Supporting Information for

Synthesis of Odd Generation Triazine Dendrimers Using a Divergent, Macromonomer Approach

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Computational Details

Computational results were obtained using the software package Materials Studio (MS) 5.0 (Accelrys, Inc). The dendrimers were built in an extended conformation using the dendrimer builder tools in MS. The conformational space of each dendrimer was sampled via 300 Simulated Annealing (SA) cycles over a period of 840 ps using the Forcite Plus program and the polymer consistent force-field (pcff) as implemented in MS 5.0. The SA runs utilized contant volume and temperature (NVT) molecular dynamics (MD) over a temperature range of 300-1000 K using the Nosé thermostat, $\Delta T = 50K$, untruncated atom-based electrostatic and van der Walls interactions, and a time step of 1 fs. The dendrimer was minimized after each annealing cycle, resulting in 300 minimized structures per dendrimer.

MALDI-TOF MS Protocol

Instrument:	Applied Biosystems Voyager STR
Mode of operation:	Reflector for molecular weight >5 kDa
	Linear for molecular weight above 5 kDa
Extraction mode:	Delayed
Polarity:	Positive
Accelerating voltage:	20000 V
Grid voltage:	65%
Mirror voltage ratio:	1.12
Guide wire:	0.002%
Extraction delay time:	275 nsec
Number of laser shots:	100/spectrum
Laser Rep Rate:	3.0 Hz
Sample concentration:	roughly 0.1 mg/ml
Matrix:	2',4',6'-Trihydroxyacetophenone monohydrate (THAP) Concentration 20 mg/ml

Matrix:Analyte ratio (1:1 v/v), 1µl of the matrix and sample mixture was spotted on a stainless steel MALDI plate.

General Procedures

Di(Boc-piperazyl) monochlorotriazine (pip-MCT) was synthesized by the method of Simanek, et al.[s1] Other chemicals were purchased from Aldrich and Acros and used without further purification. All solvents were ACS grade and used without further purification. NMR spectra were recorded on a Varian Mercury 300 MHz or Inova 300 MHz spectrometer in $CDCl_3$. All mass spectral analyses were carried out by the Laboratory for Biological Mass Spectrometry at Texas A&M.

Experimental Procedures

Compound 1. A solution of di(Boc-piperazyl) monochlorotriazine (5.0 g, 10.33 mmol), 4,7,10-trioxa-1,13-tridecanediamine (15.0 g, 68.09 mmol), and DIPEA (3.0 mL, 17.1 mmol) in THF (100 mL) was stirred for 3 h at room temperature and then refluxed for 20 h. The solution was evaporated under vacuum. The residue was dissolved in dichloromethane, washed with brine, dried over $MgSO_4$, filtered, and evaporated under vacuum. The crude product was purified by silica gel chromatography (from DCM:MeOH = 47:3 to DCM:MeOH = 7:1 w/ 1% NH_4OH) to give **1** (5.8 g, 84%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (br, 8H, NC**H$_2$**CH_2NBoc), 3.60-3.49 (m, 12H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.37 (br, 10H, NHC**H$_2$**CH_2CH_2O, NCH_2C**H$_2$**NBoc), 2.74 (t, 2H, OCH_2CH_2C**H$_2$**NH_2), 1.78 (m, 2H, OCH_2C**H$_2$**CH_2NH), 1.67 (m, 2H, OCH_2C**H$_2$**CH_2NH_2), 1.45 (s, 18H, C(C**H$_3$**)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4 (**C**$_3N_3$), 165.3 (**C**$_3N_3$), 154.9 (**C**O), 79.9 (**C**$(CH_3)_3$), 70.7 (O**C**H_2**C**H_2O), 70.3 (O**C**H_2**C**H_2O), 70.2 (O**C**H_2**C**H_2O), 69.5 (two lines, $NHCH_2CH_2$**C**H_2O, O**C**$H_2CH_2CH_2NH_2$), 43.0 (piperazine), 39.7 (NH**C**$H_2CH_2CH_2$O), 38.3 (OCH_2CH_2**C**H_2NH_2), 33.2 (OCH_2**C**$H_2CH_2NH_2$), 29.7 ($NHCH_2$**C**H_2CH_2O), 28.5 (C(**C**H_3)$_3$); MS (ESI) calcd for $C_{31}H_{57}N_9O_7$ 667.4381, found 668.3845 $(M + H)^+$.

Compound 2. Cyanuric chloride (0.54 g, 2.93 mmol) was added to a solution of **1** (4.0 g, 5.99 mmol) and DIPEA (2.0 mL, 11.4 mmol) in THF (70 mL) at 0 ^{o}C, The solution was warmed to room temperature, stirred for 24 h, and then evaporated under vacuum. The residue was dissolved in dichloromethane, washed with brine, dried over $MgSO_4$, filtered, and evaporated under vacuum. The crude product was purified by silica gel chromatography (DCM:MeOH = 15:1) to give **2** (3.8 g, 90%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70 (br, 16H, NC**H$_2$**CH_2NBoc), 3.63-3.53 (m, 24H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.40 (br, 24H, NHC**H$_2$**CH_2CH_2O, NCH_2C**H$_2$**NBoc), 1.81 (m, 8H, OCH_2C**H$_2$**CH_2NH), 1.45 (s, 36H, C(C**H$_3$**)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4 (**C**$_3N_3$), 165.9 (**C**$_3N_3$), 165.4 (**C**$_3N_3$), 154.9 (**C**O), 80.0 (**C**$(CH_3)_3$), 70.7 (O**C**H_2**C**H_2O), 70.4 (O**C**H_2**C**H_2O), 69.5 ($NHCH_2CH_2$**C**H_2O), 43.1 (piperazine), 39.1 (NH**C**$H_2CH_2CH_2$O), 38.4 (NH**C**$H_2CH_2CH_2$O), 29.7 ($NHCH_2$**C**H_2CH_2O), 29.0 ($NHCH_2$**C**H_2CH_2O), 28.5 (C(**C**H_3)$_3$); MS (MALDI-TOF) calcd for $C_{65}H_{112}ClN_{21}O_{14}$ 1445.8386, found 1446.8088 $(M + H)^+$.

Compound 3. A solution of **1** (1.79g, 2.68 mmol), **2** (1.32 g, 0.91 mmol), and DIPEA (1 mL, 5.70 mmol) in THF (20 mL) was refluxed for 24 h. The solution was evaporated under vacuum. The residue was dissolved in dichloromethane, washed with brine, dried

[s1] Chen, H. -T.; Neerman, M. F.; Parrish, A. R.; Simanek, E. E. *J. Am. Chem. Soc.* **2004**, *126*, 10044-10048.

over $MgSO_4$, filtered, and evaporated under vacuum. The crude product was purified by silica gel chromatography (DCM:MeOH = 10:1) to give **3** (1.53 g, 81%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.65 (br, 24H, NC**H$_2$**CH_2NBoc), 3.59-3.46 (m, 36H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.36 (br, 36H, NHC**H$_2$**CH_2CH_2O, NCH_2C**H$_2$**NBoc), 1.75 (m, 12H, OCH_2C**H$_2$**CH_2NH), 1.40 (s, 54H, C(C**H$_3$**)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2 (**C**$_3N_3$), 165.2 (**C**$_3N_3$), 154.7 (**C**O), 79.8 (**C**$(CH_3)_3$), 70.5 (O**C**H_2**C**H_2O), 70.2 (two lines, O**C**H_2**C**H_2O), 69.2 (two lines, $NHCH_2CH_2$**C**H_2O), 42.8 (piperazine), 38.2 (NH**C**$H_2CH_2CH_2O$), 38.1 (NH**C**$H_2CH_2CH_2O$), 29.6 ($NHCH_2$**C**H_2CH_2O), 28.4 (C(**C**$H_3)_3$); MS (MALDI-TOF) calcd for $C_{96}H_{168}N_{30}O_{21}$ 2077.3000, found 2078.3853 $(M + H)^+$.

Compound 4. A solution of **3** (0.14 g, 0.0674 mmol) in concentrated HCl (3 mL) and methanol (3 mL) was stirred for 12 h at room temperature and then evaporated under vacuum. The residue was dissolved in chloroform, washed with 5 M NaOH (aq), dried over $MgSO_4$, filtered, and evaporated under vacuum to give **4** (0.10 g, quantitative) as a white product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.64 (br, 24H, NC**H$_2$**CH_2NH), 3.57-3.51 (br m, 36H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.37 (br, 12H, NHC**H$_2$**CH_2CH_2O), 2.78 (br, 24H, NCH_2C**H$_2$**NH), 1.74 (br, 12H, OCH_2C**H$_2$**CH_2NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3 (**C**$_3N_3$), 165.2 (**C**$_3N_3$), 70.6 (O**C**H_2**C**H_2O), 70.2 (O**C**H_2**C**H_2O), 69.3 ($NHCH_2CH_2$**C**H_2O), 69.2 ($NHCH_2CH_2$**C**H_2O), 46.0 (NCH_2**C**H_2NH), 44.2 (N**C**H_2CH_2NH), 38.1 (NH**C**$H_2CH_2CH_2O$), 38.0 (NH**C**$H_2CH_2CH_2O$), 29.7 ($NHCH_2$**C**H_2CH_2O); MS (MALDI-TOF) calcd for $C_{66}H_{120}N_{30}O_9$ 1476.9855, found 1478.1023 $(M + H)^+$.

Compound 5. A solution of **2** (0.80 g, 0.553 mmol), **4** (0.10 g, 0.0677 mmol), and DIPEA (0.30 mL, 1.71 mmol) in THF (3.0 mL), methanol (0.2 mL), and H_2O (0.2 mL) was refluxed for 48 h. The solution was evaporated under vacuum. The residue was dissolved in dichloromethane, washed with brine, dried over $MgSO_4$, filtered, and evaporated under vacuum. The crude product was purified by silica gel chromatography (from DCM:EA:MeOH = 10:10:1 to DCM:MeOH = 10:1) to give **5** (0.605 g, 90%) as a white solid. The excess/unreacted **2** was recovered from the purification step and reused. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (br, 144H, NC**H$_2$**CH_2NBoc, NC**H$_2$**C**H$_2$**N), 3.61-3.47 (m, 180H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.38 (br, 156H, NHC**H$_2$**CH_2CH_2O, NCH_2C**H$_2$**NBoc), 1.78 (m, 60H, OCH_2C**H$_2$**CH_2NH), 1.43 (s, 216H, C(C**H$_3$**)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3 (**C**$_3N_3$), 165.2 (**C**$_3N_3$), 154.8 (**C**O), 79.8 (**C**$(CH_3)_3$), 70.6 (O**C**H_2**C**H_2O), 70.2 (O**C**H_2**C**H_2O), 69.3 (two lines, $NHCH_2CH_2$**C**H_2O), 42.9 (piperazine), 38.2 (NH**C**$H_2CH_2CH_2O$), 38.1 (NH**C**$H_2CH_2CH_2O$), 29.6 ($NHCH_2$**C**H_2CH_2O), 28.4 (C(**C**$H_3)_3$); MS (MALDI-TOF) calcd for $C_{456}H_{786}N_{156}O_{93}$ 9936.16, found 9945.30 $(M + H)^+$.

