

Electronic Supplementary Information

A new method for the synthesis of β -cyano substituted porphyrins and their use as sensitizers in photoelectrochemical devices

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Synthesis

General Procedures. Pyrrole was freshly distilled before use. Dichloromethane was distilled from calcium hydride under nitrogen. Tetrahydrofuran was distilled over sodium and benzophenone under argon. N-bromosuccinimide was obtained from Sigma Aldrich and recrystallized from hot water before use. Compounds 3,5-di-*t*-butylphenyldipyrromethane (**21**), 5-(4-methoxycarbonylphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (**22**),¹ 5-(4-*t*-butylphenyl)dipyrromethane (**23**),^{2,3} 5-(4-methoxycarbonylphenyl)-10,15,20-tris-(4-*t*-butylphenyl)porphyrin (**24**)⁴ 5-(2,4,6-trimethylphenyl)dipyrromethane (**25**)⁵, 5,10,15,20-tetrakis-(2,4,6-trimethylphenyl)porphyrin (**26**)⁶, 5,10,15,20-tetrakis-(4-methylphenyl)porphyrin (**27**)⁶, and 7,8,17,18-tetrabromo-5,10,15,20-tetrakis-(2,4,6-trimethylphenyl)porphyrin (**28**)⁷ were prepared following previously reported methods.

All NMR spectra were recorded on a 400 MHz Varian spectrometer. Samples were dissolved in CDCl₃ with TMS as an internal reference, unless otherwise stated. Mass spectra were obtained on an Applied Biosystems Voyager-DE STR matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF). *Trans, trans*-1,4-diphenyl-1,3-butadiene was used as a matrix for the MALDI-TOF-MS measurements, with 5,10,15,20-tetrakis-(4-methylphenyl)porphyrin as the internal reference. UV-visible absorption spectra were measured on a Shimadzu UV2100U spectrometer. Thin-layer chromatography for dipyrromethanes and porphyrins was performed on silica gel GHFL or GHL plates (Analtech). Synthesis, workup and purification were performed in a darkened laboratory.

5,10,15,20-Tetrakis-(4-*t*-butylphenyl)porphyrin (29**).** Porphyrin **29** was synthesized as a side product from the synthesis of **25** (see below). The product was purified by column chromatography on silica gel using 40% dichloromethane in toluene to yield purple crystals, mp >300 °C, yield, 150 mg (1%). ¹H NMR, δ (ppm) 8.86 (s, 8 H, pyrrolic H), 8.14 (d, *J*=7.9 Hz, 8 H, Ar), 7.75 (d, *J*=7.9 Hz, 8 H, Ar), 1.60 (s, 36 H, *t*-butyl H), -2.74 (s, 2 H, -NH); UV-visible, λ_{max} (nm, CH₂Cl₂): 419, 518, 553, 592, 648; MALDI-TOF-MS *m/z*; calcd for C₆₀H₆₂N₄ 839.16 [M⁺], obsd 838.65.

7,8,17,18-Tetrabromo-5,10,15,20-tetrakis-(4-*t*-butylphenyl)porphyrin (30**).** In an oven-dried round bottomed flask equipped with a reflux condenser and a magnetic stir

bar, **29** (150 mg, 0.179 mmol) was dissolved in dry CHCl_3 (30 mL) and stirred for 15 min at room temperature. The flask was placed in an oil bath which was brought to 80 °C, and N-bromosuccinimide (143 mg, 0.804 mmol) was added to the solution. The solution was allowed to reflux for 4 h after which pyridine (60 μL) was added and the solution was allowed to reflux for an additional 1 h. After a second addition of pyridine (60 μL) the solution was again allowed to reflux for 1h. N-bromosuccinimide (16 mg, 0.090 mmol) was added and the solution was allowed to reflux for 3 h, followed by a second addition of N-bromosuccinimide (16 mg, 0.090 mmol). After 2 h pyridine (120 μL) was added and the solution was allowed to stir for 15 min. The solvent was removed by distillation under reduced pressure and the product was removed by filtration and washed with MeOH (250 mL). The crude product was purified by column chromatography on silica gel using 40% dichloromethane in hexane as the eluent. The final product was recrystallized from CHCl_3 and MeOH to yield purple crystals, mp >300 °C, yield 150 mg (72%). $^1\text{H NMR}$, δ (ppm) 8.80 (s, 2 H, pyrrolic H), 8.74 (s, 2 H, pyrrolic H), 8.11 (d, $J=8.3$ Hz, 4 H, Ar), 7.95 (d, $J=7.9$ Hz, 4 H, Ar), 7.79 (d, $J=7.9$ Hz, 4 H, Ar), 7.67 - 7.75 (m, 4 H, Ar), 1.57 (s, 36 H, *t*-butyl H), -2.73 (br s, 2 H, -NH); UV-visible, λ_{max} (nm, CH_2Cl_2): 439, 538, 688; MALDI-TOF-MS m/z ; calcd for $\text{C}_{60}\text{H}_{58}\text{Br}_4\text{N}_4$ 1154.75 [M+], obsd 1154.20.

Zn(II) 2,3,12,13-tetrabromo-5,10,15,20-tetrakis-(4-*t*-butylphenyl)porphyrin (31). Porphyrin **30** (150 mg, 0.130 mmol) was dissolved in dichloromethane (120 mL) in a round bottomed flask equipped with a reflux condenser and a magnetic stir bar. The flask was placed in an oil bath which was brought to a temperature of 50 °C. Zinc acetate (427 mg, 1.95 mmol) was dissolved separately in MeOH (4 mL), and the resulting solution was added to the flask containing the porphyrin. The solution was stirred in an oil bath at a temperature of 50 °C for 3.5 h, after which the solvent was distilled under reduced pressure, and the product was purified by recrystallization. The resulting crystals were washed with MeOH (50 mL) to yield pure porphyrin **31** as purple crystals, mp >300 °C, yield 100 mg (63%). $^1\text{H NMR}$, δ (ppm) 8.71 (s, 4 H, pyrrolic H), 7.94 (br d, $J=1.0$ Hz, 8 H, Ar), 7.71 (d, $J=8$ Hz, 8 H, Ar), 1.59 (s, 36 H, *t*-butyl H); UV-visible, λ_{max} (nm, CH_2Cl_2): 452, 561, 601; MALDI-TOF-MS m/z ; calcd for $\text{C}_{60}\text{H}_{56}\text{Br}_4\text{N}_4\text{Zn}$ 1218.14 [M+], obsd 1218.65.

Zn(II) 2,3,12,13-tetracyano-5,10,15,20-tetrakis-(4-*t*-butylphenyl)porphyrin (1). Porphyrin **31**, zinc acetate, 1,1'-bis(diphenylphosphino)ferrocene, and Zn dust were dried under vacuum overnight before use, and all glassware was oven dried. Porphyrin **31** (100 mg, 0.082 mmol), tris-(dibenzylideneacetone)dipalladium(0) (62.6 mg, 0.1 mmol), 1,1'-bis-(diphenylphosphino)ferrocene (75.8 mg, 0.1 mmol), zinc acetate (4.7 mg, 0.02 mmol), Zn dust (2.8 mg, 0.04 mmol), and zinc cyanide (24.1 mg, 0.2 mmol) were dissolved in dimethylacetamide (10 mL) that was deoxygenated with Ar, in a Schlenk

flask equipped with a magnetic stir bar. The Schlenk flask was placed in an oil bath which was brought to 115 °C. The solution was allowed to stir under argon for 27 h, after which the solvent was removed by distillation under reduced pressure. The reaction mixture was redissolved in dichloromethane, washed 4 times with 100 mL portions of water, and dried over anhydrous sodium sulfate. The solvent was removed by distillation under reduced pressure. The product was purified by column chromatography on silica gel with 15% EtOAc in toluene as the eluent, and then recrystallized from DCM and hexane to yield porphyrin **1** as purple crystals, mp >300 °C, yield 47.9 mg (56%). ¹H NMR, δ (ppm) 8.84 (s, 4 H, pyrrolic H), 7.93 (d, *J*=7.9 Hz, 8 H, Ar), 7.74 (d, *J*=8.4 Hz, 8 H, Ar), 1.58 (s, 36 H, *t*-butyl H); UV-visible, λ_{max} (nm), (CH₂Cl₂): 443, 459, 660, 685; MALDI-TOF-MS *m/z*; calcd for C₆₄H₅₆N₈Zn 1002.59 [M⁺], obsd 1002.44.

7,8,17,18-Tetracyano-5,10,15,20-tetrakis-(4-*t*-butylphenyl)porphyrin (2).

