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Supplementary Information

Nitrone-Mediated Radical Coupling Reactions: A New Synthetic Tool Exemplified on Dendrimer Synthesis

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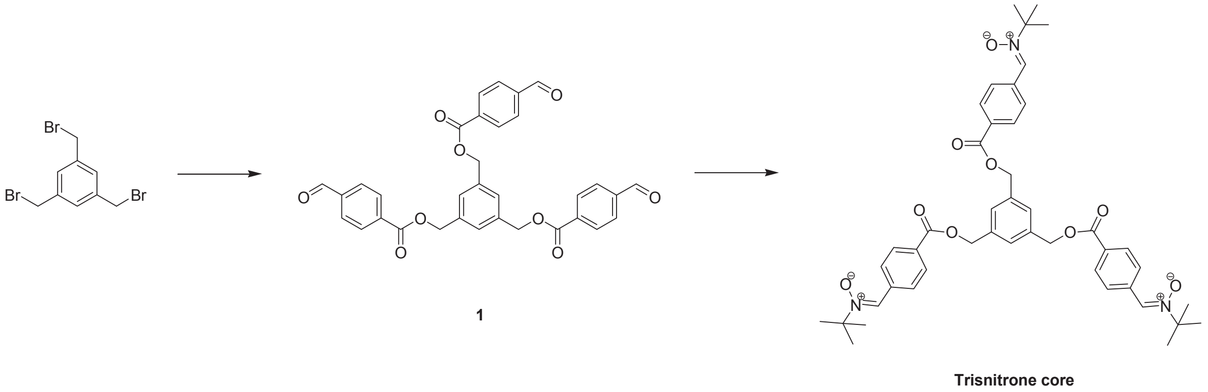
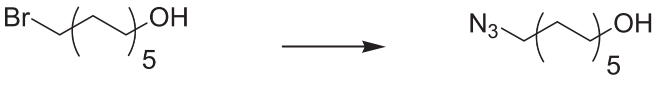
Experimental Section

Materials. 1,3,5-tris(bromomethyl)benzene (Aldrich, 97 %), 11-bromoundecanol (97%, ABCR GmbH and Co. KG), 5-hydroxyisophthalic acid (97%, Aldrich), sulfuric acid (95%, Carl Roth GmbH and Co. KG), propargyl bromide, 80 wt.% solution in toluene (80%, Acros), 2-Bromopropionyl bromide (98%, Acros), *N,N*-dimethylformamide extra dry (DMF) (99.8%, Acros), tetrahydrofuran extra dry (THF) (99.8%, Acros), triethylamine (99.7%, ABCR GmbH and Co. KG), sodium azide (99.8%, Acros), oxalyl chloride (98%, Acros), 4-formylbenzoic acid (Aldrich, 97 %), *N*-(*tert*-butyl)hydroxylamine acetate (Aldrich, 97 %), *N,N*-diisopropylethylamine (Alfa Aesar, 99 %), copper powder < 75 µm (Aldrich, 99 %), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) (Merck, 98 %), copper iodide (CuI) (Sigma-Aldrich, 98 %) were used as received. Toluene, ethanol, chloroform, dichloromethane, ethyl acetate, hexane, and cyclohexane were purchased as analytical grade and used as received.

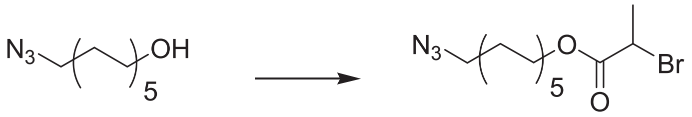


Synthesis of 1,3,5-tris((N-tert butyl-α-(4-benzoyloxy-phenyl))methyl)benzene (Trisnitrone core). To a 50 mL round bottom flask, 1,3,5-tris(bromomethyl)benzene (2.74 mmol, 0.978 g), 4-formylbenzoic acid (10.3 mmol, 1.54 g) and potassium carbonate (16.5 mmol, 2.27 g) were added before dissolving in 30 mL of dry DMF. The reaction mixture was heated under reflux at 60 °C for 24 h. Thereafter the mixture was cooled to ambient temperature and the solvent was removed under high vacuum. Approximately 40 mL of ethyl acetate was added to the flask and the contents were washed water thrice (3×50 mL) before drying the organic fraction over magnesium sulfate. The solution was filtered and concentrated, yielding appr. 1 g of the trisaldehyde compound, **1**, which was used directly in the next reaction step. Compound **1** (1.7 mmol, 0.962 g) was subsequently weighed into a 50 mL round bottom flask along with *N*-(tert butyl)hydroxylamine acetate (6.4 mmol, 0.953 g) and sodium sulfate (6.4 mmol, 0.910 g). The mixture was dissolved in 30 mL of chloroform before adding dropwise *N,N*-diisopropylethylamine (6.4 mmol, 1.12 mL). The contents in the flask were allowed to stir for 3 days at ambient temperature and kept in the dark away from any UV light source. Once the reaction time was reached, solid particulates were filtered off and the solvent was removed under high vacuum. Approximately 40 mL of water was added to the flask and the suspension was extracted with ethyl acetate (3×40 mL). The organic fraction was dried with magnesium sulfate and filtered. Ethyl acetate was removed under high vacuum. The product was further purified via column chromatography on silica gel (ethyl acetate/hexane (3:1 to 5:1 gradient) as eluent) and gave the trisnitrone core as a white foam-like product (0.717 g, 54 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 27 H), 5.40 (s, 6H), 7.52 (s, 3H), 7.63 (s, 3H), 8.07-8.10 (d, 6H), 8.32-8.50 (d, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.3, 66.3, 71.6, 127.9, 128.4, 129.0, 129.8, 130.5, 135.2, 137.0, 165.7. ESI-MS $(M+H)^+$ and $(M+Na)^+$ calcd for $C_{45}H_{51}N_3O_9$: 778.4 Da and 800.4 Da respectively, found 778.2 Da and 800.3 Da.



