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Co-initiated hyperbranched-polydendron building blocks for the direct nanoprecipitation of dendron-directed patchy particles with heterogeneous surface functionality

Electronic Supporting Information

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Methods and Synthesis

Materials

All compounds were purchased from Sigma Aldrich unless otherwise stated and used without further purification. Potassium ethyl xanthogenate, 2-bromoacetic acid, pyridine, 4-dimethylaminopyridine (DMAP), 2,2-dimethoxypropane, N,N'-dicyclohexylcarbodiimide (DCC), benzyl acrylate and 2-(dimethylamino)ethyl acrylate (DMAEA) were purchased from Alfa Aesar and used without further purification. *Para*-toluene sulfonyl ethanol (*p*-TSe) was purchased from Fluorochem and used without further purification. Dichloromethane, hexane and ethyl acetate were HPLC grade and supplied by Fisher Scientific. Analytical TLC was performed on commercial Merck plates coated with silica gel. Flash chromatography was performed using a Grace Reveleris Flash System with Silica gel Flash Cartridges.

Analysis

Nuclear magnetic resonance (NMR): Spectra were recorded using a Bruker Avance 400 spectrometer, operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, in $CDCl_3$, CD_3OD or D_2O purchased from Goss Scientific. Chemical shifts (δ) are reported in parts per million (ppm) and TMS was used as an internal standard for both ^{1}H and ^{13}C spectra.

Mass Spectrometry (MS): Chemical ionisation (CI) mass spectra were obtained using an Agilent GC/Q-TOF 7200 instrument, using methane CI gas; whilst electrospray ionisation (ESI) mass spectra was obtained using a MicroMass LCT mass spectrometer using electron ionisation and direct infusion syringe pump sampling. All samples were diluted with methanol. Matrix-assisted laser desorption/ionisation - time of flight mass spectrometry (MALDI-TOF MS) sample solutions were prepared with a 2 mg/mL concentration in THF. Matrix solution was prepared at a concentration of 10 mg/mL in THF and 1 mg/mL Na counter ion solution was prepared. 5 µL of sample solution, 20 µL of matrix solution and 1.5 µL of counter ion was added to an Eppendorf sample tube and homogenised. Solution was deposited on a stainless steel sample plate and the solvent allowed to evaporate. Spectrum acquisitions were conducted on a Bruker UltraFlex MALDI-TOF MS with SCOUT-MTP Ion source (Bruker Daltonics, Bremen) equipped with a N_2-laser (337 nm), a gridless ion source and a reflector. All spectra were acquired using a reflector-positive method with an acceleration voltage of 25 kV and a reflector voltage of 26.3 kV. The detector mass range was set to exclude everything under 1000 Da in order to exclude high intensity peaks from the lower mass range. A total of 1000 shots were performed per sample and the laser intensity was set to the lowest possible value for acquisition of high resolution spectra. The instrument was calibrated using SpheriCal™ calibrants purchased from Polymer Factory Sweden AB. The obtained spectra were analysed with FlexAnalysis Bruker Daltonics, Bremen, version 2.2.

Elemental microanalysis: Recorded on a Thermo FlashEA 1112 series CHNSO elemental analyser.

Size Exclusion Chromatography (SEC): Carried out using a Malvern Viscotek SEC Max equipped with a GPCmax VE2001 autosampler, two Viscotek T6000 columns (and a guard column), a refractive index detector VE3580 and a 270 Dual Detector (light scattering and viscometer) A mobile phase of THF containing 2%

triethylamine (v/v) at 35 °C, or DMF containing 0.01 M LiBr at 60 °C, was used as the eluent, with a flow rate of 1mL min^{-1}.

Dynamic light scattering (DLS): Measurements were carried out using a Malvern Zetasizer Nano ZS (4 mW He-Ne laser; wavelength 633 nm), at 25 °C using plastic disposable cuvettes for aqueous dispersions.

Transmission electron microscopy (TEM): Images were recorded using a Hitachi S-4800 FE-SEM at 20 kV. 10 µL of aqueous nanoparticle suspension was pipetted directly onto a Cu (holey carbon) 400 mesh 3 mm TEM grid (Agar Scientific) and blotted with filter paper.

Synthesis

Isopropylidene-2,2-bis(methoxy)propionic Acid **[$Acet_1$-G_1-COOH]**. 2,2-Bis(hydroxymethyl)-propionic acid (bis-MPA) (100 g, 0.746 mol, 1 equiv.), 2,2-dimethoxypropane (116.7 g, 137.24 mL, 1.12 mol, 1.5 equiv.), and *p*-toluenesulfonic acid monohydrate (7.09 g, 37.0 mmol, 0.05 equiv.) were added to 500 mL of acetone. The reaction mixture was stirred for 2 hours at ambient temperature (clear, colourless). After this time, the catalyst was neutralised by addition of 10 mL NH_4OH:EtOH (1:1 mixture), resulting in salt precipitation. The product was obtained by removal of acetone *in vacuo*, dissolving the crude solid in CH_2Cl_2 (750 mL), washing the organic layer twice with distilled water (2 x 300 mL), drying over $MgSO_4$ and evaporating to dryness. Yield: 100.86 g, white solid, (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (s, 3H), 1.42 (s, 3H), 1.45 (s, 3H), 3.68 (d, *J* = 12.1 Hz, 2H), 4.20 (d, *J* = 12.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.47, 21.92, 25.18, 41.86, 65.86, 98.43, 180.31. This compound was prepared by the procedure reported by Ihre *et al.*[1] Spectroscopic data agreed with those reported.

Isopropylidene-2,2-bis(methoxy)propionic Anhydride **[$Acet_2$-G_1-Anhy]**. [$Acet_1$-G_1-COOH] (88.94 g, 0.511 mol, 1 equiv.) and N,N'-Dicyclohexylcarbodiimide (DCC) (52.68 g, 0.255 mol, 0.50 equiv.) were added to 500 mL of CH_2Cl_2. The reaction mixture was stirred at ambient temperature for 48 hours. The precipitated N,N'-dicyclohexylurea (DCU) byproduct was removed by filtration and washed with a small volume of CH_2Cl_2. The crude product was purified by precipitating the filtrate into 2.5 L of cold hexane (cooled with dry ice bath) with vigorous stirring. Yield: 84.18 g, white viscous oil, (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 3H), 1.40 (s, 3H), 1.44 (s, 3H), 3.69 (d, *J* = 12.1 Hz, 4H), 4.21 (d, *J* = 12.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.70, 21.73, 25.56, 43.59, 65.64, 98.42, 169.57. This compound was prepared from [$Acet_1$-G_1-COOH] according to the procedure reported by Malkoch *et al.*[2] Spectroscopic data agreed with those reported.

General esterification procedure for divergent dendron growth, [$Acet_1$-G_1-TSe]. [$Acet_1$-G_1-Anhy] (41.88 g, 127 mmol, 1.3 equiv.), *para*-toluene sulfonyl ethanol (*p*-TSe) (19.53 g, 98 mmol, 1 equiv.) and 4-dimethylaminopyridine (DMAP) (2.38 g, 20 mmol, 0.2 equiv.) were dissolved in anhydrous pyridine (40 mL, 5 equiv. per OH-group) and anhydrous CH_2Cl_2 (120 mL 1:3 ratio of pyridine:CH_2Cl_2 (v/v)) under a nitrogen atmosphere. The reaction was left to stir at ambient temperature for 16 hours, monitoring the reaction using TLC to confirm the loss of the starting alcohol. Following this, approximately 40 mL of distilled water was added and stirred vigorously at ambient temperature for an additional 2 hours to quench the excess anhydride. The product was isolated by diluting the mixture with CH_2Cl_2 (1 L) and washing with 1 M $NaHSO_4$ (3 x 400 mL), 1M $NaHCO_3$

(3 x 400 mL), and brine (1 x 400 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. Residual solvent was removed under high vacuum overnight. Purification by liquid chromatography on silica was not required for the isolation of [$Acet_1$-G_1-TSe]. Yield: 33.69 g, colourless viscous oil, (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (s, 3H), 1.35 (s, 3H), 1.41 (s, 3H), 2.46 (s, 3H), 3.45 (t, 2H, *J* = 6.2 Hz), 3.56 (d, 2H, *J* = 11.9 Hz), 4.06 (d, 2H, *J* = 11.9 Hz), 4.45 (t, 2H, *J* = 6.2 Hz), 7.38 (d, 1H, *J* = 7.9 Hz), 7.81 (d, 1H, *J* = 7.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.26, 21.62, 22.12, 25.09, 41.69, 55.06, 58.03, 65.75, 98.05, 128.17, 130.11, 136.14, 145.28, 173.72. Calcd: $[MH]^+$ ($C_{17}H_{25}O_6S$) = 357.13 Da. Found: CI-MS: $[MH]^+$ = 357.14 Da. Anal. Calcd for $C_{17}H_{24}O_6S$: C, 57.28; H, 6.79; S, 9.00. Found: C, 57.30; H, 6.81; S, 8.89.

General deprotection procedure for removal of acetonide protecting groups, [$(OH)_2$-G_1-TSe]. DOWEX 50W-X2 (approx. 6 g) was added to a solution of [$Acet_1$-G_1-TSe] (34.73 g, 97 mmol, 1 equiv.) in methanol (350 mL) and allowed to stir at 50 °C for 3 hours. The deprotection was monitored by TLC until total disappearance of the starting material resulted. Once complete, the resin was filtered off and the solution evaporated to dryness. Residual solvent was removed under high vacuum overnight. Yield: 30.49 g, white crystals, (99%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.05 (s, 3H), 2.47 (s, 3H), 3.15 (s, br, 1H), 3.44 (t, 2H, *J* = 5.8 Hz), 3.73 (d, 2H, *J* = 11.6 Hz), 3.85 (d, 2H, *J* = 11.6 Hz), 4.53 (t, 2H, *J* = 5.8 Hz), 7.39 (d, 2H, *J* = 8.0 Hz), 7.80 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, CD_3OD): δ = 17.06, 21.74, 49.65, 55.14, 57.42, 67.96, 128.07, 130.22, 135.55, 145.57, 175.22. Calcd: $[M+Na]^+$ ($C_{14}H_{20}NaO_6S$) = 339.10 Da. Found: ESI-MS: $[M+Na]^+$ = 339.10 Da. Anal. Calcd for $C_{14}H_{20}O_6S$: C, 53.15; H, 6.37; S, 10.14. Found: C, 53.29; H, 6.44; S, 10.01.

[$Acet_2$-G_2-TSe]. [$(OH)_2$-G_1-TSe] (14.73 g, 46.56 mmol, 1 equiv.), DMAP (2.56 g, 20.95 mmol, 0.45 equiv.), [$Acet_2$-G_1-Anhy] (46.15 g, 139.68 mmol, 3 equiv.), 38 mL pyridine and 114 mL CH_2Cl_2 were reacted according to the general esterification procedure, resulting in a viscous colourless oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (10:90) increasing the polarity to EtOAc:hexane (50:50). Yield: 26.35 g, colourless viscous oil, (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (s, 6H), 1.17 (s, 3H), 1.34 (s, 6H), 1.41 (s, 6H), 2.46 (s, 3H), 3.45 (t, 2H, *J* = 6.2 Hz), 3.61 (d, 4H, *J* = 11.9 Hz), 4.13 (d, 4H, *J* = 11.9 Hz), 4.18 (d, 2H, *J* = 11.1 Hz), 4.21 (d, 2H, *J* = 11.1 Hz), 4.45 (t, 2H, *J* = 6.2 Hz), 7.38 (d, 2H, *J* = 8.1 Hz), 7.80 (d, 2H, *J* = 8.1 Hz).^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.37, 18.42, 21.65, 25.68, 42.09, 46.64, 54.83, 58.32, 65.06, 65.98, 65.98, 98.09, 128.05, 130.20, 136.24, 145.24, 171.98, 173.46. Calcd: $[M+Na]^+$ ($C_{30}H_{44}NaO_{12}S$) = 651.73 Da. Found: ESI-MS: $[M+Na]^+$ = 651.20 Da. Anal. Calcd for $C_{30}H_{44}O_{12}S$: C, 57.31; H, 7.05; S, 5.10. Found: C, 58.10; H, 7.16; S, 4.72.

[$(OH)_4$-G_2-TSe]. DOWEX 50W-X2 (approx. 5 g) and [$Acet_2$-G_2-TSe] (25.26 g, 40.18 mmol, 1 equiv) dissolved in methanol (250 mL) was reacted according to the general deprotection procedure. Yield: 20.72 g, white crystals, (99%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.13 (s, 9H), 2.46 (s, 3H), 3.58 (s, 2H), 3.66 (d, 4H, *J* = 10.8 Hz), 3.69 (d, 4H, *J* = 10.8 Hz), 4.09 (d, 2H, *J* = 11.2 Hz), 4.14 (d, 2H, *J* = 11.2 Hz), 4.43 (t, 2H, *J* = 5.6 Hz), 7.47 (d, 2H, *J* = 8.2 Hz), 7.82 (d, 2H, *J* = 8.2 Hz). ^{13}C NMR (100 MHz, CD_3OD): δ = 17.32, 18.46, 21.54, 25.56, 42.05, 46.66, 54.90, 58.35, 65.06, 66.00, 98.04, 128.15, 130.07, 136.20, 145.22, 172.06, 173.40. Calcd: $[M+Na]^+$ ($C_{24}H_{36}NaO_{12}S$) = 571.18 Da. Found: ESI-MS: $[M+Na]^+$ = 571.20 Da. Anal. Calcd for $C_{24}H_{36}O_{12}S$: C, 52.54; H, 6.61; S, 5.84. Found: C, 52.49; H, 6.56; S, 5.31.

[Acet$_4$-G$_3$-TSe]. **[**(OH)$_4$-G$_2$-TSe] (5.89 g, 11 mmol, 1 equiv.), DMAP (0.81 g, 7 mmol, 0.62 equiv.), [Acet$_2$-G$_1$-Anhy] (21.27 g, 64 mmol, 6 equiv.), 53 mL pyridine and 160 mL CH_2Cl_2 were reacted according to the general esterification procedure, resulting in a viscous colourless oil that was purified by liquid chromatography on silica, eluted from EtOAc:hexane (20:80) increasing the polarity to EtOAc:hexane (60:40). Yield: 12.46 g, colourless viscous oil, (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 12H), 1.18 (s, 3H), 1.27 (s, 6H), 1.35 (s, 12H), 1.41 (s, 12H), 2.46 (s, 3H), 3.46 (t, 2H, *J* = 6.0 Hz), 3.6 (d, 8H, *J* = 12.1 Hz) 4.08-4.22 (m, 12H), 4.25-4.35 (m, 8H), 4.48 (t, 2H, *J* = 6.0 Hz), 7.39 (d, 2H), 7.82 (d, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.25, 17.68, 18.44, 21.67, 22.01, 25.20, 42.05, 46.63, 46.93, 54.74, 58.32, 64.95, 65.76, 65.93, 65.98, 98.07, 128.15, 130.13, 136.23, 145.11, 171.67, 171.88, 173.47. Calcd: $[M+Na]^+$ ($C_{56}H_{84}NaO_{24}S$) = 1195.50 Da. Found: ESI-MS: $[M+Na]^+$ = 1195.50 Da. Anal. Calcd for $C_{56}H_{84}O_{24}S$: C, 57.32; H, 7.22; S, 2.73. Found: C, 57.33; H, 7.18; S, 2.35.

[(OH)$_8$-G$_3$-TSe]. DOWEX 50W-X2 (approx. 4 g) and [Acet$_4$-G$_3$-TSe] (22.66 g, 19 mmol, 1 equiv) dissolved in methanol (300 mL) was reacted according to the general deprotection procedure. Yield: 19.44 g, white crystals, (99%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.17 (s, 15H), 1.30 (s, 6H), 2.49 (s, 3H), 3.56- 3.73 (m, 18H), 4.14-4.38 (m, 12H), 4.49 (t, 2H, *J* = 5.5 Hz), 7.51 (d, 2H), 7.87 (d, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ = 17.40, 17.71, 18.35, 21.61, 47.74, 47.88, 51.91, 55.75, 59.77, 65.91, 66.15, 67.06, 129.38, 131.30, 138.01, 146.83, 173.33, 173.70, 175.97. Calcd: $[M+Na]^+$ ($C_{44}H_{68}NaO_{24}S$) = 1035.37 Da. Found: ESI-MS: $[M+Na]^+$ = 1035.40 Da. Anal. Calcd for $C_{44}H_{68}O_{24}S$: C, 52.17; H, 6.77; S, 3.17. Found: C, 51.97; H, 6.65; S, 3.15.

2-((Ethoxycarbonothioyl)thio)acetic acid **[Xan-COOH]**. Potassium ethyl xanthogenate (53.06 g, 331 mmol) was stirred in acetone (400 mL). A solution of 2-bromoacetic acid (38.35 g, 276 mmol) in acetone (100 mL) was added dropwise over 20 minutes. The reaction was left to stir overnight at ambient temperature. The precipitated potassium bromide by-product was filtered off and washed with a small volume of acetone. The solvent was removed under vacuum. The residue was then diluted in CH_2Cl_2 (300 mL) and washed with brine (3 x 100 mL). The organic phase was dried over $MgSO_4$ and evaporated to give [Xan-COOH] as a pale yellow solid. Yield: 36.35g (73%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (t, 3H, *J* = 7.2 Hz), 3.96 (s, 2H), 4.66 (q, 2H, *J* = 7.2 Hz), 9.12 (s, 1H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.79, 37.56, 70.99, 174.13, 212.0.

2-((Ethoxycarbonothioyl)thio)acetic anhydride **[Xan-Anhy]**. [Xan-COOH] (27.53 g, 152 mmol, 1 equiv.) was dissolved in 100 mL CH_2Cl_2. A solution N,N′-Dicyclohexylcarbodiimide (DCC) (20.76 g, 101 mmol, 0.5 equiv.) in CH_2Cl_2 was slowly added to the mixture, and the reaction allowed to stir at ambient temperature overnight. The reaction was monitored by ^{13}C NMR. Determination of reaction completion resulted by the appearance of the anhydride carbonyl carbon at 163 ppm and the disappearance of the acid carbonyl carbon at 174 ppm. The dicyclohexylurea (DCU) by-product was removed by filtration, washed with a small volume of CH_2Cl_2 and the solvent evaporated under vacuum. Yield: 26.00 g, yellow solid, (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (t, 6H, *J* = 7.1 Hz) 4.07 (s, 4H), 4.67 (q, 4H, *J* = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.64, 38.51, 71.28, 163.04, 211.44.

