

Supporting Information

Synthesis of 5, 10, 15, 20-tetrakis(4-*tert*-butyl-2, 6-dicarboxyphenyl)porphyrin : a versatile bis-faced porphyrin synthon for D_4 -symmetric chiral porphyrins

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Experimental procedures and characterization data for **1-15**.

General Considerations

All solvents were purified by standard methods. Unless otherwise noted, reagents were obtained from commercial suppliers and used without further purification. Melting points were determined on a cover glass using an electrothermal melting point apparatus and are uncorrected. NMR spectrometry was performed on a JMN-LA 300 (300 MHz, JEOL). ¹H NMR chemical shifts in CDCl₃ are reported relative to internal TMS. ¹H NMR chemical shifts in CD₂Cl₂ and ¹³C NMR chemical shifts are reported relative to the solvent peak. Mass spectrometry was performed on an SX-102 mass spectrometer (JEOL). UV-visible spectrometry was performed on a UV-1600 (Shimadzu). Silica gel column chromatography was performed on Wakogel C-200 (Wako). Preparative TLC was performed on Silica gel 60 F₂₅₄ (Merck).

4-*tert*-Butyl-2, 6-dibromotoluene **8**

Br₂ (200 g, 12.4 mol) was added dropwise to a mixture of 4-*tert*-butyltoluene (100 ml, 0.57 mol), iron powder (500 mg), and CCl₄ (60 ml) over 1 h at room temperature. Then the reaction mixture was heated mildly at 40° for 5 h. It was poured into water (100 ml), the organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was dried with Na₂SO₄, and evaporated under reduced pressure. The residue was distilled (b.p. 120-124° at 4.5 mmHg) to give an equimolar mixture (153 g) of 4-*tert*-butyl-2,6-dibromotoluene **8** (colorless oil, 77 g, 0.25 mol, 44%) and 4-*tert*-butyl-2,5-dibromotoluene **9** (77 g, 0.25 mol, 44%), which were inseparable by distillation or silica gel column chromatography. The molar ratio was determined by ¹H NMR spectral analysis; ¹H NMR (CDCl₃) δ 1.28 (9H, s), 1.40 (9H, s), 2.21 (3H, s), 2.56 (3H, s), 7.37 (1H, s), 7.47 (1H, s), 7.53 (2H, s).

4-*tert*-Butyl-2,6-dibromobenzyl alcohol **10**

N-Bromosuccinimide (30 g, 0.17 mol) and the equimolar mixture of 4-*tert*-butyl-2,6-dibromotoluene **8** and 4-*tert*-butyl-2,5-dibromotoluene **9** (50 g, total 0.16 mol) in CCl₄ (600 ml) were heated with a halogen lamp (500 W) for 6 h. After the solution was cooled to room temperature, the precipitate was removed by filtration, and the filtrate was evaporated under reduced pressure. To the residue dissolved in acetonitrile (600 ml), CH₃COOK (38 g, 0.39 mol) and trioctylmethylammonium chloride (1.5 g) were added and the whole was refluxed for 6 h. Then the reaction mixture was cooled to room temperature and evaporated. To the residue dissolved in ethanol (300 ml), 2.7 M

KOH aqueous solution (150 ml) was added. The solution was refluxed for 2.5 h, then evaporated to 70 ml, water (100 ml) was added, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was dried with Na₂SO₄ and evaporated. The residue was purified by silica gel column chromatography (CH₂Cl₂:n-hexane), which afforded an inseparable equimolar mixture (colorless oil, 44 g) of 4-*tert*-butyl-2,6-dibromobenzyl alcohol **10** (22 g, 69 mmol, 85%) and 4-*tert*-butyl-2,5-dibromobenzyl alcohol **11** (22 g, 69 mmol, 85%); ¹H NMR (CDCl₃) 1.27 (9H, s), 1.49 (9H, s), 2.05 (2H, bs), 4.64 (2H, s), 4.94 (2H, s), 7.56 (2H, s), 7.63 (1H, s), 7.68 (1H, s).

