Supporting Information

Design of Aminopolymer Structure to Enhance Performance and Stability of CO_2 Sorbents: Poly(propylenimine) vs. Poly(ethylenimine)

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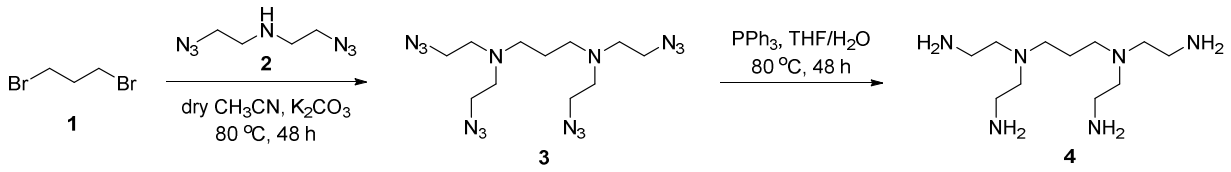
Materials and Chemical Characterization

Triethylenetetramine (TETA, Sigma-Aldrich, ≥ 97.0%) and tripropylenetetramine (TPTA, Alfa Aesar, 97%) were used directly without further purification. Chemicals for syntheses reported below were obtained from Sigma-Aldrich, Alfa Aesar and Acros Organics and used directly without further purification. Ultra-high purity N_2, ultra-high purity He, ultra-zero grade air, and 400 ppm CO_2/N_2 were obtained from Airgas.

Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light and Vogel's permanganate. ^{1}H NMR spectra were recorded on Bruker AVIII-400 instrument (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. The following abbreviations (or combinations thereof) are used to explain multiplicities: s = singlet, t = triplet, quint = quintet, m = multiplet. Coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were recorded on Bruker AVIII-400 instrument (100 MHz), and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-d. ESI-MS was performed on a Thermo Instruments Orbitrap XL mass spectrometer.



Supporting Scheme S1. Synthesis strategy for EI-den.

Synthesis of N^1,N^1,N^3,N^3-tetrakis(2-azidoethyl)propane-1,3-diamine (3)

To a solution of 1,3-dibromopropane **(1)** (0.28 mL, 2.74 mmol) and K_2CO_3 (1.90 g, 13.77 mmol) in anhydrous CH_3CN at room temperature, bis(2-azidoethyl)amine **(2)**[1] (0.85 g, 5.48 mmol) dissolved in CH_3CN was added dropwise. The mixed solution was then stirred and heated at 80 °C for 48 h. The solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel using EA/Hex = 1:1 (v/v) as the eluent. The proper fractions were combined, and the solvent was evaporated to yield compound **(3)** as yellow oil (0.81 g, 84%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.34-3.31 (t, *J* = 6.0 Hz, 8H), 2.74-2.71 (t, *J* = 6.0 Hz, 8H), 2.61-2.57 (t, *J* = 7.2 Hz, 4H), 1.69-1.62 (quint, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 53.65, 52.27, 49.41, 25.38.

ESI-MS (m/z): $[M+H]^+$ calculated for $C_{11}H_{23}N_{14}$: 351.2225, found: 351.2223.

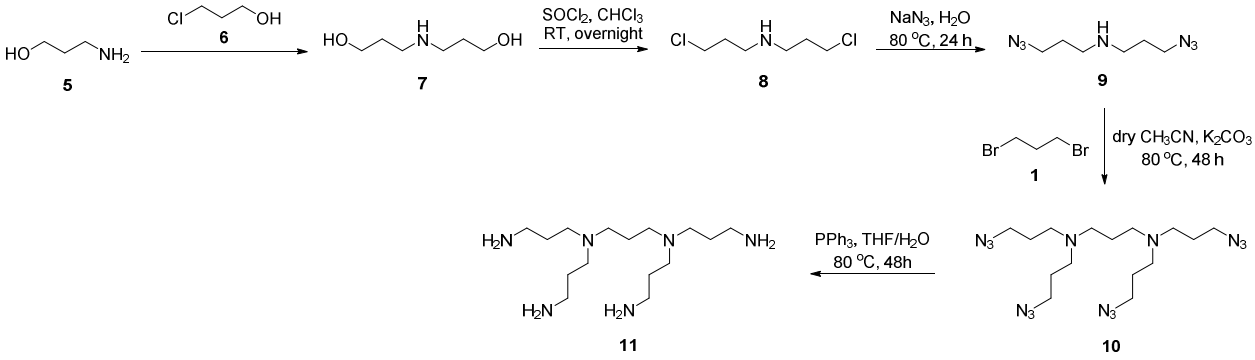
Synthesis of N^1,N^1,N^3,N^3-tetrakis(2-aminoethyl)propane-1,3-diamine (EI-den) (4)

Ph_3P (4.50 g, 17.16 mmol) was dissolved in THF and H_2O mixed solution (10:1 v/v) at room temperature, and compound **(3)** (0.5 g, 1.43 mmol) dissolved in THF was added. The solution was then stirred and heated at 80 °C for 48 h. TLC was used to monitor the completion of reaction. THF was removed by rotary evaporation and the product was extracted with iced H_2O. The product **(4)** was collected by evaporation of H_2O and obtained as light brown oil and stored at -20 °C (0.24 g, 68%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.77-2.74 (t, J = 6.0 Hz, 8H), 2.51-2.45 (m, 12H), 1.89 (s, 8H), 1.66-1.59 (quint, J = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 57.12, 52.59, 39.71, 24.96.

ESI-MS (m/z): $[M+H]^+$ calculated for $C_{11}H_{31}N_6$: 247.2605, found: 247.2604.



Supporting Scheme S2. Synthesis strategy for PI-den.

Synthesis of bis(3-chloropropyl)amine (8)

To a solution of bis(3-hydroxypropyl)amine **(7)**[2] (3.3 g, 25 mmol) in chloroform at 0 °C, thionyl chloride (11.9 g, 100 mmol) dissolved in chloroform was added dropwise. The solution was then stirred for 24 h at room temperature. The solvent was evaporated, and the crude product was purified by recrystallization from $CHCl_3$ to yield compound **(8)** as a white solid (3.9 g, 92 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.70-3.67 (t, J = 6.0 Hz, 4H), 3.26-3.15 (m, 4H), 2.21-2.14 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 49.15, 45.65, 41.74, 28.60.

ESI-MS (m/z): $[M+H]^+$ calculated for $C_6H_{14}NCl_2$: 170.0498, found: 170.0495.

Synthesis of bis(3-azidopropyl)amine (9)

A solution of compound **(8)** (1.7 g, 10 mmol) and sodium azide (3.3 g, 50 mmol) in water was heated at 80 °C for 24 h. After evaporating most of the water, the solution was made basic with sodium hydroxide and then extracted with diethyl ether. The organic phase was combined and dried over potassium carbonate. After evaporating the solvent, the residue was purified by column chromatography over silica gel using EA/Hex = 1:1 (v/v) as the eluent. The proper fractions were combined, and the solvent was evaporated to yield compound **(9)** as yellow oil (1.3 g, 71%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.39-3.36 (t, J = 6.8 Hz, 4H), 2.72-2.69 (t, J = 6.8 Hz, 4H), 1.80-1.73 (quint, J = 6.8 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 49.51, 46.87, 29.28.

ESI-MS (m/z): $[M+H]^+$ calculated for $C_6H_{14}N_7$: 184.1305, found: 184.1303.

Synthesis of N^1,N^1,N^3,N^3-tetrakis(3-azidopropyl)propane-1,3-diamine (10)

To a solution of 1,3-dibromopropane **(1)** (0.28 mL, 2.74 mmol) and K_2CO_3 (1.90 g, 13.77 mmol) in anhydrous CH_3CN at room temperature, compound **(9)** (1.00 g, 5.48 mmol) dissolved in CH_3CN was added dropwise. The mixed solution was then stirred and heated at 80 °C for 48 h. The solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel using EA/Hex = 1:1 (v/v) as the eluent. The proper fractions were combined, and the solvent was evaporated to yield compound **(10)** as yellow oil (0.96 g, 86%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.36-3.32 (t, J = 6.8 Hz, 8H), 2.49-2.46 (t, J = 6.8 Hz, 8H), 2.41-2.38 (t, J = 7.2 Hz, 4H), 1.73-1.67 (quint, J = 6.8 Hz, 8H), 1.59-1.52 (quint, J = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 52.05, 50.79, 49.40, 26.57, 24.61.

ESI-MS (m/z): $[M+H]^+$ calculated for $C_{15}H_{31}N_{14}$: 407.2851, found: 407.2845.

Synthesis of N^1,N^1,N^3,N^3-tetrakis(3-aminopropyl)propane-1,3-diamine (PI-den) (11)

Ph_3P (4.50 g, 17.16 mmol) was dissolved in THF and H_2O mixed solution (10:1 v/v) at room temperature, and compound **(10)** (0.58 g, 1.43 mmol) dissolved in THF was added. The solution was then stirred and heated at 70 °C for 48 h. TLC was used to monitor the completion of reaction. THF was removed by rotary evaporation and the product was extracted with iced H_2O. The product **(11)** was collected by evaporation of H_2O and obtained as light brown oil and stored at -20 °C (0.3 g, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.74-2.70 (t, J = 6.8 Hz, 8H), 2.47-2.43 (t, J = 7.2 Hz, 8H), 2.43-2.38 (t, J = 7.2 Hz, 4H), 1.69 (s, 8H), 1.62-1.55 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 52.22, 51.84, 40.69, 30.81, 24.51.

ESI-MS (m/z): $[M+H]^+$ calculated for $C_{15}H_{39}N_6$: 303.3231, found: 303.3230.

