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Syntheses of 2-Arylated Corroles, a Directly Linked Corrole–Porphyrin Hybrid, a 1,4-Phenylene-bridged Corrole Dimer, and 2-Hydroxy-substituted Corrole via Regioselective Ir-Catalyzed Direct Borylation of Corrole[**]

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Instrumentation and Materials

^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz) and ^{19}F NMR (565 MHz) spectra were taken on a JEOL ECA-600 spectrometer. Chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$, DMSO, CH_2Cl_2, and CH_3CN as internal references for ^{1}H NMR (δ = 7.260, 1.730, 5.320, and 1.930 ppm, respectively), and $CHCl_3$ for ^{13}C NMR (δ = 77.0 ppm). Hexafluorobenzene was used as external reference for ^{19}F NMR (δ = –162.9 ppm). UV/vis absorption and steady-state fluorescence spectra were recorded on a Shimadzu UV-2550 spectrometer and a Shimadzu RF-5300PC spectrometer, respectively. MALDI-TOF mass spectra were obtained with a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer, using negative-MALDI ionization method without matrix. High resolution ESI-TOF mass spectra were taken on a Bruker microTOF. Recycling preparative GPC-HPLC was carried out on JAI LC-908 using preparative JAIGEL-2H, 2.5H, and 3H. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Experimental Section

2-(4′4′,5′,5′-Tetramethyl[1′,3′,2′]dioxaborolan-2′-yl)-5,10,15-tris(pentafluorophenyl)corrole (2).

A flask placed with $[Ir(cod)OMe]_2$ (3.75 mg, 5.66 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (3.04 mg, 5.66 μmol), bis(pinacolate)diborane (105 mg, 0.415 mmol), and 5,10,15-tris(pentafluorophenyl)corrole (**1**) (300 mg, 0.377 mmol) was flushed with argon, and then charged with 1,4-dioxane (3 mL). The mixture was stirred at 100 °C for 24 h. After cooling, the reaction mixture was passed through a short pad of silica gel with dichloromethane. Concentration and purification by size-exclusion column chromatography gave the product **2** in 91% (315 mg, 0.342 mmol) yield. ^{1}H NMR ($CDCl_3$): δ 9.59 (d, J = 4.1 Hz, 1H, pyrrole β), 8.97 (s, 1H, pyrrole β), 8.73 (d, J = 4.6 Hz, 1H, pyrrole β), 8.70 (d, J = 4.6 Hz, 1H, pyrrole β), 8.54 (d, J = 4.6 Hz, 1H, pyrrole β), 8.51 (d, J = 4.6 Hz, 1H, pyrrole β), 8.48 (br, 1H, pyrrole β), 1.66 (s, 12H, CH_3), and –3.70 (br, 3H, NH); ^{19}F NMR ($CDCl_3$): δ –138.11 (dd, J^1 = 24.2 Hz, J^2 = 8.7 Hz, 2F), –138.53 (br, dd, 2F), –138.71 (br, dd, 2F), –153.08 (br, 1F), –153.55 (br, 1F), –153.83 (t, J = 20.7 Hz, 1F), –162.38 (br, 2F), –162.65 (br, 2F), and –162.88 (dt, J^1 = 22.5 Hz, J^2 = 8.7 Hz, 2F); UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 408 (141000), 567 (26700), and 607 (16900) nm; Fluorescence (CH_2Cl_2, λ_{ex} = 408 nm): λ_{em} = 649 nm.; HR-MS (ESI-MS): m/z =921.1529, calcd for $(C_{43}H_{21}BF_{15}N_4O_2)^-$ = 921.1531 ($[M-H]^-$).

General Procedures of Suzuki–Miyaura Cross-Coupling Reaction with 2-Borylcorrole.

