Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Inclusion of cyclodextrins in a metallosupramolecular framework via structural transformations

Supattra Somsri,[a] Naoto Kuwamura,[a] Tatsuhiro Kojima,[a] Nobuto Yoshinari,[a] Apinpus Rujiwatra,[b]
Takumi Konno [a]*

[a] *Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*
konno@chem.sci.osaka-u.ac.jp

[b] *Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 502000, Thailand.*

Experimental

Materials

The starting compounds, $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot 13H_2O$ and $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot 1/3NaOAc\cdot 10H_2O$ (**2**), were prepared according to procedures described in the literature.[S1]

Preparation of $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot 1/3NaOAc\cdot\alpha\text{-CD}$ ($\mathbf{3}^{\alpha}$)

Method A: A solid sample of $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot 13H_2O$ (100 mg, 0.060 mmol) was dissolved in 6 mL of a 0.5 M aqueous solution of NaOAc/HOAc (pH = 6.0). The dark purple solution was allowed to stand at room temperature for 20 days, yielding dark purple crystals (**2**) with a truncated hexagonal pyramidal shape. A solid sample of α-CD (87 mg, 0.09 mmol) was dissolved in the mother liquor, and then crystals of **2** were soaked in this solution. Within a day, the crystals of **2** disappeared and dark purple crystals with a hexagonal plate shape ($\mathbf{3}^{\alpha}$) appeared, and these latter crystals were collected by filtration after seven days. Yield: 19 mg (11%). Anal. Found: C, 26.81; H, 5.24; N, 2.65%. Calcd for $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot 1/3NaOAc\cdot\alpha\text{-CD}\cdot 18H_2O$ = $C_{66.6}H_{150.9}Au_3Co_2N_6Na_{3.3}O_{60.6}S_6$: C, 26.82; H, 5.10; N, 2.82%. IR spectrum (cm^{-1}, KBr disk): 2921 (ν_{CH2}), 1617 (ν_{COO^-}), 1154 (ν_{C-C}), and 1033 (δ_{OH}). ^1H NMR spectrum in D_2O (δ, ppm): 1.49 (s, 3H), 1.66 (s, 3H), 1.93 (s, 0.65H), 3.23 (s, 1H), 3.56–3.67 (m, 2H), 3.82–4.04 (m, 4H), and 5.07 (d, 1H).

Method B: To a colourless solution containing α-CD (292 mg, 0.300 mmol) in 5 mL of a 0.5 M aqueous solution of NaOAc/HOAc (pH = 6.0) was added a solution containing $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot 13H_2O$ (100 mg, 0.060 mmol) in 5 mL of a 0.5 M aqueous solution of NaOAc/HOAc (pH = 6.0). This mixture was allowed to stand at room temperature for one month, yielding dark purple crystals with a hexagonal plate shape ($\mathbf{3}^{\alpha}$), which were collected by filtration. Yield: 99 mg (55%).

Preparation of $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot 1/3NaOAc\cdot 2\gamma\text{-CD}\cdot 1/3\alpha\text{-CD}$ ($\mathbf{3}^{\alpha\gamma}$)

Method A: A solid sample of $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot 13H_2O$ (100 mg, 0.060 mmol) was dissolved in 5 mL of a 0.5 M aqueous solution of NaOAc/HOAc (pH = 6.0). The resulting dark purple solution was allowed to stand at room temperature for 20 days to give dark purple crystals (**2**) with a truncated hexagonal pyramidal shape. Solid samples of α-CD (148 mg, 0.150 mmol) and γ-CD (194 mg, 0.150 mmol) were dissolved in the mother liquor, and then crystals of **2** were soaked in this solution. Within a day, the crystals of **2** disappeared and dark purple crystals with a hexagonal plate shape ($\mathbf{3}^{\alpha\gamma}$) appeared, and the latter crystals were collected by filtration after seven days. Yield: 50 mg (15%). Anal. Calcd for $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot1/3NaOAc\cdot1/3\alpha\text{-CD}\cdot2\gamma\text{-CD}\cdot56H_2O$ = $C_{138.5}H_{346.8}Au_3Co_2N_6Na_{3.3}O_{158.7}S_6$: C, 29.65; H, 6.23; N, 1.51%. Found: C, 29.65; H, 6.09; N, 1.52%. IR spectrum (cm^{-1}, KBr disk): 2928 (ν_{CH2}), 1613 (ν_{COO^-}), 1159 (ν_{C-C}), and 1029 (δ_{OH}). ^1H NMR spectrum in D_2O (δ, ppm): 1.49 (s, 3H), 1.66 (s, 3H), 1.95 (s, 0.65H), 3.24 (s, 1H), 3.57–3.69 (m, 6.47H), 3.83–4.04 (m, 12.93H), 5.07 (d, 0.39H), and 5.13 (d, 2.78H).

