Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

The desalting/salting pathway: a route to form metastable aggregates with tuneable morphologies and lifetimes

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Form factor of PAA@γ-Fe_2O_3 nanoparticles in solution.

It has been measured in dilute solution (0.05%v/v). It was fitted by a model of a pearl necklace with spherical pearls with the *Sasview* software (https://www.sasview.org). The mean radius of the spheres is R_{mean}= 4.7 nm with a lognormal distribution (σ = 0.22), the number of spheres/necklace is 4 and the distance between spheres 1.6 nm (*Macromol. Symp.* 211 (2004) 25-42). Such distance correspond to the PAA shells. Please note that this shell was not explicitly modelled because its scattering is negligible with respect to those of γ-Fe_2O_3 nanoparticles for contrast reasons (see Materials and Methods in main text).

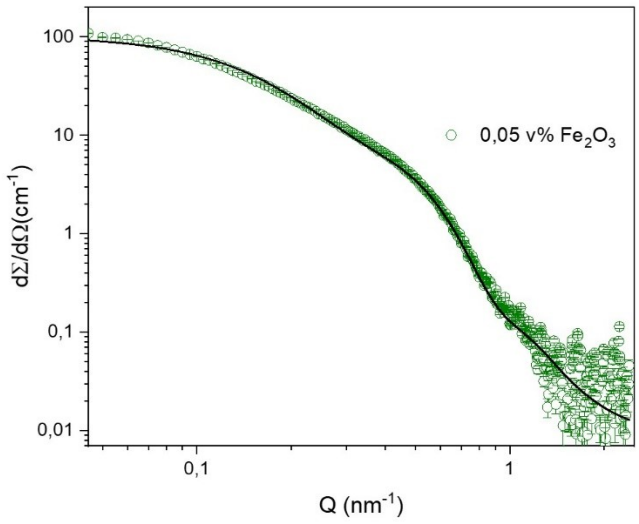

Figure S1. Experimental Form factor of PAA@γ-Fe_2O_3 nanoparticles (green circles), fitted by a pearl necklace model (black continuous line).

Parameters of the fits of the structure factor of the complexes for I_{target} ≥ 0.5 M.

The structure factor has been fitted by the sum of a Percus-Yevick structure factor and a *k* q^{-4} term, where *k* is a constant factor, in order to account for the q^{-4} Porod behaviour in the low q region of the experimental scattering curve.

I_{target} (NH_4Cl mol/L)	R_{HS} (nm)	Φ_{HS}	*k* (Porod prefactor)
0.5M	5.5±0.6	0.33±0.09	3.10±0.45e^{-09}
0.52M	5.6±0.6	0.31±0.09	2.45±0.45e^{-09}
0.56M	5.6±0.7	0.26±0.08	1.73±0.45e^{-09}
0.6M	5.7±0.9	0.195±0.07	1.40±0.45e^{-09}

Table S1. Parameters of the fits of the structure factor of Figure 4.b in the main text.

Evolution of the correlation peak of the structure factor as function of I_{target}.

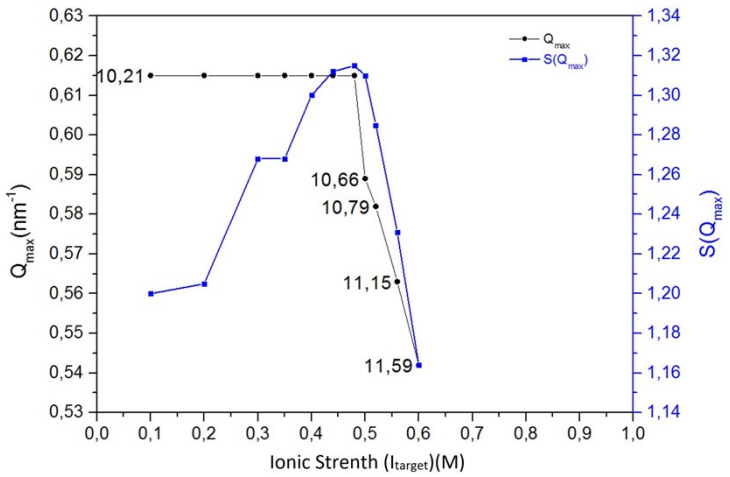

Figure S2. (a) Plot of Q_{max} and $S(Q_{max})$ versus target ionic strength (I_{target}), as calculated from the SAXS scattering curves of the PAA@γ-Fe_2O_3 nanoparticles/PDADMAC system upon desalting from 1M NH_4Cl by quenching at Z = 0.2. The numbers with the Q_{max} data points represent the interparticle distance d (nm) calculated from the peak position ($d=2\pi/Q_{max}$).

