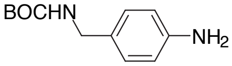
Supplementary Material

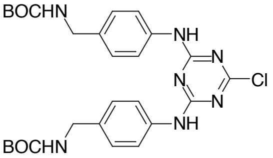
Preparation and Characterization of Dendrimers

4-(*N*-*t*-Butoxycarbonylaminomethyl)aniline. To a solution of 4-aminobenzylamine (2.00g; 16.4 mmol) in 15 ml THF, di-*t*-butyl dicarbonate (3.57g, 16.4 mmol) and 3.2 ml of *N,N*-diisopropylethylamine were added. The reaction mixture was stirred for 4 h at 0°C and then warmed to room temperature. Stirring was continued for 12 h. The solution was filtered and the solvent was evaporated. The residue was dissolved in 120 ml of toluene, washed with brine, 0.1 N KOH, brine again, and dried over $MgSO_4$. After removing toluene, the crude product was recrystallized from $CHCl_3$-hexanes to give 2.74 g (12.3 mmol, 75%) of the desired product as a white solid.



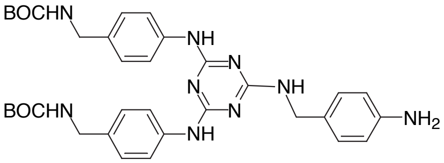
^{1}H NMR(300 MHz, $CDCl_3$) δ 7.05(d, *J*=14.4 Hz, 2H), 6.64(d, *J*=14.4 Hz, 2H), 4.75(br s, 1H), 4.17(d, *J*=8.0 Hz, 2H), 3.25(br s, 2H), 1.42(s, 9H).
^{13}C NMR (75 MHz, DMSO) δ 156.12, 147.78, 128.41, 127.60, 114.11, 77.90, 43.57, 28.73.

Intermediate 2. 4-(*N*-*t*-butoxycarbonylaminomethyl)aniline (2.74g, 12.3 mmol) was dissolved in 10 ml THF, cyanuric chloride (1.08 g, 5.88 mmol) and 2 ml of *N,N*-diisopropylethylamine were added to the solution. The reaction was stirred at 0°C for 2h, and then at room temperature for 24 h. The solution was filtered and the solvent was evaporated. The residue was dissolved in a minimum amount of THF and purified by flash chromatography (eluted with ethyl acetate) to give 3.01 g (5.40 mmol, 92%) of product as an off-white solid.



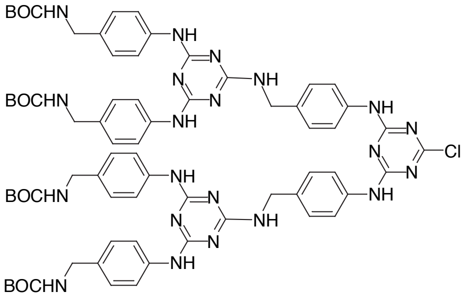
^{1}H NMR(300 MHz, $CDCl_3$) δ 7.70 (br, 2H), 7.47 (d, *J*=11Hz, 4H), 7.24 (d, *J*=11 Hz, 4H), 4.85(br, 2H), 4.28 (br, 4H), 1.45(s, 18H).
^{1}H NMR(300 MHz, DMSO) δ 10.25 (s, 1H), 10.20 (s, 1H), 7.54 (d, *J*=11Hz, 4H), 7.34 (t, 2H), 7.16 (d, *J*=11 Hz, 4H), 4.07 (d, *J*=8.0Hz, 4H), 1.38(s, 18H).
^{13}C NMR (75 MHz, DMSO) δ 168.73, 164.52, 156.47, 137.62, 136.05, 127.90, 121.58, 78.43, 43.71, 28.94.
MS: Calcd, 556(M^+); Found (FAB/DP$^+$) 556 (M^+).