Compound 6. A solution of **5** (0.58 g, 0.0583 mmol) in concentrated HCl (5 mL) and methanol (5 mL) was stirred for 12 h at room temperature and then evaporated under vacuum. The residue was dissolved in chloroform, washed with 5 M NaOH (aq), dried over $MgSO_4$, filtered, and evaporated under vacuum to give **6** (0.44 g, quantitative) as a white product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.65 (br, 144H, NC**H$_2$**CH_2NH, NC**H$_2$**C**H$_2$**N), 3.57-3.45 (m, 180H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.38 (br, 60H,

NHC**H$_2$**CH$_2$CH$_2$O), 2.79 (br, 96H, NCH$_2$C**H$_2$**NH), 1.76 (m, 60H, OCH$_2$C**H$_2$**CH$_2$NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3 (**C**$_3$N$_3$), 165.2 (**C**$_3$N$_3$), 70.6 (O**C**H$_2$**C**H$_2$O), 70.2 (O**C**H$_2$**C**H$_2$O), 69.3 (NHCH$_2$CH$_2$**C**H$_2$O), 69.2 (NHCH$_2$CH$_2$**C**H$_2$O), 46.0 (NCH$_2$**C**H$_2$NH), 44.2 (N**C**H$_2$CH$_2$NH), 42.9 (N**C**H$_2$**C**H$_2$N), 38.1 (NH**C**H$_2$CH$_2$CH$_2$O), 29.7 (NHCH$_2$**C**H$_2$CH$_2$O); MS (MALDI-TOF) calcd for $C_{336}H_{594}N_{156}O_{45}$ 7534.90, found 7520.91 $(M + H)^+$.

Compound 7. A solution of **2** (1.0 g, 0.691 mmol), **6** (0.10 g, 0.0133 mmol), and DIPEA (0.30 mL, 1.71 mmol) in THF (4.0 mL), methanol (0.25 mL), and H_2O (0.25 mL) was refluxed for 48 h. The solution was evaporated under vacuum. The residue was dissolved in chloroform, washed with brine, dried over $MgSO_4$, filtered, and evaporated under vacuum. The crude product was purified by silica gel chromatography (from EA:MeOH = 40:1 to DCM:MeOH = 9:1) to give **7** (0.49 g, 89%) as a white solid. The excess/unreacted **2** was recovered from the purification step and reused. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (br, 624H, NC**H$_2$**CH$_2$NBoc, NC**H$_2$**C**H$_2$**N), 3.62-3.49 (m, 756H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.40 (br, 636H, NHC**H$_2$**CH$_2$CH$_2$O, NCH$_2$C**H$_2$**NBoc), 1.79 (m, 252H, OCH$_2$C**H$_2$**CH$_2$NH), 1.45 (s, 864H, C(C**H$_3$**)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4 (**C**$_3$N$_3$), 165.3 (**C**$_3$N$_3$), 154.9 (**C**O), 79.8 (**C**(CH$_3$)$_3$), 70.7 (O**C**H$_2$**C**H$_2$O), 70.3 (O**C**H$_2$**C**H$_2$O), 69.4 (two lines, NHCH$_2$CH$_2$**C**H$_2$O), 42.9 (piperazine), 38.3 (NH**C**H$_2$CH$_2$CH$_2$O), 29.7 (NHCH$_2$**C**H$_2$CH$_2$O), 28.5 (C(**C**H$_3$)$_3$); MS (MALDI-TOF) calcd for $C_{1896}H_{3258}N_{660}O_{381}$ 41371.59, found 41258.42 $(M + H)^+$.

Compound 8. A solution of **7** (0.48 g, 0.0116 mmol) in concentrated HCl (5 mL) and methanol (5 mL) was stirred for 12 h at room temperature and then evaporated under vacuum. The residue was dissolved in chloroform, washed with 5 M NaOH (aq), dried over $MgSO_4$, filtered, and evaporated under vacuum to give **8** (0.37 g, quantitative) as a white product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (br, 624H, NC**H$_2$**CH$_2$NH, NC**H$_2$**C**H$_2$**N), 3.58-3.47 (br m, 756H, C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**C**H$_2$**OC**H$_2$**), 3.39 (br, 252H, NHC**H$_2$**CH$_2$CH$_2$O), 2.83 (br, 384H, NCH$_2$C**H$_2$**NH), 1.77 (br, 252H, OCH$_2$C**H$_2$**CH$_2$NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3 (**C**$_3$N$_3$), 165.2 (**C**$_3$N$_3$), 70.6 (O**C**H$_2$**C**H$_2$O), 70.2 (O**C**H$_2$**C**H$_2$O), 69.3 (two lines, NHCH$_2$CH$_2$**C**H$_2$O), 45.8 (NCH$_2$**C**H$_2$NH), 43.9 (N**C**H$_2$CH$_2$NH), 43.0 (N**C**H$_2$**C**H$_2$N), 38.2 (NH**C**H$_2$CH$_2$CH$_2$O), 29.7 (NHCH$_2$**C**H$_2$CH$_2$O); MS (MALDI-TOF) calcd for $C_{1416}H_{2490}N_{660}O_{189}$ 31766.55, found 31764.04 $(M + H)^+$.

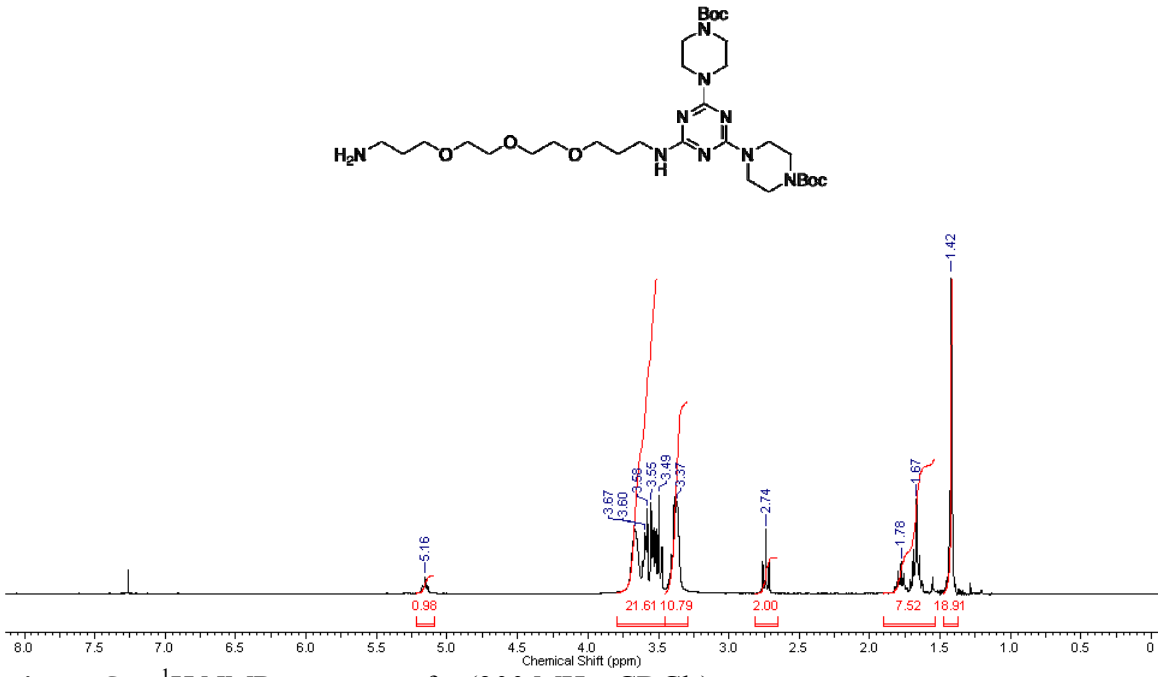


Figure S1. ^{1}H NMR spectrum of **1** (300 MHz, $CDCl_3$).

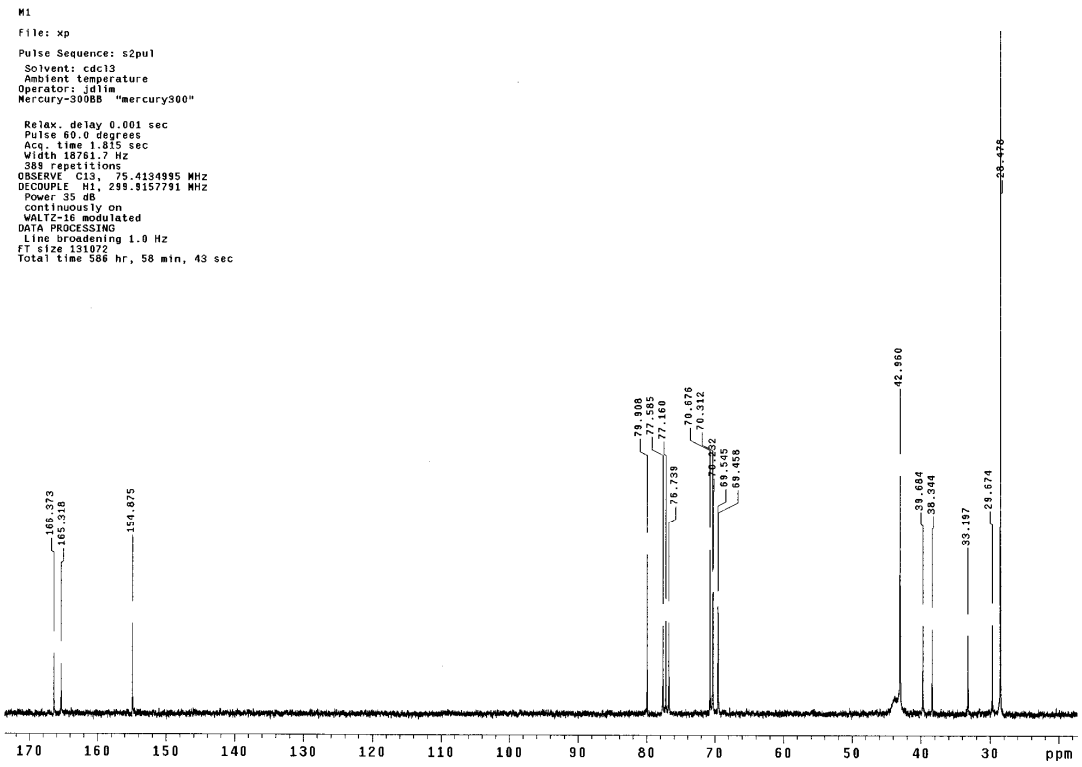
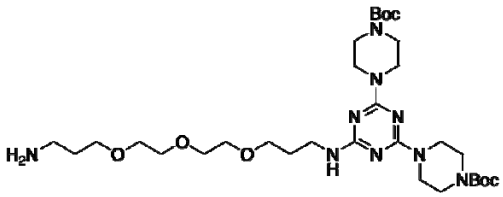


Figure S2. ^{13}C NMR spectrum of **1** (75 MHz, $CDCl_3$).



