Supplementary information for:

Tuning the properties of pH responsive Nanoparticles to control cellular interactions in vitro and ex vivo

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Synthesis of pentafluorophenyl methacrylate

Pentafluorophenol (5.0 g, 2.7 mmol), triethylamine (4.1 g, 41 mmol) and 4-dimethylaminopyridine (0.67 g, 27 mmol) were dissolved in dry DCM (30 ml). Nitrogen was bubbled through the solution for 5 min at 0˚C. Methacrylic anhydride (6.1 ml, 41 mmol) was added slowly via a syringe with vigorous stirring. The resulting solution was stirred at room temperature for 12 h under a nitrogen atmosphere. The solution was diluted with DCM (20 ml) and washed with 0.1 M HCl (50 mL), water (50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by automated column chromatography with a gradient of *n*-hexane and ethyl acetate to give pentafluorophenol methacrylate as a colourless liquid (4.2 g, 61%). ^{1}H NMR (400 MHz; $CDCl_3$): ∂/ppm: 6.45 (quintet, J = 1 Hz), 5.91 (qd, J = 1.6, 1.3 Hz), 2.09 (dd, J = 1.6, 1.0 Hz); ^{19}F NMR (376 MHz; $CDCl_3$): ∂/ppm: -152.77 (d, 2F, J = 16 Hz, *ortho*), -158.17 (1F, t, J = 22 Hz, *para)*, -162.46 (2F, dd, J = 16, 22 Hz, *meta*).

Table S1. Polymer synthesis

Polymer	Monomer:CTA:AIBN	Time (h)
$PEGMA_8$	28:1:0.1	16
$PEGMA_{37}$	176:1:0.1	16
PEG_{45}-b-$PDEAEMA_{97}$	100:1:0.1	15
$PEGMA_8$-b-$PDEAEMA_{100}$	110:1:0.1	18
$PEGMA_{37}$-b-$PDEAEMA_{90}$	110:1:0.1	16
PDEAEMA	500:10:1	16
PDEAEMA-r-PPFPMA	500:10:1	16

*All polymers were synthesized in 1,4-Dioxane at 60˚C.

Table S2. Polymer characterization

Polymer	PEG/PEGMA Mn (NMR)	PDEAEMA Mn (NMR)	Mn (GPC)	Mw (GPC)	PDI
PEG_{45}-b-$PDEAEMA_{97}$	2,000	17,700	16,962	19,086	1.13
$PEGMA_8$-b-$PDEAEMA_{100}$	2,400	18,200	16,818	21,847	1.30
$PEGMA_{37}$-b-$PDEAEMA_{90}$	11,100	16,700	55,151	90,038	1.63
PDEAEMA	-	36,000	-	-	-
PDEAEMA-r-PPFPMA	-	49,000	27,940	42,540	1.52

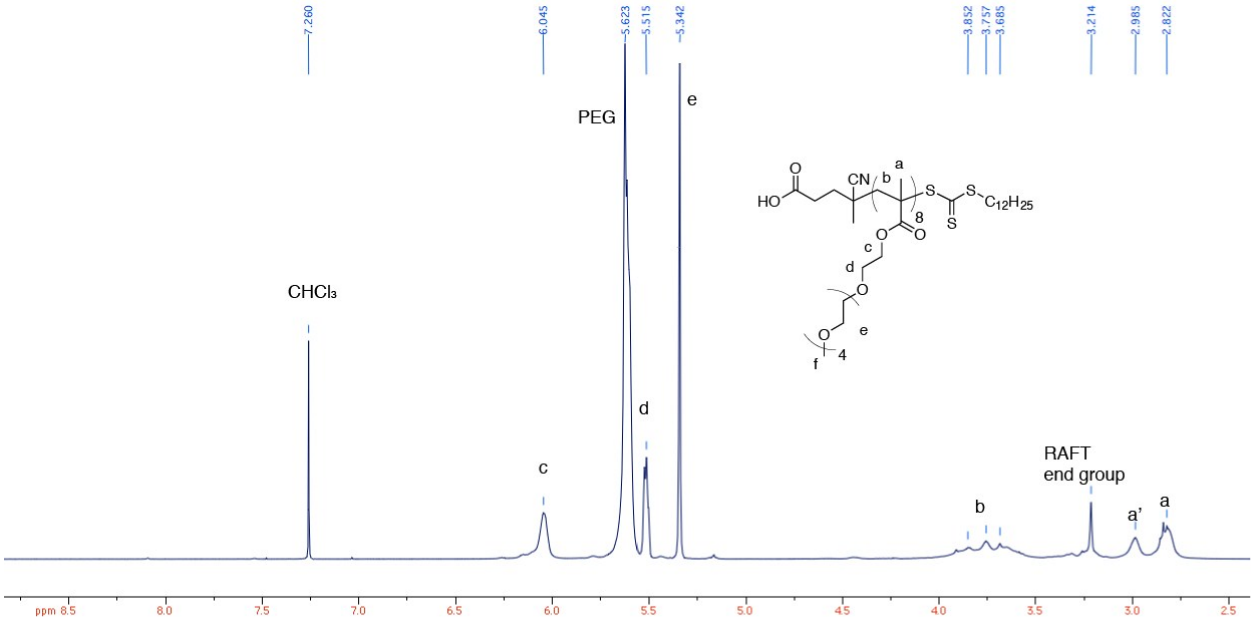


Figure S1. ^{1}H NMR of $PEGMA_8$ macro RAFT agent ($CDCl_3$).

