Supplementary Material/*Organic Letters*

Ortho-(bromomethyl) substituted tetraarylporphyrin building blocks

Norbert Jux

Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestr. 42, 91054 Erlangen

jux@organik.uni-erlangen.de

Experimental procedures and selected physical data for compounds **1**, **3-17**

2,6-Bis(methoxymethyl)-4-*t*-butyl benzaldehyde 1:
4-*t*-Butyl-2,6-bis(methoxymethyl)-bromobenzene (30.1 g, 100 mmol) was dissolved in 250 mL of dry Et_2O and cooled to -78 °C. At this temperature a solution of n-butyl lithium (70 mL of a 1.6 M solution in hexanes, 112 mmol) was added dropwise. After stirring for 2 h at -78 °C dry DMF (11.0 g, 11.6 mL, 150 mmol) was added dropwise and the mixture stirred for another hour at this temperature. After warming up to room temperature a saturated solution of NH_4Cl was added. After aqueous workup with Et_2O as eluent the organic layers were combined and dried ($MgSO_4$). The solvent was removed in vacuo and the residue purified by column chromatography (silica gel, column: length 20 cm, diameter 7 cm, eluent: CH_2Cl_2/hexanes 1:1). The material obtained by this procedure was recrystallized from EtOH. Yield 23 g (92 %), white needles, m. p. 44 °C.
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 10.45 (s, 1 H, CHO), 7.55 (s, 2 H, Ar-H), 4.80 (s, 4 H, CH_2O), 3.45 (s, 6 H, OCH_3), 1.35 (s, 9 H, *t*-butyl); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 192.5, 156.8, 141.2, 128.6, 124.9, 72.7, 58.3, 35.2, 30.8; MS (DI): *m/z* (%) = 250 (M^+, 9), 218 (50), 203 (100).

5,10,15,20-Tetrakis[2',6'-bis(methoxymethyl)-4'-*t*-butylphenyl]porphyrin 3:
2,6-Bis(methoxymethyl)-4-*t*-butyl benzaldehyde **1** (2.50 g, 10 mmol) was dissolved in 1 L of CH_2Cl_2 containing 10 mL of dry EtOH. Pyrrole (0.67 g, 0.69 mL, 10 mmol) was added and the reaction purged with argon for 30 min. BF_3*OEt_2 (0.47 g, 0.42 mL, 3.3 mmol) was added and the mixture stirred for 2 h in the dark. DDQ (1.70 g, 7.5 mmol) was added and the reaction mixture stirred for another 2 h. Evaporation of the solvent and pre-cleaning of the dark residue through a silica gel plug with CH_2Cl_2/ethyl acetate 10:1 as eluent yielded a dark bluish material. Column chromatography (silica gel, column: length 25 cm, diameter 7 cm, eluent: CH_2Cl_2/EtOAc 19:1; twice) gave the desired porphyrin. Yield 0.21 g (7 %); bluish needles, m. p. ca. 250 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.61 (s, 8 H, β-pyrr.), 7.86 (s, 8 H, Ar-H), 3.93 (s, 16 H, CH_2O), 2.78 (s, 24 H, OCH_3), 1.56 (s, 36 H, *t*-butyl), -2.55 (br. s, 2 H, NH); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 152.1, ca. 147, 139.5, 134.9, ca. 131, 122.2, 115.1, 73.1, 58.0, 35.2, 31.7; MS (FAB, NBA): *m/z* (%) = 1190 (M^+, 100), 1160 (14); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 308 (14100), 370 (24600), 420 (492000), 515 (21200), 547 (5000), 591 (6200), 646 (1800).

