Electronic Supplementary Material (ESI) for Polymer Chemistry.

Model studies of the sequential and simultaneous statistical modification of dendritic functional groups and their implications within complex polymer architecture synthesis.

Electronic Supporting Information

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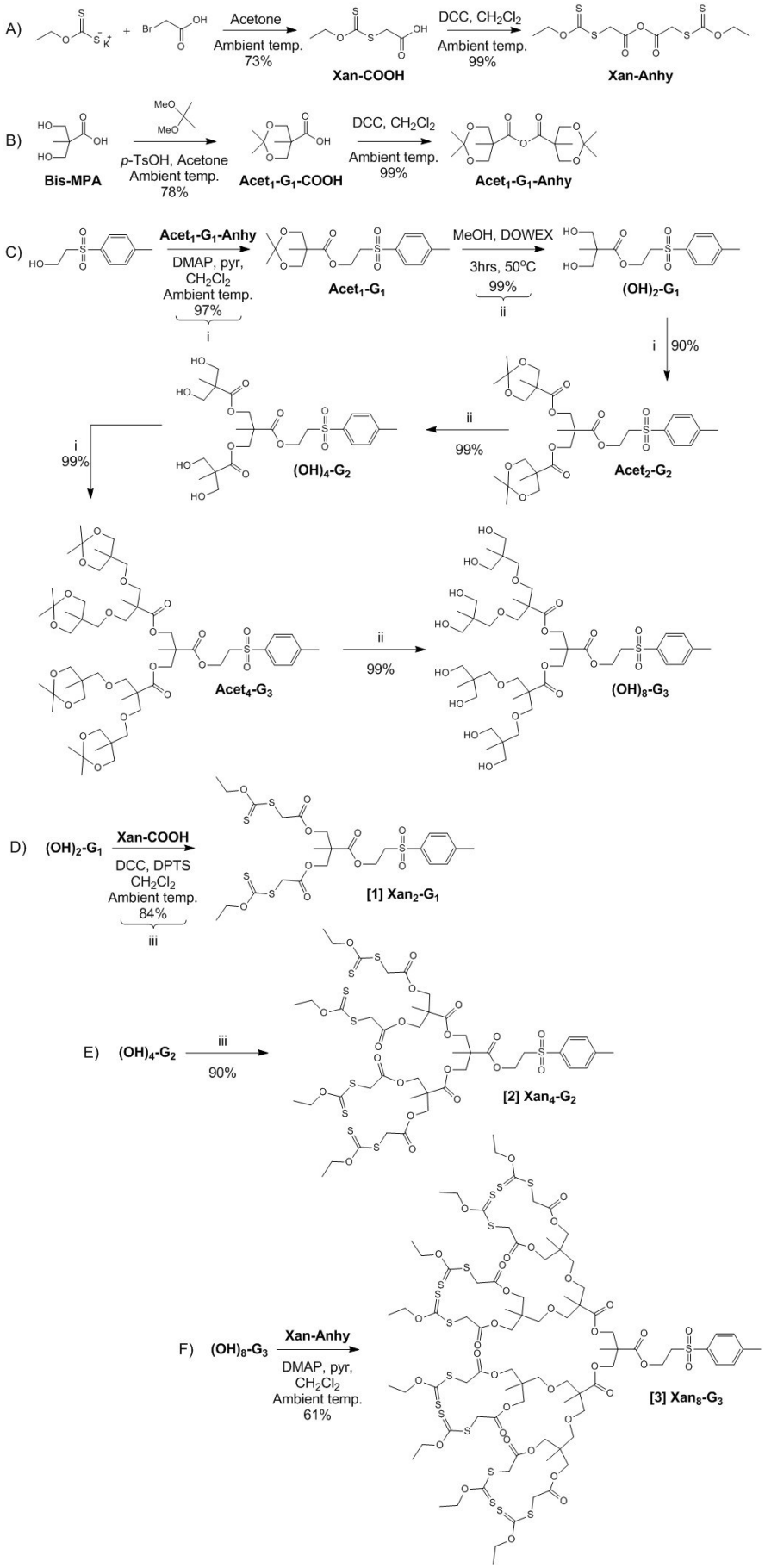
Methods and Synthesis

Materials

2,2-Bis(hydroxymethyl)propionic acid (bis-MPA), *n*-butylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Sigma Aldrich and were used without further purification. Potassium ethyl xanthate, 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 were used without further purification. *Para*-toluene sulfonyl ethanol was purchased from Fluorochem and used without further purification. Dimethylaminopyridinium *p*-toluenesulfonate (DPTS) was prepared using literature procedures.[1] Dichloromethane, hexane and ethyl acetate were HPLC grade and supplied from Fisher. Analytical TLC was performed on commercial Merck plates coated with silica. Flash chromatography was performed using a Grace Reveleris flash system with 80g silica Reveleris flash cartridges.

Analysis

Triple detection SEC was performed to measure molecular weights and molecular weight distributions using a Malvern Viscotek instrument. The instrument was equipped with a GPCmax VE2001 autosampler, two Viscotek T6000 columns (and a guard column), a refractive index (RI) detector VE3580 and a 270 Dual Detector (light scattering and viscometer) with a mobile phase of THF containing 2 v/v % of trimethylamine at 35 °C with a flow rate of 1 mL min^{-1}. NMR spectra were obtained using a Bruker Avance 400 MHz. ^{1}H spectra were recorded at 400 MHz and ^{13}C spectra were recorded at 100 MHz. $CDCl_3$ and CD_3OD containing tetramethylsilane (TMS) purchased from Goss Scientific were used as NMR solvents. Chemical shifts (δ) are reported in parts per milliom (ppm) and TMS was used as an internal standard for both ^{1}H and ^{13}C spectra. Electrospray ionisation mass spectrometry (ESI-MS) data 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 tetrahydrofuran (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.



Scheme S1. Synthetic strategy for the synthesis of the focal-point protected dendrons used within the study

Synthesis

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 at ambient temperature for 18 hours. The precipitated potassium bromide by-product was removed by filtration 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 **[3]**. Yield: 36.35g, pale yellow solid (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. 2-((Ethoxycarbonothioyl)thio)acetic acid (27.53 g, 152 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (100 mL). A solution of N,N″-dicyclohexylcarbodiimide (DCC) (20.76 g, 101 mmol, 0.5 equiv.) in CH_2Cl_2 (100 mL) was slowly added to the mixture whilst cooling with an ice bath. The reaction allowed to stir at ambient temperature overnight. Determination of reaction completion was monitored by ^{13}C NMR, indicated by the appearance of the anhydride carbonyl carbon resonance at 163 ppm and the disappearance of the acid carbonyl carbon resonance 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, orange-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.

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, 37.2 mmol, 0.05 equiv.) were stirred in acetone (500 mL) for 3 hours at ambient temperature, becoming clear as the reaction proceeded. Following this, the catalyst was neutralised by adding a 1:1 mixture of NH_4OH:EtOH (10 mL), resulting in salt precipitation. The product was obtained by removal of acetone under vacuum, redissolving 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, 41.67, 65.83, 98.43, 180.31. This compound was prepared by the procedure reported by Ihre et al.[2] Spectroscopic data agreed with those reported.

Isopropylidene-2,2-bis(methoxy)propionic Anhydride, $Acet_1$-G_1-Anhy. Isopropylidene-2,2-bis(methoxy)propionic acid (93.22 g, 0.535 mol, 1 equiv.) and N,N'-dicyclohexylcarbodiimide (DCC) (55.21 g, 0.268 mol, 0.50 equiv.) were stirred in CH_2Cl_2 (500 mL) at ambient temperature for 48 hours. The precipitated dicyclohexylurea (DCU) by-product was removed by filtration. The crude product was purified by reducing the volume of CH_2Cl_2 and precipitating the residue into cold hexane (cooled with an acetone/dry ice bath). Yield: 88.23 g, colourless 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 = 17.77, 21.63, 25.49, 43.68, 65.75, 98.43, 169.58. This compound was prepared from **6** according to the procedure reported by Malkoch et al.[3] Spectroscopic data agreed with those reported.

General esterification procedure for divergent dendron growth, $Acet_1$-G_1-TSe. Isopropylidene-2,2-bis(methoxy)propionic anhydride (41.88 g, 127 mmol, 1.3 equiv.), *para*-toluene sulfonyl ethanol (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), 1 M $NaHCO_3$ (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 **[9]**. 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. Six spatulas of DOWEX 50W-X2 was added to a solution of Acet-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 solid, (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), 3.73-3.85 (dd, 4H, *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: $[MNa]^+$ ($C_{14}H_{20}NaO_6S$) = 339.10 Da. Found: ESI-MS: $[MNa]^+$ = 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.), $Acet_1$-G_1-Anhy (46.15 g, 139.68 mmol, 3 equiv.), pyridine (38 mL) and CH_2Cl_2 (114 mL) were reacted according to the general esterification procedure, resulting in a colourless viscous oil that was purified by liquid chromatography on silica, eluted from ethyl acetate:hexane (10:90) increasing the polarity to ethyl acetate: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), 4.19 (dd, 4H, *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: $[MNa]^+$ ($C_{30}H_{44}NaO_{12}S$) = 651.26 Da. Found: ESI-MS: $[MNa]^+$ = 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. Five spatulas of DOWEX 50W-X2 and $Acet_2$-G_2-TSe (25.26 g, 40.18 mmol, 1 equiv) dissolved in methanol (250 mL) were reacted according to the general deprotection procedure. Yield: 20.72 g, white solid, (99%). ^{1}H NMR (400 MHz, CD_3OD): δ = 1.13 (s, 9H), 2.46 (s, 3H), 3.58 (s, 2H), 3.64 (dd, 4H, *J* = 11.2 Hz), 4.10 (d, 4H, *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: $[MNa]^+$ ($C_{24}H_{36}NaO_{12}S$) = 571.19 Da. Found: ESI-MS: $[MNa]^+$ = 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.), $Acet_1$-G_1-Anhy (21.27 g, 64 mmol, 6 equiv.), pyridine (53 mL) and CH_2Cl_2 (160 mL) were reacted according to the general esterification procedure, resulting in a colourless viscous oil that was purified by liquid chromatography on silica, eluted from ethyl acetate:hexane (20:80) increasing the polarity to ethyl acetate: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), 4.31 (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: $[MNa]^+$ ($C_{56}H_{84}NaO_{24}S$) = 1195.50 Da. Found: ESI-MS: $[MNa]^+$ = 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. Four spatulas of DOWEX 50W-X2 and $Acet_4$-G_3-TSe (22.66 g, 19 mmol, 1 equiv) dissolved in methanol (300 mL) were reacted according to the general deprotection procedure. Yield: 19.44 g, white solid, (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: $[MNa]^+$ ($C_{44}H_{68}NaO_{24}S$) = 1035.37 Da. Found: ESI-MS: $[MNa]^+$ = 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.

General procedure for functionalisation with Xanthate surface groups using DCC/DPTS chemistry, Xan_2-G_1-TSe [1]. This compound was prepared by the procedure reported by Auty et al.[4] The hydroxyl-terminated dendron OH_2-G_1-TSe (10.23 g, 32 mmol, 2.5 equiv.), 2-((ethoxycarbonothioyl)thio)acetic acid, Xan-COOH (17.55 g, 97 mmol, 7.5 equiv.) and DPTS
(3.81 g, 13 mmol, 1 equiv.) were dissolved in anhydrous CH_2Cl_2 (100 mL) under a nitrogen atmosphere. Dicyclohexylcarbodiimide (DCC) (22.01 g, 107 mmol, 8.25 equiv.) was added in anhydrous CH_2Cl_2 (50 mL) slowly whilst cooling with an ice bath. The reaction mixture was left to stir at ambient temperature for 18 hours. The precipitated dicyclohexylurea (DCU) by-product was removed by filtration and washed with a small volume of CH_2Cl_2. The crude product was purified by liquid chromatography on silica, eluting with hexane gradually increasing to ethyl acetate:hexane (40:60). Yield: 17.36 g, orange viscous oil (84%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (s, 3H), 1.42 (t, 6H, *J* = 7.1 Hz), 2.46 (s, 3H), 3.44 (t, 2H, *J* = 6.0 Hz), 3.91 (s, 4H), 4.17 (dd, 4H, *J* = 11.0), 4.46 (t, 2H, *J* = 6.0 Hz), 4.65 (q, 4H, *J* = 7.1 Hz), 7.39 (d, 2H, *J* = 8.0 Hz), 7.81 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.80, 17.52, 21.74, 37.77, 46.22, 54.99, 58.36, 66.13, 70.86, 128.09, 130.12, 136.20, 145.31, 167.26, 171.82, 212.50. Calcd: $[MNa]^+$ ($C_{24}H_{32}NaO_{10}S_5$) = 663.06. Found ESI-MS: $[MNa]^+$ = 663.00. Calcd for $C_{24}H_{32}O_{10}S_5$: C, 44.98; H, 5.03; S, 25.02. Found: C, 45.61; H, 5.15; S, 25.68.

Xan_4-G_2-TSe [2]. The hydroxyl-terminated dendron OH_4-G_2-TSe, Xan-COOH, DPTS (3.07 g, 10 mmol) and DCC (17.76 g, 86 mmol) were allowed to react according to the general esterification procedure in anhydrous CH_2Cl_2 (200 mL) for 18 hours. The crude product was purified by liquid chromatography on silica, eluting with hexane gradually increasing to ethyl acetate:hexane (50:50). Yield: 14.04 g, orange viscous oil (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (s, 3H), 1.25 (s, 6H), 1.42 (t, 12H, *J* = 7.1 Hz), 2.46 (s, 3H), 3.46 (t, 2H, *J* = 5.9 Hz), 3.94 (s, 8H), 4.20 (s, 4H), 4.26 (dd, 8H, *J* = 11.0), 4.46 (t, 2H, *J* = 5.9 Hz), 4.64 (q, 8H, *J* = 7.1 Hz), 7.40 (d, 2H, *J* = 8.0 Hz), 7.82 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.76, 17.37, 17.90, 21.69, 37.70, 46.44, 46.64 54.85, 58.48, 65.58, 66.24, 70.85, 128.12, 130.24, 136.35, 145.26, 167.36, 171.65, 171.82, 212.56. Calcd: $[MNa]^+$ ($C_{44}H_{60}NaO_{20}S_9$) = 1219.12. Found MALDI-TOF MS: $[MNa]^+$ = 1219.10. Calcd for $C_{44}H_{60}O_{20}S_9$: C, 44.13; H, 5.05; S, 24.10. Found: C, 44.83; H, 5.19; S, 24.34.

General procedure for functionalisation with Xanthate surface groups using anhydride chemistry, Xan_8-G_3-TSe [3]. This compound was prepared by the procedure reported by Auty et al.[5] 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, 2-((ethoxycarbonothioyl)thio)acetic anhydride, 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 18 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), 1 M $NaHCO_3$ (3 x 200 mL), and brine (1 x 200 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by liquid chromatography on silica, eluting from ethyl acetate:hexane (15:85) gradually increasing the polarity to ethyl acetate: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: $[MNa]^+$ ($C_{84}H_{116}NaO_{40}S_{17}$) = 2331.22 Da. Found: MALDI-TOF MS: $[MNa]^+$ = 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) - The xanthate functionalised dendron was dissolved in anhydrous CH_2Cl_2 and 1.3 equivalents of 1,8- diazabicyclo[5.4.0]undec-7-ene (DBU) added. 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_2-G_1-COOH – The removal of the *para*-toluene sulfonyl (*p*-TSe) protecting group was carried out as described above using Xan_2-G_1-TSe **[1]** (4.60 g, 7.18 mmol, 1.0 equiv), and DBU (1.40 mL, 9.33 mmol, 1.3 equiv). Yield: 3.10 g, orange viscous oil (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 3H), 1.42 (t, *J* = 7.10, 6H), 2.47 (s, 3H), 3.94 (s, 4H), 4.30 (d, *J* = 11.1 Hz, 2H), 4.36 (d, *J* = 11.1 Hz, 2H), 4.64 (q, *J* = 7.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.74, 17.86, 37.74, 46.06, 66.13, 70.87, 167.45, 177.80, 212.53. Calcd: $[M+Na]^+$ ($C_{15}H_{22}NaO_8S_4$) m/z = 481.02. Found: ESI-MS: $[M+Na]^+$ m/z = 481.00. Anal. Calcd for $C_{15}H_{22}O_8S_4$: C, 39.29; H, 4.84; S, 27.97. Found: C, 40.06; H, 5.06 S, 25.82.

Xan_4-G_2-COOH – The removal of the *para*-toluene sulfonyl (*p*-TSe) protecting group was carried out as described above using Xan_4-G_2-TSe **[2]** (5.02 g, 4.18 mmol, 1.0 equiv), and DBU (0.81 mL, 5.43 mmol, 1.3 equiv). Yield: 4.05 g, orange viscous oil (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 6H), 1.33 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 12H), 3.94 (s, 8H), 4.21-4.36 (m, 12H), 4.64 (q, *J* = 7.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.67, 17.89, 37.64, 46.46, 65.83, 66.40, 71.00, 167.46, 171.68, 175.13, 212.71. Calcd: $[M+Na]^+$ ($C_{35}H_{50}NaO_{18}S_8$) m/z = 1037.07. Found ESI-MS: $[M+Na]^+$ m/z = 1037.1. Anal. Calcd for $C_{35}H_{50}O_{18}S_8$: C, 41.40; H, 4.96; S, 25.27. Found: C, 42.06; H, 5.15; S, 24.82.

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 (m, *J* = 4.7 Hz, 2H), 4.32 (m, *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 Matyjaszewski *et al.*[6] The above spectroscopic data agreed with that reported.

General procedure for focal point modification to α-bromoisobutyrate moiety, Xan_2-G_1-BiB [4] - Xan_2-G_1-COOH (8.25 g, 18 mmol, 1 equiv.), HEBiB (5.70 g, 27 mmol, 1.5 equiv.), and DPTS (1.06 g, 3.6 mmol, 0.2 equiv.) were dissolved in 80 mL of anhydrous CH_2Cl_2 under a nitrogen atmosphere. DCC (7.43 g, 36 mmol, 2 equiv.) was added to the mixture in a small volume of CH_2Cl_2, and stirring continued at ambient temperature for 16 hours. The product was isolated by diluting the mixture with CH_2Cl_2 (150 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: 6.39 g, yellow viscous oil, (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 6H), 1.94 (s, 6H), 3.93 (s, 4H), 4.31 (d, *J* = 11.1 Hz, 2H), 4.35 (d, *J* = 11.1 Hz, 2H), 4.40 (s, 4H), 4.65 (q, *J* = 7.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.67, 17.89, 30.74, 37.84, 46.28, 55.28, 62.76, 63.34, 66.21, 70.82, 167.46, 171.49, 172.06, 212.52. Calcd: $[M+Na]^+$ ($C_{21}H_{31}BrNaO_{10}S_4$) m/z = 673.0. Found: ESI-MS: $[M+Na]^+$ m/z = 673.0 Anal. Calcd for $C_{21}H_{31}BrO_{10}S_4$: C, 38.71; H, 4.80; S, 19.68. Found: C, 40.08; H, 4.98; S, 19.50.

Xan_4-G_2-BiB [5] – Xan_4-G_2-COOH (6.52 g, 6.42 mmol, 1 equiv.), HEBiB (2.03 g, 9.63 mmol, 1.5 equiv.), DPTS (0.38 g, 1.28 mmol, 0.2 equiv.), DCC (2.65 g, 12.84 mmol, 2 equiv.) in anhydrous CH_2Cl_2 (60 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 (20:80), gradually increasing the polarity to ethyl acetate:hexane (60:40). Yield: 4.53 g, yellow viscous oil, (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 6H), 1.29 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 12H), 1.94 (s, 6H), 3.95 (s, 8H), 4.19-4.36 (m, 12H), 4.36-4.49 (m, 4H), 4.64 (q, *J* = 7.1 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.67, 17.65, 17.87, 30.74, 37.64, 46.27, 46.67, 55.48, 62.90, 63.34, 65.66, 66.21, 70.82, 167.46, 171.37, 171.67, 171.86, 212.71. Calcd: $[M+Na]^+$ ($C_{41}H_{59}BrNaO_{12}S_8$) m/z = 1229.04. Found: ESI-MS: $[M+Na]^+$ m/z = 1229.17. Anal. Calcd for $C_{41}H_{59}BrO_{20}S_8$: C, 40.75; H, 4.92; S, 21.23. Found: C, 39.69; H, 4.92; S, 18.48.

p[(Xan_2-G_1)-^{t}BuMA_{50}] and p[(Xan_4-G_2)-^{t}BuMA_{50}] - A**tom transfer radical polymerisation (ATRP) of tertiary butyl methacrylate (^{t}BuMA) in IPA/H_2O with Xan_2-G_1-BiB [4] or Xan_4-G_2-BiB [5] –** In a typical synthesis, targeting DP_n = 50 monomer units for the primary chains, Xan_2-G_1-BiB **[4]** (0.1744 g, 0.281 mmol, 1 equiv.), ^{t}BuMA **[6]** (2 g, 14.1 mmol, 50 equiv.) and bpy (0.105 g, 0.563 mmol, 2 equiv.) were placed into a 10 mL round-bottomed flask. IPA/H_2O (92.5/7.5 v/v) was added to the flask (50 wt% based on ^{t}BuMA, 2g, 2.6 mL) and the solution was stirred and deoxygenated using a nitrogen purge for 10 minutes. Cu(I)Cl (0.028 g, 0.281 mmol, 1 equiv) was added to the flask, whilst maintaining a positive flow of nitrogen, and the solution was left to polymerise at 30 °C. The reaction was terminated when conversion reached >95%, indicated by ^{1}H NMR after 18 hours, by exposure to oxygen and addition of THF. The solution was passed through a neutral alumni column to remove the catalytic system, and precipitated twice into cold hexane (cooled using an acetone/dry ice bath). After drying the precipitated sample overnight under high vacuum to remove residual solvents, the polymer was obtained as a white solid.

p[(Xan_2-G_1)-^{t}BuMA_{50}-EGDM$A_{0.8}$] and p[(Xan_4-G_2)-^{t}BuMA_{50}-EGDM$A_{0.8}$] - A**tom transfer radical polymerisation (ATRP) of tertiary butyl methacrylate (^{t}BuMA) in IPA/H_2O with Xan_2-G_1-BiB [4] or Xan_4-G_2-BiB [5] –** In a typical synthesis, targeting DP_n = 50 monomer units for the primary chains, Xan_2-G_1-BiB **[4]** (0.1744 g, 0.281 mmol, 1 equiv.), ^{t}BuMA **[6]** (2 g, 14.1 mmol, 50 equiv.), bpy (0.105 g, 0.563 mmol, 2 equiv.) and bifunctional monomer ethylene glycol dimethacrylate, EGDMA **[7]** (0.045 g, 0.225 mmol, 0.8 equiv.) were placed into a 10 mL round-bottomed flask. IPA/H_2O (92.5/7.5 v/v) was added to the flask (50 wt% based on ^{t}BuMA, 2g, 2.6 mL) and the solution was stirred and deoxygenated using a nitrogen purge for 10 minutes. Cu(I)Cl (0.028 g, 0.281 mmol, 1 equiv) was added to the flask, whilst maintaining a positive flow of nitrogen, and the solution was left to polymerise at 30 °C. The reaction was terminated when conversion

reached >98%, indicated by ^{1}H NMR after 18 hours, by exposure to oxygen and addition of THF. The solution was passed through a neutral alumni column to remove the catalytic system, and precipitated twice into cold hexane (cooled using an acetone/dry ice bath). After drying the precipitated sample overnight under high vacuum to remove residual solvents, the polymer was obtained as a white solid.

