Supporting Information

Dual-Gated Supramolecular Star Polymers based on Cyclodextrin Complexation

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Additional preparation procedures

Synthesis of ferrocene end functionalized PDMA (Fc-PDMA$_{191}$)

The ferrocene functionalized polymers were obtained according to a literature procedure.[1] In a 50 mL vial DMA (3.0 g, 30.27 mmol, 159 eq.), Fc-CTA (91.0 mg, 0.19 mmol, 1.0 eq.) and AIBN (6.6 mg, 0.04 mmol, 0.2 eq.) were dissolved in 1,4-dioxane (15 mL). The vial was capped with a septum and the mixture bubbled with Argon for 30 min. Next, the polymerization was conducted at 60 °C for 3 h. Afterwards the mixture was cooled with liquid nitrogen and the vial opened to air. The product was precipitated twice in cold diethyl ether, the solid was collected and dried under vacuum. Finally, the product was obtained as an orange solid (2.42 g, 78%). $M_{nSEC} = 19300$ g·mol^{-1}, $Đ = 1.11$, $M_{nNMR} = 19400$ g·mol^{-1}.

Synthesis of ferrocene end functionalized PDMA (Fc-PDMA$_{322}$)

The ferrocene functionalized polymers were obtained according to a literature procedure.[1] In a 50 mL vial DMA (3.0 g, 30.27 mmol, 300 eq.), Fc-CTA (48.5 mg, 0.10 mmol, 1.0 eq.) and AIBN (3.2 mg, 0.02 mmol, 0.2 eq.) were dissolved in 1,4-dioxane (15 mL). The vial was capped with a septum and the mixture bubbled with Argon for 30 min. Next, the polymerization was conducted at 60 °C for 5 h. Afterwards the mixture was cooled with liquid nitrogen and the vial opened to air. The product was precipitated twice in cold diethyl ether, the solid was collected and dried under vacuum. Finally, the product was obtained as an orange solid (2.51 g, 82%). $M_{nSEC} = 33800$ g·mol^{-1}, $Đ = 1.15$, $M_{nNMR} = 32400$ g·mol^{-1}.

Synthesis of ferrocene end functionalized PDEA (Fc-PDEA$_{173}$)

The ferrocene functionalized polymers were obtained according to the literature.[1] In a 50 mL vial DEA (3.0 g, 23.44 mmol, 157 eq.), Fc-CTA (72.0 mg, 0.15 mmol, 1.0 eq.) and AIBN (4.9 mg, 0.03 mmol, 0.2 eq.) were dissolved in 1,4-dioxane (15 mL). The vial was capped with a septum and the mixture bubbled with Argon for 30 min. Subsequently, the polymerization was conducted at 60 °C for 4 h. Afterwards the mixture was cooled with liquid nitrogen and the vial opened to air. The product was precipitated twice in cold hexane, the solid was collected and dried under vacuum. Finally, the product was obtained as an orange solid (2.76 g, 90%). M_{nSEC} = 17800 g·mol^{-1}, $Đ$ = 1.13, M_{nNMR} = 22500 g·mol^{-1}.

Synthesis of ferrocene end functionalized PDEA (Fc-PDEA$_{370}$)

The ferrocene functionalized polymers were obtained according to the literature.[1] In a 50 mL vial DEA (3.0 g, 23.02 mmol, 300 eq.), Fc-CTA (37.8 mg, 0.079 mmol, 1.0 eq.) and AIBN (2.6 mg, 0.016 mmol, 0.2 eq.) were dissolved in 1,4-dioxane (15 mL). The vial was capped with a septum and the mixture bubbled with Argon for 30 min. Next, the polymerization was conducted at 60 °C for 6 h. Afterwards the mixture was cooled with liquid nitrogen and the vial opened to air. The product was precipitated twice in cold hexane, the solid was collected and dried under vacuum. Finally, the product was obtained as an orange solid (2.77 g, 91%). M_{nSEC} = 31400 g·mol^{-1}, $Đ$ = 1.17, M_{nNMR} = 47500 g·mol^{-1}.

Additional method information

DLS via PSS Nicomp: DLS was performed on a 380 DLS spectrometer (Particle Sizing Systems, Santa Barbara, USA) with a 90 mW laser diode operating at 658 nm equipped with an avalanche

photo diode detector. The scattered light was recorded at an angle of 90° to the incident beam. Every measurement was performed at 10 °C and the data was evaluated with an inverse Laplace algorithm. All hydrodynamic diameters (D_h) in the text are the averages of the number weighted distributions. The samples were prepared in Milli-Q water with a concentration of 2 mg mL^{-1} and filtered with a 0.2 μm regenerated cellulose syringe filter (Roth, Rotilabo).

Table S1. DOSY measurement parameters (temperature 298 K).

