Supporting Information

Degradable polycaprolactone nanoparticles stabilized via supramolecular host-guest interactions with pH-responsive polymer-pillar[5]arene conjugates

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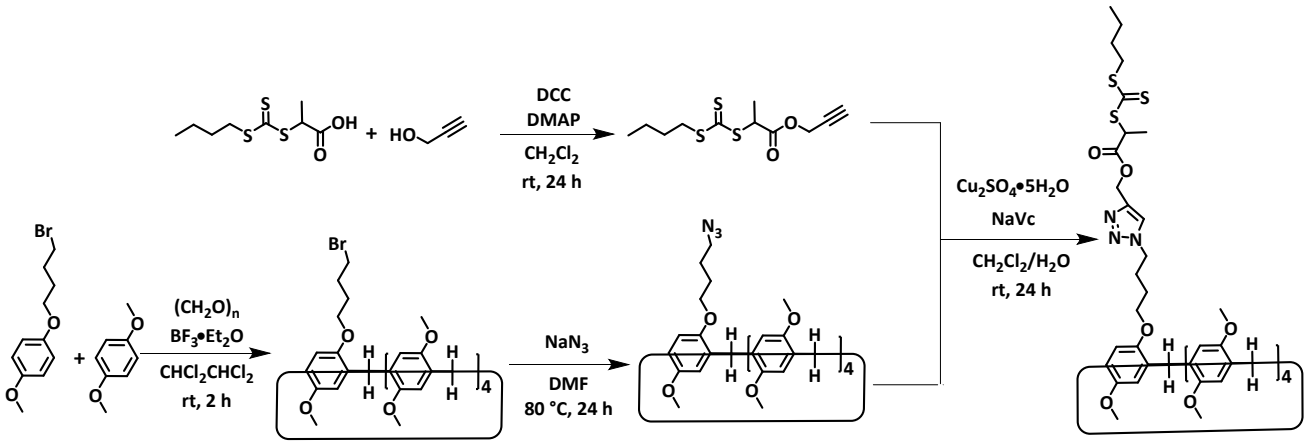


Scheme S1 Synthetic route of pillar[5]arene modified CTA.

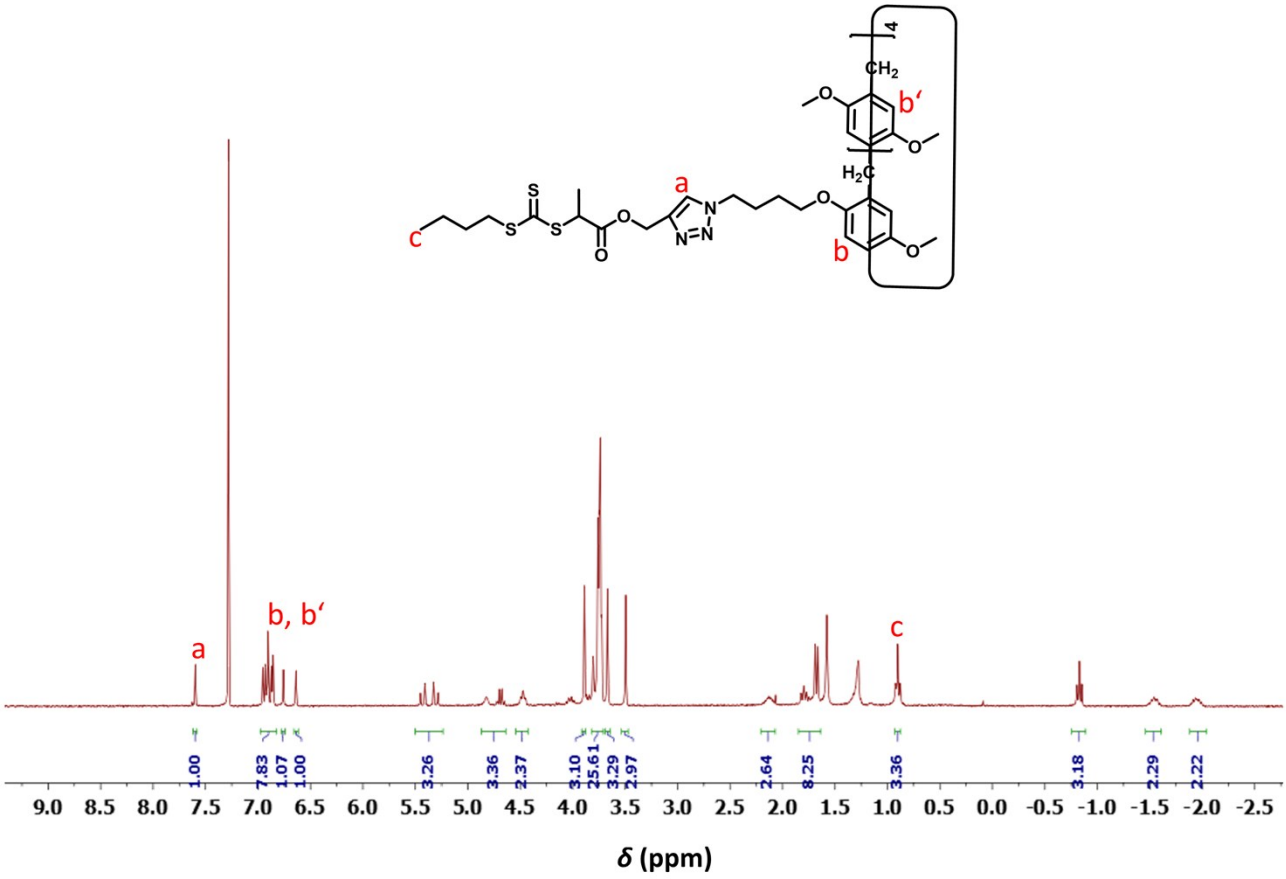


Figure S1 ^1H NMR ($CDCl_3$, 300 MHz) spectrum of the pillar[5]arene modified chain transfer agent (CTA).

