

Hyperbranched Polydendrons: a new controlled macromolecular architecture with self-assembly in water and organic solvents.

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Supplementary Information

Methods

Materials. All starting materials, 1,3-dibenzyloxy-2-propanol (97 %), 1,1'-carbonyldiimidazole ($\geq 97\%$), diethylenetriamine (99 %), β -butyrolactone (98 %), α -bromoisobutyryl bromide (98 %), 4-(dimethylamino)pyridine ($\geq 99\%$), triethylamine ($\geq 99\%$), hydroxypropyl methacrylate (97 %), ethylene glycol dimethacrylate (98 %) Cu(I)Cl ($\geq 99\%$), 2,2'-bipyridyl ($\geq 99\%$), poly(ethylene glycol) monomethyl ether (average Mn 750 g/mol) were purchased from Aldrich and used as received. Anhydrous toluene and methanol, silica gel used for column chromatography, Dowex® Marathon™ MSC (hydrogen form) ion exchange resin beads and potassium hydroxide (KOH) were purchased from Aldrich and used as received. All other solvents were analytical grade and purchased from Fisher.

Characterisation. Molecular weights and molecular weight distributions were measured using a Viscotek 270max triple detection GPC equipped with two T6000M columns with a mobile phase of THF at 35 °C and a flow rate of 1.0 mL/min. NMR spectra were recorded using a Bruker DPX-400 spectrometer operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C , in CDCl_3 , D_2O or DMSO. Electrospray mass spectrometry data was recorded in the Mass Spectrometry Laboratory at the University of Liverpool. The data was obtained using a MicroMass LCT mass spectrometer using electron ionisation and direct infusion syringe pump sampling. All materials were diluted with methanol. Elemental analyses were obtained from a Thermo FlashEA 1112 series CHNSO elemental analyser. Nanoparticle characterisation utilised a Malvern Zetasizer Nano ZS dynamic light scattering (DLS) instrument. Scanning electron microscopy SEM images were obtained using a Hitachi S-4800 FE-SEM. Samples in solvent mixtures of acetone and hexane were dropped directly onto an aluminium stub. Aqueous nanoparticle samples (1.0 mg/mL or 0.1 mg/mL in water) were either dropped onto a glass cover slide or silicon wafer mounted on an aluminium stub with a carbon tab, dried overnight at ambient temperature then Au coated at 20 mA for 2 minutes. ^1H / ^{13}C NMR and mass spectra are presented in Figs. S2-4 and 6-17. Fluorescence spectra were obtained on a PerkinElmer Luminescence spectrometer LS55. Emission spectra for Nile Red containing samples were recorded between 550 nm and 700 nm, exciting at 552 nm. The slit widths for emission and excitation were 5 nm and 10 nm, respectively, with a scan rate of 100 nm/min. Emission spectra for pyrene labelled samples were recorded between 330 nm and 500 nm, exciting at 335 nm. The slit widths for emission and excitation were 5 nm and 5 nm, respectively, with a scan rate of 100 nm/min.

Generation 1 dendron initiator (**G₁-Br**) synthesis

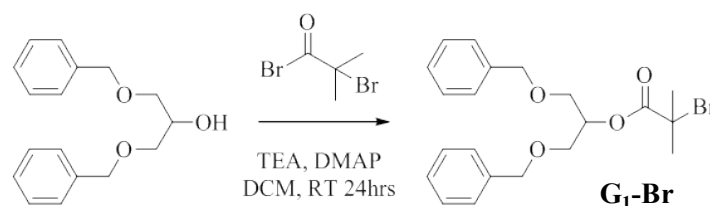


Fig. S1 – Synthetic strategy for **G₁-Br** dendron initiator

1,3-Dibenzyloxy-2-propanol, **1**, (9.80 g, 36.0 mmol) was weighed into a 2-neck round bottom flask which was equipped with magnetic stirrer and dry N₂ inlet. Dichloromethane (DCM) (100 mL) was added followed by 4-(dimethylamino)pyridine (DMAP) (0.44 g, 3.6 mmol) and triethylamine (TEA) (7.53 mL, 54.0 mmol). The reaction was cooled to 0 °C in an ice-bath and α -bromoisobutyryl bromide (5.34 mL, 43.2 mmol) was added dropwise over 20 minutes. After complete addition the reaction was warmed to room temperature and left stirring overnight. Reaction could be observed by the formation of a white precipitate. After 24 hours the precipitate was removed by filtration, the resulting crude reaction medium was washed first with a saturated solution of NaHCO₃ (3 x 100 mL) followed by distilled water (3 x 100 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give a pale yellow oil (81 %). Found, C, 59.55; H, 6.02 %. C₂₁H₂₅BrO₄ requires, C, 59.86; H, 5.98; Br, 18.96; O, 15.19 %. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.35-7.20 (m, 10H), 5.26 (m, 1H), 4.55 (m, 4H), 3.69 (d, 4H), 1.93 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 171.2, 138.0, 128.4, 127.7, 127.6, 73.3, 68.5, 55.8, 30.7. *m/z* (ES MS) 443.1 [M+Na]⁺, 461.1 [M+K]⁺, *m/z* required 420.1 [M]⁺.

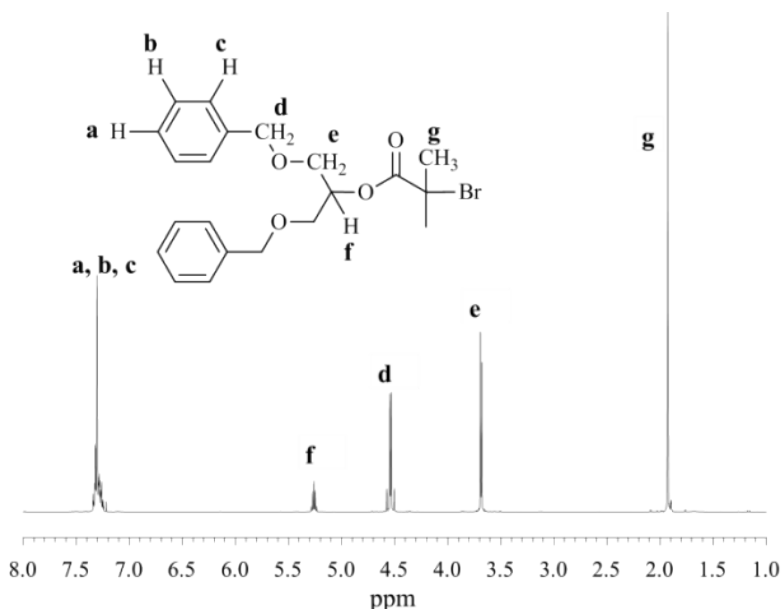


Fig. S2 - ¹H NMR (CDCl₃, 400 MHz) spectrum of **G₁-Br** dendron initiator

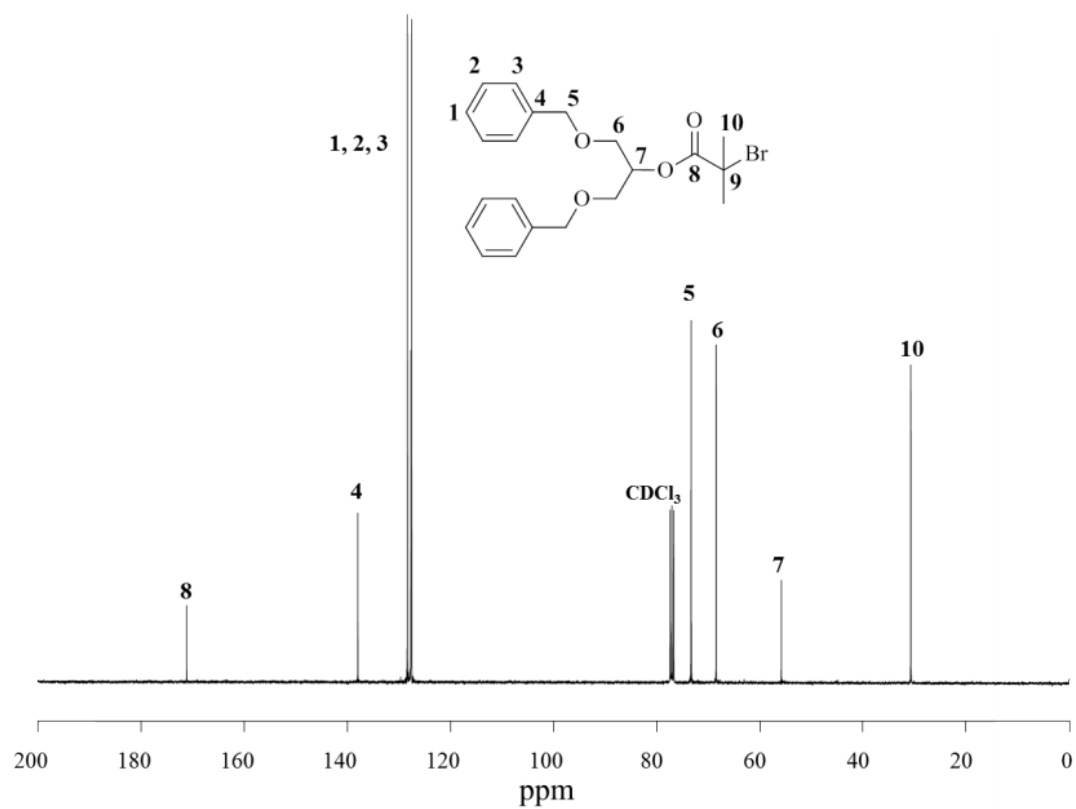


Fig. S3 - ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of $\text{G}_1\text{-Br}$ dendron initiator

