

## Electronic Supplementary Information (ESI)

### 1: Methods

Methods: NMR spectra were recorded on a Jeol NMR instrument with 500MHz magnetic field at 30 °C. The transmission electron microscope was a ZEISS Libra 120 that operates with 120 kV. TEM samples were prepared at room temperature by dropping a certain solution on a copper grid, afterwards the solvent was evaporated and the solid was analysed. Electron diffraction (ED) was carried out during TEM analysis. Scanning electron microscope (SEM) images were acquired using a Zeiss field-emission (FE)-SEM Auriga Crossbeam operating at 10 kV. Furthermore, a Zeiss GeminiSEM 500 was used operating at 5 kV. Samples were prepared using a silicon wafer in the particle solution and increasing the temperature to 70°C to induce the precipitation. Recrystallization was achieved by removing the solvent, adding new water, using a VWR ultrasound cleaning bath USC 300 TH and increasing the temperature afterwards to repeat the superstructure formation. Silicon wafers were used as received, no sputtering was used. Energy-dispersive X-ray spectroscopy (EDX) measurements were recorded on a Hitachi TM3000 Tabletop SEM using 15 kV acceleration voltage and a Quantax EDX detector. The powder X-ray diffractograms were recorded on a Bruker AXS D8 Advance powder diffractometer with  $\text{CuK}_\alpha$  radiation. DLS particle analysis was carried out in a Malvern Zetasizer

### 2: Experimental procedure

#### 2.1: Particle synthesis and superstructure formation

All syntheses were performed in oxygen-free  $\text{N}_2$ -atmosphere at room temperature. To synthesize MNPs, 39 mg of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.14 mmol) and 14 mg of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (0.07 mmol) were dissolved in 10 mL MilliQ water and degassed for 30 min. Afterwards, 0.15 mL of  $\text{NH}_4\text{OH}$  (25%wt.) were added. The immediately formed black MNPs were washed to neutrality and analysed via TEM and PXRD measurements.

For modification during synthesis, 25 mg of the polymer  $\text{EOEOVE}_{100}\text{-AEVE}_{68}$ , 39 mg of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.14 mmol) and 14 mg of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (0.07 mmol) were dissolved in 10 mL MilliQ water and degassed for 30 min. Afterwards 0.15 mL of  $\text{NH}_4\text{OH}$  (25%wt.) was added. The instantly obtained PMNPs were neutralized by washing and analysed via TEM and turbidity measurements.

Post-synthesis modification and superstructure formation:

To 0.5 mL of a 1 mM polymer  $\text{EOEOVE}_{100}\text{-AEVE}_{68}$  solution, 0.03 mmol MNPs were added and the solution mixed via ultra-sonication. Afterwards, 1 mL of a 3 mM PMNP solution was used to induce the formation of superstructures onto a silicon wafer. Slow precipitation was provided by increasing the temperature to 65 °C, a temperature slightly above the LCST of the polymer. The superstructure formation occurred after 3 days of keeping the temperature at 65 °C. Superstructures were analysed via SEM measurements.

