

Supporting Information

Synthesis of Well-Defined Core-Shell Nanoparticles based on Bifunctional Poly(2-oxazoline) Macromonomer Surfactants and a Microemulsion Polymerization Process

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Experimental Section:

NMR Experiments. The NMR spectra were recorded on 500 MHz spectrometer AVANCE-III HDX-500 with 5mm nitrogen cooled Prodigy H(C,N) probe from Bruker BioSpin GmbH or on a 400 MHz NMR spectrometer Nanobay AVANCE-III HD-400 with 5mm BBFOsmart probe from Bruker BioSpin GmbH. The spectra were calibrated using the solvent signals (CDCl_3 7.26 ppm).

Zeta potential. Zeta potential measurements were performed using a Brookhaven ZetaPALS. The experiments were carried out in 1.5 mL PS cuvette and a dipping cell at 25°C. For all measurements a 1 mg/mL aqueous NP-solution was used. For calculating the zeta potential particle solutions software were used (Version 3.1.1.3909).

UV/vis spectroscopy. UV/vis spectra were recorded on a UV-6300 PC Double Beam Spectrophotometer (VWR). Samples were measured at $c=1$ mg/mL unless otherwise stated.

ESI-MS: The ESI-MS spectra were recorded on a TSQ-system composed of quadrupole mass spectrometer with an API (Atmospheric Pressure Ionization) inlet and a coupled HPLC (Spectra SYSTEM). The mass were detected with UV6000LP (Spectra SYSTEM).

Ninhydrin test. 5 mg of **P2** was dissolved in 5 mL CHCl_3 and 100 mg K_2CO_3 was added. After 1h stirring at room temperature the salt was filtered off and the organic solvent was removed under high pressure. The residue was dissolved in 2 mL abs. ethanol and 2 mL of 11.2 mM ninhydrin solution (0.1 g ninhydrin in 50 mL abs. ethanol) was added. Then the reaction mixture was refluxed at 90°C for 30 minutes. The solution turned blue and was analyzed via UV/vis spectroscopy at $\lambda_{\text{max}}=577$ nm. The formation of the Ruhemann's complex was observed and the presence of amine groups was verified.

Amine quantification by ^1H NMR-spectroscopy. 20 mg of polymer **P2** (4.7 μmol), 1.6 mg of 2-bromomethyl naphthalene (7.0 μmol), 1.4 mg of K_2CO_3 (10.3 μmol) and cat. amounts of NaI in 5 mL dry acetonitrile were refluxed for 72h. The salt was removed by filtration and the organic solvent was removed. The residue was dissolved in CHCl_3 and precipitated in cold diethylether. The polymer was purified by reprecipitation in cold diethylether (3x). The precipitated polymer was removed by centrifugation and dried under high pressure.

