

– Supporting Information –

Social Self-Sorting: Alternating Supramolecular Oligomer Consisting of Isomers

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- S19 **Figure S6.** The crystal structure of 2-CiO- α -CD (a). Carbon and oxygen of α -CD are shown in gray and red respectively. Cinnamoyl group is shown in blue and right green, respectively. The packing structure of 2-CiO- α -CD (b, Cross-section of the **ac** plane). The crystal structure of 2-CiO- α -CD with thermal ellipsoids (c). Water molecules were omitted.
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- S21 **Figure S7.** Plots of diffusion coefficients (D_s) of 2-CiO- α -CD (\diamond), 3-CiO- α -CD (\circ) and the mixture of 2-CiO- α -CD and 3-CiO- α -CD (\blacklozenge , \bullet). D_s of 2-CiO- α -CD and 3-CiO- α -CD were calculated by using a **2a** proton of 2-CiO- α -CD and a **3a** proton of 3-CiO- α -CD, respectively, in D₂O at 30 °C. D_s of the mixture of 2-CiO- α -CD and 3-CiO- α -CD were calculated by using a **2a** proton of 2-CiO- α -CD (plotted with \blacklozenge) and a **3a** proton of 3-CiO- α -CD (plotted with \bullet), respectively, in D₂O at 30 °C.

Note; The CIF file is uploaded in Supporting Information.

Materials

α -Cyclodextrin (α -CD) was obtained from Junsei Chemical Co., Ltd. *m*-Nitrophenol was obtained from Wako Pure Chemical Industries, Ltd. *trans*-Cinnamic acid and *N, N'*-dicyclohexylcarbodiimide were obtained from Nacalai Tesque Inc. α -CD was recrystallized twice from distilled water. The other materials were used without further purification.

Measurements

The ^1H NMR spectra were recorded at 500 MHz with a JEOL JNM LA-500 NMR spectrometer. Chemical shifts were referenced to the solvent values (δ 2.49 ppm for DMSO and δ 4.79 ppm for HOD). The ^{13}C NMR spectra were recorded at 150 MHz with a VARIAN-UNITY plus 600 NMR spectrometer. Chemical shifts were referenced to the external standard (δ 1.47 ppm for acetonitrile in D_2O). 2D NMR (gCOSY, TOCSY, ROESY, HMQC, and gHMBC) experiments were performed with D_2O as a solvent at 20 $^\circ\text{C}$ at 600 MHz with a VARIAN-INONA-600 NMR spectrometer.

Determination of diffusion coefficient: The pulse field gradient spin-echo (PFGSE) NMR spectra were recorded at 600 MHz in D₂O on a VARIAN INOVA NMR spectrometer at 30.0 °C. The bipolar pulse pair stimulated echo (BPPSTE) sequence was applied for PFGSE NMR measurement. The pulsed gradients' strength was increased from 6.36×10^{-1} to 43.1 (gauss/cm). The time separation of pulsed field gradients and their duration were 0.10 and 1.0×10^{-3} (s). The sample was not spun and the airflow was disconnected. The shape of the gradient pulse was rectangular, and its strength varied automatically during the course of the experiments. The D values were determined from the slope of the regression line $\ln(I/I_0)$ versus G^2 , according to the Stejskal and Tanner's Equation (1).

$$\ln(I/I_0) = -\gamma^2 G^2 \delta^2 (\Delta - \delta/3 - \tau/2) D \quad (1)$$

I/I_0 : observed spin echo intensity / intensity without gradients, D : diffusion coefficient,

G : gradient strength, δ : gradient length

Δ : delay between the midpoints of the gradients, τ : 90 °-180 ° pulse distance.

The calibration of the gradients was carried out by a diffusion measurement of H₂O ($D_{\text{H}_2\text{O}} = 2.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) at 25 °C. According to the Stejskal and Tanner's reports, when $\ln I/I_0$ versus g^2 were plotted, where I and g are the echo intensity and (pulsed) gradient strength, respectively, the slope of the line is given by $D/(\Delta - \delta/3)\gamma^2\delta^2$. The calibration of the gradients was carried out by a diffusion measurement of H₂O ($D_{\text{H}_2\text{O}} = 2.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) at 25 °C.

Hydrodynamic radius was calculated using Stokes-Einstein equation (2).

$$R_h = \frac{k T}{6 \pi \eta D} \quad (2)$$

R_h : Hydrodynamic radius

k : Boltzmann's constant ($1.38 \times 10^{-23} \text{ J/K}$)

T : Absolute temperature

η : Viscosity of deuterium oxide at 30 °C (1.0 mPa·s)

D : Diffusion coefficient

References

Stibs, P. *Prog. NMR Spectrosc.* **1987**, *19*, 1-45.

Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288-292.

Variable-concentration ^1H NMR and determination of homo association constants:

A 24 mM stock solution of 2-CiO- α -CD (or 3-CiO- α -CD) was prepared in D_2O . Serial dilutions were carried out to produce 18, 12, 8.0, 4.0, 2.0, 1.0, 0.50 and 0.25 mM stocks. A 0.60 mL of each solution was injected to 8 sample tubes, and then all sample tubes were lyophilized immediately. After the lyophilization, 0.60 ml of D_2O was poured into each sample tube just before the ^1H NMR measurement. All NMR measurements were carried out at 30 $^\circ\text{C}$ in 15 minutes.

Single crystal X-ray analysis of 2-CiO- α -CD exhibited the formation of double threaded dimer. On the basis of the result of 2-CiO- α -CD, 2-CiO- α -CD is supposed to form dimer in an aqueous solution less than 24 mM. 3-CiO- α -CD is estimated to form dimer less than 24 mM because the D of 3-CiO- α -CD is similar to that of 2-CiO- α -CD.