#### 2.2: Polymer synthesis

Synthesis of block copolymer poly( $\text{EOEOVE-}b\text{-AEVE}$ ) was performed under a dry nitrogen atmosphere. A typical example for the sequential block copolymerization of 2-(2-ethoxy)ethoxyethyl vinyl ether (EOEOVE) and 2-phthalimidoethyl vinyl ether (PIVE) is as follows. The reaction was initiated by the addition of a  $\text{Et}_{1.5}\text{AlCl}_{1.5}$  solution (1.20 mL; 200 mM in toluene) with a syringe into a mixture of EOEOVE (0.39 mL), 1,4-dioxane (0.52 mL), 2,6-di-*tert*-butylpyridine (0.12 mL; 100mM in toluene), and cationogen [ $\text{CH}_3\text{CH}(\text{O}i\text{Bu})\text{OCOCH}_3$ ] (0.60 mL; 40 mM in toluene) in toluene at 0 °C. When EOEOVE had been consumed almost quantitatively, a mixture solution (6.0 mL) of PIVE (300 mM) and 2,6-di-*tert*-butylpyridine (8.0 mM) in  $\text{CH}_2\text{Cl}_2$  at 0 °C was added to the polymerization mixture. The reaction was quenched with prechilled methanol containing a small amount of aqueous ammonia solution (3.0 mL; 0.1 wt%), to yield the block copolymer poly( $\text{EOEOVE-}b\text{-PIVE}$ ) ( $M_n = 16.9 \times 10^3$ ,  $M_w/M_n = 1.13$ ). To remove the pendant phthalimide groups, the phthalimide-containing copolymer (0.45 g) was dissolved in a mixture of 1,4-dioxane and methanol (2:1 v/v; 27 mL), and hydrazine monohydrate (0.35 mL) was added. Afterwards, the solution was heated to reflux while stirring for 3 h, and then neutralized with 0.5M HCl aq. The insoluble byproduct (phthalhydrazide) was removed by filtration. The filtrate was neutralized with 1.0 M aqueous sodium hydroxide, and the polymer product was purified by dialysis against distilled water for at least 2 days followed by Milli-Q water for a day (MWCO of dialysis tubes is 12000-14000 g/mol). After purification, a white powder, polymer poly( $\text{EOEOVE-}b\text{-AEVE}$ ) (100:68), was obtained. We can indicate the preparation of block copolymer by  $^1\text{H}$  NMR and GPC. SI-Figure 1 a) shows the MWD of poly( $\text{EOEOVE}$ ) obtained by the first-stage polymerization of EOEOVE. The homopolymer had a very narrow

MWD ( $M_w/M_n=1.10$ ). After addition of PIVE, the second-stage polymerization of PIVE proceeded smoothly. As shown in SI-Figure

1 a), a clear shift in the MWD to a higher MW region was observed while maintaining a narrow MWD ( $M_w/M_n=1.13$ ). The polymer structure was confirmed by  $^1\text{H}$  NMR spectroscopy. The spectrum of the deprotected block copolymer (SI-Figure 1 b) contained both segments of EOEOVE and AVEE (mole ratio of 100:68), and no peaks associated with side reactions. All these results indicated that the first- and second-stage polymerizations proceeded in a living manner, to give the block copolymer selectively. The LCST was determined by multi-wavelength turbidity measurements of a 0.3 mM polymer solution selectively (SI-Figure 2). The turbidity measurements resulted in a LCST of 48 °C.

$^1\text{H-NMR}$  (500 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 1.26$  (t,  $^3J=7,3$  Hz, h), 1.74-2.00 (m, a,i), 3.11 (m, l), 3.63-3.80 (m, b-g,j,k).

