Electronic Supplementary Information (ESI)

Intermediate snapshots of a 116-nuclear metallosupramolecular cage-of-cage in a homogeneous single-crystal-to-single-crystal transformation

Benny Wahyudianto, Kento Imanishi, Tatsuhiro Kojima, Nobuto Yoshinari & Takumi Konno*

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

E-mail: konno@chem.sci.osaka-u.ac.jp

Materials

Preparation of $[Cd_4Na_4\{Au_6Cd_3(tdme)_2(D\text{-}pen)_6\}_{12}](NO_3)_{12}$ ($\mathbf{1}_{CdNa}$).

To a white suspension containing $[Au_3(tdme)(D\text{-}Hpen)_3]\cdot 5H_2O$ (250 mg, 0.145 mmol) in 25 mL of ethanol was added 0.1 M aqueous NaOH (4.3 mL, 0.43 mmol) and 0.1 M aqueous $Cd(NO_3)_2$ (4.3 mL, 0.43 mmol). The mixture was stirred at room temperature for 6 h to afford a smoky solution. After 4 days, colourless cubic crystals ($\mathbf{1}_{CdNa}$) were collected by filtration. Yield: 142.1 mg (56.8%). Found: C, 32.17; H, 4.10; N, 2.43%. Anal. Calcd for $[Cd_4Na_4\{Au_6Cd_3(tdme)_2(D\text{-}pen)_6\}_{12}(H_2O)_{16}](NO_3)_{12}\cdot 262H_2O = C_{1344}H_{2140}Au_{72}Cd_{40}N_{84}Na_4O_{458}P_{72}S_{72}$: C, 32.21; H, 4.30; N, 2.35%. IR spectrum (cm^{-1}, KBr disk): 1436 (νPh), 745 (νPh), 1100 (νP–Ph), 1585 (νCOO), 1386 (νNO_3).

Preparation of $[Co_8\{Au_6Co_3(tdme)_2(D\text{-}pen)_6\}_{12}](NO_3)_{16}$ ($\mathbf{1}_{Co}$).

Single crystals of $\mathbf{1}_{CdNa}$ (425 mg, 8.5 μmol) were soaked in 1 M aqueous $Co^{II}(NO_3)_2$ (3 mL, 3 mmol). After the mixture was allowed to stand at room temperature for 6 days, the colour of the crystals changed from colourless to blue ($\mathbf{1}_{Co}$), and the crystal shape was retained. Yield: 83.8 mg (19.7%). Found: C, 31.42; H, 3.90; N, 3.14%. Anal. Calcd for $[Co_8\{Au_6Co_3(tdme)_2(D\text{-}pen)_6\}_{12}(H_2O)_{16}](NO_3)_{16}\cdot 18Co(NO_3)_2\cdot 244H_2O = C_{1344}H_{2104}Au_{72}Co_{62}N_{124}O_{560}P_{72}S_{72}$: C, 31.45; H, 4.13; N, 3.38%. IR spectrum (cm^{-1}, KBr disk): 1433 (νPh), 743 (νPh), 1100 (νP–Ph), 1577 (νCOO), 1382 (νNO_3).

Elemental analysis for $\mathbf{1}^{1h}$, $\mathbf{1}^{6h}$, $\mathbf{1}^{1d}$, $\mathbf{1}^{2d}$, and $\mathbf{1}^{4d}$

$\mathbf{1}^{1h}$: Found: C, 30.99; H, 3.99; N, 2.97%. Anal. Calcd for $[Cd_4Co_4\{Au_6Cd_{2.97}Co_{0.03}(tdme)_2(D\text{-}pen)_6\}_{12}(H_2O)_{16}](NO_3)_{16}\cdot 18Co(NO_3)_2\cdot 193H_2O = C_{1344}H_{2002}Au_{72}Cd_{39.64}Co_{22.36}N_{124}O_{509}P_{72}S_{72}$: C, 30.73; H, 3.84; N, 3.31%.

$\mathbf{1}^{6h}$: Found: C, 31.02; H, 3.80; N, 3.36%. Anal. Calcd for $[Cd_{2.92}Co_{5.08}\{Au_6Cd_{2.19}Co_{0.81}(tdme)_2(D\text{-}pen)_6\}_{12}(H_2O)_{16}](NO_3)_{16}\cdot 18Co(NO_3)_2\cdot 196H_2O = C_{1344}H_{2008}Au_{72}Cd_{29.2}Co_{32.8}N_{124}O_{512}P_{72}S_{72}$: C, 31.03; H, 3.89; N, 3.34%.

$\mathbf{1}^{1d}$: Found: C, 31.12; H, 3.95; N, 3.41%. Anal. Calcd for $[Cd_{2.66}Co_{5.34}\{Au_6Cd_{1.46}Co_{1.54}(tdme)_2(D\text{-}pen)_6\}_{12}(H_2O)_{16}](NO_3)_{16}\cdot 18Co(NO_3)_2\cdot 204H_2O = C_{1344}H_{2024}Au_{72}Cd_{20.18}Co_{41.82}N_{124}O_{520}P_{72}S_{72}$: C, 31.23; H, 3.95; N, 3.36%.

$\mathbf{1}^{2d}$: Found: C, 31.72; H, 4.00; N, 3.26%. Anal. Calcd for $[Cd_{1.53}Co_{6.47}\{Au_6Cd_{0.59}Co_{2.41}(tdme)_2(D\text{-}pen)_6\}_{12}(H_2O)_{16}](NO_3)_{16}\cdot 18Co(NO_3)_2\cdot 181H_2O = C_{1344}H_{1978}Au_{72}Cd_{8.61}Co_{53.36}N_{124}O_{497}P_{72}S_{72}$: C, 31.87; H, 3.94; N, 3.43%.

$\mathbf{1}^{\mathbf{4d}}$: Found: C, 30.97; H, 3.84; N, 3.37%. Anal. Calcd for $[Co_8\{Au_6Cd_{0.05}Co_{2.95}(tdme)_2(D\text{-}pen)_6\}_{12}(H_2O)_{16}](NO_3)_{16}\cdot 18Co(NO_3)_2\cdot 264H_2O$ = $C_{1344}H_{2144}Au_{72}Cd_{0.6}Co_{61.4}N_{124}O_{580}P_{72}S_{72}$: C, 31.21; H, 4.18; N, 3.36%.

Physical measurements

The IR spectra in the range of 4000-400 cm^{-1} were measured on a JASCO FT/IR-4100 spectrometer by using KBr pellets. Elemental analyses (C, H, N) were performed at Osaka University using YANACO MT-5 or MT-6. X-ray fluorescence spectrometry was performed on a SHIMADZU EXD-7000 spectrometer. Diffuse reflectance spectra in the range of 900−300 nm were measured on a JASCO V-670 spectrophotometer. CD spectra in the range of 900−300 nm were measured on a JASCO J-820 spectropolarimeter. Powder X-ray diffraction patterns were recorded under a controlled temperature in transmission mode [synchrotron radiation λ=1.0 Å; 2θ range=2–78°; step width=0.018; data collection time=1 min] on a diffractometer equipped with a MYTHEN microstrip X-ray detector (Dectris Ltd.) at the SPring-8 BL02B2 beamline. To prevent the loss of crystallinity, microcrystals of each compound were loaded into a glass capillary tube (diameter=0.3 mm), together with the mother liquor.

Single-crystal X-ray analysis

The diffraction data for $\mathbf{1}_{\mathbf{CdNa}}$, $\mathbf{1}_{\mathbf{Co}}$, $\mathbf{1}^{\mathbf{1h}}$, $\mathbf{1}^{\mathbf{6h}}$, $\mathbf{1}^{\mathbf{1d}}$, $\mathbf{1}^{\mathbf{2d}}$ and $\mathbf{1}^{\mathbf{4d}}$ were recorded at 100 K with a Rayonix MX225HS CCD area detector with synchrotron radiation (λ = 0.6500 Å) at the 2D beamline at the Pohang Accelerator Laboratory. The intensity data were processed using the HKL3000 program and collected by using the ω-scan technique. The empirical absorption correction was performed using HKL3000. The diffraction data for $\mathbf{1}_{\mathbf{CdZn}}$ and $\mathbf{1}_{\mathbf{CdMn}}$ were recorded at 100 K with Hybrid Pixel Array Detector. The intensity data were processed using the CrysAlisPro (1.171.40.75a) program and collected by using the ω-scan technique. The Numerical absorption correction was performed using CrysAlisPro (1.171.40.75a). The structures were solved by direct methods using SHELXS-2014. Structure refinements were carried out using full-matrix least-squares (SHELXL-2018/3). ISOR, DELU and SIMU restraints were applied for coordinated water molecules. Global SIMU were applied. All nonhydrogen atoms were refined anisotropically. Considering the elemental and X-ray fluorescence analytical results, the porous spaces in $\mathbf{1}_{\mathbf{CdNa}}$ are considered to contain a large number of water molecules of crystallization, while those in $\mathbf{1}^{\mathbf{1h}}$, $\mathbf{1}^{\mathbf{6h}}$, $\mathbf{1}^{\mathbf{1d}}$, $\mathbf{1}^{\mathbf{2d}}$ and $\mathbf{1}^{\mathbf{4d}}$ contain not only water molecules but also aqua Co^{II} species and nitrate anions, although they were not found in the X-ray structures. The contributions of aqueous Co^{II} species, NO_3^- ions, and solvated water molecules were excluded using the SQUEEZE program in the PLATON package (ver. 20221). Some diffractions were

omitted to improve the data quality. For **1**$^{\mathbf{1h}}$, **1**$^{\mathbf{6h}}$, **1**$^{\mathbf{1d}}$, **1**$^{\mathbf{2d}}$, and **1**$^{\mathbf{4d}}$, each metal centre at M_1, M_2, M_3, M_4, and M_5 was refined as two positionally disordered metal ions (Na^{I}/Co^{II} or Cd^{II}/Co^{II}) with variable site occupancies. EADP and EXYZ constraints were applied for these positionally disordered two metal centres.