Method B: To a colourless solution containing α-CD (146 mg, 0.150 mmol) and γ-CD (195 mg, 0.150 mmol) in 5 mL of a 0.5 M aqueous solution of NaOAc/HOAc (pH = 6.0) was added a solution containing $Na_3[Au_3Co_2(\textsc{d}\text{-pen})_6]\cdot13H_2O$ (100 mg, 0.060 mmol) in 5 mL of a 0.5 M aqueous solution of NaOAc/HOAc (pH = 6.0). The mixture was allowed to stand at room temperature for two weeks to give dark purple crystals with a hexagonal plate shape ($\mathbf{3}^{\alpha\gamma}$), which were collected by filtration. Yield: 33 mg (10%).

Physical measurements

The IR spectra were recorded with a JASCO FT/IR-4100 infrared spectrophotometer using KBr pellets at room temperature. The electronic spectra were recorded with a JASCO V-630 spectrometer at room temperature. The circular dichroism spectra were recorded with a J820 spectrometer at room temperature. X-ray fluorescence analyses were performed on a SHIMADZU EDX-7000 spectrometer. Elemental analyses (C, H, N) were performed at Osaka University using a Yanaco CHN Corder MT-5. The ^1H NMR spectra were recorded with a JEOL ECS400 (400 MHz) spectrometer in D_2O. High-quality powder X-ray diffraction (PXRD) was performed at room temperature in transmission mode (synchrotron radiation λ = 1.0 Å; 2θ range = 2–78°; step width = 0.01°; data collection time 1 min) on a diffractometer equipped with a MYTHEN microstrip X-ray detector (Dectris Ltd) at the SPring-8 BL02B2 beamline. Crystals were loaded into a glass capillary tube (diameter = 0.3 mm) together with a mother liquor, which was rotated during the measurements. Simulated powder diffraction patterns were generated from the single-crystal X-ray structures using Mercury 3.9.

X-ray structural determinations

The diffraction data for $\mathbf{3}^{\alpha}$ and $\mathbf{3}^{\alpha\gamma}$ were recorded at 100 K with a PILATUS3 X CdTe 1M with synchrotron radiation ($\lambda = 0.41330$ Å) at SPring-8 (BL02B1 beamline). The intensity data were collected by the ω-scan technique and processed with a CrysAlisPro program for $\mathbf{3}^{\alpha}$ and RAPID-AUTO for $\mathbf{3}^{\alpha\gamma}$. Empirical absorption corrections were applied for both $\mathbf{3}^{\alpha}$ and $\mathbf{3}^{\alpha\gamma}$. The structures were solved by the direct method using SHELXS-2018.[S2] The structure refinements were carried out by full-matrix least-squares (SHELXL-2018).[S2] All calculations were carried out using the WingGX software package.[S3]

For $\mathbf{3}^{\alpha}$, global ISOR, SIMU, RIGU and BUMP restraints were applied. DFIX and SAME were applied to model the D-glucose moiety in α-cyclodextrin. All nonhydrogen atoms except for the water molecules of crystallization were refined anisotropically. All of the H atoms except those of the water molecules were placed at the calculated positions by using a riding model. The contributions of undetermined Na^+ and OAc^- ions and water molecules of crystallization were excluded using the SQUEEZE program in the PLATON package.[S4] A total of 28625 electrons were found in the void with a volume of 30620 Å^3 per unit cell by the mask calculation. The number of electrons is not consistent with the presence of 8/3 Na, 1/3 OAc^-, and 13.67 H_2O per formula unit, which gives 3180 electrons per unit cell. This difference in electron numbers is most likely due to the loss of water molecules of crystallization in the course of the isolation of the bulk sample and its elemental analysis. While the X-ray analysis of $\mathbf{3}^{\alpha}$ showed a relatively high Flack parameter (χ = 0.208(6)), the correctness of the absolute structure of $\mathbf{3}^{\alpha}$ was confirmed by the absolute configurations of the asymmetric carbon centres of D-pen and α-cyclodextrin.

For $\mathbf{3}^{\alpha\gamma}$, global ISOR, RIGU and BUMP restraints were applied. DFIX and SAME were applied to model the D-glucose moiety in α-cyclodextrins. All nonhydrogen atoms except for the water molecules of crystallization were refined anisotropically. All of the H atoms except those in water molecules were placed at the calculated positions by using a riding model. The contributions of undetermined Na^+ and OAc^- ions and water molecules of crystallization were excluded using the SQUEEZE program in the PLATON package.[S4] A total of 9943 electrons were found in the void with a volume of 19764 Å^3 per unit cell by the mask calculation. The number of electrons is not consistent with the presence of Na, 1/3 OAc and 49 H_2O per formula unit, which gives 5968 electrons per unit cell. This difference in electron numbers is most likely due to the loss of water molecules of crystallization in the course of the isolation of the bulk sample and its elemental analysis.