General procedure for functionalisation with Xanthate surface groups using anhydride chemistry, [Xan$_8$-G$_3$-TSe]. This compound was prepared by the procedure reported by Auty *et al.*[3] [(OH)$_8$-G$_3$-TSe] (7.24 g, 7 mmol,

1 equiv.) and DMAP (1.40 g, 11 mmol, 1.6 equiv.) were dissolved in anhydrous pyridine (40 mL). After cooling the mixture in an ice bath, [Xan-Anhy] (25.41 g, 74 mmol, 10.4 equiv.) in anhydrous CH_2Cl_2 (80 mL) was added slowly under a nitrogen atmosphere. After stirring at ambient temperature for 16 hours, approximately 15 mL of distilled water was added and stirred vigorously at ambient temperature for an additional 2 hours to quench the excess anhydride. The product was isolated by diluting the mixture with CH_2Cl_2 (350 mL) and washing with 1 M $NaHSO_4$ (3 x 1200 mL), 1M $NaHCO_3$ (3 x 200 mL), and brine (1 x 200 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. Purification by liquid chromatography on silica, eluted from EtOAc:hexane (15:85) increasing the polarity to EtOAc:hexane (50:50). Residual solvent was removed under high vacuum overnight. Yield: 10.10 g, orange viscous oil, (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20-1.30 (m, 21H), 1.42 (t, 24H, *J* = 7.2 Hz), 2.47 (s, 3H), 3.47 (t, 2H, *J* = 5.8 Hz), 3.94 (s, 16H), 4.16-4.36 (m, 28H), 4.49 (t, 2H, *J* = 5.8 Hz), 4.64 (q, 16H, *J* = 7.2 Hz) 7.40 (d, 2H), 7.81 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.67, 17.28, 17.63, 17.89, 21.73, 37.64, 46.27, 46.51, 46.75, 54.71, 58.35, 65.44, 66.23, 70.82, 128.15, 130.26, 136.39, 145.22, 167.46, 171.48, 171.63, 171.68, 212.71. Calcd: $[M+Na]^+$ ($C_{84}H_{116}NaO_{40}S_{17}$) = 2331.22 Da. Found: MALDI-TOF MS: $[M+Na]^+$ = 2331.42 Da. Anal. Calcd for $C_{84}H_{116}O_{40}S_{17}$: C, 43.66; H, 5.06; S, 23.59. Found: C, 44.01; H, 5.04; S, 23.86.

General procedure for deprotection of *para*-toluene sulfonyl ester (TSe) - 1,8- diazabicyclo[5.4.0]undec-7-ene (DBU) (1.3 equiv.) added to xanthate functional dendron dissolved in anhydrous CH_2Cl_2. The reaction was stirred under a nitrogen atmosphere for 16 hours and monitored by using TLC (40:60 ethyl acetate:hexane). The product was isolated by diluting the mixture with CH_2Cl_2 (100 mL) and washing with 1 M $NaHSO_4$ (2 x 100 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The product was then precipitated three times into hexane:ethyl acetate (9:1). Any residual solvent was removed under high vacuum to yield a viscous oil.

[Xan_8-G_3-COOH]. The removal of the *para*-toluene sulfonyl (*p*-TSe) protecting group was carried out as described above with [Xan_8-G_3-TSe] (9.07 g, 3.93 mmol, 1.0 equiv), and DBU (0.76 mL, 5.10 mmol, 1.3 equiv). Yield: 7.97 g, orange viscous oil (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 12H), 1.29 (s, 6H), 1.35 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 24H), 3.95 (s, 16H), 4.21-4.36 (m, 28H), 4.64 (q, *J* = 7.1 Hz, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.70, 17.98, 37.70, 46.41, 66.30, 70.91, 167.70, 171.65, 172.95, 212.57. Calcd: $[M+Na]^+$ ($C_{75}H_{106}NaO_{38}S_{16}$) m/z = 2149.19. Found MALDI-TOF: $[M+Na]^+$ m/z = 2151.7. Anal. Calcd for $C_{75}H_{106}O_{38}S_{16}$: C, 42.32; H, 5.02; S, 28.56. Found: C, 43.15; H, 5.09; S, 23.79.

2-Hydroxyethyl-2-bromoisobutyrate, **[HEBiB]**. Ethylene glycol (272 mL, 4.85 mol, 50 equiv.) and triethylamine (TEA) (28 mL, 0.20 mol, 2 equiv.) were dissolved in anhydrous THF (100 mL). α-Bromoisobutyryl bromide (12 mL, 97.1 mmol, 1 equiv.) was added dropwise over 30 minutes whilst cooling with an ice bath. The reaction was left to stir at ambient temperature under a nitrogen atmosphere for 16 hours. The product was isolated by pouring the crude mixture into distilled water (800 mL) and extracting the aqueous phase with CH_2Cl_2 (6 x 100 mL). The combined organic layers were washed with 1 M HCl (pH 4) (2 x 300mL), dried over $MgSO_4$ and evaporated to dryness. Residual solvent was removed under high vacuum overnight. Yield: 15.64 g, pale yellow oil, (76%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (s, 6H), 3.88 (t, *J* = 4.7 Hz, 2H), 4.32 (t, *J* = 4.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.70, 55.86, 60.82, 67.47, 171.94. Calcd: $[M+NH_4]^+$

($C_6H_{15}BrNO_3$) m/z = 228.02. Found: CI MS: $[M+NH_4]^+$ m/z = 228.02. Anal. Calcd for $C_6H_{11}BrO_3$: C, 34.14; H, 5.25. Found: C, 34.63; H, 5.30. This compound was prepared by Jakubowski *et al.*[4] The above spectroscopic data agreed with that reported.

4-(Dimethylamino)pyridinium *p*-toluenesulfonate **[DPTS]** – *p*-toluenesulfonic acid monohydrate (7.80 g, 41 mmol, 1 equiv) was dried by azeotropic distillation with 50 mL anhydrous toluene using a dean-stark head (approximately 4 hours). [Note: the solution turned dusty pink during the loss of water]. Following this, the mixture was cooled to 60 °C and 4-dimethylaminopyridine (DMAP) (5 g, 41 mmol, 1 equiv.) in 30 mL of anhydrous toluene at 60 °C added slowly. An off-white precipitate immediately formed upon addition, and the solution was left to stir at 60 °C for 1 hour. The mixture was then cooled and filtered to yield DPTS. The product was recrystallised once from 1,2-dichloroethane to yield white crystals. Yield: 11.83 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 3.17 (s, 6H), 6.76 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 8.16 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.34, 40.15, 106.86, 126.00, 128.72, 139.49, 142.76, 157.26. Anal. Calcd for $C_{14}H_{18}N_2O_3S$: C, 57.12; H, 6.16; N, 9.52; S, 10.89. Found: C, 57.30; H, 6.12; N, 9.51; S, 10.84. This compound was prepared by the procedure reported by Moore and Stupp. The above spectroscopic data agreed with that reported.[5]

General procedure for focal point modification to α-bromoisobutyrate moiety, [Xan_1-G_0-BiB]. **[**Xan-COOH] (2.42 g, 13 mmol, 1 equiv.), [HEBiB] (2.83 g, 13 mmol, 1 equiv.), and DPTS (4.33 g, 15 mmol, 1.1 equiv.) were dissolved in CH_2Cl_2 (anhydrous, 35 mL) under a nitrogen atmosphere. DCC (3.04 g, 15 mmol, 1.1 equiv.) in CH_2Cl_2 (anhydrous, 15 mL) was added and the reaction left to stir at ambient temperature for 16 hours. The precipitated DCU by-product was removed by filtration and the product isolated by diluting the mixture with CH_2Cl_2 (100 mL), washing with distilled water (2 x 100 mL) and brine (1 x 100 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was purified by liquid chromatography on silica, eluting from ethyl acetate:hexane (10:90), gradually increasing the polarity to ethyl acetate:hexane (30:70). Residual solvent was removed under high vacuum overnight. Yield: 3.74 g, yellow oil, (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 7.1 Hz, 3H), 1.94 (s, 6H), 3.96 (s, 2H), 4.41 (s, 4H), 4.65 (q, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.48, 30.36, 37.44, 55.09, 62.95, 70.43, 167.46, 171.10, 212.14. Calcd: $[M+Na]^+$ ($C_{11}H_{17}BrNaO_5S_2$) m/z = 394.97. Found: ESI-MS: $[M+Na]^+$ m/z = 395.0 Anal. Calcd for $C_{11}H_{17}BrO_5S_2$: C, 35.39; H, 4.59; S, 17.18. Found: C, 35.76; H, 4.57; S, 16.76.

[Xan_8-G_3-BiB]. **[**Xan_8-G_3-COOH] (3.98 g, 1.87 mmol, 1 equiv.), [HEBiB] (0.40 g, 1.87 mmol, 1 equiv.), DPTS (0.61 g, 2.06 mmol, 1.1 equiv.), DCC (0.42 g, 2.06 mmol, 1.1 equiv.) in anhydrous CH_2Cl_2 (40 mL) were reacted according to the general procedure for focal point modification resulting in a viscous orange oil that was purified by liquid chromatography on silica, eluting from ethyl acetate:hexane (15:85), gradually increasing the polarity to ethyl acetate:hexane (50:50). Yield: 2.47 g, orange viscous oil, (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 12H), 1.28 (s, 6H), 1.32 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 24H), 1.94 (s, 6H), 3.95 (s, 16H), 4.21-4.38 (m, 28H), 4.21 (s, 4H), 4.64 (q, *J* = 7.1 Hz, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.67, 17.89, 30.74, 37.64, 46.27, 55.48, 60.85, 66.21, 70.82, 167.46, 171.67, 212.71. Calcd: $[M+Na]^+$ ($C_{81}H_{115}BrNaO_{40}S_{16}$) m/z = 2341.17. Found:

MALDI-TOF: $[M+Na]^+$ m/z = 2341.4. Anal. Calcd for $C_{81}H_{115}BrO_{40}S_{16}$: C, 41.91; H, 4.99; S, 22.09. Found: C, 43.15; H, 5.14; S, 21.85.

Linear ATRP of *n*-butyl methacrylate (*n*-BuMA) in methanol with [Xan_1-G_0-BiB] and [Xan_8-G_3-BiB], targeting DP_n = 100 monomer units; G_0-p(*n*-BuMA)$_{100}$, G_3-p(*n*-BuMA)$_{100}$. In a typical synthesis, targeting DP_n = 100 monomer units for the primary chains, [Xan_1-G_0-BiB] (46 mg, 0.0702 mmol, 1 equiv.), *n*-BuMA (1 g, 7.03 mmol, 100 equiv.) and 2,2'-bipyridyl (bpy) (22 mg, 0.141 mmol, 2 equiv.) were placed into a 5 mL round-bottomed flask. Methanol was added (50 wt% based on *n*-BuMA; 2g, 2.6 mL) and the solution stirred and deoxygenated using a nitrogen purge for 30 minutes. Cu(I)Cl (7 mg, 0.0702 mmol, 1 equiv) was added to the flask, whilst maintaining a positive flow of nitrogen, and the solution left to polymerise at 60 °C. The reaction was terminated when conversion reached >95%, indicated by ^{1}H NMR after 21 hours, by exposure to oxygen and addition of THF. The solution was passed through a neutral alumina column to remove the catalytic system, and precipitated twice into cold petroleum ether (40-60 °C). After drying the precipitated sample overnight under high vacuum, the polymer was obtained as a white solid. This compound was prepared by the procedure reported by Hern *et al*.[6]

[PEG_{45}-BiB]. Monomethoxy poly(ethylene glycol) ($M_w \approx 2000$ g mol^{-1}) (10.25 g, 5.13 mmol, 1 equiv.) was dissolved in THF (anhydrous, 100 mL) at 40 °C, and degassed with dry N_2 for 20 minutes. DMAP (6.26 mg, 0.0512 mmol, 0.01 equiv.) and TEA (1.57 mL, 11 mmol, 2.2 equiv.) were added and the reaction cooled to 0 °C in an ice bath. α-Bromoisobutyryl bromide (1.27 mL, 10 mmol, 2 equiv.) was added dropwise over 20 minutes and a white precipitate immediately formed ($Et_3NH^+Br^-$ salt). After 24 hours, the precipitate was removed by filtration, THF removed and the crude material precipitated twice from acetone into petroleum ether (30-40 °C). ^{1}H NMR (400 MHz, D_2O): δ = 4.30-4.35 (m, 2H), 3.59-3.80 (m, 186H), 3.35 (s, 3H), 1.93 (s, 6H).

p(PEG_{45}-*b*-*n*-$BuMA_{100}$). In a kinetics study, targeting DP_n = 100 monomer units for the primary chains, [PEG_{45}-BiB] (0.302 g, 0.141 mmol, 1 equiv.), *n*-BuMA (2 g, 14 mmol, 100 equiv.) and bpy (44 mg, 0.282 mmol, 2 equiv.) were placed into a 10 mL round-bottomed flask. Methanol was added (50 wt% based on *n*-BuMA; 2g, 2.6 mL) and the solution stirred and deoxygenated using a nitrogen purge for 30 minutes. Cu(I)Cl (14 mg, 0.141 mmol, 1 equiv) was added to the flask, whilst maintaining a positive flow of nitrogen, and the solution left to polymerise at 60 °C. To determine the kinetics of the reaction, samples (~0.1 mL) were taken at regular intervals and analysed by ^{1}H NMR and SEC. The reaction was terminated when conversion reached >94%, indicated by ^{1}H NMR after 28 hours, by exposure to oxygen and addition of THF. The solution was passed through a neutral alumina column to remove the catalytic system, and precipitated twice into cold petroleum ether (40-60 °C). After drying the precipitated sample overnight under high vacuum, the polymer was obtained as a white solid.

General procedure for the co-initiated branched copolymerisation of *n*-BuMA and EGDMA with [Xan_1-G_0-BiB] and [PEG_{45}-BiB]; [$(G_0)_{0.01}$-$(PEG_{45})_{0.99}$]-p(*n*-$BuMA_{100}$-*co*-$EGDMA_{0.8}$), [$(G_0)_{0.075}$-$(PEG_{45})_{0.925}$]-p(*n*-$BuMA_{100}$-*co*-$EGDMA_{0.8}$), [$(G_0)_{0.1}$-$(PEG_{45})_{0.9}$]-p(*n*-$BuMA_{100}$-*co*-$EGDMA_{0.8}$). The co-initiated copolymerisation of *n*-BuMA and bifunctional monomer EGDMA was carried out with varying molar equivalents of [PEG_{45}-BiB]

and [Xan_1-G_0-BiB] (99:1, 92.5:7.5, 90:10). In a typical synthesis, targeting DP_n = 100 monomer units for the primary chains, [PEG_{45}-BiB], [Xan_1-G_0-BiB], *n*-BuMA (5 g, 35 mmol, 100 equiv.), bpy (110 mg, 0.703 mmol, 2 equiv.) and EGDMA (56 mg, 0.280 mmol, 0.8 equiv.) were placed into a 20 mL round-bottomed flask. Methanol was added (50 wt% based on *n*-BuMA, 5g, 7.5 mL) and the solution stirred and deoxygenated using a nitrogen purge for 30 minutes. Cu(I)Cl (35 mg, 0.352 mmol, 1 equiv) was added to the flask, whilst maintaining a positive flow of nitrogen, and the solution was left to polymerise at 60 °C. The reaction was terminated when conversion reached >98%, indicated by ^{1}H NMR after 70 hours, by exposure to oxygen and addition of THF. The solution was passed through a neutral alumina column to remove the catalytic system, and precipitated twice into cold petroleum ether (40-60 °C). After drying the precipitated sample overnight under high vacuum, the polymer was obtained as a white solid.

General procedure for the co-initiated branched copolymerisation of *n*-BuMA and EGDMA with [Xan_8-G_3-BiB] and [PEG_{45}-BiB]; [$(G_3)_{0.01}$-$(PEG_{45})_{0.99}$]-p(*n*-$BuMA_{100}$-*co*-$EGDMA_{0.8}$), [$(G_3)_{0.014}$-$(PEG_{45})_{0.986}$]-p(*n*-$BuMA_{100}$-*co*-$EGDMA_{0.8}$), [$(G_3)_{0.05}$-$(PEG_{45})_{0.95}$]-p(*n*-$BuMA_{100}$-*co*-$EGDMA_{0.8}$). The co-initiated copolymerisation of *n*-BuMA and bifunctional monomer EGDMA was carried out with varying molar equivalents of [PEG_{45}-BiB] and [Xan_8-G_3-BiB] (99:1, 98.6:1.4, 95:5). In a typical synthesis, targeting DP_n = 100 monomer units for the primary chains, [PEG_{45}-BiB], [Xan_8-G_3-BiB], *n*-BuMA (5 g, 35 mmol, 100 equiv.), bpy (110 mg, 0.703 mmol, 2 equiv.) and EGDMA (56 mg, 0.280 mmol, 0.8 equiv.) were placed into a 20 mL round-bottomed flask. Methanol was added (50 wt% based on *n*-BuMA, 5g, 7.5 mL) and the solution stirred and deoxygenated using a nitrogen purge for 30 minutes. Cu(I)Cl (35 mg, 0.352 mmol, 1 equiv.) was added to the flask, whilst maintaining a positive flow of nitrogen, and the solution was left to polymerise at 60 °C. The reaction was terminated when conversion reached >98%, indicated by ^{1}H NMR after 72 hours, by exposure to oxygen and addition of THF. The solution was passed through a neutral alumina column to remove the catalytic system, and precipitated twice into cold petroleum ether (40-60 °C). After drying the precipitated sample overnight under high vacuum, the polymer was obtained as a white solid.

4 nm GNP synthesis. Prepared by the Inverse Turkevich procedure reported by Piella *et al.*[7] Sodium citrate (2.2 mM, 150 mL), tannic acid (2.5 mM, 0.1 mL) and K_2CO_3 (150 mM, 1 mL) were stirred at 70°C, followed by addition of $HAuCl_4$ (25 mM, 1 mL), then allowed to react for 20 minutes with vigorous stirring. The solution was then cooled to ambient temperature and stored in polyethylene centrifuge tubes.

General procedure for the deprotection of peripheral xanthate groups of co-initiated HPDs, and subsequent nanoprecipitation and coordination of 4 nm GNPs. Peripheral xanthate groups of each polymer (200 mg, 1 equiv.) were deprotected with excess *n*-butylamine (10 equiv.) in THF (anhydrous, 2 mL) for 1.5 hours. The deprotected polymer was precipitated twice into hexane and dried under vacuum. The deprotected polymer was dissolved in acetone at an initial concentration of 5 mg/mL. The dissolved polymer was rapidly added to water with stirring at ambient temperature. The solvent was allowed to evaporate overnight to give nanoprecipitates with a final concentration of 1 mg/mL of polymer in water. A 1:9 ratio of polymer nanoprecipitates:4 nm GNPs was mixed and stirred for 24 hours, before imaging by TEM.

TEM preparation. TEM grids (3 mm, 400 mesh Cu(holey carbon)) were prepared by pipetting 10 µL of the polymer/GNP samples directly onto the carbon coated side of the grid, and immediately wicking away excess water with filter paper. The grids were allowed to dry for 24 hours before imaging.