4-*tert*-Butyl-2,6-dibromobenzaldehyde **12**

To a mixture of benzyl alcohols **10** and **11** (126 g, total 0.39 mol), 4-methoxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (1.43 g, 7.7 mmol) and KBr (4.5 g, 38 mmol) in CH₂Cl₂ (1.2 L) was added a mixture of 1.4 M NaOCl aqueous solution (278 ml) and saturated NaHCO₃ aqueous solution (644 ml) at 0° under argon. The reaction mixture was warmed slowly to room temperature and stirred for 3 h. Then the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water and saturated NaHCO₃ aqueous solution, dried with Na₂SO₄ and evaporated. The undesired aldehyde was removed by silica gel column chromatography (CH₂Cl₂:n-hexane) to recover 4-*tert*-butyl-2,6-dibromobenzyl alcohol **10** as a single isomer (54 g 0.17 mol, 85%). To the benzyl alcohol **10** dissolved in acetonitrile (217 ml), molecular sieves 4A (40 g) and tetra-*n*-propylammonium perruthenate (1.2 mg, 3.4 mmol) were added, and the whole was stirred under argon at room temperature. *N*-Methylmorpholine *N*-oxide (22 g, 0.19 mol) dissolved in acetonitrile (200 ml) was added to the reaction mixture over 15 min, and stirring was continued for a further 3 h at room temperature. Then the solution was passed through a silica gel short column with CH₂Cl₂ as the eluent, and evaporated under reduced pressure. 4-*tert*-Butyl-2,6-dibromobenzaldehyde **12** (35 g, 0.11 mol, 65%) was purified by silica gel column chromatography (CH₂Cl₂:n-hexane). Recrystallized from Et₂O to give colorless needles; mp 65-66°; ¹H NMR (CDCl₃) δ 1.26 (9H, s), 7.56 (2H, s), 10.18 (1H, s); ¹³C NMR (CDCl₃) δ 30.7, 35.3, 125.1, 129.7, 131.1, 158.6, 190.9; MS (EI+) *m/z* (relative intensity) 303 (52), 305 (100), 307 (50), 318 (18), 320 (36), 322 (18); Anal. Calcd for C₁₁H₁₂OBr₂ C 41.28%, H 3.78%, Found C 41.07%, H 3.77%.

5,10,15,20-Tetrakis(4-*tert*-butyl-2,6-dibromophenyl)porphyrin **13**

To 4-*tert*-butyl-2,6-dibromobenzaldehyde **12** (6.9 g, 22 mmol) dissolved in CHCl₃ (1.5 L), molecular sieves 4A (7 g) was added and the reaction mixture was purged with argon for 1 h at room temperature. Under argon, pyrrole (1.5 ml, 22 mmol) was added and then boron trifluoride diethyl etherate (1.9 ml) was added dropwise via a syringe over 5 min. The reaction mixture was stirred overnight excluding light. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (3.9 g, 17 mmol) was added and stirring was continued for a further 2 h at room temperature. At the end of the reaction, triethylamine (3.2 ml) was added, and the reaction mixture was passed through a silica gel short column with CH₂Cl₂ as the eluent. After evaporation to dryness, the residue was washed with methanol and the porphyrin **13** (1.7 g, 1.2 mmol, 22%) was purified as a brown powder by silica gel column chromatography (CH₂Cl₂:n-hexane); ¹H NMR (CDCl₃) δ -2.52 (2H, s), 1.24 (36H, s), 7.49 (8H, s), 8.57 (8H, s); ¹³C NMR (CDCl₃) δ 31.3, 35.3, 118.5, 126.0, 128.1, 128.7, 140.4, 149.0, 155.0; MS (FAB, 3-nitrobenzyl

alcohol) m/z (relative intensity) 1468 (59), 1469 (64), 1470(76), 1471 (75), 1472 (73), 1473 (62); UV (benzene) λ_{\max} 424 nm ($\epsilon=223000\text{ cm}^{-1}\text{M}^{-1}$), 517 (12500), 594 (3600).

[5,10,15,20-Tetrakis(4-*tert*-butyl-2,6-dibromophenyl)porphyrinato]zinc 14

5,10,15,20-Tetrakis(4-*tert*-butyl-2,6-dibromophenyl)porphyrin **13** (1.7 g, 1.2 mmol), zinc acetate dihydrate (2.6 g, 12 mmol), and 2,4,6-trimethylpyridine (4.3 ml) were added to dimethylformamide (300 ml) and the mixture was refluxed under argon for 2.5 h. Then the solution was poured into water (1.5 L), and the precipitate was collected and washed with water and methanol to give the zinc complex **14** as a red-purple powder (1.4 g, 0.94 mmol, 80%); ^1H NMR (CDCl_3) δ 1.58 (36H, s), 7.99 (8H, s), 8.72 (8H, s); ^{13}C NMR (CDCl_3) δ 31.3, 35.3, 119.3, 128.1, 128.7, 131.2, 140.5, 149.6, 154.7; MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 1534 (100), 1535 (63), 1536 (35); UV (benzene) λ_{\max} 428 nm ($\epsilon=280000\text{ cm}^{-1}\text{M}^{-1}$), 555 (21900).

