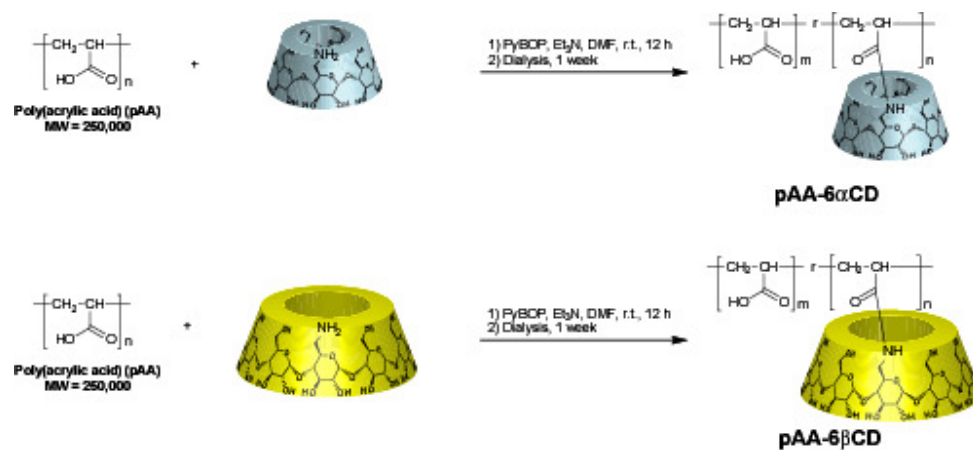
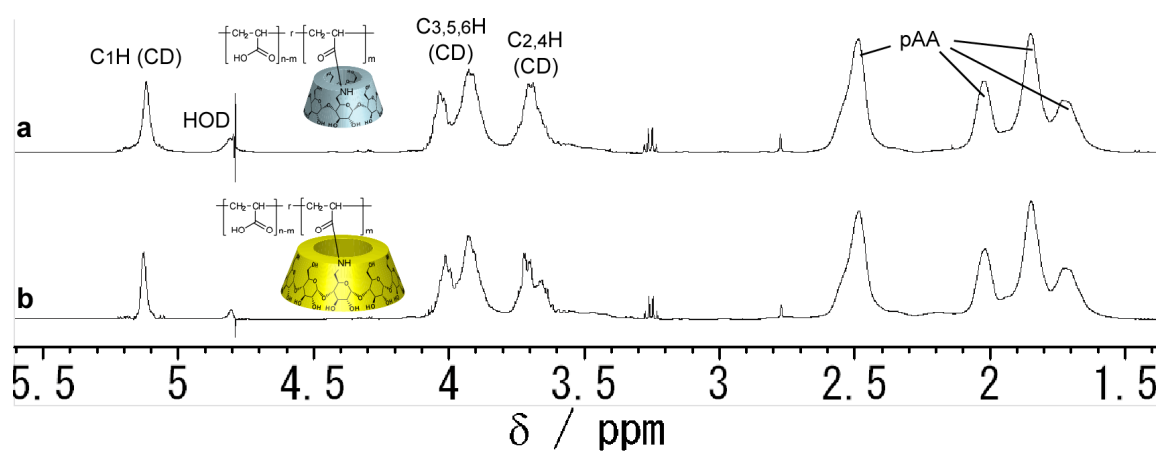
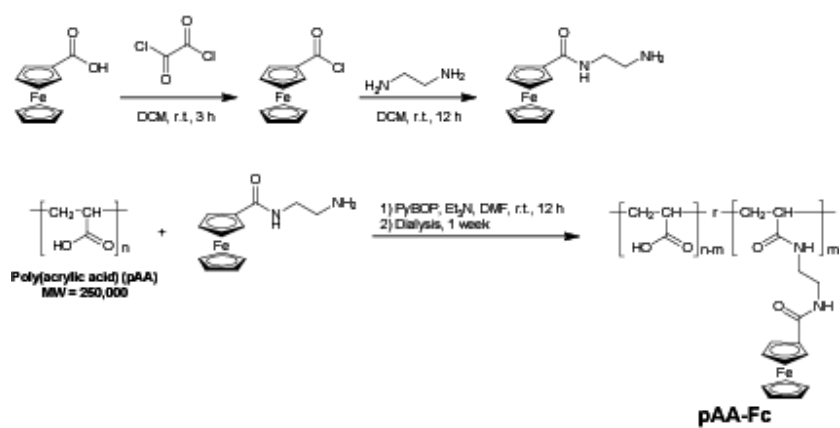




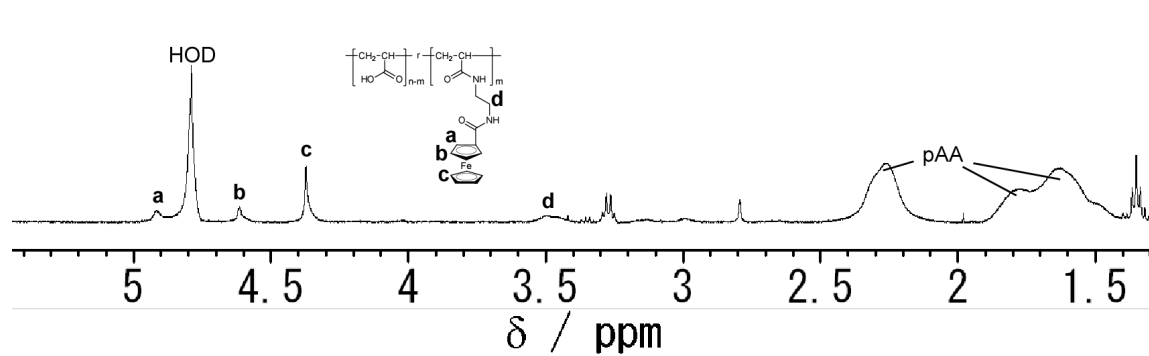
Supplementary Figure S1. Preparation of pAA-CDs.



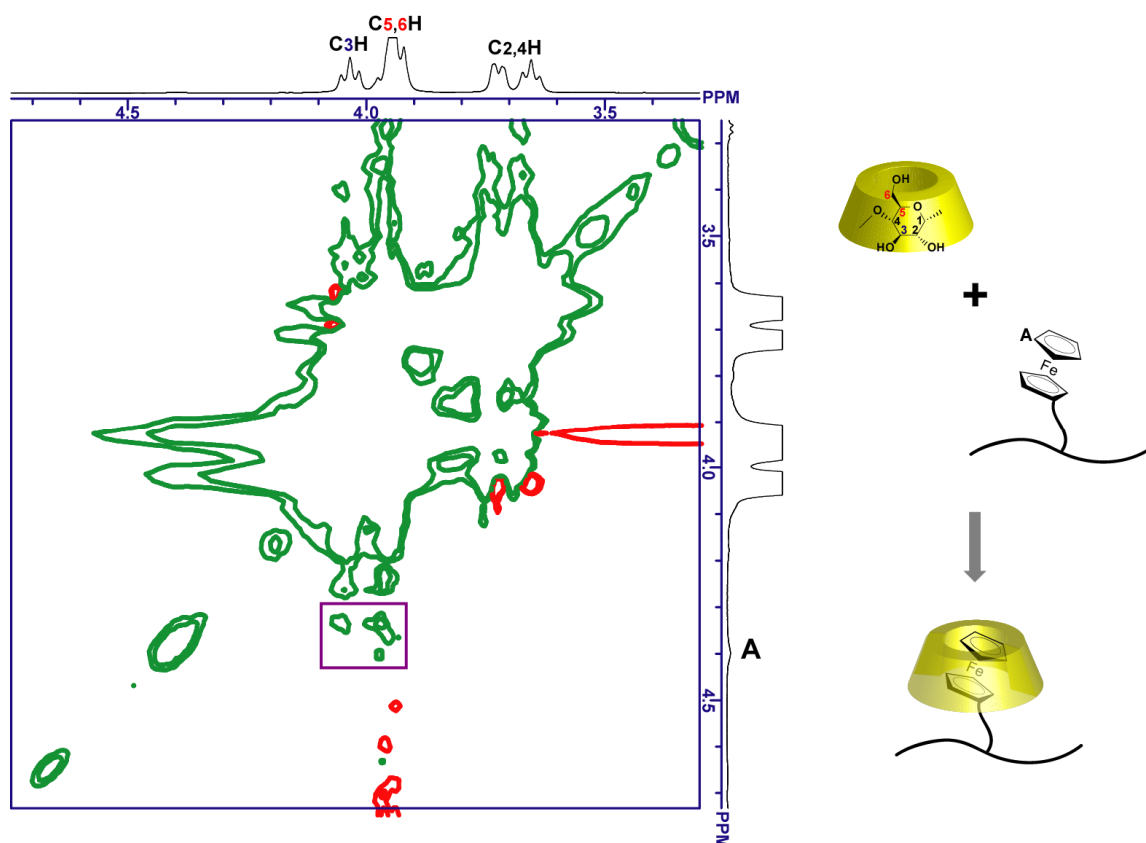
Supplementary Figure S2. Characterization of pAA-CDs. **a**, ^1H NMR spectrum of pAA-6 α CD (500 MHz, pD 9 buffer, 30 $^\circ\text{C}$). **b**, ^1H NMR spectrum of pAA-6 β CD (500 MHz, pD 9 buffer, 30 $^\circ\text{C}$).



