

Facile Synthesis of Polyamide Dendrimers from Unprotected AB₂ Building Block

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Supporting Information

Syntheses and characterization of G1 (Scheme 1S), G2 (Scheme 2S), G3 dendrons (Scheme 3S), and a G3 dendrimer (Scheme 4S)

Figure 1S. ^1H NMR spectrum of G1 dendron (2)

Figure 2S. ^{13}C NMR spectrum of G1 dendron (2)

Figure 3S. ^1H NMR spectrum of G2 dendron (3)

Figure 4S. ^{13}C NMR spectrum of G2 dendron (3)

Figure 5S. MALDI-TOF Mass spectrum of G2 dendron (3)

Figure 6S. ^1H NMR spectrum of G3 dendron (4)

Figure 7S. MALDI-TOF Mass spectrum of G3 dendron (4)

Figure 8S. ^1H NMR spectrum of G3 dendrimer (5)

Figure 9S. MALDI-TOF Mass spectrum of G3 dendrimer (5)

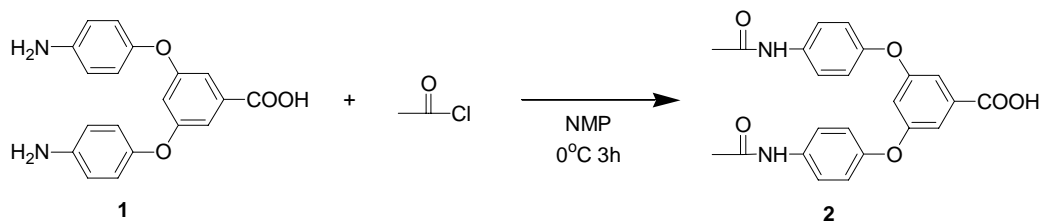
Measurement. Infrared spectra were recorded on a Horiba FT-720 spectrophotometer.

^1H and ^{13}C NMR spectra were obtained on a BRUKER DPX-300 spectrometer at ^1H , 300 MHz and ^{13}C , 75 MHz, respectively. Deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) was used as a solvent with tetramethylsilane as an internal standard. Matrix-assisted laser desorption ionization with time of flight (MALDI-TOF) mass spectra were recorded on a Kratos Kompact MALDI instrument operated in linear detection mode to generate positive ion spectra using dithranol as a matrix, THF as a solvent, sodium trifluoroacetate as an additive agent.

Materials. *N*-Methyl-2-pyrrolidinone (NMP) was distilled under reduced pressure over calcium hydride and then stored over 4-Å molecular sieves. Thionyl chloride was distilled under nitrogen over triphenyl phosphite and then stored at 0 °C under nitrogen. The other reagents and solvents were obtained commercially and used as received.

Synthesis of 1st Generation (G1) Dendron (**2**)

To a solution of dendron **1** (4.880 g, 14.51 mmol) in 25 ml of 1-methyl-2-pyrrolidinone (NMP), 3.0 equiv of acetyl chloride (4.556 g, 58.04 mmol) to **1** were added at 0 °C, and stirred for 3 h. The reaction mixture was poured into water and the precipitate was collected and dried. The precipitate was redissolved in NMP, and the solution was reprecipitated with water. The precipitate was collected, and dried *in vacuo* at 120 °C to give a white solid. The yield was 98%.



Scheme 1S

IR (KBr): ν (cm⁻¹) = 2700~3700 (-OH, st), 3294 (N-H, st), 1697 (C=O(OH), st), 1658 (C=O(N-H), st), 1597, 1504 (phenyl, st). ¹H-NMR (300 MHz, (CD₃)₂SO) δ (ppm) = 2.03 (s, -CH₃, 6H), 6.82, 7.06 (t, d, J=2.4 Hz, phenyl-(O)₂, 3H), 7.05, 7.61 (d, d, J=9.0, phenyl-(NH), 8H), 9.89 (N-H, 2H). ¹³C NMR (67.5 MHz, (CD₃)₂SO) δ (ppm) = 23.9, 111.1, 111.7, 120.2, 120.8, 133.7, 136.1, 150.5, 159.2, 166.1, 168.2.

