

## Supporting information

### Responsive Supramolecular Microgels with Redox-Triggered Cleavable Crosslinks

**Synthesis of mono-(6-O-(p-toluenesulfonyl))-beta-cyclodextrin.** The synthesis of mono-(1H-1,2,3-triazole-4-yl)(methyl)2-methacryloyl- $\beta$ -cyclodextrin was performed according to the literature.<sup>[33–35]</sup> In the first step, 16.7 g of  $\beta$ -CD (14.7 mmol) was dissolved in 200 mL of water and stirred at 60 °C until the  $\beta$ -CD was completely dissolved. After cooling the solution down to room temperature, 5.0 g of p-toluenesulfonyl imidazole (22.5 mmol) was added slowly to the solution. After stirring for 2 h at room temperature, 50 mL of aqueous NaOH (3.75 g, 93.8 mmol) was added to the solution over 20 min and the mixture was stirred for 10 min. The unreacted p-toluenesulfonyl imidazole was separated by filtration. The reaction was quenched by the addition of 10.1 g of NH<sub>4</sub>Cl (0.37 mol). The mixture was concentrated 2 d in the fume hood and the resulting solid was collected. The white solid product was washed two times with ice water and acetone and dried in vacuo overnight.

FT-IR (Si): 3324 (OH), 2928 (CH), 1361 (S=O), 1154 (S-O), 1078 (OH), 1026 (CH), 754 (OH) cm<sup>-1</sup>. <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 7.75 (d, J = 8.05 Hz, Ar-H (ortho), 2H), 7.43 (d, J = 8.08 Hz, Ar-H (meta), 2H), 5.84 – 5.63 (m, C-2, -3-OH, 14H), 4.83 (s, H-1, 5H), 4.76 (s, H-1\*, 2H), 4.54 – 4.43 (m, C-6-OH, 6H), 4.38 – 4.29 (m, H-6, 1H), 4.18 (dd, J = 11.4 Hz, J = 6.4 Hz, 1H), 3.70 – 3.21 (Overlap with HDO, m, H-6,-3,-5,-4,-2, 49H), 2.42 (s, Ar-CH<sub>3</sub>, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H}-NMR (101 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 144.8, 132.7, 129.9, 127.6, 102.0, 81.5, 73.1, 72.5, 72.1, 69.0, 68.9, 59.9, 21.1 ppm. MALDI-TOF: m/z = 1311.4 g/mol [M + Na]<sup>+</sup>.

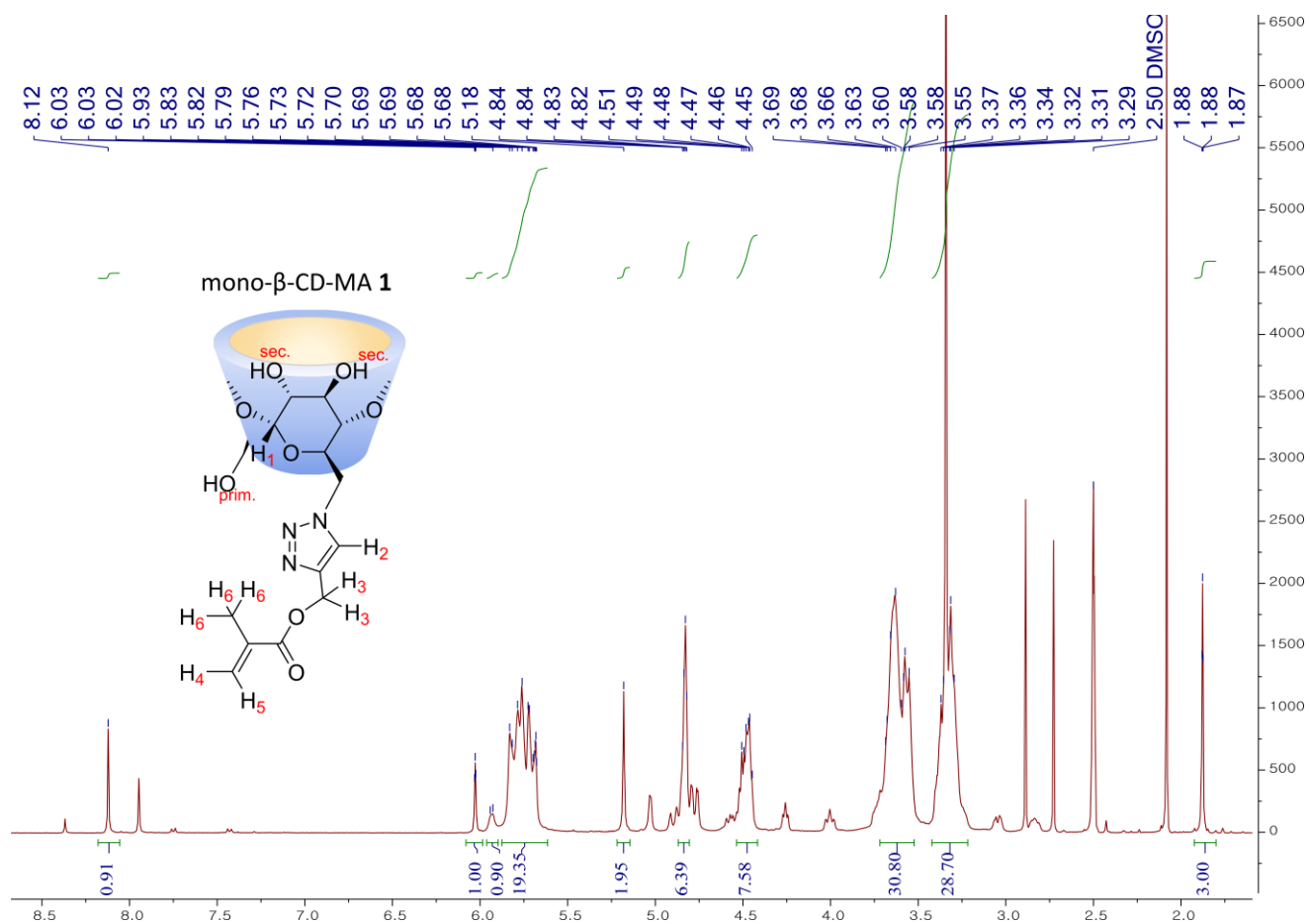
**Synthesis of mono-(6-O-azido-6-desoxy)-beta-cyclodextrin.** 9.0 g of mono-tosylated  $\beta$ -CD (6.93 mmol) was suspended in 200 mL of dry DMF under nitrogen condition and heated to 80 °C, followed by addition of an excess of 6.20 g of NaN<sub>3</sub> (95.4 mmol). The reaction was stirred further at 80 °C for 6 h until the mixture turned transparent. The crude product was precipitated in acetone and recrystallized several times from acetone-water to remove residual inorganic azide. The product was dried in vacuo overnight.