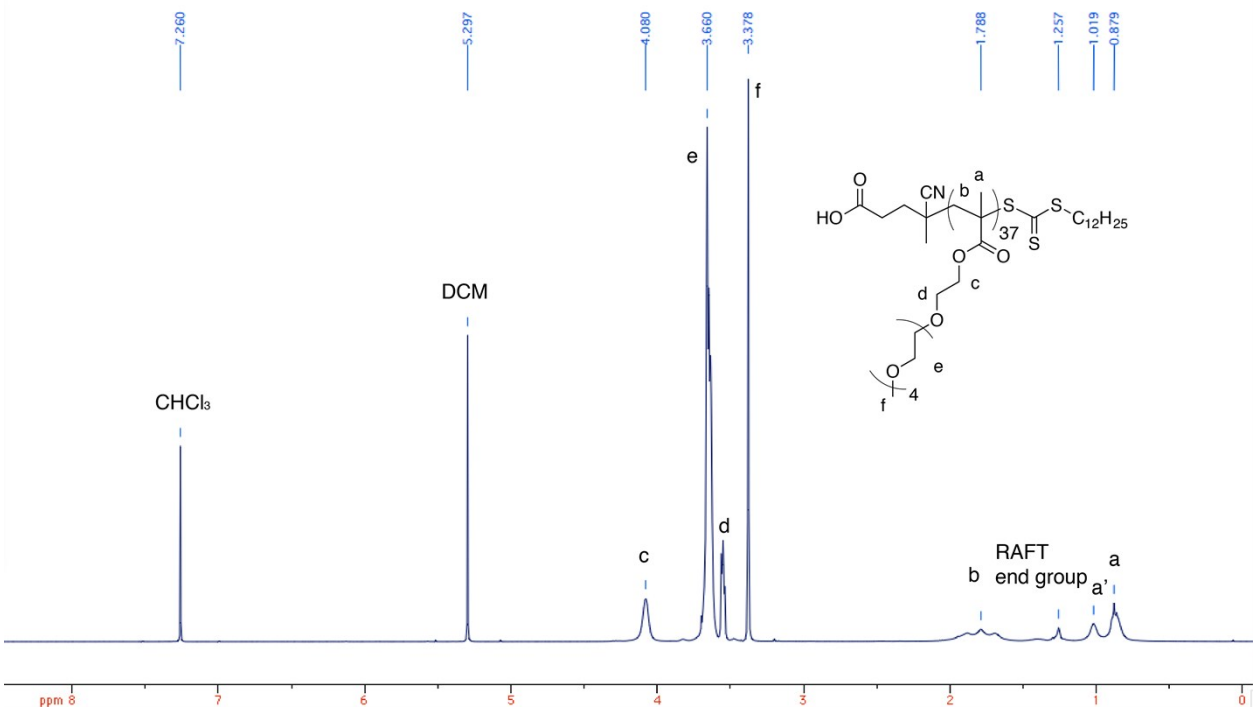


Figure S2. ^{1}H NMR of $PEGMA_{37}$ macro RAFT agent ($CDCl_3$).

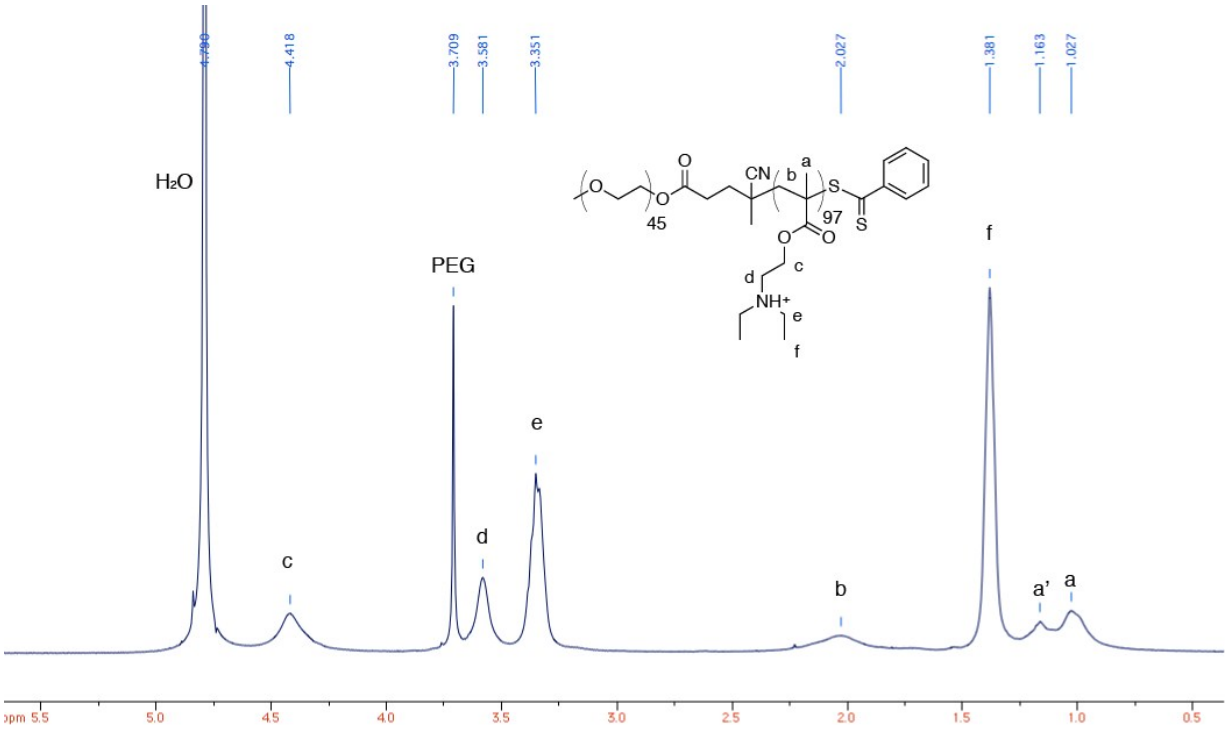


Figure S3. ^{1}H NMR of PEG_{45}-b-$PDEAEMA_{97}$ (D_2O).