Synthesis of SBA-15

SBA-15 was synthesized according to our previously reported procedure.[3] 24 g of Pluronic P123 block copolymer ($(EO)_{20}(PO)_{70}(EO)_{20}$) was dissolved in 636 g of deionized water and 120 mL of 12.1 M HCl. The components were stirred vigorously for 3 h, until everything dissolved. 46.6 g of tetraethyl orthosilicate (TEOS) was added dropwise to the mixture and stirred at 40 °C for 20 h, during which time a white precipitate formed. The solution was then heated to 100 °C and held for 24 h in the absence of stirring. The reaction was quenched with 400 mL deionized water and the precipitate was filtered and washed copiously with deionized water. The filtered precipitate was dried for 12 h in an oven at 75 °C, and then calcined according to the following program: heat to 200 °C at 1.2 °C/min, hold at 200 °C for 1 h, heat to 550 °C at 1.2 °C/min, hold at 550 °C for 12 h, cool to room temperature. The resulting white powder was stored in ambient lab conditions.

Aminopolymer/SBA-15 Composite Preparation

SBA-15 was impregnated with the liquid aminopolymers by wet impregnation. SBA-15 was dried overnight at 110 °C under vacuum (< 20 mTorr). The desired amount of amine was dissolved in 10 mL methanol and was added to 200 mg SBA-15. The mixture was allowed to stir for at least 6 h. Methanol was removed *in vacuo* at room temperature. The resulting powder was dried overnight at room temperature under vacuum (< 20 mTorr). The resulting dried powder composites were stored in ambient lab conditions.

Physical Characterization

Nitrogen adsorption isotherms were obtained on a MicrotracBEL BELSORP-max at 77 K. Prior to analysis, the samples were degassed under vacuum on a BELPREP-vac II below 10^{-2} kPa for 2 h at 70 °C. The free space measurement was performed after analysis. Surface area was analyzed by applying BET theory in the range of P/P_0 from 0.05 to 0.2, and pore volume was calculated based on the total amount of N_2 adsorbed at P/P_0 of 0.95.

Scanning electron microscopy (SEM) was performed on a Hitachi SU8230 with a cold field emission gun at an accelerating voltage of 1 kV and an emission current of 2 μA. Transmission electron microscopy (TEM) was performed on a FEI Tecnai F30 with a thermally-assisted field emission gun at an accelerating voltage of 300 kV.

Organic content of the samples was measured on a Netzsch STA409PG TGA. Mass loss from 125 to 900 °C under a flow of nitrogen diluted air was recorded and normalized by the residual mass at 900 °C.

CO_2 Adsorption

Equilibrium CO_2 adsorption capacities were measured gravimetrically on a TA Instruments Q500 TGA. The samples were pretreated by heating to 70 °C at a ramp rate of 5 °C/min under a flow of N_2 and held for 2 h. The samples were cooled to 35 °C and equilibrated at this analysis temperature for 1 h. Subsequently, the gas flow was switched to a premixed gas containing 400 ppm CO_2/N_2 for 3 h. The mass gain was recorded and normalized by the dry mass of the sample.

Cyclic adsorption/desorption experiments were performed to determine that, for these small molecules, 70 °C was the maximum temperature at which regeneration could be performed to avoid evaporation of these molecules from the sorbent while still desorbing water and CO_2 (Figure S5).

Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra were recorded under vacuum on a Bruker Vertex 80v optical bench with a DLaTGS detector. Approximately 2 mg of the sample was diluted by 100 mg KBr and pelletized for analysis.

Additional IR experiments were performed in diffuse-reflectance (DRIFTS) mode on a Thermo Nicolet iS10 with an MCT detector using a Harrick Praying Mantis DRIFTS High Temperature Reaction Chamber. The sample was placed in the reaction chamber, sealed under a dome equipped with ZnSe windows, and placed in a constant flow of 50 sccm He. The sample temperature was increased to 70 °C and held for 30 min to desorb atmospheric CO_2. All spectra were acquired at 25 °C. SBA-15 exposed to the same conditions was used as the background spectrum. The results of these experiments are reported in Figure S6.

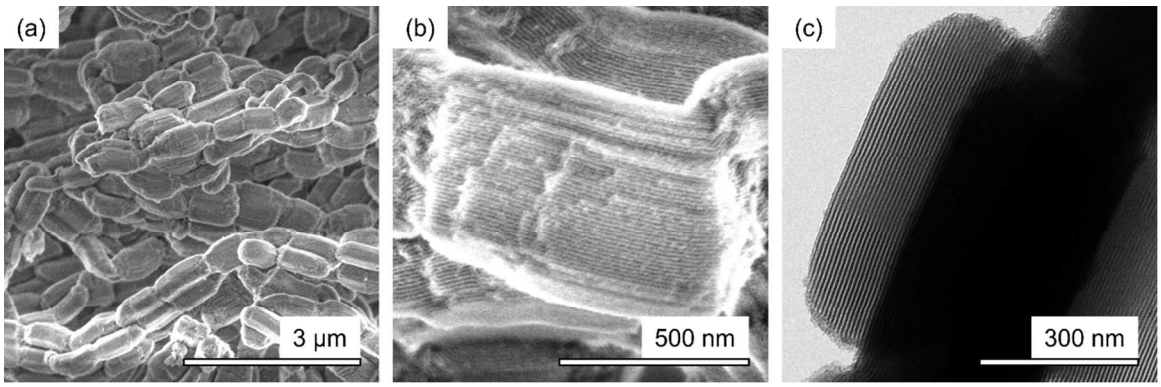
Aminopolymer Oxidation Studies

Aminopolymers were oxidatively treated by exposure to a flow of ultra-zero grade air at elevated temperature. Approximately 100 mg neat liquid aminopolymer was placed in a two-neck round-bottom flask equipped with reflux condenser. A flow of ultra-zero grade air was introduced into the flask via a needle and bubbled into the liquid. While stirring, the liquid was heated to the desired oxidation temperature (typically 110 °C) and held for 24 h. Subsequently, the liquid was cooled to room temperature. Oxidatively-treated-aminopolymer/SBA-15 composites were prepared via the same procedure listed above.

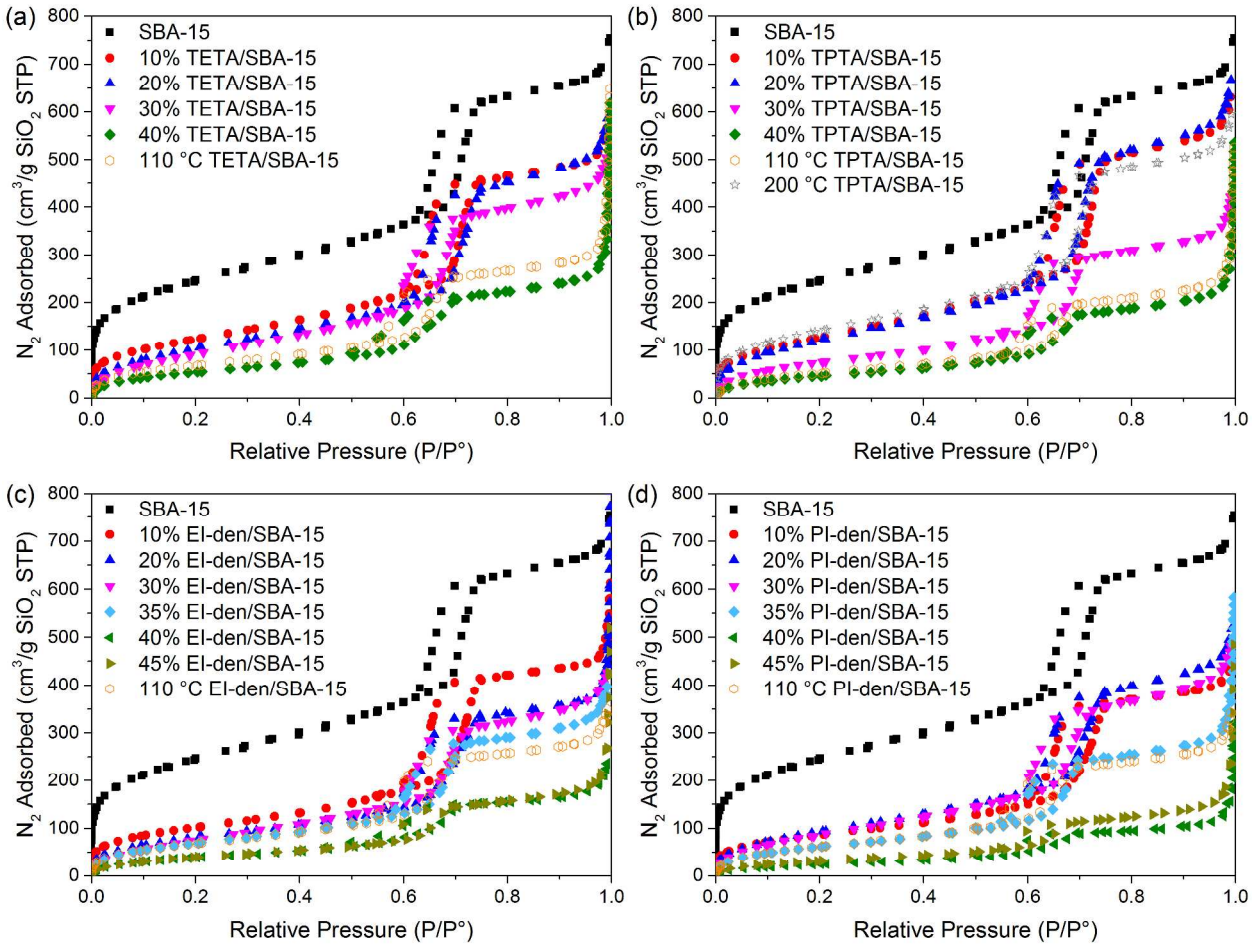
Oxidation experiments were also performed on as-prepared aminopolymer/SBA-15 composites, to ensure that trends observed with oxidation of liquid-phase aminopolymers would also exist for the silica-supported aminopolymers (Figure S7). In a TA Instruments Q500 TGA, unoxidized samples were heated to the desired oxidation temperature (typically 110 °C) at a ramp rate of 5 °C/min under a flow of ultra-zero grade air and held for 24 h. Over the course of the experiment, a small amount of steady mass loss was observed, suggesting evaporation of aminopolymer during the oxidative treatment.