2

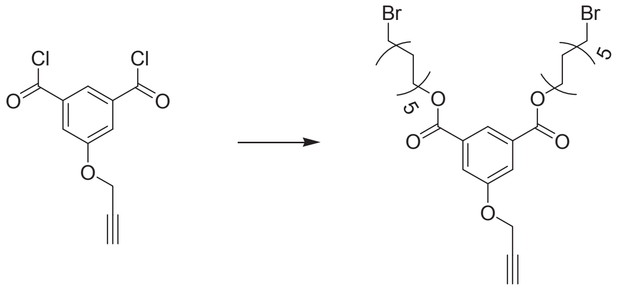
Synthesis of 11-azidoundecan-1-ol (2). 11-bromoundecan-1-ol (11.9 mmol, 3 g) was dissolved in 20 mL of DMF and sodium azide (59.7 mmol, 3.88 g) was added to the solution. The reaction mixture was stirred at 80 °C for 24 h and subsequently cooled to ambient temperature. Distilled water was added to the solution and the product was extracted three times with diethyl ether. The combined organic phases were dried over sodium sulfate, filtered and evaporated. Product **2** was quantitatively isolated as clear liquid. (2.54 g, 83 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.28-1.36 (m, 14H), 1.54-1.61 (m, 4H), 3.23-3.27 (t, 2H), 3.62-3.63 (t, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.7, 26.7, 28.1, 29.1, 29.4, 29.4 29.5, 29.6, 32.8, 51.5, 63.1.



2 **AB monomer**

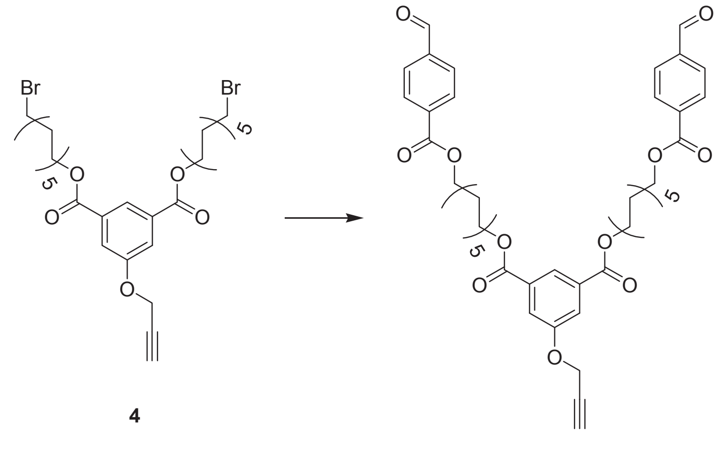
Synthesis of 11-azidoundecyl-2-bromopropanoate (AB monomer). Compound **2** (11.7 mmol, 2.5 g) was dissolved in 30 mL of dry THF. Triethylamine (17.5 mmol, 2.43 mL) was added to the solution and cooled to 0 °C. 2-Bromopropionyl bromide (15.2 mmol, 1.59 mL) was dissolved in 10 mL of dry THF and subsequently added dropwise to the reaction mixture within 30 min. After the addition, the reaction mixture was warmed to ambient temperature and stirred further for 5 h. Solids were filtered off, the filtrate was concentrated and diluted with 100 mL of dichloromethane, and the mixture was extracted two times with 50 mL of a saturated aqueous solution of sodium hydrogen carbonate. The organic phase was dried over sodium sulfate. The solution was purified by column chromatography on silica gel with ethyl acetate/hexane (1:10) to give the product **AB monomer** as pale yellow liquid (4.2 g, 93%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.28-1.36 (m, 14H), 1.54-1.61 (m, 4H), 1.81-1.83 (d, 6H), 3.23-3.27 (t, 2H), 4.12-4.19 (t, 2H), 4.32-4.40 (q, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.2, 25.7, 26.7, 28.1, 29.1, 29.4, 29.4 29.5, 29.6, 32.8, 40.1, 51.5, 64.6, 168.7.

Synthesis of 5-(prop-2-ynyloxy)isophthaloyl dichloride (3). This chemical was synthesized in identical fashion according to the reported literature.[1]



3 **4**

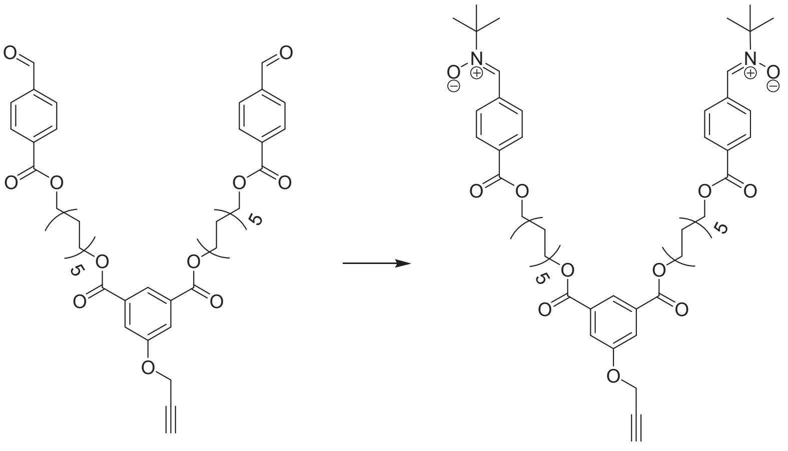
Synthesis of bis(11-bromoundecyl) 5-(prop-2-ynyloxy)benzene-1,3-dioate (4). A solution of compound **3** (3.89 mmol, 1 g) in dry THF (20 mL) was added dropwise to a solution of 11-bromoundecan-1-ol (2.34 g, 9.33 mmol) and triethylamine (1.62 mL, 11.67 mmol) in dry THF (20 mL) at 0 °C. The solution was stirred at ambient temperature for 16 h, the residue filtered off and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:4) to give the product **4** as white solid. (2.18 g, 82%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.18-1.82 (m, 36H), 2.54-2.56 (t, 1H), 3.37-3.43 (t, 4H), 4.30-4.36 (t, 4H), 4.77-4.78 (d, 2H), 7.82-7.83 (d, 2H), 8.31-8.33 (t, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.0, 28.2, 28.7, 29.5, 32.8, 34.1, 56.3, 65.6, 120.1, 123.8, 132.3, 157.5, 165.6.



4

5

Synthesis of bis(11-(4-formylbenzoyloxy)undecyl) 5-(prop-2-ynyloxy)benzene-1,3-dioate (5). To a 50 mL round bottom flask, compound **4** (1.46 mmol, 1.0 g), 4-formylbenzoic acid (3.65 mmol, 0.55 g), potassium carbonate (5.84 mmol, 0.80 g) were added before dissolving with 20 mL of dry DMF. The reaction mixture was heated under reflux at 60 ^{o}C for 24 h. Thereafter the mixture was cooled to ambient temperature and the solvent was removed under high vacuum. Approximately 30 mL of ethyl acetate was added to the flask and the contents were washed water thrice (3×30 mL) before drying the organic fraction over magnesium sulfate. The solution was filtered and concentrated, yielding compound **5** (1.1 g, 91 %) which was subsequently used in the next step without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.18-1.82 (m, 36H), 2.54-2.56 (t, 1H), 4.28-4.35 (m, 8H), 4.77-4.78 (d, 2H), 7.82-7.83 (d, 2H), 7.91-8.00 (d, 4H), 8.23-8.28 (d, 4H), 8.31-8.33 (t, 1H), 10.01-10.04 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.0, 28.7, 29.3, 29.5, 59.3, 65.6, 65.8, 120.1, 123.8, 129.5, 130.2, 132.3, 135.5, 139.1, 157.5, 165.6, 191.7.