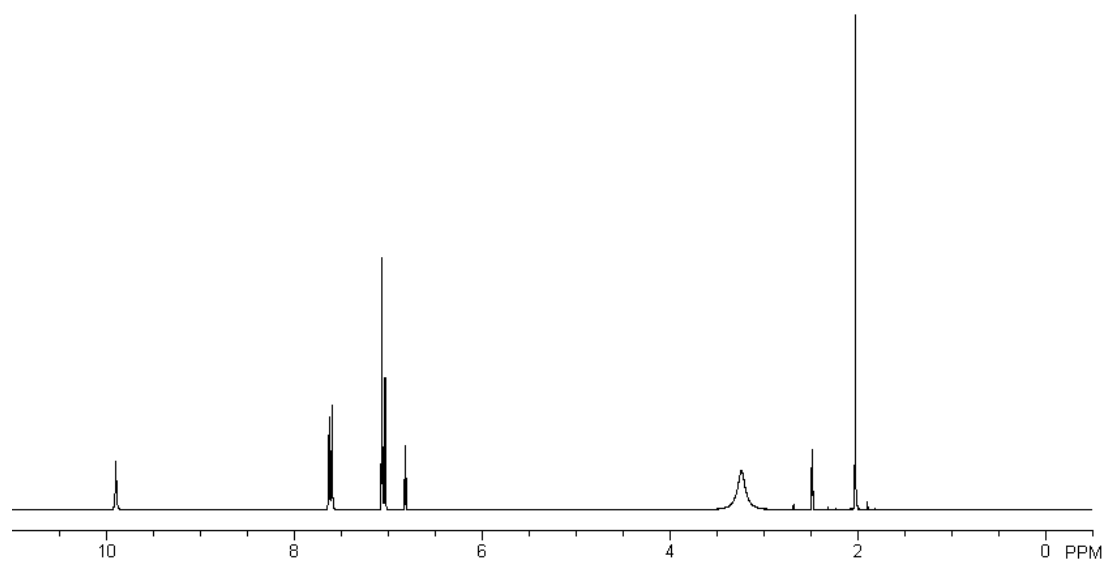


Figure 1S.

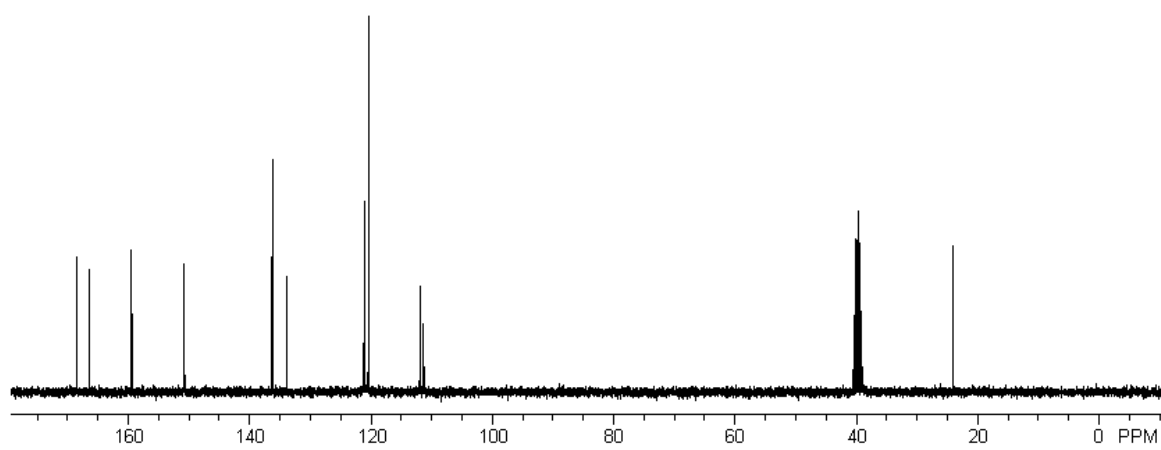
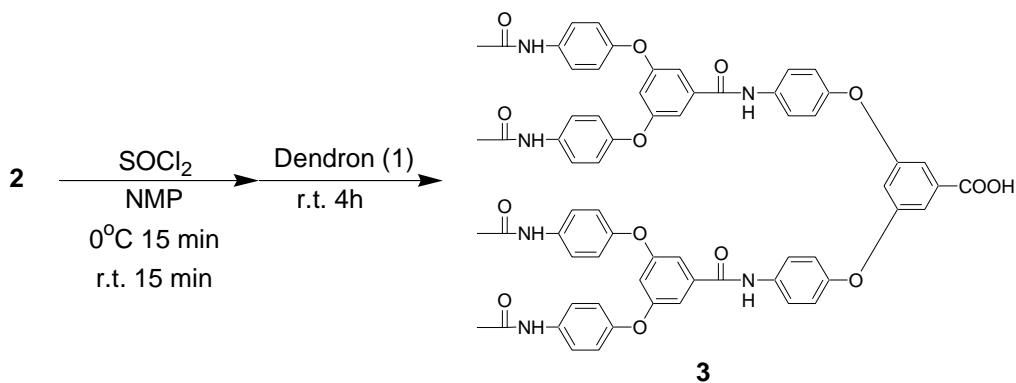


Figure 2S.

Synthesis of 2nd Generation (G2) Dendron (**3**)

1.04 equiv of thionyl chloride (1.150 g, 9.665 mmol) to **2** were added to a solution of **2** (3.907 g, 9.293 mmol) in 20 ml of NMP at 0 °C under nitrogen, and stirred for 15 min at that temperature, and for 15 min at room temperature. Then, 0.48 equiv of **1** (1.488 g, 4.425 mmol) to **2** were added to the solution and the reaction was carried out for 4 h at room temperature. The reaction mixture was poured into water and the precipitate was collected and dried. The crude product was redissolved in NMP, and diluted with methanol, and the resulting solution was reprecipitated with water (MeOH/H₂O 1/1 in volume ratio). The precipitate was collected and dried *in vacuo* at 120 °C to give a white solid. The yield was 92%.