Supporting Table S1. Summary of physical properties for all aminopolymer/SBA-15 sorbent materials studied. Organic content and amine loading were determined by TGA. Surface area and pore volume were calculated from nitrogen physisorption isotherms reported in Figure S2. Surface area was analyzed by applying BET theory in the range of P/P_0 from 0.05 to 0.2, and pore volume was calculated based on the total amount of N_2 adsorbed at P/P_0 of 0.95.

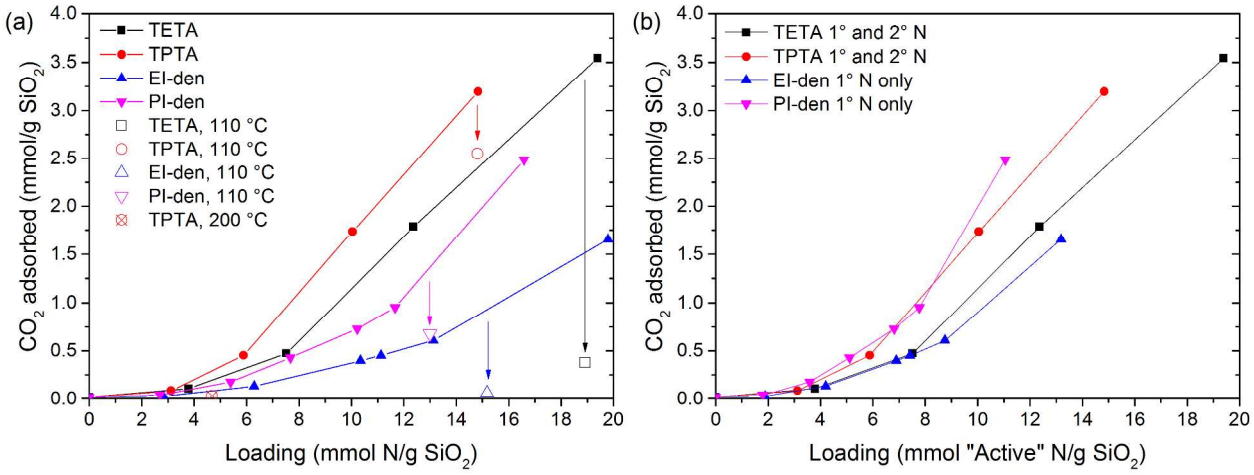
	Organic Content (wt%)	Amine Loading (mmol N/g SiO_2)	Surface Area (m^2/g SiO_2)	Pore Volume (cm^3/g SiO_2)
SBA-15	0%	0.0	880	1.00
10% TETA/SBA-15	12%	3.8	450	0.77
20% TETA/SBA-15	22%	7.5	400	0.78
30% TETA/SBA-15	31%	12	360	0.69
40% TETA/SBA-15	41%	19	210	0.39
110 °C TETA/SBA-15	41%	19	250	0.46
10% TPTA/SBA-15	13%	3.1	470	0.86
20% TPTA/SBA-15	22%	5.9	470	0.88
30% TPTA/SBA-15	32%	10	290	0.53
40% TPTA/SBA-15	41%	15	180	0.34
110 °C TPTA/SBA-15	41%	15	200	0.37
200 °C TPTA/SBA-15	18%	4.7	520	0.80
10% EI-den/SBA-15	10%	2.8	370	0.69
20% EI-den/SBA-15	21%	6.3	370	0.71
30% EI-den/SBA-15	30%	10	310	0.57
35% EI-den/SBA-15	31%	11	270	0.51
40% EI-den/SBA-15	35%	13	150	0.27
45% EI-den/SBA-15	45%	20	150	0.29
110 °C EI-den/SBA-15	38%	15	260	0.44
10% PI-den/SBA-15	12%	2.7	320	0.61
20% PI-den/SBA-15	21%	5.4	360	0.69
30% PI-den/SBA-15	28%	7.7	340	0.64
35% PI-den/SBA-15	34%	10	240	0.45
40% PI-den/SBA-15	37%	12	100	0.18
45% PI-den/SBA-15	46%	17	120	0.24
110 °C PI-den/SBA-15	40%	13	240	0.42



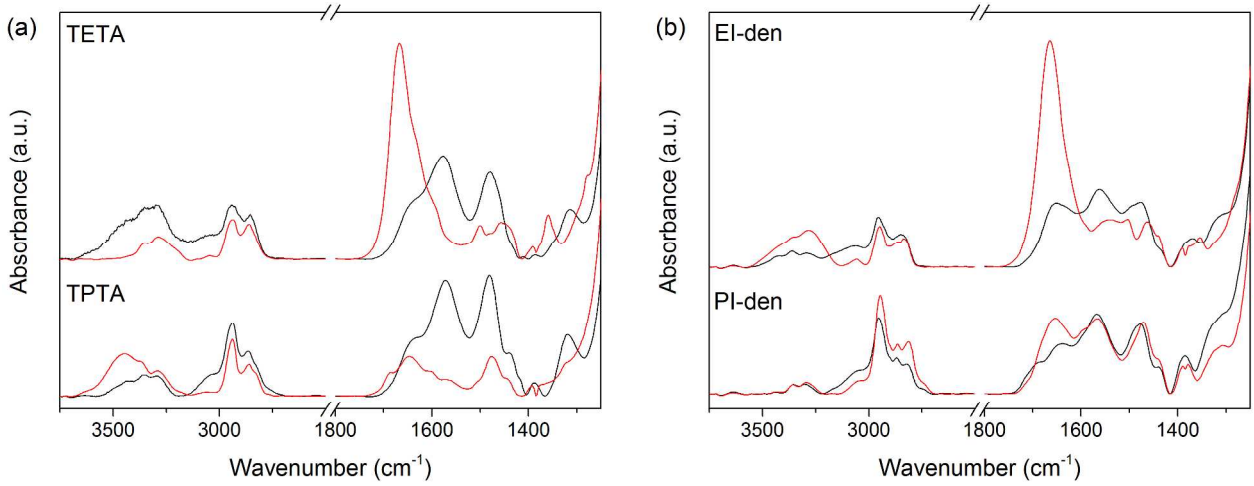
Supporting Figure S1. (a, b) SEM and (c) TEM images of the as-prepared SBA-15 mesoporous silica, showing the pore structure with 8 nm diameter pores.



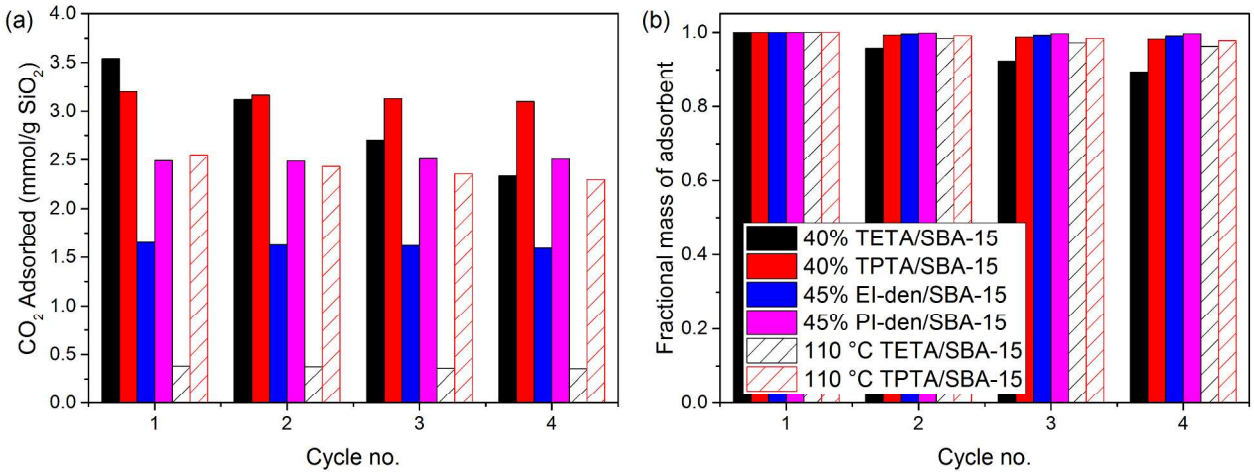
Supporting Figure S2. Nitrogen physisorption isotherms obtained at 77 K for all aminopolymer/SBA-15 sorbent materials studied. Open symbol isotherms indicate samples exposed to oxidative treatment at the listed temperature.



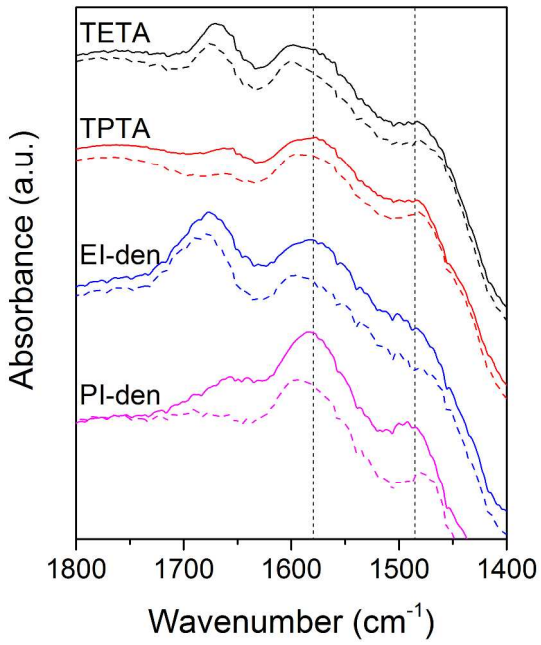
Supporting Figure S3. (a) CO_2 capacities of aminopolymers impregnated in SBA-15 at 400 ppm CO_2/N_2 and 35 °C over a range of amine loading, (b) normalized to the number of amines that are active for CO_2 capture under dry conditions (1° and 2° only). Open symbols indicate samples exposed to oxidative treatment at the listed temperature.