FT-IR (Si): 3330 (OH), 2931 (CH), 2104.3 (N=N), 1646 (C=C), 1363 (OH), 1153 (C-N), 1078 (OH), 1026.3 (CH), 946, 846, 753 (NH), 703 (CH) cm<sup>-1</sup>. <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 5.79 – 5.62 (m, C-2,-3 OH, 14H), 4.87 (d, J = 3.53 Hz, C-1, 1H), 4.83 (d, J = 3.78 Hz, C-1, 6H), 4.55 – 4.50 (m, C-6 OH, 2H), 4.47 – 4.44 (m, C-6 OH, 5H), 3.66 – 3.55 (m, C-2, -3, -5, 28H), 3.40 – 3.27 (m, C-6, 14H) ppm.

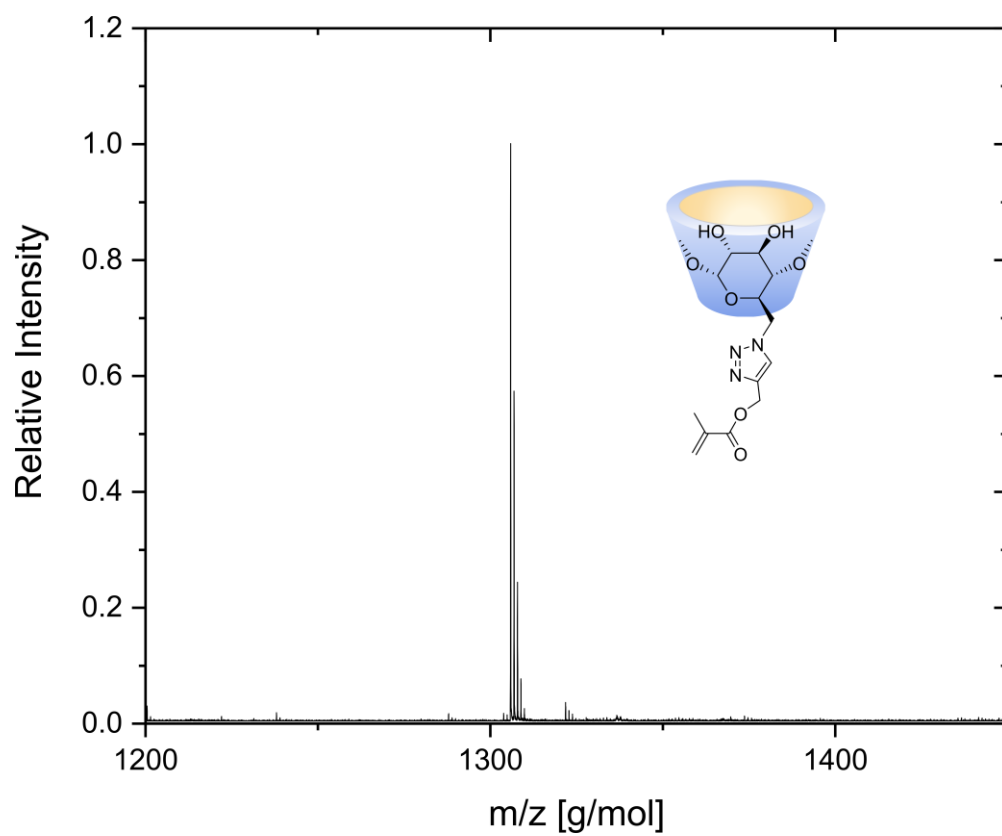
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  = 102.0, 81.6, 73.1, 72.4, 72.0, 60.0, 30.7 ppm. MALDI-TOF:  $m/z$  = 1182.2 g/mol  $[\text{M} + \text{Na}]^+$ .

**Synthesis of mono- $\beta$ -cyclodextrin triazole-methacrylate (1).** 6.00 g of mono-azide- $\beta$ -CD (5.16 mmol) was dissolved in 120 mL of dry DMF. 1.28 g of propargyl methacrylate (10.3 mmol), 0.10 g of sodium ascorbate (0.48 mmol), and 0.06 g of copper(II) sulfate pentahydrate (0.24 mmol) were added to the solution. The mixture was stirred under nitrogen at room temperature for 7 d. The residual catalyst was removed over diatomaceous earth. The solvent was removed until the clear solution turned turbid. 500 mL of acetone was added and the precipitated product was collected via simple filtration. The collecting white solid was washed three times with acetone and dried in vacuo overnight.

