Supporting Information
Model-based Design and Synthesis of Ferrocene Containing Microgels†

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Experimental

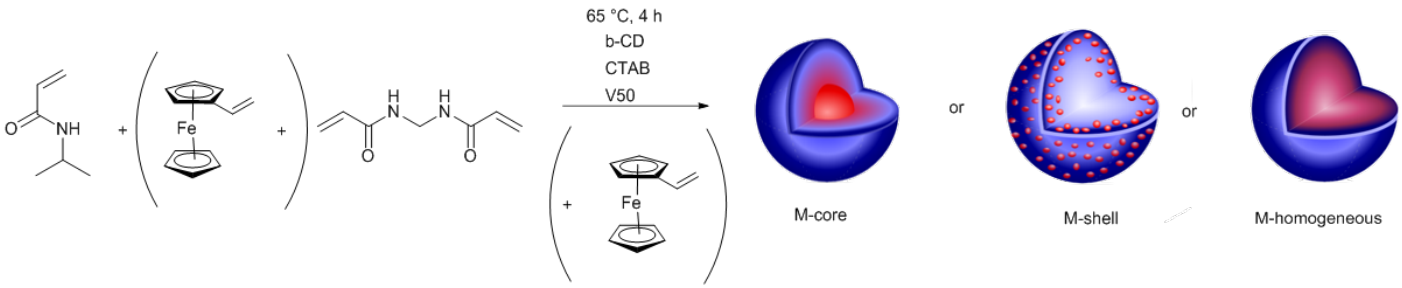
Synthesis

Synthesis of M-middle - VFc-rich intermediate shell

1.347 g NIPAM (0.012 mol), 0.108 g BIS (0.70 mmol), 5 mol %), 0.004 g CTAB (12.5 % of critical micelle concentration 0.92 mmol) were dissolved in 80 mL water. The solution was purged with nitrogen and heated to 65 °C for 1 hour. 0.054 g V50 (0.20 mmol were dissolved in 5 mL and degassed with nitrogen for at least 30 min 0.104 g Vinylferrocene (0.50 mmol) and 0.642 g CD were dissolved in 15 mL (M-shell) or 7.5 mL (M-homogeneous) bidestilled water, heated to 70 °C and degassed with nitrogen for at least 45 min. The reaction was started by injecting the degassed initiator solution into the reaction flask. The hot vinylferrocene solution was added after 75 s. The reaction was continued for 4 h and aborted by letting the reaction solution cool down to room temperature. The solution was filtered over glass wool and purified by dialysing against water (MiliQ, MWCO 12-14 kDa, 110 mL reaction volume vs 1.6 mL water) for 2 weeks.

^{1}H-NMR

^{1}H-NMR spectra were recorded from 10 to 20 mg/L% microgel solutions in DMSO with a 400-MHz Bruker DRX 400 NMR spectrometer at room temperature. The chemical shifts are shown in parts per million downfield from the TMS standard using DMSO as reference.



Scheme S1 Schematic illustration of P(NIPAM-*co*-VFc) microgel synthesis.

Results

^{1}H-NMR spectra of the synthesised and purified microgels (Scheme S1 and Figure S1) show the absence of any *beta*-cyclodextrin after dialysis. The colloidal stability of the microgels is ensured through the PNIPAM network. Whereas during the M-core synthesis no aggregates are formed, some aggregates are found during the M-shell and M-homogeneous synthesis. This small amount of aggregates was removed through filtering over glass wool subsequent to the synthesis.