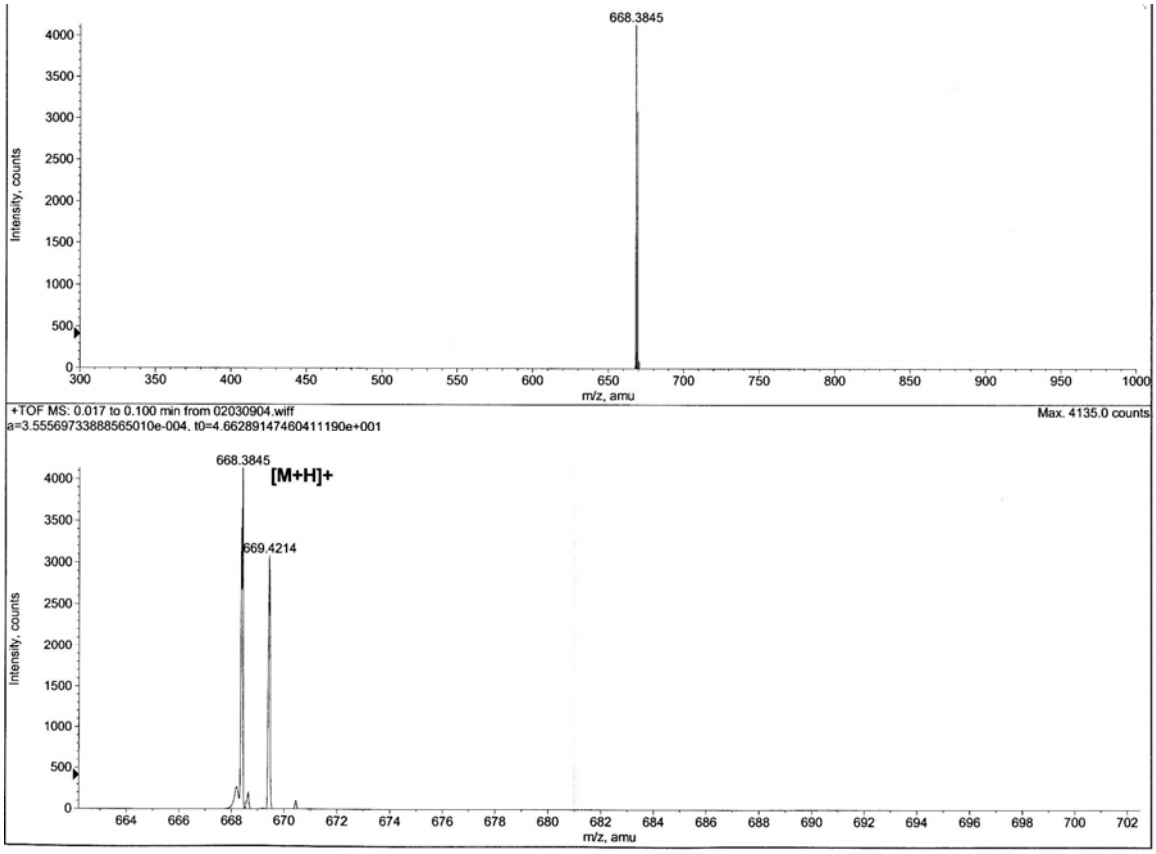


Figure S3. ESI-TOF mass spectrum of **1**.

Chemical Formula: $C_{31}H_{57}N_9O_7 + H^+$
Exact Mass: 668.4459
Molecular Weight: 668.8483
m/z: 668.4459 (100.0%), 669.4493 (33.5%), 670.4526 (5.4%), 669.4430 (3.3%), 670.4502 (1.4%), 670.4463 (1.1%)
Error: 9×10^{-5}; 90 ppm

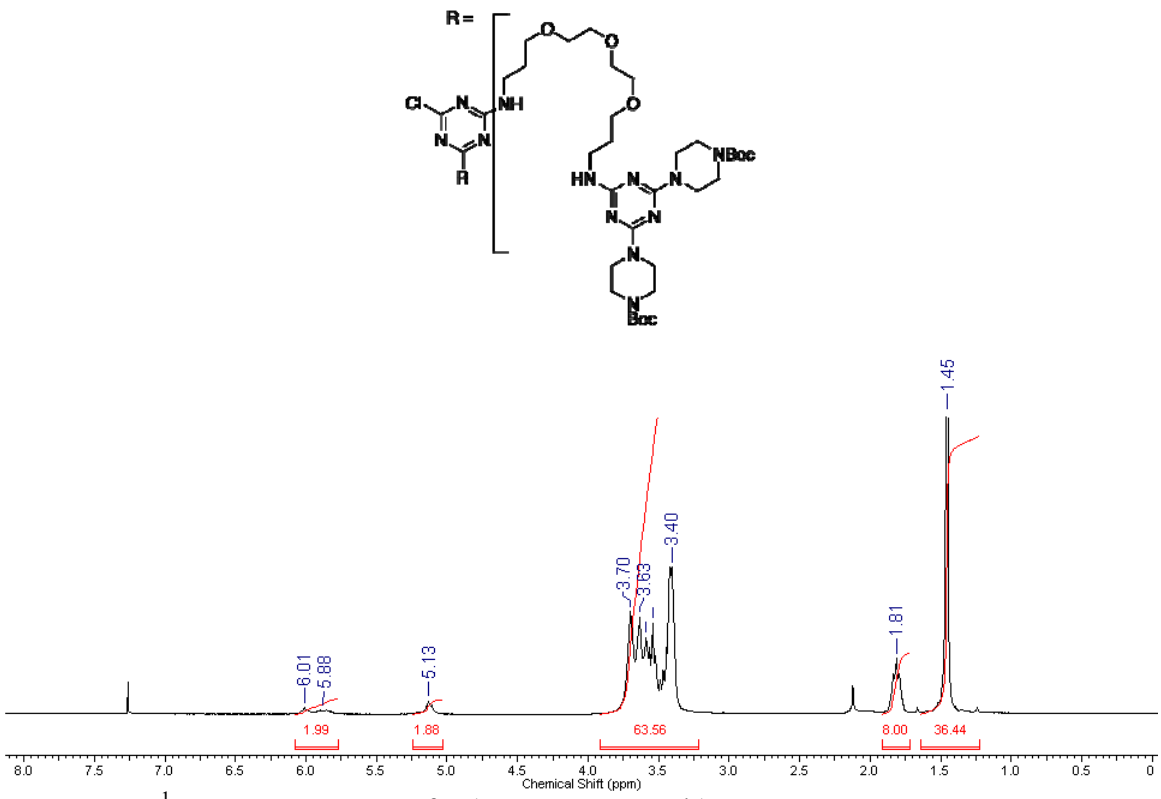


Figure S4. ^{1}H NMR spectrum of **2** (300 MHz, $CDCl_3$).

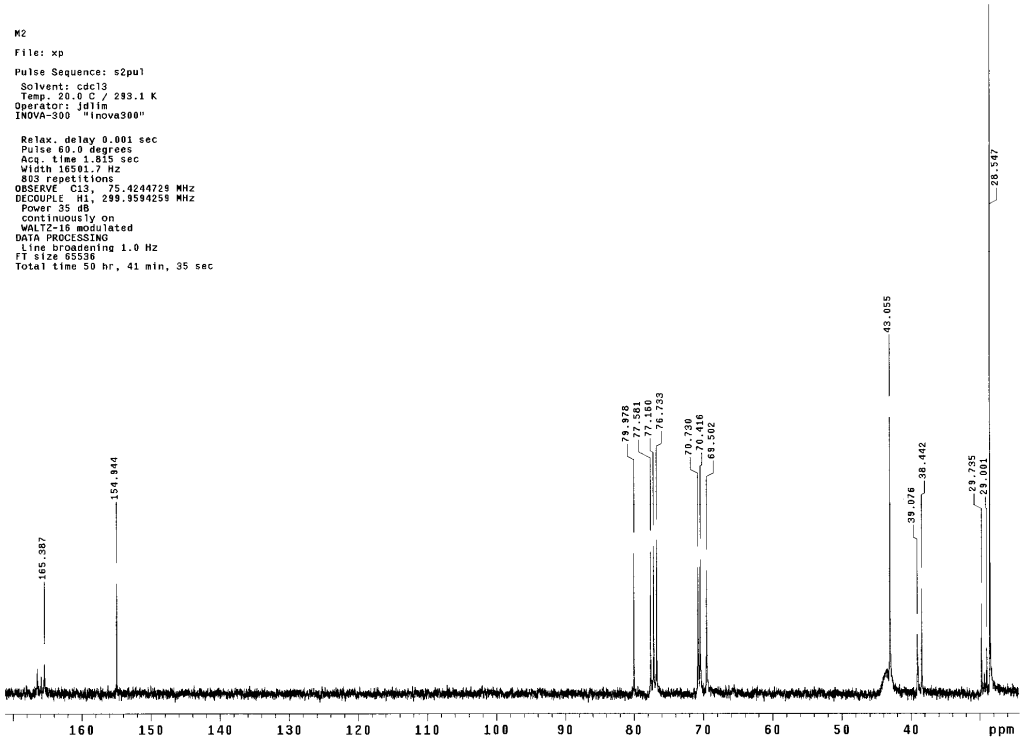


Figure S5. ^{13}C NMR spectrum of **2** (75 MHz, $CDCl_3$).

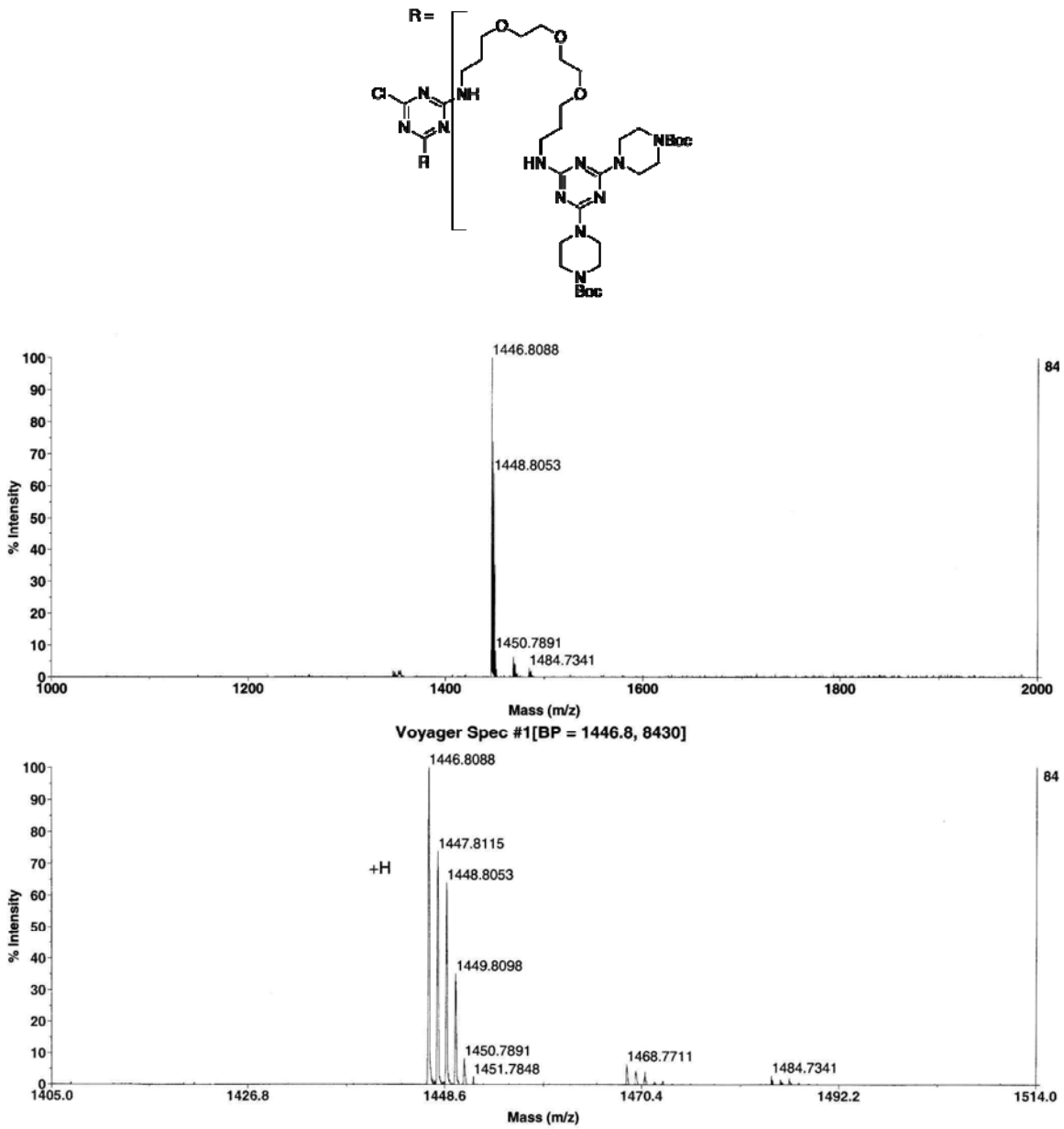


Figure S6. MALDI mass spectrum of **2**. Lines at lower m/z correspond to loss of a BOC group, a commonly observed feature in these traces.