General procedure for Sequential thiol-Michael addition reaction of dendrons - The xanthate-terminated dendron (200 mg) was dissolved in anhydrous THF (2 mL) and degassed for 5 minutes under a nitrogen atmosphere. *n*-butylamine (1 equiv per xanthate group) was added and the reaction left for 1.5 hours or until completion by TLC (40:60 ethyl acetate:hexane). The 2-(dimethylamino)ethyl acrylate (DMAEA) monomer (1.5 equiv per thiol) was added and the reaction mixture stirred at ambient temperature for 16 hours. The product was isolated by precipitating twice into hexane. Any residual solvent was removed under high vacuum to yield an orange viscous oil. The product was then dissolved in anhydrous THF (2 mL) and degassed for 5 minutes under a nitrogen atmosphere. *n*-butylamine (1.2 equiv per remaining xanthate group) was added and the reaction left for 1.5 hours or until completion by TLC (40:60 ethyl acetate:hexane). The benzyl acrylate monomer (1.5 equiv per thiol) was added and the reaction mixture stirred at ambient temperature for 16 hours. The product was isolated by precipitating twice into hexane. Any residual solvent was removed under high vacuum to yield an orange viscous oil.

General procedure for Simultaneous thiol-Michael addition reaction of dendrons - The xanthate-terminated dendron (200 mg) was dissolved in anhydrous THF (2mL) and degassed for 5 minutes under a nitrogen atmosphere. *n*-butylamine (1.2 equiv per xanthate group) was added and the reaction left for 1.5 hours or until completion by TLC (40:60 ethyl acetate: hexane). A mixture of acrylate monomers (1 equiv per thiol) was added and the reaction mixture stirred at ambient temperature for 16 hours. The product was isolated by precipitating twice into hexane. Any residual solvent was removed under high vacuum to yield an orange viscous oil.

$Bz_{1\text{-}2}$-$Am_{1\text{-}2}$-G_1 – The sequential and simultaneous thiol Michael addition procedures were carried out as described above using Xan_2-G_1-TSe **[1]**, (0.2 g, 0.136 mmol) and *n*- butylamine (74 µL, 0.7 mmol, 2.4 equiv.) stirred in anhydrous THF (2 mL) for 1.5 hours, followed by addition of 2-(dimethylamino)ethyl acrylate (Am) and benzyl acrylate (Bz), then stirred for 16 hours. The product was isolated by precipitating twice into hexane. Any residual solvent was removed under high vacuum to yield an orange viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14-1.19 (m, 3H), 2.31 (s), 2.42-2.49 (m), 2.58-2.64 (m), 2.64-2.75 (m, 4H), 2.83-2.96 (m, 4H), 3.18-3.30 (m, 4H), 3.43 (t, *J* = 5.8 Hz, 2H), 4.12-4.24 (m), 4.46 (t, *J* = 5.8 Hz, 2H), 5.13 (s), 7.29-7.43 (m), 7.79 (d, 2H, *J* = 8.0 Hz). Calcd: $[MNa]^+$ ($C_{35}H_{47}NaO_{12}S_3$) = 792.23 Da. Found: MALDI-TOF MS: $[MNa]^+$ = 796.81 Da.

$Bz_{1\text{-}4}$-$Am_{1\text{-}4}$-G_2 – The sequential and simultaneous thiol Michael addition procedures were carried out as described above using Xan_4-G_2-TSe **[2]**, (0.2 g, 0.136 mmol) and *n*- butylamine (79 µL, 0.8 mmol, 4.8 equiv.) stirred in anhydrous THF (2 mL) for 1.5 hours, followed by addition of 2-(dimethylamino)ethyl acrylate (Am) and benzyl acrylate (Bz), then stirred for 16 hours. The product was isolated by precipitating twice into hexane. Any residual solvent was removed under high vacuum to yield an orange viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15-1.21 (m, 3H), 1.21-1.30 (m, 6H), 2.28 (s), 2.44 (s, 3H), 2.54-2.61 (m), 2.62-2.73 (m, 4H), 2.83-2.94 (m, 4H), 3.20-3.30 (m, 4H), 3.4-3.48 (m, 2H), 4.13-4.34 (m), 4.45 (m, 2H), 5.13 (s), 7.28-7.41 (m), 7.80 (d, 2H, *J* = 8.6 Hz).

$Bz_{1\text{-}8}$-$Am_{1\text{-}8}$-G_3 – The sequential and simultaneous thiol Michael addition procedures were carried out as described above using Xan_8-G_3-TSe **[3]**, (0.2 g, 0.136 mmol) and *n*- butylamine (82 µL, 0.8 mmol, 9.6 equiv.) stirred in anhydrous THF (2 mL) for 1.5 hours, followed by addition of 2-(dimethylamino)ethyl acrylate (Am) and benzyl acrylate (Bz), then stirred for 16 hours. The product was isolated by precipitating twice into hexane. Any residual solvent was removed under high

vacuum to yield an orange viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16-1.30 (m, 3H), 2.27 (s), 2.45 (s, 3H), 2.52-2.59 (m), 2.61-2.72 (m, 4H), 2.82-2.93 (m, 4H), 3.26 (s, br, 4H), 3.43 (m, 2H), 4.11-4.34 (m), 4.47 (m, 2H), 5.13 (s), 7.28-7.41 (m), 7.80 (d, 2H, *J* = 7.5 Hz).

General procedure for Sequential thiol-Michael addition reaction of polymer dendron hybrids - The xanthate-terminated polymer dendron hybrid (200 mg) was dissolved in anhydrous THF (2 mL) and degassed for 5 minutes under a nitrogen atmosphere. Varying equivalents of *n*-butylamine (relative to the DP_n of primary chains by ^{1}H NMR) were added and the reaction left for 1.5 hours or until completion by TLC (60:40 hexane:ethyl acetate). Calibration curves of the percentage of xanthate groups deprotected (calculated by ^{1}H NMR) vs equivalents *n*-butylamine added were plotted for each polymer. The benzyl acrylate monomer (Bz) (5 equiv per xanthate – relative to DP_n of primary chains by ^{1}H NMR) was added and the reaction mixture stirred at ambient temperature for 16 hours. The product was isolated by precipitating twice into hexane or petroleum ether (40-60 °C). Any residual solvent was removed under high vacuum to yield a white solid. The product was then dissolved in anhydrous THF (2 mL) and degassed for 5 minutes under a nitrogen atmosphere. *n*-butylamine (2.5 equiv per xanthate group – relative to DP_n of primary chains by ^{1}H NMR) was added and the reaction left for 1.5 hours or until completion by TLC (40:60 ethyl acetate:hexane). The 2-(dimethylamino)ethyl acrylate (DMAEA) monomer (Am) (5 equiv per xanthate – relative to DP_n of primary chains by NMR) was added and the reaction mixture stirred at ambient temperature for 16 hours. The product was isolated by precipitating twice into petroleum ether (40-60 °C). Any residual solvent was removed under high vacuum to yield a white solid.

General procedure for Simultaneous thiol-Michael addition reaction of polymer dendron hybrids - The xanthate-terminated polymer dendron hybrid (100 mg) was dissolved in anhydrous THF (2mL) and degassed for 5 minutes under a nitrogen atmosphere. *n*-butylamine (1.2 equiv per xanthate group – calculated using the calibration curve of the % xanthate groups deprotected vs equivalents *n*-butylamine added for the polymer) was added and the reaction left for 1.5 hours or until completion by TLC (40:60 ethyl acetate:hexane). A mixture of Bz and Am acrylate monomers (1 equiv per thiol – calculated using the calibration curve for the polymer) was added and the reaction mixture was stirred at ambient temperature for 16 hours. The product was isolated by precipitating twice into hexane. Any residual solvent was removed under high vacuum to yield a white solid.

p[($Bz_{1\text{-}4}$-$Am_{1\text{-}4}$-G_2)-^{t}$BuMA_{50}$] – The sequential and simultaneous thiol Michael addition procedures were carried out as described above using **p[(Xan_4-G_2)-^{t}$BuMA_{50}$]**, (0.2 g, 0.019 mmol) and *n*- butylamine dissolved in anhydrous THF (2 mL) for 1.5 hours, followed by addition of benzyl acrylate (Bz) and 2-(dimethylamino)ethyl acrylate (Am) and stirred at ambient temperature for 16 hours. The product was isolated by precipitating twice into hexane. Any residual solvent was removed under high vacuum to yield a white solid.

p[($Bz_{1\text{-}4}$-$Am_{1\text{-}4}$-G_2)-^{t}$BuMA_{50}$-$EGDMA_{0.8}$] – The sequential and simultaneous thiol Michael addition procedures were carried out as described above using **p[(Xan_4-G_2)-^{t}$BuMA_{50}$-$EGDMA_{0.8}$]**, (0.2 g, 0.021 mmol) and *n*- butylamine dissolved in anhydrous THF (2 mL) for 1.5 hours, followed by addition of benzyl acrylate (Bz) and 2-(dimethylamino)ethyl acrylate (Am) and stirred at ambient temperature for 16 hours. The product was isolated by precipitating twice into hexane. Any residual solvent was removed under high vacuum to yield an orange viscous oil.

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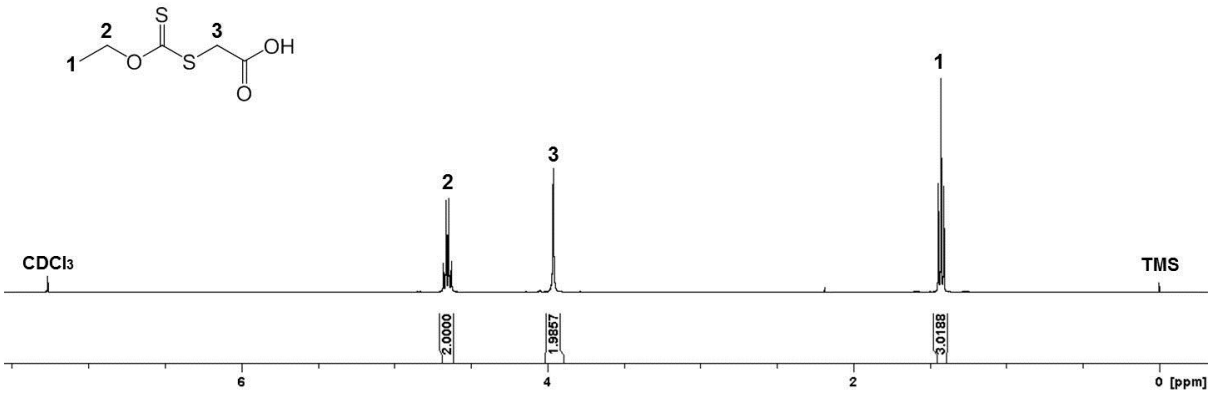

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of **2-((Ethoxycarbonothioyl)thio)acetic acid**

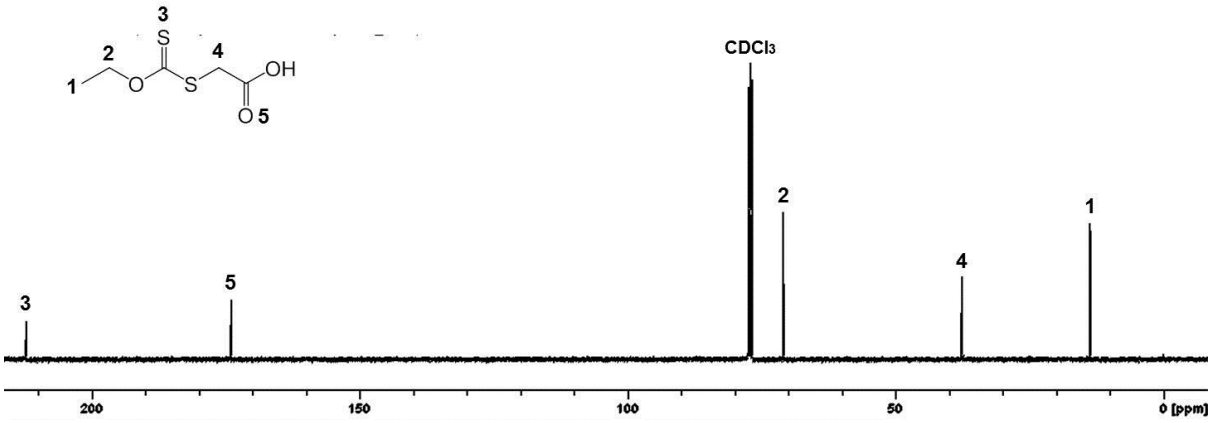

Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) of **2-((Ethoxycarbonothioyl)thio)acetic acid**

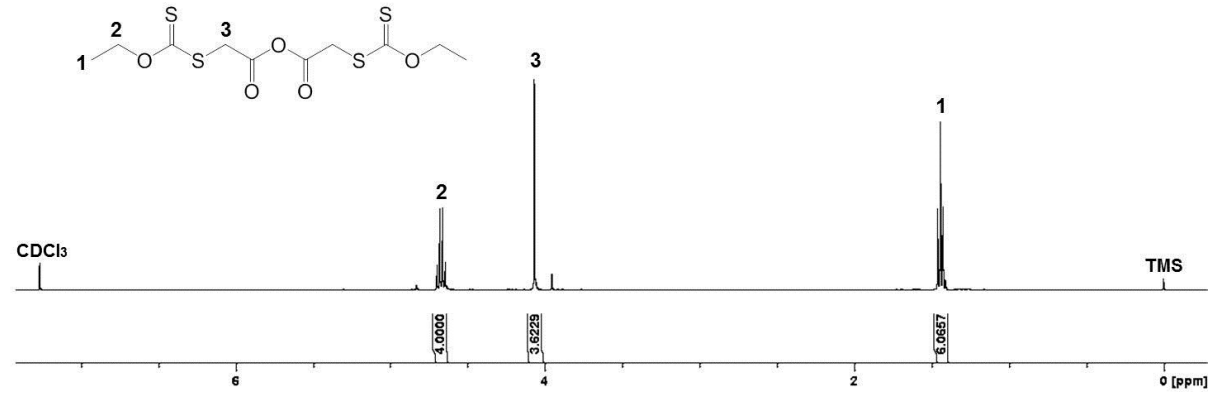

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of **2-((Ethoxycarbonothioyl)thio)acetic anhydride**

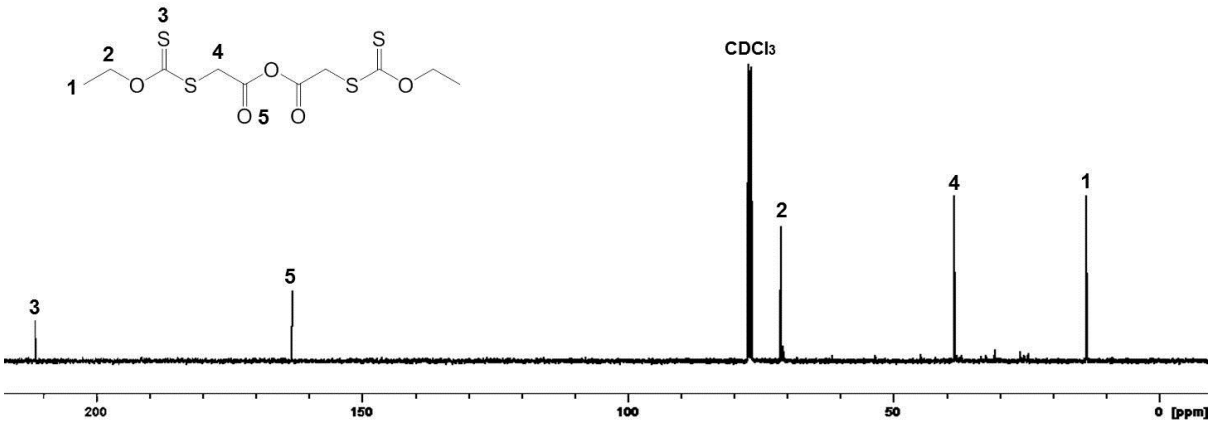

Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) of **2-((Ethoxycarbonothioyl)thio)acetic anhydride**

