Supplementary Material (ESI) for Chemical Communications

Supporting information

Taking multicalixarenes into the nanoworld: First third-generation calixarene dendrimer

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General Experimental Details

All chemicals were purchased from Sigma-Aldrich Ltd. (Aldrich, Sigma and Fluka/Riedel de Haën brands), Lancaster or Acrôs Organics, and unless specified, were used without further purification. Deuterated solvents for NMR use were purchased from Cambridge Isotope Laboratories, Inc. or Apollo Scientific. Analytical thin layer chromatography (TLC) was performed using Merck Kieselgel 60 F_{254} silica gel plates. Column chromatography was run using silica gel 60 (70-230 mesh ASTM). Visualisation was by UV light (254 nm). NMR spectra were recorded at 293 K, unless otherwise stated, using a 400 MHz Varian Unity Plus Spectrometer, operating at 399.92 MHz or 399.96 MHz (proton), 100.56 MHz or 100.57 MHz (carbon) and 376.24 MHz (fluorine), or a 300 MHz Gemini 2000 spectrometer operating at 300.05 MHz (proton) and 75.45 MHz (carbon). Shifts are referenced relative to the internal reference standard, tetramethylsilane (TMS), with chemical shifts expressed in ppm or δ downfield from the standard and coupling constants (*J*) expressed in Hz. NMR data were processed using MestReC software. MALDI-TOF mass spectra were recorded by the EPSRC National Mass Spectrometry Service, Swansea, or using a Kratos Axima CFR MALDI Mass Spectrometer. ESI mass spectra were recorded on a Shimadzu LC-MS 2010EV Spectrometer, with HPLC grade CH_3OH, water or CH_3CN as carrier solvents. Melting points were measured using an Electrothermal Mel-temp® melting point apparatus and are reported uncorrected. Infrared spectra were recorded using an Avatar 360 FT-IR spectrometer.

5,11,17,23-*p*-*Tert*-butyl-25,26,27-tripropoxy-28-(3-ethoxycarbonyl)propoxycalix[4]-arene 6

Sodium hydride (95%, 1.23 g, 51.2 mmol) and DMF (225 mL) were added to a stirred solution of **5**[1] (10.00 g, 12.85 mmol) inDMF(175 mL) under an atmosphere of argon. After 1 h, ethyl 4-bromobutyrate (7.35 mL, 51.4 mmol) was added and the solution was stirred for 5 d. Water (300 mL) was added and the aqueous solution was extracted with dichloromethane. The organic phase was washed with aq. hydrochloric acid (10%, 2 × 50 mL) and brine (2 × 50 mL) and the solvent was removed under reduced pressure to yield **6** (9.73 g, 85%) as a pale green glassy solid. **Mp** 138-139 °C; **IR** *ν*C(O) = 1738 cm^{-1}, *ν*C(O)O = 1248 cm^{-1}, 1122 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 6.80 (4 H, s, Ar*H*), 6.78 (4 H, s, Ar*H*), 4.40 (2 H, d, *J* = 13.6 Hz, ArC*H*$_2$Ar), 4.39 (2 H, d, *J* = 13.4 Hz, ArC*H*$_2$Ar), 4.15 (2 H, q, *J* = 7.2 Hz, $CH_2CO_2CH_2CH_3$), 3.86 (2 H, m, OCH_2CH_2), 3.80 (6 H, t, *J* = 7.2 Hz, $OCH_2CH_2CH_3$), 3.12 (4 H, d, *J* = 13.6 Hz, ArC*H*$_2$Ar), 3.11 (4 H, d, *J* = 13.4 Hz, ArC*H*$_2$Ar), 2.51 (2 H, m, $OCH_2CH_2CH_2CO_2Et$), 2.33 (2 H, m, $OCH_2CH_2CH_2CO_2Et$), 1.98 (6 H, m, $OCH_2CH_2CH_3$), 1.27 (3 H, t, *J* = 6.8 Hz, OCH_2CH_3), 1.10 (9 H, s, $(CH_3)_3Ar$), 1.09 (9 H, s, $(CH_3)_3Ar$), 1.06 (18 H, s, $(CH_3)_3Ar$), 0.98 (9 H, m, $OCH_2CH_2CH_3$); **^{13}C NMR** (100 MHz, $CDCl_3$); 173.6, 153.8, 153.7, 153.6, 144.5, 144.3, 134.0, 133.9, 133.8, 133.6, 125.0, 124.9, 124.8, 74.1, 60.19, 33.7, 33.6, 31.3, 30.9, 25.5, 23.2, 23.1, 14.1, 10.1; **M/z (MALDI-TOF)** *m/z* 911.74 $[M + Na]^+$.

