Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information

Molecular engineering of two-dimensional π-conjugation: Expected and unexpected photophysical consequences of simple particle-in-a-box approach

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2,6-Dibromo-4-iodoaniline (8)
To a MeOH (50 mL) solution of 2,6-dibromoaniline (5.00 g, 20.1 mmol) and KI (6.67 g, 40.2 mmol) at 0 ˚C was added dropwise conc H_2SO_4 (3.94 g, 40.2 mmol) over a period of 15 min. After 5 min of stirring at 0 ˚C, a portion of H_2O_2 (30% aqueous solution, 9.11 g, 80.4 mmol) was added to the reaction mixture over a period of 15 min. The resulting mixture was warmed to room temperature, stirred for 5 h, treated with H_2O (100 mL), and extracted with CH_2Cl_2 (100 mL × 3). The combined extracts were dried over anhyd $MgSO_4$ and filtered. Voltaile fractions were removed under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes : ethyl acetate = 9:1) to afford **8** as a white solid (7.22 g, 19.3 mmol, 96%). The ^{1}H NMR spectrum of this compound was identical to that of the same material prepared from the reaciton between 3,5-dibromosulfanilic acid and ICl in aqueous AcOH.[S1] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (s, 2H), 4.52 (bs, 2H).

2,6-Dibromo-4-phenylaniline (9)
A mixture of **8** (2.00 g, 5.34 mmol), phenylboronic acid (0.716 g, 5.87 mmol), $Pd(PPh_3)_4$ (0.300 g, 0.260 mmol), and Na_2CO_3 (4.00 g, 32.0 mmol) in anhydrous benzene (30 mL) was heated at reflux under nitrogen for 63 h. The reaction was cooled to room temperature, treated with H_2O (100 mL), and extracted with CH_2Cl_2 (100 mL × 3). The combined extracts were dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (CH_2Cl_2 : EtOAc = 5 : 1) afforded **9** as white crystals (1.33g, 3.99 mmol, 76%). The ^{1}H NMR spectrum of this compound was identical to that of the same material prepared by direct bromination of 4-aminobiphenyl with BTMA·Br_3.[S2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 4.49 (bs, 2H).

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-phenylaniline (10)
A Et_3N (30 mL) solution of **9** (1.31 g, 4.01 mmol), 2-methyl-3-butyn-2-ol (1.01 g, 12.0 mmol), $Pd(PPh_3)_4$ (93 mg, 81 μmol), and CuI (23 mg, 0.12 mmol) was evacuated and backfilled with nitrogen in three cycles using a Schlenk line. The reaction mixture was heated at 90 ˚C under nitrogen for 24 h and cooled to room temperature. A portion of H_2O (100 mL) was added and the organic layer was extracted with CH_2Cl_2 (100 mL × 3). The combined extracts were dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. The product was isolated as yellow crystals (1.31 g, 3.93 mmol, 98%) after flash column chromatography on SiO_2 (CH_2Cl_2 : EtOAc = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.48 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 4.75 (bs, 2H), 2.22 (s, 2H), 1.66 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 139.7, 131.0, 130.4, 128.7, 126.7, 126.2, 107.3, 99.8, 78.3, 65.8, 31.7. FT-IR (thin film on NaCl, cm^{-1}): 3371, 2980, 2931, 2216, 1610, 1459, 1362, 1231, 1165. HRMS (CI) calcd for $C_{22}H_{23}NO_2$ $[M]^+$ 333.1723, found 333.1732.

2,6-Dibromo-4-styrylaniline (11a)
A mixture of **8** (1.00 g, 2.67 mmol), styrene (0.253 g, 2.43 mmol), $Pd(OAc)_2$ (18 mg, 80 μmol), PPh_3 (42 mg, 0.16 mmol), and Et_3N (10 mL) in toluene (20 mL) was evacuated and backfilled with nitrogen in three cycles using a Schlenk line. The reaction mixture was heated at reflux under nitrogen for 24 h and cooled to room temperature. A portion of H_2O (100 mL) was added and the organic layer was extracted with CH_2Cl_2 (100 mL × 3). The combined extracts were dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (hexanes → hexane : CH_2Cl_2 = 50 : 1) afforded **11a** as a

white solid (0.382 g, 1.09 mmol, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 2H), 7.46 (d, *J* = 7.6 Hz, 7.35 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 16.4 Hz, 1H), 6.86 (d, *J* = 16.4 Hz, 1H), 4.61 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 137.0, 129.7, 129.6, 128.7, 127.5, 127.4, 126.3, 125.9, 108.9. FT-IR (thin film on NaCl, cm^{-1}): 3411, 3310, 2922, 2853, 2111, 1733, 1684, 1653, 1616, 1595, 1510, 1481, 1075, 970. HRMS (CI) calcd for $C_{14}H_{11}NBr_2$ $[M]^+$ 350.9258, found 350.9219.

2,6-Dibromo-4-(4-methoxystyryl)aniline (11b)
This compound was prepared with **8** (1.00 g, 2.67 mmol), 4-methoxystyrene (0.358 g, 2.67 mmol), $Pd_2(dba)_3$ (37 mg, 40 μmol), P^tBu_3 (45 mg, 0.22 mmol), and $^iPr_2NH$ (0.75 mL, 5.3 mmol) in anhyd dioxane (15 mL) by a procedure analogous to that used to prepare **11a**. The product was isolated as a yellow solid (0.518 g, 1.36 mmol, 51%) after flash column chromatography on SiO_2 (Hexane : EtOAc = 100 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 2H), 7.39 (d, *J* = 11.6 Hz, 2H), 6.89 (d, *J* = 11.6 Hz, 2H), 6.85 (d, *J* = 21.2 Hz, 1H), 6.72 (d, *J* = 21.6 Hz, 1H), 4.57 (bs, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 140.8, 130.0, 129.8, 129.4, 127.5, 127.0, 123.8, 114.1, 109.0, 55.3. FT-IR (thin film on NaCl, cm^{-1}): 3435, 3346, 3017, 2962, 2933, 2834, 1869, 1610, 1576, 1511, 1463, 1401, 1248, 1267, 1181, 1137, 959. HRMS (CI) calcd for $C_{15}H_{13}NOBr_2$ $[M]^+$ 380.9364, found 380.9378.