Porphyrin **1** (10 mg, 0.01 mmol) was dissolved in dichloromethane (50 mL) in a round bottomed flask equipped with a magnetic stir bar. Trifluoroacetic acid (7 mL) was added dropwise and the solution was stirred for 4 h at ambient temperature. Triethylamine (0.2 mL) was added and the solution was washed with a saturated solution of NaHCO₃ in water (100 mL) and then water (2 × 100 mL). The product was purified by preparative thin layer chromatography with 15% ethyl acetate in toluene as the solvent to give porphyrin **2** as purple crystals, mp >300 °C, yield 7.00 mg (74.6%). ¹H NMR, δ (ppm) 8.97 - 9.06 (m, 4 H, pyrrolic H), 8.05 (d, *J*=8.3 Hz, 8 H, Ar), 7.84 (d, *J*=8.3 Hz, 8 H, Ar), 1.61 (s, 36 H, *t*-butyl H), -2.41 (br s, 2 H, -NH); UV-visible, λ_{max} (nm), CH₂Cl₂): 441, 454, 556, 600, 670, 738; MALDI-TOF-MS *m/z*; calcd for C₆₄H₅₈N₈ 939.20 [M⁺], obsd 940.08.

7,8,17,18-Tetrabromo-5-(4-methoxycarbonylphenyl)-10,15,20-tris-(4-*t*-butylphenyl)porphyrin (32). Porphyrin **24** (500 mg, 0.6 mmol) was dissolved in 100 mL of chloroform stabilized with ethanol (0.75%) in a round bottomed flask equipped with a magnetic stir bar and a reflux condenser. N-bromosuccinimide (476 mg, 2.68 mmol) was added, the flask was placed in an oil bath which was heated to a temperature of 55 °C, and the solution was stirred for 1h. Pyridine (0.6 mL, 7.7 mmol) was added dropwise, and the solution was stirred for an additional 3.5 h. N-bromosuccinimide (106 mg, 0.596 mmol) was added and after 0.5 h pyridine (0.4 mL, 4.5 mmol) was added and the solution was stirred for an additional 1.5 h. A third portion of N-bromosuccinimide (212 mg, 1.19 mmol) and pyridine (0.4 mL, 4.8 mmol) was added and the solution was stirred for 3 h. The solvent was removed by distillation under reduced pressure and the product was purified by column chromatography on silica gel using 40% hexane in dichloromethane as the eluent. Final purification was done by recrystallization from dichloromethane and hexane, and the resulting purple crystals were washed with methanol to give pure porphyrin **32**, mp >300 °C, yield 377 mg (54.8%); ¹H NMR (400 MHz), δ (ppm) 8.68 - 8.86 (m, 3 H, pyrrolic H), 8.59 (d, *J*=4.8 Hz, 1 H, pyrrolic H), 8.45 (d, *J*=7.9 Hz, 2 H, Ar), 8.28 (d,

$J=7.9$ Hz, 2 H, Ar), 8.00 - 8.17 (m, 6 H, Ar), 7.79 (d, $J=7.9$ Hz, 6 H, Ar), 4.11 (s, 3 H, methoxy H), 1.59 (s, 27 H, *t*-butyl), -2.75 (br s., 2 H, -NH); UV-visible, λ_{max} (nm, CH_2Cl_2): 440, 538, 613, 690; MALDI-TOF-MS m/z ; calcd for $\text{C}_{58}\text{H}_{52}\text{Br}_4\text{N}_4\text{O}_2$ 1156.68 [M^+], obsd 1156.10.

Zn(II) 2,3,12,13-tetrabromo-5-(4-methoxycarbonyl)-10,15,20-tris-(4-*t*-butylphenyl)porphyrin (33). Porphyrin **32** (370 mg, 0.303 mmol) was dissolved in deaerated dichloromethane (50 mL) in a dry round bottomed flask equipped with a magnetic stir bar. Zinc acetate (1.1 g, 4.8 mmol) was dissolved in methanol (15 mL) in a separate vial and added to the round bottomed flask, and the solution was stirred at room temperature for 1 h. The reaction mixture was washed three times with water and the organic layer was dried over anhydrous sodium sulfate. The product was purified by recrystallization from methanol/hexane to give porphyrin **33** as purple crystals, mp >300 °C, yield 367 mg (94.0%). ^1H NMR (400 MHz, δ (ppm) 8.65 - 8.81 (m, 3 H, pyrrolic H), 8.56 (d, $J=5.1$ Hz, 1 H, pyrrolic H), 8.37 (d, $J=7$ Hz, 2 H, Ar), 8.16 (d, $J=7$ Hz, 2 H, Ar), 7.94 (d, $J=7.8$ Hz, 6 H, Ar), 7.71 (d, $J=7.0$ Hz, 6 H, Ar), 4.10 (s, 3 H, methoxy H), 1.59 (s, 27 H, *t*-butyl H); UV-visible, λ_{max} (nm, 2 % MeOH in CH_2Cl_2): 437, 569, 612; MALDI-TOF-MS m/z ; calcd for $\text{C}_{58}\text{H}_{50}\text{Br}_4\text{N}_4\text{O}_2\text{Zn}$ 1220.07 [M^+], obsd 1220.57.

Zn(II) 2,3,12,13-tetracyano-5-(4-methoxycarbonylphenyl)-10,15,20-tris-(4-*t*-butylphenyl)porphyrin (3). Porphyrin **33**, $\text{Zn}(\text{OAc})_2$, 1,1'-bis(diphenylphosphino)ferrocene, and Zn dust were dried under vacuum overnight and all glassware was oven dried over night before use. Dimethylacetamide was stirred with BaO for 24 h, refluxed over BaO for 1 h, and distilled under reduced pressure before use. Porphyrin **33** (350 mg 0.287 mmol), tris(dibenzylideneacetone)dipalladium(0) (210 mg, 0.229 mmol), 1,1'-bis(diphenylphosphino)ferrocene (255 mg, 0.460 mmol), zinc acetate (16 mg, 0.09 mmol), Zn dust (9 mg, 0.1 mmol), and zinc cyanide (81 mg, 0.69 mmol) were dissolved in deaerated dimethylacetamide (40 mL) in a Schlenk flask equipped with a magnetic stir bar. The Schlenk flask was placed in an oil bath which was brought to a temperature of 115 °C and the reaction mixture was stirred under argon for 20 h. Dichloromethane (60 mL) was added, the solution was washed 5 times with water (100 mL), the organic layer was collected and the solvent was removed by distillation under reduced pressure. The product was purified by column chromatography on silica gel with 20% ethyl acetate in toluene as the eluent. A final purification was done by recrystallization from dichloromethane and hexane to yield porphyrin **3** as purple crystals, mp >300 °C, yield, 115 mg (39.8%). ^1H NMR, δ (ppm) 8.73 - 8.86 (m, 3 H, pyrrolic H), 8.60 (d, $J=4.8$ Hz, 1 H, pyrrolic H), 8.43 (d, $J=8.3$ Hz, 2 H, Ar), 8.17 (d, $J=8.3$ Hz, 2 H, Ar), 7.89 - 8.02 (m, 6 H, Ar), 7.67 - 7.83 (m, 6 H, Ar), 4.09 (s, 3 H, methoxy H), 1.60 (s, 27 H, *t*-butyl H); UV-visible, λ_{max} (nm, 2 % MeOH in CH_2Cl_2): 443, 458, 657, 677; MALDI-TOF-MS m/z ; calcd for $\text{C}_{62}\text{H}_{50}\text{N}_8\text{O}_2\text{Zn}$ 1004.5 [M^+], obsd 1002.87.

Zn(II) 2,3,12,13-tetracyano-5-(4-carboxyphenyl)-10,15,20-tris-(4-*t*-butylphenyl)-porphyrin (4). Porphyrin **3** (40 mg, 0.04 mmol) was dissolved in a solution of 33% methanol in tetrahydrofuran (17.4 mL) in a round bottomed flask equipped with a magnetic stir bar. A solution of 10% KOH in water (w/w) was added dropwise (3 mL) and the solution was stirred at room temperature for 3 h. Dichloromethane (10 mL) was added and the solution was washed 2 times with water (50 mL) and dried over anhydrous sodium sulfate, and the solvent was distilled under reduced pressure. The product was purified by recrystallization from toluene and ethyl acetate to give porphyrin **4** as purple crystals, mp >300 °C, yield 30 mg (76%). ¹H NMR, δ (ppm) 8.73 - 8.87 (m, 3 H, pyrrolic H), 8.63 (d, *J*=4.8 Hz, 1 H, pyrrolic H), 8.45 (d, *J*=8.3 Hz, 2 H, Ar), 8.17 (d, *J*=7.9 Hz, 2 H, Ar), 7.97 (m, 6 H, Ar), 7.73 - 7.84 (m, 6 H, Ar), 1.53 - 1.69 (m, 27 H, *t*-butyl H); UV-visible, λ_{max} (nm, 2 % MeOH in CH₂Cl₂): 443, 458, 659, 681; MALDI-TOF-MS *m/z*; calcd for C₆₁H₄₈N₈O₂Zn 990.5 [M⁺], obsd 988.95.