5,15-Bis[2',6'-bis(methoxymethyl)-4'-*t*-butylphenyl]-10,20-bis(4'-*t*-butylphenyl)porphyrin 4:
4-*t*-Butyl-2,6-bis(methoxymethyl)phenyl-dipyrromethane **6** (1.83 g, 5 mmol) and 4-*t*-butyl benzaldehyde (0.81 g, 5 mmol) were dissolved in 1 L of dry CH_2Cl_2 containing 10 mL of dry EtOH. The reaction was purged with argon for 30 min. BF_3*OEt_2 (0.47 g, 0.42 mL, 3.3 mmol) was added and the mixture stirred for 2 h in the dark. DDQ (1.70 g, 7.5 mmol) was added and the reaction mixture stirred for another 2 h. Evaporation of the solvent and pre-cleaning of the dark residue through a silica gel plug with CH_2Cl_2 yielded a bluish material. Column chromatography (silica gel, column: length 25 cm, diameter 7 cm, eluent: CH_2Cl_2) gave the desired porphyrin. Yield 0.53 g (21 %); bluish needles, m. p. ca. 250 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.85 (d, 4 H, β-pyrr., ^3J = 4.8 Hz), 8.65 (d, 4 H, β-pyrr., ^3J = 4.8 Hz), 8.14 (d, 4 H, Ar-H, ^3J = 8.2 Hz), 7.87 (s, 4 H, Ar-H), 7.77 (d, 4 H, Ar-H, ^3J = 8.2 Hz), 3.93 (s, 8 H, CH_2O), 2.78 (s, 12 H, OCH_3), 1.63 (s, 18 H, *t*-butyl), 1.60 (s, 18 H, *t*-butyl), -2.63 (br. s, 2 H, NH); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 151.9, 150.6, ca. 147 (2C), 139.5, 138.7, 135.2, 134.5, ca. 131 – 130 (2C), 123.7, 122.2, 120.1, 114.8, 73.0, 58.1, 35.2, 34.9, 31.7, 31.6; MS (FAB, NBA): *m/z* (%) = 1015 (M^+, 100), 1001 (11), 983 (11); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 302 (13900), 368 (21400), 420 (444000), 516 (18200), 551, (71000), 592 (5300), 647 (3500).

5-[2',6'-Bis(methoxymethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin 5:
4-*t*-Butyl-2,6-bis(methoxymethyl)phenyl-dipyrromethane **6** (0.92 g, 2.5 mmol), 4-*t*-butyl benzaldehyde (1.22 g, 7.5 mmol), and pyrrole (0.34 g, 0.35 mL, 5 mmol) were dissolved in 1 L of dry CH_2Cl_2 containing 10 mL of dry

EtOH. The reaction was purged with argon for 30 min. BF_3*OEt_2 (0.47 g, 0.42 mL, 3.3 mmol) was added and the mixture stirred for 2 h in the dark. DDQ (1.70 g, 7.5 mmol) was added and the reaction mixture stirred for another 2 h. Evaporation of the solvent and pre-cleaning of the dark residue through a silica gel plug with CH_2Cl_2 yielded a bluish material. Column chromatography (silica gel, column: length 25 cm, diameter 7 cm, eluent: CH_2Cl_2/hexanes 2:1) gave the desired porphyrin, which eluted as second band after tetrakis(4-*t*-butylphenyl)porphyrin. Yield 0.29 g (12.5 %); bluish needles, m. p. ca. 250 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.88 (s, 4 H, β-pyrr.), 8.83 (d, 2 H, β-pyrr., ^3J = 4.6 Hz), 8.64 (d, 2 H, β-pyrr., ^3J = 4.6 Hz), 8.14 (m, 6 H, Ar-H), 7.87 (s, 2 H, Ar-H), 7.76 (m, 6 H, Ar-H), 3.94 (s, 4 H, CH_2O), 2.75 (s, 6 H, OCH_3), 1.63 (s, 9 H, *t*-butyl), 1.61 (s, 9 H, *t*-butyl), 1.60 (s, 18 H, *t*-butyl), -2.68 (br. s, 2 H, NH); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 151.8, 150.5, ca. 147 - 145 (4C), 139.6 (2 C), 139.3, 139.0, 135.3, 134.5, 134.5, ca. 132 – 130 (4C), 123.6, 123.6, 122.2, 120.6, 120.1, 114.2, 73.0, 58.1, 35.2, 34.9 (2C), 31.9, 31.7 (2C); MS (FAB, NBA): *m/z* (%) = 927 (M^+, 100), 912 (12), 895 (10); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 299 (13800), 378 (21400), 420 (451000), 516 (16900), 552 (8200), 591(4900), 648 (4000).