2,6-Dibromo-4-(4-cyanostyryl)aniline (11c)
This compound was prepared with **8** (4.60 g, 12.2 mmol), 4-cyanostyrene (1.43 g, 11.1 mmol), $Pd(OAc)_2$ (82 mg, 0.37 mmol), PPh_3 (96 mg, 0.37 mmol), and Et_3N (10 mL) in toluene (20 mL) by a procedure analogous to that used to prepare **11a**. The product was isolated as a white solid (2.80 g, 7.45 mmol, 61%) after flash chromatography on SiO_2 (Hexane : EtOAc = 9 : 1 to Hexane : EtOAc = 4 : 1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.76 (s, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 7.27 (d, J = 16.4 Hz, 1H), 7.19 (d, J = 16.4 Hz, 1H), 5.63 (s, 2H); ^{13}C NMR (100 MHz, DMSO d_6): δ 142.0, 142.1, 132.6, 130.4, 129.8, 127.4, 126.7, 124.6, 119.1, 108.9, 107.8. FT-IR (thin film on NaCl, cm^{-1}): 3475, 3375, 2959, 2925, 2851, 2223, 1616, 1457, 1056. HRMS (CI) calcd for $C_{15}H_{10}N_2Br_2$ $[M]^+$ 375.9211, found 375.9198.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-styrylaniline (12a)
This compound was prepared with **11a** (0.785 g, 2.24 mmol), 2-methyl-3-butyn-2-ol (0.565 g, 6.71 mmol), $Pd(PPh_3)_4$ (52 mg, 45 μmol), and CuI (13 mg, 68 μmol) in Et_3N (20 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a yellow solid (0.798 g, 2.22 mmol, 99%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 1 → 1 : 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 6.8Hz), 6.84 (s, 2H), 4.89 (bs, 2H), 3.44 (bs, 2H), 1.65 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 137.4, 130.4, 130.3, 128.5, 127.1, 126.8, 126.2, 126.0, 107.4, 99.8, 78.0, 65.6, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3374, 3024, 2980, 2929, 2215, 1607, 1496, 1465, 1362, 1265, 1230, 1153, 959. HRMS (CI) calcd for $C_{24}H_{25}NO_2$ $[M]^+$ 359.1880, found 359.1877.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-(4-methoxystyryl)-aniline (12b)
This compound was prepared with **11b** (0.680 g, 1.79 mmol), 2-methyl-3-butyn-2-ol (0.452 g, 5.37 mmol), $Pd(PPh_3)_4$ (41 mg, 36 μmol), and CuI (10 mg, 53 μmol) in Et_3N (10 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a pale yellow solid (0.689 g, 1.77 mmol, 99%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 2 : 3 → EtOAc only). ^{1}H NMR (400 MHz, CD_3OH): δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.33 (s, 2H), 6.88–6.75 (m, 4H), 3.79 (s, 3H), 1.60 (s, 12H); ^{13}C NMR (100 MHz, CD_3OD): δ 154.7, 143.6, 125.8, 122.9, 122.7, 121.2, 120.5, 109.6, 102.8, 95.6, 73.4, 61.2, 50.8, 27.0. FT-IR (thin film on NaCl, cm^{-1}): 3375, 2979, 2932, 2739, 2029, 1605, 1511, 1251, 1174, 1111, 1034, 956. HRMS (CI) calcd for $C_{25}H_{27}NO_3$ $[M]^+$ 389.1985, found 389.1990.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-(4-cyanostyryl)-aniline (12c)
This compound was prepared with **11c** (1.00 g, 2.66 mmol), 2-methyl-3-butyn-2-ol (0.671 g, 7.98 mmol), $Pd(PPh_3)_4$ (61 mg, 53 μmol), and CuI (15 mg, 79 μmol) in Et_3N (15 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a pale yellow solid (1.01 g, 2.63 mmol, 99%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 1 → EtOAc only). ^{1}H NMR (400 MHz, CD_3OH): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.40 (s, 2H), 6.97 (d, *J* = 15.6 Hz, 1H), 6.84 (d, *J* = 16.0 Hz, 1H), 4.88 (bs, 2H), 2.30 (bs, 2H), 1.66 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 142.0, 132.4, 130.92, 130.85, 126.4, 125.6, 123.9, 119.2, 109.8, 107.3, 100.1, 77.7, 65.7, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3377,

2979, 2925, 2853, 2226, 1599, 1465, 1363, 1265, 1229, 1165, 959. HRMS (CI) calcd for $C_{25}H_{24}N_2O_2$ $[M]^+$ 384.1832, found 384.1831.

