Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

Conversion of 12-Membered $\textsc{d}_3$- and $\textsc{l}_3$-$Co^{III}_3Cd^{II}_3$ Metallorings into a 24-Membered $\textsc{d}_3\textsc{l}_3$-$Co^{III}_6Cd^{II}_6$ Metalloring

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Experimental Section

Materials.

N,*N*'-ethylenebis(D-penicillamine) (D-H_4ebp) and *N*,*N*'-ethylenebis(L-penicillamine) (L-H_4ebp) were prepared from D-penicillamine and L-penicillamine, respectively, *via* 5,5-dimethylthiazolidine-4-carboxylic acid[S1] using a modified synthetic method of *N*,*N*'-ethylenebis(L-cysteine).[S2] $Na_3[Co(CO_3)_3]\cdot 3H_2O$ was freshly prepared according to the literature method.[S3] Other chemicals and solvents were of commercial reagent grade and used without further purification.

Preparation of Na[Co(D- or L-ebp)].

This complex has been previously prepared by using $[Co(NH_3)_6]Cl_3$ as a starting complex[S4] but isolated as a double salt containing NaCl, Na[Co(D-ebp)]·0.5NaCl. To avoid contamination with chloride ions, $Na_3[Co(CO_3)_3]$ was used as the starting complex in this study.

An aqueous suspension (30 mL) containing D-H_4ebp (300 mg, 0.92 mmol) and $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (350 mg, 0.97 mmol) was stirred at room temperature for 1 h, which gave a brown solution. The brown solution was evaporated to dryness, and then methanol (8 mL) and 1-hexanol (8 mL) were added to the residue to give a brown suspension. After filtration, 1-hexanol (12 mL) was added to the filtrate. The brown solution was concentrated to a small volume to give a dark brown powder. The brown powder was collected by filtration, washed with diethyl ether, and then dried in vacuo. Yield: 245 mg (57 %). Anal. Calcd for Na[Co(D-ebp)]·3.5H_2O = $C_{12}H_{27}CoN_2NaO_{7.5}S_2$: C, 30.97; H, 5.85; N, 6.02 %. Found: C, 30.62; H, 5.57; N, 6.00 %. ^{1}H NMR spectrum in D_2O (δ, ppm from DSS): 3.54 (s, 2H), 3.51 (d, J = 8.6 Hz, 2H), 2.93 (d, J = 8.6 Hz, 2H), 1.79 (s, 6H), 1.29 (s, 6H). Diffuse reflection spectrum (λ, nm): 538. Solid CD spectrum (λ, nm): 405 (–), 453 (–), 547 (+), 669 (+)

A similar reaction using L-H_4ebp, instead of D-H_4ebp, gave Na[Co(L-ebp)]. Yield: 55 %. Anal. Calcd for Na[Co(L-ebp)]·3.5H_2O = $C_{12}H_{27}CoN_2NaO_{7.5}S_2$: C, 30.97; H, 5.85; N, 6.02 %. Found: C, 30.91; H, 5.87; N, 5.81 %. Diffuse reflection spectrum (λ, nm): 539. Solid CD (λ, nm): 400 (+), 460 (+), 558 (–), 670 (–)

Preparation of $[Cd_3\{Co(D\text{-ebp})\}_3I_3]$ (D_3-**1**$_I$) and $[Cd_3\{Co(L\text{-ebp})\}_3I_3]$ (L_3-**1**$_I$).

To a brown solution containing Na[Co(D-ebp)]·3.5H_2O (50 mg, 0.11 mmol) in H_2O (5 mL) was added a colourless solution of CdI_2 (59 mg, 0.16 mmol) in H_2O (4 mL). The brown solution was slowly evaporated at room temperature for 2 weeks, which gave purple block crystals of D_3-**1**$_I$, together with a small amount of a white precipitate. The white precipitate was removed by decantation, and the purple crystals were collected by filtration and washed with a small amount of H_2O. One of the crystals was used for single-crystal X-ray analysis. Yield: 53 mg (73 %). Anal. Calcd for $[Cd_3\{Co(D\text{-ebp})\}_3I_3]\cdot 8H_2O$ = $C_{36}H_{76}Cd_3Co_3I_3N_6O_{20}S_6$: C, 21.62; H, 3.83; N, 4.20 %. Found: C, 21.63; H, 3.61; N, 4.19 %. Diffuse reflection spectrum (λ, nm): 525. Solid CD spectrum (λ, nm): 438 (–), 525 (+), 612 (–).