Scheme 2S

IR (KBr): ν (cm⁻¹)= 2700~3700 (-OH, st), 3417 (N-H, st), 1666 (C=O(N-H), st), 1589, 1504 (phenyl ring, st). ¹H-NMR (300 MHz, (CD₃)₂SO) δ (ppm)=2.03 (s, -CH₃, 12H), 6.70, 7.28 (t, d, J=2.4 Hz, -(O)₂-phenyl-(CONH), 6H), 6.89, 7.10 (t, d, J=2.7, -(O)₂-phenyl-(COOH), 3H), 7.04, 7.60 (d, d, J=8.7, (CH₃-CONH)-phenyl(-O), 16H), 7.09, 7.76 (d, d, J=9.0, (-CONH)-phenyl(-O), 8H), 9.87 (CH₃CO-NH, 4H), 10.23

((phenyl)-CONH-(phenyl), 2H). ^{13}C NMR (67.5 MHz, $(\text{CD}_3)_2\text{SO}$) δ (ppm)=23.8, 109.8, 111.1, 111.5, 111.8, 119.7, 119.9, 120.7, 122.4, 133.7, 135.3, 135.8, 137.7, 150.7, 151.2, 158.7, 159.0, 164.0, 166.0, 168.1. Calcd.: $[\text{M}]^+$ m/z = 1141.1. Found: MALDI-TOFMS: $[\text{M}+\text{H}]^+=1141.3$, $[\text{M}+\text{Na}]^+=1163.0$, $[\text{M}+\text{K}]^+=1179.3$.

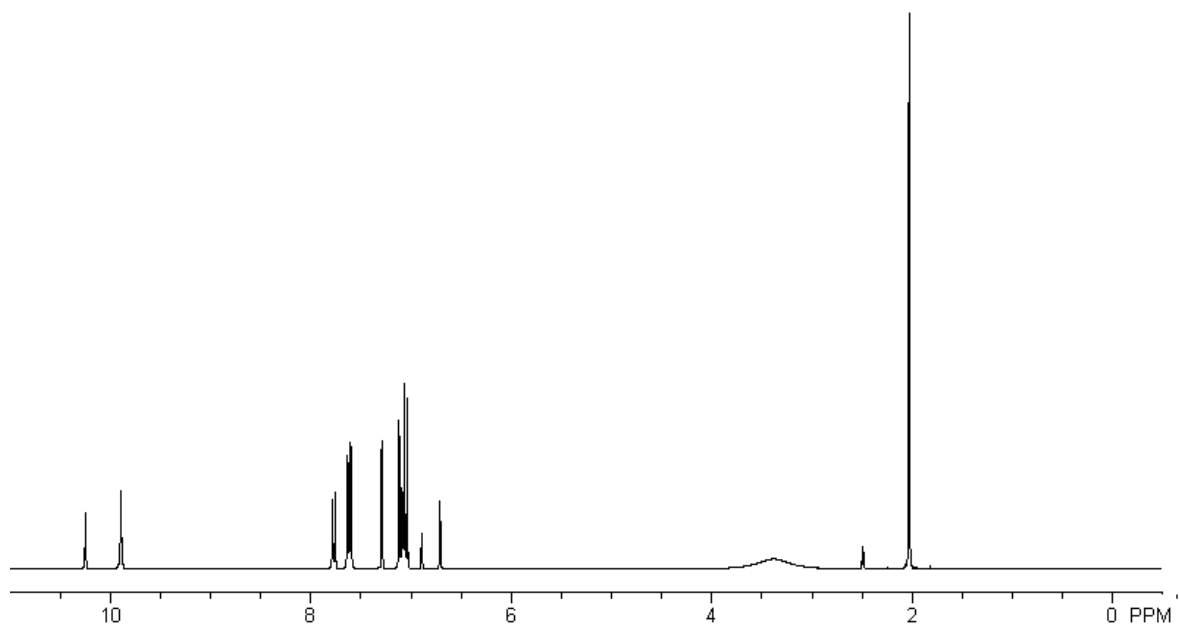


Figure 3S.

