Electronic Supplementary Material (ESI) for Polymer Chemistry.

Enhanced cytocompatibility and functional group content of poly(L-Lysine) dendrimers by grafting with poly(oxazolines)

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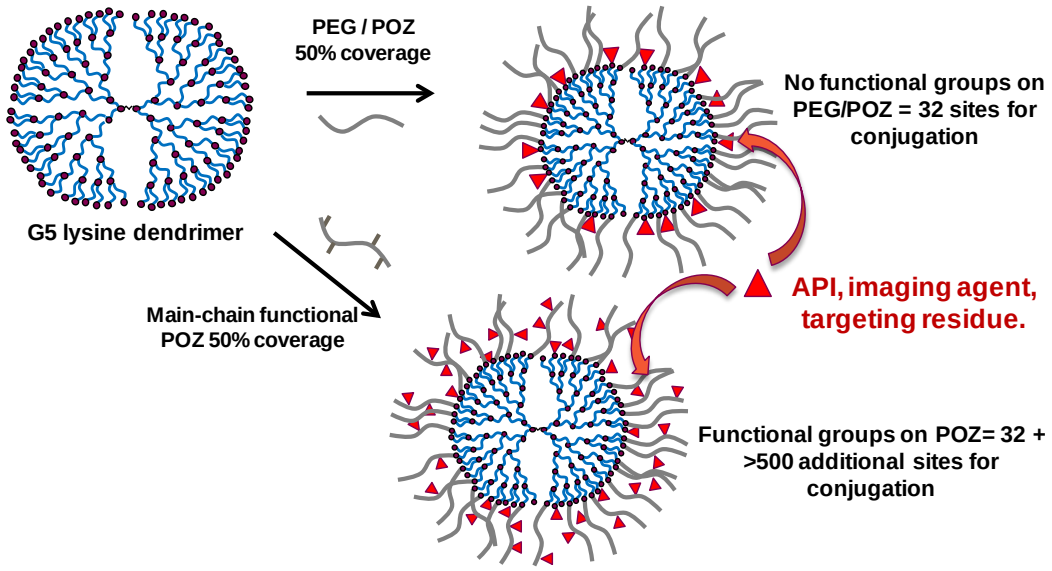


Supporting S1 - Methods

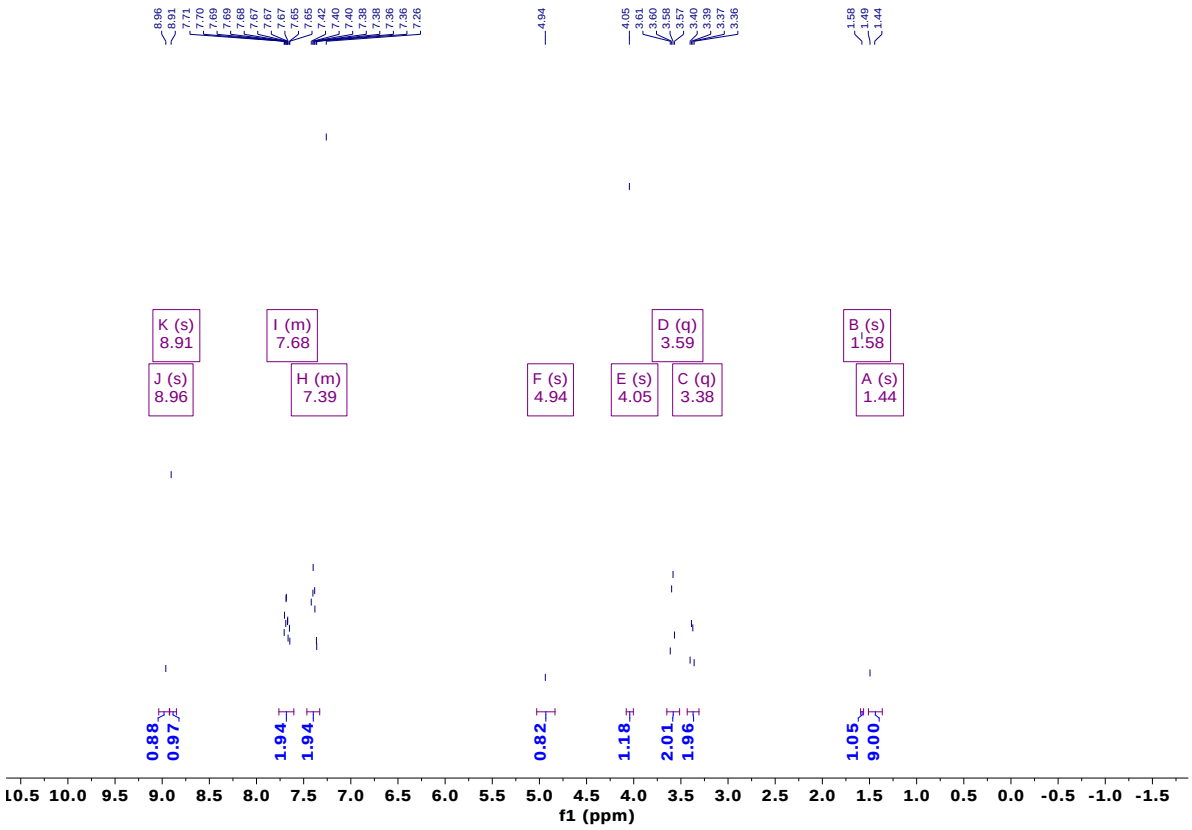
G5 L-lysine dendrimer synthesis

Table 1. Conditions used for the synthesis of the generation 5 L-lysine dendrimer.

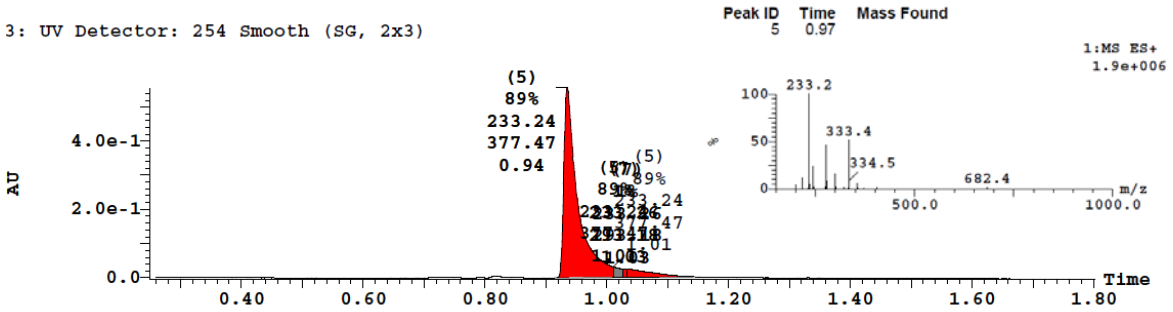
Dendrimer generation	Boc-L-Lys(Boc)-ONp equivalents (to lysine $-NH_2$ groups of previous generation/core molecule)	Triethylamine equivalents (to lysine $-NH_2$ groups of previous generation)	Reaction time (days)	Yield %
G1	1.1	3	0.5	99
G2	1.5	1.25	2	90
G3	1.5	1.5	3	98
G4	1.5	1.5	3	82
G5	1.5	2.5	5	90

The reaction molarity was 10-30mmolar in anhydrous DMF. Initial quantity of 1,3-diaminopropane was 0.5g. Purifications from G3-G5 were performed by precipitation of the reaction mixture into 20x excess of 0.2M NaOH solution to obtain a yellow precipitate. The precipitate was partially dried and then taken up in a acetonitrile/methanol mixture 95:5 before slow addition of 0.2M NaOH to form a precipitate. The precipitate was filtered and dried before finally suspending in a large volume of acetonitrile (cooled with ice bath) with rapid stirring until a white precipitate formed which was filtered and washed with cold acetonitrile before drying overnight in a vacuum oven at 30°C. Approximately half of the materials for each generation was stored for future work and analysis and a final quantity of G5PLLNH$_2$ of 7.88g was obtained.