2,6-Dibromo-4-(phenylethynyl)aniline (13a)
A resealable tube equipped with a Teflon-lined screw cap was loaded with **8** (1.00 g, 2.67 mmol), phenylacetylene (0.25 g, 2.4 mmol), $Pd(PPh_3)_4$ (62 mg, 54 μmol), CuI (15 mg, 79 μmol), and $^iPr_2NH$ (10 mL). The reaction mixture was evacuated and backfilled with nitrogen in three cycles using a Schlenk line. The tube was sealed and heated at 90 ˚C for 18 h. The reaction mixture was cooled to room temperature, treated with H_2O (100 mL) and extracted with CH_2Cl_2 (100 mL × 3). The combined extracts were dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography of the crude product on SiO_2 (hexanes) frunished **13a** as a white solid (0.750 g, 2.15 mmol, 88%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 2H), 7.49–7.47 (m, 2H), 7.34–7.32 (m, 3H), 4.73(bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 134.6, 131.4, 128.3, 128.1, 123.0, 114.2, 107.8, 88.9, 87.1. FT-IR (thin film on NaCl, cm^{-1}): 3418, 3284, 2923, 2849, 2100, 1616, 1411, 1064, 870. HRMS (CI) calcd for $C_{14}H_9NBr_2$ $[M]^+$ 348.9102, found 348.9083.

2,6-Dibromo-4-[(4-methoxyphenyl)ethynyl]aniline (13b)
This compound was prepared with **8** (1.00 g, 2.67 mmol), 1-ethynyl-4-methoxybenzene (0.321 g, 2.43 mmol), $Pd(PPh_3)_4$ (62 mg, 54 μmol), CuI (15 mg, 79 μmol), and $^iPr_2NH$ (10 mL) in a manner similar to that described for **13a**. The product was isolated as a yellow solid (0.786 g, 2.07 mmol, 85%) after flash column chromatography on SiO_2 (hexanes : CH_2Cl_2 = 9 : 1 → hexanes : EtOAc = 10 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.7 (bs, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 141.9, 134.6, 132.9, 155.1, 114.7, 114.0, 107.9, 88.9, 85.8, 55.3. FT-IR (thin film on NaCl, cm^{-1}): 3480, 3378, 2932, 2835, 2538, 2209, 1611, 1509, 1478, 1328, 1248, 1173, 1045. HRMS (CI) calcd for $C_{15}H_{11}NOBr_2$ $[M]^+$ 378.9202, found 378.9211.

2,6-Dibromo-4-[(4-cyanophenyl)ethynyl]aniline (13c)
This compound was prepared with **8** (1.00 g, 2.67 mmol), 4-ethynylbenzonitrile (0.309 g, 2.43 mmol), $Pd(PPh_3)_4$ (62 mg, 54 μmol), CuI (15 mg, 79 μmol), and $^iPr_2NH$ (10 mL) in a manner similar to that described for **13a**. The product was isolated as a white solid (0.842 g, 2.25 mmol, 93%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 20 : 1). ^1H NMR (400 MHz, DMSO-d_6): δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.66 (s, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 5.87 (bs, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 144.3, 135.0, 132.6, 131.9, 127.6, 118.6, 110.7, 106.9, 92.0, 87.4. FT-IR (thin film on NaCl, cm^{-1}): 3479, 3374, 3012, 2927, 2225, 2206, 1700, 1652, 1558, 1141, 1102, 831. HRMS (CI) calcd for $C_{15}H_9N_2Br_2$ $[M]^+$ 374.9127, found 374.9115.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-(phenylethynyl)-aniline (14a)
This compound was prepared with **13a** (0.895 g, 2.57 mmol), 2-methyl-3-butyn-2-ol (0.674 g, 7.70 mmol), $Pd(PPh_3)_4$ (59 mg, 51 μmol), and CuI (15 mg, 79 μmol) in Et_3N (20 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a yellow solid (0.910 g, 2.55 mmol, 99%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 1 to EtOAc only). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.45 (m, 2H), 4.40 (s, 2H), 7.33–7.29 (m, 3H), 1.63 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 135.5, 131.3, 128.3, 127.9, 123.5, 107.1, 100.1, 88.5, 87.6, 77.5, 65.7, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3384, 3056, 2978, 2931, 2872, 2515, 2210, 1959, 1734, 1610, 1492, 1465, 1363, 1264, 1229, 1161, 948. HRMS (CI) calcd for $C_{24}H_{23}NO_2$ $[M]^+$ 357.1723, found 357.1710.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-[(4-methoxyphenyl)-ethynyl]aniline (14b)
This compound was prepared with **13b** (0.775 g, 2.05 mmol), 2-methyl-3-butyn-2-ol (0.516 g, 6.14 mmol), $Pd(PPh_3)_4$ (47 mg, 41 μmol), and CuI (12 mg, 63 μmol) in Et_3N (20 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a white solid (0.784 g, 2.02 mmol, 99%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 1 to EtOAc only). ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 6.8 Hz, 2H), 7.38 (s, 2H), 6.85 (d, *J* = 6.8 Hz, 2H), 4.85 (bs, 2H), 3.82 (s, 3H), 1.64 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 148.4, 135.4, 132.8, 114.0, 112.2, 107.1, 101.9, 100.0, 87.5, 87.1, 77.6, 65.8, 55.3, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3379, 2975, 2926, 2841, 2091, 1653, 1558, 1456, 1436, 1245, 1102. HRMS (CI) calcd for $C_{25}H_{25}NO_3$ $[M]^+$ 387.1829, found 387.1835.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-[(4-cyanophenyl)-ethynyl]aniline (14c)
This compound was prepared with **13c** (0.842 g, 2.25 mmol), 2-methyl-3-butyn-2-ol (0.569 g, 6.76 mmol), $Pd(PPh_3)_4$ (52 mg, 45 μmol), and CuI (13 mg, 68 μmol) in Et_3N (20 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a pale yellow solid (0.866 g, 2.32 mmol, 99%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 1 to EtOAc only). ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.41 (s, 2H), 4.97 (bs, 2H), 2.24 (bs, 2H), 1.64 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 135.8, 135.7, 132.0, 131.7, 128.5, 118.6, 110.9, 110.6, 107.1, 100.3, 93.4, 86.3, 65.8, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3376, 2979, 2925, 2853, 2515, 2227, 2207, 1700, 1652, 1616, 1506, 1362, 1228, 1169, 1115. HRMS (CI) calcd for $C_{25}H_{23}N_2O_2$ $[M]^+$ 373.1754, found 373.1751.