1. H. Ihre, A. Hult, J. M. J. Fréchet en I. Gitsov, *Macromolecules*, 1998, **31**, 4061–4068.
2. M. Malkoch, E. Malmström en A. Hult, *Macromolecules*, 2002, **35**, 8307–8314.
3. S. E. R. Auty, O. C. J. Andrén, F. Y. Hern, M. Malkoch en S. P. Rannard, *Polym. Chem.*, 2014, **6**, 573–582.
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6. F. Y. Hern, S. E. R. Auty, O. C. J. Andren, M. Malkoch en S. P. Rannard, *Polym. Chem.*, 2017, **8**, 1644–1653.
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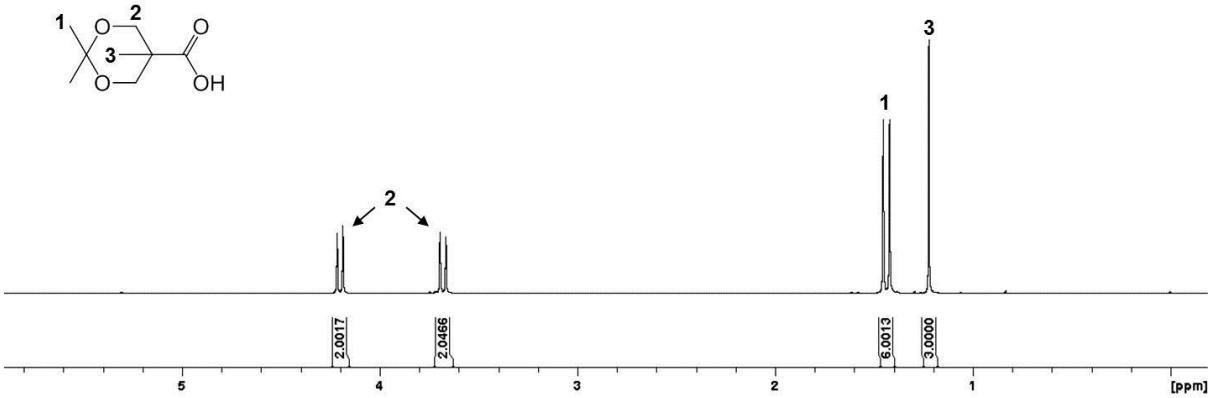


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of **[Acet$_1$-G$_1$-COOH]**

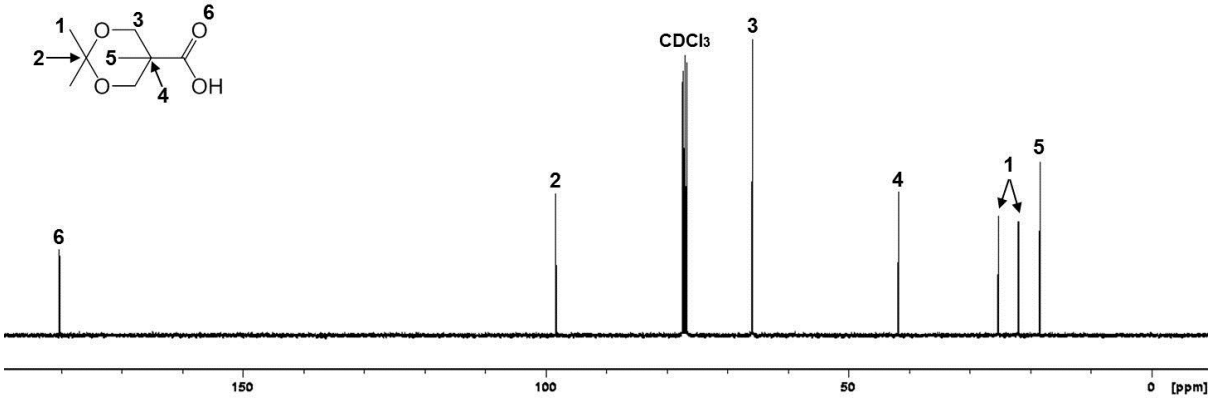


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) of **[Acet$_1$-G$_1$-COOH]**

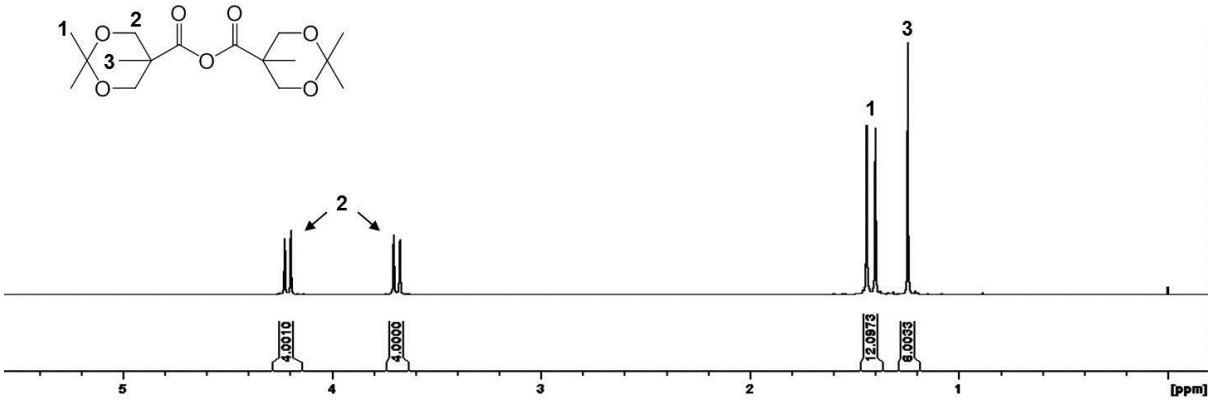


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of **[Acet$_1$-G$_1$-Anhy]**

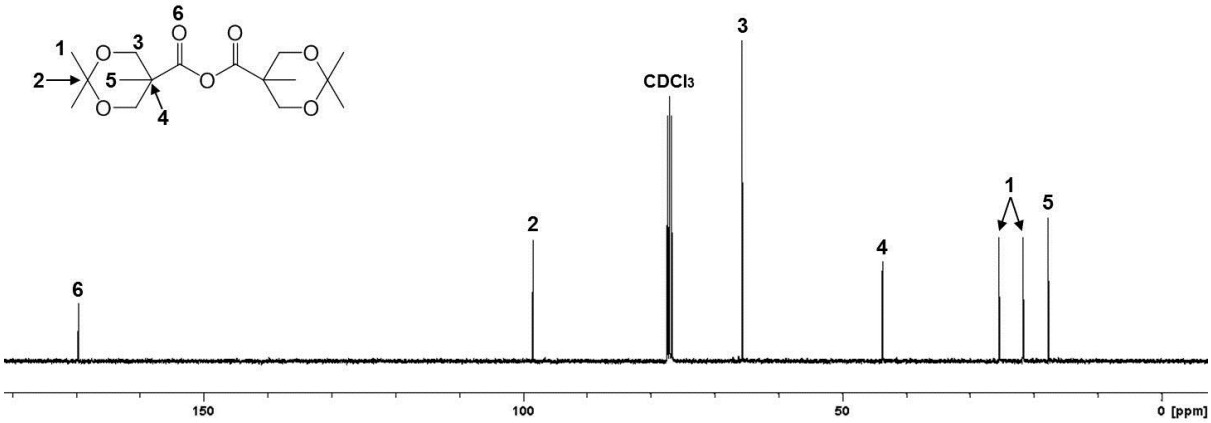


Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) of **[Acet$_1$-G$_1$-Anhy]**

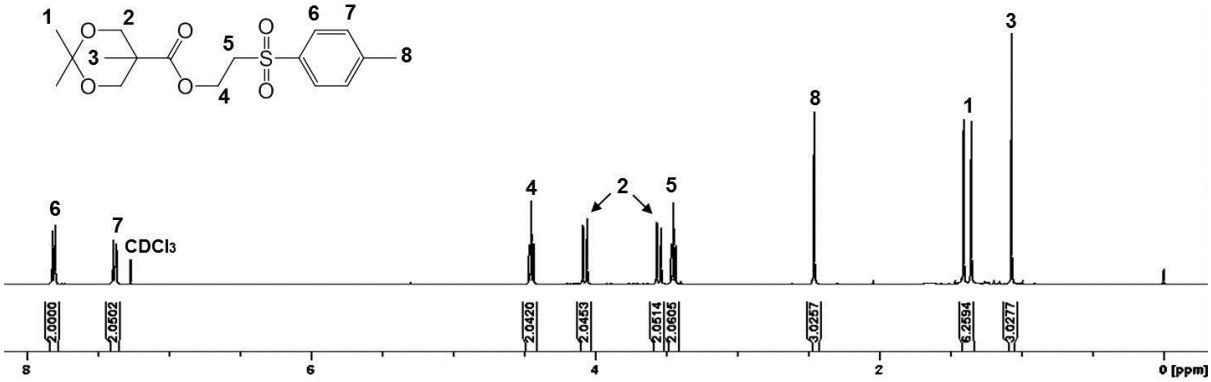


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of **[Acet$_1$-G$_1$-TSe]**

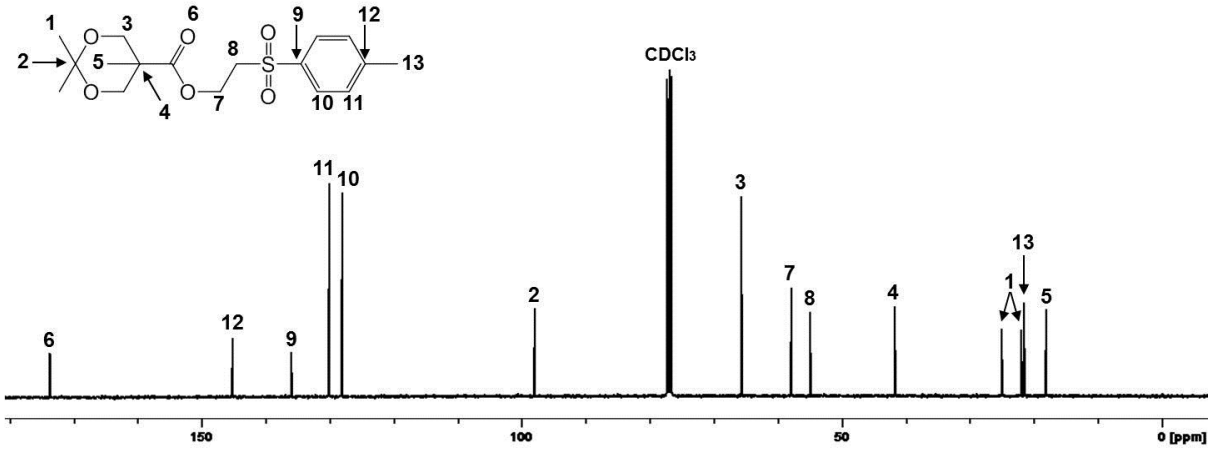


Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$) of **[Acet$_1$-G$_1$-TSe]**

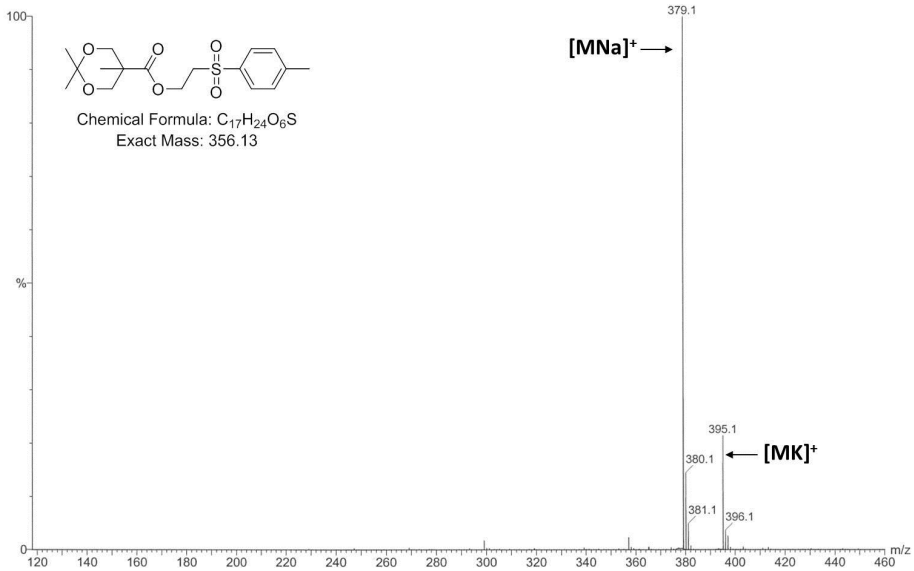


Figure S7. ESI MS (MeOH) of **[Acet$_1$-G$_1$-TSe]**

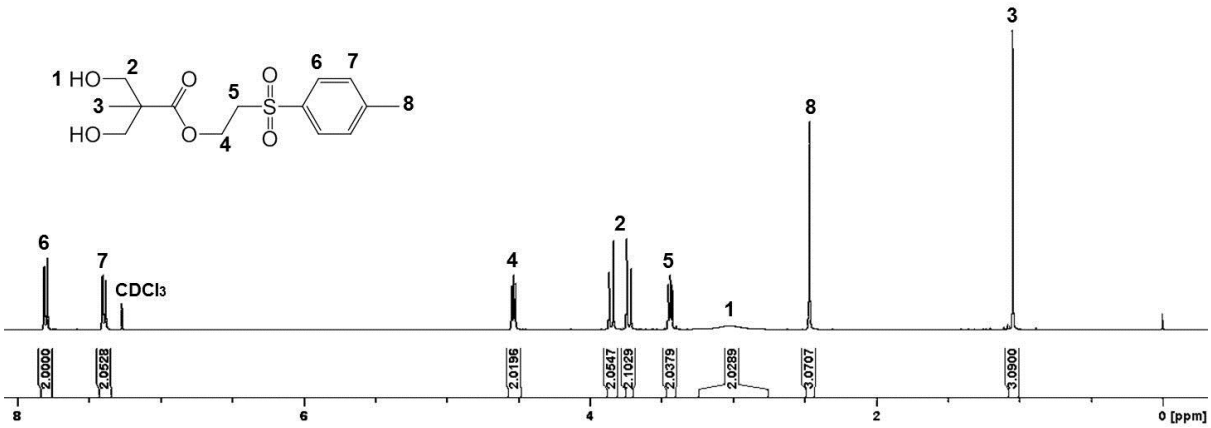


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of **[(OH)$_2$-G$_1$-TSe]**

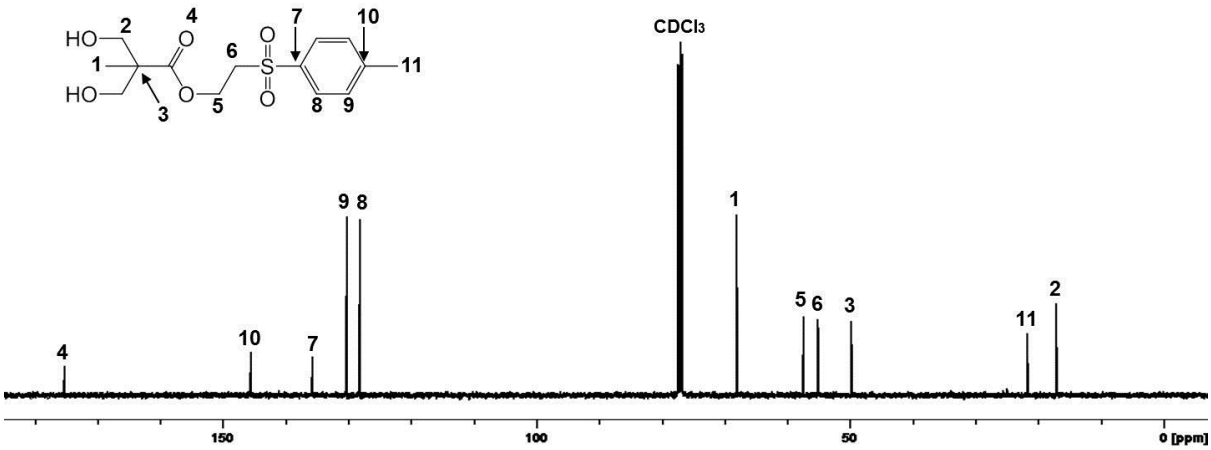


Figure S9. ^{13}C NMR (100 MHz, $CDCl_3$) of **[(OH)$_2$-G$_1$-TSe]**

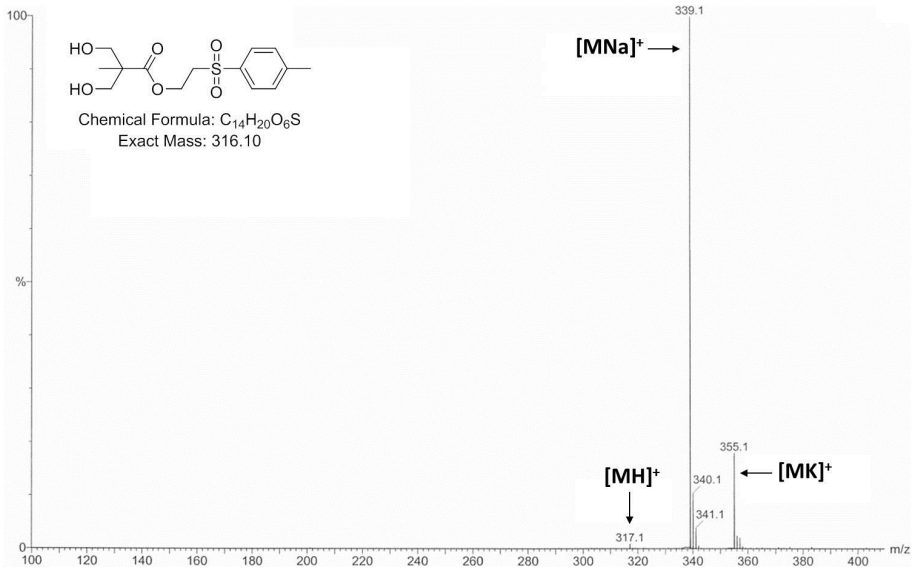


Figure S10. ESI MS (MeOH) of **[(OH)$_2$-G$_1$-TSe]**

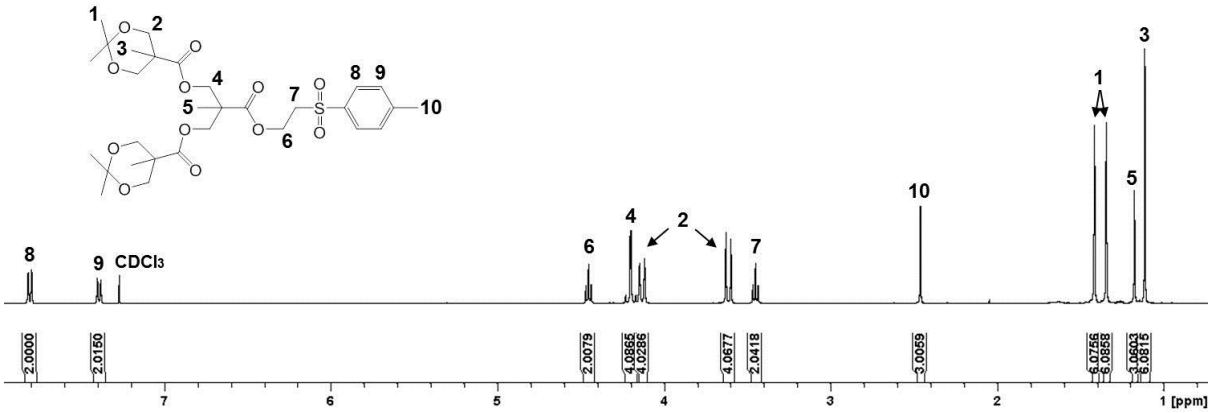


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of **[Acet$_2$-G$_2$-TSe]**

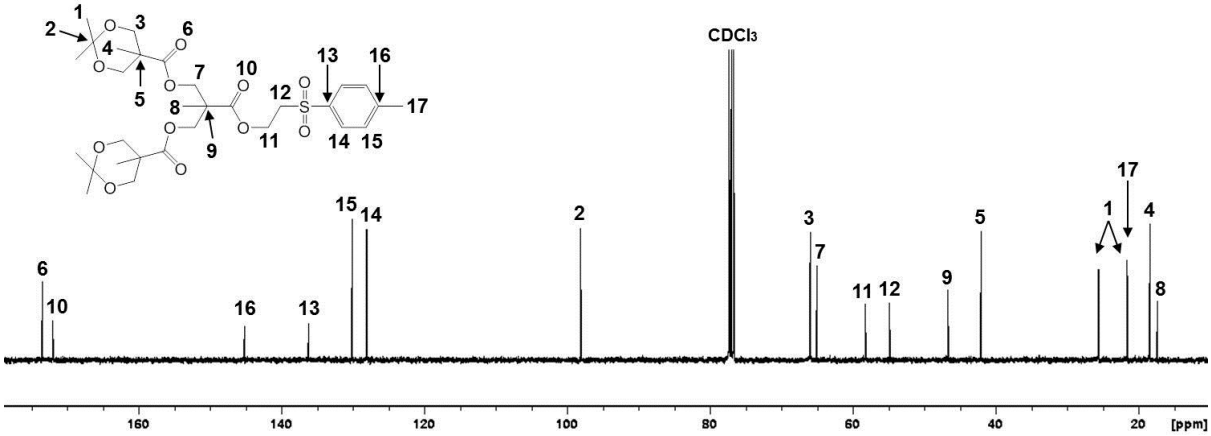


Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) of **[Acet$_2$-G$_2$-TSe]**