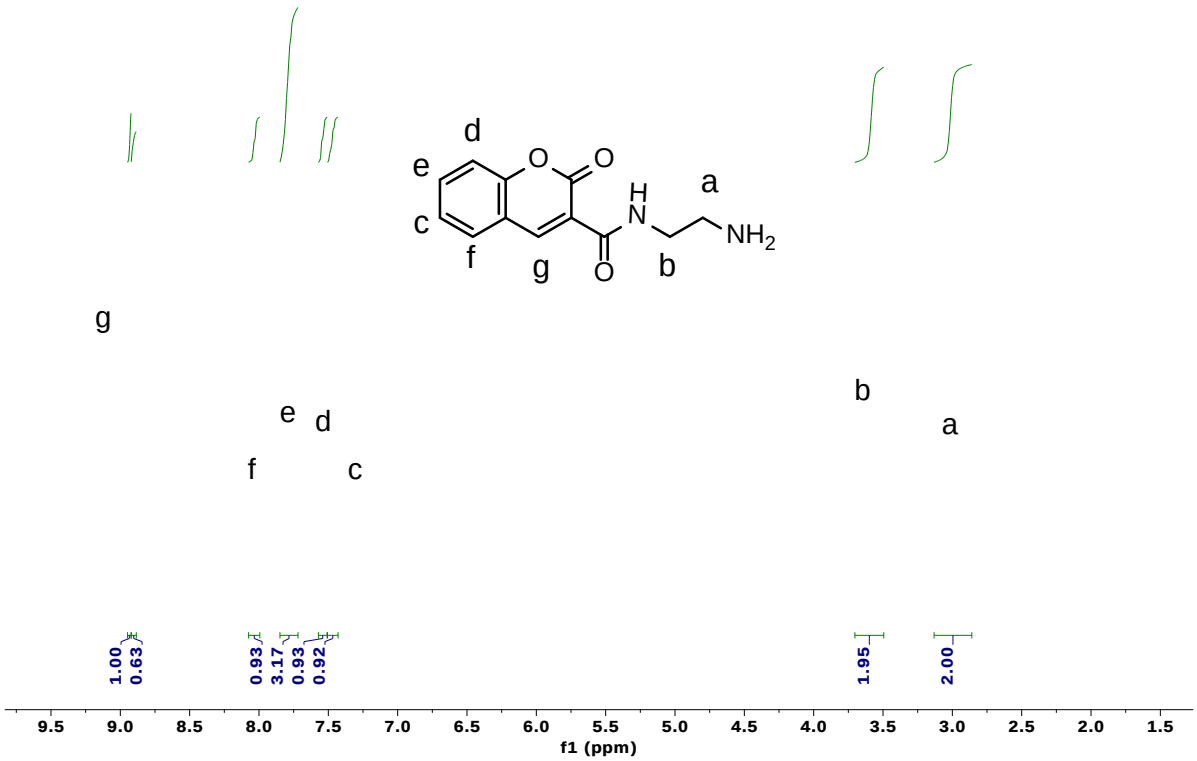
Supporting S2 – Analytical section



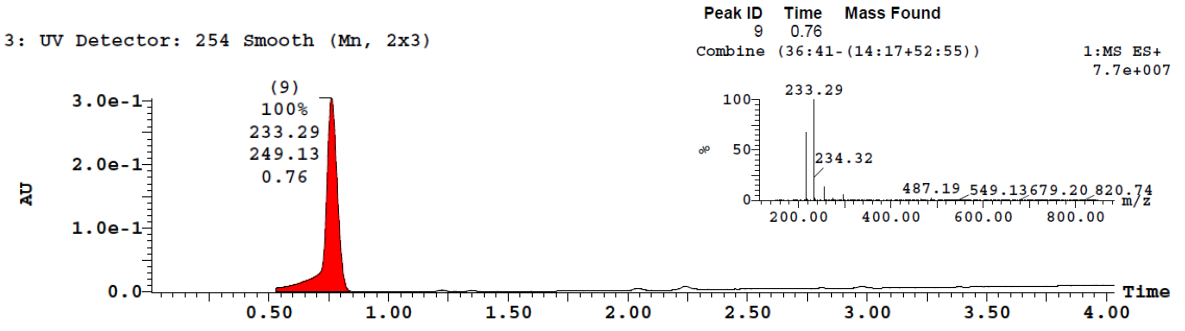
SI Figure 1. ^{1}HNMR (400MHz, $CDCl_3$) spectra for tert-butyl (2-(2-oxo-2H-chromene-3-carboxamido)ethyl)carbamate (boc-aminocoumarin).



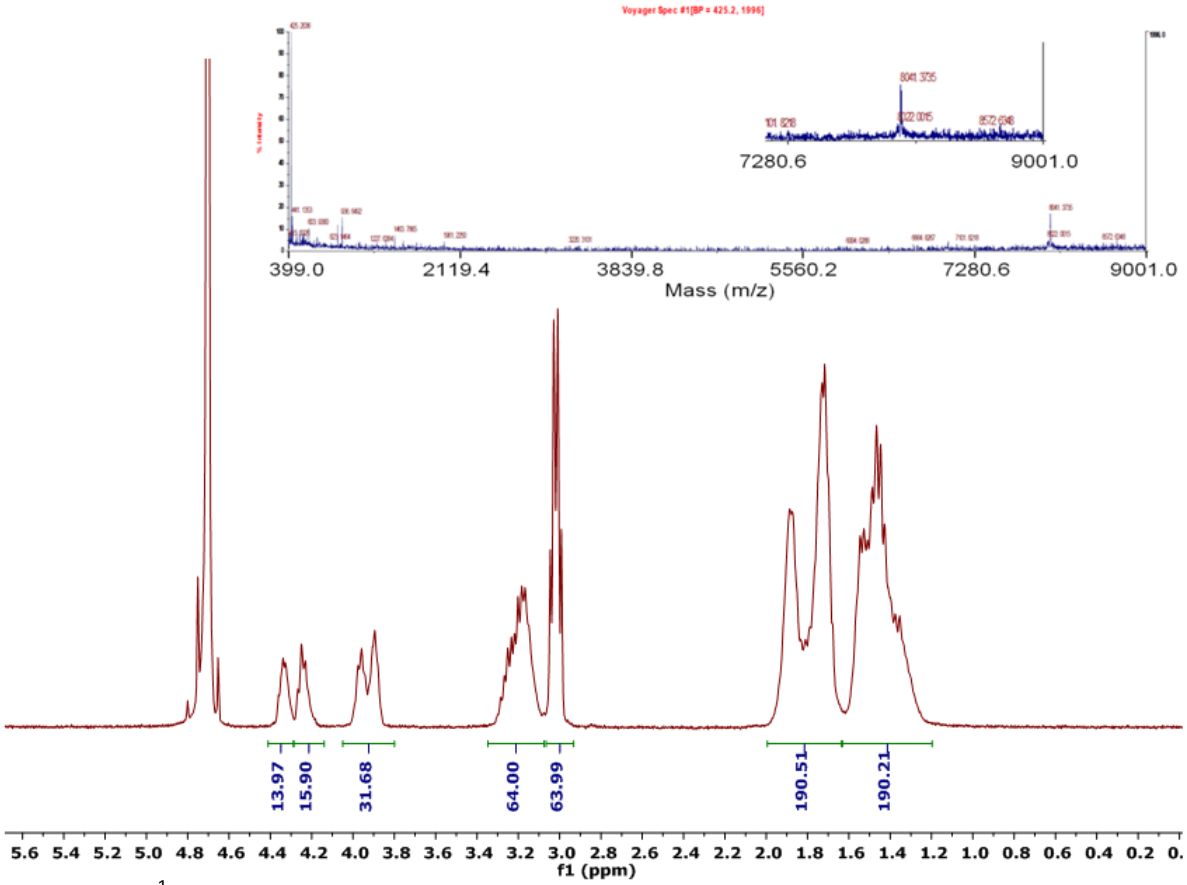
SI Figure 2. UPLC-UV-MS spectra for tert-butyl (2-(2-oxo-2H-chromene-3-carboxamido)ethyl)carbamate (boc-aminocoumarin).