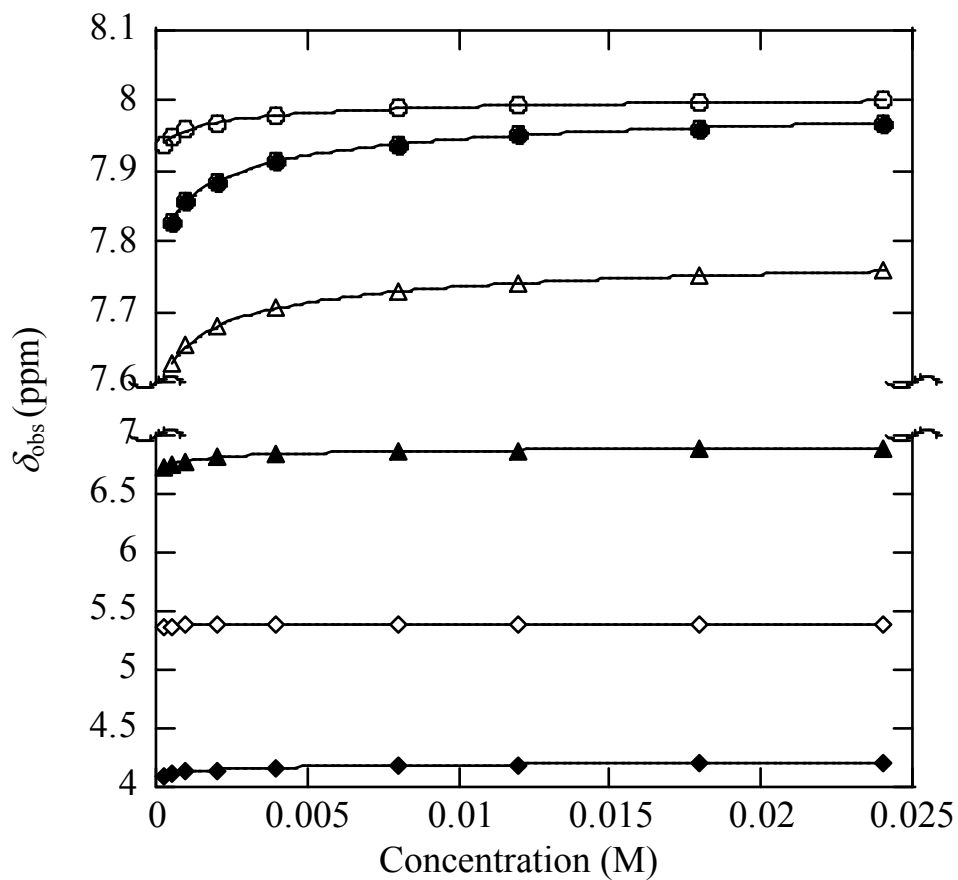
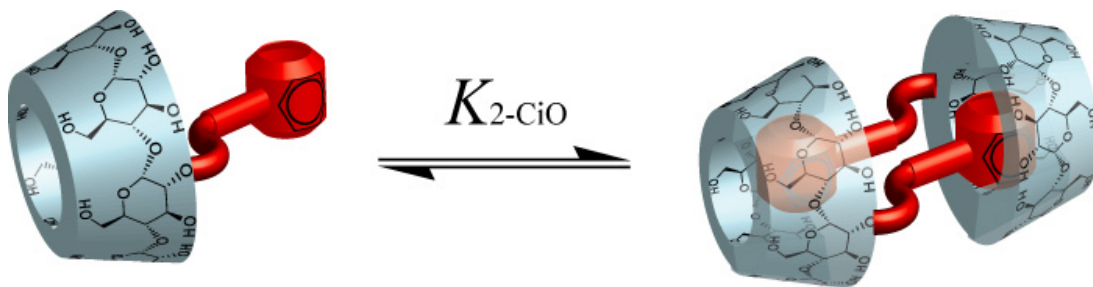
As observed above, supposing that 2-CiO- α -CD and 3-CiO- α -CD, respectively, form monomer or dimer less than 24 mM, the association constants of 2-CiO- α -CD and 3-CiO- α -CD, respectively, were determined by curve-fitting technique for the following equation.

$$\delta_{\text{obs}} = \delta_{\text{mon}} + (\delta_{\text{dimer}} - \delta_{\text{mon}}) \left(\frac{(4 K_a C_0 - 1) - \sqrt{8 K_a C_0 + 1}}{4 K_a C_0} \right) \quad (3)$$

C_0 = total concentration of CiO- α -CD

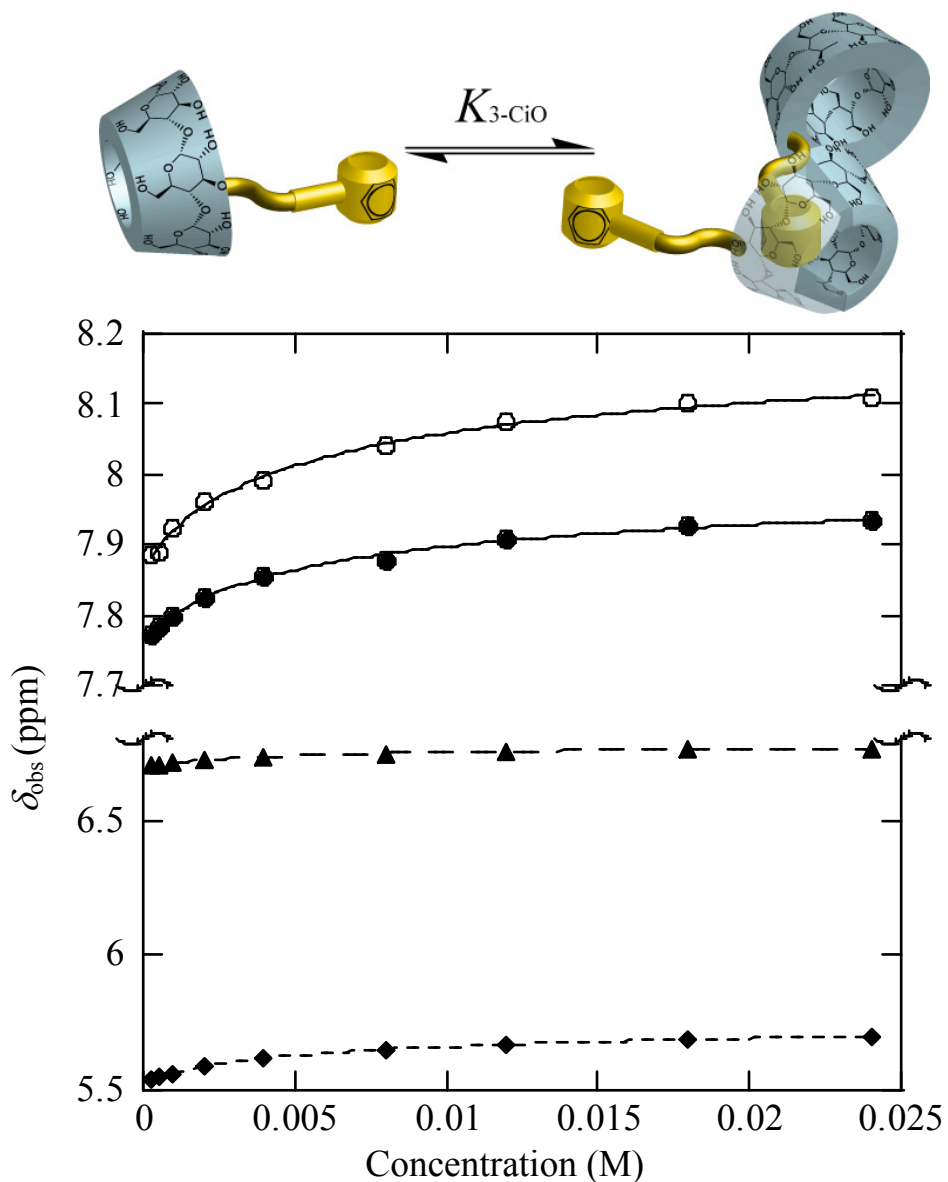
K_a = association constant

δ_{obs} = observed chemical shift



	b (○)	d (●)	c (△)	a (▲)	C(1)H (◇)	C(3)H (◆)
$K_{2\text{-CiO}}$ ($\times 10^2 \text{ M}^{-1}$)	4.1 ± 0.48	4.0 ± 0.26	3.9 ± 0.33	5.3 ± 1.16	3.1 ± 0.79	4.2 ± 0.32
δ_{mon} (ppm)	7.9254	7.7717	7.5723	6.6807	5.369	4.0617
δ_{dim} (ppm)	8.0189	8.0195	7.8062	6.9396	5.4021	4.2442
R^2	0.99905	0.99983	0.9997	0.99696	0.9948	0.99957