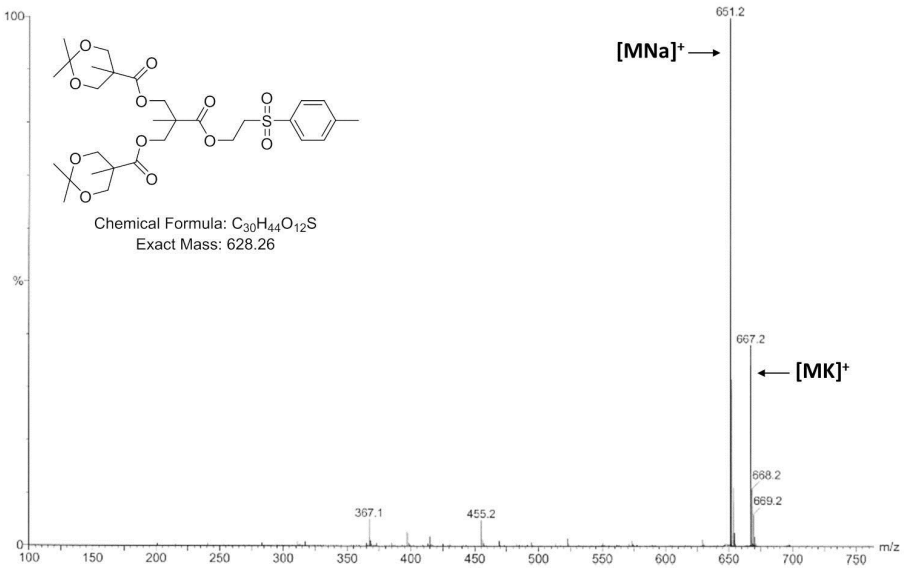


Figure S13. ESI MS (MeOH) of **[Acet$_2$-G$_2$-TSe]**

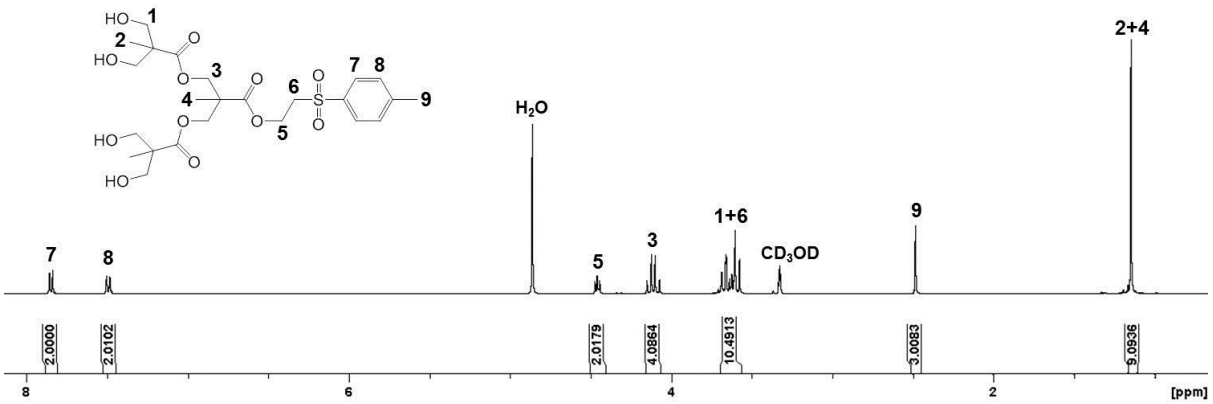


Figure S14. ^{1}H NMR (400 MHz, CD_3OD) of **[(OH)$_4$-G$_2$-TSe]**

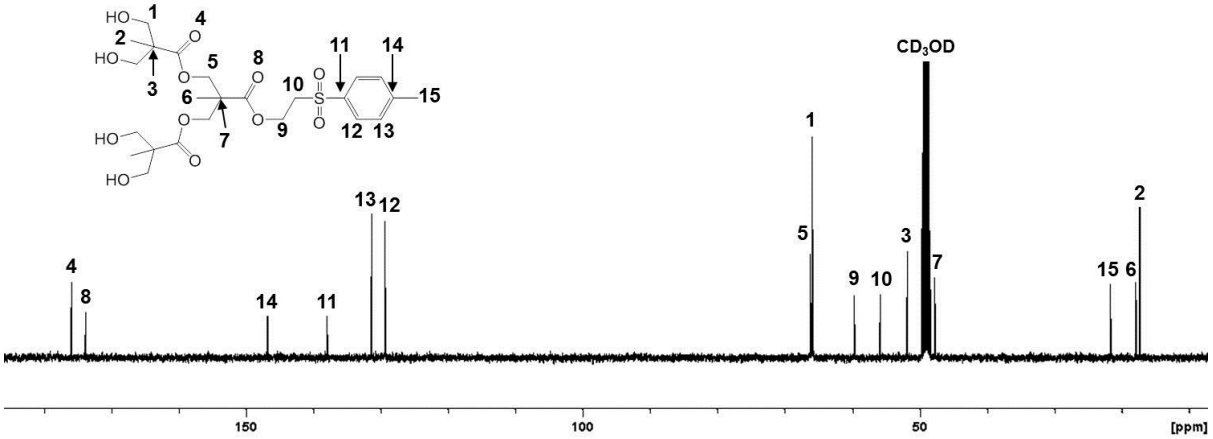


Figure S15. ^{13}C NMR (100 MHz, CD_3OD) of **[(OH)$_4$-G$_2$-TSe]**

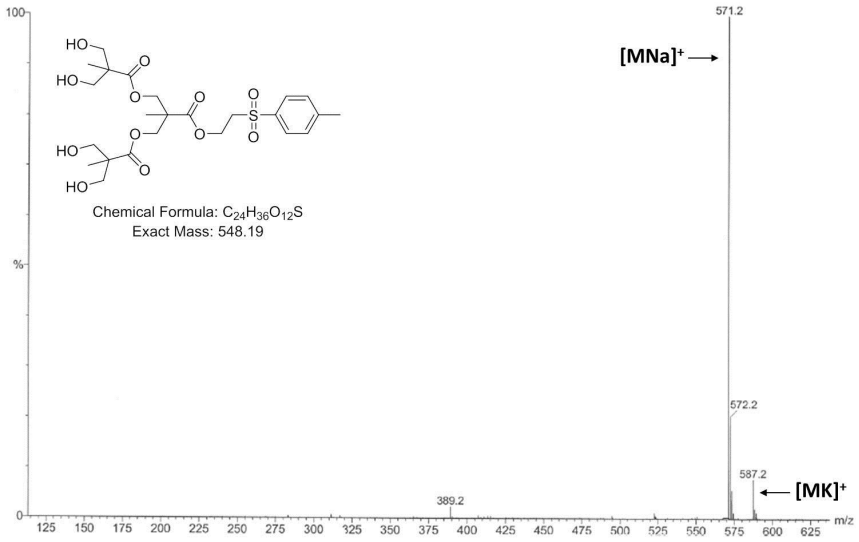


Figure S16. ESI MS (MeOH) of **[(OH)$_4$-G$_2$-TSe]**

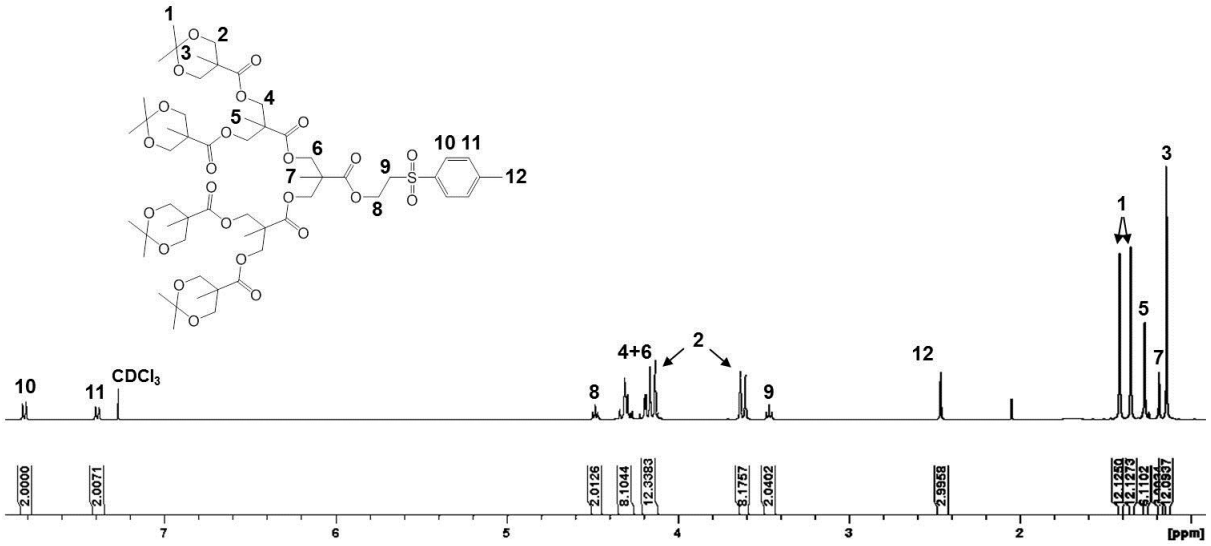


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) of **[Acet$_4$-G$_3$-TSe]**