A similar reaction using Na[Co(L-ebp)]·3.5H_2O, instead of Na[Co(D-ebp)]·3.5H_2O, gave L_3-**1**. Yield: 51 %. Anal. Calcd for $[Cd_3\{Co(ebp)\}_3I_3]\cdot 8H_2O$ = $C_{36}H_{76}Cd_3Co_3I_3N_6O_{20}S_6$: C, 21.62; H, 3.83; N, 4.20 %. Found: C, 21.74; H, 3.61; N, 4.22 %. Diffuse reflection spectrum (λ, nm): 525. Solid CD spectrum (λ, nm): 435 (+), 522 (–), 614 (+).

Preparation of $[\mathrm{Cd_6(H_2O)_6\{Co(D\text{-}ebp)\}_3\{Co(L\text{-}ebp)\}_3I_6}]$ ($\mathrm{D_3L_3}$-$\mathbf{2}_\mathrm{I}$).

Method A.

To a brown solution containing $\mathrm{Na[Co(D\text{-}ebp)]\cdot 3.5H_2O}$ (15 mg, 0.033 mmol) and $\mathrm{Na[Co(L\text{-}ebp)]\cdot 3.5H_2O}$ (15 mg, 0.033 mmol) in $\mathrm{H_2O}$ (6 mL) was added a colourless solution containing $\mathrm{CdI_2}$ (72 mg, 0.13 mmol) in $\mathrm{H_2O}$ (2 mL). The resulting brown solution was slowly evaporated at room temperature for a week, which gave purple hexagonal plate crystals of $\mathrm{D_3L_3}$-$\mathbf{2}_\mathrm{I}$. The crystals were collected by filtration and washed with a small amount of $\mathrm{H_2O}$. One of the crystals was used for single-crystal X-ray analysis. Yield: 29 mg (67 %). Anal. Calcd for $\mathrm{[Cd_6(H_2O)_6\{Co(epen)\}_6I_6]\cdot 12H_2O = C_{72}H_{156}Cd_6Co_6I_6N_{12}O_{42}S_{12}}$: C, 21.42; H, 3.90; N, 4.16 %. Found: C, 21.36; H, 3.72; N, 4.07 %. Diffuse reflection spectrum (λ, nm): 525. Solid CD spectrum: silent.

Method B.

$\mathrm{D_3}$-$\mathbf{1}_\mathrm{I}$ (10 mg, 5.0 μmol) and $\mathrm{L_3}$-$\mathbf{1}_\mathrm{I}$ (10 mg, 5.0 μmol) were dissolved in $\mathrm{H_2O}$ (6 mL), which gave a brown solution. To the solution was added a 0.3 M aqueous NaI solution (650 μL, 195 μmol). The mixture was slowly evaporated at room temperature for 3 weeks, which gave purple hexagonal plate crystals of $\mathrm{D_3L_3}$-$\mathbf{2}_\mathrm{I}$. The crystals were collected by filtration and washed with a small amount of $\mathrm{H_2O}$. Yield: 17 mg (84 %).

Preparation of $[\mathrm{Cd_2(H_2O)_2\{Co(D\text{-}ebp)\}_2\{Co(L\text{-}ebp)\}_2}]$ ($\mathrm{D_2L_2}$-$\mathbf{3}$).