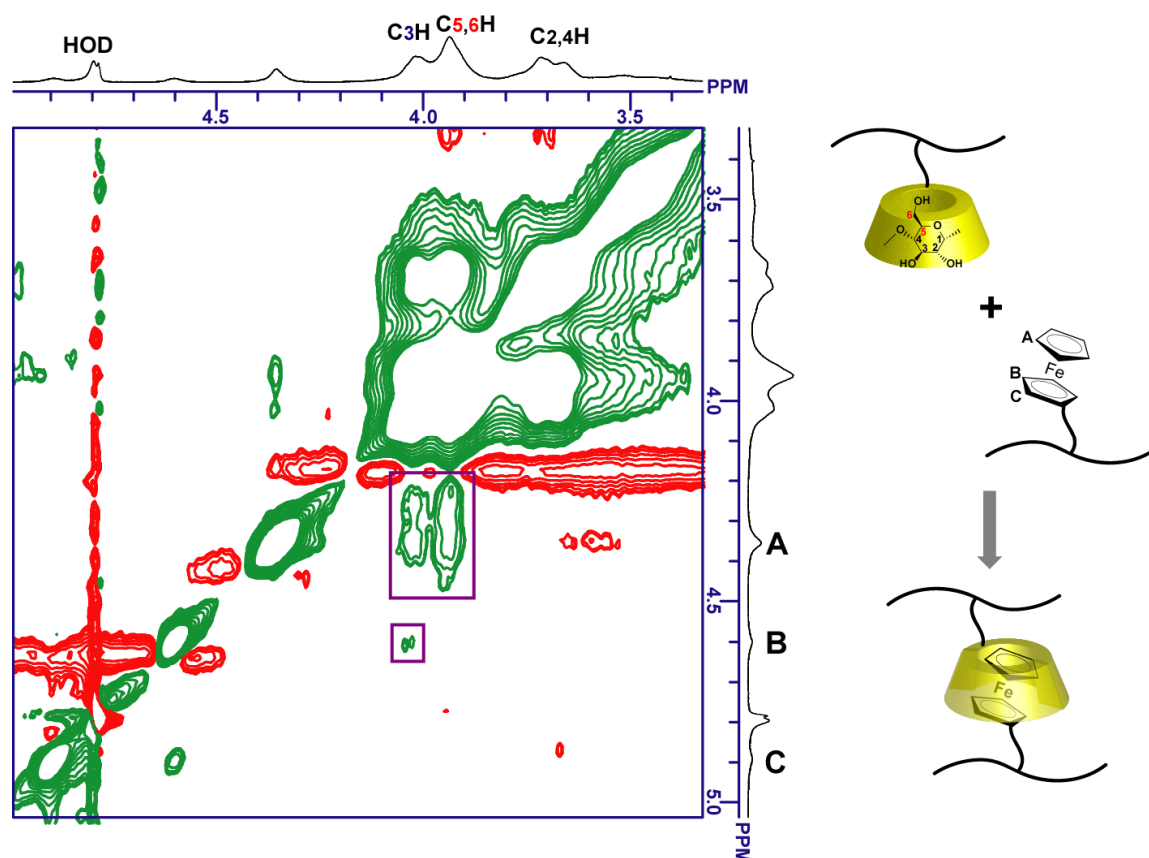
Supplementary Figure S3. Preparation of pAA-Fc.



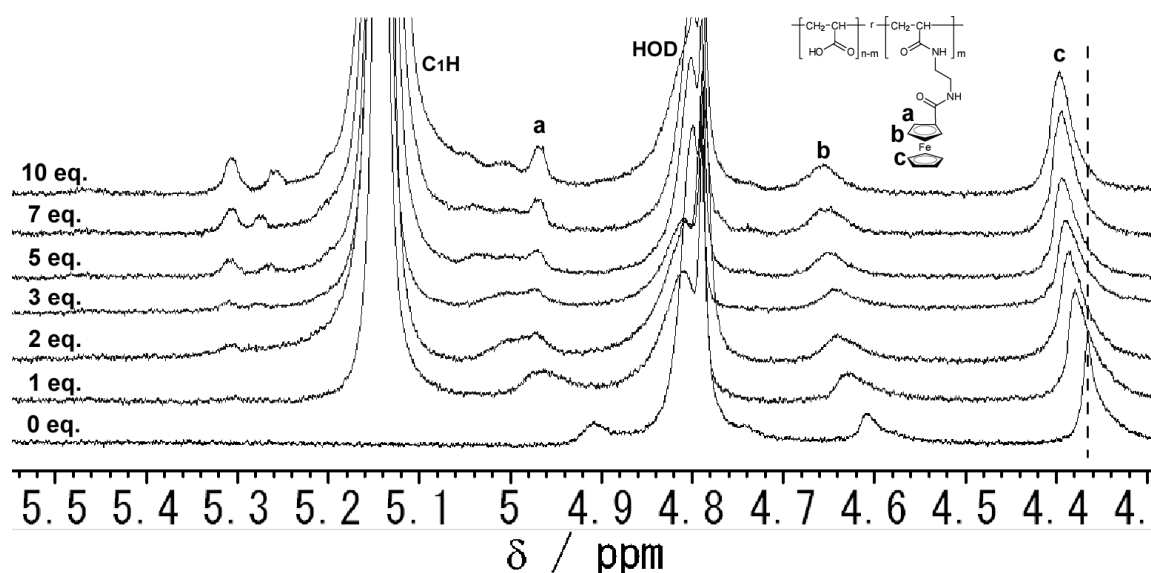
Supplementary Figure S4. Characterization of pAA-Fc. ^1H NMR spectrum of pAA-Fc (500 MHz, pD 9 buffer, 30 °C).



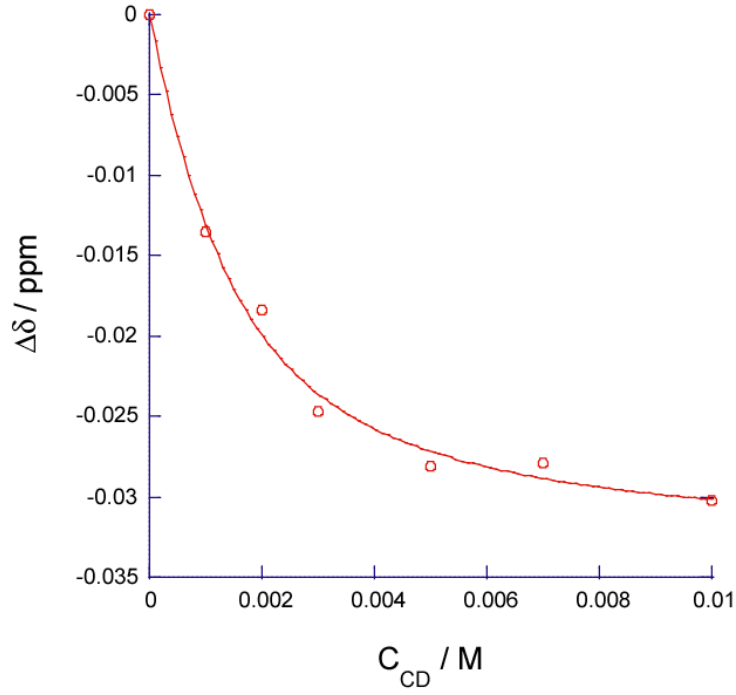
Supplementary Figure S5. 2D NOESY NMR of β -CD with pAA-Fc. 2D NOESY NMR spectrum of the mixture of β -CD (10 mM) and pAA-Fc ([Fc] = 1 mM) (500 MHz, pD 9 buffer, 30°C, left) and proposed structure of inclusion complex at side chain of pAA-Fc (right). The NOESY NMR spectrum showed that the inner protons of β -CD were correlated to the protons of the Fc group of pAA-Fc. Peak intensities between C(5,6)H protons (wider rim of β -CD) and the A proton of the Fc group was greater than that of the C(3)H proton, indicating that the Fc group is included from the wider rim of the β -CD cavity in aqueous solutions.