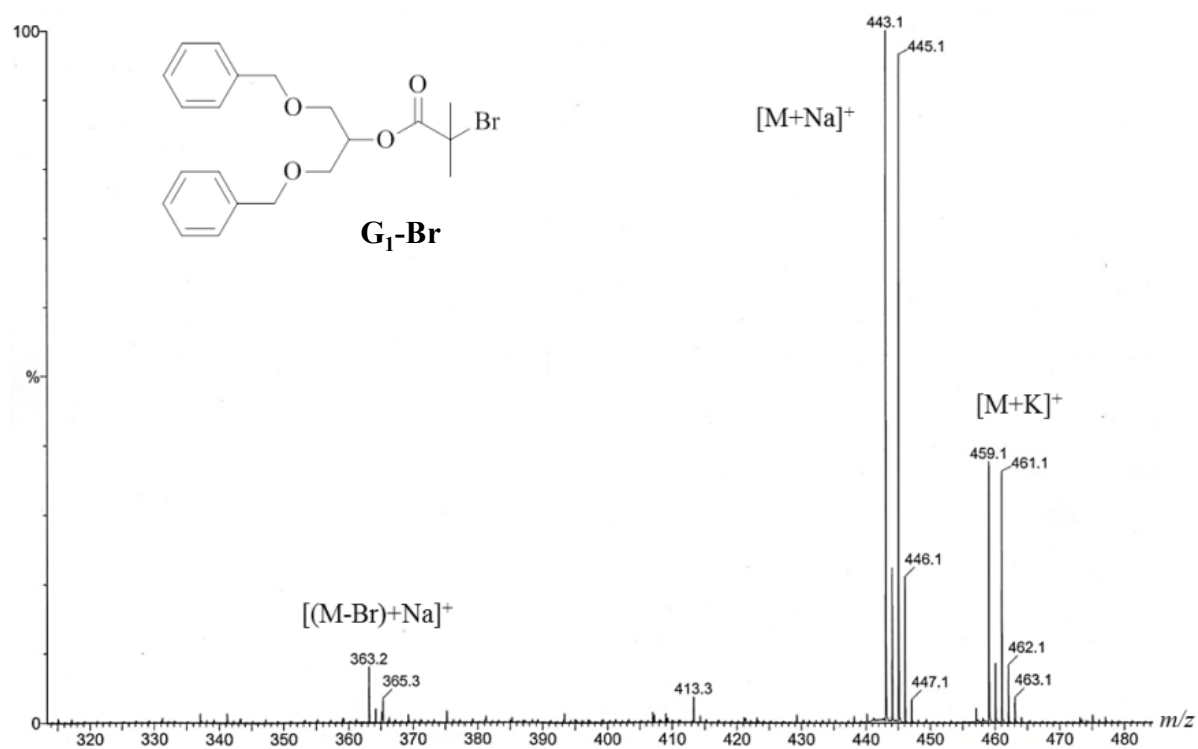


Fig. S4 - Mass spectrum (ES-MS) of **G₁-Br** dendron initiator

Generation 2 dendron initiator **G₂-Br** synthesis

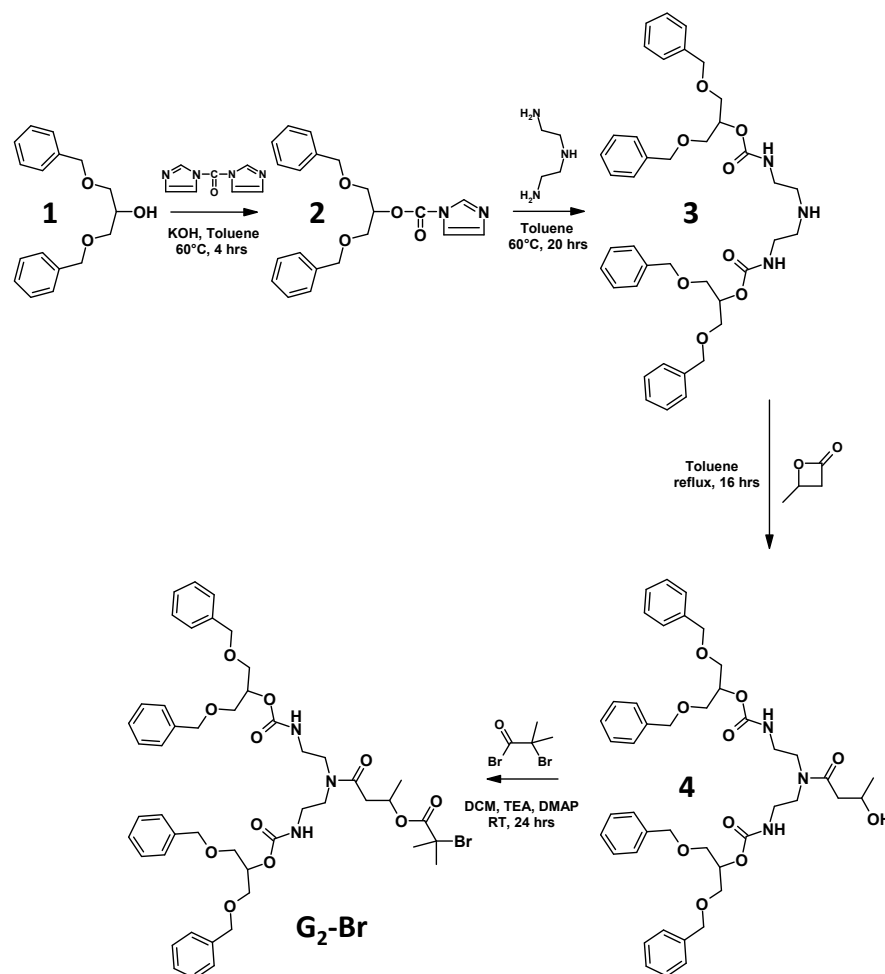


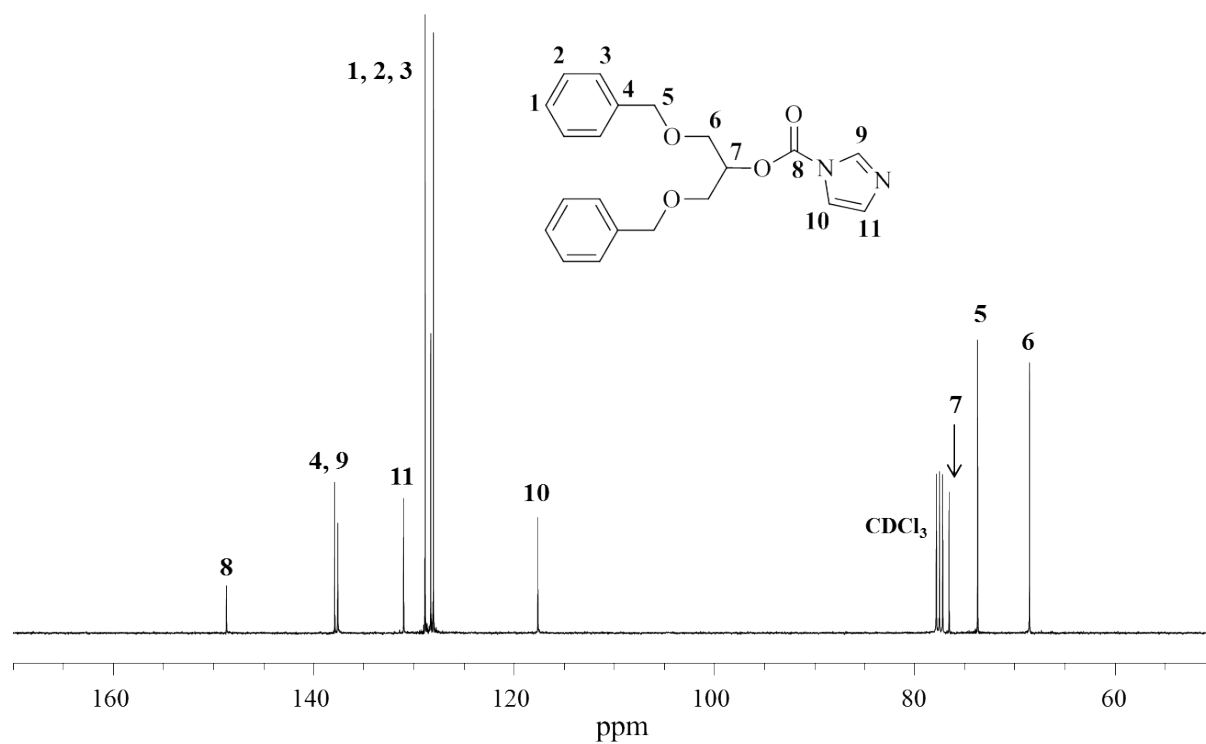
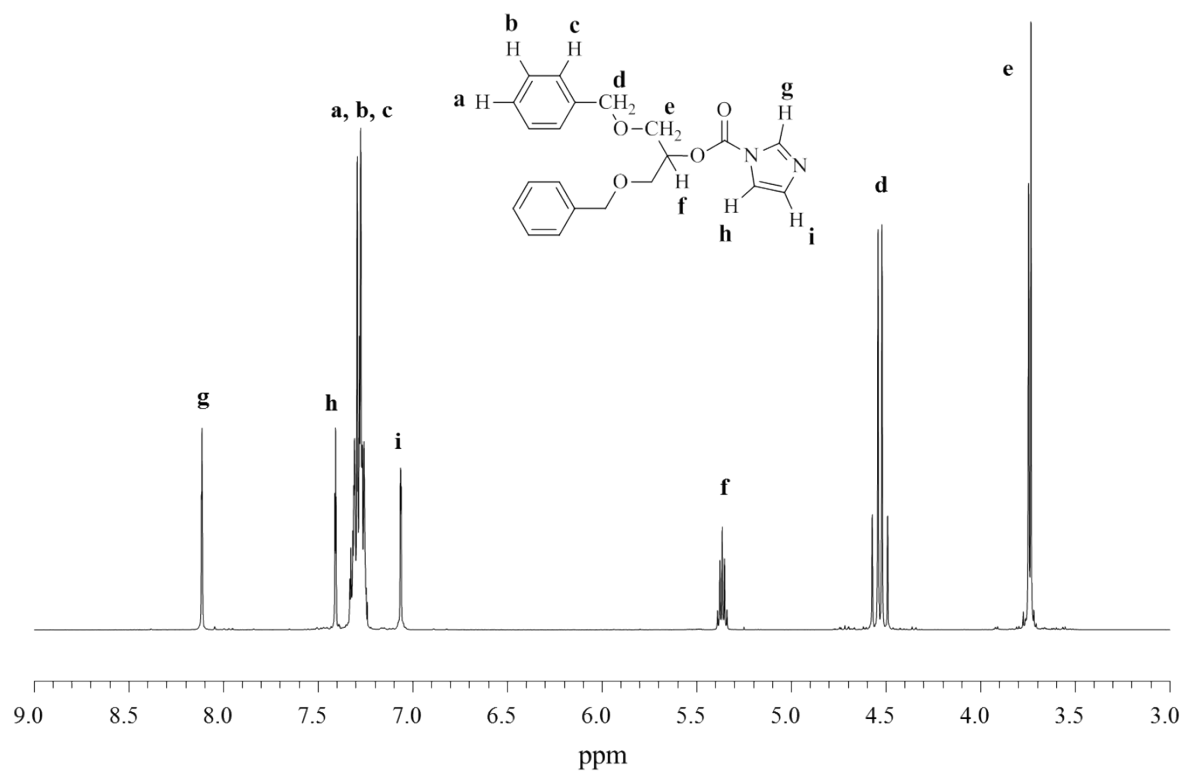
Fig. S5 – Synthetic strategy for **G₂-Br** dendron initiator

1,1'-Carbonyldiimidazole (CDI) (9.73 g, 60.0 mmol) was weighed into a 2-neck round bottom flask and equipped with magnetic stirring, condenser and dry N₂ inlet. Anhydrous toluene (100 mL) was added, followed by KOH (0.34 g, 6.0 mmol) and **1** (12.35 mL, 50.0 mmol). The reaction was heated to 60 °C for 6 hours. Toluene was removed *in vacuo*, the crude mixture was dissolved in DCM (50 mL) and washed with distilled water (3 x 50 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give **2** as a pale yellow oil (97 %). Found C, 68.64; H, 6.10; N, 7.85 %. C₂₁H₂₂N₂O₄ requires C, 68.84; H, 6.05; N, 7.65; O, 17.47 %. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.11 (s, 1H), 7.41 (s, 1H), 7.33-7.23 (m, 10H), 7.06 (s, 1H), 5.36 (qn, 1H), 4.53 (m, 4H), 3.75 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 148.3, 137.5, 137.2, 130.6, 128.4, 127.9, 127.6, 117.2, 76.1, 73.3, 68.1. *m/z* (ES MS) 367.2 [M+H]⁺, 389.2 [M+Na]⁺, 405.1 [M+K]⁺, *m/z* required 366.2 [M]⁺.