$\mathrm{D_3}$-$\mathbf{1}_\mathrm{I}$ (10 mg, 5.0 μmol) and $\mathrm{L_3}$-$\mathbf{1}_\mathrm{I}$ (10 mg, 5.0 μmol) were dissolved in $\mathrm{H_2O}$ (6 mL), which gave a brown solution. The mixture was slowly evaporated at room temperature for 2 weeks, which gave purple hexagonal plate crystals of $\mathrm{D_3L_3}$-$\mathbf{2}_\mathrm{I}$ and green block crystals of $\mathrm{D_2L_2}$-$\mathbf{3}$. The product was recrystallized from $\mathrm{H_2O}$, which gave only green block crystals of $\mathrm{D_2L_2}$-$\mathbf{3}$. The green crystals were collected by filtration and washed with a small amount of $\mathrm{H_2O}$. One of the green crystals was used for single-crystal X-ray analysis. Yield: 3 mg (20 %). Found: C, 30.37; H, 5.06; N, 5.88 %. Calcd for $\mathrm{[Cd_2\{Co(ebp)\}_4]\cdot 9H_2O = C_{48}H_{98}Cd_2Co_4N_8O_{25}S_8}$: C, 30.27; H, 5.19; N, 5.88 %. Diffuse reflection spectrum (λ, nm): 543. Solid CD spectrum: silent. Fluorescence X-ray analysis: Cd, Co, S. The bulk purity of the sample was confirmed by powder X-ray diffraction measurement.

Preparation of $[\mathrm{Cd_3\{Co(D\text{-}ebp)\}_3Br_3}]$ ($\mathrm{D_3}$-$\mathbf{1}_\mathrm{Br}$) and $[\mathrm{Cd_3\{Co(L\text{-}ebp)\}_3Br_3}]$ ($\mathrm{L_3}$-$\mathbf{1}_\mathrm{Br}$).

To a brown solution containing $\mathrm{Na[Co(D\text{-}ebp)]\cdot 3.5H_2O}$ (50 mg, 0.11 mmol) in $\mathrm{H_2O}$ (6 mL) was added $\mathrm{CdBr_2}$ (32 mg, 0.12 mmol). After stirring at room temperature for 3 days, a small amount of a white precipitate was filtered off. The brown filtrate was slowly evaporated at room temperature for 2 weeks. The resulting purple block crystals of $\mathrm{D_3}$-$\mathbf{1}_\mathrm{Br}$ were collected by filtration and washed with a small amount of $\mathrm{H_2O}$. One of the crystals was used for single-crystal X-ray analysis. Yield: 49 mg (74 %). Anal. Calcd for $\mathrm{[Cd_3\{Co(ebp)\}_3Br_3]\cdot 8H_2O = C_{36}H_{76}Br_3Cd_3Co_3N_6O_{20}S_6}$: C, 23.26; H, 4.12; N, 4.52 %. Found: C, 23.41; H, 3.99; N, 4.63 %. Diffuse reflection spectrum (λ, nm): 523. Solid CD spectrum (λ, nm): 435 (–), 523 (+), 610 (–).

A similar reaction using $\mathrm{Na[Co(L\text{-}ebp)]\cdot 3.5H_2O}$ instead of $\mathrm{Na[Co(D\text{-}ebp)]\cdot 3.5H_2O}$ gave $\mathrm{L_3}$-$\mathbf{1}_\mathrm{Br}$. Yield: 62 %. Anal. Calcd for $\mathrm{[Cd_3\{Co(ebp)\}_3Br_3]\cdot 8H_2O = C_{36}H_{76}Br_3Cd_3Co_3N_6O_{20}S_6}$: C, 23.26; H, 4.12; N, 4.52 %. Found: C, 23.13; H, 4.03; N, 4.53 %. Diffuse reflection spectrum (λ, nm): 526. Solid CD spectrum (λ, nm): 434 (+), 525 (–), 610 (+).

Preparation of [$Cd_6(H_2O)_6$\{Co(D-ebp)\}$_3$\{Co(L-ebp)\}$_3Br_6$] (**D3L3-2Br**).

Method A.