5,11,17,23-*p*-*Tert*-butyl-25,26,27-tripropoxy-28-(3-carboxypropoxy)calix[4]arene 7

Tetramethylammonium hydroxide (25% aq., 36.90 mL, 101.2 mmol) was added to a stirred solution of **6** (9.00 g, 10.1 mmol) in tetrahydrofuran (200 mL) and the solution heated at reflux overnight. After cooling, the mixture was acidified with conc. aq. hydrochloric acid (37%, 40 mL) and stirred for 6 h at RT; the resultant precipitate was filtered and washed with H_2O (2 × 50 mL) to give **7** (6.60 g, 76%) as a white powder. **Mp** 144-145°C; **IR** *ν*OH = 2960 cm^{-1}, *ν*C(O) = 1731 cm^{-1}, *ν*CO = 1202 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 6.98 (4 H, bs, Ar*H*), 6.77 (2 H, s, Ar*H*), 6.73 (2 H, s, Ar*H*), 4.39 (4 H, d, *J* = 12.5 Hz, ArC*H*$_2$Ar, coincident), 4.12-4.05 (4 H, m, $OCH_2CH_2CH_2CO_2H$), 3.68 (2 H, t, *J* = 7.2 Hz, $OCH_2CH_2CH_3$), 3.57 (4 H, t, *J* = 7.2 Hz, $OCH_2CH_2CH_3$), 3.10 (2 H, d, *J* =

12.5 Hz, ArC*H*$_2$Ar), 3.09 (2H, d, *J* = 12.5 Hz, ArC*H*$_2$Ar), 1.99 (4 H, m, OCH$_2$C*H*$_2$CH$_2$CO$_2$H, OCH$_2$C*H*$_2$CH$_3$, coincident), 1.89 (4 H, m, OCH$_2$C*H*$_2$CH$_3$), 1.08-0.89 (45 H, m, (C*H*$_3$)$_3$Ar, OCH$_2$CH$_2$C*H*$_3$, coincident); **^{13}C NMR** (100 MHz, $CDCl_3$); 179.3, 154.0, 153.7, 153.3, 144.7, 144.3, 144.2, 134.3, 134.2, 133.5, 133.3, 125.1, 125.0, 124.9, 124.8, 73.87, 33.75, 33.73, 33.63, 31.5, 31.4, 31.3, 30.9, 25.2, 23.2, 23.1, 10.19, 10.0 ***M/z*** **(MALDI TOF)** *m/z* 883.05 $[M + Na]^+$.

5,11,17,23-*p*-*Tert*-butyl-25,26,27-tripropoxy-28-(4-oxo-4-pentafluorophenoxybutyl)calix[4]arene 8

