
Electronic Supporting Information

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Methods and Synthesis

Methods

2,2-Bis(hydroxymethyl)propanoic acid, Benzaldehyde dimethyl acetal, Potassium ethyl xanthogenate, Triethanolamine, Butylamine, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), Benzyl acrylate, 2-(Dimethylamino)ethyl acrylate, oligo(ethylene glycol) methyl ether acrylate $M_n = 480$, Dichloromethane (anhydrous) and p-Toluenesulfonic acid monohydrate were purchased from Sigma Aldrich and were used without further purification. Palladium Hydroxide 20% on Carbon (Pearlman’s Catalyst), 2-Bromoacetic acid, Pyridine (anhydrous), 4-Dimethylaminopyridine (DMAP) and N,N′-Dicyclohexylcarbodiimide (DCC) were purchased from Alfa Aesar and were used without further purification. Para-toluene sulfonyl ethanol was purchased from Fluorochem. DPTS was prepared using literature procedures [1]. Compounds [5], [6] were prepared by literature procedures [2]. Compounds [8], [9], [10] and [11] were also prepared by literature procedures [3]. Dichloromethane, Hexane and Ethyl Acetate were HPLC grade and supplied from Fisher. Analytical TLC was performed on commercial Merck Plates coated with silica gel. Flash chromatography was performed using a Grace Reveleris Flash System with 80g Silica Reveleris Flash Cartridges. NMR spectra were collected 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$_3$OD containing Tetramethylsilane (TMS) purchased from Goss Scientific were used as NMR solvents. Chemical shifts ($\delta$) are reported in parts per million (ppm) and TMS was used as an internal standard for both $^1$H and $^{13}$C spectra. Electrospray mass spectrometry data was obtained using a MicroMass LCT mass spectrometer using Electron ionisation and direct infusion syringe pump sampling. All samples were diluted with methanol. Gel Permeation Chromatography (GPC) was carried out using a Malvern Viscoatke GPC Max connected to a Viscoatke 270 Light Scattering detector, Viscometer and Reflective index (RI) triple detection system. HPLC grade tetrahydrofuran THF (Fisher) containing 2% triethylamine (Sigma Aldrich) was used as the eluent, with a flow rate of 1mL/min. GPC Columns were mixed bed columns supplied by Viscoatke. The column oven was set at 35 °C. The obtained spectra were analyzed using Malvern OmiSec software calibrated by a universal calibration calculation relative to a narrow linear polystyrene standard (105k). Matrix-assisted laser desorption/ionization-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 10mg/ml in THF and a 1mg/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 a eppendorf sample tube and homogenized. 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 (337nm), a grid less ion source and reflector design. 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 preformed per sample and the laser intensity was set to the lowest possible value for acquisition of high resolution spectra. The instrument was calibrated using SpheriCalTM calibrants purchased from Polymer Factory Sweden AB. The obtained spectra were analyzed with FlexAnalysis Bruker Daltonics, Bremen, version 2.2.

**Synthesis**

[2-((Ethoxycarbonothioyl)thio)acetic acid]; [3] - Potassium ethyl xanthogenate [1] (53.06g, 167 mmol) was added to 400 mL acetone. A solution of 2-bromoacetic acid [2] (38.35g, 103 mmol) in acetone (100 mL) was added dropwise at ambient temperature over a period of 20 min. Stirring was continued overnight at ambient temperature. The precipitated Potassium Bromide byproduct was removed by filtration and washed with a small volume of acetone to afford a clear pale yellow solution. The filtrate was concentrated under vacuum leaving a yellow viscous liquid that was dissolved in dichloromethane (300 mL) and washed three times with brine (100 mL). The organic phase was dried over MgSO4 and evaporated to dryness to afford 24.23 g (50%) of a white solid.

1H NMR (400 MHz, CDCl3): δ = 1.43 (t, J = 7.1 Hz, 3H), 3.98 (s, 2H) 4.67 (q, J = 7.1 Hz, 2H), 4.53. 13C NMR (100 MHz, CDCl3): δ = 13.68, 37.60, 70.93, 174.30, 212.0.

[Benzylidene-2,2-bis(oxymethyl)propionic Acid]; [5] - 2,2-Bis(hydroxymethyl)-propionic acid [4] (100 g, 0.756 mol), benzaldehyde dimethyl acetal (170.20 g, 1.12 mol), and p-toluenesulfonic acid monohydrate (7.10 g, 37.3 mmol) were added to 750 mL of acetone. The reaction mixture was stirred for 4h at ambient temperature. After storage of the reaction mixture in the refrigerator overnight, the solids were filtered off and washed with cold acetone to give [4] as white crystals: 92.50 g (56%). 1H NMR (400 MHz, CDCl3): δ = 1.11 (s, 3H), 3.70 (d, J = 11.7 Hz, 2H), 4.63 (d, J = 11.6 Hz), 5.49 (s, 1H), 7.34 (m, 3H), 7.47 (m, 2H). 13C NMR (100 MHz, CDCl3): 17.75, 42.15, 73.44, 101.95, 126.17, 128.29, 129.09, 137.49, 178.69.