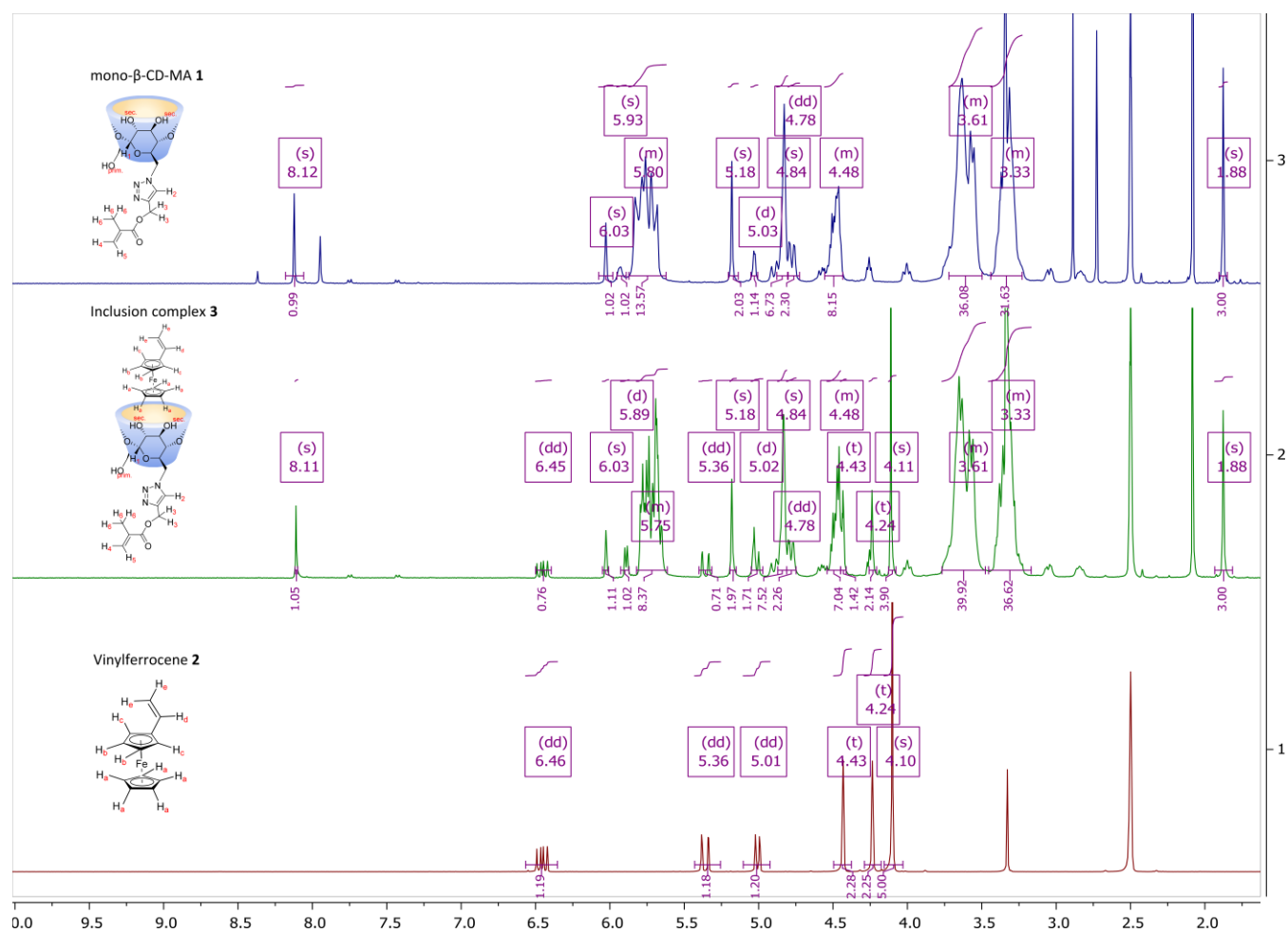
FT-IR (Si): 3319 (OH), 2930 (CH), 1715 (C=O), 1657 (C=C), 1331 (OH), 1297, 1153 (C-N), 1078 (OH), 1028 (CH), 946 (C=C), 843, 755 (NH), 704 (CH)  $\text{cm}^{-1}$ .  $^1\text{H}$ -NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 8.12 (s, H-2, 1H), 6.03 (s, H-4, 1H), 5.93 (s, H-5, 1H), 5.83 – 5.68 (m, Hsec. (OH-2,3), 14H), 5.18 (s, H-3, 2H), 4.83 (s, H-1, 7H), 4.51 – 4.45 (m, Hprim. (OH-6), 6H), 3.69 – 3.55, 3.37 – 3.29 (m, Hglucose, 42H), 1.88, (s, H-6, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  = 102.0, 81.5, 73.1, 72.4, 72.0, 59.9, 35.8, 30.7, 18.0 ppm. MALDI-TOF:  $m/z$  = 1306.22 g/mol  $[\text{M} + \text{Na}]^+$ .



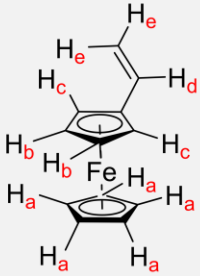
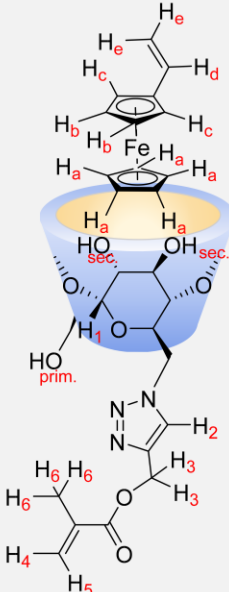
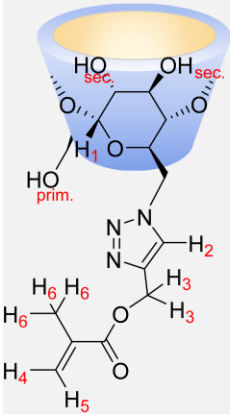
**Figure S1. <sup>1</sup>H-NMR of mono-β-CD-MA in DMSO-d<sub>6</sub>.**



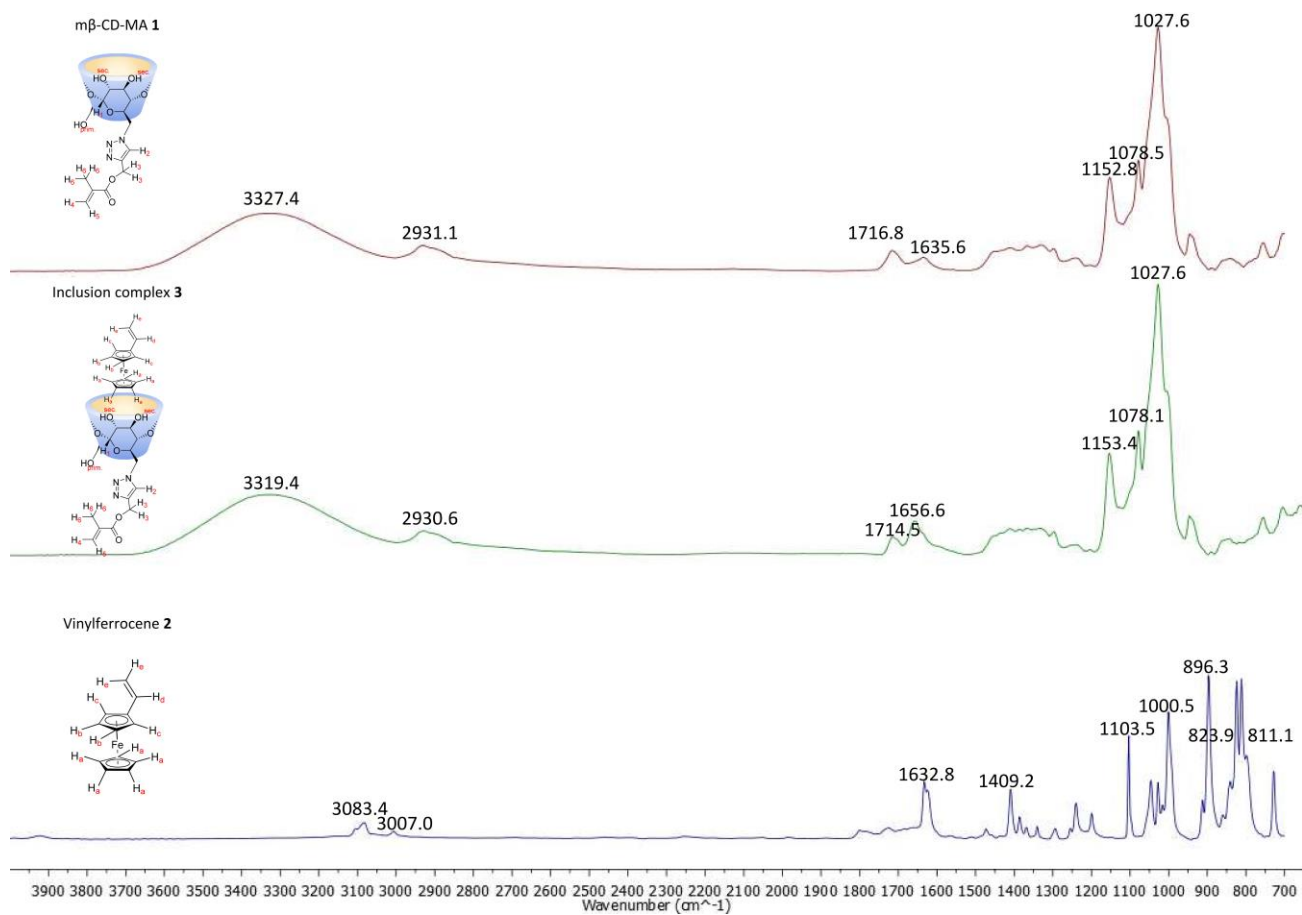
**Figure S2. MALDI-TOF spectra of mono-β-CD-MA.**