Supplementary Figure S6. 2D NOESY NMR of pAA-6 β CD with pAA-Fc. 2D NOESY NMR spectrum of the mixture of pAA-6 β CD ([β CD] = 1 mM) and pAA-Fc ([Fc] = 1 mM) (500 MHz, pD 9 buffer, 30 °C, left) and proposed structure of inclusion complex at side chain of each polymer (right). The NOESY NMR spectrum showed that the inner protons of the β -CD unit were correlated to the protons of the Fc group of pAA-Fc, indicating that the side chain group of pAA-Fc is included in the cavity of β -CD at side chain of pAA-6 β CD in aqueous solutions.



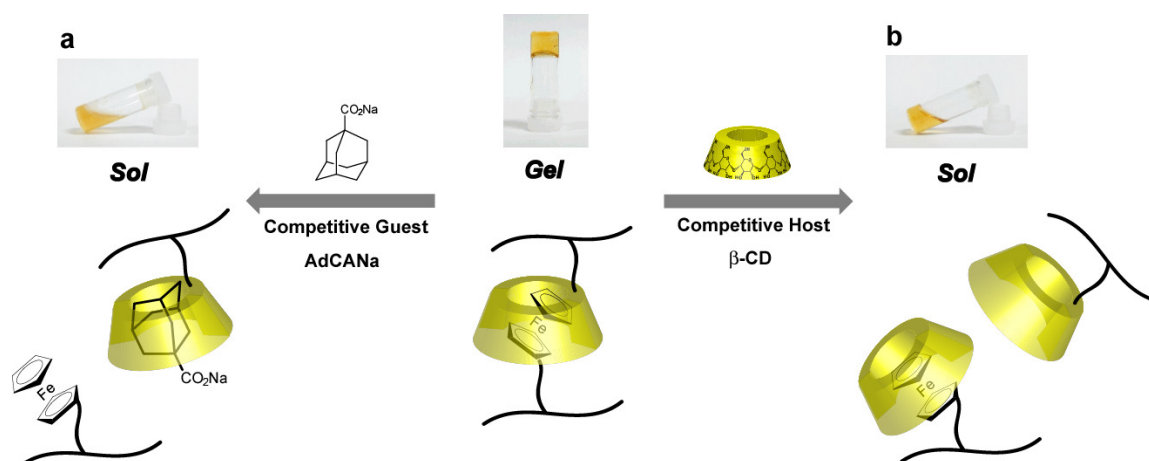
Supplementary Figure S7. Partial ^1H -NMR spectra of pAA-Fc in the presence of β -CD. ^1H NMR spectra for pAA-Fc ($[\text{Fc}] = 1 \text{ mM}$) in the presence of various concentrations (0 mM, 1 mM, 2 mM, 3 mM, 5 mM, 7 mM, and 10 mM) of β -CD (C_{CD}) (500 MHz, pD 9 buffer, 30 $^\circ\text{C}$). As C_{CD} is increased, clear down-field shifts was observed, indicating the interaction of β -CD with Fc group.



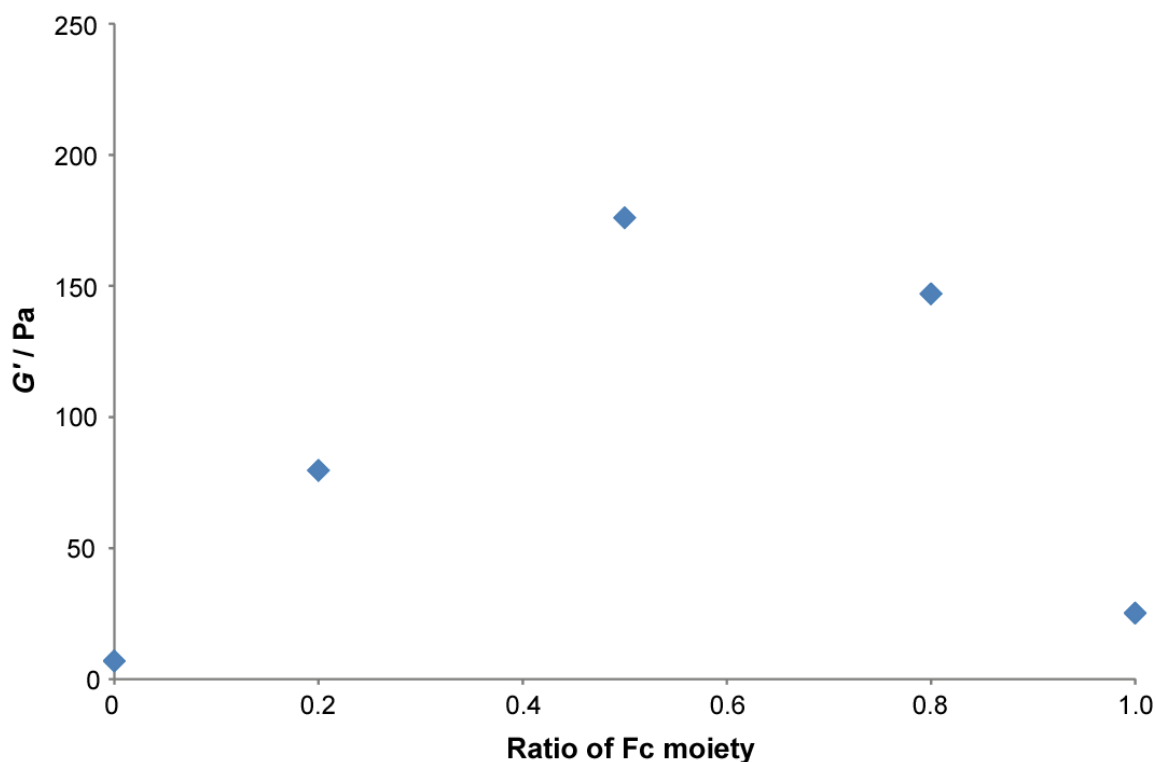
Supplementary Figure S8. Nonlinear least-squares plot. We investigated the interaction of β -CD with the Fc group of pAA-Fc by ^1H NMR to estimate apparent association constant (K) using nonlinear least-squares method. From ^1H NMR spectra (Supplementary Figure S7), the peak shifts for the signal due to the c protons of the Fc group ($\Delta\delta$) were calculated and plotted against C_{CD} . As can be seen in Figure S8, the plots show a good accordance with (S1), indicating that the interaction of β -CD with Fc group can be analyzed based on the formation of one-to-one complexes. The apparent K value was determined to be $1.1 \times 10^3 M^{-1}$ by

$$\Delta\delta = \frac{\Delta\delta}{2K[Fc]_0} [1 + K[CD]_0 + K[Fc]_0 - \{(1 + K[CD]_0 + K[Fc]_0)^2 - 4K^2[CD]_0[Fc]_0\}^{\frac{1}{2}}] \quad (S1)$$