[Benzylidene-2,2-bis(oxymethyl)propionic Anhydride]; [6] - Benzylidene-2,2-bis(oxymethyl)propionic Acid [5] (92 g, 0.414 mol) and N,N’-Dicyclohexylcarbodiimide (DCC) (47.04 g, 0.228 mol) were added to 700 mL of CH2Cl2. The reaction mixture was stirred overnight for 24 hours. The precipitated urea DCC byproduct was removed by filtration and washed with a small volume of CH2Cl2. The crude product was purified by precipitating the filtrate into 2.5 L of hexane under vigorous stirring for 30 mins. After filtration, [6] was isolated as white crystals: 84.82 g (88%). 1H NMR (400 MHz, CDCl3): δ = 1.11 (s, 6H), 3.68 (d, J = 11.7 Hz, 2H), 4.65 (d, J = 11.7 Hz, 2H), 7.32 (m, 6H), 7.44 (m, 4H). 13C NMR (100 MHz, CDCl3): 16.90, 44.23, 73.21, 102.15, 126.31, 128.27, 129.14, 137.61, 169.16

General procedure for divergent dendron growth ([8], and [10]) - Benzylidene protected anhydride [6], para-toluene sulfonyl ethanol [7] or compound [9], and 4-dimethylaminopyridine (DMAP) were dissolved in an anhydrous 1:1 ratio of CH2Cl2:pyridine (v/v) under a nitrogen atmosphere. After stirring at ambient temperature for 18 h, approximately 2 mL of water was added and the reaction was stirred for an additional 2h in order to quench the excess anhydride. The product was isolated by diluting the mixture with CH2Cl2 (150 mL) and washing with 1 M NaHSO4 (3 x 150 mL), 1M NaHCO3 (2 x 150 mL), and brine (150 mL). The organic layer was dried over MgSO4 and evaporated to dryness. Any residual solvent was removed under high vacuum overnight.

General Procedure for deprotection of Benzylidene protecting groups ([9], and [11]) - To a Parr Vessel suitable for catalytic hydrogenation, the benzylidene protected dendron [8] or [10] was dissolved in a 1:1 mixture of CH2Cl2 : MeOH (v/v). Pd(OH)2 on Carbon (20%) was added and the apparatus was evacuated and back-filled with hydrogen three times (H2 pressure: 10 atm). After hydrogenation under vigorous stirring for 16 h, the catalyst was filtered off through a celite plug and carefully washed with methanol. The filtrate was evaporated to give the desired hydroxyl terminated dendron as white crystals.
General procedure for functionalisation with Xanthate surface groups ([12] and [14]) - The hydroxyl-terminated dendron ([9] or [11]), 2-((Ethoxycarbonothioyl)thio)acetic acid ([3], and 4-(Dimethylamino)pyridinium 4-toluene sulfonate (DPTS) were dissolved in CH₂Cl₂ under a nitrogen atmosphere. Dicyclohexylcarbodiimide (DCC) was added in CH₂Cl₂ and the reaction mixture was stirred overnight for 24 hours. The precipitated urea DCC byproduct was removed by filtration and washed with a small volume of CH₂Cl₂. The product was purified by liquid chromatography on silica gel, eluting with hexane gradually increasing to 40:60 ethyl acetate/hexane to give a viscous oil.

General procedure for deprotection of para-toluene sulfonyl ester (TSe) ([13] and [15]) - The Xanthate functionalised dendron ([12] or [14]) was dissolved in dry CH₂Cl₂ and 1.3 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added. The reaction was stirred under a nitrogen atmosphere for 16 hrs and monitored until completion by TLC (60:40 hexane:ethyl acetate). The product was isolated by diluting the mixture with CH₂Cl₂ (100 mL) and washing with 1 M NaHSO₄ (2 x 100 mL). The organic layer was dried over MgSO₄ and evaporated to dryness. The product was then precipitated three times into hexanes and ethyl acetate (9:1). Any residual solvent was removed under high vacuum to yield a viscous oil.