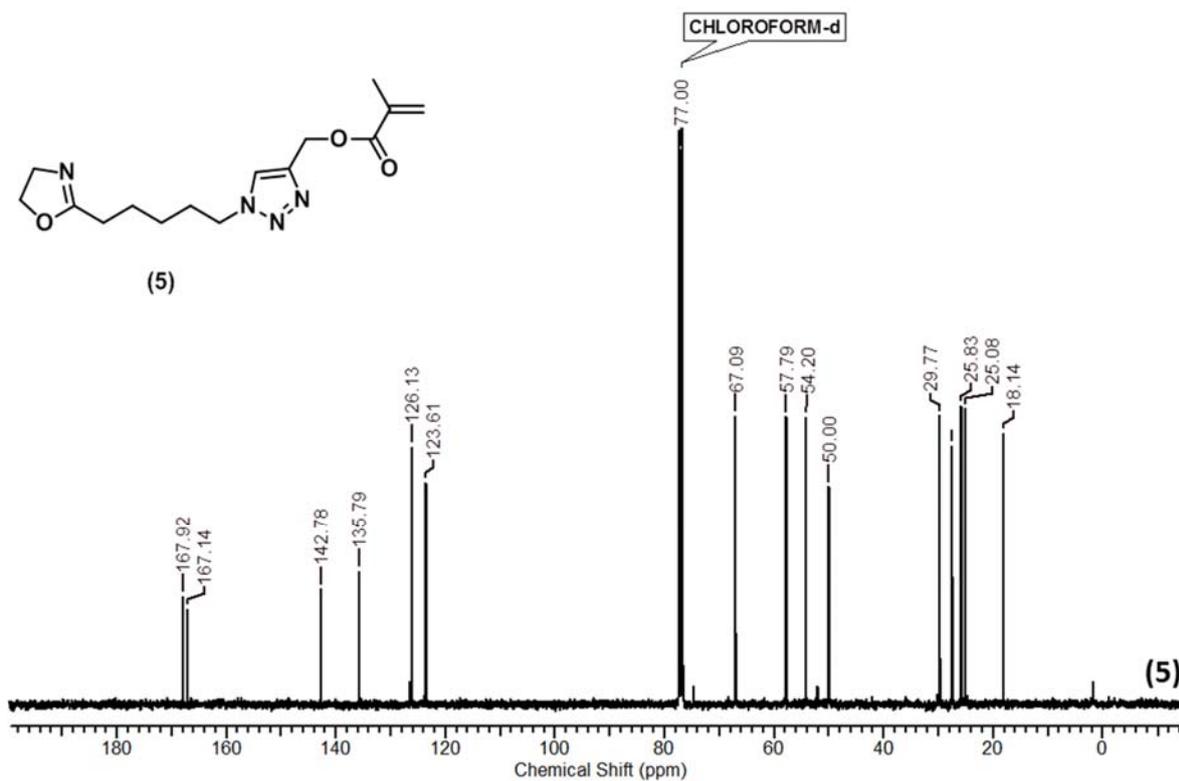


Figure S1. ^{13}C -NMR of 2-(5-pentyl-[(1,2,3-triazol)-4-yl-methacrylat]) oxazoline 5.

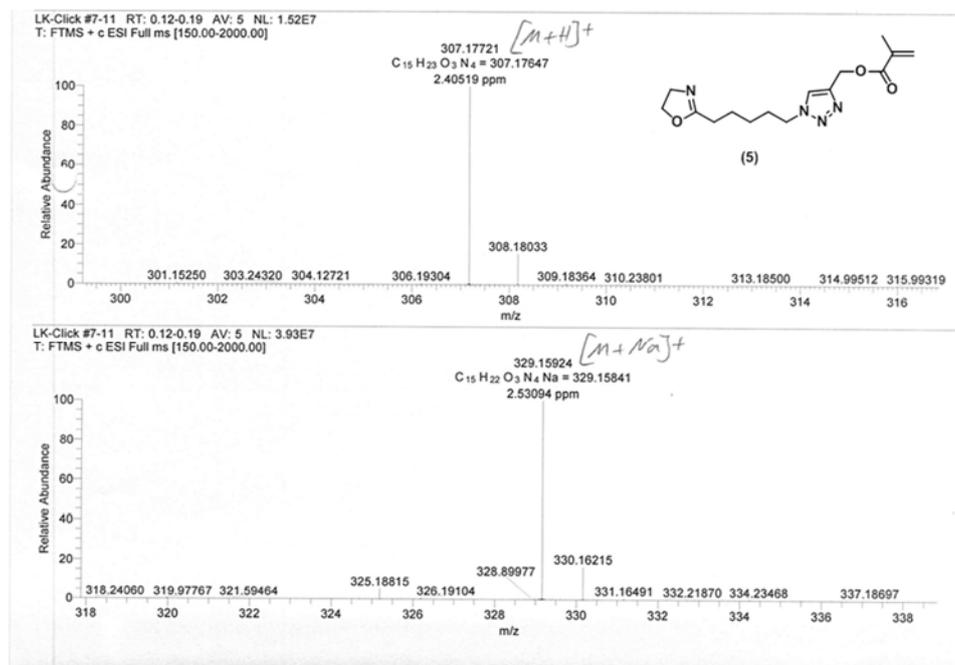


Figure S2. MS (ESI) of 2-(5-pentyl-[(1,2,3-triazol)-4-yl-methacrylat]) oxazoline 5.