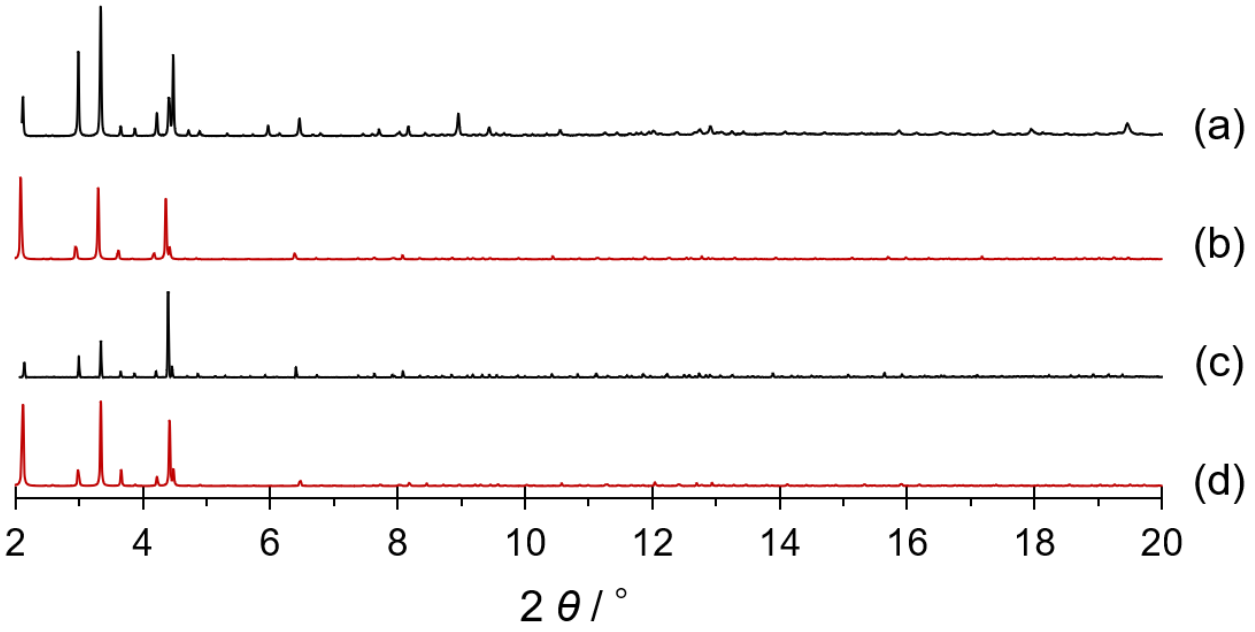

Fig. S1. The PXRDs that were measured in capillaries containing the mother liquor (λ = 1.000 Å) (a) $\mathbf{1}_{CdNa}$ and (c) $\mathbf{1}_{Co}$. The PXRDs that were simulated from single-crystal X-ray data collected at 100 K (λ = 1.000 Å) (b) $\mathbf{1}_{CdNa}$ and (d) $\mathbf{1}_{Co}$.

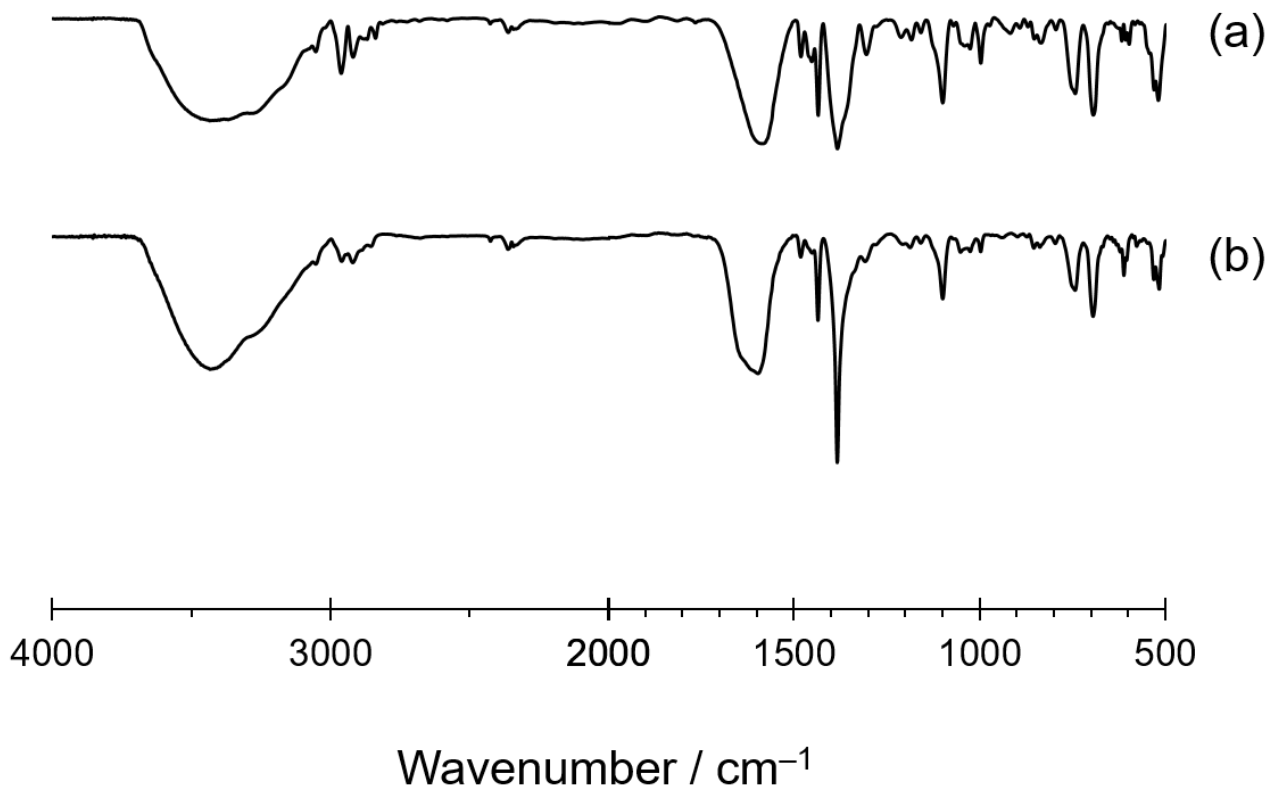

Fig. S2. IR spectra (KBr disk) of (a) $\mathbf{1}_{\mathbf{CdNa}}$ and (b) $\mathbf{1}_{\mathbf{Co}}$.

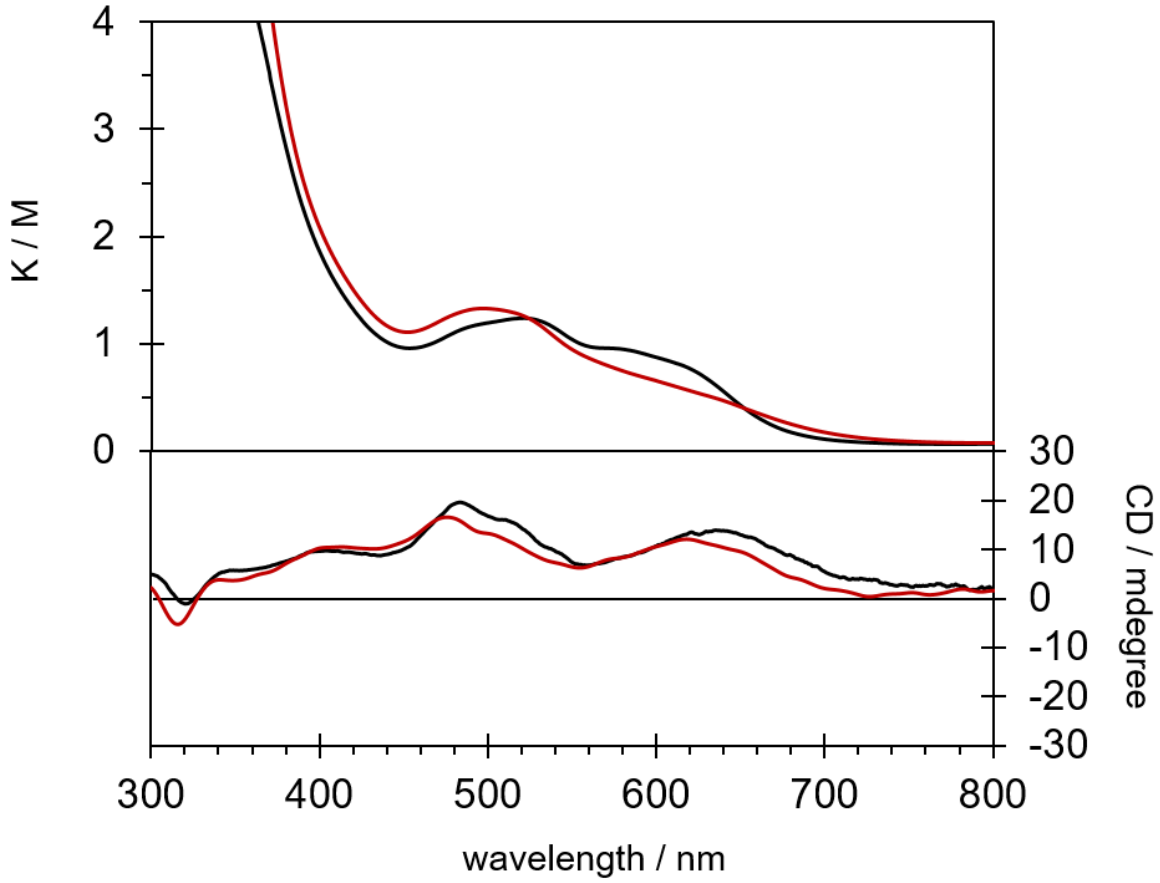

Fig. S3. Diffuse reflectance (top) and CD (bottom) spectra of $\mathbf{1}_{\mathbf{Co}}$ (black) and $[Co^{II}_3(L^{Au3})_2]$ (red) in the solid state.

