Electronic Supplementary Information (ESI)

Self-assembly of Cyclic Hexamers of γ-Cyclodextrin in a Metallosupramolecular Framework with D-Penicillamine

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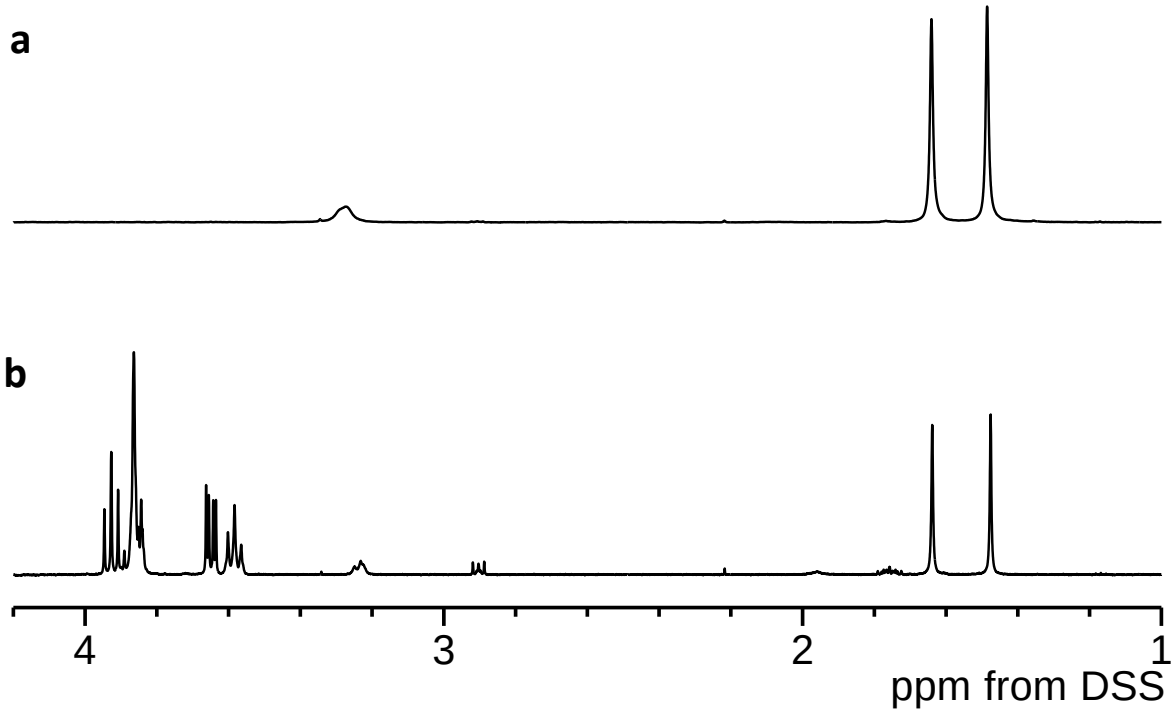

Fig. S1. ^{1}H NMR spectra of (a) $[Co(H_2O)]_3[\mathbf{1^D}]_2$ and (b) $[Co(H_2O)]_3[\mathbf{1^D}]_2\cdot 2(\gamma\text{-CD})$ in D_2O. $[Co(H_2O)]_3[\mathbf{1^D}]_2\cdot 2(\gamma\text{-CD})$ gives rise to additional multiplet signals in the range of 3.5-4.0 ppm due to the γ-CD molecules.

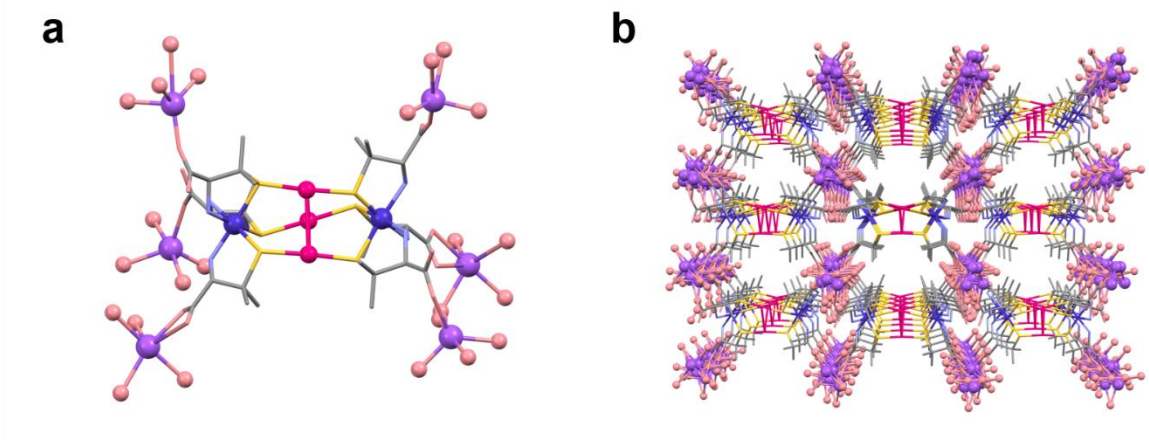

Fig. S2. Crystal structure of $Na_3[\mathbf{1^D}]\cdot 0.5$acetone.[S1] (a) Coordination environment around $[\mathbf{1^D}]^{3-}$. (b) The 3D dense framework. Colour code: Co, dark blue; Au, magenta; S, yellow; O, pink; Na, purple; N, blue; C, grey. S1: Konno, T., Toyota, A., Igashira-Kamiyama, A. coordination behaviour of a D-penicillaminato aurate(I) metalloligand toward cobalt(III) centres. *J. Chin. Chem. Soc.* **2009**, *56*, 26-33.