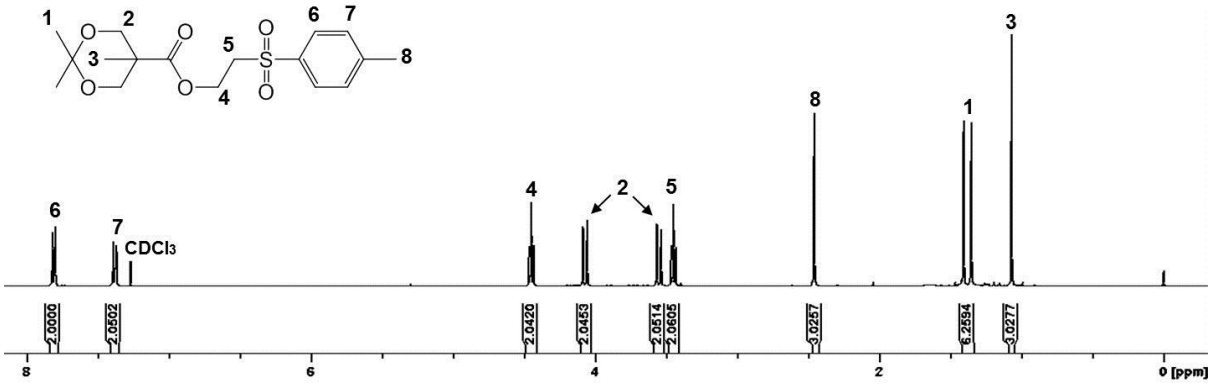

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of **Acet-G_1-TSe**

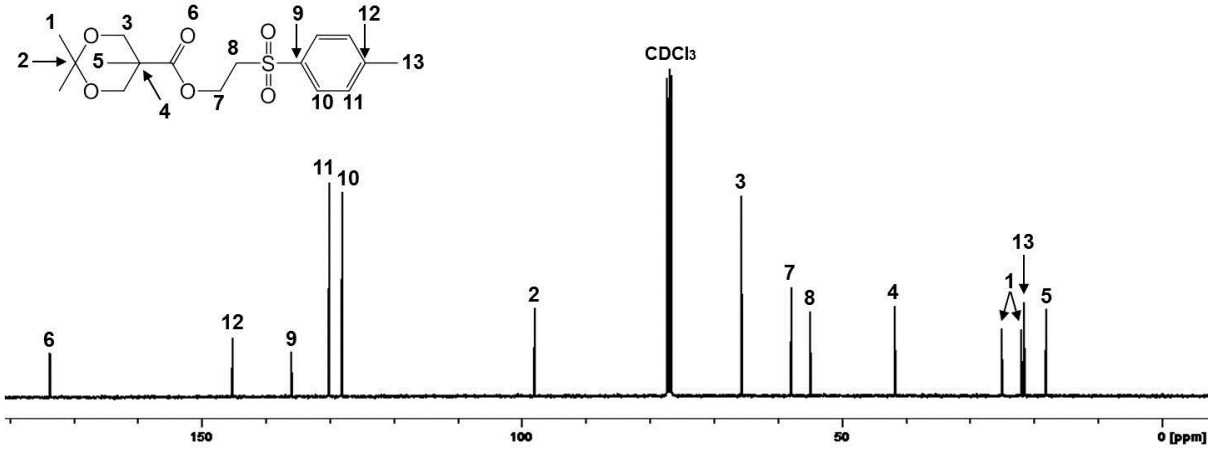

Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$) of **Acet-G_1-TSe**

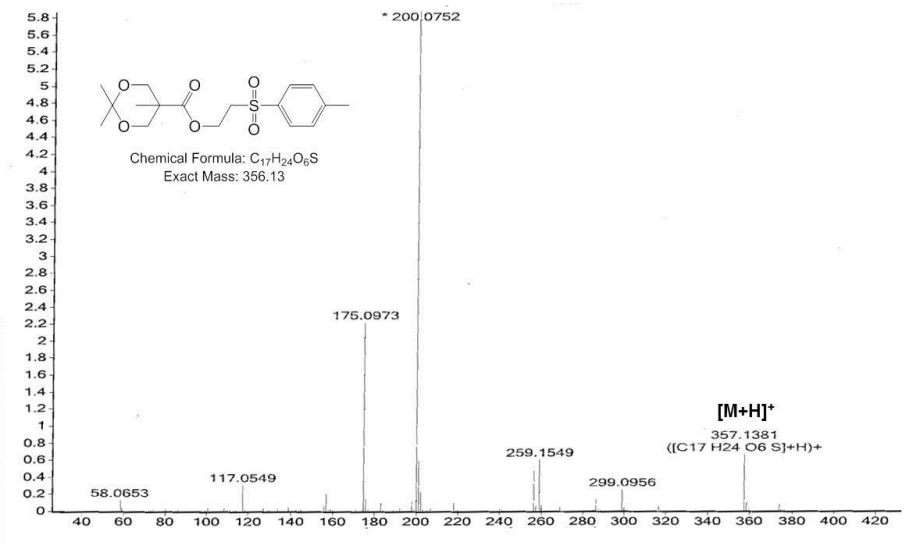

Figure S7. CI-MS (MeOH) of **Acet-G_1-TSe**

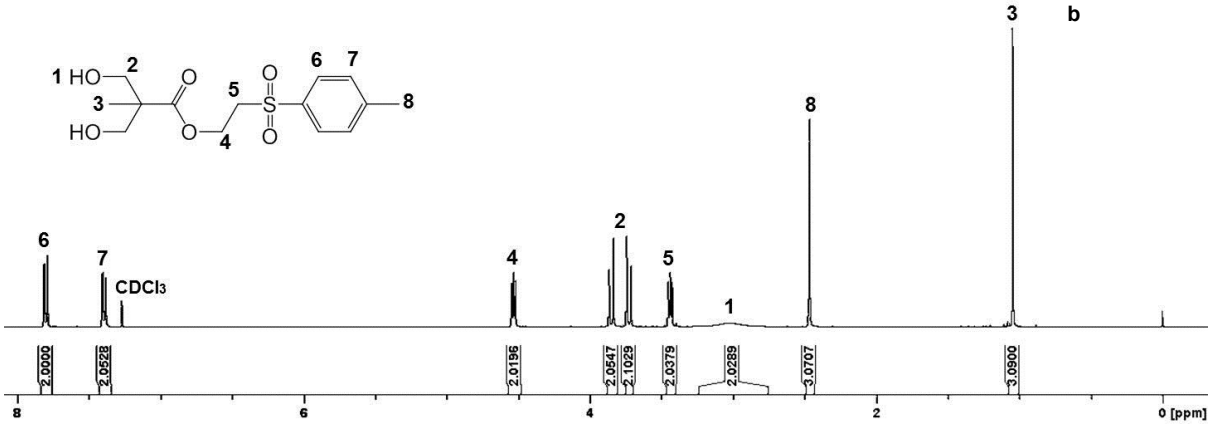

Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of **OH_2-G_1-TSe**

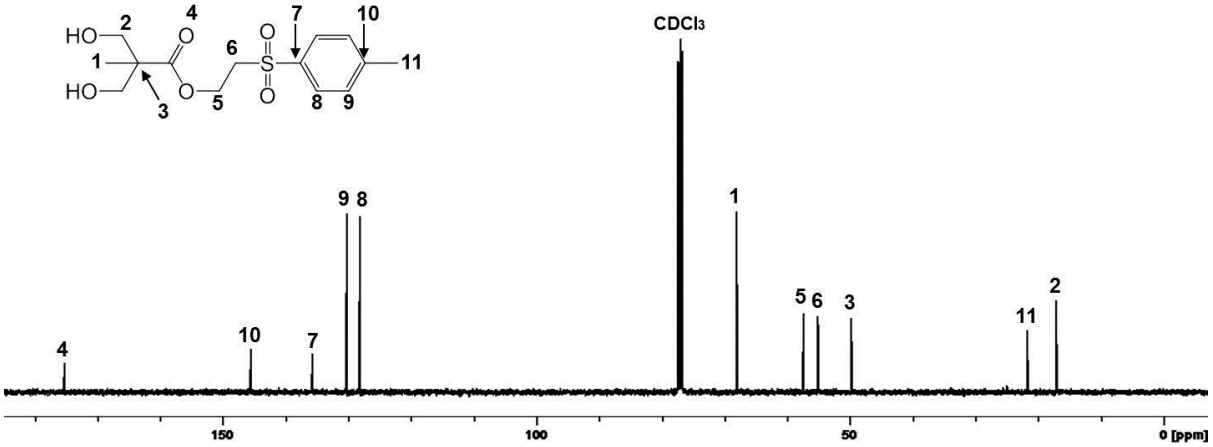

Figure S9. ^{13}C NMR (100 MHz, $CDCl_3$) of **OH_2-G_1-TSe**

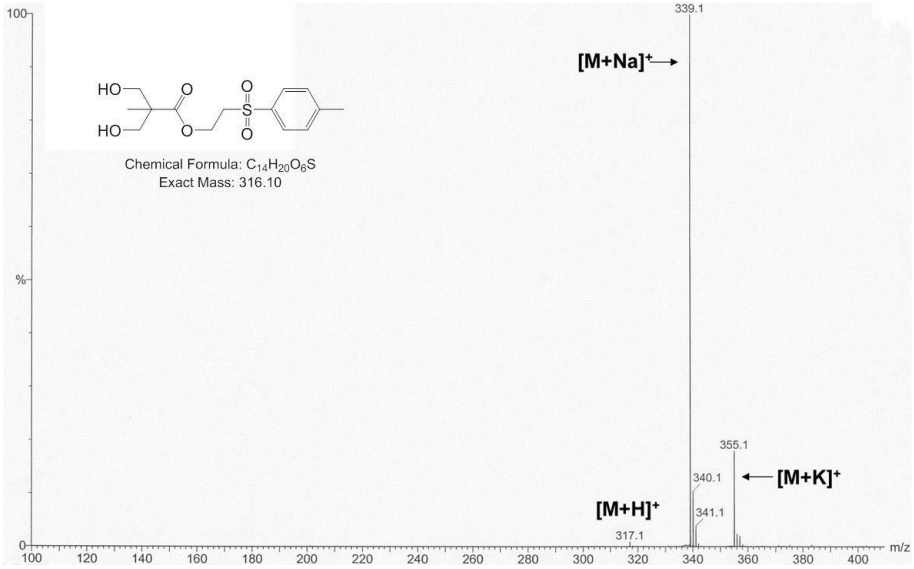

Figure S10. ESI-MS (MeOH) of **OH_2-G_1-TSe**

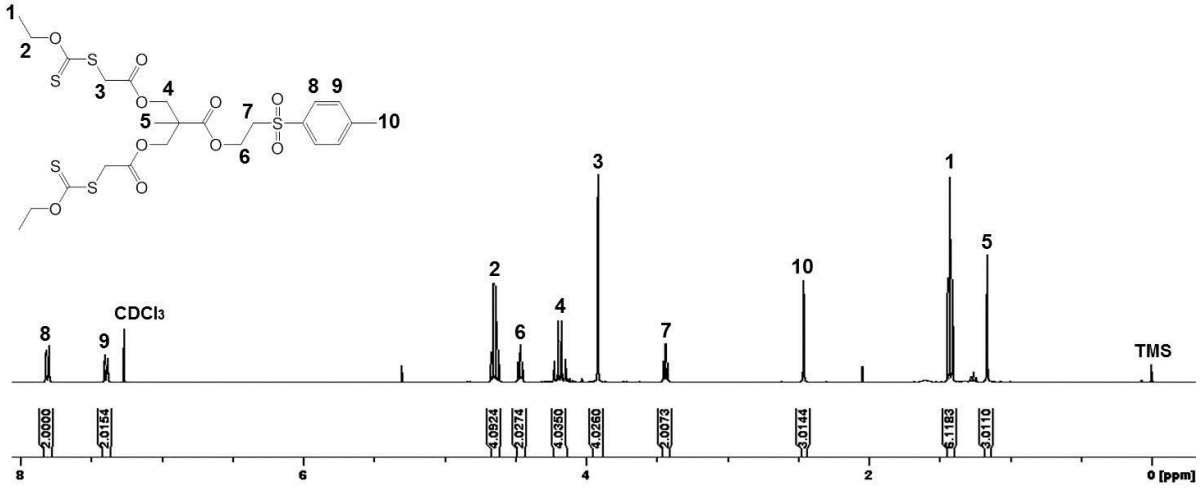

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_2-G_1-TSe [1]**

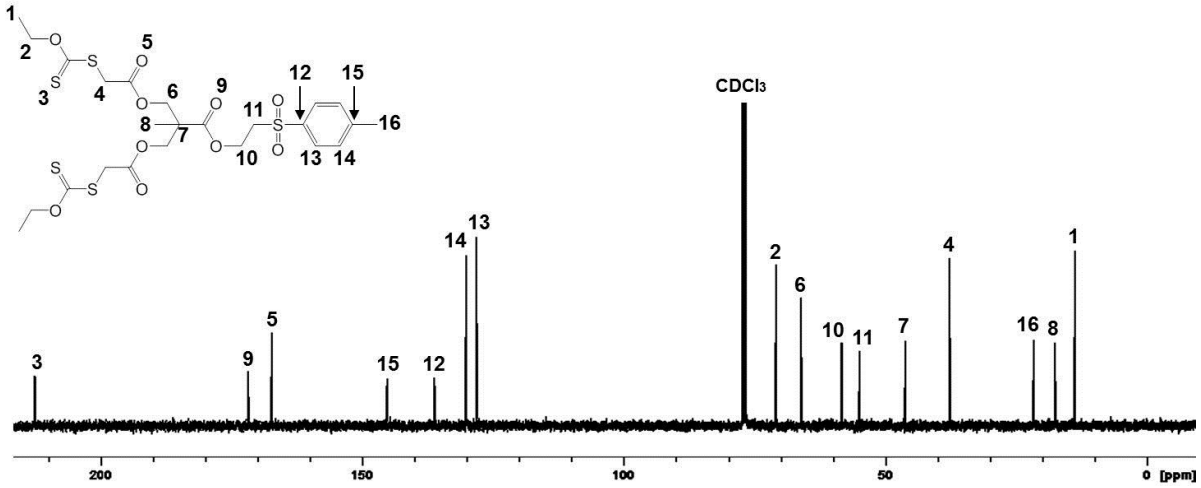

Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) of **Xan_2-G_1-TSe [1]**

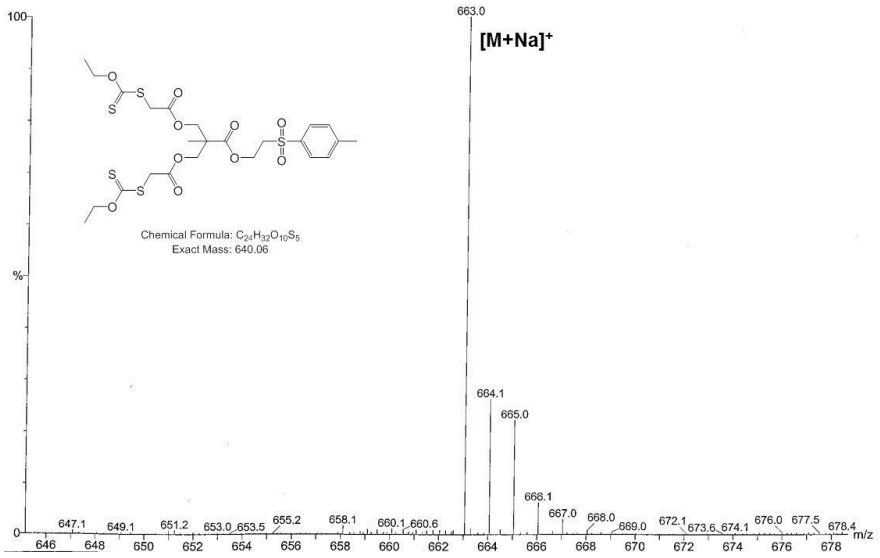

Figure S13. ESI-MS (MeOH) of **Xan_2-G_1-TSe [1]**

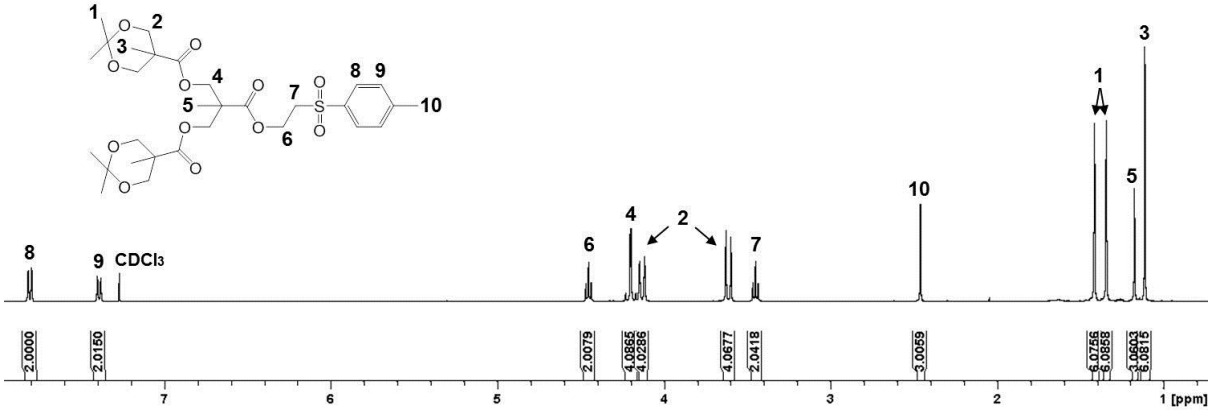

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) of **$Acet_2$-G_2-TSe**

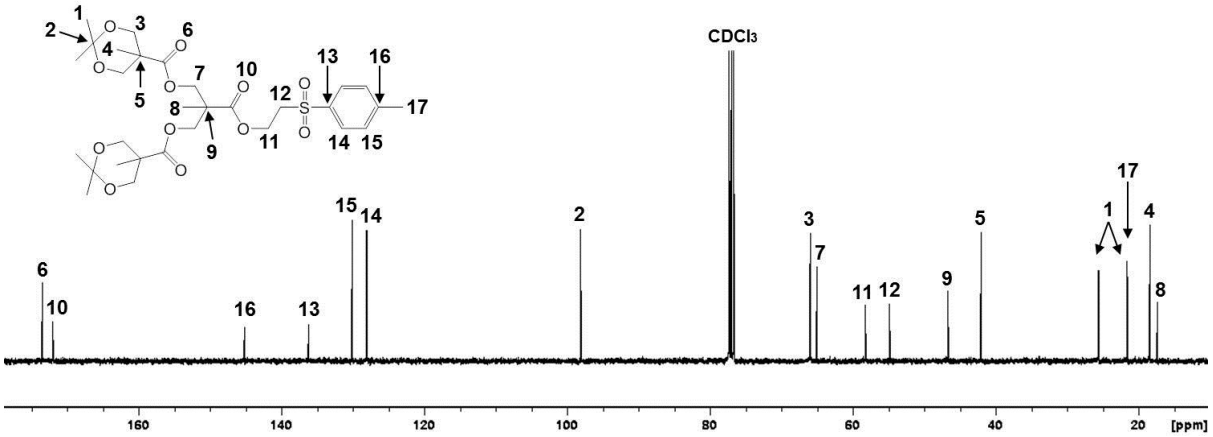

Figure S15. ^{13}C NMR (100 MHz, $CDCl_3$) of **$Acet_2$-G_2-TSe**

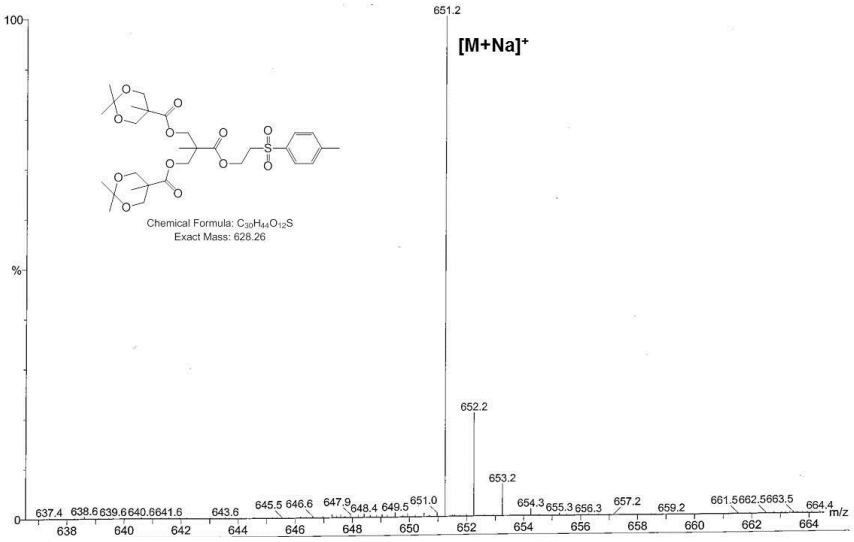

Figure S16. ESI-MS (MeOH) of **Acet$_2$-G$_2$-TSe**