Chemical Formula: $C_{65}H_{112}ClN_{21}O_{14} + H^+$
Exact Mass: 1446.8464
Molecular Weight: 1448.1780
m/z: 1446.8464 (100.0%), 1447.8498 (70.3%), 1448.8435 (32.0%), 1448.8531 (24.3%), 1449.8468 (22.5%), 1450.8502 (7.8%), 1447.8435 (7.8%), 1449.8565 (5.5%), 1448.8468 (5.5%), 1448.8507 (2.9%), 1449.8405 (2.5%), 1449.8540 (2.0%), 1449.8502 (1.9%), 1451.8536 (1.8%), 1450.8439 (1.7%), 1447.8527 (1.3%)
Error: 2.6×10^{-5}; 26 ppm

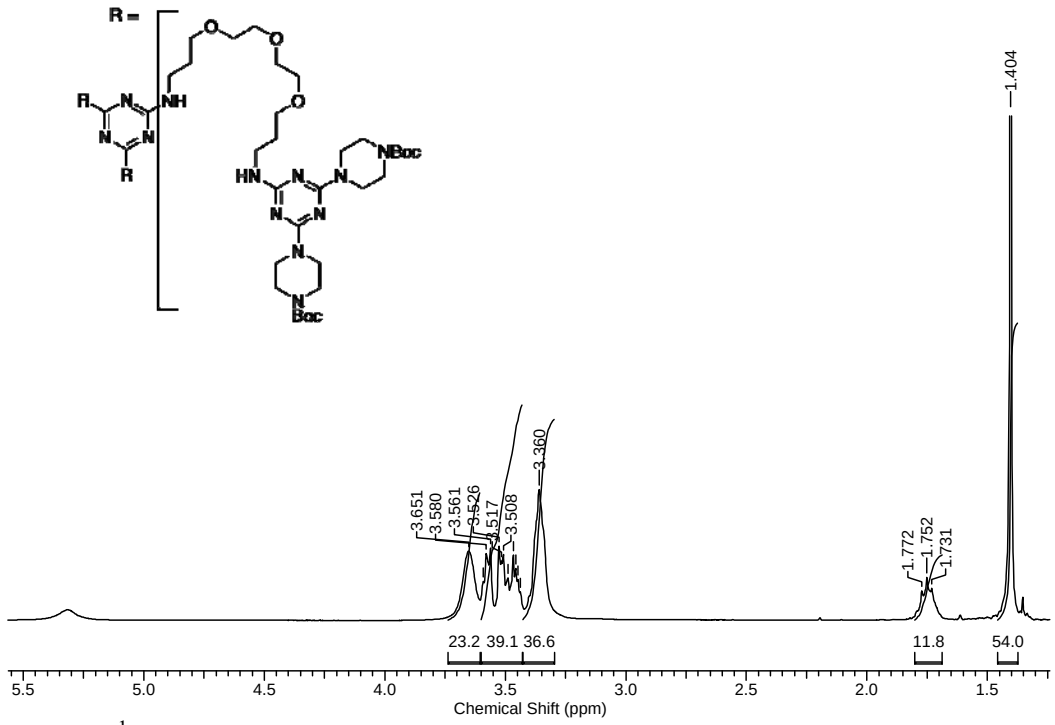


Figure S7. ^{1}H NMR spectrum of dendrimer **3** (300 MHz, $CDCl_3$)

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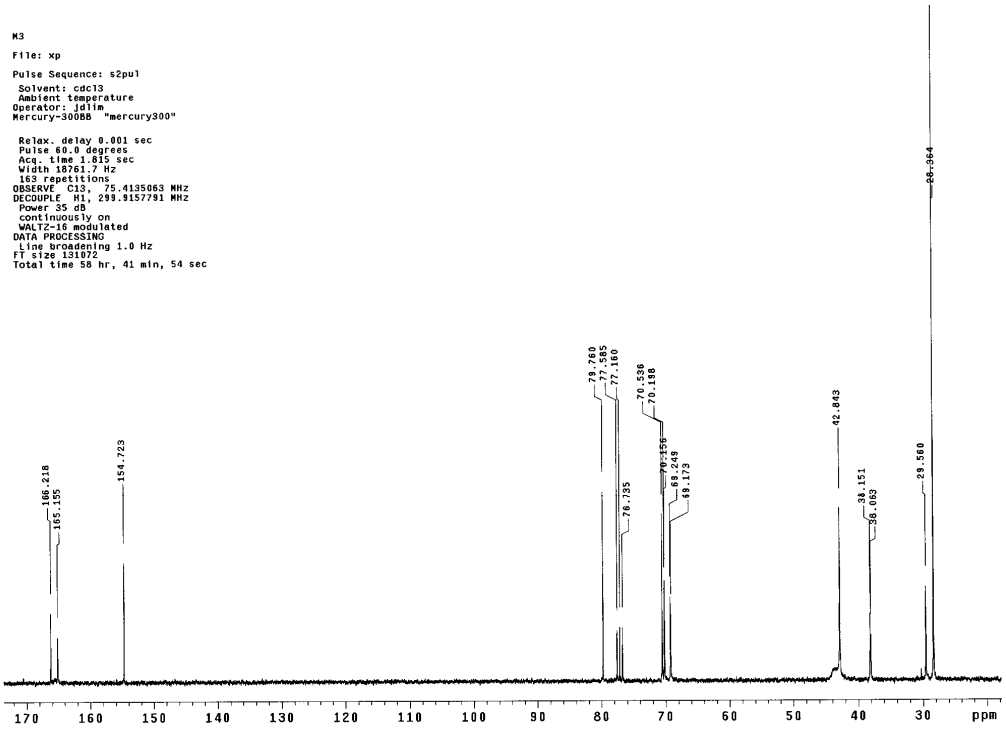

Figure S8. ^{13}C NMR spectrum of dendrimer **3** (75 MHz, $CDCl_3$).

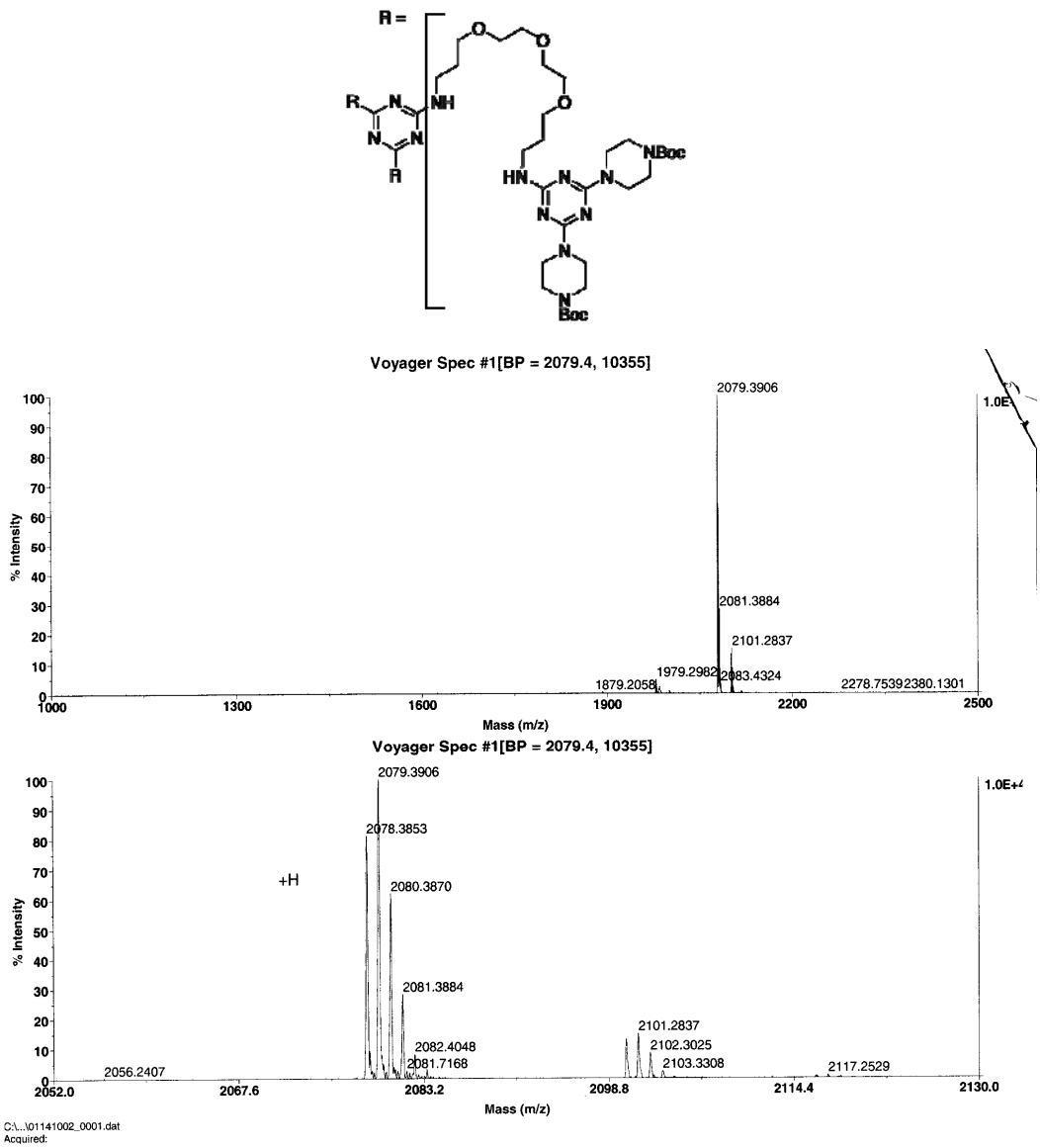

Figure S9. MALDI mass spectrum of dendrimer **3**. Loss of a BOC group is seen.

Chemical Formula: $C_{96}H_{168}N_{30}O_{21} + H^+$
Exact Mass: 2078.3079
Molecular Weight: 2079.5575
m/z: 2079.3112 (100.0%), 2078.3079 (96.3%), 2080.3146 (51.4%), 2081.3179 (17.4%), 2080.3082 (11.1%), 2079.3049 (10.7%), 2081.3116 (5.7%), 2082.3213 (4.4%), 2081.3155 (4.3%), 2080.3121 (4.2%), 2082.3188 (2.2%), 2080.3175 (1.9%), 2082.3150 (1.9%), 2079.3141 (1.9%)
Error: 4.5×10^{-4}; 450 ppm

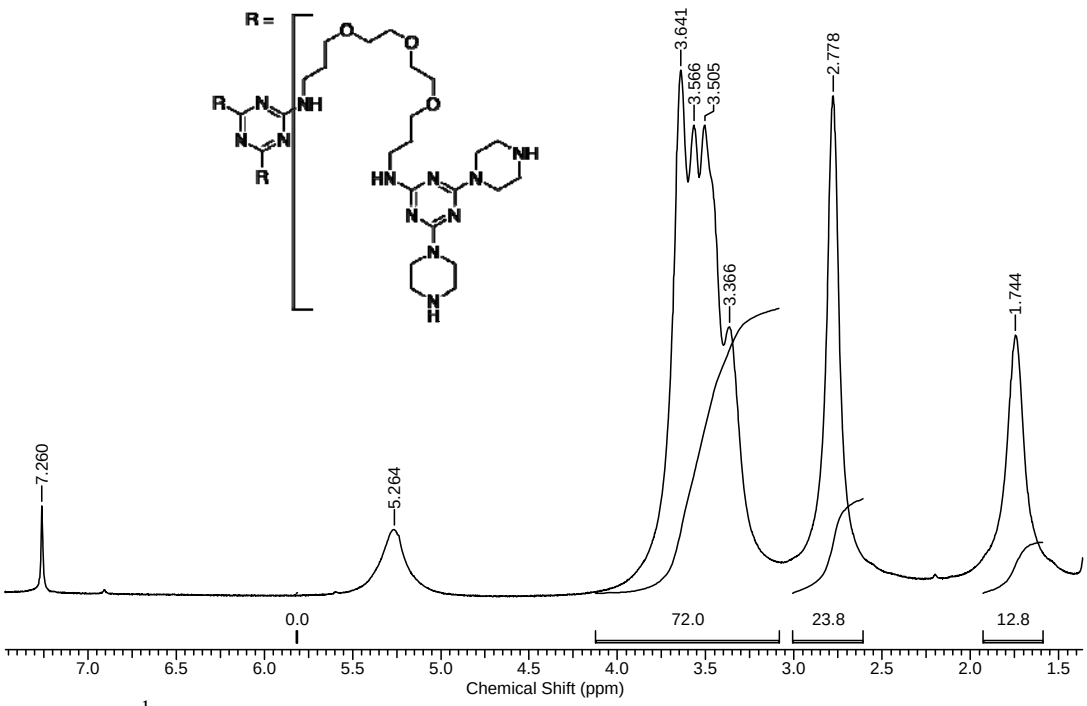

Figure S10. ^{1}H NMR spectrum of dendrimer **4** (300 MHz, $CDCl_3$).