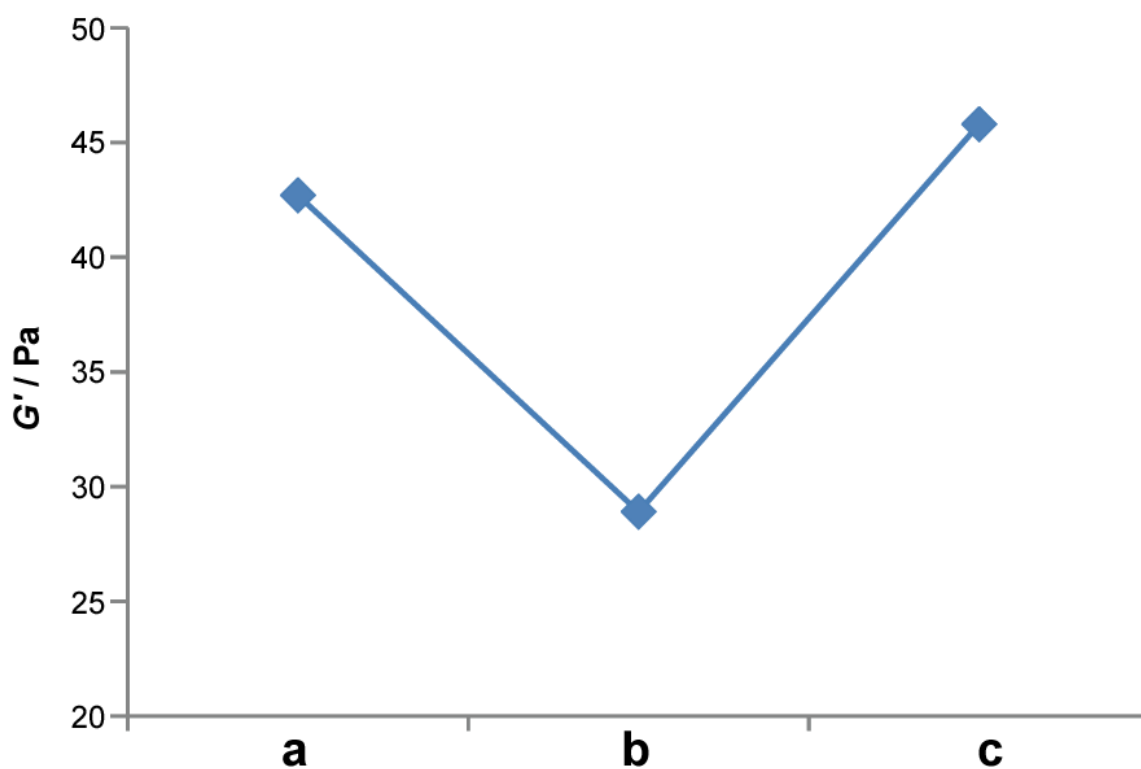
About 72% of the Fc groups were included in the cavity of the β -CD group to form a hydrogel by applying K for the pAA-6 β CD/pAA-Fc hydrogel (2 wt%).



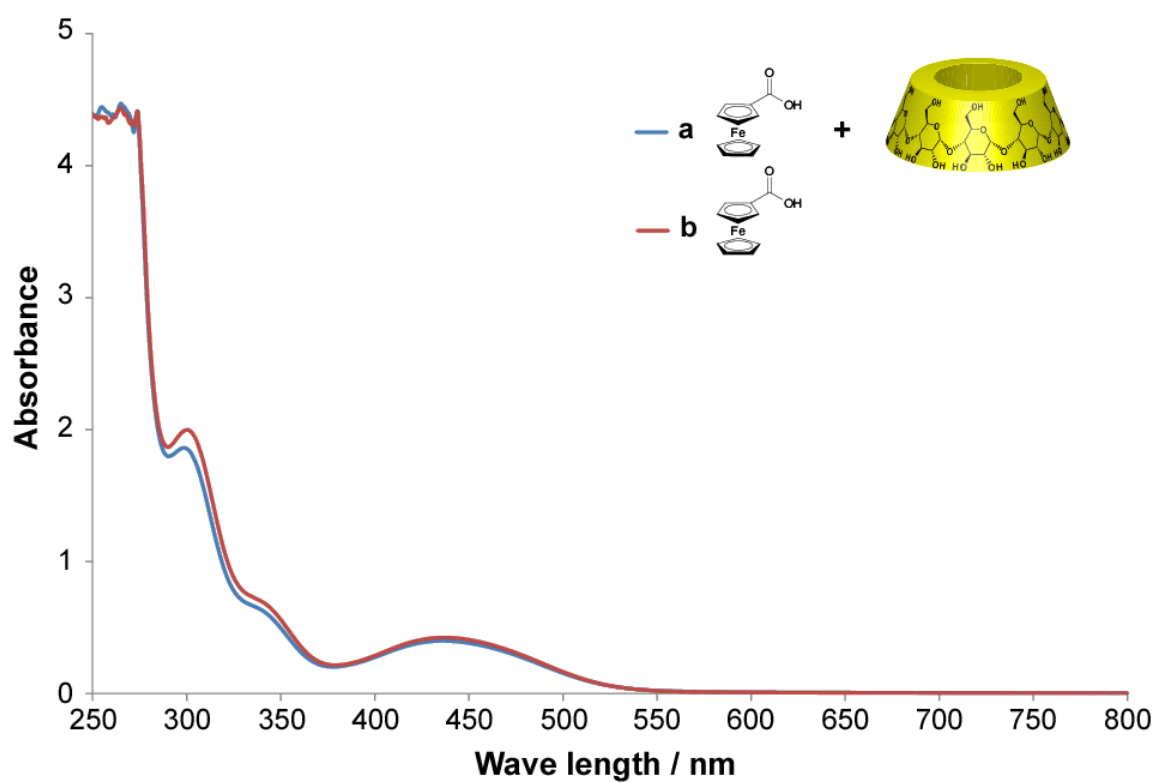
Supplementary Figure S9. Competitive guest / host experiment. Addition of AdCANA as a competitive guest and β -CD as a competitive host into the pAA-6 β CD/pAA-Fc hydrogel (2 wt%). Adding AdCANA (10 eq. for the β CD group of pAA-6 β CD) into the pAA-6 β CD/pAA-Fc hydrogel led to a sharp drop in the elasticity from 176 Pa to 23.3 Pa to form the sol state (a). Similar to adding AdCANA, adding β -CD (10 eq. for the Fc group of pAA-Fc) as a competitive host into the pAA-6 β CD/pAA-Fc hydrogel induced a phase transition into the sol state (b).



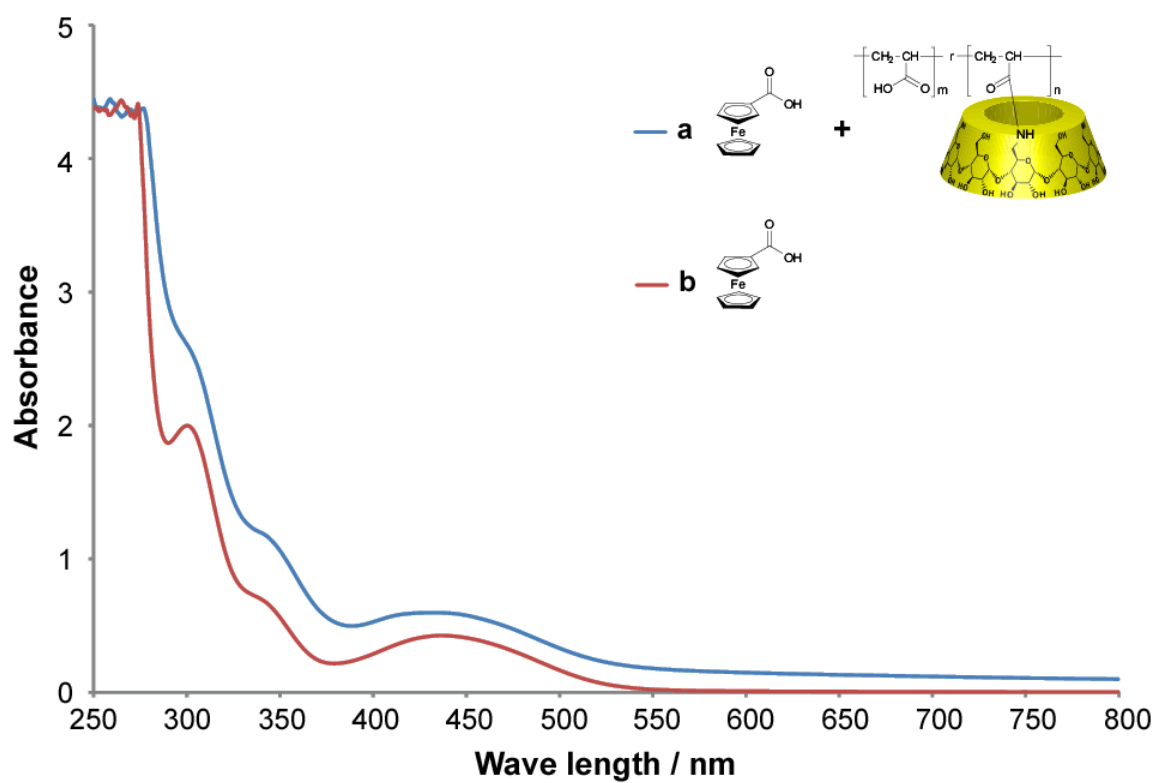
Supplementary Figure S10. G' (storage elastic modulus) against the molar ratio of Fc. The elasticity of pAA-6 β CD/pAA-Fc was estimated by varying the ratio of pAA-6 β CD and pAA-Fc in the monomer unit equivalent ($\omega = 10$ rad / s, Strain = 0.1%, pH 9 buffer, 25 °C). Values of G' were plotted against the ratio of ferrocene moiety of pAA-Fc against β CD moiety of pAA-6 β CD.