Figure S1. Association constants ($K_{2\text{-CiO}}$) and chemical shifts in free form (δ_{mon}) and the double threaded dimer (δ_{dim}) of 2-CiO- α -CD determined by fitting the chemical shift changes of various protons (a (▲), b (○), c (△), d (●), C(1)H (◇), and C(3)H (◆)) as a concentration of 2-CiO- α -CD.



	b (○)	c (△)	a (▲)	C(3)H (◆)
$K_{3\text{-CiO}} (\times 10^2 \text{ M}^{-1})$	1.0 ± 0.19	1.0 ± 0.15	1.1 ± 0.18	1.0 ± 0.15
δ_{mon} (ppm)	7.8652	7.7597	6.6932	5.5239
δ_{dim} (ppm)	8.2569	8.0402	6.8052	5.8036
R^2	0.99608	0.99758	0.99714	0.99957

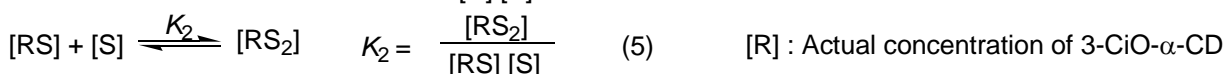
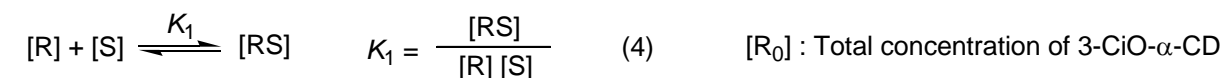
Figure S2. Association constants ($K_{3\text{-CiO}}$) and chemical shift in free form (δ_{mon}) and the pure complex form (δ_{dim}) of 3-CiO- α -CD determined by fitting the chemical shift changes of various protons (a (▲), b (○), c (△), and C(3)H (◆)) as a concentration of 3-CiO- α -CD.

Determination of hetero association constants:

A 24 mM stock solution of 2-CiO- α -CD was prepared in D₂O. Serial 2-fold and 3-fold dilutions were carried out to produce 12, 8.0, 6.0, 4.0, 3.0, 2.0, and 1.0 mM stocks. A 0.60 mL amount of each solution was transferred to 7 sample tubes. A 2.0 mM stock solution of 3-CiO- α -CD was prepared in D₂O, and then 60 μ L of the 3-CiO- α -CD stock was dispensed to all sample tubes including various concentrations of 2-CiO- α -CD. After the divided injection, all sample tubes were lyophilized immediately, and then 0.60 ml of D₂O was poured into each sample tube just before the ¹H NMR measurement. All NMR measurements were carried out at 30 °C in 15 minutes.

The ROESY NMR results of the mixture of 2-CiO- α -CD and 3-CiO- α -CD indicate that the cinnamoyl group of 2-CiO- α -CD inserted from the wider rim to the cavity of 3-CiO- α -CD and vice versa, resulting that the mixture of 2-CiO- α -CD and 3-CiO- α -CD forms an alternating supramolecular complex, and not self-supramolecular complex.

As observed above, we assumed the association equilibrium of 2-CiO- α -CD for 3-CiO- α -CD.



$$[R_0] = [R] + [RS] + [RS_2] \quad (6) \quad [S] : \text{Actual concentration of 2-CiO-}\alpha\text{-CD}$$

K_1 : Association constant for the fotation of dimer
(Meaning $K_{\text{Hetero-1}}$ in the manuscript)

K_2 : Association constant for the fotation of trimer
(Meaning $K_{\text{Hetero-2}}$ in the manuscript)

Deformations of equations (4), (5), and (6) are summarized as follows.

$$[R] = \frac{K_1 [R_0][S]}{1 + K_1[S] + K_1 K_2 [S]^2} \quad (7) \quad [RS] = \frac{K_1 K_2 [R_0][S]^2}{1 + K_1[S] + K_1 K_2 [S]^2} \quad (8)$$

Apparent chemical shifts are described as follows because the formation rate of the supramolecular complexes are faster than the NMR time scale.

$$\delta_{\text{obs}} = \frac{1}{[R_0]} \{ [R]\delta_R + [RS]\delta_{RS} + [RS_2]\delta_{RS2} \} \quad (9)$$

δ_{obs} : Apparent chemical shift

δ_R : Chemical shift of uncomplexed 3-CiO- α -CD

δ_{RS} : Chemical shift of complexed 3-CiO- α -CD

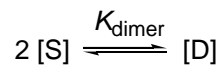
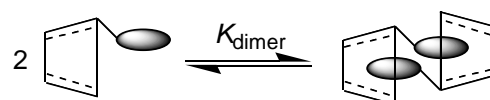
Equation (10) is derived from the assignment equations (7) and (8) to (9).

$$\delta_{\text{obs}} = \frac{\delta_R + K_1[S]\delta_{RS} + K_1K_2[S]^2\delta_{RS2}}{1 + K_1[S] + K_1K_2[S]^2} \quad (10)$$

δ_R is the chemical shift of are substituted by 5.524 (C(3)H), 6.693 (a proton), and 7.865 (b proton) of 3-CiO- α -CD, which are calculated by the extrapolation to 0 mM.

The concentration of uncomplexed 2-CiO- α -CD, [S], is calculated by an equation (11) because [S] is not equal to [S₀] due to the formation of supramolecular dimer incorporating 2-CiO- α -CD. If [2-CiO- α -CD] >> [3-CiO- α -CD], it is assumed that the change of [2-CiO- α -CD] can be ignored in the formation of hetero dimer.

The complex formation of 3-CiO- α -CD in the mixture of 2-CiO- α -CD and 3-CiO- α -CD is involved in only creating hetero supramolecular complexes, because 6% of the total 3-CiO- α -CD forms the homo supramolecular dimer at 0.20 mM, which is calculated by equation (12). On the basis of these results, the formation of supramolecular dimer incorporating 3-CiO- α -CD can be ignored.