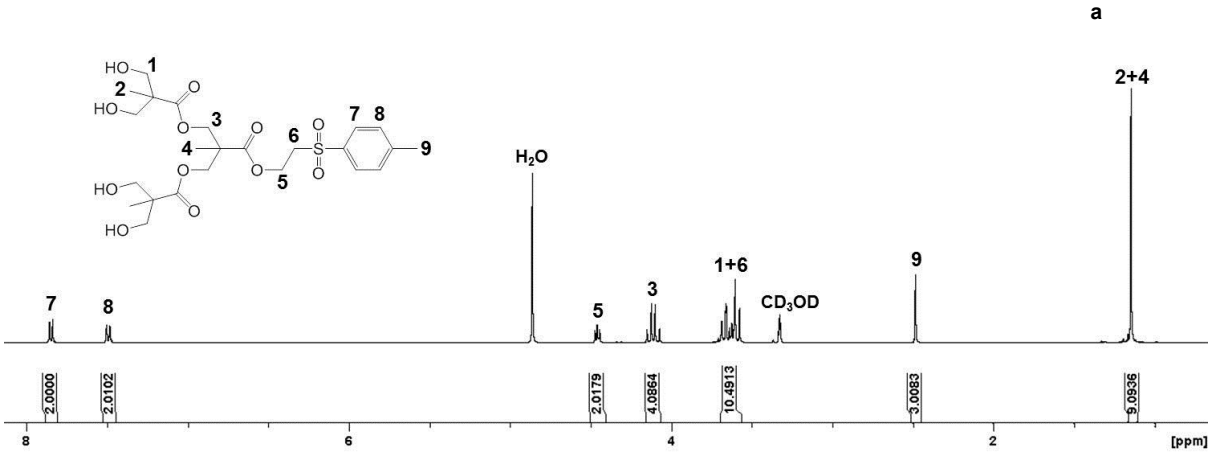

Figure S17. ^{1}H NMR (400 MHz, CD_3OD) of **OH$_4$-G$_2$-TSe**

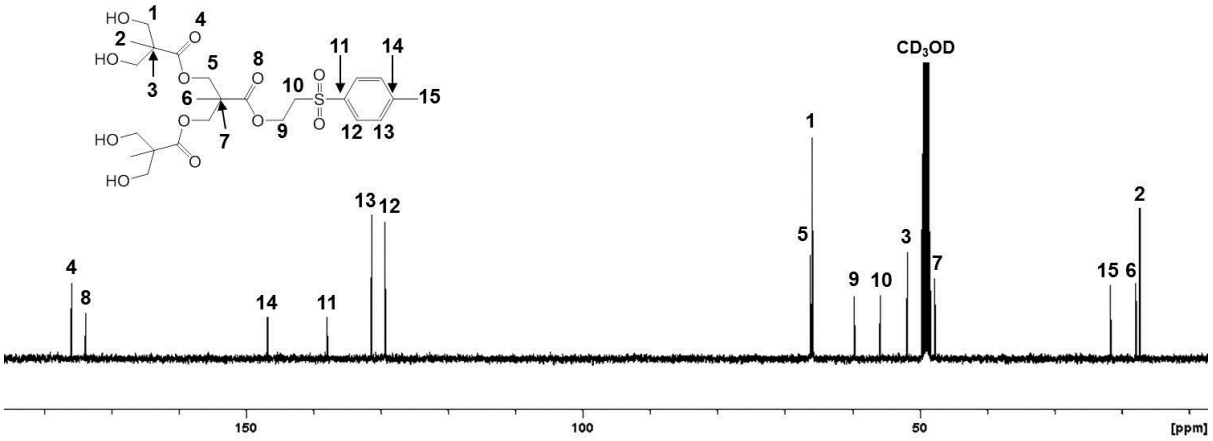

Figure S18. ^{13}C NMR (100 MHz, CD_3OD) of **OH$_4$-G$_2$-TSe**

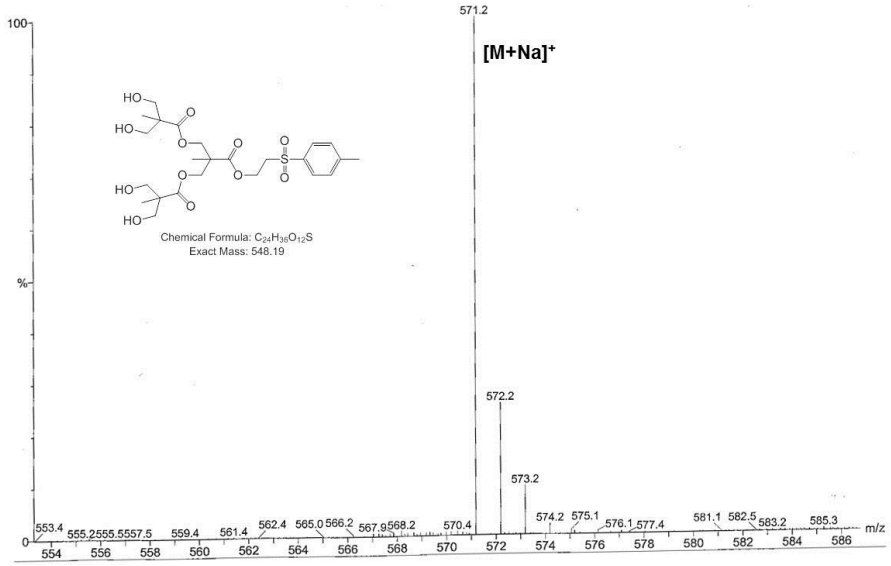

Figure S19. ESI-MS (MeOH) of **OH_4-G_2-TSe**

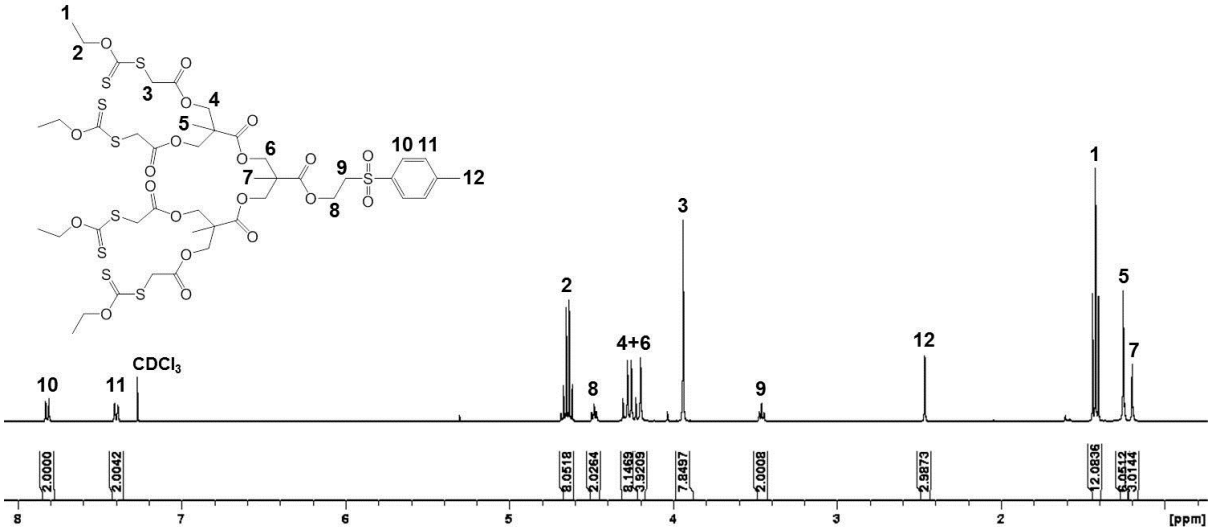

Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_4-G_2-TSe [2]**

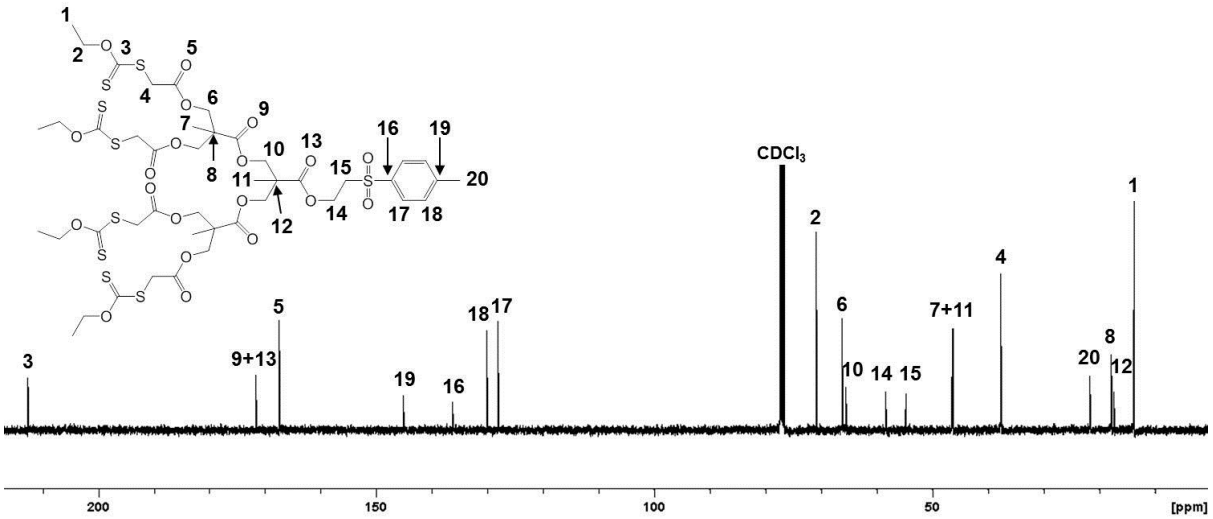

Figure S21. ^{13}C NMR (100 MHz, $CDCl_3$) of **Xan_4-G_2-TSe [2]**

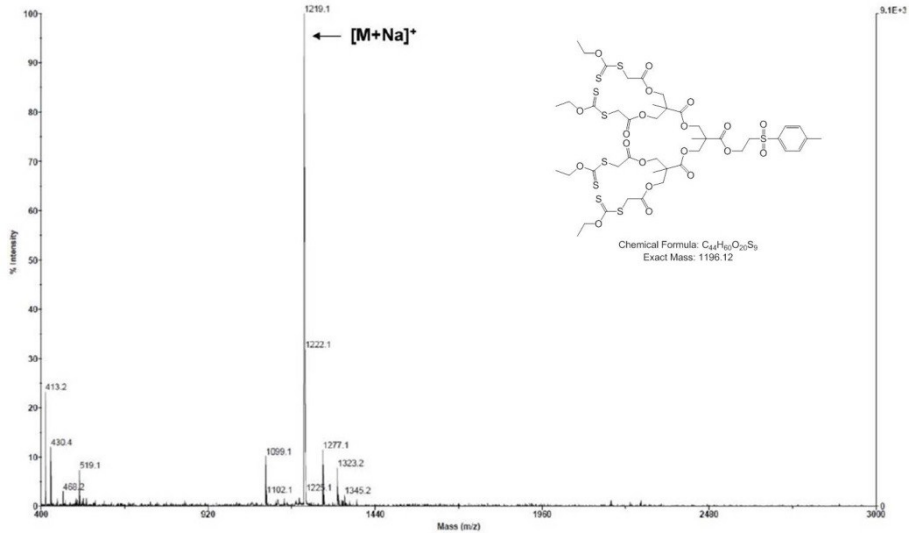

Figure S22. ESI-MS (MeOH) of **Xan_4-G_2-TSe [2]**

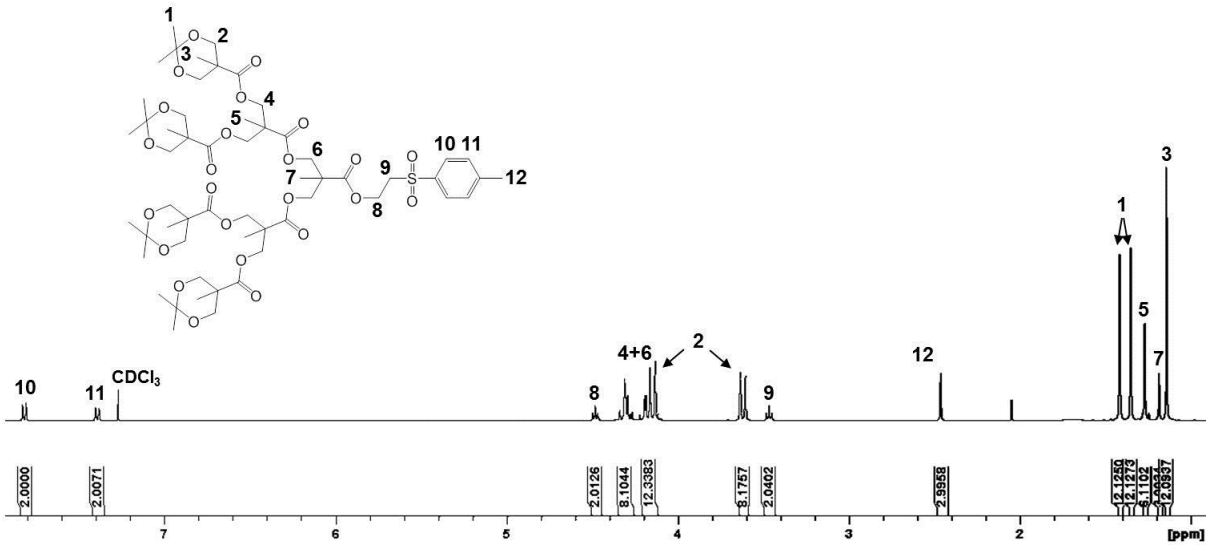

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of **$Acet_4$-G_3-TSe**

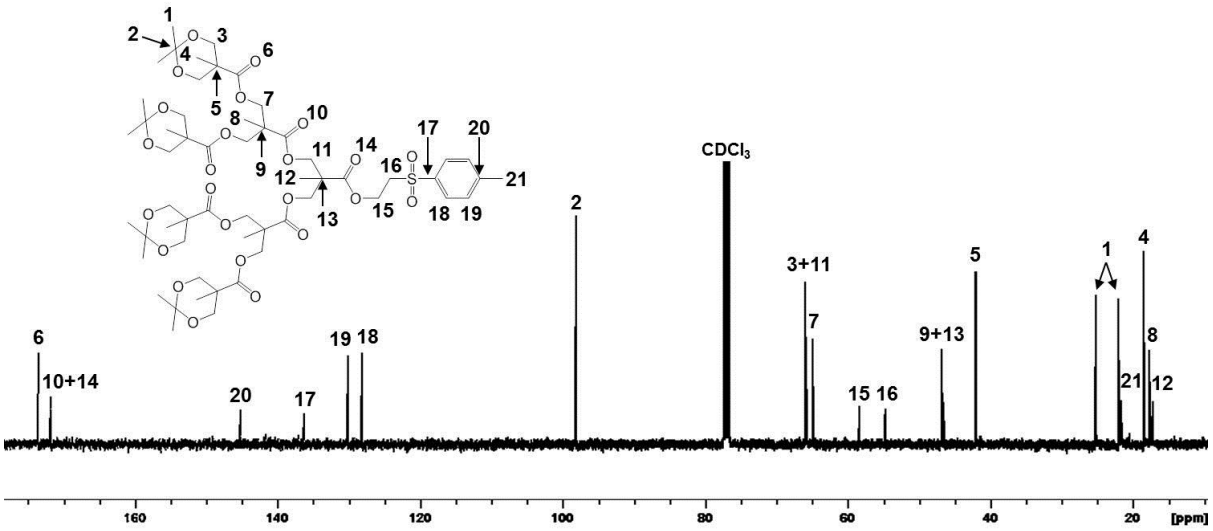

Figure S24. ^{13}C NMR (100 MHz, $CDCl_3$) of **Acet$_4$-G$_3$-TSe**

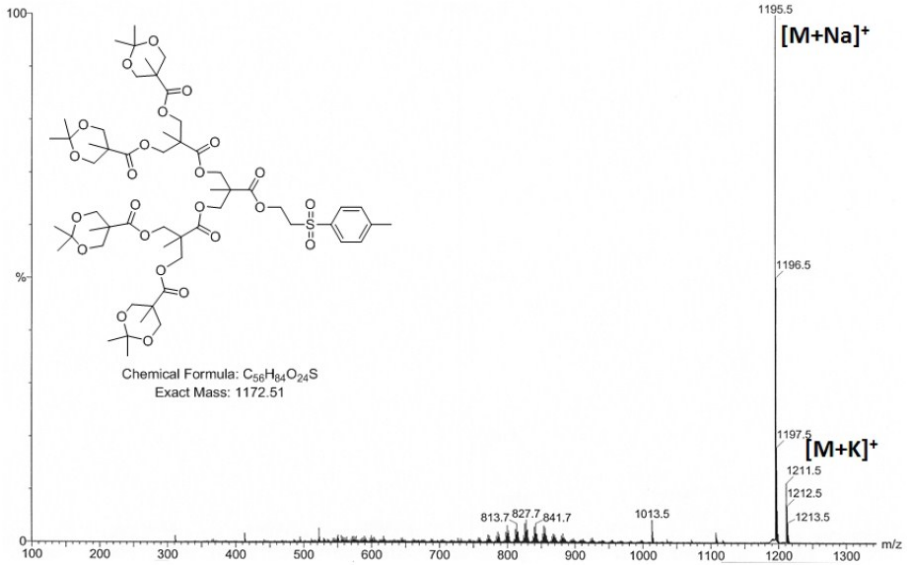

Figure S25. ESI- MS (MeOH) of **Acet$_4$-G$_3$-TSe**

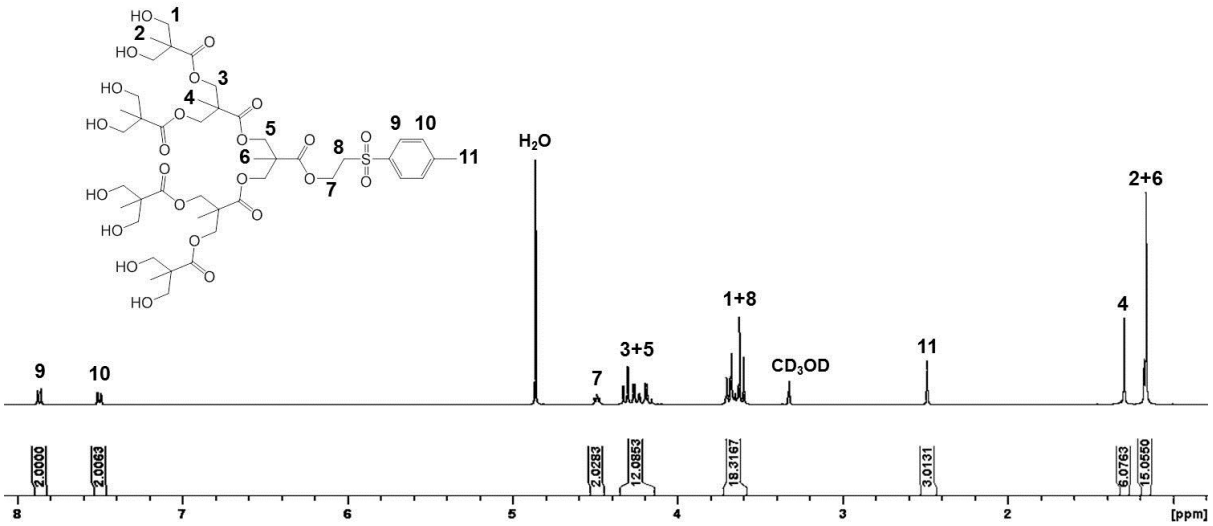

Figure S26. ^{1}H NMR (400 MHz, CD_3OD) of **OH_8-G_3-TSe**

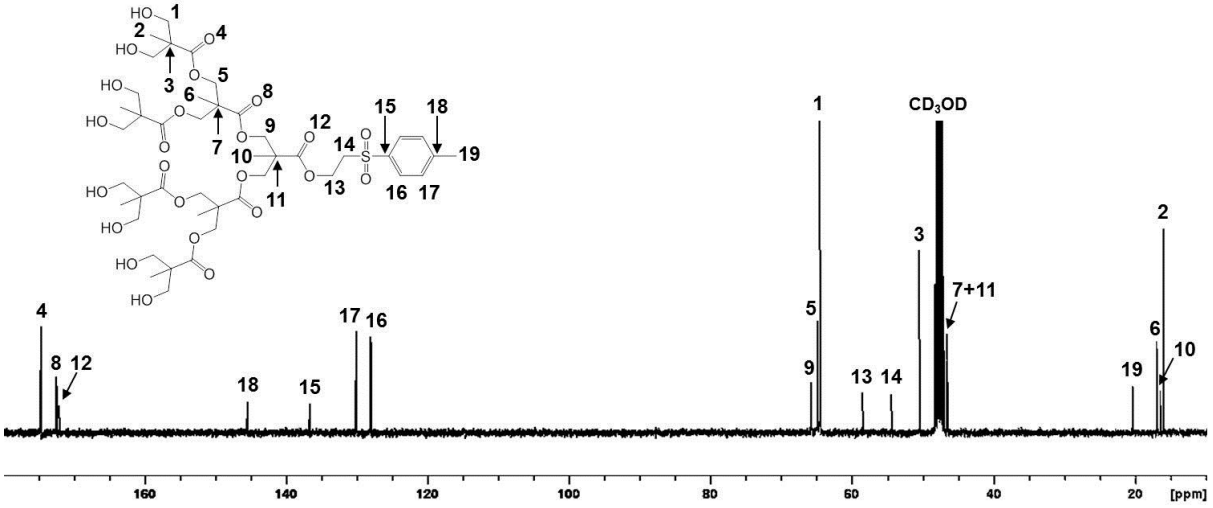

Figure S27. ^{13}C NMR (100 MHz, CD_3OD) of **OH_8-G_3-TSe**

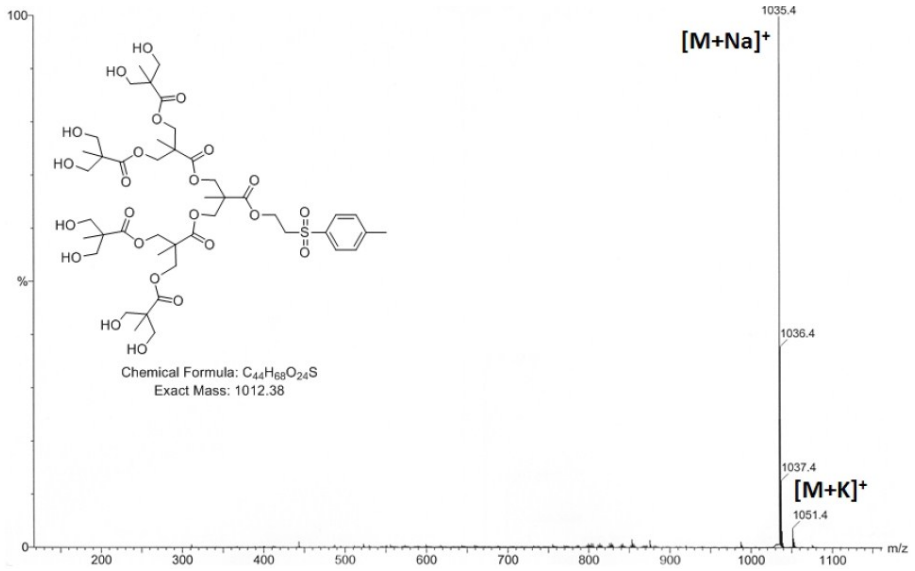

Figure S28. ESI MS (MeOH) of **OH_8-G_3-TSe**

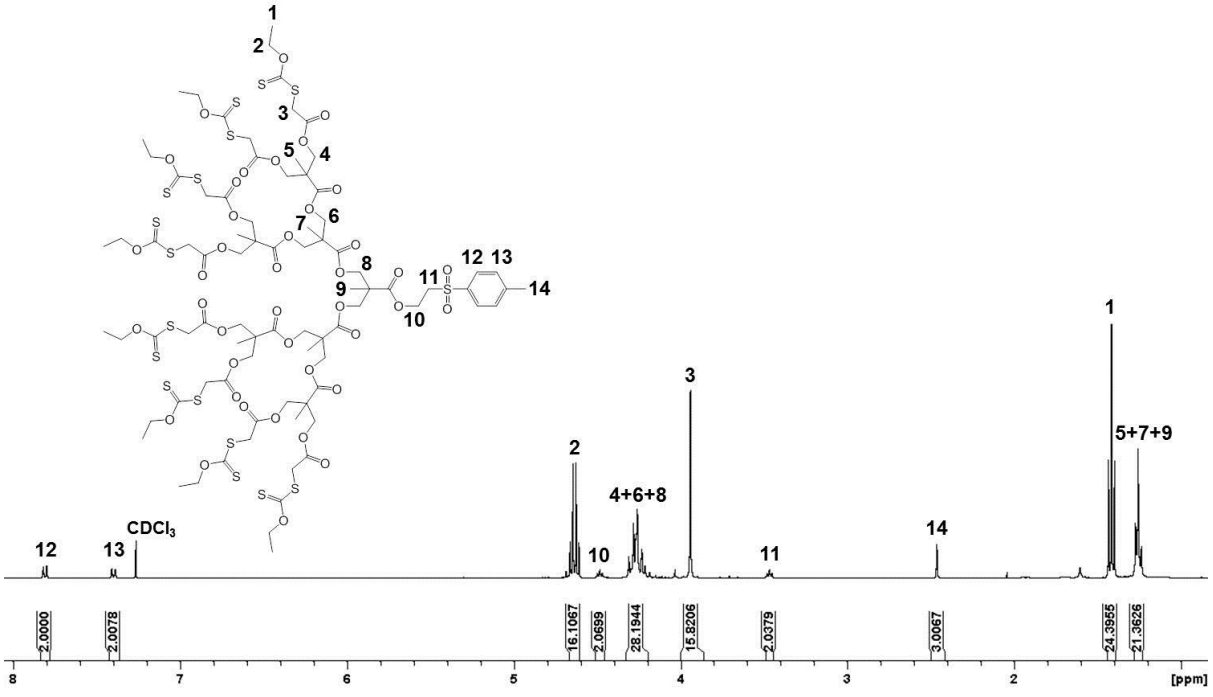

Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_8-G_3-TSe [3]**