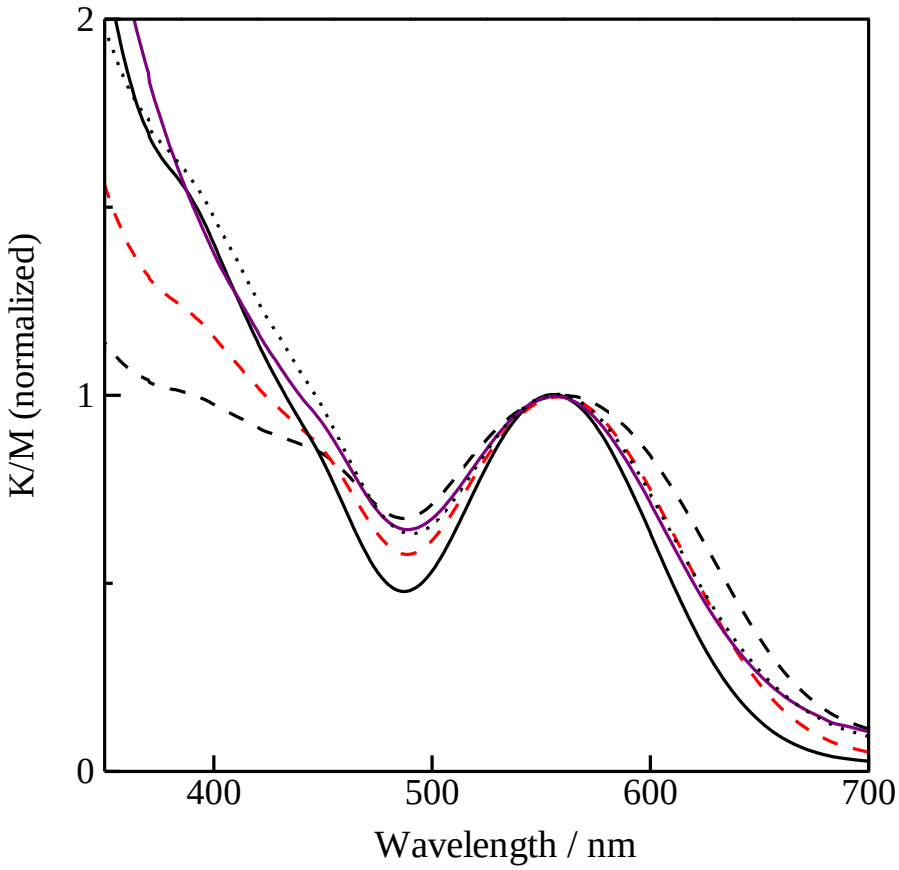

Fig. S3. Diffuse reflection spectra in the solid state for Na_3[**1**$^{\mathbf{D}}$] (black dotted line), **2**$^{\mathbf{D}}$ (black dashed line), **2**$^{\mathbf{L}}$ (red dashed line), **2**$^{\mathbf{DL}}$ (purple solid line), and **3**$^{\mathbf{D}}$ (black solid line). The K/M intensity was normalized to the intensity maxima of the band at 550-600 nm.

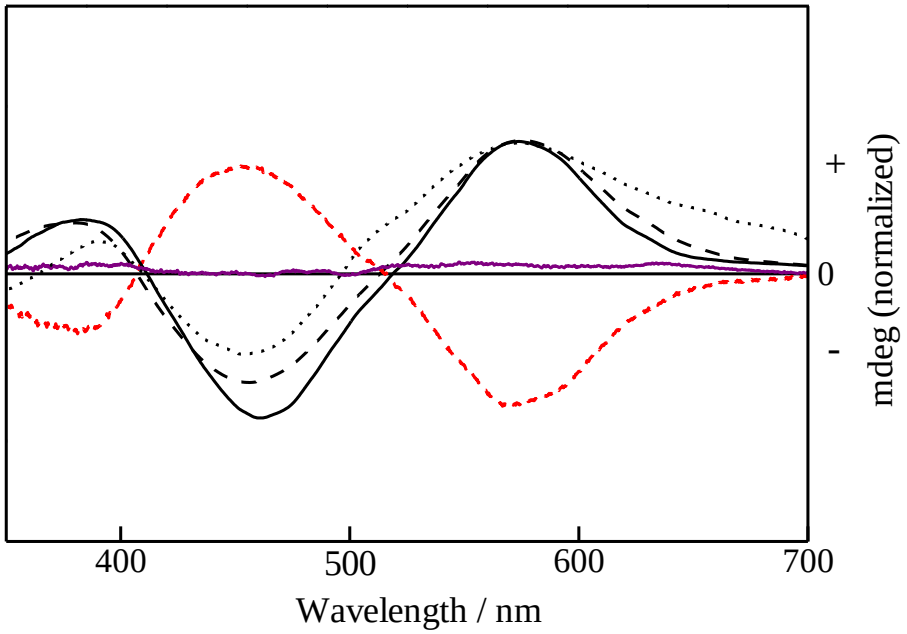

Fig. S4. CD spectra in the solid state for Na_3[**1**$^{\mathbf{D}}$] (black dotted line), **2**$^{\mathbf{D}}$ (black dashed line), **2**$^{\mathbf{L}}$ (red dashed line), **2**$^{\mathbf{DL}}$ (purple solid line), and **3**$^{\mathbf{D}}$ (black solid line). The CD intensity was normalized to the intensity maxima of the band at 550-600 nm, except for **2**$^{\mathbf{DL}}$.

