- Electronic Supplementary Information -

Redox-Responsive Supramolecular Polymeric Networks Having Double-Threaded Inclusion Complexes

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1. Experimental details

Materials

Acrylamide (AAm) and *N*-(hydroxymethyl)acrylamide were purchased from Wako Pure Chemical Industries, Ltd. α-Cyclodextrin (αCD), β-cyclodextrin (βCD), and γ-cyclodextrin (γCD) were obtained from Junsei Chemical Co. Ltd. *p*-Toluenesulfonic acid monohydrate, potassium peroxodisulfate (KPS), *N,N,N′,N′*–tetramethylethylenediamine (TEMED) and *N,N′*–methylenebis(acrylamide) (MBAAm) were purchased from Nacalai Tesque Inc. DMSO-d_6 was obtained from Merck & Co., Inc. The water used for the preparation of the aqueous solutions was purified with a Millipore Elix 5 system. Other reagents were used without further purification. Mono-6*O*-Acrylamido-methyl-αCD and βCD (αCDAAmMe and βCDAAmMe) and 4-(11-acryloyloxyundecyl)-4'-(methyl)-bipyridinium dichloride (VC11 monomer) were prepared according to our previous reports.[1-2]

Measurements

^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM–ECA 500 NMR spectrometer (500 MHz). Solid–state ^{1}H field gradient magic angle spinning (FG-MAS) NMR spectra were recorded with a JEOL JNM–ECA 400 NMR spectrometer (400 MHz, with a sample spinning rate of 7.0 kHz). All chemical shifts were referenced to the residual solvent peaks as internal standards (for ^{1}H NMR: δ = 0 ppm for tetramethylsilane (TMS) and 2.49 ppm for DMSO-d_6, ^{13}C NMR: δ = 0 ppm for TMS and 39.5 ppm for DMSO-d_6).

Matrix-assisted LASER desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was conducted on a Bruker instrument.

UV/Vis spectra were recorded by a JASCO V-650 in water with a 1-mm quartz cell at room temperature.

FT-IR spectra were acquired using a JASCO FT/IR–410 spectrometer with ATR method.

Isothermal titration calorimetry (ITC) measurements were performed by Malvern MicroCal iTC200 system.

The fracture stress and strain of the hydrogels were determined by the tensile tensing system (Autograph AG-X plus, Shimadzu).

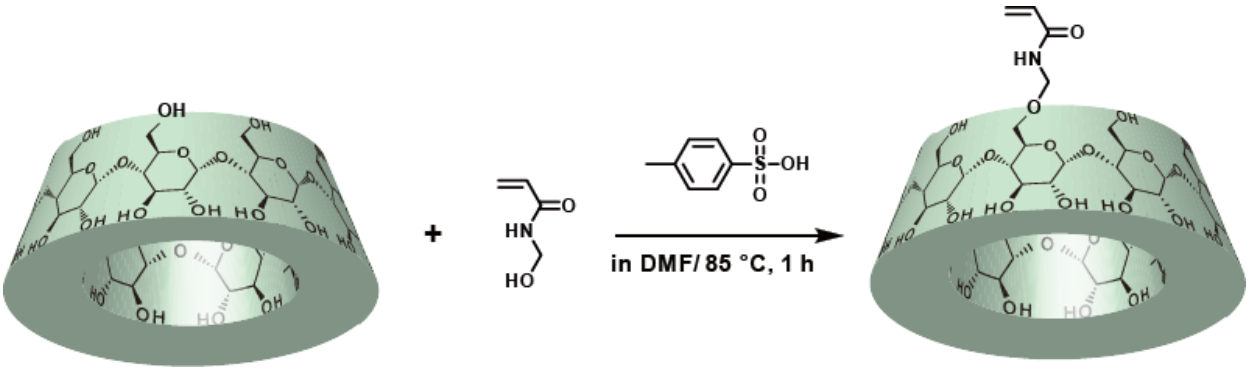
The Young's modulus of each hydrogel was determined by compression tests (Creep meter, RE-33005B, Yamaden Ltd.), where initial slope of stress-strain curve (λ < 5%) was employed to calculate the Young's modulus.

The size of the hydrogel was measured using a digital inverted microscope (EVOS AME i2111, Advanced Microscopy Group).

Dynamic mechanical measurement (DMA) were observed by dynamic shear rheometer to investigate dynamic viscoelasticity of the obtained materials. (Equipment: Anton Paar MCR302 rheometer with D-PP08 and P-PTD200. Application: RHEOPLUS/32 V3.62. Mode; Amplitude Sweep, Number of Data Points in Single Measurement: 31, Amplitude gamma = 0.01 ... 1 % log; |Slope| = 15 Pt. / dec. Angular Frequency omega = 10 rad/s.)

All the error bars in the charts were obtained through more than three experimental replicates. The errors bars indicate standard deviation of the replication.

2. Preparation of host monomer[1,2] (γCDAAmMe)



Scheme S1. Preparation of γCDAAmMe.

γ-Cyclodextrin (γCD, 13 g, 10 mmol) and *N*-(hydroxymethyl)acrylamide (1.0 g, 10 mmol) were dissolved in DMF (100 mL). *p*-Toluenesulfonic acid monohydrate (500 mg, 2.9 mmol) was added to the solution, and the solution was stirred for 1 hour at 80 °C. The resulting solution was poured into acetone (500 mL) to precipitate the crude product, which was collected by filtration and washed with acetone. The filtrate was dried in vacuo at 50 °C for 12 hours. The obtained product was purified by medium-pressure liquid chromatography to give γCDAAmMe (3.0 g, 22% yield).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.80 (t, J = 6.7 Hz, 1H), 6.14-6.25 (m, 2H), 5.66-5.82 (m, 17H), 4.85-4.89 (m, 8H), 4.54-4.69 (m, 9H), 3.53-3.73 (br, 32H), 3.34-3.38 (br, overlapped with HOD) (see **Figure S1**).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 165.8, 132.0, 127.1, 102.2, 84.2, 73.4, 73.1, 72.7, 71.0, 70.2, 60.5 (see **Figure S2**).

MALDI-TOF MS: *m*/*z*

Calcd. for $C_{52}H_{85}NO_{41}Na$ ($[M + Na]^+$): 1402.45;

Found: 1402.717

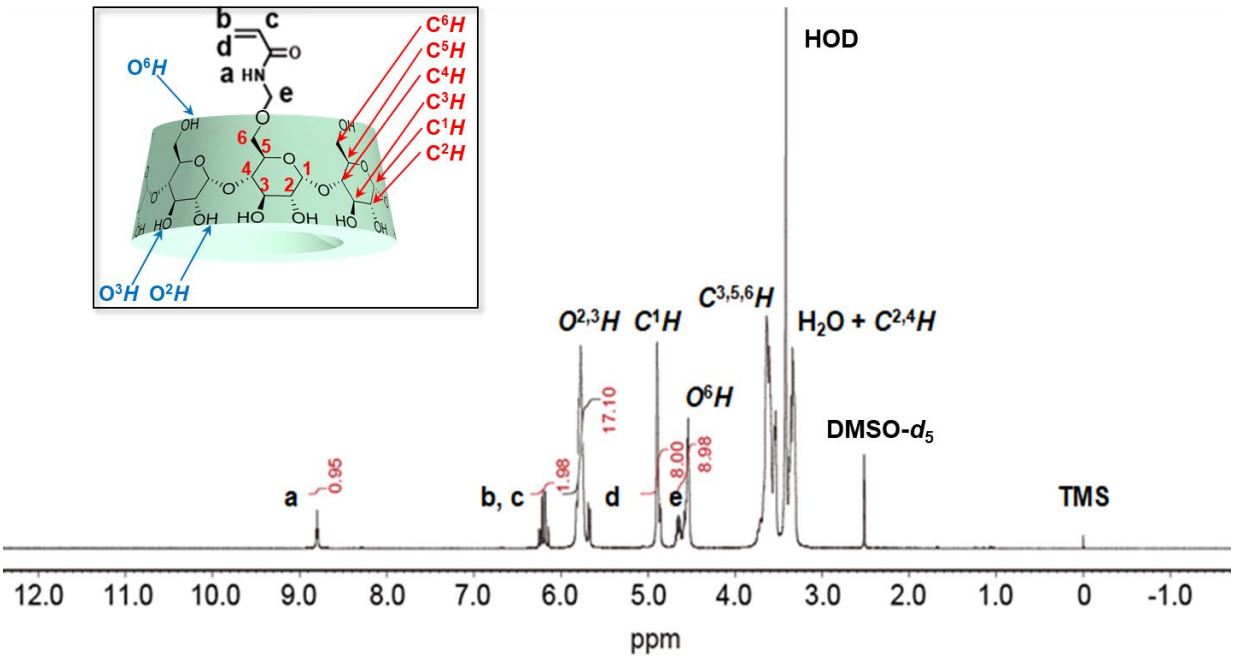


Figure S1. 500 MHz ^{1}H NMR spectrum of γCDAAmMe in DMSO-d_6.

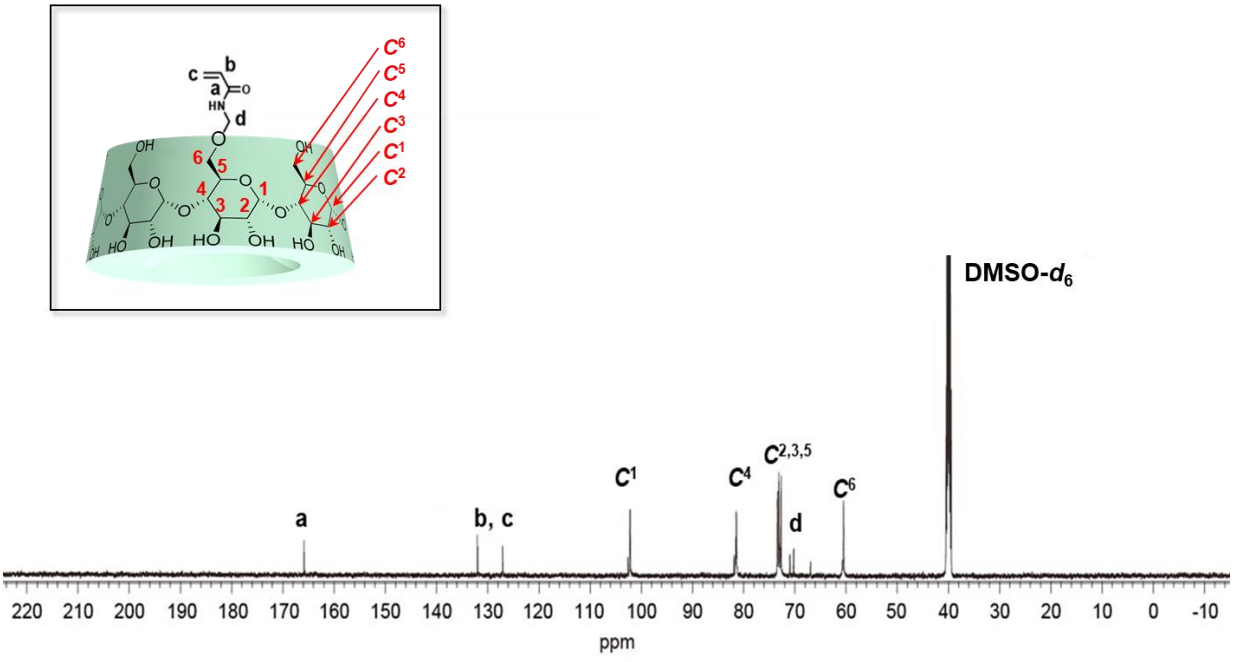


Figure S2. 125 MHz ^{13}C NMR spectrum of γCDAAmMe in DMSO-d_6.

3. Formation of the inclusion complexes of CDs with VC11

3-1. Formation of the inclusion complexes of αCD with VC11

Figure S3 shows the 2D ROESY NMR spectrum of the mixture of αCD with VC11 in D_2O. Correlations were observed between the inner protons ($C^{3,5,6}H$) of the αCD residues and the protons of the alkyl chain of VC11, indicating that the alkyl group of VC11 is included in the αCD.

(Note: Cyclodextrins (MW = ~10^3) have improper rotational correlation time τ, that unfortunately results in $\omega\tau$ = ~1 (ω: Larmor frequency), giving the lowest nuclear Overhauser effect in the laboratory frame (NOESY). Therefore, ROESY (in the rotating frame) was employed.)

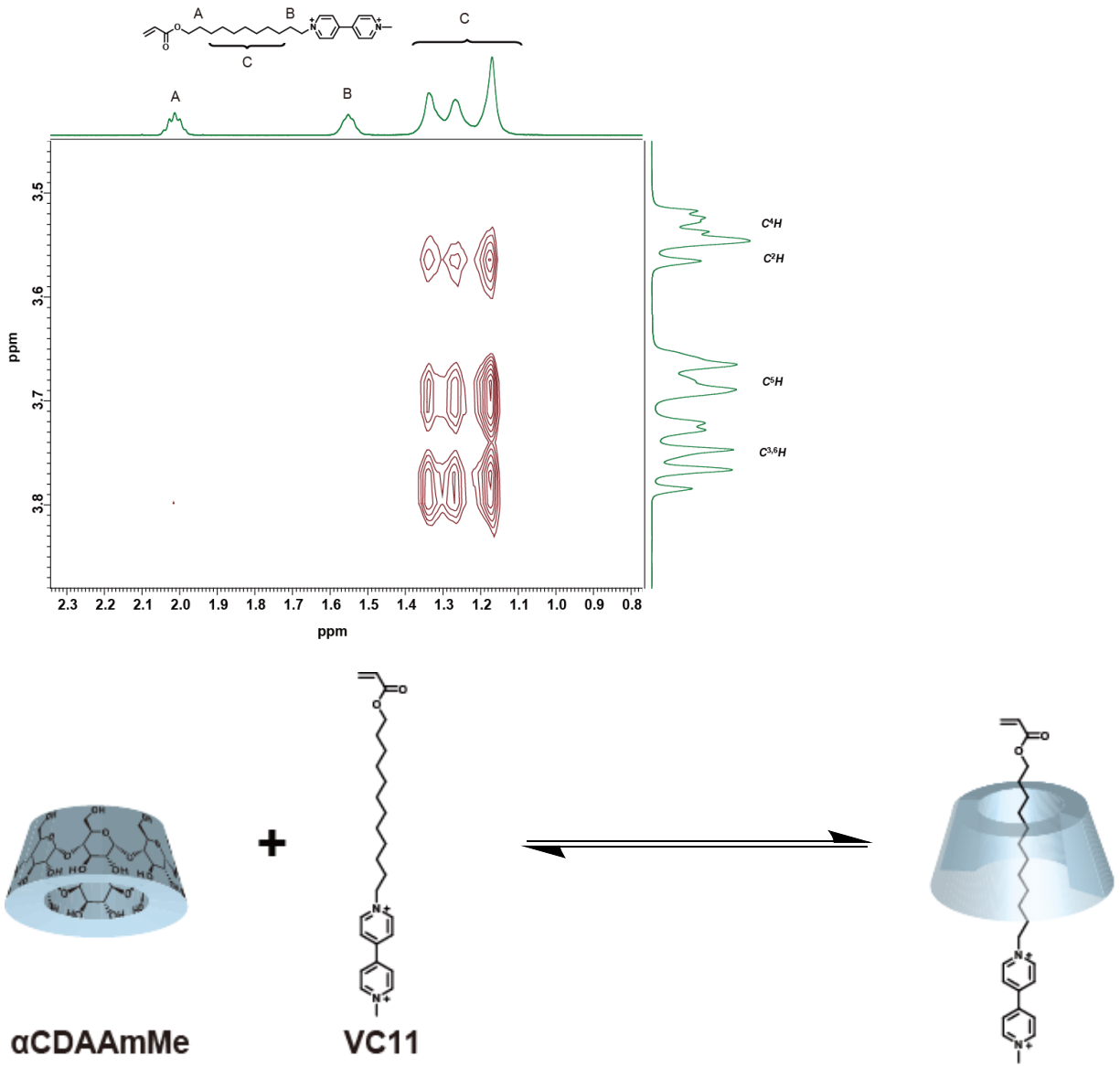


Figure S3. 500 MHz 2D ROESY NMR spectrum of a mixture of αCD (10 mM) and VC11 (10 mM) in D_2O at 25 °C (mixing time τ = 600 ms) and the proposed structure of the inclusion complex.