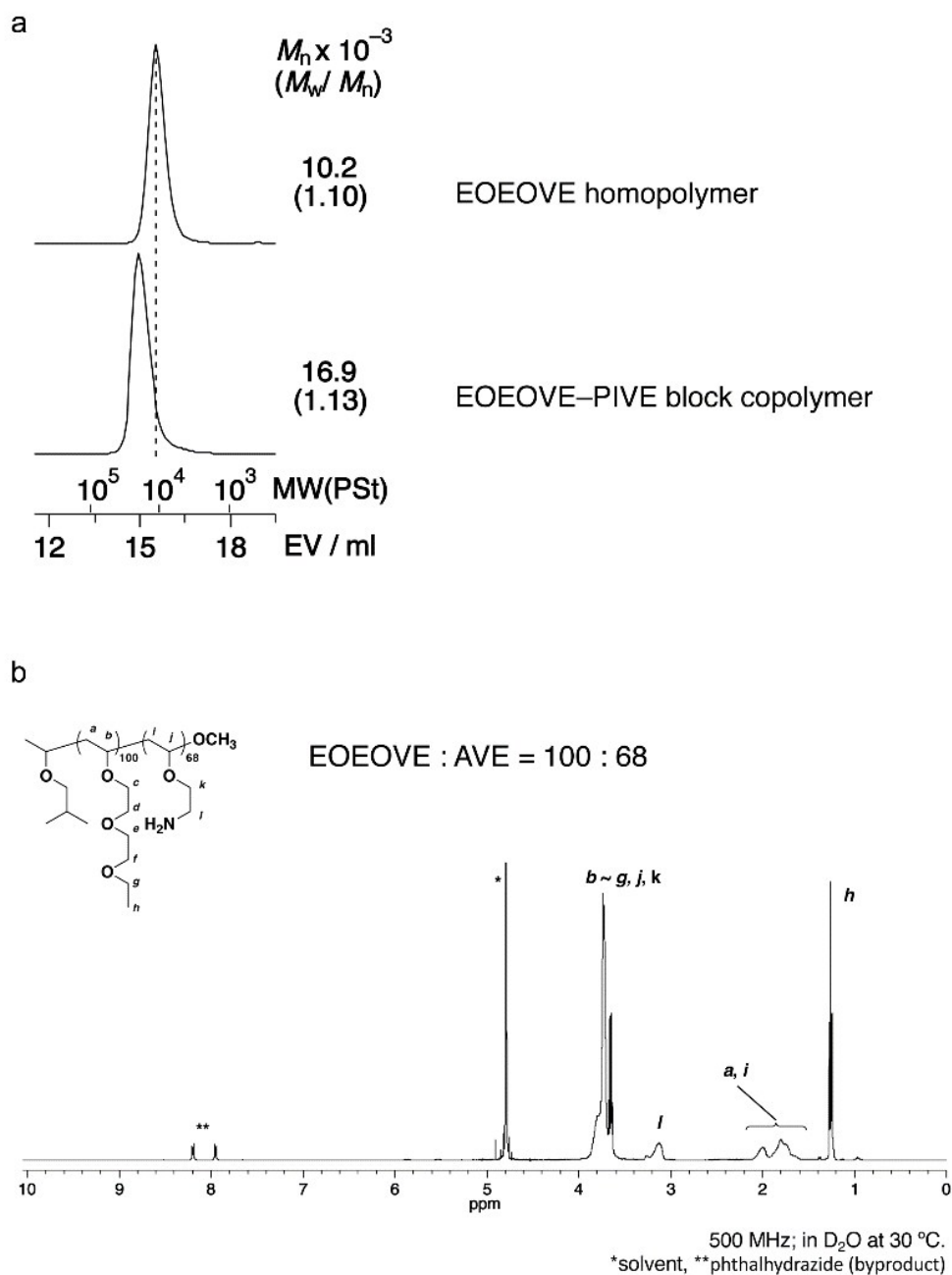


Figure S1 a: GPC measurements and b:  $^1\text{H}$  NMR spectrum of polymer EOEOVE<sub>100</sub>-AVEE<sub>68</sub>.

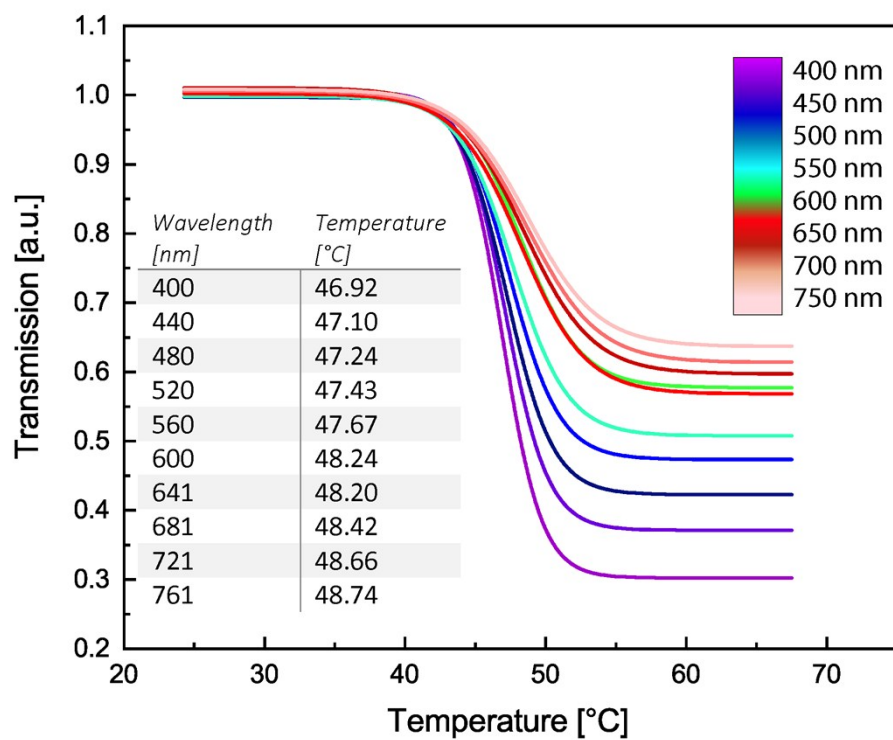


Figure S2: Temperature dependent multi-wavelength turbidity measurements of pure polymer in water.