General procedure for Xanthate Dendrimer synthesis by convergent growth ([16], [18], [22] - The Xanthate-terminated dendron ([13] or [15]) or 2-((Ethoxycarbonothioyl)thio)acetic acid ([3], Triethanolamine (TEA) and 4-(Dimethylamino)pyridinium 4-toluene sulfonate (DPTS) were dissolved in CH₂Cl₂ under a nitrogen atmosphere. Dicyclohexylcarbodiimide (DCC) was added in CH₂Cl₂ and the reaction mixture was stirred overnight for 24 hours. The precipitated urea DCC byproduct was removed by filtration and washed with a small volume of CH₂Cl₂. The product was isolated by diluting the mixture with CH₂Cl₂ (100 mL) and washing with 1 M NaHSO₄ (2 x 100 mL). The organic layer was dried over MgSO₄ and evaporated to dryness. The product was purified by liquid chromatography on silica gel, eluting with hexane gradually increasing to 40:60 ethyl acetate/hexane to give a viscous oil.

General procedure for Thiol Michael Addition Click Reactions - The Xanthate-terminated dendrimer ([16], [18] or [14]) was dissolved in anhydrous THF and degassed for 10 minutes under a nitrogen atmosphere. n-butylamine (1.1 eqv per Xanthate group) was added and the reaction left for 1.5 hrs or until completion by TLC (60:40 hexane:ethyl acetate). The acrylate monomer (1.1 eqv per thiol) was added and the reaction mixture was stirred overnight for 18 hours. The product was isolated by diluting the mixture with CH₂Cl₂ (100 mL) and washing with 1 M NaHSO₄ (2 x 100 mL). The organic layer was dried over MgSO₄ and evaporated to dryness. The product was then precipitated twice into hexanes. Any residual solvent was removed under high vacuum to yield a pale orange viscous oil.

[OBz-G₃-TSe]:89(119,150),(935,948) - The dendron growth step was carried out as described above, using para-toluene sulfonyl ethanol ([7] (10 g, 50 mmol), benzylidene anhydride (42.65 g, 100 mmol, 2 equiv) and DMAP (2.57 g, 21 mmol) dissolved in 220 mL of dry CH₂Cl₂ and 120 mL of pyridine, and stirred for 16 h at ambient temperature. Yield: 19.78 g, white foam (98%). 1H NMR (400 MHz, CDCl₃): δ = 0.96 (s, 3H), 2.43 (s, 3H), 3.46 (t, J = 6.2 Hz, 2H), 3.60 (d, J = 11.6 Hz, 2H) 4.47 (t, J = 6.2 Hz, 2H), 4.52 (d, J = 11.6 Hz, 2H), 5.43 (s, 1H), 7.27-7.44 (m, 7H). 13C NMR (100 MHz, CDCl₃): δ = 17.52, 21.64, 42.46, 55.13, 58.20, 73.32, 101.72, 126.15, 128.19, 128.23, 129.01, 130.09, 134.11, 149.86, 173.52. GPC: Mₙ = 390, Mₘ = 430, Mₜ/Mₙ = 1.09

[OH₂-G₃-TSe]:(136,958),(941,958) - Deprotection of [8] (5.5 g, 13.60 mmol) in 210 mL of CH₂Cl₂ : MeOH (1:1, v/v) was carried out as above for 16 h at ambient temperature under 10 bar H₂ atmosphere. 0.55 g Pd(OH)₂ was used. Yield: 4.3 g, white foam (99%). 1H NMR (400 MHz, CD₃OD): δ = 1.03 (s, 3H), 2.45 (s, 3H), 3.49 (dd, J = 10.9 Hz, 4H), 3.59 (t, J = 5.9 Hz, 2H), 4.40 (t, J = 5.8 Hz, 2H), 7.47 (d, J = 8.2 Hz 2H), 7.83 (d, J = 8.6 Hz, 2H). 13C NMR (100 MHz, CD₃OD): δ = 17.07, 21.61, 51.58, 55.90, 58.93, 65.66, 129.30, 131.22, 137.76, 146.71, 175.89.
[OBz-G2-TSe]: [10] - The dendron growth step was carried out as described above, using [9] (4.10 g, 12.96 mmol), benzylidene anhydride (16.58 g, 39 mmol, 3 equiv) and DMAP (0.71 g, 5.38 mmol) dissolved in 70 mL of dry CH2Cl2 and 35 mL of pyridine, and stirred for 16 h at ambient temperature. Yield: 8.68 g, white foam (93%). 1H NMR (400 MHz, CDCl3): δ = 0.95 (s, 6H), 1.09 (s, 3H), 2.37 (s, 3H), 3.10 (t, J = 5.8 Hz, 2H), 3.60 (d, J = 12.4 Hz, 4H) 4.20 (m, 6H), 4.56 (m, 4H), 5.42 (s, 2H), 7.27-7.43 (m, 12H), 7.68 (d, J = 8.3 Hz, 2H). 13C NMR (100 MHz, CDCl3): δ = 17.33, 17.72, 21.56, 42.60, 46.70, 54.65, 58.32, 65.20, 73.46, 73.53, 101.63, 126.12, 128.05, 128.16, 128.91, 130.00, 136.29, 137.78, 145.00, 172.00, 173.17. Calcd.: [M]+ m/z = 724.26. Found ESI-MS: [M + Na]+ = 747.20, [M + K]+ = 763.2. GPC: Mw = 680, Mn = 760, Mw/Mn = 1.12