5

CD$_2$ monomer

Synthesis of bis(11-(N-tert butyl-α-(4-benzoyloxy-phenyl))undecyl) 5-(prop-2-ynyloxy)benzene-1,3-dioate (CD$_2$ monomer). To a 50 mL round bottom flask containing **5** (0.95 mmol, 0.78 g), *N*-(tert butyl)hydroxylamine acetate (2.4 mmol, 0.35 g) and sodium sulfate (2.4 mmol, 0.34 g) were added before dissolving with 25 mL of chloroform. *N,N*-diisopropyethylamine (2.4 mmol, 412 μL) was added dropwise to the reaction mixture and the contents of the flask were allowed to stir for 2 days at room temperature in the dark. After the reaction time was reached, the solid particulates in the flask were filtered off and the solvent was subsequently removed under high vacuum. Water (30 mL) was then added to the flask and the suspension was extracted with ethyl acetate (3×30 mL). The organic fraction was dried over magnesium sulfate, filtered and concentrated before finally purified by column chromatography on silica gel (ethyl acetate/hexane (1:1) as eluent) yielding CD$_2$ monomer (0.72 g, 85 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.18-1.82 (m, 36H), 1.62 (s, 18H), 2.54-2.56 (t, 1H), 4.28-4.35 (m, 8H), 4.77-4.78 (d, 2H), 7.62 (s, 2H), 7.81-7.82 (d, 2H), 8.04-

8.08 (d, 4H), 8.31-8.35 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.0, 28.3, 28.6, 29.2, 29.5, 59.2, 65.3, 65.6, 71.6, 120.1, 123.8, 128.3, 129.0, 129.6, 131.2, 132.2, 134.8, 157.4, 165.6, 166.1. ESI-MS $(M+Na)^+$ calcd for $C_{57}H_{78}N_2O_{11}$: 989.6 Da, found 989.4 Da.

Synthesis of G1-[N$_3$]$_6$. The trisnitrone core (0.43 mmol, 0.335 g), AB monomer (6.46 mmol, 2.25 g) and copper powder (6.46 mmol, 0.411 g) were weighed into a 100 mL round bottom flask. Toluene (50 mL) was added into the flask before sealing with a rubber septum and the reaction mixture was purged with nitrogen for 45 minutes in an ice bath. Degassed PMDETA (6.46 mmol, 1.36 mL) was transferred into the 100 mL round flask while keeping the nitrogen gas on. The reaction mixture was then reacted at 60 ^{o}C in a thermostated oil bath for 4 h. Copper complexes were removed by passing over a column of basic alumina. Both the flask and column were rinsed thoroughly with ethyl acetate to ensure maximum product recovery. The organic solutions – now free of copper – were collected and concentrated under high vacuum. The first generation dendrimer was finally purified by column chromatography on silica gel (ethyl acetate:cyclohexane (1:10 to 1:7 gradient) as eluent) (0.98 g, 95 %). ^{1}H-NMR (400 MHz, $CDCl_3$, both diastereomers) δ 0.65-0.76 (dd, 27H), 0.87-1.00 (m, 18H), 1.10-1.80 (m, 108H), 3.02-3.38 (m, 3H), 3.20-3.28 (m, 12H), 3.60-3.64 (m, 3H), 4.00-4.24 (m, 12H), 4.26-4.56 (m, 3H), 5.36-5.39 (d, 6H), 7.51-8.03 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$, both diastereomers) δ 14.1, 15.5, 15.7, 16.4, 18.2, 19.1, 19.3, 22.7, 25.6-26.0, 26.7, 27.8-28.3, 28.5-29.5, 31.6, 44.2, 51.5, 60.8-61.7, 64.2-65.1, 66.1-66.5, 67.6-67.7, 127.9-131.6, 137.0, 166.3, 173.9, 175.1, 176.2. ESI-MS $(M+Na)^+$ calcd for $C_{129}H_{207}N_{21}O_{21}$: 2410.6 Da, found 2410.1 Da.

Synthesis of G2-[Nit]$_{12}$. A solution consisting of G1-[N$_3$]$_6$ (94 μmol, 225 mg), CD$_2$ monomer (0.62 mmol, 600 mg) and CuI (0.62 mmol, 118 mg) in toluene (10 mL) in a sealed 25 mL round bottom flask was purged with nitrogen gas for 20 minutes in an ice bath. A degassed solution of PMDETA (0.62 mmol, 130 μL) in 1 mL toluene was injected into the flask using a degassed syringe. The mixture was stirred at room temperature for 4 h upon reaction completion. Copper complexes were removed by passing the solution over a column of basic alumina. To ensure maximum product recovery, both the flask and column were rinsed with ethyl acetate and tetrahydrofuran. The organic solution was concentrated and the product was purified by dialysis in ethanol/chloroform mixture using a dialysis membrane (Spectrum Laboratories Inc., Spectra/por Dialysis Membrane MWCO 3500 molecular porous membrane tubing) with a molecular weight cut-off of 3500 g·mol^{-1} yielding G2-[Nit]$_{12}$ (480 mg, 62 %).

^{1}H-NMR (400 MHz, $CDCl_3$, both diastereomers) δ 0.65-0.76 (dd, 27H), 0.87-1.00 (m, 18H), 1.10-1.80 (m, 432H), 3.02-3.16; 3.29-3.38 (m, 3H), 3.60-3.64 (m, 3H), 3.72-3.76 (m, 12H), 4.00-4.35 (m, 60H), 4.26-4.56 (m, 3H), 5.26 (s, 12H), 5.36-5.39 (d, 6H), 7.51-8.03 (m, 15H), 7.62 (s, 12H), 7.65 (s, 6H), 7.82-7.83 (d, 12H), 8.04-8.07 (d, 24H), 8.29-8.34 (m, 30H). ^{13}C-NMR (100 MHz, $CDCl_3$, both diastereomers) δ 14.1, 22.7, 25.3-26.0, 26.5, 28.4-29.7, 31.9, 50.5, 62.5, 65.3-65.6, 71.6, 119.9, 122.6, 123.4, 127.5, 128.2, 129.0, 129.6, 131.2, 132.3, 134.9, 143.1, 158.3, 165.6, 166.1. SEC-ESI-MS $(M+5Na)^{+5}$ calcd for $C_{471}H_{675}N_{33}O_{87}$: 1661.3 Da, found 1660.9 Da.