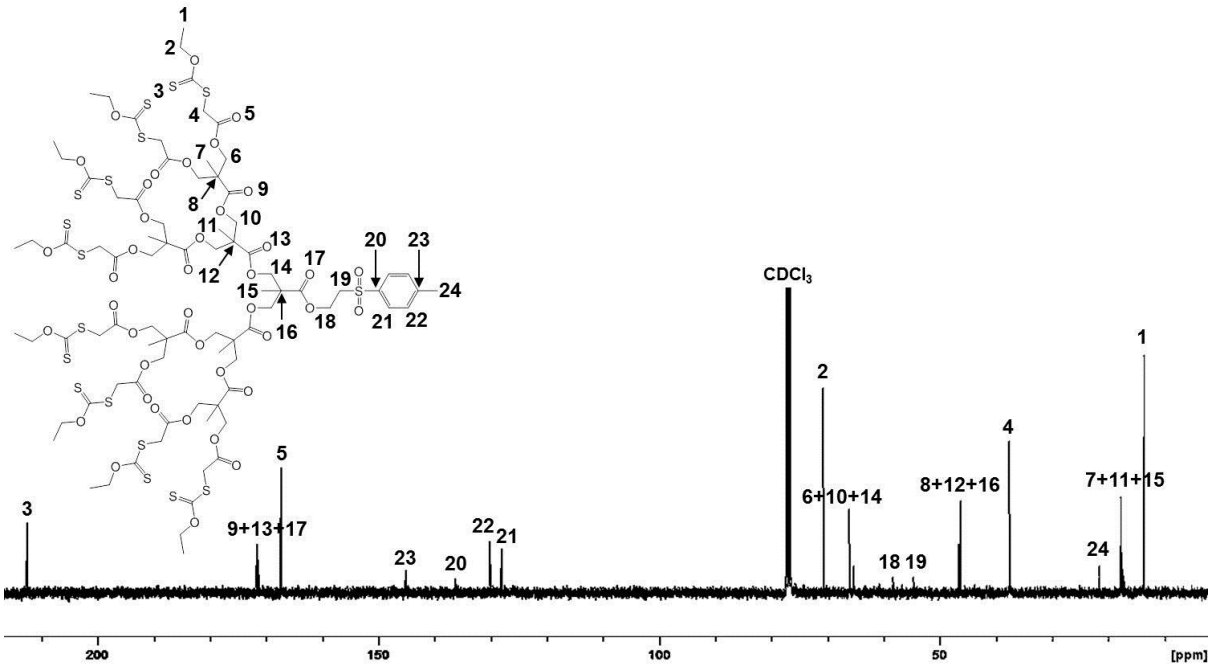

Figure S30. ^{13}C NMR (100 MHz, $CDCl_3$) of **Xan_8-G_3-TSe [3]**

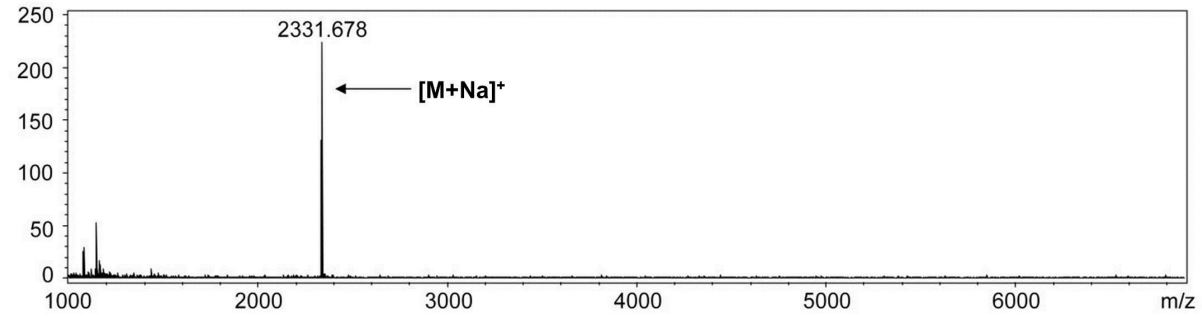

Figure S31. MALDI-TOF analysis of **Xan_8-G_3-TSe [3]**

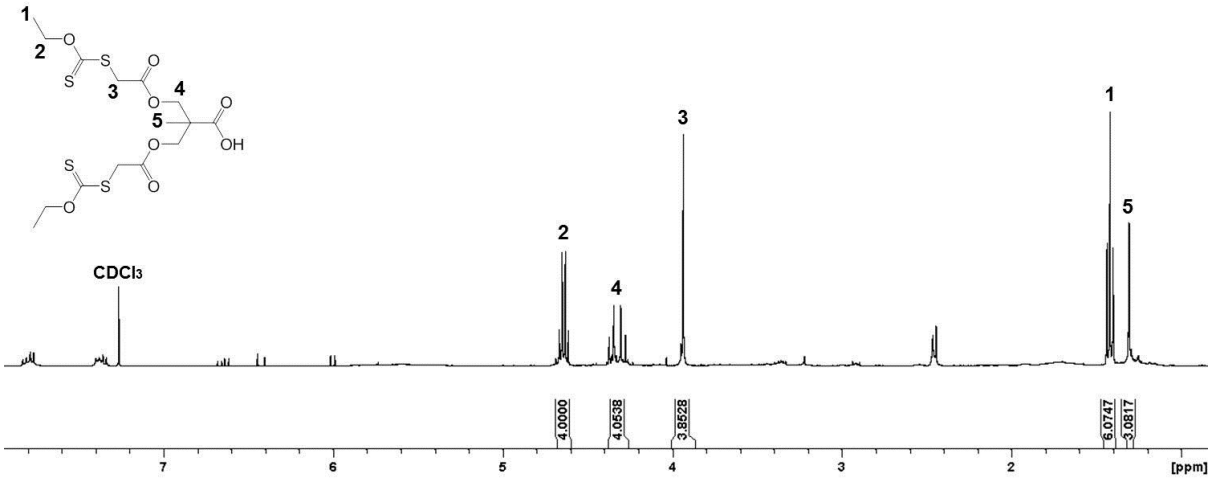

Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_2-G_1-COOH**

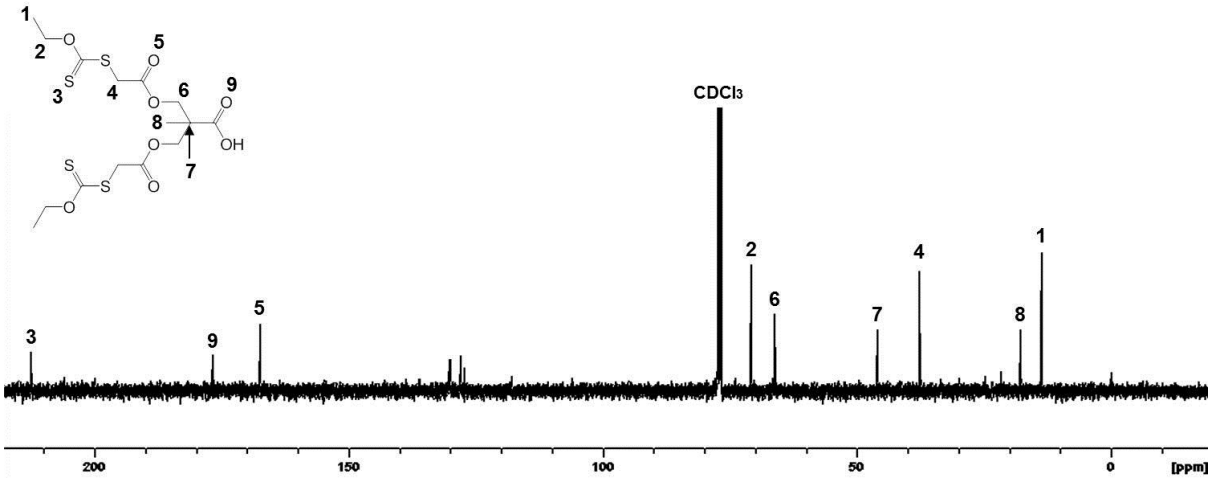

Figure S33. ^{13}C NMR (100 MHz, $CDCl_3$) of **Xan_2-G_1-COOH**

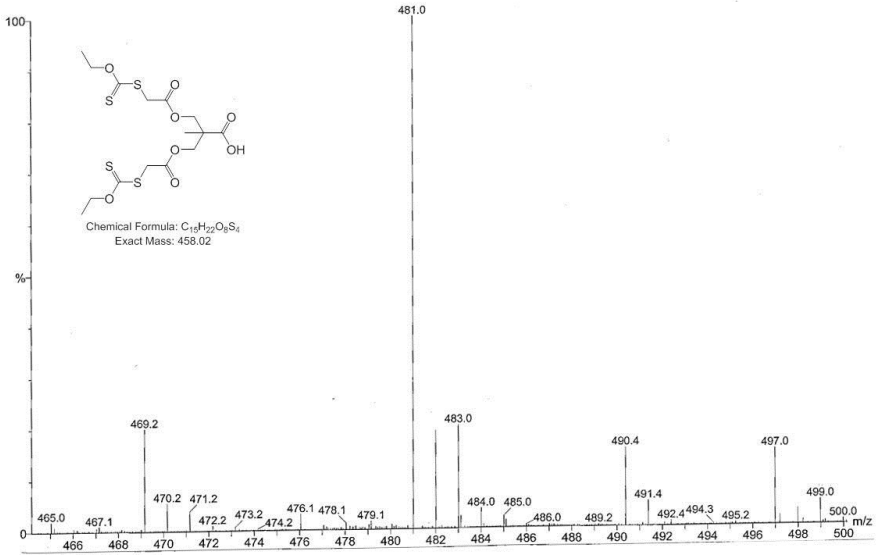

Figure S34. ESI MS (MeOH) of **Xan_2-G_1-COOH**

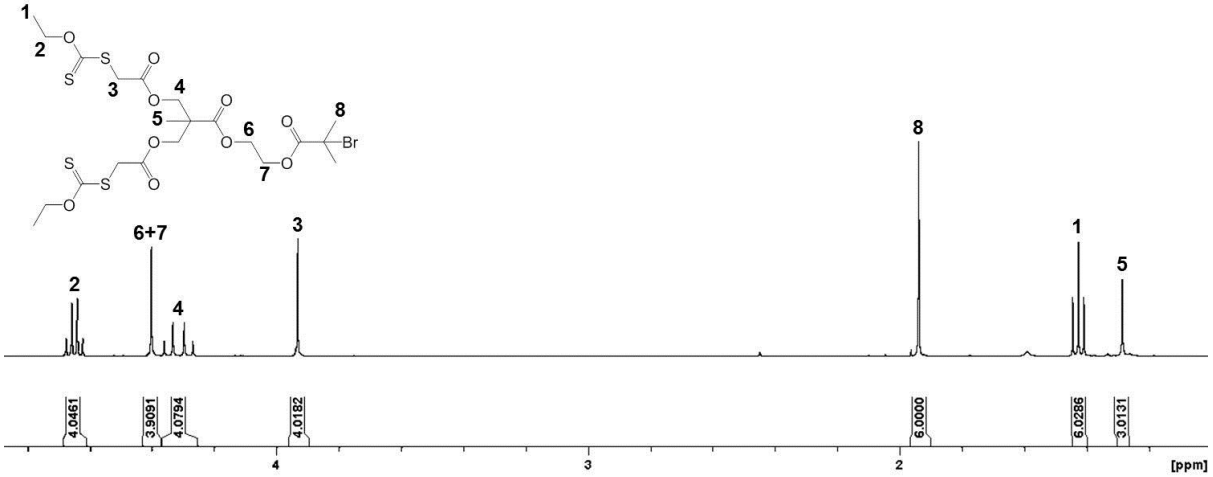

Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_2-G_1-BiB [4]**

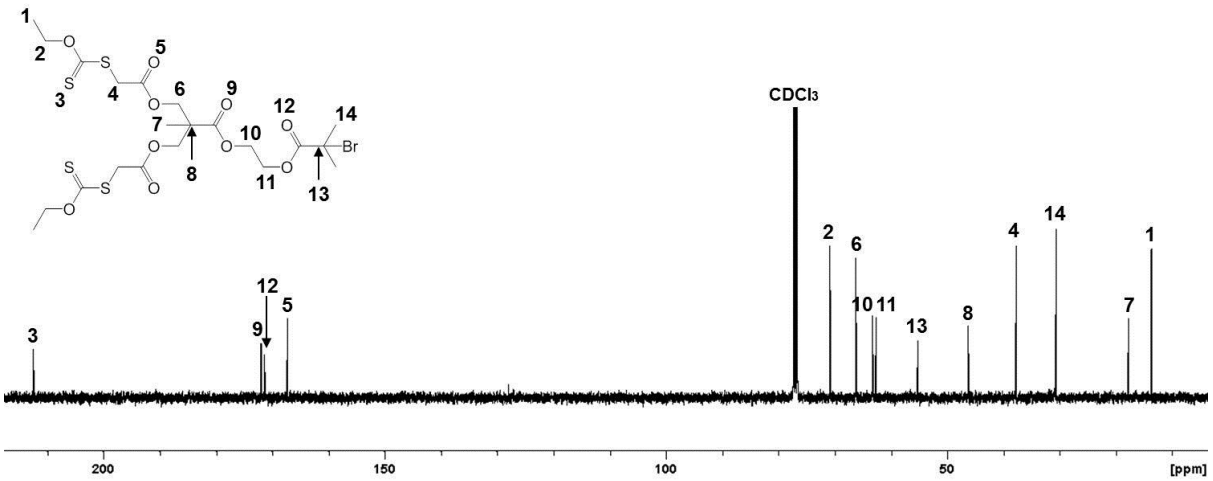

Figure S36. ^{13}C NMR (100 MHz, $CDCl_3$) of **Xan_2-G_1-BiB [4]**

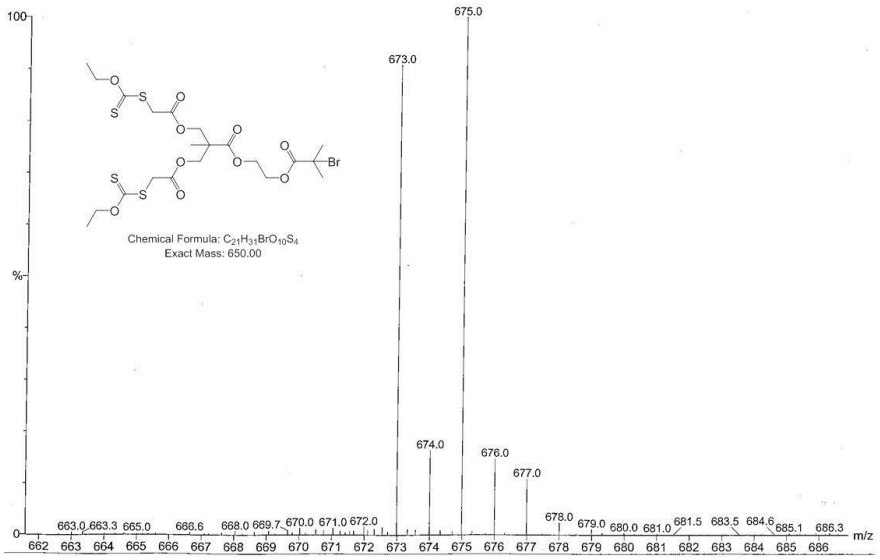

Figure S37. ESI MS (MeOH) of **Xan_2-G_1-BiB [4]**

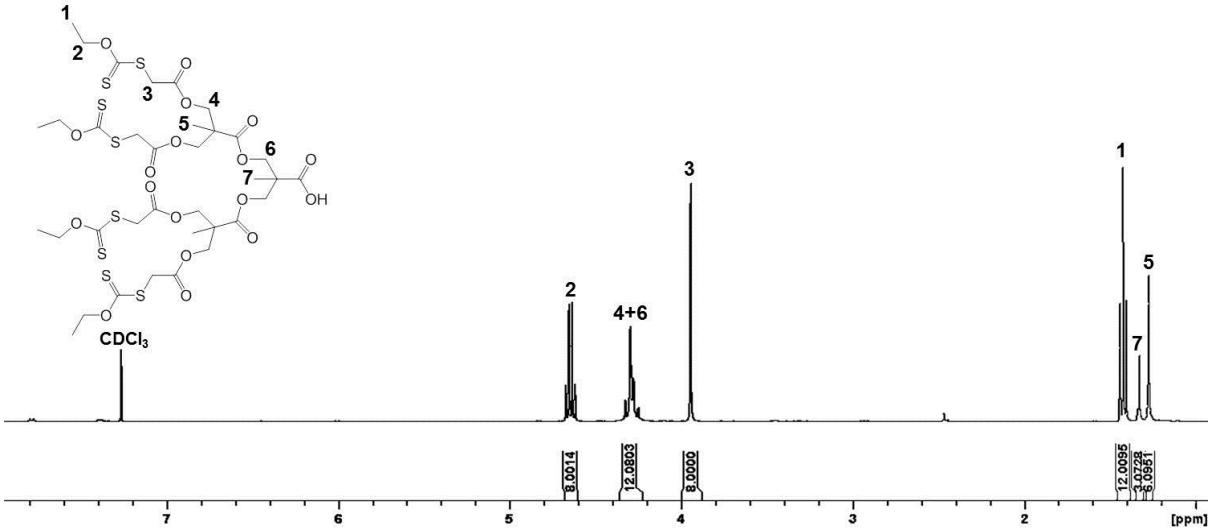

Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan_4-G_2-COOH**

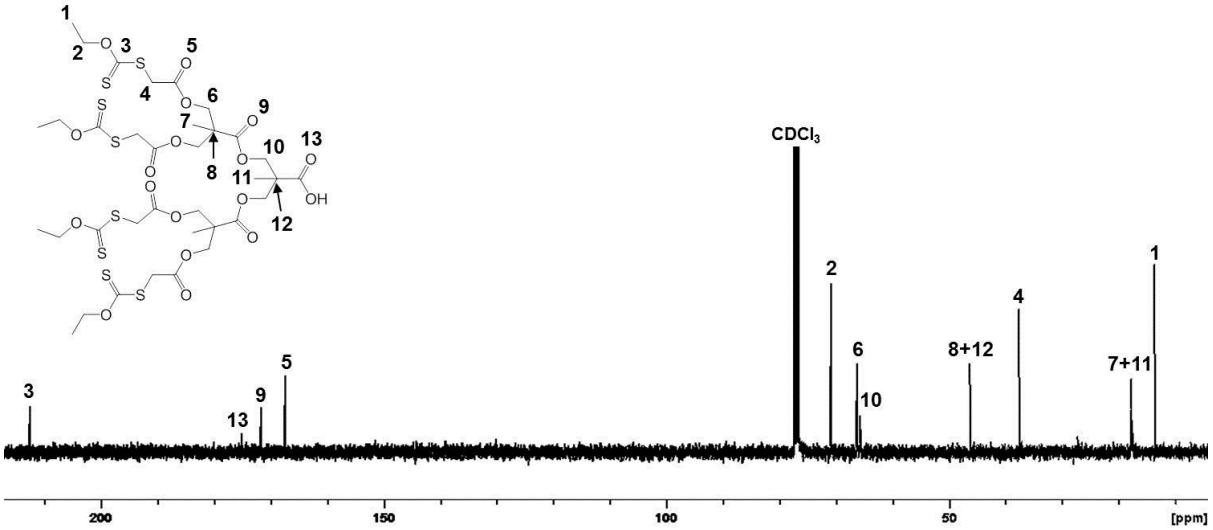

Figure S39. ^{13}C NMR (100 MHz, $CDCl_3$) of **Xan_4-G_2-COOH**

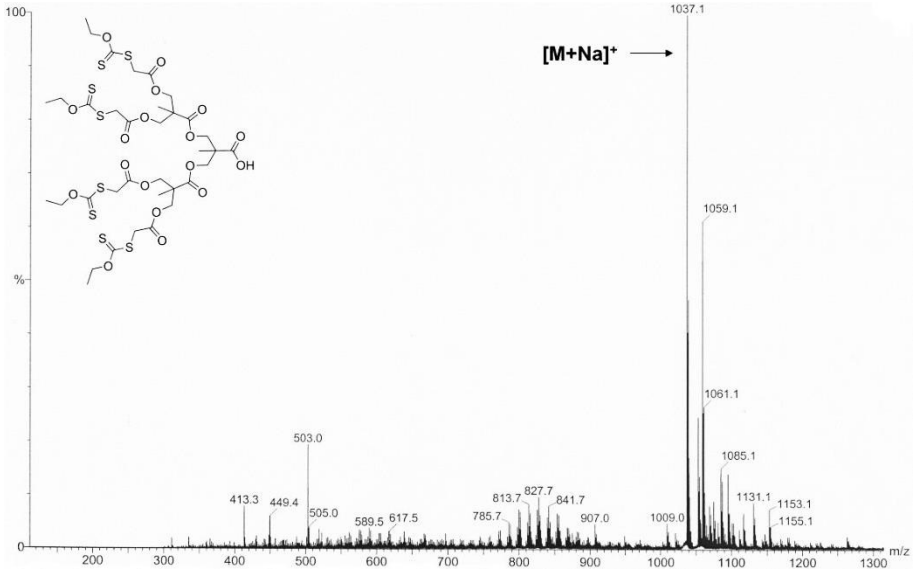

Figure S40. ESI MS (MeOH) of **Xan_4-G_2-COOH**

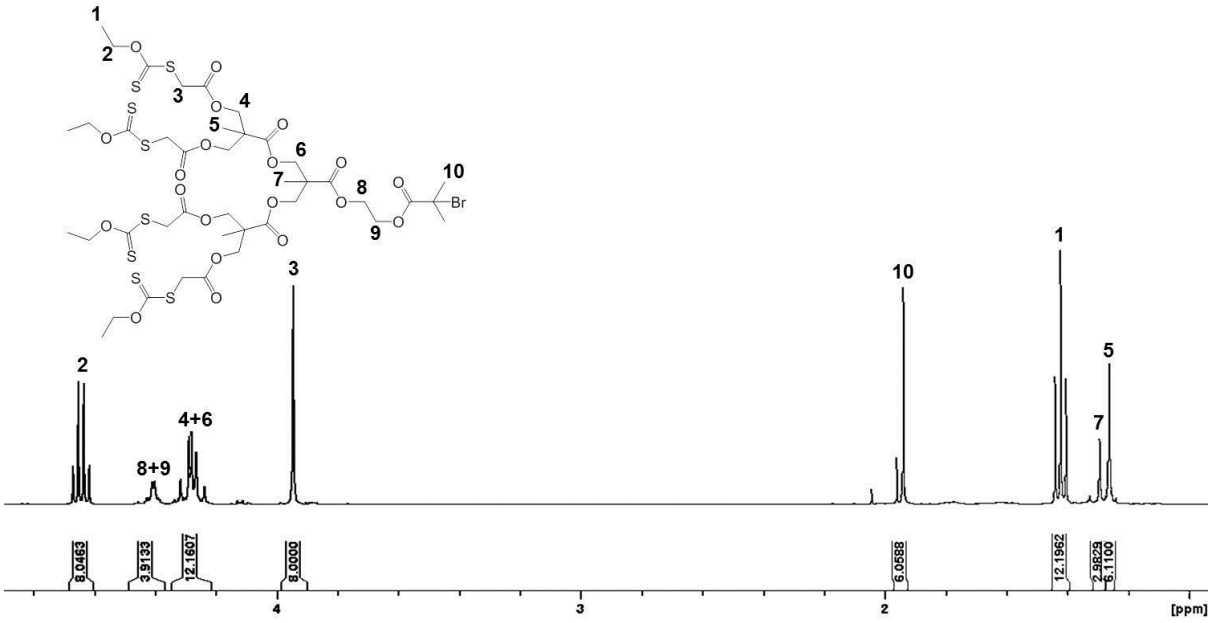

Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) of **Xan$_4$-G$_2$-BiB [5]**