2 (16.84 g, 46.0 mmol) was weighed into a 2-neck round bottom flask which was equipped with magnetic stirring, condenser and dry N₂ inlet. Anhydrous toluene (120 mL) was added followed by diethylenetriamine (DETA) (2.48 mL, 23.0 mmol). The reaction was heated to 60 °C for 48 hours. Toluene was removed *in vacuo*, the resulting crude mixture was dissolved in DCM (100 mL) and washed with distilled water (3 x 100 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give **3** as a yellow oil (93 %). Found C, 68.50; H, 7.13; N, 6.00 %. C₄₀H₄₉N₃O₈ requires, C, 68.65; H, 7.06; N, 6.00; O, 18.29 %. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.27-7.16 (m, 20H), 5.23 (s, br, NH), 5.03 (qn, 2H), 4.44 (m, 8H), 3.57 (d, 8H), 3.12 (m, 4H), 2.58 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 156.6, 138.4, 128.8, 128.1, 73.7, 72.1, 69.4, 49.0, 41.2. *m/z* (ES MS) 700.4 [M+H]⁺, 722.3 [M+Na]⁺, 738.3 [M+K]⁺, *m/z* required 699.4 [M]⁺.

3 (15.01 g, 21.4 mmol) was weighed into a 2-neck round bottom flask, equipped with magnetic stirrer, condenser and dry N₂ inlet. Anhydrous toluene (90 mL) was added followed by dropwise addition of β-butyrolactone (2.62 mL, 32.2 mmol). The reaction was heated at reflux for 16 hours. Toluene was removed *in vacuo*, the resulting crude mixture was dissolved in DCM (50 mL) and washed with distilled water (3 x 50 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give a yellow oil. The crude product was purified by silica gel column chromatography with a mobile phase gradient of DCM:MeOH (100:0 - 95:5 - 90:10) to give **4** as a pale yellow oil (45 %). Found C, 65.35; H, 6.72; N, 5.10 %. C₄₄H₅₅N₃O₁₀ requires, C, 67.24; H, 7.05; N, 5.35; O, 20.36 %. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.34-7.25 (m, 20H), 5.35 (br, NH), 5.31 (br, NH), 5.11 (m, 2H), 4.50 (m, 8H), 4.14 (s, 1H), 3.62 (m, 8H), 3.46-3.18 (m, br, 8H), 2.45-2.22 (m, 2H), 1.18-1.05 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 174.4, 156.8, 156.6, 138.4, 138.3, 128.8, 128.1, 128.0, 73.7, 73.6, 72.6, 72.4, 69.5, 69.3, 65.1, 48.5, 46.5, 41.2, 40.3, 39.9, 22.9. *m/z* (ES MS) 808.4 [M+Na]⁺, *m/z* required 785.4 [M]⁺.

4 (9.31 g, 11.85 mmol) was dissolved in DCM (100 mL) and transferred to a round bottom flask which was equipped with magnetic stirring and a dry N₂ inlet. DMAP (0.14 g, 1.19 mmol), TEA (3.30 mL, 23.7 mmol) were added and the reaction mixture was cooled to 0 °C in an ice bath followed by dropwise addition of α-bromoisobutyryl bromide (2.19 mL, 17.78 mmol). The reaction was warmed to room temperature for 24 hours. A colour change from pale orange to a dark orange/brown colour was observed over time. No precipitate was observed, the crude reaction mixture was washed with a saturated NaHCO₃ solution (3 x 100 mL) and distilled water (3 x 100 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give the G₂ dendron initiator **G₂-Br** as an orange oil (81 %). Found C, 59.50; H, 6.31; N, 4.39 %. C₄₈H₆₀BrN₃O₁₁ requires, C, 61.67; H, 6.47; Br, 8.55; N, 4.49; O, 18.82 %. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.35-7.23 (m, 20H), 5.33 (s, br, NH), 5.10 (m, 2H), 4.52 (m, 8H), 3.71-3.53 (s, 8H), 3.52-3.12 (m, br, 8H), 2.76 (d of d, 1H), 2.47 (d of d, 1H), 1.87 (s, 6H), 1.29 (d, 3H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 192.5, 170.8, 156.3, 156.1, 137.9, 134.5, 128.4, 127.7, 127.6, 73.2, 73.1, 72.2, 71.8, 70.2, 69.1, 69.0, 68.8, 56.1, 48.3, 46.3, 39.6, 39.4, 38.9, 30.8, 30.7, 30.6, 19.7. *m/z* (ES MS) 958.3 [M+Na]⁺, 974.3 [M+K]⁺, *m/z* required 933.3 [M]⁺.