7,8,17,18-Tetracyano-5-(4-carboxyphenyl)-10,15,20-tris-(4-*t*-butylphenyl)-porphyrin (5). Porphyrin **4** (30 mg) was dissolved in a solution of 13.8% ethyl acetate in dichloromethane (58 mL) in a round bottomed flask equipped with a magnetic stir bar. Trifluoroacetic acid (7 mL) was added dropwise and the solution was stirred overnight at ambient temperature. Triethylamine (0.2 mL) was added and the solution was washed with 5% (w/w) NaHCO₃ (100 mL) and then water (2 × 100 mL). The product was purified by preparative thin layer chromatography with 20% ethyl acetate in toluene as the solvent to give porphyrin **5** as purple crystals, mp >300 °C, yield, 25 mg (89%). ¹H NMR, δ (ppm) 8.98 - 9.10 (m, 3 H, pyrrolic H), 8.83 (d, *J*=4.9 Hz, 1 H, pyrrolic H), 8.53 (d, *J*=7.9 Hz, 2 H, Ar), 8.25 (d, *J*=7.9 Hz, 2 H, Ar), 7.97 - 8.09 (m, 6 H, Ar), 7.76 - 7.88 (m, 6 H, Ar), 1.51 - 1.68 (m, 27 H, *t*-butyl), -2.44 (d, *J*=7.9 Hz, 2 H, -NH); UV-visible, λ_{max} (nm, CH₂Cl₂): 445, 459, 555, 602, 672, 738; MALDI-TOF-MS *m/z*; calcd for C₆₁H₄₈N₈O₂Zn 927.10 [M⁺], obsd 927.59.

5-(3-Methoxycarbonylphenyl)-10,15,20-tris-(4-*t*-butylphenyl)porphyrin (34). Dipyrro-methane **23**. (10g, 0.04 mol), 4-*t*-butylbenzaldehyde (3 mL, 0.02 mol), and methyl 3-formylbenzoate (3 g, 0.02 mol) were dissolved in dry and deoxygenated dichloromethane (1.8 L) under argon in a round bottomed flask equipped with a magnetic stirrer. Trifluoroacetic acid (4.9 mL, 0.1 mol) was added dropwise and the solution was stirred for 3 h at room temperature. Next, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (12.3 g, 0.1 mol) was added and the solution was stirred for 5 h. The solvent was removed by distillation under reduced pressure and the reaction mixture was run through a silica gel pad with dichloromethane as the eluent. The product was purified by column chromatography on silica gel using a solution of 40% dichloromethane in toluene as the eluent to give porphyrin **34** as purple crystals, mp >300 °C, yield, 1.2 mg (7.9%). ¹H NMR, δ (ppm) 8.82 - 8.97 (m, 6 H, pyrrolic H), 8.74 (d,

$J=4.9$ Hz, 2 H, pyrrolic H), 8.44 - 8.52 (m, 1 H, Ar), 8.41 (dt, $J=7.7$, 1.4 Hz, 1 H, Ar), 8.07 - 8.21 (m, 6 H, Ar), 7.84 (t, $J=7.7$ Hz, 1 H, Ar), 7.71 - 7.80 (m, 6 H, Ar), 3.98 (s, 3 H, methoxy H), 1.57 - 1.65 (m, 27 H, *t*-butyl H), -2.76 (s, 2 H, -NH). UV-visible, λ_{\max} (nm, CH_2Cl_2): 419, 517, 553, 591, 647; MALDI-TOF-MS m/z ; calcd for $\text{C}_{58}\text{H}_{56}\text{N}_4\text{O}_2$ 841.09 [M+], obsd 840.63.

7,8,17,18-Tetrabromo-5-(3-methoxycarbonylphenyl)-10,15,20-tris-(4-*t*-butylphenyl)-porphyrin (35). Porphyrin **34** (300 mg, 0.4 mmol) was dissolved in chloroform (70 mL) stabilized with ethanol in a dry round bottomed flask equipped with a magnetic stir bar and reflux condenser. The round bottomed flask was placed in an oil bath which was brought to a temperature of 80 °C. N-bromosuccinimide (470 mg, 2.5 mmol) was added to the solution which was then allowed to reflux 2 h. An additional amount of N-bromosuccinimide (63 mg, 0.4 mmol) was added to the solution, which was refluxed for 1 h. After the reaction was complete as indicated by thin layer chromatography and MALDI mass spectrometry, the solvent was distilled under reduced pressure and the product was purified by column chromatography on silica gel using 0.5% triethylamine in dichloromethane as the eluent. The final purification was done by column chromatography on silica gel using 50% hexane in dichloromethane as the eluent to yield porphyrin **35** as purple crystals, mp >300 °C, yield, 319 mg (77%). ^1H NMR, δ (ppm) 8.83 - 8.91 (m, 1 H, pyrrolic H), 8.72 - 8.81 (m, 3 H, pyrrolic H), 8.59 (d, $J=5.3$ Hz, 1 H, Ar), 8.49 (d, $J=7.5$ Hz, 1 H, Ar), 8.37 (d, $J=7.5$ Hz, 1 H, Ar), 8.11 (dd, $J=7.9$, 3.1 Hz, 6 H, Ar), 7.86 (t, $J=7.7$ Hz, 1 H, Ar), 7.80 (d, $J=7.5$ Hz, 6 H, Ar), 4.03 (s, 3 H, methoxy H), 1.53 - 1.64 (m, 29 H, *t*-butyl H), -2.75 (s, 2 H, -NH); UV-visible, λ_{\max} (nm, CH_2Cl_2): 440, 538, 615, 687; MALDI-TOF-MS m/z ; calcd for $\text{C}_{58}\text{H}_{50}\text{Br}_4\text{N}_4\text{O}_2$ 1156.68[M+], obsd 1156.23.

Zn(II) 2,3,12,13-tetrabromo-5-(3-methoxycarbonylphenyl)-10,15,20-tris-(4-*t*-butyl-phenyl)porphyrin (36). Porphyrin **35** (156 mg, 0.1 mmol) was dissolved in deaerated dichloromethane (20 mL) in a round bottomed flask equipped with a magnetic stirrer. Zinc acetate (443 mg, 2 mmol) was dissolved in MeOH (2 mL) and the resulting solution was added dropwise to the porphyrin solution, which was then stirred for 1 h at room temperature. The organic layer was washed three times with water (100 mL) and dried over anhydrous sodium sulfate to yield porphyrin **36** as purple crystals, mp >300 °C, yield, 124 mg (75.3%). ^1H NMR, δ (ppm) 8.77 - 8.85 (m, 3 H, pyrrolic H), 8.69 (s, 1 H, pyrrolic H), 8.63 (d, $J=4.7$ Hz, 1 H, Ar), 8.42 (d, $J=7.4$ Hz, 1 H, Ar), 8.26 (d, $J=7.4$ Hz, 1 H, Ar), 7.95 (d, $J=6.7$ Hz, 6 H, Ar), 7.80 (t, $J=7.8$ Hz, 1 H, Ar), 7.72 (d, $J=8.2$ Hz, 6 H, Ar), 3.93 (s, 3 H, methoxy H), 1.59 (s, 27 H, *t*-butyl H); UV-visible, λ_{\max} (nm, 2% MeOH in CH_2Cl_2): 437, 570, 612; MALDI-TOF-MS m/z ; calcd for $\text{C}_{58}\text{H}_{50}\text{Br}_4\text{N}_4\text{O}_2\text{Zn}$ 1220.07 [M+], obsd 1219.95.

Zn(II) 2,3,12,13-tetracyano-5-(3-methoxycarbonylphenyl)-10,15,20-tris-(4-*t*-butylphenyl)porphyrin (6). Porphyrin **36**, zinc acetate, 1,1'-bis(diphenylphosphino)-

ferrocene, and Zn dust were dried under vacuum overnight before use, and all glassware was oven dried. Porphyrin **36** (124 mg, 0.1 mmol), tris(dibenzylideneacetone)dipalladium(0) (75 mg, 0.1 mmol), 1,1'-bis(diphenylphosphino)ferrocene (90 mg, 0.2 mmol), zinc acetate (5.6 mg, 0.3 mmol), Zn dust (3 mg, 0.05 mmol), and zinc cyanide (29 mg, 0.2 mmol) were dissolved in deaerated dimethylacetamide (10 mL) in a Schlenk flask equipped with a magnetic stirrer. The Schlenk flask was placed in an oil bath that was heated to 115 °C and the solution was allowed to stir under argon for 17.5 h, after which the solvent was removed by distillation and the reaction mixture was redissolved in dichloromethane. The solution was washed five times with water (100 mL) and dried over anhydrous sodium sulfate, and the solvent was distilled under vacuum. The product was purified by column chromatography on silica gel with 15% EtOAc in toluene as the eluent, and then recrystallized from dichloromethane and hexane to give porphyrin **6** as purple crystals, mp >300 °C, yield, 30 mg (29%). ¹H NMR, δ (ppm) 8.70 - 8.90 (m, 3 H, pyrrolic H), 8.47 (d, *J*=5.3 Hz, 1 H, pyrrolic H), 8.29 (br s, 1 H, Ar), 8.16 (d, *J*=7.5 Hz, 1 H, Ar), 7.99 (br s, 2 H, Ar), 7.57 - 7.91 (m, 11 H, Ar), 3.36 (br s, 3 H, methoxy H), 1.59 (s, 9 H, *t*-butyl H), 1.56 (s, 9 H, *t*-butyl H), 1.53 (s, 9 H, *t*-butyl H); UV-visible, λ_{max} (nm, 2% MeOH in CH₂Cl₂): 443, 459, 661, 685; MALDI-TOF-MS *m/z*; calcd for C₆₂H₅₀N₈O₂Zn 1004.52 [M⁺], obsd 1002.45.