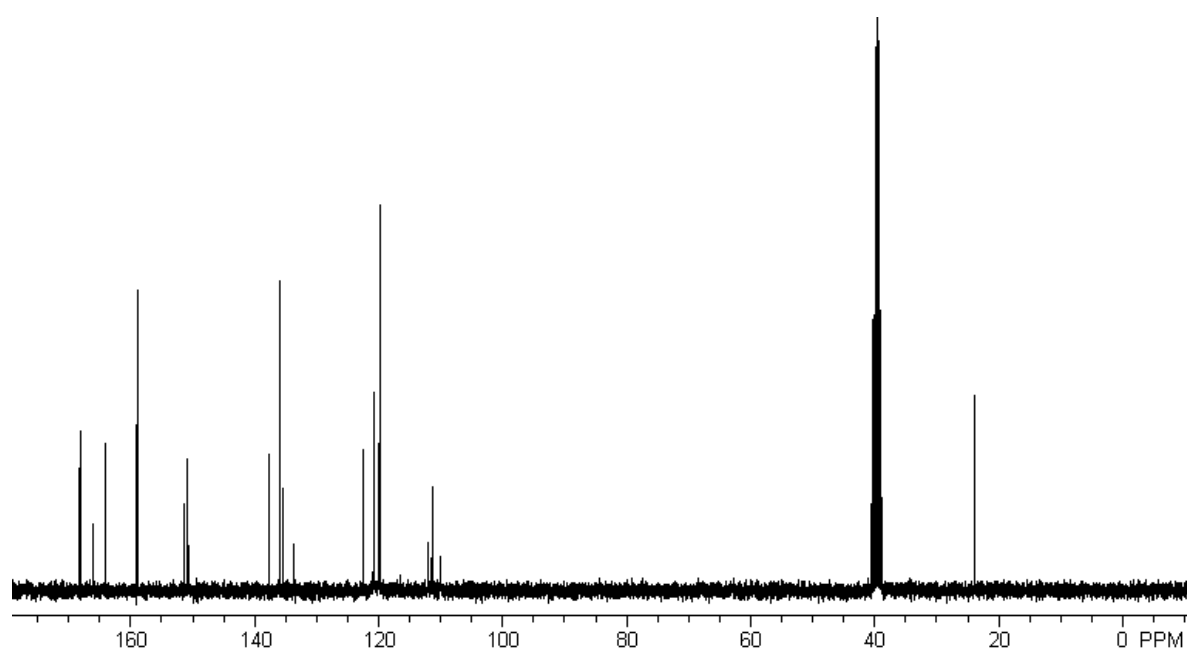


Figure 4S.

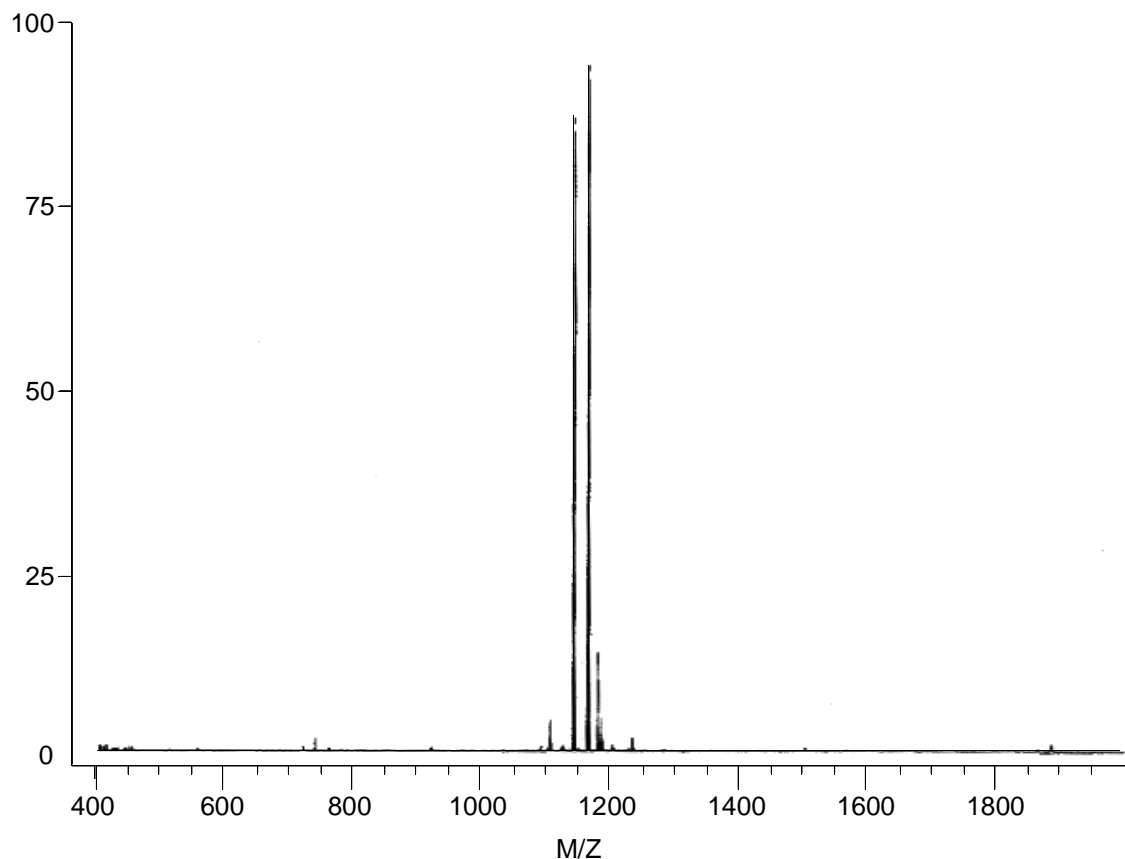
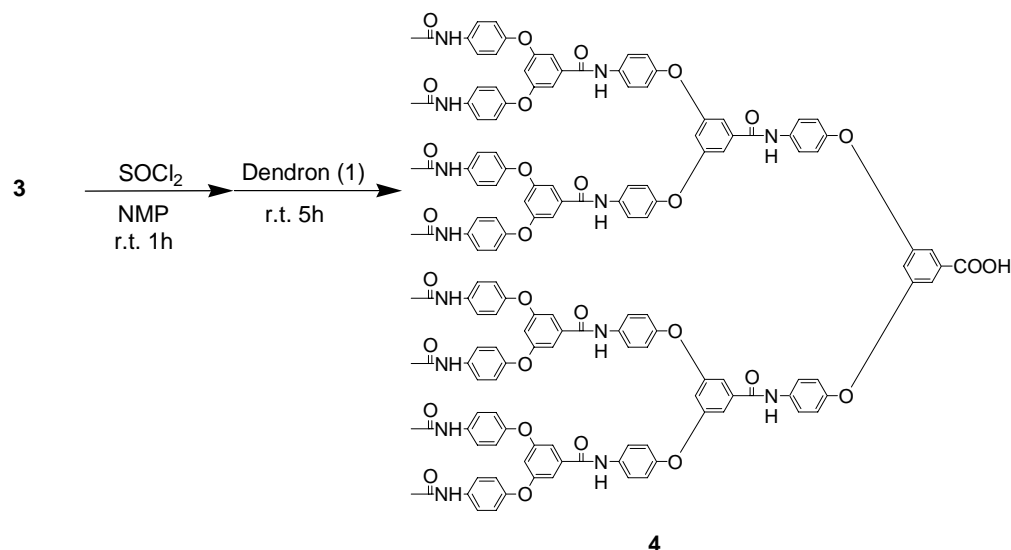