7 (3.00 g, 3.48 mmol) was suspended in EtOAc (50 mL) and cooled to 0^{o}C. N,M'-Dicyclohexylcarbodiimide (0.72 g, 3.48 mmol) and pentafluorophenol (0.64 g, 3.5 mmol) were added and the solution stirred for 18 h. The suspension was filtered, the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography over silica gel, eluting with dichloromethane, to yield **8** (1.49 g, 42%) as a white powder: **Mp** 165-167 °C; **IR** *v*C(O) = 1794 cm^{-1}, *v*CO = 1201 cm^{-1}, 1122 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 6.85 (4 H, d, *J* = 1.8 Hz, Ar*H*), 6.73 (2 H, s, Ar*H*), 6.72 (2 H, s, Ar*H*), 4.42 (2 H, d, *J* = 12.7 Hz, ArC*H*$_2$Ar), 4.38 (2 H, d, *J* = 12.4 Hz, ArC*H*$_2$Ar), 3.98 (2 H, t, *J* = 7.0 Hz, OC*H*$_2$CH$_2$CH$_2$CO$_2$PFP), 3.87-3.77 (6 H, m, OC*H*$_2$CH$_2$CH$_3$), 3.15 (2 H, d, *J* = 12.7 Hz, ArC*H*$_2$Ar), 3.12 (2 H, d, *J* = 12.4 Hz, ArC*H*$_2$Ar), 2.93 (2 H, t, *J* = 7.5 Hz, OCH$_2$CH$_2$C*H*$_2$CO$_2$PFP), 2.51 (2 H, m, OCH$_2$C*H*$_2$CH$_2$CO$_2$PFP), 1.99 (6 H, m, OCH$_2$C*H*$_2$CH$_3$), 1.13 (9 H, s, Ar(C*H*$_3$)$_3$), 1.12 (9 H, s, Ar(C*H*$_3$)$_3$), 1.03 (18 H, s, Ar(C*H*$_3$)$_3$), 0.99 (9 H, m, OCH$_2$CH$_2$C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$); 169.5, 153.9, 153.6, 153.5, 145.0, 144.5, 144.4, 134.4, 134.3, 133.7, 133.4, 125.4, 125.2, 125.1, 125.0, 77.3, 77.2, 73.7, 34.1, 34.0, 33.9, 31.7, 31.6, 31.5, 31.2, 31.1, 30.6, 30.5, 25.6, 23.6, 23.4, 10.4, 10.3; **^{19}F NMR** (376 MHz, $CDCl_3$); -153.55 (2 F, d, *J* = 21.8 Hz, F_{ortho}), -158.82 (1 F, t, *J* = 22.8 Hz, F_{para}), -163.08 (2 F, t, *J* = 21.8 Hz, F_{meta}); ***M/z*** **(MALDI TOF)** *m/z* 1063.50 $[(M - 2 H + K],^+$ 1025.28 $[M - H]^+$.

Multi-calixarene 9

A solution of **4**[2] (0.09 g, 0.11 mmol), **8** (0.45 g, 0.44 mmol), diisopropylethylamine (0.18 mL, 1.10 mmol) and a catalytic amount of DMAP in DCM (3 mL) was stirred at ambient

temperature for 6 d. Water (5 mL) and dichloromethane (5 mL) were added. The organic layer was separated and washed with aq. hydrochloric acid (10 %, 5 mL), aq. sodium hydroxide (10 %, 5 mL) and brine (10 %, 5 mL), befor being dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel, eluting with dichloromethane / hexane (5:1) to yield multi-calixarene **9** as a white foam (0.10 g, 22%). **Mp** 214-217 °C; **IR** *ν*NH = 3377 cm^{-1}, *ν*Phth = 1719 cm^{-1}, *ν*C(O) = 1677 cm^{-1}, *ν*NH = 1601 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 7.86 (2 H, dd, *J* = 5.5 Hz, *J* = 3.1 Hz, ArH_{pht}), 7.71 (2H, dd, *J* = 5.4 Hz, *J* = 3.1 Hz, ArH_{pht}), 7.05 (4 H, s, Ar*H*), 6.83-6.63 (36 H, br m, Ar*H*), 4.39 (20 H, m, ArCH_2Ar), 3.96-3.81 (50 H, m, OC$H_2$$CH_2CH_2N$, OC$H_2$$CH_2CH_3$, OCH_2CH_2CH_2N, coincident), 3.11 (20 H, m, ArCH_2Ar), 2.30 (16 H, m, OCH_2CH_2), 2.05 (16 H, m, OCH_2CH_2), 1.86 (8 H, m, OCH_2CH_2), 1.09-0.89 (189 H, br m, C(CH_3)$_3$, OCH_2CH_2CH_3, coincident); ***M/z*** **(MALDI TOF)** *m/z* 4193.8 $[M + Na]^+$.