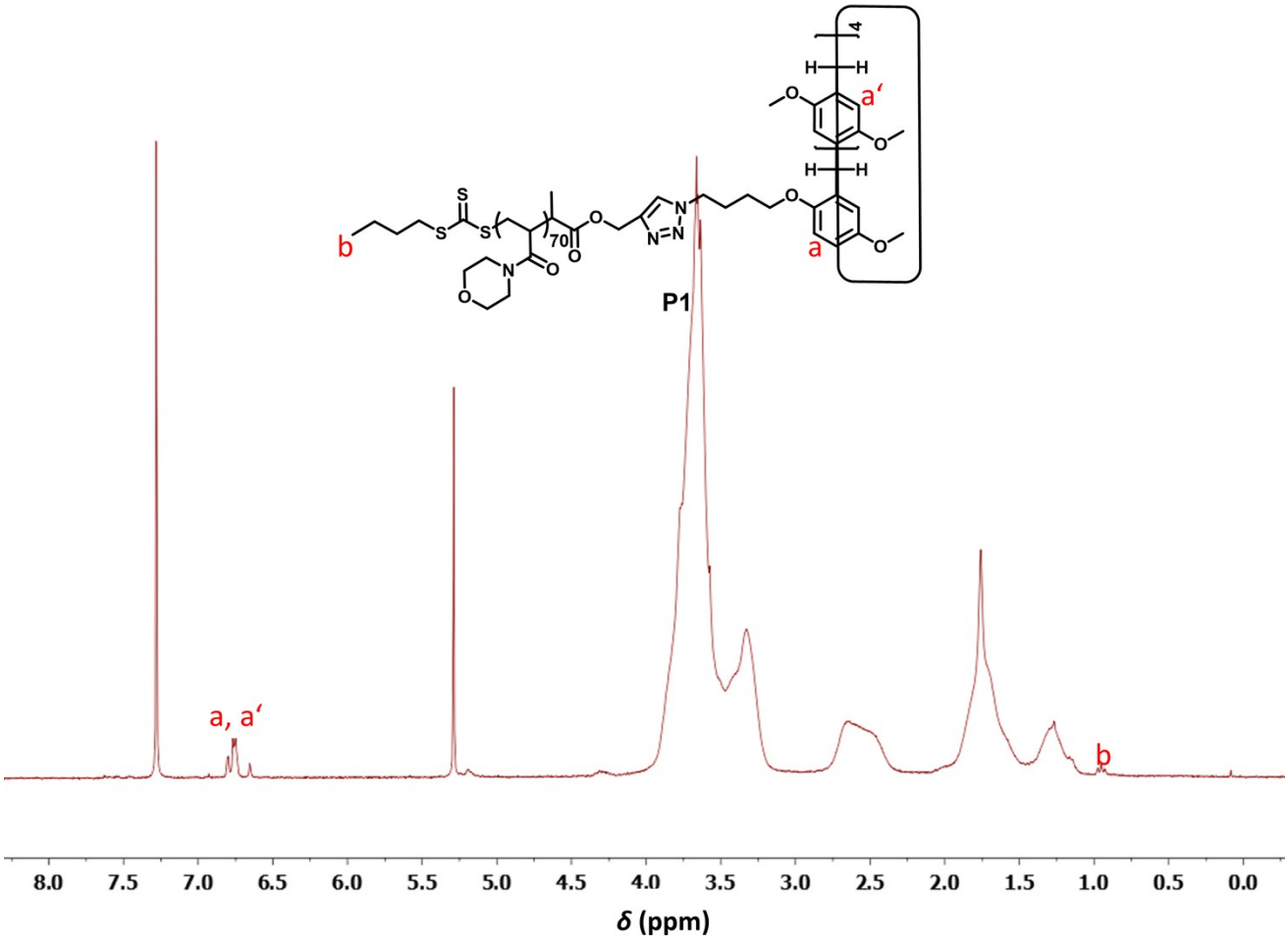


Figure S2 ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **P1** (PNAM).

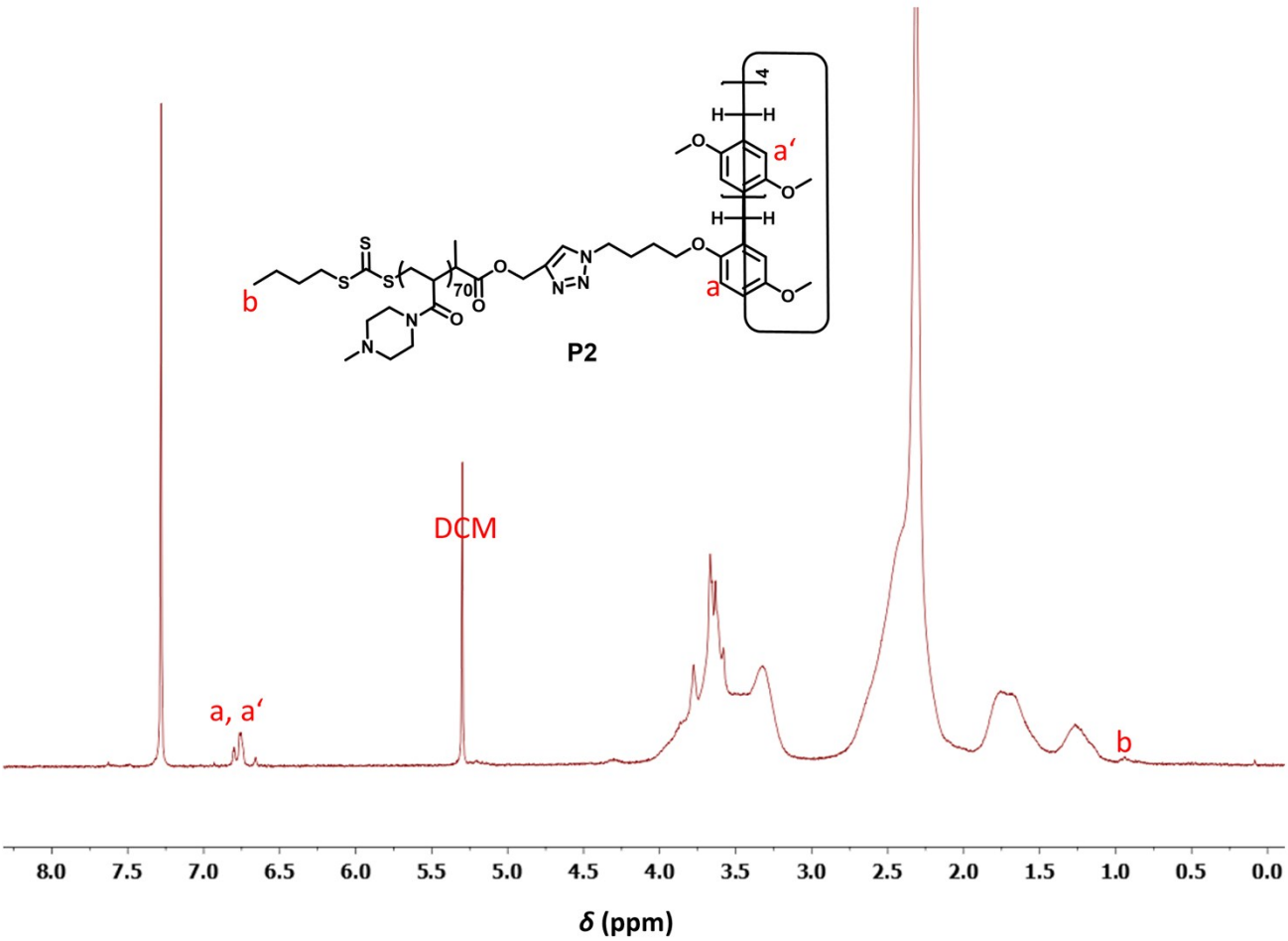


Figure S3 ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **P2** (PNAMP).