Sample	p30 (diffusion gradient length)	d20 (diffusion delay)
β-CD$_6$	2100	0.100
Fc-PDMA$_{61}$	2500	0.100
Fc-PDEA$_{84}$	2600	0.100
Fc-PDMA$_{61@}\beta$-CD$_6$	3000	0.100
Fc-PDEA$_{84@}\beta$-CD$_6$	1500	0.52499998
Fc-PDMA$_{61@}\beta$-CD$_6$ + NaOCl	1500	0.30000001
Fc-PDMA$_{61@}\beta$-CD$_6$ + NaOCl + ascorbic acid	1500	0.40000001
Fc-PDEA$_{84@}\beta$-CD$_6$ + NaOCl	1500	0.34999999
Fc-PDEA$_{84@}\beta$-CD$_6$ + NaOCl + ascorbic acid	1500	0.34999999
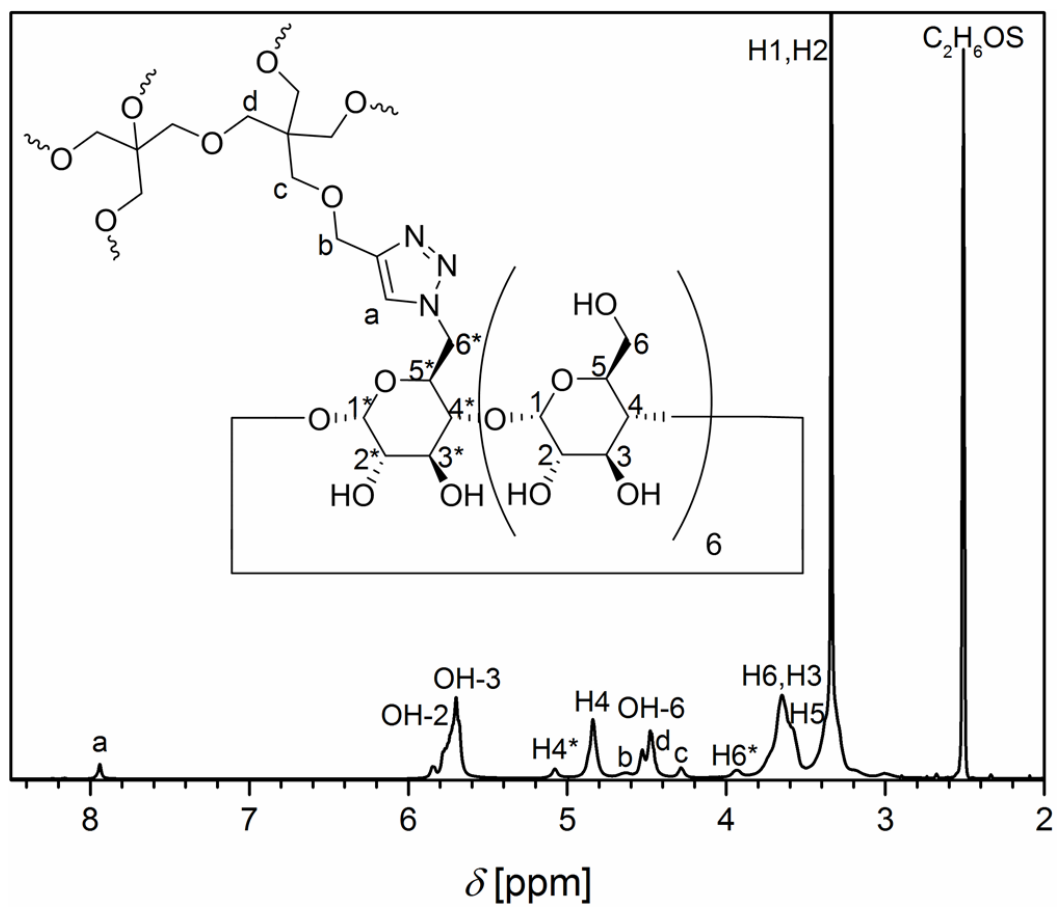
Figure S1. ^{1}H-NMR spectrum (400 MHz, DMSO) of **β-CD₆**. The numbers 1 to 6 refer to the respective positions within the *via* α-1,4 glycosidic linkage connected α-D-glucose units.
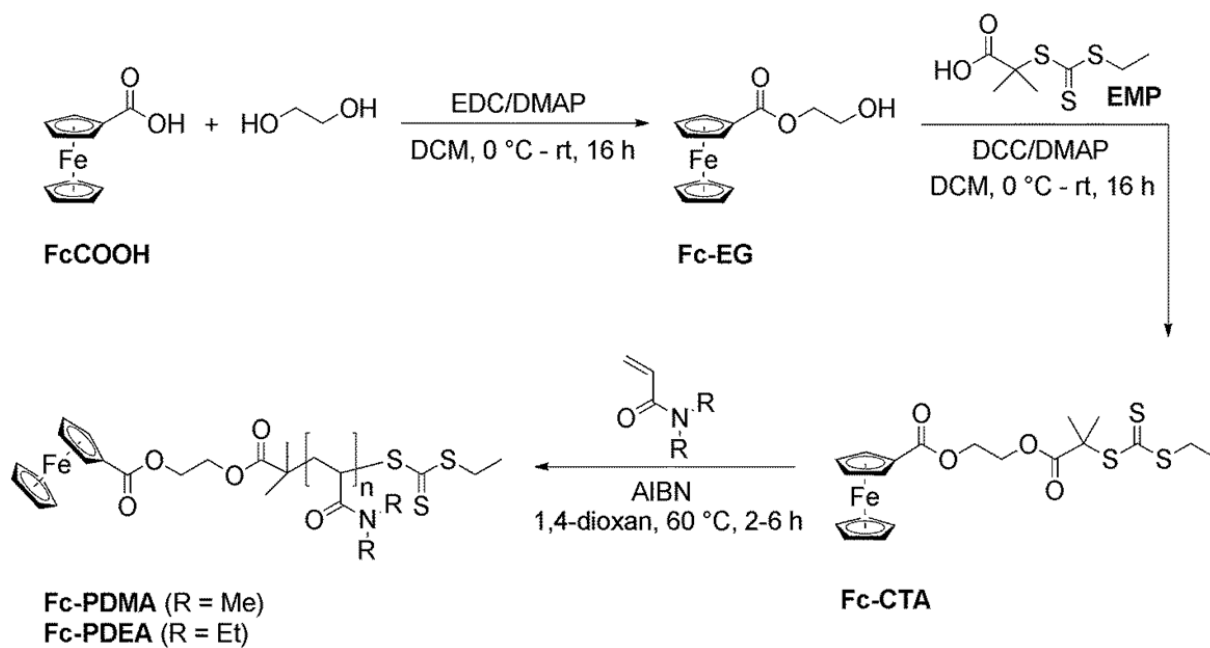
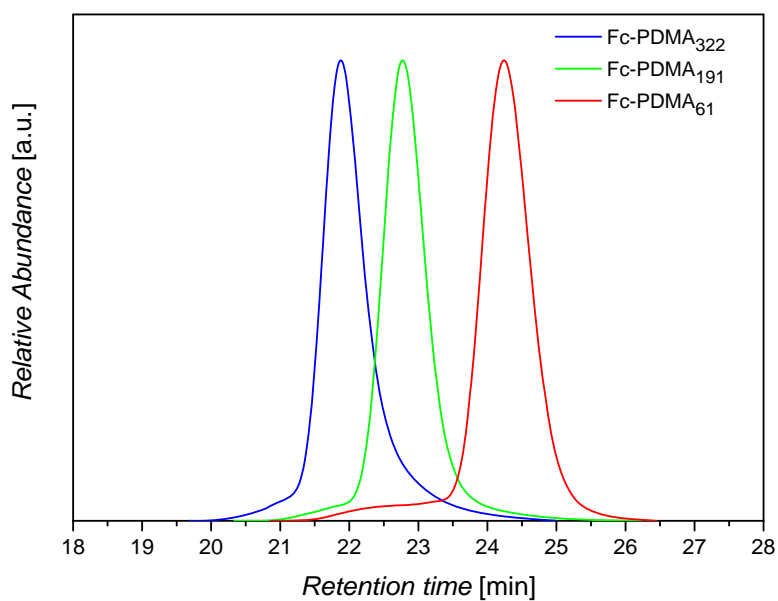**Figure S2.** Synthetic route towards Fc-CTA and Fc functionalized polymers.