NMR measurements (**Figure S4**) showed that there is a single association constant in the aqueous solution of αCD and VC11 ($K_a = 3.5\times10^3$ M^{-1}).

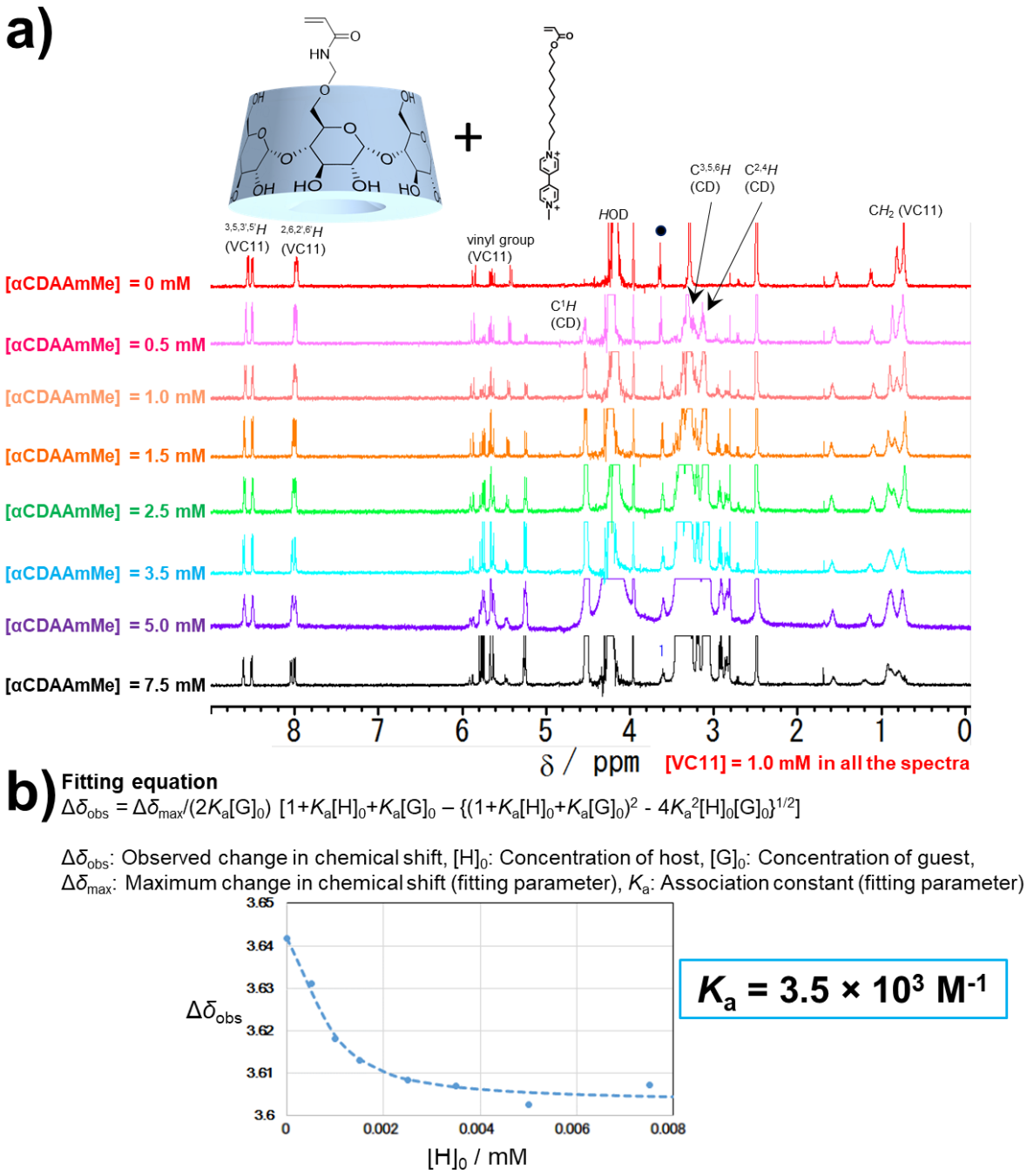


Figure S4. ^{1}H NMR spectra of a mixture of VC11 (1.0 mM) and αCD (concentrations are shown in each spectra) in D_2O **(a)**. Non-linear least squares fitting for plot of the chemical shift value and the concentration of VC11 **(b)**. Association constant of the 1:1 complex between αCD and VC11 was determined by the fitting as 3.5×10^3 M^{-1}.

3-2. Formation of the inclusion complexes of βCD with VC11

Figure S5 shows the 2D ROESY NMR spectrum of a mixture of βCD and VC11 in D_2O. Correlations were observed between the inner protons ($C^{3,5,6}H$) of the βCD residues and the protons of the alkyl chain of VC11, indicating that the alkyl group of VC11 is included in the βCD.

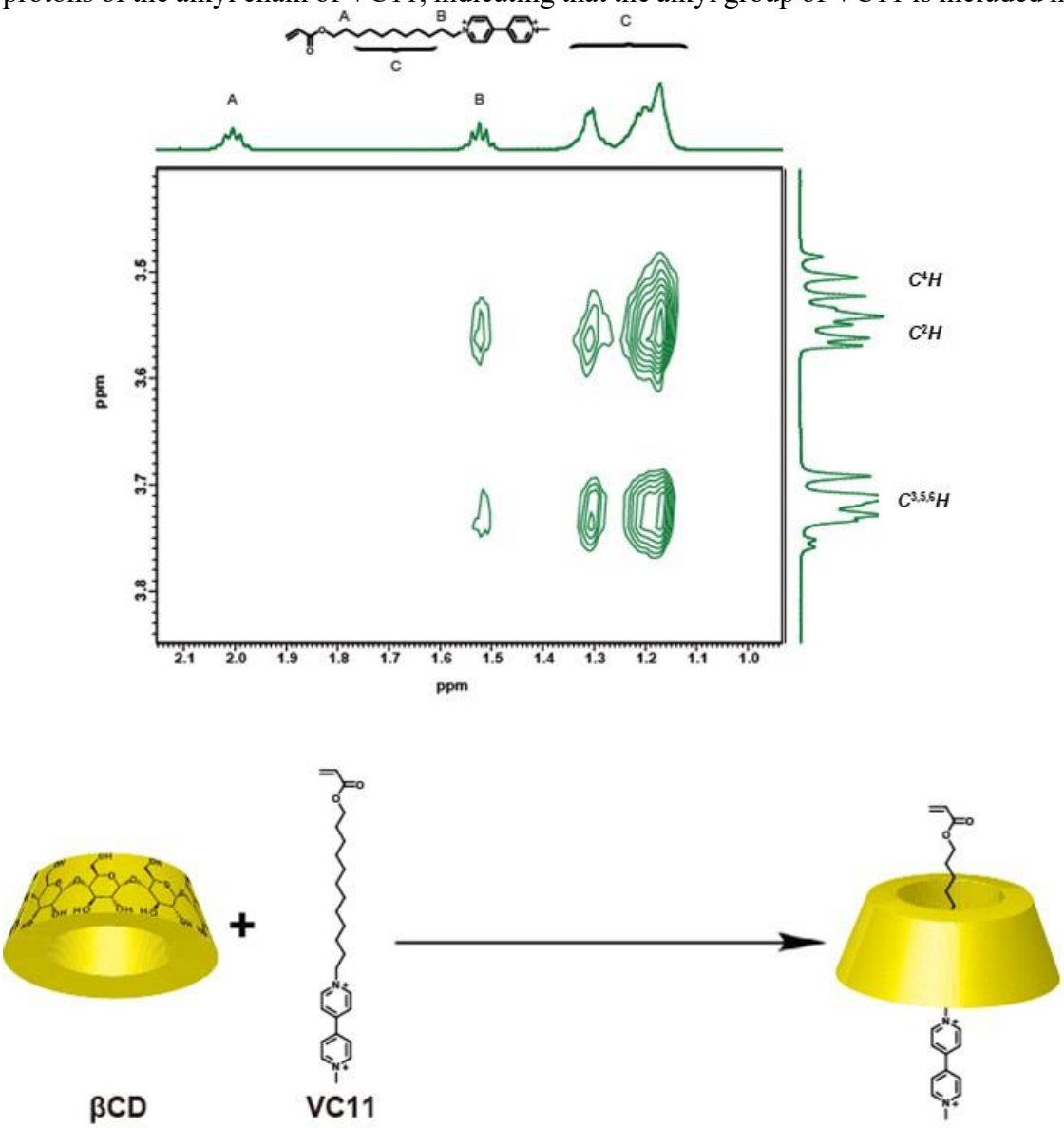


Figure S5. 500 MHz 2D ROESY NMR spectrum of a mixture of βCD (10 mM) and VC11 (10 mM) in D_2O at 25 °C (mixing time τ = 600 ms) and the proposed structure of the inclusion complex.

NMR measurements (**Figure S6**) showed that there is a single association constant in the aqueous solution of βCD and VC11 ($K_a = 5.6\times10^3$ M^{-1}).

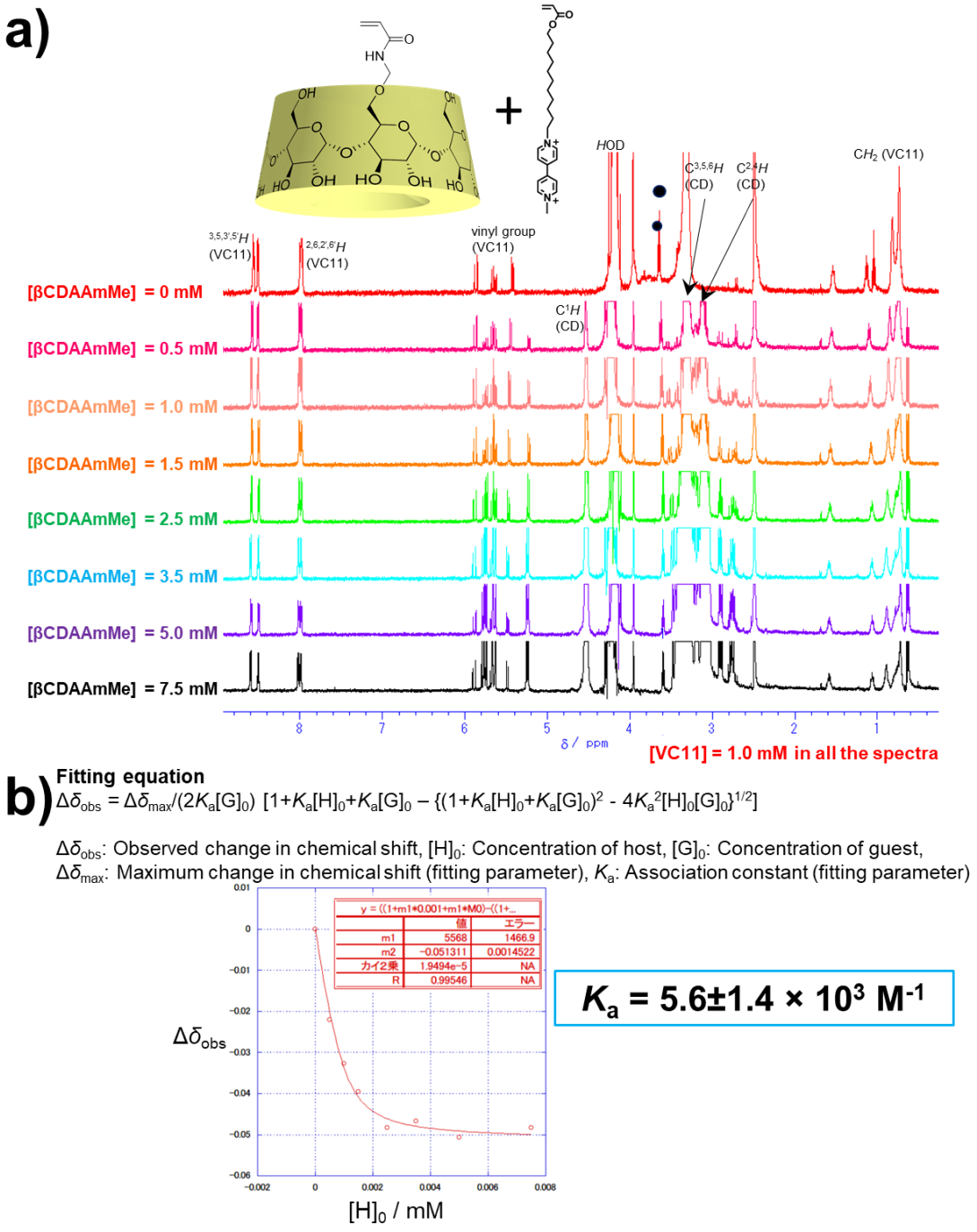


Figure S6. ^{1}H NMR spectra of a mixture of VC11 (1.0 mM) and βCD (concentrations are shown in each spectra) in D_2O **(a)**. Non-linear least squares fitting for plot of the chemical shift value and the concentration of VC11 **(b)**. Association constant of the 1:1 complex between βCD and VC11 was determined by the fitting as 5.6×10^3 M^{-1}.

3-3. Formation of the inclusion complex of γCDAAmMe with VC11

Figure S7 shows the 2D ROESY NMR spectrum of a mixture of γCD and VC11. Correlations between the inner protons ($C^{3,5,6}H$) of the γCD residue and the protons of the alkyl chain of VC11 were observed. The inner protons ($C^{3}H$) and outer protons ($C^{5,6}H$) of γCD were correlated with the protons (A or B) of the alkyl chain of VC11. These results indicate that the inclusion complex of γCD with VC11 forms a double-threaded structure in which two VC11 molecules are included in a single γCD cavity and that the VC11 molecules align with their strands antiparallel (see **Figure S7**).