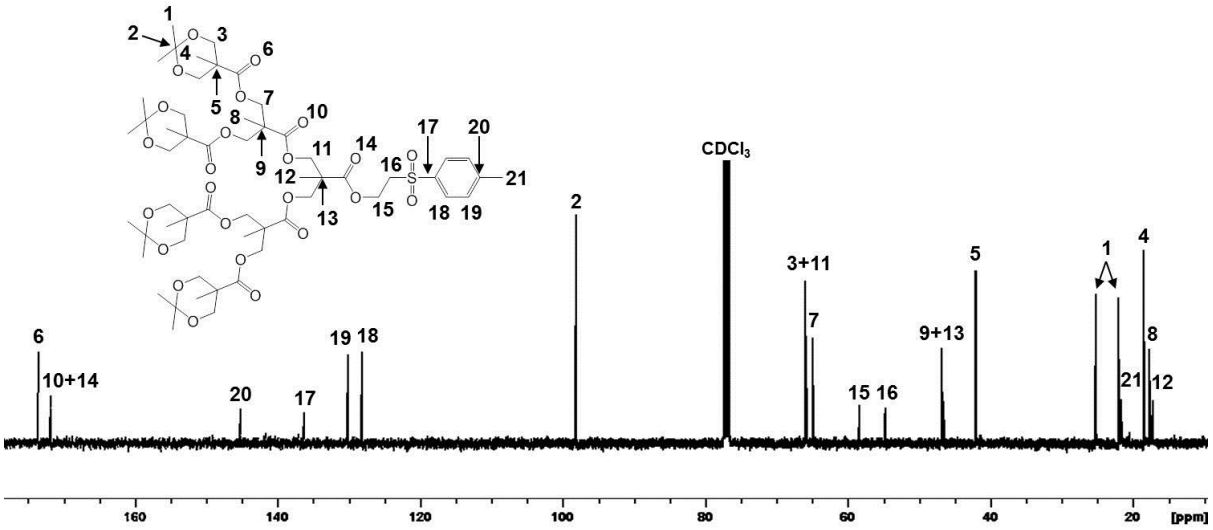


Figure S18. ^{13}C NMR (100 MHz, $CDCl_3$) of **[Acet$_4$-G$_3$-TSe]**

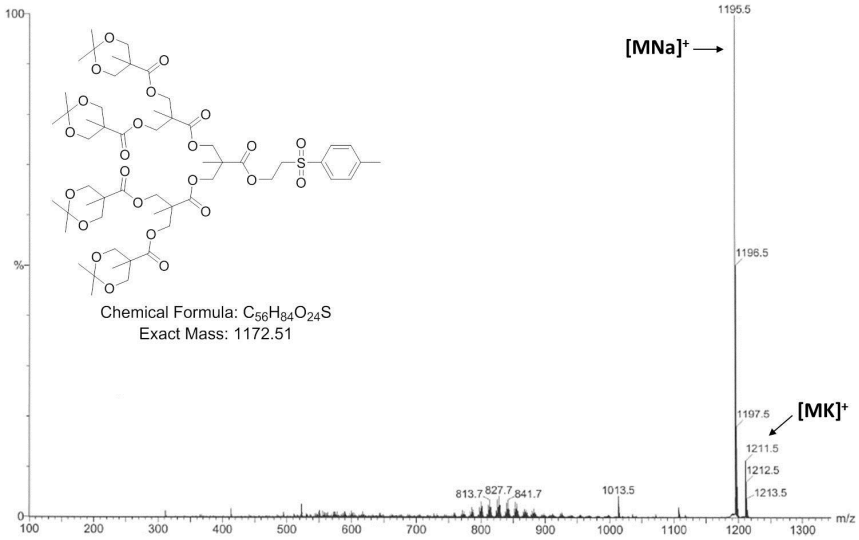


Figure S19. ESI MS (MeOH) of **[Acet$_4$-G$_3$-TSe]**

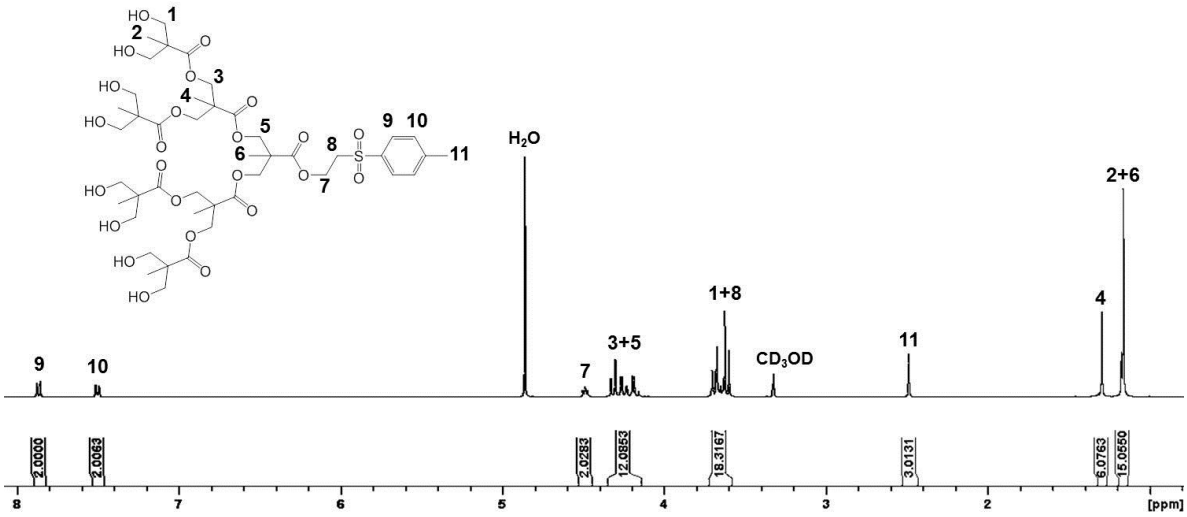


Figure S20. ^{1}H NMR (400 MHz, CD_3OD) of **[(OH)$_8$-G$_3$-TSe]**

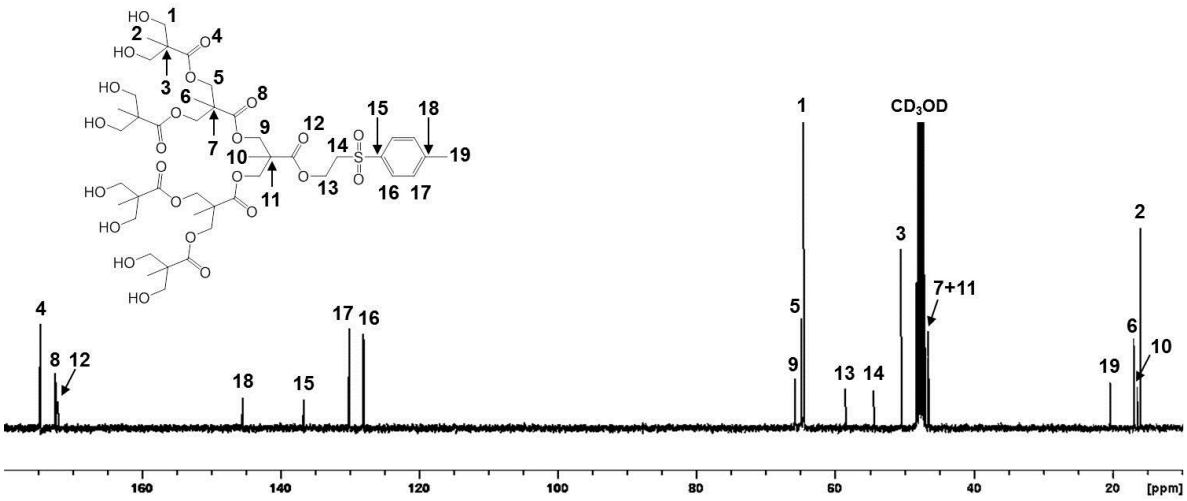


Figure S21. ^{13}C NMR (100 MHz, CD_3OD) of **[(OH)$_8$-G$_3$-TSe]**

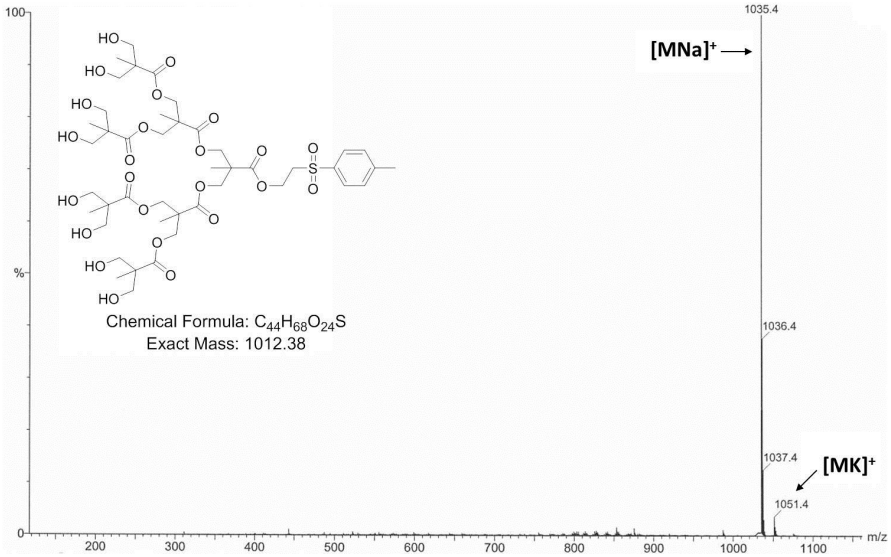


Figure S22. ESI MS (MeOH) of **[(OH)$_8$-G$_3$-TSe]**

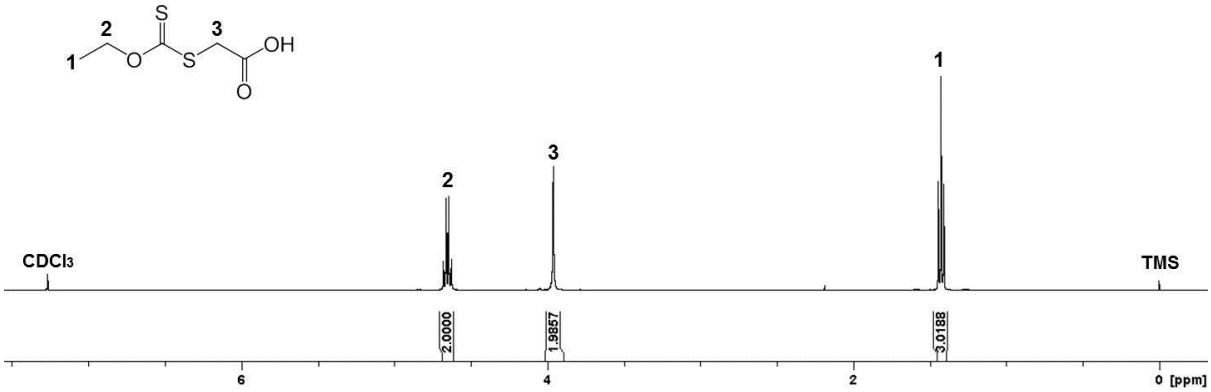


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of **2-((ethoxycarbonothioyl)thio)acetic acid [Xan-COOH]**

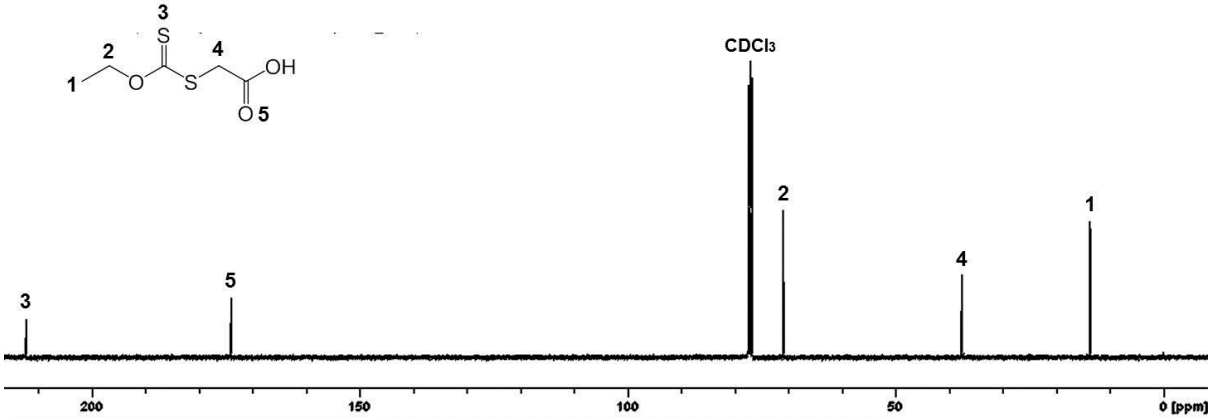


Figure S24. ^{13}C NMR (100 MHz, $CDCl_3$) of **2-((Ethoxycarbonothioyl)thio)acetic acid, [Xan-COOH]**

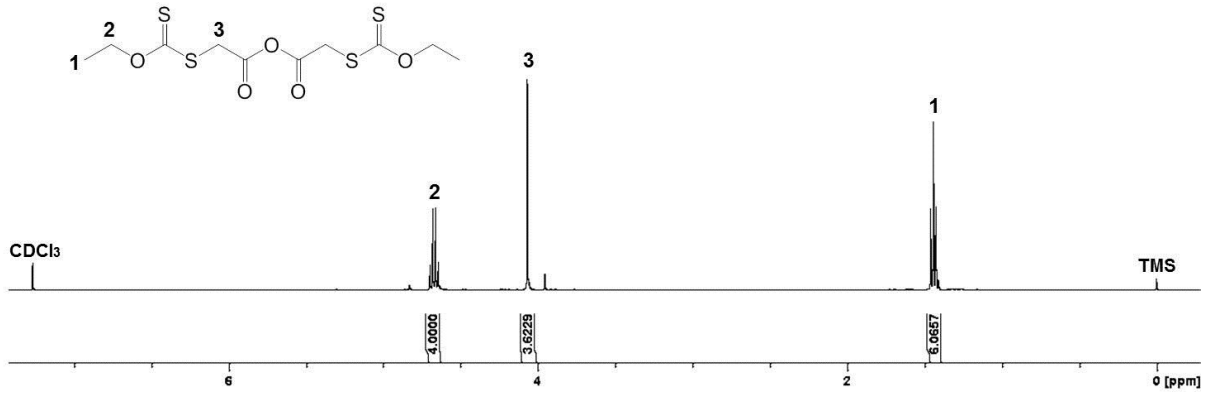


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of **2-((Ethoxycarbonothioyl)thio)acetic anhydride, [Xan-Anhy]**

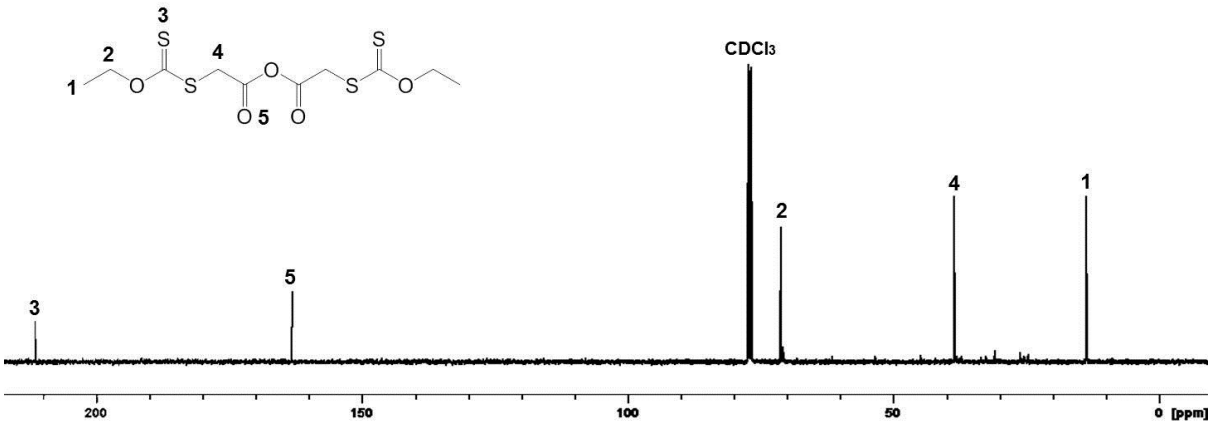


Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) of **2-((Ethoxycarbonothioyl)thio)acetic anhydride, [Xan-Anhy]**

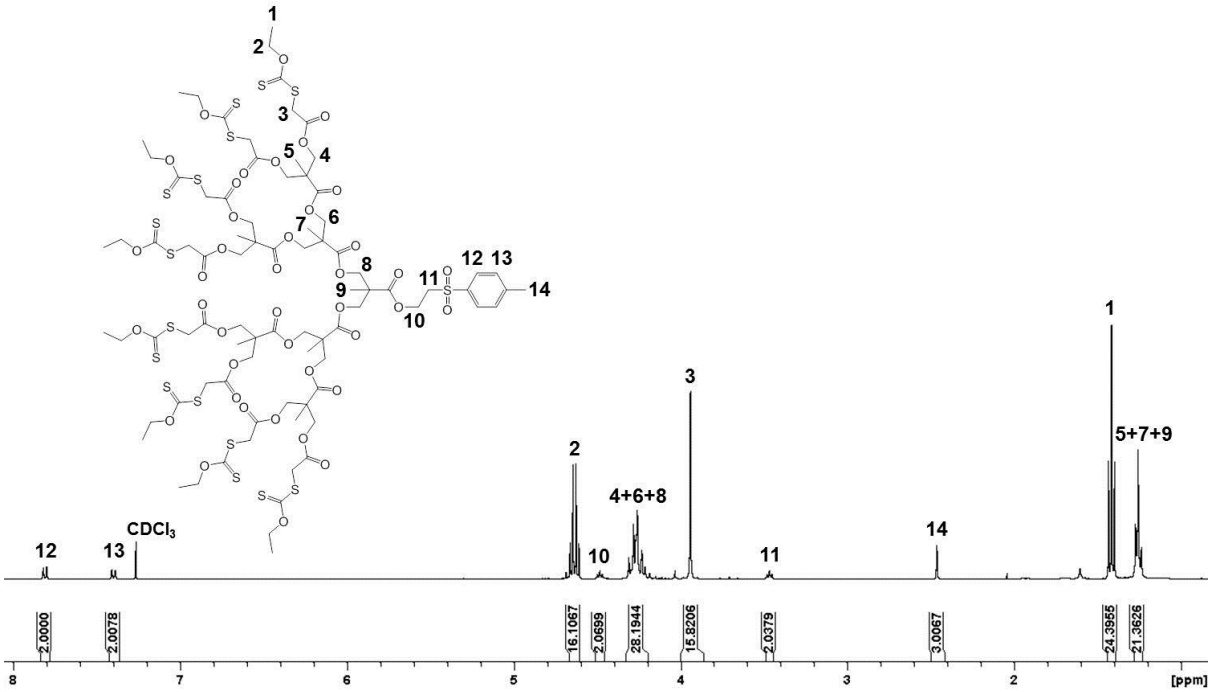


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of **[Xan$_8$-G$_3$-TSe]**

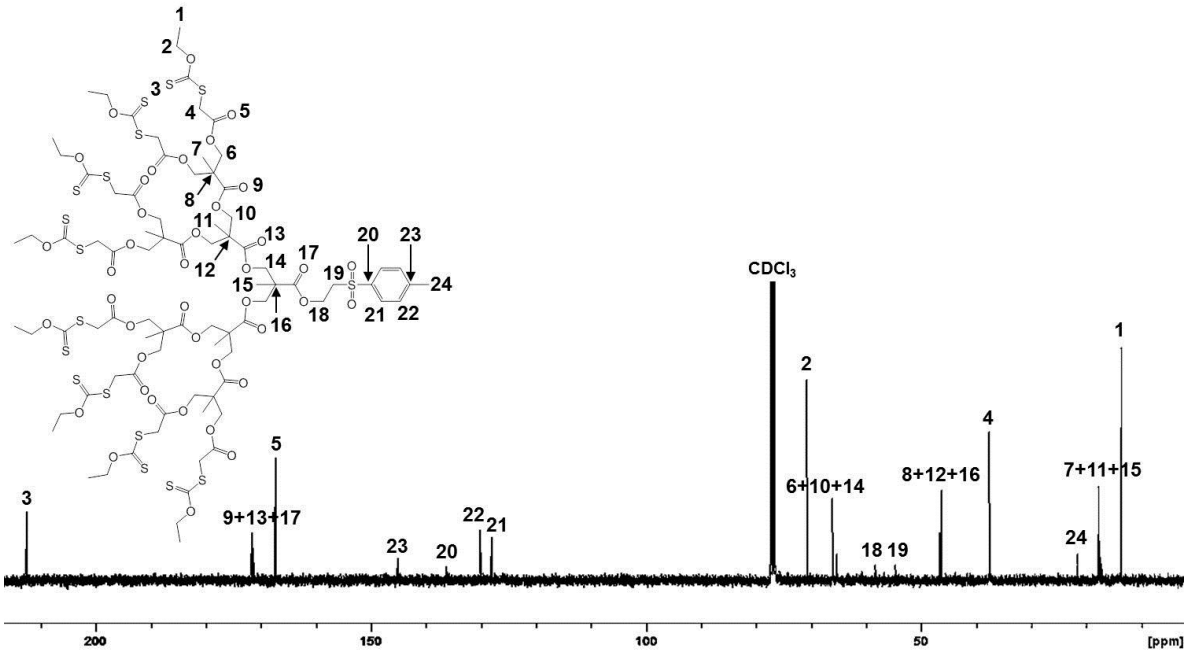


Figure S28. ^{13}C NMR (100 MHz, $CDCl_3$) of **[Xan$_8$-G$_3$-TSe]**

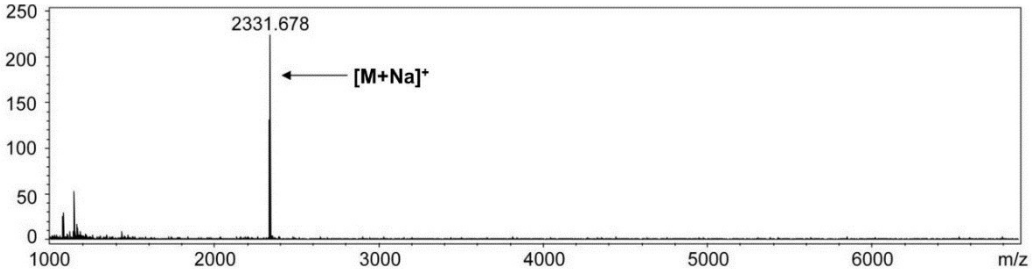


Figure S29. MALDI-TOF analysis of **[Xan$_8$-G$_3$-TSe]**

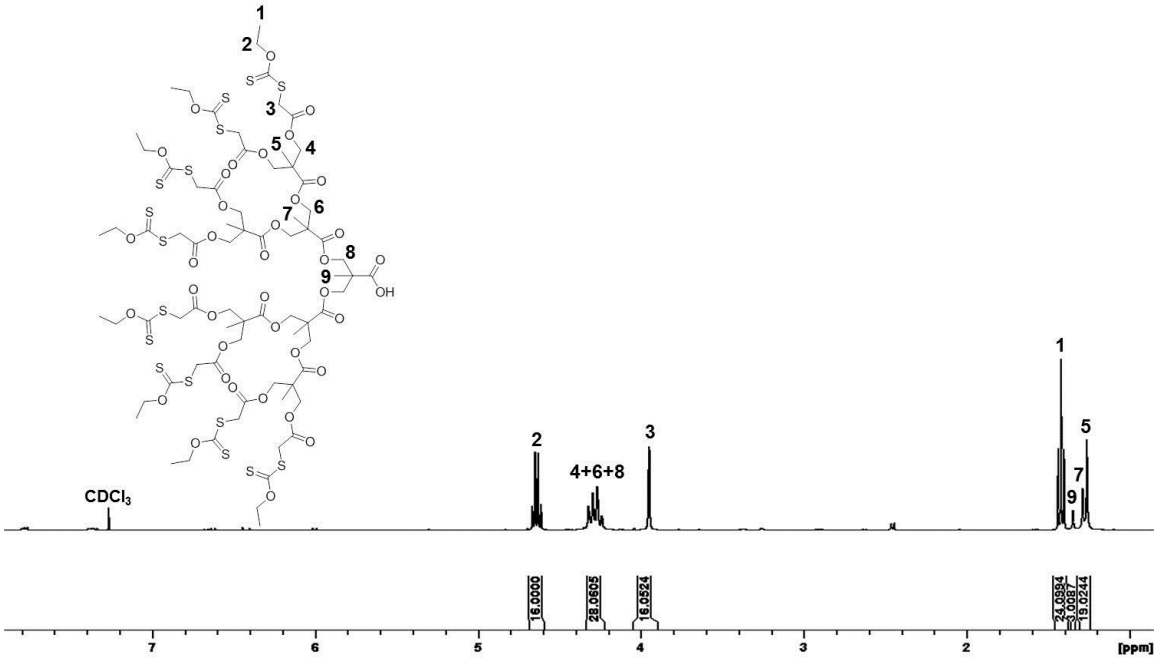


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) of **[Xan$_8$-G$_3$-COOH]**