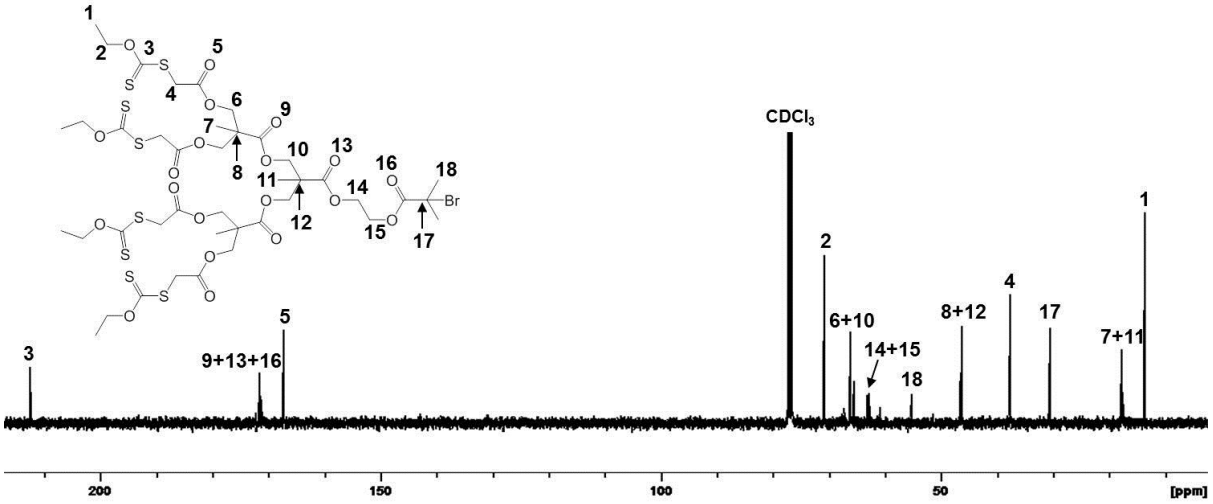

Figure S42. ^{13}C NMR (100 MHz, $CDCl_3$) of **Xan$_4$-G$_2$-BiB [5]**

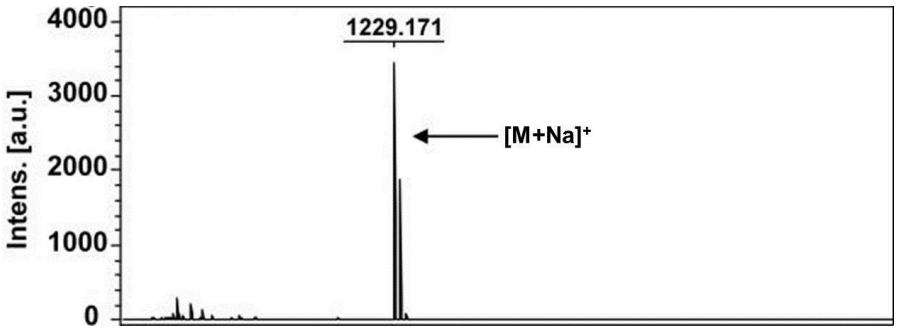

Figure S43. MALDI-TOF analysis of **Xan$_4$-G$_2$-BiB [5]**

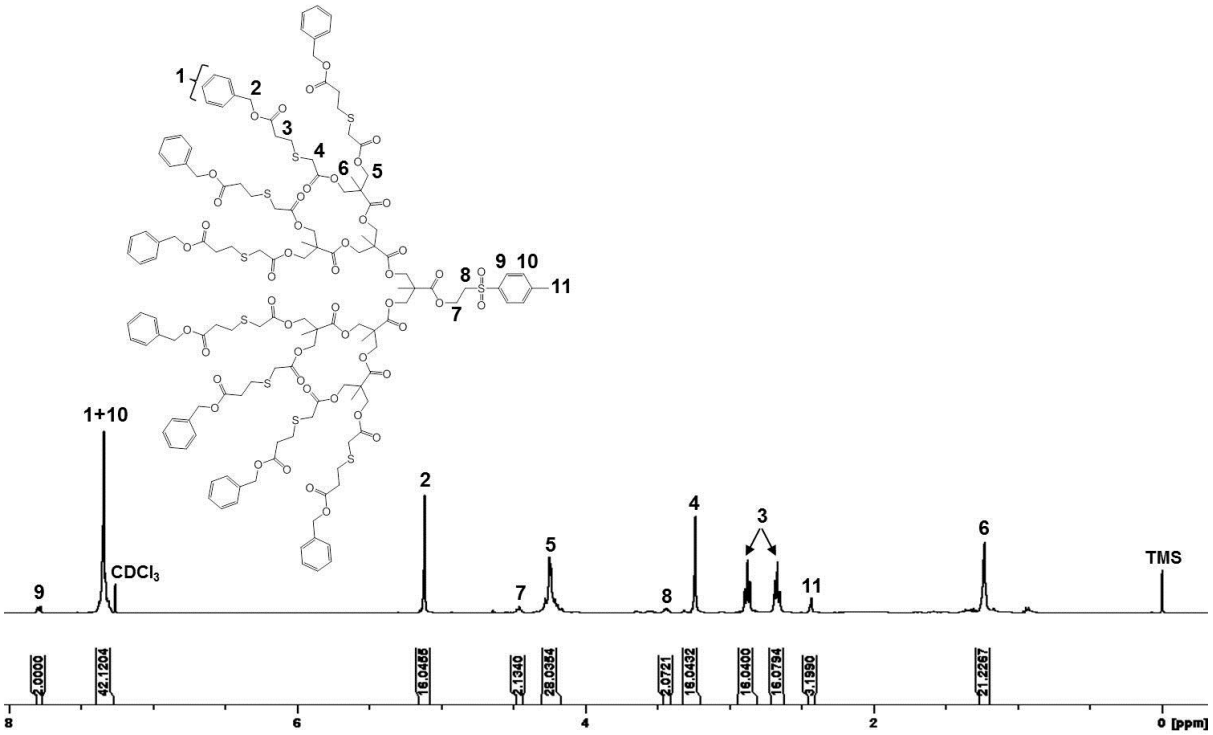

Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) of $\mathbf{Bz_8\text{-}G_3}$

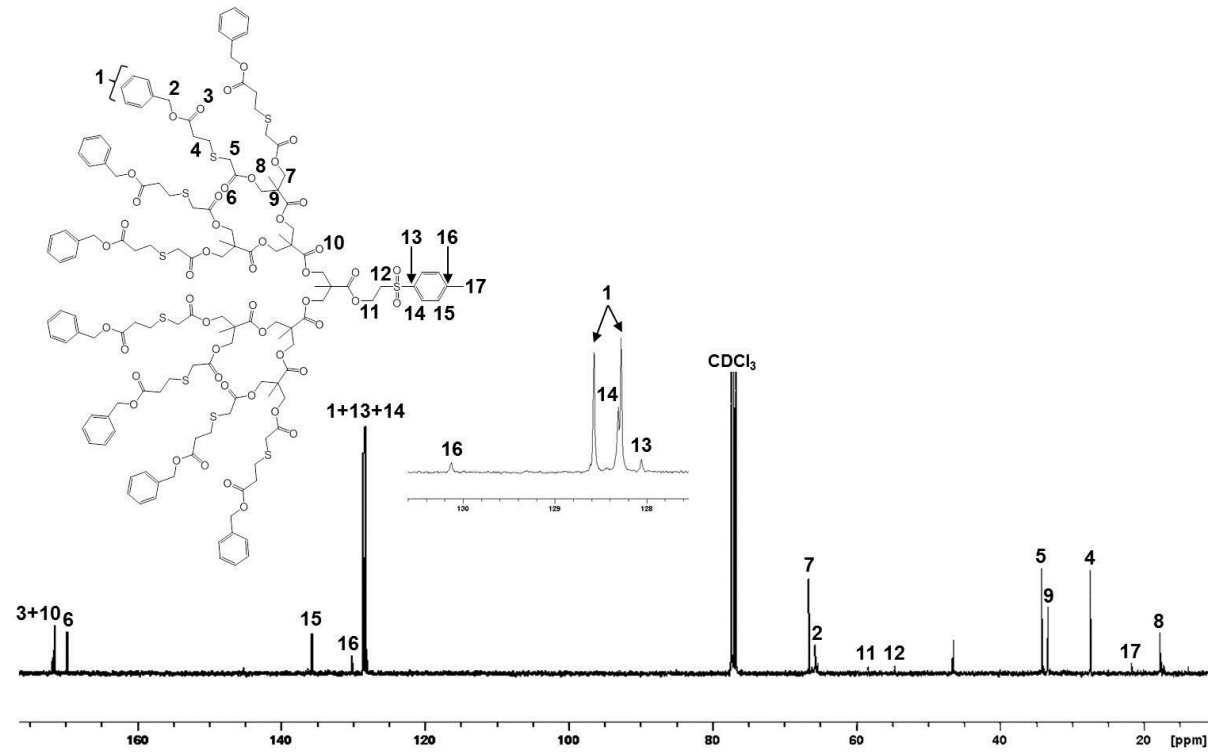

Figure S45. ^{13}C NMR (100 MHz, $CDCl_3$) of $\mathbf{Bz_8\text{-}G_3}$

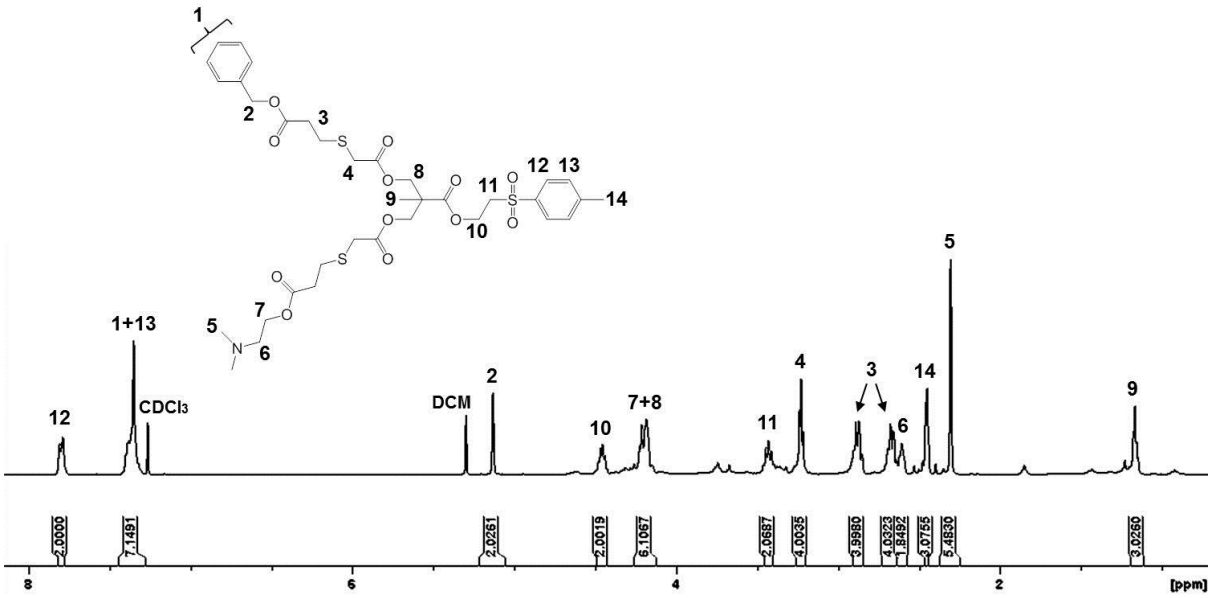

Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) of Sequential $\mathbf{Bz_{1\text{-}2}\text{-}Am_{1\text{-}2}\text{-}G_1}$

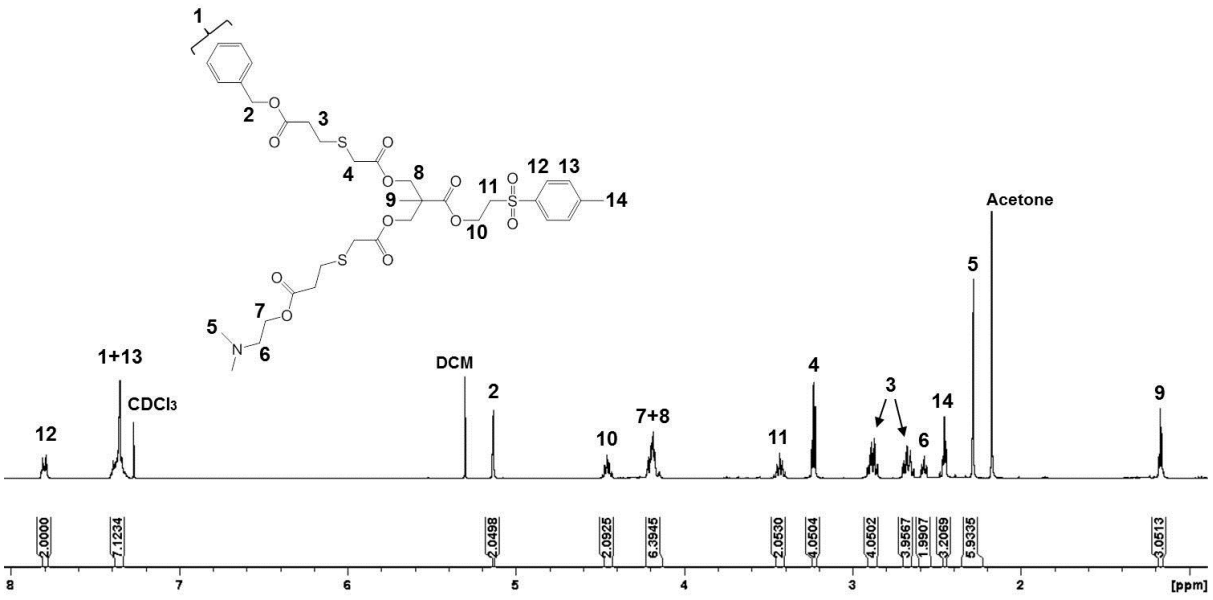

Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) of Simultaneous $\mathbf{Bz_{1\text{-}2}\text{-}Am_{1\text{-}2}\text{-}G_1}$

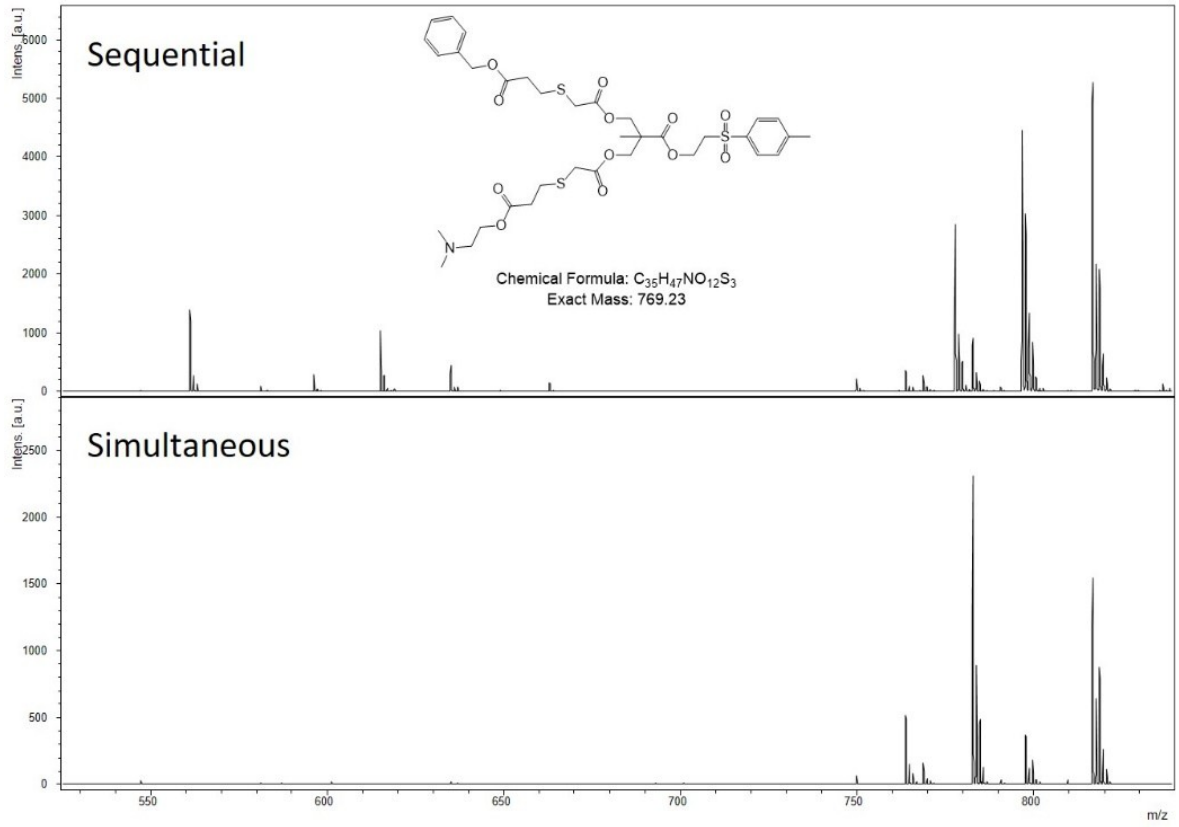

Figure S48. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous $\mathbf{Bz_{1\text{-}2}\text{-}Am_{1\text{-}2}\text{-}G_1}$

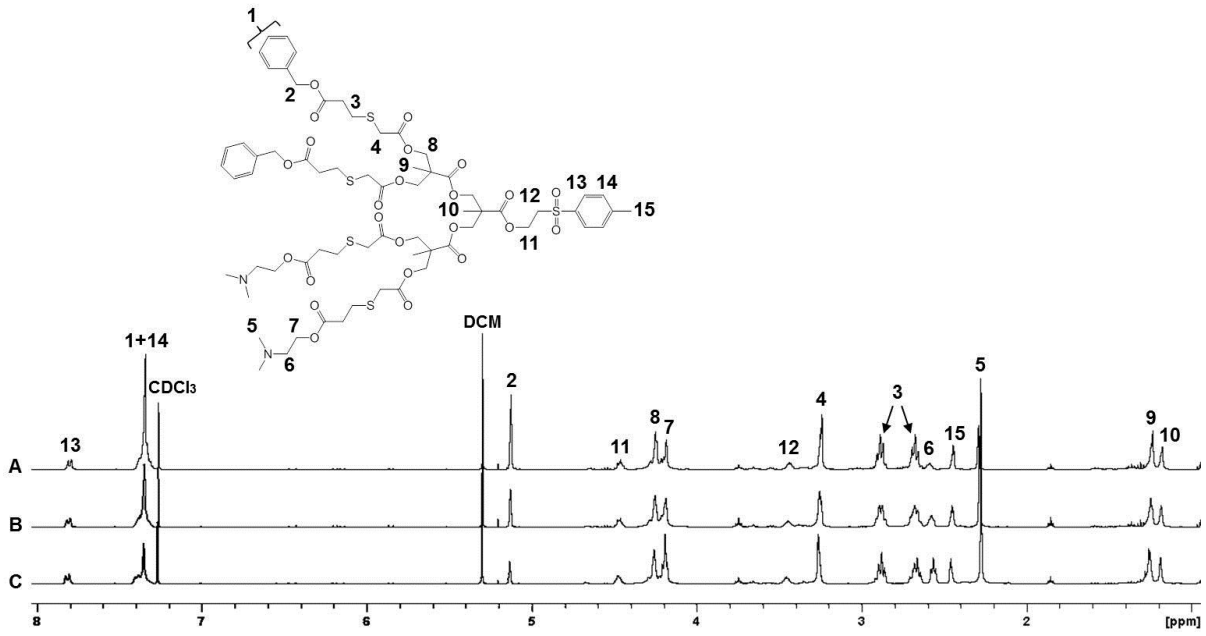

Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) of Sequential **Bz_{1-4}-Am_{1-4}-G_2**: (A) **Bz_3-Am_1-G_2**; (B) **Bz_2-Am_2-G_2**; (C) **Bz_1-Am_3-G_2**

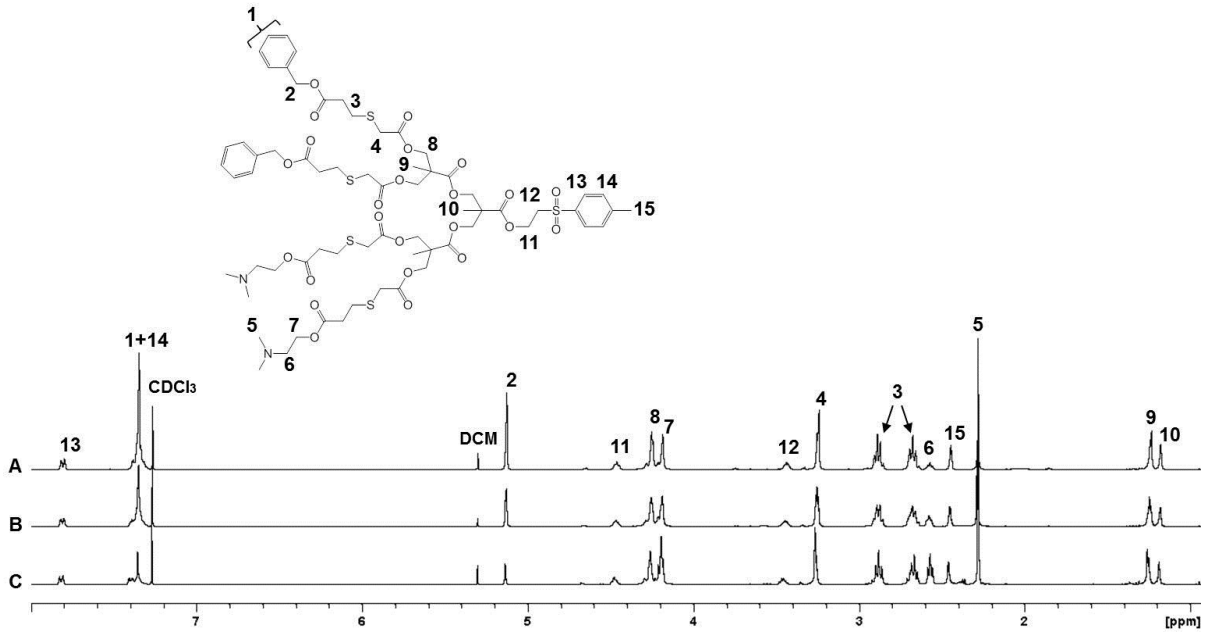

Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) of Simultaneous **Bz_{1-4}-Am_{1-4}-G_2**: (A) **Bz_3-Am_1-G_2**; (B) **Bz_2-Am_2-G_2**; (C) **Bz_1-Am_3-G_2**