To a brown solution containing Na[Co(D-ebp)]·3.5H_2O (15 mg, 0.033 mmol) and Na[Co(L-ebp)]·3.5H_2O (15 mg, 0.033 mmol) in H_2O (6 mL) was added a colourless solution containing $CdBr_2$ (54 mg, 0.20 mmol) in H_2O (2 mL). The mixture was slowly evaporated at room temperature for 5 days. The resulting purple hexagonal plate crystals of **D_3L_3-2$_{Br}$** were collected by filtration and washed with a small amount of H_2O. One of the crystals was used for single-crystal X-ray analysis. Yield: 29 mg (72 %). Anal. Calcd for [$Cd_6(H_2O)_6$\{Co(ebp)\}$_6Br_6$]·12H_2O = $C_{72}H_{156}Br_6Cd_6Co_6N_{12}O_{42}S_{12}$: C, 23.03; H, 4.19; N, 4.48 %. Found: C, 22.96; H, 4.04; N, 4.50 %. Diffuse reflection spectrum (λ, nm): 525. Solid CD spectrum: silent.

Method B.

D_3-**1**$_{Br}$ (10 mg, 5.4 μmol) and L_3-**1**$_{Br}$ (10 mg, 5.4 μmol) were dissolved in H_2O (8 mL), which gave a brown solution. To the solution was added 3 M aqueous NaBr (70 μL, 210 μmol). The mixture was slowly evaporated at room temperature for 3 weeks, which gave purple hexagonal plate crystals of D_3L_3-**2**$_{Br}$. The crystals were collected by filtration and washed with a small amount of H_2O. Yield: 15 mg (74 %).

Preparation of [CdCl\{Co(D-ebp)\}]$_n$.

To a brown solution containing Na[Co(D-ebp)]·3.5H_2O (50 mg, 0.11 mmol) in H_2O (3 mL) was added $CdCl_2$·2.5H_2O (24 mg, 0.11 mmol). After stirring at room temperature for 1 day, a small amount of a white precipitate was filtered off. The brown filtrate was slowly evaporated at room temperature for 5 days. The resulting purple block crystals of [CdCl\{Co(D-ebp)\}]$_n$ were collected by filtration and washed with a small amount of H_2O. One of the crystals was used for single-crystal X-ray analysis. Yield: 32 mg (49 %). Anal. Calcd for [CdCl\{Co(ebp)\}]·4H_2O = $C_{12}H_{28}CdCoN_2O_8S_2$: C, 24.05; H, 4.71; N, 4.67 %. Found: C, 24.11; H, 4.43; N, 4.70 %.

Preparation of [$Cd_6(H_2O)_6$\{Co(D-ebp)\}$_3$\{Co(L-ebp)\}$_3Cl_6$] (**D3L3-2Cl**).

To a brown solution containing Na[Co(D-ebp)]·3.5H_2O (15 mg, 0.033 mmol) and Na[Co(L-ebp)]·3.5H_2O (15 mg, 0.033 mmol) in H_2O (6 mL) was added a colourless solution containing $CdCl_2$·2.5H_2O (45 mg, 0.13 mmol) in H_2O (2 mL). The mixture was slowly evaporated at room temperature for 5 days. The resulting purple hexagonal plate crystals of **D_3L_3-2$_{Cl}$** were collected by filtration and washed with a small amount of H_2O. One of the crystals was used for single-crystal X-ray analysis. Yield: 27 mg (71 %). Anal. Calcd for [$Cd_6(H_2O)_6$\{Co(ebp)\}$_6Cl_6$]·12H_2O = $C_{72}H_{156}Cd_6Cl_6Co_6N_{12}O_{42}S_{12}$: C, 25.05; H, 4.44; N, 4.87 %. Found: C, 25.07; H, 4.33; N, 4.91 %.

Physical measurements.

The absorption and CD spectra in solution were recorded with a JASCO V-670 spectrophotometer and a JASCO V-670 spectrophotometer, respectively, at room temperature. The CD spectra in the solid state were recorded with a JASCO J-820 polarimeter using KBr disks at room temperature. The diffuse reflection spectra were recorded with a JASCO V-670 spectrophotometer equipped with a JASCO ISN-723 integrating sphere using $MgSO_4$ at room temperature. The CD spectra in the solid state were recorded with a JASCO J-820 polarimeter using KBr disks at room temperature. The elemental analyses (C, H, N) were performed with a Yanaco CHN Corder MT-5. The ^{1}H NMR spectra were recorded with a JEOL ECS500 spectrometer in D_2O. Sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) was used as the internal standard. Fluorescence X-ray spectra were measured with a SHIMADZU Rayny EDX-720 energy-dispersive X-ray fluorescence spectrometer. The electrospray ionization (ESI) mass spectra were recorded on BRUKER micrOTOF II-OS (1.5 mM in water-methanol (v/v = 1/1)). The TG/DTA data were measured with a SHIMADZU DTG-60 using Al_2O_3 as a reference.