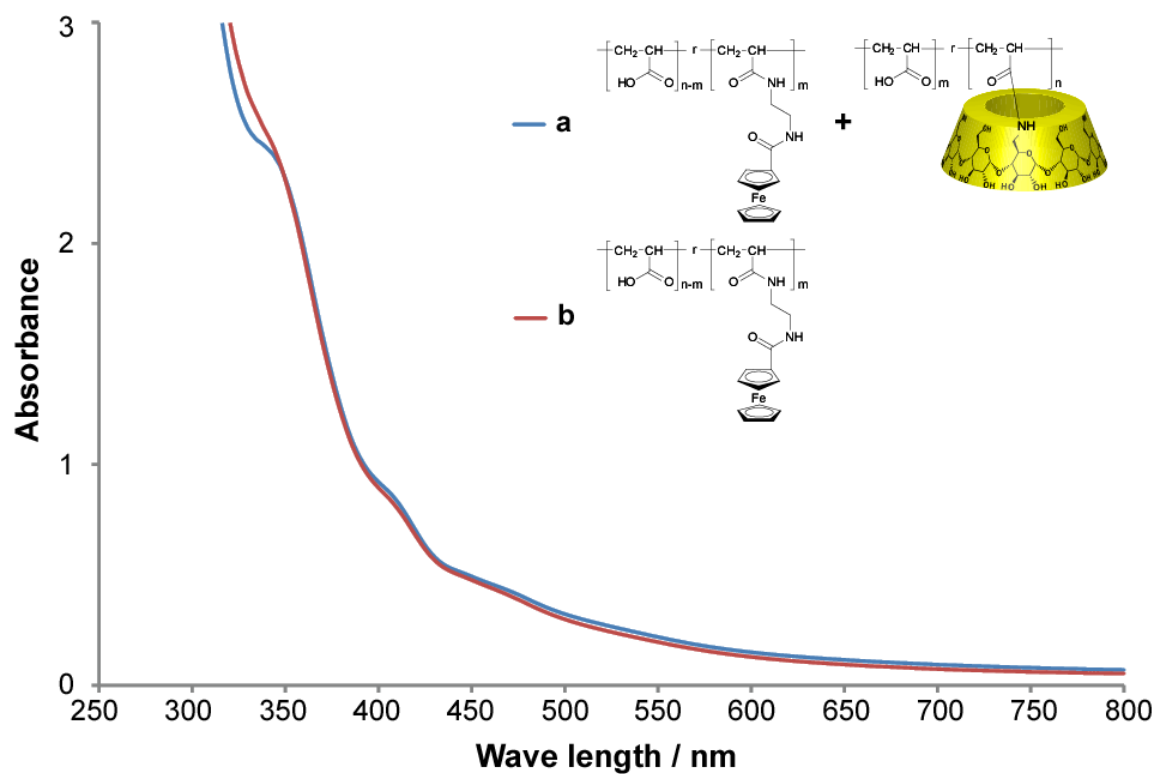
Supplementary Figure S11. Storage elastic modulus (G') switched by redox. Storage elastic modulus (G') of pAA-6 β CD/pAA-Fc hydrogel (2 wt%) before (a), after electrochemical oxidation (+1.0 V vs Ag/AgCl, 24 h) (b), and after subsequent reduction by heating (50 °C, 1 h) (c). ($\omega = 10 \text{ rad / s}$, Strain = 1%, pH 9 buffer, 25 °C)



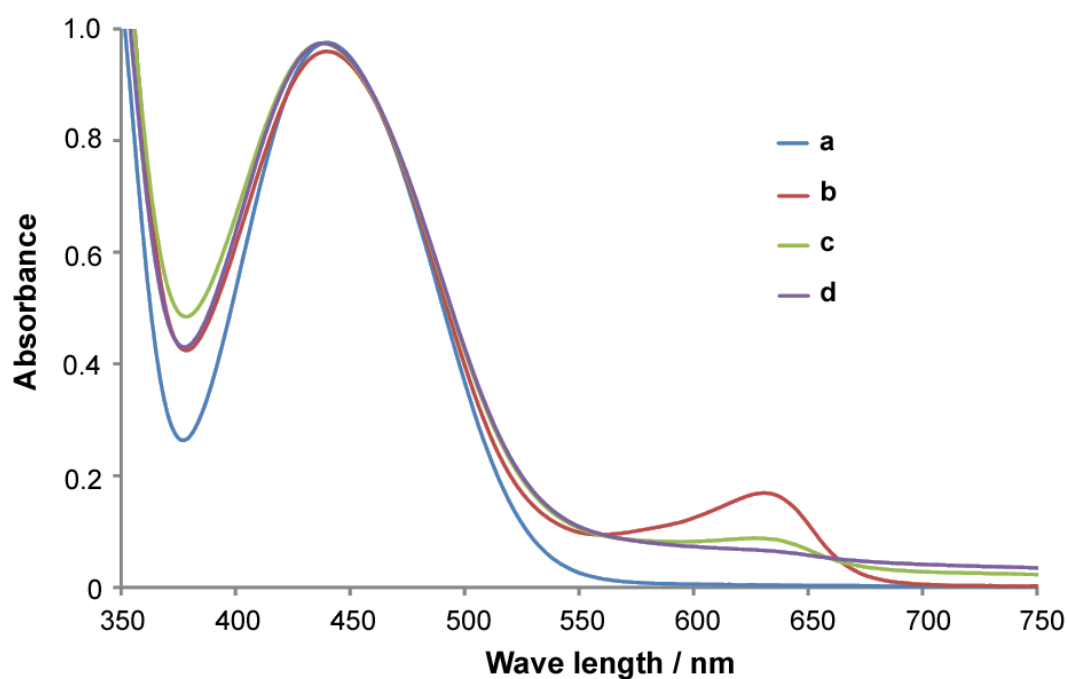
Supplementary Figure S12. UV-Vis spectra of FcCOOH and β -CD. The UV-Vis spectra of FcCOOH (2 mM) in the presence of β -CD (2 mM) (a) and absence of β -CD (b) in aqueous solutions at 25 °C.