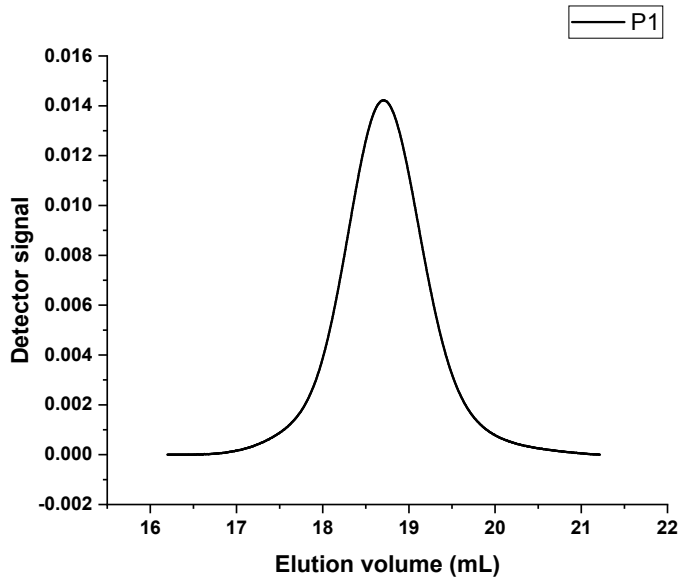


Figure S4 SEC trace of **P1** (PNAM).

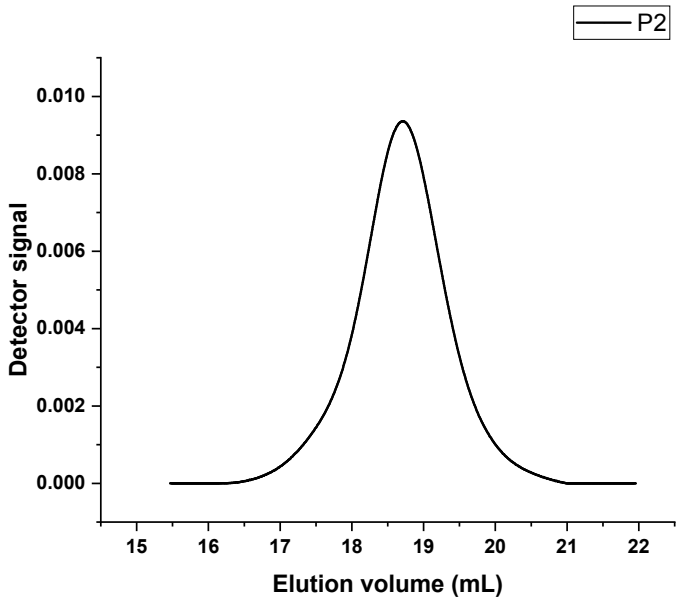


Figure S5 SEC trace of **P2** (PNAMP).

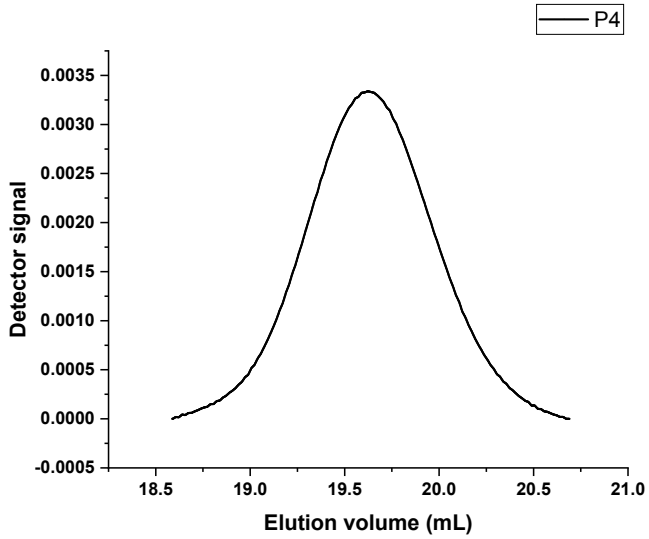


Figure S6 SEC trace of **P4** (PCL).

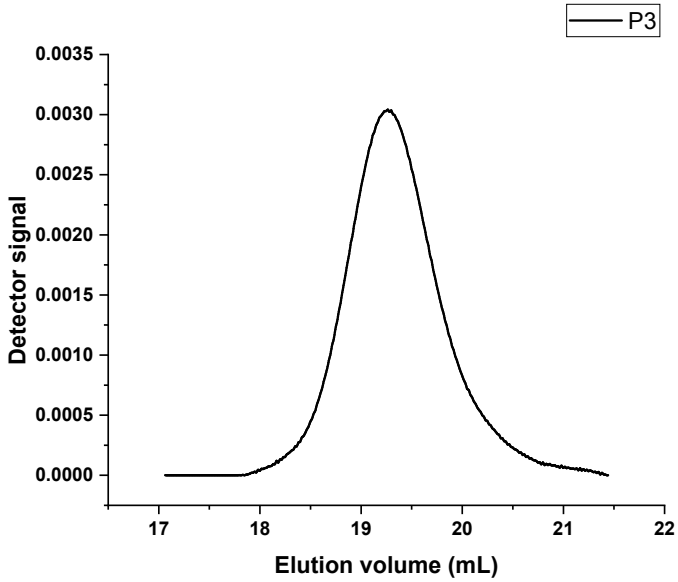


Figure S7 SEC trace of **P3** (viologen-PCL).