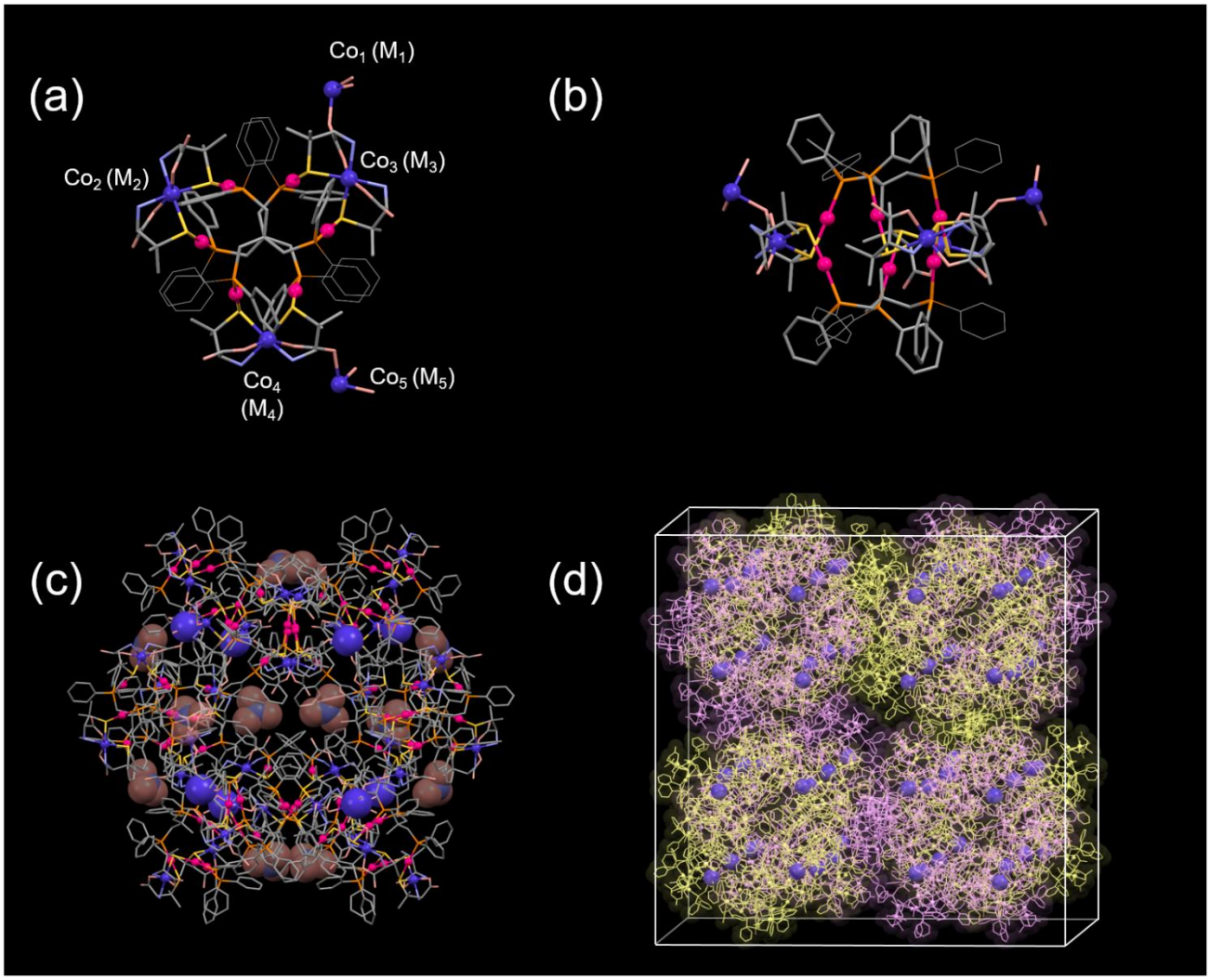

Fig. S4. Expanded illustration of Fig. 1. Crystal structures of **1**$_{Co}$. Top (a) and side (b) views of the $[Co^{II}_3(L^{Au3})_2]$ molecule with linking Co^{II} atoms. (c) The entire $Au^{I}_{72}Co^{II}_{44}$ cage-of-cage with NO_3^- anions. (d) The packing of the cage-of-cage molecules (cream and pink). Colour codes: red, Au; violet, Co; orange, P; yellow, S; pink, O; pale blue, N; grey, C.

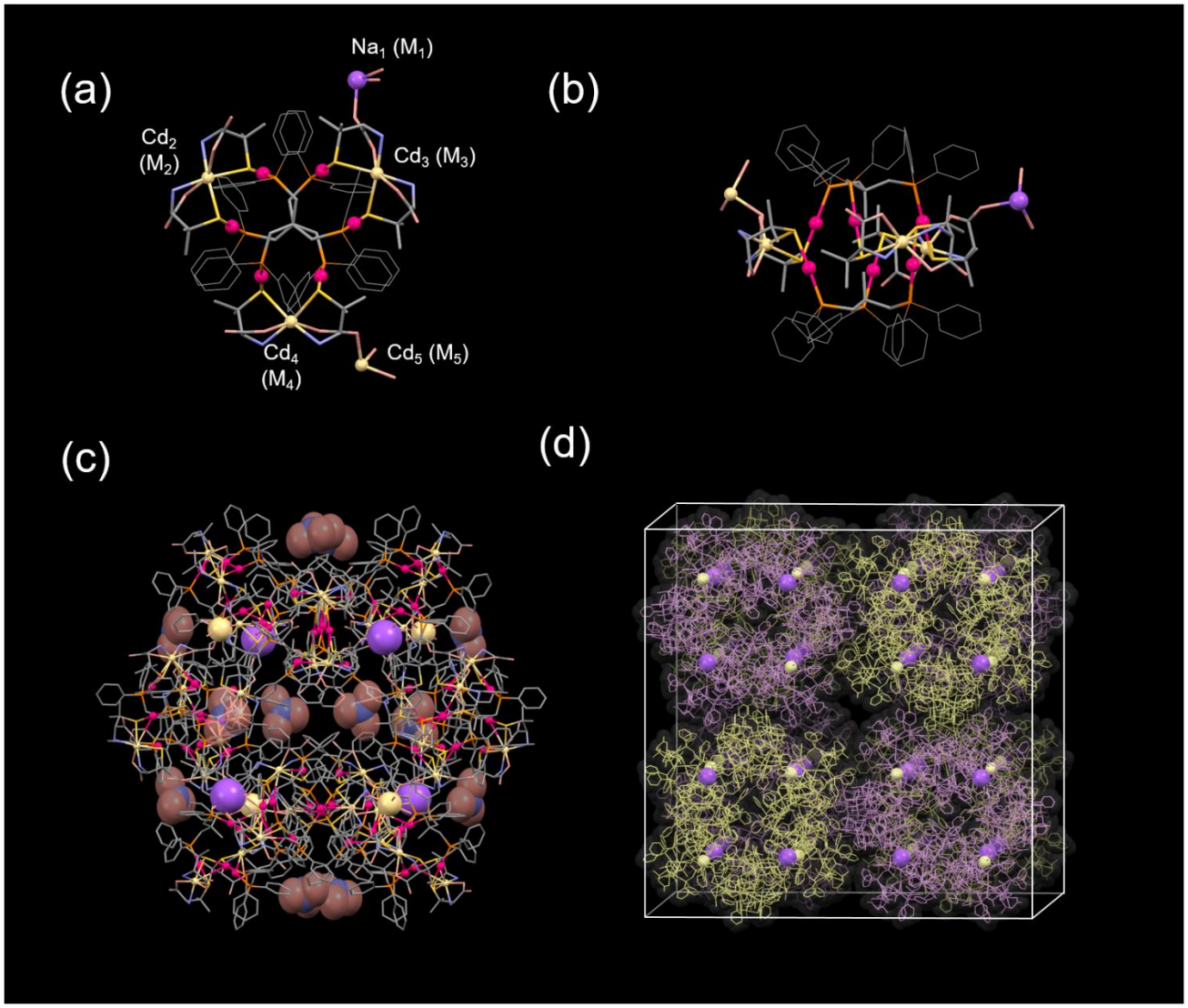

Fig. S5. Crystal structures of $\mathbf{1}_{\mathbf{CdNa}}$. (a) Top and (b) side views of the $[Cd^{II}_3(L^{Au3})_2]$ molecule linking Cd^{II} and Na^{I} atoms. (c) The entire $Au^{I}_{72}Cd^{II}_{40}Na^{I}_4$ cage-of-cage molecule with NO_3^- anions. (d) The packing of the cage-of-cage molecules (cream and pink). Colour codes: red, Au; cream, Cd; purple, Na; orange, P; yellow, S; pink, O; pale blue, N; grey, C.