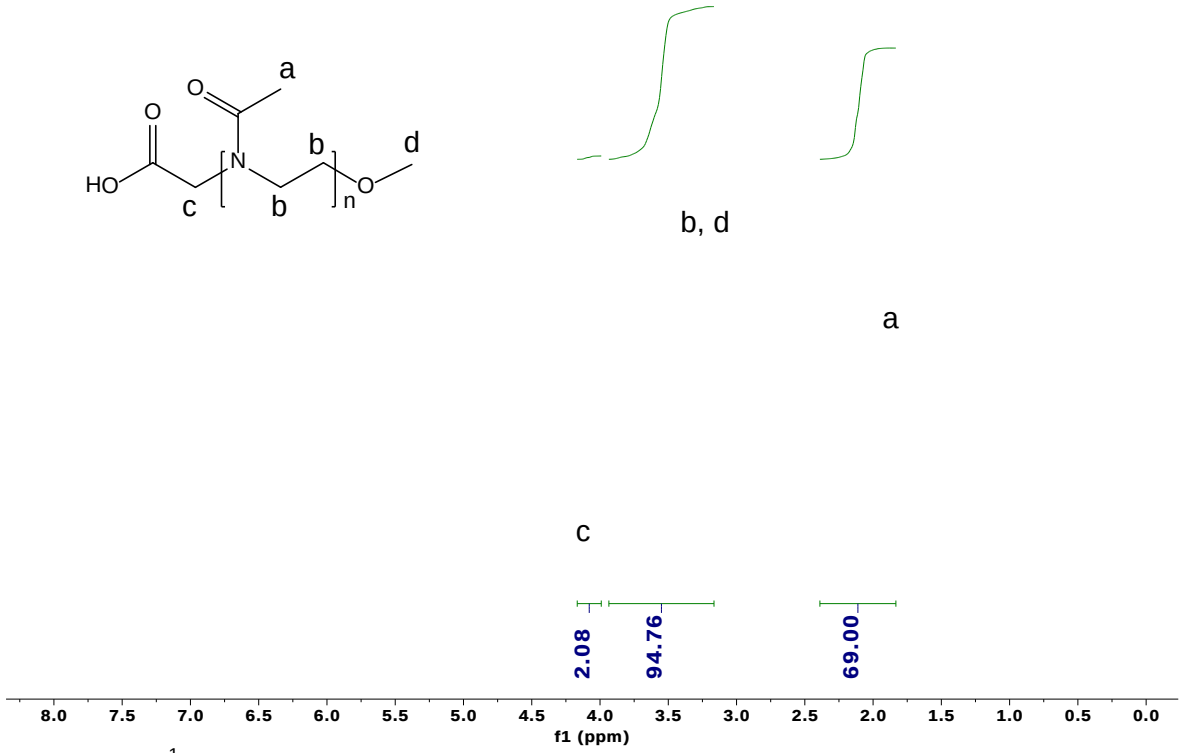
SI Figure 3. ^{1}HNMR (400MHz, d_6-DMSO) spectra for N-(2-aminoethyl)-2-oxo-2H-chromene-3-carboxamide (**coumarin-NH$_2$**)



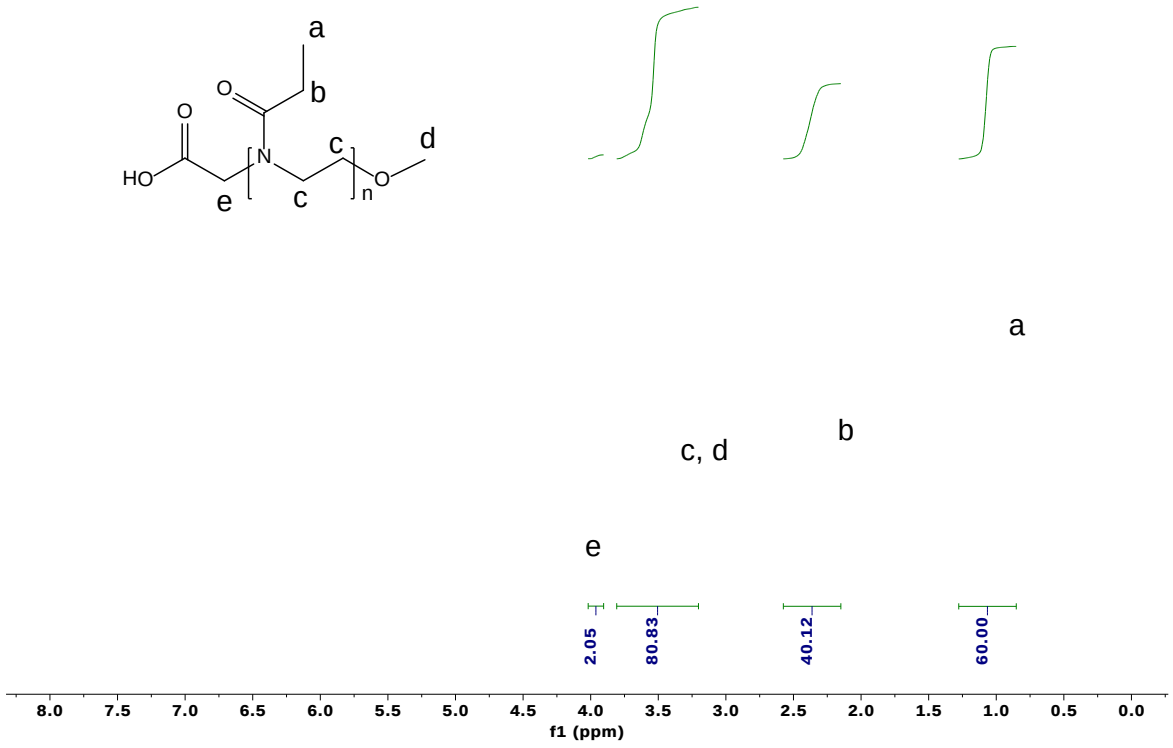
SI Figure 4. UPLC-UV-MS spectra for N-(2-aminoethyl)-2-oxo-2H-chromene-3-carboxamide (**coumarin-NH$_2$**)



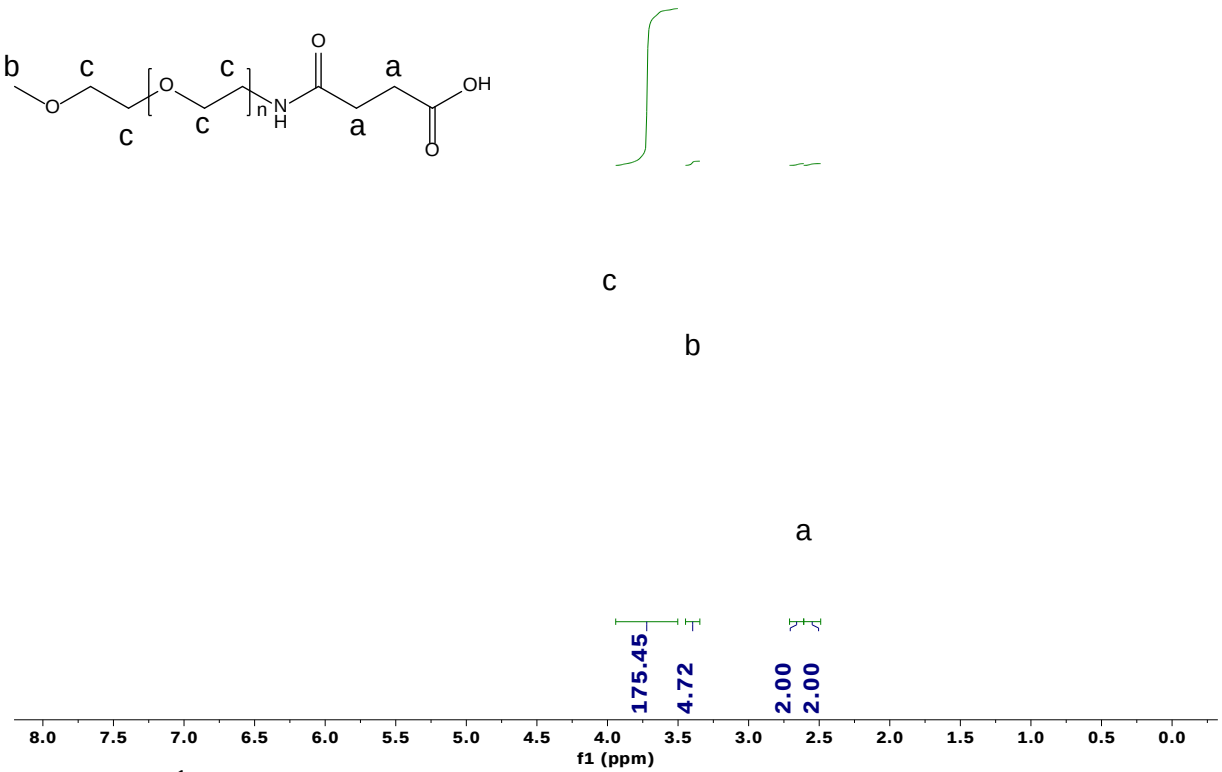
SI Figure 5. ^{1}HNMR (400MHz, D_2O) spectra with overlay of MALDI-TOF-MS spectra for generation 5 L-Lysine dendrimer.