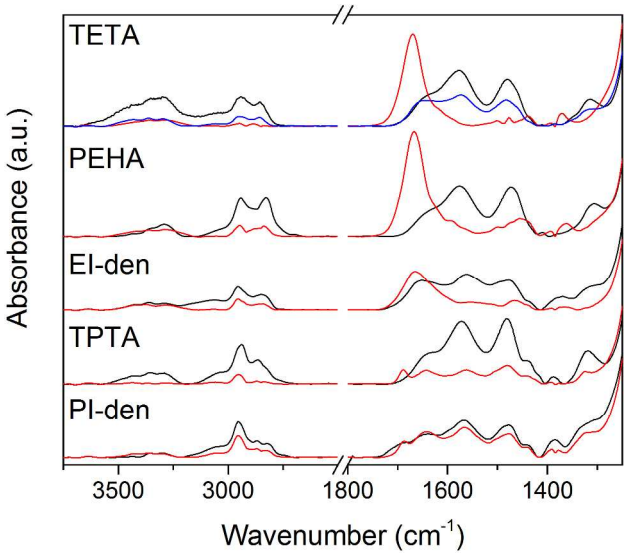
Supporting Figure S4. Complete FTIR spectra for SBA-15-supported (a) linear aminopolymers TETA and TPTA and (b) dendritic aminopolymers EI-den and PI-den, with fresh aminopolymers (black) and aminopolymers oxidatively-treated at 110 °C for 24 h (red).



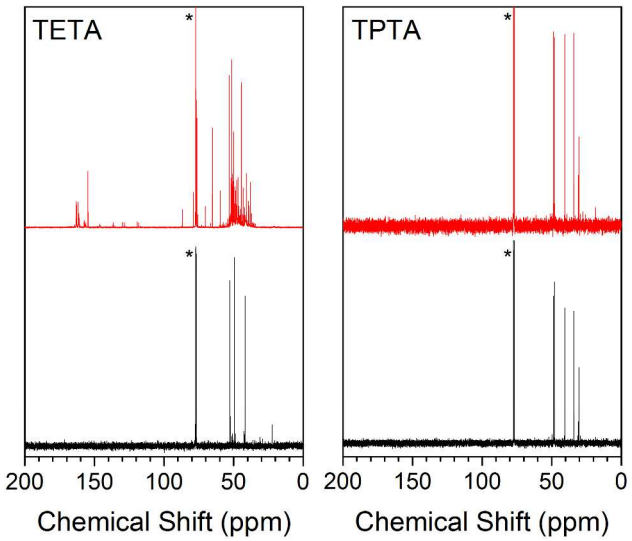
Supporting Figure S5. (a) CO_2 capacities of aminopolymers impregnated in SBA-15 at 400 ppm CO_2/N_2 and 35 °C and (b) fractional dry mass at beginning of adsorption relative to starting dry mass of adsorbent, as a function of temperature swing cycle. Desorption in between cycles was performed at 70 °C under a flow of N_2 for 2 h and adsorption was performed for 3 h, as detailed in the Methods above.



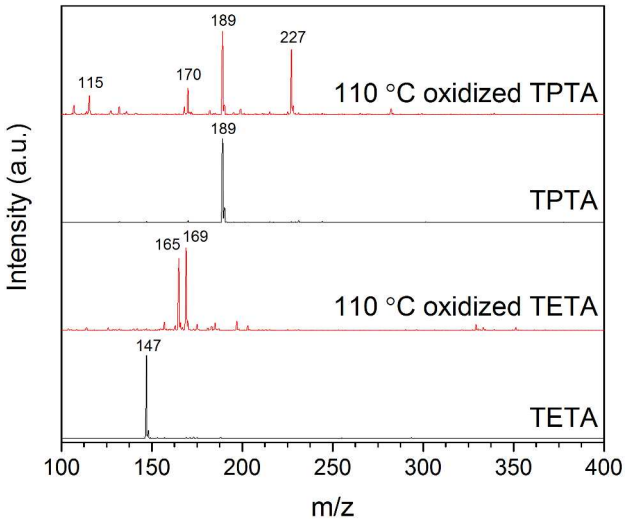
Supporting Figure S6. DRIFT spectra for aminopolymers supported in SBA-15 under a constant flow of 50 sccm He. Solid lines are prior to heating to 70 °C, dashed lines are after heating. Vertical lines at 1575 and 1485 cm^{-1} denote the location of the predominant ammonium carbamate stretches. After desorption of CO_2, resulting spectra reveal NH_2 bending (1600 cm^{-1}) and CH_2 bending (1470 cm^{-1}) modes that were previously hidden by the ammonium carbamate stretches.[4]



Supporting Figure S7. FTIR spectra for aminopolymers supported in SBA-15, after oxidative treatment at (blue) 70 °C or (red) 110 °C. Aminopolymers were supported in SBA-15 prior to oxidative treatment (see Methods above for details). PEHA = pentaethylenehexamine. TETA did not oxidize appreciably at 70 °C, suggesting that the mild sorbent regeneration conditions used in our study would not cause the sorbents to oxidize to a significant extent.

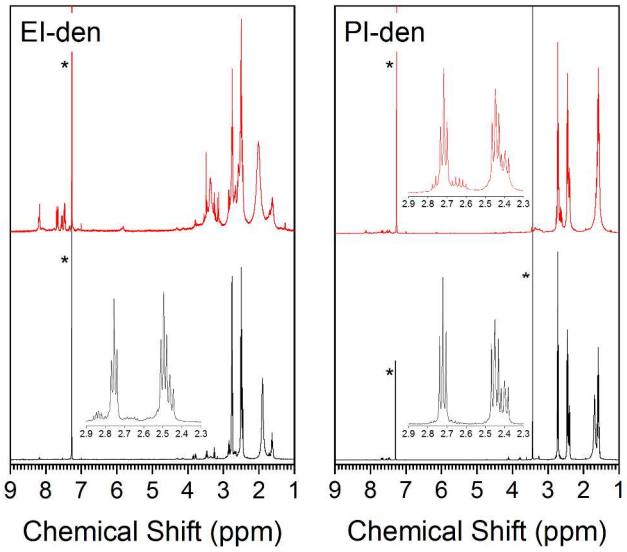


Supporting Figure S8. ^{13}C NMR spectra for linear aminopolymers TETA and TPTA, acquired in $CDCl_3$ (solvent peaks indicated by asterisks). Black, lower: fresh aminopolymers; red, upper: aminopolymers oxidatively-treated at 110 °C for 24 h.

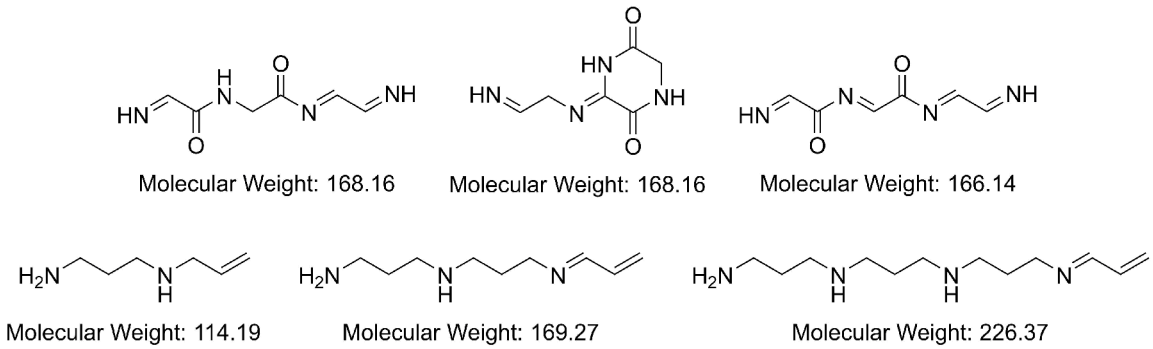


Supporting Figure S9. ESI mass spectra for (black) fresh and (red) oxidatively-treated linear aminopolymers TETA and TPTA.

Fragments produced from oxidative treatment of TETA with m/z = 165 and 169 are consistent with intramolecular cyclization reactions, as suggested previously,[5] and addition of up to two oxygen atoms. In contrast, fragments produced from oxidative treatment of TPTA with m/z = 115, 170, and 227 are consistent with loss or addition of alkylamine fragments due to thermal rearrangement (e.g. loss of $NHC_3H_6NH_2$, for m/z = 115, or addition of a C_3H_6 fragment, for m/z = 227). Loss or addition of these types of fragments is consistent with the ^{1}H and ^{13}C NMR spectra for oxidatively-treated TPTA: the molecules created by these processes are chemically similar to the fresh TPTA, resulting in very little change in the NMR spectra (Figures 3 and S8). Examples of possible structures formed from the oxidative treatment are shown in Figure S11.