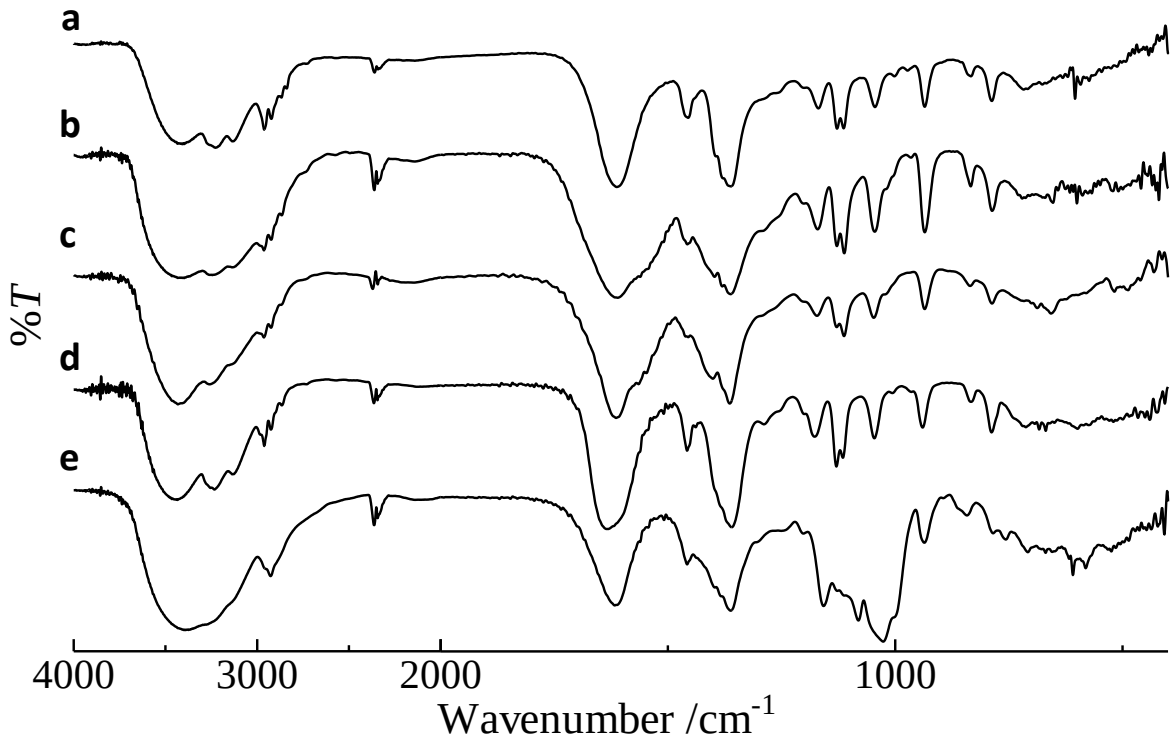

Fig. S5. IR spectra of (a) Na_3[**1**$^{\mathbf{D}}$], (b) **2**$^{\mathbf{D}}$, (c) **2**$^{\mathbf{L}}$, (d) **2**$^{\mathbf{DL}}$, and (e) **3**$^{\mathbf{D}}$. Compound **3**$^{\mathbf{D}}$ gives rise to additional bands at 1025 cm^{-1} and 1158 cm^{-1} that are assignable to $\nu_{C\text{-}C}$ and δ_{OH} of γ-CD, respectively.