Powder X-ray diffraction measurements.

Powder X-ray diffraction patterns illustrated in Figures S13 and S14 were recorded at 200 K, in transmission mode [synchrotron radiation $\lambda = 1.000$ Å; 2θ range = 0–78°; step width = 0.01°; data collection time = 1 min] on a diffractometer equipped with a white imaging plate detector at the SPring-8 BL02B2 beamline. The crystals were put into 0.3 mm glass capillary tubes, and the samples were rotated during the measurements. The diffraction patterns were collected with a large Debye−Scherrer camera. Powder X-ray diffraction patterns illustrated in Figures S17 and S18 were recorded at room temperature in reflection mode (Cu radiation $\lambda = 1.54$ Å, 2θ range = 6–30°; step width = 0.05°). The powder simulation patterns were generated from the single-crystal X-ray structures using Mercury 3.10.[S5]

X-ray Structural Determinations.

The single-crystal X-ray diffraction measurements were performed using a Rigaku FR-E Superbright rotating-anode X-ray source with a Mo-target ($\lambda = 0.71075$ Å), equipped with a Rigaku RAXIS VII imaging plate as a detector, at 200 K. The intensity data were collected via the ω-scan technique and empirically corrected for absorption. The structures of the complexes were solved by direct methods using SHELXS97.[S6] The structure refinements were carried out using the full matrix least-squares method (SHELXL-2014).[S6] The crystallographic data are summarized in Tables S1-S4. All calculations were performed using the Yadokari-XG software package.[S7] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (CCDC 1879438-1879446). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

For D$_3$-**1**$_\mathrm{I}$, L$_3$-**1**$_\mathrm{I}$, [CdCl{Co(D-ebp)}]$_n$, L$_3$-**1**$_\mathrm{Br}$, all non-hydrogen atoms except for several water molecules were refined anisotropically, while the other atoms were refined isotropically. H atoms were included in the calculated positions except those of water molecules. For D$_3$-**1**$_\mathrm{Br}$, D$_3$L$_3$-**2**$_\mathrm{Br}$, and D$_3$L$_3$-**2**$_\mathrm{Cl}$, all non-hydrogen atoms were refined anisotropically, while the other atoms were refined isotropically. H atoms were included in the calculated positions except those of water molecules. For D$_3$L$_3$-**2**$_\mathrm{I}$, all non-hydrogen atoms were refined anisotropically, while the other atoms were refined isotropically. H atoms bound to C and N atoms were placed at the calculated positions and refined using a riding model. The H atoms of water molecules were found in the Fourier map and refined with restrained displacement parameters [$U_\mathrm{iso}(\mathrm{H}) =$

1.2U_{eq}(O)]. For D_2L_2-**3**, the complex molecule was disordered over two positions (part A (occ. 90 %) and part B (occ. 10 %)). All non-hydrogen atoms belonging to the major part (part A) were refined anisotropically, while the atoms belonging to the minor part (part B) were refined isotropically. The H atoms, which were refined isotropically, were included in the calculated positions except those of water molecules. The DFIX and EADP restraints were used to model the minor part. Because the geometrical parameters of the atoms belonging to the minor part were inaccurate, their data were excluded from the discussion.

References.