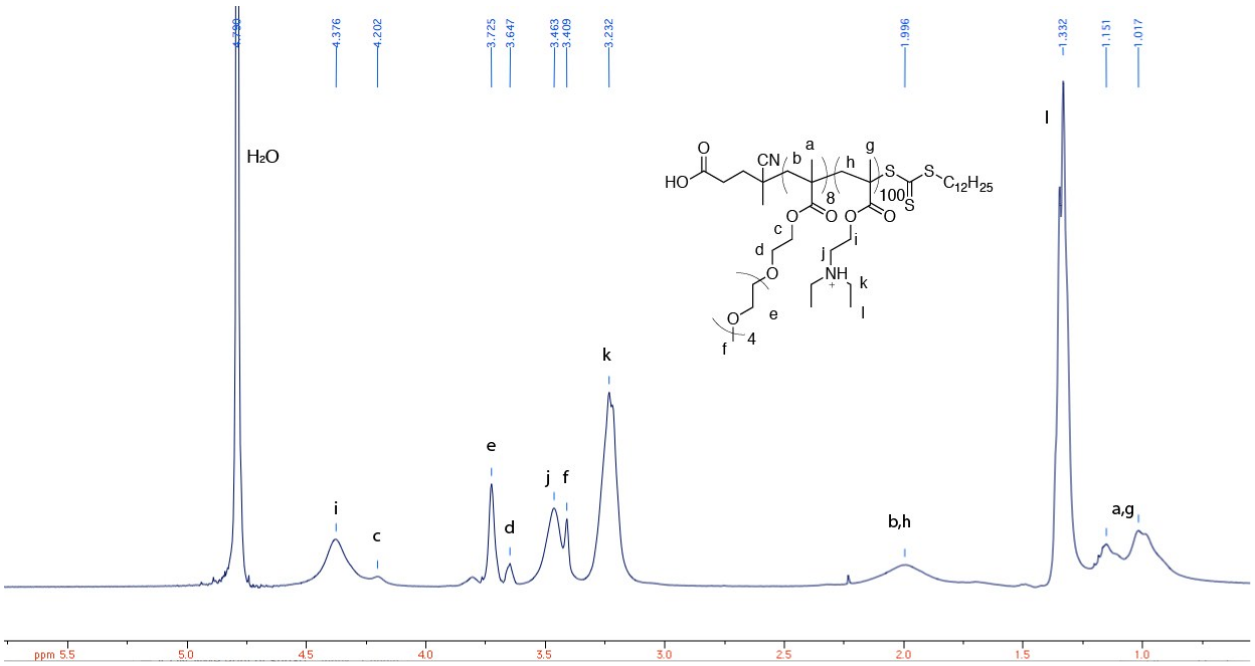


Figure S4. ^{1}H NMR of $PEGMA_8$-b-$PDEAEMA_{100}$ (D_2O).

