Electronic Supplementary Information for:

Degradable Dendrimers Divergently Synthesized via Click Chemistry

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Experimental Section

General:

Reactions were monitored by TLC using silica gel 60 F\textsubscript{254} plastic, aluminum, or glass plates (Aldrich, Merck or EMD Chemicals, Inc.) or F\textsubscript{264} basic aluminum oxide glass plates (EMD Chemicals, Inc.). Gravity and flash chromatography was performed with 32-63 micron silica gel (Merck) or activated basic aluminum oxide Brockman I with 150 mesh (Aldrich). A fluorescent indicator (green 254 nm) was added to the silica gel for chromatography performed in a quartz column. TLC bands were visualized by UV, dinitrophenylhydrazine (DNP) stain, or ninhydrin stain. Solvent ratios used as eluents are reported in v/v. Preparative size-exclusion chromatography (SEC) was performed using 13” x 1.5”, 29” x 0.75” or 26” x 2.5” columns of Bio-Beads S-X1 200-400 mesh beads (Bio-Rad) with CH\textsubscript{2}Cl\textsubscript{2} or CH\textsubscript{2}Cl\textsubscript{2}/toluene mixtures as the eluent. Analytical SEC was performed using a 2x sytrigel HR3, 1x styrigel HR4E column in series with 50mM LiBr in DMF as the eluent at a flow rate of 1.0 mL/min. Peak detection was achieved by a Viscotek triple array 300 refractive index detector. SEC-derived molecular weights were
based on calibration with linear polystyrene however the GPC reported inflated molecular weights consistently for several different dendritic compounds ran using this solvent system. Narrowness and shape of peaks are considered the valuable data from traces. The purity of the final products was obtained through $^1$H NMR, $^{13}$C NMR, melting point and/or elemental analysis.

$^1$H NMR and $^{13}$C NMR data were obtained on either a 400 or 500 MHz Varian U400 or U500 instrument at the VOICE NMR laboratory at the University of Illinois. Chemical shifts are reported in parts per million (ppm) and coupling constants were reported in Hertz (Hz). $^1$H NMR spectra obtained in CDCl$_3$ were referenced to 7.26 ppm and D$_2$O were referenced to 4.64 ppm. $^{13}$C NMR spectra obtained in CDCl$_3$ were referenced to 77.0 ppm. FDMS and ESIIMS data were collected by the Mass Spectrometry Center at the University of Illinois. MALDI-MS spectra were obtained on an Applied Biosystems Voyager-DE STR mass spectrometer. Matrices employed in the collection of MALDI spectra included dithranol, 2-(4-hydroxyphenylazo)benzoic acid (HABA), and trans-3-indoleacrylic acid (IAA). Data was calibrated to an external standard solution of insulin and cytochrome C. IR spectra were collected on a Matson FTIR 5000. Melting points were measured with a Thomas Hoover melting point apparatus and are uncorrected.

**Syntheses:**
Tri bromo core. To a solution of 1,1,1-tris(4-hydroxyphenyl)ethane (7.54 g, 24.4 mmol) and 1,3-dibromopropane (40.0 mL, 394 mmol) in acetone (40.0 mL) was added potassium carbonate (14.0 g, 101 mmol) and the suspension was heated to 80°C. After 10 minutes 18-crown-6 (2.03 g, 7.60 mmol) was added. After 25 hours, additional potassium carbonate (10.0 g, 72.3 mmol) and 1,3-dibromopropane (11.0 mL, 108 mmol) were added and the reaction was stirred for 16 more hours. The reaction was filtered and purified via flash chromatography (gradient 0:1 to 1:4 ethyl acetate : petroleum ether) to afford 11.5 g of a white solid that contained the desired tri bromo product along with elimination and C-alkylation side products. The mixture was taken on to the next step without further purification: major product: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.99 (d, $J = 8.7$ Hz, 6H), 6.79 (d, $J = 8.7$ Hz, 6H), 4.08 (t, $J = 5.7$ Hz, 6H), 3.60 (t, $J = 5.8$ Hz, 6H), 2.31 (quint, $J = 5.9$ Hz, 6H), 2.10 (s, 3H).