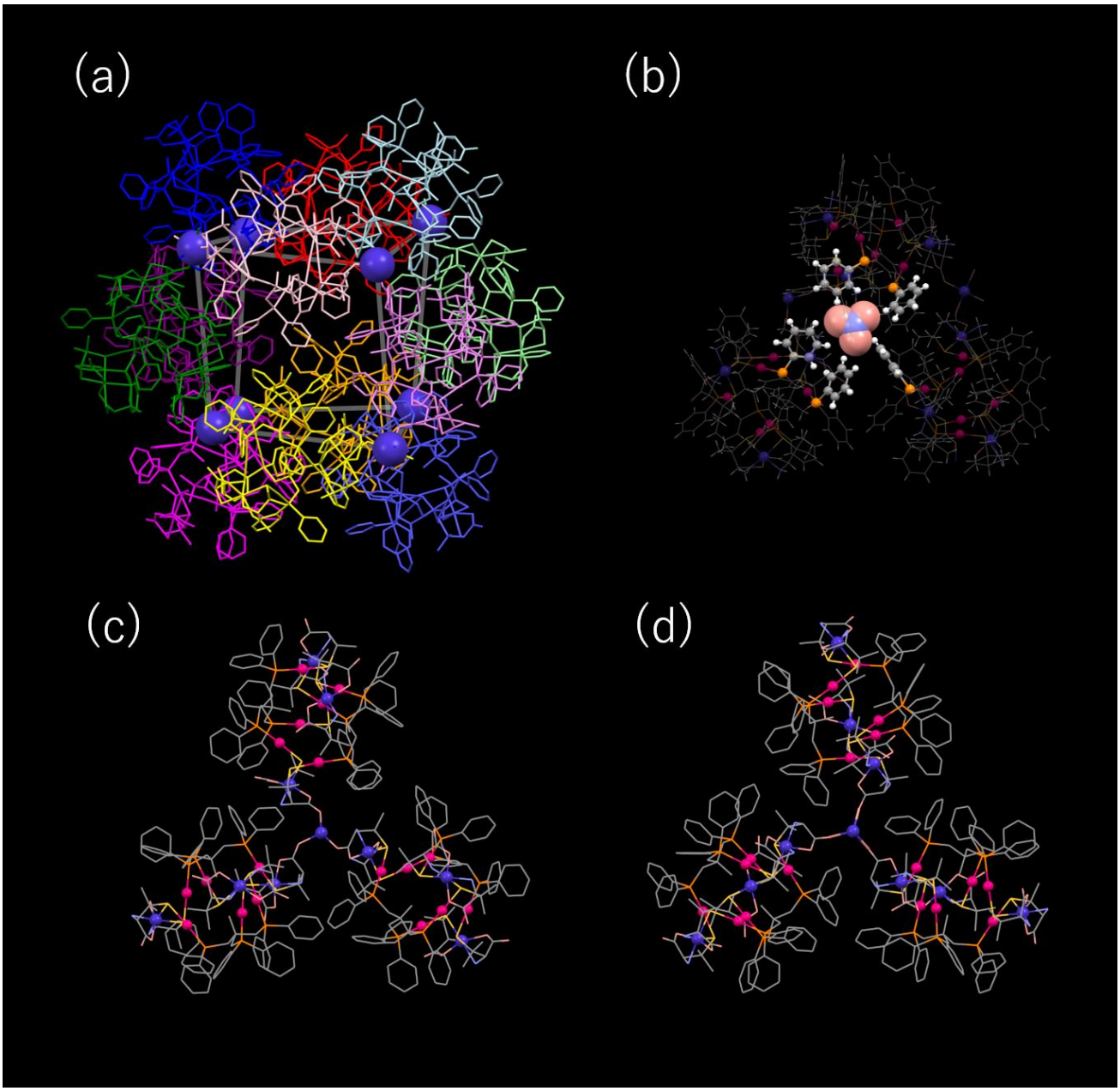

Fig. S6. (a) A perspective view of a $Au^{I}_{72}Co^{II}_{44}$ cage-of-cage cation in $\mathbf{1_{Co}}$. (b) A nitrate anion attached to the surface via CH···O interactions. (c) A Co^{II} centre (M1 site) linking three $[Co_3(L^{Au3})_2]$ molecules. (d) A Co^{II} centre (M5 site) linking three $[Co_3(L^{Au3})_2]$ molecules. Colour codes: red, Au; violet, Co; orange, P; yellow, S; pink, O; pale blue, N; grey, C.

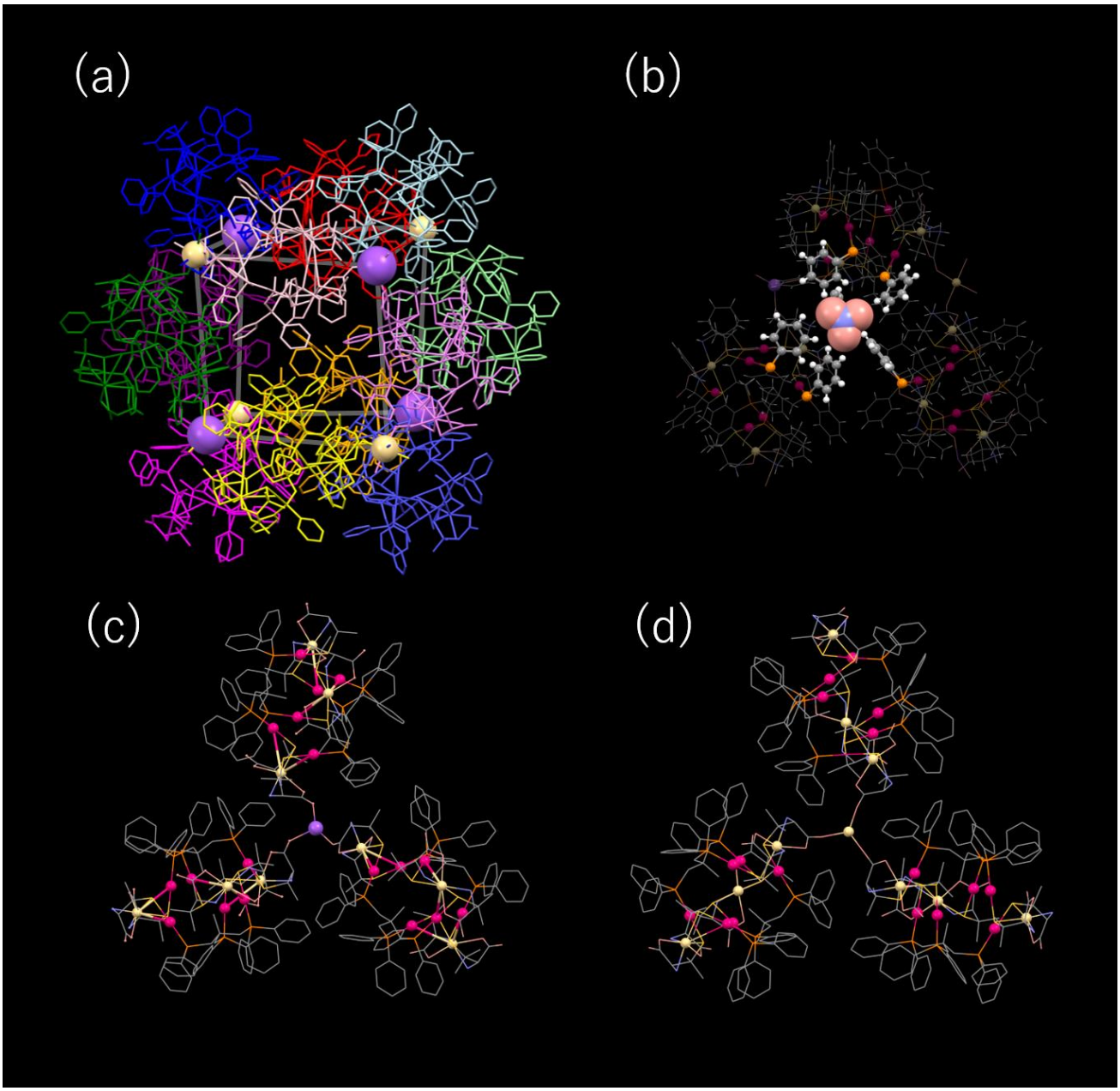

Fig. S7. (a) A perspective view of a $Au^{I}_{72}Cd^{II}_{40}Na^{I}_{4}$ cage-of-cage cation in $\mathbf{1}_{\mathbf{CdNa}}$. (b) A nitrate anion attached to the surface via CH···O interactions. (c) A Na^{I} centre (M1 site) linking three $[Cd_3(L^{Au3})_2]$ molecules. (d) A Cd^{II} centre (M5 site) linking three $[Cd_3(L^{Au3})_2]$ molecules. Colour codes: red, Au; cream, Cd; purple, Na; orange, P; yellow, S; pink, O; pale blue, N; grey, C.