Zn(II) 2,3,12,13-tetracyano-5-(3-carboxyphenyl)-10,15,20-tris-(4-*t*-butylphenyl)-porphyrin (7). Porphyrin **6** (21 mg, 0.02 mmol) was dissolved in freshly distilled tetrahydrofuran (8 mL) in a dry round bottomed flask equipped with a magnetic stir bar. Methanol (4 mL) was added, followed by the dropwise addition of 17% w/w KOH in water (1.8 mL). The solution was allowed to stir at room temperature for 2 h or until reaction was complete as indicated by thin layer chromatography and mass spectrometry. The most volatile components of the solvent were removed by distillation at reduced pressure and the product was extracted from the remaining aqueous layer with dichloromethane. The organic layer was washed with 0.1 M citric acid followed by water (100 mL), after which the organic layer was dried over anhydrous sodium sulfate. The solvent was distilled under reduced pressure and the product was dried overnight under vacuum. The product was purified by recrystallization from dichloromethane and hexane to yield porphyrin **7** as purple crystals, mp >300 °C, yield, 20 mg (97%). ¹H NMR, δ (ppm) 8.72 - 8.84 (m, 3 H, pyrrolic H), 8.68 (s, 1 H, pyrrolic H), 8.62 (d, *J*=5.3 Hz, 1 H, Ar), 8.56 (d, *J*=7.9 Hz, 1 H, Ar), 8.29 (d, *J*=7.5 Hz, 1 H, Ar), 7.95 (d, *J*=6.1 Hz, 6 H, Ar), 7.85 (t, *J*=7.7 Hz, 1 H, Ar), 7.70 - 7.80 (m, 6 H, Ar), 1.55 - 1.66 (m, 27 H, *t*-butyl H); UV-visible, λ_{max} (nm, 2 % MeOH in CH₂Cl₂): 443, 460, 662, 689; MALDI-TOF-MS *m/z*; calcd for C₆₁H₄₈N₈O₂Zn 990.50 [M⁺], obsd 988.95.

7,8,17,18-Tetracyano-5-(3'-carboxyphenyl)-10,15,20-tris-(4-*t*-butylphenyl)-porphyrin (8). Porphyrin **7** (10 mg, 0.01 mmol) was dissolved in a solution of 15% ethyl acetate in dichloromethane (60 mL) in a round bottomed flask equipped with a magnetic

stir bar. Trifluoroacetic acid (7 mL) was added dropwise and the solution was stirred for 4 h at ambient temperature. Triethylamine (0.2 mL) was added and the solution was washed with a saturated solution of NaHCO₃ in water (100 mL) and then water (2 × 100 mL). The product was purified by preparative thin layer chromatography with 20% ethyl acetate in toluene as the solvent to give porphyrin **8** as purple crystals, mp >300 °C, yield, 8 mg (85.4%). ¹H NMR, δ (ppm) 8.96 - 9.08 (m, 3 H, pyrrolic H), 8.77 - 8.89 (m, 2 H, pyrrolic H, Ar), 8.67 (d, *J*=7.9 Hz, 1 H, Ar), 8.38 (d, *J*=7.5 Hz, 1 H, Ar), 7.98 - 8.08 (m, 6 H, Ar), 7.94 (t, *J*=7.7 Hz, 1 H, Ar), 7.83 (d, *J*=8.3 Hz, 6 H, Ar), 1.56 - 1.68 (m, 27 H, *t*-butyl-H), -2.45 (br s, 2 H, -NH); UV-visible, λ_{max} (nm, 2 % MeOH in CH₂Cl₂): 441, 453, 556, 601, 668, 735; MALDI-TOF-MS *m/z*; calcd for C₆₁H₅₀Br₄N₈O₂ 926.41 [M⁺], obsd 927.40.

5,10,15,20-Tetrakis-(3,5-di-*t*-butylphenyl)porphyrin (37). Porphyrin **37** was synthesized as a side product from the synthesis of **28** (see below). The product was purified by column chromatography on silica gel using 30% dichloromethane in toluene to yield purple crystals, mp >300 °C, yield, 375 mg (14.1%); ¹H NMR, δ (ppm) 8.89 (s, 8 H, pyrrolic H), 8.08 (d, *J*=1.8 Hz, 8 H, Ar), 7.78 (t, *J*=1.8 Hz, 4 H, Ar), 1.52 (br s, 72 H, *t*-butyl H), -2.68 (s, 2 H, -NH); UV-visible, λ_{max} (nm, CH₂Cl₂): 419, 517, 553, 591, 646; MALDI-TOF-MS *m/z*; calcd for C₇₆H₉₄N₄ 1063.59 [M⁺], obsd 1063.25.

7,8,17,18-Tetrabromo-5,10,15,20-tetrakis-(3,5-di-*t*-butyl-phenyl)porphyrin (38). Porphyrin **37** (375 mg, 0.353 mmol) was dissolved in chloroform (50 mL) stabilized with ethanol in a dry round bottomed flask equipped with a magnetic stir bar and reflux condenser. The flask was placed in an oil bath which was brought to a temperature of 80 °C. N-bromosuccinimide (314 mg, 1.76 mmol) was added to the solution which was then allowed to reflux 1 h, followed by the addition of pyridine (0.142 mL, 1.76 mmol). The solution was allowed to reflux for an additional 5 h. After the reaction was complete as indicated by thin layer chromatography and MALDI mass spectrometry, the solvent was distilled under reduced pressure and the product was purified by column chromatography on silica gel using a solution of 0.5% triethylamine, and 49.5% dichloromethane in hexane as the eluent to yield porphyrin **38** as purple crystals, mp >300 °C, yield, 100 mg (20.7%). ¹H NMR, δ (ppm) 8.89 (s, 8 H, pyrrolic H), 8.08 (d, *J*=1.6 Hz, 8 H, Ar), 7.78 (s, 4 H, Ar), 1.52 (br s, 72 H, *t*-butyl H), -2.94 (s, 2 H, -NH); UV-visible, λ_{max} (nm, CH₂Cl₂): 432, 529, 663, 665; MALDI-TOF-MS *m/z*; calcd for C₇₆H₉₀Br₄N₄ 1379.17 [M⁺], obsd 1378.44.

Zn (II) 2,3,12,13-tetrabromo-5,10,15,20-tetrakis-(3,5-di-*t*-butylphenyl)porphyrin (39). Porphyrin **38** (100 mg, 0.073 mmol) was dissolved in deaerated chloroform (30 mL) in a round bottomed flask equipped with a magnetic stirrer. Zinc acetate (320 mg, 1.46 mmol) was dissolved in MeOH (3.2 mL) and the resulting solution was added dropwise to the porphyrin solution, which was then stirred for 1 h at room temperature. The organic layer was washed three times with water (100 mL) and dried over anhydrous sodium

sulfate to yield porphyrin **39** as purple crystals, mp >300 °C, yield, 60 mg (63.5%). ¹H NMR, δ (ppm) 8.76 (s, 4 H, pyrrolic H), 7.85 (s, 8 H, Ar), 7.77 (br s, 4 H, Ar), 1.48 (s, 72 H, *t*-butyl H); UV-visible, λ_{max} (nm, CH₂Cl₂): 429, 557, 597; MALDI-TOF-MS m/z; calcd for C₇₆H₈₈Br₄N₄Zn 1442.56 [M⁺], obsd 1442.43.

Zn (II) 2,3,12,13-tetracyano-5,10,15,20-tetrakis-(3,5-di-*t*-butyl-phenyl)porphyrin (9). Porphyrin **39**, zinc acetate, 1,1'-bis(diphenylphosphino)ferrocene, and Zn dust were dried under vacuum overnight before use, and all glassware was oven dried. Porphyrin **39** (20 mg, 0.014 mmol), tris(dibenzylideneacetone)dipalladium(0) (10 mg, 0.011 mmol), 1,1'-bis(diphenylphosphino)ferrocene (12 mg, 0.022 mmol), zinc acetate (1 mg, 0.0035 mmol), Zn dust (1 mg, 0.015 mmol), and zinc cyanide (4 mg, 0.034 mmol) were dissolved in deaerated N,N-dimethylacetamide (15 mL) in a Schlenk flask equipped with a magnetic stirrer. The Schlenk flask was placed in an oil bath that was heated to 115 °C and the solution was allowed to stir under argon for 17.5 h, after which the solvent was removed by distillation and the reaction mixture was redissolved in dichloromethane. The solution was washed five times with water (100 mL) and dried over anhydrous sodium sulfate, and the solvent was distilled under vacuum. The product was purified by column chromatography on silica gel with 15% EtOAc in toluene as the eluent, and then recrystallized from dichloromethane and hexane to give porphyrin **9** as purple crystals, mp >300 °C, yield, 30 mg (29%). ¹H NMR, δ (ppm) 8.76 (s, 4 H, pyrrolic H), 7.86 (t, *J*=1.8 Hz, 4 H, Ar), 7.79 (d, *J*=1.8 Hz, 8 H, Ar), 1.41 (s, 72 H, *t*-butyl H); UV-visible, λ_{max} (nm, 2 % MeOH in CH₂Cl₂): 443, 458, 655, 677; MALDI-TOF-MS m/z; calcd for C₈₀H₈₈N₈Zn 1227.02 [M⁺], obsd 1227.25.