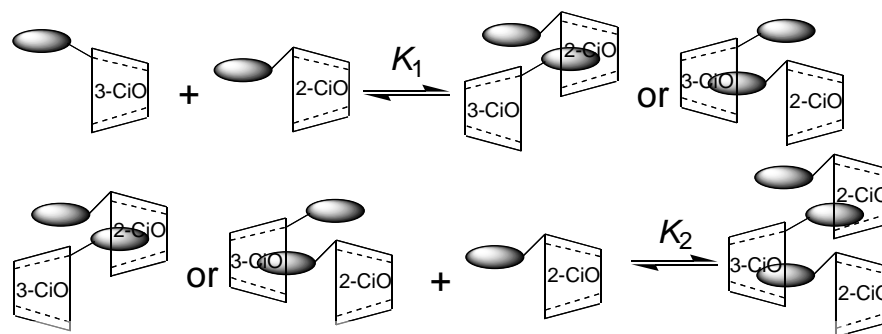


$$K_{\text{dimer}} = \frac{[D]}{[S]^2}$$

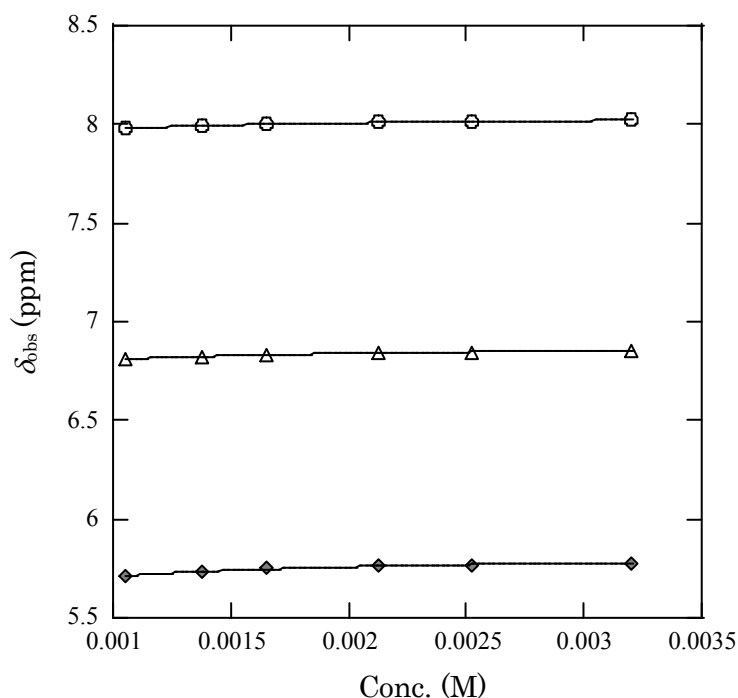
$$[S_0] = [S] + 2[D]$$

$$[S] = \frac{\sqrt{8 K_{2-\text{CiO}}[S_0] + 1} - 1}{4 K_{2-\text{CiO}}} \quad (11)$$

$$[S] = \frac{\sqrt{8 K_{3-\text{CiO}}[S_0] + 1} - 1}{4 K_{3-\text{CiO}}} \quad (12)$$



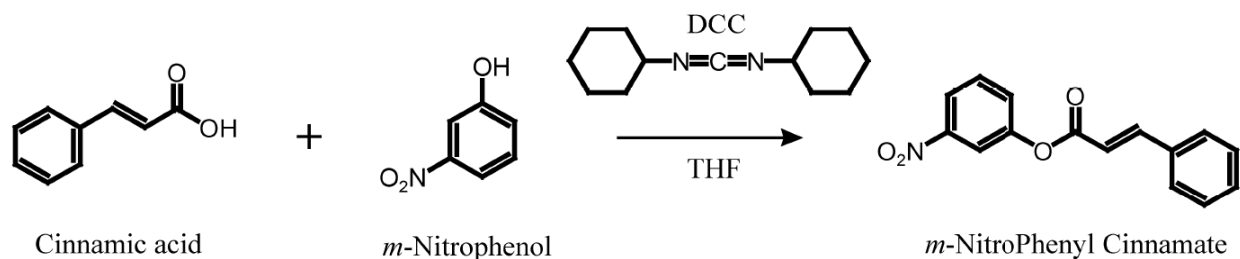
Scheme S1. The model for the determination of hetero association constants (K_1 & K_2). The total concentration of 3-CiO- α -CD is held and the total concentration of 2-CiO- α -CD is varied.



	b (○)	a (▲)	C(3)H (◆)
$K_1 (\times 10^2 \text{ M}^{-1})$	18 ± 2.9	23 ± 3.8	20 ± 3.3
$K_2 (\times 10^2 \text{ M}^{-1})$	12 ± 1.9	17 ± 2.6	15 ± 2.5
δ_R (ppm)	7.865	6.693	5.524
δ_{RS} (ppm)	7.961	6.7412	5.6364
δ_{RS2} (ppm)	8.0439	6.8793	5.8173
R^2	0.99624	0.99791	0.99774

Figure S3. Association constants (K_1 , and K_2) and the chemical shift in the pure dimer form (δ_{RS}) and the pure trimer form (δ_{RS2}) of 3-CiO- α -CD in the 1:1 mixture of 2-CiO- α -CD and 3-CiO- α -CD determined by fitting chemical shift changes of various protons (a (▲), b (○), and C(3)H (◆)) as a function of corrected 2-CiO- α -CD concentration.

Preparation of *m*-nitrophenyl cinnamate (*m*-NPC)



A solution of *trans*-cinnamic acid (6.1 g, 41 mmol), *m*-nitrophenol (5.8 g, 41 mmol), and DCC (8.5 g, 41 mmol) in THF (37 mL) was stirred over night at room temperature. After removal of the undissolved residue by filtration, filtrate was poured into 800 mL of distilled water. The resulting precipitate was washed with a saturated sodium hydrogen carbonate solution and recrystallized twice from *n*-butanol. The product was dried under vacuum at 50 °C over night. Yield : 2.8 g (25%). ¹H NMR (DMSO-*d*₆, 30 °C, 500 MHz): δ 6.90 (d, *J* = 16.1 Hz, 1H, -CH=CH-Ph), 7.44-7.50 (m, 3H, -CH=CH-3, 4, 5-Ph), 7.71-7.78 (m, 3H, 5, 6-Ph-NO₂), 7.79-7.85 (m, 2H, -CH=CH-2,6-Ph), 7.91 (d, *J* = 16.1 Hz, 1H, -CH=CH-Ph), 8.12 (m, 2H, 2, 4-Ph-NO₂). Elem. Anal. Calcd for C₁₅H₁₁NO₄: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.79; H, 3.96; N, 5.21. M.p. 107-108 °C.