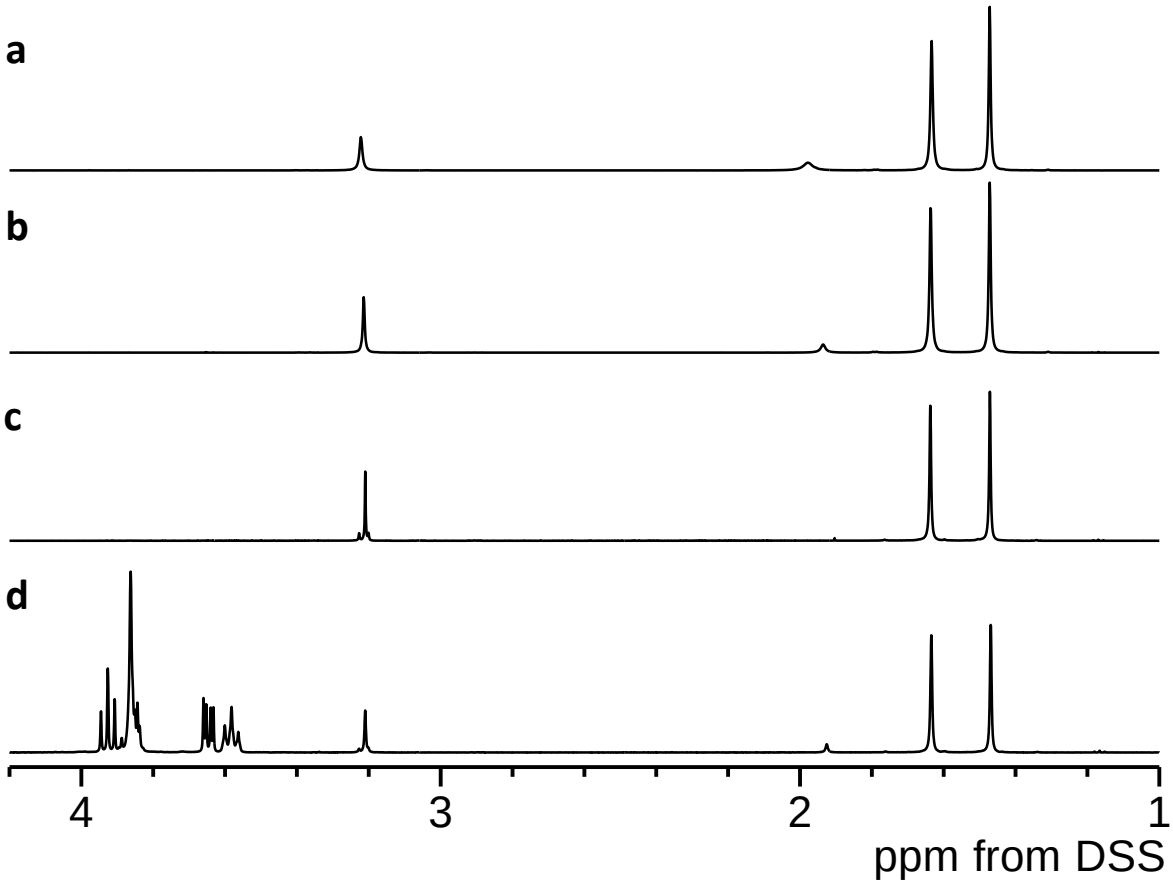

Fig. S6. ^{1}H NMR spectra of (a) $\mathbf{2^{D}}$, (b) $\mathbf{2^{L}}$, (c) $\mathbf{2^{DL}}$, and (d) $\mathbf{3^{D}}$ in D_2O. A methyl proton signal due to acetate is observed at 1.97, 1.94, and 1.92 ppm for $\mathbf{2^{D}}$, $\mathbf{2^{L}}$, and $\mathbf{2^{DL}}$, respectively. Compound $\mathbf{3^{D}}$ gives rise to additional multiplet signals in the range of 3.50-4.0 ppm due to γ-CD molecules.

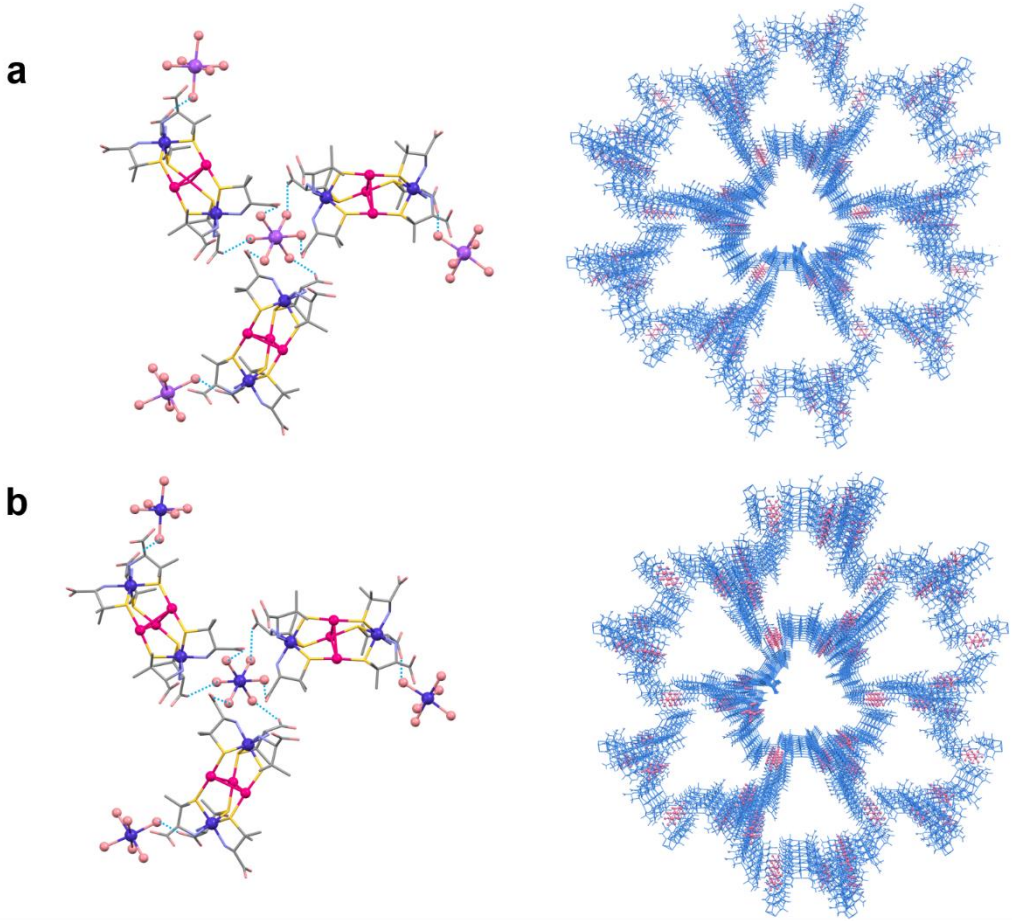

Fig. S7. Crystal structures of $\mathbf{2^D}$ and $[Co(H_2O)_6]_3[\mathbf{1^D}]_2$. (a) The linkage of $[\mathbf{1^D}]^{3-}$ anions with $[Na(H_2O)_6]^+$ cations in a 3-connected mode and the 3D porous framework constructed from $[\mathbf{1^D}]^{3-}$ anions with $[Na(H_2O)_6]^+$ cations in $\mathbf{2^D}$. (b) The linkage of $[\mathbf{1^D}]^{3-}$ anions with $[Co(H_2O)_6]^{2+}$ cations in a 3-connected mode and the 3D porous framework in $[Co(H_2O)_6]_3[\mathbf{1^D}]_2$. The blue dotted lines indicate hydrogen bonds. Colour code: Left: Co, dark blue; Au, magenta; S, yellow; O, pink; Na, purple; N, blue; and C, grey; Right: $[\mathbf{1^D}]^{3-}$, blue; $[Na(H_2O)_6]^+$, pink; and $[Co(H_2O)_6]^{2+}$, pink.