Synthesis of G3-[N_3]$_{24}$. The synthesis of G3-[N_3]$_{24}$ proceeded under similar conditions to the synthesis of the first generation dendrimer via NMRC reactions. G2-[Nit]$_{12}$ (23.5 μmol, 200 mg), AB monomer (2.26 mmol, 790 mg) and copper powder (2.26 mmol, 144 mg) were added into a 25 mL round bottom flask before adding 15 mL of toluene. The flask was sealed and the solution was purged with nitrogen for 20 minutes while keeping the temperature between 0 to 5 °C. A degassed solution of PMDETA (2.26 mmol, 475 μL) in 1 mL toluene was injected into the flask and the reaction mixture was subsequently reacted at 60 °C in a thermostated oil bath for 4 h. After the reaction time was reached, the solution was cooled to ambient temperature and passed through a column of basic alumina to the remove copper complexes. Likewise – to ensure maximum product recovery – the flask and column were rinsed with ethyl acetate and the organic solution concentrated. The final purification step included column chromatography on silica gel (ethyl acetate/hexane (1:10 gradient to 1:2) as eluent), yielding G3-[N_3]$_{24}$ (90 mg, 29 %). ^{1}H-NMR (400 MHz, $CDCl_3$, both diastereomers) δ 0.65-0.76 (dd, 135H), 0.87-1.00 (m, 90H), 1.10-1.80 (m, 756H), 3.02-3.38 (m, 15H), 3.20-3.28 (m, 48H), 3.60-3.64 (m, 15H), 3.72-3.76 (m, 12H), 4.00-4.35 (m, 108H), 4.26-4.56 (m, 15H), 5.26 (s, 12H), 5.36-5.39 (d, 6H), 7.51-8.03 (m, 60H), 7.65 (s, 6H), 7.82-7.83 (d, 12H), 8.04-8.07 (d, 24H), 8.29-8.34 (m, 30H). ^{13}C-NMR (100 MHz, $CDCl_3$, both diastereomers) δ 14.1, 15.5, 15.7, 19.2, 19.3, 22.7, 26.0, 26.7, 27.8-28.3, 28.5-29.7, 31.6, 51.5, 60.8, 64.2-65.0, 65.6, 67.7, 119.9, 127.9-132.3, 165.7, 166.3, 173.9, 175.1, 176.2.

Characterization by THF Size Exclusion Chromatography (SEC). SEC measurements were performed on a Polymer Laboratories PL-GPC 50 plus Integrated System, comprising an autosampler, a PLgel 5 μm bead-size guard column (50×7.5 mm) followed by three PLgel 5 μm Mixed-C and one PLgel 3 μm Mixed-E columns (300×7.5 mm) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 $mL \cdot min^{-1}$. The SEC system was calibrated using linear narrow polystyrene standards ranging from 160 to $6 \cdot 10^{6}$ $g \cdot mol^{-1}$. The Mark-Houwink parameters for polystyrene ($K = 14.1 \cdot 10^{-5}$ $dL \cdot g^{-1}$ and $\alpha = 0.70$)[2] were used when determining the molecular weights of the dendrimers.

Characterization by Nuclear Magnetic Resonance (NMR) Spectroscopy. The synthesized chemical structures were confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy using a Bruker AM 400 MHz spectrometer for hydrogen nuclei and 100 MHz for carbon nuclei. The samples were dissolved in $CDCl_3$ solution containing tetramethylsilane ($\delta = 0.00$ ppm) as the internal standard. The molecular weights of the dendrimers were determined via the following method:

For G1-$[N_3]_6$: The proton at 5.36-5.39 ppm (i.e. the proton **b** of the trisnitrone core (see Figure S1) and the proton shaded in ● of G1-$[N_3]_6$ (see Figure S3)) was set as the reference peak with the integral A_{exp} and compared to the sum of the α protons of the azide group at 3.20-3.28 ppm (●) and the methine proton 3.02-3.38 ppm (●), defined as integral B_{exp}. The molecular weight of G1-$[N_3]_6$ was then deduced as $M_{n,theo\ for\ G1}$ x $((B_{exp}/A_{exp})/(B_{theo}/A_{theo}))$ where $B_{theo}/A_{theo} = 15/6$.

For G2-$[Nit]_{12}$: The same proton at 5.36-5.39 ppm of the trisnitrone core was set as the reference with integral A_{exp}, and was compared to the sum of the proton of the triazole ring at 7.65 ppm (●) and the nitrone proton at 7.62 ppm (●), defined as integral C_{exp}. The molecular weight of G2-$[Nit]_{12}$ was then deduced as $M_{n,theo\ for\ G2}$ x $((C_{exp}/A_{exp})/(C_{theo}/A_{theo}))$ where $C_{theo}/A_{theo} = 18/6$.

For G3-$[N_3]_{24}$: The determination of the molecular weight of G3-$[N_3]_{24}$ is similar to that of G1-$[N_3]_6$, with the exception that the value for B_{theo}/A_{theo} of a third generation dendrimer now becomes 60/6 because of the increase in generation and therefore the number of functional groups.

Characterization by SEC/Refractive Index (RI)/Electrospray Ionization-Mass Spectrometry (ESI-MS).[3] Mass spectra were recorded on an LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the *m/z* range 195-1822 Da using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 3.5 kV and a dimensionless sheath gas of 8 and a sweep gas flow rate of 2 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature were set to 60 V, 120 V and 275 ^{o}C respectively. The LXQ was coupled to a Series 1200 HPLC-system(Agilent, Santa Clara, CA) consisting of a solvent degasser (G1322A), a binary pump (G1312A) and a high performance autosampler (G1367B), followed by a thermostated column compartment (G1316A). Separation was performed on two mixed bed size exclusion chromatography columns (Polymer Laboratories/Varian, Church Stretton, UK, Mesopore 250×4.6 mm, particle diameter 3 µm) with precolumn (Mesopore 50 x 4.6 mm) operating at 30 ^{o}C. THF at a flow rate of 0.30 mL·min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to an RI detector (G1362A with SS420x A/D). 0.27 mL·min^{-1} of the eluent was directed through the RI detector, and 30 µL·min^{-1} infused into the electrospray source after postcolumn addition of a 100 µM solution of sodium iodide in methanol at 20 µL·min^{-1} by a microflow HPLC syringe pump (Teledyne ISCO, Model 100DM). 20 µL of the sample solution with a concentration of 3-6 mg·mL^{-1} was injected into the HPLC system.