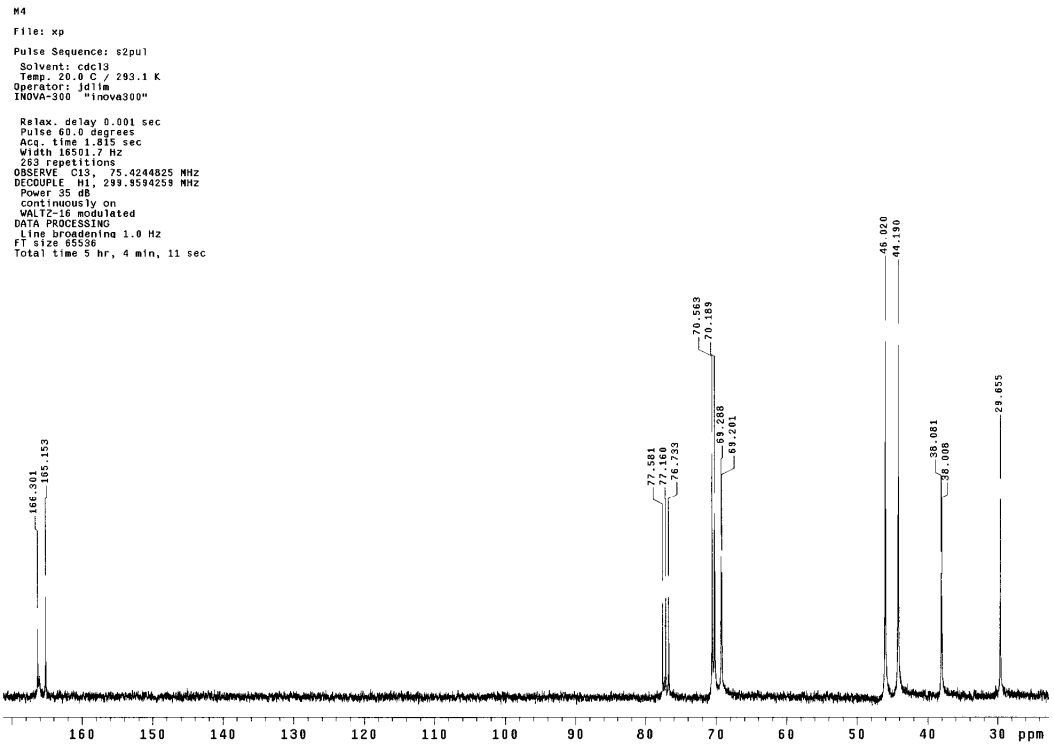

Figure S11. ^{13}C NMR spectrum of dendrimer **4** (75 MHz, $CDCl_3$).

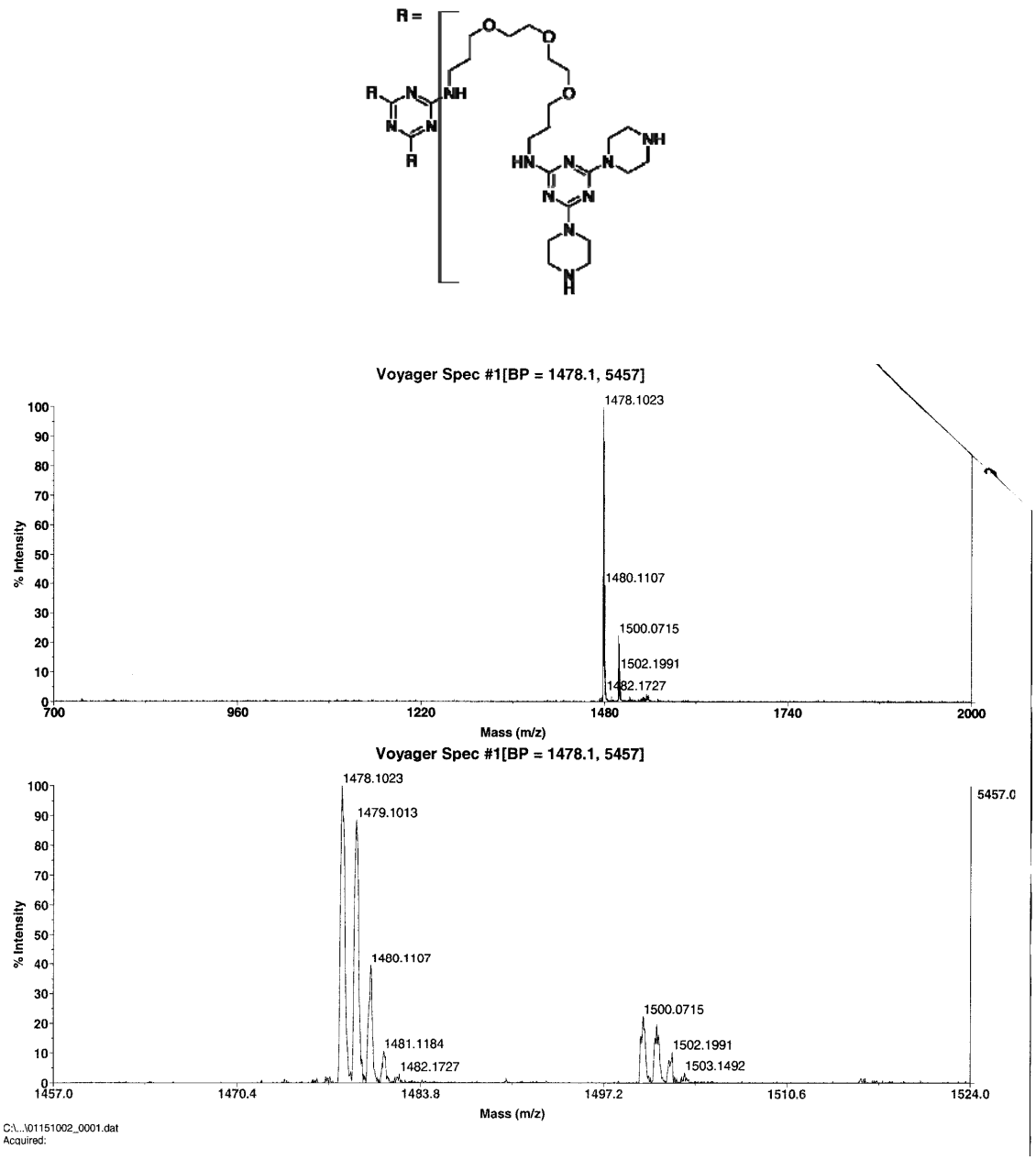

Figure S12. MALDI mass spectrum of dendrimer **4**.

Chemical Formula: $C_{66}H_{120}N_{30}O_9 + H^+$
Exact Mass: 1477.9933
Molecular Weight: 1478.8625
m/z: 1477.9933 (100.0%), 1478.9966 (71.4%), 1480.0000 (25.1%), 1478.9903 (11.1%), 1479.9937 (7.9%), 1481.0033 (5.8%), 1480.9970 (2.8%), 1479.9975 (1.8%), 1478.9996 (1.4%), 1481.0009 (1.3%)
Error: 7.4×10^{-5}; 74 ppm

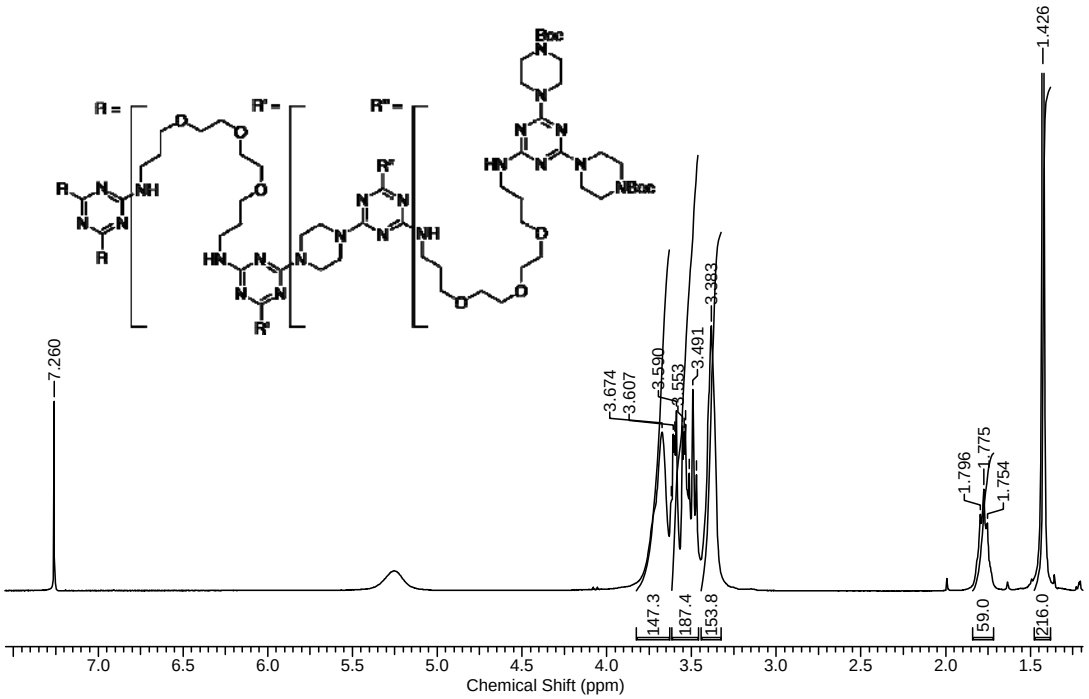

Figure S13. ^{1}H NMR spectrum of dendrimer **5** (300 MHz, $CDCl_3$).