Intermediate 7. Intermediate **2** (1.15g; 2.07 mmol) was dissolved in 10 ml THF, and 4-aminobenzylamine (505 mg, 4.14 mmol) and 0.6 ml of *N,N*-diisopropylethylamine were added to the solution. The reaction was stirred at room temperature for 12 h, and then heated to 70° C for 30 h. The solution was filtered and the solvent was evaporated. The residue was purified by flash chromatography (eluted with 1:1 ethyl acetate/petroleum ether) to give the product (1.18g, 88.7%) as a white solid.



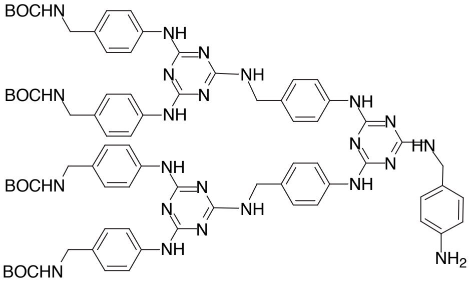
^{1}H NMR(300 MHz, $CDCl_3$) δ 7.50 (br, 2H),7.40(br, 4H), 7.06(br, 4H), 7.01(d, *J*=12Hz, 2H), 6.56(d, *J*=12Hz, 2H), 5.62(br, 1H), 4.96(br, 2H), 4.40(d, *J*=6.7Hz, 2H), 4.16(br, 4H), 3.25(br, 2H), 1.43(s, 18H).
^{1}H NMR(300 MHz, DMSO) δ 9.04 (s, 1H), 8.95 (s, 1H), 7.69 (br. 4H),7.40(br., 1H), 7.30 (t, 2H), 7.10 (d, *J*=12Hz, 4H), 7.01(d, *J*=12Hz, 2H), 6.56(d, *J*=12Hz, 2H), 4.92(br, 2H), 4.38(d, *J*=6.7Hz, 2H), 4.08(d, *J*=7.5Hz, 4H), 1.38(s, 18H).
^{13}C NMR (75 MHz, DMSO) δ 166.50, 164.90, 156.60, 148.10, 139.80, 134.05, 128.69, 127.86, 120.74, 114.50, 79.30, 43.62, 28.46.
MS: Calcd, 641 (M^+); Found (FAB/DP^+) 642 ($M+H^+$).

Intermediate 8. Intermediate **7** (896 mg, 1.40 mmol) was dissolved in 8 ml THF, and cyanuric chloride (129 mg; 0.70 mmol) and 0.5 ml of *N,N*-diisopropylethylamine were added to the solution. The mixture was stirred for 48 h at room temperature. The solvent was removed and the residue was purified by flash chromatography using ethyl acetate to afford a white solid product (940 mg, 96.4%).



^{1}H NMR(300 MHz, DMSO) δ 9.05 (s, 3H), 8.99 (s, 3H), 7.69 (br, 2H), 7.62 (br, 12H), 7.28(br, 4H), 7.10 (br, 12H), 4.50 (br, 4H), 4.04(m., 8H), 1.39(s, 36H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 168.50, 166.48, 164.77, 156.48, 139.55, 137.56, 136.30, 134.04, 127.75, 121.62, 120.67, 78.34, 43.75, 28.94.
MS: Calcd,1395.02(M^+); Found, 1396.56$(M+1)^+$, 1418.89$(M+Na)^+$

Intermediate 9. To a solution of **8** (900 mg, 0.65mmol) in 6 ml THF, 4-aminobenzylamine (252 mg, 2.07 mmol) and 0.4 ml of *N,N*-diisopropylethylamine were added. The mixture was stirred at room temperature for 12h and then heated to 70 °C for 30 h. The solution was filtered and the solvent was evaporated. The residue was purified by flash chromatography using ethyl acetate/petroleum ether(1:1) and then ethyl acetate as eluants to give a light-yellow solid product (908 mg, 95.1%).