Figure S3. SEC traces (in DMAc) of **Fc-PDMA$_{322}$** (blue line, M_n = 33800 g mol^{-1}, Đ = 1.15), **Fc-PDMA$_{191}$** (green line, M_n = 19300 g mol^{-1}, Đ = 1.11) and of **Fc-PDMA$_{61}$** (red line, M_n = 7700 g mol^{-1}, Đ = 1.16).
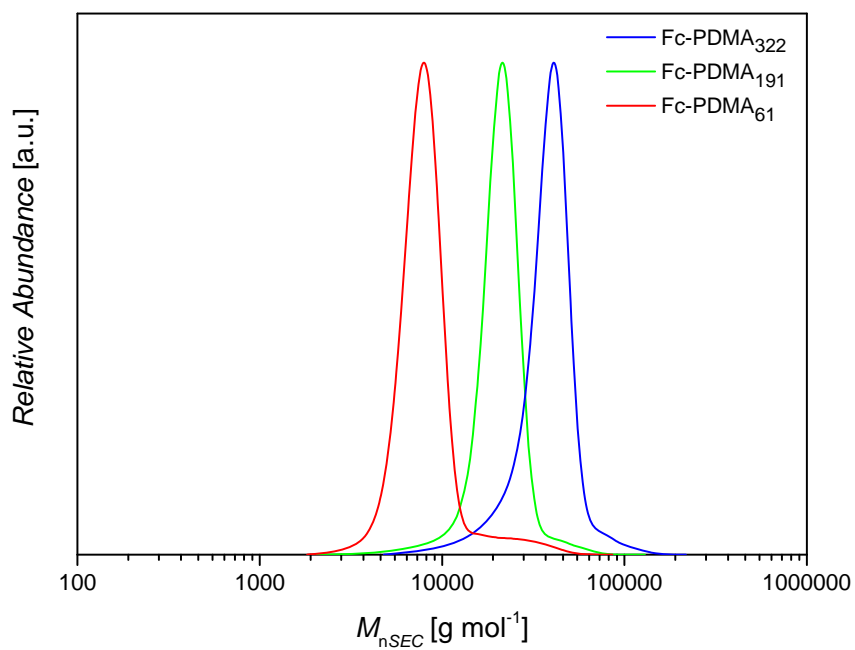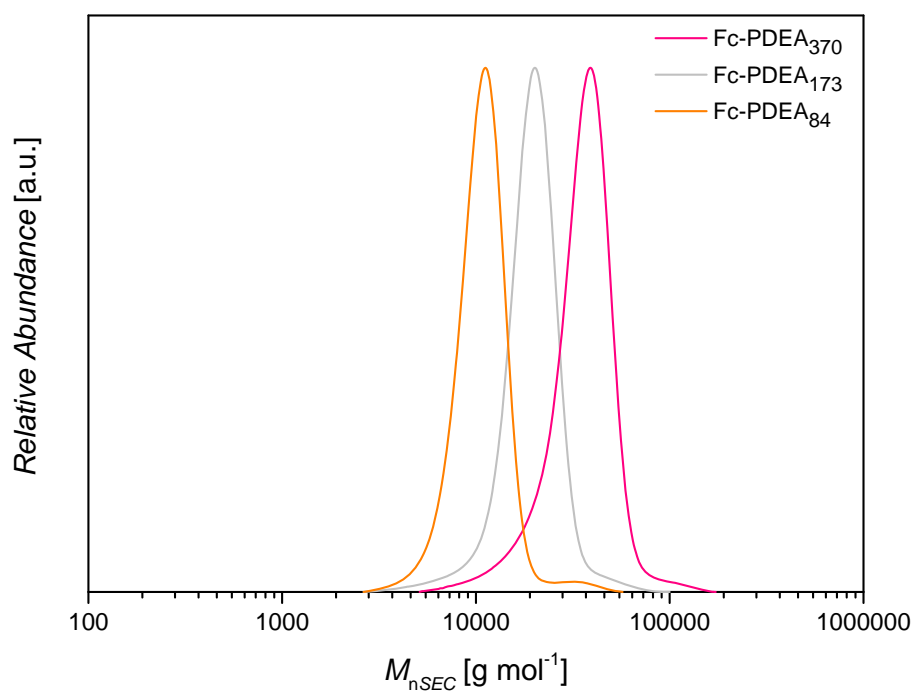
Figure S4. Molecular mass distributions (calculated via SEC in DMAc against poly(styrene)) of **Fc-PDMA₃₂₂** (blue line, M_n = 33800 g mol^{-1}, $Đ$ = 1.15), **Fc-PDMA₁₉₁** (green line, M_n = 19300 g mol^{-1}, $Đ$ = 1.11) and of **Fc-PDMA₆₁** (red line, M_n = 7700 g mol^{-1}, $Đ$ = 1.16).
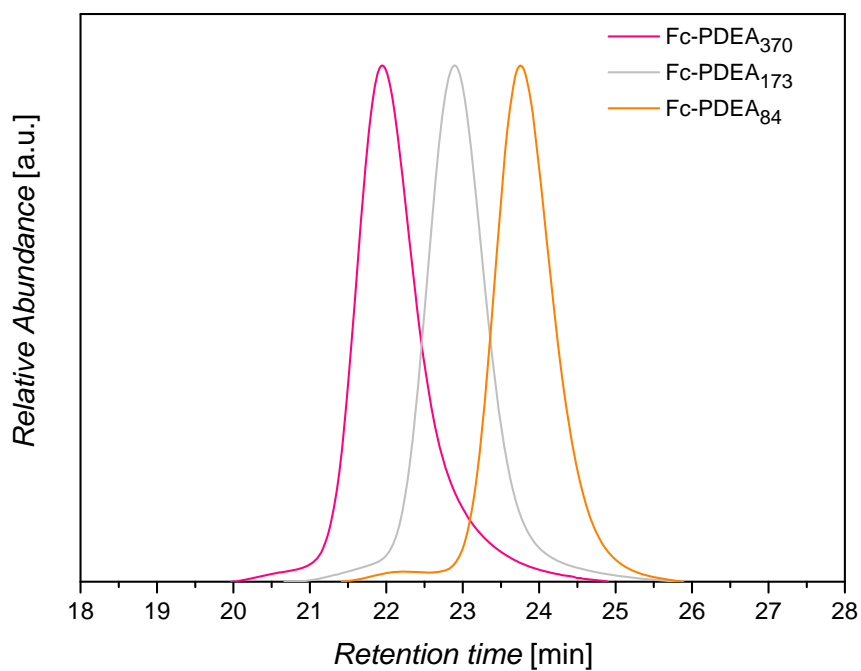
Figure S5. SEC traces (in DMAc) of **Fc-PDEA$_{370}$** (pink line, M_n = 31400 g mol^{-1}, $Đ$ = 1.17), **Fc-PDEA$_{173}$** (grey line, M_n = 17800 g mol^{-1}, $Đ$ = 1.13), **Fc-PDEA$_{84}$** (orange line, M_n = 10100 g mol^{-1}, $Đ$ = 1.11).