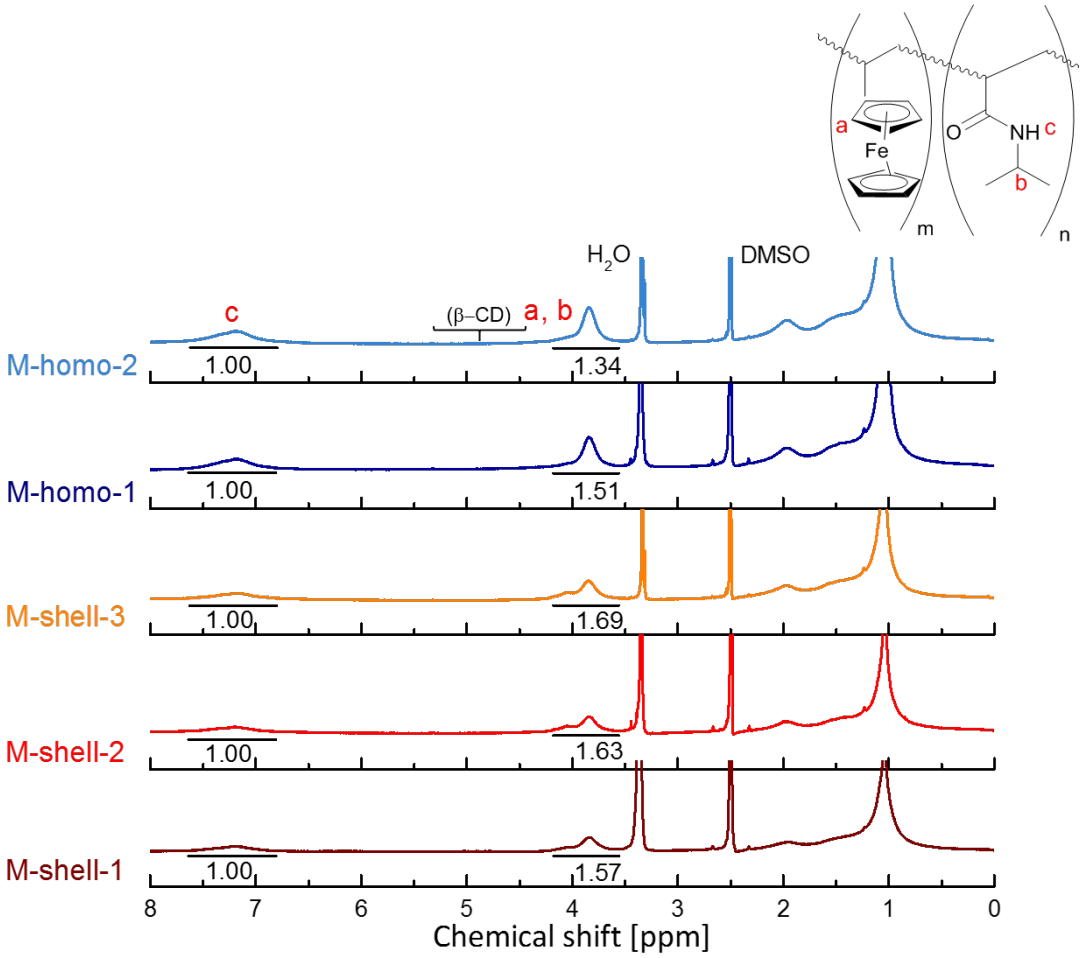


Fig. S1 1H-NMR of synthesised P(NIPAM-*co*-VFc) (peaks are assigned according to the shown polymer structure).

Iron profiles - EELS line scans

Iron profiles for the M-shell microgels confirm the reproducibility of the microgel architecture. All scans show peaks arising from the clustered iron spots. Overall, the iron content is rather low reaching the detectivity limit of the instrument setup explaining slight variations in the different spectra. In case of the M-homogeneous microgels the intensity follows the polymer density within the TEM image for all shown spectra.