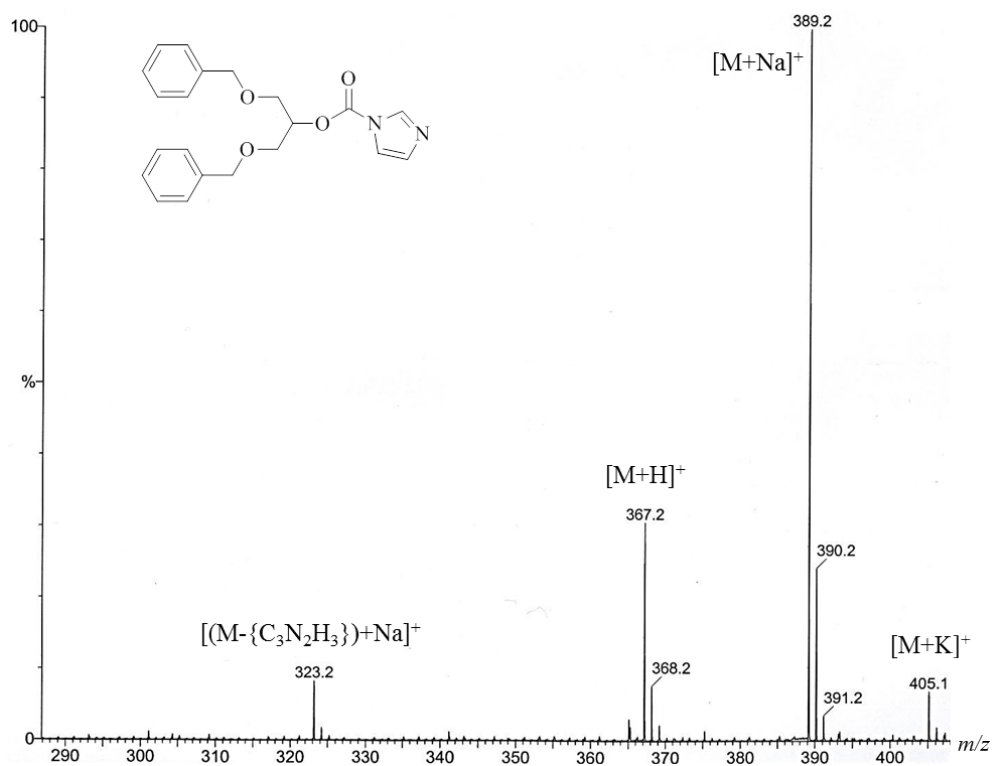


Fig. S8 - Mass spectrometry (ES-MS) of **2**

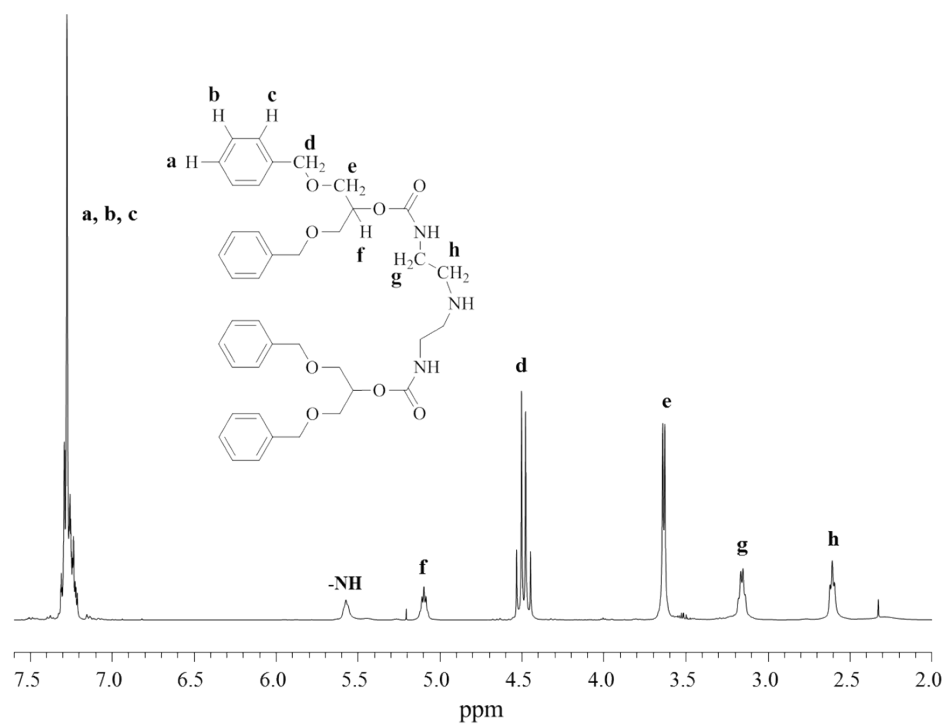


Fig. S9 - 1H NMR ($CDCl_3$, 400 MHz) spectrum of **3**

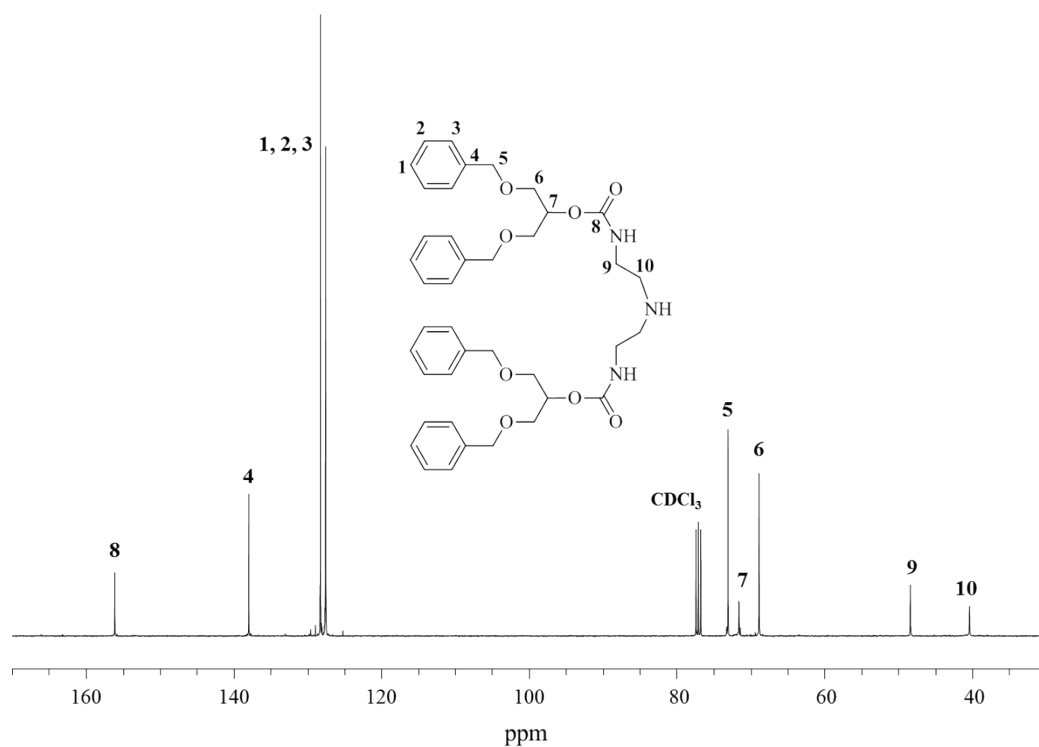


Fig. S10 - ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of **3**

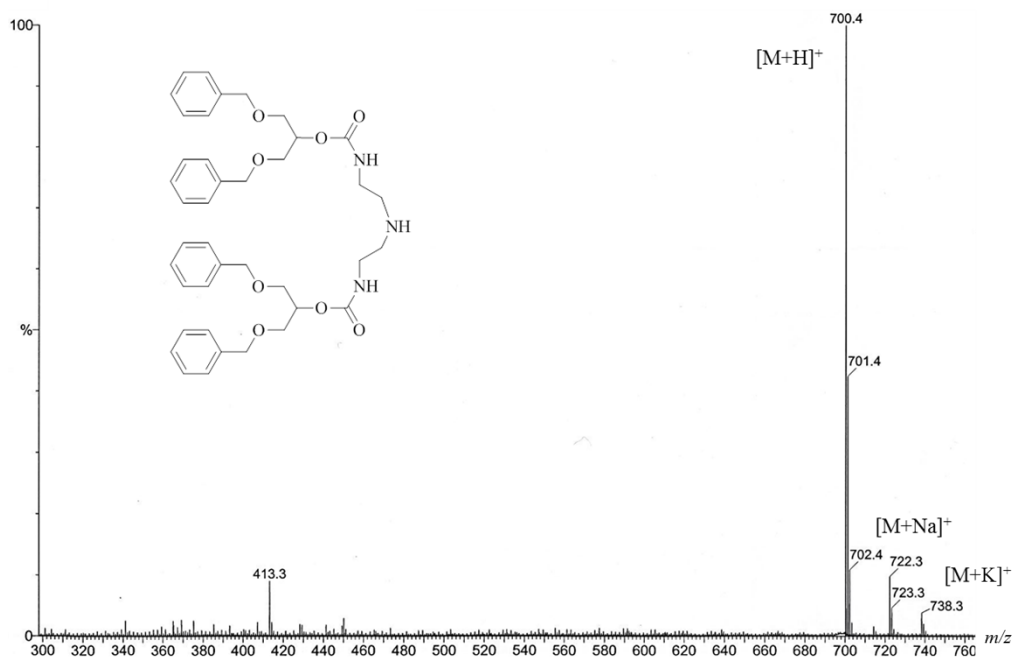


Fig. S11 - Mass spectrometry (ES-MS) of **3**

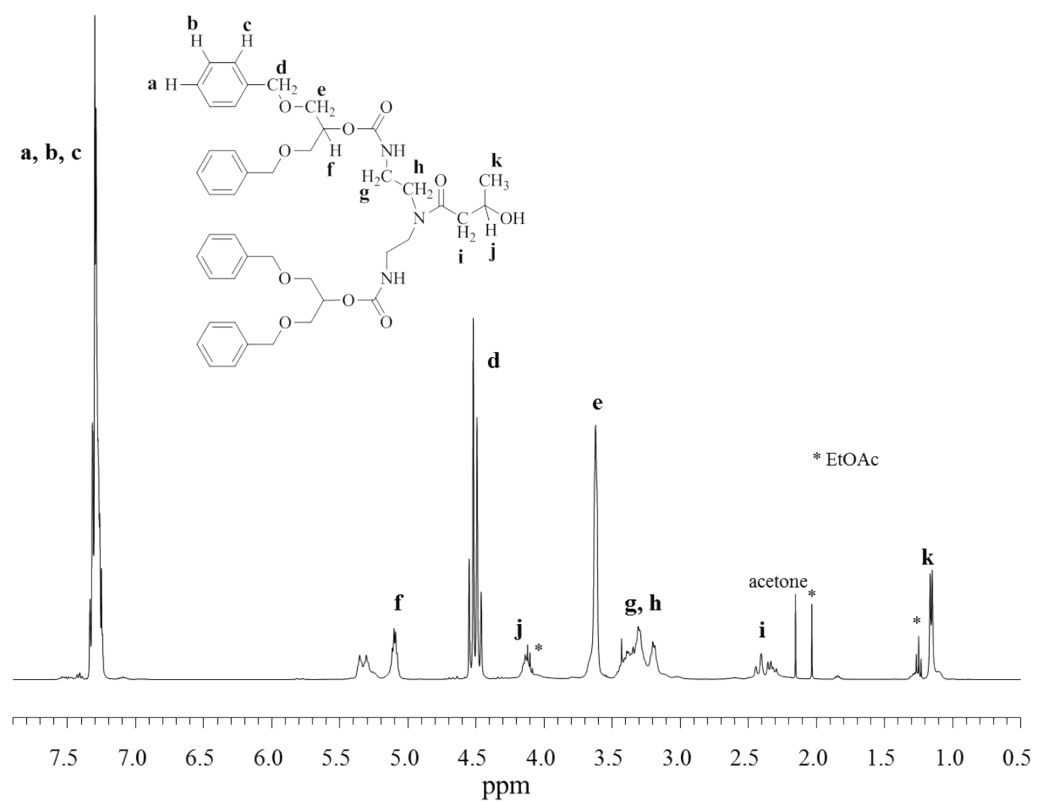


Fig. S12 - ¹H NMR (CDCl₃, 400 MHz) spectrum of **4**

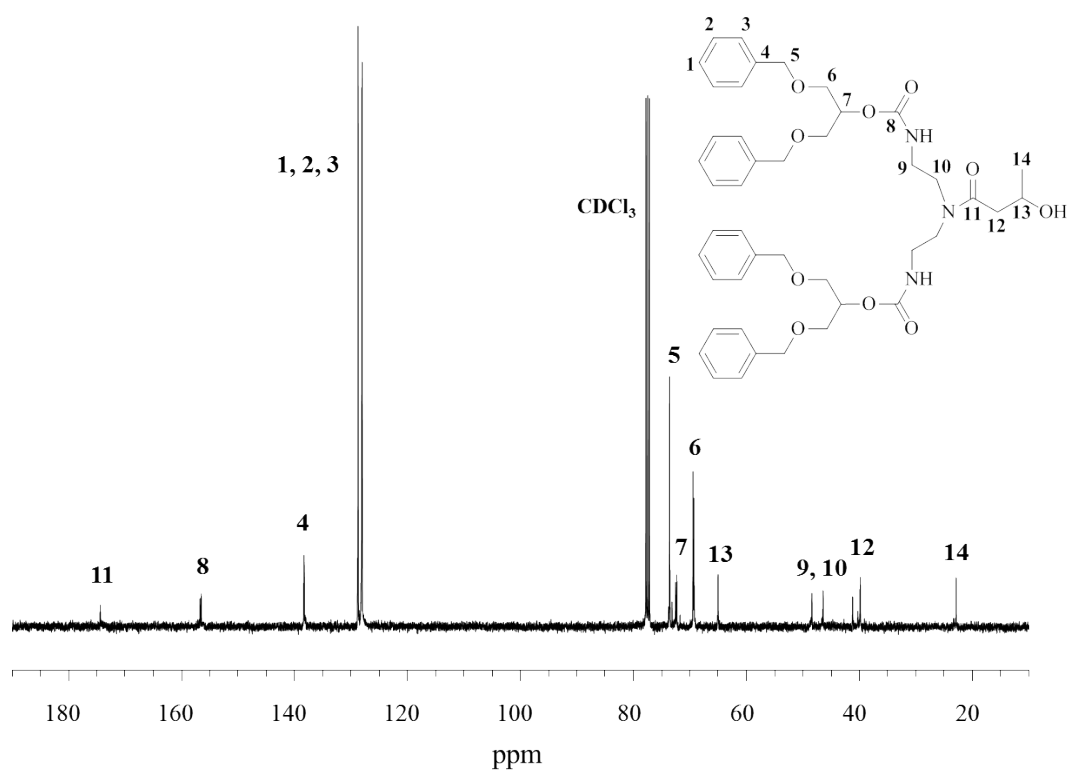


Fig. S13 - ¹³C NMR (CDCl₃, 100 MHz) spectrum of **4**

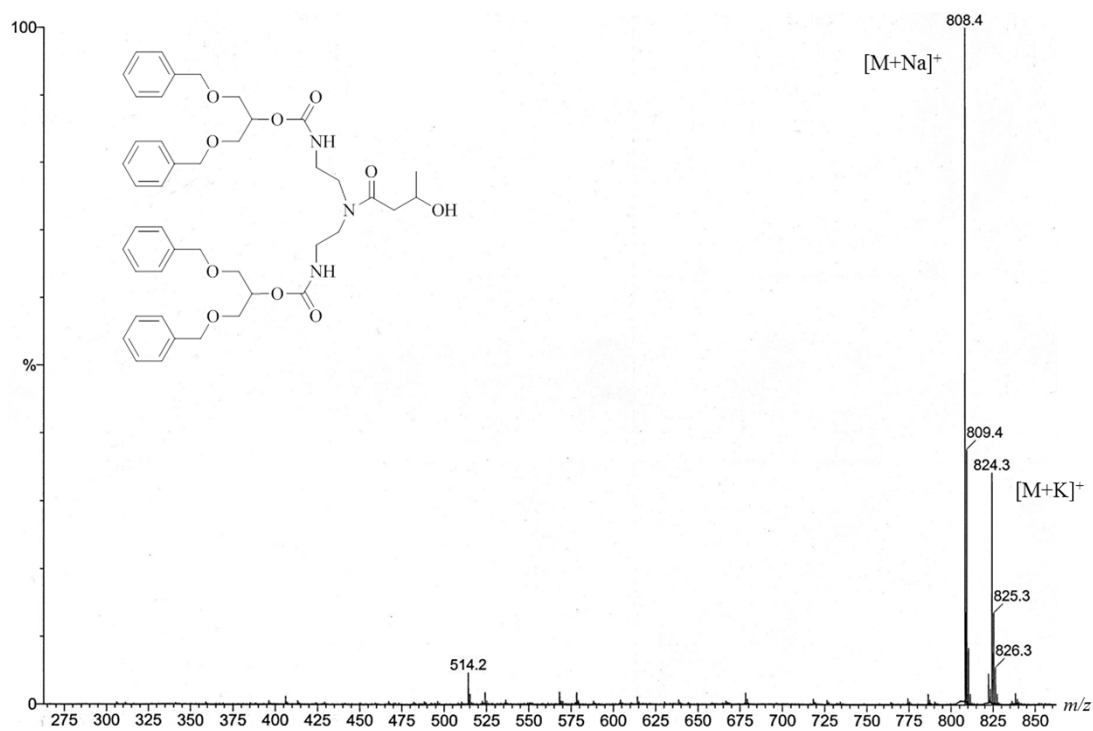


Fig. S14 - Mass spectrometry (ES-MS) of **4**

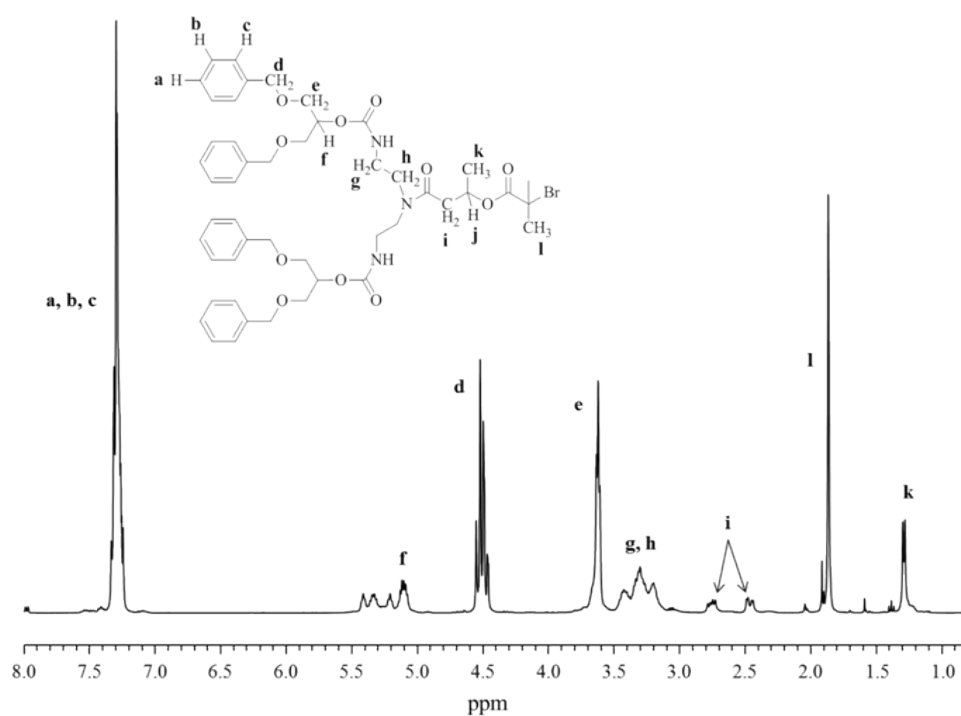
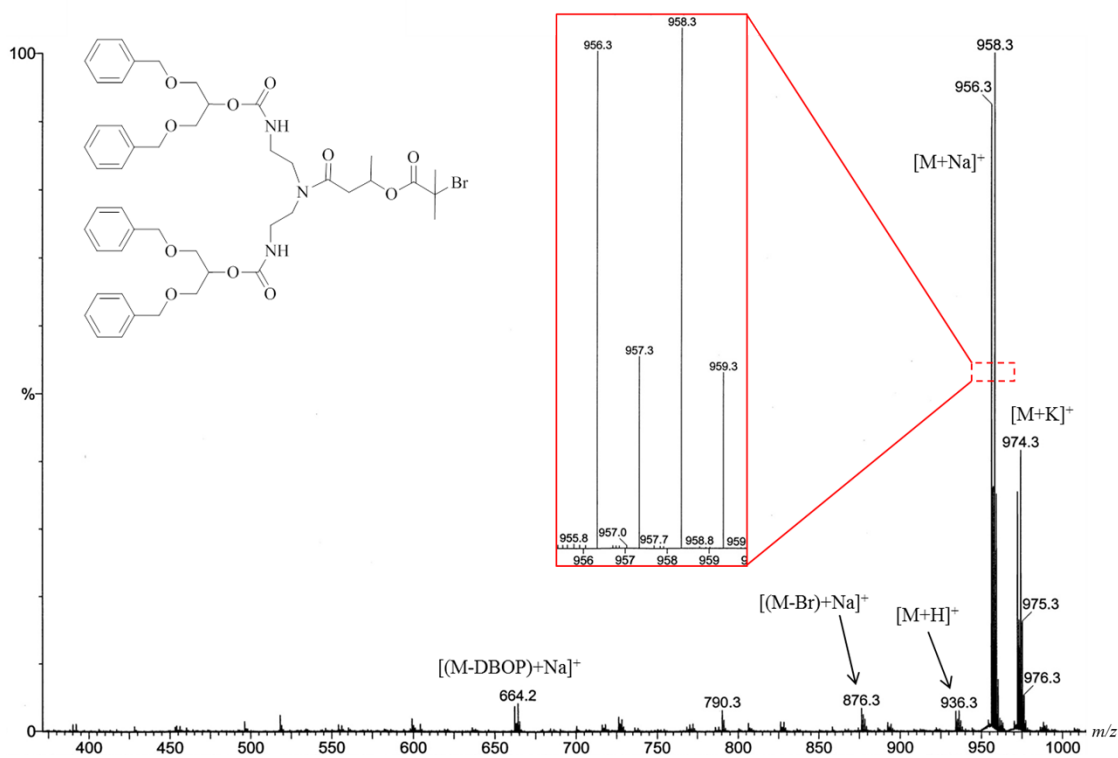
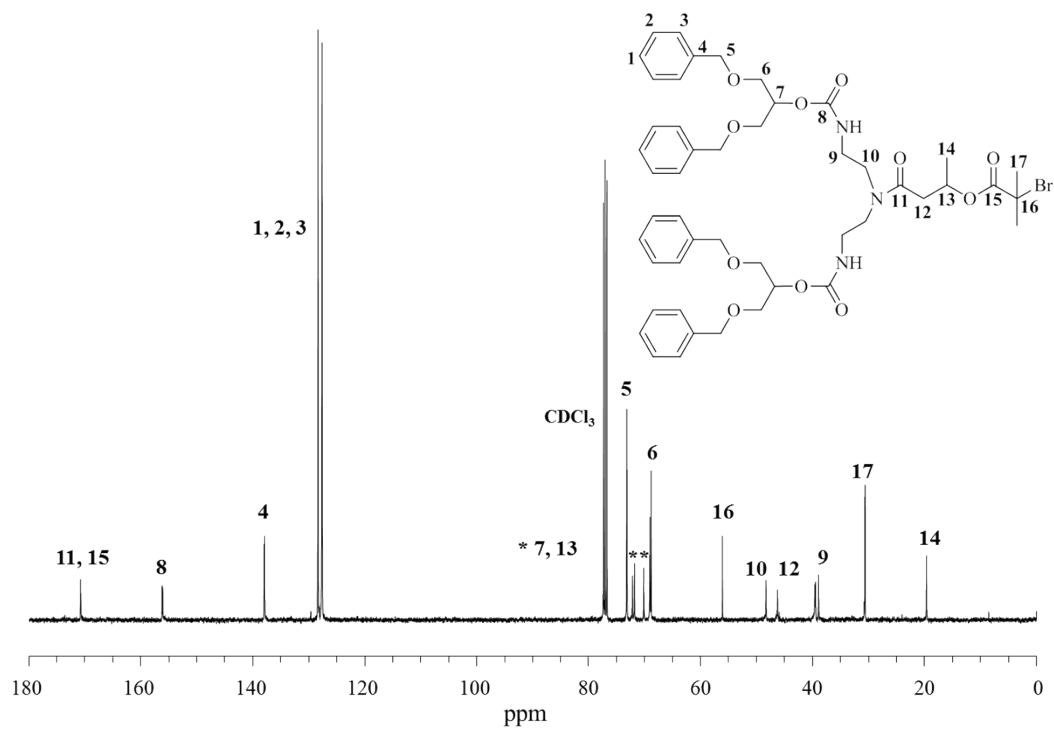


Fig. S15 - ^1H NMR (CDCl_3 , 400 MHz) of **G₂-Br** dendron initiator



Linear dendritic polymer synthesis with G₂ dendron initiator

In a typical experiment, G₂ dendron initiator, **G₂-Br**, (0.648 g, 0.69 mmol) and HPMA, **2**, (targeted DP_n = 50) (5.0 g, 34.7 mmol) were weighed into a round bottom flask. The flask was equipped with magnetic stirrer bar, sealed and degassed by bubbling with N₂ for 20 minutes and maintained under N₂ at 30 °C. Anhydrous methanol was degassed separately and subsequently added to the monomer/initiator mixture via syringe to give a 50 vol% mixture with respect to the monomer. The catalytic system; Cu(I)Cl (0.069 g, 0.69 mmol) and 2,2'-bipyridyl (bpy) (0.217 g, 1.39 mmol), were added under a positive nitrogen flow in order to initiate the reaction. The polymerisations were stopped when conversions had reached over 98 % determined by ¹H NMR using the vinyl CH₂ peaks and protons of the polymer backbone. The polymerisation was stopped by diluting with a large excess of tetrahydrofuran (THF), which caused a colour change from dark brown to a bright green colour. The catalytic system was removed using Dowex® Marathon™ MSC (hydrogen form) ion exchange resin beads and basic alumina. The resulting polymer was isolated by precipitation from the minimum amount of acetone into cold hexane. The [initiator]:[CuCl]:[bpy] molar ratios in all polymerizations were 1:1:2.

G₂ polydendron synthesis