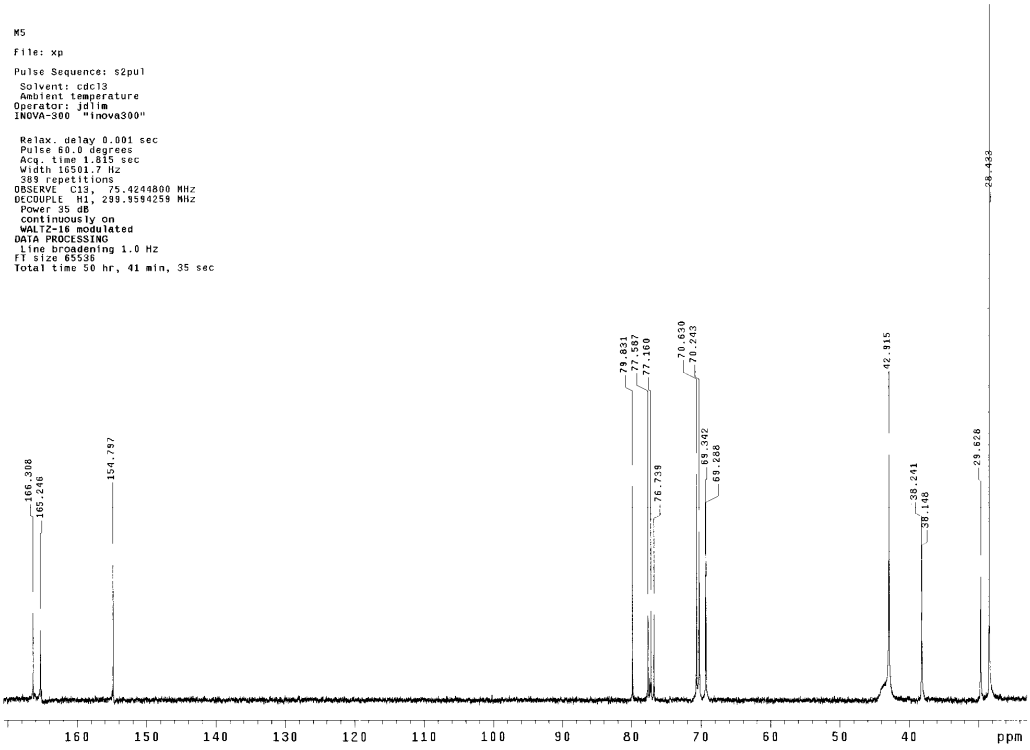

Figure S14. ^{13}C NMR spectrum of dendrimer **5** (75 MHz, $CDCl_3$).

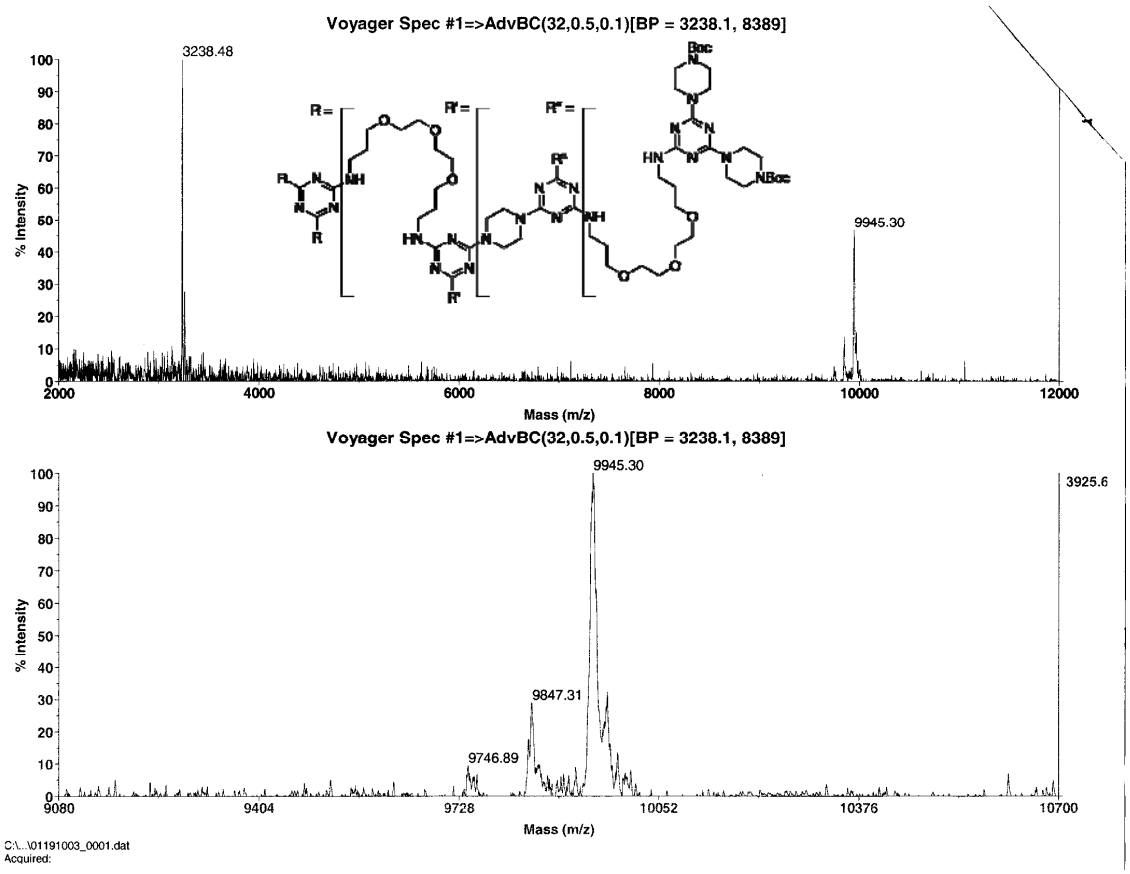

Figure S15. MALDI mass spectrum of dendrimer **5**. The minor ions correspond to loss of BOC (M+H-100).$^{+}$ The ion at 3238 (m/z) is believed to derive from the fragmentation during ionization: The peak is not observed after the following deprotection step. It corresponds to no predictable side reaction, and results from fragmentation of the flexible linker.

Chemical Formula: $C_{456}H_{786}N_{156}O_{93} + H^{+}$
Exact Mass: 9937.1649
Molecular Weight: 9943.1174
m/z: 9942.1817 (100.0%), 9941.1783 (84.3%), 9940.1750 (70.7%), 9943.1850 (67.0%), 9939.1716 (38.8%), 9938.1683 (18.8%), 9937.1649 (7.9%)
Error: 3.1×10^{-4}; 310 ppm

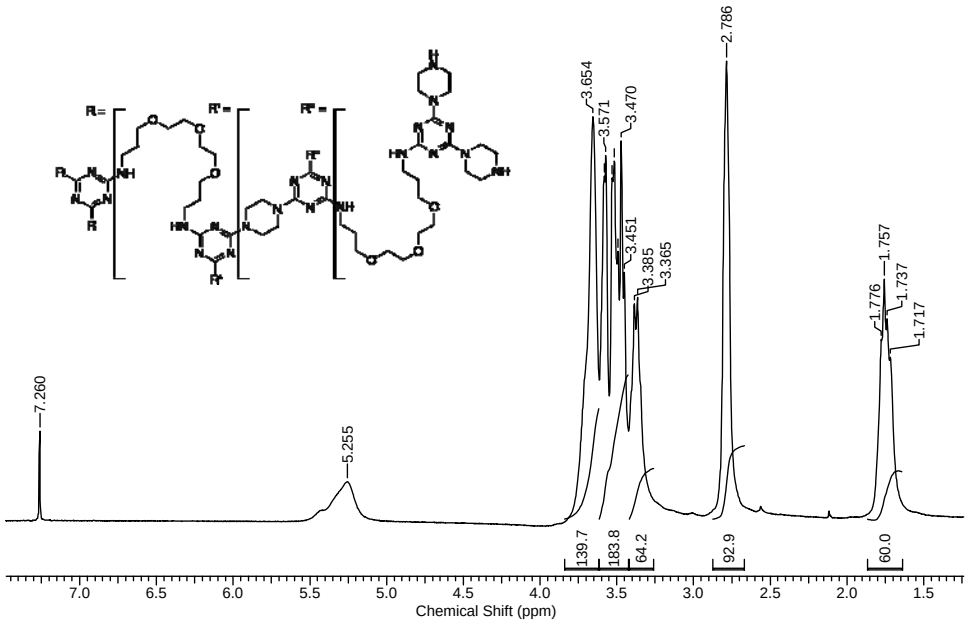

Figure S16. ^{1}H NMR spectrum of dendrimer **6** (300 MHz, $CDCl_3$).

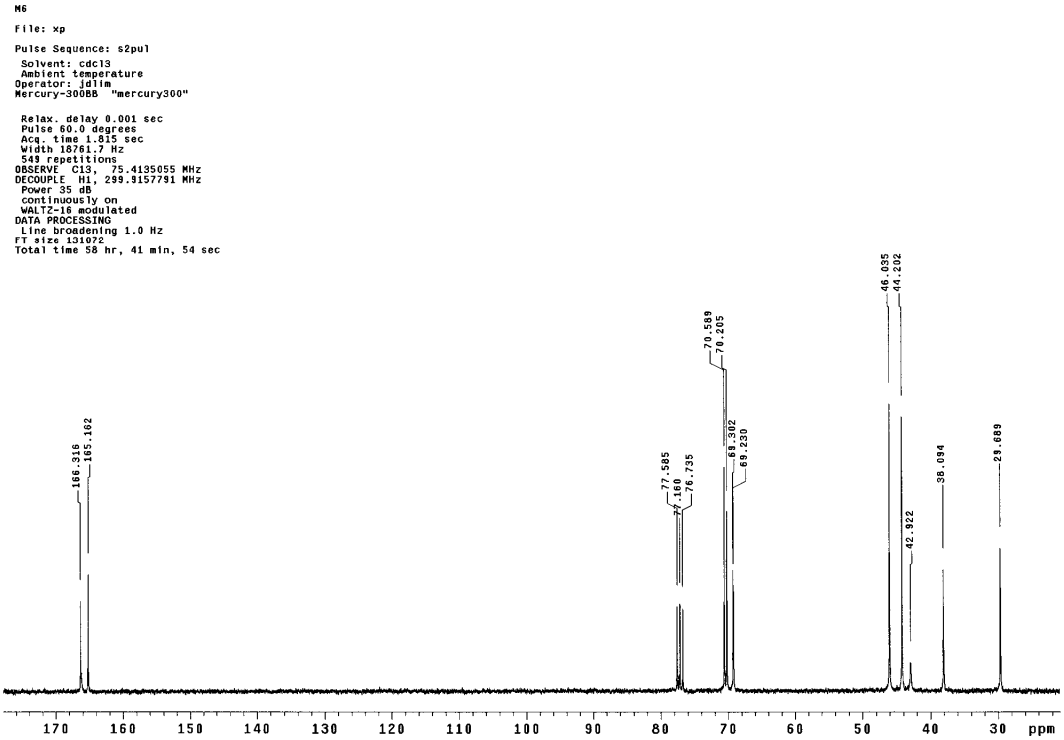

Figure S17. ^{13}C NMR spectrum of dendrimer **6** (75 MHz, $CDCl_3$).