7,8,17,18-Tetracyano-5,10,15,20-tetrakis-(3,5-di-*t*-butylphenyl)porphyrin (10). Porphyrin **9** (5.0 mg, 0.0041 mmol) was dissolved in dichloromethane (26 mL) in a round bottomed flask equipped with a magnetic stir bar. Trifluoroacetic acid (4 mL) was added dropwise and the solution was stirred for 4 h at ambient temperature. The solution was washed with a saturated solution of NaHCO₃ in water (100 mL), followed by water (2 × 100 mL). The organic solution was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The product was purified by preparative thin layer chromatography with 5% ethyl acetate in toluene as the solvent to give porphyrin **10** as purple crystals, mp >300 °C, yield, 3 mg (60.5%). ¹H NMR, δ (ppm) 8.95 (d, *J*=1.3 Hz, 4 H, pyrrolic H), 7.95-7.91 (m, 4 H, Ar), 7.90 (d, *J*=1.3 Hz, 8 H, Ar), 1.48 (s, 72 H, *t*-butyl H), -2.47 (s, 2 H, -NH); UV-visible, λ_{max} (nm, 2 % MeOH in CH₂Cl₂): 440, 453, 553, 599, 667, 730; MALDI-TOF-MS m/z; calcd for C₈₀H₉₀N₈ 1164.27 [M⁺], obsd 1163.62.

5-(3-Methoxycarbonylphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (40). Methyl 3-formylbenzoate, 3,5-di-*t*-butylbenzaldehyde, and dipyrromethane **21** were dried overnight under vacuum. Compound **21** (3.3 g, 10 mmol), 3,5-di-*t*-butylbenzaldehyde (1.1 g, 5 mmol), and methyl 3-formylbenzoate (0.8 g, 5 mmol) were

dissolved in dry and deaerated dichloromethane (600 mL) in a dry round bottomed flask equipped with a magnetic stir bar and stirred for 15 min under argon at room temperature. Trifluoroacetic acid (1.4 mL, 18 mmol) was added dropwise and stirred for 2 h, after which time 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (4.5 g, 20 mmol) was added. The reaction vessel was opened to the atmosphere and stirred for an additional 1.5 h. A portion of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.50 g, 2.2 mmol) was then added and the solution was stirred for an additional 30 min. The solvent was distilled under reduced pressure and the product was redissolved in dichloromethane and run through a short silica gel plug using dichloromethane as the eluent. The first three bands containing porphyrin were collected and the solvent was removed from each by distillation under reduced pressure. The product, the second band, was further purified by column chromatography on silica gel using 30% dichloromethane in toluene as the eluent. The final purification was done by recrystallization from hexane and dichloromethane to give porphyrin **40** as purple crystals, mp >300 °C, yield, 459 mg (9.1%). ¹H NMR, δ (ppm) 8.83 - 8.97 (m, 6 H, pyrrolic H), 8.76 (d, *J*=4.9 Hz, 2 H, pyrrolic H), 8.47 (d, *J*=7.9 Hz, 1 H, Ar), 8.42 (d, *J*=7.5 Hz, 1 H, Ar), 8.04 - 8.12 (m, 6 H, Ar), 7.84 (t, *J*=7.7 Hz, 1 H, Ar), 7.77 - 7.81 (m, 3 H, Ar), 3.97 (s, 3 H, methoxy H), 1.52 (s, 54 H, *t*-butyl H), -2.70 (s, 2 H, -NH); UV-visible λ_{max} (nm, CH₂Cl₂): 420, 517, 553, 592, 647; MALDI-TOF-MS *m/z*; calcd for C₇₀H₈₀N₄O₂ 1009.41 [M⁺], obsd 1008.85.

7,8,17,18-Tetrabromo-5-(3-methoxycarbonylphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (41). Porphyrin **40** and N-bromosuccinimide were dried overnight under vacuum. N-bromosuccinimide (405 mg, 2.3 mmol), and **40** (459 mg, 0.5 mmol) were dissolved in CHCl₃ (75 mL) in a dry round bottomed flask equipped with a reflux condenser and a magnetic stirrer. The solution was allowed to reflux for 2 h, after which time additional N-bromosuccinimide (162 mg, 0.9 mmol) was added and the solution was allowed to reflux for an additional 2 h. A third portion of N-bromosuccinimide (162 mg, 0.910 mmol) was added to the solution, which was then allowed to reflux for 2 h. Pyridine (0.2 mL, 2.5 mol) was added to the solution and the mixture was stirred for 10 min, and then the solvent was distilled under reduced pressure. The product was purified by column chromatography on silica gel using a solution of 40% dichloromethane in hexane as the eluent to give porphyrin **41** as purple crystals, mp >300 °C, yield, 417 mg (69.2%). ¹H NMR, δ (ppm) 8.84 -8.86 (m, 1 H, pyrrolic H), 8.76 - 8.86 (m, 2 H, pyrrolic H), 8.62 (d, *J*=4 Hz, 1 H, pyrrolic H), 8.49 (d, *J*=8 Hz, 1 H, Ar), 8.35 (d, *J*=7.6 Hz, 1 H, Ar), 7.92 - 8.22 (m, 6 H, Ar), 7.852 (t, *J*=7.6 Hz, 1 H, Ar), 7.84 - 7.62 (m, 3 H, Ar), 4.01 (s, 3 H, methoxy H), 1.46 - 1.60 (m, 54 H, *t*-butyl H), -2.94 (s, 2 H, -NH); UV-visible λ_{max} (nm, CH₂Cl₂): 435, 531, 604, 678; MALDI-TOF-MS *m/z*; calcd for C₇₀H₇₆Br₄N₄O₂ 1324.99 [M⁺], obsd 1324.87.

Zn(II) 2,3,12,13-tetrabromo-5-(3-methoxycarbonylphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (42). Porphyrin **41** (417 mg, 0.3 mmol) was dissolved in chloroform (120 mL), in a round bottomed flask equipped with a reflux condenser and a magnetic stirrer. The flask was placed in an oil bath that was heated to 50 °C. Zinc acetate (1.4 g, 6.3 mmol) was dissolved in methanol (7 mL), and the resulting solution was added to the round bottom flask containing the porphyrin solution. The solution was allowed to stir for 1 h. The solvent was distilled under reduced pressure, and the product was purified by column chromatography on silica gel using a solution of 50% dichloromethane and in hexane as the eluent to yield porphyrin **42** as purple crystals, mp >300 °C, yield, 304 mg (69.6%). ¹H NMR, δ (ppm) 8.86 - 8.89 (m, 2 H, pyrrolic H), 8.83 (d, *J*=4.8 Hz, 1 H, pyrrolic H), 8.69 (s, 1 H, Ar), 8.67 (d, *J*=4.8 Hz, 1 H, Ar), 8.42 (d, *J*=7.6 Hz, 1 H, Ar), 8.26 (d, *J*=7.6 Hz, 1 H, Ar), 7.88 – 7.82 (m, 6 H, Ar), 7.82 – 7.77 (m, 4 H, Ar), 3.92 (s, 3 H, methoxy H), 1.51 – 1.47 (m, 54 H, *t*-butyl H); UV-visible λ_{max} (nm, 2% MeOH in CH₂Cl₂): 435, 567, 607; MALDI-TOF-MS *m/z*; calcd for C₇₀H₇₄Br₄N₄O₂Zn 1388.39[M⁺], obsd 1388.66.