Tri azido core (6). To a solution of tri bromo core (11.5 g, 17.3 mmol) in DMF (75 mL) was added sodium azide (9.05 g, 139 mmol) and the solution was heated to 80°C for 20
hours. The reaction was partitioned between ethyl acetate (200 mL) and brine (100 mL). The organic fraction was washed with brine (4 x 50 mL), dried over Na₂SO₄, filtered, concentrated in vacuo, and purified via flash chromatography (gradient 1:9 to 1:4 ethyl acetate: petroleum ether) to give 3.70 g (22 % over two steps) of 6 as a clear, colorless oil that solidified over time: ¹H NMR (500 MHz, CDCl₃) δ 6.99 (d, J = 8.8 Hz, 6H), 6.78 (d, J = 8.8 Hz, 6H), 4.02 (t, J = 5.9 Hz, 6H), 3.51 (t, J = 6.7 Hz, 6H), 2.10 (s, 3H), 2.04 (quint, J = 6.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 156.6, 141.9, 129.6, 113.6, 64.3, 50.6, 48.2, 30.7, 28.8; FD-LRMS m/z 555.2 (M⁺). Anal. Calcd for C₂⁹H₃₃N₉O₃: C, 62.69; H, 5.99; N, 22.69. Found: C, 63.03; H, 5.93; N, 22.24.

7-[(3-propynyloxy)methyl]-2,4,6-triphenyl-1,3,5-triazaadamantane. To a solution of 7-(hydroxymethyl)-2,4,6-triphenyl-1,3,5-triazaadamantane (18.7 g, 47.0 mmol) and tetrabutylammonium iodide (637 mg, 1.69 mmol) in THF (50 mL) at 0°C was added sodium hydride (7.51 g, 188 mmol). After 30 minutes, propargyl bromide (30 mL, 270 mmol) was added and the solution was heated to reflux. After 4.5 hours the reaction was cooled in an ice bath and water was added slowly (5 mL). The solution was concentrated in vacuo and partitioned between CH₂Cl₂ (300 mL) and water (100 mL). The organic layer was washed with brine (100 mL) and water (100 mL). The combined aqueous layers were washed with CH₂Cl₂ (4 x 50 mL). The combined organic layers were dried over Na₂SO₄, filtered, concentrated in vacuo, and purified via flash chromatography (1:4
ethyl acetate : petroleum ether) to afford 21.2 g of a yellow paste that was taken on without any further purification. Crystallization in ethyl acetate/petroleum ether can produce analytically and diastereomerically pure product as a white solid: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.1$ Hz, 2H), 7.78 (d, $J = 8.1$ Hz, 4H), 7.44 (t, $J = 7.8$ Hz, 4H), 7.33 (m, 4H), 7.24 (t, $J = 7.2$ Hz, 1H), 5.64 (s, 1H), 5.42 (s, 2H), 3.91 (d, $J = 2.4$ Hz, 2H), 3.51 (d, $J = 12.9$ Hz, 2H), 3.25 (d, $J = 13.0$ Hz, 2H), 2.94 (s, 2H), 2.79 (s, 2H), 2.30 (t, $J = 2.3$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 140.0, 139.8, 128.8, 128.7, 127.4, 127.1, 126.7, 82.9, 79.8, 75.4, 74.6, 74.6, 58.6, 55.5, 46.9, 26.8; FD-LRMS $m/z$ 435.2 (M$^+$).

Anal. Calcd for C$_{29}$H$_{29}$N$_3$O: C, 79.97; H, 6.71; N, 9.65. Found: C, 80.02; H, 6.73; N, 9.60.