[OH2-G2-TSe]: [11] - Deprotection of [8] (7.90 g, 10.90 mmol) in 190 mL of CH2Cl2 : MeOH (1:1, v/v) was carried out as above for 16 h at ambient temperature under 10 bar H2 atmosphere. 0.40 g Pd(OH)2 was used. Yield: 5.93 g, white foam (99%). 1H NMR (400 MHz, CD3OD): δ = 1.15 (s, 9H), 2.48 (s, 3H), 3.57-3.69 (m, 10H), 4.09 (d, J = 11.2 Hz) 2H), 4.14 (d, J = 10.6 Hz, 2H), 4.46 (t, J = 5.2 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H). 13C NMR (100 MHz, CD3OD): δ = 17.31, 17.86, 21.67, 47.68, 51.82, 55.84, 59.68, 65.97, 66.20, 129.29, 131.36, 137.81, 146.82, 173.79, 175.95. Calcd.: [M]+ m/z = 548.19. Found ES MS: [M + Na]+ = 571.2, [M + K]+ = 587.2

[Xan-G2-TSe]: [12] – 2-(Ethoxycarbonothioyl)thio)acetic acid [3] (4.65 g, 25.80 mmol), G1-(OH)-Tse [9] (2.72 g, 8.60 mmol), DPTS (1.01 g, 3.44 mmol), and DCC (5.86 g, 28.38 mmol) were allowed to react according to the general esterification procedure in 40 mL of dry CH2Cl2 for 18 h. The crude product was purified by liquid chromatography on silica gel, eluting with hexane gradually increasing to 40:60 ethyl acetate/hexane Yield: 4.60 g, orange viscous oil (84%). 1H NMR (400 MHz, CDCl3): δ = 1.16 (s, 3H), 1.42 (t, J = 7.1, 6H), 2.46 (s, 3H), 3.44 (t, J = 6.0 Hz, 2H), 3.91 (s, 4H), 4.16 (d, J = 11.0, 2H), 4.21 (d, J = 11.0 Hz), 4.46 (t, J = 6.0 Hz, 2H), 4.64 (q, J = 7.1 Hz, 4H), 7.39 (d, J = 8.0, 2H), 7.81 (d, J = 8.3, 2H). 13C NMR (100 MHz, CDCl3): δ = 13.74, 17.56, 21.67, 37.70, 46.19, 54.97, 58.36, 66.13, 70.91, 128.12, 130.18, 136.18, 145.28, 167.33, 171.80, 212.57. Calcd.: [M]+ m/z = 640.06. Found ES MS: [M + Na]+ = 663.0, [M + K]+ = 679.0. GPC: Mw = 700, Mw = 910, Mw/Mn = 1.30

[Xan-G2-COOH]: [13] - The removal of the para-toluene sulfonyl protecting group was carried out as described above, using [12] (4.60 g, 7.18 mmol, 1.0 equiv), and DBU (1.40 mL, 9.33 mmol, 1.3 equiv) dissolved in 50 mL of CH2Cl2 and stirred for 16 h. The reaction was monitored using TLC, 40:60 ethyl acetate/hexane. Yield: 3.10 g, orange viscous oil (94%). 1H NMR (400 MHz, CDCl3): 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). 13C NMR (100 MHz, CDCl3): δ = 13.74, 17.86, 37.74, 46.06, 66.13, 70.87, 167.45, 177.80, 212.53. Calcd.: [M]+ m/z = 548.02. ES MS: [M + Na]+ = 481.0