The formation of this 1:2 inclusion complex of γCD and VC11 was confirmed by the Job plot, and the chemical shifts in the ^{1}H NMR spectra of γCD and VC11 in D_2O were evaluated (**Figure S8(b)**). Proton A of VC11 showed a downfield shift ($\Delta\delta$ in **Figure S8(b)**) due to complexation with γCD. The plot exhibits a maximum $\Delta\delta$ value at a VC11 molar ratio of 0.667, indicating that the stoichiometry of the complex of γCD and VC11 is 1:2.

ITC measurements showed that there are two association constants in the aqueous solution of γCD and VC11. One is K_1, corresponding to a very low value (one-to-one complexation, 8.7 ± 1.3 M^{-1}), and the other is K_2, which has a higher value (one-to-two complexation, $(2.8 \pm 0.4) \times 10^3$ M^{-1}) (**Figure S8(d)**), supporting the 1:2 complexation between γCD and VC11 (**Figure S8(a)**).

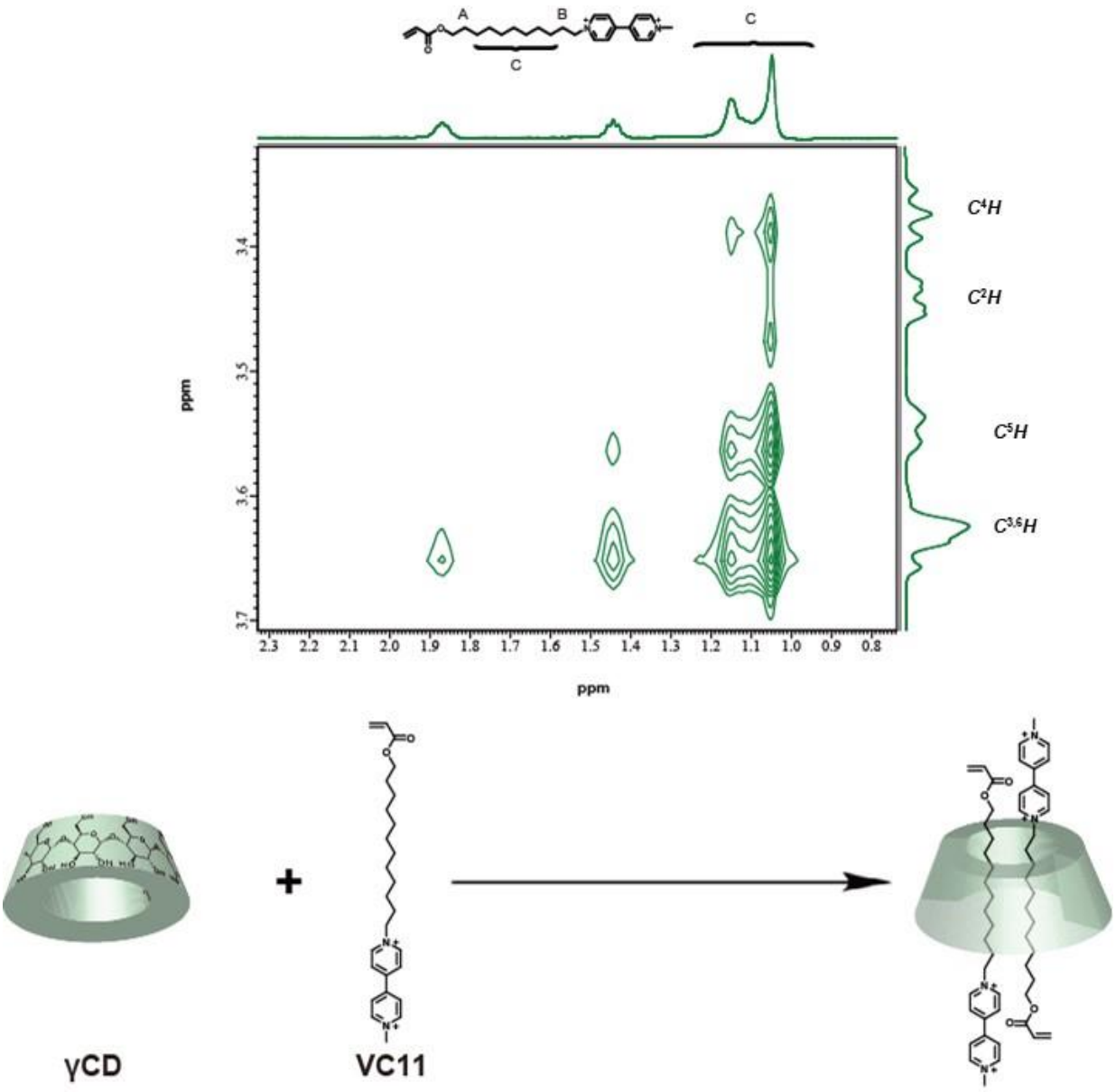


Figure S7. 500 MHz 2D ROESY NMR spectrum of a mixture of γCD (10 mM) and VC11 (10 mM) in D_2O at 25 °C (mixing time $\tau = 600$ ms) and the proposed structure of the inclusion complex.

The 1:2 complexation among the γCDAAmMe and the two VC11 monomers was observed by Job plot (**Figure S8b**), where chemical shift values of the H_a proton of VC11 showed maximum at [γCDAAmMe]/[VC11] = 1/2. Result of ITC (**Figure S8c and S8d**) showed that the association constants of the 1:2 complexation (K_1 and K_2) are 8.7±1.3 M^{-1} and 2,800±400 M^{-1}, respectively. These values also support the 1:2 complexation among the γCD and VC11 units.

Note: VC11 has potential for self-aggregation. To calculate K_1 and K_2 with ruling out effect of the self-aggregation as possible, we used subtracted results of the ITC measurements, in which the heat flow values were subtracted by those from VC11 injection to control solvent (without γCD) in the same ITC conditions.

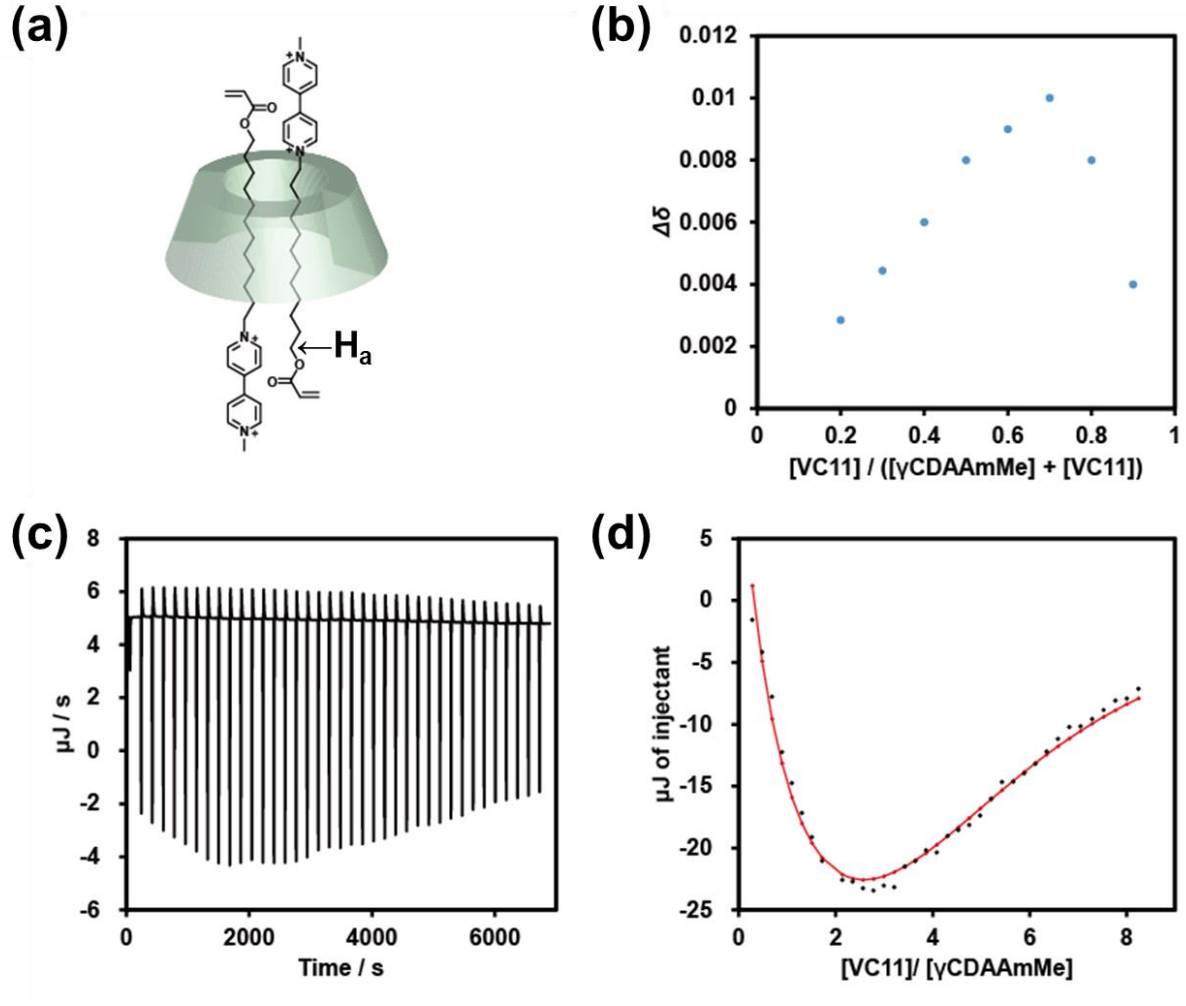
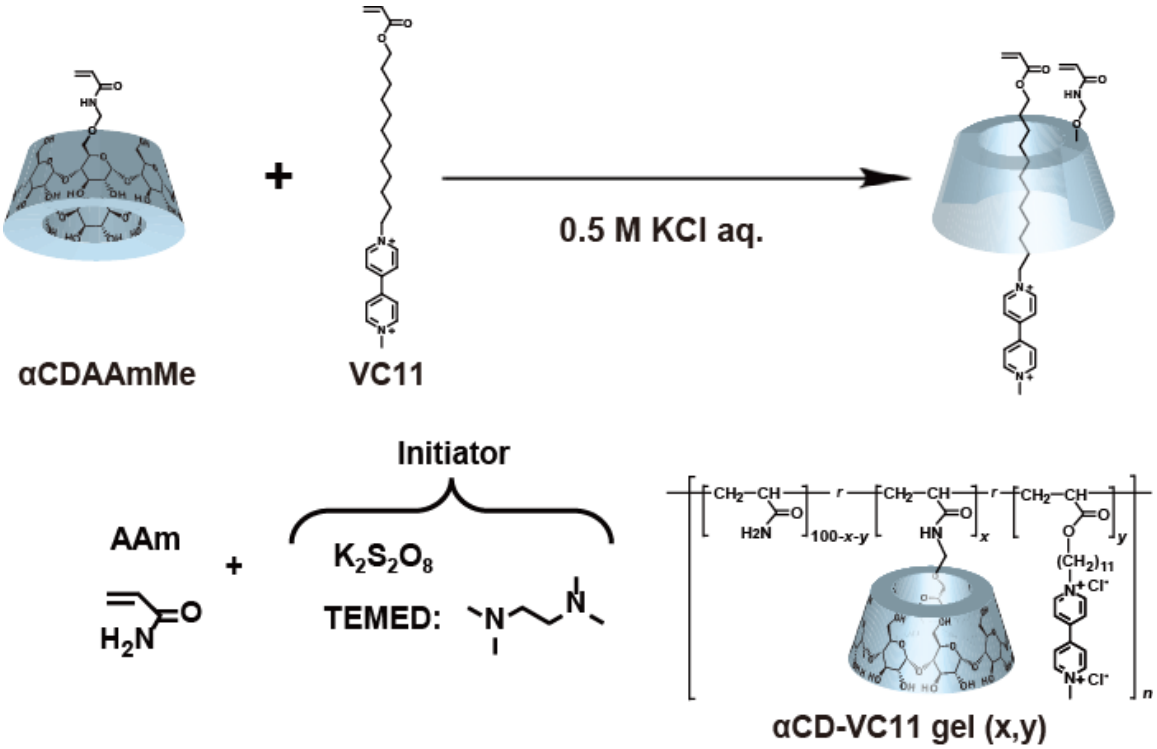


Figure S8. **(a)** Structure of the inclusion complex of γCD with VC11, **(b)** Job plot for the complexation of γCD with VC11 in D_2O at 25 °C (based on the chemical shift values of the Ha proton of VC11), **(c)** ITC isotherms for the titration of a solution of VC11 (100 mM) to a solution of γCDAAmMe (2.5 mM) at 25 °C in water, and **(d)** plot with curve fitting by using obtained K_1 and K_2.

4. Preparation of the supramolecular hydrogels

Preparation of the αCD-VC11(*x*,*y*) hydrogels



Scheme S2. Preparation of the αCD-VC11(*x*,*y*) hydrogels.

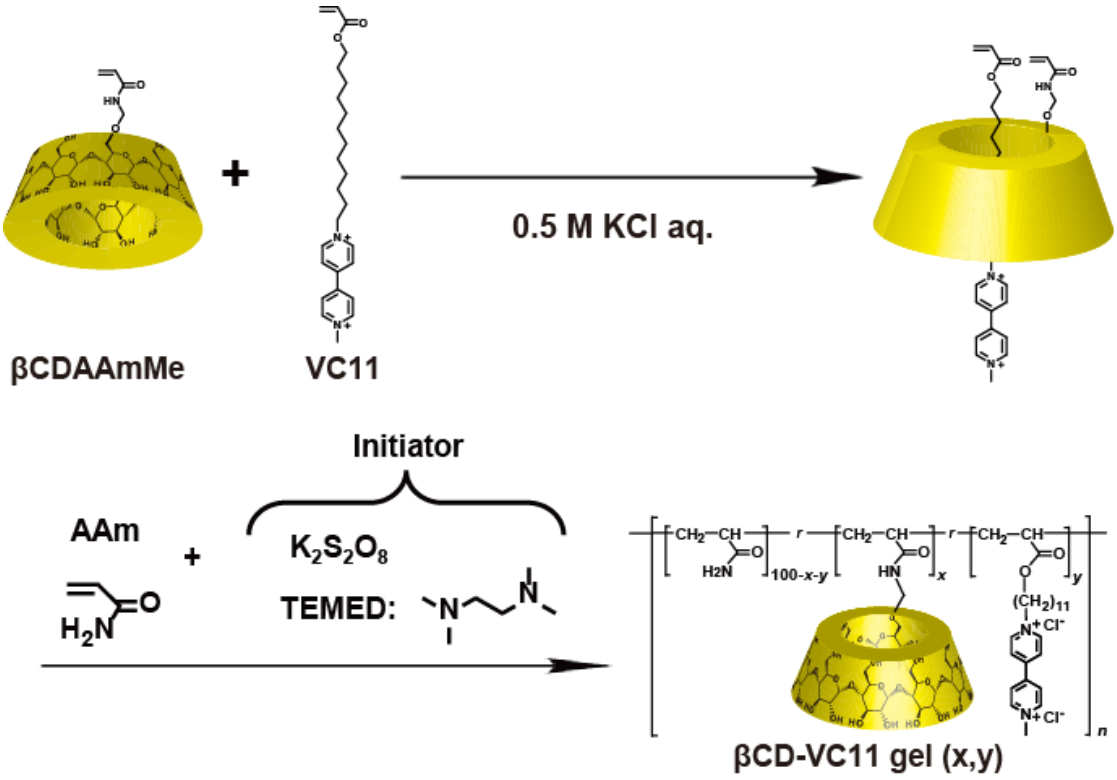
The αCDAAmMe (139 mg, 0.24 mmol) host monomer and the VC11 guest monomer (56 mg, 0.24 mmol) were mixed in water for 2 hours at room temperature to form the host-guest inclusion complex. The inclusion complex of αCDAAmMe with VC11 was copolymerized with acryl amide (AAm; the main chain monomer, 410 mg, 12 mmol) by using a redox initiator system (16 mg (0.12 mmol) of potassium persulfate ($K_2S_2O_4$) and 6.9 mg (0.12 mmol) of *N,N,N',N'*-tetramethylethylenediamine (TEMED)) at room temperature. The solution gelated within 5 minutes to give a self-standing hydrogel. The obtained hydrogel was soaked and washed in DMSO for 24 hours to remove the residual initiators and monomers. (Note: In aqueous media, some reagents can be included and captured by the CD unit in the hydrogel.) Then, the hydrogel was

then soaked in water for 24 hours to replace the solvent to obtain the pure hydrogel. The hydrogels were characterized by FG-MAS NMR and IR spectroscopy (see below). The amounts of reagents and the solvent use are summarized in **Table S1**.