In a typical experiment, G₂ dendron initiator, **G₂-Br**, (0.648 g, 0.69 mmol) and HPMA, **2**, (targeted DP = 50) (5.0 g, 34.7 mmol) were weighed into a round bottom flask. EGDMA, **3**, (105 µL, 0.55 mmol) was added and the flask was equipped with magnetic stirrer bar, sealed and degassed by bubbling with N₂ for 20 minutes and maintained under N₂ at 30 °C. Anhydrous methanol was degassed separately and subsequently added to the monomer/initiator/brancher mixture via syringe to give a 50 vol% mixture with respect to the monomer. The catalytic system; Cu(I)Cl (0.069 g, 0.69 mmol) and 2,2'-bipyridyl (bpy) (0.217 g, 1.39 mmol), were added under a positive nitrogen flow in order to initiate the reaction. The polymerisations were stopped when conversions had reached over 98 % determined by ¹H NMR using the vinyl CH₂ peaks and protons of the polymer backbone. The polymerisation was stopped by diluting with a large excess of tetrahydrofuran (THF), which caused a colour change from dark brown to a bright green colour. The catalytic system was removed using Dowex® Marathon™ MSC (hydrogen form) ion exchange resin beads and basic alumina. The resulting polymer was isolated by precipitation from the minimum amount of THF into cold hexane. The [initiator]:[CuCl]:[bpy] molar ratios in all polymerizations were 1:1:2.

Kinetics experiments

Kinetics experiments were conducted at 30 °C. To determine the kinetic parameters of polymerisations samples (~0.1 mL) were taken at regular intervals and analysed by ¹H NMR and gel permeation chromatography (GPC). Approximately one third of each sample taken was diluted into 0.8 mL of deuterated DMSO (for ¹H NMR analysis) and the other two thirds was diluted into 4mL THF (for GPC analysis). Oxidation of Cu(I) to Cu(II) was observed by a colour change from brown to turquoise in DMSO and from brown to green in THF

indicating termination of the reaction. Conversion of monomer to polymer was determined by ^1H NMR as previously discussed. The samples diluted in THF were prepared for GPC analysis by removal of the catalytic system with Dowex[®] Marathon[™] MSC (hydrogen form) ion exchange resin beads, transferred into a pre-weighed vial, removal of THF from the polymer solution by evaporation to give dry polymer residue of a known weight. The dry polymer residues of known weights were then diluted with HPLC grade THF to give polymer solutions with concentrations around 5.0 mg/mL. These were analysed by triple detection GPC consisting of refractive index (RI), light scattering (LS) and viscometer detectors.