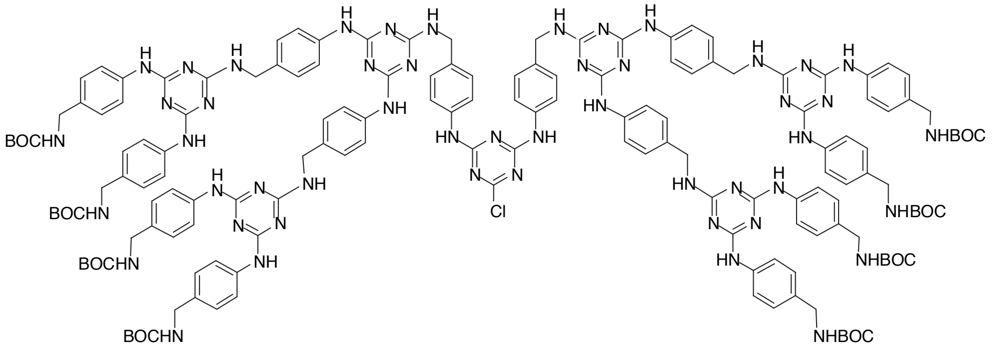
^{1}H NMR(300 MHz, $CDCl_3$) δ 7.35 (br, 12H), 7.00 (br, 12H), 6.84 (br, 2H), 6.40 (br, 2H), 5.08 (br, 2H), 4.28 (br, 4H), 4.08 (br, 14H), 1.30 (s, 36H).

^{1}H NMR(300 MHz, DMSO) δ 9.04 (br, 2H), 8.97 (br, 2H), 8.91 (br, 2H),7.68 (m, 12H), 7.52 (br, 3H), 7.28 (m, 4H), 7.18 (d, *J*=11.5Hz, 4H), 7.07 (br, 8H), 6.96 (d, *J*=11.5Hz, 2H), 6.46 (d, *J*=12Hz, 2H), 4.84 (s, 2H), 4.44 (d, *J*=8.0Hz, 4H), 4.32 (d, *J*=8.5Hz, 2H), 4.02 (d, *J*=8.0Hz, 8H), 1.36 (s, 36H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 165.22, 164.14, 155.93, 145.63, 138.08, 133.27, 128.54, 127.82, 120.61, 115.20, 79.36, 44.20, 28.44.

MS: Calcd,1480.68(M^+); Found, 1396.56$(M+1)^+$, 1480.25(M^+)

Intermediate 10. Intermediate **9** (890 mg, 0.60 mmol) was dissolved in 8 ml THF, cyauric chloride (55.3 mg, 0.30 mmol) and 0.4 ml of *N,N*-diisopropylethylamine were added to the solution. The reaction mixture was stirred for 48 h at room temperature. The solvent was removed and the residue was purified by flash chromatography (eluted with EtOAc) to give a light-yellow solid (890 mg, 96%).



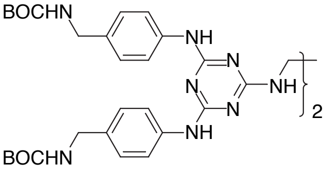
^{1}H NMR(300 MHz, $CDCl_3$) δ 6.60-8.00 (br, 56 H), 5.00(br, 14H), 4.22(br, 28H), 1.41(s, 72H).

^{1}H NMR(300 MHz, DMSO) δ 9.05 (s, 7H), 8.98 (s, 7H), 7.68 (m, 28H), 7.55 (br, 6H), 7.28 (br, 8H), 7.15 (d, *J*=11.5Hz, 12H), 7.08 (br, 16H), 4.46 (br, 12H), 4.02(br, 16H), 1.36 (s, 72H).

^{13}C NMR (75 MHz, DMSO) δ 166.50, 166.42, 164.73, 156.46, 139.54, 137.80, 136.15, 133.99, 127.73, 121.80, 120.46, 78.34, 43.72, 28.94.