### 3: Supplementary measurement data

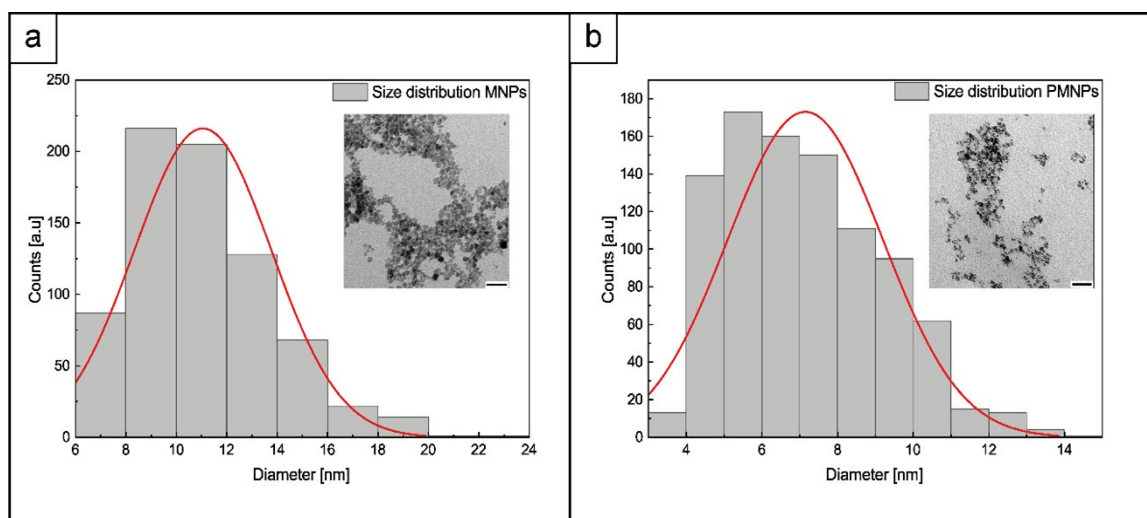


Figure S3: Size distribution of TEM measurements, a: MNPs:  $11.0 \text{ nm} \pm 2.6 \text{ nm}$ , b: PMNPs:  $7.1 \text{ nm} \pm 2.0 \text{ nm}$ , inset scale bar: 50 nm.