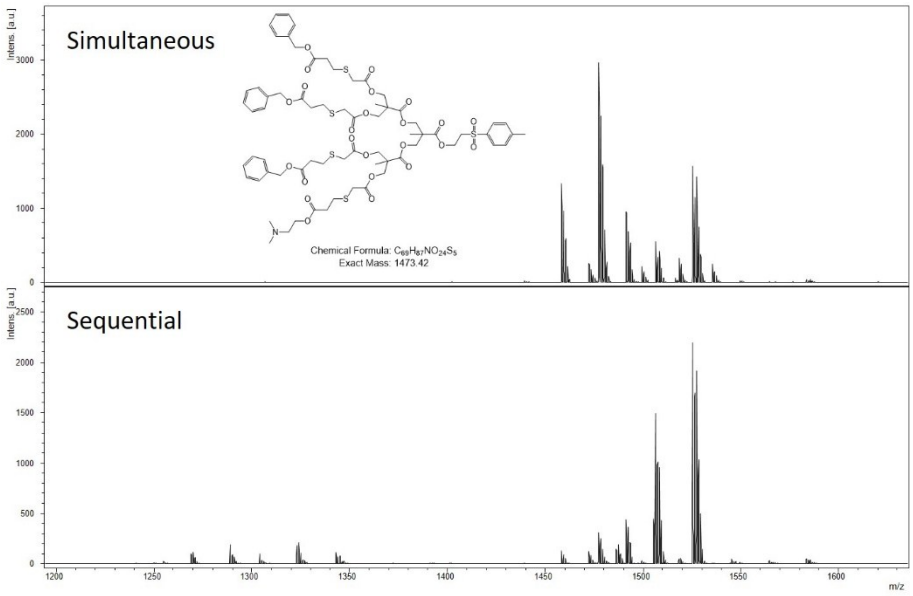

Figure S51. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous **Bz_3-Am_1-G_2**

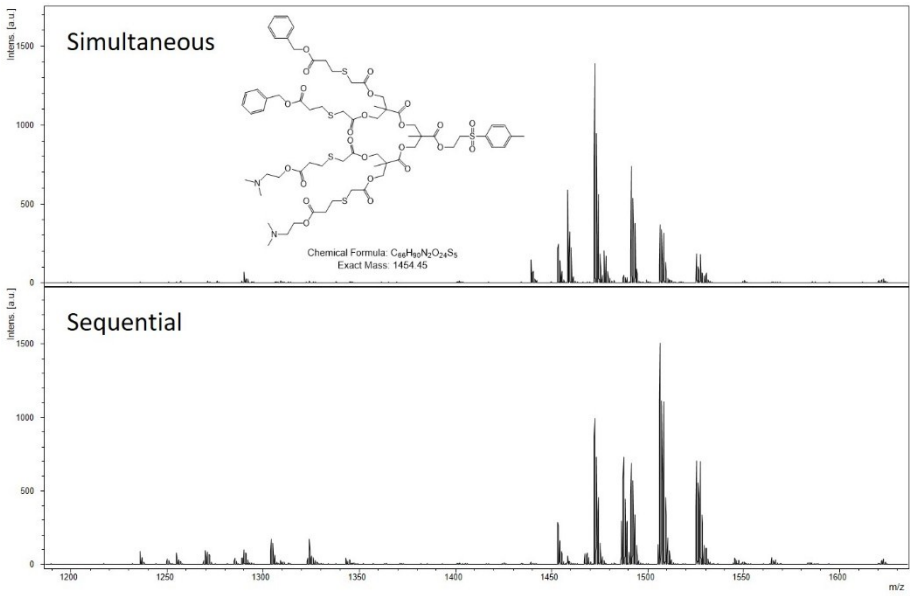

Figure S52. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous **Bz_2-Am_2-G_2**

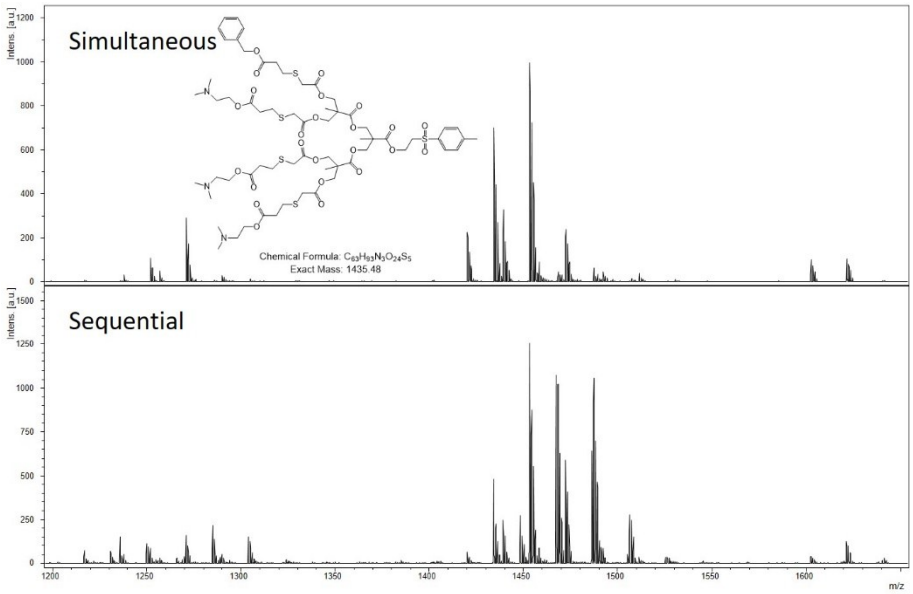

Figure S53. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous **Bz_1-Am_3-G_2**

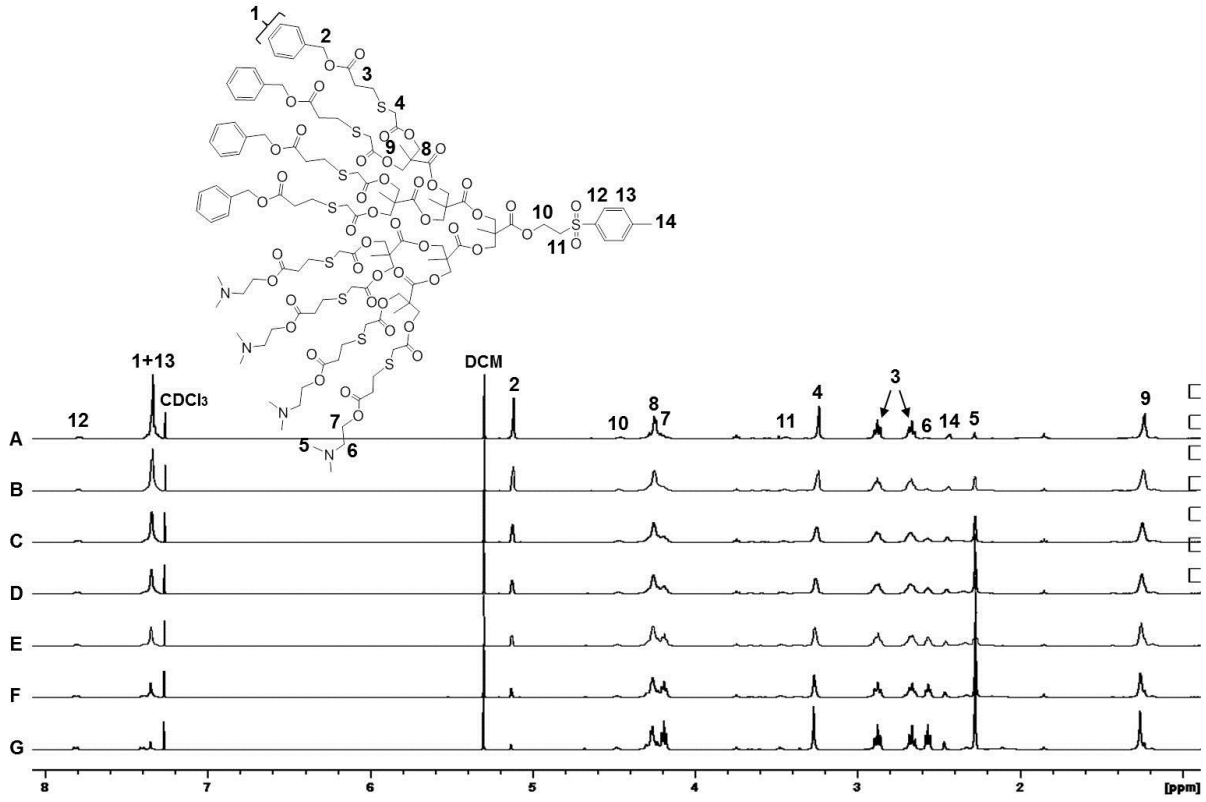

Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) of Sequential **$Bz_{1\text{-}8}$-$Am_{1\text{-}8}$-G_3**: (A) **Bz_7-Am_1-G_3**; (B) **Bz_6-Am_2-G_3**; (C) **Bz_5-Am_3-G_3**; (D) **Bz_4-Am_4-G_3**; (E) **Bz_3-Am_5-G_3**; (F) **Bz_2-Am_6-G_3**; (G) **Bz_1-Am_7-G_3**

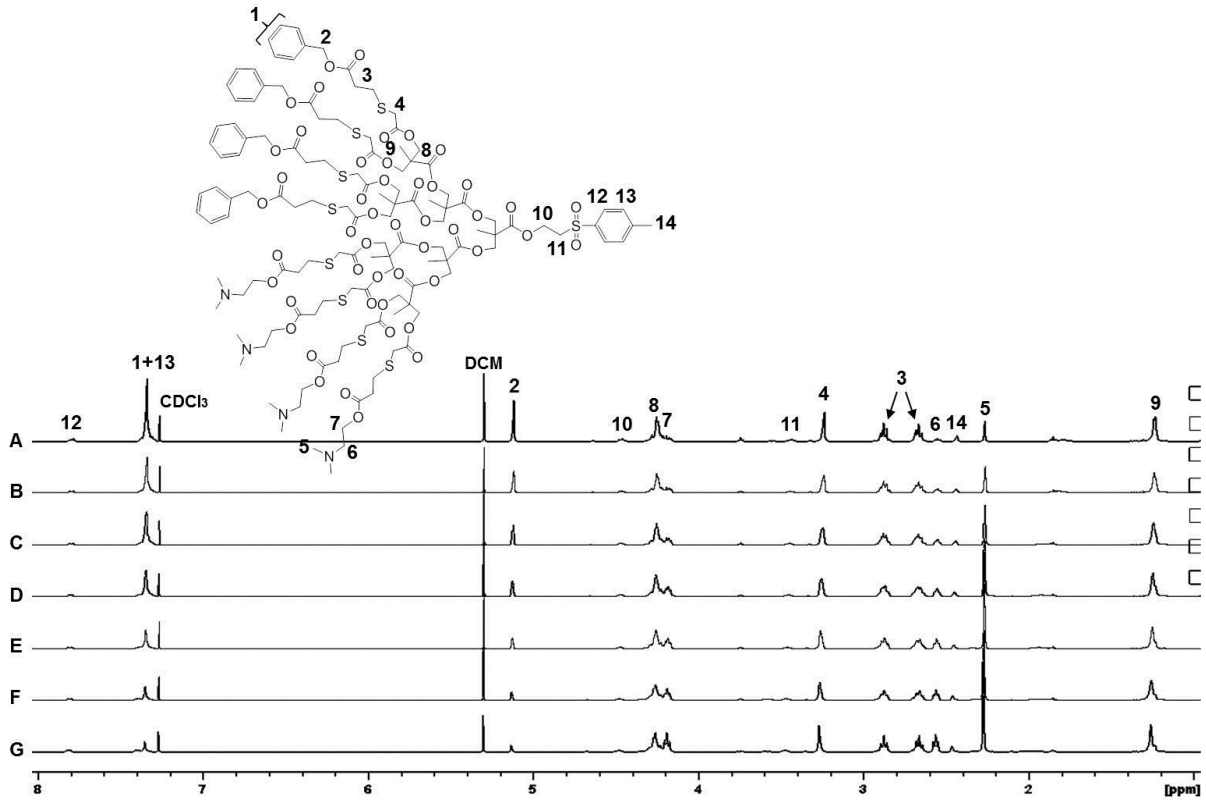

Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) of Simultaneous **$Bz_{1\text{-}8}$-$Am_{1\text{-}8}$-G_3**: (A) **Bz_7-Am_1-G_3**; (B) **Bz_6-Am_2-G_3**; (C) **Bz_5-Am_3-G_3**; (D) **Bz_4-Am_4-G_3**; (E) **Bz_3-Am_5-G_3**; (F) **Bz_2-Am_6-G_3**; (G) **Bz_1-Am_7-G_3**

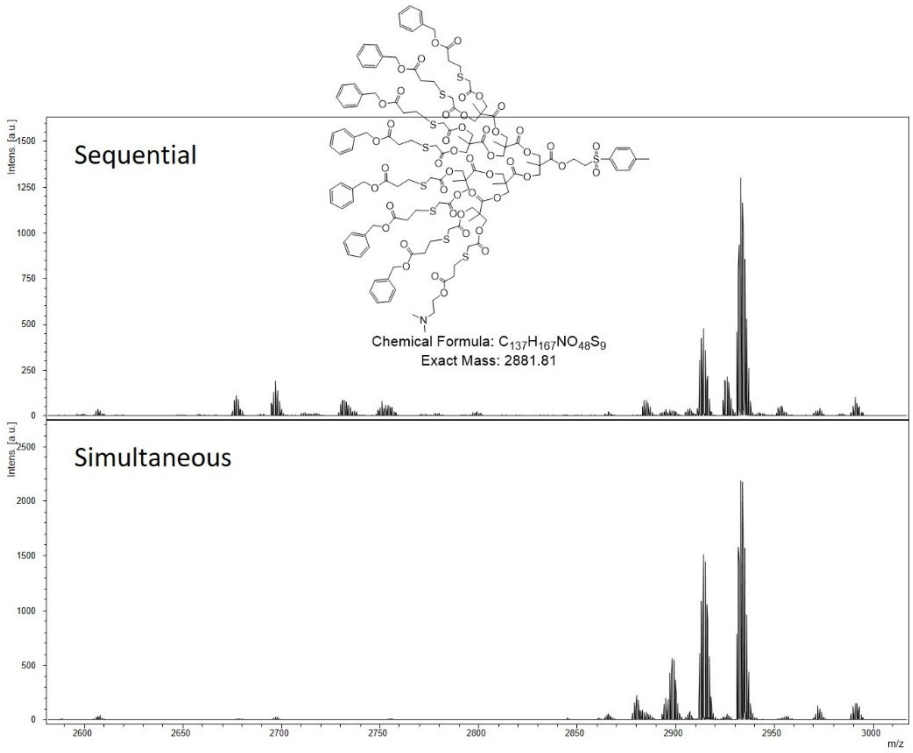

Figure S56. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous **Bz_7-Am_1-G_3**

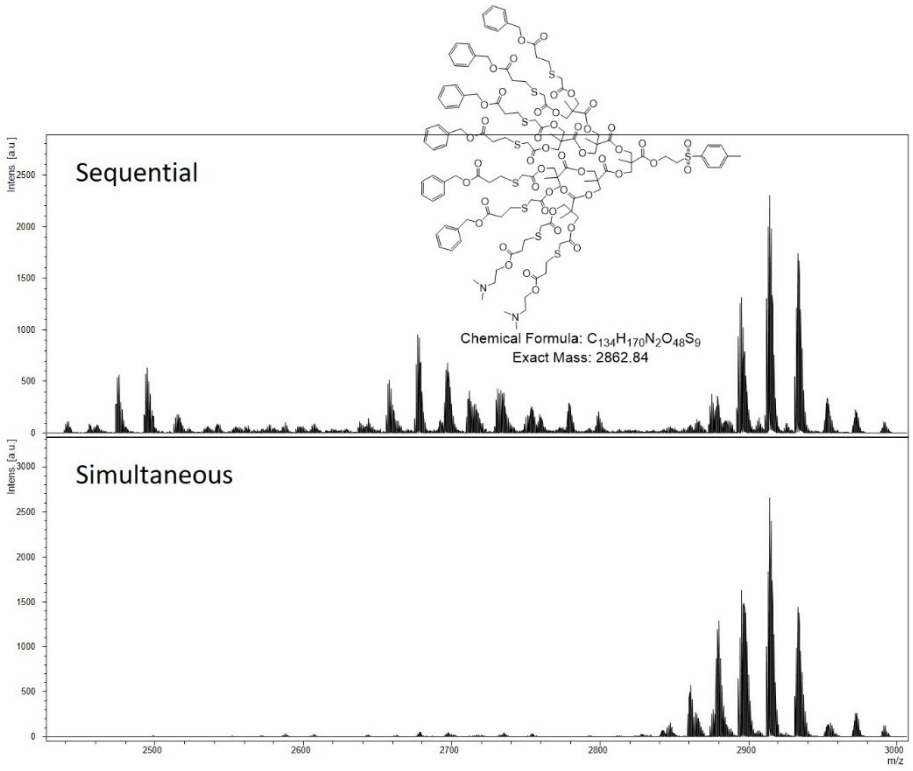

Figure S57. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous **Bz_6-Am_2-G_3**

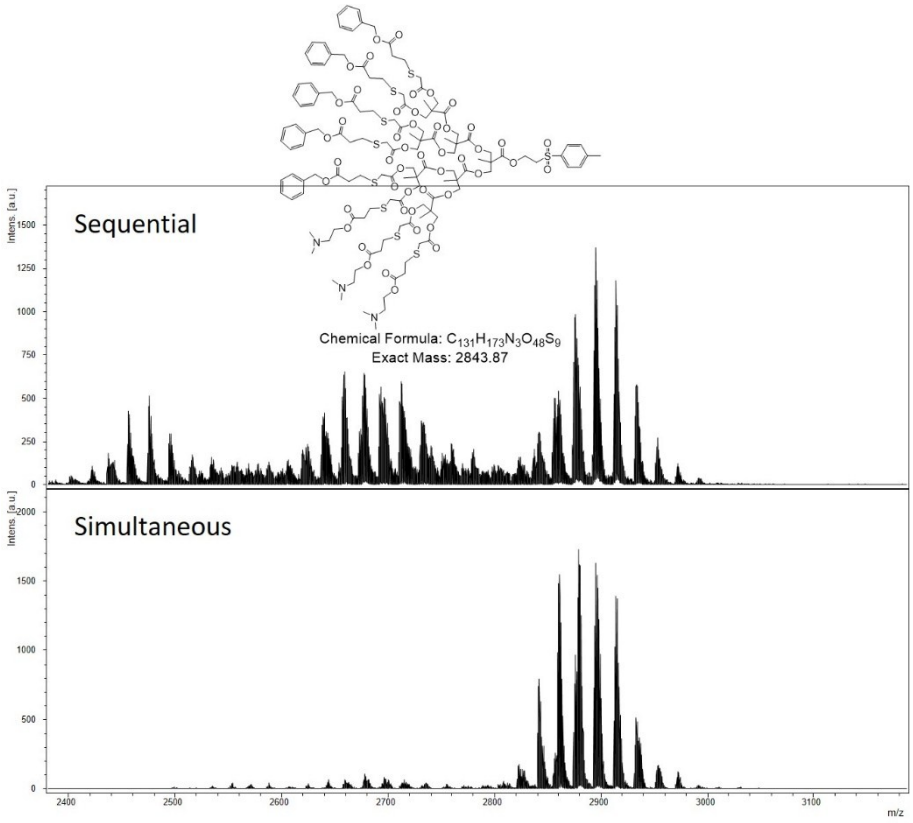

Figure S58. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous $\mathbf{Bz_5\text{-}Am_3\text{-}G_3}$

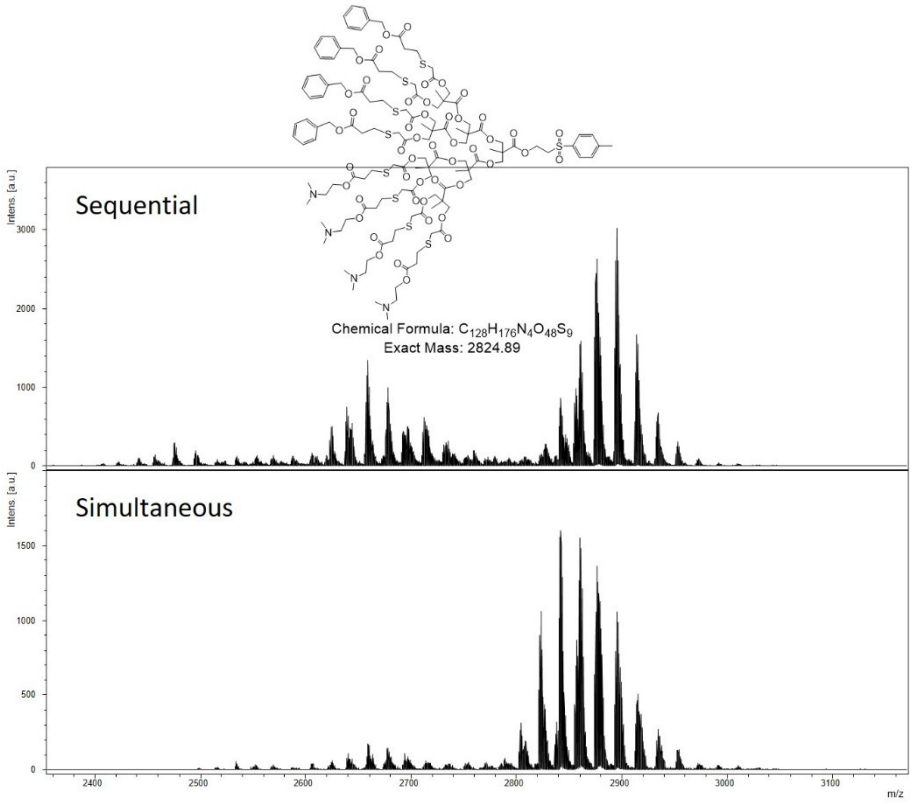

Figure S59. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous $\mathbf{Bz_4\text{-}Am_4\text{-}G_3}$