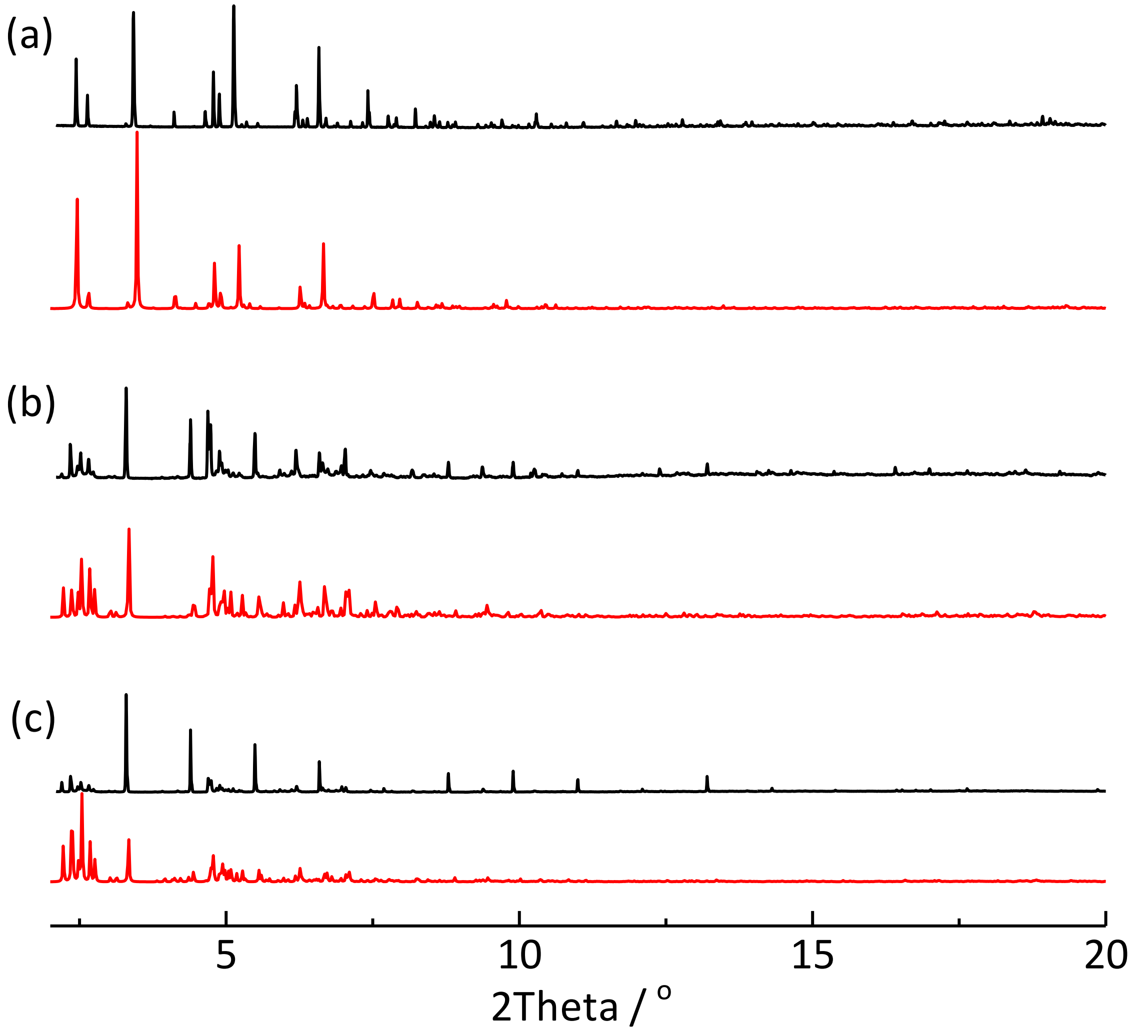

Fig. S1. Observed (black line) and simulated (red line) PXRD patterns of (a) **3**$^{\alpha}$, (b) **3**$^{\alpha\gamma}$ and (c) **3**$^{\gamma}$.