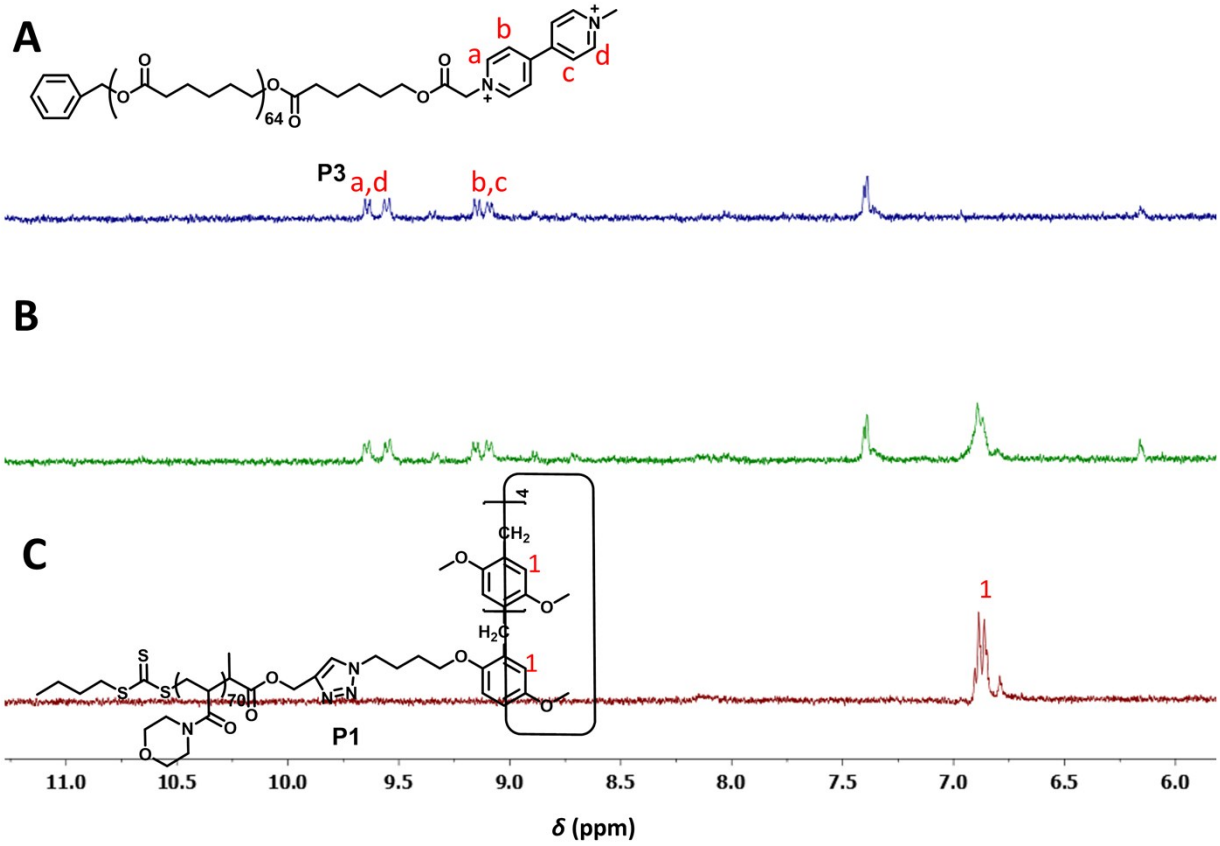


Figure S8 ^{1}H NMR (acetone-*d6*, 300 MHz) spectra of A) 4 mM **P3** (viologen-PCL), B) 1/1 mixture of **P3** (viologen-PCL) and **P1** (PNAM), C) 4 mM **P1** (PNAM) measured at 25 °C.

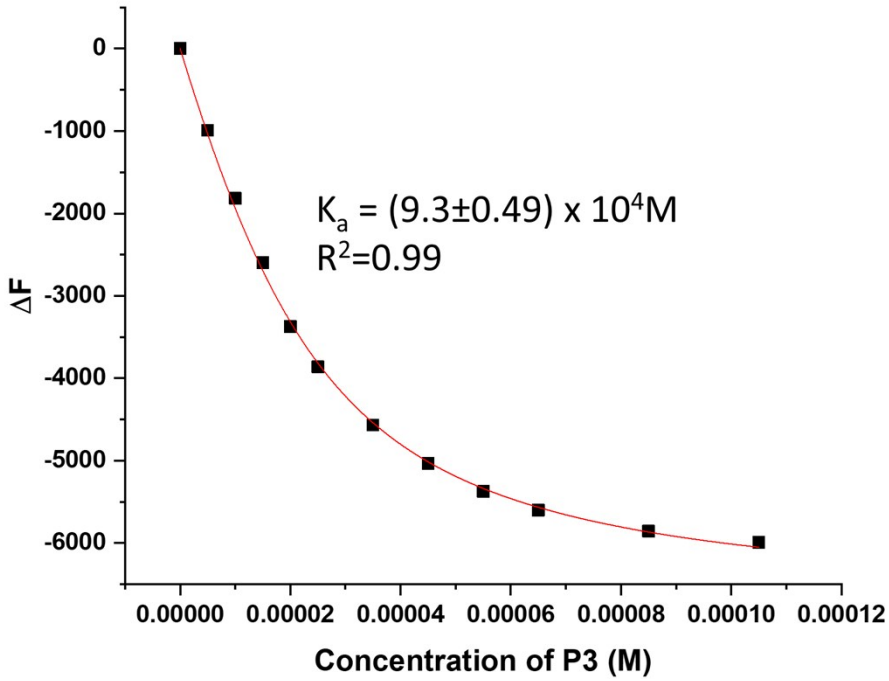


Figure S9 Change of fluorescence intensity (**P2**) with increasing concentration of **P3**. The red line represents a corresponding exponential fit from which the association constant K_a can be calculated according to: $\Delta F = (\Delta F\infty/[H]_0)(0.5[G]_0 + 0.5([H]_0 + 1/Ka) - (0.5([G]_0^2 + (2[G]_0(1/Ka - [H]_0)) + (1/Ka + [H]_0)^2)^{0.5}))$. ΔF is the difference in fluorescence intensity at 240 nm at $[H]_0$ (**P2**), $\Delta F\infty$ is the difference in fluorescence intensity at 240 nm when **P2** is completely complexed. $[H]_0$ is the fixed initial concentration of **P2** and $[G]_0$ is the initial concentration of **P3**.

