Supporting Information

Synthesis and Self-Assembly of Supramolecular Dendritic “Bow-Ties”: Effect of Peripheral Functionality on Association Constants

*Elizabeth R. Gillies and Jean M. J. Fréchet**

Table of Contents:

1. General Procedures and Materials.....pg. 2
2. Experimental Procedures for compounds **2a**, **2b**, **3a**, **4a**, **7**, **11b**, **15b**.....pg. 2-6
3. ¹H NMR Spectrum for compound **12**.....pg. 7

General Procedures and Materials. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled under a nitrogen atmosphere from Na/benzophenone immediately prior to use. Dichloromethane and pyridine were distilled from CaH₂ under a nitrogen atmosphere immediately prior to use. The combined organic layers after extractions were dried over anhydrous MgSO₄ and filtered by gravity over filter paper. Solvents were removed *in vacuo* with a rotary evaporator, followed by vacuum pump evacuation of volatile compounds. Merck Kieselgel plates coated with silica gel 60 F₂₅₄ were used for thin layer chromatography and were visualized by UV activity or using permanganate stain. Column chromatography (cc) was performed using Merck Kieselgel 60 silica gel (230-400 Mesh). ¹H NMR spectra were recorded at 400 or 500 MHz and ¹³C NMR spectra were recorded at 100 or 125 MHz. NMR chemical shifts are reported in ppm and calibrated against residual solvent signals of CDCl₃ (δ 7.26, 77.2) or MeOD (δ 3.31, 49.2). CDCl₃ was dried by filtering over activated basic alumina. All coupling constants are reported in Hz. FT-IR spectroscopic analyses were performed using a thin film from CH₂Cl₂ or THF on a reflective mirror surface and are reported in cm⁻¹.

(Benzyldiene)₂-[G-2]-trimethylsilylethyl ester (2a). **1b** (0.62 g, 2.6 mmol, 1.0 equiv.) and DMAP (0.26 g, 2.1 mmol, 0.80 equiv.) were dissolved in 20 mL of CH₂Cl₂ and 10 mL of pyridine were added. Benzyldiene-2,2-bis(oxymethyl)propionic anhydride (4.5 g, 11 mmol, 4.0 equiv.) was added, and the reaction mixture was stirred at rt overnight. The reaction was quenched and worked up as for **1a** to give 1.6 g (93 %) of **2a** as a colorless glass. IR (film from CH₂Cl₂): 1740. ¹H NMR (500 MHz, CDCl₃): δ -

0.03 (s, 9H), 0.91-0.95 (m, 2H), 0.96 (s, 6H), 1.25 (s, 3H), 3.61 (dd, 4H, $J = 11.4, 3.2$), 4.11-4.15 (m, 2H), 4.37 (d, 2H, $J = 11.0$), 4.43 (d, 2H, $J = 11.0$), 4.59 (d, 4H, $J = 11.4$), 5.42 (s, 2H), 7.30-7.33 (m, 6H), 7.40-7.42 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ -1.4, 17.5, 17.9, 18.0, 42.8, 46.8, 63.8, 65.8, 73.7, 102.0, 126.4, 128.3, 129.1, 138.0, 173.1, 173.5. MS: calcd $[\text{M}+\text{Li}]^+$ ($\text{C}_{34}\text{H}_{46}\text{LiO}_{10}\text{Si}$): 649.3020. Found: (HRFAB) 649.3032. Anal. calcd for $\text{C}_{34}\text{H}_{46}\text{O}_{10}\text{Si}$: C, 63.53; H, 7.21. Found: C, 63.36; H, 7.05.

(HO)₄-[G-2]-trimethylsilylethyl ester (2b). **2a** (1.50 g, 2.34 mmol) was dissolved in 15 mL of CH_2Cl_2 and was diluted with 15 mL of methanol. 150 mg of 10% w/w Pd/C were added. The procedure described above for **1b** was repeated to give 1.05 g (96 %) of **2b** as a white solid. MP: 56-58 °C. IR (film from CH_2Cl_2): 3430, 1722. ^1H NMR (500 MHz, CDCl_3): δ 0.04 (s, 9H), 0.97-1.00 (m, 2H), 1.05 (s, 6H), 1.27 (s, 3H), 3.48 (br s, 4H), 3.68 (t, 4H, $J = 10.9$), 3.79 (dd, 4H, $J = 11.3, 4.7$), 4.19-4.23 (m, 4H), 4.41 (d, 2H, $J = 11.1$). ^{13}C NMR (125 MHz, CDCl_3): δ -1.4, 17.3, 17.6, 18.3, 46.4, 49.9, 64.2, 65.1, 67.5, 173.4, 175.3. MS: calcd $[\text{M}+\text{H}]^+$ ($\text{C}_{20}\text{H}_{39}\text{O}_{10}\text{Si}$): 467.2312. Found: (HRFAB) 467.2320. Anal. calcd for $\text{C}_{20}\text{H}_{38}\text{O}_{10}\text{Si}$: C, 51.48; H, 8.21. Found: C, 51.70; H, 8.02.