4-*t*-Butyl-2,6-bis(methoxymethyl)phenyl-dipyrromethane 6:
2,6-Bis(methoxymethyl)-4-*t*-butyl benzaldehyde **1** (2.5 g, 10 mmol) was dissolved in 50 mL of dry pyrrole (distilled from calcium hydride). The solution was purged with argon for 30 min. BF_3*OEt_2 (0.41 g, 0.37 mL, 3 mmol) was added and the mixture stirred for 30 min. in the dark. 100 mL of CH_2Cl_2 were added followed by immediate addition of 100 mL of a 0.1N sodium hydroxide solution. After separation of the layers the aqueous layer was extracted twice with 50 mL of CH_2Cl_2. The organic layers were combined and dried (Na_2SO_4). CH_2Cl_2 was removed under reduced pressure, the excess of pyrrole was distilled off in high vacuum. Column chromatography (silica gel, column: length 25 cm, diameter 7 cm, eluent: hexanes/EtOAc/NEt_3 80:20:1) yielded the desired pyrromethane, which eluted as second band after tiny amounts of pyrrole. The pyrromethane was recognized easily on thin layer sheets by its purple color when bromine was used as colorant. The material so obtained was recrystallized from hexanes at -18°C. Yield 2.11 g (58%); yellowish platelets, m. p. 95 °C.
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.81 (br. s, 2 H, NH), 7.34 (s, 2 H, Ar-H), 6.64 (m, 2 H, α-pyrr.), 6.12 (m, 2 H, β-pyrr.), 6.02 (m, 3 H, γ-pyrr. + C-H), 4.26 (br. s, 4H, CH_2O), 3.30 (br. s, 6 H, OCH_3), 1.31 (s, 9 H, *t*-butyl); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 149.8, 136.7, 136.3, 131.3 128.3, 116.7, 107.9, 106.6, 73.4, 58.1, 37.8, 34.3, 21.2; MS (DI): *m/z* (%) = 366 (M^+, 37), 334 (72), 301 (90) 245 (100).

5,10,15,20-Tetrakis[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]porphyrin 7:
5,10,15,20-Tetrakis[2',6'-bis(methoxymethyl)-4'-*t*-butylphenyl]porphyrin **3** (119 mg, 0.1 mmol) was dissolved in 20 mL of CH_2Cl_2. 30 mL of a 33%-solution of HBr in glacial acetic acid was added and the mixture stirred overnight at room temperature. The reaction mixture was quenched with water, the layers were separated, the organic layer washed with a saturated Na_2CO_3-solution and dried ($MgSO_4$). The solvent was removed in vacuo and the bluish residue purified by column chromatography (silica gel, column: length 25 cm, diameter 3 cm, eluent: hexanes/CH_2Cl_2 3:1). The desired porphyrin eluted as first band. Yield 139 mg (88%); bluish powder, m. p. ca. 220 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8. 61 (s, 8 H, β-pyrr.), 7.86 (s, 8 H, Ar-H), 4.07 (s, 16 H, CH_2Br), 1.61 (s, 36 H, *t*-butyl), -2.46 (br. s, 2 H, NH); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 153.2, ca. 147, 139.5, 137.5, ca. 131, 127.3, 113.6, 35.1, 32.1, 31.5; MS (FAB, NBA): *m/z* (%) = 1583 (M^+, 100), 1503 (21), 1421 (7); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 312 (16200), 378 (24400), 423 (402000), 516 (19800), 542 (3300), 587 (6100), 643 (1000).