2,6-Dibromo-4-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]aniline (15)
An anhydrous DMF (20 mL) solution of **8** (2.02 g, 5.38 mmol), 1-[(*E*)-buta-1,3-dienyl]benzene (0.700 g, 5.38 mmol), $Pd(OAc)_2$ (60 mg, 0.27 mmol), PPh_3 (0.141 g, 0.548 mmol), and Et_3N (10 mL) was stirred under nitrogen at room temperature for 1 h. The reaction mixture was heated at 90 ˚C for 18 h and cooled to room temperature. A portion of H_2O (100 mL) was added and the organic layer was extracted with Et_2O (100 mL × 3). The combined extracts were dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatogrpahy on SiO_2 afforded **15** as a bright brown solid (1.28 g, 3.40 mmol, 63%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.89 (dd, *J* = 15.6Hz, 1H), 6.75 (dd, *J* = 15.6 Hz, 1H), 6.63 (d, *J*= 15.6 Hz, 1H), 6.42 (d, *J* = 15.5 Hz, 1H), 4.61 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 137.3, 132.6, 129.9, 129.7, 129.6, 128.9, 128.6, 128.0, 127.5, 126.3, 108.9. FT-IR (thin film on NaCl, cm^{-1}): 3376, 3378, 3024, 2924, 2854, 1609, 1576, 1479, 1479, 1403, 1301, 1056, 990. HRMS (CI) calcd for $C_{16}H_{13}NBr_2$ $[M]^+$ 376.9409, found 376.9419.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]aniline (16)
This compound was prepared with **15** (0.260 g, 0.690 mmol), 2-methyl-3-butyn-2-ol (0.173 g, 2.06 mmol), $Pd(PPh_3)_4$ (16 mg, 14 μmol), and CuI (4 mg, 0.02 mmol) in Et_3N (10 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a pale yellow solid (0.240 g, 0.623 mmol, 90%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 2 to EtOAc only). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.32–7.29 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.88 (dd, *J* = 15.6Hz, 1H), 6.74 (dd, *J* = 15.6 Hz, 1H), 6.58 (d, *J*= 15.6 Hz, 1H), 6.43 (d, *J* = 15.5 Hz, 1H), 3.52 (bs, 2H), 1.65 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 137.5, 131.7, 131.3, 130.4, 129.3, 128.6, 127.3, 127.0, 126.9, 126.2, 107.3, 99.8, 78.1, 65.7, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3365, 2978, 2928, 2855, 2517, 2216, 1153, 1612, 1465, 1362, 1264, 1227, 1168, 959. HRMS (CI) calcd for $C_{26}H_{27}NO_2$ $[M]^+$ 385.2036, found 385.2047.

2,6-Dibromo-4-[2-(trimethylsilyl)ethynyl]aniline (17)
A resealable tube equipped with a Teflon-lined screw cap was charged with **8** (5.00 g, 12.3 mmol), trimethysilylacetylene (1.43 g, 14.6 mmol), $Pd(PPh_3)_4$ (0.307 g, 0.266 mmol), CuI (76 mg, 0.40 mmol), and Et_3N (30 mL) and purged with nitrogen. The reaction mixture was heated at 50 ˚C for 18 h and cooled to room temperature. A portion of H_2O (100 mL) was added and the mixture was extracted with CH_2Cl_2 (150 mL × 3). The combined extracts were dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. The product was isolated (4.19 g, 12.1 mmol, 91%) by flash column chromatography on SiO_2 (pentanes). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 2H), 4.71 (bs, 2H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.34, 135.1, 114.1, 107.6, 102.7, 93.7, –0.1. FT-IR (thin film on NaCl, cm^{-1}): 3488, 3386, 3066, 2958, 2899, 2148, 1611, 1582, 1469. HRMS (CI) calcd for $C_{11}H_{13}NBr_2Si$ $[M]^+$ 344.9179, found 344.9188.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-[2-(trimethylsilyl)-ethynyl]aniline (18)
This compound was prepared with **17** (0.350 g, 1.01 mmol), 2-methyl-3-butyn-2-ol (0.256 g, 3.04 mmol), $Pd(PPh_3)_4$ (23 mg, 20 μmol), and CuI (6 mg, 0.03 mmol) in Et_3N (10 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a yellow amorphous solid (0.384 g, 1.09 mmol, 99%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 2H), 4.85 (bs, 2H), 2.45 (bs, 2H), 1.59 (s, 12H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 135.9, 111.7, 106.9, 104.2, 100.0, 92.0, 77.4, 65.7, 31.6, 0.0. FT-IR (thin film on NaCl, cm^{-1}): 3356, 2981, 2933, 2153, 1609, 1464, 1363, 1249, 1163, 1000, 954, 858. HRMS (CI) calcd for $C_{21}H_{27}NO_2Si$ $[M]^+$ 353.1806, found 353.1808.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-ethynylaniline (19)
A MeOH (10 mL) solution of **18** (0.200 g, 0.566 mmol) and KF·2H_2O (75 mg, 0.80 mmol) was stirred for 18 h at room temperature. Volatile fractions were removed under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 2) to furnish **19** as a yellow solid (100 mg, 0.356 mmol, 67%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.17 (s, 2H), 5.59 (bs, 2H), 5.55 (s, 2H), 3.87 (s, 1H), 1.48 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.5, 134.6, 108.9, 106.6, 101.9, 82.7, 78.3, 75.9, 63.8, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3355, 2979, 2928, 2854, 2218, 2103, 1733, 1610, 1461. HRMS (CI) calcd for $C_{18}H_{19}NO_2$ $[M]^+$ 281.1410, found 281.1411.