^{1}H-NMR Spectra

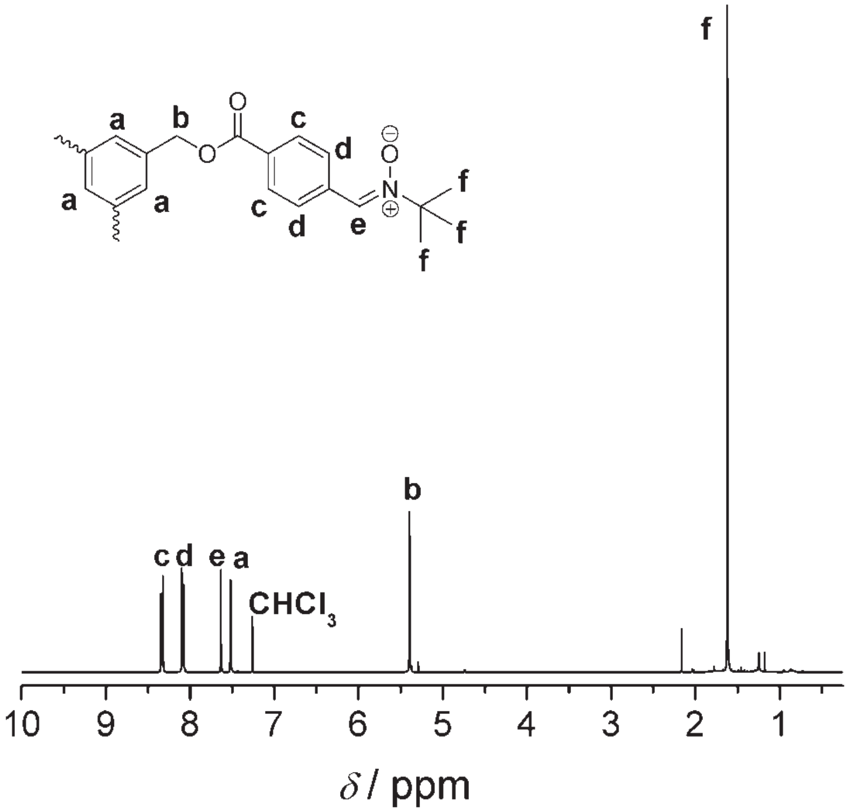


Figure S1. Full ^{1}H-NMR spectra of trisnitrone core.

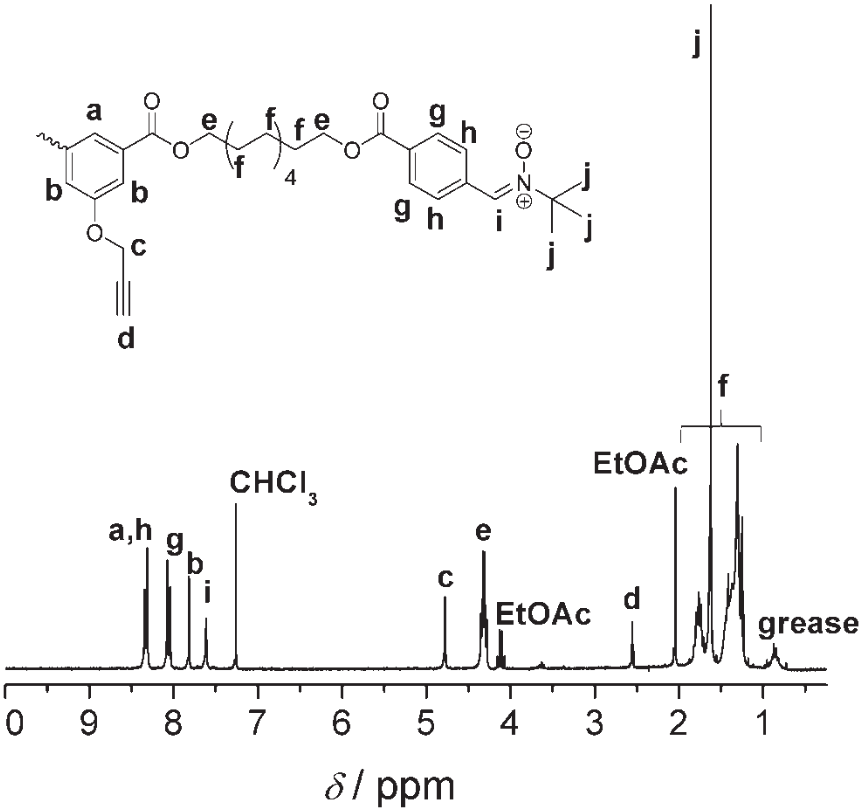


Figure S2. Full ^{1}H-NMR spectra of CD_2 monomer.