Figure S6. Molecular mass distributions (calculated via SEC in DMAc against poly(styrene)) of **Fc-PDEA$_{370}$** (pink line, M_n = 31400 g mol^{-1}, Đ = 1.17), **Fc-PDEA$_{173}$** (grey line, M_n = 17800 g mol^{-1}, Đ = 1.13), **Fc-PDEA$_{84}$** (orange line, M_n = 10100 g mol^{-1}, Đ = 1.11).
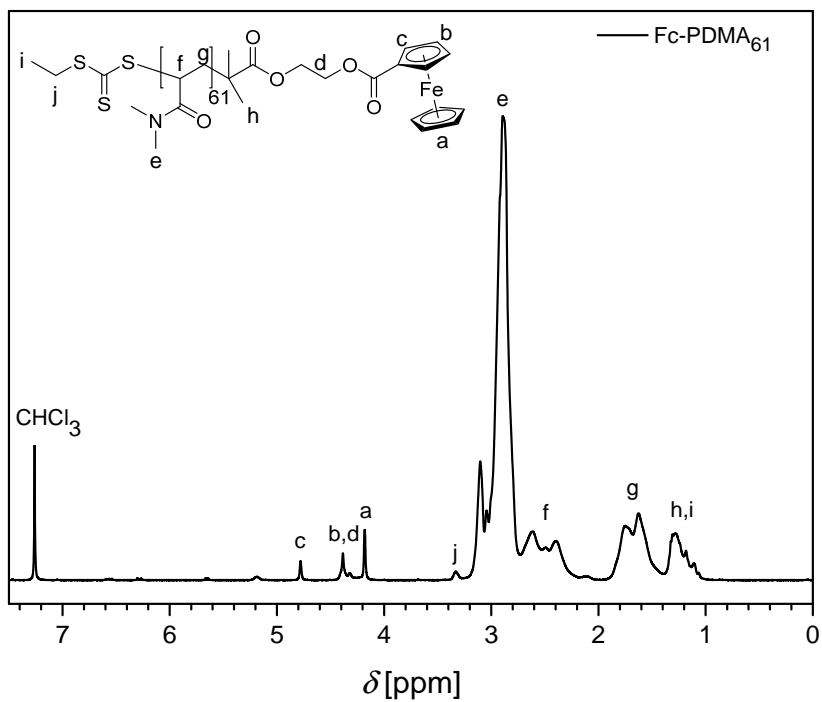
Figure S7. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of **Fc-PDMA$_{61}$**. M_n and P_n values were obtained by comparing the integrals of the signals of H$_a$ and H$_g$ (refer to Table 1 in the main text).
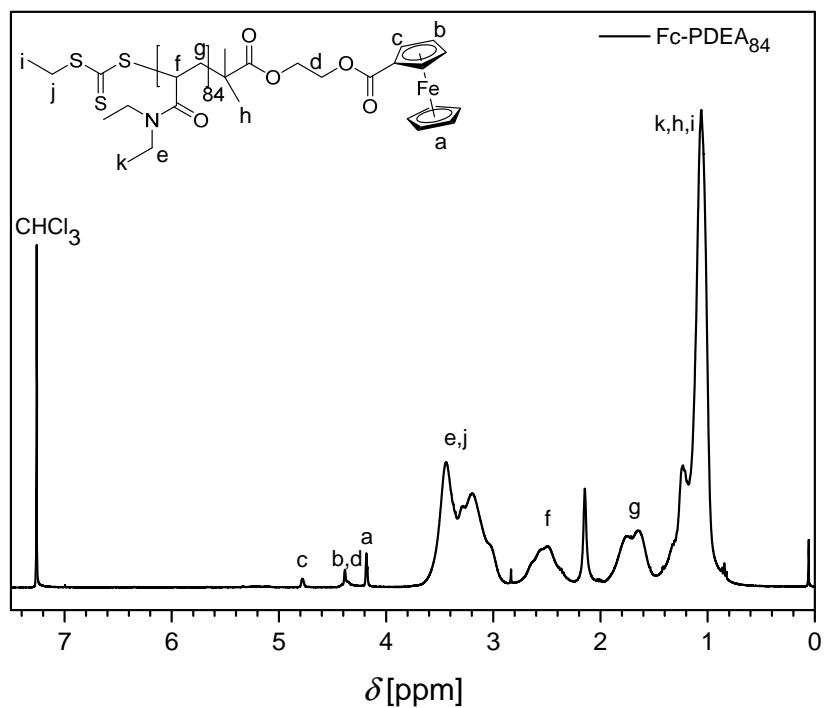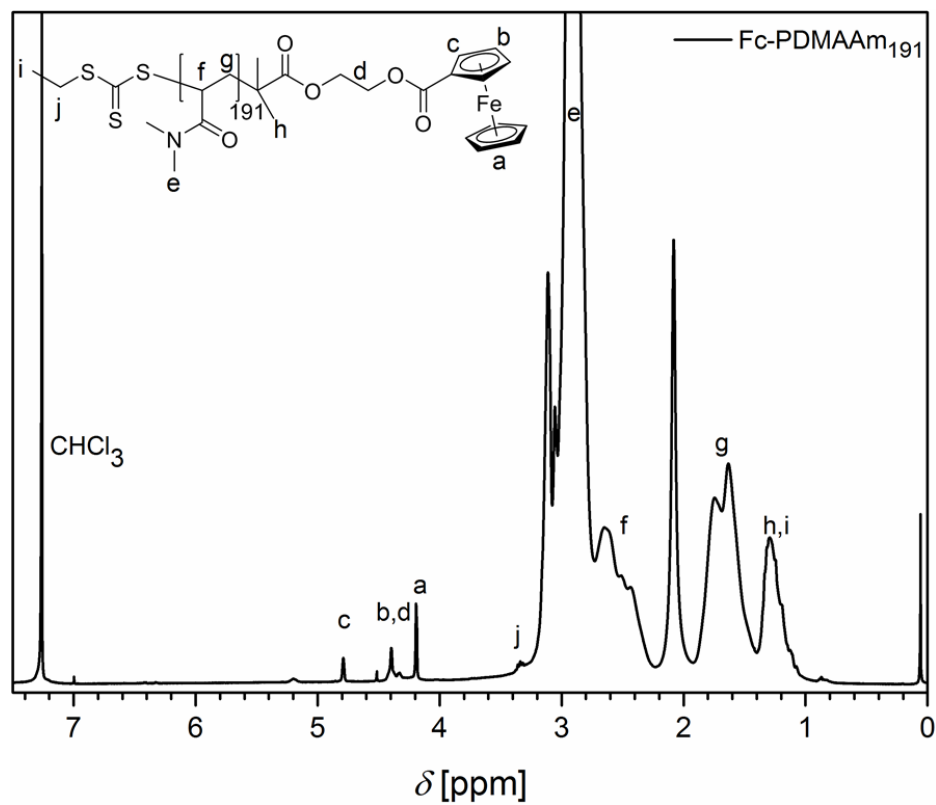
Figure S8. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of **Fc-PDEA$_{84}$**. M_n and P_n values were obtained by comparing the integrals of the signals of H$_a$ and H$_g$ (refer to Table 1 in the main text).
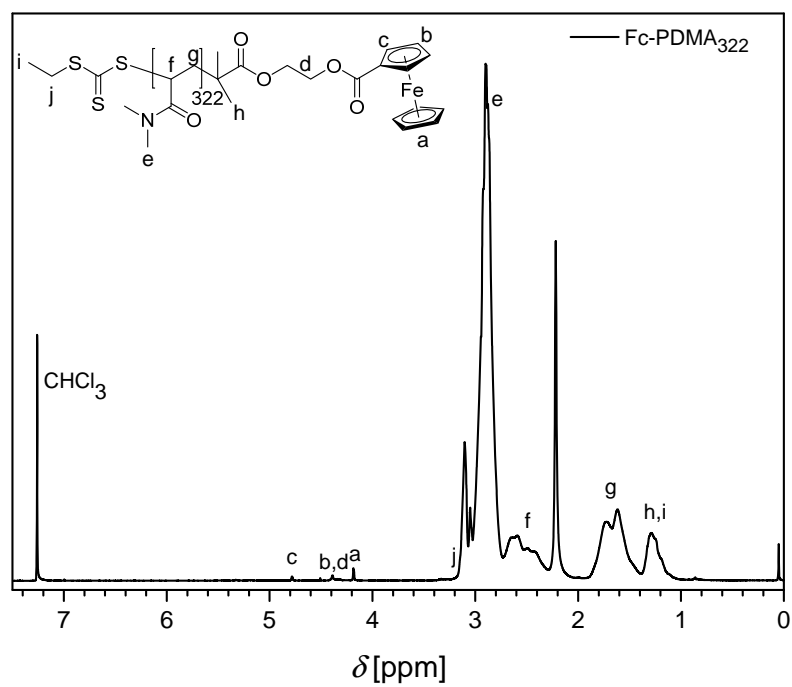
Figure S9. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of **Fc-PDMA$_{191}$**. M_n and P_n values were obtained by comparing the integrals of the signals of H$_a$ and H$_g$ (refer to Table 1 in the main text).

Figure S10. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of **Fc-PDMA$_{322}$**. M_n and P_n values were obtained by comparing the integrals of the signals of H$_a$ and H$_g$ (refer to Table 1 in the main text).