2,6-Di(3-methyl-3-hydroxy-1-butynyl)-4-(4-phenylbuta-1,3-diynyl)aniline (20)
A MeOH (10 mL) solution of **19** (0.400 g, 1.42 mmol), 1-(2-bromoethynyl)benzene (0.257 g, 1.42 mmol), CuBr (20 mg, 0.14 mmol), hydroxylamine hydrochloride (20 mg, 0.28 mmol), and piperidine (0.35 mL) was stirred for 2 days at room temperature to afford a dark red brown solution. The reaction mixture was concentrated under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 1) to furnish **20** (0.285 g, 0.663 mmol, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.58 (m, 2H), 7.44–7.37 (m, 5H), 5.18 (bs, 2H), 3.40 (bs, 2H), 1.72 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 136.2, 132.3, 128.9, 128.3, 121.9, 109.8, 107.2, 100.3, 81.0, 80.9, 77.1, 74.2, 72.3, 65.6, 31.5. FT-IR (thin film on NaCl, cm^{-1}): 3376, 2980, 2932, 2866, 2525, 2217, 2141, 1608, 1467, 1369 ,1230, 959. HRMS (CI) calcd for $C_{26}H_{23}NO_2$ $[M]^+$ 381.1723, found 381.1721.

3,5-Dibromophenylethnyltrimethylsilane (21)
A resealable tube equipped with a Teflon-lined screw cap was charged with 1,3,5-tribromobenzene (1.00 g, 3.18 mmol), trimethylsilylacetylene (0.312 g, 3.18 mmol), $PdCl_2(PPh_3)_2$ (45 mg, 64 μmol), CuI (18 mg, 95 μmol), and Et_3N (10 mL). The reaction vessel was purged with nitrogen, sealed, and heated at 50 ˚C for 4 h and cooled to room temperature. A portion of H_2O (100 mL) was added and the organic layer was extracted into CH_2Cl_2 (100 mL × 3). The combined extracts were dried over anhyd $MgSO_4$, filtered, and concentrated under reduced presssure. Flash column chromatography on SiO_2 (hexanes) afforded **21** as a clear oil (0.90 g, 2.7 mmol, 85%), which contained small amount of unreacted 1,3,5-tribromobenzene as well as the dicoupling product 3,5-di(trimethylsilylethynyl)bromobenzene. Since these contaminants could readily be removed in the next step (see below), further purification was not attempted. The ^{1}H-NMR data of **21** obtained by this route was identical to that of the same material prepared by 5-step synthesis from 4-nitroaniline.[S3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 2H), 7.53 (s, 1H), 0.25 (s, 9H).

3,5-Di(phenylethynyl)-1-(trimethylsilylyethynyl)benzene (22a)
This compound was prepared using crude **21** (1.10 g, ca 3.31 mmol), phenylacetylene (1.01 g, 9.94 mmol), $Pd(PPh_3)_4$ (76 mg, 66 μmol), and CuI (19 mg, 0.10 mmol) in ^{i}Pr_2NH (5 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a white solid (0.840 g, 2.25 mmol) after flash column chromatography on SiO_2 (pentanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.61 (d, *J* = 1.6 Hz, 2H), 7.56–7.53 (m, 4H), 7.39–7.36 (m, 6H), 0.28 (s, 9H).[S4]

3,5-Di[(4-methoxyphenyl)ethynyl]-1-(trimethylsilylyethynyl)-benzene (22b)
This compound was prepared using crude **21** (1.00 g, ca 3.01 mmol), 4-ethynylanisole (0.954 g, 7.22 mmol), $Pd(PPh_3)_4$ (70 mg, 61 μmol), and CuI (17 mg, 89 μmol) in ^{i}Pr_2NH (10 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a white solid (1.18 g, 2.72 mmol) after flash column chromatography on SiO_2 (hexanes : EtOAc = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 1.6 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 2H), 7.56 (d, *J* = 11.2 Hz, 4H), 6.97 (d, *J* = 11.2 Hz, 4H), 3.89 (s, 6H), 0.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 133.8, 133.1, 124.2, 123.7, 114.8, 114.0, 103.5, 95.4, 90.5, 86.6, 55.2, −0.2. FT-IR (thin film on NaCl, cm^{-1}): 2958, 2836, 2542, 2211, 2154, 2054, 1606, 1579, 1511, 1465, 1294, 1254, 1172, 1033, 974, 855. HRMS (CI) calcd for $C_{29}H_{26}O_2Si$ $[M]^+$ 434.1697, found 434.1687.

3,5-Di[(4-cyanophenyl)ethynyl]-1-(trimethylsilylyethynyl)-benzene (22c)
This compound was prepared using crude **21** (2.63 g, ca 7.92 mmol), 4-ethynylbenzonitrile (3.01 g, 23.8 mmol), $Pd(PPh_3)_4$ (0.183 g, 0.158 mmol), and CuI (45 mg, 0.24 mmol) in ^{i}Pr_2NH (20 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a white solid (1.62 g, 3.82 mmol) after

flash column chromatography on SiO_2 (hexanes : EtOAc = 40 : 1 to 20 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 2H), 7.63 (s, 5H), 7.60 (s, 2H), 7,57 (s, 2H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.2, 134.3, 132.1, 127.4, 124.3, 123.1, 118.3, 112.0, 102.6, 96.7, 91.6, 88.9, –0.2. FT-IR (thin film on NaCl, cm^{-1}): 3053, 2957, 2900, 2728, 2227, 2158, 1918, 1603, 1580, 1500, 1412, 1250, 1206, 978, 869. HRMS (CI) calcd for $C_{29}H_{20}N_2Si$ $[M]^+$ 424.1390, found 424.1398.