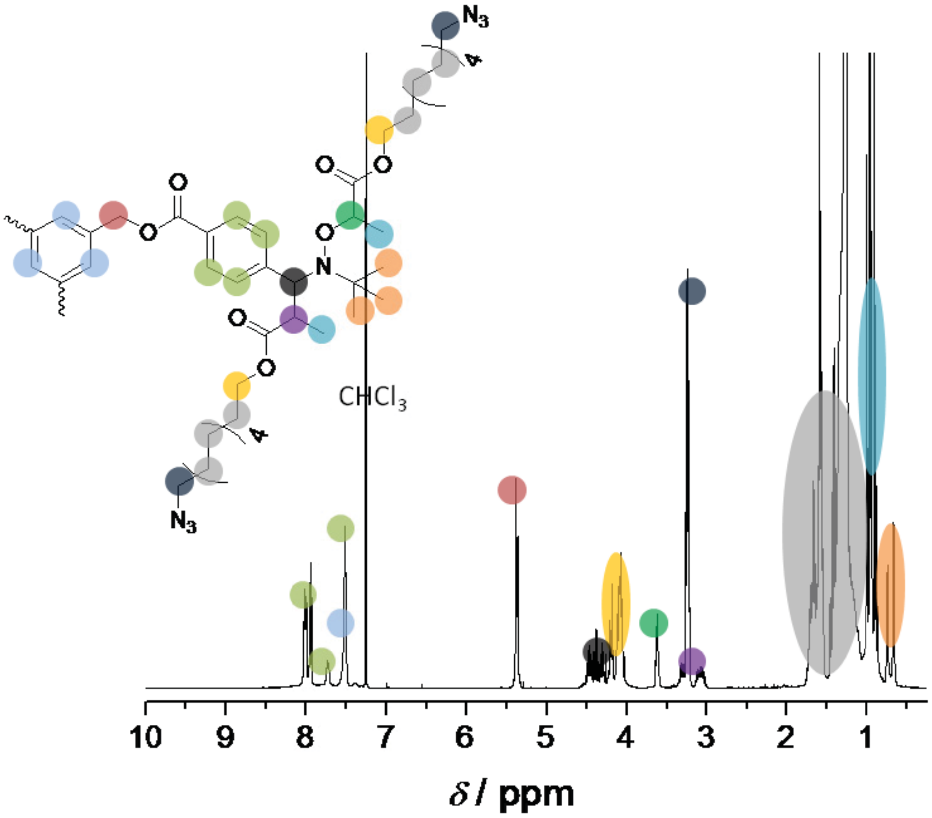


Figure S3. Full ^{1}H-NMR spectra of G1-[N_3]$_6$.

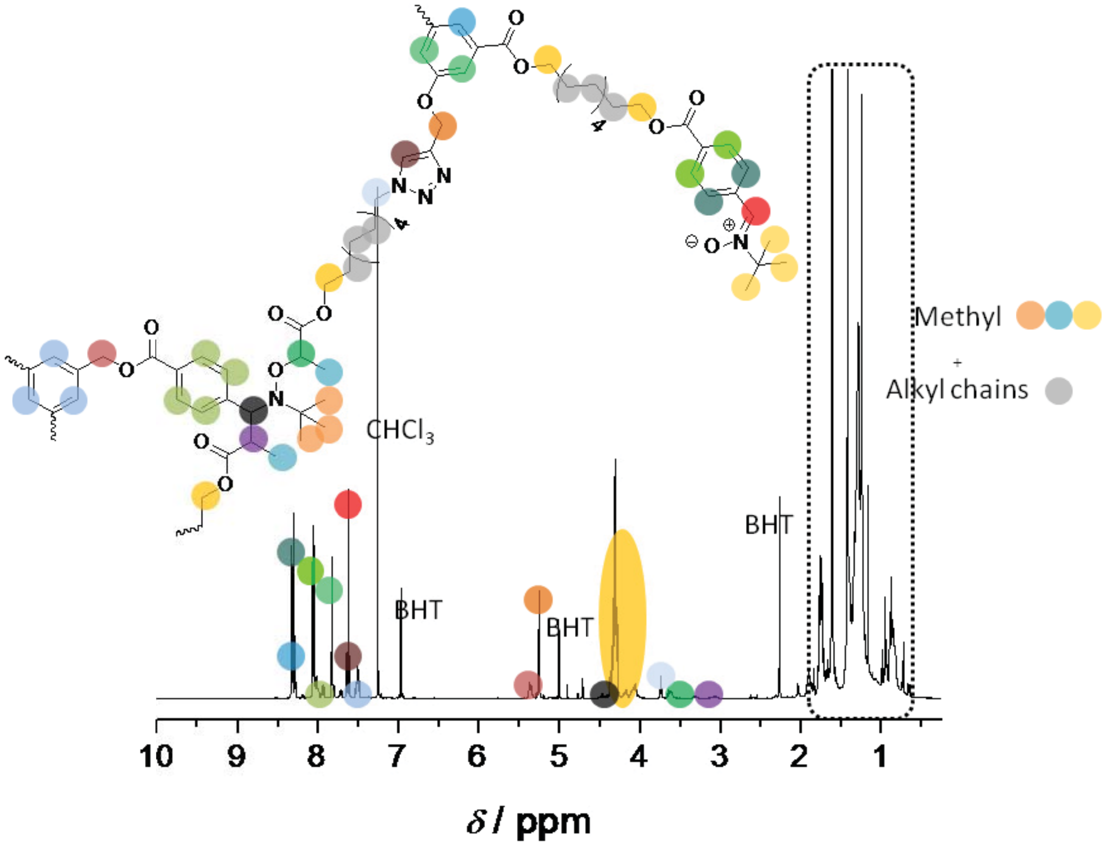


Figure S4. Full ^{1}H-NMR spectra of G2-[Nit]$_{12}$. BHT is an abbreviation for 2,6-dimethyl-4-*tert*-butylphenol.