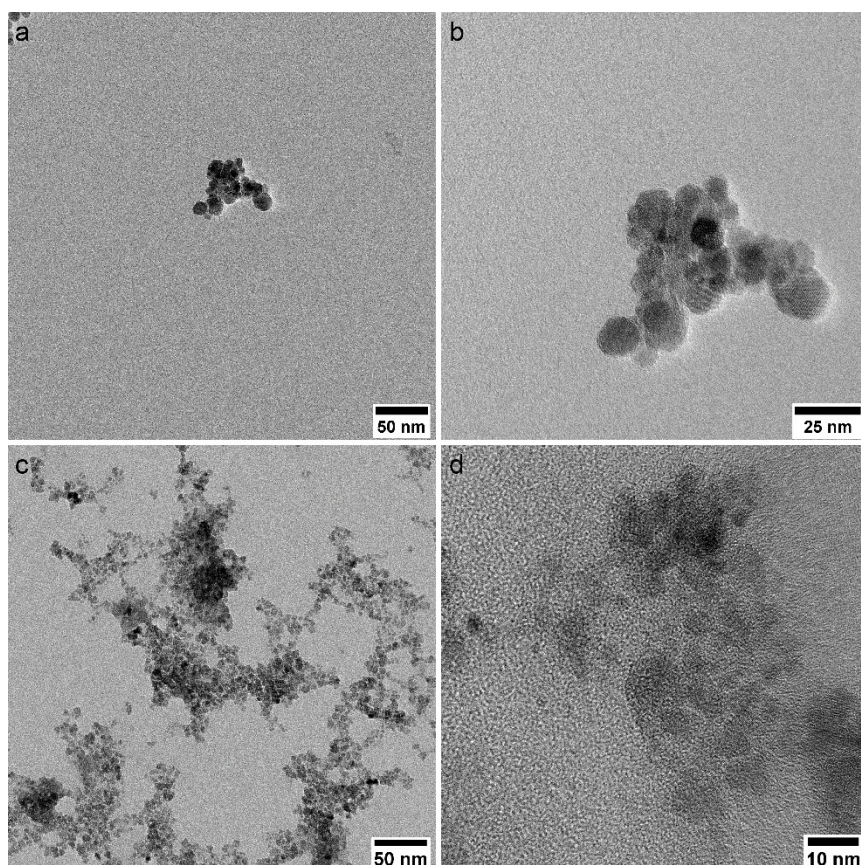


Figure S4 a, b: HR-TEM images of MNPs without polymer influence, c, d: HR-TEM images of synthesis functionalized PMNPs.

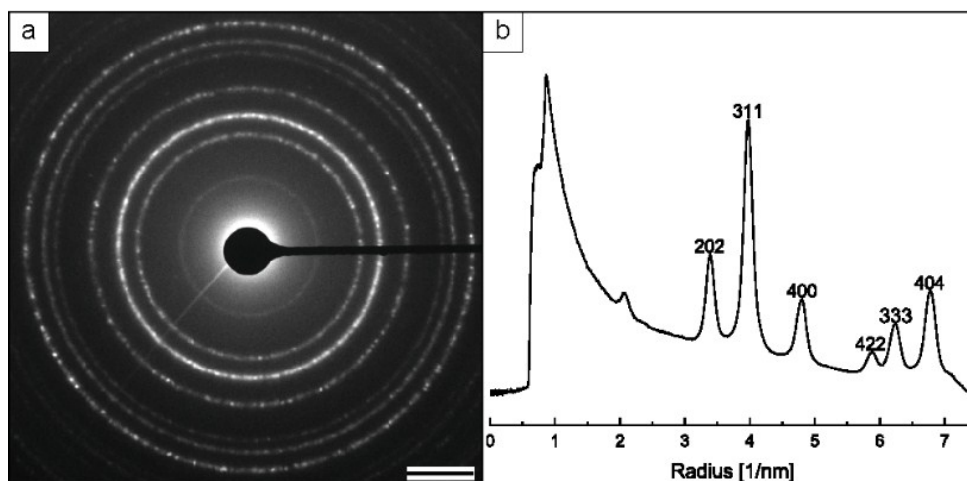


Figure S5 a: Electron diffraction (ED) pattern, scale bar  $2 \text{ nm}^{-1}$  and b: ED analysis of MNPs.

DLS measurements were performed to determine the stability of the different particles (SI-Table 1, SI-Figure 4: without polymer influence, synthesis functionalized and post-synthesis functionalized):

The DLS data show the particle sizes after different times at room temperature to analyse the stability in aqueous phase. The sizes are number weighted values, calculated out of the intensity weighted values, which are actually measured by DLS. A trend is clearly visible. PMNPs are both stable for hours. If the error bars (calculated by averaging five measurements) are considered, it can be seen that the measurements of post-synthesis functionalized particles show smaller errors. Also, the sizes are not changing much indicating the post-synthesis modified PMNPs as the most stable particles. Also considering the autocorrelation functions, the correlation curves are most reasonable for the post-synthesis functionalized particles. Considering the correlation function of the during synthesis functionalized PMNPs, fluctuations in the correlation function are visible. Despite the fluctuations a stability over 24 hours can be clearly shown. Comparing the results with MNPs without polymer influence, the trend clearly shows agglomeration followed by precipitation of the MNPs. The numerical values then show small particles in solution, but if the correlation function is taken into account, it is clear that agglomeration takes place between 1.5 h and 5 h, which increases the correlation function and leaves a few particles in solution due to precipitation of the particles, which reduces the amplitude of the correlation function to 0.1. Although these data provide reasonable results for stability, size distributions should be treated with caution due to the  $d^6$ -dependency of the scattering intensity in light scattering experiments.

Table S1: Time dependent mean number-weighted size values of synthesis modified PMNPs, post-synthesis PMNPs and MNPs without polymer influence.