2-Borylcorrole (**2**, 20.0 mg, 21.7 μmol), aryl halide (21.7 μmol, 1.0 equiv), Cs_2CO_3 (10.6 mg, 32.6 μmol, 1.5 equiv), CsF (9.89 mg, 65.1 μmol, 3.0 equiv), $Pd_2(dba)_3$ (1.00 mg, 1.09 μmol, 5 mol%), and triphenylphosphine (1.14 mg, 4.34 μmol, 20 mol%) were dissolved in a mixture of toluene (1.5 mL), DMF (0.75 mL) and water (0.1 mL). The solution was deoxygenated via three times freeze-pump-thaw degas cycle, and the resulting mixture was stirred at 90 °C under argon atmosphere. After 5 h, the reaction was quenched with water and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated. Purification by silica-gel column chromatography afforded the coupling product.

2-(Anthracen-9′-yl)-5,10,15-tris(pentafluorophenyl)corrole (3a).

Following the general procedure, the reaction with 9-bromoanthracene (5.58 mg, 21.7 *μ*mol) gave **3a** in 94 % (19.8 mg, 20.3 *μ*mol) yield. ^{1}H NMR ($CDCl_3$): δ 8.91 (d, J = 4.1 Hz, 1H, pyrrole *β*), 8.86 (s, 1H), 8.80 (s, 1H, pyrrole *β*), 8.71 (d, J = 4.1 Hz, 1H, pyrrole *β*), 8.66 (d, J = 4.1 Hz, 1H, pyrrole *β*), 8.27 (d, J = 8.7 Hz, 2H), 8.16 (s, 1H, pyrrole *β*), 7.79 (d, J = 8.7 Hz, 1H), 7.63 (br , 1H, pyrrole *β*), 7.52 (m, 2H), and 7.19 (br, 2H); ^{19}F NMR ($CDCl_3$): δ –139.12 (dd, J^1 = 24.2 Hz, J^2 = 8.7 Hz, 2F), –138.44 (br, d, J = 19.0 Hz, 2F), –139.85 (br, d, J = 19.0 Hz, 2F), –153.11 (br, 2F), –153.59 (t, J = 20.7 Hz, 1F), –162.32 (br, 4F), and –162.75 (dt, J^1 = 21.6 Hz, J^2 = 8.7 Hz, 2F); UV/Vis (CH_2Cl_2): λ_{max} = 413, 567, and 610 nm; HR-MS (ESI-MS): *m*/*z* = 971.1301, calcd for $(C_{51}H_{18}F_{15}N_4)^-$ = 971.1297 ($[M - H]^-$).

2-(2′,5′-Dimethoxyphenyl-1′-yl)-5,10,15-tris(pentafluorophenyl)corrole (3b).

Following the general procedure, the reaction with 1-bromo-2,5-dimethoxybenzene (3.27 *μ*L, 21.7 *μ*mol) gave **3b** in 75 % (15.2 mg, 16.3 *μ*mol) yield. ^{1}H NMR (CD_2Cl_2): δ 8.89 (d, J = 4.1 Hz, 1H, pyrrole *β*), 8.83 (d, J = 4.1 Hz, 1H, pyrrole *β*), 8.80 (d, J = 4.6 Hz, 1H, pyrrole *β*), 8.69 (br, 1H, pyrrole *β*), 8.65 (d, J = 4.6 Hz, 1H, pyrrole *β*), 8.63 (d, J = 4.1 Hz, 1H, pyrrole *β*), 8.51 (br, 1H, pyrrole *β*), 7.76 (br, 1H), 7.29 (d, J = 8.8 Hz, 1H), 7.17 (dd, J^1 = 9.2 Hz, J^2 = 3.2 Hz, 1H), 3.92 (s, 3H, OCH_3), and 3.89 (s, 3H, OCH_3); ^{19}F NMR (CD_2Cl_2): δ –139.19 (d, J = 19.0 Hz, 2F), –139.56 (br, 2F), –139.68 (br, 2F), –154.47 (br, 2F), –155.02 (br, 1F), –163.51 (br, 4F), and –163.90 (br, 2F); UV/Vis (CH_2Cl_2): λ_{max} = 414, 568, and 612 nm; HR-MS (ESI-MS): *m*/*z* = 931.1201, calcd for $(C_{45}H_{18}O_2F_{15}N_4)^-$ = 931.1196 ($[M - H]^-$).