Preparation of cinnamoyl modified α -cyclodextrin (CiO- α -CD) at the secondary hydroxyl group.

α -CD (1.5 g, 1.6 mmol) was dissolved in 300 mL of sodium carbonate solution (4.0×10^{-4} mol / L). The α -CD solution was added to 180 mL of acetonitrile. *m*-NPC (0.60 g, 2.2 mmol) dissolved in 30 mL of acetonitrile was gradually added to the α -CD solution with stirring. The pH of the reaction medium was adjusted to 8-9 by addition of 0.10 M NaOH solution at room temperature. After 2 hours, the reaction solution was adjusted to pH 3.0 with some drops of 1.0 M HCl solution. The reaction mixture was lyophilized to give a colorless powder. The crude powder was washed with water (200 mL) to eliminate insoluble compounds. The contaminants in the filtrate were extracted with 600 mL of ether. An aqueous layer was lyophilized to give cinnamate α -CD containing two isomers.

Reversed-phase preparative HPLC was performed to separate these isomers. A lyophilized powder was dissolved in 50 mL of distilled water and an aliquot of the solution (5.0 mL) was injected onto the HPLC system. A typical chromatogram of the mixture of two isomers is shown in Figure S4. The instrumental parameters are given in Table S1. Lyophilization of each eluent gave 74 mg of Fraction 1 (the former peak of two main peaks) and 41 mg of Fraction 2 (the latter peak of two main peaks).

Fractions 1 and 2 were identified as 3-CiO- α -CD and 2-CiO- α -CD, respectively, as characterized by ^1H NMR, ^{13}C NMR, and various 2D NMR (COSY, TOCSY, and HMQC). An accurate determination of the substituted position in the cyclodextrin derivatives was provided by an HMBC correlation between the carbon signal of the carbonyl carbon and the corresponding proton signal of the substituted site in α -CD.

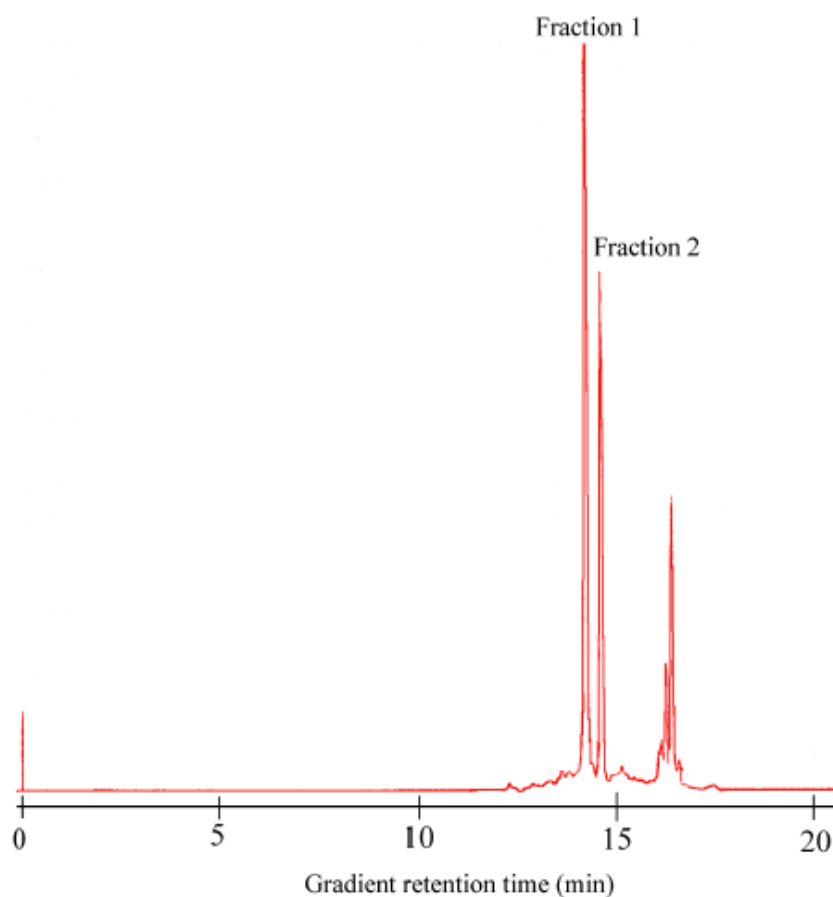


Figure S4. Typical chromatogram of the mixture of 2-CiO- α -CD and 3-CiO- α -CD.

Table S1. The instrumental parameters of preparative HPLC

Control system	Waters 600 Controller	Gradient program	
Detector	Waters 2487 Dual l Absorbance Detector	Time (min)	H ₂ O / acetonitrile (% v/v)
Pump	Waters Delta 600	Initial	100 / 0
Column	SunFire C18 OBD 19×150 mm	15	50 / 50
Recorder	SEKOINIC SS-250F	20	0 / 100
Flow rate	14 mL / min.	25	0 / 100
Temperature	40 °C (ambient)	30	100 / 0
Detection	UV@ 254 nm		

Characteristic data of 2-CiO- α -CD

^1H NMR (D_2O , 20 °C, 32 mM, 600 MHz): δ 3.51 ($\text{C}^{\text{D}}(2)\text{H}$), 3.52 ($\text{C}^{\text{A}}(4)\text{H}$, $\text{C}^{\text{B}}(2)\text{H}$), 3.53 ($\text{C}^{\text{F}}(4)\text{H}$, $\text{C}^{\text{C}}(2)\text{H}$), 3.60 ($\text{C}^{\text{F}}(2)\text{H}$), 3.62 ($\text{C}^{\text{C}}(4)\text{H}$, $\text{C}^{\text{E}}(2)\text{H}$), 3.84 ($\text{C}^{\text{C}}(3)\text{H}$, $\text{C}^{\text{F}}(3)\text{H}$), 3.89 ($\text{C}^{\text{E}}(4)\text{H}$), 3.93 ($\text{C}^{\text{A}}(3)\text{H}$), 3.47-3.98 ($\text{C}^{\text{A-F}}(5)\text{H}$, $\text{C}^{\text{A-F}}(6)\text{H}$, $\text{C}^{\text{B}}(4)\text{H}$, $\text{C}^{\text{C}}(3-4)\text{H}$), 4.03 ($\text{C}^{\text{B}}(3)\text{H}$), 4.11 ($\text{C}^{\text{E}}(3)\text{H}$), 4.67 ($\text{C}^{\text{A}}(3)\text{H}$), 4.67 ($\text{C}^{\text{A}}(2)\text{H}$), 4.91 ($\text{C}^{\text{D}}(1)\text{H}$), 4.98 ($\text{C}^{\text{C}}(1)\text{H}$), 5.00 ($\text{C}^{\text{B}}(1)\text{H}$), 5.01 ($\text{C}^{\text{E}}(1)\text{H}$), 5.07 ($\text{C}^{\text{F}}(1)\text{H}$), 5.29 ($\text{C}^{\text{A}}(1)\text{H}$), 6.82 (d, $J = 16.0$ Hz, 1H, $-\text{CH}=\text{CH}-\text{Ph}$), 7.51 (t, $J = 7.2$ Hz, 1H, $-\text{CH}=\text{CH}-4-\text{Ph}$), 7.65 (t, $J = 7.4$ Hz, 2H, $-\text{CH}=\text{CH}-3,5-\text{Ph}$), 7.86 (d, $J = 8.0$ Hz, 2H, $-\text{CH}=\text{CH}-2,6-\text{Ph}$), 7.88 (d, $J = 16.0$ Hz, 1H, $-\text{CH}=\text{CH}-\text{Ph}$).