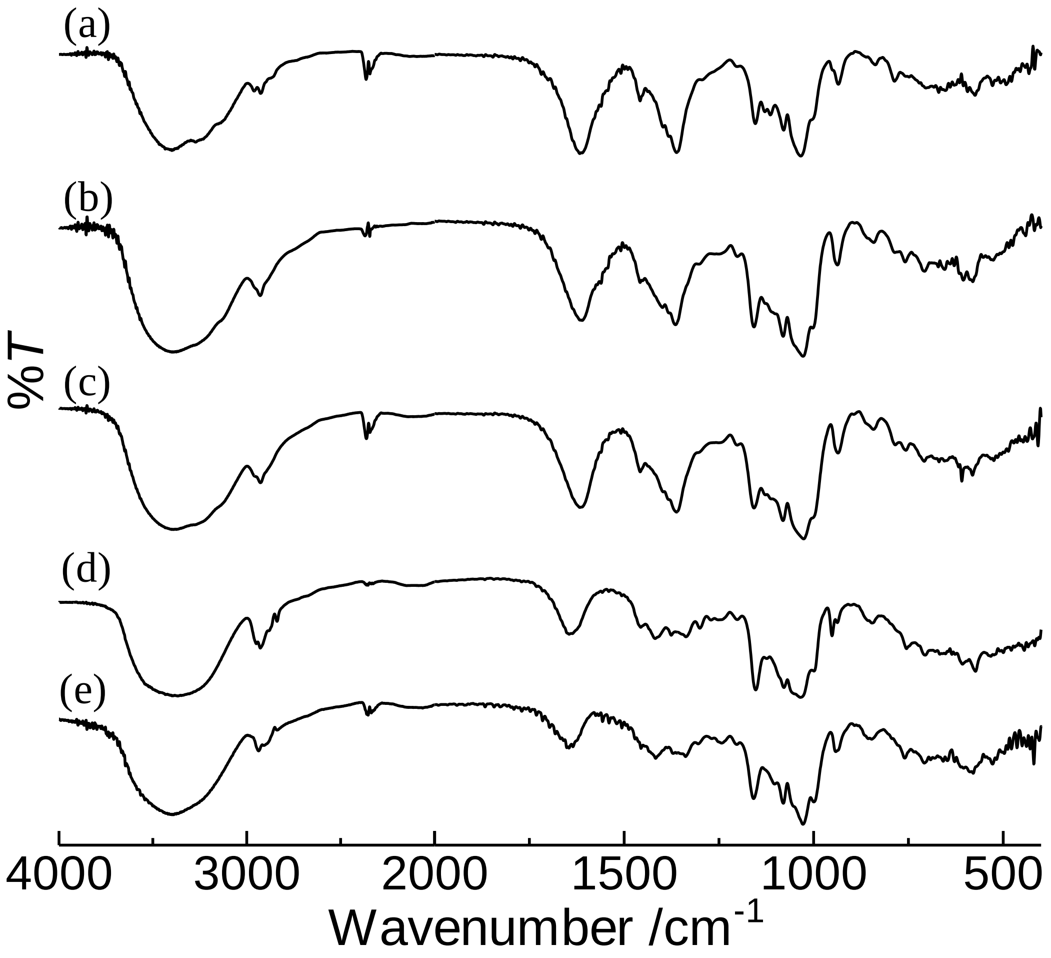

Fig. S2. IR spectra of (a) $\mathbf{3}^{\alpha}$, (b) $\mathbf{3}^{\alpha\gamma}$, (c) $\mathbf{3}^{\gamma}$, (d) α-CD and (e) γ-CD.