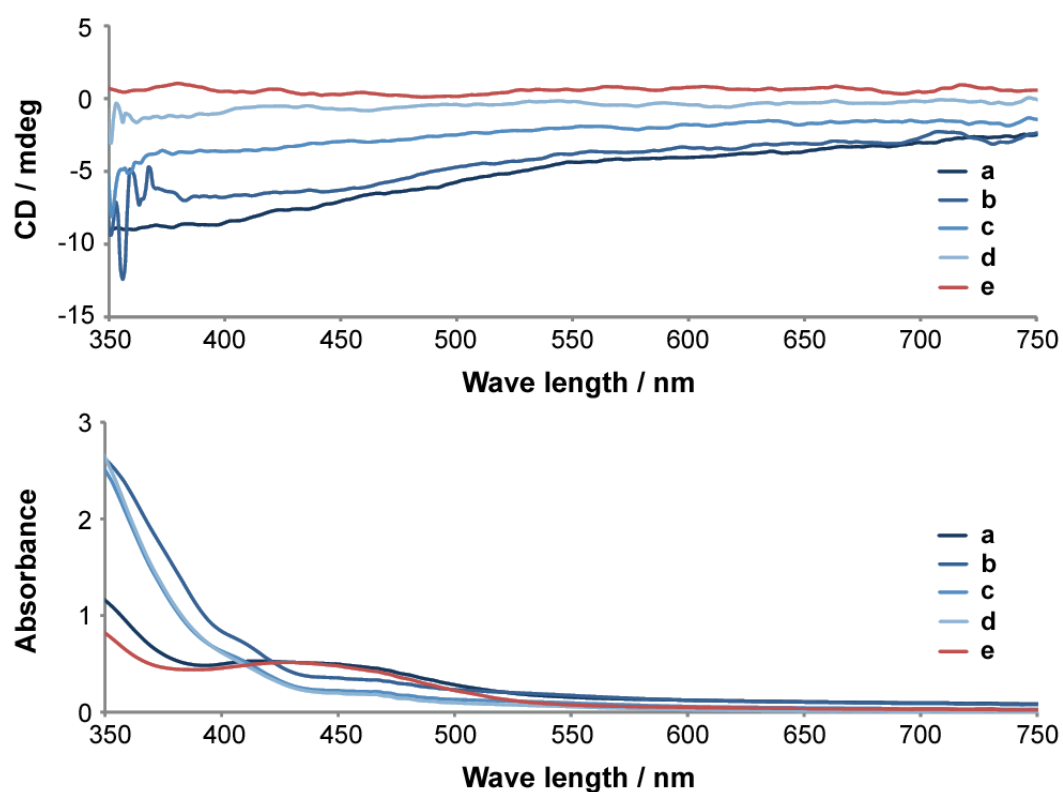
Supplementary Figure S13. UV-Vis spectra of FcCOOH and pAA-6βCD. The UV-Vis spectra of FcCOOH (2 mM) in the presence of pAA-6βCD ([βCD] = 2 mM) (a) and absence of pAA-6βCD (b) in aqueous solutions at 25 °C.



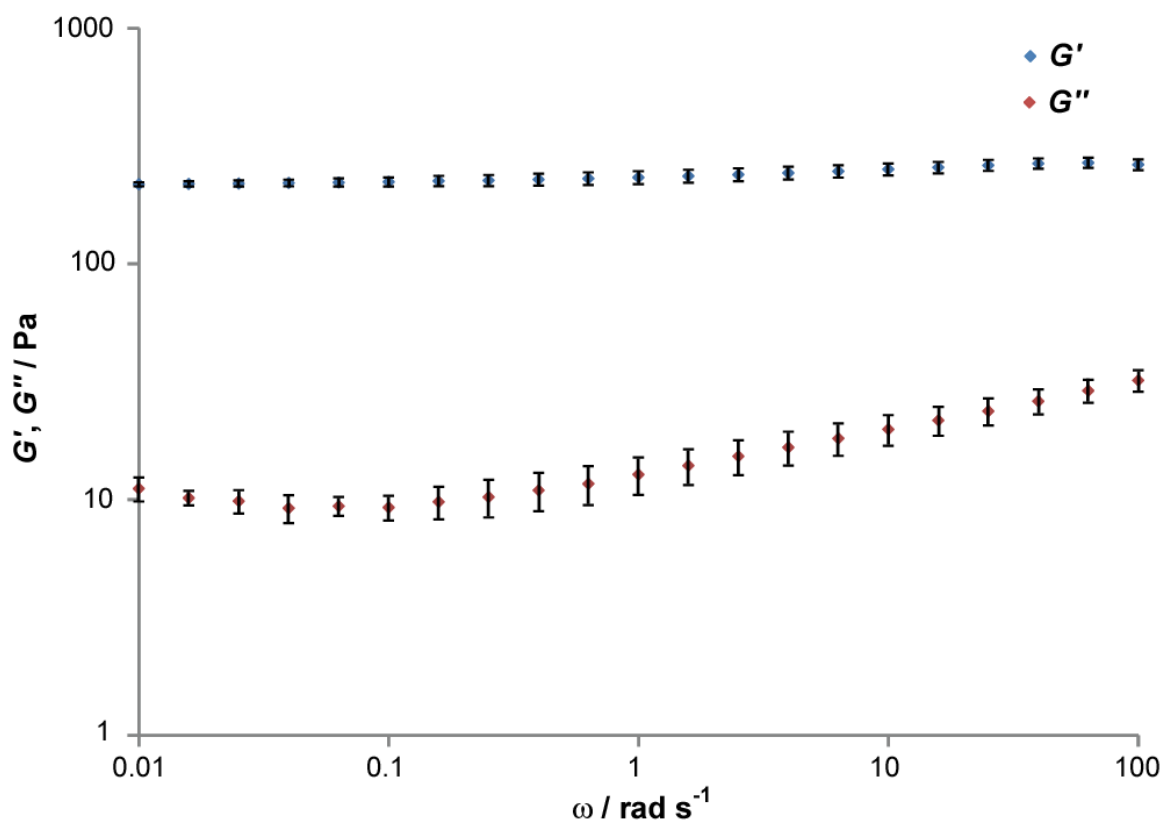
Supplementary Figure S14. UV-Vis spectra of pAA-Fc and pAA-6βCD. The UV-Vis spectra of pAA-Fc ([Fc] = 1 mM) in the presence of pAA-6βCD ([βCD] = 1 mM) (a) and absence of pAA-6βCD (b) in aqueous solutions at 25 °C.



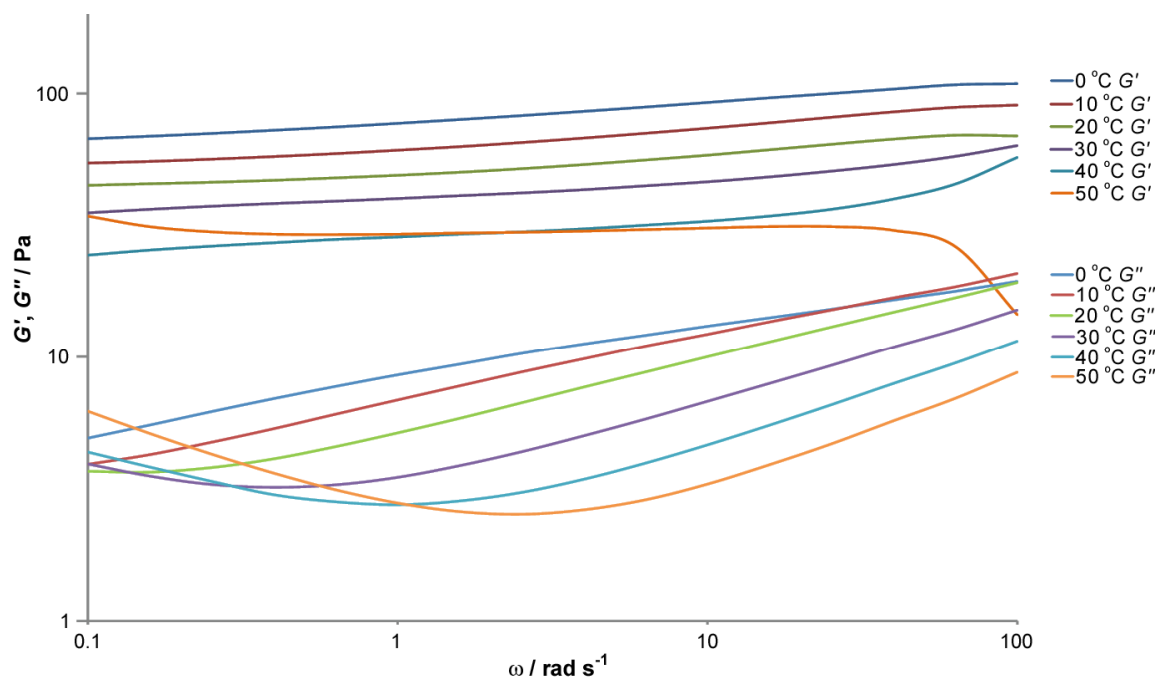
Supplementary Figure S15. Change of UV-Vis spectra by redox. The UV-Vis spectra of Fc-COOH (5 mM) in 0.1 M NaBr aqueous solution (a), after electrochemical oxidation (+0.5 V vs Ag/AgCl, 10 min.) (b), after subsequent heating (50 °C, 10 min.) (c), and after heating (50 °C, 40 min.) (d) in aqueous solutions at 25 °C. The peak around 630 nm due to Fc^+ in its oxidized state was observed by oxidation, and was disappeared by subsequent heating.