Multi-calixarene 10

A stirred solution of multi-calixarene **9** (0.12 g, 0.03 mmol) and hydrazine hydrate (0.09 mL, 3 mmol) in ethanol (3 mL) was heated at reflux for 4 d. Water (3 mL) and dichloromethane (6 mL) were added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 6 mL), the organic layers were combined and the solvent was evaporated under reduced pressure to yield **10** as a white glass (0.11 g, quantitative). **Mp** 211-212 °C; **IR** *ν*NH_2 = 3289 cm^{-1}, 3418 cm^{-1}, *ν*C(O) = 1641 cm^{-1}, *ν*NH = 1547 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 7.02 (4 H, br s, Ar*H*), 6.79-6.58 (36 H, m, Ar*H*), 4.40 (20 H, m, ArCH_2Ar), 3.98-3.87 (48 H, m, OC$H_2$$CH_2CH_2N$, OC$H_2$$CH_2CH_3$, OCH_2CH_2CH_2N, coincident), 3.11 (22 H, m, ArCH_2Ar, OCH_2CH_2CH_2N, coincident), 2.36 (16 H, m, OCH_2CH_2), 2.02 (16 H, m, OCH_2CH_2), 1.83 (8 H, m, OCH_2CH_2), 1.10 (72 H, s, C(CH_3)$_3$), 1.08 (36 H, s, C(CH_3)$_3$), 1.07 (36 H, s, C(CH_3)$_3$), 0.98 (45 H, m, OCH_2CH_2CH_3); ***M/z*** **(MALDI TOF)** *m/z* 4063.7 $[M+Na]^+$.

Multi-calixarene MC1

A solution of multi-calixarene **10** (0.13 g, 0.03 mmol), **11**[2] (0.01 g, 0.008 mmol), diisopropylethylamine (0.01 mL, 0.08 mmol) and a catalytic amount of 4-

dimethylaminopyridine in dichloromethane (1 mL) was stirred at ambient temperature for 5 days. Water (2 mL) and dichloromethane (2 mL) were added and the organic layer was separated and washed with aq. hydrochloric acid (10 %, 2 mL), aq. sodium hydroxide (10 %, 2 mL), brine (10 %, 2 mL), before being dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel, eluting with hexane / ethyl acetate (10:1) gradient to hexane / ethyl acetate (5:1), to yield **MC1** as a white powder (68.30 mg, 50%). **Mp** 240-242 °C; **IR** *ν*NH = 3421 cm^{-1}, *ν*C(O) = 1652 cm^{-1}, *ν*NH = 1539 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 7.30-6.42(180 H, m, Ar + NH) 6.83-6.64 (140 H, m, Ar*H*), 4.39 (80 H, m, ArC*H*$_2$Ar), 3.89-3.57 + 3.46-3.28 (210 H, br m, b m, OC*H*$_2$CH$_2$CH$_3$, OC*H*$_2$CH$_2$C*H*$_2$N, OC*H*$_2$C(O)NH, ArC*H*$_2$Ar, coincident), 3.09 (80 H, m, ArC*H*$_2$Ar), 2.46-2.15 (40 H, m, OCH$_2$C*H*$_2$), 1.98-1.89 (120 H, m, OCH$_2$C*H*$_2$), 1.08-0.89 (756 H, m, OCH$_2$CH$_2$C*H*$_3$, C(C*H*$_3$)$_3$, coincident); ***M/z* (MALDI TOF)** *m/z* 16747 $[M + H]^+$.

5,11,17,23- *p-Tert*-butyl-25,26,27-tripropoxy-28-(3-aminopropoxy)calix[4]arene (13)
A solution of **12**[2] (8.00 g, 8.37 mmol) and hydrazine hydrate (2.60 mL, 83.7 mmol) in ethanol (75 mL) was heated to reflux for 4 h. The reaction was followed by TLC (dichloromethane) until only a single spot was observed on the base line, using ninhydrin as an indicator. After cooling, water (40 mL) was added to dilute the mixture, the precipitate was extracted with dichloromethane and the solvent was evaporated to give **13** as a white solid (6.15 g, 88%). **Mp** 204-206 °C; **IR** *ν*NH = 3437 cm^{-1}, 3324 cm^{-1}, 1597 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 6.76 (8 H, m, Ar*H*), 4.42 (2 H, d, *J* = 12.4 Hz, ArC*H*$_2$Ar), 4.39 (2 H, d, *J* = 12.4 Hz, ArC*H*$_2$Ar), 3.92 (2 H, t, *J* = 7.2 Hz, OC*H*$_2$CH$_2$CH$_2$NH$_2$), 3.83 (6 H, m, OC*H*$_2$CH$_2$CH$_3$), 3.14 (2 H, d, *J* = 12.4 Hz, ArCH$_2$Ar), 3.13 (2 H, d, *J* = 12.4 Hz, ArCH$_2$Ar), 2.90 (2 H, m, OCH$_2$CH$_2$C*H*$_2$NH$_2$), 2.16 (2 H, m, OCH$_2$C*H*$_2$CH$_2$NH$_2$), 2.01 (6 H, m, OCH$_2$C*H*$_2$CH$_3$), 1.65 (2 H, br s, OCH$_2$CH$_2$CH$_2$N*H*$_2$), 1.06 (45 H, m, (C*H*$_3$)$_3$Ar, OCH$_2$CH$_2$C*H*$_3$, coincident); **^{13}C NMR** (100 MHz; $CDCl_3$); 153.8, 153.6, 153.5, 144.5, 144.4, 144.3, 144.2, 134.0, 133.9, 133.8, 125.1, 125.0, 124.9, 124.9, 73.0, 39.5, 34.0, 33.7, 31.4, 31.0, 23.2, 23.1, 10.16 **ESI MS** *m/z* 832.3 $[M]^+$.