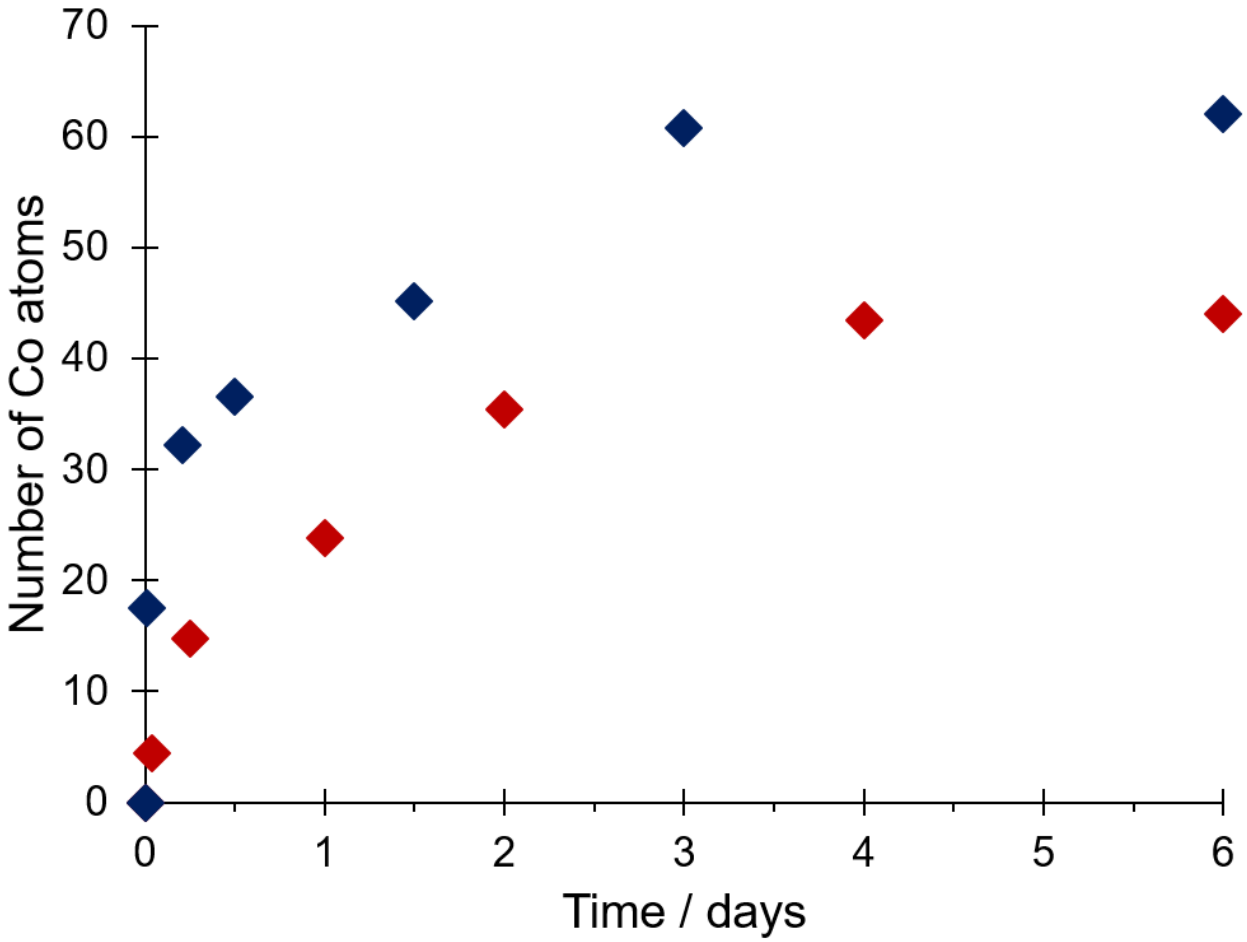

Fig. S8. Time-dependent changes in the numbers of Co^{II} atoms per cage-of-cage molecule determined by X-ray fluorescence analysis (blue) and single-crystal X-ray diffraction analysis (red). The difference in the numbers of Co^{II} atoms between these methods corresponds to aqua Co^{II} species existing in the crystal interstices, which could not be located in the X-ray structure.

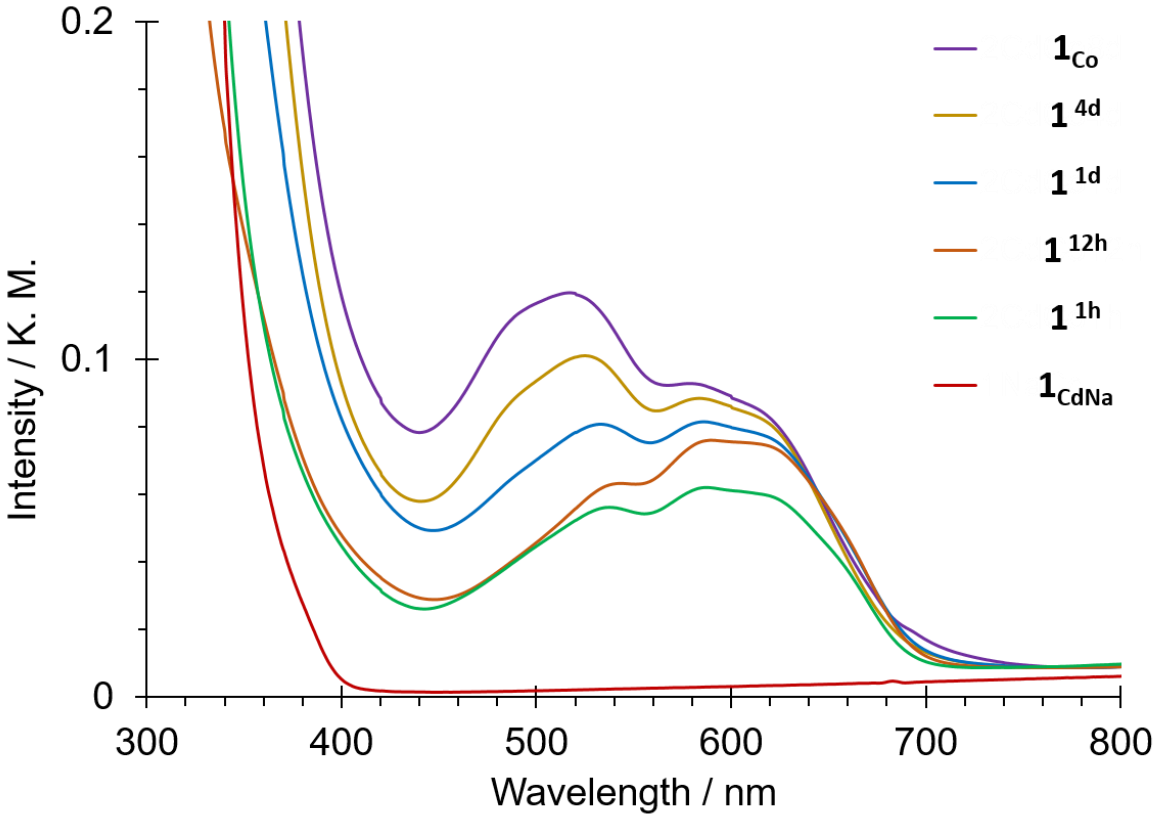

Fig. S9. Diffuse reflection spectra of $\mathbf{1}_{CdNa}$, $\mathbf{1}^{1h}$, $\mathbf{1}^{12h}$, $\mathbf{1}^{1d}$, $\mathbf{1}^{4d}$, and $\mathbf{1}_{Co}$.