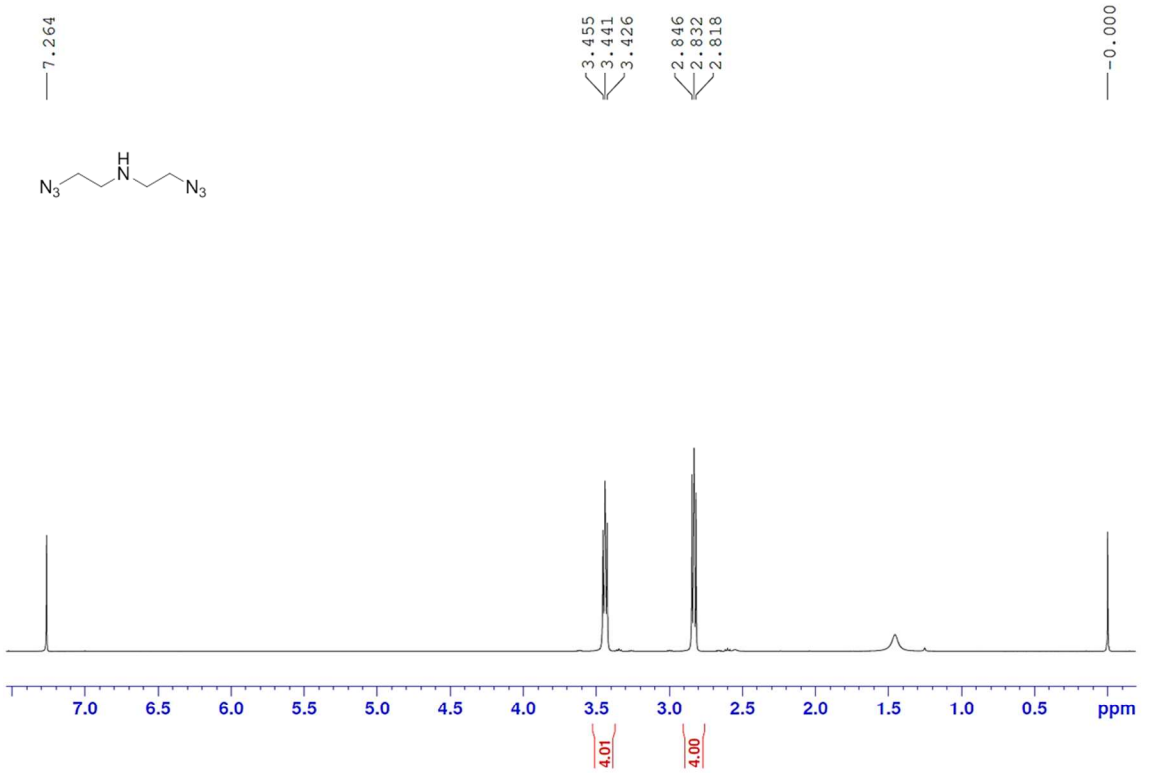


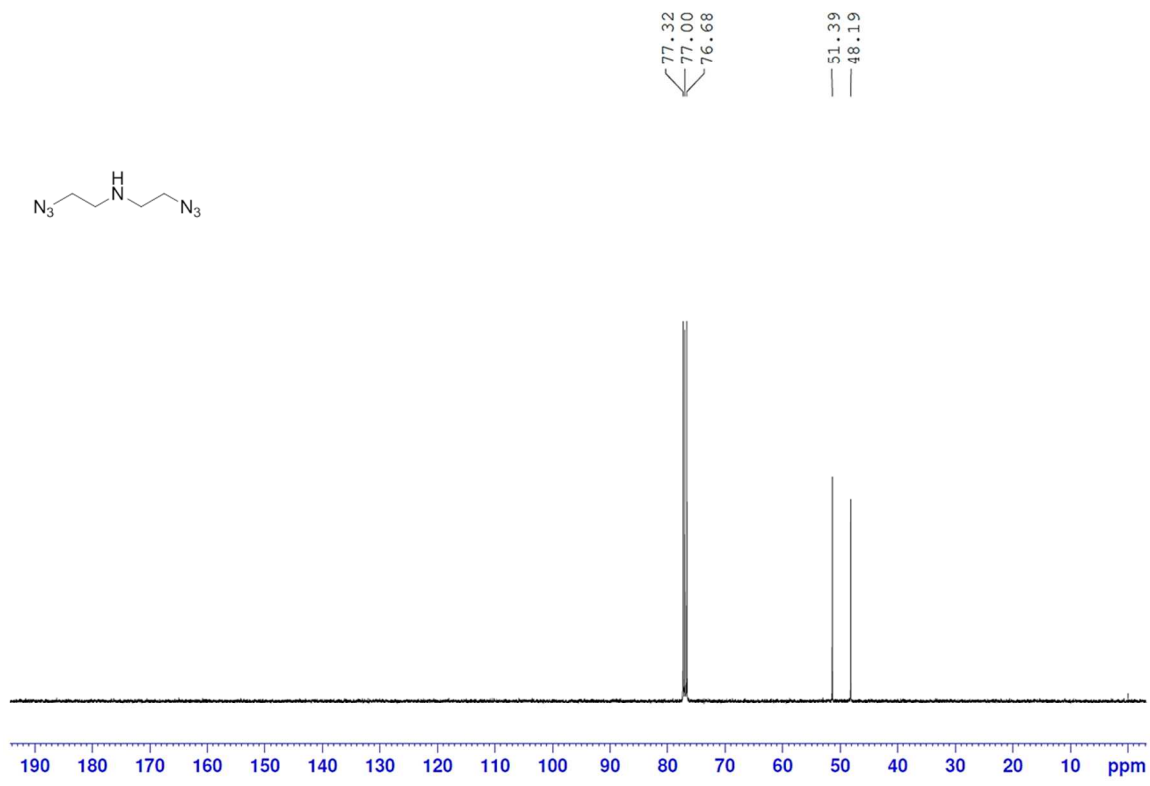
Supporting Figure S10. ^{1}H NMR spectra for dendritic aminopolymers EI-den and PI-den, acquired in $CDCl_3$ (solvent peak and residual methanol indicated by asterisks). Black, lower: fresh aminopolymers; red, upper: aminopolymers oxidatively-treated at 110 °C for 24 h.

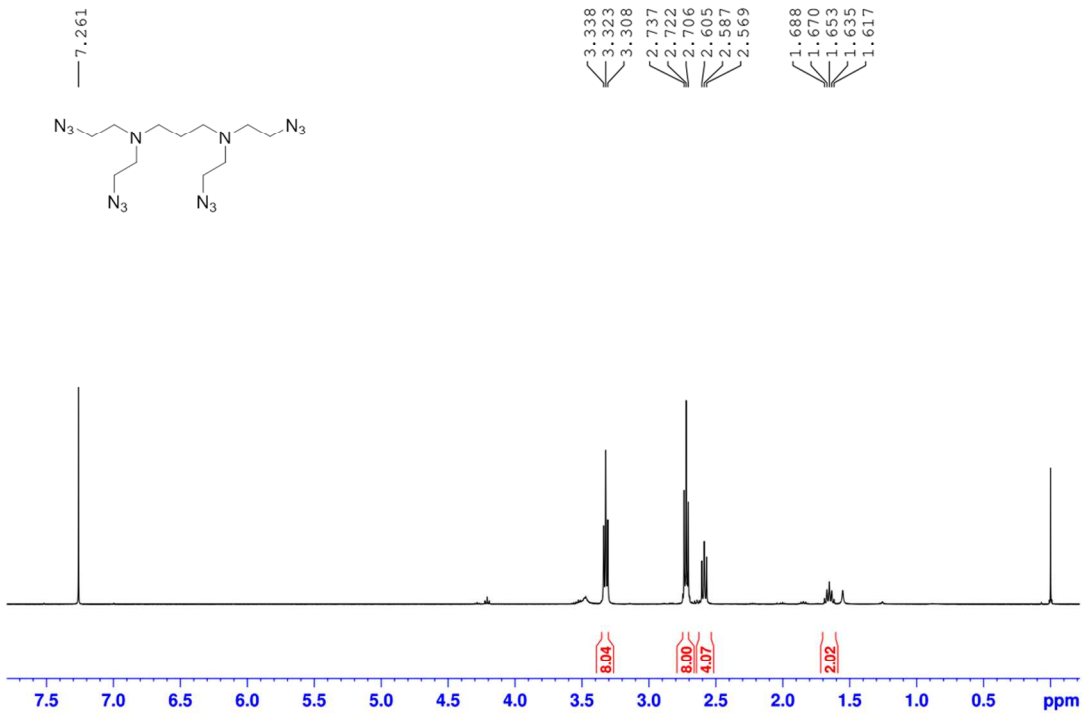


Supporting Figure S11. Examples of possible structures formed from the oxidative treatment of TETA (top row) and TPTA (bottom row), with masses consistent with ESI-MS data. These structures are not proposed to be the only structures formed during the oxidative treatment, but are rather representative of the various intramolecular cyclization and/or alkylamine chain transfer reactions that could occur during the oxidative treatment.