[Xan-G2-TSe]: [14] - 2-(Ethoxycarbonothioyl)thio)acetic acid [3], (9.97 g, 55.32 mmol), G2-(OH)-Tse [11], (5.06 g, 9.22 mmol), DPTS, (2.17 g, 7.38 mmol), and DCC (12.56 g, 60.85 mmol) were allowed to react according to the general esterification procedure in 170 mL of dry CH2Cl2 for 18 h. The crude product was purified by liquid chromatography on silica gel, eluting with hexane gradually increasing to 50:50 ethyl acetate/hexane: Yield: 9.65 g, orange viscous oil (88%). 1H NMR (400 MHz, CDCl3): δ = 1.20 (s, 3H), 1.25 (s, 6H), 1.42 (t, J = 7.1, 12H), 2.46 (s, 3H), 3.46 (t, J = 5.9 Hz, 2H), 3.94 (s, 8H), 4.17-4.33 (m, 12H) 4.46 (t, J = 5.9 Hz, 2H), 4.64 (q, J = 7.1 Hz, 8H), 7.40 (d, J = 9.2, 2H), 7.82 (d, J = 8.3, 2H). 13C NMR (100 MHz, CDCl3): 13.75, 17.37, 17.86, 21.69, 37.72, 46.36, 46.58, 54.81, 58.41, 65.58, 66.24, 70.89, 128.12, 130.16, 136.28, 145.20, 167.43, 171.64, 171.68, 212.61. Calcd.: [M]+ m/z = 1196.92. Found MALDI-TOF: [M+Na]+ = 1219.1. GPC: Mw = 1080, Mm = 1235, Mw/Mn = 1.14
[Xan$_2$G$_2$-COOH]; [15] - The removal of the para-toluene sulfonyl protecting group was carried out as described above, using [12] (9.50 g, 7.93 mmol, 1.0 equiv), and DBU (1.54 mL, 9.33 mmol, 1.3 equiv) dissolved in 100 mL of CH$_2$Cl$_2$ and stirred for 16 h. The reaction was monitored using TLC, 40:60 ethyl acetate/hexane. Yield: 7.44 g, orange viscous oil (93%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.27$ (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$_3$): $\delta = 13.75$, 17.65, 17.85, 46.37, 65.71, 66.33, 70.90, 167.50, 171.68, 175.89, 212.62. Calcd.: [M$^+$] $m/z = 1014.08$. Found ESI-MS: [M+Na]$^+$ = 1037.1. GPC: $M_n = 1690$, $M_w = 2570$, $M_d/M_w = 1.52$.

[Xan$_2$G$_4$]; [16] - 2-(Ethoxycarbonothioyl)thio)acetic acid [3], (1.54 g, 8.54 mmol), TEA, (0.32 g, 2.14 mmol), DPTS, (1.51 g, 9.40 mmol), and DCC (1.94 g, 9.40 mmol) were allowed to react according to the general esterification procedure in 30 mL of dry CH$_2$Cl$_2$ for 18 h. The crude product was purified by liquid chromatography on silica gel, eluting with hexane gradually increasing to 40:60 ethyl acetate/hexane. Yield: 1.01 g, orange viscous oil (88%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.43$ (t, $J = 7.1$ Hz, 9H), 2.88 (t, $J = 5.8$ Hz, 6H), 3.95 (s, 6H), 4.21 (t, $J = 5.8$ Hz, 2H), 4.65 (q, $J = 7.1$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.76$, 17.39, 53.18, 64.10, 70.76, 167.86, 212.72. Calcd.: [M$^+$] $m/z = 658.0$. Found ESI-MS: [M+Na]$^+$ = 658.0, [M+K]$^+$ = 674.0. GPC: $M_n = 890$, $M_w = 1400$, $M_d/M_w = 1.57$.

[Bz$_2$G$_4$]; [17] - The thiol Michael addition click procedure was carried out as described above using the general Michael addition procedure, using [Xan$_2$G$_4$]; [16], (0.2 g, 0.315 mmol) and n-butylamine (0.076 g, 103 µL, 1.04 mmol) dissolved in 3 mL of dry THF for 1.5 hr. Benzyl acrylate (0.154 g, 1.73 mmol), DPTS, (1.53 g, 5.19 mmol), and DCC (1.50 g, 9.27 mmol) were added and stirred according to the general esterification procedure in 15 mL of dry CH$_2$Cl$_2$ for 18 h. The crude product was purified by liquid chromatography on silica gel, eluting with 10:90 hexane/ethyl acetate/hexane. Yield: 0.25 g, pale yellow oil (92%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.27$, 1.33 (s, 9H), 1.42 (t, $J = 7.1$ Hz, 18H), 2.87 (t, $J = 6.3$ Hz, 6H), 3.93 (s, 12H), 4.17 (t, $J = 6.3$ Hz, 6H), 4.25 (d, $J = 11.0$ Hz, 6H), 4.33 (d, $J = 11.0$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.76$, 17.92, 37.75, 46.21, 53.09, 63.38, 66.30, 70.90, 167.39, 172.19, 212.55. Calcd.: [M$^+$] $m/z = 1492.2$. Found ESI-MS: [M+Na]$^+$ = 1492.2 GPC: $M_n = 1540$, $M_w = 1795$, $M_d/M_w = 1.16$.

