Novel Phenylazomethine Dendrimers: Synthesis and Structural Properties

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Supporting Information

Synthesis of DPA dendron G2: Benzophenone (25.7 g, 141 mmol), 4,4'-diaminobenzophenone (3.00 g, 14.1 mmol), and 1,4-diazabiclo[2.2.2]octane (DABCO) (9.51 g, 84.8 mmol) were dissolved in chlorobenzene (90 mL). Titanium(IV) tetrachloride (4.02 g, 21.2 mmol) was added dropwisely. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated, the dendron G2 (3.63 g, 6.71 mmol, 48%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:7 - 1:4, including 1% Et_3N, R_f = 0.32 in the solution of ethyl acetate:hexane = 1:5). **DPA dendron G2**: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.76 (br, 4H), 7.57 (d, *J* = 8.4 Hz, 4H), 7.46 (br, 2H), 7.40 (br, 4H), 7.26 (br, 6H), 7.12 (br, 4H), 6.76 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 195.02, 168.67, 155.11, 139.00, 135.62, 132.53, 131.03, 130.92, 129.40, 129.27, 128.88, 128.20, 127.99, 120.27; IR (KBr, cm^{-1}): 1647 (C=O), 1618 (C=N), 1581 (phenyl), 848, 781, 697; EI-MS: 540 $[M]^+$; Anal. Calcd for $C_{39}H_{28}N_2O$: C, 86.64; H, 5.22; N, 5.18; Found: C, 86.87, H, 4.92; N, 5.09.

Synthesis of DPA dendron G3: The dendron G2 (4.85 g, 8.97 mmol), 4,4'-diaminobenzophenone (380 mg, 1.79 mmol), and DABCO (1.21 g, 10.8 mmol) were dissolved in chlorobenzene (40 mL). Titanium(IV) tetrachloride (510 mg, 2.69 mmol) was added dropwisely. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated, the dendron G3 (1.43 g, 1.14 mmol, 64%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:5 - 1:3, including 1% Et_3N, R_f = 0.24 in solution of ethyl acetate:hexane = 1:4). **DPA dendron G3**: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.77-7.66 (m, 8H), 7.58 (d, *J* = 8.4 Hz, 4H), 7.53 (d, *J* = 8.0 Hz, 4H), 7.49-7.32 (m, 12H), 7.29 (br, 6H), 7.14 (br, 10H), 6.98 (br, 4H), 6.86 (d, *J* = 7.6 Hz, 4H), 6.74 (d, *J* = 8.0 Hz, 4H), 6.69 (d, *J* = 8.4 Hz, 4H), 6.56 (d, *J* = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 194.89,

169.00, 168.48, 155.57, 153.98, 152.06, 139.25, 139.07, 135.85, 135.60, 133.97, 132.22, 130.95, 130.16, 130.05, 129.37, 128.80, 128.17, 128.02, 127.84, 120.68, 120.53, 120.28; IR (KBr, cm^{-1}): 1647 (C=O), 1617 (C=N), 1581 (phenyl), 848, 781, 697; FAB-MS: 1257 $[M+1]^+$; Anal. Calcd for $C_{91}H_{64}N_6O$: C, 86.91; H, 5.13; N, 6.68; Found: C, 86.59, H, 4.79; N, 6.51.

Synthesis of DPA dendron G4: Dendron G3 (9.52 g, 7.57 mmol), 4,4'-diaminobenzophenone (268 mg, 1.26 mmol), DABCO (849 mg, 7.57 mmol) were dissolved in chlorobenzene (120 mL). Titanium(IV) tetrachloride (358 mg, 1.89 mmol) was added dropwisely. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 44 h. The precipitate was removed by filtration. The filtrate was concentrated, the dendron G4 (668 mg, 0.248 mmol, 20%) was isolated by silica gel column chromatography (ethyl acetate:hexane:dichloromethane = 1:6:6 - 1:3:3, including 1% Et_3N, R_f = 0.377 in the solution of ethyl acetate:hexane:dichloromethane = 1:5:5). **DPA dendron G4**: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.74-6.35 (m, 136H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 194.68, 168.87, 168.43, 168.23, 168.12, 155.46, 154.39, 153.78, 152.07, 139.28, 139.05, 135.83, 134.24, 133.66, 132.36, 130.90, 130.60, 130.21, 130.08, 129.98, 129.36, 128.80, 128.17, 128.01, 127.83, 120.89, 120.74, 120.50, 120.28, 120.04; IR (KBr, cm^{-1}): 1647 (C=O), 1617 (C=N), 1578 (phenyl), 848, 784, 695; MALDI-TOF-MS: Calcd: 2690.11 $[M+H]^+$, Found: 2690.36; Anal. Calcd for $C_{195}H_{136}N_{14}O$: C, 87.03; H, 5.09; N, 7.29; Found: C, 87.11, H, 5.24; N, 6.89.

Synthesis of DPA G1: Benzophenone (1.69 g, 9.25 mmol), *p*-phenylenediamine (500 mg, 4.62 mmol), and DABCO (3.11 g, 27.7 mmol) were dissolved in chlorobenzene (40 mL). Titanium(IV) tetrachloride (1.32 g, 6.93 mmol) was added dropwisely. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated, DPA G1 (1.83 g, 4.19 mmol, 91%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:10, R_f = 0.4). **DPA G1**: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.70 (d, *J* = 7.6 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 7.6, 7.6 Hz, 4H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 7.6, 7.6 Hz, 4H), 7.05 (d, *J* = 7.6 Hz, 4H), 6.51 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 167.97, 146.83, 139.74, 136.28, 130.47, 129.47, 129.14, 128.34, 128.06, 127.84, 121.33; IR (KBr, cm^{-1}): 1618 (C=N), 1596 (phenyl), 840, 781, 697; EI-MS: 436 $[M]^+$; Anal. Calcd for $C_{33}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42; Found: C, 88.19, H, 5.35; N, 6.40.