Figure 5S.

Synthesis of 3rd Generation (G3) Dendron (**4**)

Compound **3** (2.062 g, 1.807 mmol) was placed in a two-necked flask, and heated at 150 °C under reduced pressure for 4 h. Into the flask cooled in a water bath, 7.5 ml of NMP and 1.10 equiv of thionyl chloride (0.2365 g, 1.988 mmol) to **3** were added under nitrogen. The reaction mixture was stirred for 10 min at that temperature, and 50 min at room temperature. Then, 0.48 equiv of **1** (0.2894 g, 0.8605 mmol) to **3** were added to the solution and the reaction was performed for 5 h at room temperature. The reaction

mixture was poured into water and the precipitate was collected and dried. The crude product was redissolved in NMP, and this was reprecipitated with EtOH. The precipitate was collected, and dried *in vacuo* at 120 °C to give a white solid. The yield was 72%.



Scheme 3S

IR (KBr): ν (cm⁻¹)=3421 (N-H, st), 1658 (C=O(N-H), st), 1589, 1504 (phenyl ring, st).

¹H-NMR (300 MHz, (CD₃)₂SO) δ (ppm)=2.01 (s, -CH₃, 24H), 6.68, 7.26 (t, d, J=2.1 Hz, (CH₃-CONH-phenyl-O)₂-phenyl-(CONH-), 12H), 6.77, 7.31 (t, d, J=2.1 Hz, (-CONH-phenyl-O)₂-phenyl-(CONH-), 6H), 6.89, 7.07 (t, d, J=2.7, -(O)₂-phenyl-(COOH), 3H), 7.03, 7.58 (d, d, J=8.7, (CH₃-CONH)-phenyl(-O), 32H), 7.09, 7.75 (d, d, J=9.3, (-CONH)-phenyl(-O), 16H), 7.09, 7.75 (d, d, J=9.3, (-CONH)-phenyl(-O-phenyl-COOH), 8H), 9.87 (CH₃CO-NH, 8H), 10.21 ((phenyl)-CONH-(phenyl), 4H), 10.24 ((phenyl)-CONH-(phenyl)-COOH), 2H). Calcd.: [M]⁺ m/z = 2582.6. Found: MALDI-TOFMS: [M+Na]⁺ = 2606.3.