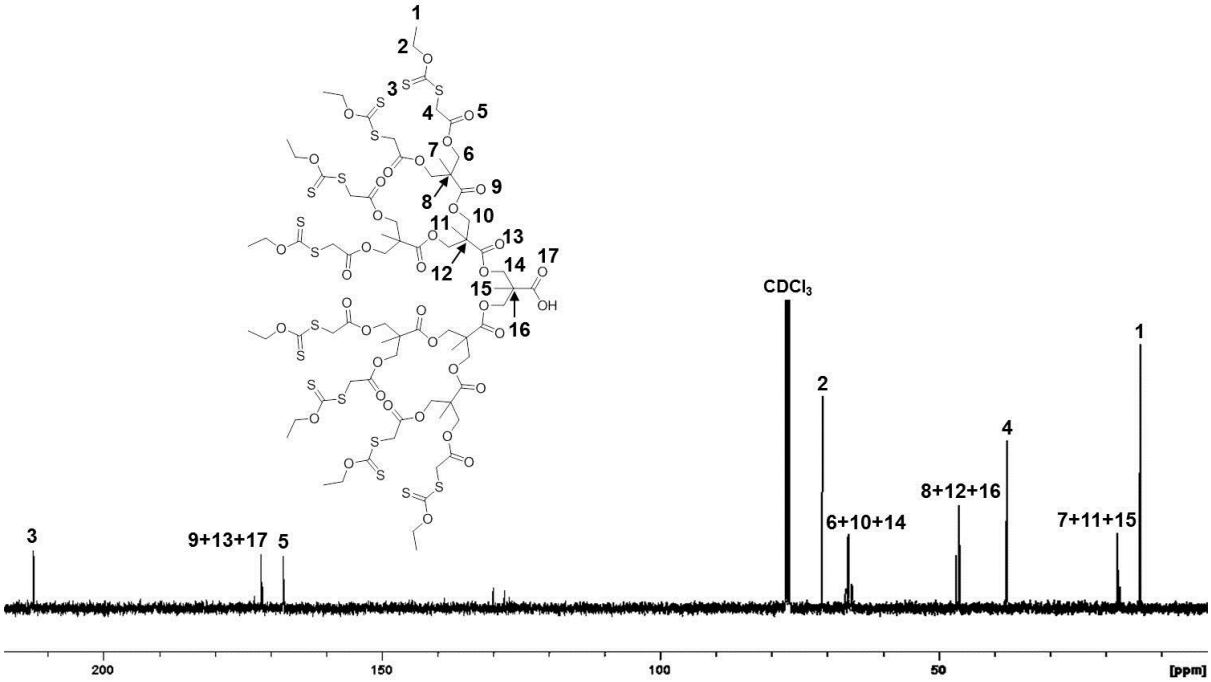


Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$) of **[Xan$_8$-G$_3$-COOH]**

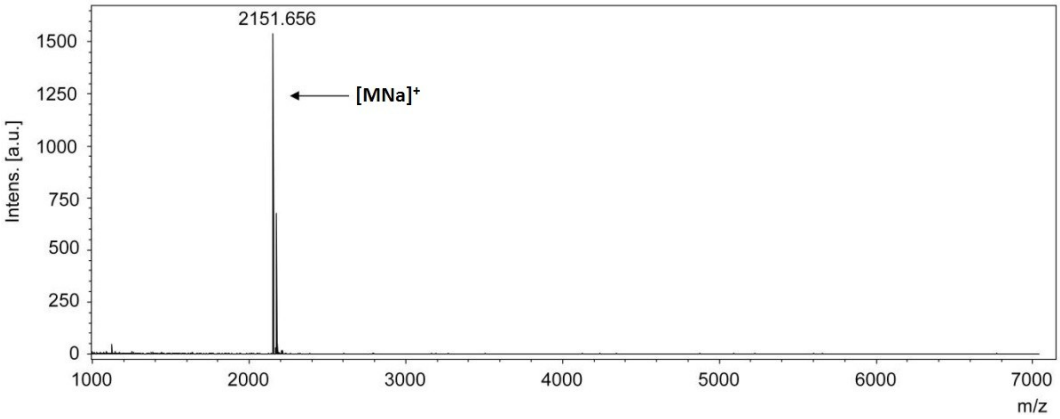


Figure S32. MALDI-TOF analysis of **[Xan$_8$-G$_3$-COOH]**

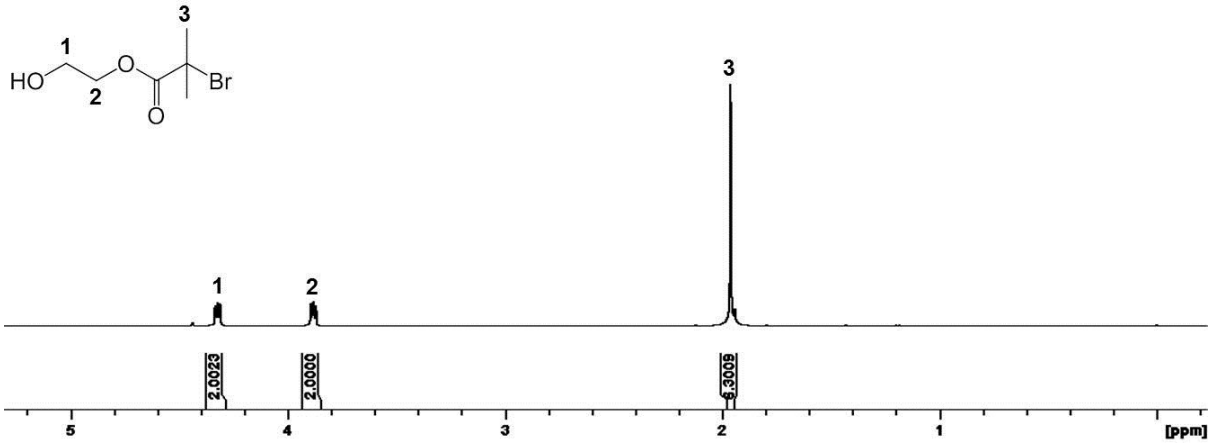


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of **[HEBiB]**

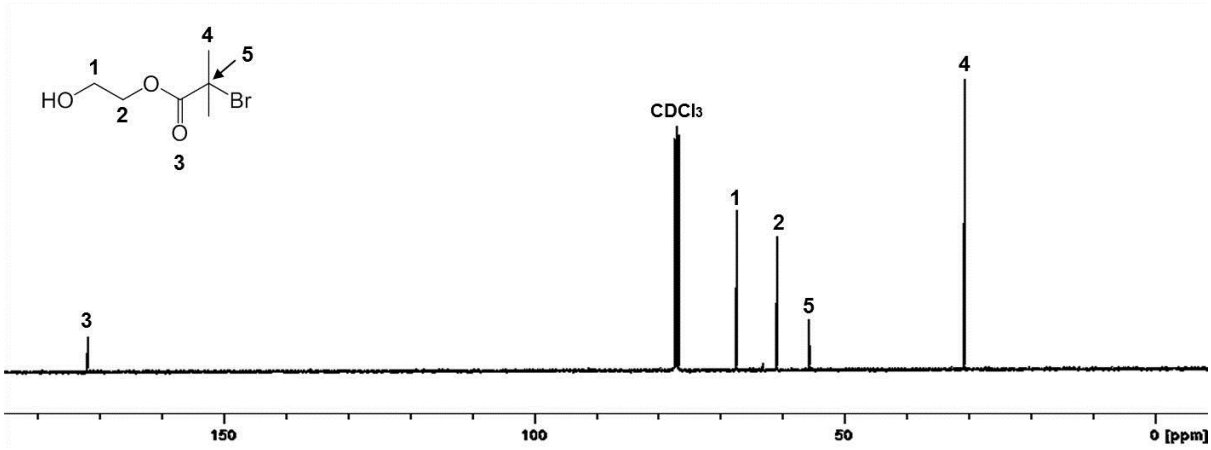


Figure S34. ^{13}C NMR (100 MHz, $CDCl_3$) of **[HEBiB]**

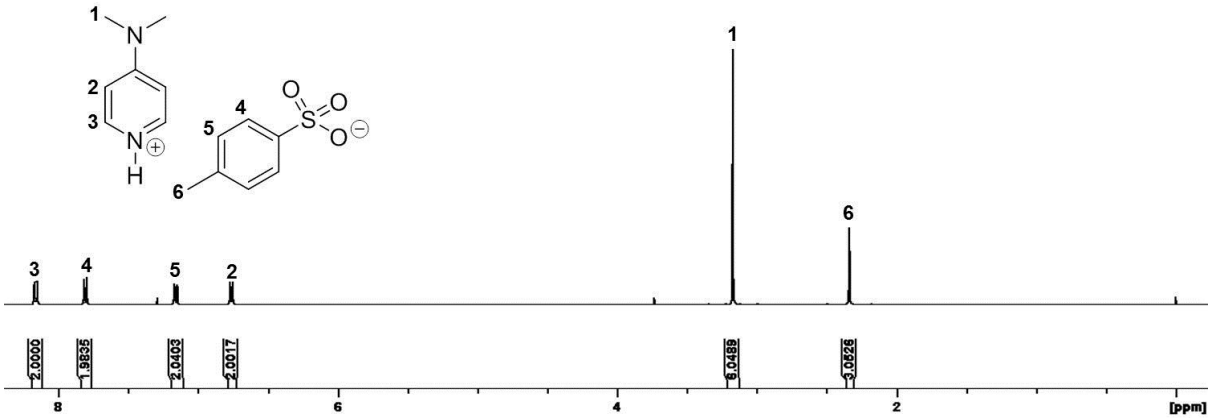


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of **DPTS**

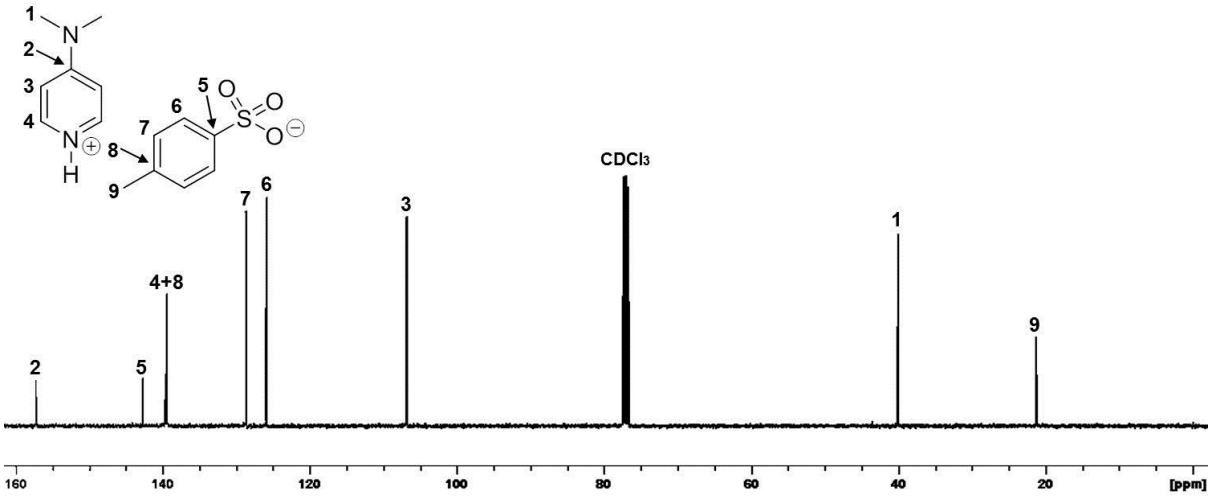


Figure S36. ^{13}C NMR (100 MHz, $CDCl_3$) of **DPTS**

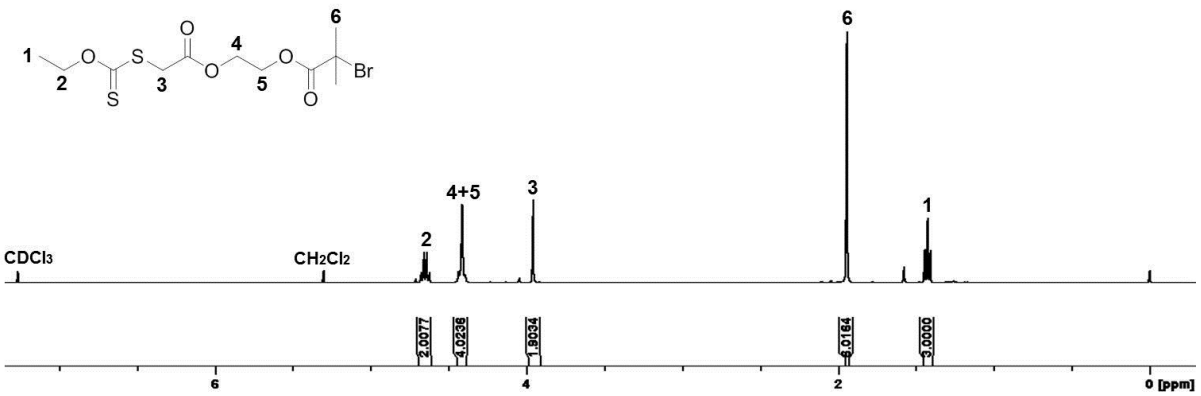


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of **[Xan$_1$-G$_0$-BiB]**

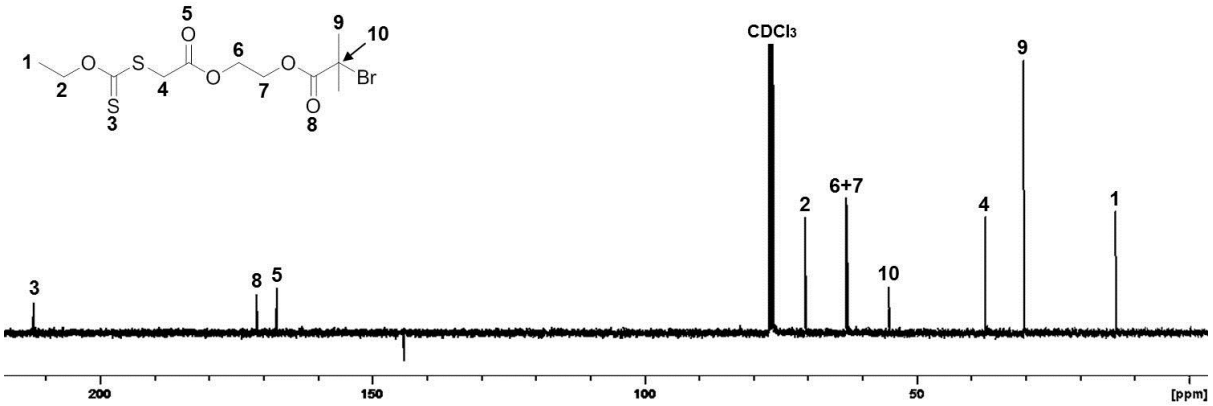


Figure S38. ^{13}C NMR (100 MHz, $CDCl_3$) of **[Xan$_1$-G$_0$-BiB]**

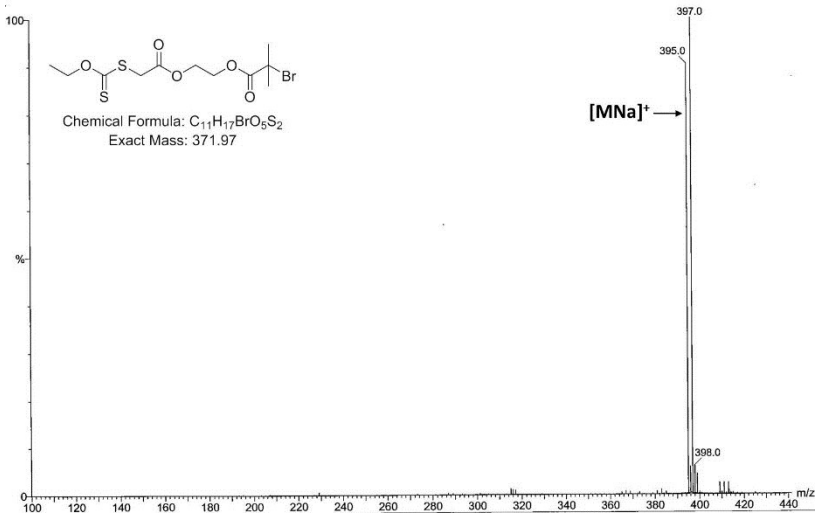


Figure S39. ESI-MS (MeOH) of **[Xan$_1$-G$_0$-BiB]**

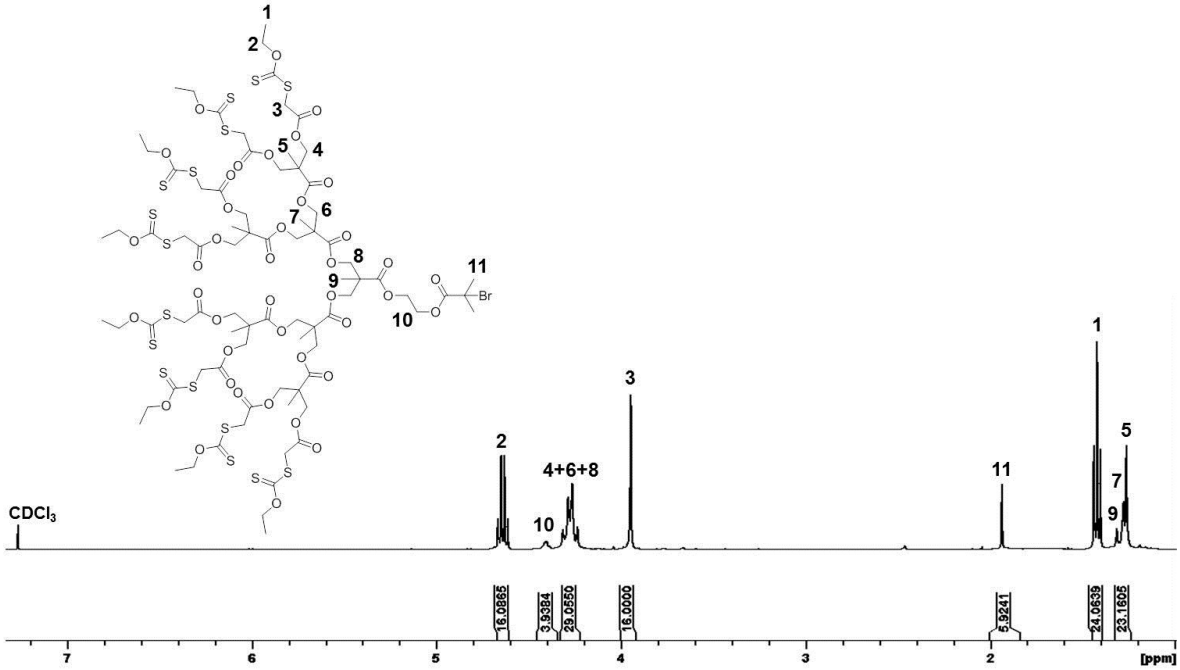


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) of **[Xan$_8$-G$_3$-BiB]**