2-Propargyl-1,1,1-tris(aminomethyl)ethane trihydrochloride (2). To a solution of 7-[(3-propynyloxy)methyl]-2,4,6-triphenyl-1,3,5-triazaadamantane (21.1 g, 48.4 mmol) in THF (440 mL) was added HCl (1.25 M, 250 mL). After 1 hour the THF was removed in vacuo and the resultant solution was washed with ether (3 x 130 mL). The combined ether layers were washed with HCl (2 x 70 mL). The combined aqueous layers were concentrated in vacuo and ether/ethyl acetate were added to precipitate out 10.8 g (82 % over 2 steps) of 2 as a white solid: $^1$H NMR (500 MHz, D$_2$O) $\delta$ 4.28 (s, 2H), 3.82 (s, 2H), 3.31 (s, 6H), 2.97 (s, 1H); $^{13}$C NMR (125 MHz, 1% MeOH in CDCl$_3$) $\delta$ 79.1, 77.8, 69.8, 59.4, 41.1, 39.4; ESI-LRMS $m/z$ 172.2 (M + H$^+$). Anal. Calcd for C$_8$H$_{20}$Cl$_3$N$_3$O: C, 34.24; H, 7.18; Cl, 37.90; N, 14.97. Found: C, 34.32; H, 7.14; Cl, 38.02; N, 14.59; mp = 257 °C (decomp).
2-(2-Chloroethoxy)ethylamine hydrochloride. To a solution of 2-(2-aminoethoxy)-ethanol (7.13 g, 66.4 mmol) in toluene (70 mL) was added SOCl₂ (5.30 mL, 72.8 mmol). The solution instantly turned yellow and gave off heat. After one hour the solvent was decanted to produce a brown oil that was dried in vacuo to produce 11.4 g (assumed quantitative conversion for calculations in the next step) of a brown solid that was taken on without further purification: ¹H NMR (500 MHz, CDCl₃) δ 8.33 (br s, 3H), 3.85 (t, J = 5.2 Hz, 2H), 3.81 (t, J = 5.7 Hz, 2H), 3.72 (t, J = 5.7 Hz, 2H), 3.27 (sext, J = 5.2 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 71.3, 66.7, 43.0, 39.6; ESI-LRMS m/z 124.1 (M + H⁺).

N-[2-(2-Chloro-ethoxy)-ethyl]-4-formyl-benzamide (4). To a suspension of 4-carboxybenzaldehyde dimethoxyacetal (8.52 g, 43.4 mmol) and N-hydroxsuccinimide (5.64 g, 48.0 mmol) in CH₂Cl₂ (200 mL) was added dropwise a solution of N,N'-dicyclohexylcarbodiimide (9.70 g, 46.5 mmol) in CH₂Cl₂ (50 mL) over 35 minutes. After 3 hours the precipitate was filtered and 2-(2-chloroethoxy)ethylamine hydrochloride (11.4 g, 66.4 mmol (theoretical from previous step)) and triethylamine (12.2 mL, 87.5 mmol) were added. Trifluoroacetic acid was added (16.0 mL, 206 mmol) after 4 hours and again 2 hours later (10.0 mL, 129 mmol). After 1 hour the solution was washed with NaHCO₃ (100 mL). The organic layer was washed with NaHCO₃ (2 x 100 mL) and brine (50 mL), dried over Na₂SO₄, filtered, concentrated in vacuo, and purified via flash chromatography (4:1 ethyl acetate : petroleum ether) to afford 8.86 g (80 %) of
4 as a white solid: \(^1\text{H NMR (500 MHz, CDCl}_3\text{) \(\delta\) 10.08 (s, 1H), 7.95 (s, 4H), 6.82 (br s, 1H), 3.79 (t, J = 5.6 Hz, 2H), 3.71 (m, 4H), 3.68 (t, J = 5.6 Hz, 2H);} \(^{13}\text{C NMR (125 MHz, CDCl}_3\text{) \(\delta\) 191.8, 166.5, 139.6, 138.2, 129.9, 127.8, 70.9, 69.4, 43.3, 39.8; ESI-LRMS m/z 256.3 (M + H\(^+\));} \text{Anal. Calcd for C}_{12}\text{H}_{14}\text{ClNO}_3: C, 56.37; H, 5.52; Cl, 13.87; N, 5.48. Found: C, 56.28; H, 5.55; Cl, 14.41; N, 5.51; mp = 83.8 – 86.4 °C.}