2-[10′,15′,20′-Tris(3″,5″-di-*tert*-butylphenyl)porphyrin-5′-yl]-5,10,15-tris(pentafluorophenyl) corrole (3c).

Following the general procedure, the reaction with 5-bromo-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (20.7 mg, 21.7 *μ*mol) gave **3c** in 72 % (26.3 mg, 15.7 *μ*mol) yield. ^{1}H NMR ($CDCl_3$): δ 9.45 (s, 1H, pyrrole *β*), 9.09 (d, J = 4.6 Hz, 2H, pyrrole *β*), 9.07 (d, J = 4.6 Hz, 2H, pyrrole *β*), 9.01 (d, J = 4.6 Hz, 2H, pyrrole *β*), 8.96 (d, J = 4.6 Hz, 1H, pyrrole *β*), 8.93 (d, J = 4.6 Hz, pyrrole *β*), 8.77 (d, J = 4.6 Hz, 1H, pyrrole *β*), 8.73 (d, J = 4.6 Hz, 1H, pyrrole *β*), 8.65 (d, J = 5.0 Hz, 1H, pyrrole *β*), 8.15 (m, 4H), 8.09 (m, 2H), 7.88 (d, J =

4.6 Hz, 1H, pyrrole *β*), 7.84 (m, 1H), 7.75 (m, 2H), 7.19 (d, *J* = 4.1 Hz, 1H, pyrrole *β*), 1.56 (m, 18H, CH_3), 1.48 (s, 18H, CH_3), 1.46 (s, 18H, CH_3), and –2.35 (s, 2H, NH); ^{19}F NMR ($CDCl_3$): δ –138.06 (dd, J^1 = 24.2 Hz, J^2 = 8.7 Hz, 2F), –138.34 (br, 2F), –138.89 (br, 2F), –153.15 (br, 2F), –153.56 (t, *J* = 17.8 Hz, 1F), –162.17 (br, 2F), –162.44 (br, 2F), and –162.72 (dt, J^1 = 22.5 Hz, J^2 = 8.7 Hz, 2F); UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}\,cm^{-1}$]) = 421 (270000), 438 (256000), 520 (28000), 568 (32800), 612 (26500), and 652 (13200) nm; Fluorescence (CH_2Cl_2, λ_{ex} = 421 nm): λ_{em} = 661 nm; HR MS (ESI-MS): *m*/*z* = 1668.6401, calcd for $(C_{99}H_{82}F_{15}N_8)^-$ = 1668.6461 ([*M* – *H*]$^-$).

1,4-bis[5′,10′,15′-tris(pentafluorophenyl)corrole-2′-yl]benzene (3d).

Following the general procedure, the reaction of 2-borylcorrole (30.0 mg, 32.5 *μ*mol) and 1,4-dibromobenzene (2.55 mg, 10.8 *μ*mol) gave **3d** in 56 % (10.1 mg, 6.06 *μ*mol) yield. ^{1}H NMR ($CDCl_3$): δ 9.30 (d, *J* = 4.6 Hz, 2H, pyrrole *β*), 8.99 (m, 4H, phenyl), 8.87 (s, 2H, pyrrole *β*), 8.81 (m, 4H, pyrrole *β*), 8.63 (d, *J* = 5.0 Hz, 2H, pyrrole *β*), 8.62 (d, *J* = 4.6 Hz, 2H, pyrrole *β*), 8.51 (br, 2H, pyrrole *β*); ^{19}F NMR ($CDCl_3$): δ –138.10 (d, *J* = 13.8 Hz, 2F), –138.41 (d, *J* = 20.7 Hz, 2F), –138.73 (d, *J* = 22.0 Hz, 2F), –152.79 (br, 1F), –152.98 (br, 1F), –153.50 (t, *J* = 20.7 Hz, 1F), –162.20 (br, 4F), and –162.69 (t, *J* = 20.7 Hz, 2F); UV/Vis (CH_2Cl_2): λ_{max} = 414, 569, and 620 nm; HR-MS (ESI-MS): *m*/*z* = 832.0740, calcd for $(C_{80}H_{22}F_{30}N_8)^{2-}$ = 832.0750 ([*M* – 2*H*]$^{2-}$).