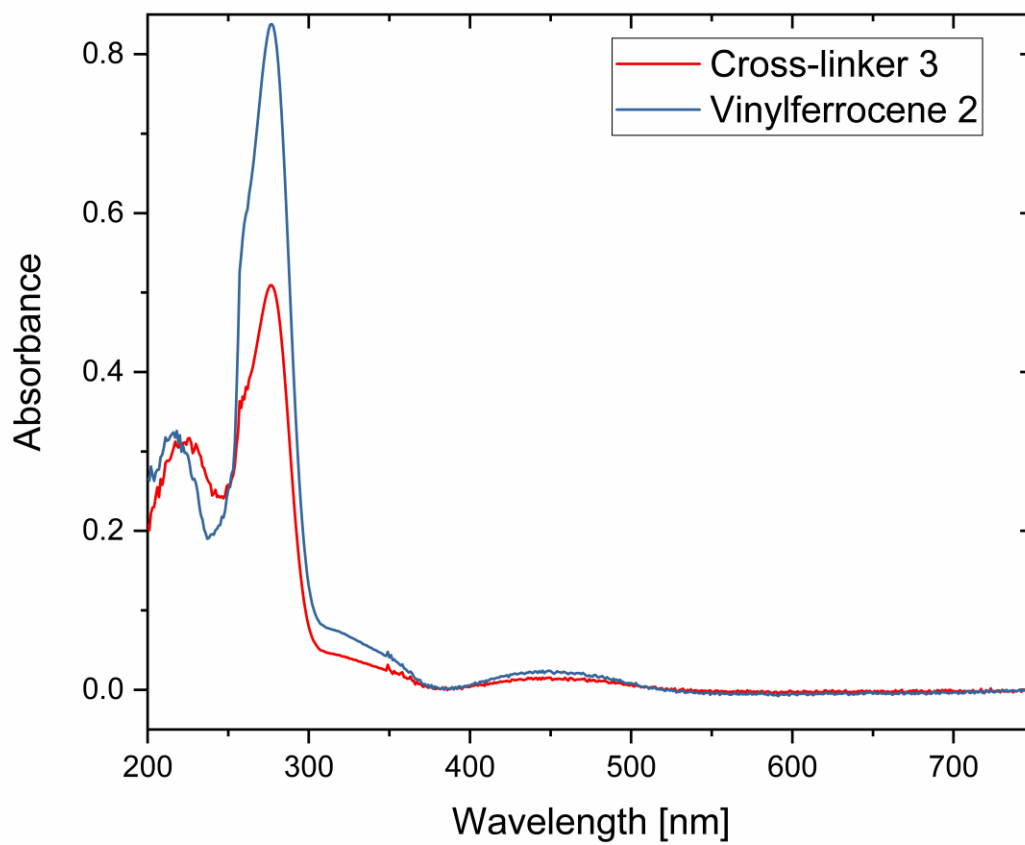
**Figure S3. <sup>1</sup>H-NMR of mono-β-CD-Ma (top), inclusion complex (middle), and VFc(bottom) in DMSO-d<sub>6</sub>.**

	Protons [ppm]	Reactants [ppm]	Chemical shifts [ppm]	Inclusion complex [ppm]	
	H <sub>a</sub>	4.10	(-0.01)	4.11	
	H <sub>b</sub>	4.43	(-)	4.43	
	H <sub>c</sub>	4.24	(-)	4.24	
	H <sub>d</sub>	6.46	(-0.01)	6.45	
	H <sub>e</sub>	5.36	(-)	5.36	
		5.10	(-)	5.10	
	H <sub>1</sub>	4.83	(-)	4.83	
	H <sub>2</sub>	8.12	(-0.01)	8.11	
	H <sub>3</sub>	5.18	(-)	5.18	
	H <sub>4</sub>	6.03	(-)	6.03	
	H <sub>5</sub>	5.90	(-0.01)	5.89	
	H <sub>6</sub>	1.88	(-)	1.88	
	H <sub>prim.</sub>	4.51–4.44	(-)	4.51–4.43	
	H <sub>sec.</sub>	5.80–5.66	(-)	5.80–5.67	
	H <sub>glucose</sub>	3.64–3.54	(-)	3.67–3.55	
		3.40–3.28	(-)	3.38–3.28	

**Table S1.** <sup>1</sup>H-NMR chemical shifts in comparison between inclusion complex (right) and host, guest molecules (left).