Nanoprecipitation method. Polydendrons were dissolved in THF for a minimum of 6 hours at various concentrations. Once fully dissolved, polymer in THF (1 mL, 5 mg/mL) was added quickly to a vial of water (5 mL) stirring at 30 °C. The solvent was allowed to evaporate overnight in a fume cupboard to give a final concentration of 1 mg/mL polymer in water. By adjusting the starting concentration and the volume of water used, the size of the corresponding nanoparticles were controlled.

Encapsulation of guest molecules – Nile Red and pyrene. Polydendrons were dissolved in THF for a minimum of 6 hours at various concentrations. The fluorescent dyes, Nile Red and pyrene, were dissolved in THF to give a stock solution (0.1 mg/mL). The stock solution (50 μL , 0.1 mg/mL) was added to an empty vial and the THF was allowed to evaporate to leave 5 μg of dye. The polymer dissolved in THF (1 mL, 5 mg/mL) was added to the dry Nile Red or pyrene to give a mixture containing 5 mg polymer, 5 μg dye dissolved in 1 mL of THF. This was then added quickly to a vial of water (5 mL) stirring at 30 °C. The solvent was allowed to evaporate overnight in a fume cupboard to give a final concentration of 1 mg/mL polymer and 1 $\mu\text{g/mL}$ Nile Red or pyrene (0.1 w/w%) in water. The Nile Red containing samples were measured at their final concentration. The pyrene-containing samples were diluted 8-fold (0.125 mg/ml polymer, 0.125 $\mu\text{g/ml}$ pyrene). Blanks were measured under the same conditions as each loaded sample.

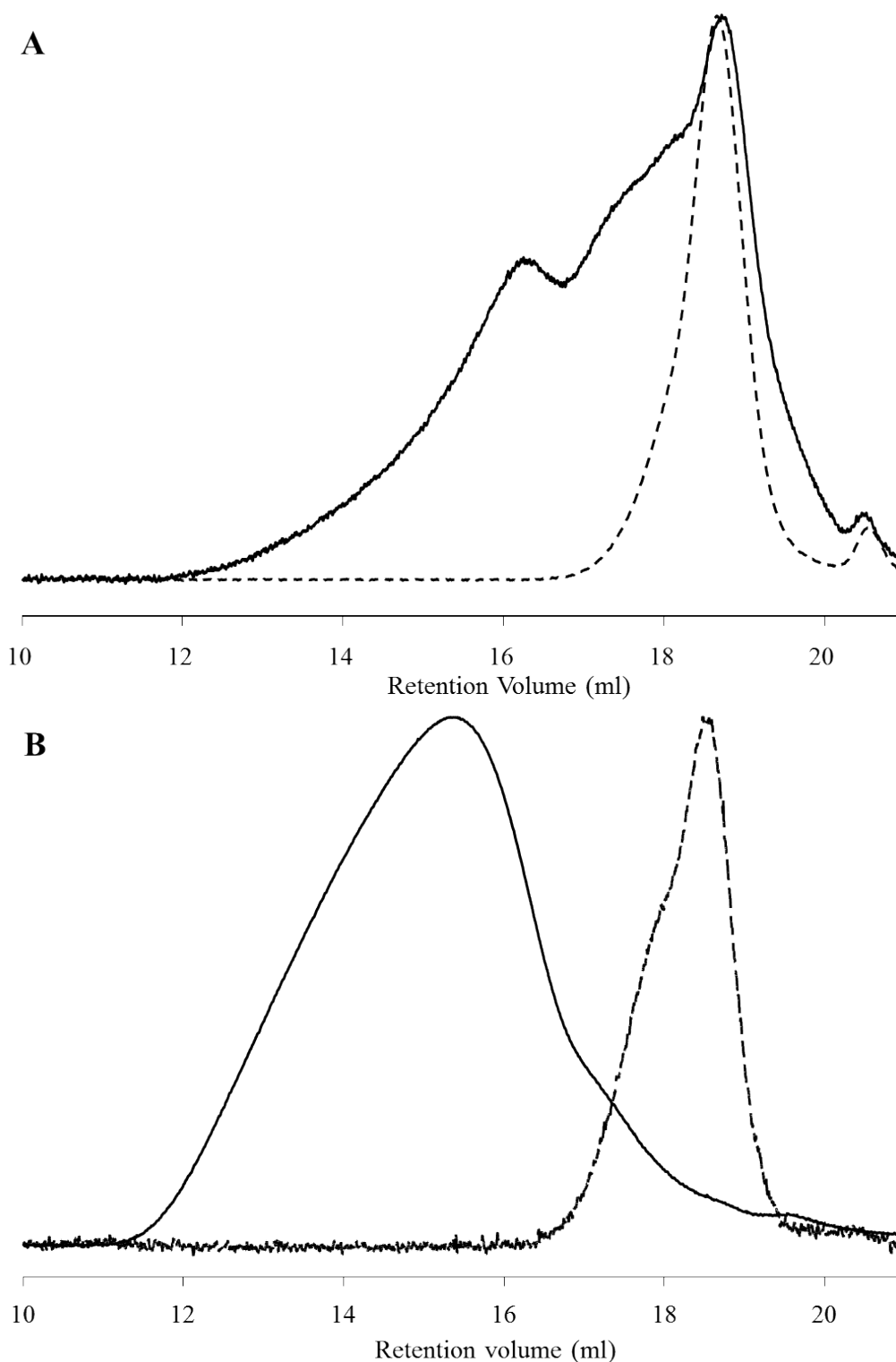


Fig. S18 – Triple detection Gel Permeation Chromatography (GPC) overlays of A) refractive index detector and B) right angle light scattering detector for **G₂-Br** initiated ATRP of HPMA – target DP_n = 50 monomer units. The figures show analysis of both linear dendritic polymer hybrids (dotted lines) and branched polymerisations (solid line). A small shoulder is seen in the RALS signal for the linear-dendritic polymer analogue, possibly due to a small amount of bifunctional monomer within the commercial sample as purchased.

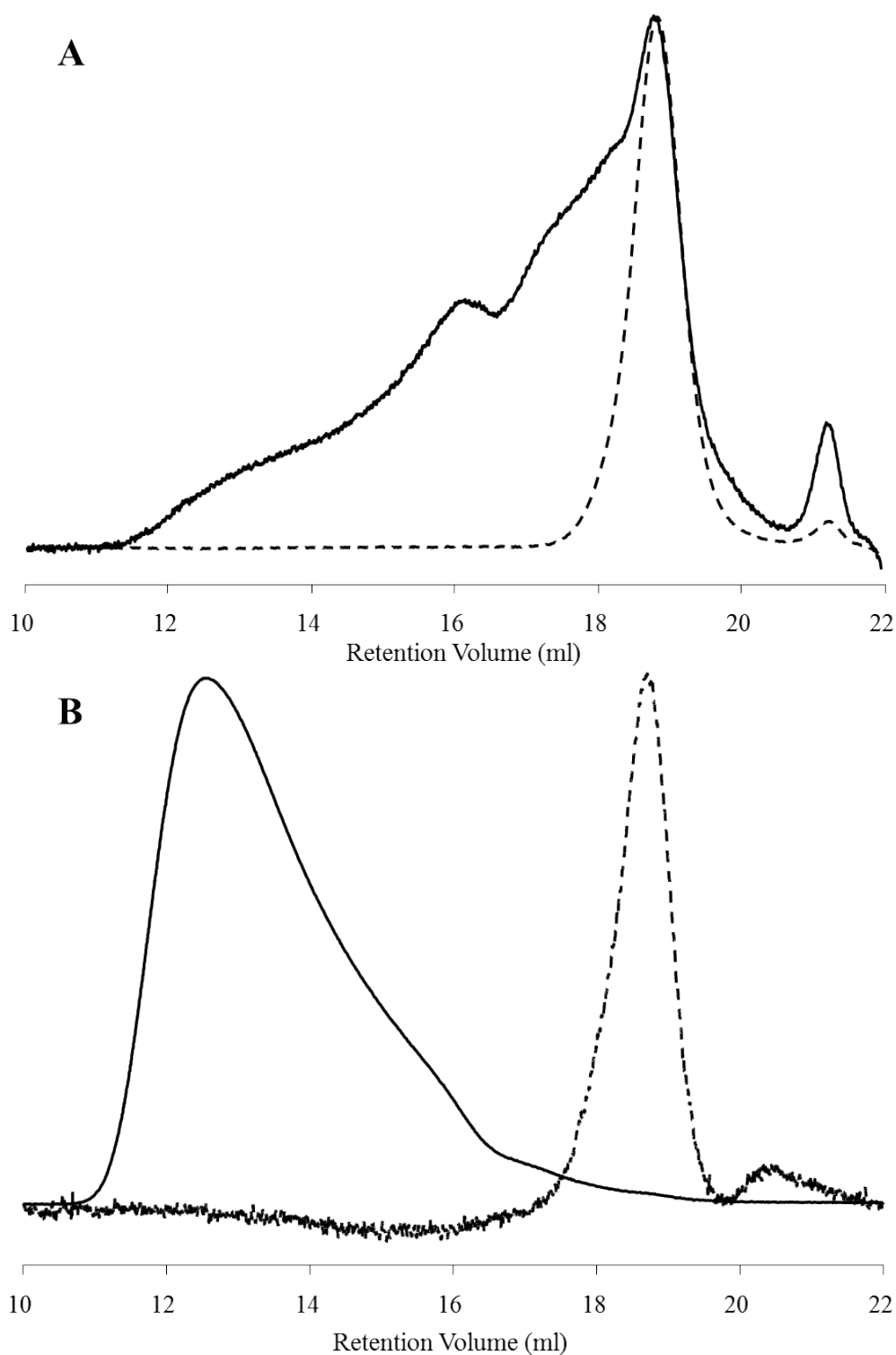


Fig. S19 – Triple detection Gel Permeation Chromatography (GPC) overlays of A) refractive index detector and B) right angle light scattering detector for **G₁-Br** initiated ATRP of HPMA – target DP_n = 50 monomer units. The figures show analysis of both linear dendritic polymer hybrids (dotted lines) and branched polymerisations (solid line). A small shoulder is seen in the RALS signal for the linear-dendritic polymer analogue, possibly due to a small amount of bifunctional monomer within the commercial sample as purchased.