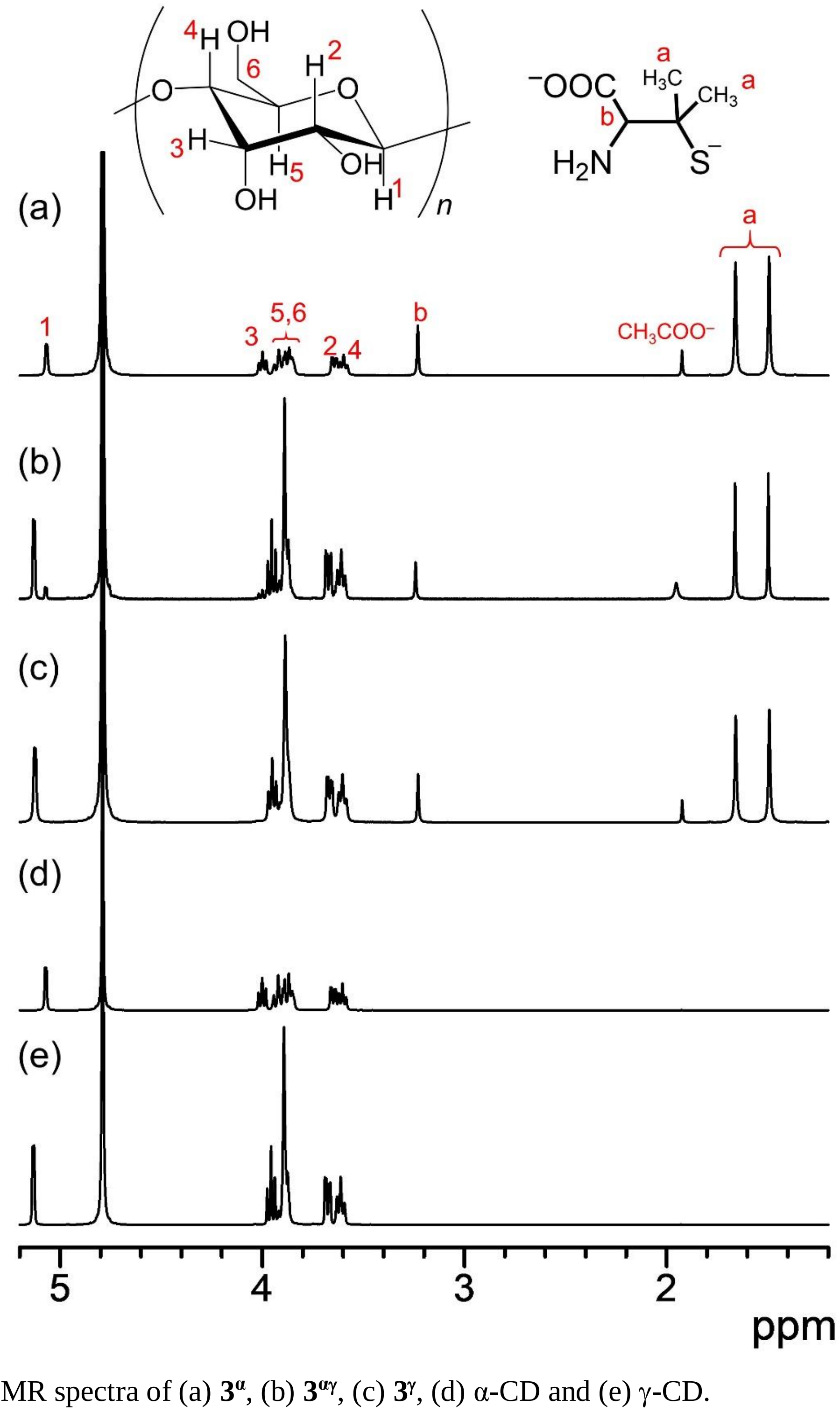

Fig. S3. ^{1}H NMR spectra of (a) $\mathbf{3}^{\alpha}$, (b) $\mathbf{3}^{\alpha\gamma}$, (c) $\mathbf{3}^{\gamma}$, (d) α-CD and (e) γ-CD.

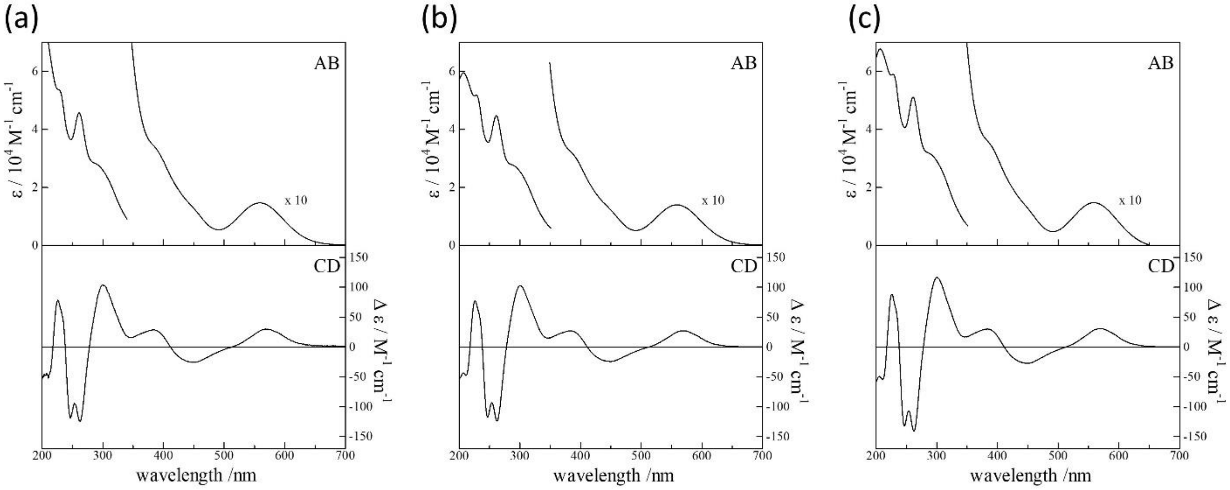

Fig. S4. Absorption and circular dichroism spectra of (a) **2**, (b) $\mathbf{3}^{\alpha}$ and (c) $\mathbf{3}^{\alpha\gamma}$ in H_2O.