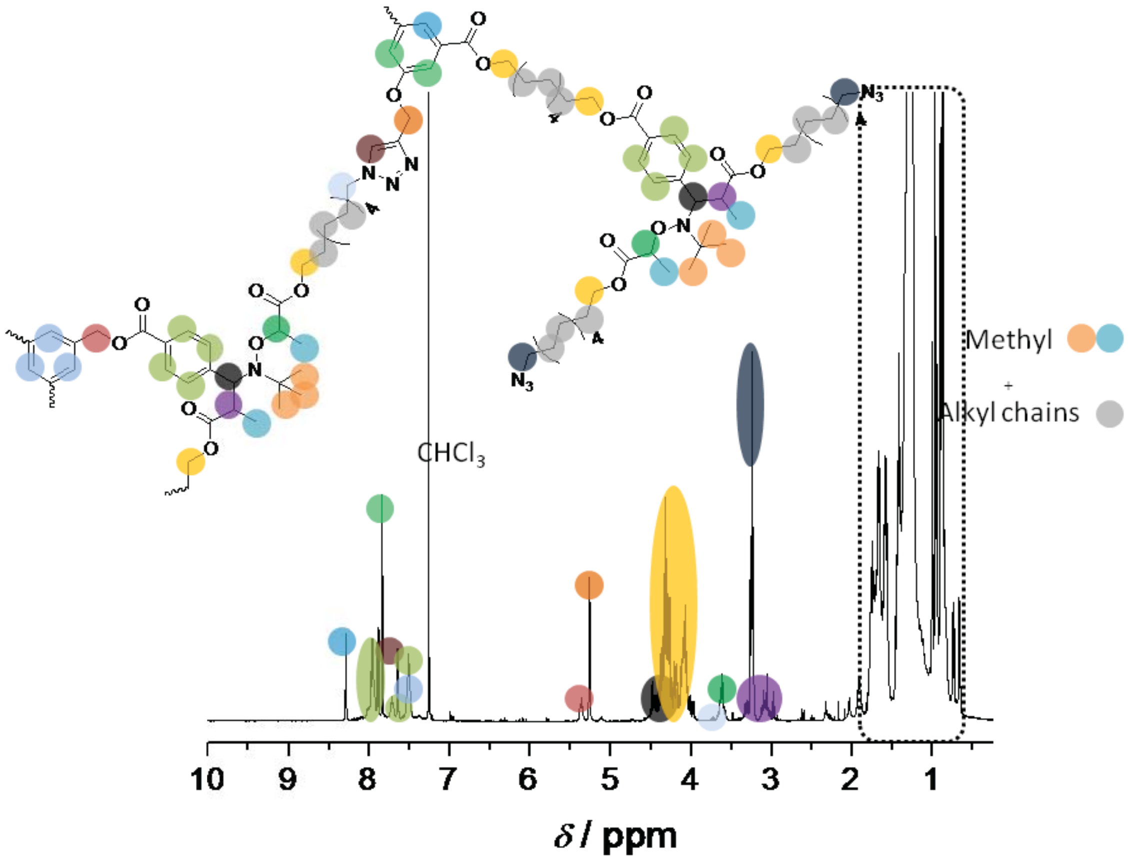


Figure S5. Full ^{1}H-NMR spectra of G3-$[N_3]_{24}$.

(SEC)-ESI-MS Spectra

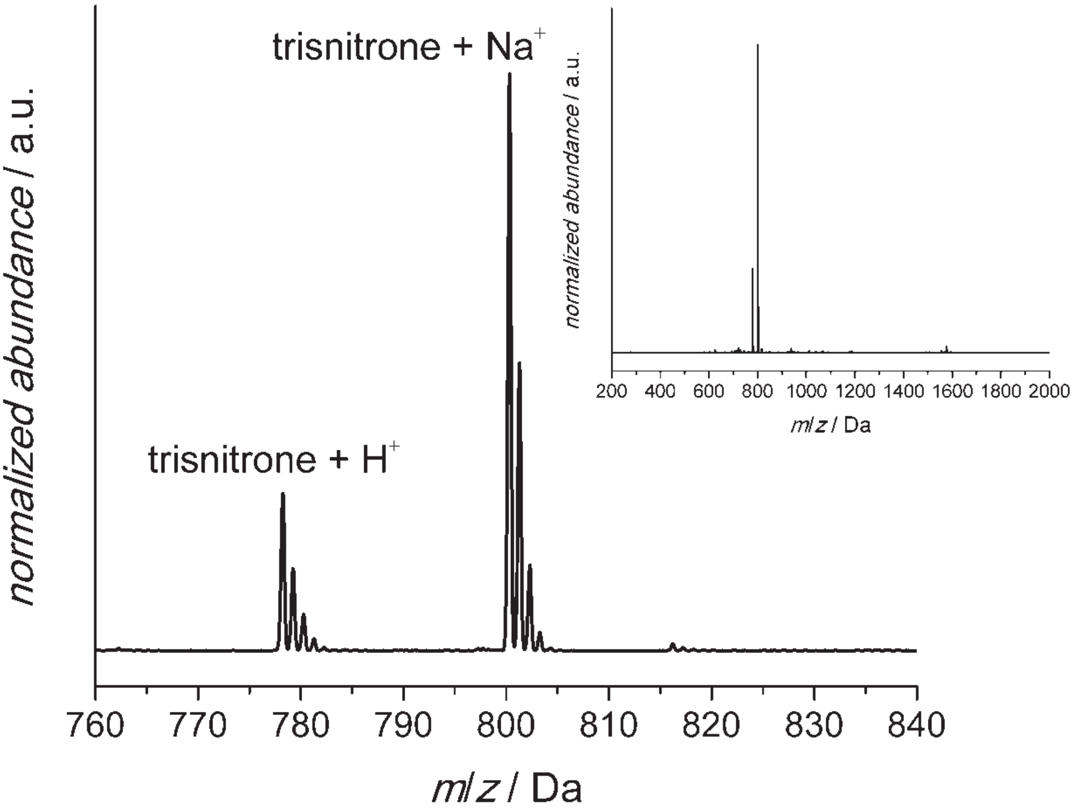


Figure S6. Mass spectrum of the trisnitrone core obtained via electrospray ionization-mass spectrometry analysis. The insert shows the full mass spectrum (from 200 – 2000 Da) of the ion product.

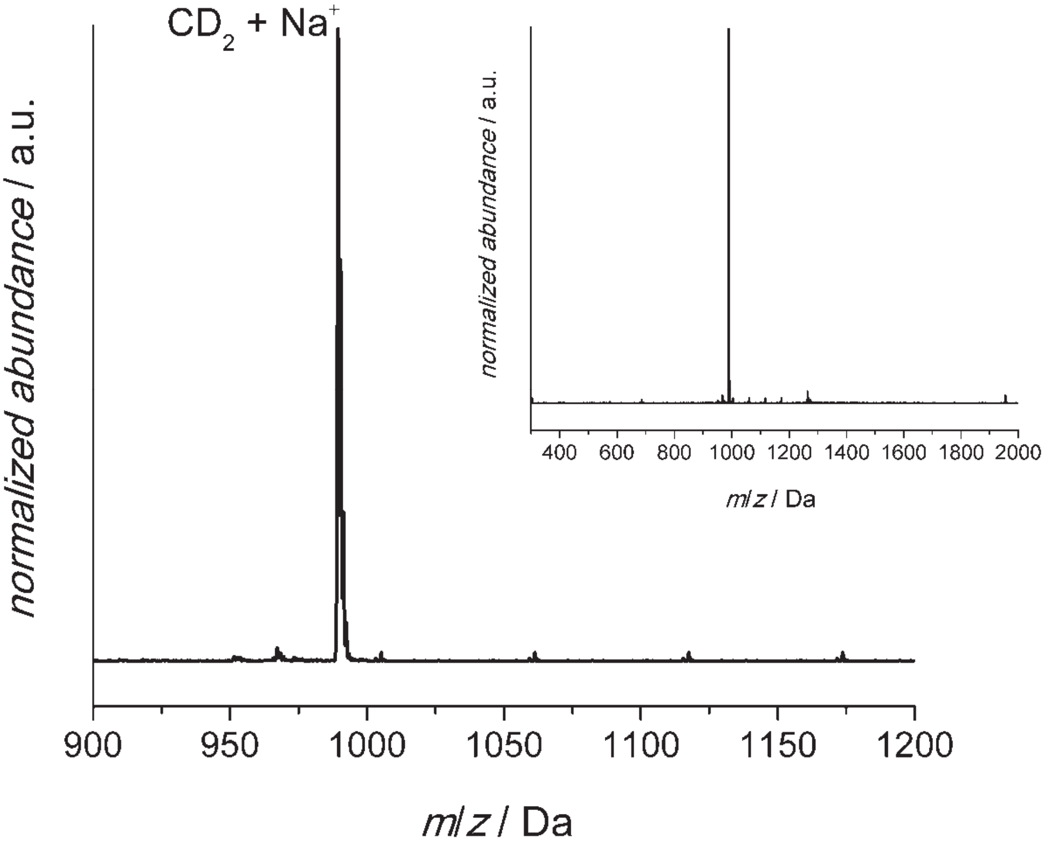


Figure S7. Mass spectrum of the CD$_2$ monomer obtained via electrospray ionization-mass spectrometry analysis. The insert shows the full mass spectrum (from 300 – 2000 Da) of the ion product.