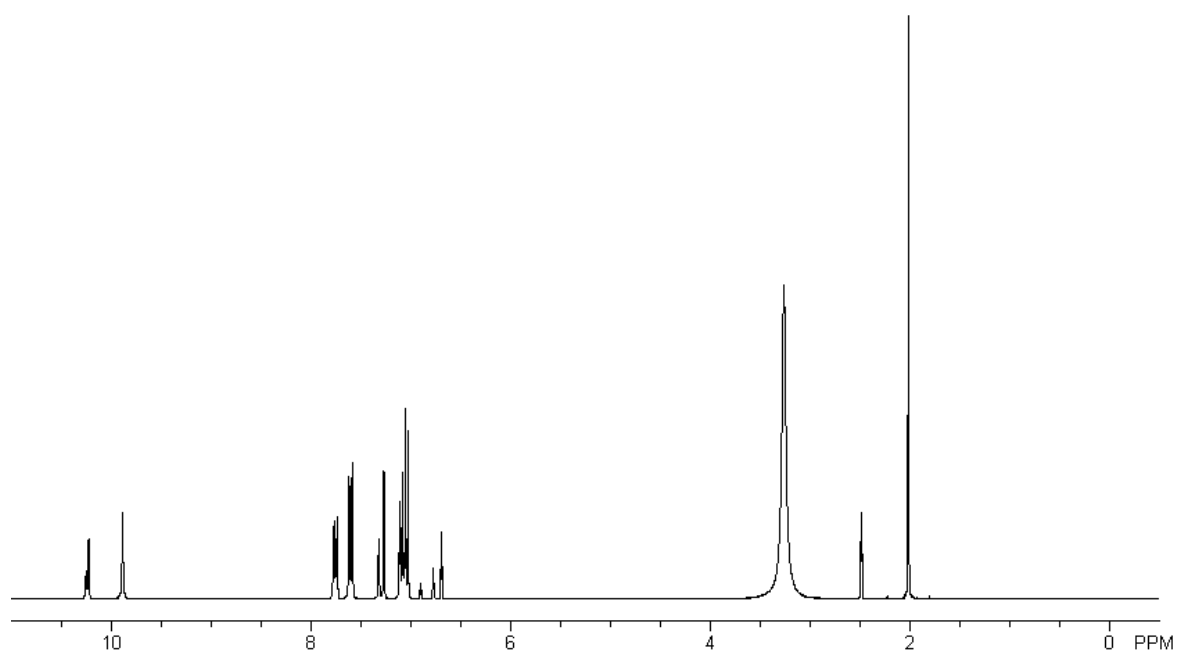


Figure 6S.

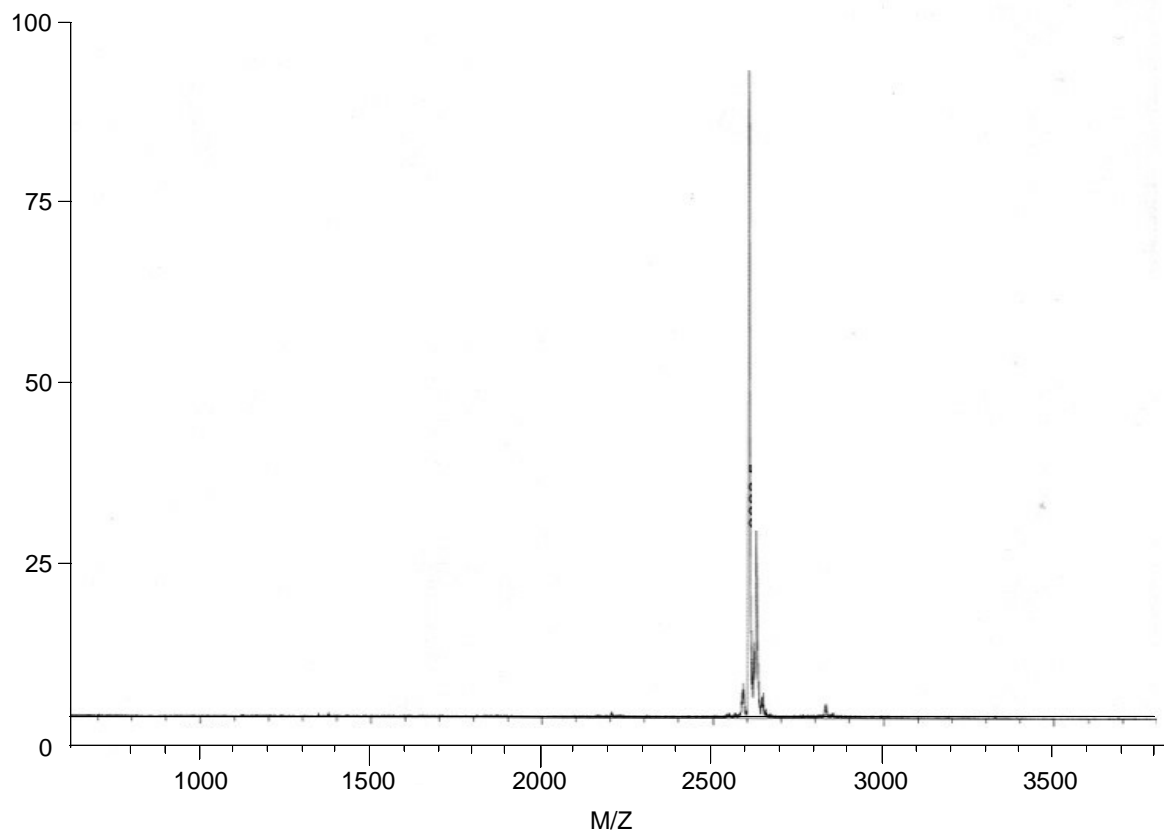
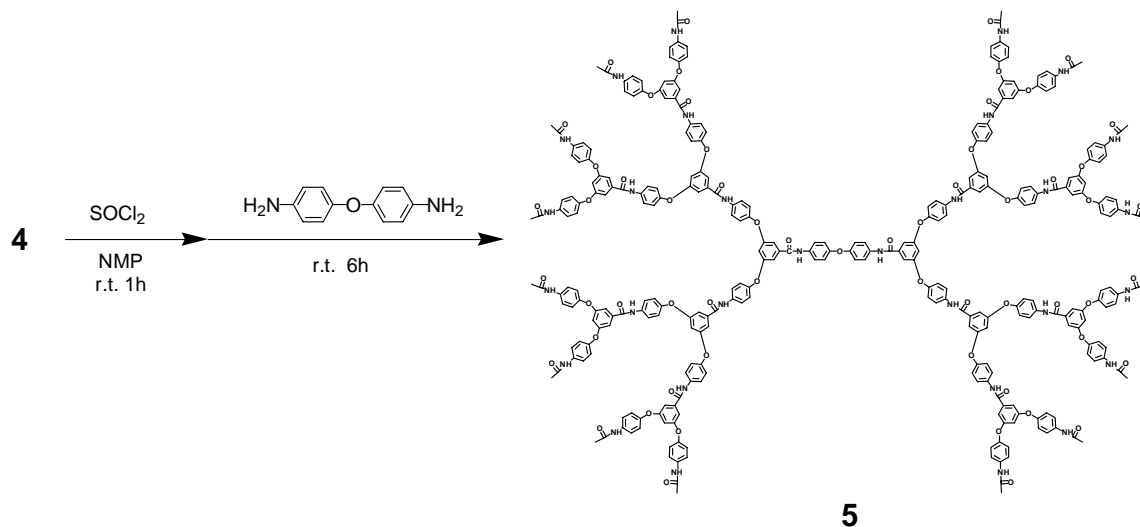