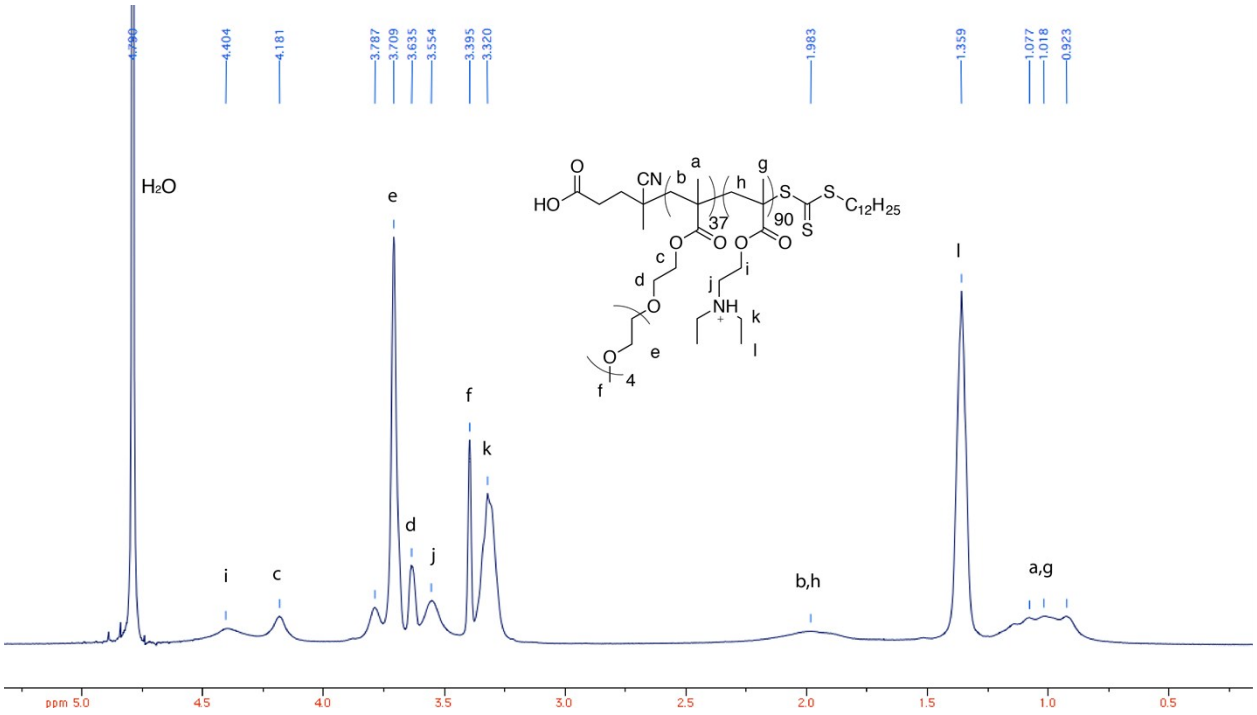


Figure S5. ^{1}H NMR of $PEGMA_{37}$-b-$PDEAEMA_{90}$ (D_2O)

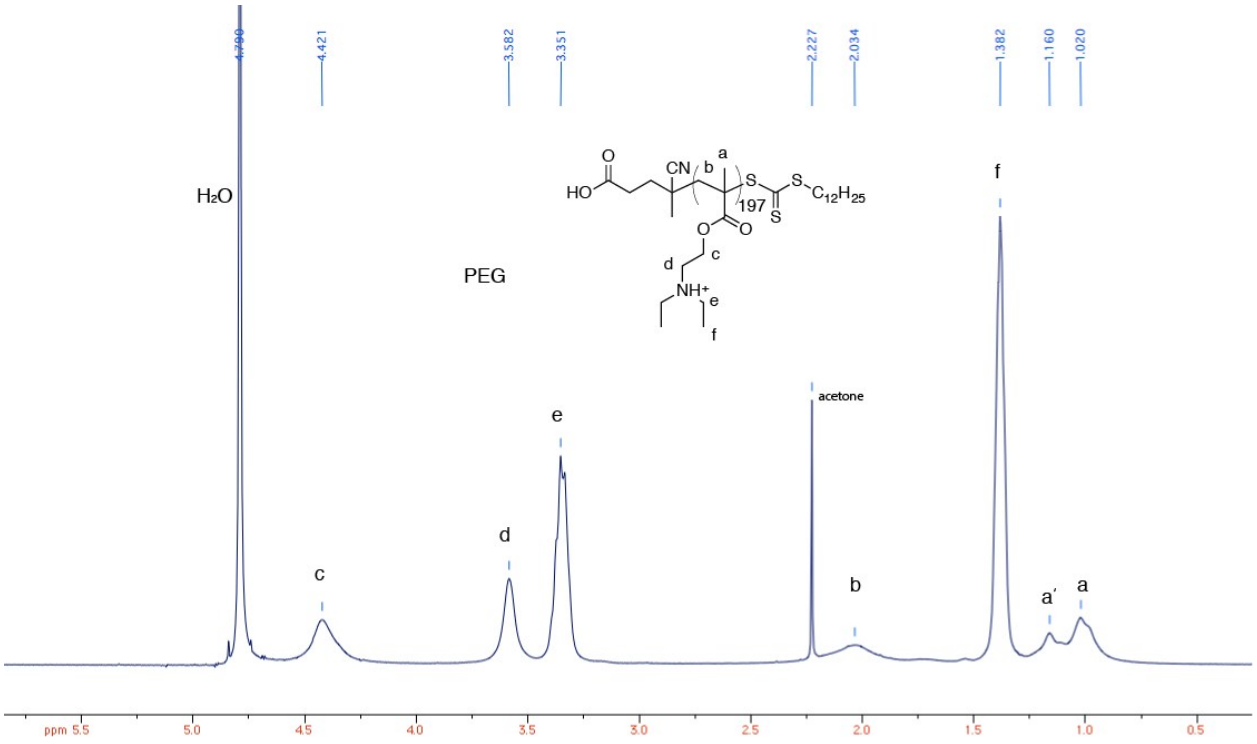


Figure S6. ^{1}H NMR of PDEAEMA (D_2O).