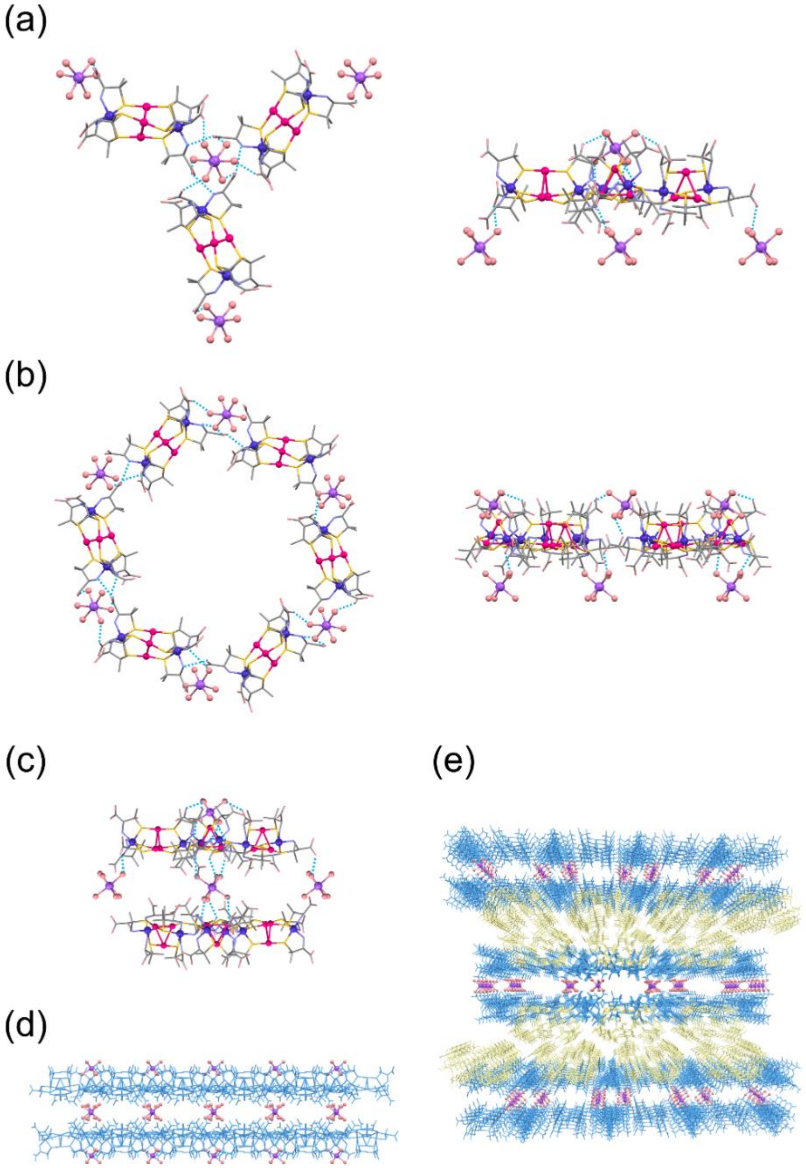

Fig. S5. Crystal structure of **3**$^{\alpha}$. (a) [**1**]$^{3-}$ anions connected by [Na(H$_2$O)$_6$]$^+$ cations through O-H···OOC hydrogen bonds. (b) A hexagon composed of six [**1**]$^{3-}$ anions. (c) Two hexagons linked by [Na(H$_2$O)$_6$]$^+$ cations. (d) A double layer structure linked by [Na(H$_2$O)$_6$]$^+$ cations. (e) A multilayer structure composed of double layers of the honeycomb framework and double layers of α-CD. Colour codes: Co, violet; Au, red; S, yellow; O, pink; Na, purple; N, blue; C, grey. Honeycomb framework and α-CD trimer are represented by blue and yellow colours, respectively.