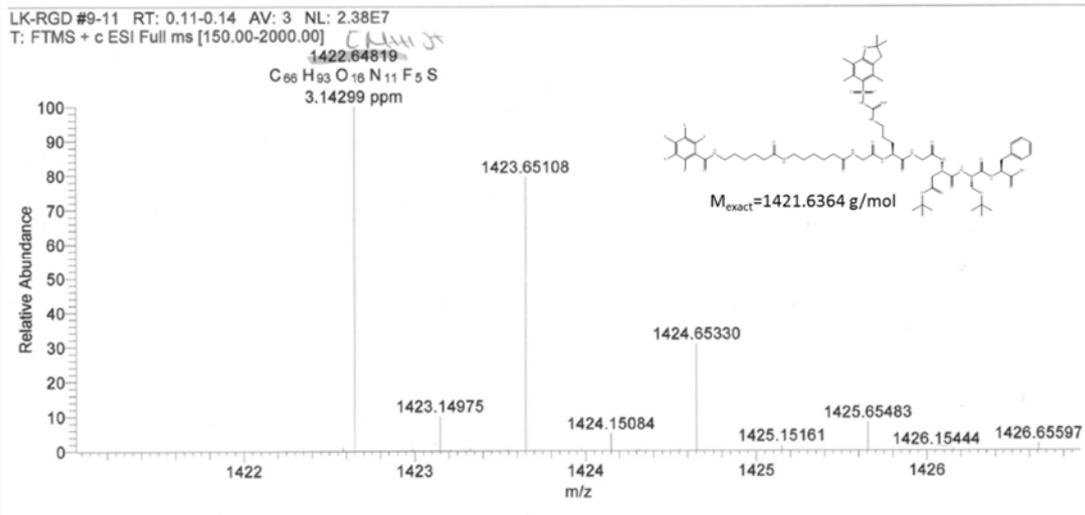


Figure S3. MS (ESI) of the peptide sequence GRGDS6Ahx6AhxF.