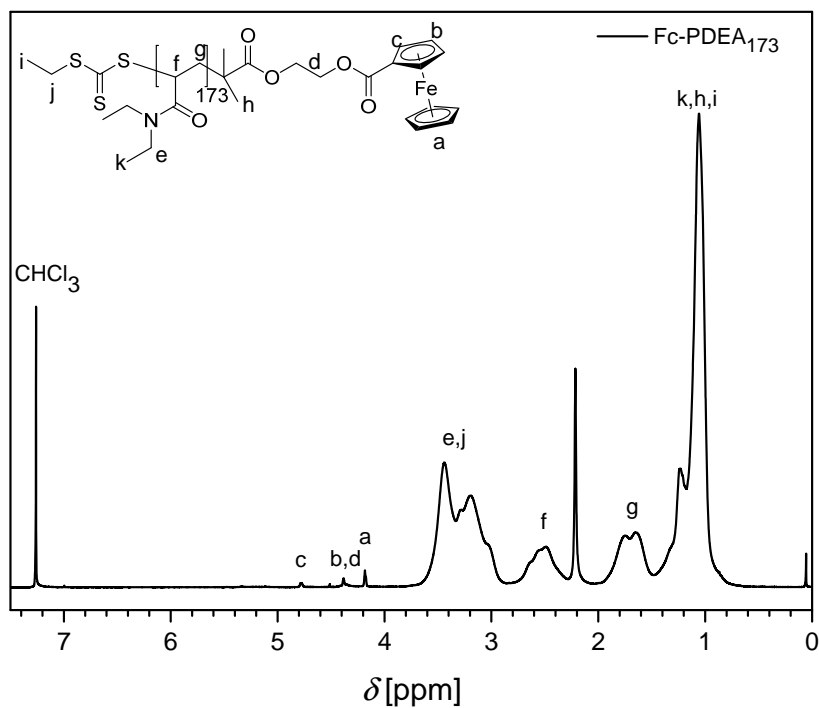**Figure S11.** ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of **Fc-PDEA$_{173}$**. M_n and P_n values were obtained by comparing the integrals of the signals of H$_a$ and H$_g$ (refer to Table 1 in the main text).
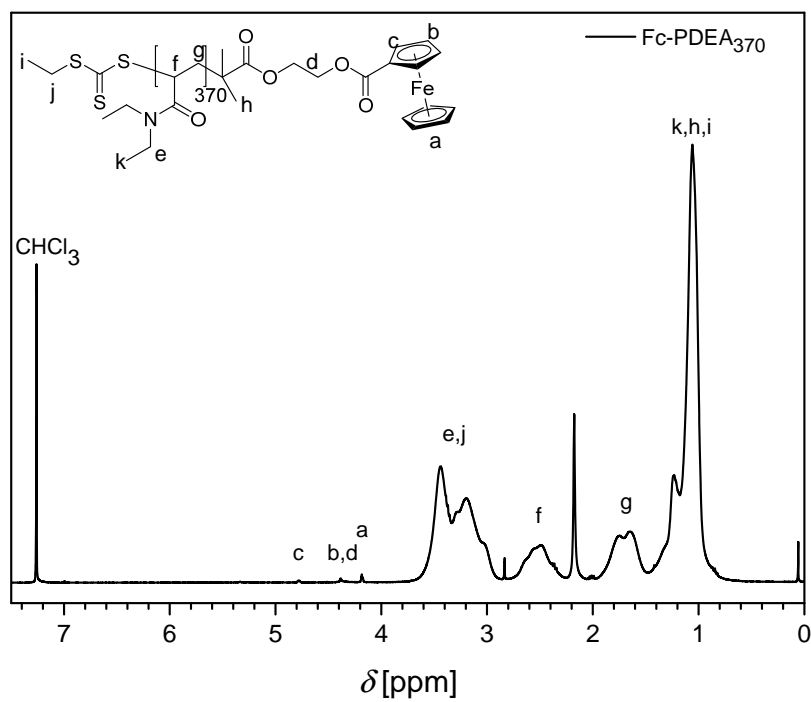
Figure S12. ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of **Fc-PDEA$_{370}$**. M_n and P_n values were obtained by comparing the integrals of the signals of H$_a$ and H$_g$ (refer to Table 1 in the main text).
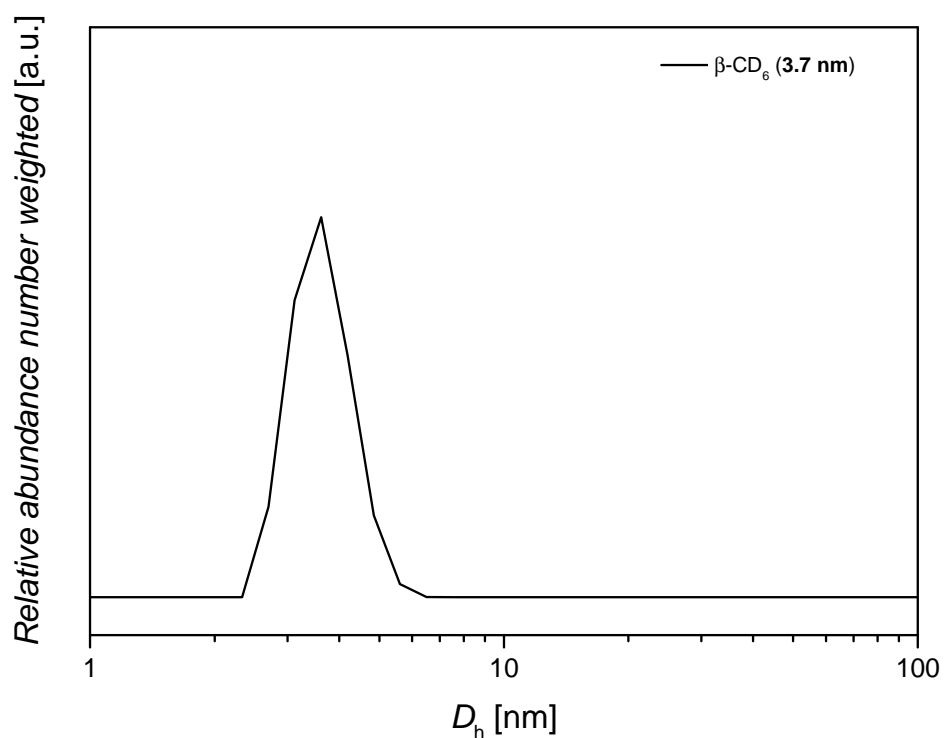
Figure S13. Particle size distribution of β-CD$_6$ at 10 °C measured via DLS at a concentration of 0.86 mg mL^{-1}.

Table S2. Hydrodynamic diameters (D_h) of precursors, six-arm star polymers before oxidation, after oxidation with NaOCl and after reduction with ascorbic acid.

Polymer	$D_{h,crude}$ [nm]	$D_{h,polymer@β-CD6}$ [nm]	expansion ratio
Fc-PDMA$_{191}$[a]	5.5	6.9	1.3
Fc-PDMA$_{322}$[a]	7.7	10.2	1.3
Fc-PDEA$_{173}$[b]	4.9	6.5	1.3
Fc-PDEA$_{370}$[b]	7.9	9.8	1.2

a) measured via DLS in water at 10 °C and 2 mg mL^{-1} via PSS Nicomp

Table S3. Hydrodynamic diameters (D_h) of precursors, six-arm star polymers before oxidation, after oxidation/sonication with NaOCl and after reduction with ascorbic acid.