3,5-Di(phenylethynyl)-1-ethynylbenzene (23a)
This compound was prepared with **22a** (0.270 g, 0.721 mmol) and KF·$2H_2O$ (0.102 g, 1.08 mmol) in a manner similar to that described for **19**. The product was isolated as white crystals (0.218 g, 0.721 mmol, 99%) after flash column chromatography on SiO_2 (hexanes). ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.65 (d, *J* = 1.2 Hz, 2H), 7.60–7.58 (m, 4H), 7.41–7.39 (m, 6H), 3.17 (s, 1H).[S4]

3,5-Di[(4-methoxyphenyl)ethynyl]-1-ethynylbenzene (23b)
This compound was prepared using **22b** (0.220 g, 0.507 mmol) and KF·$2H_2O$ (72 mg, 0.77 mmol) in MeOH (10 mL) in a manner similar to that described for **19**. The product was isolated as a white solid (0.176 g, 0.486 mmol, 96%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 15 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.57 (d, *J* = 2.0 Hz, 2H), 7.47 (d, *J* = 11.6 Hz, 4H), 7.89 (d, *J* = 11.6 Hz, 4H), 3.83 (s, 6H), 3.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 134.3, 134.0, 133.1, 124.3, 122.7, 114.8, 114.0, 90.7, 86.5, 82.2, 78.1, 55.2. FT-IR (thin film on NaCl, cm^{-1}): 3288, 3002, 2958, 2933, 2836, 2541, 2207,2053, 1605, 1579, 1509, 1440, 1293, 1251, 1180, 1025, 831. HRMS (CI) calcd for $C_{26}H_{18}O_2$ $[M]^+$ 362.1301, found 362.1314.

3,5-Di[(4-cyanophenyl)ethynyl]-1-ethynylbenzene (23c)
This compound was prepared using **22c** (1.58 g, 3.72 mmol) and KF·$2H_2O$ (0.53 g, 5.6 mmol) in MeOH (30 mL) in a manner similar to that described for **19**. The product was isolated as a yellow solid (0.984 g, 2.79 mmol, 75%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 9 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.60–7.53 (m, 11H), 3.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.0, 134.5, 131.92, 131.87, 127.1, 123.1, 123.0, 118.1, 111.8, 91.2, 89.0, 81.2, 79.2. FT-IR (thin film on NaCl, cm^{-1}): 3293, 3067, 3018, 2228, 1604, 1580, 1501, 1403, 1272, 889, 838. HRMS (CI) calcd for $C_{26}H_{12}N_2$ $[M]^+$ 352.0995, found 352.0987.

4-[3,5-Di(phenylethynyl)phenylethynyl]-2,6-dibromoaniline (24a)
This compound was prepared with **8** (0.459 g, 1.22 mmol), **23a** (0.370 g, 1.22 mmol), $Pd(PPh_3)_4$ (61 mg, 53 μmol), CuI (15 mg, 79 μmol), and $^iPr_2NH$ (15 mL) in a manner similar to that described for **10**. The product was isolated as a white solid (0.635 g, 1.15 mmol, 94%) after flash column chromatography on SiO_2 (hexanes : CH_2Cl_2 = 9 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.59 (d, *J* = 1.2 Hz, 2H), 7.58 (s, 2H), 7.56–7.53 (m, 4H), 7.38–7.36 (m, 6H), 4.77 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 134.8, 134.0, 133.8, 131.7, 128.6, 128.4, 124.1, 123.8, 122.8, 113.7, 107.9, 90.3, 88.3, 87.8, 87.4. FT-IR (thin film on NaCl, cm^{-1}): 3380, 3380, 2921, 2849, 2605, 2208, 1868, 1616, 1582, 1481, 1102, 1071, 869. HRMS (CI) calcd for $C_{30}H_{17}NBr_2$ $[M]^+$ 548.9722, found 548.9705.

4-{3,5-Di[(4-methoxyphenyl)ethynyl]phenylethynyl}-2,6-dibromoaniline (24b)
This compound was prepared with **8** (0.399 g, 1.07 mmol), **23b** (0.386 g, 1.07 mmol), $Pd(PPh_3)_4$ (25 mg, 22 μmol), CuI (6 mg, 0.03 mmol), and $^iPr_2NH$ (20 mL) in a manner similar to that described for **10**. The product was isolated as a white solid (0.540 g, 0.883 mmol, 83%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 9 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (t, *J* = 2.0 Hz, 1H), 7.57 (s, 2H), 7.55 (d, *J* = 1.6 Hz, 2H), 7.49 (d, *J* = 11.6 Hz, 4H), 7.89 (d, *J* = 11.6 Hz, 4H), 4.75 (bs, 2H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 142.4, 134.7, 133.6, 133.3, 133.1, 124.2, 123.6, 114.8, 114.0, 113.7, 107.8, 90.5, 88.1, 87.6, 86.7, 55.2. FT-IR (thin film on NaCl, cm^{-1}): 3368, 2958, 2832, 2206, 2060, 1877, 1607, 1576, 1507, 1479, 1294, 1246, 1168, 1033, 869, 819, 741. HRMS (CI) calcd for $C_{32}H_{21}N_1O_2Br_2$ $[M]^+$ 608.9939, found 608.9900.