5,11,17,23-Tetra(pentafluorophenoxycarbonyl)-25,26,27,28-tetrapropoxycalix[4]arene (14)

A solution of 25,26,27,28-tetrapropoxycalix[4]arene-5,11,17,23-tetracarboxylic acid[3] (2.00 g, 2.92 mmol) in ethyl acetate (30 mL) was cooled to 0°C. N,N'-Dicyclohexylcarbodiimide (2.41 g, 11.6 mmol) and pentafluorophenol (2.15 g, 11.6 mmol) were added and the solution was stirred for 18 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in EtOAc and filtered to yield **14** as a white solid (1.10 g, 39%). **Mp** 245-247 °C; **IR** *ν*C(O)O = 1758 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 7.58 (8 H, s, Ar*H*), 4.54 (4 H, d, *J* = 13.7 Hz, ArC*H*$_2$Ar), 3.99 (8 H, t, *J* = 7.4 Hz, OC*H*$_2$CH$_2$CH$_3$), 3.39 (4 H, d, *J* = 13.7 Hz, ArC*H*$_2$Ar), 1.96 (8 H, m, OCH$_2$C*H*$_2$CH$_3$), 1.04 (12 H, t, *J* = 7.4 Hz, OCH$_2$CH$_2$C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$); 162.1, 161.9, 140.4, 135.4, 131.6, 125.5, 121.5, 114.5, 94.6, 77.6, 31.0, 23.5, 10.4; **^{19}F NMR** (376 MHz, $CDCl_3$); -152.7 (8 F, d, *J* = 18.4 Hz, F_{ortho}), -159.6 (4 F, t, *J* = 22.8 Hz, F_{para}), -164.0 (8 F, t, *J* = 24 Hz, F_{meta}); **ESI MS** *m/z* 1454.85 $[M + Na]^+$.

Multi-calixarene MC2

A solution of **11** (2.40 g, 1.81 mmol), **13** (6.03 g, 7.25 mmol), diisopropylethylamine (2.99 mL, 18.12 mmol) and a catalytic amount of 4-dimethylaminopyridine in dichloromethane (100 mL) was stirred for 48 h. The solution was diluted with water (60 mL), washed with aq. hydrochloric acid (10%, 2 × 50 mL), aq. sodium hydroxide (10%, 2 × 50 mL), brine (2 × 50 mL), and dried ($MgSO_4$). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography over silica gel, eluting with dichloromethane running to ethyl acetate, to yield **MC2** (5.24 g, 74%) as a white solid. **Mp** 201-203 °C; **IR** *ν*C(O)NH = 3413 cm^{-1}, 1688 cm^{-1}, 1529 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 6.90 (8 H, d, *J* = 7.6 Hz, Ar*H*), 6.87 (8 H, s, Ar*H*), 6.86 (8 H, s, Ar*H*), 6.65 (16 H, s, Ar*H*), 6.57 (4 H, t, *J* = 7.6 Hz, Ar*H*), 6.32 (4 H, t, *J* = 5.6 Hz, N*H*), 4.45 (8 H, d, *J* = 12.4 Hz, ArC*H*$_2$Ar), 4.39 (8 H, d, *J* = 12.4 Hz, ArC*H*$_2$Ar), 3.95 (8 H, t, *J* = 7.4 Hz, OC*H*$_2$CH$_2$CH$_2$N), 3.86 (16 H, m, OC*H*$_2$CH$_2$CH$_3$), 3.74 (8H , t, *J* = 7.4 Hz, OC*H*$_2$CH$_2$CH$_3$), 3.61 + 3.55 (16 H, 2 × s, ArC*H*$_2$Ar, OC*H*$_2$C(O)N), 3.35 (8 H, m, OCH$_2$CH$_2$C*H*$_2$N), 3.12 (8 H, d, *J* = 12.4 Hz, ArC*H*$_2$Ar), 3.11 (8 H, d, *J* = 12.4 Hz,