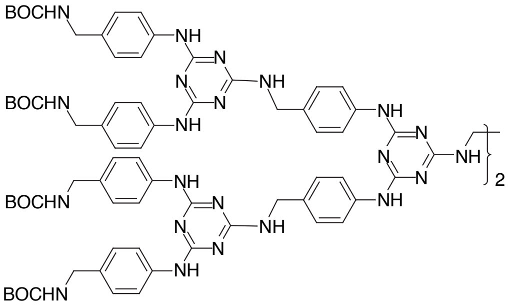
MS: Calcd, 3072.97(M^+); Found(MALDITOF): 3076.02$(M+3)^+$, 3097.89$(M+Na)^+$.

Dendrimer(Generation 1) 3. Intermediate **2** (1.11 g; 2.0 mmol) was dissolved in 10 ml *p*-dioxane, containing 0.4 ml of *N,N*-diisopropylethylamine. Ethylenediamine (60 mg;1 mmol) was added to the solution. The solution was sealed in a parr vessel and heated at 80° C under stirring for 12 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate to afford the product as a light-yellow solid (867 mg, 0.79 mmol, 79%).



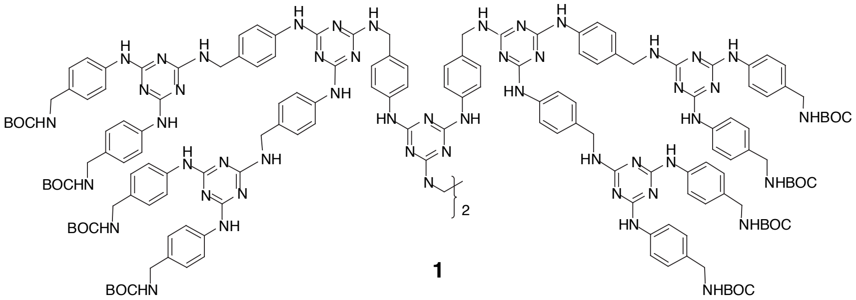
^{1}H NMR(300 MHz, DMSO) δ 9.07 (s, 2H), 8.95 (s, 2H), 7.70 (br. 8H), 7.29 (br., 4H), 7.10 (d, J=11.8 Hz, 8H), 4.05 (d, J=7.4Hz, 8H), 3.54 (br., 4H), 1.39(s, 36H).
^{13}C NMR (75 MHz, DMSO) δ 166.48, 164.73, 156.47, 139.60, 133.98, 127.75, 120.48, 78.36, 67.05, 43.74, 28.97.
MS: Calcd, 1100(M^+); Found(FAB/DP$^+$), 1100(M^+)

Dendrimer (Generation 2) 5. Intermediate **8** (350 mg, 0.25 mmol) was dissolved in 8 ml dioxane. To the solution ethylenediamine (7.5 mg; 0.125 mmol) and 0.1 ml of *N,N*-diisopropylethylamine were added. The solution was sealed in a Parr vessel and heated at 100°C and stirred for 24 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was purified by column chromatography on silica gel using CH_2Cl_2:CH_3OH (19:1) as eluent to give the product as a light-yellow solid (246 mg, 71%).



^{1}H NMR(300 MHz, DMSO) δ 9.03(s. 6H), 8.96 (s. 6H), 7.70 (br. 24H), 7.62 (br. 4H), 7.22 (t. 8H), 7.10(br. 24H), 6.98 (br., 2H), 4.47 (br. 8H), 4.04 (br. 16H), 3.50 (br. 2H), 3.41 (d, 2H), 1.38 (s, 72H).
^{13}C NMR (75 MHz, DMSO) δ 166.49, 164.80, 156.47, 139.57, 133.10, 127.73, 120.46, 78.36, 67.05, 43,74, 28.95.
MS: Calcd, 2777.26 (M^+); Found(MALDITOF): 2778.08 (M^+), 2800.52(M+Na$^+$)

Dendrimer(Generation 3) 1. Intermediate **10** (240 mg; 0.079 mmol) was dissolved in 6 ml dioxane. To this solution 0.1 ml of *N,N*-diisopropylethylamine and ethylenediamine (2.40 mg; 0.04 mmol) of were added to the solution. The solution was sealed in a Parr vessel and heated at 100°C with stirring for 36 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was purified by chromatography using CH_2Cl_2:CH_3OH (16:1, 10:1) afford the product as a light-yellow solid (145 mg, 60%).