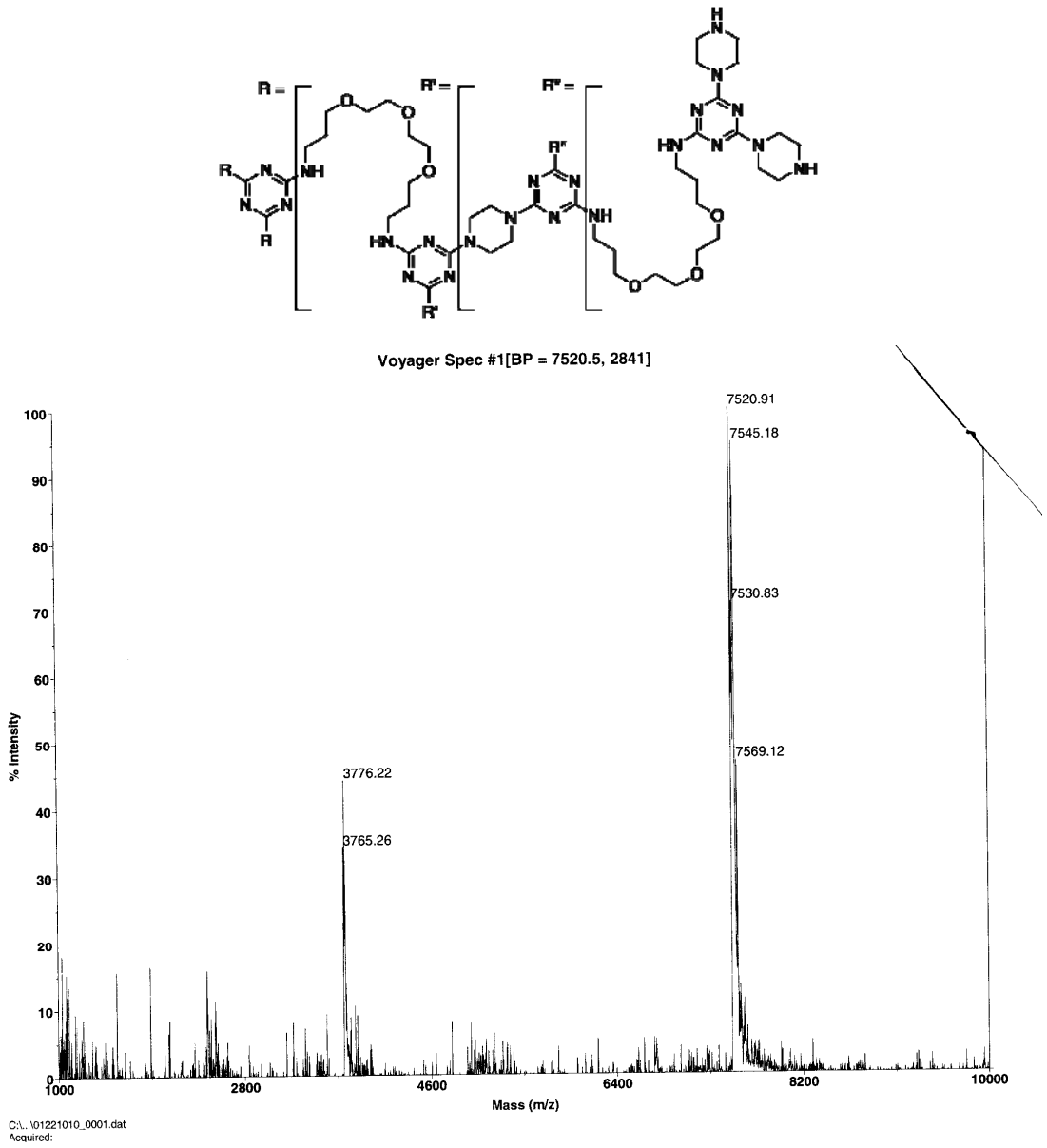

Figure S18. MALDI mass spectrum of dendrimer **6**. The doubly charged [M + $2H^+$] is observed with the expected peak at m/z ~3765.

Chemical Formula: $C_{336}H_{594}N_{156}O_{45} + H^+$
Exact Mass: 7535.9066
Molecular Weight: 7540.3377
m/z: 7538.9167 (100.0%), 7539.9200 (75.7%), 7537.9133 (68.3%), 7540.9234 (34.7%), 7536.9100 (33.1%), 7535.9066 (13.8%)
Error: 2.3×10^{-3}; 2300 ppm

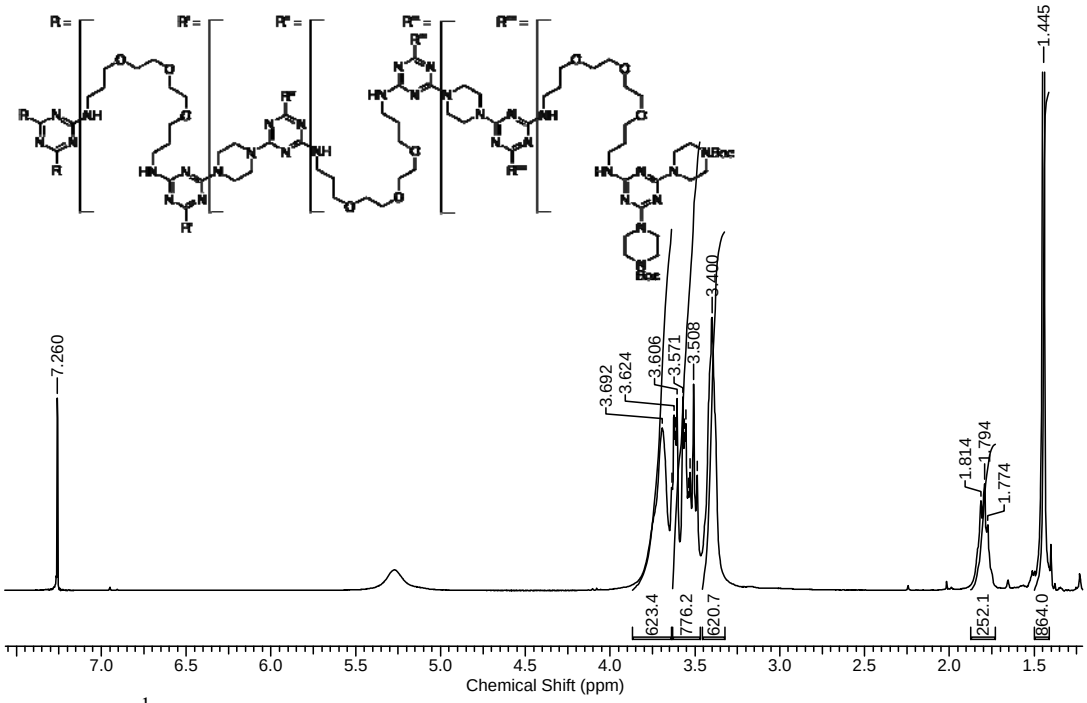

Figure S19. ^{1}H NMR spectrum of dendrimer **7** (300 MHz, $CDCl_3$).

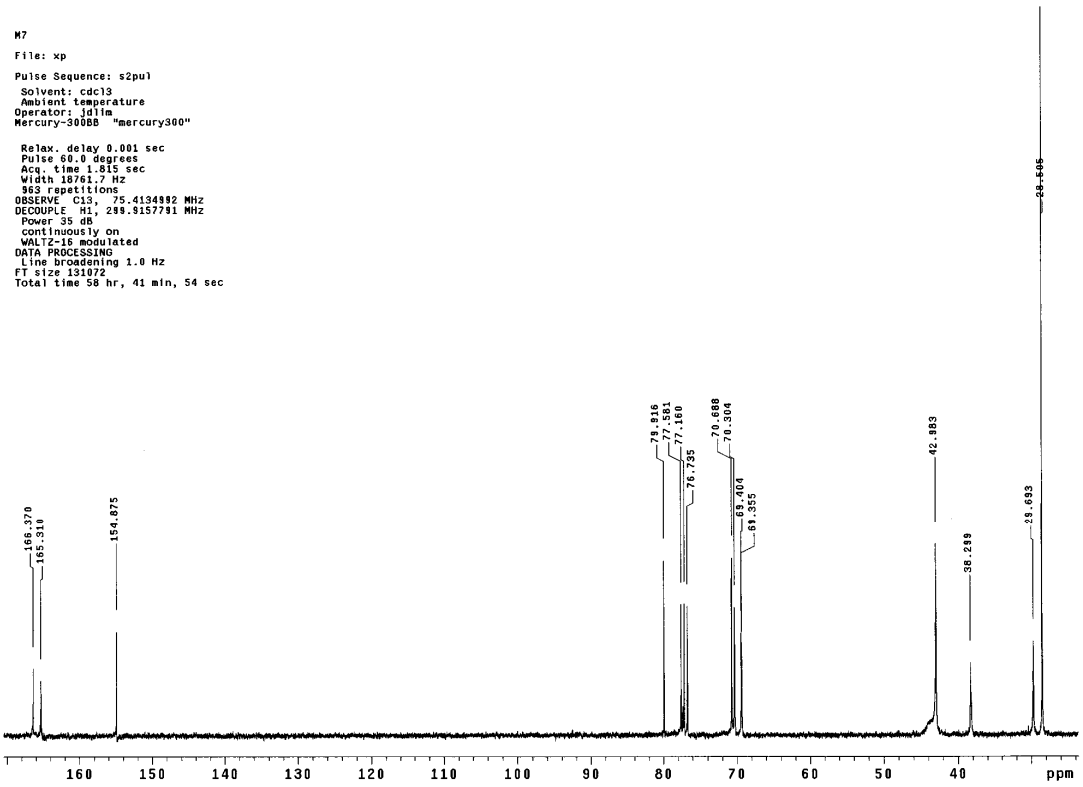

Figure S20. ^{13}C NMR spectrum of dendrimer **7** (75 MHz, $CDCl_3$).

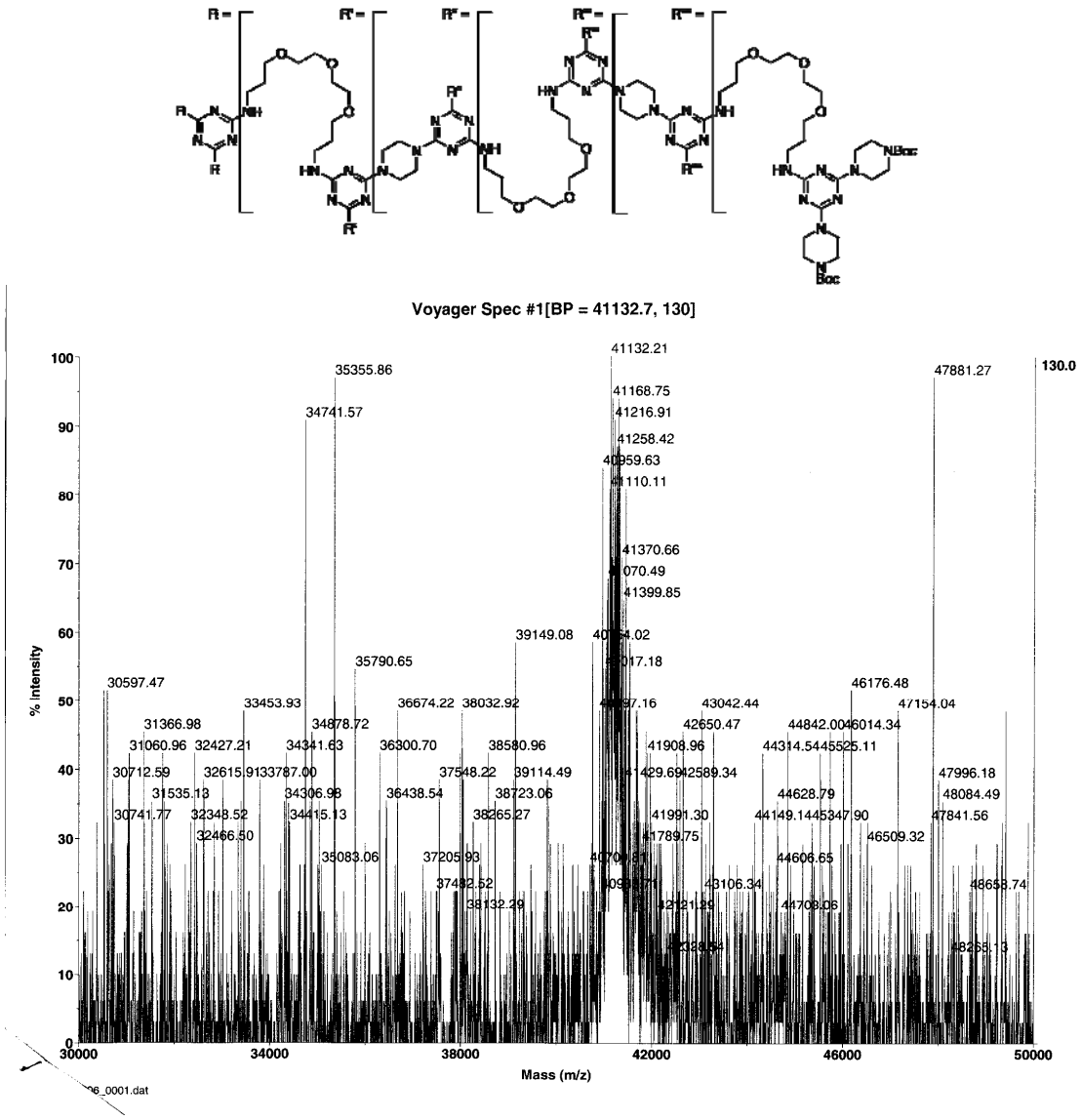

Figure S21. MALDI mass spectrum of dendrimer **7**. Obtained at the analytical limits of the instrument, this data is more compelling considering the trace of the incompletely reacted material (next).