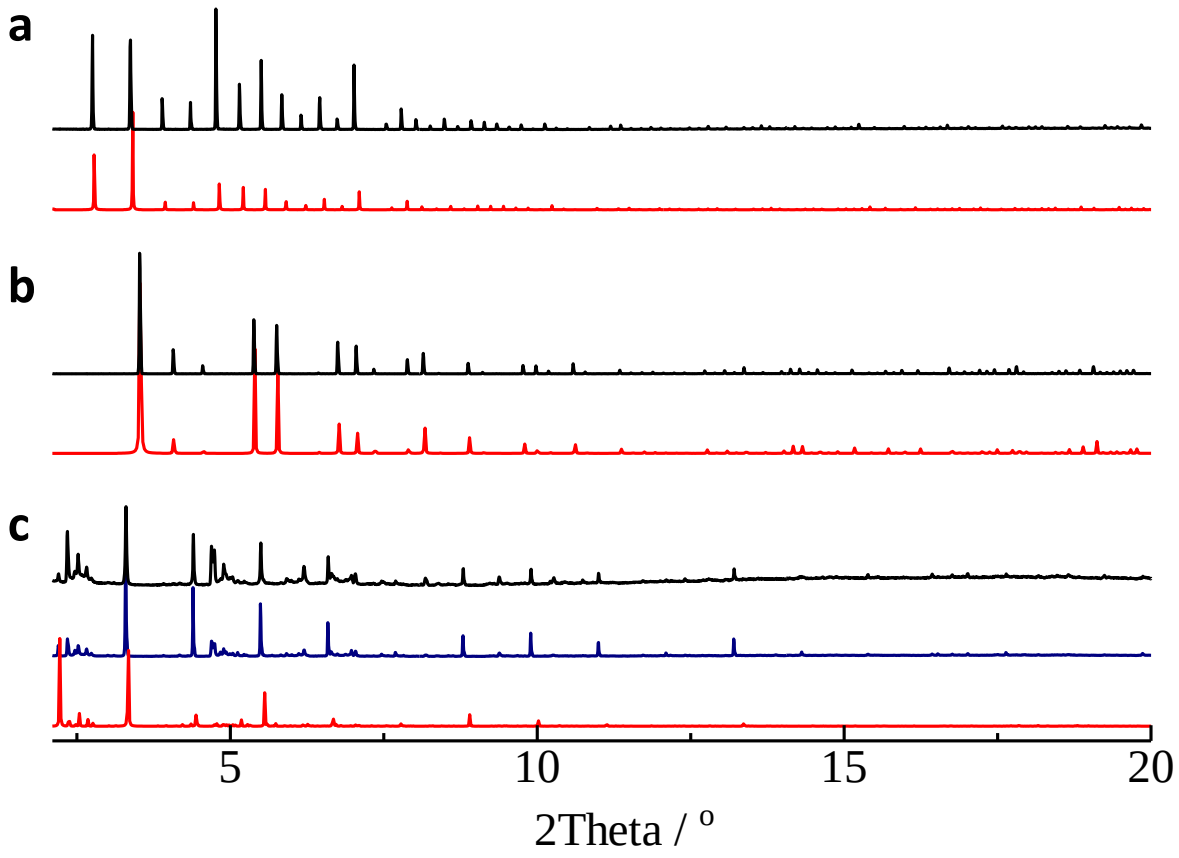

Fig. S8. Observed (black) and simulated (red) PXRD patterns for (a) $\mathbf{2^{D}}$, (b) $\mathbf{2^{DL}}$, and (c) $\mathbf{3^{D}}$ soaking method (black), co-crystallization method (blue).

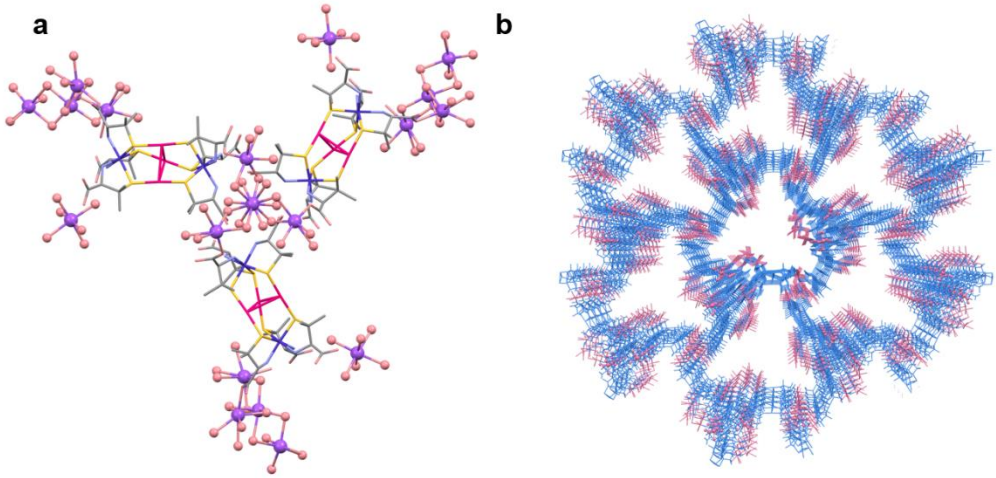

Fig. S9. Crystal structures of $\mathbf{2^L}$ crystallized in the cubic space group of $I2_13$. (a) The linkage of $[\mathbf{1^D}]^{3-}$ anions with $[Na_4(H_2O)_{15}]^{4+}$ and $[Na(H_2O)_6]^{+}$ cations in a 3-connected mode. (b) The 3D porous framework. The homogeneity of the bulk sample of $\mathbf{2^L}$ was confirmed by the PXRD pattern that matches the pattern simulated from the single-crystal X-ray data (Fig. S8). Colour codes: (a) Co, dark blue; Au, magenta; S, yellow; O, pink; Na, purple; N, blue; and C, grey; (b) $[\mathbf{1^D}]^{3-}$, blue; $[Na_4(H_2O)_{15}]^{4+}$, pink.