ArC*H*$_2$Ar), 2.21 (8 H, m, OCH$_2$C*H*$_2$CH$_2$N), 2.04 (24 H, m, OCH$_2$C*H*$_2$CH$_3$), 1.14 (72 H, s, (C*H*$_3$)$_3$Ar), 0.99 (108 H, m, (C*H*$_3$)$_3$Ar, OCH$_2$CH$_2$C*H*$_3$, coincident); **M/z (MALDI-TOF)** *m/z* 3953 $[M + K]^+$, 3937.34 $[M + Na]^+$.

Multi-calixarene MC3

A solution of **14** (0.60 g, 0.42 mmol), **13** (1.39 g, 1.67 mmol), diisopropylethylamine (0.69 mL, 4.18 mmol) and a catalytic amount of 4-dimethylaminopyridine in dichloromethane (20 mL) was stirred for 48 h. The solution was diluted with water (20 mL), washed with aq. hydrochloric acid (10%, 2 × 10 mL), aq. sodium hydroxide (10%, 2 × 10 mL) and water (2 × 10 mL) and was dried ($MgSO_4$). The solvent was evaporated under reduced pressure. The solid was re-precipitated from dichloromethane / methanol to yield multi-calixarene **MC3** (1.27 g, 75%) as a white powder. **Mp** 185-187 °C; **IR** *v*C(O)NH = 3343 cm^{-1},1658 cm^{-1}, 1596 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$); 7.08 (4 H, s, Ar*H*), 6.77 (36 H, m, Ar*H*), 6.23 (4 H, t, *J* = 5.4 Hz, N*H*C(O)), 4.48 (4 H, d, *J* = 13.6 Hz, ArC*H*$_2$Ar), 4.40 (8 H, d, *J* = 12.8 Hz, ArC*H*$_2$Ar), 4.37 (8 H, d, *J* = 12.8 Hz, ArC*H*$_2$Ar), 3.90 (16 H, m, OC*H*$_2$CH$_2$CH$_3$, OC*H*$_2$CH$_2$CH$_2$N, coincident), 3.78 (24 H, t, *J* = 7.6 Hz, OC*H*$_2$CH$_2$CH$_3$), 3.48 (8 H, m, OCH$_2$CH$_2$C*H*$_2$N), 3.26 (4 H, d, *J* = 13.6 Hz, ArC*H*$_2$Ar), 3.10 (16 H, d, *J* = 12.8 Hz, ArC*H*$_2$Ar, coincident), 2.28 (8 H, m, OCH$_2$C*H*$_2$CH$_2$N), 1.98 (24 H, m, OCH$_2$C*H*$_2$CH$_3$), 1.88 (8 H, m, OCH$_2$C*H*$_2$CH$_3$), 1.39-1.04 (144 H, m, C(C*H*$_3$)$_3$), 0.96 (48 H, m, OCH$_2$CH$_2$C*H*$_3$); **M/z (MALDI-TOF)** *m/z* 4047.8 $[M+Na]^+$, 4025.77 $[M]^+$.