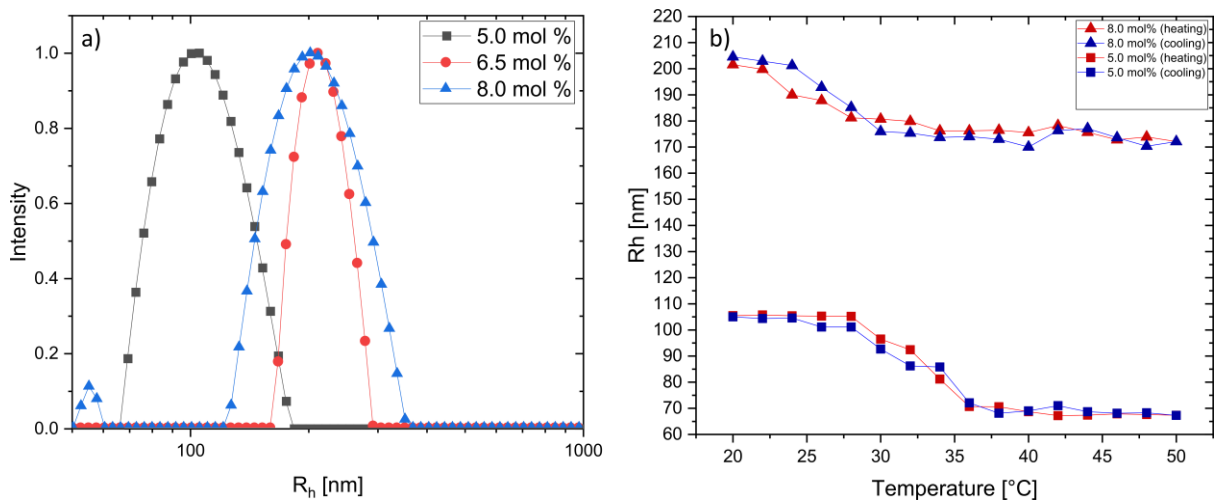


**Figure S4. FT-IR spectra of mono-β-CD-MA (top), inclusion complex (middle), and vinylferrocene (bottom).**

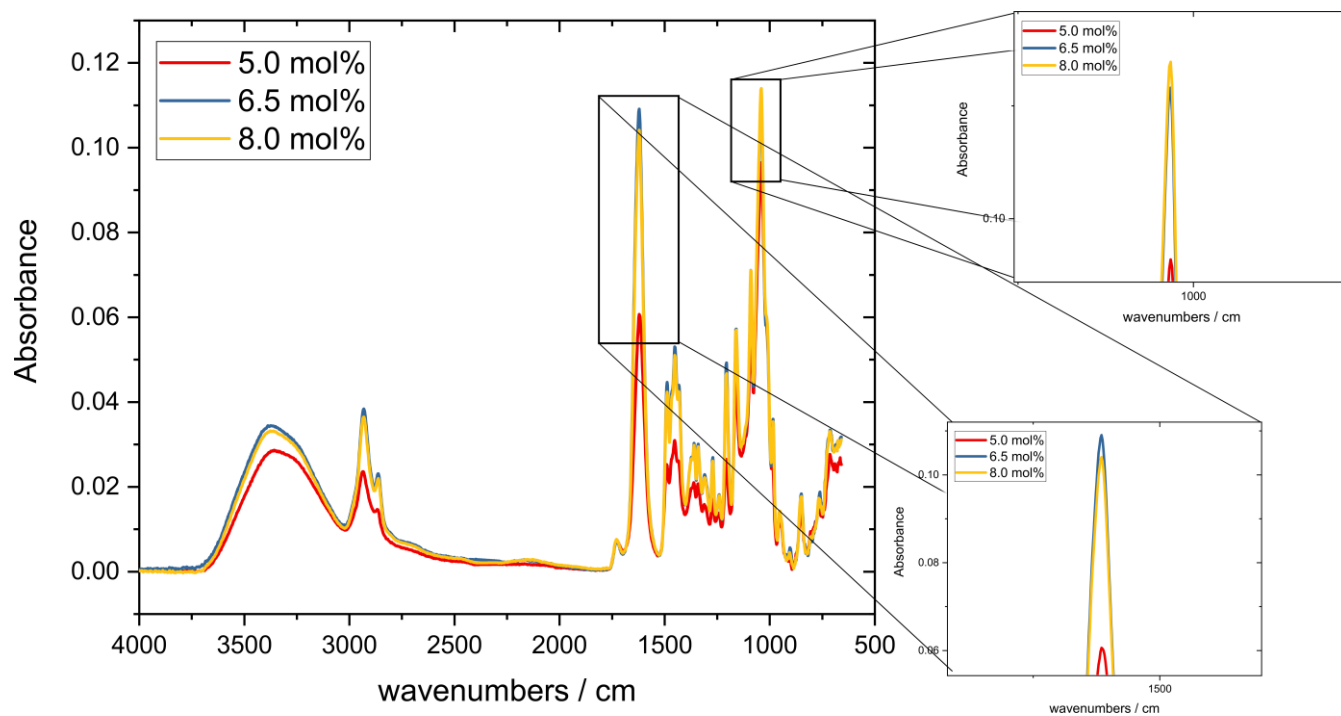


**Figure S5. UV-VIS spectra of crosslinker (3) and vinylferrocene (2).**

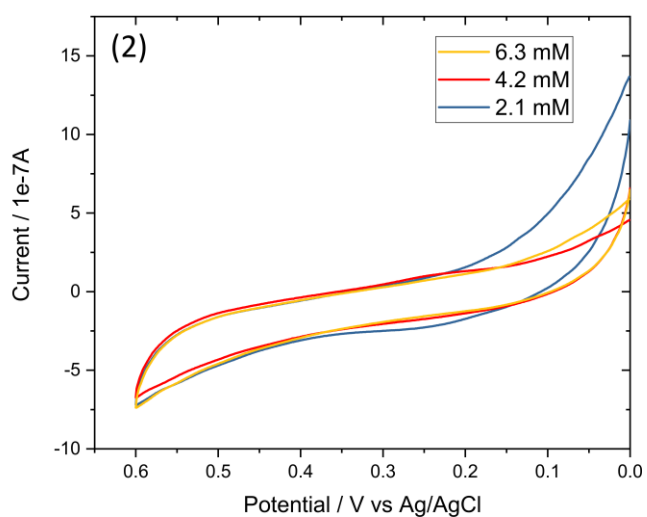
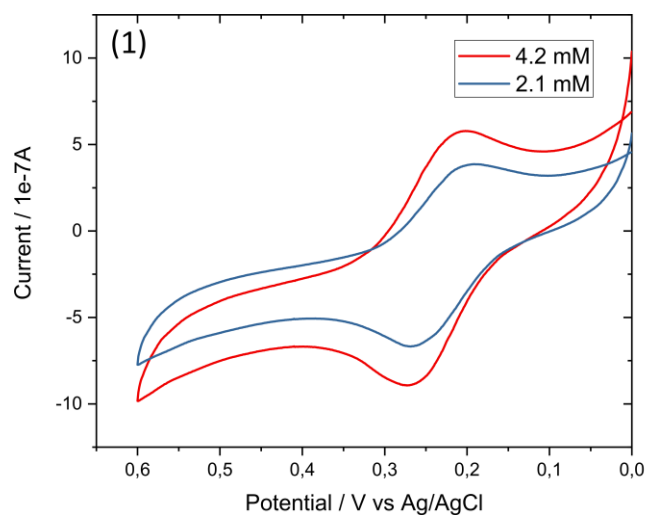