^{13}C NMR (D_2O 20 °C, 150 MHz): δ 60.5, 70.5, 71.5, 73.6, 82.1, 99.0 ($\text{C}^{\text{A}}(1-6)$ of CD moiety), 60.3, 60.7, 60.9, 71.7, 71.8, 71.9, 72.1, 72.2, 72.3, 72.4, 72.6, 73.1, 73.3, 73.4, 73.9, 81.4, 81.7, 101.7, 101.8, 101.9 ($\text{C}^{\text{B-F}}(1-6)$ of CD moiety), 117.4 ($-\text{CH}=\text{CH}-\text{Ph}$), 128.8 ($-\text{CH}=\text{CH}-2,6-\text{Ph}$), 129.5 ($-\text{CH}=\text{CH}-3,5-\text{Ph}$), 130.7 ($-\text{CH}=\text{CH}-4-\text{Ph}$), 134.4 ($-\text{CH}=\text{CH}-1-\text{Ph}$), 146.6 ($-\text{CH}=\text{CH}-\text{Ph}$), 168.9 ($-\text{O}-\text{C}=\text{O}$)

MALDI-TOF MS ; $m/z = 1126.1$ ($[\text{C}_{45}\text{H}_{66}\text{O}_{31} + \text{Na}]^+ = 1125.4$), 1142.2 ($[\text{C}_{45}\text{H}_{66}\text{O}_{31} + \text{K}]^+ = 1141.3$).

Elemental Anal. Calcd for $\text{C}_{45}\text{H}_{66}\text{O}_{31}(\text{H}_2\text{O})_6$: C, 44.63; H, 6.49. Found: C, 44.81; H, 6.28.

Characteristic data of 3-CiO- α -CD

^1H NMR (D_2O , 20 °C, 32 mM, 600 MHz): δ 3.41 ($\text{C}^{\text{B}}(2)\text{H}$, $\text{C}^{\text{B}}(4)\text{H}$), 3.51 ($\text{C}^{\text{B}}(3)\text{H}$), 3.53 ($\text{C}^{\text{E}}(4)\text{H}$, $\text{C}^{\text{C}}(2)\text{H}$), 3.58 ($\text{C}^{\text{F}}(2)\text{H}$), 3.60 ($\text{C}^{\text{E}}(2)\text{H}$), 3.62 ($\text{C}^{\text{D}}(4)\text{H}$), 3.64 ($\text{C}^{\text{B}}(5)\text{H}$, $\text{C}^{\text{F}}(5)\text{H}$), 3.65 ($\text{C}^{\text{D}}(6)\text{H}$), 3.66 ($\text{C}^{\text{D}}(2)\text{H}$), 3.82 ($\text{C}^{\text{D}}(5)\text{H}$), 3.83 ($\text{C}^{\text{E}}(3)\text{H}$), 3.84 ($\text{C}^{\text{F}}(3)\text{H}$), 3.85 ($\text{C}^{\text{A}}(6)\text{H}$), 3.87 ($\text{C}^{\text{A}}(2)\text{H}$), 3.89 ($\text{C}^{\text{E}}(5)\text{H}$), 3.91 ($\text{C}^{\text{A}}(4)\text{H}$, $\text{C}^{\text{F}}(4)\text{H}$), 3.37-4.05 ($\text{C}^{\text{B,E,F}}(6)\text{H}$, $\text{C}^{\text{C}}(3-6)\text{H}$), 4.01 ($\text{C}^{\text{A}}(5)\text{H}$), 4.14 ($\text{C}^{\text{D}}(3)\text{H}$), 4.91 ($\text{C}^{\text{C}}(1)\text{H}$), 4.94 ($\text{C}^{\text{B}}(1)\text{H}$), 5.01 ($\text{C}^{\text{F}}(1)\text{H}$), 5.06 ($\text{C}^{\text{D}}(1)\text{H}$), 5.08 ($\text{C}^{\text{E}}(1)\text{H}$), 5.13 ($\text{C}^{\text{A}}(1)\text{H}$), 5.66 ($\text{C}^{\text{A}}(3)\text{H}$), 6.70 (d, J = 16.0 Hz, 1H, -CH=CH-Ph), 7.53 (t, J = 7.2 Hz, 1H, -CH=CH-4-Ph), 7.59 (t, J = 7.5 Hz, 2H, -CH=CH-3, 5-Ph), 7.88 (d, J = 7.6 Hz, 2H, -CH=CH-2, 6-Ph), 8.06 (d, J = 16.0 Hz, 1H, -CH=CH-Ph).

^{13}C NMR (D_2O 20 °C, 150 MHz): δ 71.4, 73.7, 75.6, 79.7, 81.6, 101.8 ($\text{C}^{\text{A}}(1-6)$ of CD moiety), 60.8, 61.0, 61.1, 61.2, 71.5, 72.2, 72.3, 72.5, 72.6, 72.7, 72.9, 73.3, 73.5, 73.8, 74.3, 81.8, 81.9, 82.0, 82.1, 102.0, 102.1, 102.2, 102.3 ($\text{C}^{\text{B-F}}(1-6)$ of CD moiety), 118.2 (-CH=CH-Ph), 129.3 (-CH=CH-2,6-Ph), 129.7 (-CH=CH-3,5-Ph), 131.1 (-CH=CH-4-Ph), 135.1 (-CH=CH-1-Ph), 147.0 (-CH=CH-Ph), 170.0 (-O-C=O).

MALDI-TOF MS ; m/z = 1125.4 ($[\text{C}_{45}\text{H}_{66}\text{O}_{31} + \text{Na}]^+ = 1125.4$), 1142.3 ($[\text{C}_{45}\text{H}_{66}\text{O}_{31} + \text{K}]^+ = 1141.3$).

Elemental Anal. Calcd for $\text{C}_{45}\text{H}_{66}\text{O}_{31}(\text{H}_2\text{O})_5$: C, 45.30; H, 6.42. Found: C, 45.02; H, 6.35.