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\begin{align*}
\text{TAA monomer (5). To a solution of 2 (3.14 g, 11.2 mmol) and triethylamine (5.50 mL, 39.5 mmol) in MeOH (50 mL) was added 4 (8.74 g, 34.2 mmol) in MeOH (40 mL) and the solution was heated at reflux. After 75 minutes the majority of the solvent was removed in vacuo and resultant solution was partitioned between CHCl}_3 (100 mL) and H\textsubscript{2}O (50 mL). The organic layer was washed again with H\textsubscript{2}O (50 mL). The combined aqueous layers were washed with CHCl}_3 (2 x 20 mL). The combined organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, concentrated in vacuo, and purified via flash chromatography (gradient from 2% TEA in CH\textsubscript{2}Cl\textsubscript{2} to 2% TEA and 2% MeOH in CH\textsubscript{2}Cl\textsubscript{2}) to afford 7.11 g (72%) of 5 as an off-white foam: \(^1\text{H NMR (500 MHz, CDCl}_3\text{) \(\delta\) 7.85 (m, 12H), 6.67 (br t, 2H), 6.56 (br t, 1H), 5.65 (s, 1H), 5.37 (s, 2H), 3.91 (d, J = 2.3 Hz, 2H), 3.80 (t, J = 5.7 Hz, 4H), 3.73 (m, 10H), 3.69 (t, J = 5.7 Hz, 4H), 3.66 (m, 4H), 3.63 (t, J = 5.7 Hz, 2H), 3.45 (d, J = 13.4 Hz, 2H), 3.24 (d, J = 13.4 Hz, 2H), 2.90 (s, 2H), 2.77 (s, 2H), 2.31 (t, J = 7.4 Hz, 2H), 2.09 (s, 2H); ESI-LRMS m/z 256.3 (M + H\(^+\));} \text{Anal. Calcd for C}_{12}\text{H}_{14}\text{ClNO}_3: C, 56.37; H, 5.52; Cl, 13.87; N, 5.48. Found: C, 56.28; H, 5.55; Cl, 14.41; N, 5.51; mp = 83.8 – 86.4 °C.}
\end{align*} \]
$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.4, 167.1, 142.9, 142.6, 133.5, 133.3, 127.5, 127.3, 126.5, 126.4, 82.4, 79.3, 75.2, 74.7, 73.8, 70.7, 70.6, 69.4, 69.4, 58.2, 55.0, 46.6, 43.1, 42.9, 39.5, 39.5, 26.4; FD-LRMS $m/z$ 884.2 (M$^+$); Anal. Calcd for C$_{44}$H$_{53}$Cl$_3$N$_6$O$_7$: C, 59.76; H, 6.04; N, 9.50. Found: C, 59.58; H, 6.07; N, 9.37, SEC (0.05 M LiCl in DMF) calcd $M_w = 3189$, PDI = 1.03.