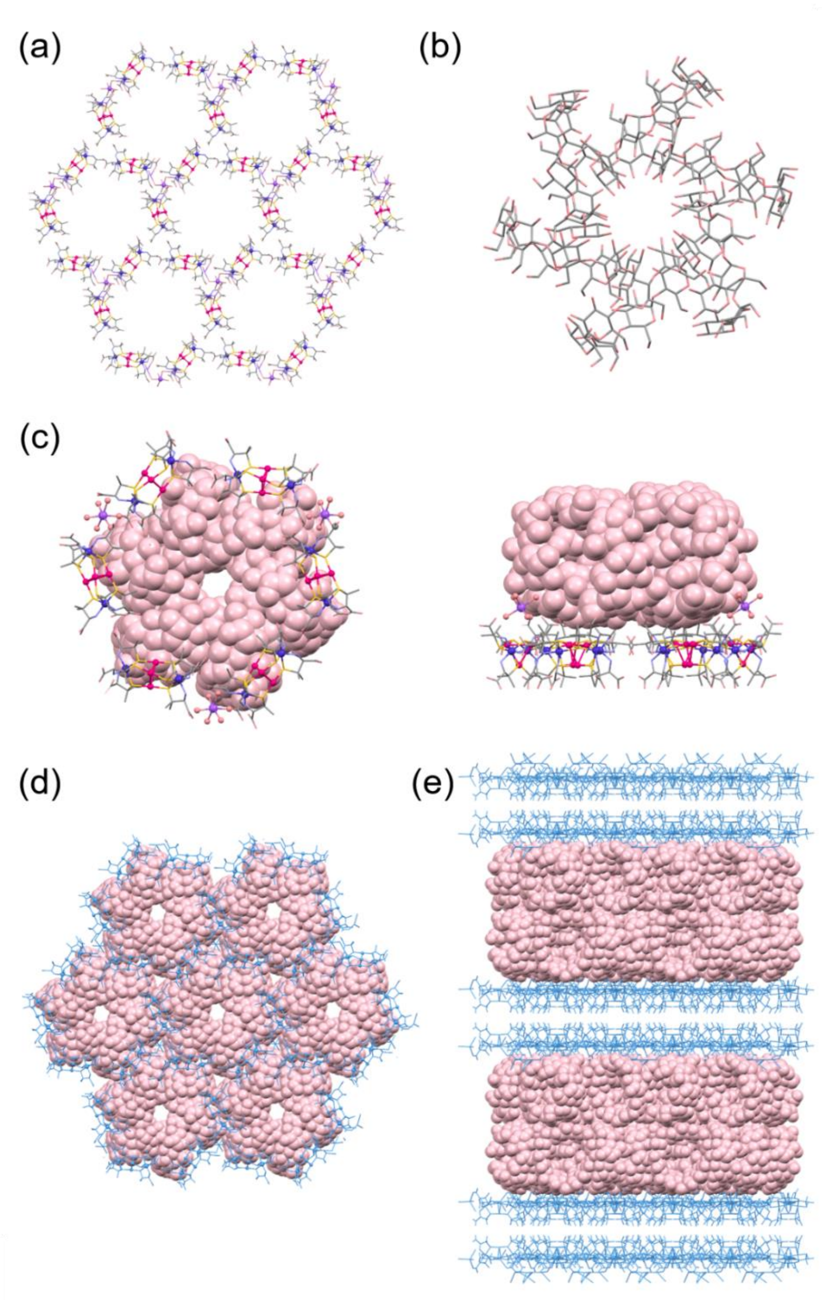

Fig. S6. Crystal structures of **3**$^{\gamma}$. (a) A honeycomb layer framework composed of [**1**]$^{3-}$ anions that are linked by $[Na_4(H_2O)_9]^{4+}$ cations. (b) A hexameric assembly of γ-CD molecules. (c) A hexagonal cavity covered by a γ-CD hexamer. (d) A honeycomb layer framework with γ-CD hexamers. (e) A multilayer structure composed of double layers of the honeycomb framework and double layers of γ-CD hexamers. Colour codes: Co, violet; Au, red; S, yellow; O, pink; Na, purple; N, blue; C, grey. Honeycomb framework and γ-CD hexamer are represented by blue and pink colours, respectively.