(Benzylidene)₄-[G-3]-trimethylsilylethyl ester (3a). **2b** (1.3 g, 2.7 mmol, 1.0 equiv.) and DMAP (0.40 g, 3.3 mmol, 1.2 equiv.) were dissolved in 50 mL of CH_2Cl_2 and 5 mL of pyridine were added. Benzylidene-2,2-bis(oxymethyl)propionic anhydride (7.0 g, 16 mmol, 6.0 equiv.) was added, and the reaction mixture was stirred at rt overnight. The reaction was quenched and worked up as for **1a** to give 3.2 g (92 %) of **3a** as a colorless glass. IR (film from CH_2Cl_2): 1745. ^1H -NMR (500 MHz, CDCl_3): δ 0.02 (s, 9H), 0.93-0.97 (m, 14H), 1.04 (s, 3H), 1.21 (s, 6H), 3.58 (dd, 8H, $J = 11.6, 2.4$), 4.05 (d, 2H, $J = 11.0$), 4.09-4.15 (m, 4H), 4.33-4.39 (m, 8H), 4.57 (dd, 8H, $J = 8.9, 2.8$), 5.40 (s, 4H),

7.29-7.33 (m, 12H), 7.39 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3): δ -1.8, 17.5, 17.6, 17.87, 17.90, 42.8, 46.6, 47.1, 64.0, 65.4, 66.2, 73.7, 101.9, 126.4, 128.3, 129.0, 138.0, 172.1, 172.5, 173.4. MS: calcd $[\text{M}+\text{Na}]^+$ ($\text{C}_{68}\text{H}_{86}\text{NaO}_{22}\text{Si}$): 1306.4. Found: (MALDI-TOF) 1305.2. Anal. calcd for $\text{C}_{68}\text{H}_{86}\text{O}_{22}\text{Si}$: C, 63.63; H, 6.75. Found: C, 63.20; H, 6.92.

N, N-Bis(2-cyanoethyl)-ethanolamine (4a). This compound was prepared according to a previously reported procedure. Some spectral data was not previously reported.²³ ^1H NMR (500 MHz, CDCl_3): δ 2.48 (t, 4H, $J = 6.7$), 2.63 (s, 1H), 2.66 (t, 2H, $J = 5.3$), 2.86 (t, 4H, $J = 6.7$), 3.57 (t, 2H, $J = 5.3$). ^{13}C NMR (125 MHz, CDCl_3): δ 17.1, 49.8, 55.6, 59.5, 118.9.

(HO)₈-[G-3]-(Adamantylurea)₂ (7). **6** (80 mg, 0.047 mmol) was dissolved in 5 mL of CH_2Cl_2 and was diluted with 5 mL of MeOH. 60 mg of 10% w/w Pd/C were added. The procedure described above for **1b** was followed, then the resulting residue was taken up in THF and washed with 0.1 M NaOH in saturated brine. The organic phase was dried and evaporated to provide 51 mg (81 %) of the unprotonated amine **7** as a colorless glass. IR (film from THF): 3390, 1732, 1641. ^1H NMR (500 MHz, MeOD): 1.15 (s, 12H), 1.30 (s, 6H), 1.41 (s, 3H), 1.61-1.66 (m, 4H), 1.74 (br s, 12H), 1.94-1.98 (m, 12H), 2.04 (br s, 6H), 2.56 (t, 4H, $J = 7.0$), 2.78 (t, 2H, $J = 6.5$), 3.10 (t, 4H, $J = 6.7$), 3.60 (d, 8H, $J = 10.9$), 3.68 (dd, 8H, $J = 10.8$, 2.3), 4.23-4.26 (m, 6H), 4.28-4.34 (m, 8H). ^{13}C NMR (125 MHz, MeOD): 17.5, 18.3, 18.5, 28.9, 31.2, 37.7, 38.9, 43.7, 48.0, 48.1, 51.6, 52.0, 53.1, 53.3, 66.0, 66.3, 67.4, 69.0, 160.4, 173.9, 174.1, 176.0. MS: calcd $[\text{M}+\text{H}]^+$ ($\text{C}_{65}\text{H}_{108}\text{N}_5\text{O}_{24}$): 1342.5. Found: (MALDI-TOF) 1341.2. Anal. calcd for $\text{C}_{65}\text{H}_{107}\text{N}_5\text{O}_{24}$: C, 58.15; H, 8.03; N, 5.22. Found: C, 57.78; H, 8.28; N, 4.88.