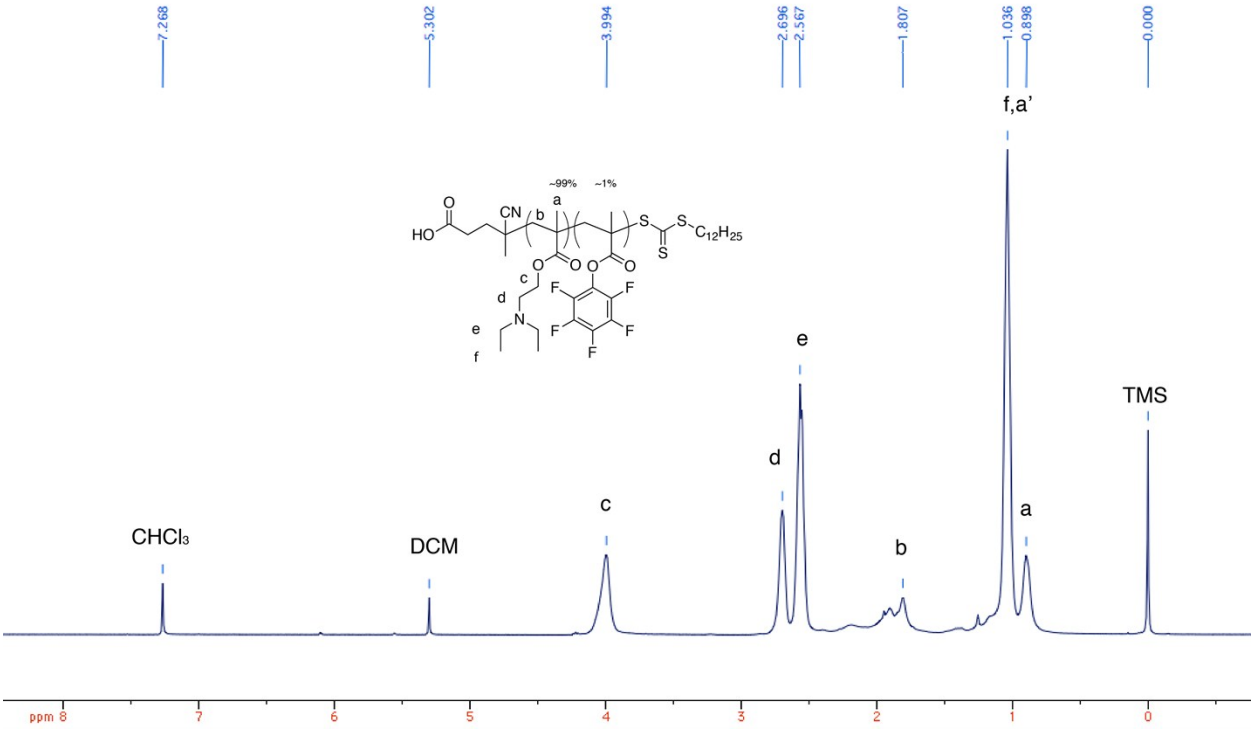


Figure S7. ^{1}H NMR of P(PDEAEMA-r-PFPMA) ($CDCl_3$).

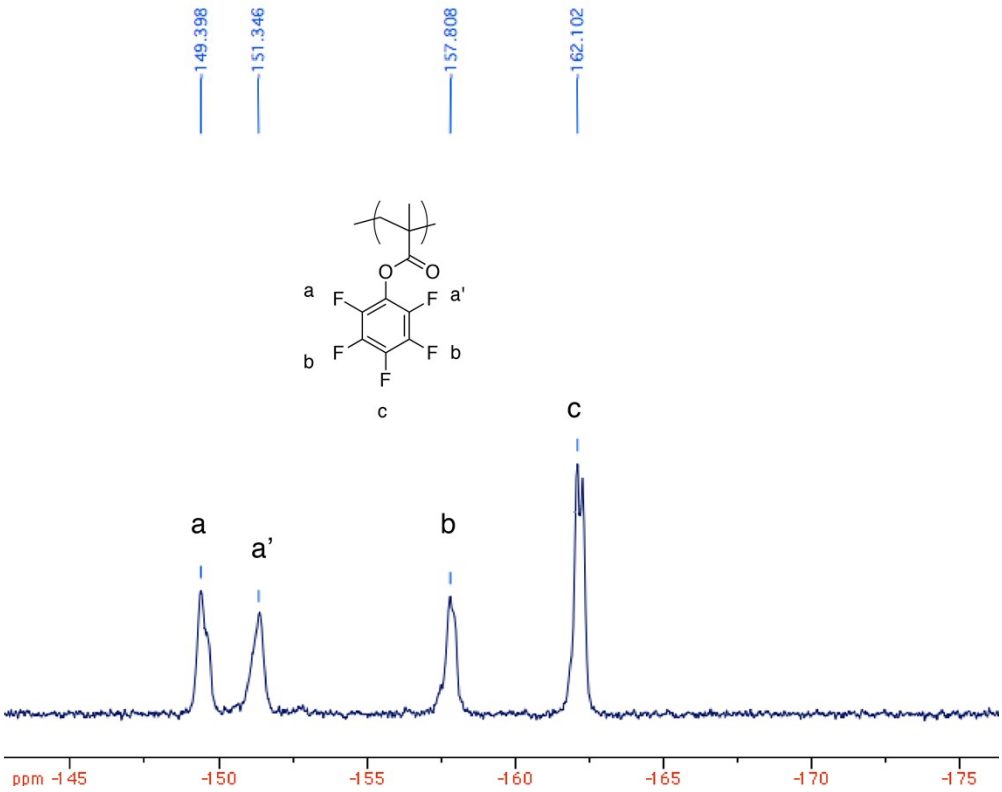


Figure S8. ^{19}F NMR of P(PDEAEMA-r-PFPMA).