Polymer	$D_{h,crude}$ [nm]	$D_{h,polymer@\beta\text{-}CD6}$ [nm]	expansion ratio	$D_{h,polymer@\beta\text{-}CD6}$ after oxidation [nm]	$D_{h,polymer@\beta\text{-}CD6}$ after reduction [nm]
Fc-PDMA$_{61}$[a]	3.6	6.9	1.9	3.2-3.9[b]	-[c]

a) measured via DLS (Malvern instrument) in water at 10 °C and 2 mg mL^{-1}, b) after ultrasonication due to aggregate formation see discussion; c) no reasonable value could be obtained see discussion
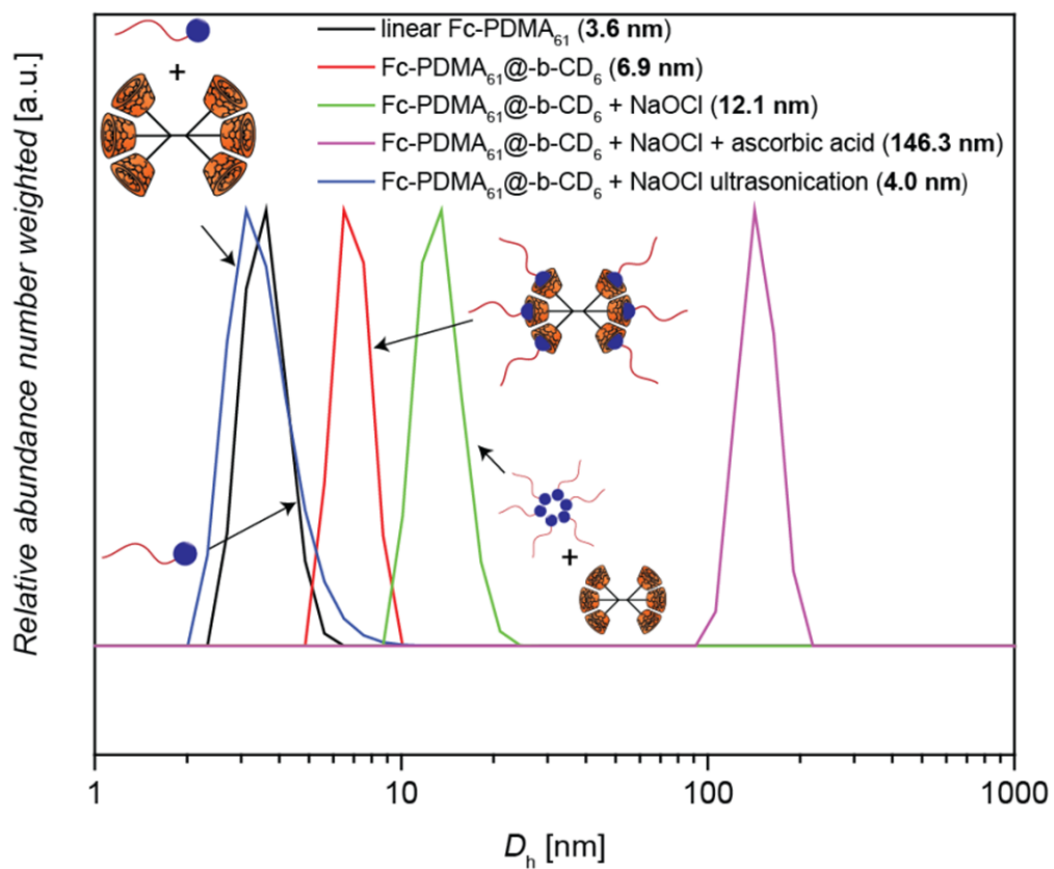
Figure S14. Redox-responsive dissociation of six-arm star polymer Fc-PDMA$_{61}$@β-CD$_6$ at 10 °C measured via DLS at a concentration of 2 mg mL^{-1} before addition of NaOCl (red trace), after addition of NaOCl (green trace), after addition of excess ascorbic acid (purple trace) and after addition of NaOCl with 1 h sonication (blue trace) as well as a linear reference sample (black trace).