[5,10,15,20-Tetrakis(4-*tert*-butyl-2,6-dicyanophenyl)porphyrinato]zinc 15

[5,10,15,20-Tetrakis(4-*tert*-butyl-2,6-dibromophenyl)porphyrinato]zinc **14** (1.47 g, 0.96 mmol) and copper (I) cyanide (7.35 g, 82 mmol) were added to *N*-methyl-2-pyrrolidone (350 ml) and the mixture was refluxed under argon for 6 h. Copper (I) cyanide (3.68 g, 41 mmol) was added again and reflux was continued for another 9 h. Then the solution was poured into 0.4 M sodium cyanide aqueous solution (1.5 L). The aqueous solution was extracted with ethyl acetate. The organic solution was dried with Na_2SO_4 , and ethyl acetate and *N*-methyl-2-pyrrolidone were evaporated under reduced pressure. The residue was purified by silica gel column chromatography and [5,10,15,20-tetrakis(4-*tert*-butyl-2,6-dicyanophenyl)porphyrinato]zinc **15** was obtained as a red-purple powder (644 mg, 0.59 mmol, 61%); ^1H NMR (CD_2Cl_2) δ 1.57 (36H, s), 8.28 (8H, s), 8.72 (8H, s); ^{13}C NMR (CDCl_3) δ 31.2, 35.9, 113.8, 117.2, 119.3, 132.3, 133.1, 146.1, 150.3, 154.4; MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 1100 (73), 1101 (100), 1102 (86), 1103 (75); IR (KBr) 2240 cm^{-1} ; UV (benzene) λ_{\max} 436 nm ($\epsilon=287000\text{ cm}^{-1}\text{M}^{-1}$), 563 (29700).

5,10,15,20-Tetrakis(4-*tert*-butyl-2,6-dicarboxyphenyl)porphyrin 1-dication

[5,10,15,20-Tetrakis(4-*tert*-butyl-2,6-dicyanophenyl)porphyrinato]zinc **15** (200 mg, 0.18 mmol) in a mixture of water (20 ml), H_2SO_4 (20 ml) and acetic acid (40 ml) was refluxed under argon for 20 h. It was allowed to cool to room temperature, trifluoroacetic acid (2.0 ml) and ethyl acetate (100 ml) were added, and the organic layer was washed with water. The organic layer was dried with Na_2SO_4 , and evaporated under reduced pressure to dryness to give dicationic porphyrin **1**, which was directly used in the next reaction without further purification.

Typical procedure for condensation of 5,10,15,20-tetrakis(4-*tert*-butyl-2,6-dicarboxyphenyl)porphyrin 1-dication and amines

To a solution of 5,10,15,20-tetrakis(4-*tert*-butyl-2,6-dicarboxyphenyl)porphyrin 1-dication (30 mg) in CH_2Cl_2 (3 ml) was added oxalyl chloride (0.8 ml) and the mixture was refluxed for 2 h. The solvent was evaporated under reduced pressure and the residue was dried with a vacuum pump. The residue was dissolved in CH_2Cl_2 (2 ml), and amine (80 equiv. to porphyrin) dissolved in CH_2Cl_2 (2 ml) was added dropwise to the solution cooled with an ice-bath over 5 min. Then the reaction mixture was warmed

to room temperature and stirred for 15 h. CH₂Cl₂ (30 ml) was added, and the organic layer was washed with 2 N HCl and 2N NaOH, dried with Na₂SO₄, and evaporated. Brown powder (40-65% based on octacyanoporphyrin) was obtained after purification by preparative TLC.

5,10,15,20-Tetrakis(2,6-bis(*N*-*tert*-butylcarbamoyl)-4-*tert*-butylphenyl)porphyrin 3

Yield based on the octacyanoporphyrin **15** was 52%; ¹H NMR (CDCl₃) δ -2.44 (2H, s), 0.05 (72 H, s), 1.63 (36H, s), 5.15 (8H, s), 7.89 (8H, s), 8.65 (8H, s); ¹³C NMR (CDCl₃) δ 23.6, 27.8, 31.5, 50.8, 114.3-167.8 (weak signals); MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 1632 (100), 1633 (77); IR (KBr) 3412 cm⁻¹, 1669; UV (benzene) λ_{max} 427 nm (ε=233000 cm⁻¹M⁻¹), 521 (11400), 598 (3300).