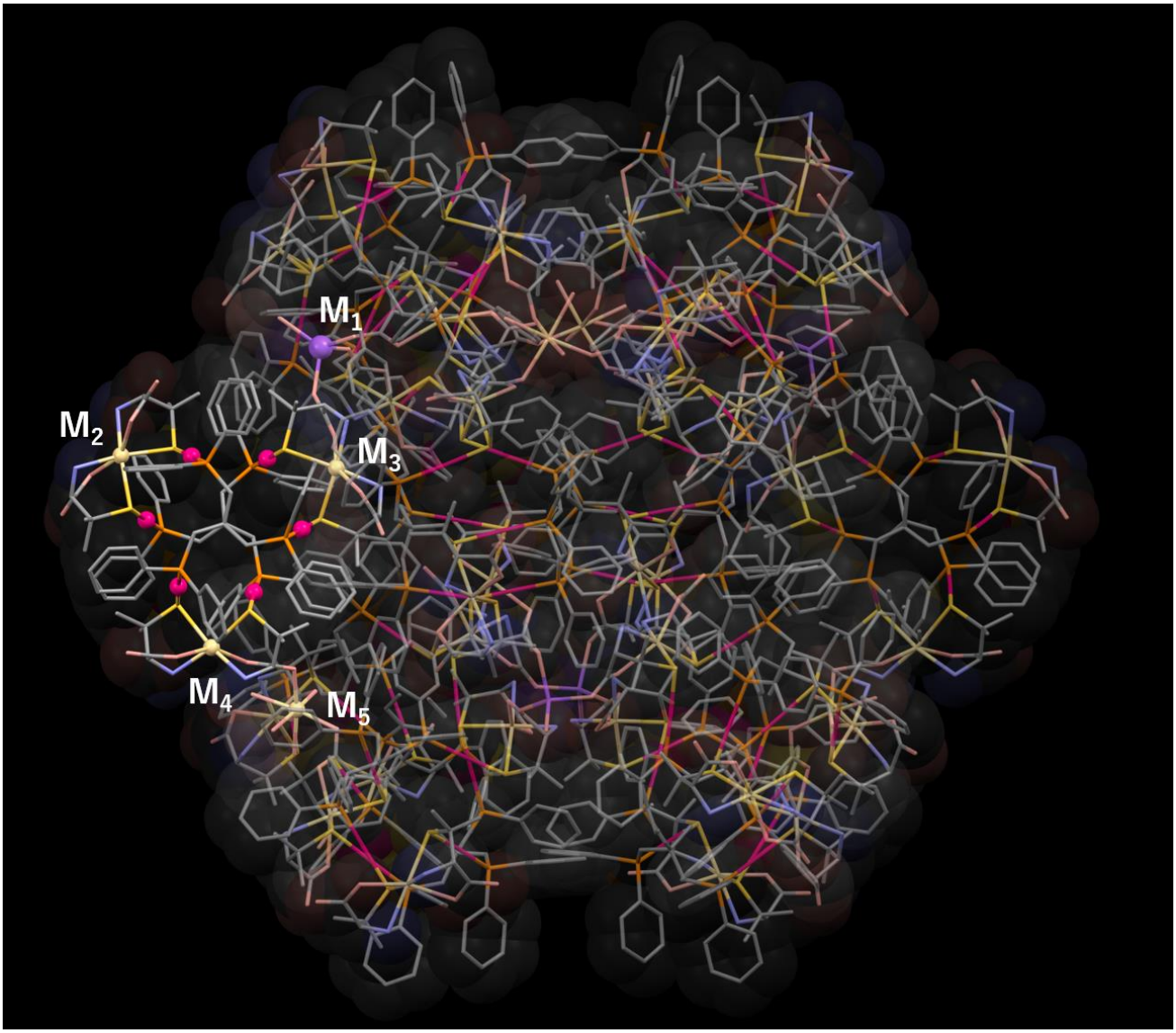

Fig. S10. The entire $Au^{I}_{72}Cd^{II}_{40}Na^{I}_{4}$ cage-of-cage molecule. Colour codes: red, Au; cream, Cd; purple, Na; orange, P; yellow, S; pink, O; pale blue, N; grey, C.

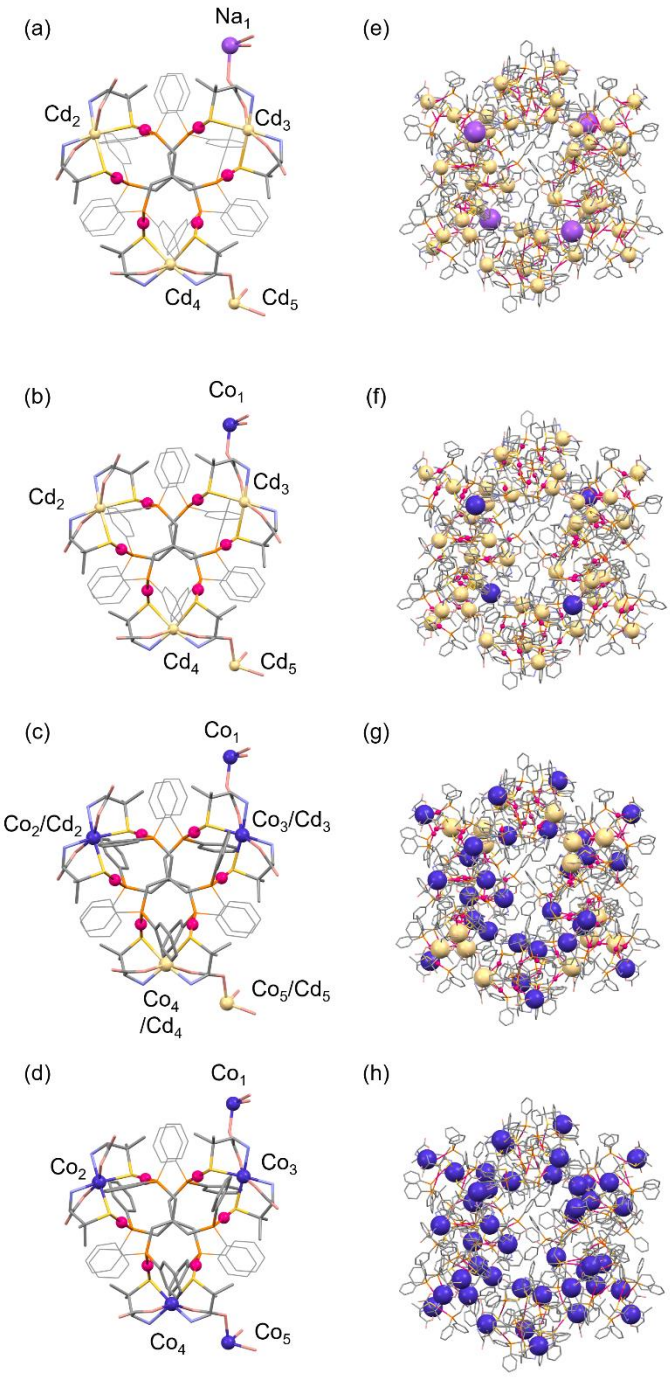

Fig. S11. Expanded illustration of Fig. 4. Crystal structures of (a-d) the asymmetric units and (e-h) the cage-of-cage molecules in $\mathbf{1}_{\mathbf{NaCd}}$, $\mathbf{1}^{\mathbf{1h}}$, $\mathbf{1}^{\mathbf{1d}}$, and $\mathbf{1}_{\mathbf{Co}}$. (a) $\mathbf{1}_{\mathbf{NaCd}}$. (b) $\mathbf{1}^{\mathbf{1h}}$: Cd^{II} and Co^{II} atoms are disordered at the M_2 metal centre with site occupancies of 0.97 and 0.03, respectively. (c) $\mathbf{1}^{\mathbf{1d}}$: Co^{II} and Cd^{II} atoms are disordered at M_2, M_3, M_4, and M_5 metal centres with site occupancies of 0.71/0.29 for M_2, 0.57/0.43 for M_3, 0.25/0.75 for M_4, and 0.33/0.67 for M_5, respectively. (d) $\mathbf{1}_{\mathbf{Co}}$. Colour codes: red, Au; cream, Cd; purple, Na; violet, Co; orange, P; yellow, S; pink, O; pale blue, N; grey, C.

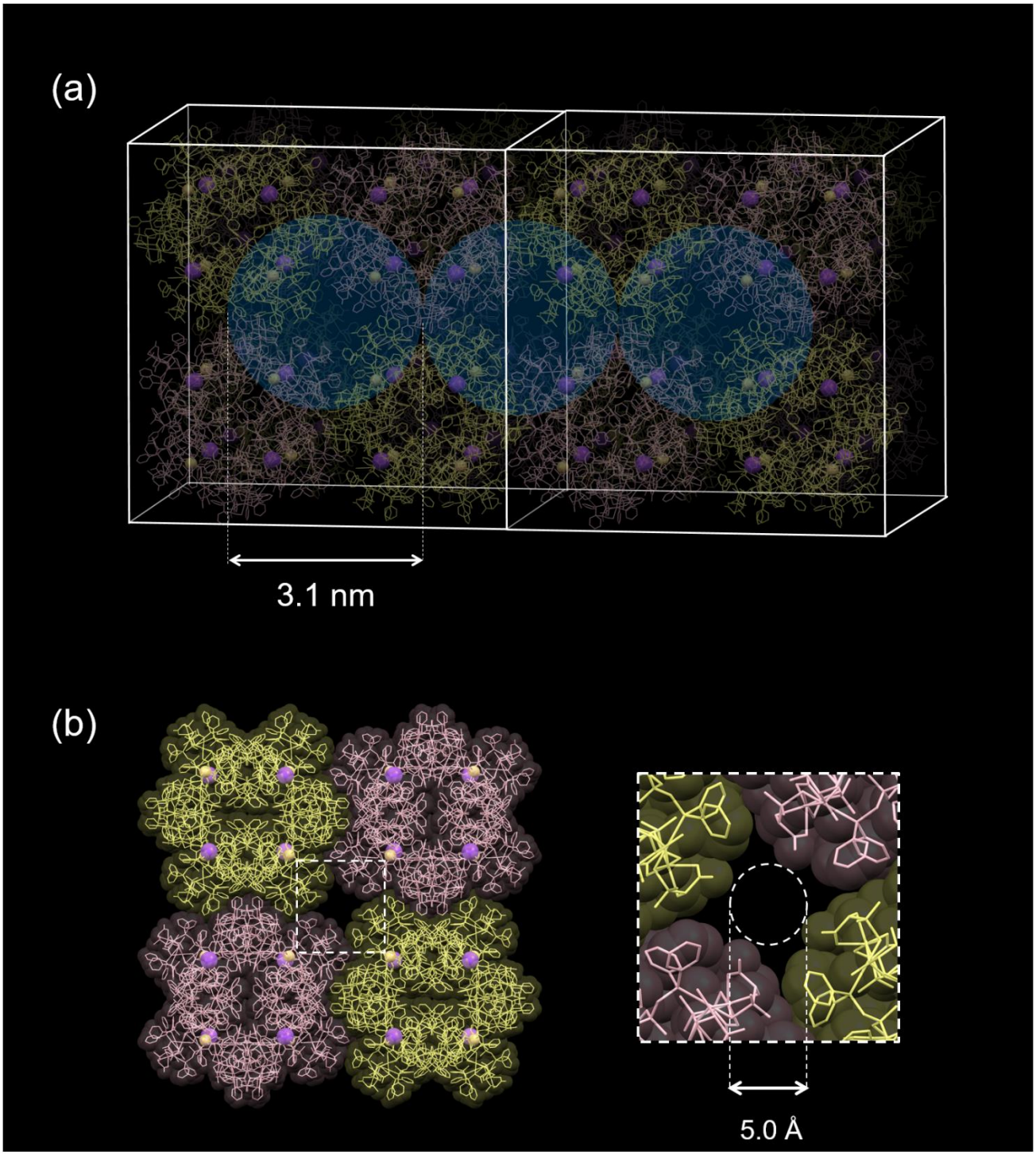

Fig. S12. Crystal structures of $\mathbf{1}_{\mathbf{CdNa}}$. Perspective views that show (a) the large interstices (diameters of ~3.1 nm) and (b) the pore window with the shortest diameter of 5.0 Å.