[Xan$_2$G$_1$]-[18]-[Xan$_2$G$_1$]-COOH; [13] (3.01 g, 6.56 mmol), TEA, (0.258 g, 1.73 mmol), DPTS, (1.53 g, 5.19 mmol), and DCC (1.50 g, 7.27 mmol) were added and stirred according to the general esterification procedure in 15 mL of dry CH$_2$Cl$_2$ for 18 h. The crude product was purified by liquid chromatography on silica gel, eluting with 10:90 hexane/ethyl acetate/hexane. Yield: 1.65 g, orange viscous oil (65%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.27$, 1.33 (s, 9H), 1.43 (t, $J = 7.1$ Hz, 18H), 2.87 (t, $J = 6.3$ Hz, 6H), 3.93 (s, 12H), 4.17 (t, $J = 6.3$ Hz, 6H), 4.25 (d, $J = 11.0$ Hz, 6H), 4.33 (d, $J = 11.0$ Hz, 6H), 4.64 (q, $J = 7.1$ Hz, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.76$, 17.92, 37.75, 46.21, 53.09, 63.38, 66.30, 70.90, 167.39, 172.19, 212.55. Calcd.: [M$^+$] $m/z = 1469.1$. Found ESI-MS: [M+Na]$^+$ = 1470.1. Found MALDI-TOF: [M+Na]$^+$ = 1492.2 GPC: $M_n = 1540$, $M_w = 1795$, $M_d/M_w = 1.16$.

[Bz$_2$G$_1$]; [19] - The thiol Michael addition click procedure was carried out as described above using the general Michael addition procedure, using G1-(Xan)$_n$-TEA [18], (0.2 g, 0.136 mmol) and n-butylamine (89 µL, 0.90 mmol) dissolved in 3 mL of dry THF for 1.5 hr. Benzyl acrylate (125 µL, 0.816 mmol) was then added and stirred for 16 hr. Yield: 0.24 g, pale yellow oil (92%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.25$ (s, 9H), 2.67 (t, $J = 7.2$ Hz, 12H), 2.88 (t, $J = 7.2$ Hz, 12H), 3.22 (s, 12H), 4.27 (m, 18H), 5.12 (s, 12H), 7.34 (m, 30H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 17.73$, 27.51, 33.41, 34.26, 46.33, 52.94, 62.47, 65.83, 66.60, 128.27, 128.33, 128.59, 135.69, 169.75, 171.44, 172.22. Calcd.: [M$^+$] $m/z = 1913.6$. Found MALDI-TOF: [M+H]$^+$ = 1914.8, [M+Na]$^+$ = 1936.8, [M+K]$^+$ = 1952.8. GPC: $M_n = 2145$, $M_w = 2320$, $M_d/M_w = 1.08$. 

[12] = 2-(Ethoxycarbonothioyl)thio)acetic acid.
The thiol Michael addition click reaction was carried out as described above using the general Michael addition procedure, using \( \text{G1}-\text{Xan}_n \)-TEA \([18]\), (0.2 g, 0.136 mmol) and N-butylamine (89 µL, 0.90 mmol) dissolved in 3 mL of dry THF for 1.5 hr. 2-(Dimethylamino)ethyl acrylate (88.0 µL, 0.576 mmol) was then added and stirred for 16 hr. Yield: 0.216 g, pale yellow oil (89%).

The thiol Michael addition click procedure was carried out as described above using the general Michael addition procedure, using \( \text{G1}-\text{Xan}_n \)-TEA \([18]\), (0.2 g, 0.136 mmol) and N-butylamine (89 µL, 0.90 mmol) dissolved in 3 mL of dry THF for 1.5 hr. 2-oligo(ethylene glycol) methyl ether acrylate (0.394 g, 0.816 mmol) was then added and stirred for 16 hr. Yield: 0.11 g, pale yellow oil (89%).