5,10,15,20-Tetrakis(2,6-bis(*N*-((*S*)-1-phenylethyl)carbamoyl)-4-*tert*-butylphenyl)porphyrin 4

Yield based on the octacyanoporphyrin **15** was 41%; ¹H NMR (CDCl₃) δ -2.32 (2H, s), -1.26 (24H, d, J=6.9 Hz), 1.51 (36H, s), 3.72 (8H, m), 5.36 (8H, d, J=9.0 Hz), 6.6-7.3 (40H, m), 7.85 (8H, s), 8.85 (8H, s); ¹³C NMR (CDCl₃) δ 19.4, 31.4, 36.6, 47.6, 126.0, 127.3, 128.5, 141.0, 142.0, 151-167 (weak signals); MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 2015 (100); IR (KBr) 3416 cm⁻¹, 1667; UV (benzene) λ_{max} 426 nm (ε=227000 cm⁻¹M⁻¹), 520 (11700), 596 (4300).

5,10,15,20-Tetrakis(2,6-bis(*N*-bornylcarbamoyl)-4-*tert*-butylphenyl)porphyrin 5

Yield based on the octacyanoporphyrin **15** was 40%; ¹H NMR (CDCl₃) δ -3.01 (2H, s), -1.04-2.71 (128H, m), 1.13 (36H, s), 4.76 (8H, d, J=9.1 Hz), 7.50 (8H, s), 8.24 (8H, s); ¹³C NMR (CDCl₃) δ 13.7, 18.3, 19.5, 27.2, 27.3, 31.4, 35.1, 35.2, 44.3, 47.1, 49.3, 52.9, 115.8, 125.4, 132.5, 136.4, 137.6, 142.2, 152.3, 168.0; MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 2178 (100); IR (KBr) 3424 cm⁻¹, 1670; UV (benzene) λ_{max} 429 nm (ε=266000 cm⁻¹M⁻¹), 524 (12900), 602 (3600).

5,10,15,20-Tetrakis(2,6-bis(*N*-((*S*)-1-(ethoxycarbonyl)ethyl)carbamoyl)-4-*tert*-butylphenyl)porphyrin 6

Yield based on the octacyanoporphyrin **15** was 41%; ¹H NMR (CDCl₃) δ -2.62 (2H, s), -1.09 (24H, d, J=7.1 Hz), 1.00 (24H, t, J=7.1 Hz), 1.61 (36H, s), 3.30 (8H, quint, J=8.0 Hz), 3.88 (16H, m), 5.67 (8H, d, J=8.0 Hz), 7.97 (8H, s), 8.74 (8H, s); ¹³C NMR (CDCl₃) δ 14.1, 16.1, 31.7, 35.7, 47.3, 61.5, 115.4, 125.4, 132.9, 140.8, 149.9, 153.5, 153.6, 167.8, 171.9; MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 1984 (100); IR (KBr) 3416 cm⁻¹, 1739, 1668; UV (benzene) λ_{max} 426 nm (ε=278000 cm⁻¹M⁻¹), 521 (17200), 598 (5000).

5,10,15,20-Tetrakis(2,6-bis(*N*-((*S*)-1-(methoxycarbonyl)-2-methylpropyl)carbamoyl)-4-*tert*-butylphenyl)porphyrin 7

Yield based on the octacyanoporphyrin **15** was 40%; ¹H NMR (CDCl₃) δ -2.59 (2H, s), -0.62 (24H, d, J=6.8 Hz), -0.34 (24H, d, J=6.8 Hz), 0.81 (8H, m), 1.62 (36H, s), 3.28 (8H, m), 3.30 (24H, s), 5.80 (8H, d, J=8.1 Hz), 8.01 (8H, s), 8.65 (8H, s); ¹³C NMR (CDCl₃) δ 17.3, 17.5, 29.8, 31.4, 35.2, 51.6, 57.5, 115.3, 125.8, 129.9, 133.7, 140.8, 150.4, 152.4, 167.8, 171.7; MS (FAB, 3-nitrobenzyl alcohol) m/z 2096 (100); IR (KBr) 3418

cm^{-1} , 1740, 1672; UV (benzene) λ_{max} 428 nm ($\epsilon=279000 \text{ cm}^{-1}\text{M}^{-1}$), 523 (16500), 600 (4700).