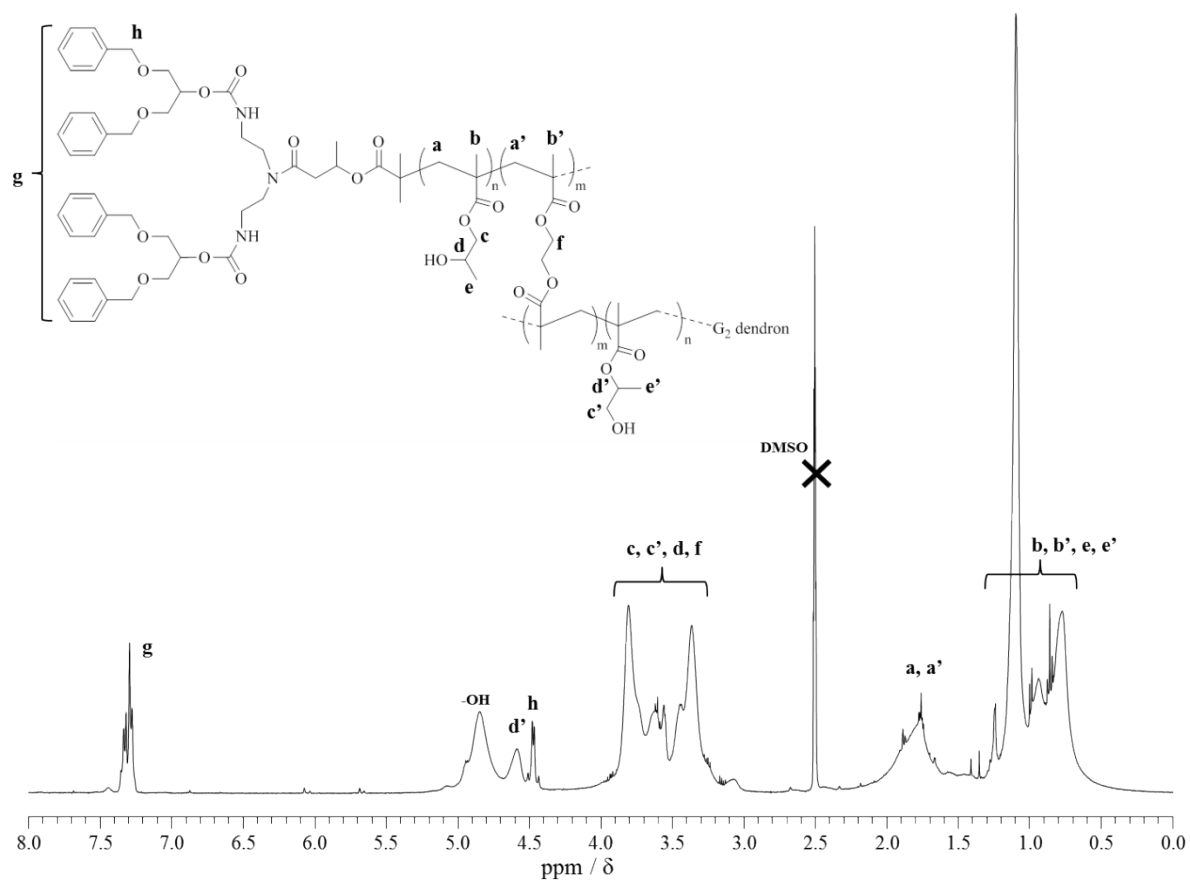


Fig. S20 - ^1H NMR (CDCl_3 , 400 MHz) spectrum of $\text{G}_2\text{-(HPMA}_{50}\text{-co-EGDMA}_{0.8})$

Fraction of hexane added (Φ)	p (HPMA ₅₀)		G ₁ -(HPMA ₅₀)		G ₂ -(HPMA ₅₀)	
	Z-Ave (d.nm)	PDI	Z-Ave (d.nm)	PDI	Z-Ave (d.nm)	PDI
0	-	-	-	-	-	-
0.09	-	-	-	-	-	-
0.17	-	-	-	-	-	-
0.23	-	-	-	-	-	-
0.29	-	-	-	-	454.1	0.203
0.33	351.9	0.210	407.5	0.212	1001.0	0.438
0.43	528.7	0.173	657.7	0.250	539.9	0.119
0.50	589.8	0.075	976.6	0.228	666.0	0.165
0.67	559.3	0.046	580.7	0.148	492.5	0.104
0.75	565.8	0.091	460.0	0.136	1754.0	0.294
0.80	567.9	0.076	393.7	0.048	-	-
Fraction of hexane added (Φ)	p (HPMA ₅₀ -EGDMA _{0.8})		G ₁ -(HPMA ₅₀ -EGDMA _{0.8})		G ₂ -(HPMA ₅₀ -EGDMA _{0.8})	
	Z-Ave (d.nm)	PDI	Z-Ave (d.nm)	PDI	Z-Ave (d.nm)	PDI
0	41.57	0.396	45.96	0.369	37.25	0.382
0.09	-	-	42.18	0.361	34.85	0.371
0.17	181.4	0.055	39.85	0.325	33.32	0.349
0.23	147.9	0.005	162.1	0.021	178.2	0.018
0.29	137.0	0.014	140.5	0.027	155.1	0.017
0.33	134.7	0.038	149.3	0.075	155.1	0.036
0.43	134.0	0.058	140.4	0.056	152.3	0.050
0.50	128.5	0.043	136.2	0.072	141.6	0.056
0.67	128.3	0.037	132.6	0.060	144.7	0.054
0.75	151.0	0.020	160.6	0.033	169.6	0.007
0.80	194.5	0.019	201.2	0.013	233.4	0.097

Table S1 z-Average diameter (nm) and polydispersity indices (PDI) for all nanoparticles with a starting concentration of 5 mg/mL polymer in acetone and varying hexane non-solvent fractions.

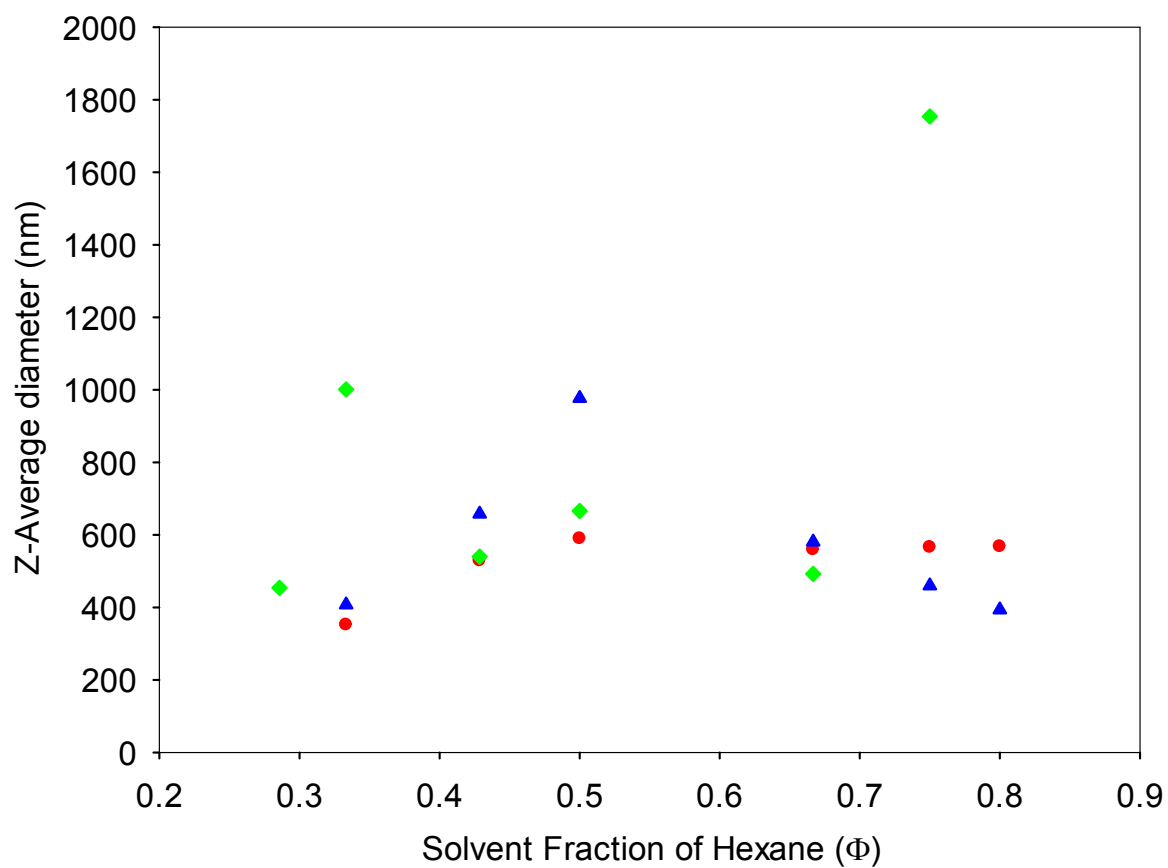


Fig. S21 Impact of hexane solvent fraction on the self-assembly behaviour of linear polymers (z-average diameters) for p(HPMA₅₀) (red circles), G₁-(HPMA₅₀) (blue triangles) and G₂-(HPMA₅₀) (green diamonds) with addition of hexane (bad solvent) to acetone (good solvent) solutions