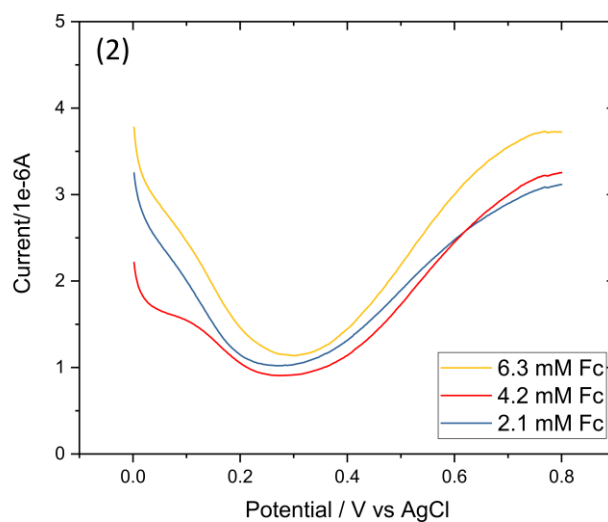
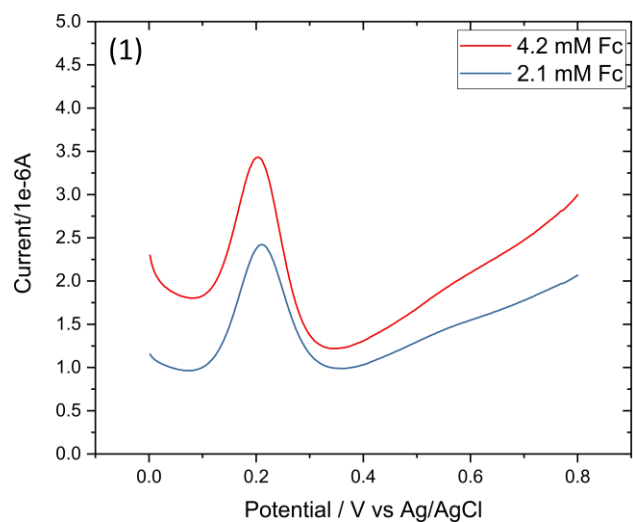
**Figure S6. A) DLS size distribution curves for synthesized microgels with three different crosslinker content 5.0 mol % to 8.0 mol % at 20°C. B) Dependence of hydrodynamic radii on temperature for microgel with 5.0 and 8.0 mol% crosslinker.**



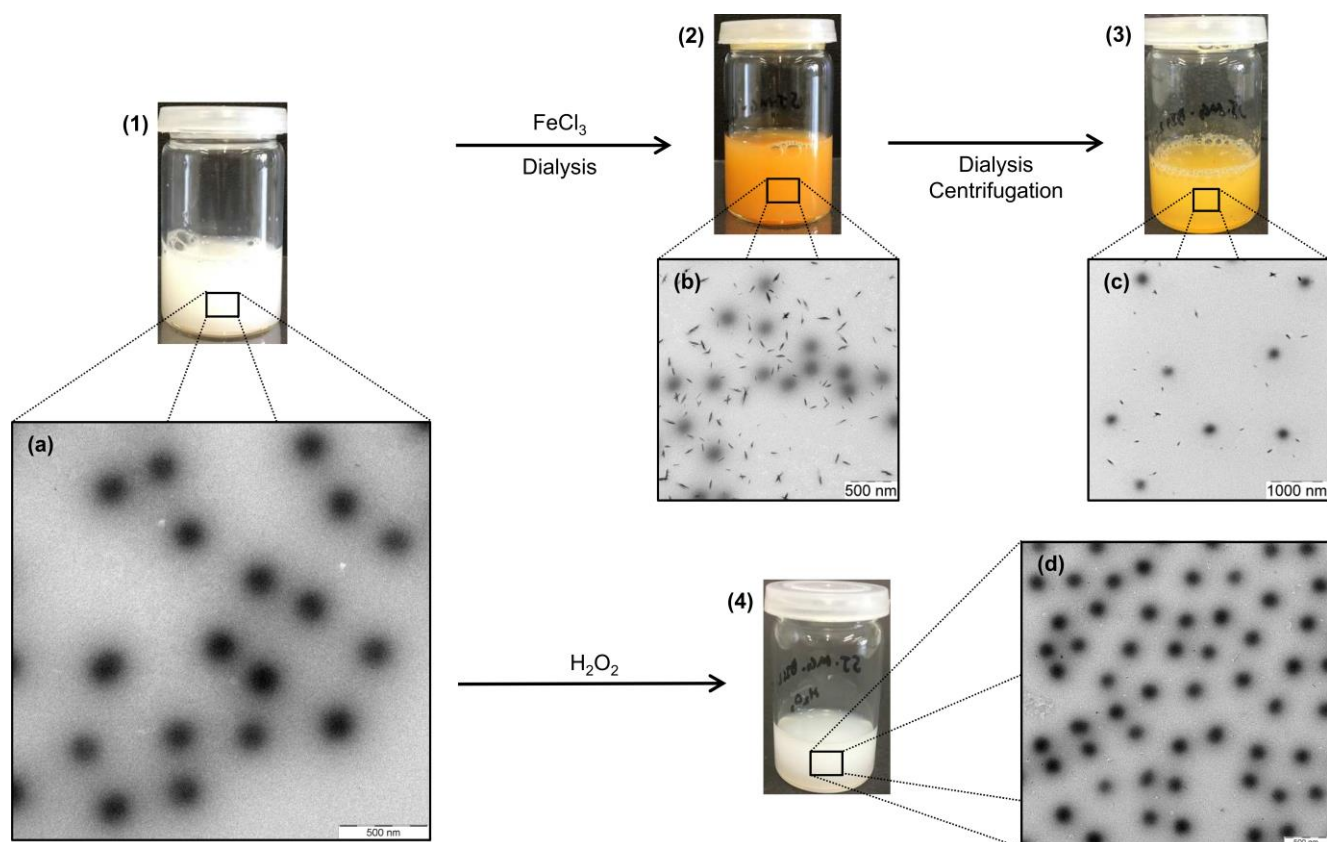
**Figure S7. FT-IR spectra of synthesized microgels with three different ferrocene contents.**