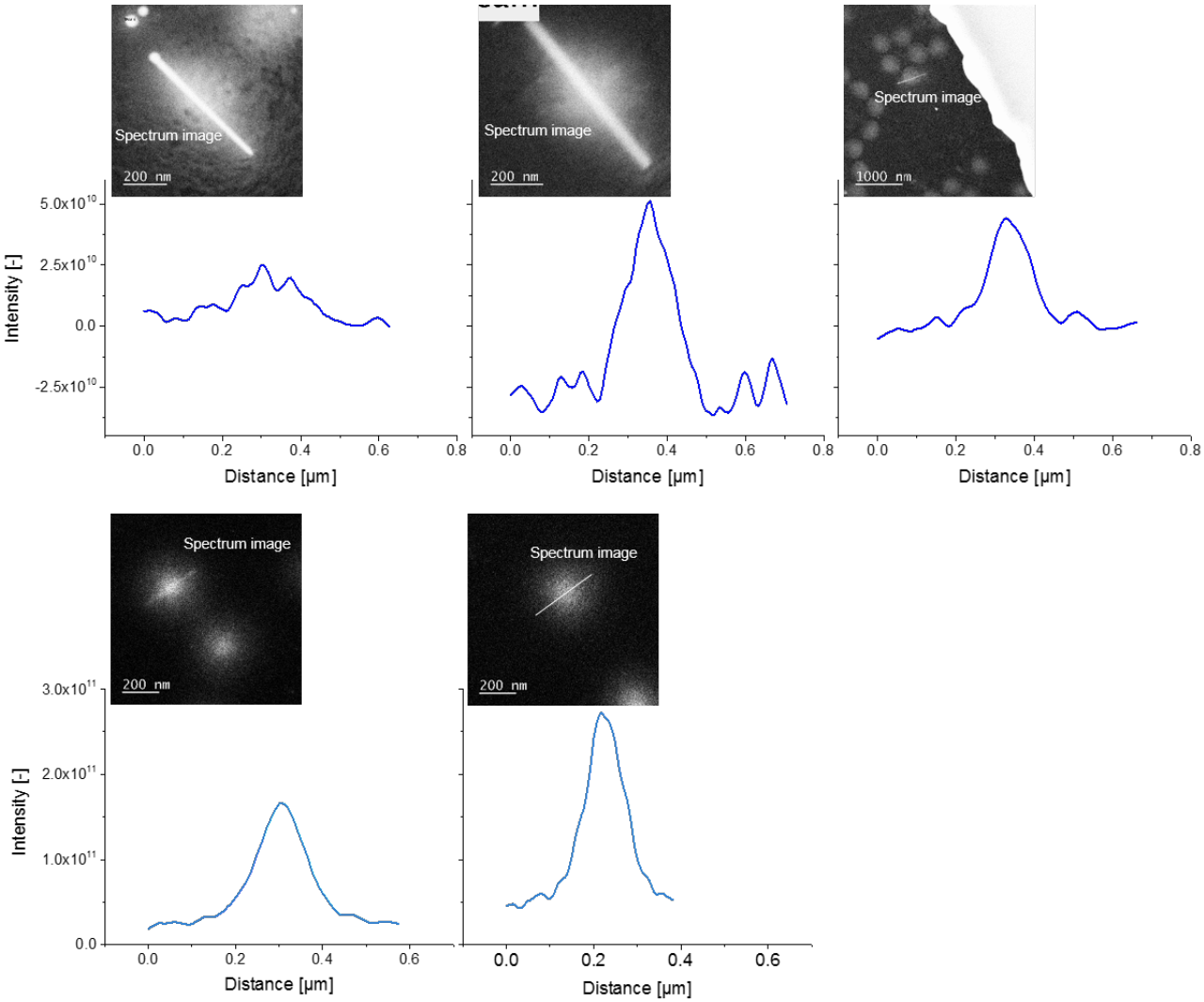


Fig. S2 Iron profiles determined by EELS line scan in STEM with the corresponding spectrum image for dried microgel dispersion ($0.5\,\mathrm{g/L}$ to $1.5\,\mathrm{g/L}$) of M-homogeneous-1 (top, dark blue) and M-homogeneous-2 (bottom, light blue)