Figure 7S.

Synthesis G3 Polyamide Dendrimer (**5**)

Compound **4** (0.4833 g, 0.1828 mmol) was placed in a two-necked flask, and dried at 150 °C under the reduced pressure for 6 h. Into the flask cooled with a water bath, 1.7 ml of NMP and 1.50 equiv of thionyl chloride (0.03262 g, 0.2742 mmol) to **4** were added under nitrogen. The reaction mixture was stirred for 10 min at that temperature, and 50 min at room temperature. Then, 0.5 equiv of 4,4'-oxydianiline (0.01785 g, 0.08917 mmol) to **4** were added to the solution and the reaction was performed for 6 h at room temperature. The reaction mixture was poured into water and the precipitate was collected and dried.

The crude product was dissolved in *N,N*-dimethylformamide, and this was reprecipitated with THF. The precipitate was collected, and dried *in vacuo* at 120 °C to give a white solid. The yield was 78%.



Scheme 4S

IR (KBr): ν (cm⁻¹)=3421 (N-H, st), 1654 (C=O(N-H), st), 1608, 1504 (phenyl ring, st).

¹H-NMR (300 MHz, (CD₃)₂SO) δ (ppm)=2.01 (s, -CH₃, 48H), 6.68, 7.26 (t, d, J=2.4 Hz, (CH₃-CONH-phenyl-O)₂-phenyl-(CONH-), 24H), 6.75, 7.32 (t, d, J=2.1 Hz, (-CONH-phenyl-O-phenyl-CONH-), 8H), 7.03, 7.59 (d, d, J=9.0 Hz, (CH₃-CONH)-phenyl(-O), 64H), 7.03, 7.58 (d, d, J=8.7, (CH₃-CONH)-phenyl(-O), 32H), 7.08, 7.74 (d, d, J=9.3, (-CONH)-phenyl(-O), 24H), 7.08, 7.75 (d, d, J=9.3, (-CONH)-phenyl(-O-phenyl-COOH), 16H), 9.85 (CH₃CO-NH, 16H), 10.17(s, (-CONH-phenyl-O-phenyl-CONH-, 2H), 10.20 (s, (phenyl)-CONH-(phenyl), 8H), 10.24 ((phenyl)-CONH-(phenyl)-COOH), 4H). Calcd.: [M]⁺ m/z = 5329.4. Found: MALDI-TOFMS: [M+Na]⁺ = 5354.3.