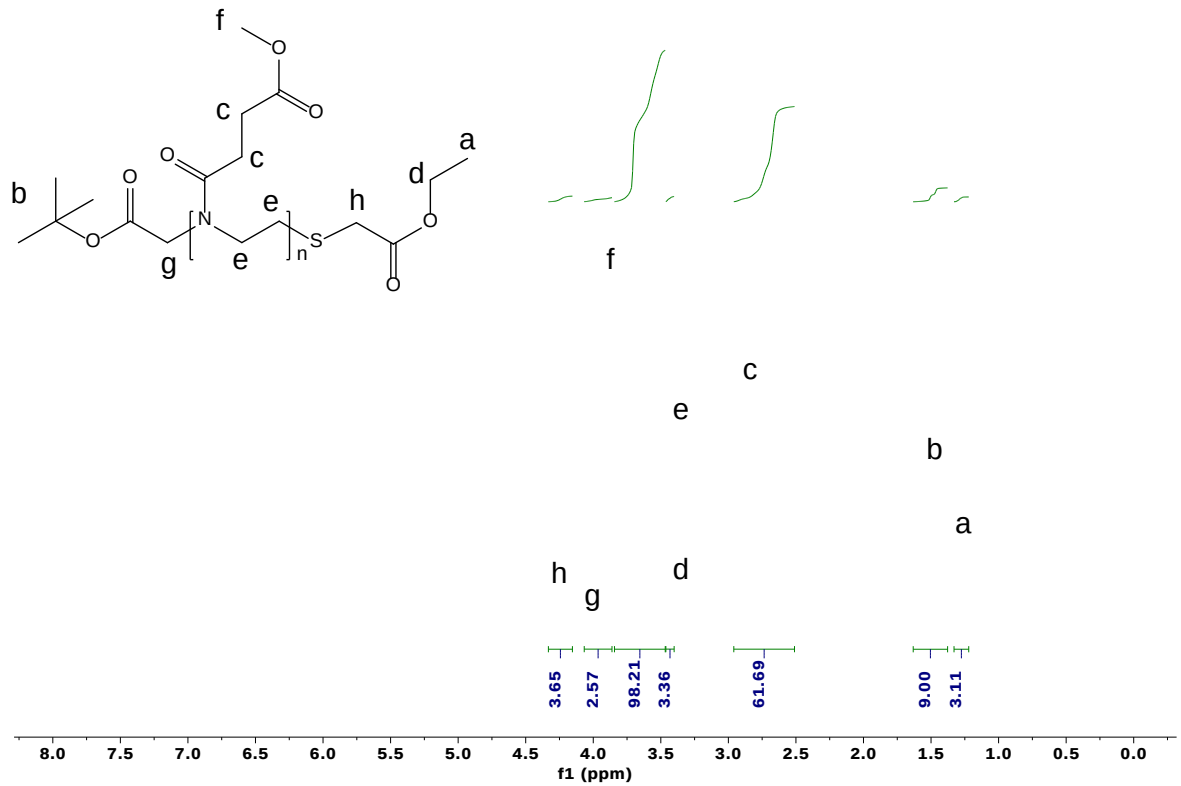
SI Figure 6. ^{1}HNMR (400MHz, D_2O) spectra for HOOC-PMOx-OMe.



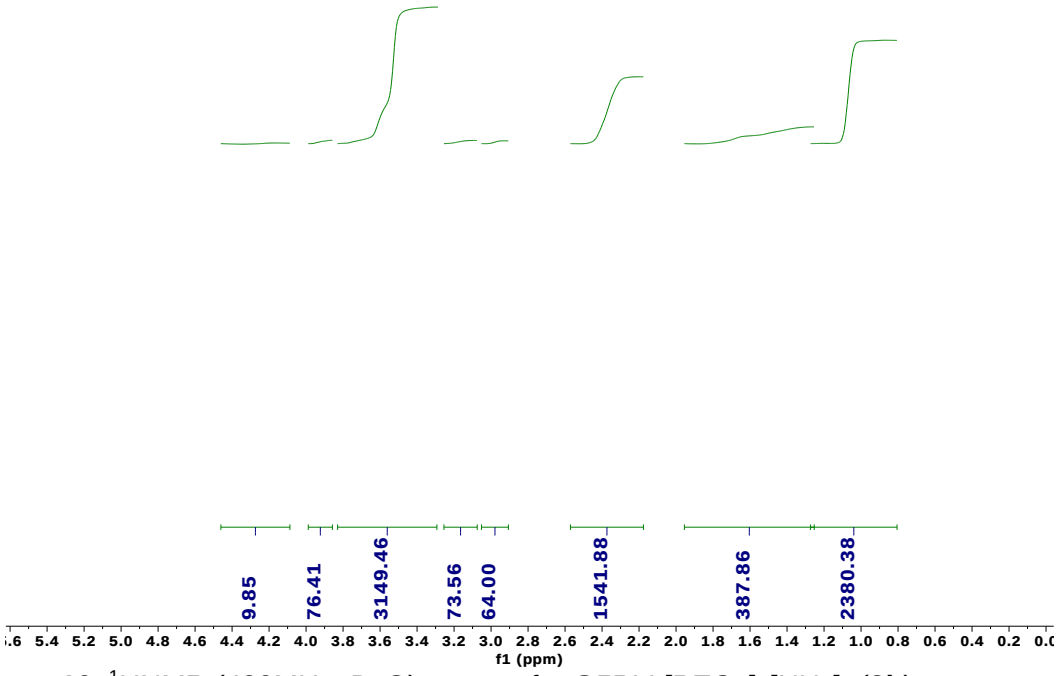
SI Figure 7. ^{1}HNMR (400MHz, D_2O) spectra for HOOC-PEOx-OMe.



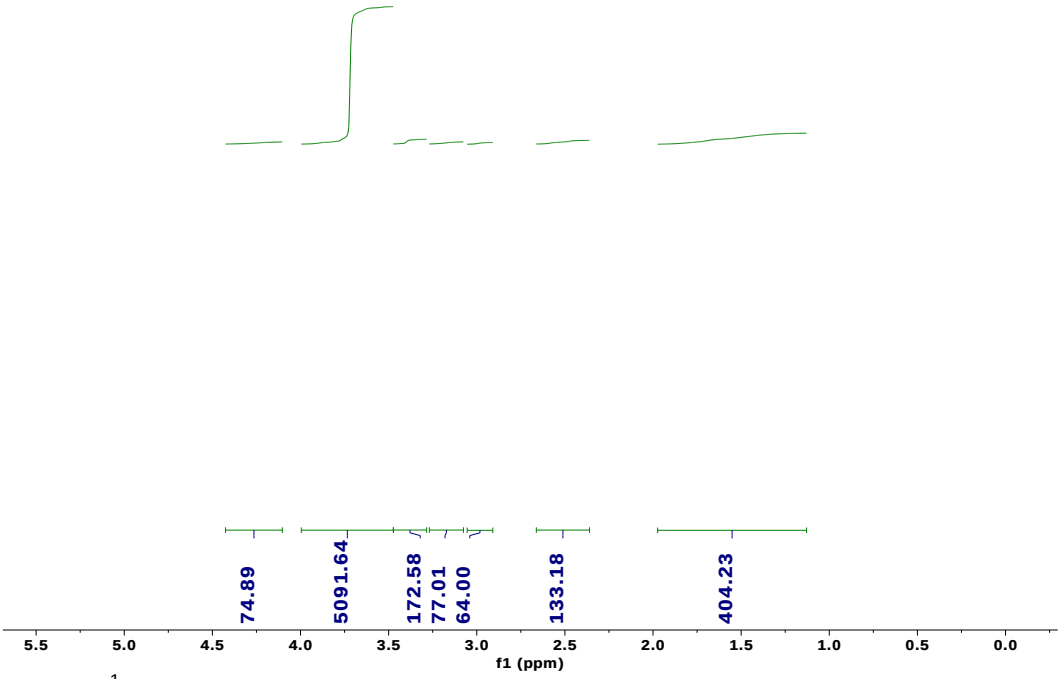
SI Figure 8. ^{1}HNMR (400MHz, D_2O) spectra for HOOC-PEG-OMe.