Chemical Formula: $C_{1897}H_{3258}N_{660}O_{381} + H^+$
Exact Mass: 41372.5931
Molecular Weight: 41397.3570
Error: 2.7×10^{-3}; 2700 ppm

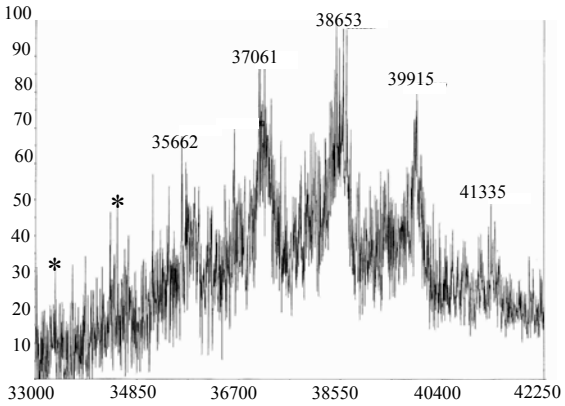

Figure S22. Mass spectrum of **7** shows the desired product (m/z 41335) and features corresponding to targets missing 1-4 macromonomers. Additional clues of defects (targets missing 5 and 6 hypermonomers) are indicated with a *.

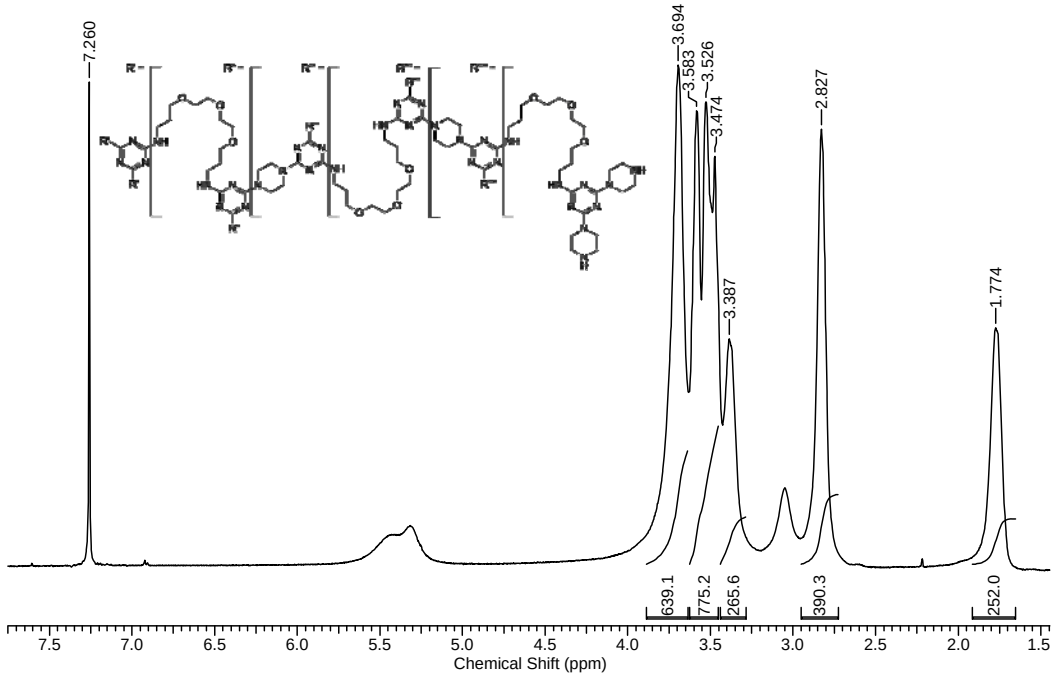

Figure S23. ^{1}H NMR spectrum of dendrimer **8** (300 MHz, $CDCl_3$).

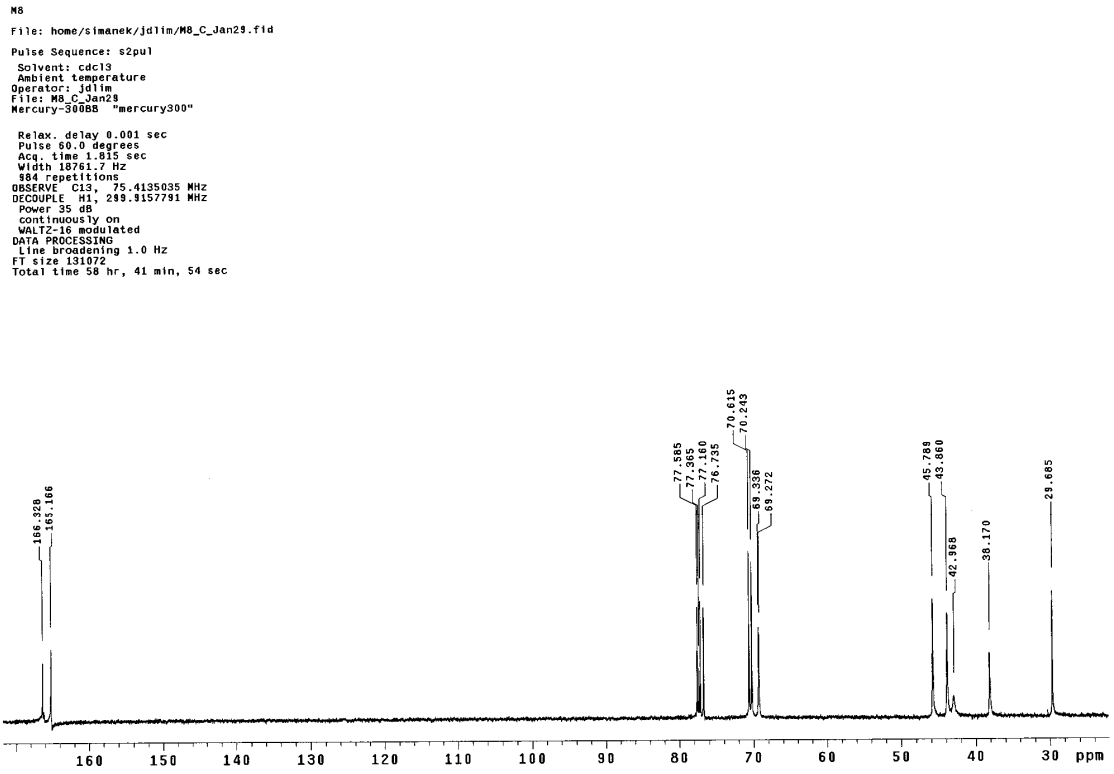

Figure S24. ^{13}C NMR spectrum of dendrimer **8** (75 MHz, $CDCl_3$).

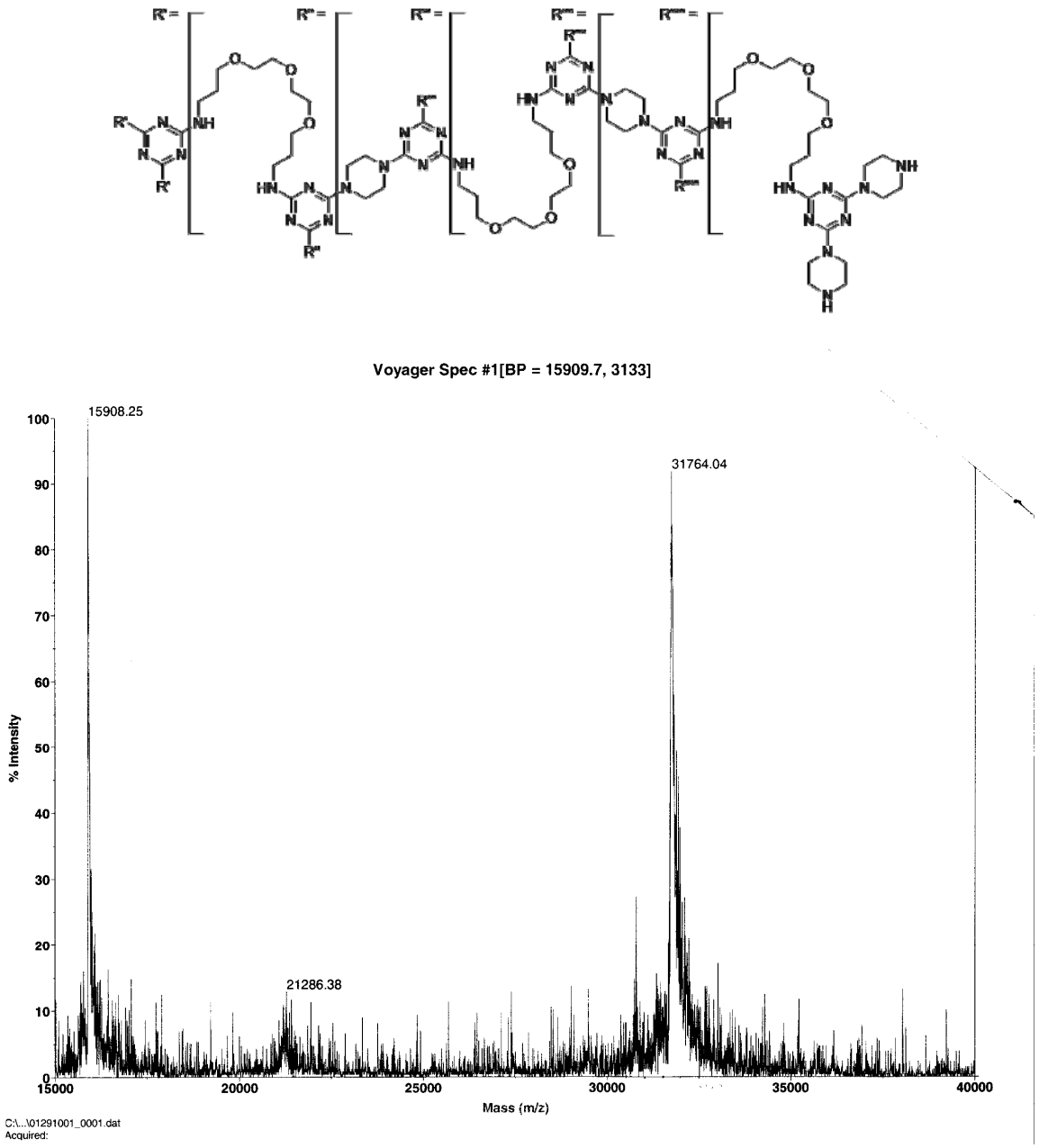

Figure S25. MALDI mass spectrum of dendrimer **8**. The ions of [M + $2H^+$] appears at 15908. The line at 21286 could be attributed to [2M + $3H^+$], fragmentation or an impurity. We interpret this line presently to be a fragmentation product resulting from cleavage within the hydrophilic diamine linker.

Chemical Formula: $C_{1416}H_{2490}N_{660}O_{189} + H^+$
Exact Mass: 31767.5599
Molecular Weight: 31786.2383
Error: 1.1 x 10^{-4}; 110 ppm