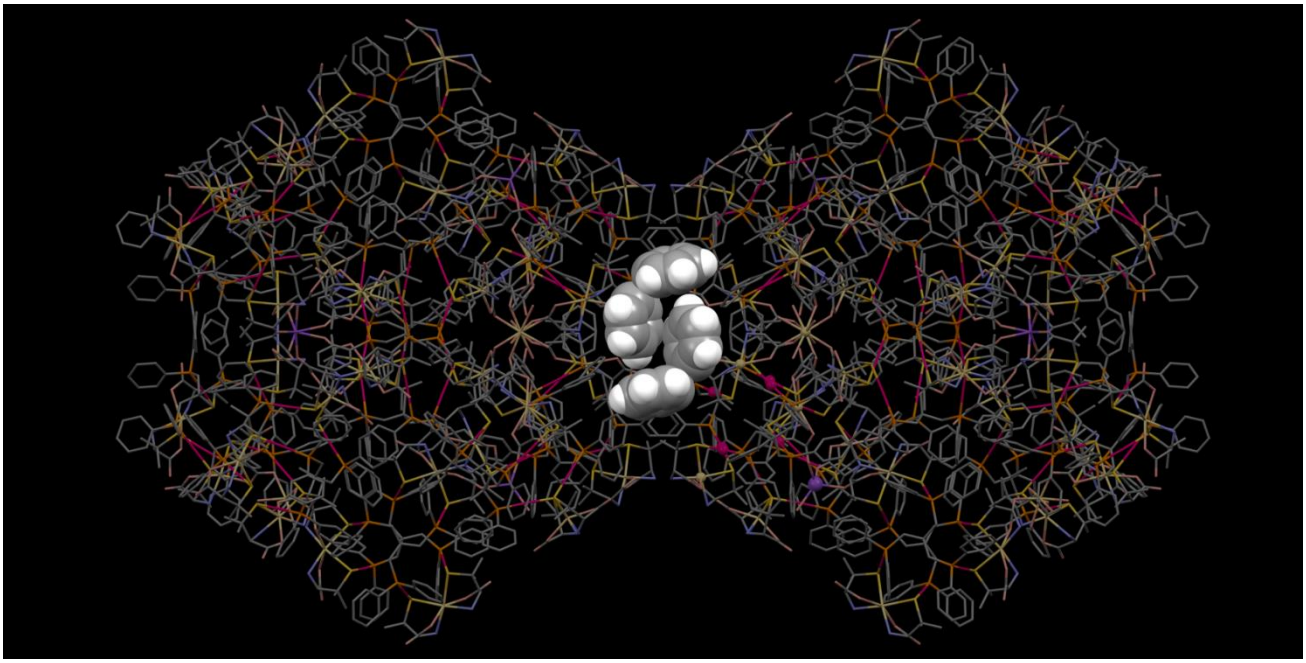

Fig. S13. A perspective view that shows the contact between the two cage-of-cage molecules through CH---π and π---π interactions. Colour codes: red, Au; cream, Cd; purple, Na; orange, P; yellow, S; pink, O; pale blue, N; grey, C.

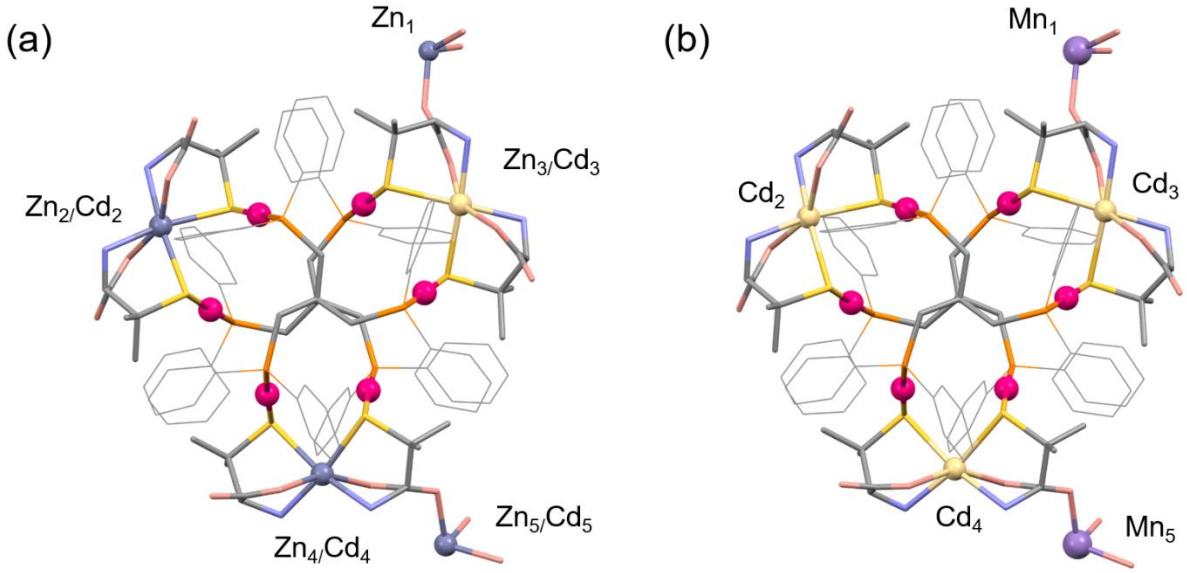

Fig. S14. Crystal structures of the asymmetric units of $\mathbf{1}_{\mathbf{CdZn}}$ and $\mathbf{1}_{\mathbf{CdMn}}$, which were obtained by soaking crystals of $\mathbf{1}_{\mathbf{CdNa}}$ in 1M aqueous $Zn(NO_3)_2$ and $Mn(NO_3)_2$, respectively, for 2 weeks. (a) $\mathbf{1}_{\mathbf{CdZn}}$: Zn^{II} and Cd^{II} atoms were disordered at M_2, M_3, M_4 and M_5 metal centres with site occupancies of Zn/Cd = 0.68/0.32, 0.33/0.67, 0.59/0.41 and 0.83/0.17 for M_2, M_3, M_4 and M_5 , respectively, while M_1 site was refined as a Zn atom. Crystallographic data, Cubic *F*432, $a = b = c = 77.1192(5)$ Å, $V = 458{,}656(9)$ Å^3, R_1 (I>2σ(I)) = 0.0640, Rw_2 (all data) = 0.2074 (CCDC 2080059). (b) $\mathbf{1}_{\mathbf{CdMn}}$: M_1 and M_5 metal centres were refined as a Mn atom, while M_2, M_3 and M_4 centres were refined as a Cd atom, indicative of the replacement of Cd^{II} in $\mathbf{1}_{\mathbf{CdNa}}$ by Mn^{II} at only linking metal sites of M_1 and M_5. Crystallographic data, Cubic *F*432, $a = b = c = 77.5594(4)$ Å, $V = 466{,}556(7)$ Å^3, R_1 (I>2σ(I)) = 0.0572, Rw_2 (all data) = 0.1827 (CCDC 2080060). Colour codes: red, Au; cream, Cd; pale purple, Zn; light purple, Mn; orange, P; yellow, S; pink, O; pale blue, N; grey, C.

Table S1. Crystallographic data for $\mathbf{1}_{\mathbf{CdNa}}$, $\mathbf{1}^{\mathbf{1h}}$, $\mathbf{1}^{\mathbf{6h}}$, $\mathbf{1}^{\mathbf{1d}}$, $\mathbf{1}^{\mathbf{2d}}$, $\mathbf{1}^{\mathbf{4d}}$, and $\mathbf{1}_{\mathbf{Co}}$.