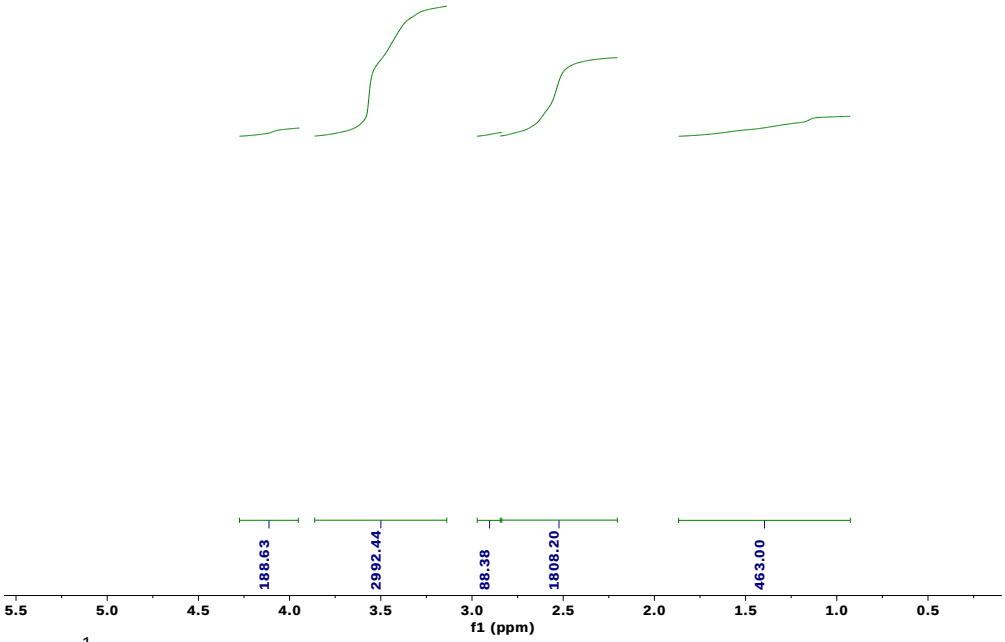
SI Figure 9. ^{1}HNMR (400MHz, D_2O) spectra for t-butylester-Poly(methyl-4-oxobutanoate-2-oxazoline)-methyl-3-thiopropanoate



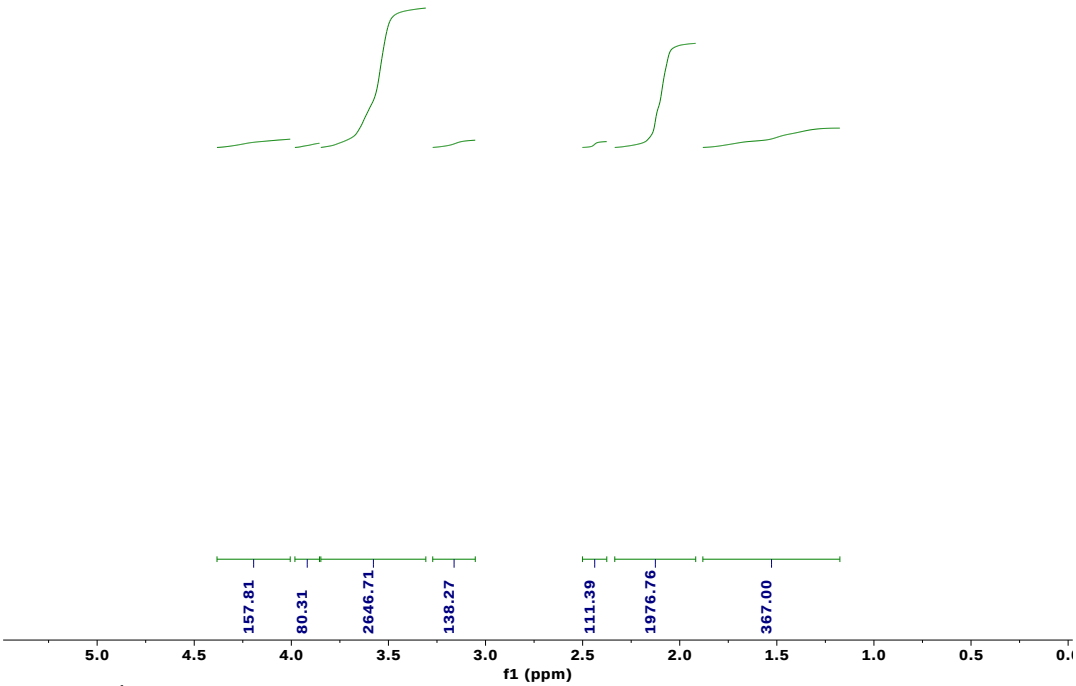
SI Figure 10. ^{1}HNMR (400MHz, D_2O) spectra for G5PLL[PEOx]$_x$[NH_2]$_y$ (**2b**)



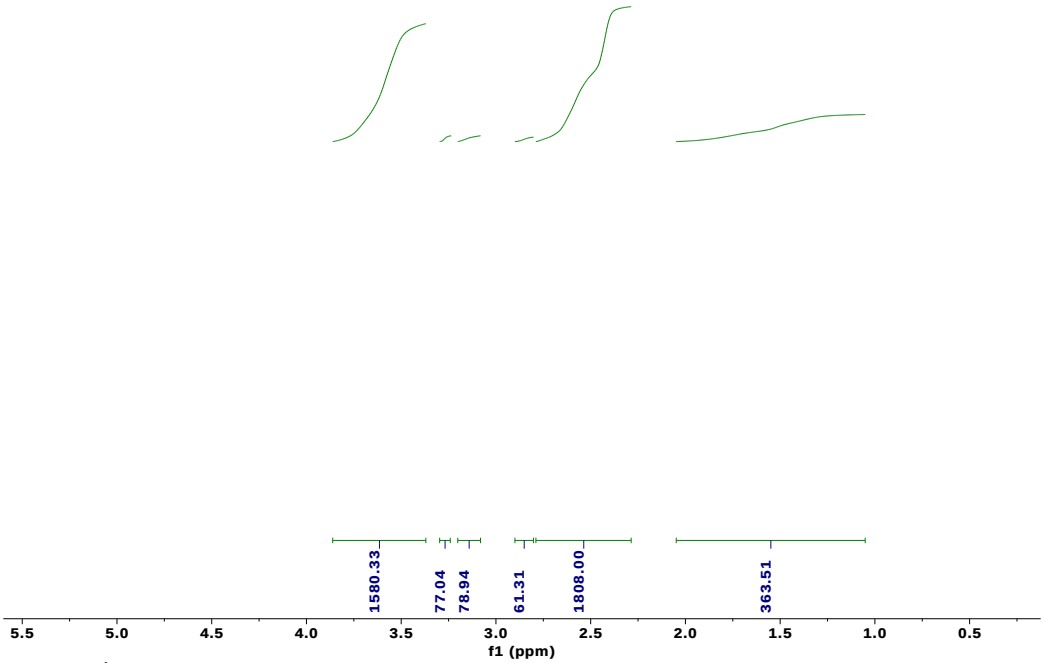
SI Figure 11. ^{1}HNMR (400MHz, D_2O) spectra for G5PLL[PEG]$_x$[NH_2]$_y$ (**2c**)



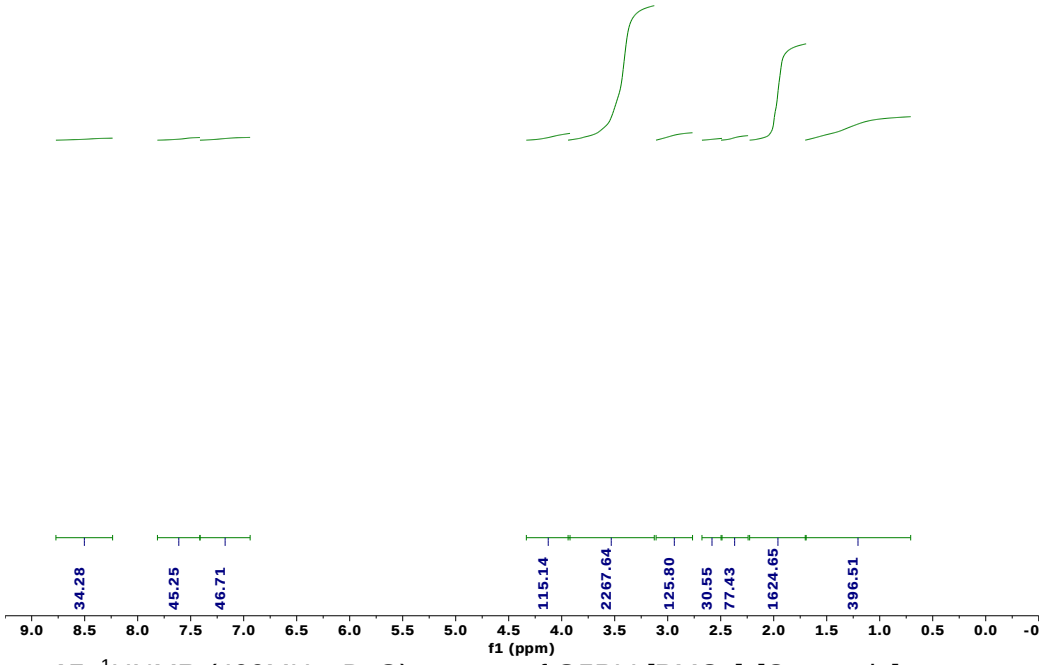
SI Figure 12. ^{1}HNMR (400MHz, D_2O) spectra for G5PLL[PEsterOx]$_x$[NH_2]$_y$ (**2d**)