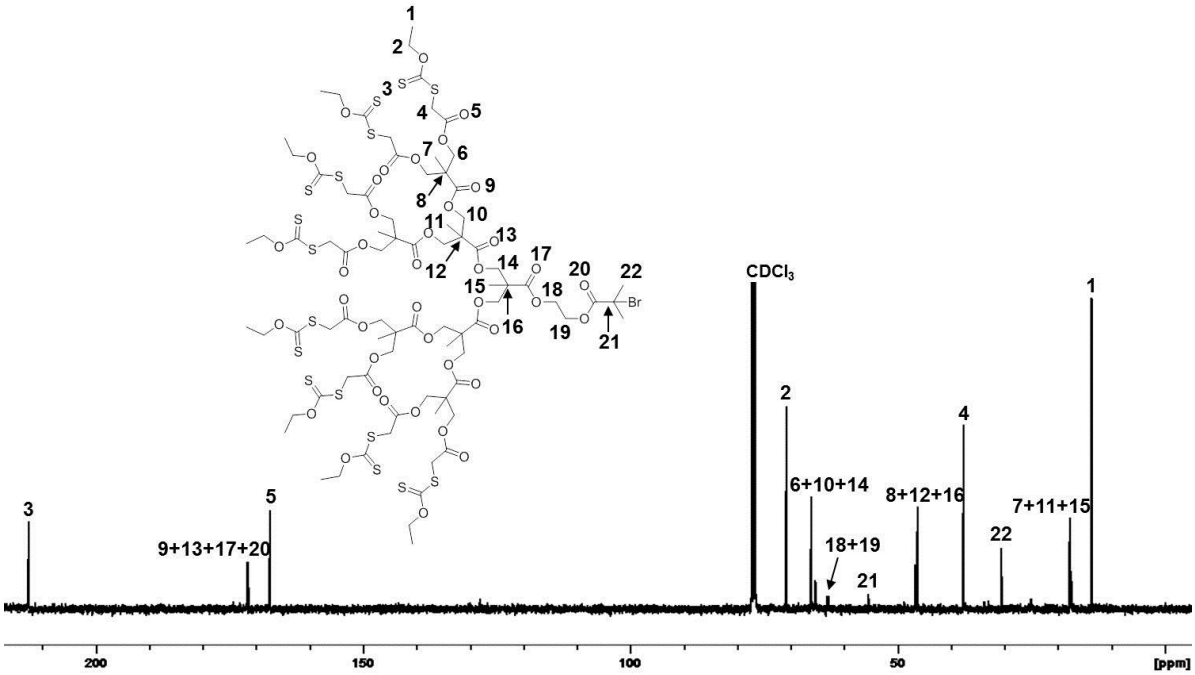


Figure S41. ^{13}C NMR (100 MHz, $CDCl_3$) of **[Xan$_8$-G$_3$-BiB]**

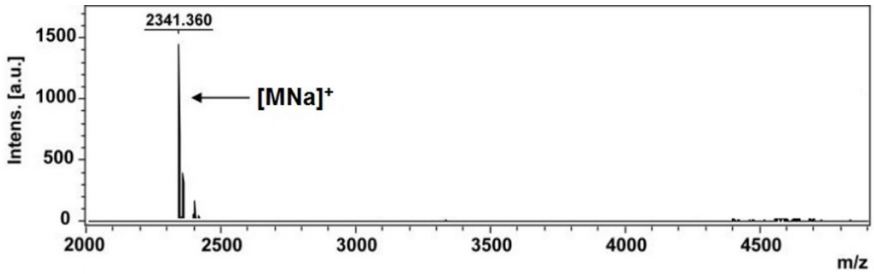


Figure S42. MALDI-TOF analysis of **[Xan$_8$-G$_3$-BiB]**

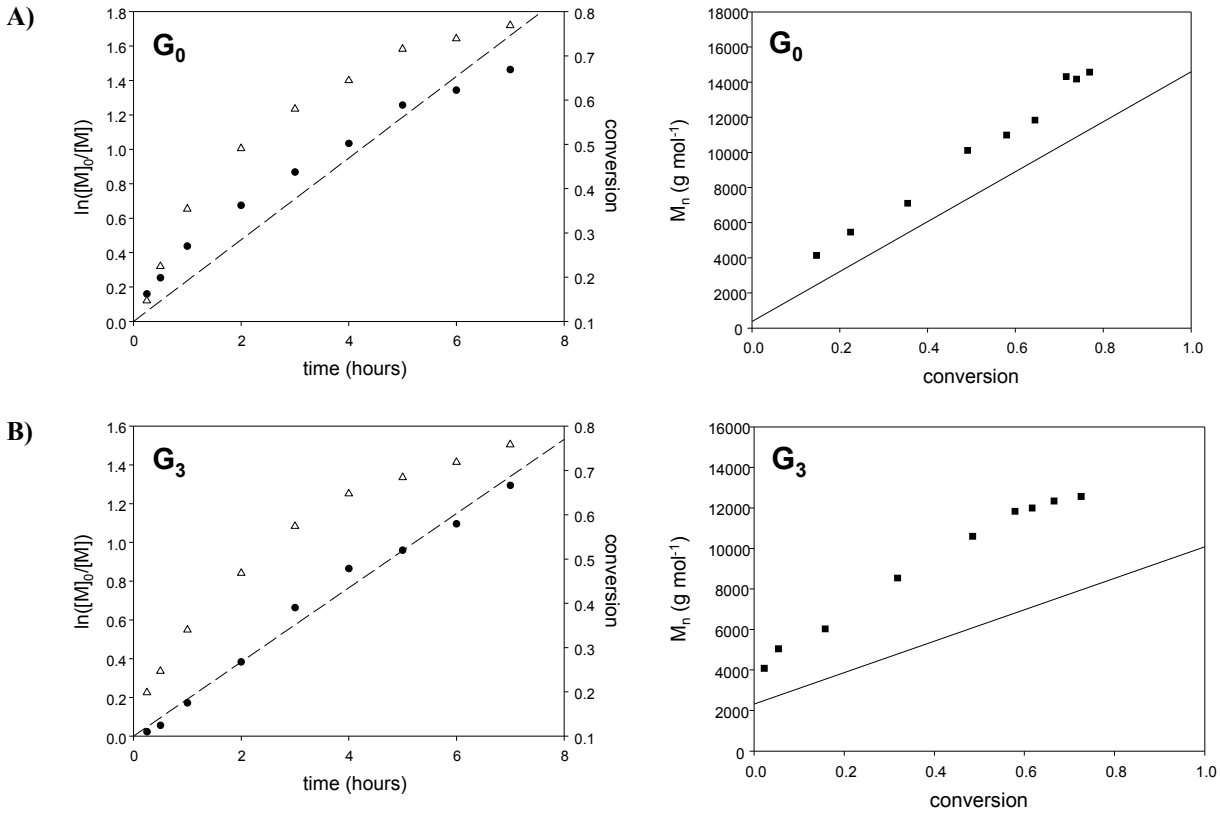


Figure S43. Kinetic studies of the ATRP of *n*-BuMA: A) **G_0-p(*n*-BuMA$_{100}$)**; and B) **G_3-p(*n*-BuMA$_{50}$)**. Conversion *vs*. time (open triangles) with corresponding semi-logarithmic plots (closed black circles); dashed line represents linear regression of semi-logarithmic plot. M_n *vs*. conversion (closed black squares) and theoretical M_n *vs*. conversion (solid line).

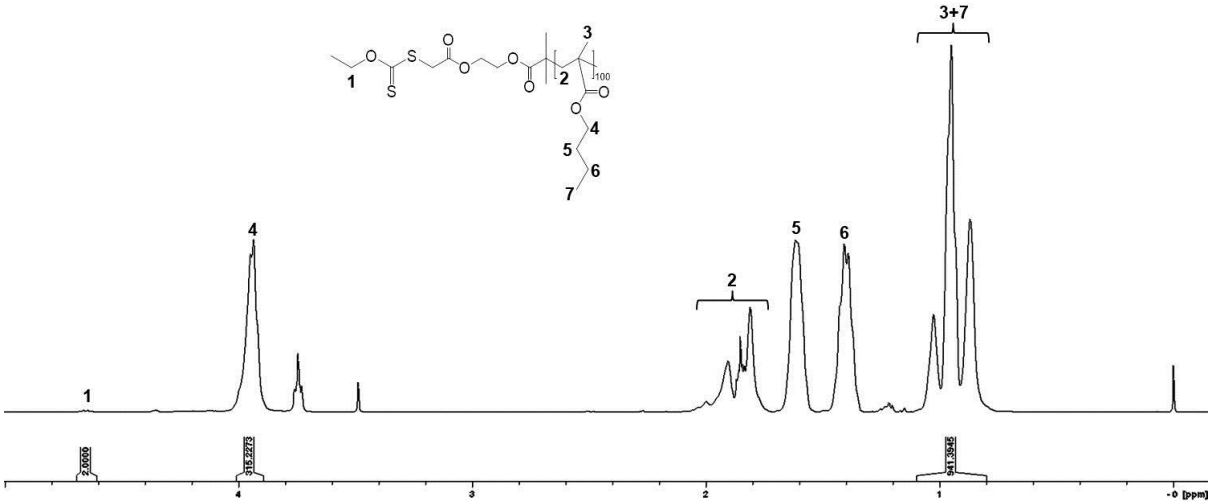


Figure S44. ^{1}H NMR (400MHz, $CDCl_3$) of **G_0-p(*n*-BuMA)$_{100}$**

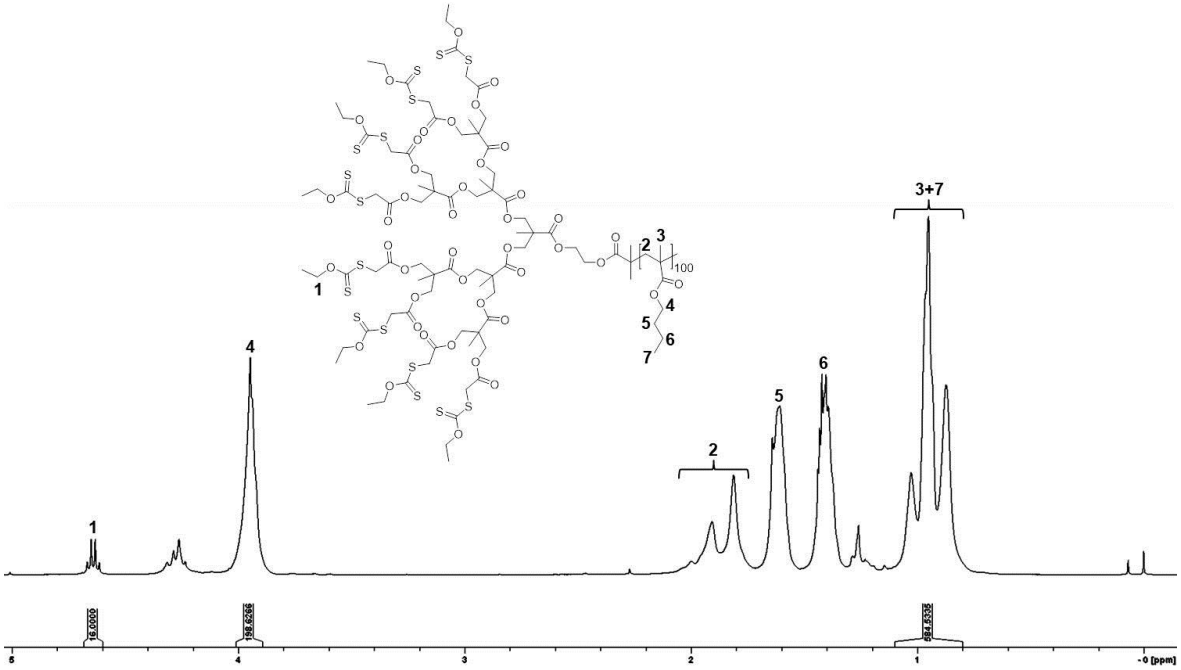


Figure S45. ^{1}H NMR (400MHz, $CDCl_3$) of **G_3-p(*n*-BuMA)$_{100}$**

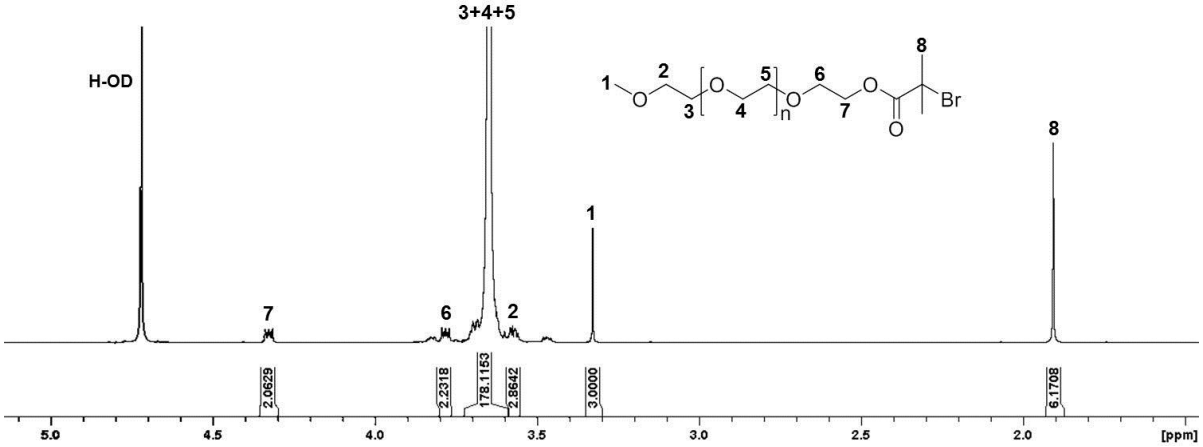


Figure S46. ^{1}H NMR (400 MHz, D_2O) of **[PEG$_{45}$-BiB]**

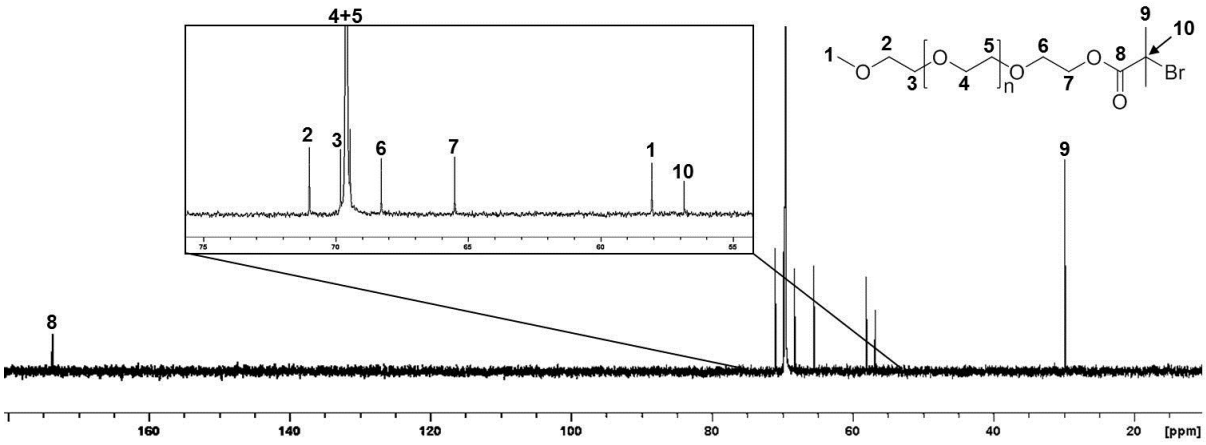


Figure S47. ^{13}C NMR (100 MHz, $CDCl_3$) of **[PEG$_{45}$-BiB]**

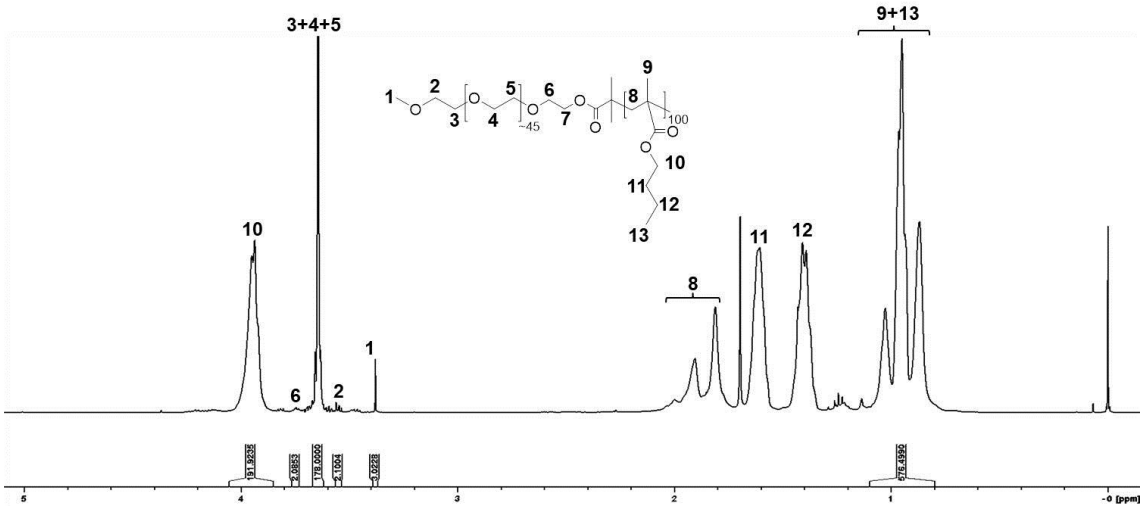


Figure S48. ^{1}H NMR (400MHz, $CDCl_3$) of **p(PEG$_{45}$-*b*-*n*-BuMA$_{100}$)**

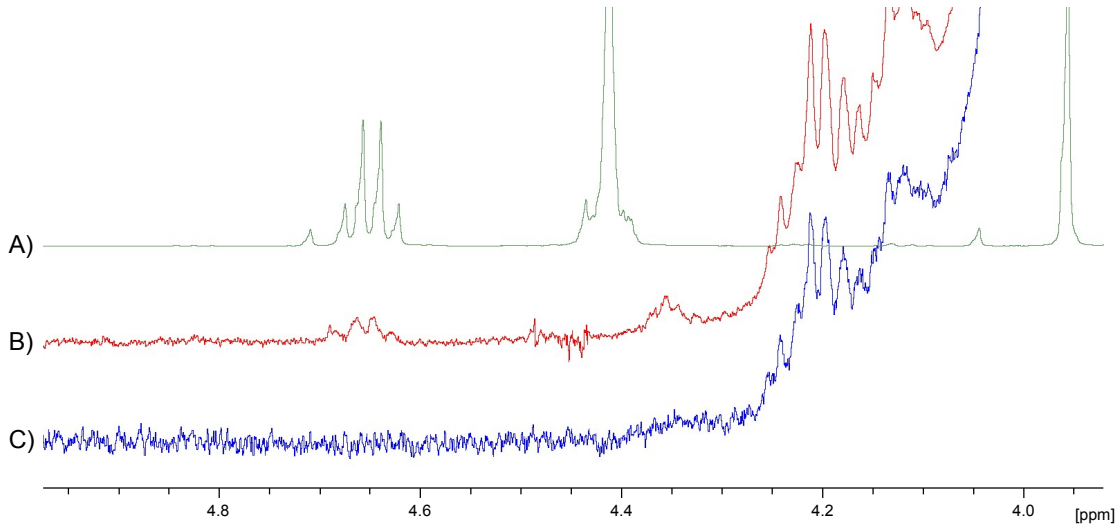


Figure S49. ^{1}H NMR (400MHz, $CDCl_3$) of: A) **[Xan$_1$-G$_0$-BiB]**; B) **[(G$_0$)$_{0.1}$-(PEG$_{45}$)$_{0.9}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**; and C) deprotected **[(G$_0$)$_{0.1}$-(PEG$_{45}$)$_{0.9}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**