Table S1. Amounts of reagents and solvents used in the preparation of the αCD-VC11(*x*,*y*) hydrogel.

	H_2O /mL	AAm /mg	αCDAAmMe /mg	VC11 /mg	KPS /mg	TEMED /μL
αCD-VC11(2,2) hydrogel	3.0	410	139	56	16	8.9

Preparation of the βCD-VC11(*x*,*y*) hydrogels



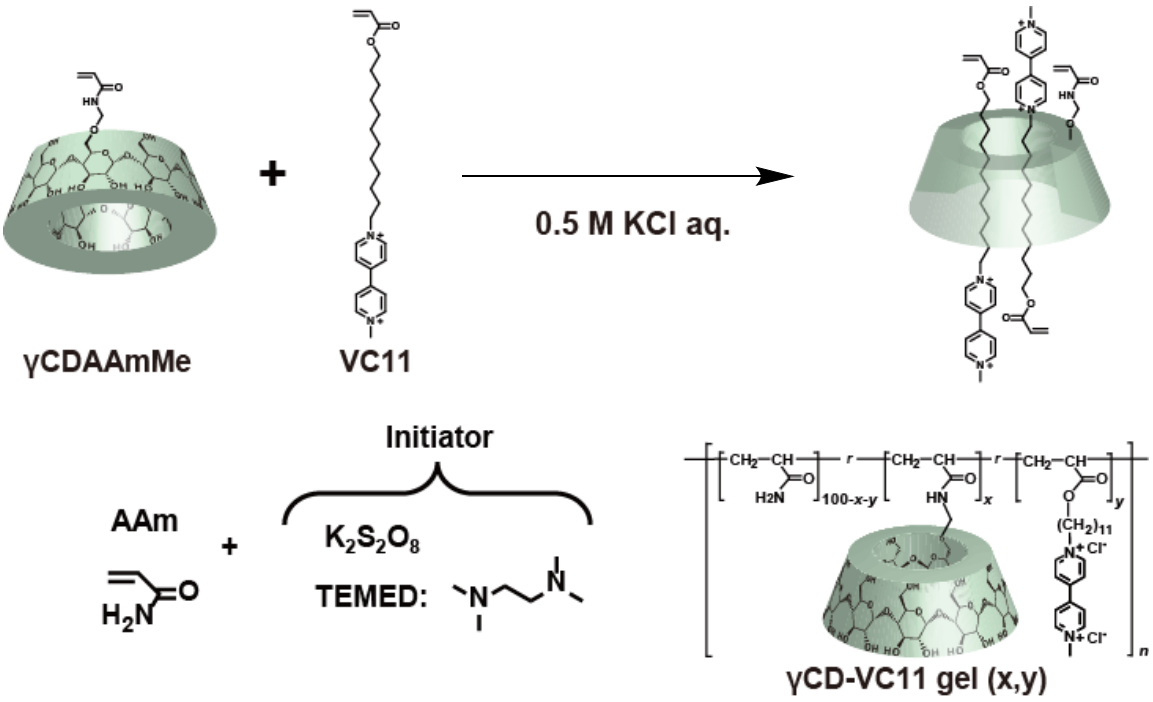
Scheme S3. Preparation of the βCD-VC11(*x*,*y*) hydrogels

The βCD-VC11(*x*,*y*) hydrogels were prepared in the same manner as the αCD-VC11(*x*,*y*) hydrogels. The hydrogels were characterized by FG-MAS NMR and IR spectrometry (see below). The amounts of the reagents and the solvents use are summarized in **Table S2**.

Table S2. Amounts of reagents and solvents used in the preparation of the βCD-VC11(*x*,*y*) hydrogel.

	H_2O /mL	AAm /mg	βCDAAmMe /mg	VC11 /mg	KPS /mg	TEMED /μL
βCD-VC11 (2,2) hydrogel	3.0	410	146	29	16	8.9

Preparation of the γCD-VC11(*x*,*y*) hydrogels



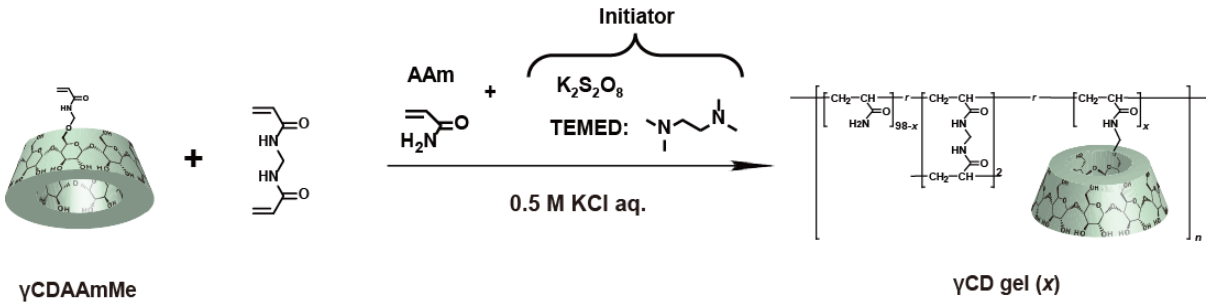
Scheme S4. Preparation of the γCD-VC11(*x*,*y*) hydrogels

The γCD-VC11(*x*,*y*) hydrogels were prepared in the same manner as the αCD-VC11(*x*,*y*) hydrogels. The hydrogels were characterized by FG-MAS NMR and IR spectroscopy (see below). The amounts of reagents and the solvent use are summarized in **Table S3**.

Table S3. Amounts of reagents and solvents used in the preparation of the γCD-VC11(*x*,*y*) hydrogel.

	H_2O /mL	AAm /mg	γCDAAmMe /mg	VC11 /mg	KPS /mg	TEMED μL
γCD-VC11(1,1) hydrogel	3.0	418	82.8	28	16	8.9
γCD-VC11(2,2) hydrogel	3.0	410	166	56	16	8.9
γCD-VC11(3,3) hydrogel	3.0	400	248	84	16	8.9
γCD-VC11(4,4) hydrogel	3.0	392	331	112	16	8.9
γCD-VC11(5,5) hydrogel	3.0	383	414	140	16	8.9

Preparation of the γCD hydrogel



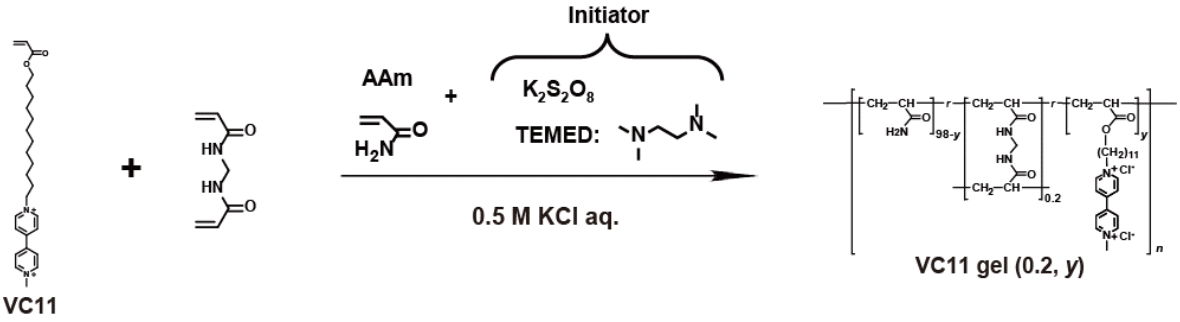
Scheme S5. Preparation of the γCD hydrogel

N',N'-Methylenebis(acrylamide) (MBAAm; 18 mg, 0.24 mmol), γCDAAmMe (166 mg, 0.24 mmol) and AAm (410 mg, 12 mmol) were solubilized in water. The aqueous monomer solution was copolymerized using a redox initiator system ($K_2S_2O_8$ and TEMED). The obtained hydrogel was soaked and washed in DMSO for 24 hours to remove the residual initiators and monomers. (Note: In aqueous media, some reagents can be included and captured by the CD unit in the hydrogel.) Then, the hydrogel was then soaked in water for 24 hours to replace the solvent to obtain the pure hydrogel. The hydrogels were characterized by FG-MAS NMR and IR spectroscopy (see below). The amounts of reagents and the solvent use are summarized in **Table S4**.

Table S4. Preparation of the γCD hydrogel.

	H_2O /mL	AAm /mg	MBAAm /mg	γCDAAmMe /mg	KPS /mg	TEMED /μL
γCD hydrogel	3.0	410	18	166	16	8.9

Preparation of the VC11(0.2,*y*) hydrogel



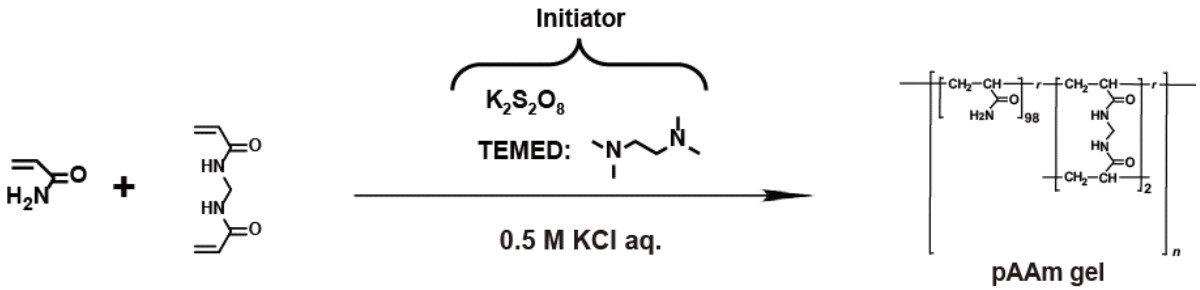
Scheme S6. Preparation of the VC11(0.2,*y*) hydrogel

MBAAm (1.9 mg, 0.024 mmol), VC11 (56 mg, 0.24 mmol) and AAm (410 mg, 12 mmol) were dissolved in water. The monomer solution was copolymerized using a redox initiator system ($K_2S_2O_8$ and TEMED). The obtained hydrogel was soaked and washed in DMSO for 24 hours to remove the residual initiators and monomers. Then, the hydrogel was then soaked in water for 24 hours to replace the solvent to obtain the pure hydrogel. The hydrogels were characterized by FG-MAS NMR and IR spectroscopy (see below). The amounts of reagents and the solvent use are summarized in **Table S5**.

Table S5. Preparation of the VC11(0.2,*y*) hydrogel.

	H_2O /mL	AAm /mg	MBAAm /mg	VC11 monomer /mg	KPS /mg	TEMED /μL
VC11(0.2,*y*) hydrogel	3.0	410	1.9	56	16	8.9

Preparation of the pAAm hydrogel



Scheme S7. Preparation of the pAAm hydrogel

MBAAm (18 mg, 0.24 mmol) and AAm (418 mg, 12 mmol) were dissolved in water. The monomer solution was copolymerized using a redox initiator system ($K_2S_2O_8$ and TEMED). The obtained hydrogel was soaked and washed in DMSO for 24 hours to remove the residual initiators and monomers. Then, the hydrogel was then soaked in water for 24 hours to replace the solvent to obtain the pure hydrogel. The hydrogels were characterized by FG-MAS NMR and IR spectroscopy (see below). The amounts of reagents and the solvent use are summarized in **Table S6**.

Table S6. Preparation of the pAAm hydrogel.

	H_2O	AAm	MBAAm	KPS	TEMED
	/mL	/mg	/mg	/mg	/μL
pAAm hydrogel	3.0	418	18	16	8.9

5. Characterization of the hydrogels.

FT-IR spectra

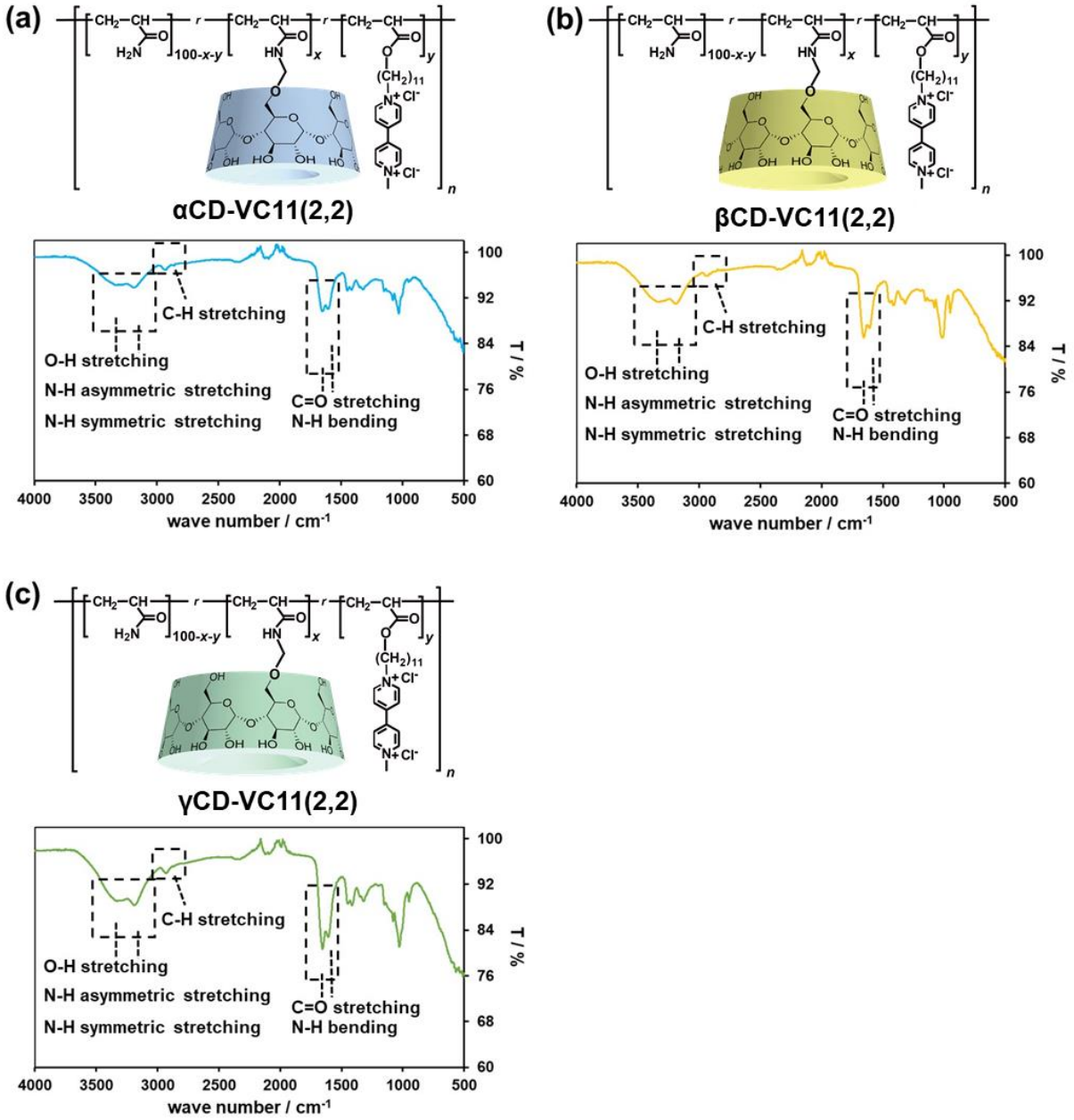


Figure S9. FT-IR spectra (ATR method) of **(a)** the αCD-VC11(2,2) hydrogel, **(b)** βCD-VC11(2,2) hydrogel, and **(c)** γCD-VC11(2,2) hydrogel. In the measurements, all the hydrogels were dried to remove strong IR absorption signals derived from water.