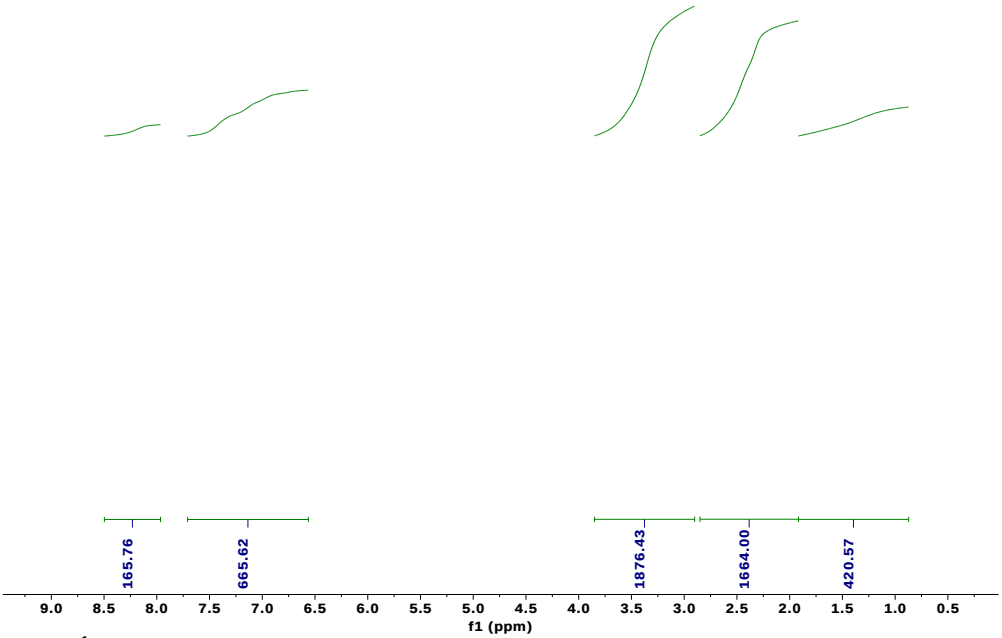
SI Figure 13. ^{1}HNMR (400MHz, D_2O) spectra for G5PLL[PMOx]$_x$[COOH]$_y$ (**3a**)



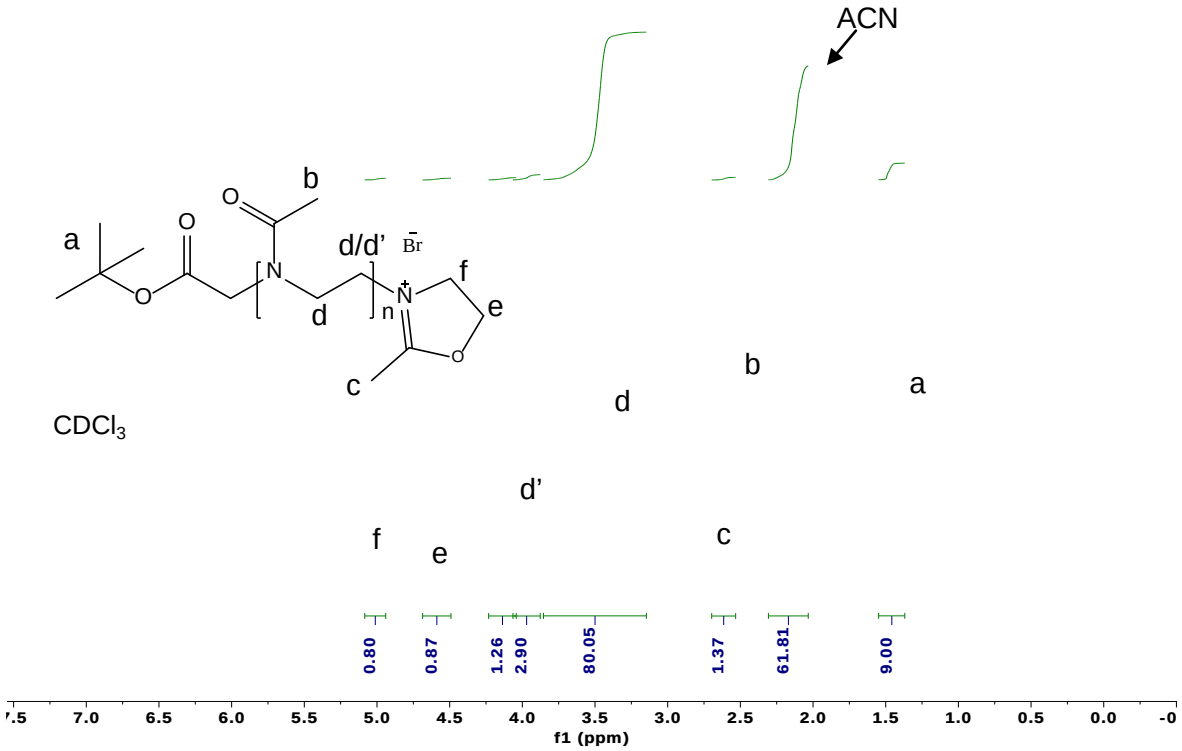
SI Figure 14. ^{1}HNMR (400MHz, D_2O) spectra for G5PLL[PAcidOx]$_x$[COOH]$_y$ (**4d**)



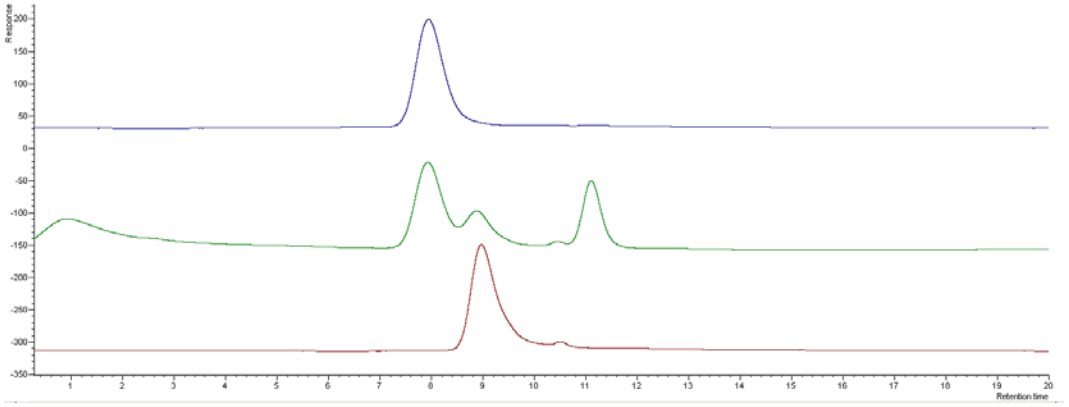
SI Figure 15. ^{1}HNMR (400MHz, D_2O) spectra of G5PLL[PMOx]$_x$[Coumarin]$_y$



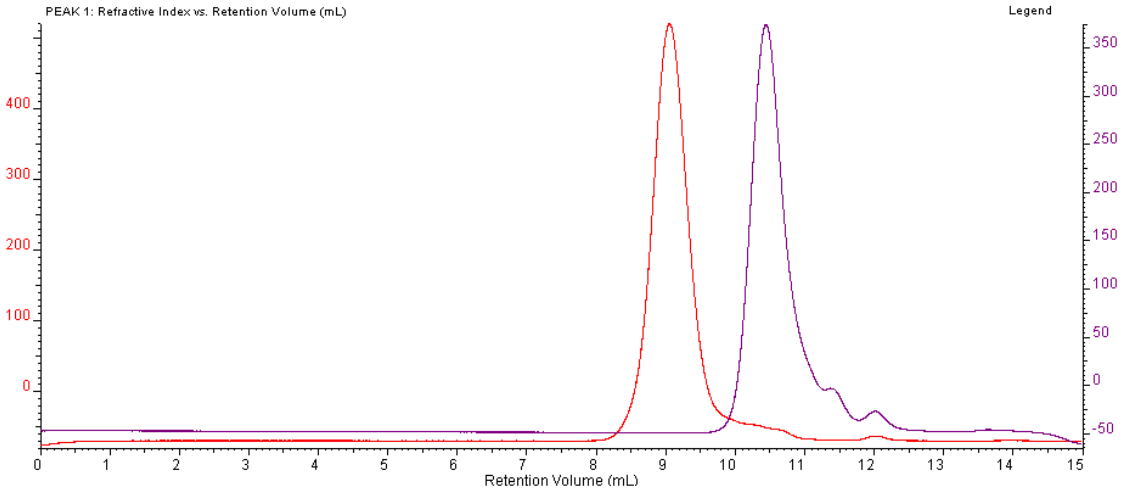
SI Figure 16. ^{1}HNMR (400MHz, D_2O) spectra of G5PLL[PAcid]$_x$[Coumarin]$_y$ (**5d**)