Zn(II) 2,3,12,13-tetracyano-5-(3-methoxycarbonylphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (14). Porphyrin **42**, zinc cyanide, zinc dust, and zinc acetate were dried overnight under vacuum. All glassware was oven dried. Porphyrin **42** (135 mg, 0.1 mmol), zinc cyanide (25 mg, 0.2 mmol), zinc dust (2.5 mg, 0.04 mmol), tris-(dibenzylideneacetone)dipalladium(0) (17 mg, 0.02 mmol), tri(*o*-tolyl)phosphine (11.8, 0.04 mmol), and zinc acetate (2.8 mg, 0.02 mmol) were dissolved in dry and deaerated *N,N*-dimethylformamide (10 mL), in a dry Schlenk flask equipped with a magnetic stirrer. The Schlenk flask was immersed in an oil bath, and the temperature of the oil was brought to 110 °C. The mixture was stirred under argon for 72 h, after which time zinc cyanide (50 mg, 0.4 mmol), zinc dust (5 mg, 0.1 mmol), tris-(dibenzylideneacetone)dipalladium(0) (35 mg, 0.04 mmol), tri(*o*-tolyl)phosphine (24 mg, 0.08 mmol), and zinc acetate (6 mg, 0.03 mmol) were added and the solution was stirred under argon for an additional 48 h. The solvent was distilled under reduced pressure and the reaction mixture was redissolved in dichloromethane and washed with water (250 mL) 4 times. The organic layer was dried over anhydrous sodium sulfate, and the solvent was distilled under reduced pressure. The crude product was further dried overnight under reduced pressure, and then purified by column chromatography on silica gel using dichloromethane as the eluent. A final purification was done with column chromatography using 5% ethyl acetate in toluene as the eluent to yield porphyrin **14** as purple crystals, mp >300 °C, yield, 15 mg (12.9%). ¹H NMR, δ (ppm) 8.83 - 8.90 (m, 2 H), 8.81 (d, *J*=4.9 Hz, 1 H), 8.66 (d, *J*=4.9 Hz, 1 H), 8.55 (br s, 1 H), 8.47 (d, *J*=7.5 Hz, 1 H), 8.26 (d, *J*=7.9 Hz, 1 H), 7.93 (m, *J*=1.8 Hz, 3 H), 7.78 - 7.89 (m, 7 H), 3.84 (s, 3 H), 1.40 - 1.59 (m, 54 H); UV-visible λ_{max} (nm, 2% MeOH in

CH₂Cl₂): 445, 459, 659, 681; MALDI-TOF-MS m/z; calcd for C₇₄H₇₄N₈O₂Zn 1172.84 [M⁺], obsd 1171.30.

Zn(II) 2,3,12,13-tetracyano-5-(3-carboxyphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)-porphyrin (15). Porphyrin **14** (15 mg 0.01 mmol), was allowed to dissolved in tetrahydrofuran (4.6 mL) in a round bottom flask equipped with a magnetic stirrer, and the solution was allowed to stir for 10 min. Methanol (2.3 mL) was added followed by the dropwise addition of 17% w/w KOH in water (1 mL), and the solution was allowed to stir at room temperature for 2 h. The product was extracted with dichloromethane and washed with a solution of 0.1 M citric acid (20 mL) followed by two water washes (20 mL). The organic phase was collected and the solvent was distilled under reduced pressure and the residue was dried under vacuum. The product was purified by preparative thin layer chromatography with toluene containing 5% ethyl acetate as the eluent to give porphyrin **15** as purple crystals, mp >300 °C, yield, 15 mg (98%). ¹H NMR (400 MHz, Methanol-d₄) δ (ppm) 8.70 - 8.75 (m, 3 H, pyrrolic H), 8.66 (d, J=5.4 Hz, 1 H, pyrrolic H), 8.56 (d, J=8.3 Hz, 1 H, Ar), 8.35 (d, J=7.8 Hz, 1 H, Ar), 7.84 - 8.02 (m, 10 H, Ar), 7.69 - 7.82 (m, 1 H, Ar), 1.43 - 1.56 (m, 54 H, *t*-butyl H); UV-visible λ_{max} (nm, 2% MeOH in CH₂Cl₂): 445, 460, 661, 685; MALDI-TOF-MS m/z; calcd for C₇₃H₇₂N₈O₂Zn 1158.82 [M⁺], obsd 1157.04.

7,8,17,18-Tetracyano-5-(3-carboxyphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)-porphyrin (16). Porphyrin **15** (7 mg) was dissolved in a solution of 9% ethyl acetate in dichloromethane (11 mL) in a round bottomed flask equipped with a magnetic stir bar. Trifluoroacetic acid (2.2 mL) was added dropwise and the solution was stirred for 4 h at ambient temperature. The solution was washed with water (50 mL) follow by wash with a saturated solution of NaHCO₃ in water (50 mL) and then a second wash with water (50 mL). The solution was dried over anhydrous sodium sulfate, and the solvent was removed under vacuum. The product was purified by preparative thin layer chromatography with 5% methanol in dichloromethane as the solvent to give porphyrin **16** as purple crystals, mp >300 °C, yield, 5 mg (75.4%). ¹H NMR, δ (ppm) 8.93 - 9.09 (m, 3 H), 8.86 (d, J=4.8 Hz, 1 H), 8.82 (s, 1 H), 8.65 (d, J=8.3 Hz, 1 H), 8.36 (d, J=7.0 Hz, 1 H), 7.96 (s, 3 H), 7.92 (s, 7 H), 1.51 (s, 54 H), -2.45 (d, J=6.6 Hz, 2 H); UV-visible λ_{max} (nm, CH₂Cl₂): 443, 453, 555, 600, 669, 730; MALDI-TOF-MS m/z; calcd for C₇₃H₇₄N₈O₂ 1095.42 [M⁺], obsd 1096.23.

7,8,17,18-Tetrabromo-5-(4-methoxycarbonylphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (43). Porphyrin **22** and N-bromosuccinimide were dried overnight under vacuum. N-bromosuccinimide (200 mg, 1.13 mmol), and **22** (350 mg, 0.347 mmol) were dissolved in CHCl₃ (60 mL) in a dry round bottomed flask equipped with a reflux condenser and a magnetic stirrer. The solution was allowed to reflux for 2.5 h, after which time pyridine (0.050 mL, 0.621 mmol) was added to the solution, which was then allowed to continue to reflux for an additional 2 h. N-bromosuccinimide (115 mg, 0.650

mmol) was added and the solution was allowed to reflux for an additional 0.5 h, after which pyridine (0.250 mL, 4.36 mmol) was added. The reaction mixture was cooled to room temperature and stirred for 3 h, after which a third portion of N-bromosuccinimide (50.0 mg, 0.283 mmol) was added to the solution, which was then brought to reflux and allowed to stir for 1 h. The solvent was distilled under reduced pressure, and the product was purified by column chromatography on silica gel using a solution of 40% DCM in hexane as the eluent to give porphyrin **43** as purple crystals, mp >300 °C, yield, 417 mg (69.2%). ¹H NMR, δ (ppm) 8.78 - 8.84 (m, 3 H, pyrrolic H), 8.63 (d, *J*=5.4 Hz, 1 H, pyrrolic H), 8.44 (d, *J*=8.3 Hz, 2 H, Ar), 8.27 (d, *J*=8.3 Hz, 2 H, Ar), 7.93 - 8.00 (m, 6 H, Ar), 7.79 - 7.84 (m, 3 H, Ar), 4.10 (s, 3 H, methoxy H), 1.52 (s, 54 H, *t*-butyl H), -2.91 (s, 2 H, -NH); UV-visible λ_{max} (nm, CH₂Cl₂): 434, 531, 605, 676; MALDI-TOF-MS *m/z*; calcd for C₇₀H₇₆Br₄N₄O₂ 1324.99 [M⁺], obsd 1324.67.

Zn(II) 2,3,12,13-tetrabromo-5-(4-methoxycarbonylphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (44). Porphyrin **43** (150 mg, 0.113 mmol) was dissolved in dichloromethane (70 mL), in a round bottomed flask equipped with a reflux condenser and a magnetic stirrer. The round bottomed flask was placed in an oil bath that was heated to 50 °C. Zinc acetate (500 mg, 2.28 mmol) was dissolved in methanol (4 mL), and the resulting solution was added to the round bottom flask containing the porphyrin. The solution was heated to 45°C allowed to stir for 3 h. The solvent was distilled under reduced pressure, and the product was purified by column chromatography on silica gel using a solution of 50% dichloromethane in hexane as the eluent to yield porphyrin **44** as purple crystals, mp >300 °C, yield, 145 mg (92.2%); ¹H NMR, δ (ppm) 8.85 - 8.90 (m, 2 H, pyrrolic H), 8.83 (d, *J*=4.8 Hz, 1 H, pyrrolic H), 8.68 (d, *J*=4.8 Hz, 1 H, Ar), 8.36 (d, *J*=7.9 Hz, 2 H, Ar), 8.15 (d, *J*=7.9 Hz, 2 H, Ar), 7.84 (s, 6 H, Ar), 7.79 (s, 3 H, Ar), 4.07 (s, 3 H, methoxy H), 1.48 (s, 54 H, *t*-butyl H); UV-visible λ_{max} (nm, 2% MeOH in CH₂Cl₂): 430, 558, 596; MALDI-TOF-MS *m/z*; calcd for C₇₀H₇₄Br₄N₄O₂Zn 1388.39 [M⁺], obsd 1388.68.