FG-MAS NMR spectra

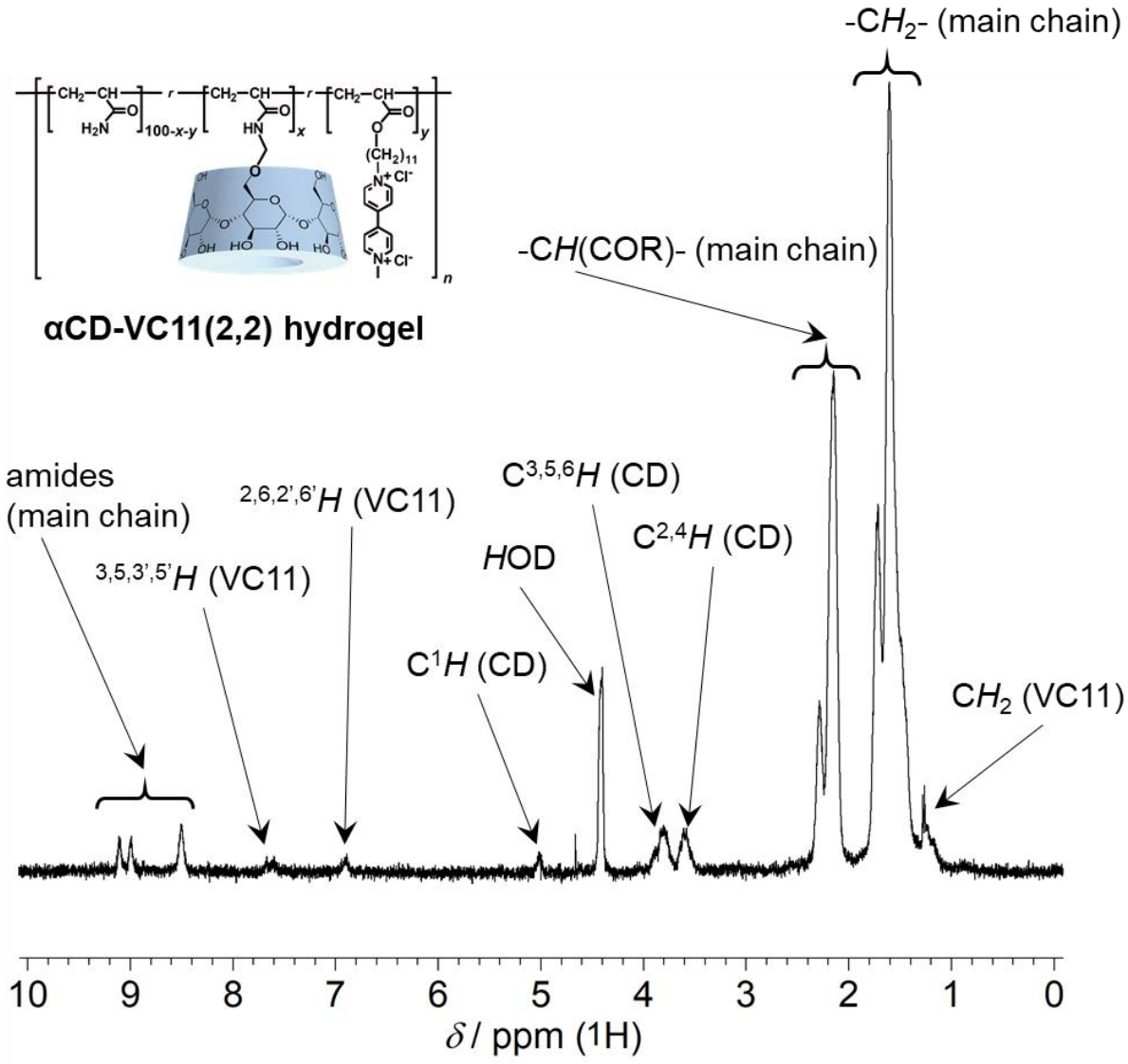


Figure S10. 400 MHz ^{1}H FG-MAS NMR spectrum of the αCD-VC11(2,2) hydrogel (immersed in D_2O) at 30 °C. The frequency of the magic angle spinning was 7 kHz. The same labels indicating CD's proton in **Figure S1** are used.

Amount of each residues

In the preparation: [αCD] / [VC11] / [AAm] = 2.0 / 2.0 / 96.0.
Calculated from the spectrum: [αCD] / [VC11] / [AAm] = 2.1 / 2.0 / 95.9.

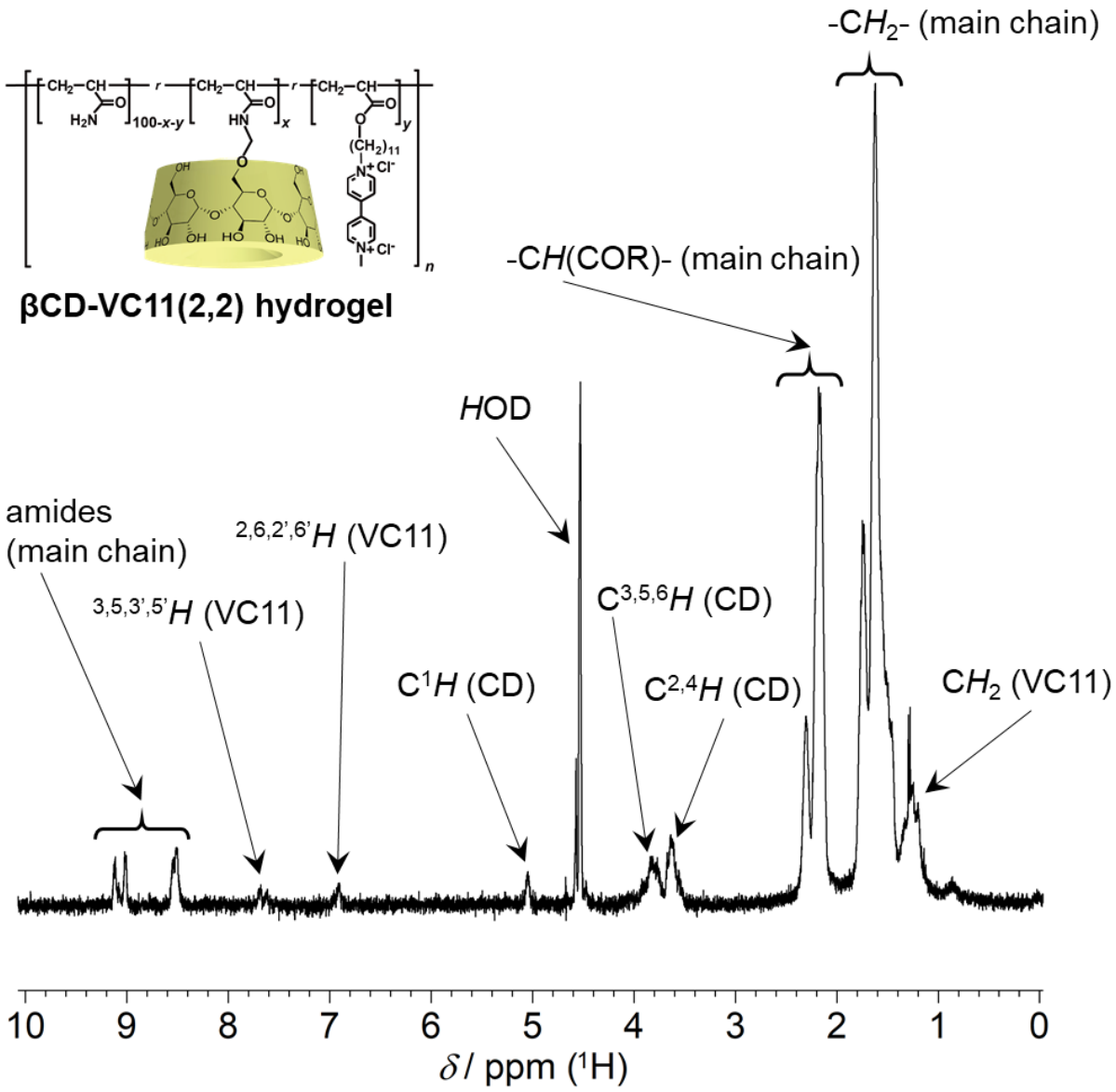


Figure S11. 400 MHz ^{1}H FG-MAS NMR spectrum of the βCD-VC11(2,2) hydrogel (immersed in D_2O) at 30 °C. The frequency of the magic angle spinning was 7 kHz. The same labels indicating CD's proton in **Figure S1** are used.

Amount of each residues

In the preparation: [βCD] / [VC11] / [AAm] = 2.0 / 2.0 / 96.0.
Calculated from the spectrum: [βCD] / [VC11] / [AAm] = 2.2 / 2.1 / 95.5.

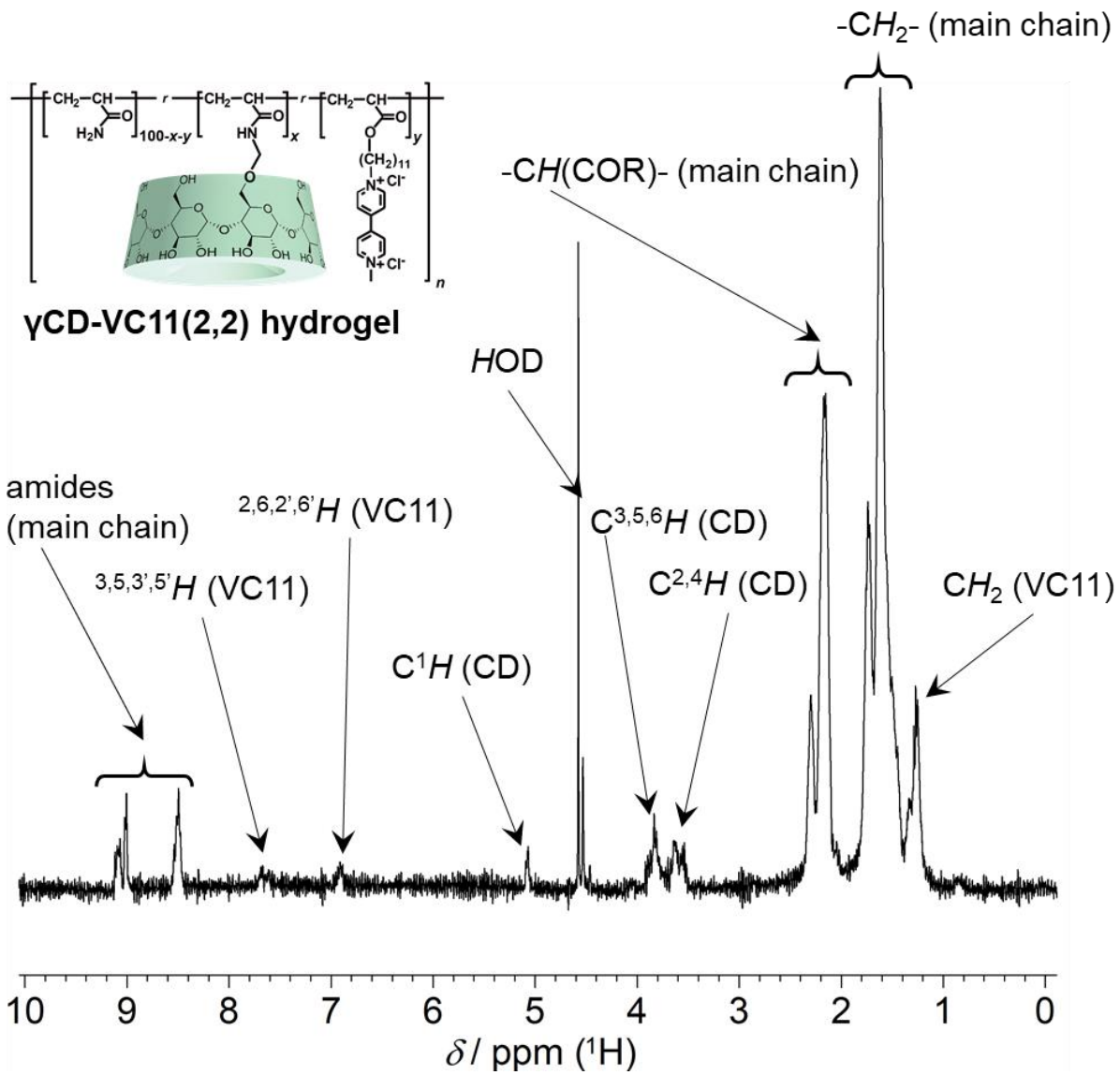


Figure S12. 400 MHz ^{1}H FG-MAS NMR spectrum of the γCD-VC11(2,2) hydrogel (immersed in D_2O) at 30 °C. The frequency of the magic angle spinning was 7 kHz. The same labels indicating CD's proton in **Figure S1** are used.

Amount of each residues

In the preparation: [γCD] / [VC11] / [AAm] = 2.0 / 2.0 / 96.0.
Calculated from the spectrum: [γCD] / [VC11] / [AAm] = 2.8 / 2.6 / 94.6.