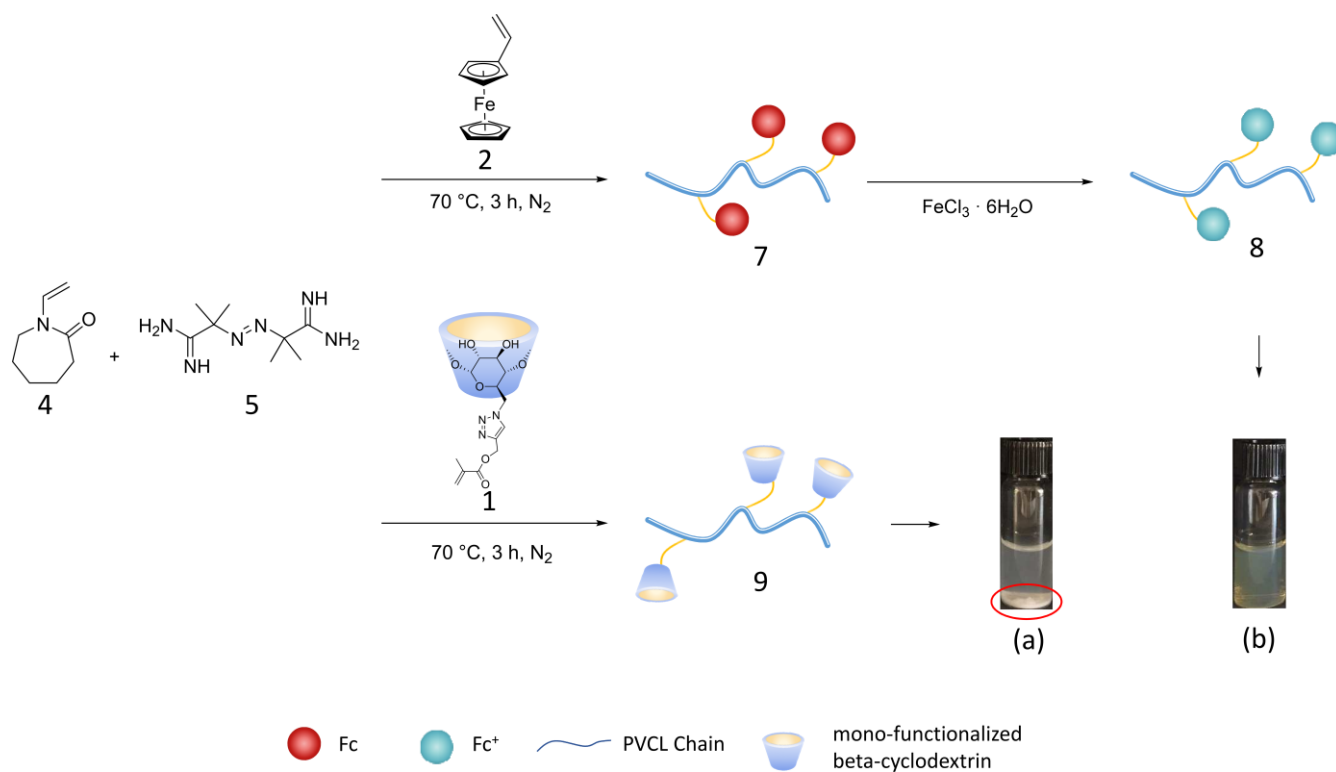
**Figure S8. Cyclic voltammograms of crosslinker 3 with two different concentration (1) (2.1 and 4.2 mM of fc-content) and microgel with 6.5 mol% with three different concentration (2) (2.1, 4.2, and 6.3 mM of fc-content).**



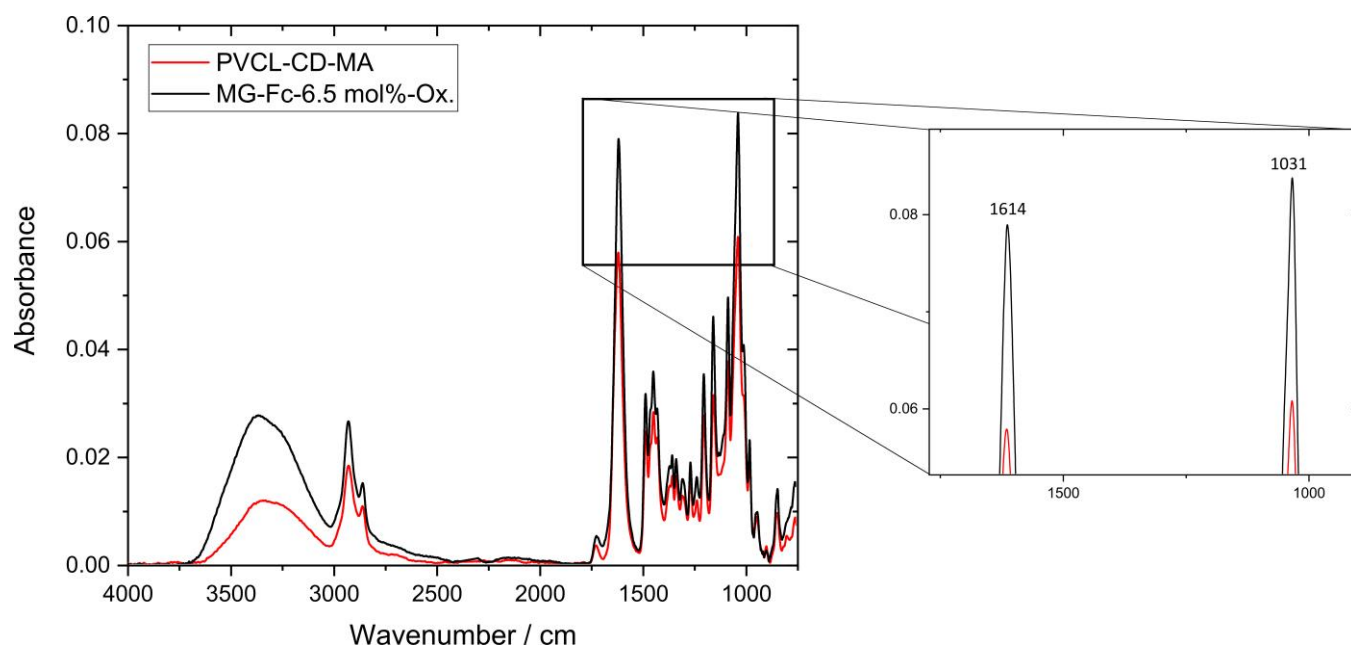
**Figure S9. differential pulse voltammetry of crosslinker 3 with two different concentration (1) (2.1 and 4.2 mM of fc-content) and microgel with 6.5 mol % with three different concentration (2) (2.1, 4.2, and 6.3 mM of fc-content).**