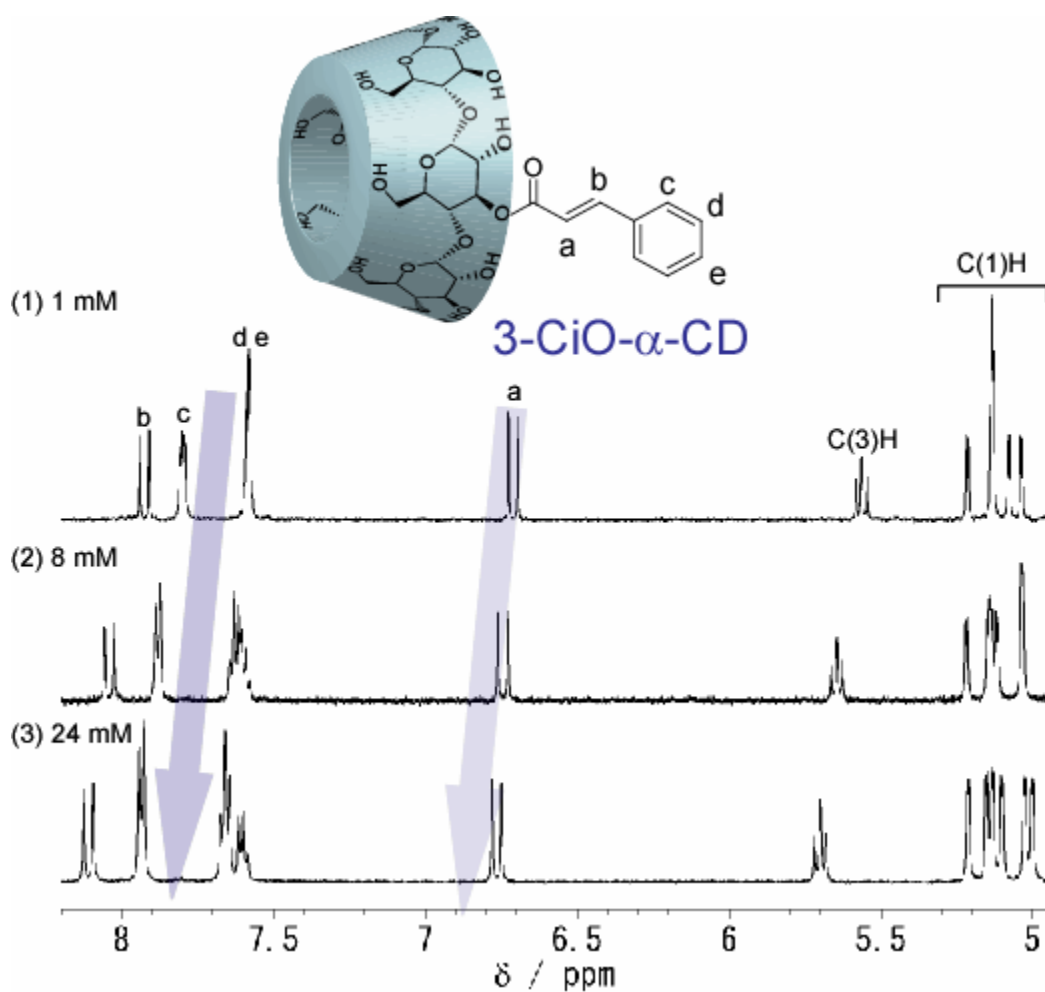


Figure S5. ^1H NMR spectra of various concentrations of 3-CiO- α -CDs in D_2O at 30°C . (1.0 mM, 2.0 mM, 4.0 mM, 8.0 mM, and 16mM).

The resonance peaks of 3-CiO- α -CD showed the peak shifts as well as 2-CiO- α -CD. The peaks of 3-CiO- α -CD shifted to a lower field with an increase in the concentration, affording the intermolecular supramolecular complex in aqueous solutions.