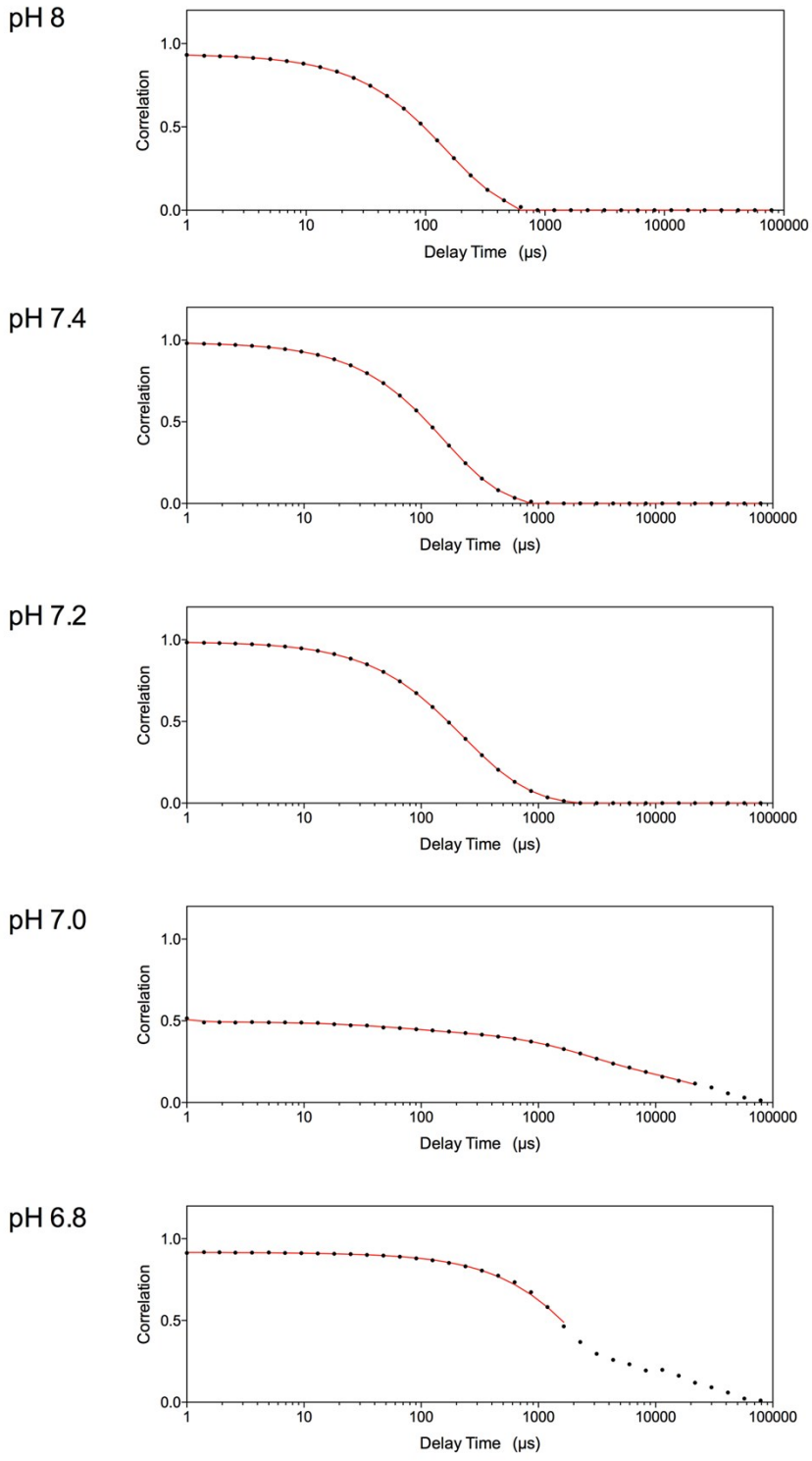


Figure S9. pH-dependent disassembly of nanoparticles analysis by DLS. Correlation function (black circles) and fitting function (red line) for $PEGMA_8$ NPs adjusted to selected pH values at 37˚C.

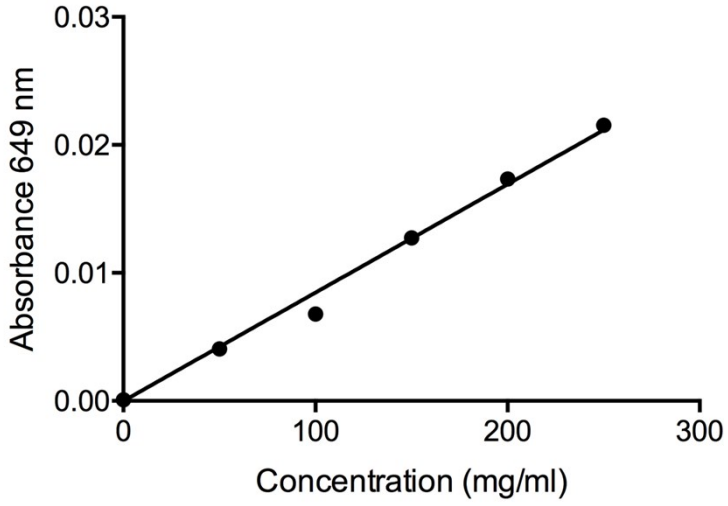
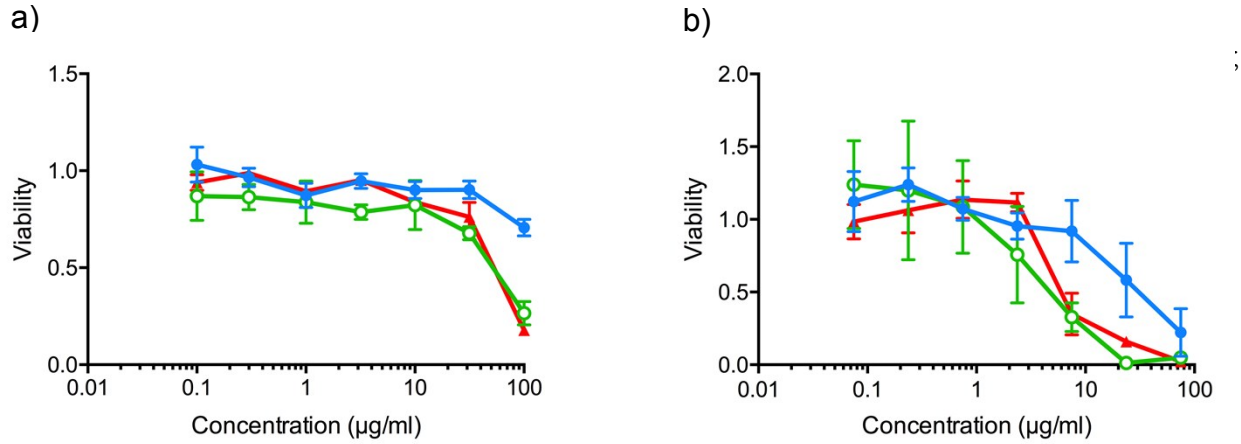


Figure S10. Cy5-labelled PDEAEMA standard curve.