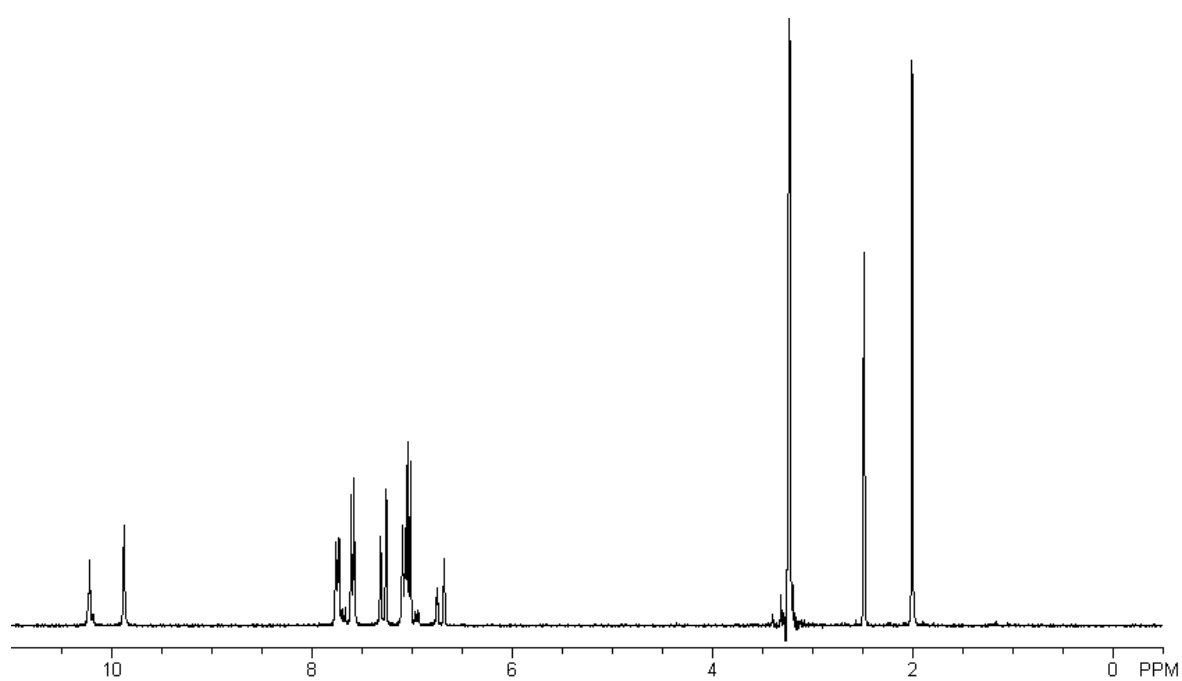


Figure 8S.

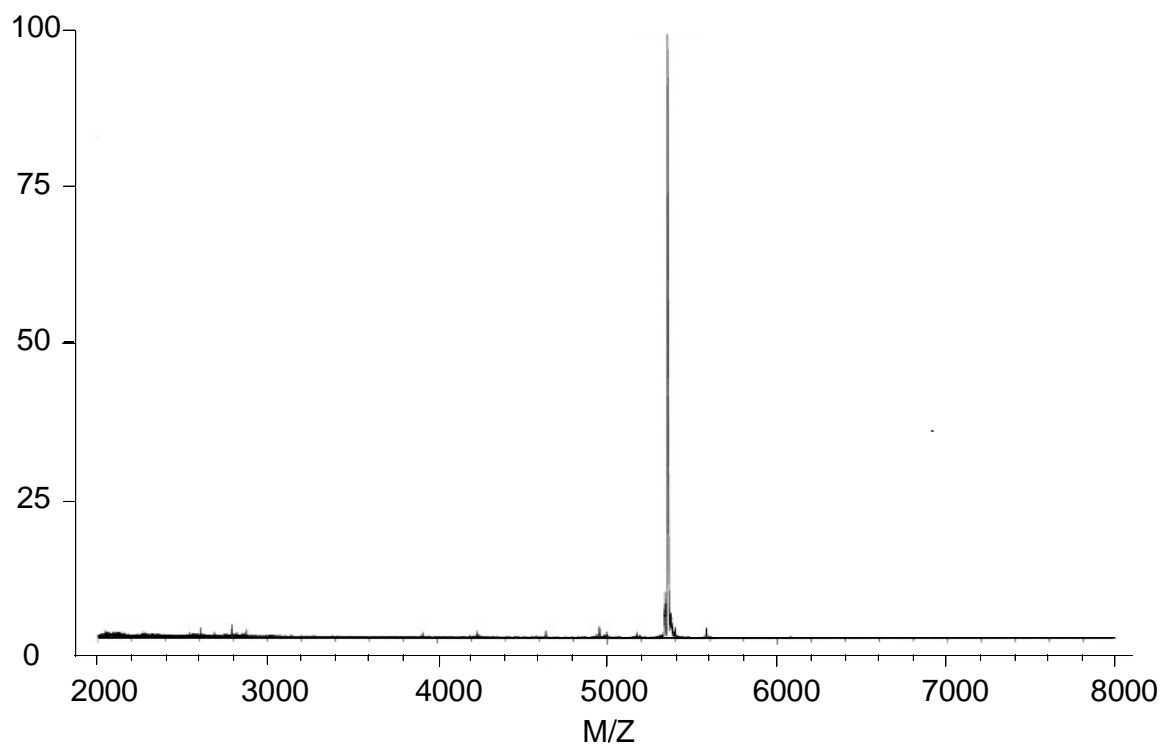


Figure 9S.