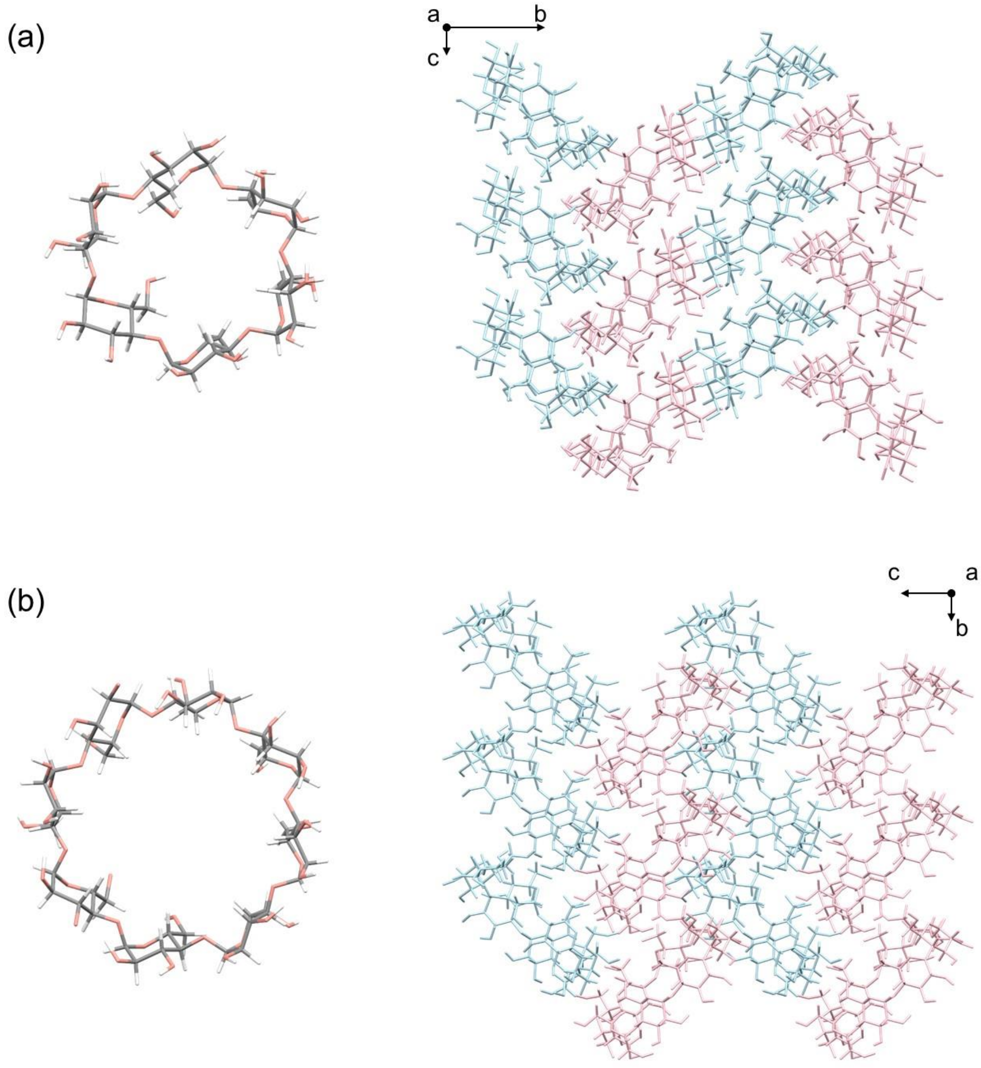

Fig. S7. Herringbone-type packing structures of CD molecules in (a) α-CD·6H_2O and (b) γ-CD·14.1H_2O.[S5,S6] Only the CD molecules are illustrated to emphasize their arrangement in the crystal lattice.

Table S1. Crystallographic data for **3^{α}**, **$3^{\alpha\gamma}$**, and **3^{γ}**.

	3^{α}	**$3^{\alpha\gamma}$**	**3^{γ}**
Formula	$C_{66.67}H_{151}Au_3Co_2N_6$ $Na_{3.33}O_{60.67}S_6$	$C_{138.67}H_{347}Au_3Co_2N_6$ $Na_{3.33}O_{158.67}S_6$	$C_{126}H_{204.33}Au_3Co_2N_6$ $Na_{3.33}O_{100.5}S_6$
Colour, form	Purple, plate	Purple, plate	Purple, plate
Crystal size / mm^3	0.08 × 0.08 × 0.005	0.12 × 0.10 × 0.005	0.85 × 0.67 × 0.12
M	2985.35	5615.62	4389.03
Crystal system	Trigonal	Monoclinic	Monoclinic
Space group	$P3_221$	$C2$	$C2$
a / Å	27.74680(10)	48.5735(19)	48.570(8)
b / Å	27.74680(10)	28.0506(11)	28.050(8)
c / Å	98.7723(5)	52.270(2)	52.051(10)
α / °	90	90	90
β / °	90	97.789(7)	97.93(4)
γ / °	120	90	90
V / Å^3	65855.4(6)	70562(5)	70236(28)
Z	18	12	12
T / K	100(2)	100(2)	100(2)
$F(000)$	27036	34968	26760
ρ_{calcd} / g· cm^{-3}	1.355	1.586	1.245
μ(Mo Kα) / mm^{-1}	0.829 ($\lambda = 0.4133$)	0.488 ($\lambda = 0.4132$)	1.629 ($\lambda = 0.6500$)
$2\theta_{max}$(°)	21.851	14.413	29.821
$R1$ (I>2σ(I)) [a]	0.1565	0.1375	0.0809
w$R2$ (all data) [b]	0.3824	0.3794	0.2033
GOF	1.298	0.943	0.866
Flack parameter	0.208(6)	0.094(17)	0.074(5)
CCDC No.	2108598	2108597	2006557

[a] $R_1 = (\Sigma|(|F_o|-|F_c|)|)/(\Sigma|F_o|)$ [b] $wR_2 = [\{\Sigma w(F_o^2-F_c^2)^2\}/(\Sigma w|F_o^2|^2]^{1/2}$

References

[S1] S. Somsri, N. Kuwamura, T. Kojima, N. Yoshinari and T. Konno, *Chem. Sci.*, 2020, **11**, 9246-9253.
[S2] G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122.
[S3] L. J. Farrugia, *J. Appl. Cryst.* 2012, **45**, 849-854.
[S4] A. L. Spek, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2009, **65**, 148-155.
[S5] B. Klar, B. Hingerty and W. Saenger, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 1154–1165.
[S6] K. Harata, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2763–2767.