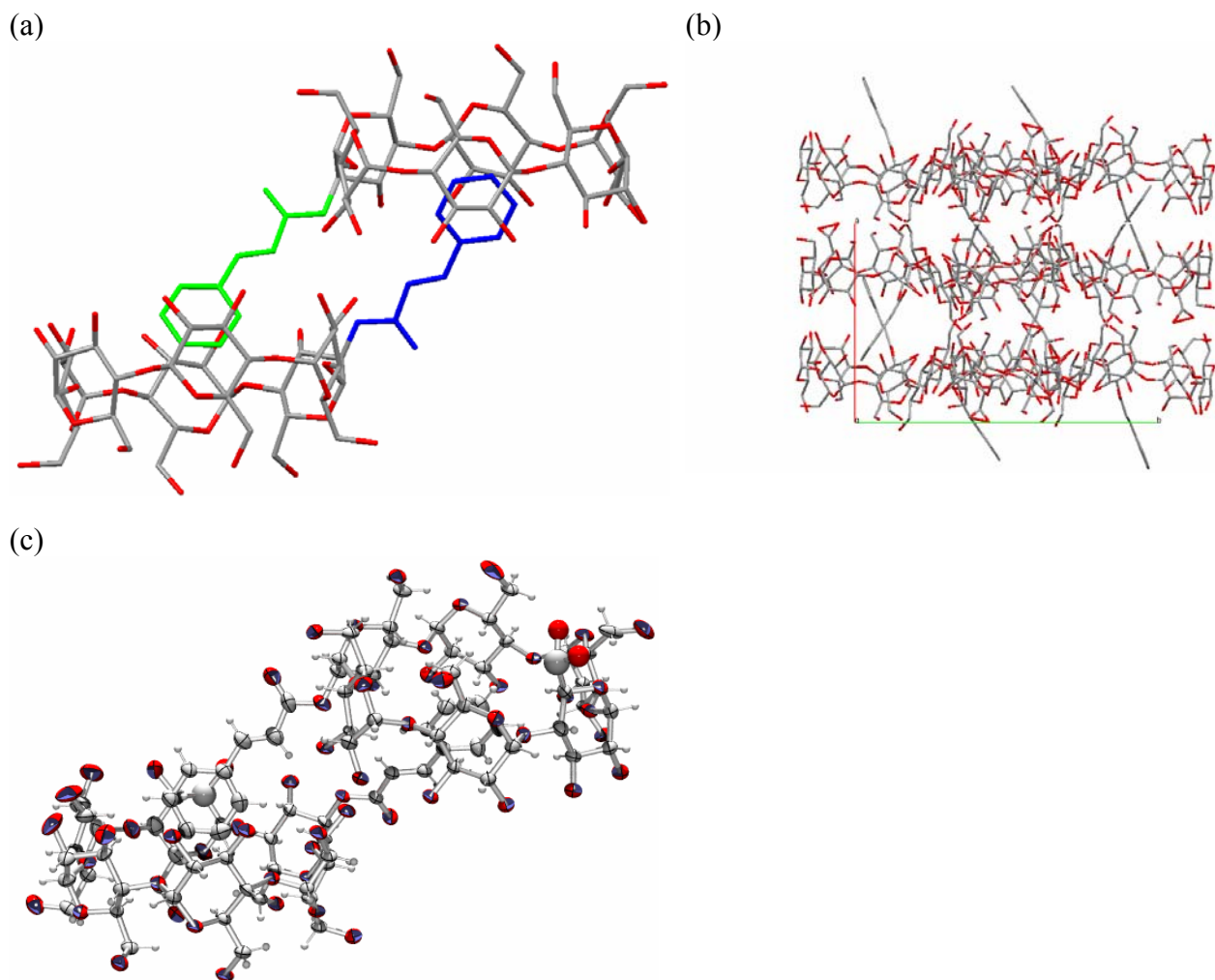


Figure S6. The crystal structure of 2-CiO- α -CD (a). Carbon and oxygen of α -CD are shown in gray and red respectively. Cinnamoyl group is shown in blue and right green, respectively. The packing structure of 2-CiO- α -CD (b, Cross-section of the **ac** plane). The crystal structure of 2-CiO- α -CD with thermal ellipsoids (c). Water molecules were omitted.

The movie file of the crystal structure of 2-CiO- α -CD and CIF file are uploaded in Supporting Information.

Table S2. Crystal data and collection parameters for 2-CiO- α -CD.

	2-CiO-α-CD
formula	C ₄₅ H ₆₆ O ₃₁
formula weight	1103.00
crystal system	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)
<i>a</i> , Å	15.5665(4)
<i>b</i> , Å	23.5385(5)
<i>c</i> , Å	33.1929(9)
α , deg.	-
β , deg.	-
γ , deg.	-
<i>V</i> , Å ³	12162.3(5)
<i>Z</i>	8
<i>D</i> _{calcd} , g/cm ³	1.54187
<i>F</i> (000)	4672.00
μ [Cu K α], cm ⁻¹	0.892
temp, K	100.1
2 θ _{min} , 2 θ _{max} , deg	3.1, 68.3
no. of refl. Measured (Total)	11715
no. of refl. measured (Unique)	10055
no. of variables	1593
<i>R</i>	0.0753
w <i>R</i>	0.2340
GOF	1.081

A CIF file is uploaded in Supporting Information.

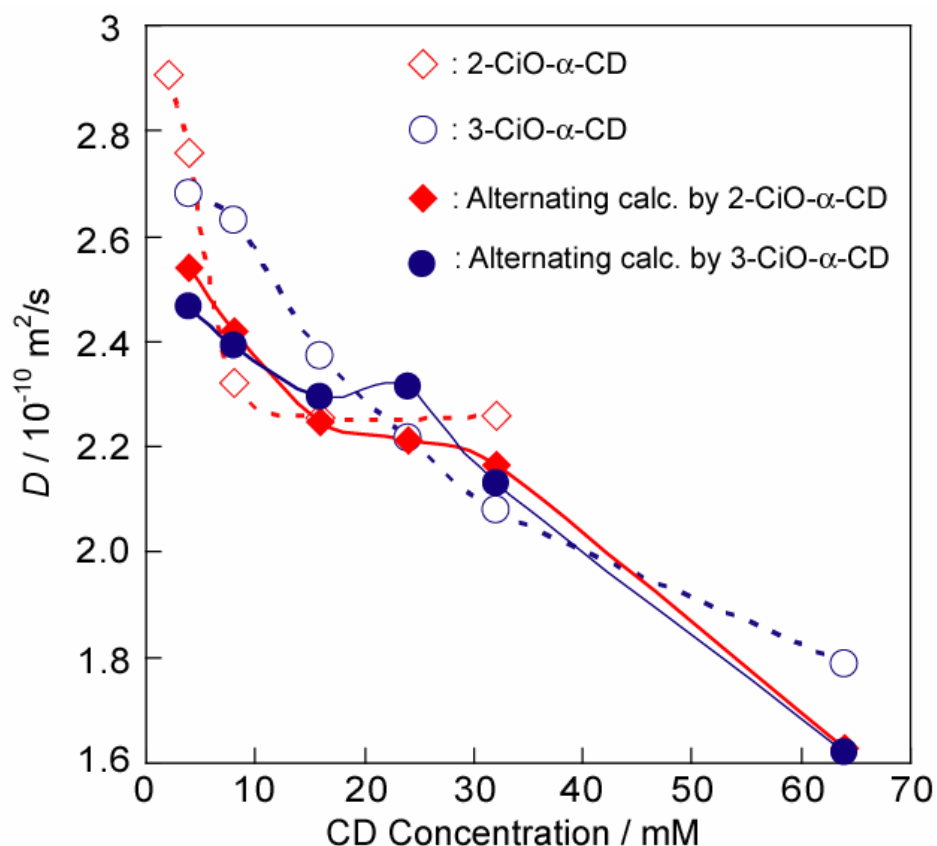


Figure S7. Plots of diffusion coefficients (D s) of 2-CiO- α -CD (\diamond), 3-CiO- α -CD (\circ) and the mixture of 2-CiO- α -CD and 3-CiO- α -CD (\blacklozenge , \bullet). D s of 2-CiO- α -CD and 3-CiO- α -CD were calculated by using a **2a** proton of 2-CiO- α -CD and a **3a** proton of 3-CiO- α -CD, respectively, in D_2O at 30 °C. D s of the mixture of 2-CiO- α -CD and 3-CiO- α -CD were calculated by using a **2a** proton of 2-CiO- α -CD (plotted with \blacklozenge) and a **3a** proton of 3-CiO- α -CD (plotted with \bullet), respectively, in D_2O at 30 °C.

The D of 2-CiO- α -CD shows an unvarying D over 10 mM and reached $2.3 \times 10^{-10} \text{ m}^2/\text{s}$ at 32 mM. The D of 3-CiO- α -CD decreases monotonously with its concentration, then reached $1.7 \times 10^{-10} \text{ m}^2/\text{s}$ at 64 mM. 2-CiO- α -CD is estimated to form double threaded dimer over 10 mM as demonstrated by the single crystal X-ray analysis. It should be noted that the D of 3-CiO- α -CD shows a concentration dependence, but D of 2-CiO- α -CD does not. These results indicate that 3-CiO- α -CD forms weak supramolecular oligomer at more than 32 mM in aqueous solutions.

The D s of the mixture of 2-CiO- α -CD and 3-CiO- α -CD were calculated by using a **2a** proton of 2-CiO- α -CD and a **3a** proton of 3-CiO- α -CD, respectively. The D s of the mixture showed much lower values than those of individual isomers, indicating that the mixture of 2-CiO- α -CD and 3-CiO- α -CD formed stable alternating supramolecular oligomers cooperatively.