2-Oxo-3-hydro-5,10,15-tris(pentafluorophenyl)corrole (4K).

A solution of **2a** (40.0 mg, 43.4 *μ*mol) in THF (2 mL) was degassed by argon bubbling for 10 min, and then an aqueous solution (0.5 mL) of Oxone® (80.0 mg, 0.130 mmol) was added. After stirring for 5 h at room temperature, the reaction was quenched with $Na_2S_2O_3$ aqueous solution then poured into a separation funnel with CH_2Cl_2. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated. Separation by silica gel column chromatography with CH_2Cl_2/hexane solution followed by recrystallization from chloroform/hexane afforded **4K** in 62% (22.0 mg, 27.1 *μ*mol) yield as purple crystals. ^{1}H NMR ($CDCl_3$): δ 9.17 (d, *J* = 4.6 Hz, 1H, pyrrole *β*), 8.67 (d, *J* = 4.6 Hz, 1H, pyrrole *β*), 8.56 (d, *J* = 4.6 Hz, 1H, pyrrole *β*), 8.42 (br, d, 1H, pyrrole *β*), 8.39 (m, 2H, pyrrole *β*), 4.75 (m, 2H, CH_2), –0.44 (s, 1H, NH), –3.05 (s, 1H, NH), and –4.84 (s, 1H, NH); ^{19}F NMR ($CDCl_3$): δ –138.61 (dd, J^1 = 22.6 Hz, J^2 = 8.7 Hz, 2F), –138.96 (m, 4F), –152.83 (m, 2F), –153.06 (t, *J* = 20.7 Hz, 1F), –162.02 –

–161.83 (m, 4F) and –162.19 (dt, J^1 = 22.4 Hz, J^2 = 6.9 Hz, 2F); ^{13}C NMR ($CDCl_3$): δ 197.9, 149.4, 147.1, 146.7, 146.3, 145.5, 145.1, 144.6, 141.0, 138.4, 135.9, 133.9, 133.2, 130.7, 126.2, 124.9, 123.4, 121.6, 120.5, 119.8, 119.6, 114.6, 113.2, 112.5, and 45.6; UV/Vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 430 (208000), 516 (13000), 552 (8350), 609 (5400), and 663 (8600) nm; Fluorescence (CH_2Cl_2, λ_{ex} = 430 nm): λ_{em} = 670 nm.; HR-MS (ESI-MS): *m*/*z* =811.0629, calcd for $(C_{37}H_{10}F_{15}N_4O)^-$ = 811.0621 ($[M-H]^-$).

2-Hydroxy-5,10,15-tris(pentafluorophenyl)corrole (4E).

^{1}H NMR ([D_6]DMSO): δ 11.9 (br, 1H, OH), 9.25 (br, 1H, pyrrole *β*), 8.81–8.95 (m, 5H, pyrrole *β*), and 7.82 (s, 1H, pyrrole *β*), –0.59 (br, 1H, NH), –1.02 (br, 1H, NH), and –3.51 (br, 1H, NH); ^{19}F NMR ([D_6]DMSO): δ –140.33 (br, d, *J* = 24.2 Hz, 2F), –140.57 (br, 2F), –140.75 (br, 2F), –155.44 (br, 1F), –155.83 (br, 1F), –156.18 (t, *J* = 20.7 Hz, 1F), –163.76 (br, t, *J* = 22.4 Hz, 2F), –163.88 (br, t, *J* = 25.9 Hz, 2F), and –164.31 (br, t, *J* = 22.5 Hz, 2F); UV/Vis (DMSO): λ_{max} (ε [M^{-1} cm^{-1}]) = 435 (183000), 587 (13400), and 616 (19600) nm; Fluorescence (DMSO, λ_{ex} = 435 nm): λ_{em} = 624 nm.