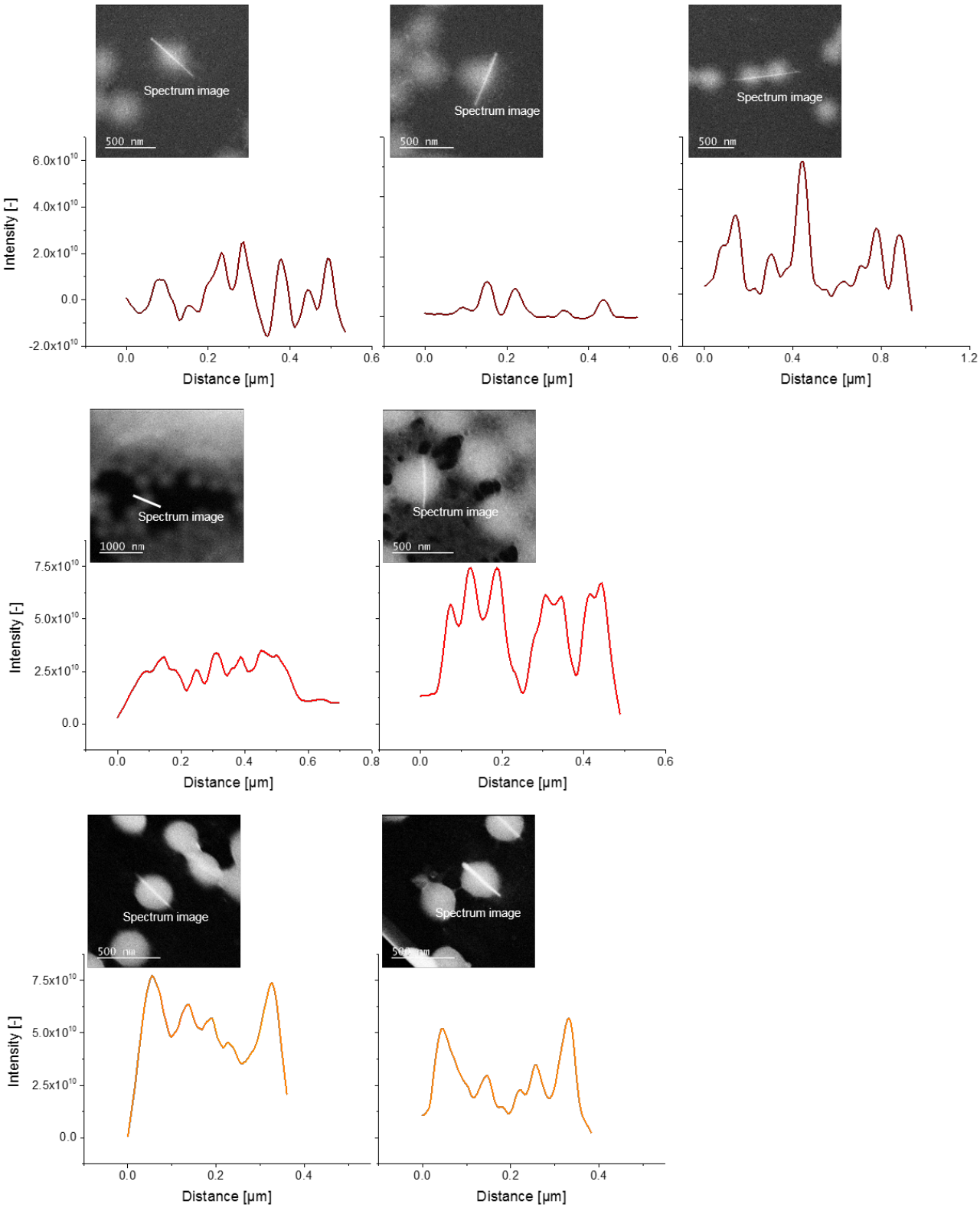


Fig. S3 Iron profiles obtained by EELS line scan in STEM with the corresponding spectrum image for dried microgel dispersion (0.5 g/L to 1.5 g/L) of M-shell-1 (top, dark red), M-shell-2 (middle, light red) and M-shell-3 (bottom, orange)

Synthesis of M-middle microgels

To yield an intermediate VFc-rich shell seems to be more complicated for this P(NIPAM-*co*-VFc) polymer system. The resulting structure when adding VFc after 75 s is indistinguishable from the M-core microgels where VFc is present from the start of the reaction (Figure S4. After initiation the solution turns strongly turbid within the first minute of the reaction. This shows the successfull initiation of the reaction and the formation of NIPAM microgels. These NIPAM cores are either too small to be visualized by Cryo-TEM or the precursor particle are able to form a VFc-rich core region after VFc addition due to coagulation. Overall, further adaption of the synthesis protocol seems to be necessary to yield a microgel with a larger NIPAM core and an intermediate VFc rich structure.

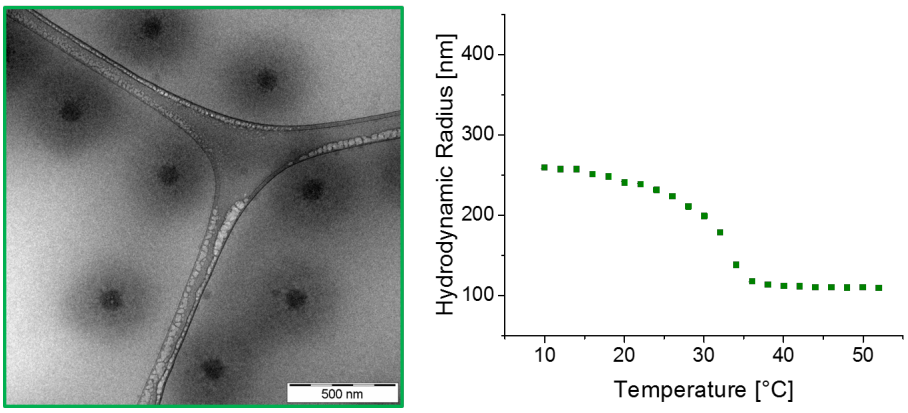


Fig. S4 Cryo-TEM image from microgel dispersions ($0.5\,\mathrm{g/L}$) and hydrodynamic radius vs. temperature of synthesised microgels with VFc addition time of 75 s.