<i>Time [h]</i>	<i>Synthesis modified PMNPs Number-weighted Size [nm]</i>	<i>Post-Synthesis modified PMNPs Number-weighted Size [nm]</i>	<i>MNPs without Polymer Number-weighted Size [nm]</i>
0	$150 \pm 47$	$55 \pm 13$	$740 \pm 332$
0.5	$58 \pm 10$	$56 \pm 9$	$1541 \pm 216$
1.5	$72 \pm 17$	$54 \pm 20$	$1084 \pm 298$
5	$113 \pm 24$	$47 \pm 13$	$224 \pm 156$
24	$98 \pm 38$	$44 \pm 16$	$86 \pm 58$

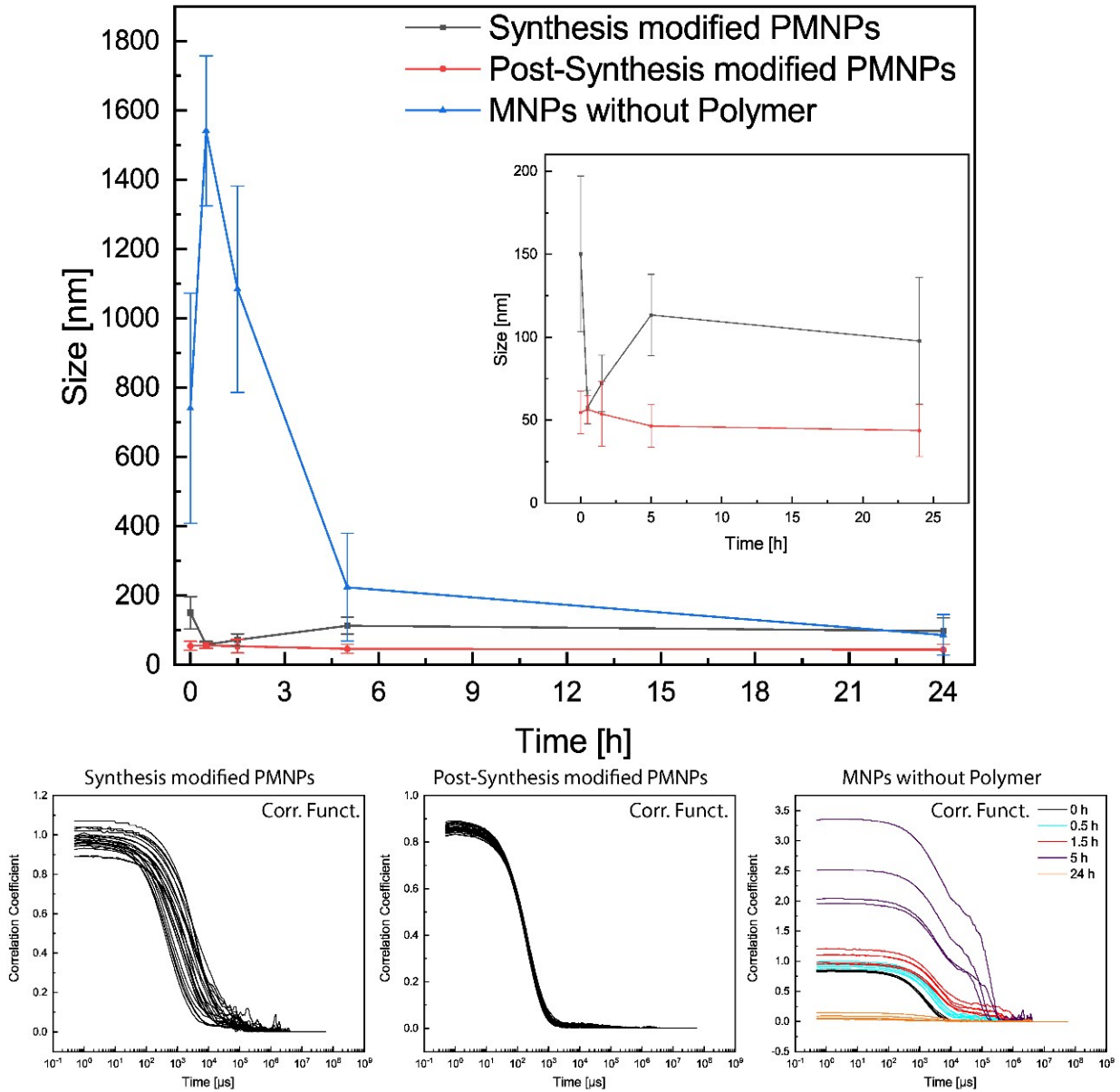


Figure S6: DLS measurements. Top: Time dependent Number-weighted size values of synthesis modified PMNPs, post-synthesis PMNPs and MNPs without polymer influence. Bottom: corresponding correlation functions.