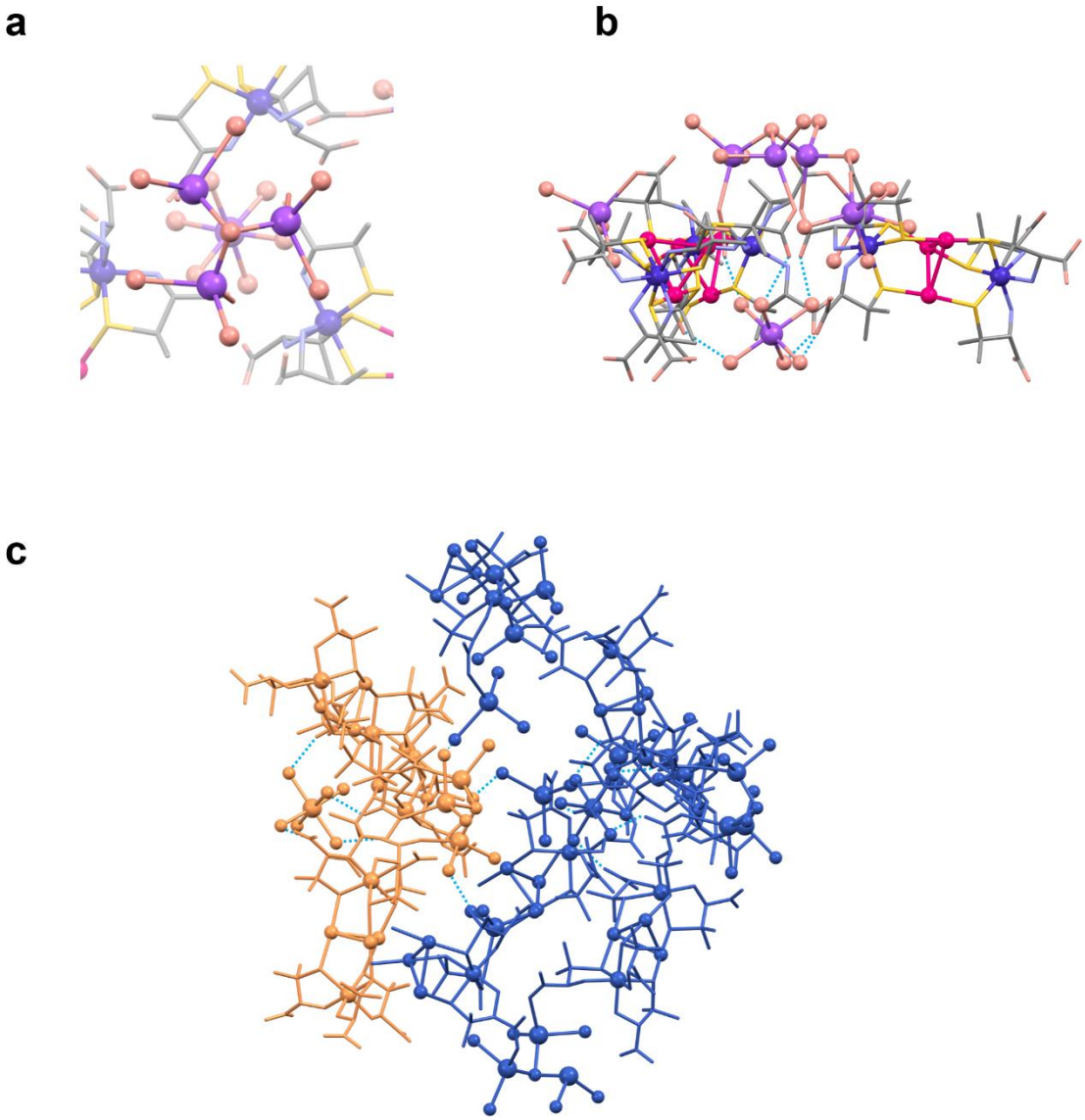

Fig. S10. Crystal structures of $\mathbf{2^{DL}}$. (a) The structure of the $[Na_3(H_2O)_7]^{3+}$ cation connecting 3 $[\mathbf{1^D}]^{3-}$ anions. (b) The linkage of $[\mathbf{1^D}]^{3-}$ anions with $[Na(H_2O)_6]^{+}$ and $[Na_3(H_2O)_7]^{3+}$ cations. (c) The interpenetration of the two enantiomeric frameworks (orange and blue) via O-H···O hydrogen bonds (blue dotted lines).