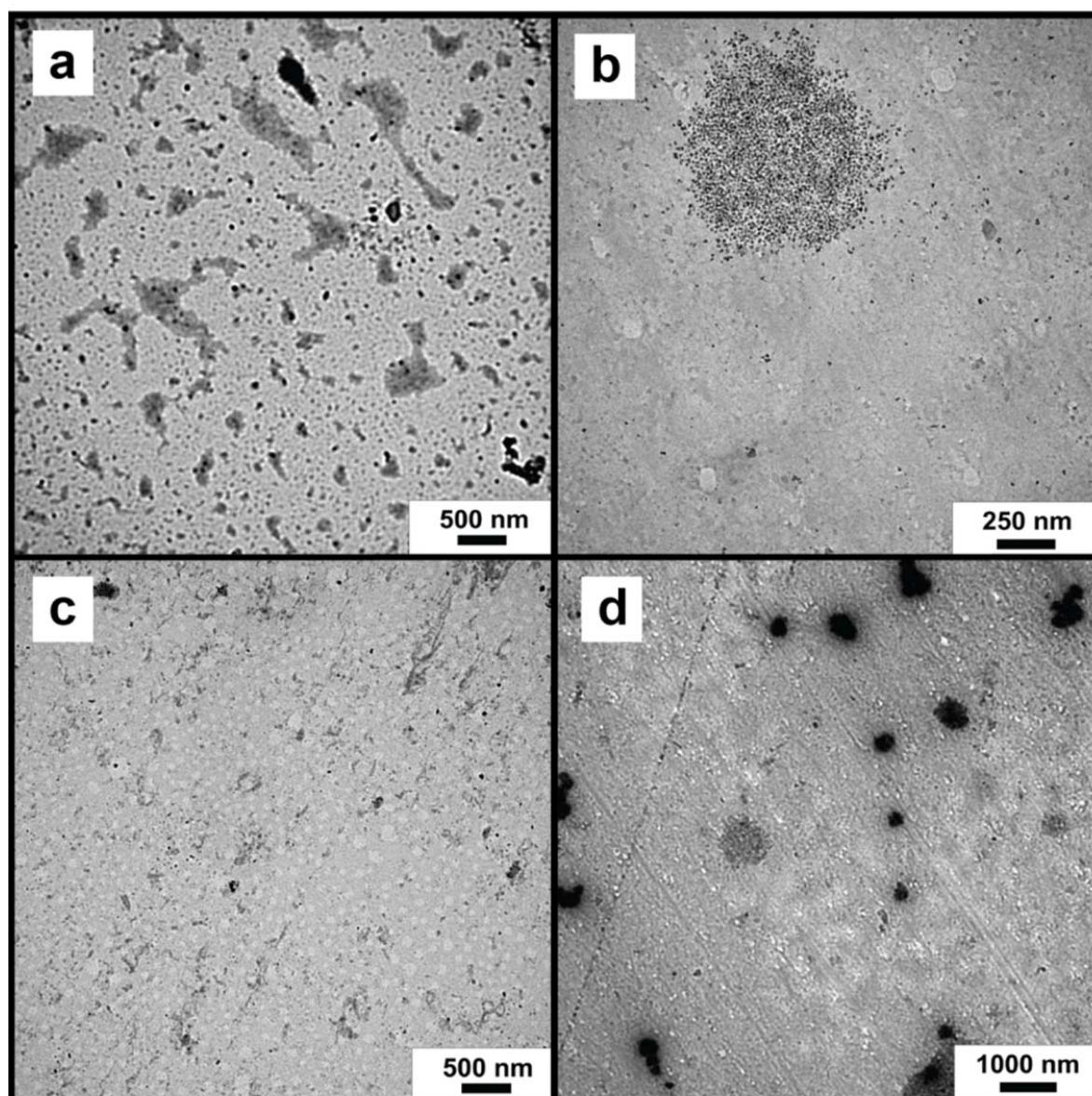
Figure S15. Investigation of the redox stimulus of six-arm star polymer via TEM: a) Fc-PDMA$_{61}$@β-CD$_6$, b) Fc-PDEA$_{84}$@β-CD$_6$, c) Fc-PDMA$_{61}$@β-CD$_6$ after oxidation with NaOCl and d) Fc-PDEA$_{84}$@β-CD$_6$ after oxidation with NaOCl.
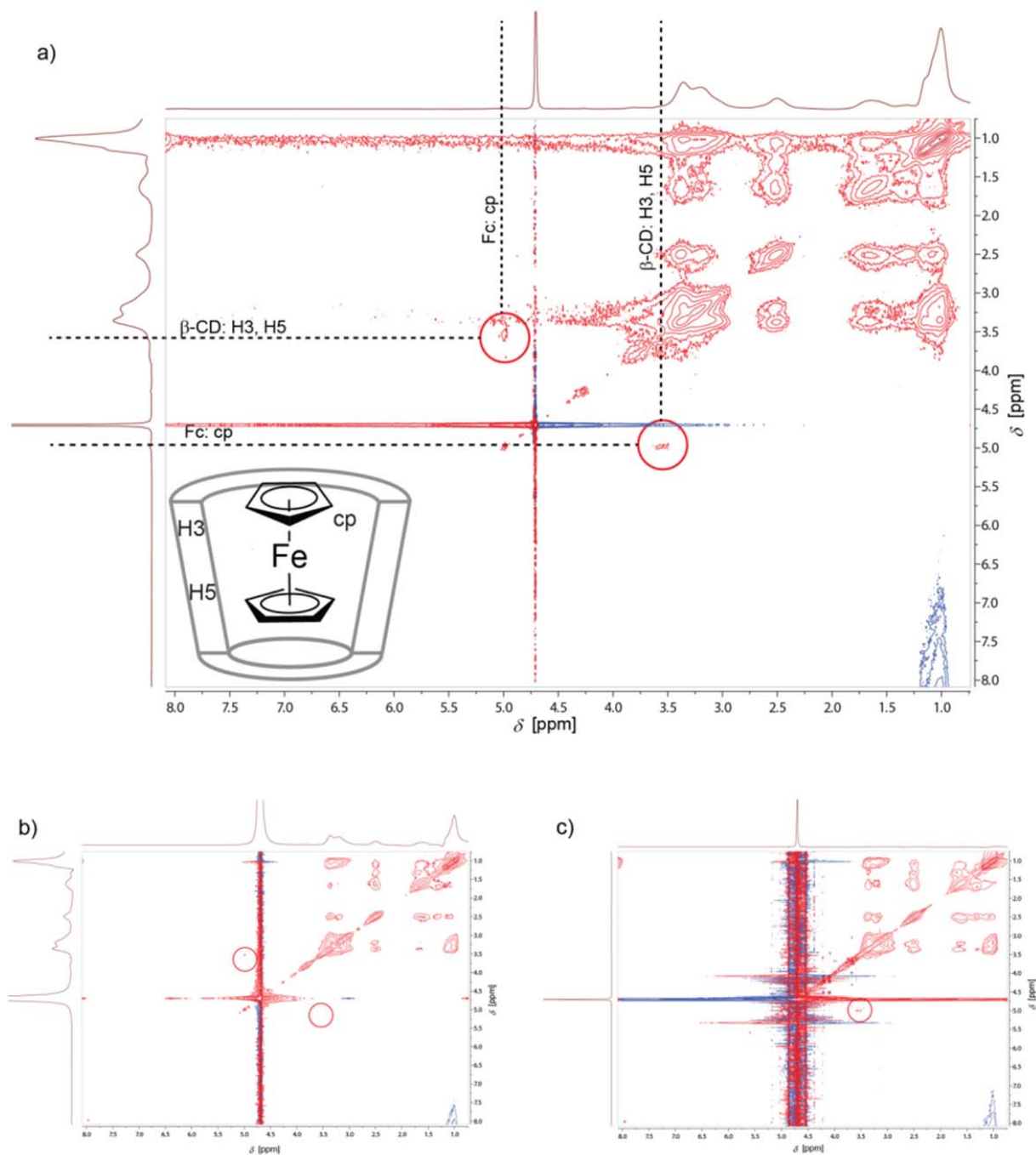
Figure S16. NOESY spectra of six-arm star polymer Fc-PDEA$_{84}$@β-CD$_6$ in D$_2$O at 25 °C and a concentration of 10 mg mL^{-1}: before oxidation (top), after oxidation with NaOCl (middle) and after reduction with excess ascorbic acid and dialysis (bottom).
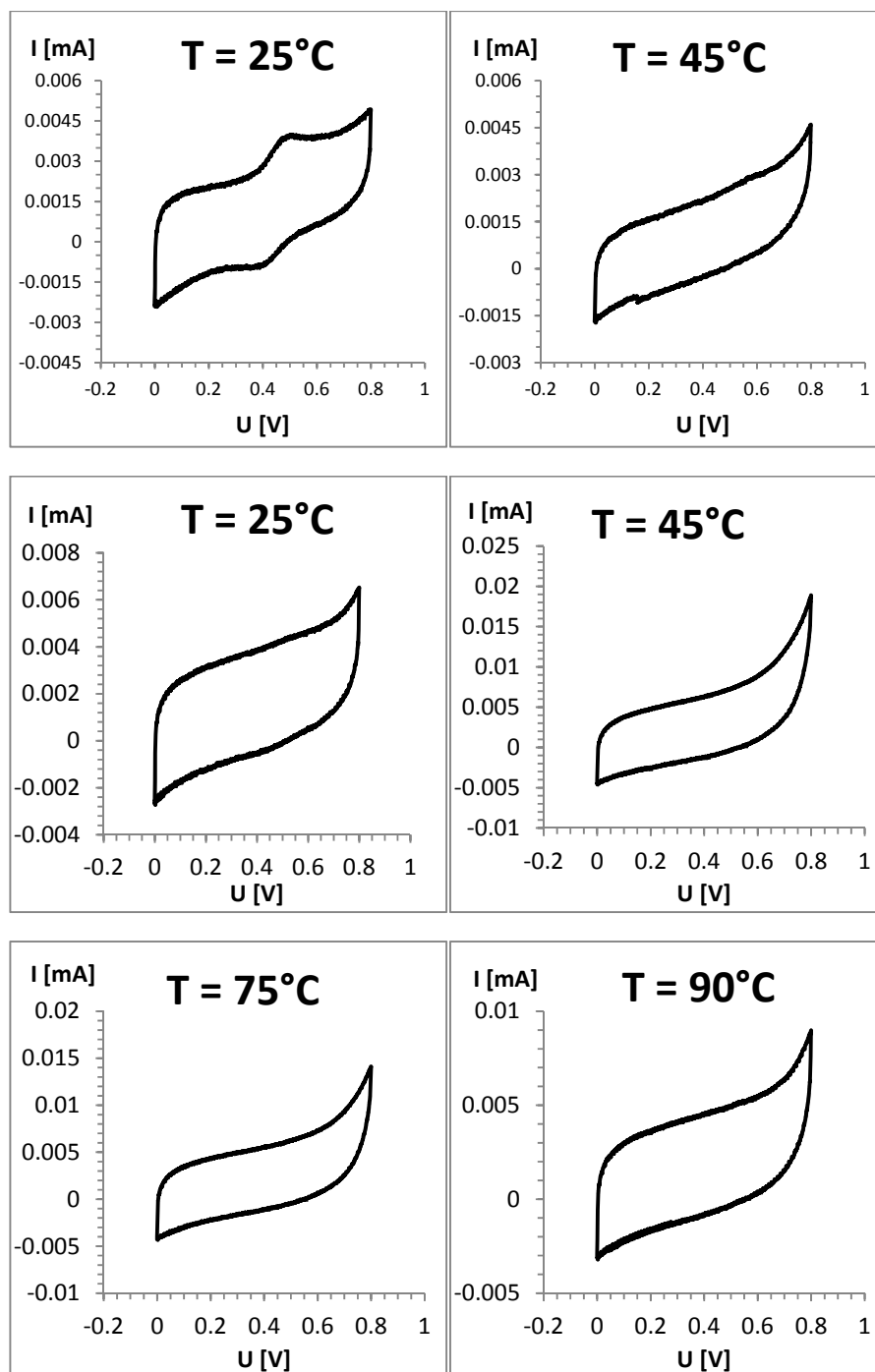
Figure S17. Investigation of the redox stimulus of six-arm star polymer via CV in 0.1 M LiCl at 20 mV s^{-1}: Fc-PDEA$_{84}$ (top) and Fc-PDEA$_{84}$@β-CD$_6$ (middle and bottom).