Zn(II) 2,3,12,13-tetracyano-5-(4-methoxycarbonylphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (11). Porphyrin **44**, zinc cyanide, zinc dust, and zinc acetate were dried overnight under vacuum. All glassware was oven dried. Porphyrin **44** (70 mg, 0.05 mmol), zinc cyanide (14.2 mg, 0.12 mmol), zinc dust (1.65 mg, 0.0504 mmol), tris-(dibenzylideneacetone)dipalladium(0) (36.92 mg, 0.0403 mmol), 1,1'-bis(diphenylphosphino)ferrocene (44.7, 0.08064 mmol), and zinc acetate (2.75 mg, 0.0125 mmol) were dissolved in dry and deaerated N,N-dimethylacetamide (10 mL), in a dry Schlenk flask equipped with a magnetic stirrer. The Schlenk flask was immersed in an oil bath, and the temperature of the oil was brought to 110 °C. The mixture was stirred under argon for 24 h. Once cooled, dichloromethane (20 mL) was added, the mixture was washed with water 5 times (200 ml), and the organic layer was collected and dried

over anhydrous sodium sulfate. The crude product was further dried overnight under reduced pressure, and then purified by column chromatography using 5% ethyl acetate in toluene as the eluent to yield porphyrin **11** as purple crystals, mp >300 °C, yield, 18 mg (30%). ¹H NMR, δ (ppm) 8.86 (q, *J*=4.9 Hz, 2 H, pyrrolic H), 8.82 (d, *J*=4.9 Hz, 1 H, pyrrolic H), 8.63 (d, *J*=4.9 Hz, 1 H pyrrolic H), 8.05 (d, *J*=8.3 Hz, 2 H, Ar), 7.93 - 8.01 (m, 2 H, Ar), 7.91 (br s, 3 H, Ar), 7.87 (d, *J*=1.0 Hz, 6 H, Ar), 3.65 - 3.77 (m, 3 H, methoxy H), 1.43 - 1.53 (m, 54 H, *t*-butyl H); UV-visible, λ_{max} (nm, 2% MeOH in CH₂Cl₂): 443, 458, 655, 679; MALDI-TOF-MS *m/z*; calcd for C₇₄H₇₄N₈O₂Zn 1172.84 [M⁺], obsd 1172.95.

Zn(II) 2,3,12,13-tetracyano-5-(4-carboxyphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (12). Porphyrin **11** (15 mg 0.01 mmol), was dissolved in tetrahydrofuran (10 mL) in a round bottom flask equipped with a magnetic stirrer, and the solution was stirred for 10 min. Methanol (2 mL) was added, followed by the dropwise addition of 17% w/w KOH in water (1.2 mL), and the solution was stirred at room temperature for 3 h. The product was extracted with dichloromethane and washed with a solution of 0.1 M citric acid (20 mL) followed by two water washes (20 mL). The organic phase was collected and dried over anhydrous sodium sulfate. The solvent was distilled under reduced pressure and the residue was dried under vacuum. The product was purified by preparative thin layer chromatography with toluene containing 5% ethyl acetate as the eluent to give porphyrin **12** as purple crystals, mp >300 °C, yield, 14 mg (98%). ¹H NMR (400 MHz, Methanol-*d*₄) δ (ppm) 8.72 - 8.81 (m, 3 H, pyrrolic H), 8.67 (d, *J*=4.8 Hz, 1 H, pyrrolic H), 8.45 (d, *J*=8.3 Hz, 2 H, Ar), 8.23 (d, *J*=8.3 Hz, 2 H, Ar), 7.87 - 8.00 (m, 9 H, Ar), 1.52 (s, 54 H, *t*-butyl H); UV-visible λ_{max} (nm, 2% MeOH in CH₂Cl₂): 443, 458, 654, 681; MALDI-TOF-MS *m/z*; calcd for C₇₃H₇₂N₈O₂Zn 1158.82[M⁺], obsd 1158.97.

7,8,17,18-Tetracyano-5-(4-carboxyphenyl)-10,15,20-tris-(3,5-di-*t*-butylphenyl)porphyrin (13). Porphyrin **12** (5 mg, 0.004 mmol) was dissolved in a solution of 7% ethyl acetate in dichloromethane (2.2 mL) in a round bottomed flask equipped with a magnetic stir bar. Trifluoroacetic acid (0.4 mL) was added and the solution was stirred for 4 h at ambient temperature. The solution was washed with water (20 mL) followed by washing with a saturated solution of NaHCO₃ in water (20 mL) and then a second wash with water (50 mL). The solution was dried over anhydrous sodium sulfate, and the solvent was removed under vacuum. The product was purified by preparative thin layer chromatography with 5% methanol in dichloromethane as the solvent to give porphyrin **13** as purple crystals, mp >300 °C, yield, 4 mg (84.4%). ¹H NMR, δ (ppm) 8.97 - 9.09 (m, 3 H, pyrrolic H), 8.89 (d, *J*=3.9 Hz, 1 H, pyrrolic H), 8.59 (d, *J*=7.9 Hz, 2 H, Ar), 8.30 (d, *J*=7.9 Hz, 2 H, Ar), 7.90 - 8.03 (m, 9 H, Ar), 1.50 - 1.58 (m, 54 H, *t*-butyl H), -2.42 (d, *J*=8.3 Hz, 2 H, -NH); UV-visible λ_{max} (nm, CH₂Cl₂): 441, 452, 554, 599, 667, 729; MALDI-TOF-MS *m/z*; calcd for C₇₃H₇₄N₈O₂ 1095.42 [M⁺], obsd 1096.08.

7,8,17,18-Tetrabromo-5,10,15,20-tetrakis-(4-methylphenyl)porphyrin (45). In an oven dried round bottomed flask equipped with a reflux condenser and a magnetic stirrer, **27** (1.0 g, 1.5 mmol) was dissolved in dry chloroform (160 mL) and stirred for 15 min at room temperature. N-bromosuccinimide (1.2 g, 6.7 mmol) was added, the temperature was brought to 80 °C, and the solution was stirred for 2h. The solvent was distilled under reduced pressure and the product was collected on a filter paper and washed with methanol (250mL). The crude product was recrystallized from chloroform and methanol, giving a mixture of **45** and the tribrominated porphyrin, which were not further purified or separated before the next synthetic step. The mixture of porphyrins were obtained as purple crystals; mp >300 °C; yield, 925 mg. MALDI-TOF-MS m/z; calcd for C₄₈H₃₄Br₄N₄ 986.43, and C₄₈H₃₅Br₃N₄ 907.53 [M⁺], obsd 984.5061 and 908.5873.

Zn(II) 2,3,12,13-tetrabromo-5,10,15,20-tetrakis-(4-methylphenyl)porphyrin (46). In a round bottomed flask equipped with a reflux condenser and a magnetic stirrer, the mixture above containing **45** (82 mg) was dissolved in a solution of dimethylformamide (12 mL) and pyridine (0.5 mL) at room temperature. Zinc acetate (181 mg, 0.825mmol) was added and the solution was allowed to reflux for 45 min, after which time the reaction was complete as indicated by thin layer chromatography. The solvent was removed by distillation under reduced pressure, and the product was washed with methanol (250 mL). The product was obtained as a mixture of **46** and the tribrominated analog, which was not further separated. The mixture consisted of purple crystals, mp >300 °C, yield, 80 mg. MALDI-TOF-MS m/z; calcd for C₄₈H₃₂Br₄N₄Zn 1049.82, and C₄₈H₃₃Br₃N₄Zn 970.92 [M⁺], obsd 1049.72 and 969.82.

Zn(II) 2,3,12,13-tetracyano-5,10,15,20-tetrakis-(4-methylphenyl)porphyrin (17). Porphyrin **46** from above containing also the tribrominated analog, Ph₃As, and K₄[Fe(CN)₆] were dried overnight under vacuum and all glassware was oven dried overnight. All reagents **46** (350 mg), tris-(dibenzylideneacetone)dipalladium(0) (60mg, 0.066 mmol), triphenylarsine (163 mg, 0.533 mmol), and potassium ferrocyanide (491 mg, 1.33 mmol) were dissolved in dry and deaerated dimethylformamide (20 mL) in a round-bottomed flask equipped with a magnetic stir bar, and under argon. The round bottomed flask was put in an oil bath which was brought to 100 °C and stirred for 48 h, after which the temperature was increased to 115 °C and stirring was continued for 7.5 h. The solution was allowed to cool to room temperature, additional tris-(dibenzylideneacetone)dipalladium(0) (60 mg, 0.066mmol) and triphenylarsine (163 mg, 0.533mmol) were added, and the solution was allowed to stir for an additional 48 h at 115 °C. The solvent was removed by distillation under reduced pressure, and the product was purified by column chromatography on silica gel using 30% hexane in dichloromethane as the eluent. Final purification was done by preparative thin layer chromatography with toluene containing 5% ethyl acetate as the eluent. This

chromatography yielded **17** (23 mg) and the corresponding tricyanoporphyrin 23.64 mg. ^1H NMR, δ (ppm) 8.76 (s, 4 H, pyrrolic H), 7.92 (d, $J=7.9$ Hz, 8 H, Ar), 7.58 (d, $J=7.9$ Hz, 8 H, Ar), 2.73 (s, 12 H, methyl H); UV-visible λ_{max} (nm, CH_2Cl_2): 443, 458, 658.5, 680; MALDI-TOF-MS m/z ; calcd for $\text{C}_{52}\text{H}_{32}\text{N}_8\text{Zn}$ 834.27 [M^+], obsd 832.68.