6. Reduction of the hydrogels

The hydrogels (5 × 5 × 1 mm^3) were reacted with sodium hydrosulfite ($Na_2S_2O_4$ as a reductant; 0.10 M) in 0.50 M phosphate buffer (pH 7.0). The soaked hydrogels immediately changed the color (from pale yellow to dark purple). These color changes are characteristic of viologen molecules, which are reduced by $Na_2S_2O_4$ to give the radical cation of the viologen unit (**Figure S13**).

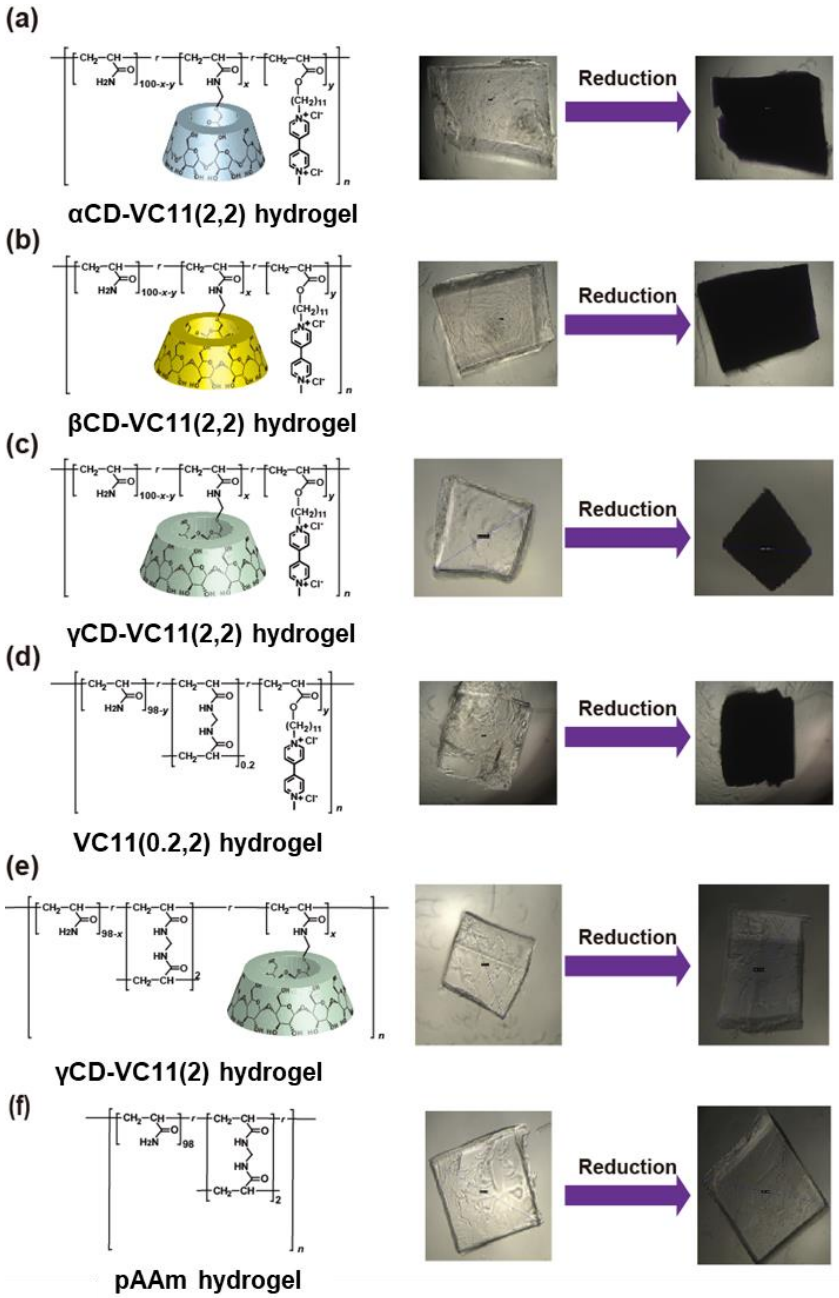


Figure S13. Structures and photographs of **(a)** αCD-VC11(2,2) hydrogel, **(b)** βCD-VC11(2,2) hydrogel, **(c)** γCD-VC11(2,2) hydrogel, **(d)** VC11(0.2,2) hydrogel, **(e)** γCD(2) hydrogel, and **(f)** pAAm hydrogel.

Figure S14 shows the UV-Vis spectra of CD-VC11 during the reduction. Whereas the viologen dication shows no peak in the 450 nm to 700 nm region, the reduced viologen moieties show two characteristic peaks at 537 nm and 604 nm.

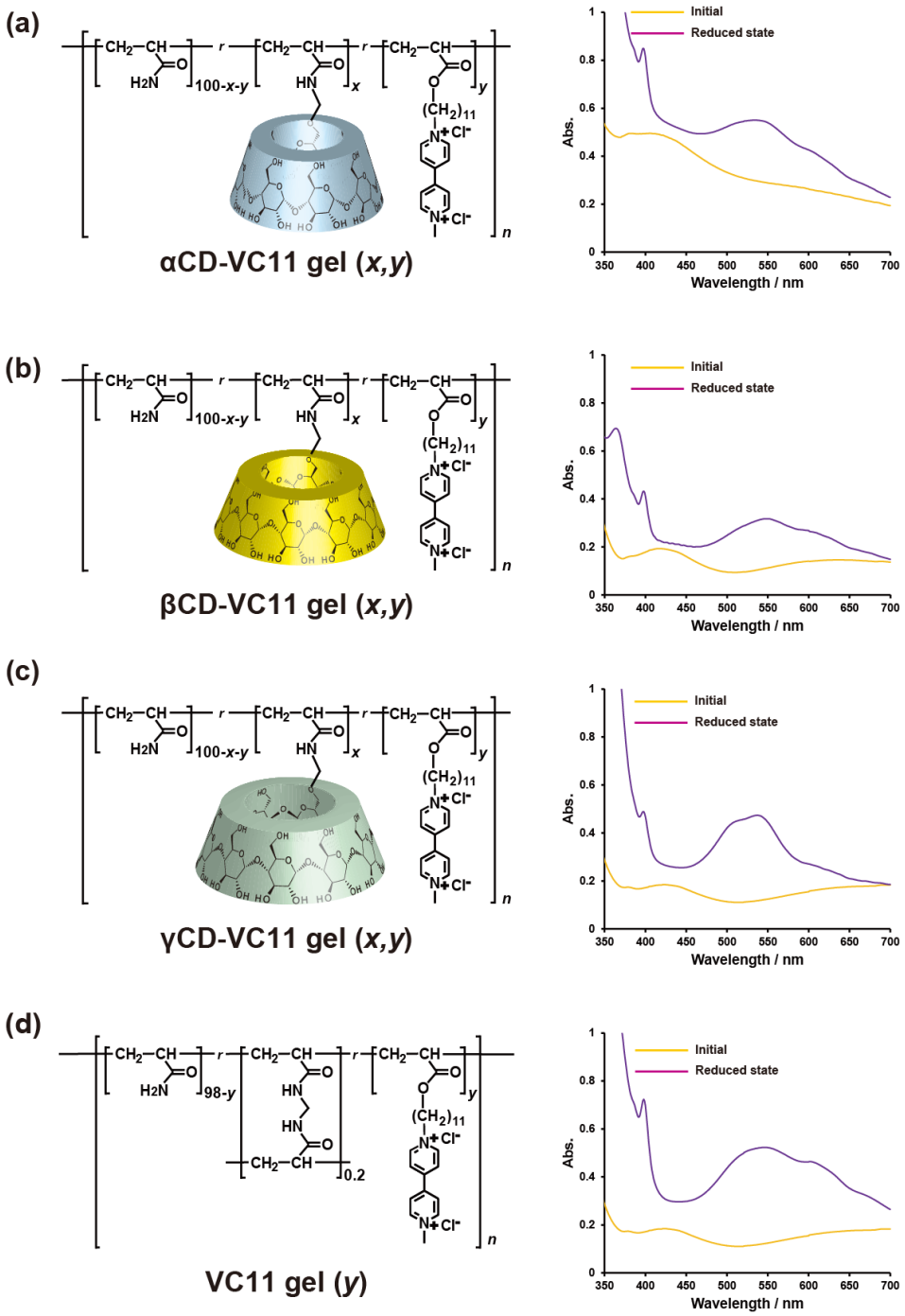


Figure S14. UV-Vis spectra of **(a)** αCD-VC11(2,2) hydrogel, **(b)** βCD-VC11(2,2) hydrogel, **(c)** γCD-VC11(2,2) hydrogel and **(d)** VC11(0.2,2) hydrogel in their initial and reduced states.

Figure S15 shows the partial spectra of the hydrogels in the reduced state. Waveform separation analysis was carried out by non-linear least-squares curve fitting method (**eq. (1)** was used for fitting). The results indicate molar content of the viologen monomer ($x_{monomer}$), dimer (x_{dimer}), and dimer included by CD ($x_{CD\text{-}dimer}$) (summarized in **Table S7**).

$$A = \sum_{i=1}^{n} \left[\frac{A_i}{\sqrt{2\pi}\sigma_i} \mathrm{Exp}\left(\frac{(\lambda-\lambda_i)^2}{{\sigma_i}^2} \right) \right] + a\lambda^2 + b\lambda + c \quad (1)$$

A (absorbance) is a function of λ (wavelength), where A_i, λ_i, σ_i, a, b and c are fitting parameters. Number of peaks (n) is 2 or 3.

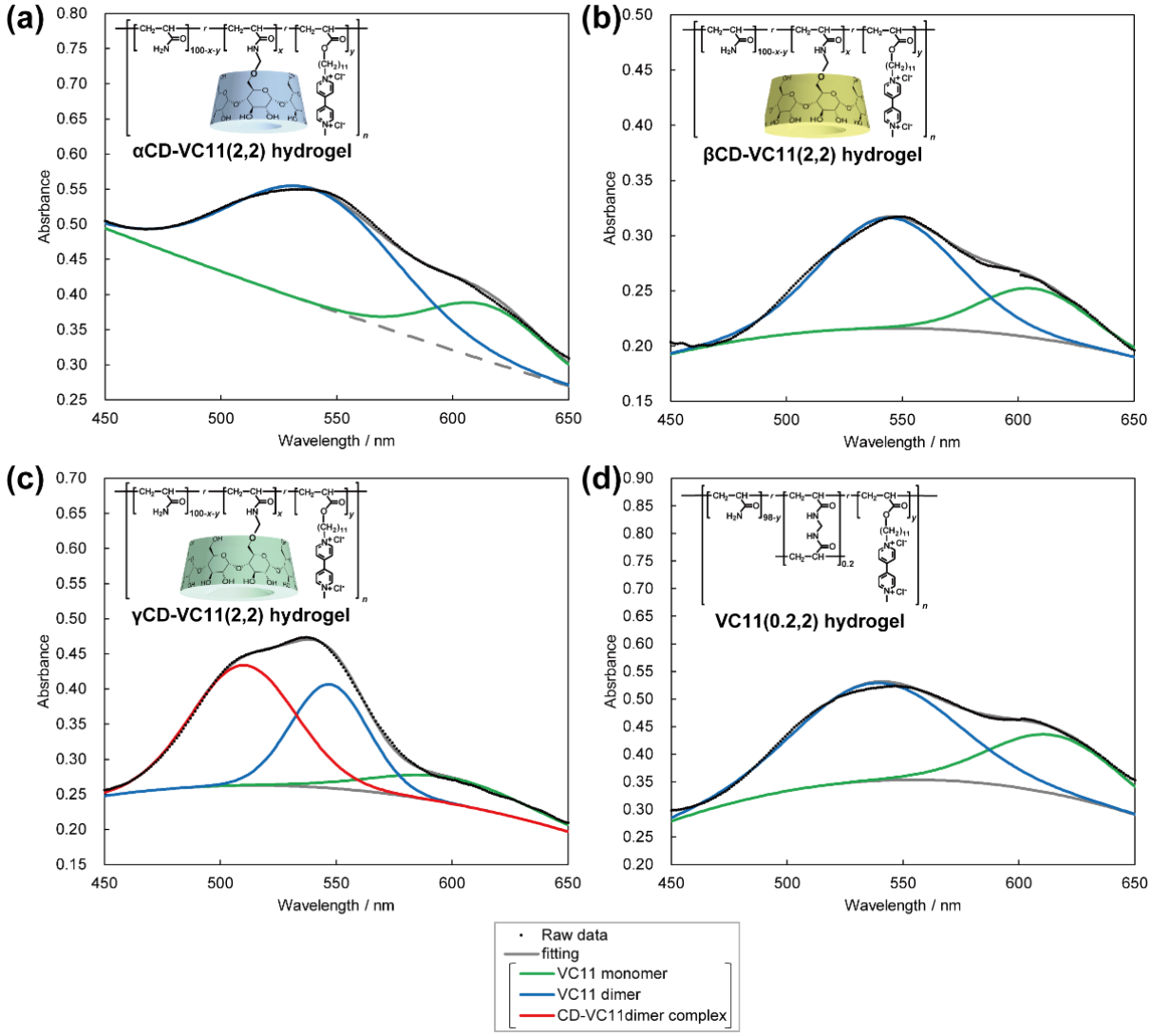
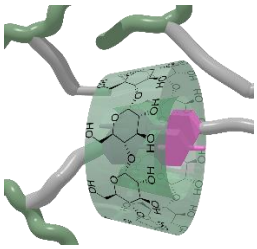


Figure S15. Partial UV/Vis spectra of the αCD-VC11(2,2) **(a)**, βCD-VC11(2,2) **(b)**, γCD-VC11(2,2) **(c)**, and VC11(0.2,2) **(d)** hydrogels in the reduced state. Waveform separation analysis are used to estimate the three state of reduced VC11 units (the monomer, dimer, and included dimer).

Table S7. Ratios of spices of the VC11 radical cations in the reduced hydrogels.

	$x_{monomer}$	x_{dimer}	$x_{CD\text{-}dimer}$
			
αCD-VC11(2,2) hydrogel	25.4	74.6	-
βCD-VC11(2,2) hydrogel	26.3	73.7	-
γCD-VC11(2,2) hydrogel	15.2	33.0	51.8
VC11(0.2,2) hydrogel	33.0	67.0	-

The molar fraction of the each viologen sciences are calculated by integral values of each peaks of the UV/Vis spectra (**Figure S15**), where we assume that the each viologen sciences have same molar absorbance coefficient value.

7. Oxidation of the reduced γCD-VC11(2,2) hydrogel

The hydrogels were oxidized with KNO_2 (KNO_2 as the oxidant; 0.1 M) in 0.50 M phosphate buffer (pH 7.0). The soaked hydrogels changed color (from dark purple to pale yellow) within 5 minutes. These color changes are characteristic of viologen molecules, which are oxidized by KNO_2 to give the dication of the viologen unit (**Figure S16**).