Determination of the inner structure of the complexes formed upon quenching at different times after quenching

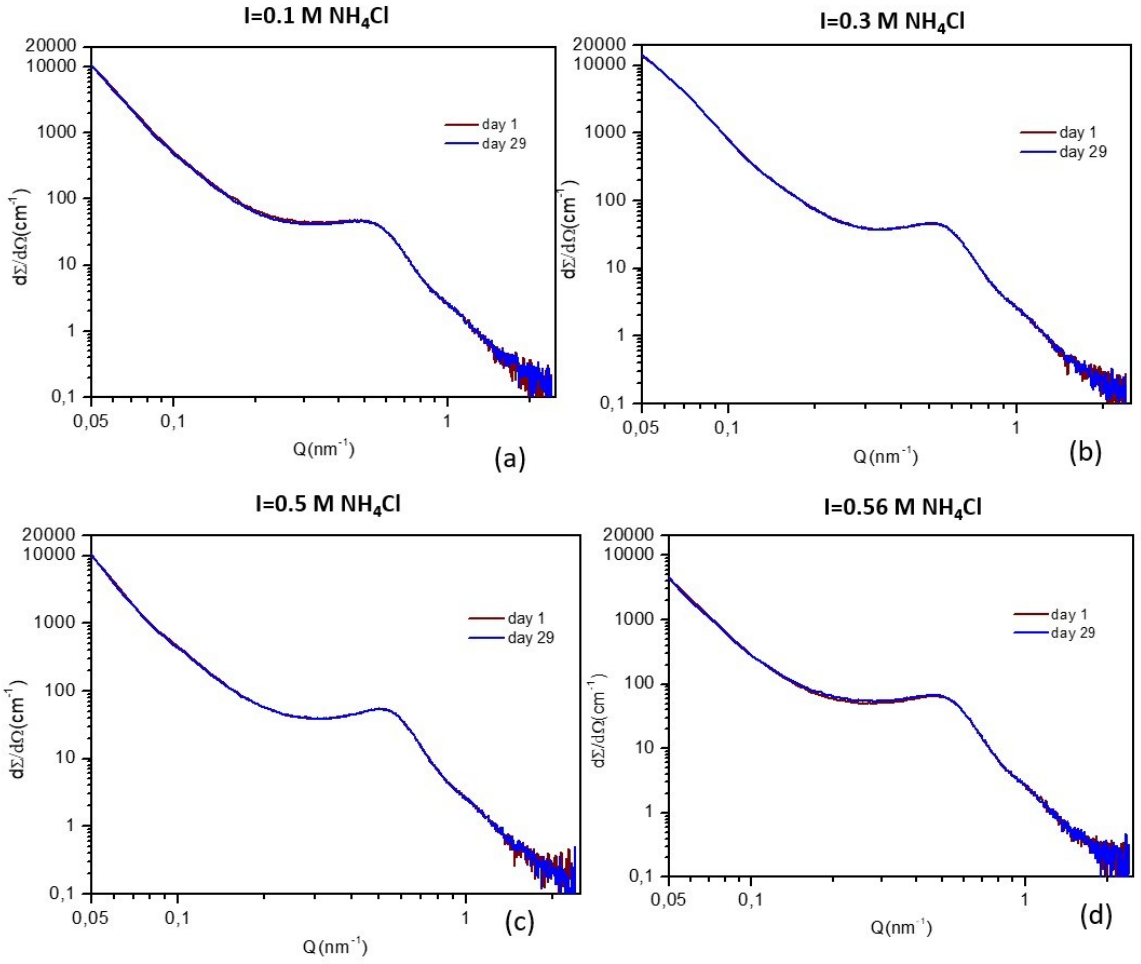

Figure S3. Comparison of the inner morphology of the complexes obtained by SAXS after different elpased times after quenching along the desalting/salting pathway in the case of the quenching mixing pathway at Z = 0.2 for various I_{target}: (a) I_{target} = 0.1 M; (b) I_{target} = 0.3 M; (c) I_{target} = 0.5 M; (d) I_{target} = 0.56 M.