7,8,12,13-Tetracyano-5,10,15,20-tetrakis-(4-methylphenyl)porphyrin (18). Porphyrin **17** (12 mg, 0.01 mmol) was dissolved in dichloromethane (7 mL) in a round bottomed flask equipped with a magnetic stir bar. Trifluoroacetic acid (0.5 mL) was added and the solution was allowed to stir for 30 min at room temperature. The solution was washed with water (2×50 mL), followed by a saturated aqueous solution of NaHCO_3 (50 mL). The product was dried over anhydrous sodium sulfate, and the solvent was distilled under reduced pressure. The product was purified by preparative thin layer chromatography using 10% ethyl acetate in toluene as the solvent to give porphyrin **18** as purple crystals, mp >300 °C, yield, 9.5 mg (84.3%). ^1H NMR (400 MHz,) δ (ppm) 8.96 (d, $J=2.00$, 4 H, pyrrolic H), 8.012 (d, $J=8$ Hz, 8 H, Ar), 7.65 (d, $J=7.6$ Hz, 8 H, Ar), 2.75 (s, 12 H, methyl H); UV-visible λ_{max} (nm, CH_2Cl_2): 441, 453, 556, 601, 677, 736; MALDI-TOF-MS m/z ; calcd for $\text{C}_{52}\text{H}_{34}\text{N}_8$ 770.88 [M^+], obsd 770.08.

Zn(II) 2,3,12-tricyano-5,10,15,20-tetrakis-(4-methylphenyl)porphyrin (21). An inseparable mixture of porphyrin 2,3,11,12-tetrabromo-5,10,15,20-tetrakis-(4-methylphenyl)porphyrin and 2,3,12-tribromo-5,10,15,20-tetrakis-(4-methylphenyl)porphyrin was synthesized as reported above for **45**. Ph_3As , and $\text{K}_4[\text{Fe}(\text{CN})_6]$ were dried overnight under vacuum and all glassware was oven dried overnight. All reagents; the mixture of the two β -brominated porphyrins (350 mg), tris-(dibenzylideneacetone)dipalladium(0) (60mg, 0.066 mmol), triphenylarsine (163 mg, 0.533 mmol), and potassium ferrocyanide (491 mg, 1.33 mmol) were dissolved in dry and deaerated dimethylformamide (20 mL) in a round-bottomed flask equipped with a magnetic stir bar, and under argon. The round bottomed flask was put in an oil bath which was brought to 100 °C and stirred for 48 h, after which the temperature was increased to 115 °C and stirring was continued for 7.5 h. The solution was allowed to cool to room temperature, additional tris-(dibenzylideneacetone)dipalladium(0) (60 mg, 0.066mmol) and triphenylarsine (163 mg, 0.533mmol) were added, and the solution was allowed to stir for an additional 48 h at 115 °C. The solvent was removed by distillation under reduced pressure, and the product was purified by column chromatography on silica gel using 30% hexane in dichloromethane as the eluent. Final purification was done by preparative thin layer chromatography with toluene containing 5% ethyl acetate as the eluent. This chromatography yielded pure **21**, mp >300 °C, yield, 24 mg. ^1H NMR δ (ppm) 9.39 (s, 1 H), 8.81 - 8.90 (m, 2 H), 8.75 - 8.80 (m, 2 H), 7.98 (d, $J=7.5$ Hz, 2 H), 7.85 - 7.95 (m, 6 H), 7.50 - 7.61 (m, 8 H), 2.68 - 2.74 (m, 12 H); UV-visible λ_{max} (nm, CH_2Cl_2): 444, 632; MALDI-TOF-MS m/z ; calcd for $\text{C}_{51}\text{H}_{33}\text{N}_7\text{Zn}$ 809.26 [M^+], obsd 807.14.

2,3,12,-Tricyano-5,10,15,20-tetrakis-(4-methylphenyl)porphyrin (22). Porphyrin **21** (12 mg, 0.01 mmol) was dissolved in dichloromethane (7 mL) in a round bottomed flask equipped with a magnetic stir bar. Trifluoroacetic acid (0.5 mL) was added and the solution was allowed to stir for 30 min at room temperature. The solution was washed with water (2 × 50 mL), followed by a saturated aqueous solution of NaHCO₃ (50 mL). The product was dried over anhydrous sodium sulfate, and the solvent was removed by distillation under reduced pressure. The product was purified by preparative thin layer chromatography using 10% ethyl acetate in toluene as the solvent to give porphyrin **22** as purple crystals, mp >300 °C, yield, 9.5 mg (44%). ¹H NMR δ (ppm) 9.29 (s, 1 H, pyrrolic H), 8.97-8.91 (m, 2 H, pyrrolic), 8.86 (d, J=2.4 Hz, 1 H, pyrrolic), 8.01-7.97 (m, 8 H, Ar), 7.62-7.57 (m, 8 H, Ar), 2.72-2.69 (m, 12 H, methyl H); UV-visible λ_{max} (nm, CH₂Cl₂): 444, 545, 586, 648, 707; MALDI-TOF-MS m/z; calcd for C₅₁H₃₅N₇ 745.87 [M⁺], obsd 745.31.

Zn(II) 2,3,12,13-tetrabromo-5,10,15,20-tetrakis-(2,4,6-trimethylphenyl)porphyrin (47). Porphyrin **47** was synthesized from 150 mg (0.137 mmol) of **28** following the method reported for the synthesis of **33**. The product was purified by recrystallization from dichloromethane and methanol to give porphyrin **47**. The product was characterized by thin layer chromatography, no further characterization was done before the next step. The material was obtained as purple crystals, mp >300 °C, yield, 128 mg (80.1%).

Zn(II) 2,3,12,13-tetracyano-5,10,15,20-tetrakis-(2,4,6-trimethylphenyl)porphyrin (19). Porphyrin **47**, Zn(OAc)₂, and Zn dust were dried under vacuum overnight before use, and all glassware was oven dried. N,N-dimethylacetamide was stirred with BaO for 24 h, then refluxed over BaO for 1 h and then distilled under reduced pressure. Porphyrin **47** (44 mg, 0.04 mmol), tris(dibenzylideneacetone)dipalladium(0) (27 mg, 0.03 mmol), 1,1'-bis(diphenylphosphino)ferrocene (34 mg, 0.1 mmol), zinc acetate (2 mg, 0.01 mmol), Zn dust (1 mg, 0.02 mmol), and zinc cyanide (11 mg, 0.1 mmol) were dissolved under argon in N,N-dimethylacetamide (20 mL) in a Schlenk flask equipped with a magnetic stir bar. The Schlenk flask was placed in an oil bath that was brought to a temperature of 115 °C and the solution was stirred under argon for 20 h. Dichloromethane (60 mL) was added to the solution, which was then washed with water (5 × 100 mL). The organic layer was dried over anhydrous sodium sulfate and then the solvent was removed by distillation under reduced pressure. The product was purified by column chromatography on silica gel using a solution of 10% ethyl acetate in toluene as the eluent. The product was further purified by recrystallization from dichloromethane and hexane to yield porphyrin **19** as purple crystals, mp >300 °C, yield, 7 mg (19.5%). ¹H NMR (400 MHz,) δ (ppm) 8.57 (s, 4 H, pyrrolic H), 7.30 (s, 8 H, Ar), 2.63 (s, 12 H, methyl H), 1.84 (s, 25 H, methyl H); UV-visible λ_{max} (nm, 2% MeOH in CH₂Cl₂): 444, 459, 662, 686; MALDI-TOF-MS m/z; calcd for C₆₀H₄₈N₈Zn 946.49 [M⁺], obsd 946.94.

7,8,17,18-Tetracyano-5,10,15,20-tetrakis-(2,4,6-trimethylphenyl)porphyrin (20). Porphyrin **19** (5.0 mg, 0.0053 mmol) was dissolved in a solution of 3.8% ethyl acetate in dichloromethane (26 mL) in a round bottomed flask equipped with a magnetic stir bar. Trifluoroacetic acid (5 mL) was added and the solution was allowed to stir for 30 min at room temperature. Concentrated HCl (0.5 mL) was added to the solution, which was stirred for an additional 5 min. The solution was washed with water (2 × 50 mL), followed by a saturated aqueous solution of NaHCO₃ (50 mL). The product was dried over anhydrous sodium sulfate, and the solvent was removed by distillation under reduced pressure. The product was purified by preparative thin layer chromatography using 10% ethyl acetate in toluene as the solvent to give porphyrin **20** as purple crystals, mp >300 °C, yield, 4 mg (85.8%). ¹H NMR, δ (ppm) 8.79 (d, *J*=1.3 Hz, 4 H, pyrrolic H), 7.33 (s, 8 H, Ar), 2.64 (s, 12 H, methyl H), 1.82 (s, 24 H, methyl H), -2.14 (br s, 2 H, -NH); UV-visible λ_{max} (nm, CH₂Cl₂): 439, 451, 552, 599, 673, 733; MALDI-TOF-MS *m/z*; calcd for C₆₀H₅₀N₈ 883.09 [M⁺], obsd 883.98.

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