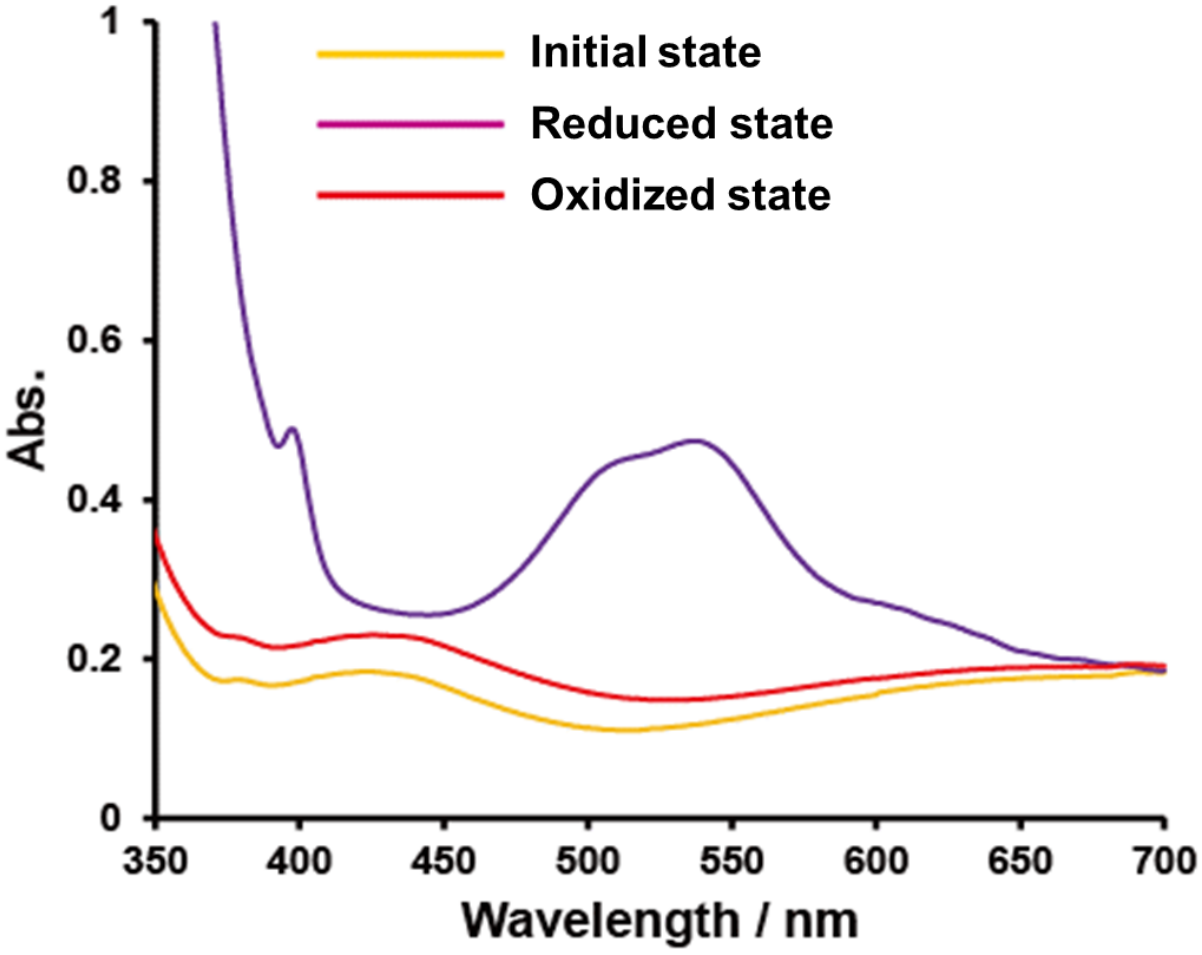


Figure S16. UV/Vis spectra of the γCD-VC11(2,2) hydrogel during the reduction/oxidation process.

8. NMR spectra of CDs in the presence of MV radical cation

Figure S17 shows the NMR spectra of CDs in the presence of the reduced VC11 monomer. The NMR spectra of βCD or γCD showed peak broadening in the presence of monocationic viologen radical. However, in the case of αCD, broadening of the NMR signals was not observed, indicating that βCD and γCD stabilize the viologen monocation dimer (Especially in γCD).

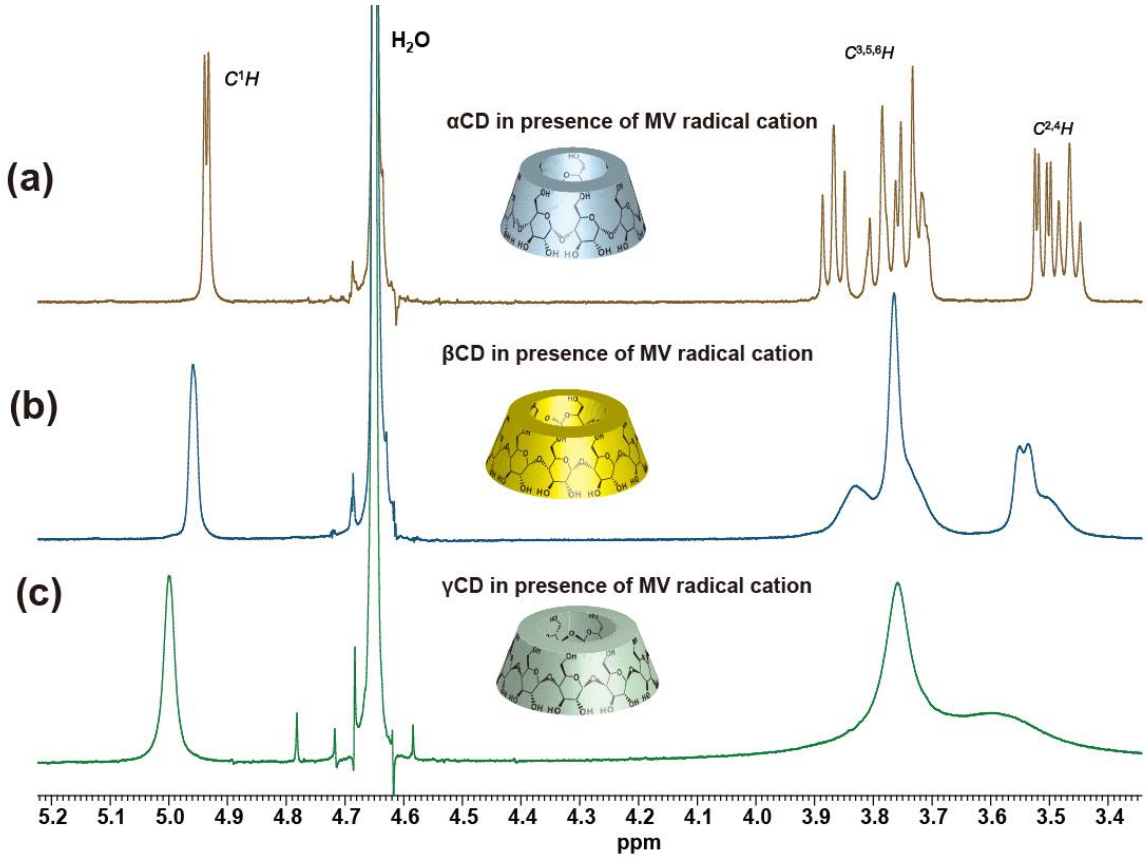


Figure S17. 500 MHz ^{1}H NMR spectra of αCD, βCD or γCD in the presence of reduced VC11 cations in D_2O.

9. UV-Vis spectra of the MV radical cation in the presence of CDs

Figure S18 shows the UV-Vis spectra of the reduced VC11 monomer in the presence of γCD. The shoulder band at 505 nm is derived from the inclusion complex of γCD with the reduced VC11 dimer (see also **Figure S15**).

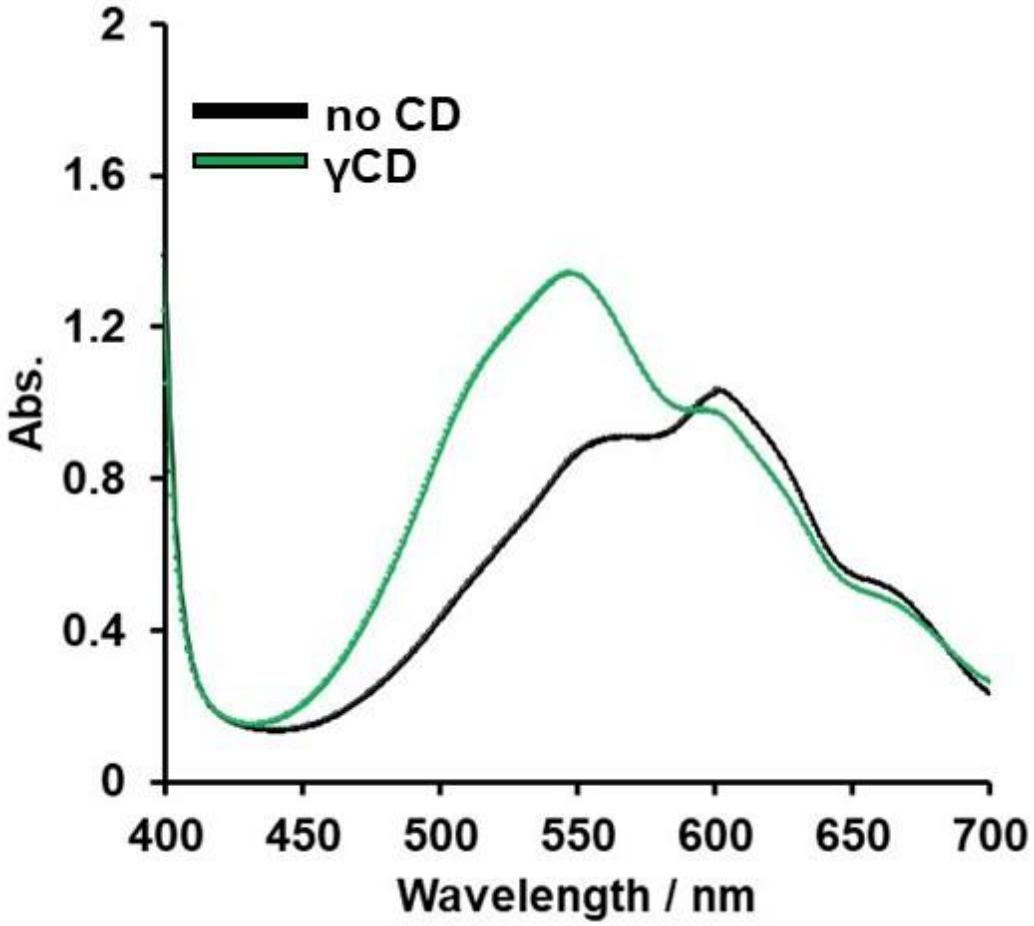


Figure S18. UV-Vis spectra of MV radical dication in the absence or presence of γCD.

10. Young's modulus of the hydrogels in their initial and reduced states.

Figure S19 shows the Young's modulus of each hydrogel in their initial and reduced states ($E_{initial}$ and $E_{reduction}$, respectively). Young's modulus values were calculated from the initial gradients of the stress-strain curves obtained from compression tests.

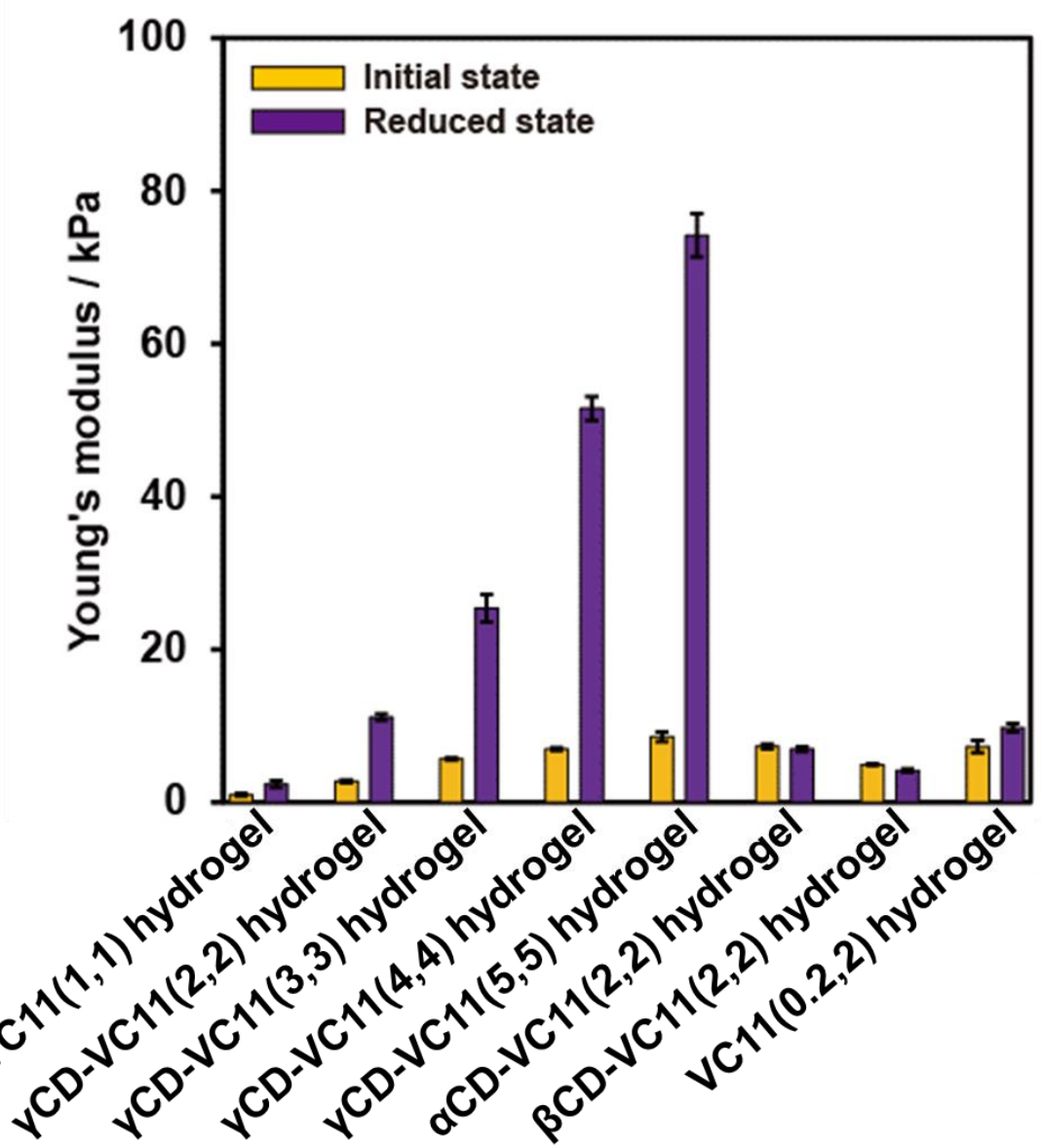


Figure S19. Young's modulus of the hydrogels in the initial and reduced states.

Figure S20 shows the 2D plots of the change in the Young's modulus ($f = E_{reduction} / E_{initial}$) and the polymer's volume fraction in the hydrogels, which were normalized by the initial state ($\varphi = \varphi_{reduction} / \varphi_{initial}$).