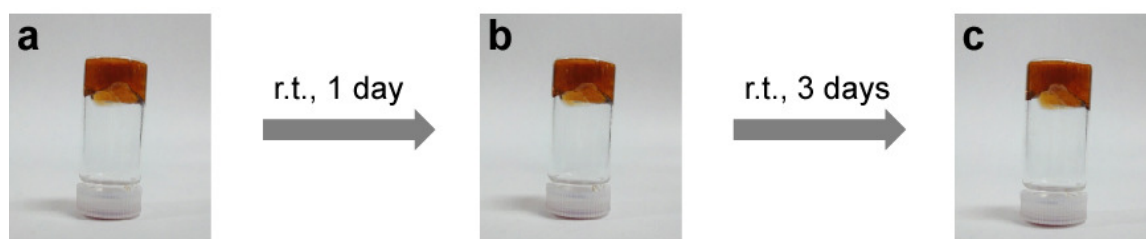
Supplementary Figure S16. Circular dichroism spectra of Fc-COOH. UV-Vis and circular dichroism spectra of Fc-COOH (2 mM). Fc-COOH (2 mM)/PAA-6 β CD ($[\beta$ CD] = 2 mM) in the absence of NaClO aq. (a) and in the presence of NaClO aq. (4.7 mM (b), 14 mM (c), and 23 mM (d)), and Fc-COOH (2 mM) (e) in aqueous solutions at 25 °C. The negative induced Cotton band around 450 nm was observed in aqueous solutions. This Cotton band is assigned to the Fc group included in asymmetric cavity of β -CD. On the contrary, the Cotton band was disappeared with the addition of NaClO aq. These results indicate that the oxidized ferricenium group was excluded from the cavity of β -CD.



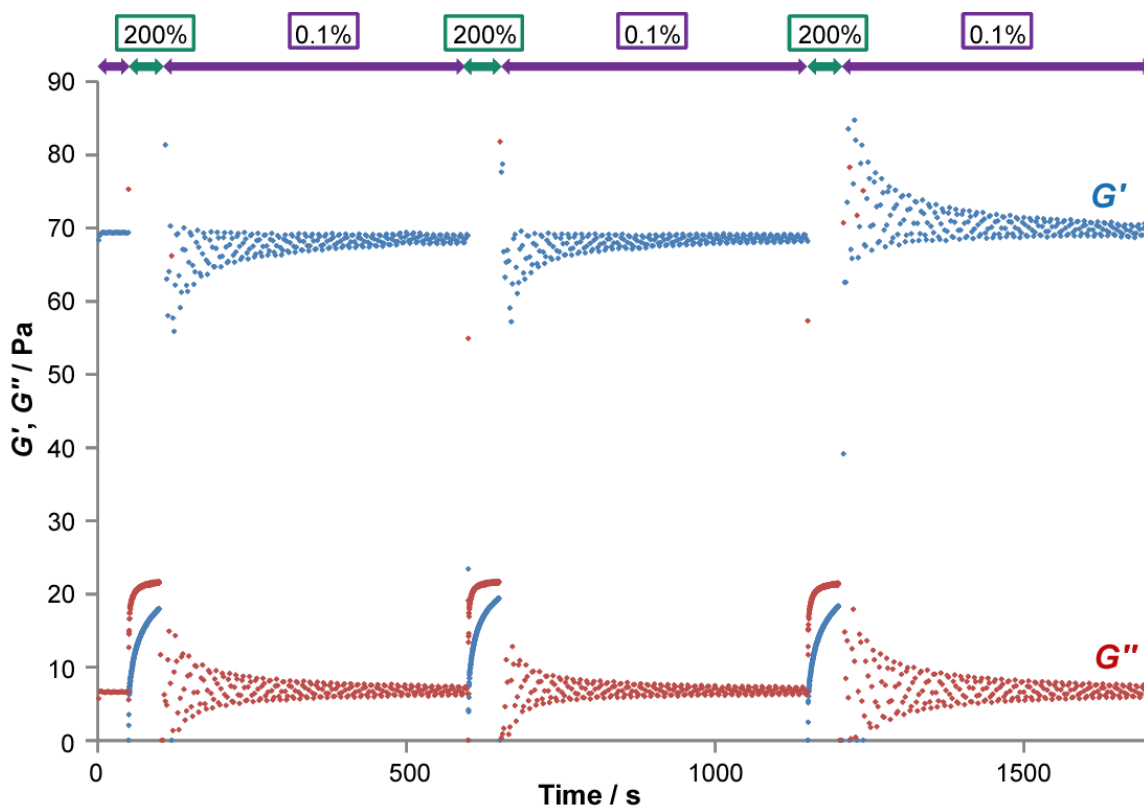
Supplementary Figure S17. Dynamic viscoelastic measurement. Dependency of the storage and loss moduli, G' and G'' on angular frequency (ω) for an aqueous solution of the mixture of pAA-6 β CD/pAA-Fc hydrogel (2 wt%). (Strain = 0.1%, pH 9 buffer, 25 °C, n=5, error bars are standard deviation.)



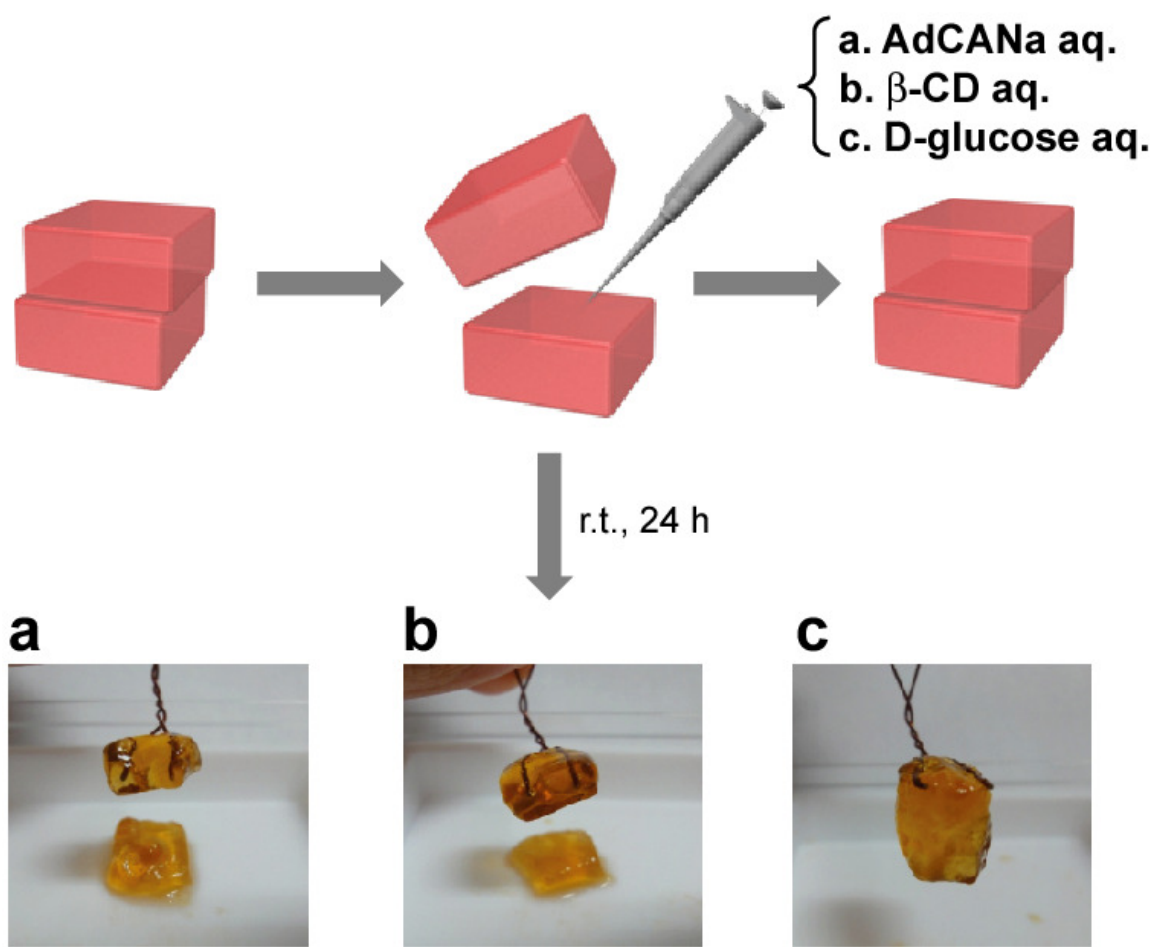
Supplementary Figure S18. Temperature dependence of G' and G'' . Storage elastic modulus (G') and loss elastic modulus (G'') of the mixture of pAA-6 β CD/pAA-Fc hydrogel (2 wt%) according to temperature. (Strain = 1%, pH 9 buffer)