^{1}H and ^{13}C NMR Spectra



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3.338
3.323
3.308
2.737
2.722
2.706
2.605
2.587
2.569
1.688
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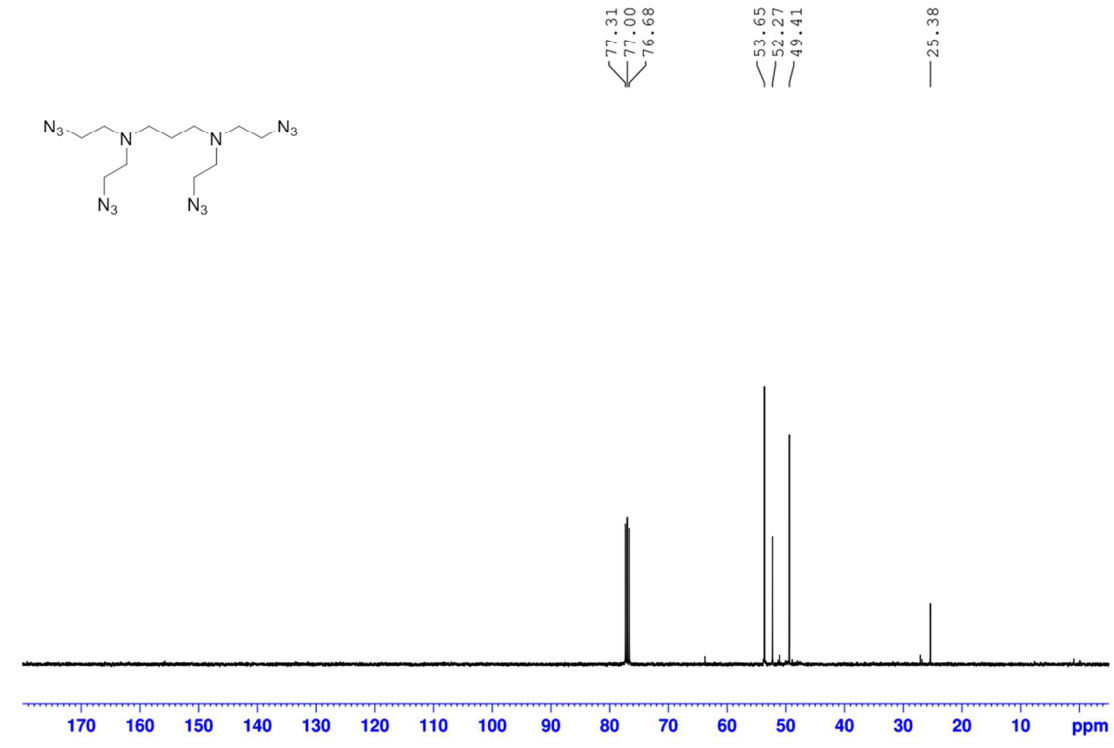
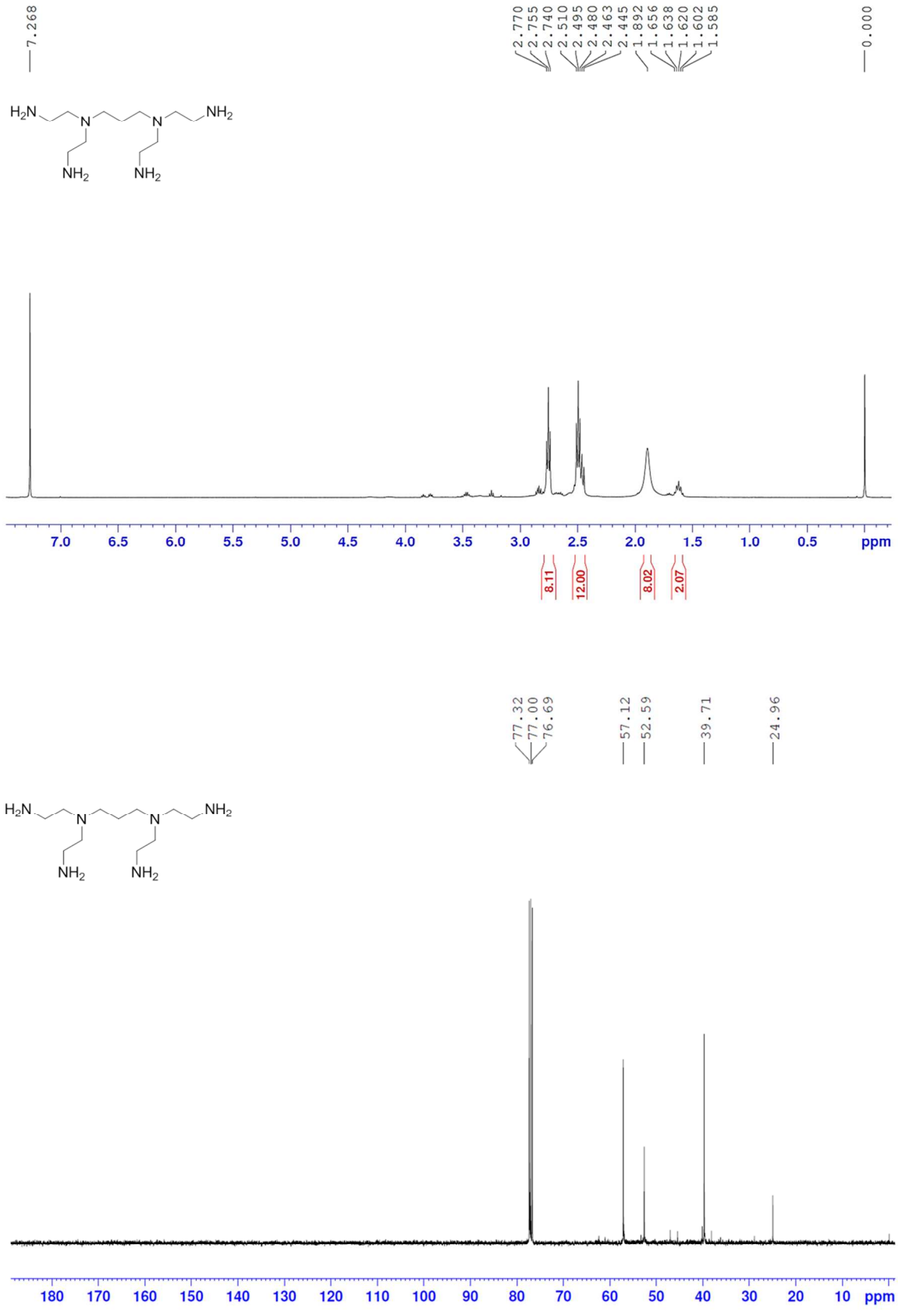
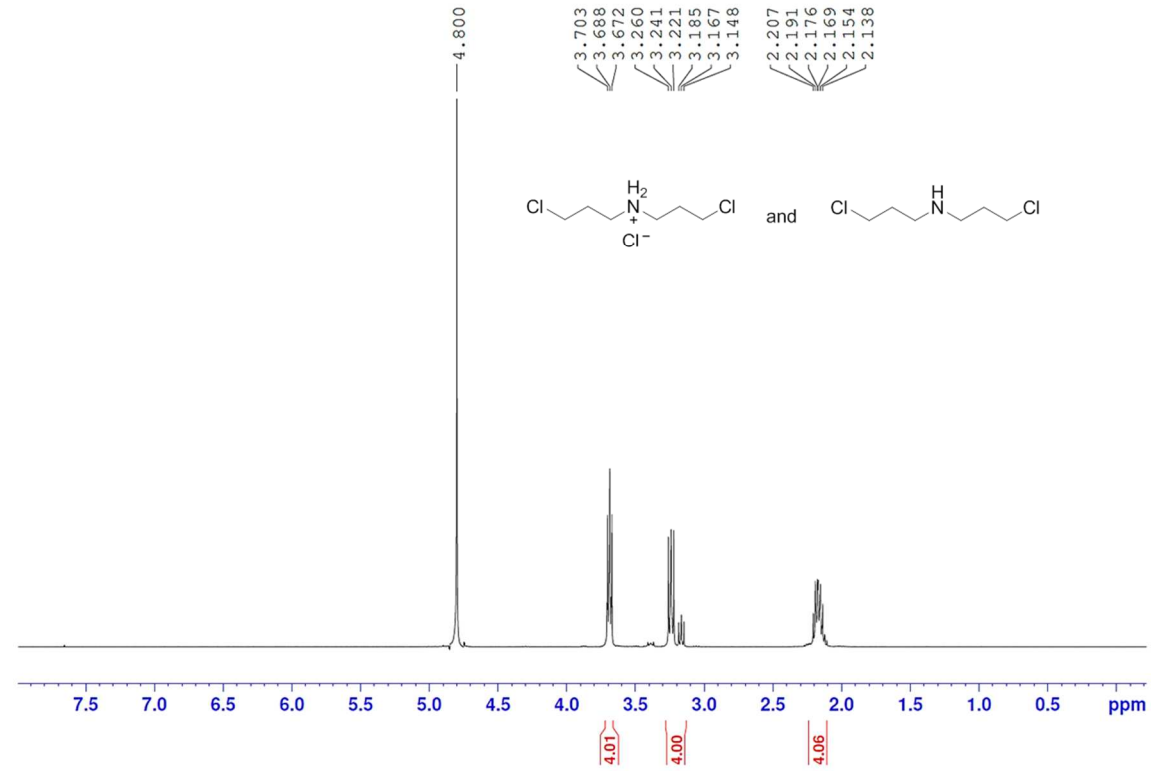
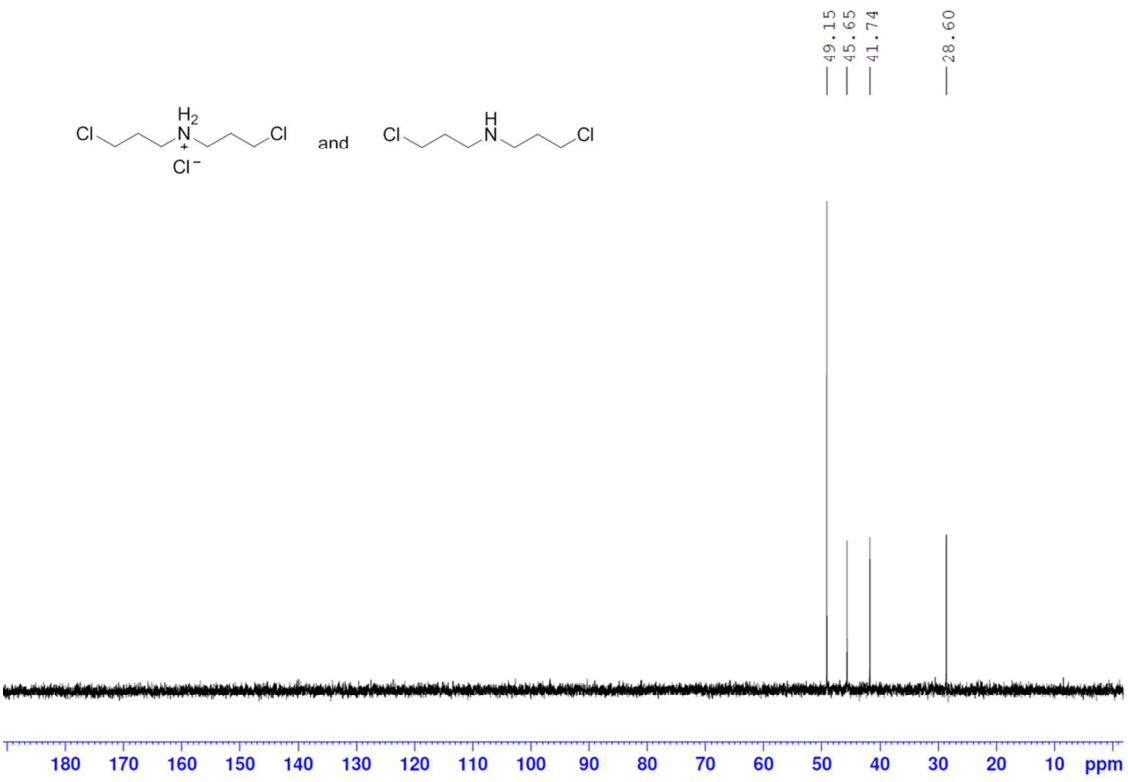
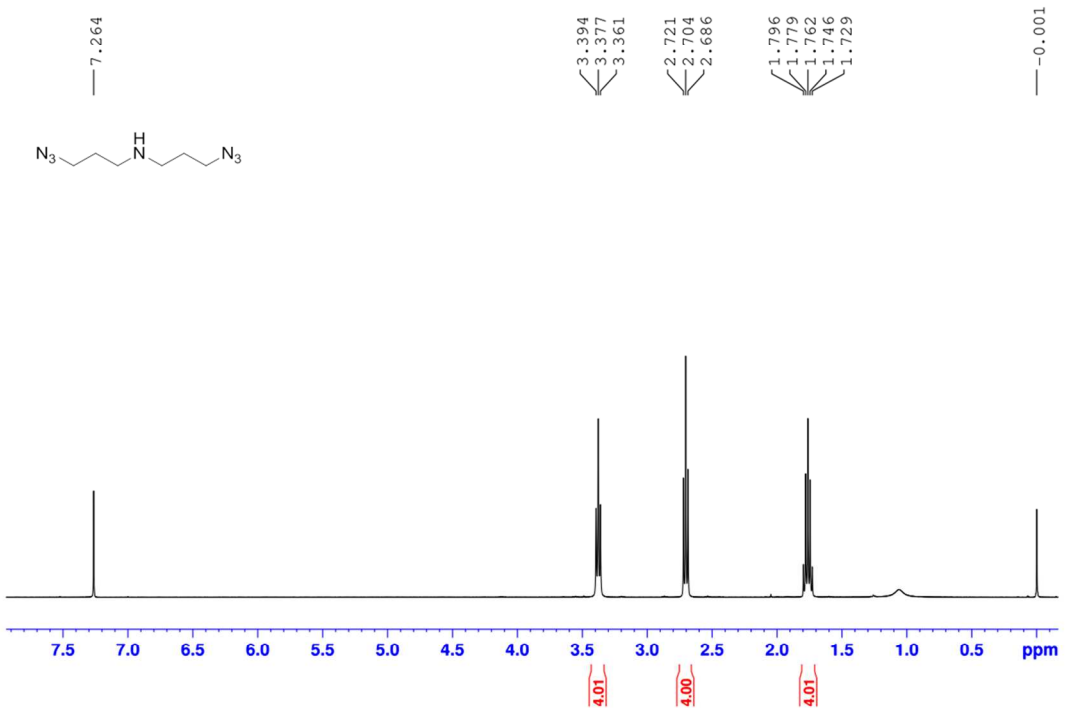
0.5
ppm