5,15-Bis[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]-10,20-bis(4'-*t*-butylphenyl)porphyrin 8:
5,15-Bis[2',6'-bis(methoxymethyl)-4'-*t*-butylphenyl]-10,20-bis(4'-*t*-butylphenyl)porphyrin **4** (102 mg, 0.1 mmol) was dissolved in 20 mL of CH_2Cl_2. 30 mL of a 33%-solution of HBr in glacial acetic acid was added and the mixture stirred overnight at room temperature. The reaction mixture was quenched with water, the layers were separated, the organic layer washed with a saturated Na_2CO_3-solution and dried ($MgSO_4$). The solvent was removed in vacuo and the bluish residue purified by column chromatography (silica gel, column: length 25 cm, diameter 3 cm, eluent: hexanes/CH_2Cl_2 2:1). The desired porphyrin eluted as first band. Yield 103 mg (85%); bluish powder, m. p. ca. 220 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.88 (d, 4 H, β-pyrr., ^3J = 4.8 Hz), 8.63 (d, 4 H, β-pyrr., ^3J = 4.8 Hz), 8.16 (d, 4 H, Ar-H, ^3J = 8.3 Hz), 7.88 (s, 4 H, Ar-H), 7.76 (d, 4 H, Ar-H, ^3J = 8.3 Hz), 4.07 (s, 8 H, CH_2Br), 1.63 (s, 18 H, *t*-butyl), 1.59 (s, 18 H, *t*-butyl), -2.61 (br. s, 2 H, NH); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 153.0, 150.7, ca. 147 (2 C), 139.5, 138.6, 137.9, 134.5, ca. 131 (2 C), 127.2, 123.7, 120.7, 112.9, 35.1, 34.9, 32.2, 31.6, 31.5; MS (FAB, NBA): *m/z* (%) = 1210 (M^+, 100), 1131 (18), 1049 (10); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 305 (18600), 376 (23400), 422 (425000), 517 (19100), 549 (6100), 591 (5900), 646 (3000).

5-[2',6'-Bis(bromomethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin 9:
5-[2',6'-Bis(methoxymethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin **5** (93 mg, 0.1 mmol) was dissolved in 20 mL of CH_2Cl_2. 30 mL of a 33%-solution of HBr in glacial acetic acid was added and the mixture stirred overnight at room temperature. The reaction mixture was quenched with water, the layers were separated, the organic layer washed with a saturated Na_2CO_3-solution and dried ($MgSO_4$). The solvent was removed in vacuo and the bluish residue purified by column chromatography (silica gel, column: length 25 cm, diameter 3 cm, eluent: hexanes/CH_2Cl_2 2:1). The desired porphyrin eluted as first band. Yield 87 mg (85%); bluish powder, m. p. ca. 250 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.88 (s, 4 H, β-pyrr.) 8.86 (d, 2 H, β-pyrr., ^3J = 4.8 Hz), 8.60 (d, 2 H, β-pyrr., ^3J = 4.8 Hz), 8.15 (m, 6H, Ar-H), 7.87 (s, 2H, Ar-H), 7.75 (m, 6H, Ar-H), 4.07 (s, 4 H, CH_2Br), 1.62 (s, 9 H, *t*-butyl), 1.60 (s, 9 H, *t*-butyl), 1.59 (s, 18 H, *t*-butyl), -2.66 (br. s, 2 H, NH); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 152.8, 150.5, ca. 147 – 145 (4C), 139.4, 139.2, 138.9, 138.0, 134.5 (2C), ca. 132 – 130 (4C), 127.2, 125.8, 123.6, 122.4, 121.1, 120.4, 111.8, 35.1, 34.9 (2C), 32.4, 31.7, 31.5, 31.2; MS (FAB, NBA): *m/z* (%) = 1025 (M^+, 100), 945 (8), 863 (8); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 302 (14800), 420 (450000), 517 (17400), 552 (7100), 590 (5100), 647 (3500).