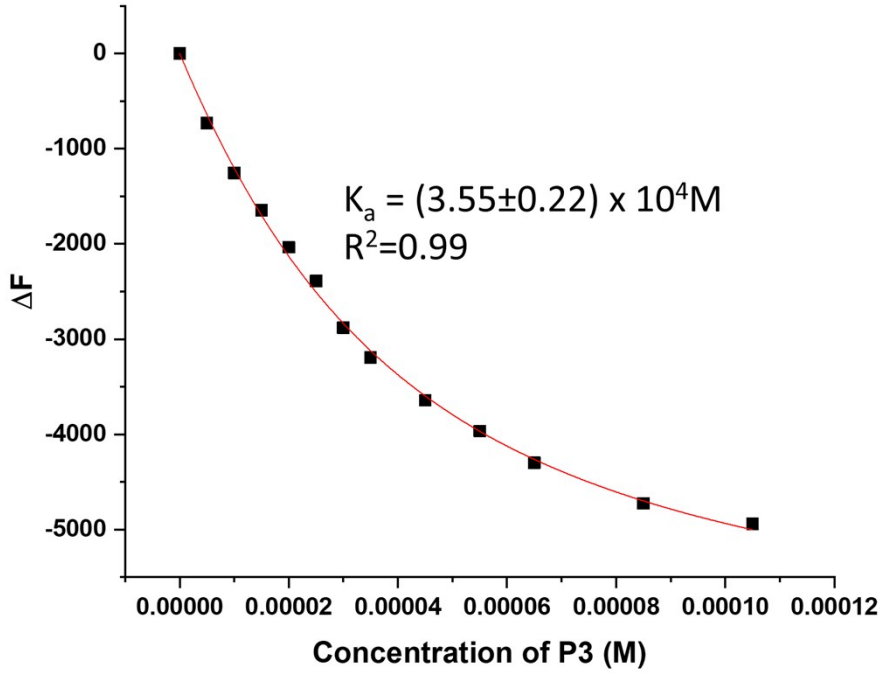


Figure S10 Change of fluorescence intensity (**P1**) with increasing concentration of **P3**. The red line represents a corresponding exponential fit from which the association constant K_a can be calculated according to: $\Delta F = (\Delta F\infty/[H]_0)(0.5[G]_0 + 0.5([H]_0 + 1/Ka) - (0.5([G]_0^2 + (2[G]_0(1/Ka - [H]_0)) + (1/Ka + [H]_0)^2)^{0.5}))$. ΔF is the difference in fluorescence intensity at 240 nm at $[H]_0$ (**P1**), $\Delta F\infty$ is the difference in fluorescence intensity at 240 nm when **P1** is completely complexed. $[H]_0$ is the fixed initial concentration of **P1** and $[G]_0$ is the initial concentration of **P3**.

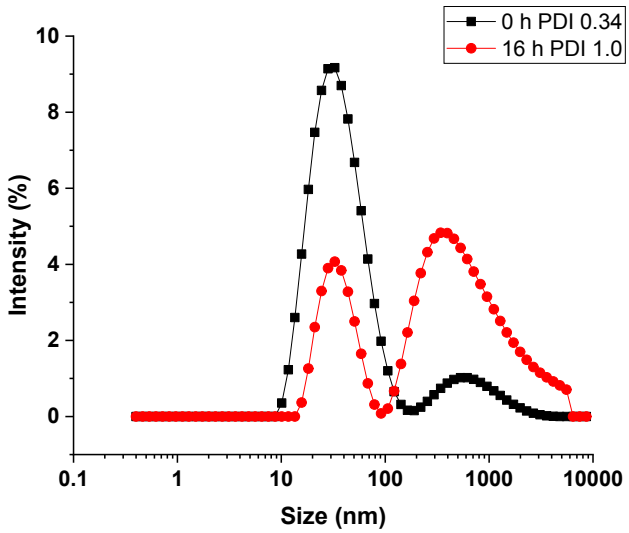


Figure S11 Size distribution (intensity weighted) of the particles formed by **P1**+**P3** after preparation (0 h) and after 16 h measured by DLS in PBS.

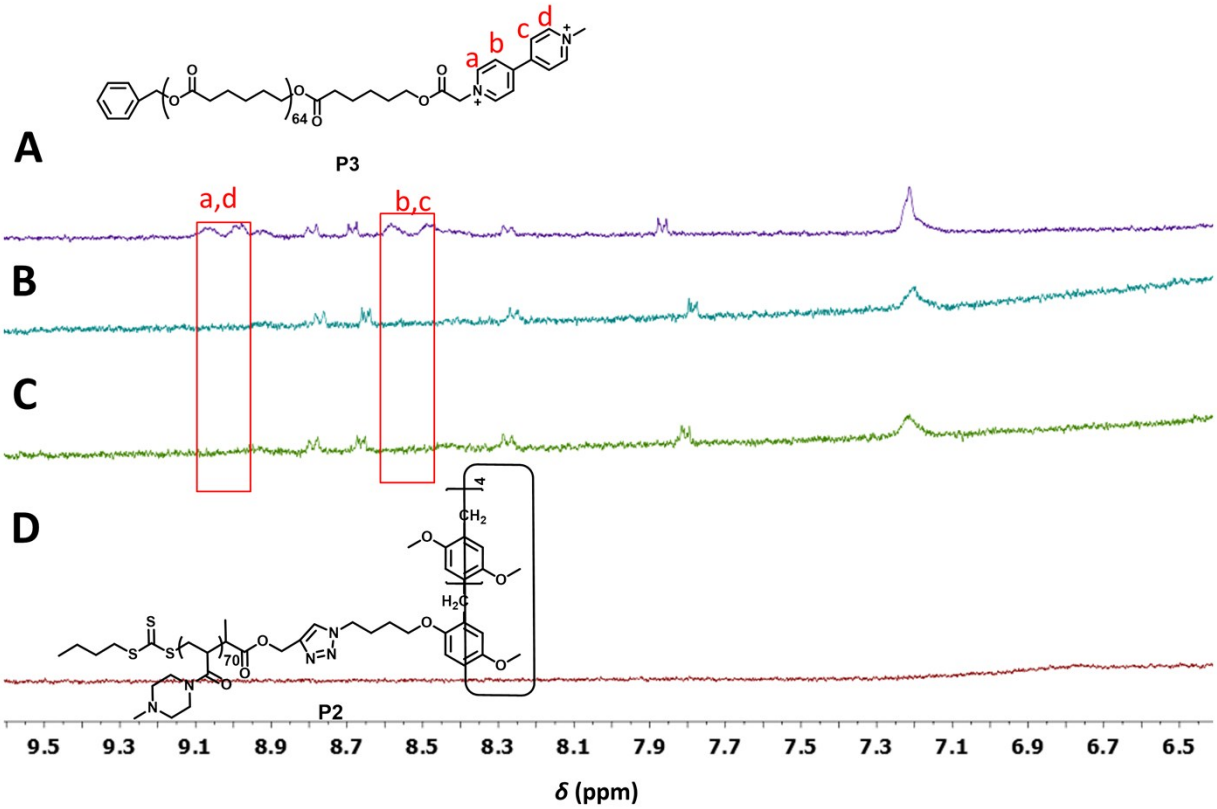


Figure S12 ^{1}H NMR (D_2O, 300 MHz) spectra of A) 4 mM **P3** (viologen-PCL), B) 1/1 mixture of **P3** (viologen-PCL) and **P2** (PNAMP), C) 1/1 mixture of **P3** (viologen-PCL) and **P2** (PNAMP) in PBS, D) 4 mM **P2** (PNAMP) measured at 25 °C. The additionally visible signals belong to small impurities (< 5%, see also Figure S8) of free viologen salts, which are intensified due to their comparably good solubility and could not fully be removed by the purification steps.