**G1-chloro dendrimer (7).** H$_2$O (6 mL) was added to a solution of 6 (207 mg, 0.373 mmol) and 5 (1.02 g, 1.16 mmol) in CH$_2$Cl$_2$ (6 mL). To the biphasic solution was added CuSO$_4$·5H$_2$O (15.0 mg, 0.0600 mmol) quickly followed by sodium ascorbate (23.0 mg, 0.116 mmol). After 7 hours the rxn was partitioned between CH$_2$Cl$_2$ (20 mL) and NaHCO$_3$ (20 mL). The aqueous layer was washed with CH$_2$Cl$_2$ (6 x 10 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered, concentrated in vacuo, and
purified via flash chromatography (gradient from 2% TEA in ethyl acetate to 2% TEA 10% MeOH in ethyl acetate in order to remove monomer, 10% MeOH in CH₂Cl₂ in order to remove product) to produce 1.03 g (86%) of 7 as a white foam: ¹H NMR (500 MHz, CDCl₃) δ 7.85 (m, 18H), 7.78 (m, 18H), 7.35 (s, 3H), 6.96 (d, J = 8.9 Hz, 6H), 6.79 (br s 6H), 6.73 (d, J = 8.8 Hz, 6H), 6.68 (br s, 3H), 5.58 (s, 3H), 5.32 (s, 6H), 4.51 (t, J = 7.0 Hz, 6H), 4.36 (s, 6H), 3.90 (t, J = 5.5 Hz, 6H), 3.77 (t, J = 5.0 Hz, 12H), 3.70 (m, 30H), 3.67 (t, J = 5.7 Hz, 12H), 3.64 (m, 12H), 3.61 (t, J = 5.5 Hz, 6H), 3.38 (d, J = 13.3 Hz, 6H), 3.18 (d, J = 13.3 Hz, 6H), 2.84 (s, 6H), 2.72 (s, 6H), 2.32 (quint, J = 6.2 Hz, 6H), 2.07 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 167.5, 167.2, 156.3, 144.5, 142.9, 142.6, 141.9, 133.5, 133.3, 129.4, 127.5, 127.3, 126.4, 126.4, 122.8, 113.4, 82.3, 75.1, 74.2, 70.6, 70.6, 69.4, 69.4, 64.3, 63.9, 55.0, 50.4, 47.0, 43.1, 43.0, 39.4, 39.4, 30.6, 29.7, 27.5, 26.6; MALDI-HRMS m/z 3208.3850 (M + H⁺); SEC (0.05 M LiCl in DMF) calcd Mₘ = 7675, PDI = 1.01.
G1-azido dendrimer (8). To a solution of 7 (926 mg, 0.299 mmol) in DMF (7 mL) was added sodium azide (632 mg, 6.73 mmol) and the solution was heated to 90°C. After 32 hours the rxn was cooled to room temperature, the insoluble material was filtered, and the solvent was removed in vacuo. Purification via preparative SEC (1 : 3 toluene : CH₂Cl₂) afforded 0.873 g (93 %) of 8 as a white foam: ¹H NMR (500 MHz, CDCl₃) δ 7.85 (m, 18H), 7.78 (m, 18H), 7.34 (s, 3H), 6.96 (d, \( J = 8.8 \) Hz, 6H), 7.73 (m, 12H), 6.63 (br s, 3H), 5.59 (s, 3H), 5.33 (s, 6H), 4.51 (t, \( J = 7.0 \) Hz, 6H), 4.36 (s, 6H), 3.91 (t, \( J = 5.6 \) Hz, 6H), 3.74-3.62 (m, 54H), 3.40 (m, 18H), 3.35 (t, \( J = 4.5 \) Hz, 6H), 3.18 (d, \( J = 13.1 \) Hz, 6H), 2.85 (s, 6H), 2.73 (s, 6H), 2.34 (quint, \( J = 6.2 \) Hz, 6H) 2.07 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 167.5, 167.2, 156.4, 144.7, 143.0, 142.8, 142.0, 133.5, 133.4, 129.6,
G2-chloro dendrimer (9). H2O (5 mL) was added to a solution of 8 (229 mg, 0.0701 mmol) and 5 (558 mg, 0.631 mmol) in CH2Cl2 (5 mL). To the biphasic solution was added CuSO4·5H2O (7.93 mg, 0.0318 mmol) quickly followed by sodium ascorbate (12.4 mg, 0.0626 mmol). After 8 hours the rxn was partitioned between 10% iPrOH in
CH$_2$Cl$_2$ (10 mL) and NaHCO$_3$ (10 mL). The aqueous layer was washed with 10% iPrOH in CH$_2$Cl$_2$ (4 x 10 mL). The combined organic layers were washed with brine (3 x 15 mL), dried over Na$_2$SO$_4$, filtered, concentrated in vacuo, dissolved in CH$_2$Cl$_2$ and precipitated out of ethyl acetate to produce 0.731 g (93%) of 9 as a white foam: MALDI-LRMS $m/z$ 11227.44 (M + H$^+$); SEC (0.05 M LiCl in DMF) calcd $M_w$ = 15580, PDI = 1.04.
**G2-azido dendrimer (10).** To a solution of 9 (62.1 mg, 0.0553 mmol) in DMF (10 mL) was added sodium azide (265 mg, 4.08 mmol) and the solution was heated to 80°C. After 27 hours the rxn was cooled to room temperature, the insoluble material was filtered, and the solvent was removed in vacuo to produce 604 mg (96%) of 10 as a tan foam that was used without further purification: MALDI-LRMS m/z 11407.22 (M + H⁺); SEC (0.05 M LiCl in DMF) calcd $M_w = 16440$, PDI = 1.06.