Zinc-5,10,15,20-tetrakis[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]porphyrin 10:
5,10,15,20-Tetrakis[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]porphyrin **7** (32 mg, 0.02 mmol) was dissolved in 5 mL of CH_2Cl_2. A solution of $Zn(OAc)_2$ (18 mg, 0.1 mmol) in 1 mL of MeOH containing 1% of glacial acetic acid was added. The mixture was stirred for 1 h at room temperature. Water was added, the layers separated and the organic layer washed with a saturated Na_2CO_3-solution. The organic layer was dried ($MgSO_4$) and evaporated. The zinc porphyrin was purified by column chromatography (silica gel, column: length 20 cm, diameter 3 cm, eluent: hexanes/CH_2Cl_2 3:1). Yield 31 mg (95%), pink powder, m. p. ca. 220 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.65 (s, 8 H, β-pyrr.), 7.85 (s, 8 H, Ar-H), 4.09 (s, 16 H, CH_2Br), 1.61 (s, 36 H, *t*-Butyl); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 152.8, 150.3, 139.2, 138.6, 132.1, 127.2, 114.2, 35.1, 32.4, 31.5; MS (FAB, NBA): *m/z* (%) = 1646 (M^+, 100), 1565 (18), 1485 (8); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 317 (17200), 345 (10700), 404 (39700), 424 (547000), 551 (21300), 589 (2900).

Zinc-5,15-bis[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]-10,20-bis(4'-*t*-butylphenyl)porphyrin 11:
5,15-Bis[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]-10,20-bis(4'-*t*-butylphenyl)porphyrin **8** (48 mg, 0.04 mmol) was dissolved in 10 mL of CH_2Cl_2. A solution of $Zn(OAc)_2$ (37 mg, 0.2 mmol) in 2 mL of MeOH containing 1% of glacial acetic acid was added. The mixture was stirred for 1 h at room temperature. Water was added, the layers separated and the organic layer washed with a saturated Na_2CO_3-solution. The organic layer was dried ($MgSO_4$) and evaporated. The zinc porphyrin was purified by column chromatography (silica gel, column: length 20 cm, diameter 3 cm, eluent: hexanes/CH_2Cl_2 2:1). Yield 48 mg (95%), pink powder, m. p. ca. 250 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.95 (d, 4 H, β-pyrr., ^3J = 4.6 Hz), 8.68 (d, 4 H, β-pyrr., ^3J = 4.6 Hz), 8.16 (d, 4 H, Ar-H, ^3J = 8.1 Hz), 7.86 (s, 4 H, Ar-H), 7.74 (d, 4 H, Ar-H, ^3J = 8.1 Hz), 4.07 (s, 8 H, CH_2Br), 1.62 (s, 18 H, *t*-butyl), 1.58 (s, 18 H, *t*-butyl); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 152.7, 150.8, 149.9 (2C), 139.4, 139.2, 134.4, 132.5, 131.6, 127.1, 123.8, 121.5, 110.5, 35.1, 34.8, 32.5, 31.7, 31.5; MS (FAB, NBA): *m/z* (%) = 1274 (M^+, 100), 1193 (12), 1113 (8); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 306 (8800), 402 (34000), 422 (461000), 550 (17900), 587 (2100).

Zinc-5-[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin 12:
5-[2',6'-Bis[bromomethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin **9** (41 mg, 0.04 mmol) was dissolved in 10 mL of CH_2Cl_2. A solution of $Zn(OAc)_2$ (37 mg, 0.2 mmol) in 2 mL of MeOH containing 1% of glacial acetic acid was added. The mixture was stirred for 1 h at room temperature. Water was added, the layers separated and the organic layer washed with a saturated Na_2CO_3-solution. The organic layer was dried ($MgSO_4$) and evaporated. The zinc porphyrin was purified by column chromatography (silica gel, column: length 20 cm, diameter 3 cm, eluent: hexanes/CH_2Cl_2 3:1). Yield 41 mg (95%), pink powder, m. p. ca. 250 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 9.00 (s, 4 H, β-pyrr.) 8. 97 (d, 2 H, β-pyrr., ^3J = 4.6 Hz), 8.70 (d, 2 H, β-pyrr., ^3J = 4.6 Hz), 8.18 (m, 6 H, Ar-H), 7.88 (s, 2 H, Ar-H), 7.76 (m, 6 H, Ar-H), 4.10 (s, 4 H, CH_2Br), 1.64 (s, 9 H, *t*-butyl), 1.63 (s, 9 H, *t*-butyl), 1.62 (s, 18 H, *t*-butyl); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 152.6, 150.6, 150.5, 150.3, 149.9, 139.8, 139.6, 139.2, 138.8, 134.4 (2C), 132.5, 132.2, 132.0, 131.3, 127.1, 123.5 (3C), 122.0, 121.3, 112.8, 35.1, 34.9 (2C), 32.6, 31.7, 31.5 (2C), 29.7; MS (FAB, NBA): *m/z* (%) = 1088 (M^+, 100), 1007 (6), 925 (60); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 306 (16300), 402 (42700), 422 (428000), 550 (22800), 587 (4000).