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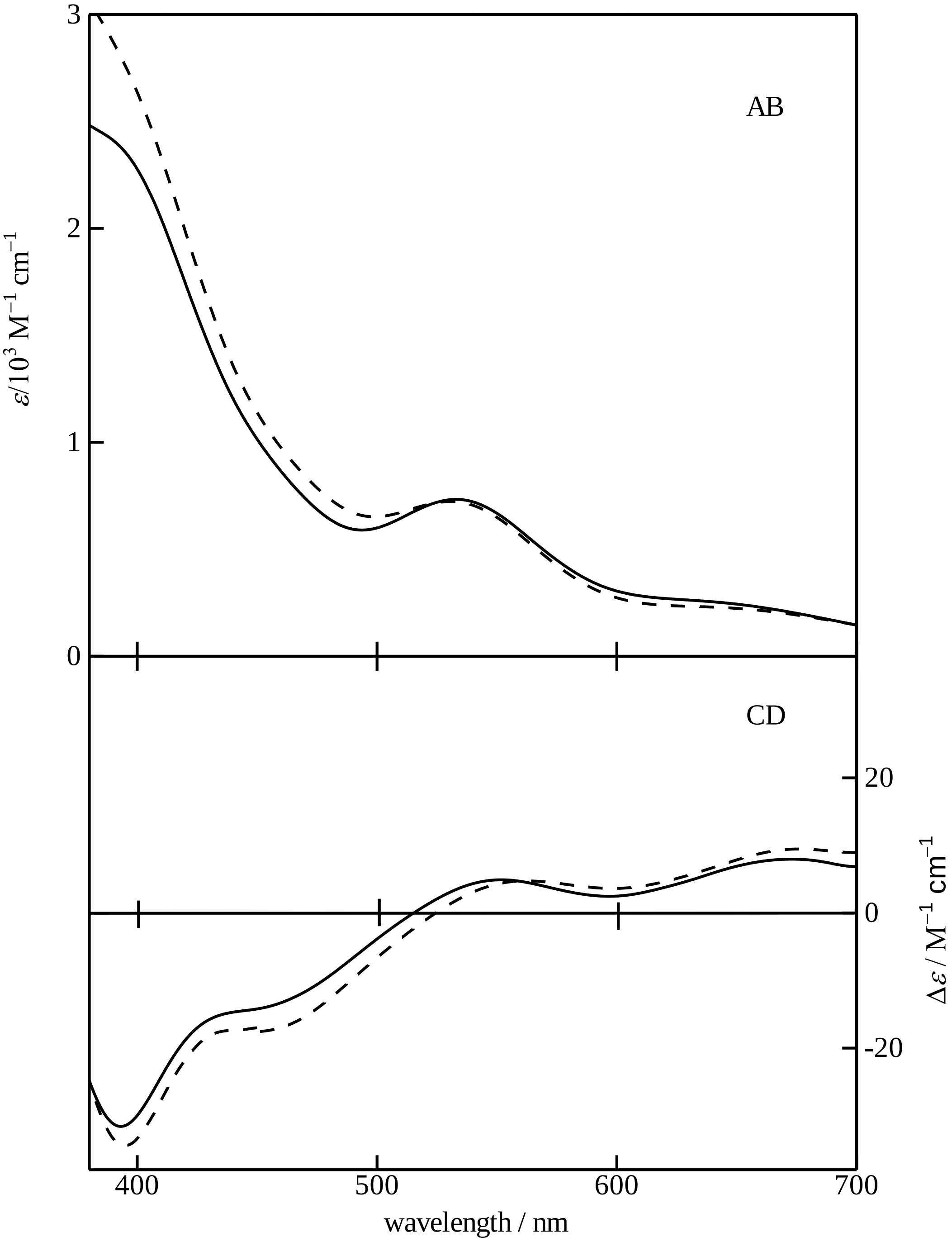

Figure S1. Absorption (AB) and CD spectra of Na[Co(D-ebp)]×3 (dashed line) and D_3-**1**$_I$ (solid line) in water.