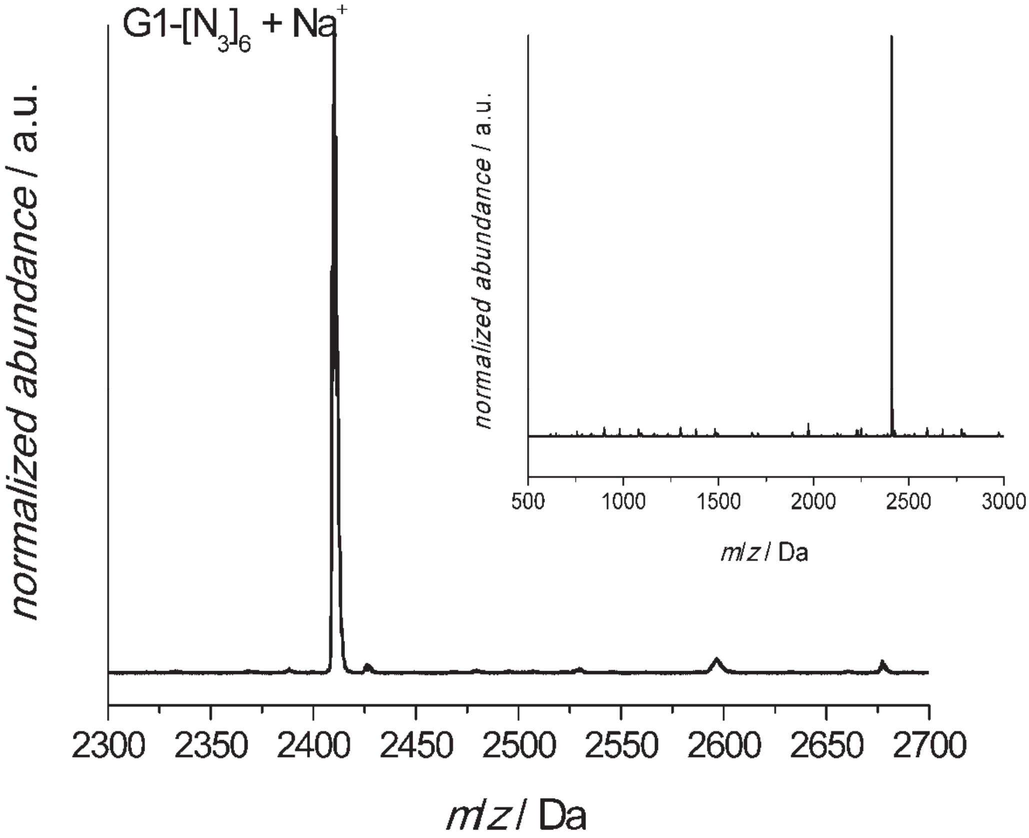


Figure S8. Mass spectrum of the first generation dendrimer, G1-$[N_3]_6$, obtained via electrospray ionization-mass spectrometry analysis. The insert shows the full mass spectrum (from 500 – 3000 Da) of the ion product.

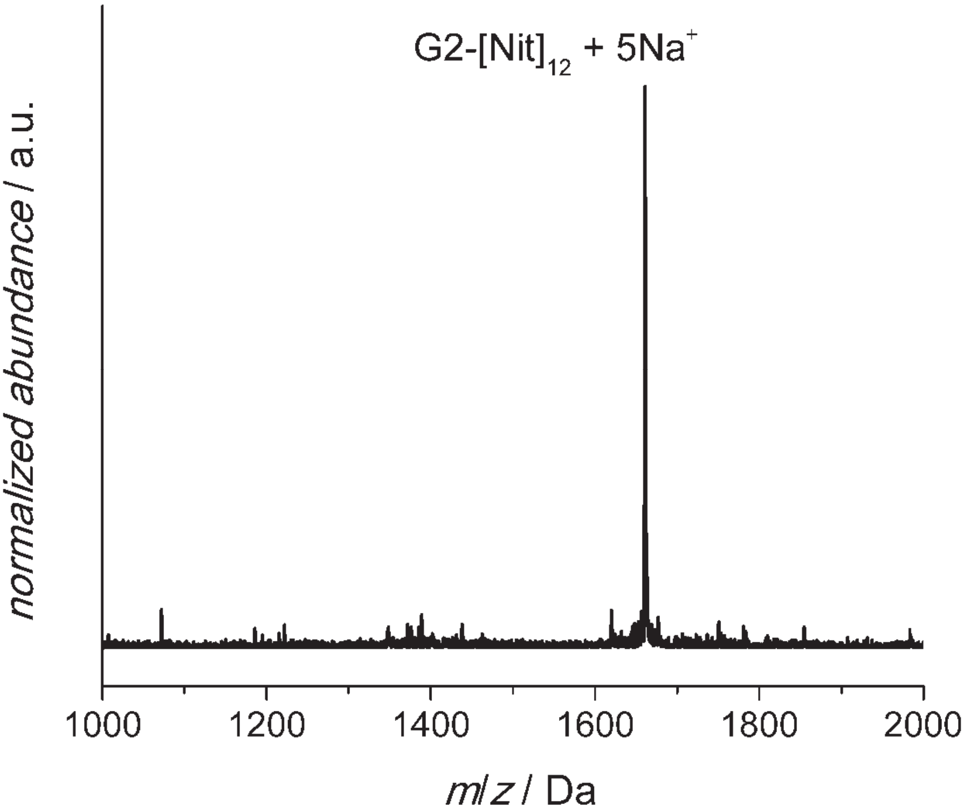


Figure S9. Mass spectrum of the second generation dendrimer, G2-[Nit]$_{12}$, obtained via electrospray ionization-mass spectrometry analysis. Note that the signal to noise ratio is relatively low due to large mass of the analysed product (> 8000 Da) and hence leading to the poor baseline.

References

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