4-{3,5-Di[(4-cyanophenyl)ethynyl]phenylethynyl}-2,6-dibromoaniline (24c)
This compound was prepared with **8** (1.00 g, 2.67 mmol), **23c** (0.942 g, 2.67 mmol), $Pd(PPh_3)_4$ (62 mg, 54 μmol), CuI (15 mg, 79 μmol), and $^iPr_2NH$ (20 mL) in a manner similar to that described for **10**. The product was isolated as a white solid (1.40 g, 2.33 mmol, 87%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 9 : 1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.67–7.55 (m, 13H), 4.79 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 134.8, 134.6, 134.0, 132.13, 132.10, 127.5, 124.3, 123.2, 118.3, 113.3, 112.0, 107.8, 91.6, 89.1, 89.0, 86.9.

FT-IR (thin film on NaCl, cm^{-1}): 3380, 3067, 2920, 2852, 2583, 2228, 2210, 1603, 1583, 1481, 1406, 1271, 1064, 881, 831. HRMS (CI) calcd for $C_{32}H_{15}N_3Br_2$ $[M]^+$ 598.9627, found 598.9637.

4-[3,5-Di(phenylethynyl)phenylethynyl]-2,6-di(3-methyl-3-hydroxyl-1-butynyl)aniline (25a)
This compound was prepared with **24a** (0.635 g, 1.15 mmol), 2-methyl-3-butyn-2-ol (0.291 g 3.46 mmol), $Pd(PPh_3)_4$ (27 mg, 23 μmol), CuI (7 mg, 0.04 mmol) in Et_3N (20 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a pale yellow solid (0.590 g, 1.06 mmol, 92%) after flash column choromatography on SiO_2 (hexanes : EtOAc = 1 : 1 to 1 : 2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (t, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 2H), 7.55–7.52 (m. 4H), 7.40 (s, 4H), 7.38–7.33 (m, 6H), 4.98 (bs, 2H), 2.09 (bs, 2H), 1.65 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 135.5, 133.7, 133.6, 131.7, 128.5, 128.4, 124.2, 123.9, 122.8, 111.2, 107.2, 100.2, 90.4, 89.8, 87.9, 86.2, 65.7, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3374, 3056, 2980, 2928, 2855, 2211, 1615, 1579, 1465, 1442, 1376, 1264, 1230, 1161, 959. HRMS (CI) calcd for $C_{40}H_{31}NO_2$ $[M]^+$ 557.2349, found 557.2341.

4-{3,5-Di[(4-methoxyphenyl)ethynyl]phenylethynyl}-2,6-di(3-methyl-3-hydroxyl-1-butynyl)aniline (25b)
This compound was prepared with **24b** (0.518 g, 0.847 mmol), 2-methyl-3-butyn-2-ol (0.215 g, 2.55 mmol), $Pd(PPh_3)_4$ (20 mg, 17 μmol), CuI (7 mg, 0.04 mmol) in Et_3N (20 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a pale yellow solid (0.520 g, 0.842 mmol, 99%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 1 to 1 : 2, and then EtOAc). ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (t, *J* = 1.6 Hz, 1H), 7.51 (d, *J* = 1.6 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 4H), 7.39 (s, 2H), 6.87 (d, *J* = 8.8 Hz, 4H), 4.95 (bs, 2H), 3.82 (s, 6H), 2.70 (bs, 2H), 1.64 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 148.8, 135.5, 133.35, 133.27, 133.1, 132.0, 124.2, 124.1, 114.9, 114.0, 111.3, 107.1, 100.2, 90.4, 89.6, 86.8, 86.4, 65.7, 55.3, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3381, 2980, 2933, 2837, 2541, 2210, 2052, 1607, 1510, 1464, 1441, 1293, 1251, 1180, 1036, 959, 831. HRMS (CI) calcd for $C_{42}H_{35}NO_4$ $[M]^+$ 617.2561, found 617.2563.

4-{3,5-Di[(4-cyanophenyl)ethynyl]phenylethynyl}-2,6-di(3-methyl-3-hydroxyl-1-butynyl)aniline (25c)
This compound was prepared with **24c** (1.17 g, 1.94 mmol), 2-methyl-3-butyn-2-ol (0.490 g, 5.81 mmol), $Pd(PPh_3)_4$ (45 mg, 39 μmol), CuI (11 mg, 58 μmol) in Et_3N (30 mL) by a procedure analogous to that used to prepare **10**. The product was isolated as a pale yellow solid (1.15 g, 1.91 mmol, 99%) after flash column chromatography on SiO_2 (hexanes : EtOAc = 1 : 1 to 1 : 2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65–7.57 (m, 11H), 7.38(s, 2H), 4.98 (bs, 2H), 2.47 (bs, 2H), 1.64 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 135.5, 134.5, 133.7, 132.11, 132.07, 127.5, 124.8, 123.1, 118.3, 111.9, 100.4, 91.8, 90.7, 88.8, 85.6, 77.2, 65.7, 31.6. FT-IR (thin film on NaCl, cm^{-1}): 3376, 2980, 2932, 2227, 1733, 1603, 1576, 1465, 1229, 1161, 838, 753. HRMS (CI) calcd for $C_{42}H_{29}N_3O_2$ $[M]^+$ 607.2254, found 607.2283.