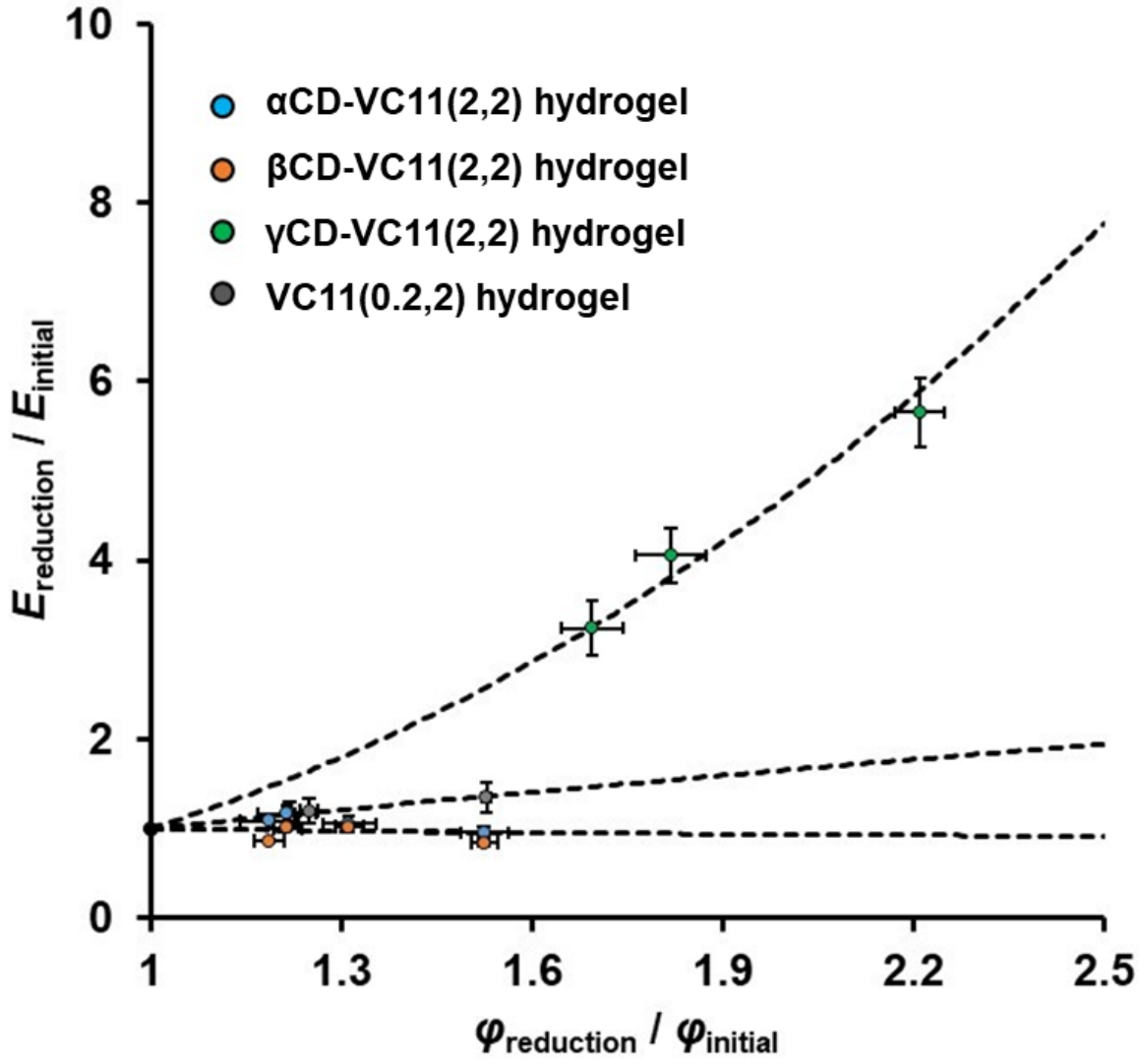


Figure S20. The plots of the change in Young's modulus ($f = E_{reduction} / E_{initial}$) as a function of the polymer's volume fraction in the hydrogel normalized by the initial state ($\varphi = \varphi_{reduction} / \varphi_{initial}$).

The curve fitting (dashed lines) was accomplished using nonlinear least-squares method with a model equation, $f = \varphi^{-\alpha}$ (α: fitting parameter). The results are shown below.

αCD-VC11(2,2) hydrogel and **βCD-VC11(2,2) hydrogel**: $f = \varphi^{-0.1}$
γCD-VC11(2,2) hydrogel: $f = \varphi^{2.2}$
VC11(0.2,2) hydrogel: $f = \varphi^{0.73}$

11. Dynamic viscoelastic measurement

Linear viscoelastic measurement of the hydrogels

Dynamic viscoelastic measurements of sheet samples with thickness of ~1 mm were performed with an Anton Paar MCR302 rheometer. Angular frequency (ω) sweep from 0.1 to 100 rad/s was performed using the parallel-plate fixture with 8 mm in diameter. The oscillatory shear strain amplitudes for all the tests were within the range of linear viscoelasticity. Results of the hydrogel at different temperatures and frequencies followed the time-temperature superposition principle. **Figure S21** shows the master curves of storage modulus *G'* and loss modulus *G''* referenced at 25 °C. Relaxation times τ were estimated by fitting master curves of *G'* and *G''* with the generalized Maxwellian model.

$$G' = \sum_{p\geq 1}^{N} G_p \frac{\omega^2 {\tau_p}^2}{1+\omega^2 {\tau_p}^2} + G_{\mathrm{N}}$$

$$G'' = \sum_{p\geq 1}^{N} G_p \frac{\omega \tau_p}{1+\omega^2 {\tau_p}^2}$$

G_p: Relaxation strength in p^{th} relaxation mode.
τ_p: Relaxation time in p^{th} relaxation mode.
G_{N}: Terminal modulus.

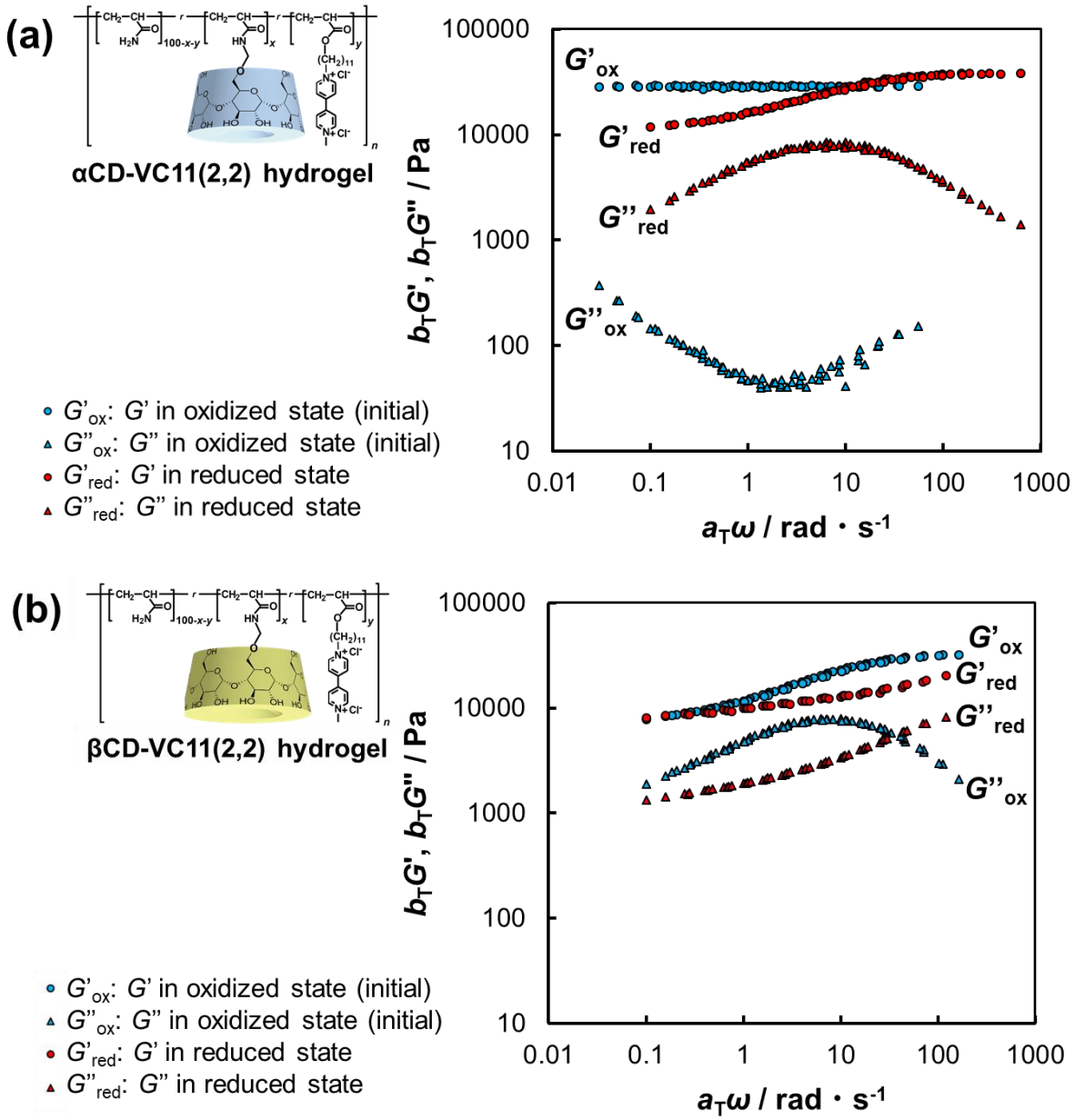


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Figure S21. Dynamic viscoelastic measurements of the αCD-VC11(2,2) **(a)**, βCD-VC11(2,2) **(b)**, γCD-VC11(2,2) **(c)**, and VC(0.2,2) hydrogels **(d)** in their oxidized (initial) and reduced states. The samples were measured at 0, 5, 10, 15, 20, and 25 ℃ to obtain the master curves with shift factor a_T (reference temperature: 25 ℃).

(Continued from the previous page)

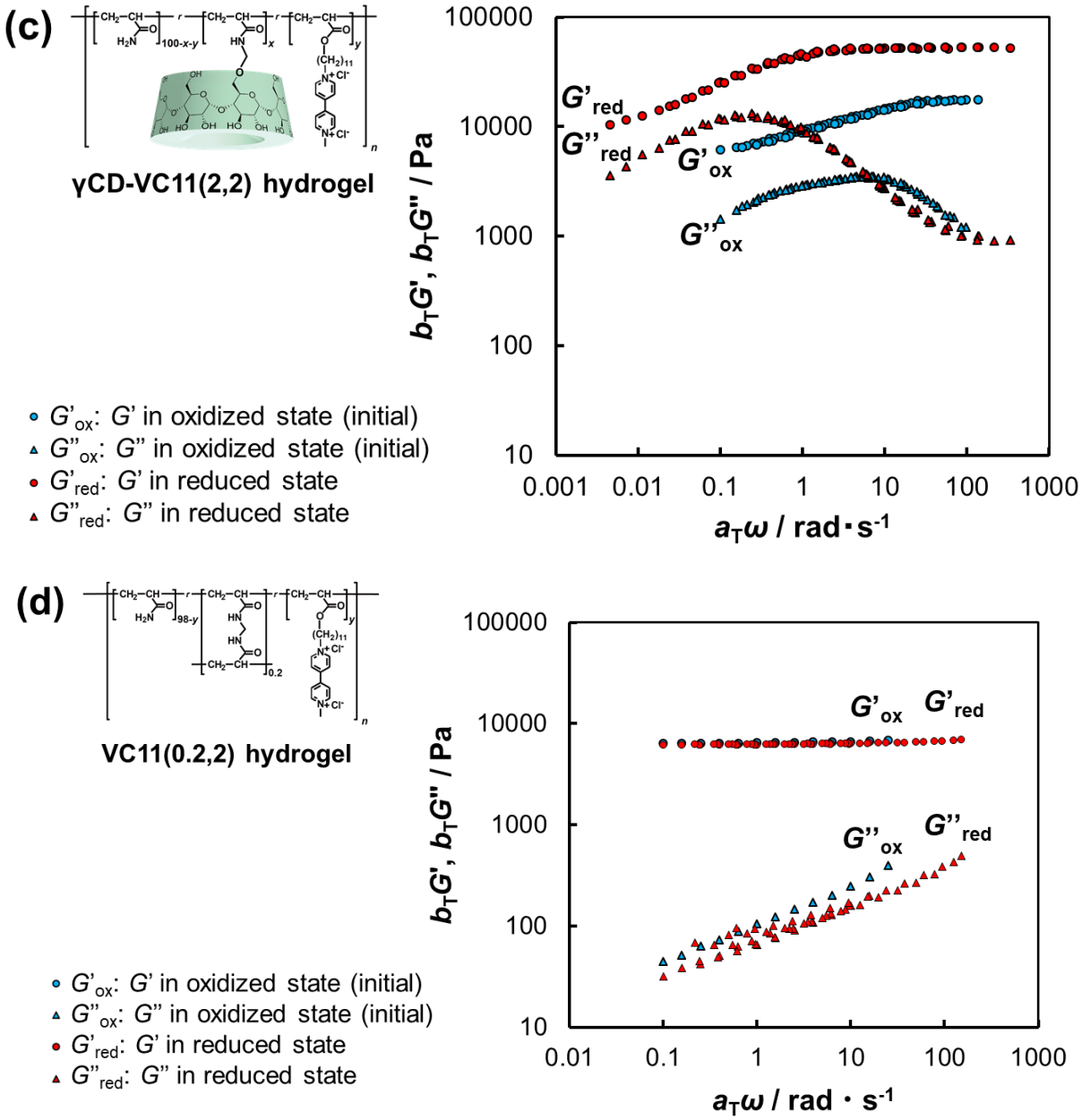

Figure S21. (Continued)

Table S8. Relaxation times (τ) of the αCD-VC11(2,2), βCD-VC11(2,2), γCD-VC11(2,2), and VC(0.2,2) hydrogels.

	Oxidized state / s (Initial state)	Reduced state / s
αCD-VC11(2,2)	4.0×10^{3}	0.14
βCD-VC11(2,2)	0.16	1.2×10^{-3}
γCD-VC11(2,2)	0.10 7.5×10^{-2}	4.0
VC(0.2,2)	n/a ($<10^{-3}$)	n/a ($<10^{-3}$)

The relaxation times are estimated by curve fitting for the master curves obtained from the dynamic viscoelastic measurements (**Figure S21**). We assume that the hydrogels behave as Maxwell material. The γCD-VC11(2,2) hydrogel showed two relaxation modes within the frequency range in the DMA measurement.

12. References

[1] Takashima, Y., Otani, K., Kobayashi, Y., Aramoto, H., Nakahata, M., Yamaguchi, H., Harada, A. Mechanical Properties of Supramolecular Polymeric Materials Formed by Cyclodextrins as Host Molecules and Cationic Alkyl Guest Molecules on the Polymer Side Chain. *Macromolecules* **2018**, *51*, 6318-6326.

[2] Takashima, Y., Sawa, Y., Iwaso, K., Nakahata, M., Yamaguchi, H., Harada, A. Supramolecular Materials Cross-Linked by Host−Guest Inclusion Complexes: The Effect of Side Chain Molecules on Mechanical Properties. *Macromolecules*, **2017**, *50*, 3254-3261.