Synthesis of DPA G2: The dendron G2 (1.00 g, 1.85 mmol), *p*-phenylenediamine (100 mg, 0.925 mmol), and DABCO (623 mg, 5.55 mmol) were dissolved in chlorobenzene (30 mL). Titanium(IV) tetrachloride (264 mg, 1.39 mmol) was added dropwisely. The additional funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated, DPA G2 (664 mg, 0.576 mmol, 62%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:6 - 1:4, including 1% Et_3N, R_f = 0.4 in the solution of ethyl acetate:hexane = 1:4). **DPA G2**: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.76 (d, *J* = 7.3 Hz, 4H), 7.71 (d, *J* = 7.3 Hz, 4H), 7.49 (d, *J* = 8.4 Hz, 4H), 7.46-7.35 (m, 12H), 7.28 (m, 6H), 7.19-7.13 (m, 10H), 7.01 (m, 4H), 6.73 (d, *J* = 8.4 Hz, 4H), 6.71 (d, *J* = 8.4 Hz, 4H), 6.54 (d, *J* = 8.4 Hz, 4H), 6.37 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 168.74, 168.44, 167.34, 153.42, 151.69, 146.96, 139.45, 139.32, 136.00, 135.80, 135.11, 131.03, 130.85, 130.47, 129.88, 129.49, 129.42, 128.80, 128.19, 128.06, 127.94, 121.71, 120.54, 120.10; IR (KBr, cm^{-1}): 1617 (C=N), 1584 (phenyl), 844, 784, 697; FAB-MS: 1153 $[M+1]^+$. Anal. Calcd for $C_{84}H_{60}N_6$: C, 87.47; H, 5.24; N, 7.29; Found: C, 87.61, H, 5.16; N, 7.13.

Synthesis of DPA G3: The dendron G3 (600 mg, 0.477 mmol), *p*-phenylenediamine (21.6 mg, 0.200 mmol), and DABCO (135 mg, 1.20 mmol) were dissolved in chlorobenzene (30 mL). Titanium(IV) tetrachloride (56.9 mg, 0.300 mmol) was added dropwisely. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated, the dendron G3 (230 mg, 0.0890 mmol, 45%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:5 - 1:2, including 1% Et_3N, R_f = 0.46 in the solution of ethyl acetate:hexane = 1:2). **DPA G3**: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.76-7.63 (m, 16H), 7.50-7.33 (m, 36H), 7.31-7.22 (m, 16H), 7.19-7.11 (m, 12H), 7.06 (br, 4H), 6.95 (br, 8H), 6.84 (d, *J* = 8.4 Hz, 4H), 6.76-6.71 (m, 12H), 6.67 (d, *J* = 8.4 Hz, 4H), 6.59 (d, *J* = 8.4 Hz, 4H), 6.54 (d, *J* = 8.4 Hz, 4H), 6.51 (d, *J* = 8.4 Hz, 4H), 6.44 (d, *J* = 8.4 Hz, 4H), 6.43 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 169.00, 168.83, 168.51, 168.41, 168.11, 167.17, 153.83, 153.78, 153.68, 152.12, 151.95, 151.87, 147.10, 139.41, 139.26, 139.08, 135.94, 135.81, 135.63, 134.56, 134.48, 134.43, 130.88, 130.78, 130.73, 130.47, 130.30, 130.16, 130.11, 129.98, 129.45, 129.30, 128.86, 128.71, 128.23, 128.08, 127.95, 127.90, 121.86, 120.82, 120.79, 120.51, 120.33, 120.00; IR (KBr, cm^{-1}): 1617 (C=N), 1581 (phenyl), 847, 783, 696; MALDI-TOF-MS: Calcd:

2587.2 $[M]^+$, Found: 2587.0; Anal. Calcd for $C_{188}H_{132}N_{14}$: C, 87.28; H, 5.14; N, 7.58; Found: C, 87.43, H, 4.84; N, 7.37.

Synthesis of DPA G4: The dendron G4 (400 mg, 0.149 mmol), *p*-phenylenediamine (8.0 mg, 0.074 mmol), and DABCO (49.8 mg, 0.444 mmol) were dissolved in chlorobenzene (20 mL). Titanium(IV) tetrachloride (21.1 mg, 0.111 mmol) was added dropwisely. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated, DPA G4 (125 mg, 0.0229 mmol, 31%) was isolated by silica gel column chromatography (ethyl acetate:hexane:dichloromethane = 1:4:4 - 1:3:3, including 1% Et_3N, R_f = 0.45 in solution of ethyl acetate:hexane:dichloromethane = 1:3:3). **DPA G4**: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ = 7.80-6.31 (m, 276H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ = 169.02, 168.79, 168.47, 168.14, 167.95, 167.78, 166.89, 154.19, 154.04, 153.78, 152.27, 151.97, 151.72, 139.39, 139.18, 139.00, 135.89, 135.70, 134.48, 134.33, 134.17, 130.93, 130.70, 130.35, 130.14, 129.43, 128.86, 128.66, 128.22, 128.07, 127.92, 121.67, 121.05, 120.87, 120.79, 120.52, 120.33, 120.05; IR (KBr, cm^{-1}): 1617 (C=N), 1578 (phenyl), 848, 784, 696; MALDI-TOF-MS: Calcd: 5451.26 $[M+H]^+$, Found: 5451.48.