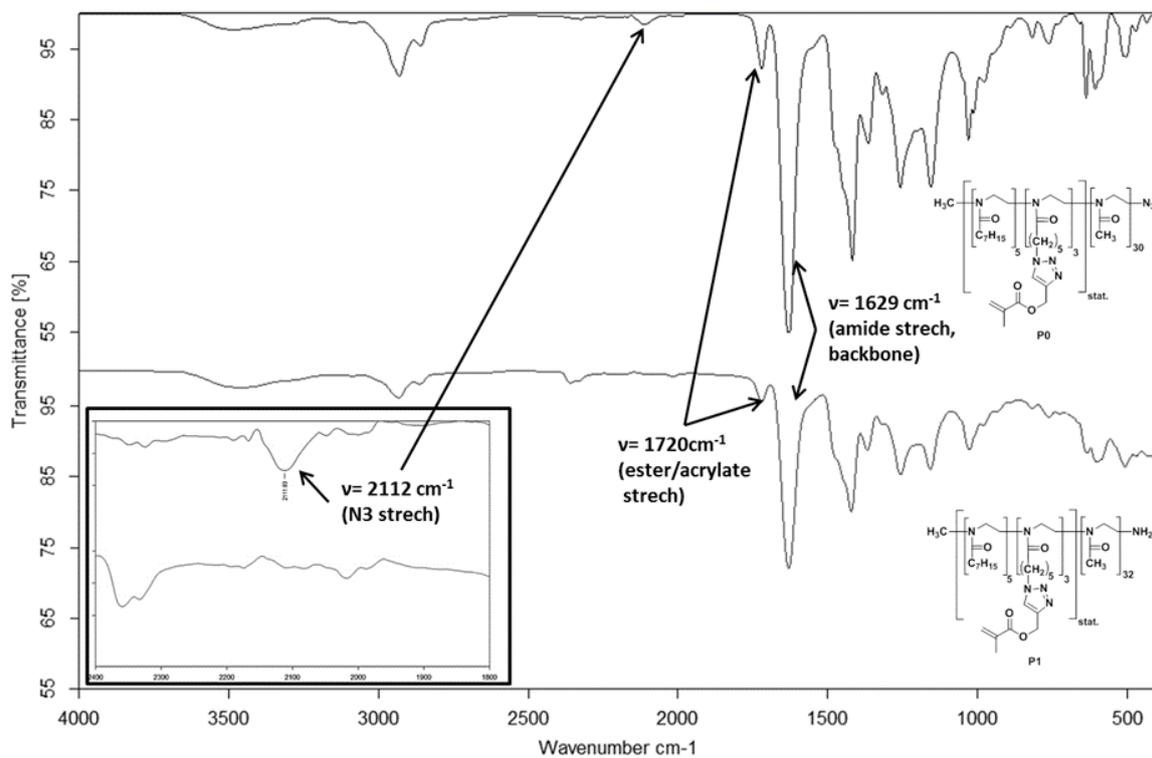


Figure S4. FTIR spectra of P1 and P2.

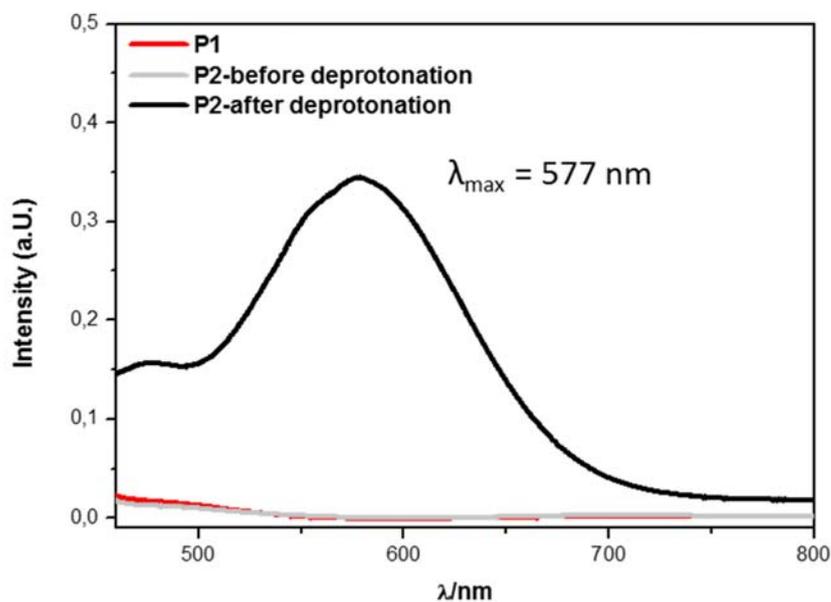


Figure S5. A) Ninyhdrin test of **P2** to determine the primary amino end group.