X-Ray Crystallographic Studies
Intensity data were collected on a Bruker diffractometer equipped with a SMART 6000 CCD detector. A typical single crystal was selected from the bulk sample and afffixed to the tip of glass fiber with the use of silicone grease, and the mounted sample was transferred to the goniostat and cooled to –144 ˚C (for **2**) or –150 ˚C (for **6**) for characterization and data collection. Frames were measured for 20 seconds each (for 2) with a frame width of 0.3 degrees in omega. Data were corrected for absorption, instrumental effects, interframe scaling differences, and other systematic errors via the SADABS program.[S5] Equivalent reflections were averaged. The structure was solved by direct methods and completed by Fourier techniques using the SHELXTL software package.[S6] For **6**, the program SQUEEZE was employed to model some regions of highly disordered lattice solvent.

Although most hydrogen sites of **2** were computed based on molecular geometry, many corresponded closely to difference electron density maxima. The positions for the hydrogen atoms of the hydroxyl groups were chosen directly from difference electron density maps and refined freely as isotropic contributors; all other hydrogen positions were refined with a riding model. Disordered, near-overlapping carbon atoms C(74A)–C(79A) and C(74B)–C(79B) were refined isotropically, and all other nonhydrogen atoms were refined anisotropically. Geometric and thermal displacement restraints were applied to stabilize refinement against the effects of high correlations among the atomic parameters of several disordered groups.

The structure of **2** exhibits multiple distinct disorders. First, similarly to the situation in **1**,[S7] it exhibits the "core disorder", in which two alternative orientations of the coplanar central region of the

molecule, i.e. atoms O(1)–N(5), O(30)–N(34), and O(59)–N(63), are present at the same molecular site. These two orientations are related to each other by a non-crystallographic 180° rotation about an axis lying in the plane of the core. Second, the structure exhibits a slight disorder in the terminal phenyl group of one of the molecular arms, where the two alternative positions are mutually coplanar and mostly overlapping; it could have been adequately modeled by hyper-elongated atomic displacement ellipsoids, but the chosen disorder model seems more reflective of the true nature of the structure. Third, all three chlorobenzene solvent molecules are disordered as if by inversion through their molecular centroids (computed considering hydrogen atoms); in one of the three cases, the centroid is at a crystallographic inversion center. Finally, two of the three solvent positions are only partially occupied.

The structure of **6** contains one unique half of a molecule of the compound, $C_{87}H_{69}N_3O_9$, and both dioxane and pentane solvent molecules. The unique half of the molecule **6** is related to its other half by a crystallographic twofold rotation. The structure exhibits both a "core disorder" (see above) and a disorder in the orientation of some of its alcohol groups. The core disorder involves two orientations of the planar, C_{3h}-symmetric core, related by a twofold rotation through an axis in the plane (or equivalently, by an inversion through the centroid). In this structure the twofold rotation is a crystallographic symmetry operation, so the component ratio is exactly 1:1. Despite the disorder, the core atoms were successfully refined without geometric restraints. The alcohol disorders reflect simple differences in torsions of the affected groups around their sp^3–sp bonds to the rest of the molecule. Disorder component ratios are approximately 7:3 and 1:1. These groups were refined with geometric restraints to stabilize the refinement in the presence of the atomic near overlaps. Atomic displacement restraints were applied to all atoms. The structure also contains a considerable amount of disordered solvent. Two dioxane molecules were resolved, one disordered about a center of symmetry and one partially occupied and disordered with (presumably) a highly-disordered pentane molecule; these dioxane molecules were refined, but the rest of the solvent was modeled by use of the SQUEEZE algorithm of program PLATON. Overall solvent content was estimated based on the refined solvent occupancy factors and SQUEEZE's estimates of the void sizes and electron counts.

Compound **4b** crystallizes in monoclinic space group *Cc* with a = 14.424(4) Å, b = 33.079(8) Å, c = 15.929(4) Å, β = 92.505(6)°, and Z = 4. Although the chemical connectivity of this compound was unambigously established by crystallographic analysis, the structure was not fully refined due to extremely weak diffraction data and disorder problems associated with lattice solvent molecules. In the preliminary structure refinement, the model geometry and atomic displacements were extensively restrained, taking into account the molecule's symmetry and the geometric demands of aromatic fragments.

Comparative Conformational Analysis

The conformational analysis consists of verification of the planarity of the cores and arms of each molecule, computation of the core–arm interplanar angles (τ_1), and computation of the intra-arm dihedral angles (τ_2) between aryl functionalities. The crystallographic mode manipulation program XP from the SHELXTL suite[S6] was used to perform the computations. Planarity analyses were performed by computing the plane for which the sum over the atoms of interest of squared atom-plane distances was minimum, i.e. the "least-squares plane". The program provides the individual and mean atomic deviations from this plane and angles to other planes. All 15 non-hydrogen atoms were used for each core plane. For the arm planes, the central phenyl group and the first three atoms of the 2- and 6-substituents were used. For the intra-arm dihedral angles, the second plane in each case was based on the six aryl carbon atoms.

Compound **2** exhibits a core disorder of a type common to this class of compounds, wherein the two disorder components are related by a non-crystallographic twofold rotation in the core plane. For this analysis, all atoms of both disorder components were used to determine the core plane (30 atoms in all). Moreover, the outside *para*-methoxyphenyl substituents on one arm are disordered over two roughly coplanar (mean deviation 0.092 Å, maximum 0.209 Å) orientations; the mean plane over both orientation was used to compute the intra-arm dihedral angle.

Compound **6** has crystallographic two-fold symmetry, with the axis running in the plane of the core and passing through the center of one of the two arms. This imposes a well-resolved core disorder, which was ignored, and makes two of the arms equivalent. The third arm contains crystallographic symmetry; this was taken into account by including the full arm in the computation, including symmetry-equivalent atoms where appropriate.

References

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