Zinc-5-[2',6'-bis(azidomethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin 13:
Zinc-5-[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin **12** (43 mg, 0.04 mmol) was dissolved in 5 mL of dry THF. NaN_3 (10 mg, 0.15 mmol) and [18]crown-6 (5 mg, 0.02 mmol) were

added. The mixture was refluxed overnight. Water was added, the layers separated and the organic layer washed with water. The organic layer was dried ($MgSO_4$) and evaporated. The porphyrin was purified by column chromatography (silica gel, column: length 20 cm, diameter 3 cm, eluent: hexanes/CH_2Cl_2 3:1). Yield 37 mg (92%), pink powder, m. p. ca. 200 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.96 (d, 2 H, β-pyrr., ^3J = 5.0 Hz), 8.94 (d, 2 H, β-pyrr., ^3J = 5.0 Hz), 8.81 (d, 2 H, β-pyrr., ^3J = 4.4 Hz), 8.28 (d, 2 H, β-pyrr., ^3J = 4.4 Hz), 8.14 (d, 2 H, Ar-H, ^3J = 8.3 Hz), 8.07 (d, 4 H, Ar-H, ^3J = 8.3 Hz), 7.75 (d, 2 H, Ar-H, ^3J = 8.3 Hz), 7.72 (d, 4 H, Ar-H, ^3J = 8.3 Hz), 7.15 (br. s, 2 H, Ar-H, ^3J = 8.3 Hz), 3.10 (br. s, 4 H, CH_2N_3), 1.62 (s, 18 H, *t*-butyl), 1.59 (s, 18 H, *t*-butyl); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 152.0, 150.6, 150.5, 150.3, 150.2, 149.0, 139.8, 139.6, 137.5, 136.7, 134.3, 134.2, 133.0, 132.3, 132.1, 129.7, 123.6, 123.4, 122.0, 121.2, 11.6, 52.4, 34.9, 34.7, 31.9, 31.7, 31.5, 29.7; MS (FAB, NBA): *m/z* (%) = 1011 (M^+, 90), 984 (M^+-N_2, 30), 956 (M^+-2N_2, 92), 940 (100); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 306 (16800), 350 (12600), 401 (44100), 420 (429000), 549 (22500), 587 (4700).