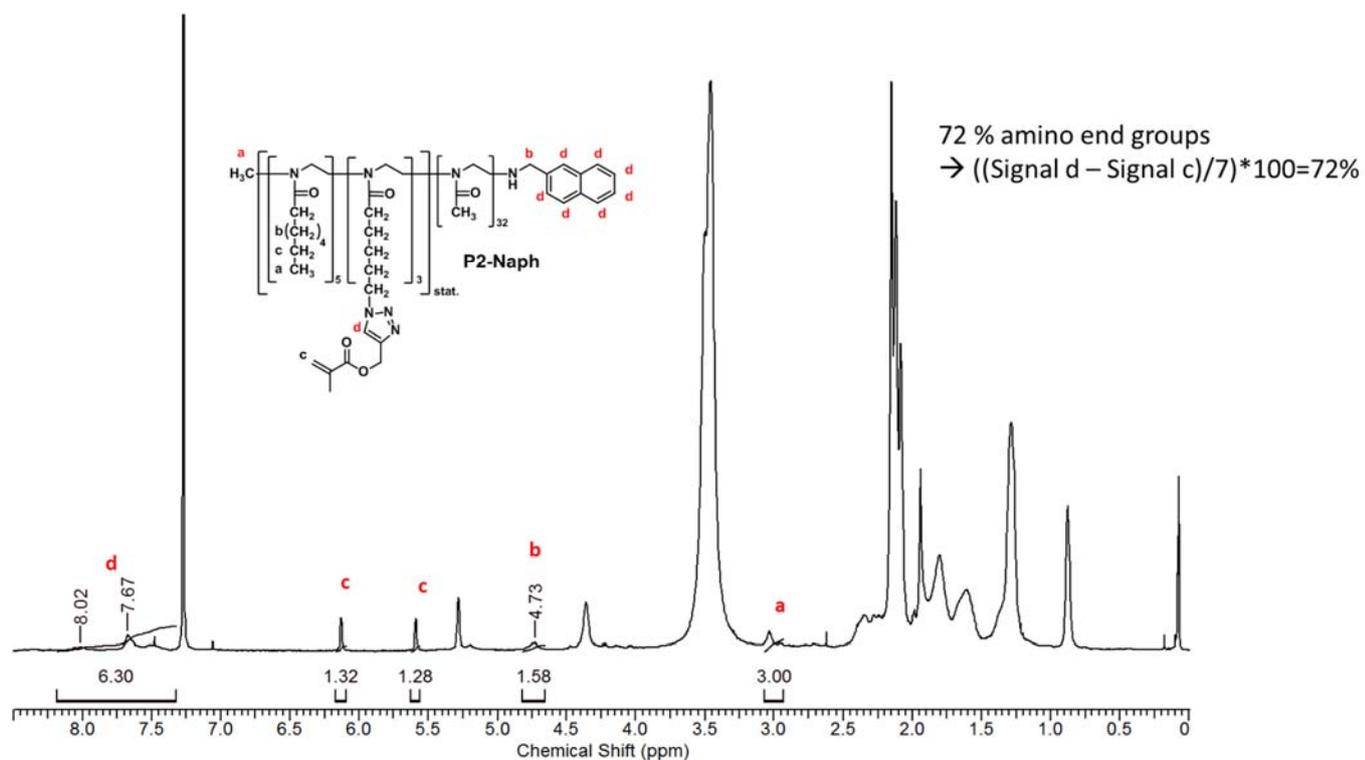


Figure S5. B) Endgroup modification of **P2** with 2-(bromomethyl)naphthalene and characterization by ^1H NMR spectroscopy