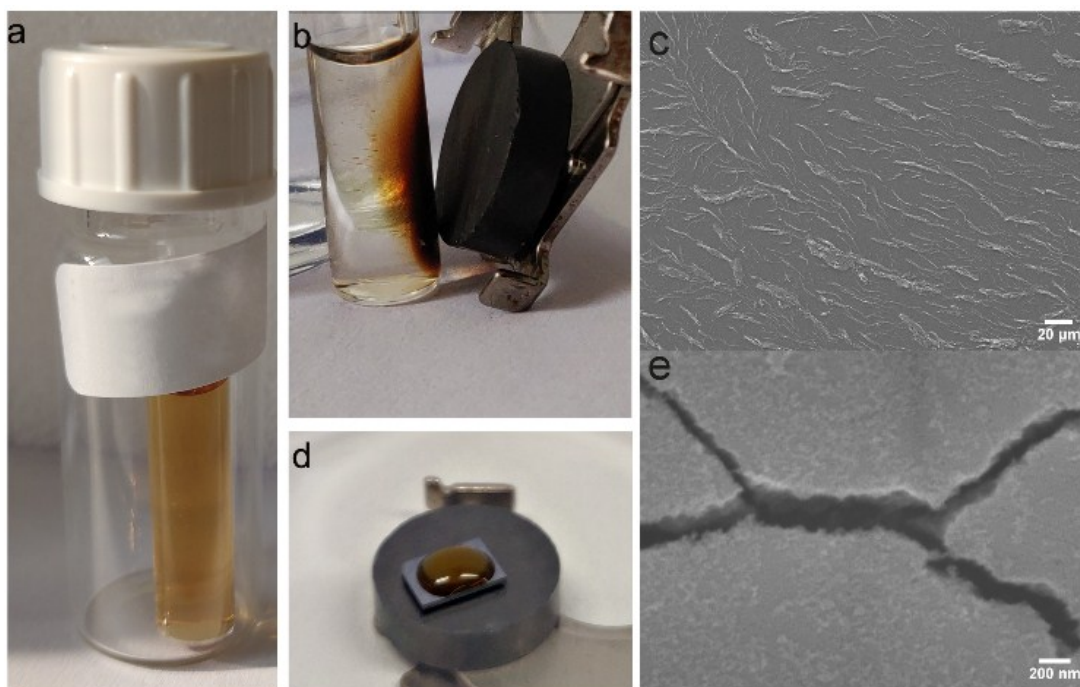


Figure S7 a: Stable PMNP solution, b: PMNPs precipitated in an external magnetic field, c: particles precipitated in magnetic field lines, d: Drop of stable PMNP solution on silicon wafer in an external magnetic field to obtain external field directed self-assembled superstructures, e: higher magnification showing dense packing of PMNPs.

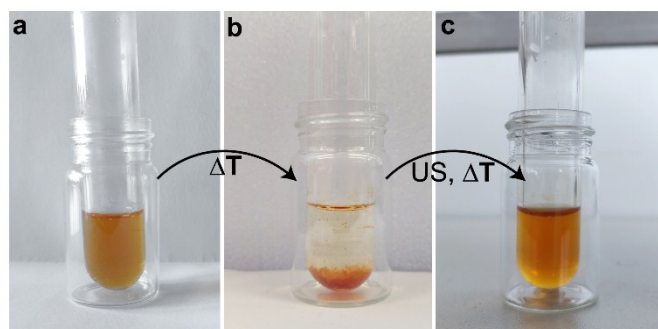


Figure S8: Precipitation and dissolution cycle. a: stable PMNP dispersion, b: after increasing temperature to 70 °C for 30 min aggregation is induced, c: reversible dissolution of aggregates using ultrasound and room temperature.