Zinc-5-[2'-(bromomethyl)-6'-(cyanomethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin 14:
Zinc-5-[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin **9** (43 mg, 0.04 mmol) was dissolved in 5 mL of THF. KCN (3 mg, 0.05 mmol) and [18]crown-6 **13** (5 mg, 0.02 mmol) were added. The mixture was stirred overnight. Water was added, the layers separated and the organic layer washed with water. The organic layer was dried ($MgSO_4$) and evaporated. The porphyrin was purified by column chromatography (silica gel, column: length 20 cm, diameter 3 cm, eluent: hexanes/CH_2Cl_2 2:1). The first band contained unreacted starting material, the second band the desired product. The dicyanoporphyrin was found in the third band. Yield 39 mg (95%), pink powder, m. p. ca. 250 °C (decomp.).
^{1}H NMR ($CDCl_3$/TMS, 400 MHz, 25 °C): δ = 8.98 (s, 4 H, β-pyrr.), 8.96 (d, 2 H, β-pyrr., ^3J = 4.7 Hz), 8.63 (d, 2 H, β-pyrr., ^3J = 4.7 Hz), 8.14 (m, 6 H, Ar-H), 7.91 (d, 1 H, Ar-H, ^4J = 2.0 Hz), 7.89 (d, 1 H, Ar-H, ^4J = 2.0 Hz), 7.79 (m, 6 H, Ar-H), 4.12 (s, 2 H, CH_2Br), 3.21 (s, 2 H, CH_2CN), 1.64 (s, 9 H, *t*-butyl), 1.61 (s, 9 H, *t*-butyl), 1.60 (s, 18 H, *t*-butyl); ^{13}C NMR ($CDCl_3$/TMS, 100.5 MHz, 25 °C): δ = 152.9,150.7, 150.5, 150.4 (2C), 149.2, 139.6, 139.5, 139.1, 138.5, 134.3, 133.1, 132.4, 132.2, 130.2, 126.8, 124.7, 123.5, 122.2, 121.5, 117.8, 112.4, 35.2, 34.9, 32.4, 31.7, 31.5, 23.3; MS (FAB, NBA): *m/z* (%) = 1033 (M^+, 100), 953 (25); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 311 (13000), 350 (9300), 401 (38000), 421 (498000), 549 (19900), 587 (3700).

Zinc-5,10,15,20-Tetrakis[2',6'-bis(*N*-methylene-[4''-*t*-butylpyridinium])-4'-*t*-butylphenyl]porphyrin octa-bromide 15:
Zinc-5,10,15,20-tetrakis[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]porphyrin **10** (33 mg, 0.02 mmol) was dissolved in 5 mL of dry toluene. 4-*t*-Butyl pyridine (220 mg, 1.6 mmol) was added. The mixture was refluxed overnight. After the mixture was cooled to room temperature, dry Et_2O was added to the stirred solution. The precipitate was collected, washed with ether and redissolved in dry methanol. Again, ether was added, the precipitate collected and dried. The material obtained by this procedure was clean according to NMR. Yield 47 mg (86%), brownish powder, m. p. ca. 220 °C (decomp.).
^{1}H NMR (MeOH, 400 MHz, 25 °C): δ = 8.32 (d, 16 H, pyridine-H, ^3J = 6.8 Hz), 8.28 (s, 8 H, Ar-H), 7.93 (s, 8 H, β-pyrr.), 7.85 (d, 16 H, pyridine-H, ^3J = 6.8 Hz), 5.49 (s, 16 H, CH_2N), 1.60 (s, 36 H, *t*-butyl), 1.29 (s, 72 H, *t*-butyl pyridine); ^{13}C NMR (MeOH, 100.5 MHz, 25 °C): δ = 173.2, 151.4, 145.4, 141.5, 139.0, 137.1, 133.0, 128.9, 126.5, 114.8, 63.6, 37.6, 36.4, 31.7, 30.4; MS (FAB, NBA): *m/z* (%) not available so far; UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 218 (128000), 327 (23200), 368 (18700), 416 (37300), 437 (288000), 482 (17600), 567 (15700), 606 (6400), 747 (5100).