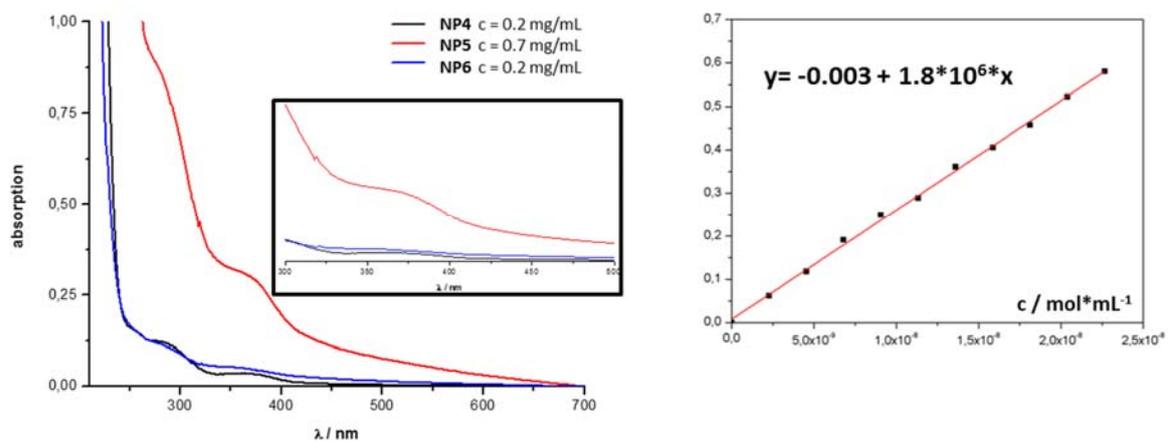


Figure S6. UV/vis spectra of NP4-NP6 FA (left) and the calibration of folic acid in 1 M NaOH solution (right).

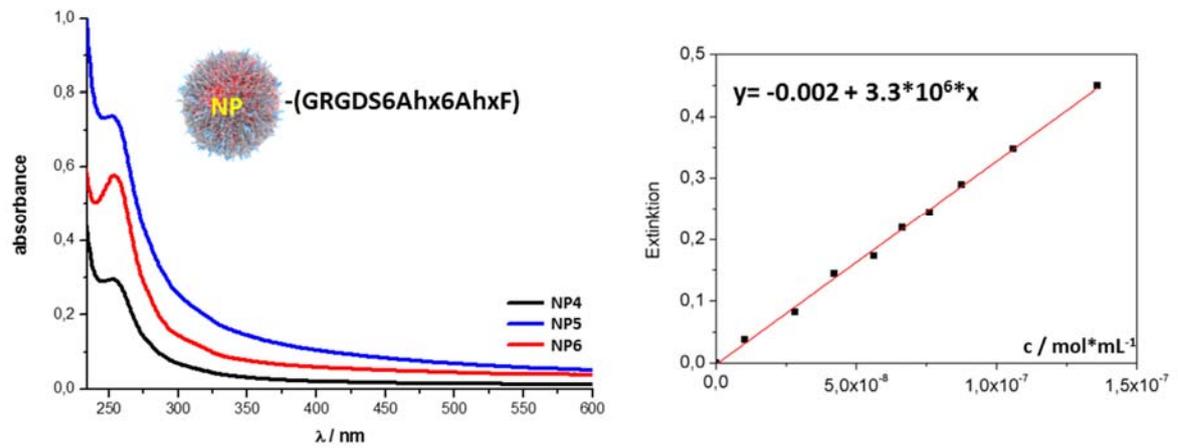


Figure S7. UV/vis spectra of NP4-NP6 P (left) and the calibration of RGD-peptide in water (right).