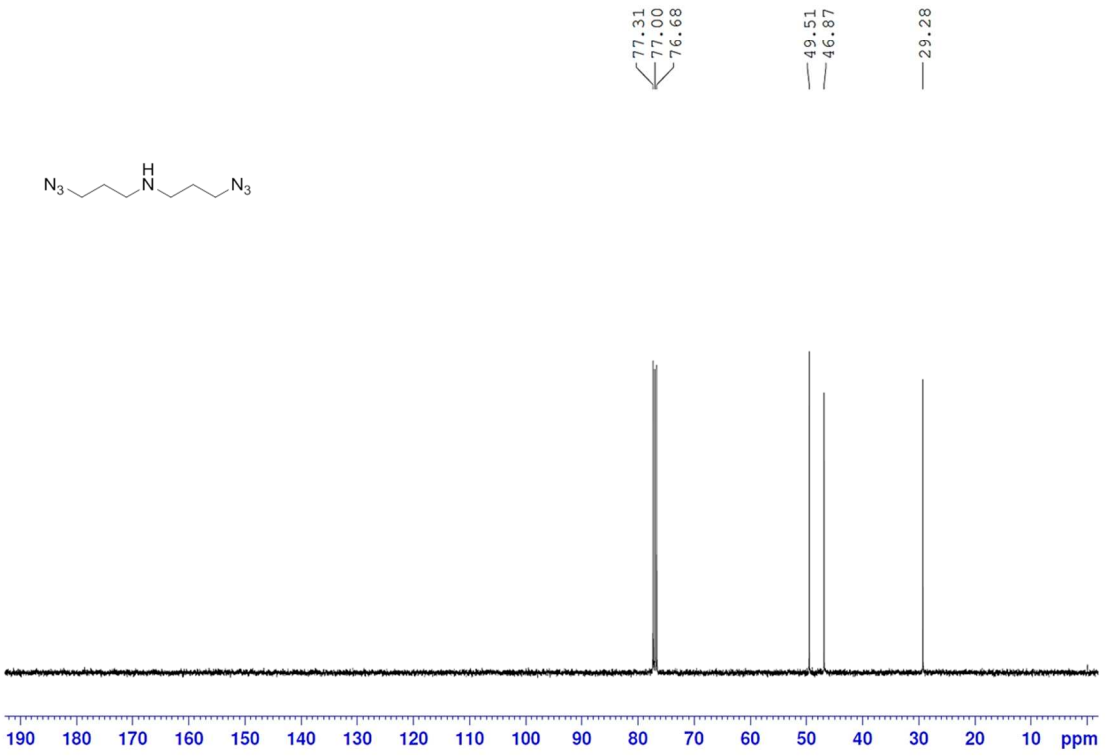

77.31
77.00
76.68
53.65
52.27
49.41
25.38
N3
N
N3
N3
N3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

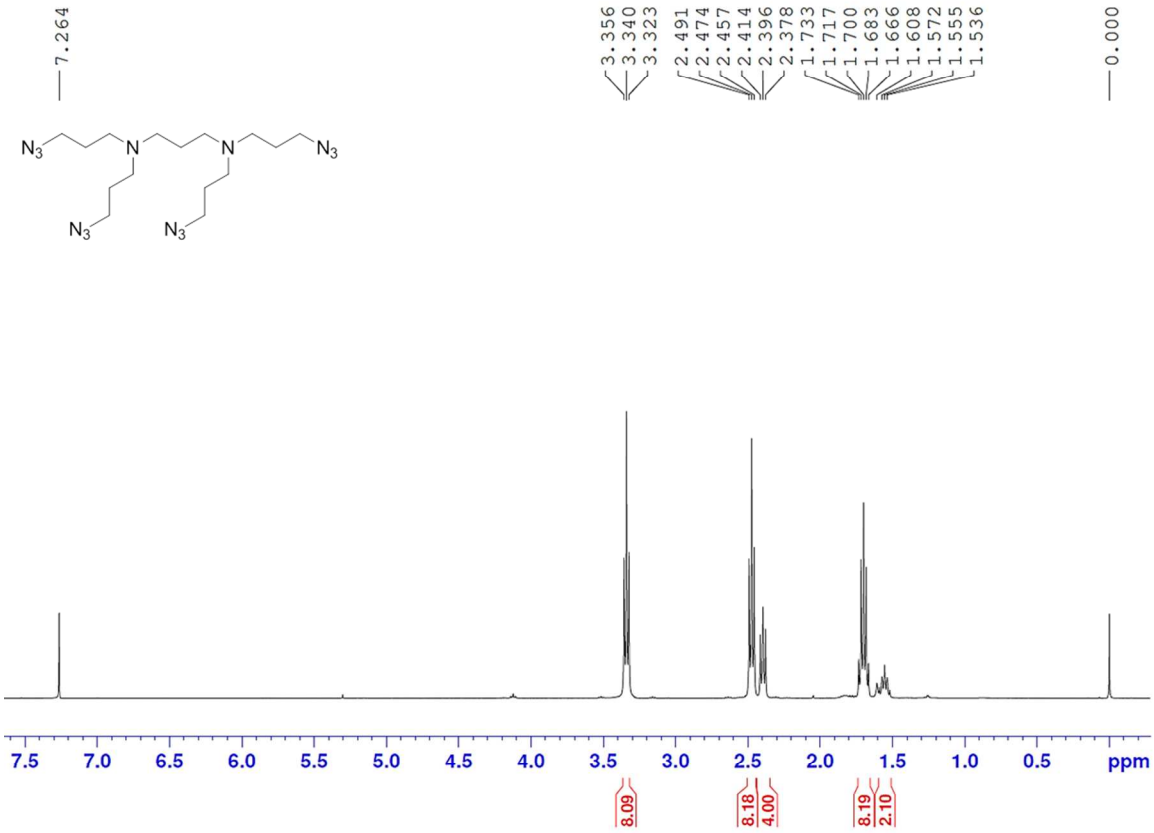

7.268
2.770
2.755
2.740
2.510
2.495
2.480
2.463
2.445
1.892
1.656
1.638
1.620
1.602
1.585
0.000
H2N
N
N
NH2
NH2
NH2
NH2
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
8.11
12.00
8.02
2.07
77.32
77.00
76.69
57.12
52.59
39.71
24.96
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