Zinc-5,15-Bis[2',6'-bis(*N*-methylene-[4''-*t*-butylpyridinium])-4'-*t*-butylphenyl]-10,20-bis(4'-*t*-butylphenyl)-porphyrin tetrabromide 16:
Zinc-5,15-bis[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]-10,20-bis(4'-*t*-butylphenyl)porphyrin **11** (38 mg, 0.03 mmol) was dissolved in 5 mL of dry toluene. 4-*t*-Butyl pyridine (160 mg, 1.2 mmol) was added. The mixture was refluxed overnight. After the mixture was cooled to room temperature, dry Et_2O was added to the stirred solution. The precipitate was collected, washed with ether and redissolved in dry methanol. Again, ether was added, the precipitate collected and dried. The material obtained by this procedure was clean according to NMR. Yield 49 mg (90%), blue powder, m. p. ca. 220 °C (decomp.).
^{1}H NMR (MeOH, 400 MHz, 25 °C): δ = 8.56 (d, 4 H, β-pyrr., ^3J = 4.6 Hz), 8.53 (s, 4 H, Ar-H), 8.16 (d, 4 H, Ar-H, ^3J = 8.3 Hz), 7.91 (d, 4 H, β-pyrr., ^3J = 4.6 Hz), 7.81 (d, 4H, Ar-H, ^3J = 8.3 Hz), 7.17 (d, 8 H, pyridine-H, ^3J = 6.8 Hz), 6.94 (d, 8 H, pyridine-H, ^3J = 6.8 Hz), 5.44 (s, 8 H, CH_2N), 1.82 (s, 18 H, *t*-butyl), 1.61 (s, 18 H, *t*-butyl), 1.04 (s, 36 H, *t*-butyl pyridine); ^{13}C NMR (MeOH, 100.5 MHz, 25 °C): δ = 172.0, 156.2, 152.2, 152.0, 150.2, 144.2, 144.0, 140.6, 137.1, 136.3, 135.2, 131.7, 129.5, 125.5, 124.7, 123.5, 112.4, 63.9, 37.1, 36.6, 35.8, 32.1, 32.0, 30.1; MS (FAB, NBA): *m/z* (%) = 1735 (M^+ - Br, 2), 1654 (M^+ - 2Br, 3), 1023 (100); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 218 (61600), 323 (20700), 349 (13900), 435 (413000), 565 (16900), 613 (8300).

Zinc-5-[2',6'-bis(*N*-methylene-[4''-*t*-butylpyridinium])-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)-porphyrin dibromide 12:

Zinc-5-[2',6'-bis(bromomethyl)-4'-*t*-butylphenyl]-10,15,20-tris(4'-*t*-butylphenyl)porphyrin **12** (43 mg, 0.04 mmol) was dissolved in 5 mL of dry toluene. 4-*t*-Butyl pyridine (110 mg, 0.8 mmol) was added. The mixture was refluxed overnight. After the mixture was cooled to room temperature, dry Et_2O was added to the stirred solution. The precipitate was collected, washed with ether and redissolved in dry methanol. Again, ether was added, the precipitate collected and dried. The material obtained by this procedure was clean according to NMR. Yield 52 mg (95%), blue crystals, m. p. ca. 220 °C (decomp.).

^{1}H NMR (MeOH, 400 MHz, 25 °C): δ = 8.94 (s, 4 H, β-pyrr.) 8. 61 (d, 2 H, β-pyrr., ^3J = 4.5 Hz), 8.52 (s, 2 H, Ar-H), 8.15 (m, 6 H, Ar-H), 7.95 (d, 2 H, β-pyrr., ^3J = 4.5 Hz), 7.85 (m, 6 H, Ar-H),), 6.66 (d, 4 H, pyridine-H, ^3J = 7.0 Hz), 6.46 (d, 4 H, pyridine-H, ^3J = 7.0 Hz), 5.49 (s, 4 H, CH_2N), 1.82 (s, 9 H, *t*-butyl), 1.64 (s, 9 H, *t*-butyl), 1.62 (s, 18 H, *t*-butyl), 0.80 (s, 18 H, *t*-butyl pyridine); ^{13}C NMR (MeOH, 100.5 MHz, 25 °C): δ = 171.9, 152.6, 152.4, 152.0, 151.1, 149.2, 143.9, 143.8, 140.9, 137.4, 136.0, 135.5, 134.6, 133.7, 133.5, 131.8, 128.8, 124.7 (2C), 123.1, 64.4, 37.9, 36.8, 36.6, 35.8, 32.1, 32.0, 29.9; MS (FAB, NBA): *m/z* (%) = 1277 (M^+-Br, 54), 926 (100); UV/VIS (CH_2Cl_2): λ_{max}[nm] (ε) = 217 (69300), 233 (62600), 315 (11100), 352 (8700), 427 (262000), 559 (13100), 598 (5800).