**G3-chloro dendrimer (11).** H₂O (5 mL) was added to a solution of 10 (201 mg, 0.0176 mmol) and 5 (423 mg, 0.478 mmol) in CH₂Cl₂ (5 mL). To the biphasic solution was
added CuSO₄ • 5H₂O (5.84 mg, 0.0234 mmol) quickly followed by sodium ascorbate (9.53 mg, 0.0481 mmol). After 26 hours CuSO₄ • 5H₂O (5.82 mg, 0.0233 mmol), sodium ascorbate (9.77 mg, 0.0493 mmol), and MeOH (1 mL) were added. After 10 hours the rxn was partitioned between 5% iPrOH in CH₂Cl₂ (20 mL) and NaHCO₃ (10 mL). The aqueous layer was washed with 10% iPrOH in CH₂Cl₂ (4 x 20 mL). The combined organic layers were washed with brine (20 mL) and H₂O (20 mL), dried over Na₂SO₄, filtered, concentrated in vacuo, and purified via preparative SEC (CH₂Cl₂) to afford 348 mg (56%) of 11 as a pale green solid: MALDI-LRMS m/z 352.79.06 (M + H⁺); SEC (0.05 M LiCl in DMF) calcd Mₘ = 54419, PDI = 1.38.

Degradation Study:
To a solution of dendrimer 10 (84.5 mg, 7.52 µmol) in THF/MeOH (0.70 mL/0.10 mL) was added 1.00 mL 1M HCl. The solution was stirred for one hour after which it was partitioned between CH₂Cl₂ (5 mL) and H₂O (10 mL). The aqueous layer was washed with CH₂Cl₂ (3 x 5 mL). The combined organic layers were dried over Na₂SO₄, filtered, concentrated in vacuo to afford 49.1 mg (0.192 mmol) of 4 as a white solid. This structure was confirmed by ¹H NMR and ESI-LRMS. The aqueous layer was concentrated in vacuo to afford 49.2 mg of a tan solid that consisted of a mixture of the hydrolyzed dendrimer core S₁ and aldehyde S₂. Core S₁: ¹H NMR (500 MHz, D₂O) δ 7.99 (s, 3H), 6.70 (d, J = 8.7 Hz, 6H), 6.50 (d, J = 8.7 Hz, 6H), 4.66 (s, 6H), 4.49 (t, J = 6.9 Hz, 6H), 3.79 (m, 12H), 3.70 (s, 18H), 2.24 (quint, J = 6.3 Hz, 6H), 1.88 (s, 3H); ESI-LRMS m/z 357.4 (M + 3H⁺); Aldehyde S₂: ¹H NMR (500 MHz, D₂O) δ 9.96 (s, 1H), 8.01 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 4.60 (t, J = 4.9 Hz, 2H), 4.45 (s, 2H), 3.95 (t, J = 4.9 Hz, 2H), 3.70 (s, 2H), 3.67 (t, J = 5.3 Hz, 2H), 3.49 (t, J = 5.2 Hz, 2H), 3.29 (s, 6H); ESI-LRMS m/z 256.2 (M + H⁺); Mixture consists of a 1:9 ratio or S₁:S₂ as evidenced by ¹H NMR.

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Spectra

Degradation Study $^1$H NMR:

Organic Layer

Aqueous Layer
GPC:

Byproduct Ratio

Retention Volume (mL)
IR:

![IR spectra](image)

MALDI:

![MALDI spectrum](image)
High res MALDI-TOF MS
Dendrimer 8

MALDI-TOF MS
Dendrimer 9
MALDI-TOF MS
Dendrimer 10

MALDI-TOF MS
Dendrimer 11

m/z

8000 9000 10000 11000 12000 13000

20000 25000 30000 35000 40000

M + H⁺