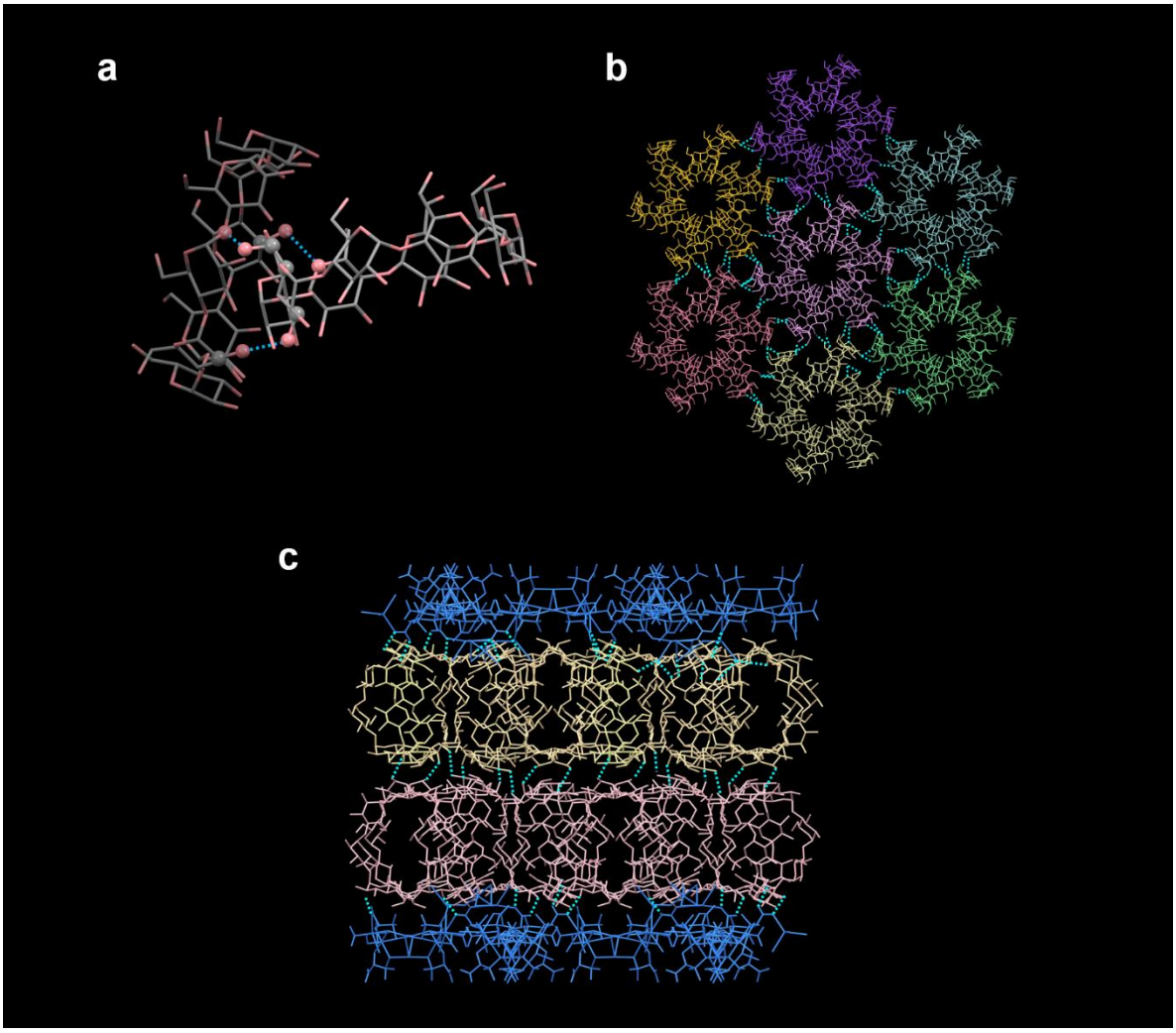

Fig. S11. Crystal structures of $\mathbf{3^D}$. (a) OH···O hydrogen bonds between the γ-CD molecules in a cyclic hexamer. (b) A cyclic hexamer of γ-CD surrounded by 6 adjacent hexamers by forming OH···O hydrogen bonds in the 2D layer. (c) The double layer structure of γ-CD, in which two layers are stacked through OH···O hydrogen bonds. Each hexamer is illustrated with different colors in (b). The blue molecules represent $[\mathbf{1^D}]^{3-}$, and the yellow and pink molecules are γ-CD molecules in (c). The blue dotted lines indicate hydrogen bonds.

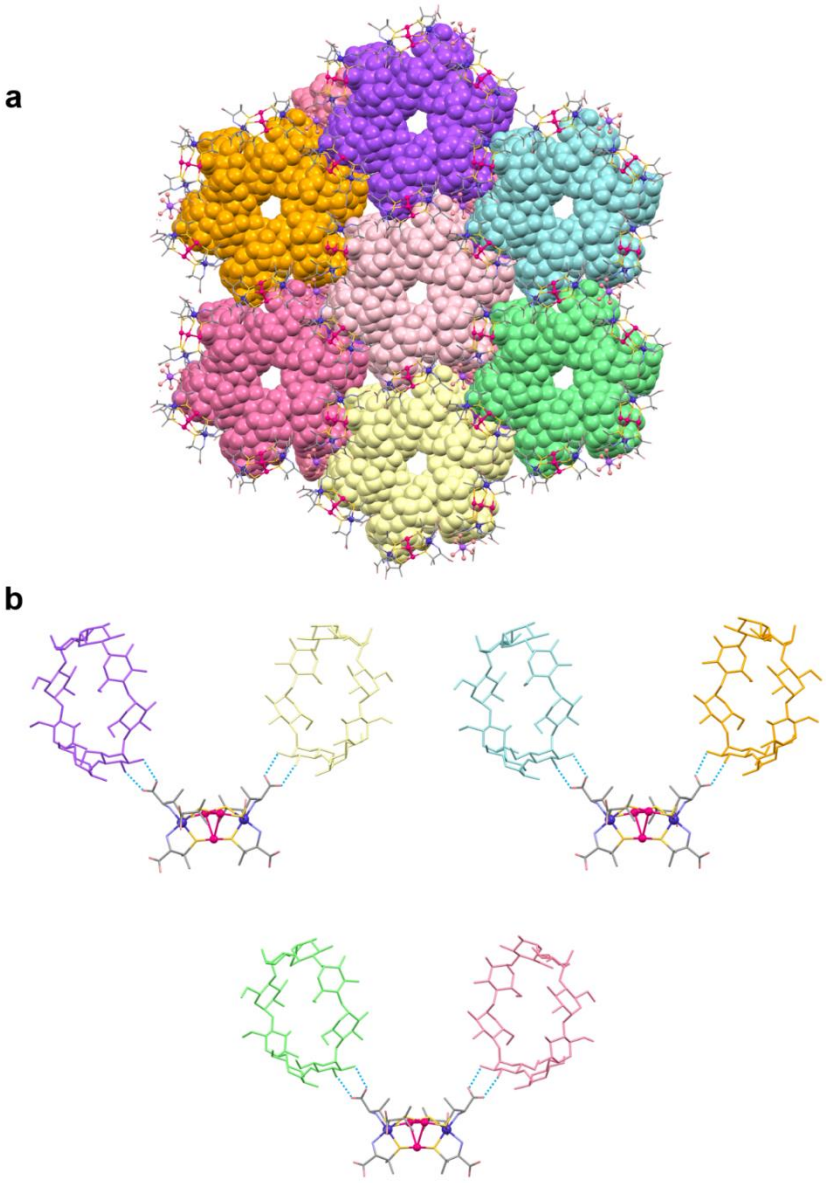

Fig. S12. Crystal structures of **3^{D}**. (a) γ-CD molecules located on the hexagonal cavities of the 2D porous framework. (b) OH···O hydrogen bonding interaction of each [**1^{D}**]$^{3-}$ anion with γ-CD molecules. Colour code: Co, dark blue; Au, magenta; S, yellow; O, pink; Na, purple; N, blue; C, grey for [**1^{D}**]$^{3-}$. The cyclodextrins are illustrated with different colours. The blue dotted lines indicate hydrogen bonds.