	$\mathbf{1}_{\mathbf{CdNa}}$	$\mathbf{1}^{\mathbf{1h}}$	$\mathbf{1}^{\mathbf{6h}}$	$\mathbf{1}^{\mathbf{1d}}$
CCDC No.	2054688	2054689	2056446	2054592
Formula	$C_{1344}H_{2140}Au_{72}Cd_{40}N_{84}Na_4O_{458}P_{72}S_{72}$	$C_{1344}H_{2002}Au_{72}Cd_{39.64}Co_{22.46}N_{124}O_{509}P_{72}S_{72}$	$C_{1344}H_{2008}Au_{72}Cd_{29.20}Co_{32.80}N_{124}O_{512}P_{72}S_{72}$	$C_{1344}H_{2024}Au_{72}Cd_{20.18}Co_{41.82}N_{124}O_{520}P_{72}S_{72}$
Colour, form	Colourless, cubic	Pale purple, block	Pale purple, block	Purple, cubic
Crystal size/ mm^3	0.11×0.11×0.11	0.14×0.14×0.11	0.14×0.14×0.14	0.19×0.19×0.19
Wavelength/ Å	0.6500			
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	*F*432	*F*432	*F*432	*F*432
$a = b = c$ / Å	77.714(9)	77.522(9)	77.518(9)	77.485(9)
$\alpha = \beta = \gamma$ / °	90	90	90	90
V/ $Å^3$	469,342(159)	465,879(159)	465,809(159)	465,209(160)
Z	8	8	8	8
T/ K	100(2)	100(2)	100(2)	100(2)
Flack parameter	0.013(1)	0.006(1)	0.001(1)	0.001(1)
R_1 ($I>2\sigma(I)$)	0.0403	0.0451	0.0470	0.0508
Rw_2 (all data)	0.1139	0.1477	0.1580	0.1875
GOF	1.054	1.038	1.064	1.023

Table S1. (Continued)

	$\mathbf{1}^{2d}$	$\mathbf{1}^{4d}$	$\mathbf{1}_{Co}$
CCDC No.	2054593	2054594	2054595
Formula	$C_{1344}H_{1978}Au_{72}Cd_{8.61}Co_{53.39}N_{124}O_{497}P_{72}S_{72}$	$C_{1344}H_{2144}Au_{72}Cd_{0.60}Co_{61.40}N_{124}O_{580}P_{72}S_{72}$	$C_{1344}H_{2104}Au_{72}Co_{62}N_{124}O_{560}P_{72}S_{72}$
Colour, form	Purple, cubic	Purple, cubic	Purple, cubic
Crystal size/ mm^3	0.12×0.12×0.12	0.10×0.10×0.10	0.09×0.08×0.06
Wavelength/ Å	0.6500		
Crystal system	Cubic	Cubic	Cubic
Space group	*F*432	*F*432	*F*432
$a = b = c$ / Å	77.370(9)	76.326(9)	76.541(9)
$\alpha = \beta = \gamma$ / °	90	90	90
V/ $Å^3$	463,149(160)	444,649(154)	448,417(155)
Z	8	8	8
T/ K	100(2)	100(2)	100(2)
Flack parameter	0.001(1)	0.012(2)	0.003(3)
R_1 (I>2σ(I))	0.0505	0.0510	0.0540
Rw_2 (all data)	0.1827	0.1824	0.1945
GOF	1.032	0.920	0.983

Table S2. Selected bond length (Å) for $\mathbf{1_{CdNa}}$, $\mathbf{1^{1h}}$, $\mathbf{1^{6h}}$, $\mathbf{1^{1d}}$, $\mathbf{1^{2d}}$, $\mathbf{1^{4d}}$, and $\mathbf{1_{Co}}$.

	Bond length /Å			
	$\mathbf{1_{CdNa}}$	$\mathbf{1^{1h}}$	$\mathbf{1^{6h}}$	$\mathbf{1^{1d}}$
M_1–O_{10}	2.234(6)	2.042(10)	2.067(14)	2.054(17)
M_2–S_1/S_4	ave. 2.646 2.636(2)/2.656(2)	ave. 2.649 2.647(3)/2.651(4)	ave.2.598 2.596(4)/2.600(4)	ave. 2.538 2.537(4)/2.539(5)
M_2–O_1/O_7	ave. 2.353 2.364(8)/2.342(8)	ave. 2.338 2.345(11)/2.331(9)	ave. 2.249 2.255(13)/2.243(10)	ave. 2.176 2.191(15)/2.162(12)
M_2–N_1/N_4	ave. 2.335 2.324(9)/2.346(9)	ave. 2.310 2.314(13)/2.306(11)	ave. 2.286 2.302(14)/2.271(14)	ave. 2.211 2.197(17)/2.226(15)
M_3-S_2/S_5	ave. 2.637 2.630(2)/2.644(2)	ave. 2.627 2.623(3)/2.631(3)	ave. 2.614 2.592(7)/2.636(8)	ave. 2.536 2.530(5)/2.542(4)
M_3-O_3/O_9	ave. 2.366 2.380(6)/2.351(5)	ave. 2.363 2.319(10)/2.408(8)	ave. 2.286 2.252(15)/2.320(11)	ave. 2.207 2.136(17)/2.279(11)
M_3-N_2/N_5	ave. 2.338 2.355(8)/2.321(6)	ave. 2.325 2.311(10)/2.340(10)	ave. 2.277 2.272(15)/2.282(14)	ave. 2.228 2.217(14)/2.240(15)
M_4-S_3/S_6	ave. 2.645 2.658(2)/2.633(17)	ave. 2.648 2.658(3)/2.638(3)	ave. 2.636 2.644(4)/2.629(3)	ave. 2.614 2.610(5)/2.618(4)
M_4-O_5/O_{11}	ave. 2.384 2.395(7)/2.372(5)	ave. 2.368 2.386(10)/2.360(6)	ave. 2.357 2.358(12)/2.357(7)	ave. 2.321 2.316(15)/2.337(8)
M_4-N_3/N_6	ave. 2.328 2.302(8)/2.354(6)	ave. 2.323 2.306(12)/2.340(10)	ave. 2.335 2.325(15)/2.346(11)	ave. 2.302 2.266(19)/2.339(14)
M_5–O_{12}	2.243(5)	2.221(6)	2.206(7)	2.209(9)

Table S2. (Continued)

	Bond length /Å		
	1^{2d}	**1^{4d}**	**1_{Co}**
M_1–O_{10}	2.058(14)	2.102(13)	2.079(16)
M_2–S_1/S_4	ave. 2.503 2.508(4)/2.496(5)	ave. 2.458 2.451(6)/2.465(5)	ave. 2.472 2.460(7)/2.485(7)
M_2–O_1/O_7	ave. 2.125 2.146(12)/2.113(11)	ave. 2.094 2.087(15)/2.108(13)	ave. 2.119 2.117(19)/2.122(16)
M_2–N_1/N_4	ave. 2.191 2.201(14)/2.186(13)	ave. 2.189 2.147(15)/2.231(13)	ave. 2.119 2.125(19)/2.213(16)
M_3-S_2/S_5	ave. 2.498 2.499(4)/2.496(4)	ave. 2.414 2.407(6)/2.423(5)	ave. 2.417 2.413(8)/2.421(7)
M_3-O_3/O_9	ave. 2.110 2.021(14)/2.203(10)	ave. 2.049 2.039(15)/2.062(12)	ave. 2.044 2.011(19)/2.077(15)
M_3-N_2/N_5	ave. 2.150 2.152(13)/2.159(13)	ave. 2.135 2.130(16)/2.127(16)	ave. 2.114 2.14(2)/2.089(19)
M_4-S_3/S_6	ave. 2.544 2.528(5)/2.560(4)	ave. 2.447 2.445(5)/2.450(5)	ave. 2.446 2.449(7)/2.444(6)
M_4-O_5/O_{11}	ave. 2.243 2.220(15)/2.274(9)	ave. 2.124 2.097(12)/2.141(10)	ave. 2.130 2.115(15)/2.146(12)
M_4-N_3/N_6	ave. 2.222 2.197(18)/2.255(14)	ave. 2.142 2.132(17)/2.144(15)	ave. 2.168 2.16(2)/2.176(19)
M_5–O_{12}	2.165(9)	2.125(11)	2.132(15)

Table S3. Site occupancies of metal centres (M_1, M_2, M_3, M_4, M_5) for $\mathbf{1_{CdNa}}$, $\mathbf{1^{1h}}$, $\mathbf{1^{6h}}$, $\mathbf{1^{1d}}$, $\mathbf{1^{2d}}$, $\mathbf{1^{4d}}$, and $\mathbf{1_{Co}}$.

	Site occupancy			
	$\mathbf{1_{CdNa}}$	$\mathbf{1^{1h}}$	$\mathbf{1^{6h}}$	$\mathbf{1^{1d}}$
Co_1/Na_1 (M_1)	0.0/1.0	1.0/0.0	1.0/0.0	1.0/0.0
Co_2/Cd_2 (M_2)	0.0/1.0	0.03(1)/0.97(1)	0.38(1)/0.62(1)	0.71(1)/0.29(1)
Co_3/Cd_3 (M_3)	0.0/1.0	0.0/1.0	0.29(1)/0.71(1)	0.57(1)/0.43(1)
Co_4/Cd_4 (M_4)	0.0/1.0	0.0/1.0	0.14(1)/0.86(1)	0.26(1)/0.74(1)
Co_5/Cd_5 (M_5)	0.0/1.0	0.0/1.0	0.27(2)/0.73(2)	0.33(2)/0.67(2)
Total Co atoms per cage-of-cage[a]	0.0	4.4	14.8	23.8

	Site occupancy		
	$\mathbf{1^{2d}}$	$\mathbf{1^{4d}}$	$\mathbf{1_{Co}}$
Co_1/Na_1 (M_1)	1.0/0.0	1.0/0.0	1.0/0.0
Co_2/Cd_2 (M_2)	0.98(1)/0.02(1)	1.0/0.0	1.0/0.0
Co_3/Cd_3 (M_3)	0.85(1)/0.15(1)	1.0/0.0	1.0/0.0
Co_4/Cd_4 (M_4)	0.58(1)/0.42(1)	0.96(1)/0.04(1)	1.0/0.0
Co_5/Cd_5 (M_5)	0.62(1)/0.38(1)	1.0/0.0	1.0/0.0
Total Co atoms per cage-of-cage[a]	35.4	43.5	44.0

a: Calculated from $4\times Co_1+12\times Co_2+12\times Co_3+12\times Co_4+4\times Co_5$