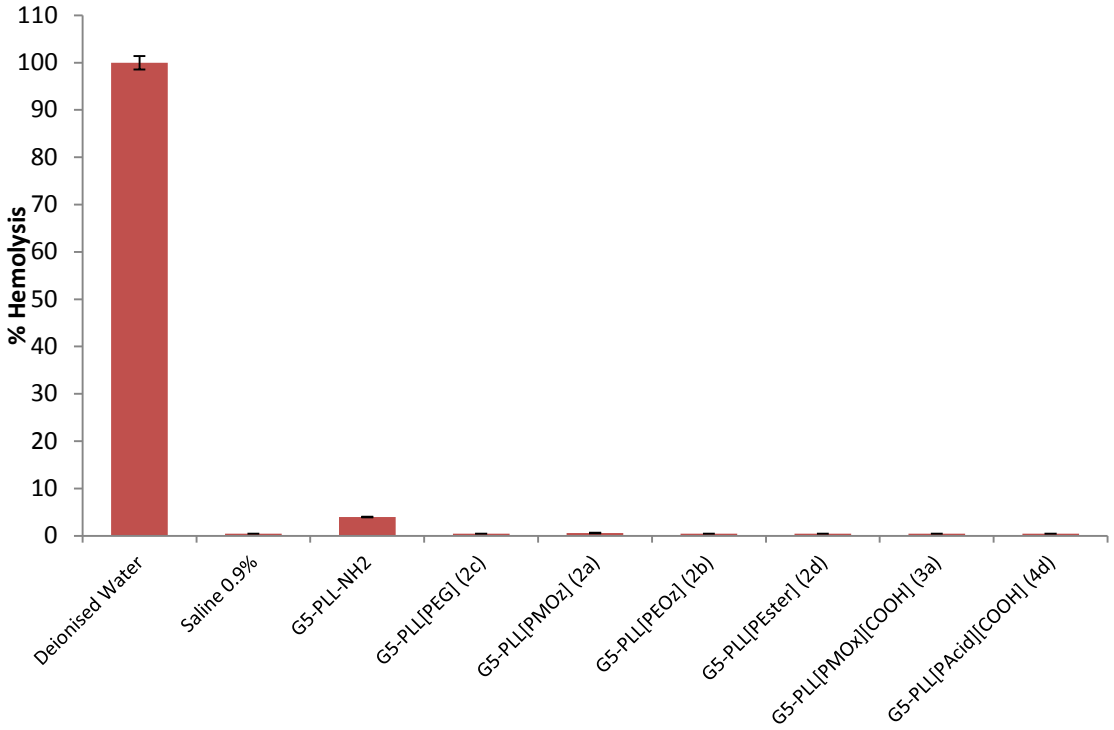
SI Figure 17. ^{1}HNMR (400MHz, $CDCl_3$) spectra for the reaction mixture of PMOz before quenching with NaOMe.



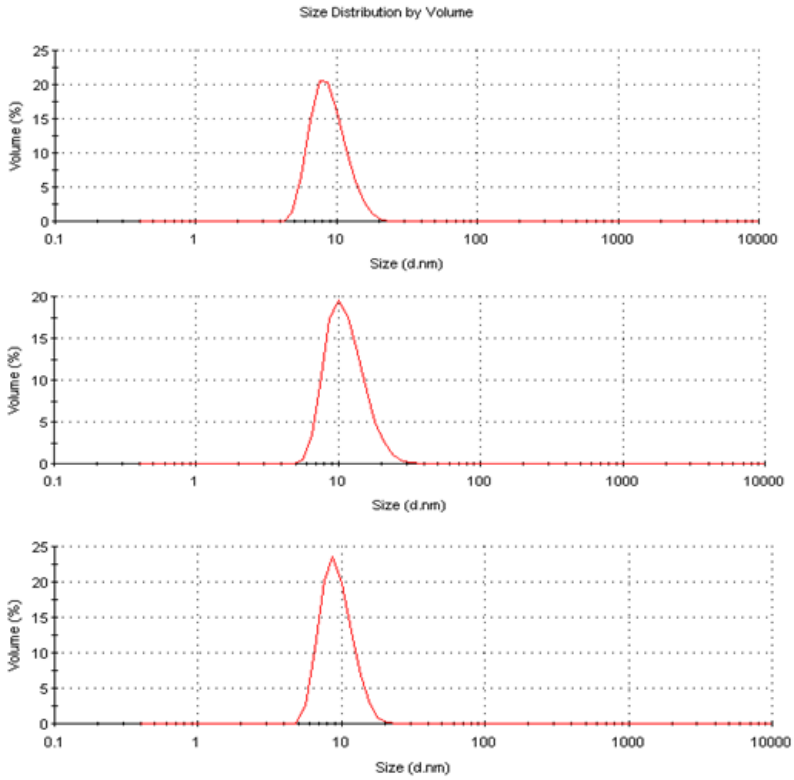
SI Figure 18. HPLC-SEC-UV (220nm) showing PMOx2000 (red), reaction mixture (72hrs, green) and purified PMOx modified dendrimer (blue).



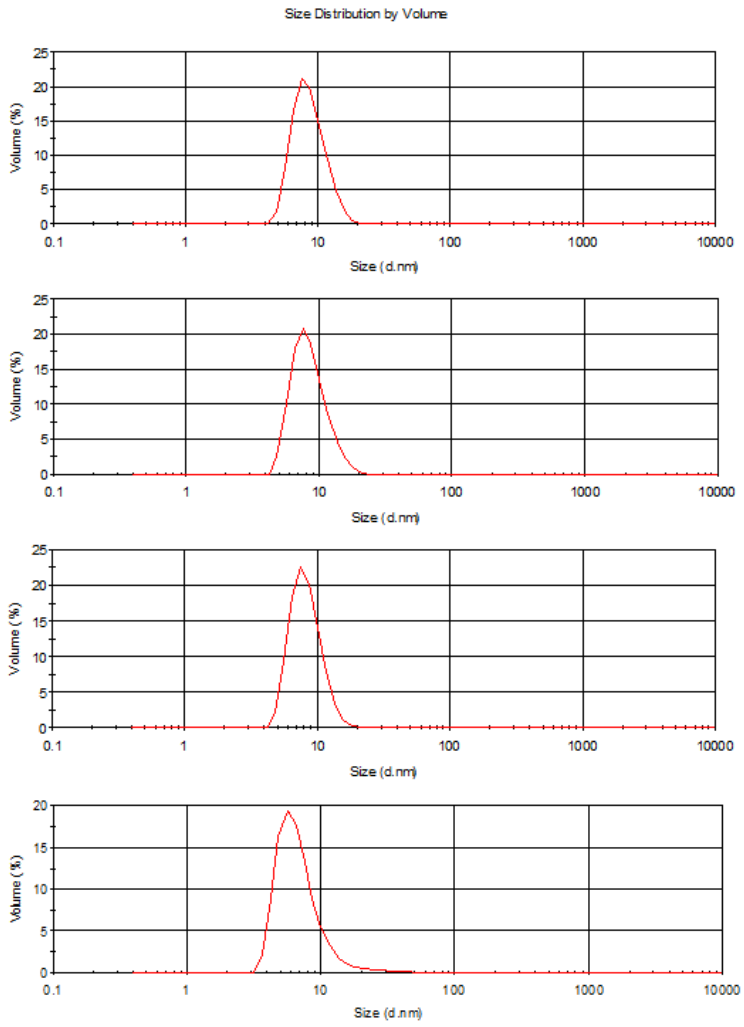
SI Figure 19. Aqueous GPC overlay chromatogram (TSKgel GMPWxl, 40:10mM $NaNO_3$: NaH_2PO_4) for HOOC-PMOx-OMe (**1a**) and G5-PLL[PMOx][NH_2] (**2a**)



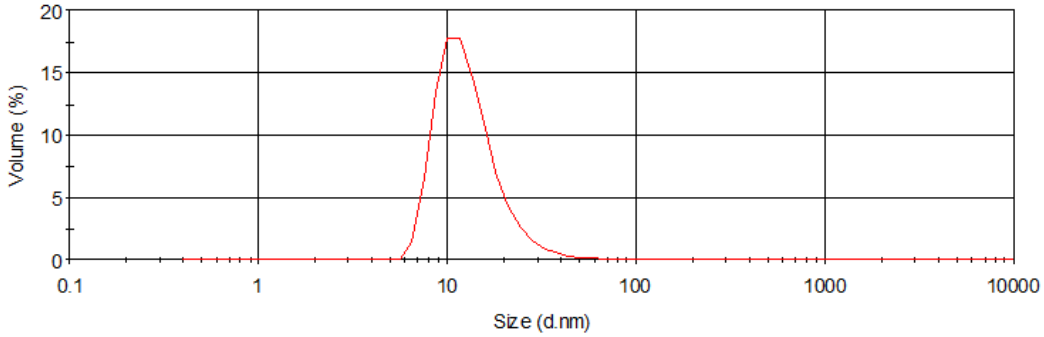
SI Figure 20. Haemolysis data for the unmodified and POZ and PEG modified G5 L-Lysine dendrimer. Saline and coated dendrimers haemoglobin levels lower than limit of detection and marked as 0.3%.