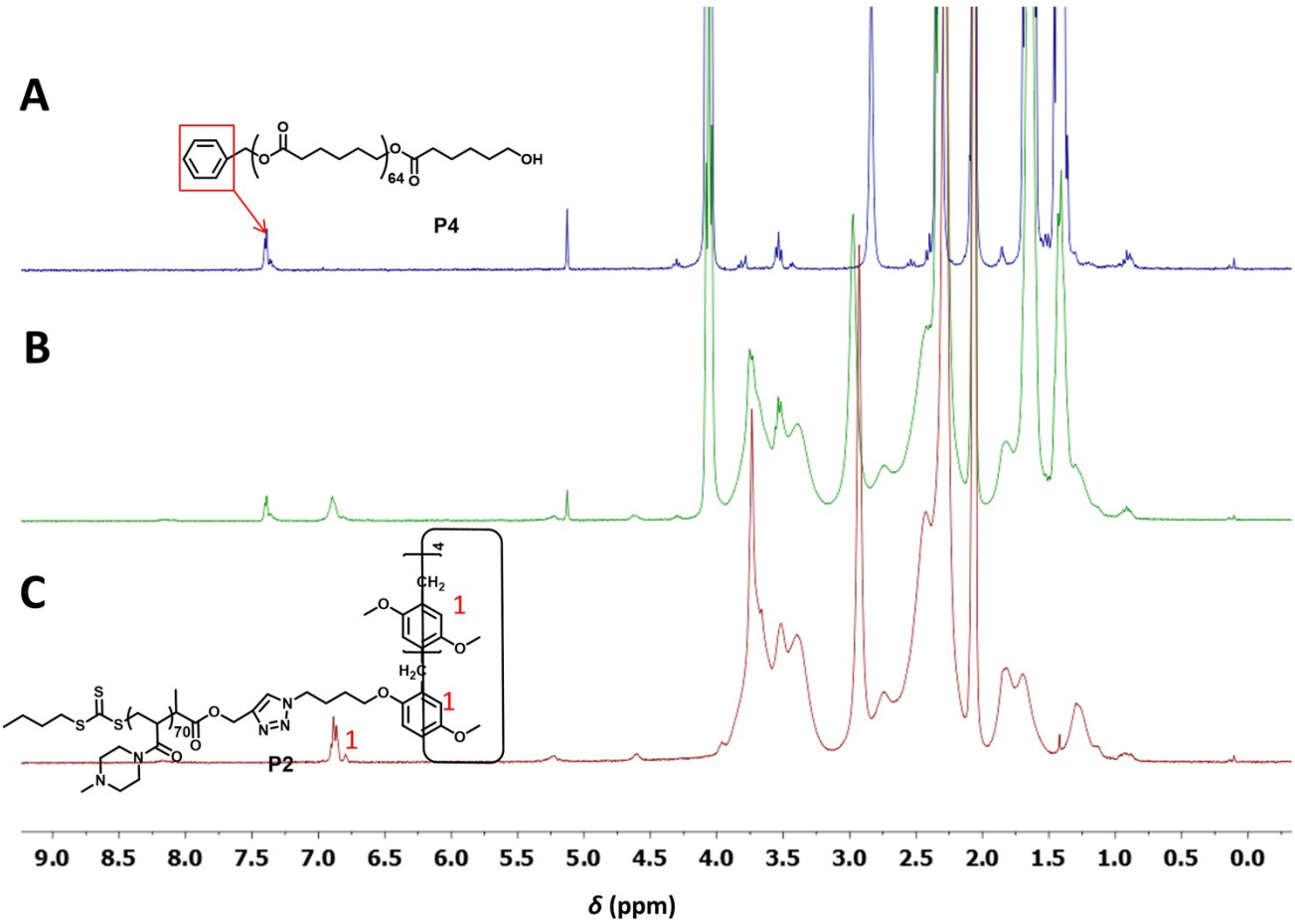


Figure S13 ^{1}H NMR (acetone-*d6*, 300 MHz) spectra of A) 4 mM **P4** (PCL), B) 1/1 mixture of **P4** (PCL) and **P2** (PNAMP), C) 4 mM **P2** (PNAMP) measured at 25 °C.

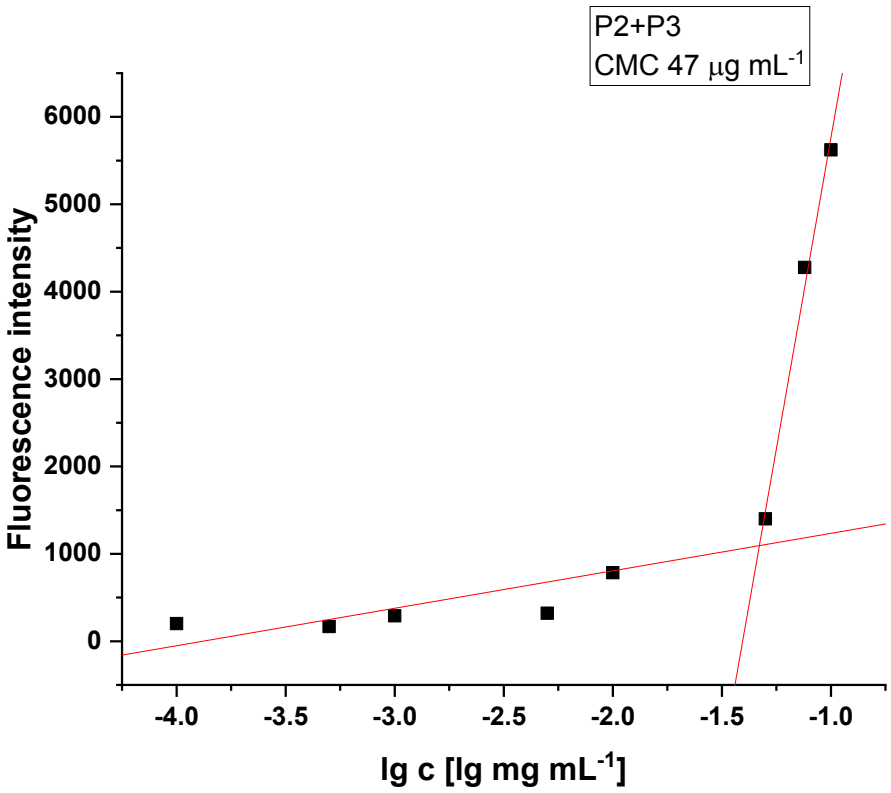


Figure S14 Fluorescence intensity of Nile Red at various concentrations of **P2**+**P3**. The CMC was determined as the intersection of the corresponding linear fits (red lines).