(Isopropylidene)₄-[G-3]-Glyciny lurea (11b). The ester **11a** (0.24 g, 1.9 mmol) was dissolved in 15 mL of EtOAc and 30 mg of 10% w/w Pd/C were added. The procedure described above for **1b** was followed, stopping the reaction after 3 h to provide 0.21 g (92 %) of **11b** as a colorless glass. IR (film from CH₂Cl₂): 3400, 1740, 1644, 1567. ¹H NMR (500 MHz, CDCl₃): 1.09 (s, 12H), 1.23 (s, 3H), 1.24 (s, 6H), 1.31 (s, 12H), 1.31-1.35 (m, 4H), 1.38 (s, 12H), 1.43-1.51 (m, 2H), 1.58-1.64 (m, 2H), 3.13 (s, 2H), 3.59 (d, 8H, *J* = 12.5), 3.88 (d, 2H, *J* = 3.5), 4.07-4.12 (m, 10H), 4.19-4.30 (m, 12H), 5.55 (s, 1H), 5.66 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): 17.7, 17.8, 18.5, 21.7, 25.6, 25.8, 26.4, 28.4, 29.8, 40.4, 42.2, 42.9, 46.8, 47.0, 65.1, 65.6, 66.1, 66.2, 98.3, 159.4, 172.0, 172.3, 173.1, 173.8. MS: calcd [M+H]⁺ (C₅₆H₉₁N₂O₂₅): 1191.3. Found: (MALDI-TOF) 1192.0. Anal. calcd for C₅₆H₉₀N₂O₂₅: C, 56.46; H, 7.62; N, 2.35. Found: C, 56.54; H, 7.48; N, 2.44.

Oligo(ethylene oxide)-[G-3]-Glyciny lurea (15b). The ester **15a** (0.13 g, 40 μmol) was dissolved in 8 mL of EtOAc and 20 mg of 10% w/w Pd/C were added. The procedure described above for **1b** was followed, stopping the reaction after 3 h to provide 0.13 g (100 %) of **15b** as a colorless glass. IR (film from CH₂Cl₂): 3400, 1754, 1727. ¹H NMR (500 MHz, CDCl₃): 1.15 (s, 15H), 1.19 (s, 3H), 1.24-1.30 (m, 4H), 1.37-1.42 (m, 2H), 1.53-1.59 (m, 2H), 3.04-3.10 (m, 2H), 3.28 (s, 24H), 3.45 (m, 16H), 3.54-3.57 (m, 48H), 3.61-3.67 (m, 20H), 3.82 (d, 2H, *J* = 6.3), 4.03 (t, 2H, *J* = 8.1), 4.15-4.23 (m, 72H), 5.43 (s, 1H), 5.55 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): 17.5, 17.7, 25.6, 26.3, 28.3, 30.0, 40.1, 42.7, 46.3, 46.5, 46.6, 59.0, 64.0, 65.2, 65.3, 65.6, 66.4, 67.7, 67.9, 68.8, 70.47, 70.50, 71.8, 159.1, 169.3, 169.7, 171.4, 171.6, 172.0, 172.3. MS: calcd

$[M+Na]^+$ ($C_{132}H_{218}NaN_2O_{81}$): 3152.1. Found: (MALDI-TOF) 3153.7. Anal. calcd for $C_{132}H_{218}N_2O_{81}$: C, 50.67; H, 7.02; N, 0.90. Found: C, 50.70; H, 6.88; N, 0.98.

Compound 12