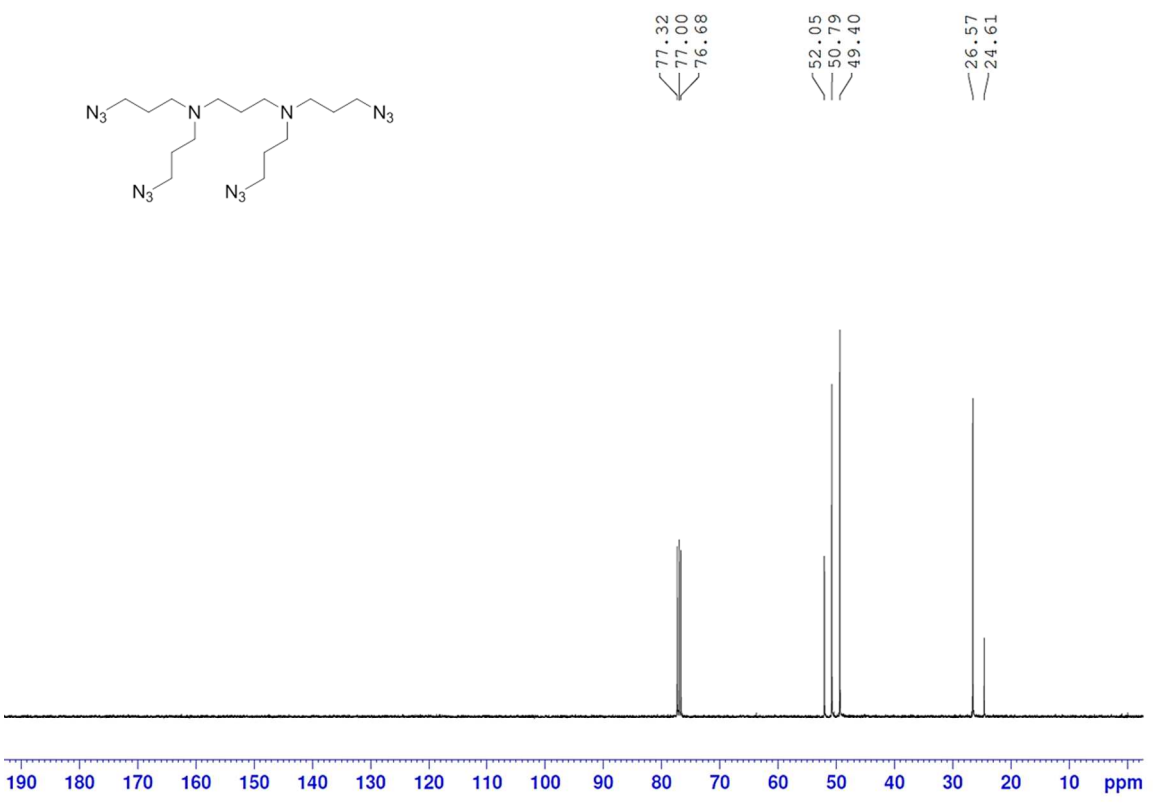

4.800
3.703
3.688
3.672
3.260
3.241
3.221
3.185
3.167
3.148
2.207
2.191
2.176
2.169
2.154
2.138
Cl
H2
N
+
Cl⁻
Cl
and
Cl
H
N
Cl
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.01
4.00
4.06

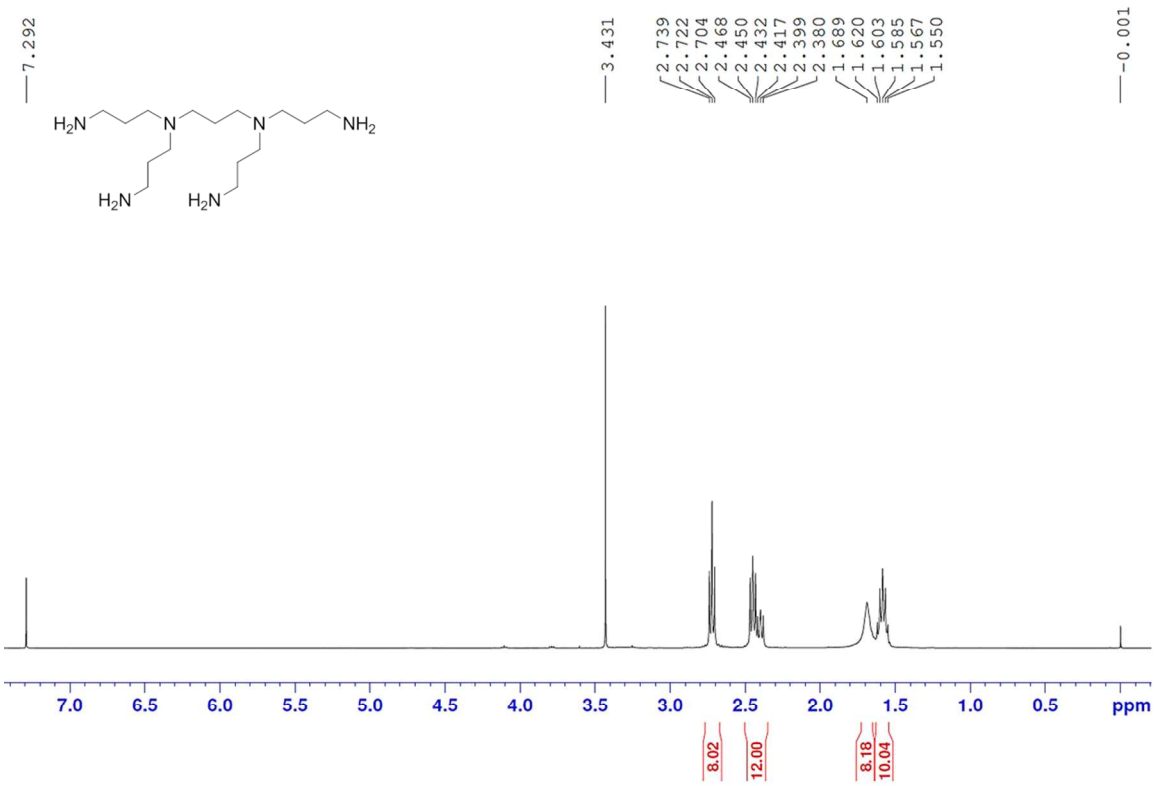

49.15
45.65
41.74
28.60
Cl
H2
N
+
Cl⁻
Cl
and
Cl
H
N
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

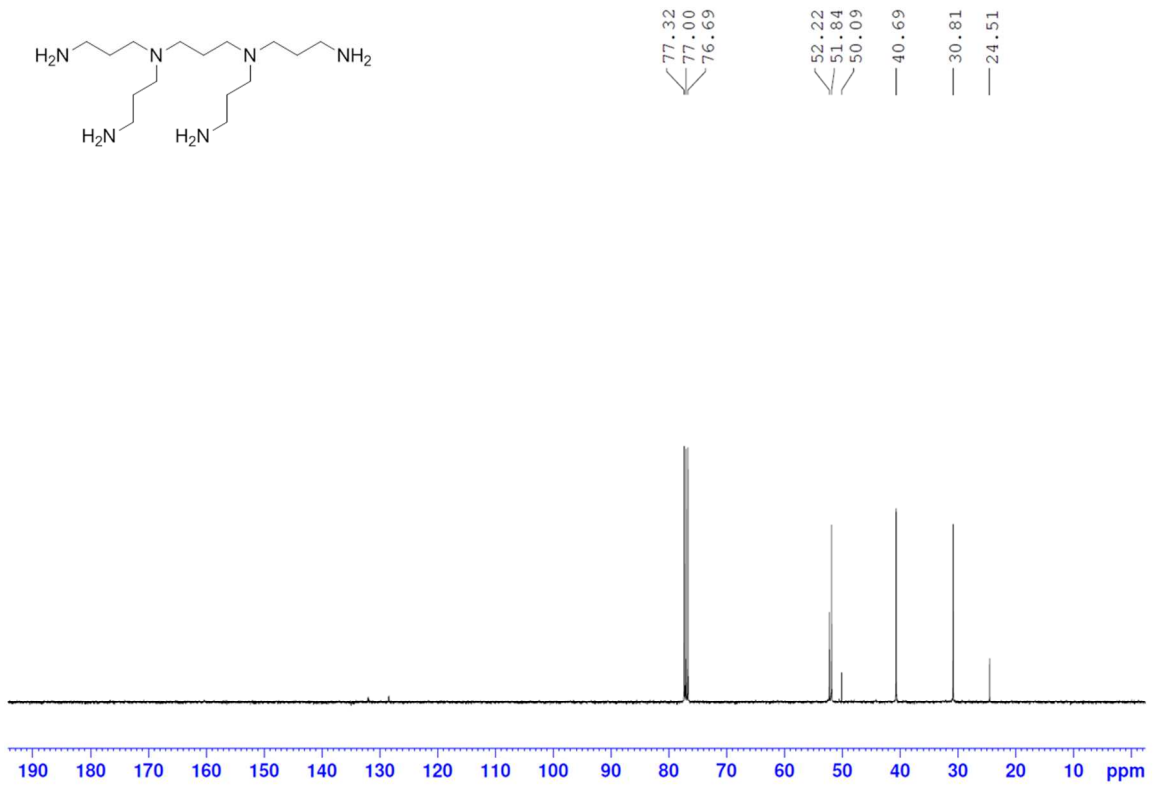

7.264
3.394
3.377
3.361
2.721
2.704
2.686
1.796
1.779
1.762
1.746
1.729
0.001
N3
H
N
N3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.01
4.00
4.01


77.31
77.00
76.68
49.51
46.87
29.28
N3
H
N
N3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.264
3.356
3.340
3.323
2.491
2.474
2.457
2.414
2.396
2.378
1.733
1.717
1.700
1.683
1.666
1.608
1.572
1.555
1.536
0.000
N3
N
N
N3
N3
N3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
8.09
8.18
4.00
8.19
2.10


77.32
77.00
76.68
52.05
50.79
49.40
26.57
24.61
N3
N
N
N3
N3
N3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.292
3.431
2.739
2.722
2.704
2.468
2.450
2.432
2.417
2.399
2.380
1.689
1.620
1.603
1.585
1.567
1.550
0.001
H2N
N
N
NH2
H2N
H2N
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
8.02
12.00
8.18
10.04


77.32
77.00
76.69
52.22
51.84
50.09
40.69
30.81
24.51
H2N
N
N
NH2
H2N
H2N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

References

(1) Gao, Y.; Chen, L.; Zhang, Z.; Gu, W.; Li, Y. *Biomacromolecules* **2010**, *11*, 3102.

(2) Chen, S.; Gopalakrishnan, R.; Schaer, T.; Marger, F.; Hovius, R.; Bertrand, D.; Pojer, F.; Heinis, C. *Nat. Chem.* **2014**, *6*, 1009.

(3) Moschetta, E. G.; Sakwa-Novak, M. A.; Greenfield, J. L.; Jones, C. W. *Langmuir* **2015**, *31*, 2218.

(4) Bacsik, Z.; Hedin, N. *Vib. Spectrosc.* **2016**, *87*, 215.

(5) Lepaumier, H.; Picq, D.; Carrette, P.-L. *Ind. Eng. Chem. Res.* **2009**, *48*, 9068.