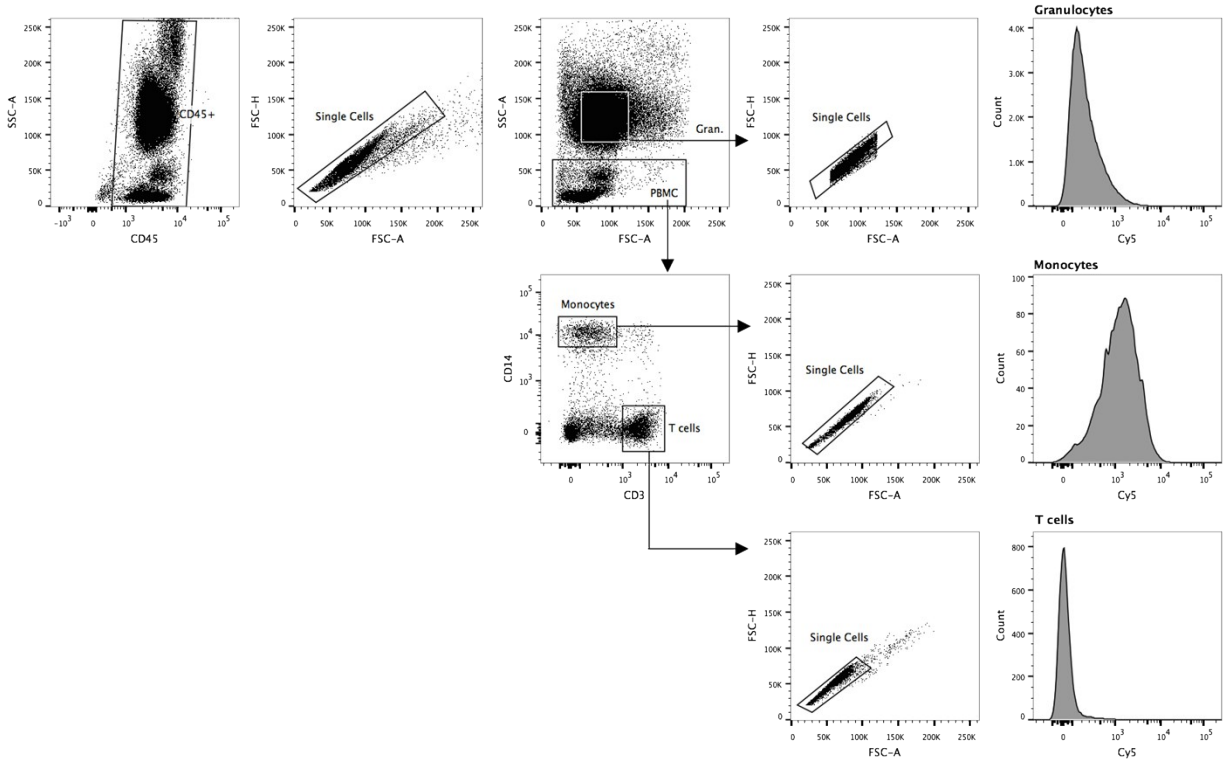
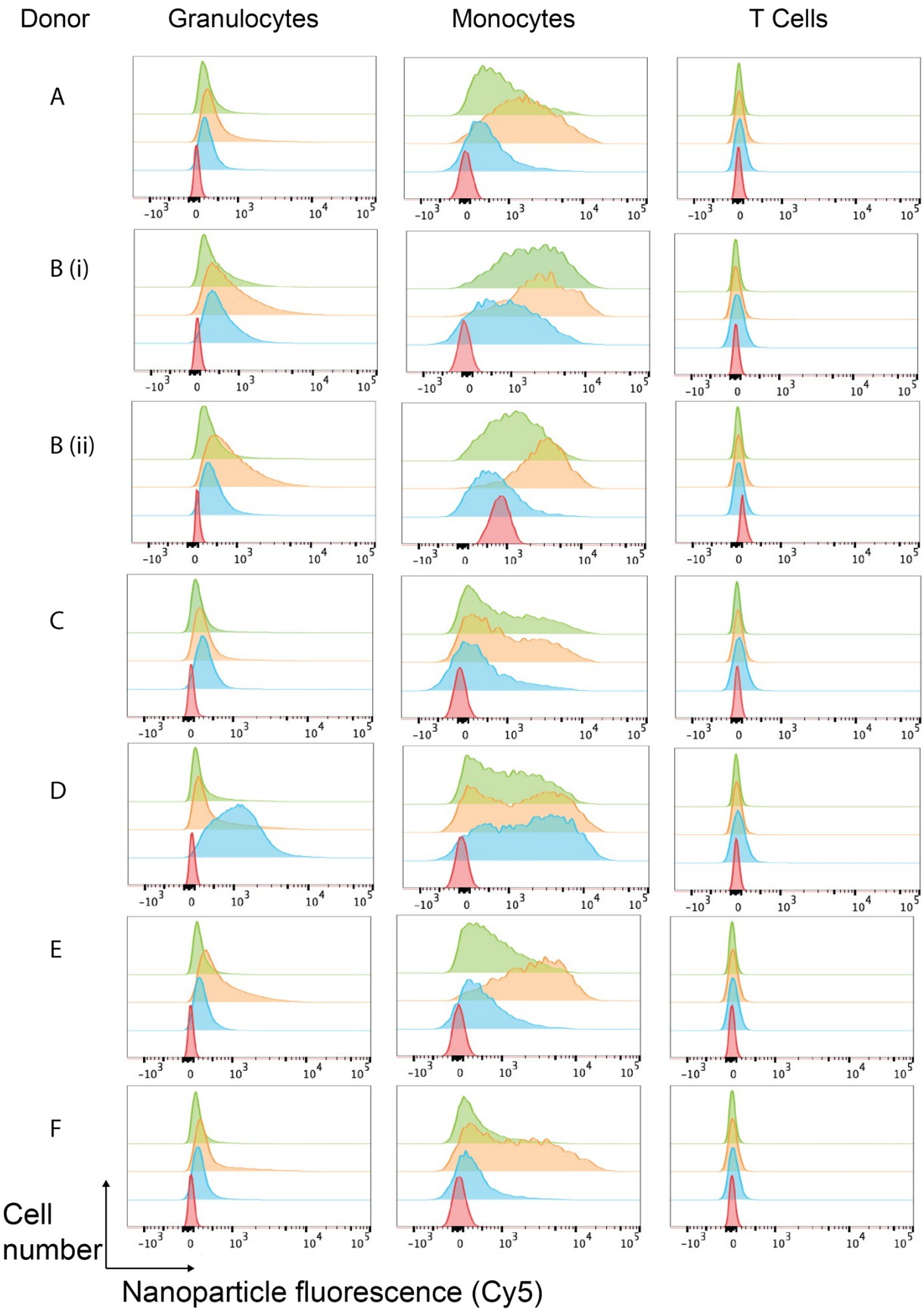