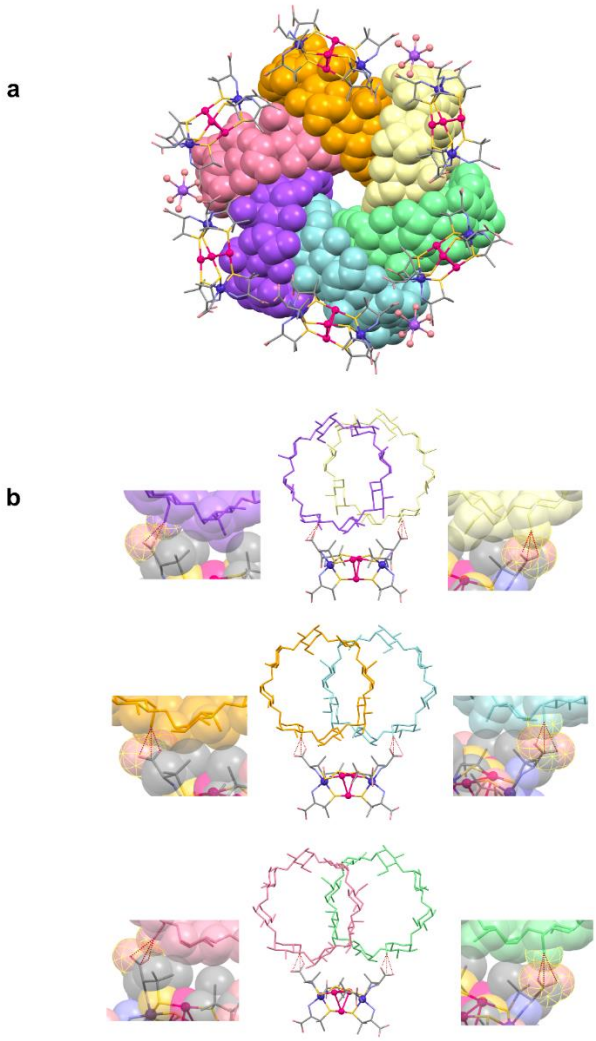

Fig. S13. Model structure. (a) γ-CD molecules located on the hexagonal cavity of the 2D porous framework of $[\mathbf{1}^{\mathbf{L}}]^{3-}$. (b) Short contacts of each $[\mathbf{1}^{\mathbf{L}}]^{3-}$ anion with the γ-CD molecules, represented by red dotted lines (2.2-2.5 Å). The 2D porous framework of $[\mathbf{1}^{\mathbf{L}}]^{3-}$ was modeled by using the inverted coordinates of the single-crystal X-ray data of $\mathbf{3}^{\mathbf{D}}$. The coordinates of the γ-CD molecules were translated from those in the single-crystal X-ray data of $\mathbf{3}^{\mathbf{D}}$. Colour code: Co, dark blue; Au, magenta; S, yellow; O, pink; Na, purple; N, blue; C, grey for $[\mathbf{1}^{\mathbf{D}}]^{3-}$. The cyclodextrins are illustrated with different colours.

Table S1. Crystallographic data for **2^{D}**, **2^{L}**, **2^{DL}**, and **3^{D}**.

	2^{D}	**2^{L}**	**2^{DL}**	**3^{D}**
Formula	$C_{30}H_{54}Au_3Co_2N_6Na_{3.33}O_{45}S_6$	$C_{30}H_{54}Au_3Co_2N_6Na_{3.33}O_{45}S_6$	$C_{30}H_{54}Au_3Co_2N_6Na_{3.33}O_{28}S_6$	$C_{378}H_{613}Au_9Co_6N_{18}Na_{10}O_{301.50}S_{18}$
Colour, form	Purple, truncated hexagonal pyramid	Purple, truncated hexagonal pyramid	Purple, tetrahedron	Purple, hexagonal thin plate
M	2196.54	2196.54	1924.54	13167.09
Crystal system	cubic	cubic	cubic	monoclinic
Space group	$I2_13$	$I2_13$	I-43d	$C2$
a / Å	41.171(5)	41.407(3)	39.2235(11)	48.570(8)
b / Å	41.171(5)	41.407(3)	39.2235(11)	28.050(8)
c / Å	41.171(5)	41.407(3)	39.2235(11)	52.051(10)
α / °	90	90	90	90
β / °	90	90	90	97.93(4)
γ / °	90	90	90	90
V / Å^3	69787(24)	70996(17)	60345(5)	70236(28)
Z	12	12	24	4
T /K	100(2)	100(2)	100(2)	100(2)
λ / Å	0.6100	0.4248	0.4248	0.6500
F(000)	12716	12716	22168	26760
ρ_{calcd} /g cm^{-3}	0.627	0.617	1.271	1.245
μ(Mo Kα) /mm^{-1}	1.363	0.526	1.264	1.629
Crystal size /mm^3	0.14×0.12×0.04	0.30×0.30×0.20	0.10×0.10×0.10	0.85×0.67×0.12
R_1[a] (I>2σ(I))	0.0970	0.0479	0.0213	0.0809
wR_2[b] (all data)	0.3054	0.1093	0.0548	0.2033
GOF	0.885	0.923	1.081	0.866
Flack parameter	0.116(6)	0.015(8)	0.014(8)	0.074(5)
CCDC No.	2006554	2006555	2006556	2006557

[a] $R_1 = (\Sigma|(|F_o| - |F_c|)|)/(\Sigma|F_o|)$

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