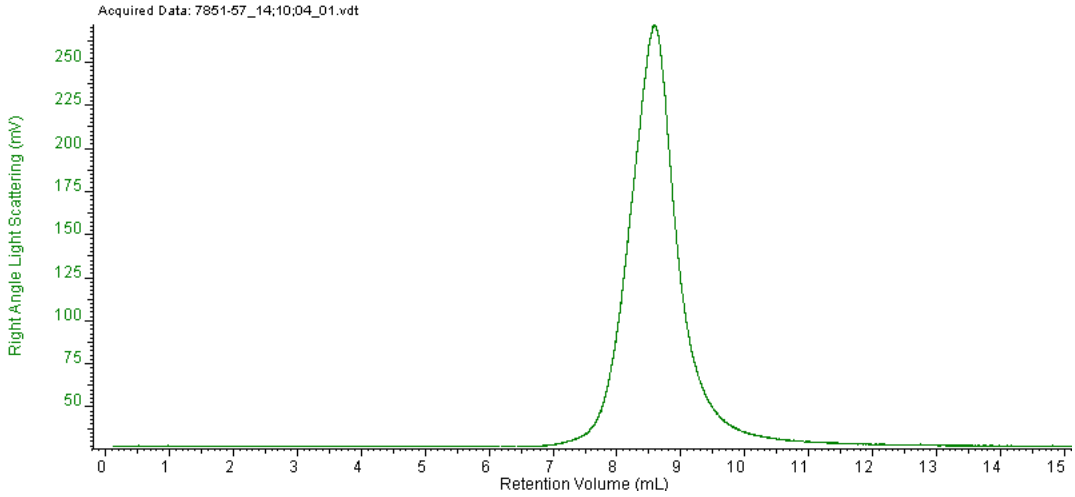
SI Figure 21. DLS spectra (size distribution by volume) for PMOx modified L-lysine dendrimers and coumarin conjugated dendrimer (top to bottom) **2a, 3a** and **4a**



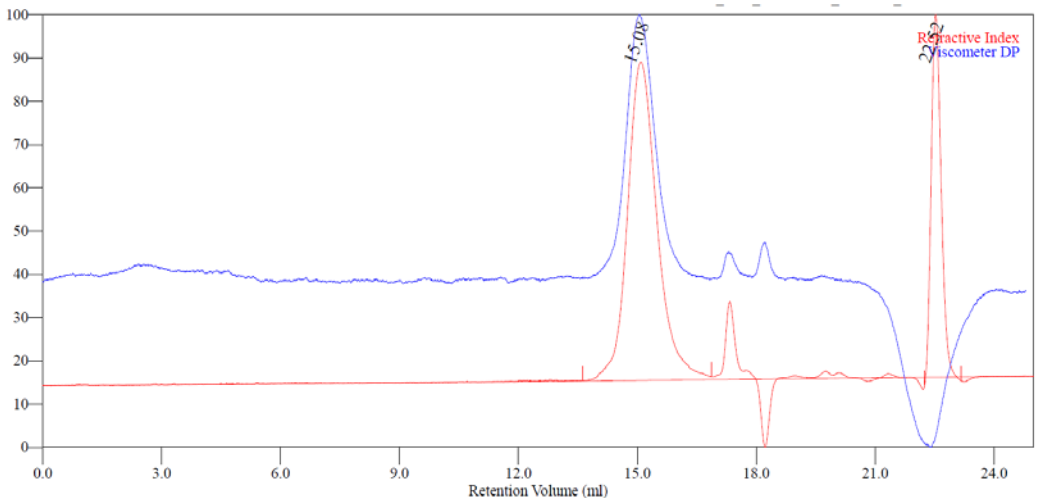
SI Figure 22. DLS spectra (size distribution by volume) for the Ester POZ modified L-lysine dendrimers, after deprotection and courmarin loaded (10mM NaCl) (top to bottom **2d, 3d, 4d, 5d**)



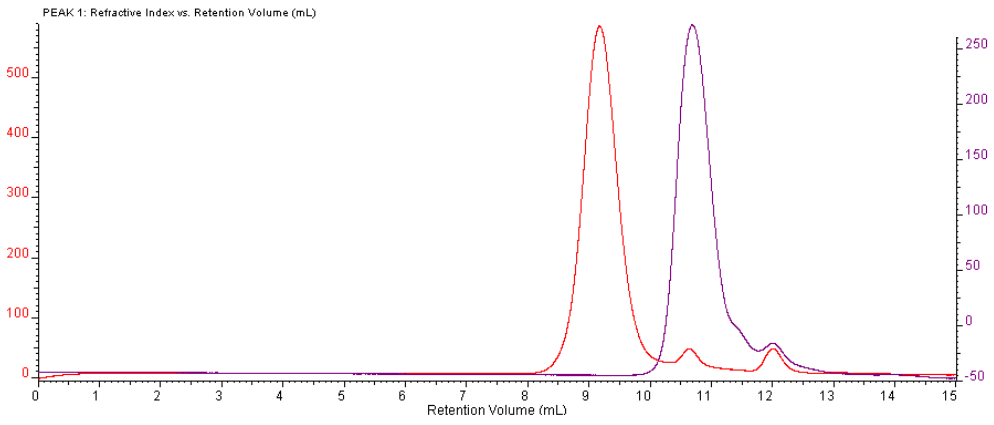
SI Figure 23. DLS spectra for G5PLL[PAcid][Coumarin] **5d** using the GPC eluent 40:10 mM $NaNO_3$: NaH_2PO_4



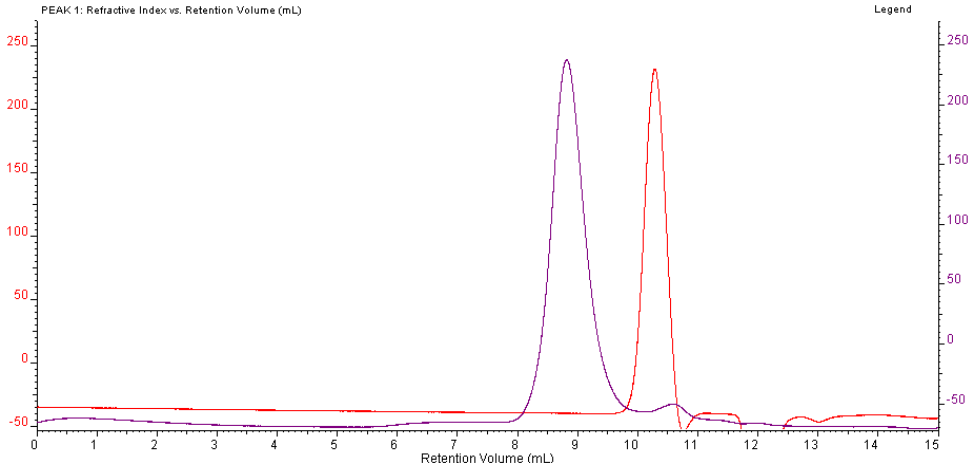
SI Figure 24. Aqueous GPC Light scattering chromatogram (TSKgel GMPWxl 40:10mM $NaNO_3$: NaH_2PO_4) for G5-PLL[PAcid][Coumarin] (**5d**).



SI Figure 25. Organic GPC (DMF/LiBr, Mixed-D) chromatogram for HOOC-PEster-COOMe (**1d**)



SI Figure 26. Aqueous GPC overlay chromatogram (TSKgel GMPWxl 40:10mM $NaNO_3$: NaH_2PO_4) for HOOC-PEOx-OMe (**1b**) and G5-PLL[PEOx][NH_2] (**2b**)



SI Figure 27. Aqueous GPC overlay chromatogram (TSKgel GMPWxl 40:10mM $NaNO_3$: NaH_2PO_4) for HOOC-PEG-OMe (**1c**) G5-PLL[PEG][NH_2] (**2c**)