The thiol Michael addition click procedure was carried out as described above using the general Michael addition procedure, using \( \text{G1}-\text{Xan}_n \)-TEA \([18]\), (0.2 g, 0.136 mmol) and N-butylamine (89 µL, 0.90 mmol) dissolved in 3 mL of dry THF for 1.5 hr. 2-(Dimethylamino)ethyl acrylate (125 µL, 0.816 mmol) was then added and stirred for 16 hr. Yield: 0.107 g, pale orange oil (87%).
The thiol Michael addition click procedure was carried out as described above using the general Michael addition procedure, using [Xan$_{12}$-G$_2$];[22], (0.19 g, 0.061 mmol) and N-butylamine (87 µL, 0.461 mmol) dissolved in 3mL of dry THF for 1.5 hr. 2 oligo(ethylene glycol) methyl ether acrylate (0.583g, 1.1 mmol) was then added and stirred for 16 hr. Yield: 0.350 g, pale yellow oil (73%) $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.26$ (s, 27H), 2.67 (t, $J = 7.1$ Hz, 24H), 2.88 (t, $J = 7.2$ Hz, 24H), 3.28 (s, 24H), 3.38 (s, 36H), 3.52-3.79 (m, 397H), 4.07-4.42 (m, 48H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 17.82, 27.39, 33.35, 34.09, 46.50, 59.04, 63.85, 65.66, 69.04, 70.58, 71.95, 169.70, 171.56, 171.75, 172.01$. Calcd.: [M]$^+$ m/z = 7868 Found MALDI-TOF: [M+Na]$^+$ = 7897.0. GPC: $M_a = 8585, M_w = 9795, M_w/M_a = 1.14$.

Figure S1. $^{13}$C NMR (100 MHz, CDCl$_3$) of [2-((Ethoxycarboxthioyl)thio)acetic acid]; [3]

Figure S2. $^{13}$C NMR (100 MHz, CDCl$_3$) of [2-((Ethoxycarboxthioyl)thio)acetic acid]; [3]
Scheme S1. Synthesis of [Xan$_3$-G$_0$]; xanthate functional dendrimer and subsequent one-pot deprotection/thiol Michael addition with Benzyl acrylate to yield [Bz$_3$-G$_0$].

Figure S3. $^1$H NMR (400 MHz, CDCl$_3$) of [Xan$_3$-G$_0$]; [16].
Figure S4. $^{13}$C NMR (100 MHz, CDCl$_3$) of [Xan$_3$-G$_o$]; [16].

Figure S5. ESI-MS (MeOH) of [Xan$_3$-G$_o$]; [16].
Figure S6. GPC (Refractive index) of \([\text{Xan}_3\text{-Go}]\); [16]

Figure S7. – Deprotection of \([\text{Xan}_3\text{-Go}]\); [16] using 1.1 eqvs of n-butylamine analysed using \(^1\text{H NMR}\)
Figure S8. $^1$H NMR (400 MHz, CDCl$_3$) of [Bz$_3$-G$_n$]; [17].

Figure S9. GPC (Refractive index) of [Bz$_3$-G$_n$]; [17]
Figure S10. $^{13}$C NMR (100 MHz, CDCl$_3$) of [Bz$_3$-G$_3$]; [17].

Figure S11. ESI-MS (MeOH) of [Bz$_3$-G$_3$]; [17].
Figure S12. $^1$H NMR (400 MHz, CDCl$_3$) of [Xan$_2$-G$_1$-TSe]; [12]

Figure S13. ESI-MS (MeOH) of [Xan$_2$-G$_1$-TSe]; [12]
Figure S14. $^{13}$C NMR (100 MHz, CDCl$_3$) of [Xan$_2$-G$_1$-TSe]; [12]

Figure S15. $^1$H NMR (400 MHz, CDCl$_3$) of [Xan$_2$-G$_2$-TSe]; [14]
Figure S16. $^{13}$C NMR (100 MHz, CDCl$_3$) of [Xan$_4$-G$_2$-TSe]; [14]

Figure S17. MALDI-TOF (Dith, THF) of [Xan$_4$-G$_2$-TSe]; [14]
Figure S18. $^1$H NMR (400 MHz, CDCl$_3$) of [Xan$_2$-G$_1$-COOH]; [13]

Figure S19. $^{13}$C NMR (100 MHz, CDCl$_3$) of [Xan$_2$-G$_1$-COOH]; [13]

Figure S20. ESI-MS (MeOH) of [Xan$_2$-G$_1$-COOH]; [13]
Figure S21. $^1$H NMR (400 MHz, CDCl$_3$) of [Xan$_4$-G$_2$-COOH]; [15]

Figure S22. $^{13}$C NMR (100 MHz, CDCl$_3$) of [Xan$_4$-G$_2$-COOH]; [15]
Figure S23. ESI-MS (MeOH) of [Xan-G2-COOH]; [15]
Scheme S2. Synthesis of $[\text{Xan}_{12}-\text{G}_1]$ xanthate functional dendrimer and subsequent one-pot deprotection/thiol Michael addition with various acrylates.
Figure S24. $^1$H NMR (400 MHz, CDCl$_3$) of [Xan$_6$-G$_1$];[18].