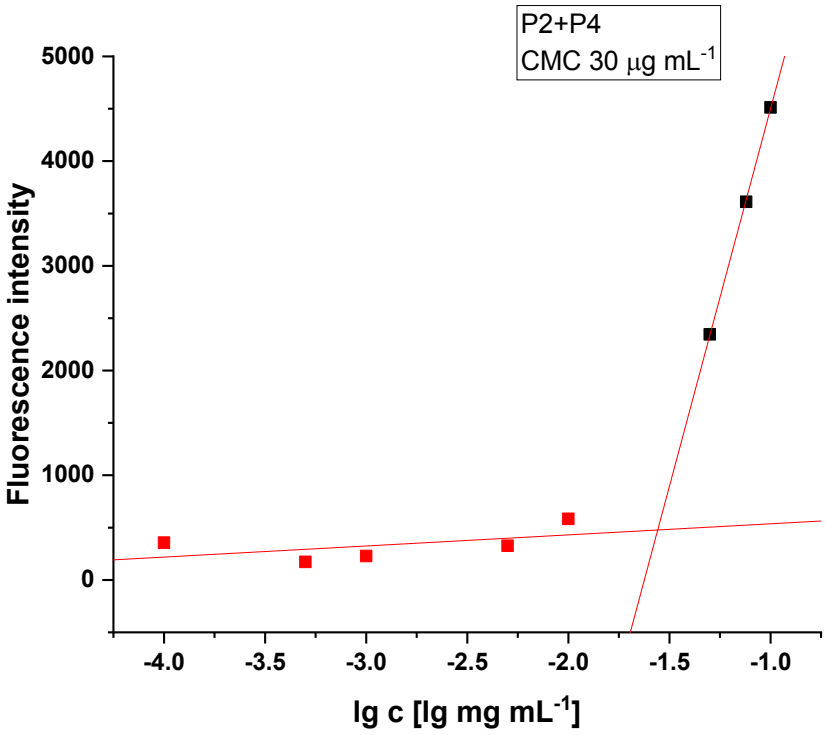


Figure S15 Fluorescence intensity of Nile Red at various concentrations of **P2**+**P4**. The CMC was determined as the intersection of the corresponding linear fits (red lines).

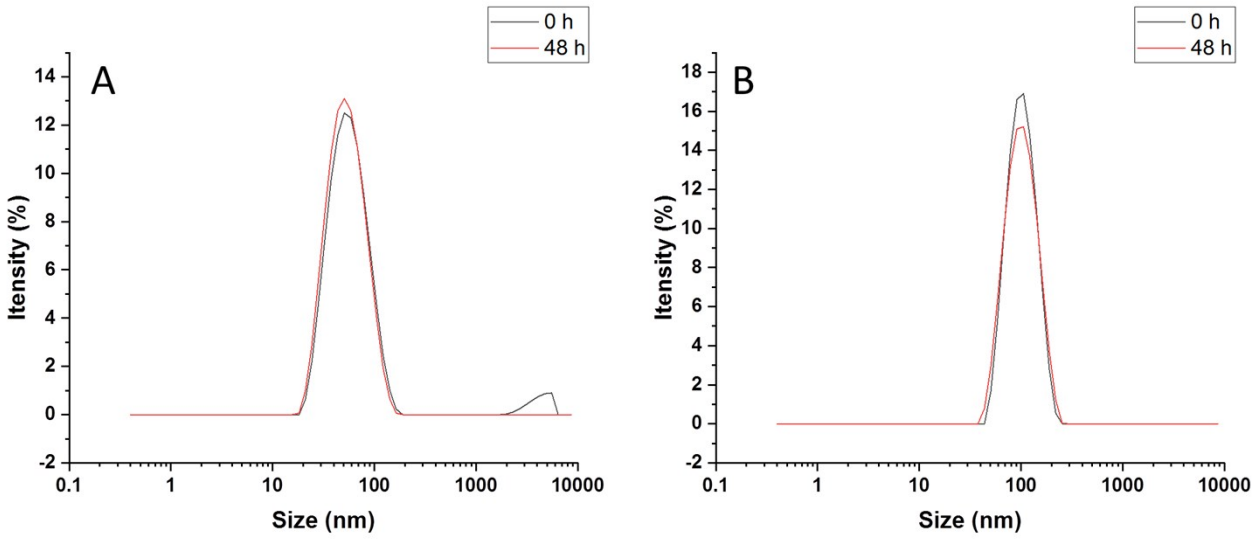


Figure S16 Size distribution (intensity weighted) of the particles formed by A) **P2**+**P3** and B) **P2**+**P4** in cell culture medium after 48 h.

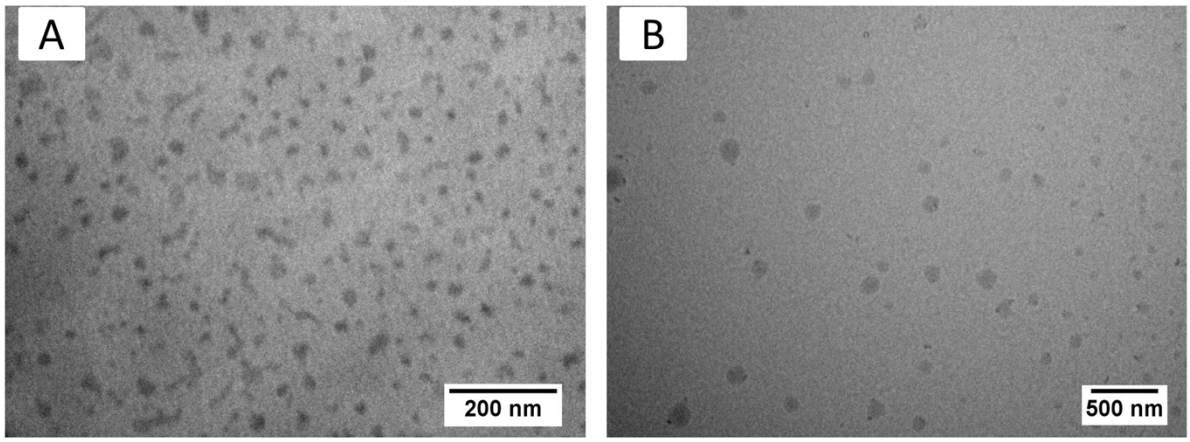


Figure S17 TEM images of A) **P3** and B) **P4**.