Figure S12. Gating strategy for identification of monocyte, granulocyte and T cell association with nanoparticles. Representative flow cytometry plots from a single donor after association with $PEGMA_8$. Leukocytes are identified as CD45+ before selecting single cells, Granulocytes and peripheral blood mononuclear cells (PBMC) identified by forward (FSC) and side scatter (SSC) properties. PBMC are identified as monocytes (CD14+ CD3-) and T cells (CD3+ CD14-). After again gating on single cells, Cy5 signals were analyzed to identify nanoparticle association.


Donor
Granulocytes
Monocytes
T Cells
A
B (i)
B (ii)
C
D
E
F
Cell number
Nanoparticle fluorescence (Cy5)

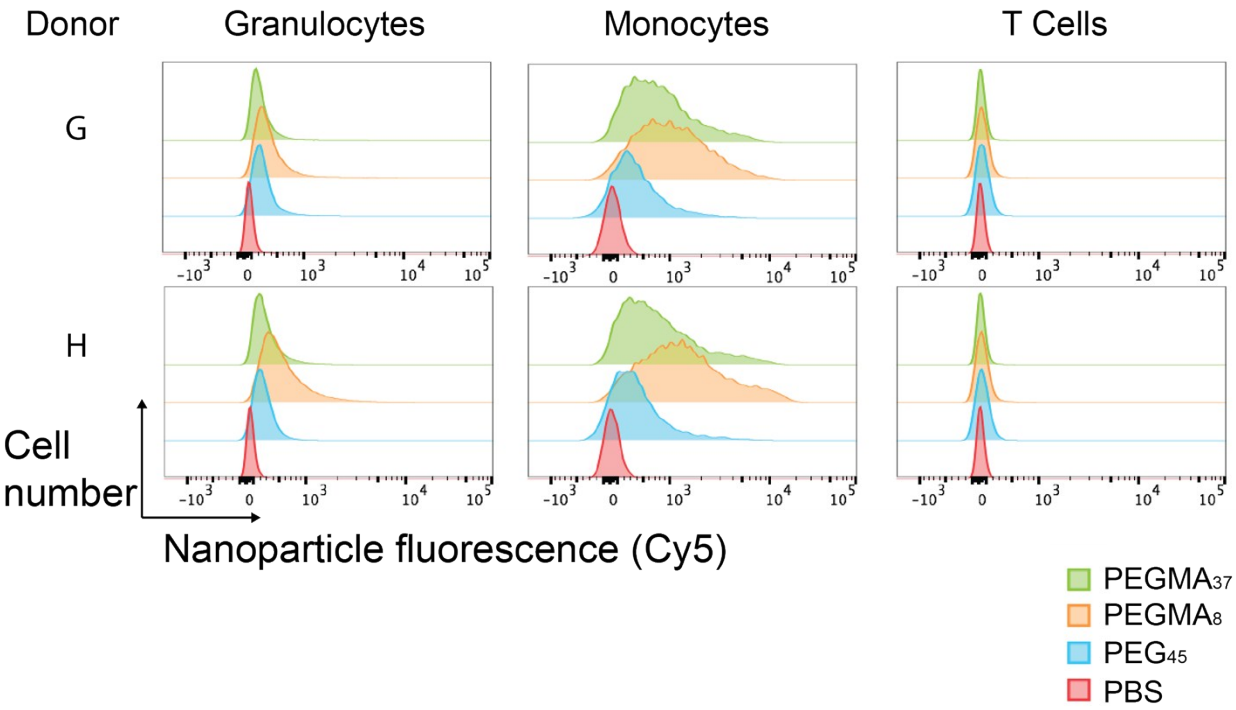


Figure S13. Flow cytometry histograms for monocyte, granulocyte and T-cell association of nanoparticles in 8 donors. The fluorescence was normalized to account for the different concentration of fluorescent labeling of the particles.