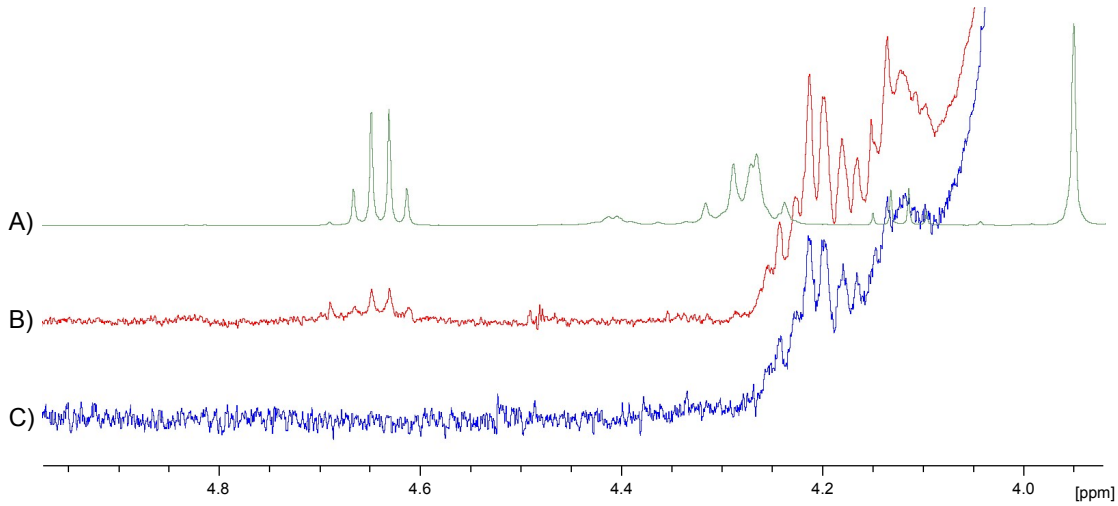


Figure S50. ^{1}H NMR (400MHz, $CDCl_3$) of: A) **[Xan$_8$-G$_3$-BiB]**; B) **[(G$_3$)$_{0.014}$-(PEG$_{45}$)$_{0.986}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**; and C) deprotected **[(G$_3$)$_{0.014}$-(PEG$_{45}$)$_{0.986}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**

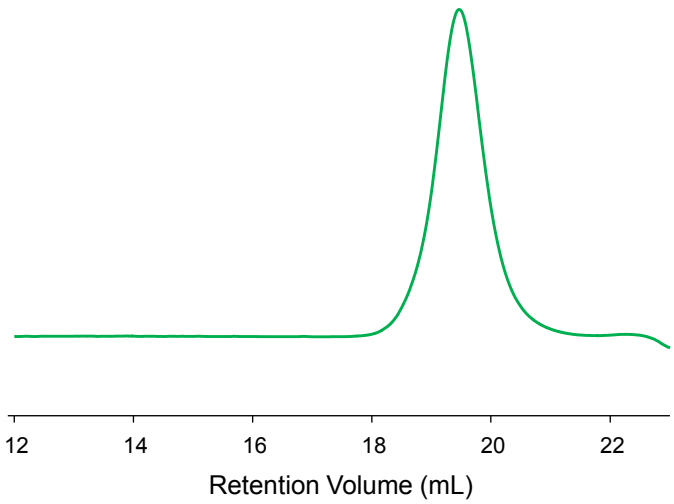


Figure S51. SEC chromatogram (RI) of linear polymer **G_0-p(*n*-BuMA)$_{100}$**

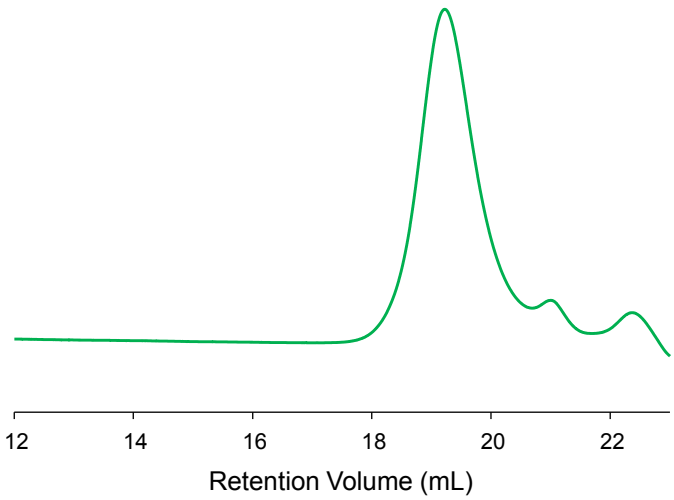


Figure S52. SEC chromatogram (RI) of linear dendritic hybrid polymer **G_3-p(*n*-BuMA)$_{100}$**

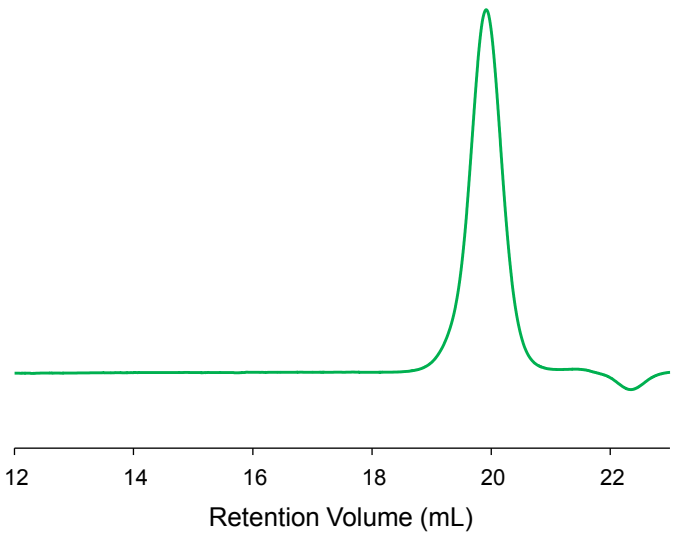


Figure S53. SEC chromatogram (RI) of linear block copolymer **p(PEG$_{45}$-*b*-*n*-BuMA$_{100}$)**

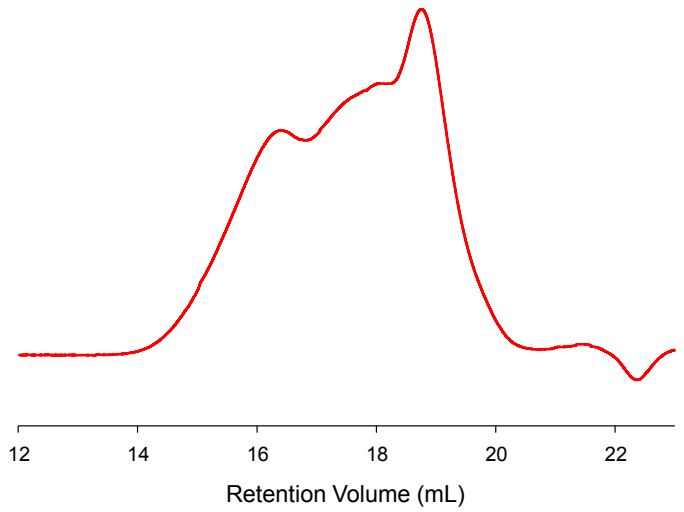


Figure S54. SEC chromatogram (RI) of HPD **[$(G_0)_{0.01}$-$(PEG_{45})_{0.99}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**

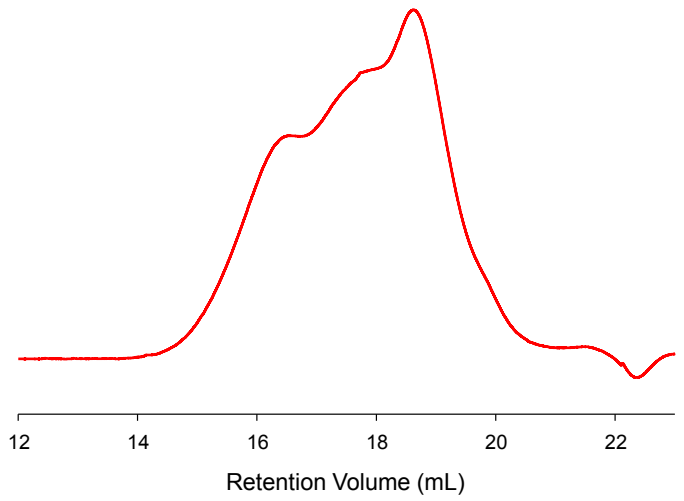


Figure S55. SEC chromatogram (RI) of HPD **[$(G_0)_{0.075}$-$(PEG_{45})_{0.925}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**

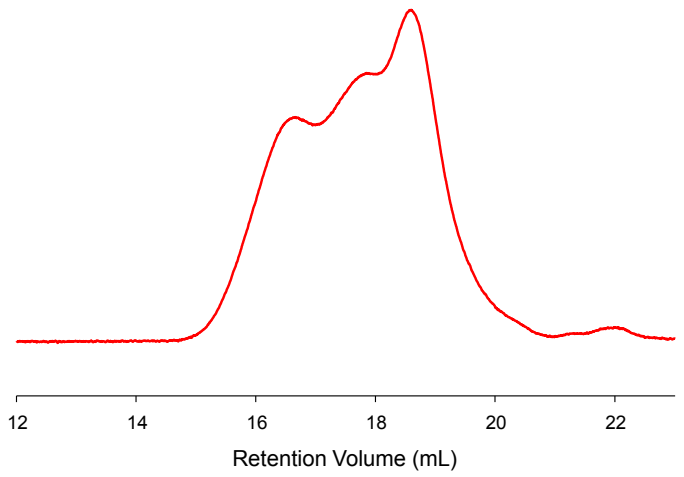


Figure S56. SEC chromatogram (RI) of HPD **[$(G_0)_{0.1}$-$(PEG_{45})_{0.9}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**

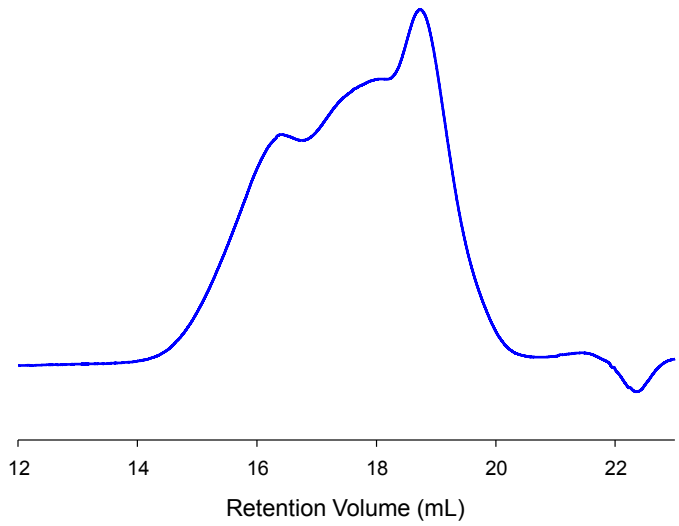


Figure S57. SEC chromatogram (RI) of HPD **[$(G_3)_{0.01}$-$(PEG_{45})_{0.99}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**

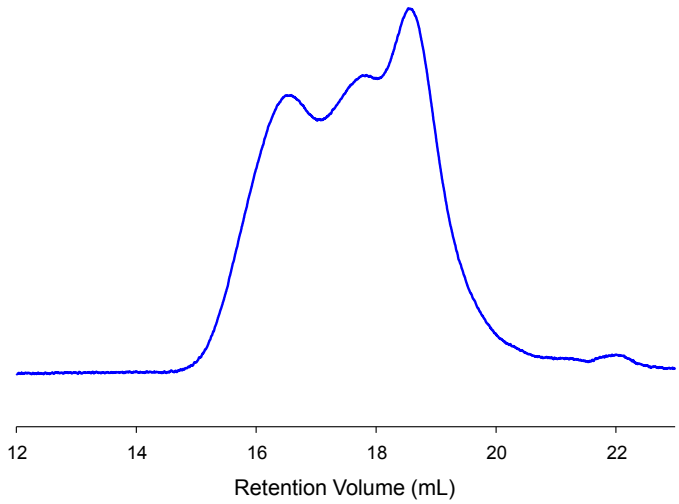


Figure S58. SEC chromatogram (RI) of HPD **[$(G_3)_{0.014}$-$(PEG_{45})_{0.986}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**

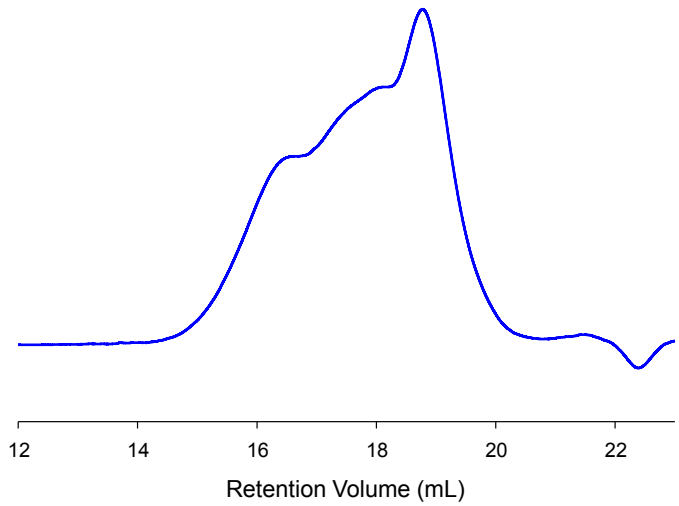


Figure S59. SEC chromatogram (RI) of HPD **[$(G_3)_{0.05}$-$(PEG_{45})_{0.95}$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**

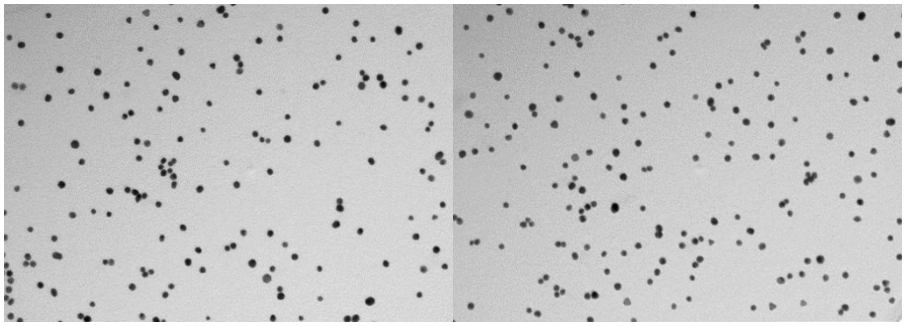
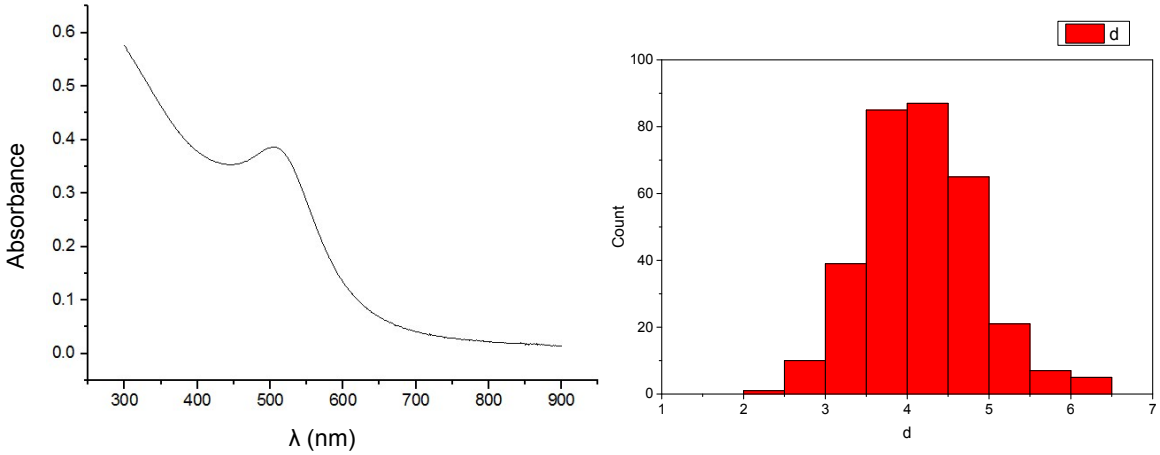


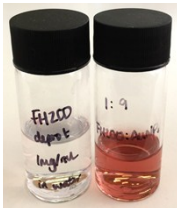
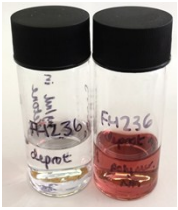
Figure S60. TEM images of 4 nm GNPs synthesised by the Inverse Turkevich method



	N total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
d	323	4.13583	0.77112	1335.87358	0.51586	4.07093	6.30369

Figure S61. Size determination of GNPs by UV-Vis spectroscopy

Table S1. DLS data for: **[$(G_0)_x$-$(PEG_{45})_y$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**; **a** (x = 0.01, y = 0.99); **b** (x = 0.075, y = 0.925); **c** (x = 0.1, y = 0.9); and **[$(G_3)_x$-$(PEG_{45})_y$]-p(*n*-BuMA$_{100}$-*co*-EGDMA$_{0.8}$)**; **d** (x = 0.01, y = 0.99); **e** (x = 0.014, y = 0.986); **f** (x = 0.05, y = 0.95) nanoprecipitates 1 year stability studies at ambient temperature with coordinated 4 nm GNPs

Material	Initiator (%)			GNPs	Original		1 year			
	G_0	G_3	PEG_{45}		D_z	PdI	D_z	PdI	polymer nanoparticle suspension	polymer nanoparticle suspension + 4 nm GNPs
a	1	0	99	-	53	0.128	56	0.101		
a	1	0	99	✓	60	0.230	55	0.078		
b	7.5	0	92.5	-	52	0.083	56	0.063		
b	7.5	0	92.5	✓	64	0.224	54	0.082		
c	10	0	90	-	65	0.097	65	0.100		
c	10	0	90	✓	74	0.235	61	0.134		
d	0	1	99	-	51	0.105	53	0.094		
d	0	1	99	✓	54	0.124	60	0.102		
e	0	1.4	98.6	-	61	0.141	62	0.107		
e	0	1.4	98.6	✓	66	0.190	78	0.167		
f	0	5	95	-	52	0.101	55	0.065		
f	0	5	95	✓	56	0.101	56	0.083		