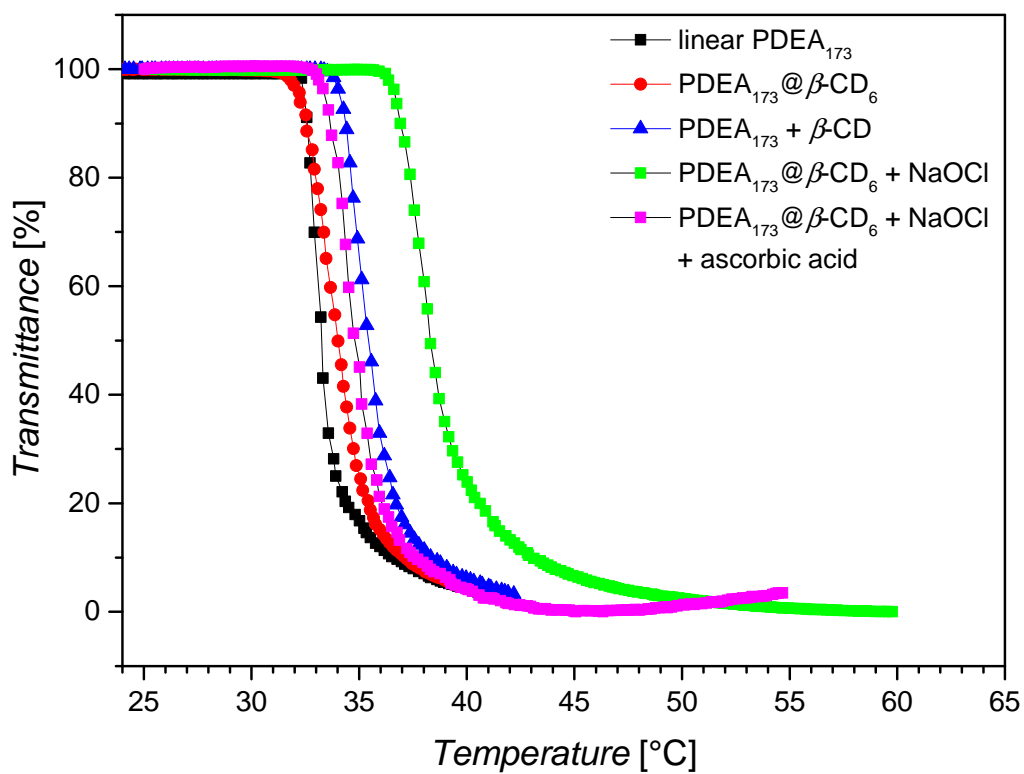
Figure S18. Turbidimetry measurements of six-arm star polymer Fc-PDEA$_{173}$@β-CD$_6$ and reference samples in water at a concentration of 1 mg mL^{-1}.
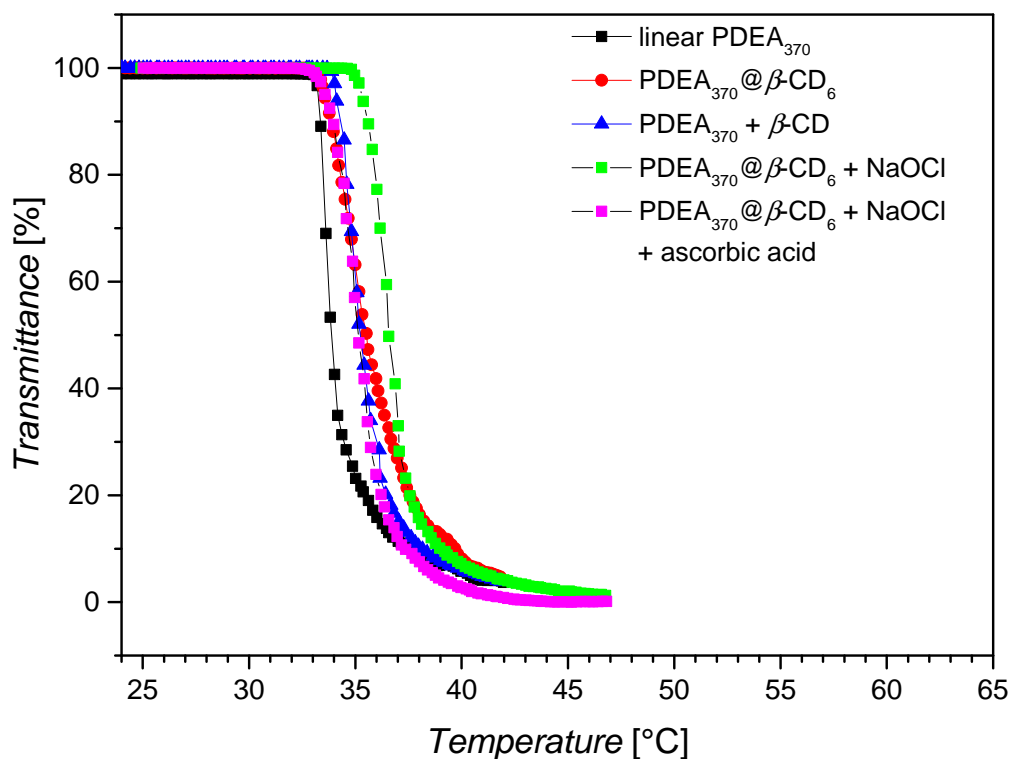
Figure S19. Turbidimetry measurements of six-arm star polymer Fc-PDEA$_{370}$@β-CD$_6$ and reference samples in water at a concentration of 1 mg mL^{-1}.

Table S4. Cloud points of PDEA and PDEA star polymers obtained via turbidimetry in water.

Polymer	$T_{c,crude}$	$T_{c,polymer@β-CD6}$	$T_{c,polymer@β-CD}$	$T_{c,polymer@β-CD6}$ after oxidation	$T_{c,polymer@β-CD6}$ after reduction
Fc-PDEA$_{84}$	31.0	34.0	34.6	46.3	34.7
Fc-PDEA$_{173}$	33.2	34.0	35.5	38.2	34.9
Fc-PDEA$_{370}$	33.9	35.5	35.3	36.6	35.1

REFERENCES

1.   Du, P.; Liu, J.; Chen, G.; Jiang, M. *Langmuir* **2011,** 27, (15), 9602-9608.