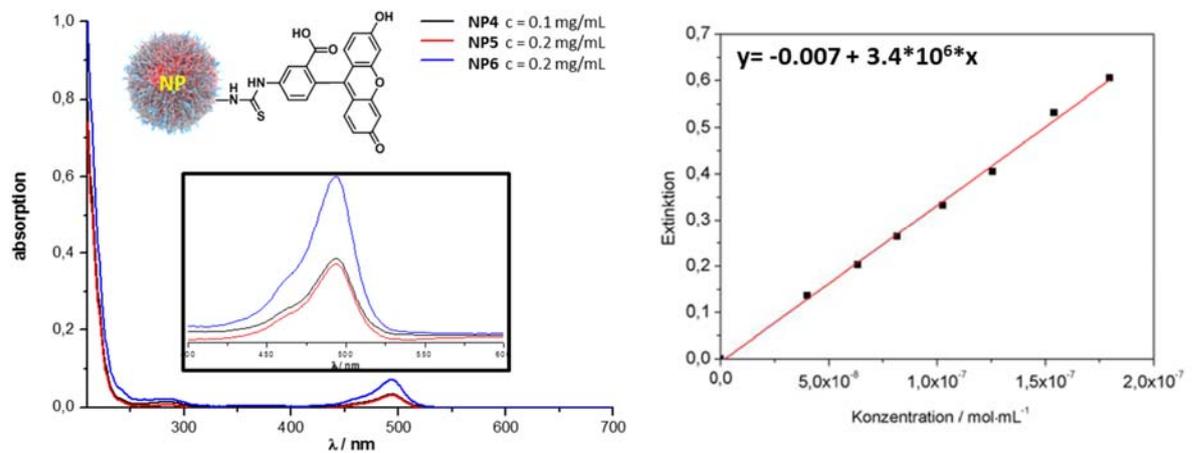


Figure S8. UV/vis spectra of NP4-NP6 FITC (left) and the calibration of FITC in 0.1 M NaHCO $_3$ solution (right).

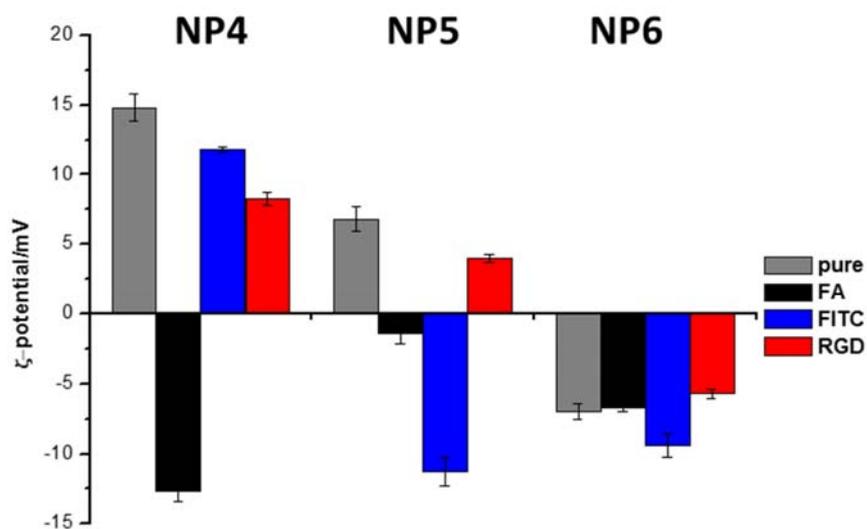


Figure S9. Zeta potential of the pure nanoparticles NP4 – NP6 before and after surface modification.

Table S1. Change in particle volume in water or methanol for the particles NP1 – NP6.

Nanoparticle	r_h / nm (H ₂ O)	V / nm ³ (H ₂ O)	r_h / nm (MeOH)	V / nm ³ (MeOH)	Volume shrinkage / %
NP1	12.815	8 815	10.4	4 712	-47
NP2	23.52	54 499	20.74	37 369	-32
NP3	36.32	201 684	33.995	164 563	-18.5
NP4	13.075	9 363	9.33	3 402	-64
NP5	20.06	39 126	18.9	28 280	-28
NP6	35.125	181 525	34.69	174 864	-3.7

Particle volume has been calculated as follows: $V = \frac{4}{3}\pi r^3$

Table S2. Zeta potential data of the pure nanoparticles **NP4** – **NP6** before and after surface modification.

Nanoparticle	ζ-potential / mV (pure nanoparticles)	ζ-potential / mV (after modification)	
NP4	14.84 ± 0.94	Folic acid	-12.64 ± 0.79
		FITC	11.84 ± 0.17
		RGD	8.30 ± 0.48
NP5	6.83 ± 0.88	Folic acid	-1.36 ± 0.86
		FITC	-11.23 ± 1.01
		RGD	3.96 ± 0.29
NP6	-9.08 ± 0.50	Folic acid	-6.66 ± 0.34
		FITC	-9.09 ± 0.83
		RGD	-5.70 ± 0.31