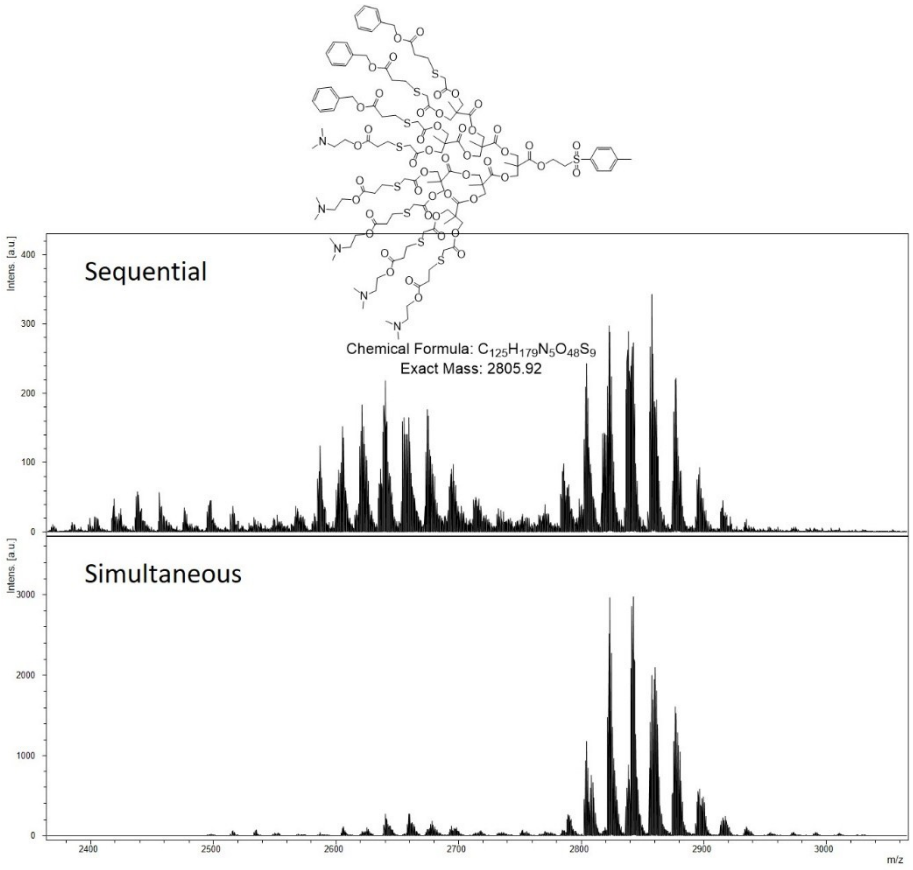

Figure S60. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous **Bz_3-Am_5-G_3**

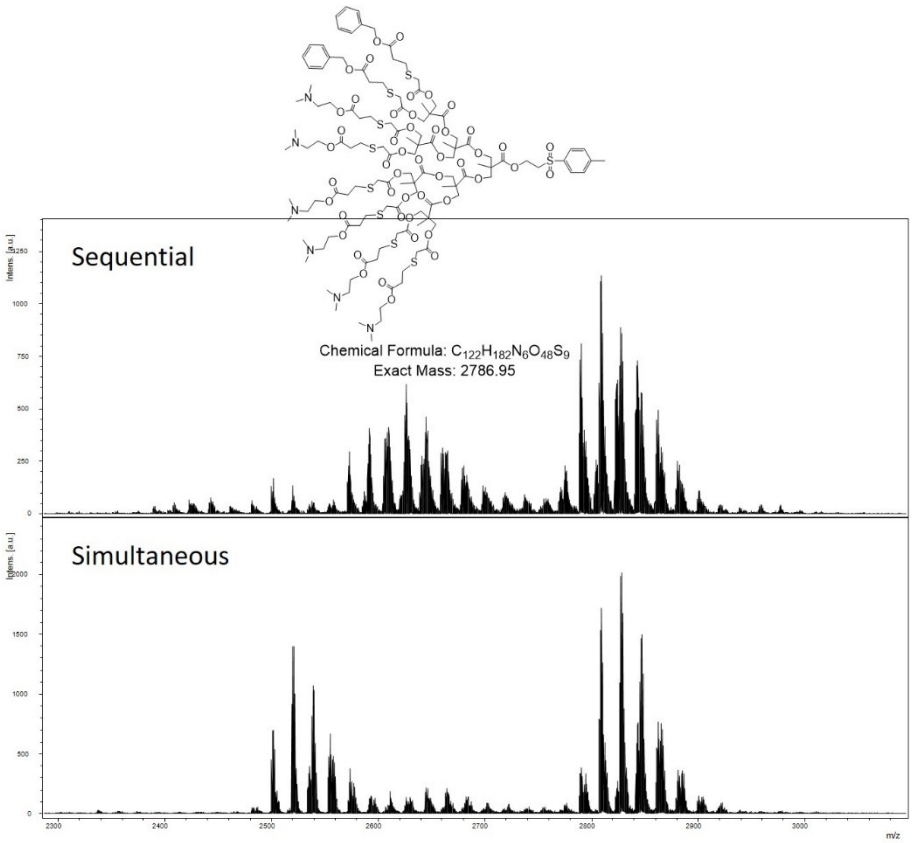

Figure S61. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous **Bz_2-Am_6-G_3**

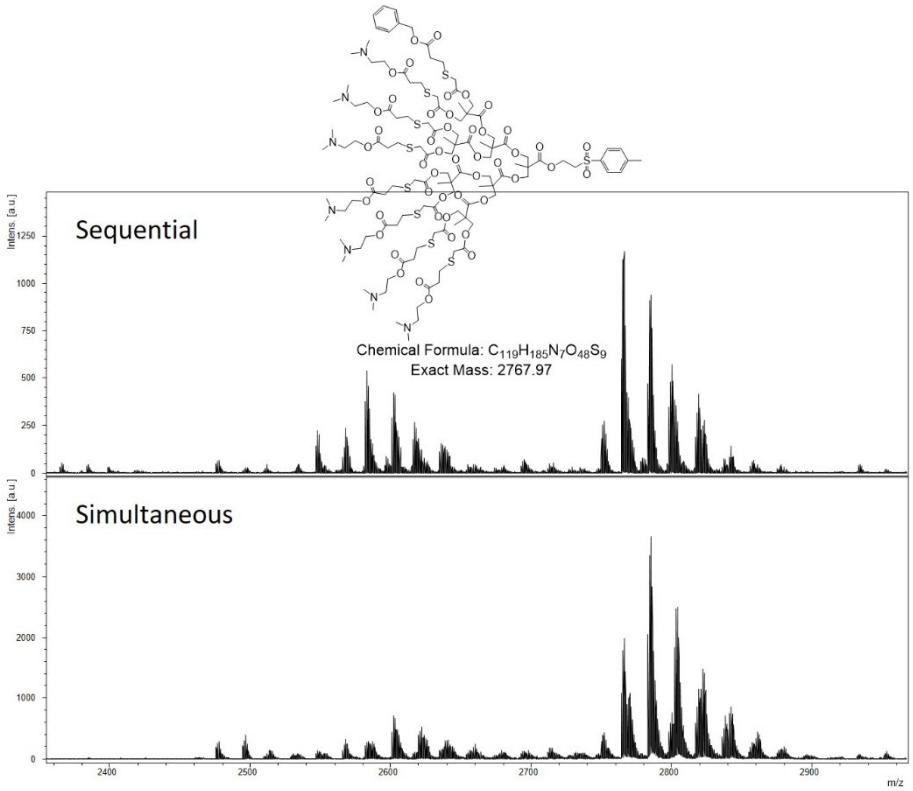

Figure S62. MALDI-TOF MS (Dith, THF) comparison of Sequential vs. Simultaneous **Bz_1-Am_7-G_3**

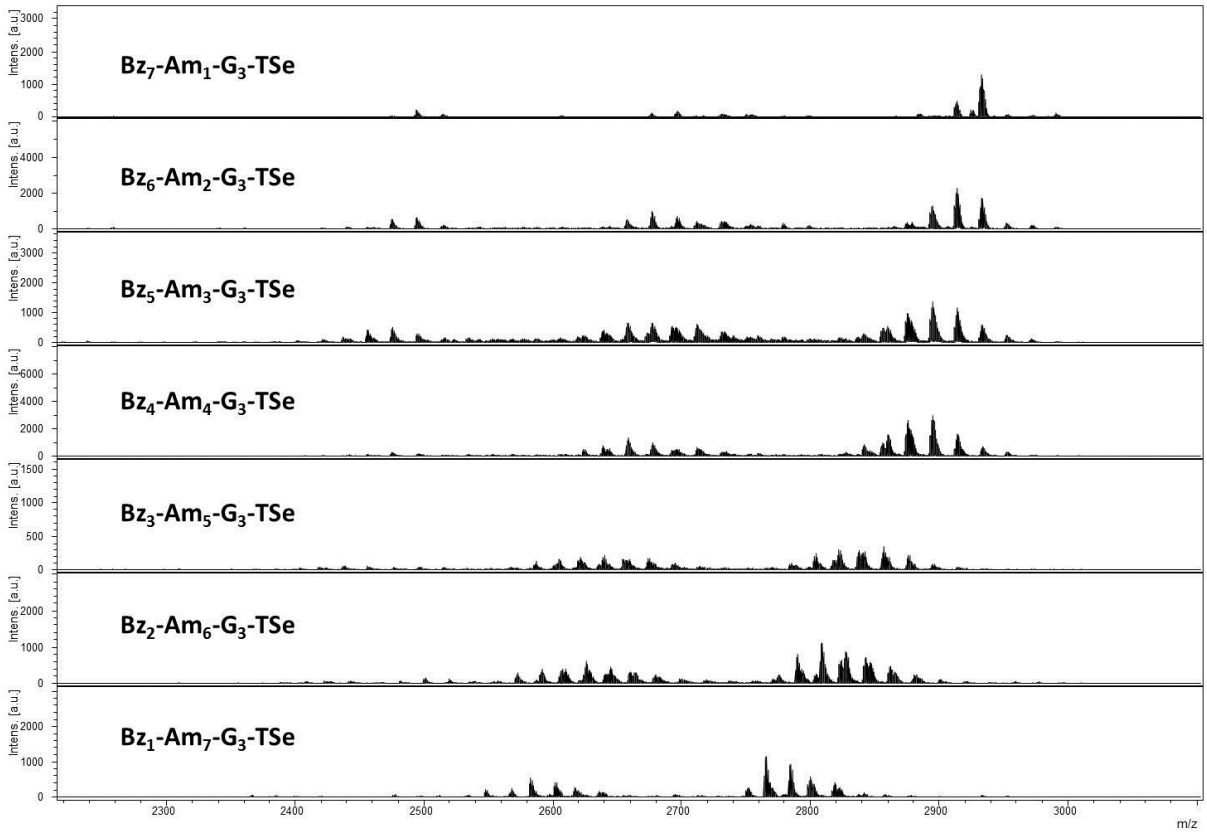

Figure S63. MALDI-TOF MS (Dith, THF) comparison of Sequential $\mathbf{Bz_{1\text{-}8}\text{-}Am_{1\text{-}8}\text{-}G_3}$

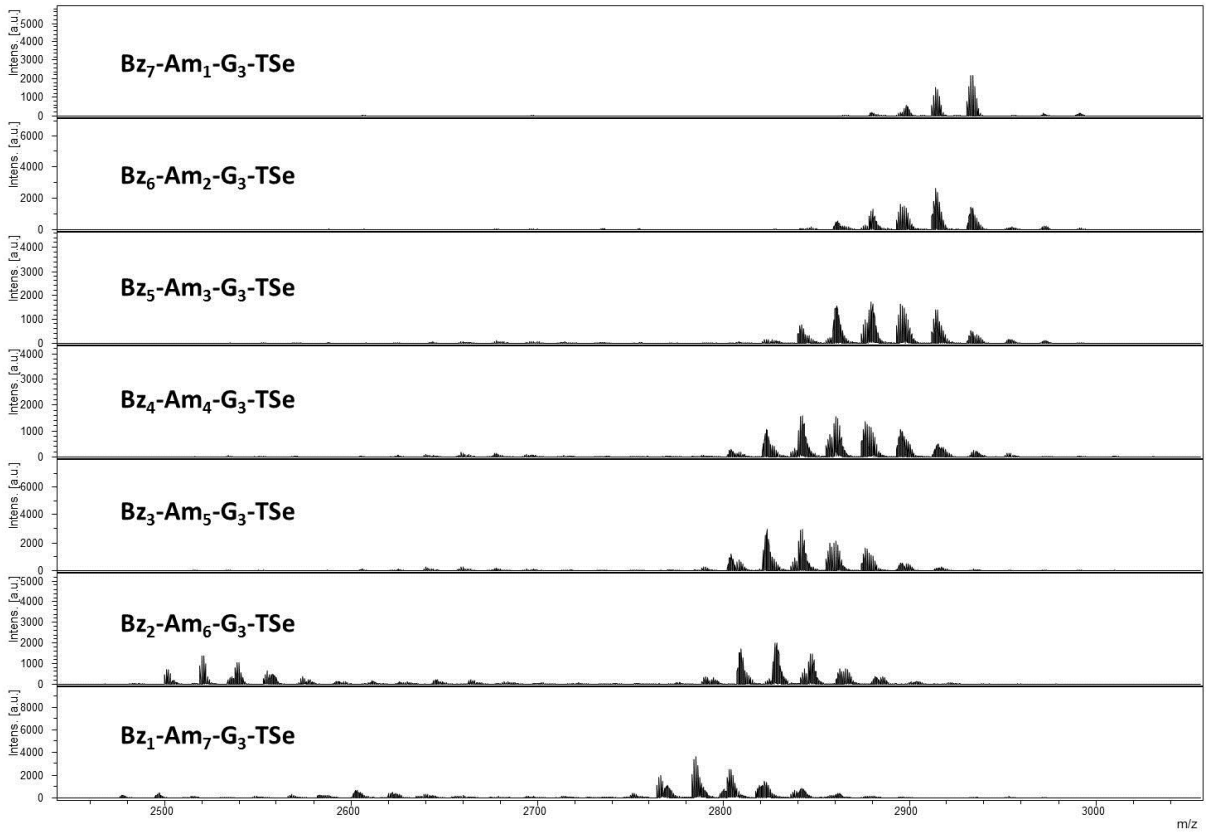

Figure S64. MALDI-TOF MS (Dith, THF) comparison of Simultaneous $\mathbf{Bz_{1\text{-}8}\text{-}Am_{1\text{-}8}\text{-}G_3}$

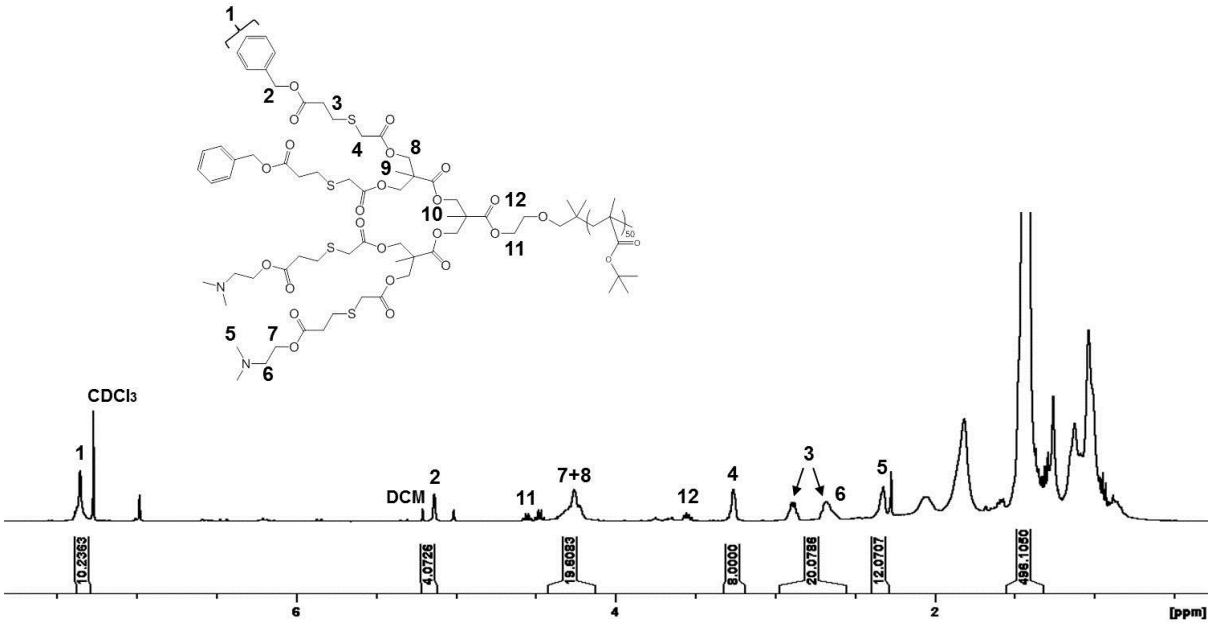

Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) of Simultaneous **p[($Bz_{1\text{-}4}$-$Am_{1\text{-}4}$-G_2)-^{t}BuMA$_{50}$]**

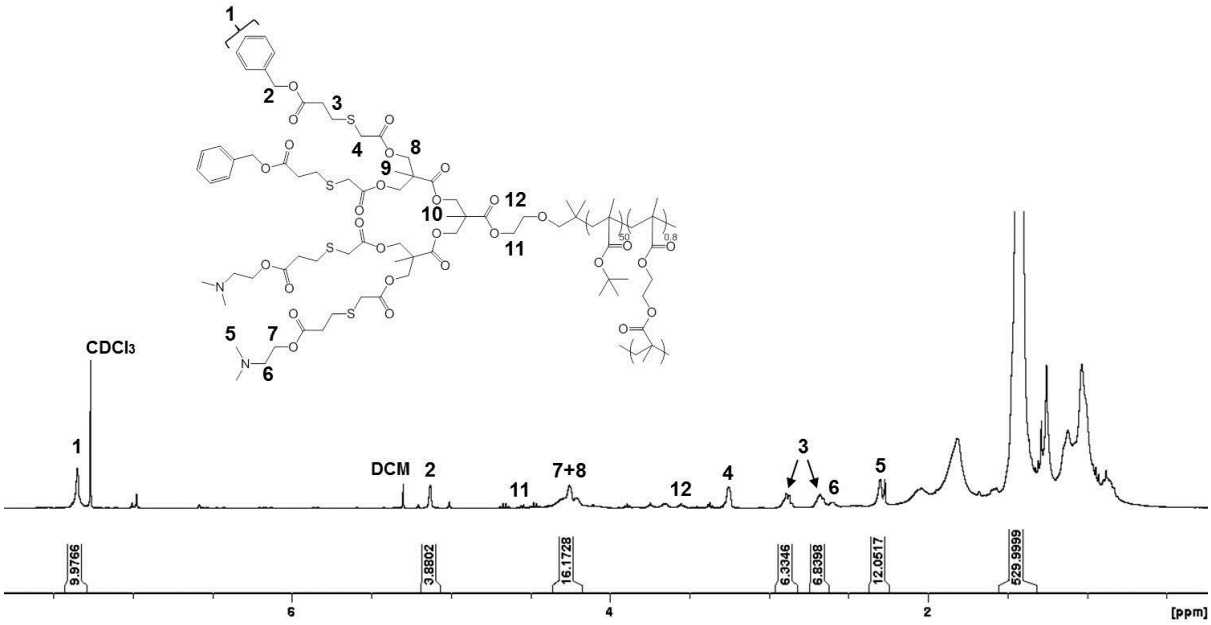

Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of Simultaneous **p[($Bz_{1\text{-}4}$-$Am_{1\text{-}4}$-G_2)-^{t}BuMA$_{50}$-EGDMA]**

Table S1. Peaks identified and assigned within the MALDI-TOF spectrum of [Am_6-G_3] – see Figure 4 in main manuscript

Peak	Species assignment	Theoretical Exact mass m/z+1 (Da)	Peak identified m/z (Da)
1	[Am_3-G_3]H^+ + 48	2525	2526.9
2	[Am_3-G_3]K^+ + 32	2547	2546.9
3	[Am_3-G_3]K^+ + 48	2563	2561.0
4	[Am_4-G_3]K^+ + 16	2586	2582.0
5	[Am_4-G_3]H^+ + 64	2596	2596.0
6	[Am_4-G_3]K^+ + 48	2618	2618.9
7	[Am_5-G_3]H^+ + 48	2635	2635.6
8	[Am_5-G_3]K^+ + 16	2641	2641.1
9	[Am_5-G_3]K^+ + 32	2657	2656.1
10	[Am_6-G_3]K^+ + 16	2696	2694.6
11	[Am_6-G_3]H^+ + 64	2706	2708.6
12	[Am_7-G_3]K^+ + 16	2751	2750.0
13	[Am_7-G_3]K^+ + 32	2767	2764.1
14	[Am_7-G_3]K^+ + 48	2783	2781.2
15	[Am_8-G_3]H^+ + 48	2800	2800.1
16	[Am_8-G_3]K^+ + 16	2806	2805.9
17	[Am_8-G_3]H^+ + 64	2816	2817.1
18	[Am_8-G_3]K^+ + 32	2822	2822.1
19	[Am_8-G_3]K^+ + 48	2838	2836.2