Figure S25. $^{13}$C NMR (100 MHz, CDCl$_3$) of [Xan$_n$-G$_1$];[18].
Figure S26. MALDI-TOF of [Xan₆-G₁]:[18]. (Matrix = trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB))

Figure S27. GPC (Refractive index) of [Xan₆-G₁]:[18]
Figure S28. $^1$H NMR (400 MHz, CDCl$_3$) of [Xan$_{12}$-G$_2$];[22]
Figure S29. $^{13}$C NMR (400 MHz, CDCl$_3$) of [Xan$_{12}$-G$_2$];[22]

Figure S30. MALDI-TOF of [Xan$_{12}$-G$_2$];[22] A - (Matrix = trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)) 20% Laser. B - (Matrix = trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)) 24% Laser.
Figure S31. $^1$H NMR (400 MHz, CDCl$_3$) of [Bz$_6$-G$_1$]-[19].

Figure S32. $^{13}$C NMR (100 MHz, CDCl$_3$) of [Bz$_6$-G$_1$]-[19].
Figure S33. MALDI-TOF of $[\text{Bz}_6\text{-G}_1];\text{[19]}$. A - 9-Nitroanthracene (9-antra) B - (Matrix = trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB))

Figure S34. GPC (Refractive index) of $[\text{Bz}_6\text{-G}_1];\text{[19]}$
Figure S35. $^1$H NMR (400 MHz, CDCl$_3$) of [Am$_6$-G$_1$];[20]

Figure S36. $^{13}$C NMR (100 MHz, CDCl$_3$) of [Am$_6$-G$_1$];[20]
Figure S37. MALDI-TOF of [Am$_6$-G$_1$];[20]. (Matrix = 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA))

Figure S38. GPC (Refractive index) of [Am$_x$-G$_1$];[20]
Figure S39. $^1$H NMR (400 MHz, CDCl$_3$) of [OEG$_6$-G$_1$];[21]

Figure S40. $^{13}$C NMR (100 MHz, CDCl$_3$) of [OEG$_6$-G$_1$];[21]
**Figure S41.** GPC (Refractive index) of [OEG₆-G₁]:[21]

**Figure S42.** MALDI-TOF of [OEG₆-G₁]:[21]. (Matrix = 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA))
Figure S43. MALDI-TOF of $[\text{OEG}_6\text{-G}_1]_{[21]}$. (Matrix = 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA))

Figure S44. $^1$H NMR (400 MHz, CDCl$_3$) of $[\text{Xan}_{12}\text{-G}_2]_{[22]}$
Figure S45. $^{13}$C NMR (400 MHz, CDCl$_3$) of [Xan$_{12}$-G$_{2}$]:[22]
Figure S46. $^{13}$C NMR (400 MHz, CDCl$_3$) of $G_2$-(Benzyl)$_{12}$-TEA [23]. A - 9-Nitroanthracene (9-antra) B - (Matrix = trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB))

Figure S47. GPC (Refractive index) of $G_2$-(Benzyl)$_{12}$-TEA [23].
Figure S48. $^1$H NMR (400 MHz, CDCl$_3$) of [Am$_{12}$-G$_2$];[24].

Figure S49. GPC (Refractive index) of [Am$_{12}$-G$_2$];[24].
Figure S50. $^{13}$C NMR (400 MHz, CDCl$_3$) of [Am$_{12}$-G$_2$];[24].

Figure S51. MALDI-TOF of [Am$_{12}$-G$_2$];[24]. (Matrix = 2-(4’-Hydroxybenzeneazo)benzoic acid (HABA))
Figure S52. $^1$H NMR (400 MHz, CDCl$_3$) of [OEG$_{12}$-G$_2$]; [25].

Figure S53. GPC (Refractive index) of [OEG$_{12}$-G$_2$]; [25].
Figure S54. $^{13}$C NMR (400 MHz, CDCl$_3$) of [OEG$_{12}$-G$_2$]; [25].
Figure S55. MALDI-TOF of [OEG_{12}-G_2]; [25]. (Matrix = trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB))

Figure S56. MALDI-TOF of [OEG_{12}-G_2]; [25]. (Matrix = trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB))
Figure S57. – ESI-MS of reaction of a G2 dendron with an additional methyl group between peripheral ester and xanthate using DBU.

Figure S58. – $^1$H NMR(400 MHz, CDCl$_3$) of reaction of a G2 dendron with an additional methyl group between peripheral ester and xanthate using DBU.