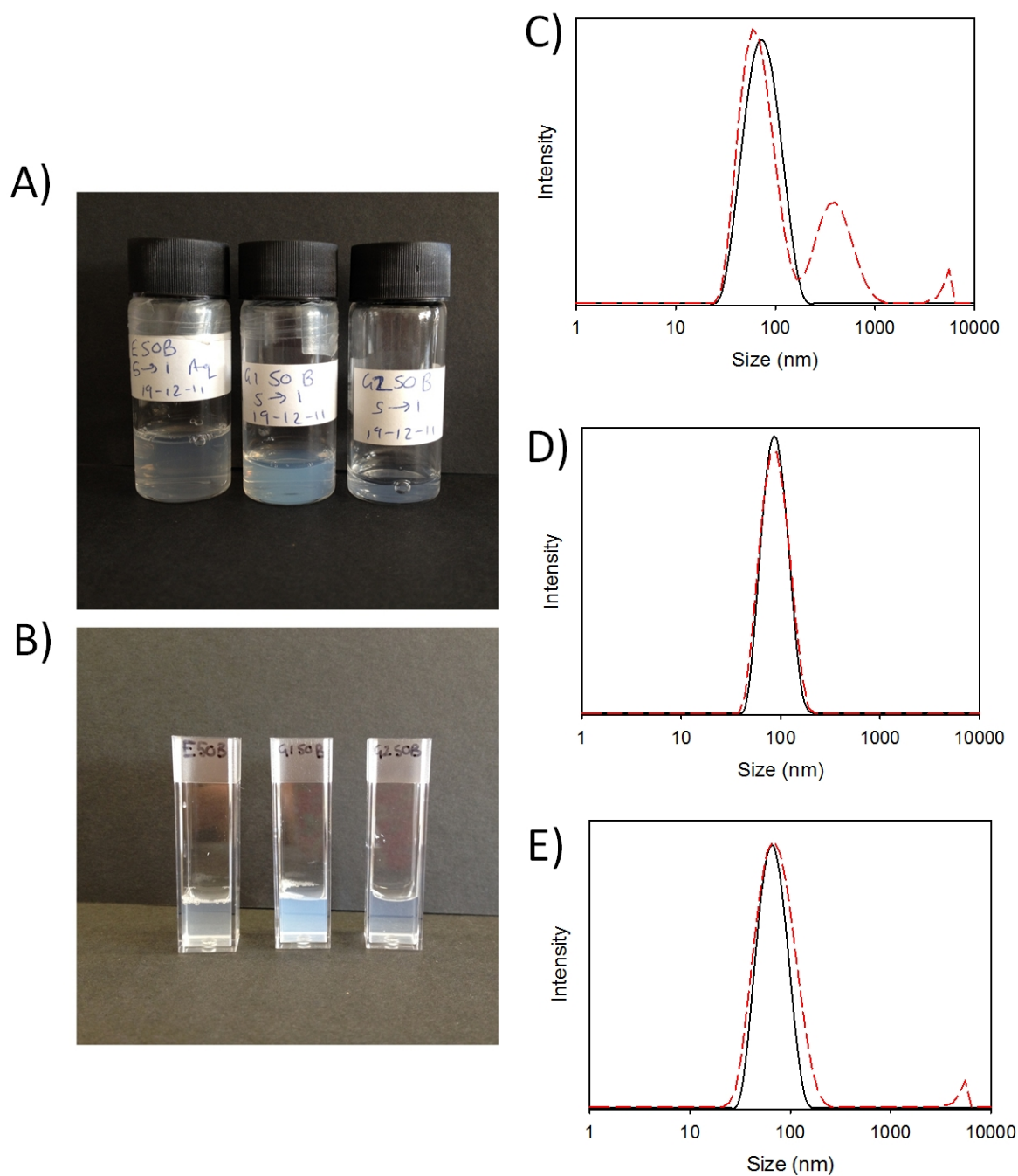


Fig. S22 – Aqueous nanoprecipitates after 23 month storage at ambient temperature: A) Photograph: storage in vials under ambient conditions for two years, and B) Photograph: the samples in cuvettes after DLS evaluation after 2 years in vials. In both images: left = $p(\text{HPMA}_{50}\text{-co-EGDMA}_{0.8})$, middle = $G_1\text{-(HPMA}_{50}\text{-co-EGDMA}_{0.8})$, right = $G_2\text{-(HPMA}_{50}\text{-co-EGDMA}_{0.8})$; C) DLS of $p(\text{HPMA}_{50}\text{-co-EGDMA}_{0.8})$ – solid line = initial measurement, red dashed line = 23 months old; D) DLS of $G_1\text{-(HPMA}_{50}\text{-co-EGDMA}_{0.8})$ – solid line = initial measurement, red dashed line = 23 months old; E) DLS of $G_2\text{-(HPMA}_{50}\text{-co-EGDMA}_{0.8})$ – solid line = initial measurement, red dashed line = 23 months old

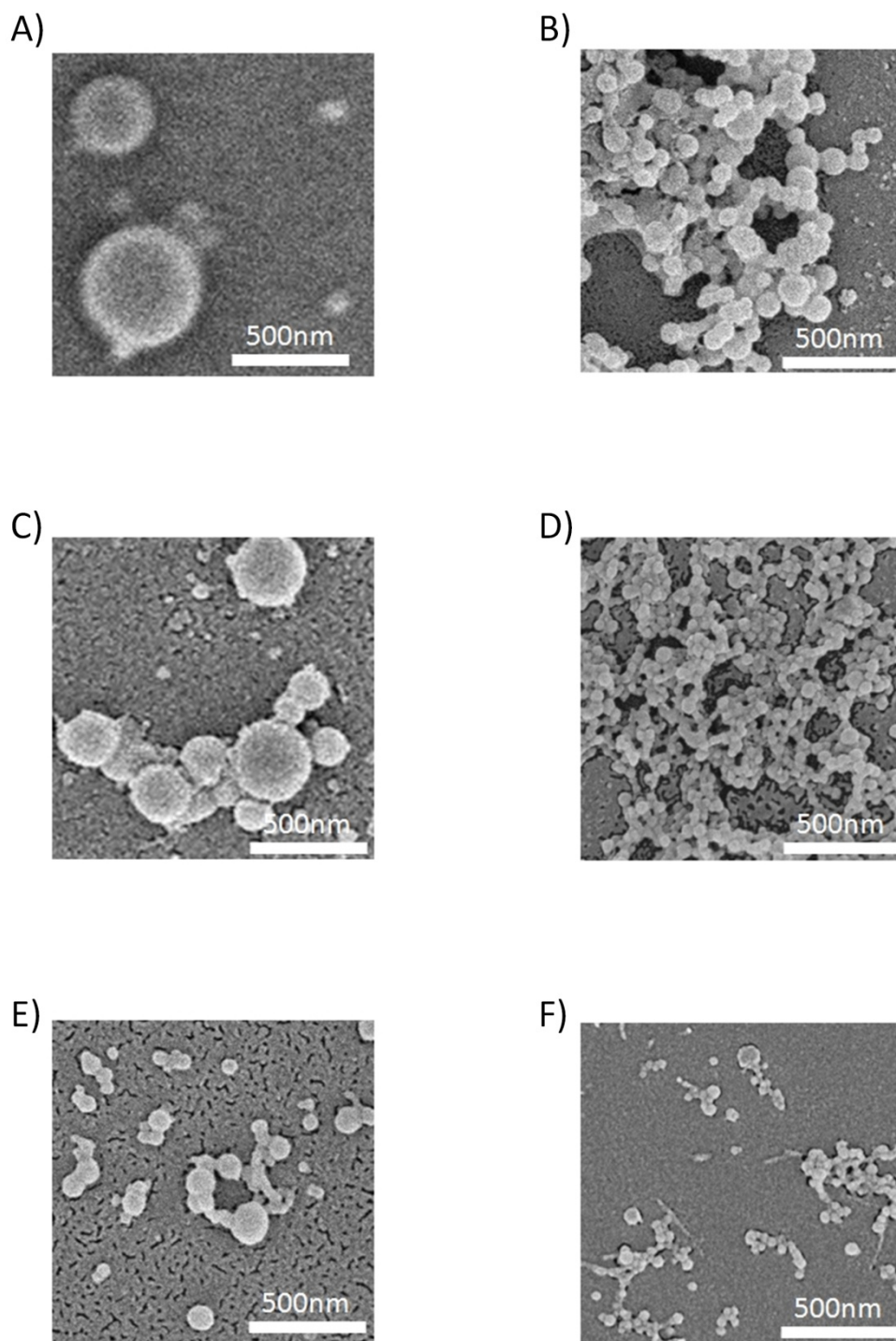
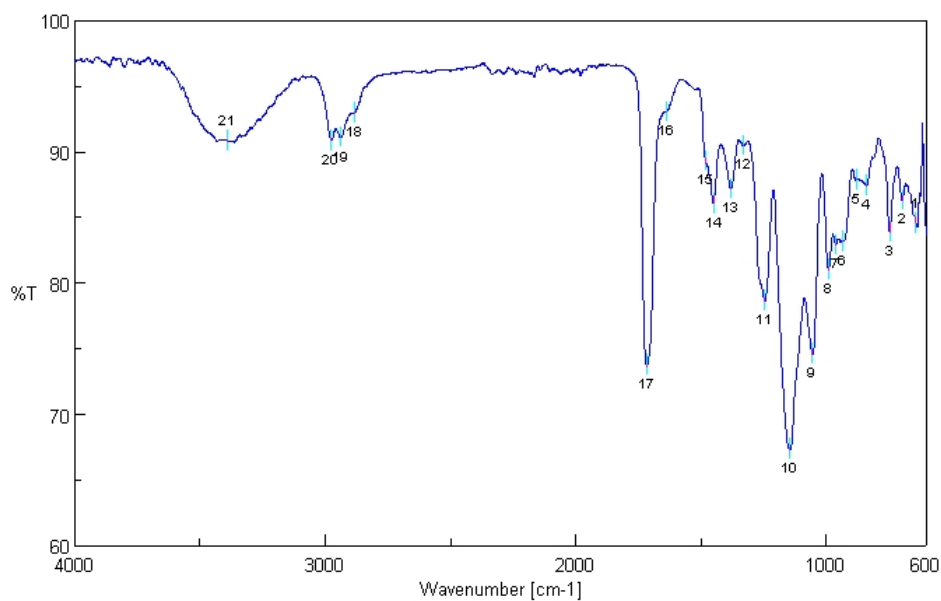


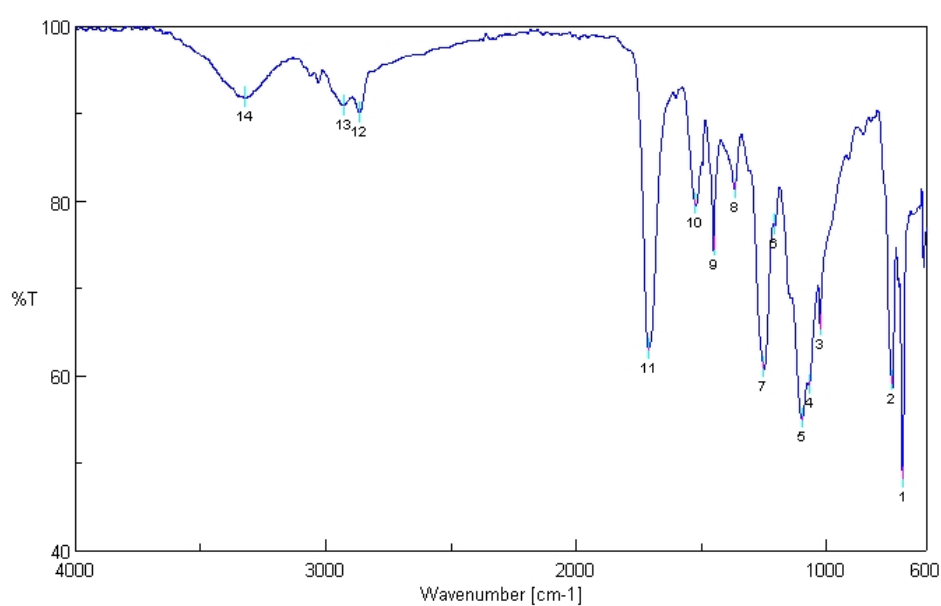
Fig. S23 Scanning Electron Microscopy of aqueous nanoprecipitates. A) $p(\text{HPMA}_{50})$; B) $p(\text{HPMA}_{50}\text{-}co\text{-EGDMA}_{0.8})$; C) $G_1\text{-(HPMA}_{50})$; D) $G_1\text{-(HPMA}_{50}\text{-}co\text{-EGDMA}_{0.8})$; E) $G_2\text{-(HPMA}_{50})$; F) $G_2\text{-(HPMA}_{50}\text{-}co\text{-EGDMA}_{0.8})$. Samples prepared by adding polymer dissolved in THF (5 mg/mL) into water to generate a final aqueous concentration of 1 mg/mL of polymer. The nanoparticles were diluted to 0.1 mg/mL for imaging on silicon wafers mounted on SEM stubs with a carbon tab. Coated with Au for 2 min at 20 mA. All images shown at identical magnification.



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	643.144	84.57735	2	697.141	86.29539	3	748.245	83.89655
4	841.776	87.46597	5	881.309	87.88566	6	935.306	83.18613
7	964.233	82.89297	8	993.16	81.03697	9	1057.76	74.60351
10	1148.4	67.32793	11	1245.79	78.65697	12	1331.61	90.47348
13	1382.71	87.16720	14	1451.17	86.05636	15	1482.99	89.29661
16	1638.23	93.03705	17	1714.41	73.75591	18	2882.09	93.00178
19	2939.95	91.10515	20	2975.62	90.88644	21	3394.1	90.87970

Fig. S24 Infrared spectrum for G₂-(HPMA₅₀-co-EGDMA_{0.8})



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	697.141	48.29034	2	740.531	59.47196	3	1024.98	65.80569
4	1072.23	58.99309	5	1097.3	55.12243	6	1209.15	77.25484
7	1252.54	60.92254	8	1368.25	81.38580	9	1451.17	74.82487
10	1526.38	79.70846	11	1710.55	63.06964	12	2864.74	90.13382
13	2929.34	90.93573	14	3325.64	91.85768			

Fig. S25 Infrared spectrum for G₂-Br