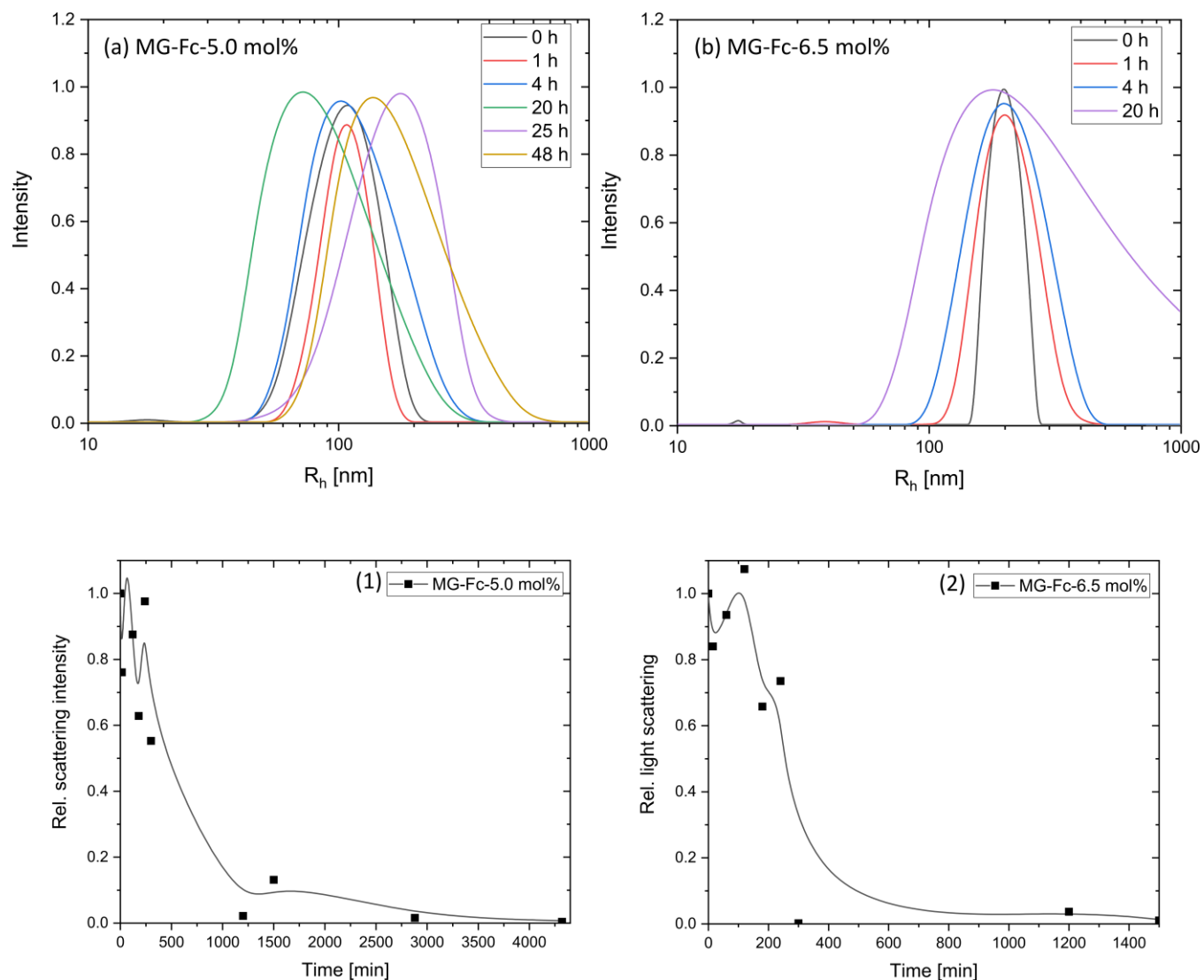
**Figure S10.** Picture of PVCL-BIS 2.5 mol % microgel (1), after addition of FeCl<sub>3</sub> (2), (3) and after addition of H<sub>2</sub>O<sub>2</sub> (4). TEM images of PVCL-BIS 2.5 mol% microgel (a), after addition of FeCl<sub>3</sub> (b) and (c) and after addition of H<sub>2</sub>O<sub>2</sub> (d).



**Figure S11. Scheme of synthesis of PVCL-co-Fc<sup>+</sup> 8 and PVCL-co-CD-MA 9. Pictures (a) and (b) show the synthesized products.**

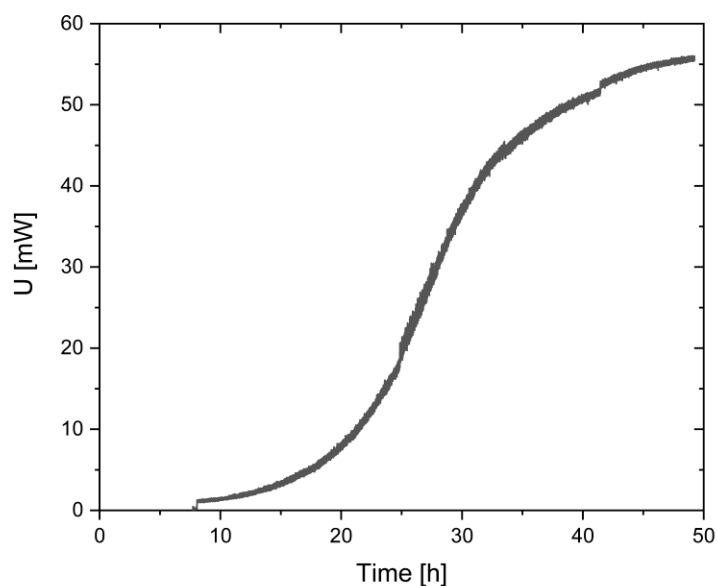


**Figure S12. FT-IR spectra of precipitates of oxidized MG-Fc-6.5 mol% and PVCL-CD-MA (9).**



**Figure S13. Degradation rate via DLS as a function of time. The degradable microgels with 5.0 mol % (a) and 6.5 mol % (b) crosslinker show the size change in the presence of hydrogen peroxide. Also, the scattering intensity change is plotted over the degradation time (1) and (2).**





**Figure S14.** Turbidity measurement of degradation of microgel with Fc-8.0 mol % using hydrogen peroxide as oxidant. The transmission intensity  $U(\text{mW})$ , which displays detected residual light after scattering and absorption, was shown as a function of time. Low transmission intensity indicates high turbidity of the solution.