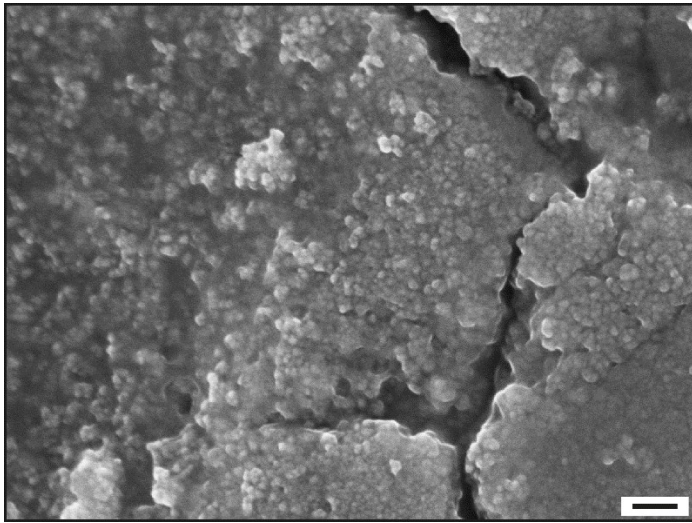


Figure S9: Higher magnification SEM image of densely packed PMNPs after recrystallization, scale bar: 100 nm.

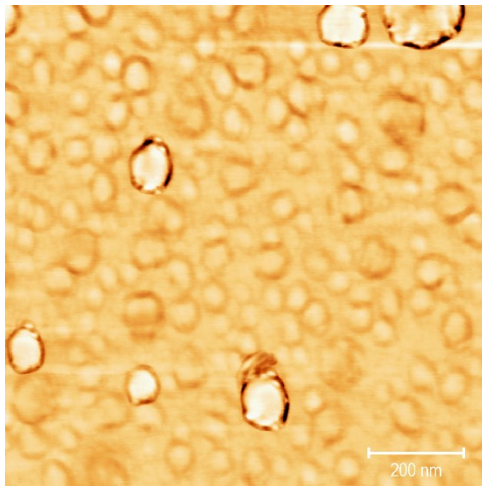


Figure S10: Phase contrast image of synthesis functionalized PMNPs measured by AFM.



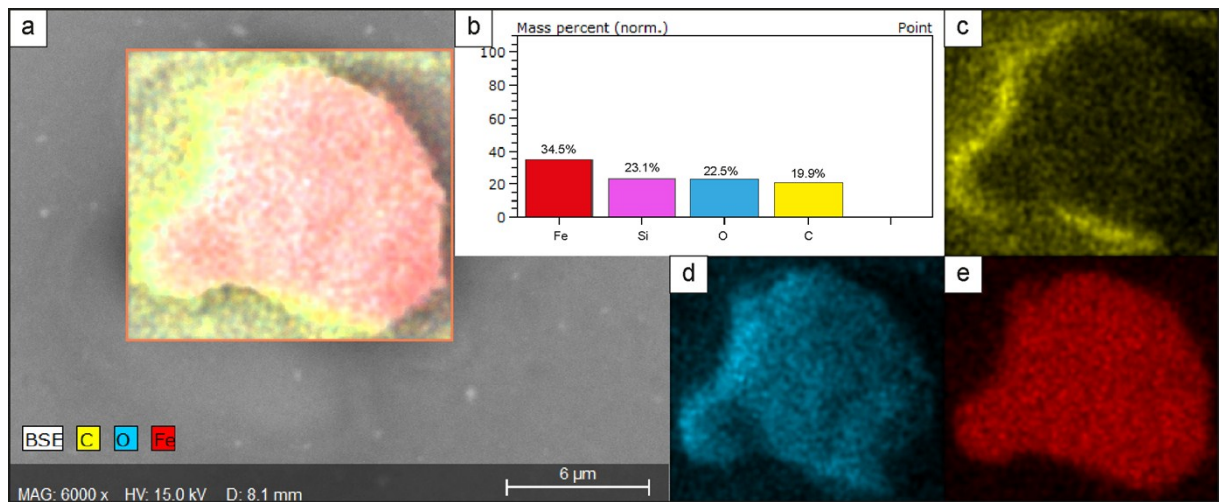


Figure S11: Energy-dispersive X-ray spectroscopy (EDX) of temperature-induced PMNP superstructures a: overview, b: mass percent distribution of iron, silicon (due to a silicon wafer), oxygen and carbon, c: yellow-colored: carbon indicating organic layer, d: blue-colored: oxygen, e: red-colored: iron.