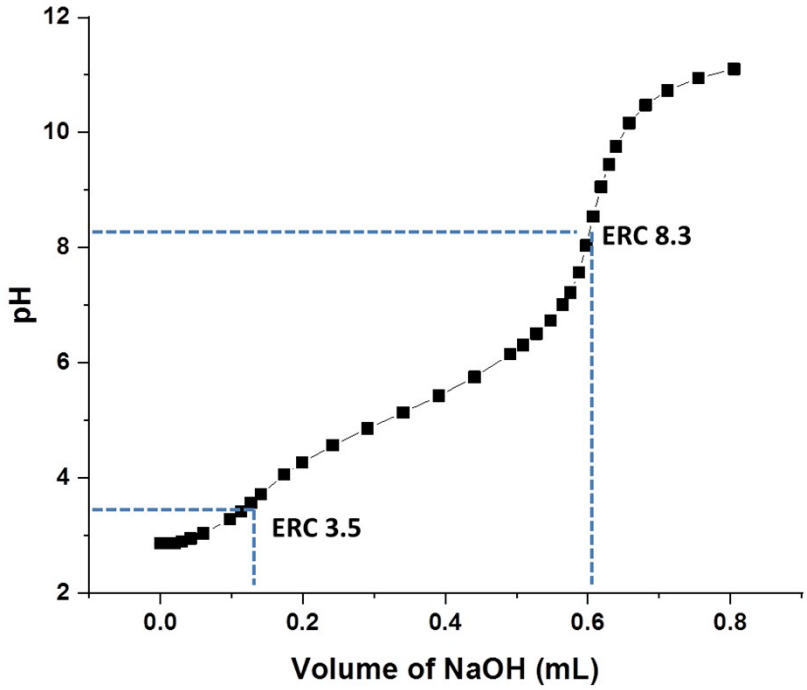


Figure S18 Titration of **P2** (1 mg mL^{-1}) at 25 °C with NaOH (0.1 M) after acidification with HCl (0.1 M). NaCl (0.1 M) was added to simulate physiological conditions.

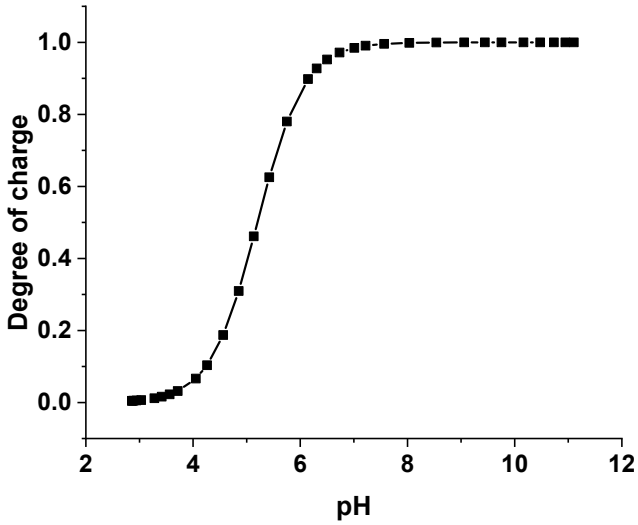


Figure S19 Degree of charge of PNAMP (**P2**) segments as a function of pH; the dashed line corresponds to the behavior of a dilute **P2** solution (intrinsic pK_a 5.2).

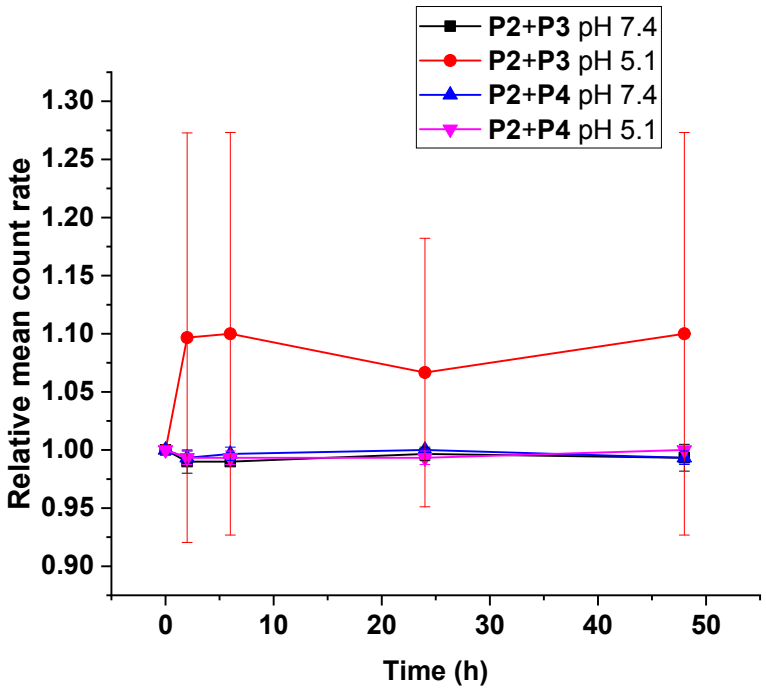
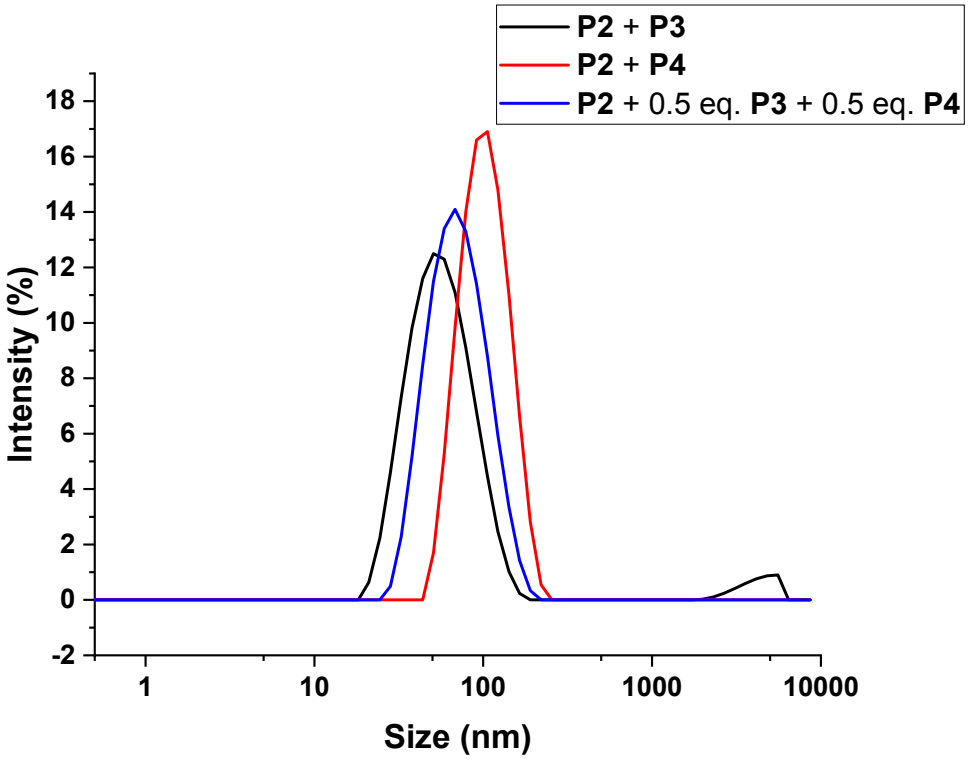


Figure S20: Relative mean count rate of the respective dispersions at different pH at 37 °C determined by DLS.



1

2 **Figure S21**: Size distributions (intensity weighted) of the respective nanoparticles measured by DLS.