AFM Experiments

General Sample Preparation

A 9 μL drop of the sample solution at 4 μg.mL^{-1} in dichloromethane was deposited onto freshly cleaved muscovite mica (Agar Scientific, UK). The sample was inserted into the liquid cell of the AFM (ECS, Cambridge, England). Imaging was carried out in an 'intermittent contact mode' under redistilled *n*-butanol (Sigma, UK) using 100 μm long oxide-sharpened Nanoprobe levers (NP-S, Veeco Instruments Inc., USA) with a quoted force constant of k = 0.38 Nm^{-1}. These tips have a quoted radius of curvature of 5-40 nm. The scan velocity of the tip was 0.8 μms^{-1}, which approximates to a scan rate of 2 Hz. The cantilever was oscillated just below its resonance frequency. Typical drive

frequencies and voltages were in the region of 13 kHz and 30 mV respectively. The resultant amplitude of oscillation of the cantilevers was approximately 8-15 nm.

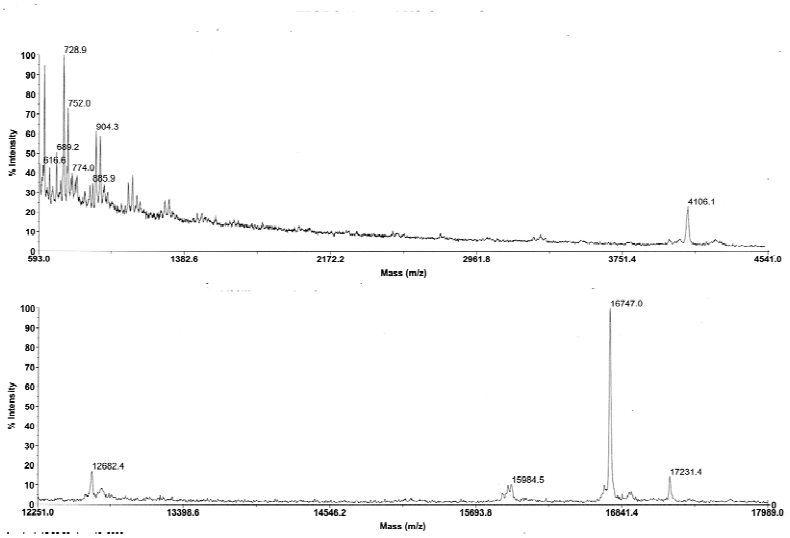

Figure 1: Full MALDI TOF (+ve mode) Mass Spectrum of **MC1**

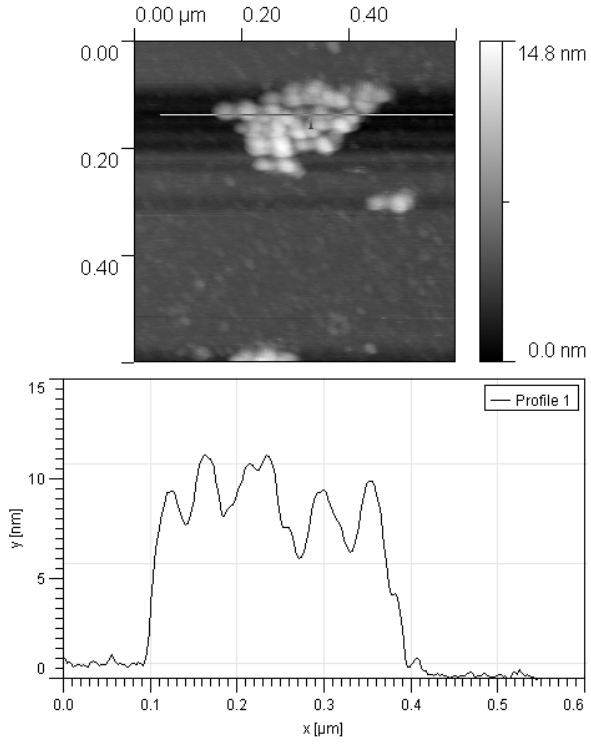

Figure 2 : Measurement of height of dendrimer **MC1** aggregates

References

1) K. Iwamoto, K. Araki and S. Shinkai, *Tetrahedron*, 1991, **47**, 4325.

2) R. Lalor, J. DiGesso, A. Mueller and S. E. Matthews, *Chem. Commun*., 2007, 4907.

3) F. Sansone, S. Barboso, A. Casnati, M. Fabbi, A. Pochini, F. Ugozzoli and R. Ungaro, R. *Eur. J. Org. Chem.* **1998**, 897-905.