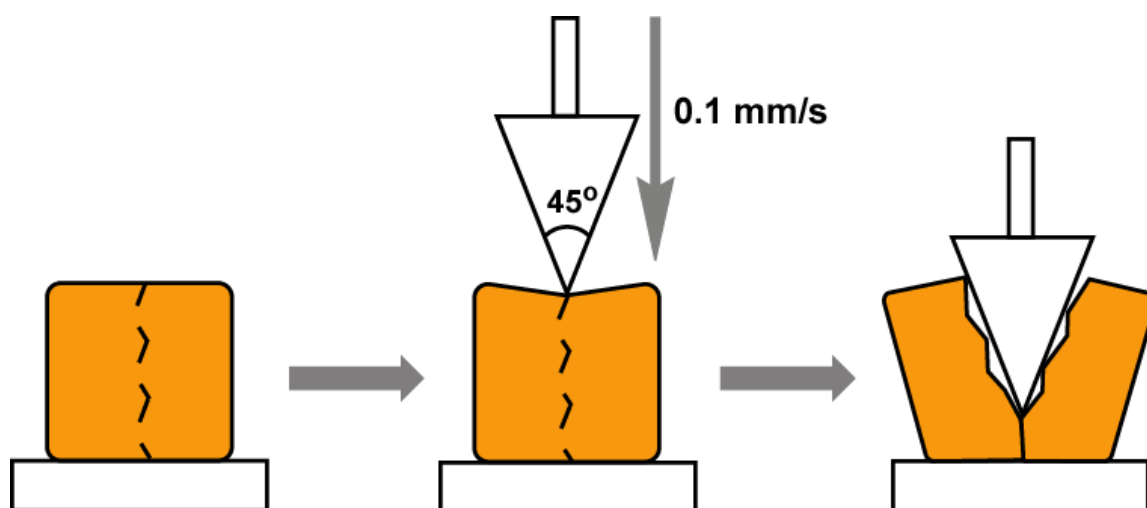
Supplementary Figure S19. Photographs of the gel. Photographs of gels soon after making (a), after 1 day (b), and after 3 days (c). No flowing was observed.



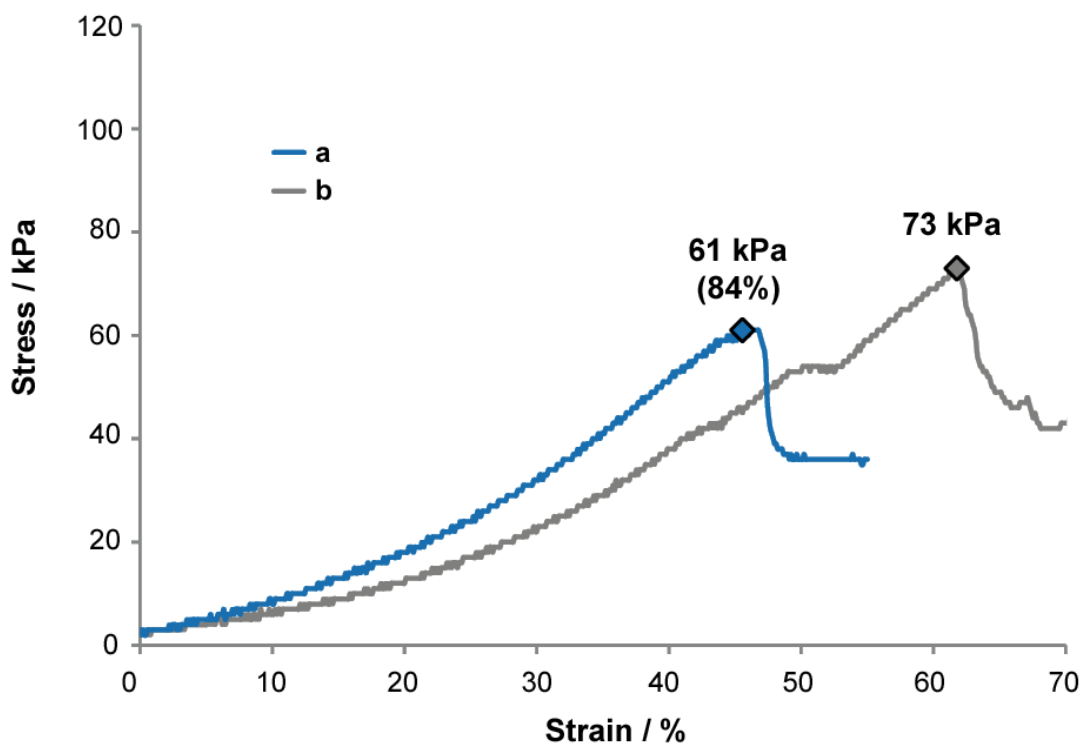
Supplementary Figure S20. Step strain measurements. G' (blue dots) and G'' (red dots) values of the pAA-6 β CD/pAA-Fc hydrogel (2 wt%) in continuous step strain measurements (25 °C). Large strain (200%) inverted the values G' and G'' to give the sol state. On the other hand, G' was recovered under a small strain (0.1%) within 20 seconds.



Supplementary Figure S21. Self-healing experiments using competitive guest / host molecules. 1 cm cube-shaped 2 wt% gels were cut in half, and the cut surfaces were coated with aqueous solutions of AdCANa (3 mM, 20 μ L) (a), β -CD (3 mM, 20 μ L) (b), or D-glucose (3 mM, 20 μ L) (c). Then the two pieces were reattached according to the experimental operation. After 24 hours, gels coated with aqueous solutions of AdCANa (3 mM, 20 μ L) or β -CD (3 mM, 20 μ L) did not show healing. However, the surface coated with D-glucose aq. showed healing.



Supplementary Figure S22. Schematic illustration of breaking stress measurement. Breaking stress of the pAA-6 β CD/pAA-Fc hydrogel was measured by a creep meter with a wedge-shaped plunger.



Supplementary Figure S23. Self-healing property. Stress-strain curve of pAA-6βCD/pAA-Fc hydrogel (3 wt%) after standing for 24 h (a) compared with the sample without crack (b). Peaks indicate the breaking points, and the stress values at that point were regarded as breaking stress.

Supplementary Table S1. Degree of side chain modification (per acrylic acid unit) for each polymer. Degree of side chain modification was calculated from ^1H NMR data. In the case of pAA-CDs, values of integral were compared between pAA protons and C_1H protons. In the case of pAA-Fc, values of integral were compared between pAA protons and c protons.

Polymer	pAA-6 α CD	pAA-6 β CD	pAA-Fc
Side chain modification ratio [%]	4.6	4.0	2.7