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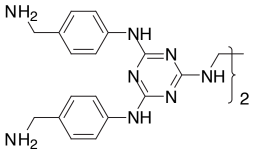
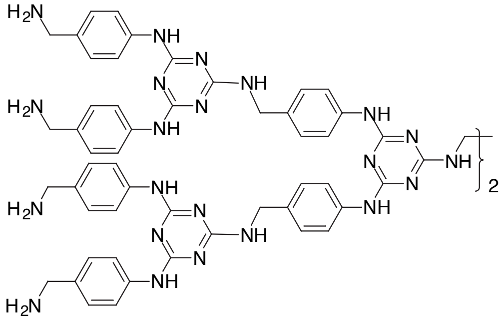
^1H NMR(300 MHz, DMSO) δ 9.08 (s. 14H), 9.06 (s. 14H), 7.72 (br, 56H), 7.68 (br, 12H), 7.32 (br, 16H), 7.22 (br, 24H), 7.10 (br, 32H), 4.47(br, 24H), 4.05 (br, 32H), 3.57(br, 4H), 1.38(s, 144H).
^{13}C NMR (75 MHz, DMSO) δ 166.48, 164.78, 156.47, 139.55, 134.00, 127.74, 120.47, 78.37, 67.06, 43,74, 28.95.
MS: Calcd, 6133.18 (M^+); Found(MALDITOF): 6157.55($M+Na^+$)

II. Divergent Approach

Intermediate 4. Intermediate **3** (460 mg; 0.42 mmol) was dissolved in 4 ml of CH_2Cl_2 /TFA (1:1). The mixture was stirred for 4 h at room temperature. The solvent and TFA was removed to afford a range solid of **4** $[G\text{-}1\text{-}(NH_3^+\ OOCCF_3^-)_4]$(490 mg, 0.4 mmol, 100%). This product was used without purification.



Dendrimer(G-2) 5. Intermediate **4** (1 equi,) was dissolved in 10 ml of THF. To the solution **2** (934 mg; 1.08 mmol) of and 0.7 ml of *N,N*-diisopropylethylamine was added. The solution was sealed in a Parr vessel and heated at 80 °C for 20 h. After cooling to room temperature, the solid was filtered and solvent was evaporated. The residue was dissolved in a mixed solution of CH_2Cl_2/CH_3OH (19:1) and then purified by flash chromatography using CH_2Cl_2/CH_3OH (19:1, 15:1, 10:1)to afford the product as a light-yellow solid (94 mg, 0.034 mmol, 8.01%).



(The spectral data are the same as the G-2 obtained from convergent approach).

Intermediate 6. Dendrimer **5** (450 mg; 0.16 mmol) was dissolved in 10 ml of CH_2Cl_2/TFA (1:1). The mixture was stirred for 48 h at room temperature. The solvent and TFA was removed to afford **6** [G-2-$(NH_3^+\ OOCCF_3^-)_8$] as a light-yellow solid (470 mg, 0.16 mmol, 100%). This product was used without further purification.

Dendrimer(G-3) 1. Intermediate **6** (470 mg, 0.16 mmol)) was suspended in 15 ml of THF. To the solution 0.5 ml of *N,N*-diisopropylethylamine and **2** (890 mg; 1.60 mmol) was added. The solution was sealed in a Parr vessel and heated at 80° C for 24 h. The reaction mixture was cooled to room temperature. The solvent was removed and the residue was dissolved in CH_2Cl_2/CHOH (19:1) and purified by chromatography with CH_2Cl_2/CHOH (19:1, 10:1, 1:1) to give G-3 (75 mg., 7.64%).
(The spectral data are the same as the G-3 obtained from convergent approach).