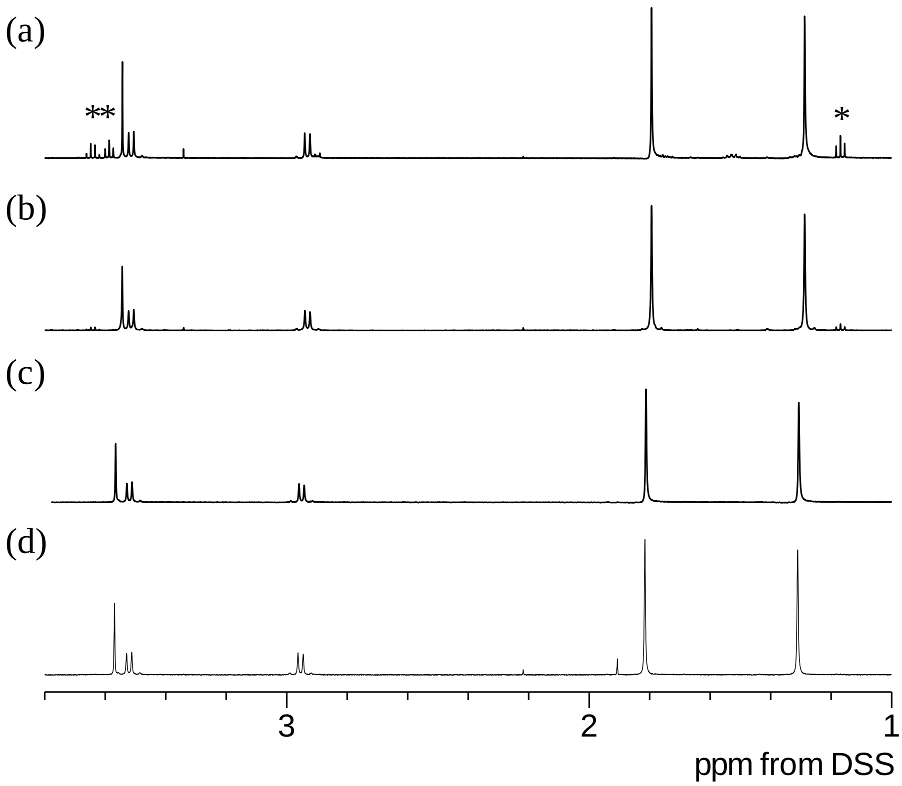

Figure S2. ^{1}H NMR spectra of (a) Na[Co(D-ebp)], (b) Na[Co(L-ebp)], (c) D$_3$-**1**$_\mathrm{I}$, and (d) L$_3$-**1**$_\mathrm{I}$ in D_2O. (* denotes the signals from solvents)

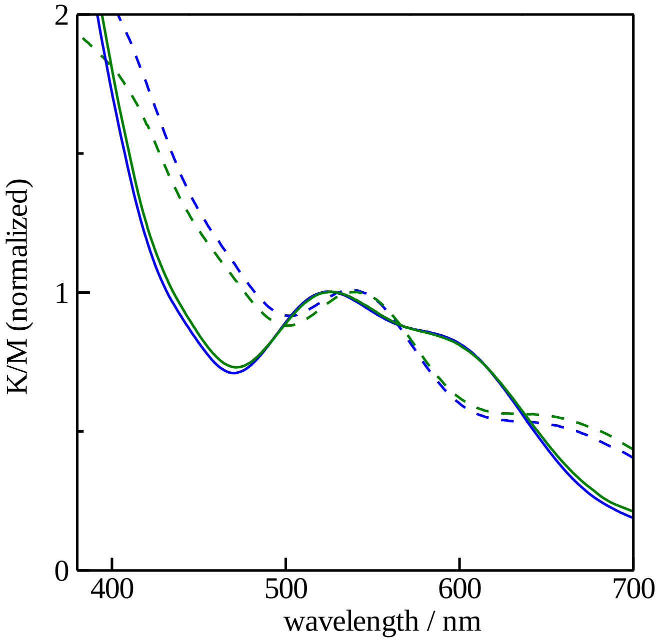

Figure S3. Diffuse reflection spectra of Na[Co(D-ebp)] (blue dashed line), Na[Co(L-ebp)] (green dashed line), D$_3$-**1**$_\mathrm{I}$ (blue solid line), and L$_3$-**1**$_\mathrm{I}$ (green solid line) in the solid state. The reflection intensity was normalized at the absorption band approximately 500-550 nm.

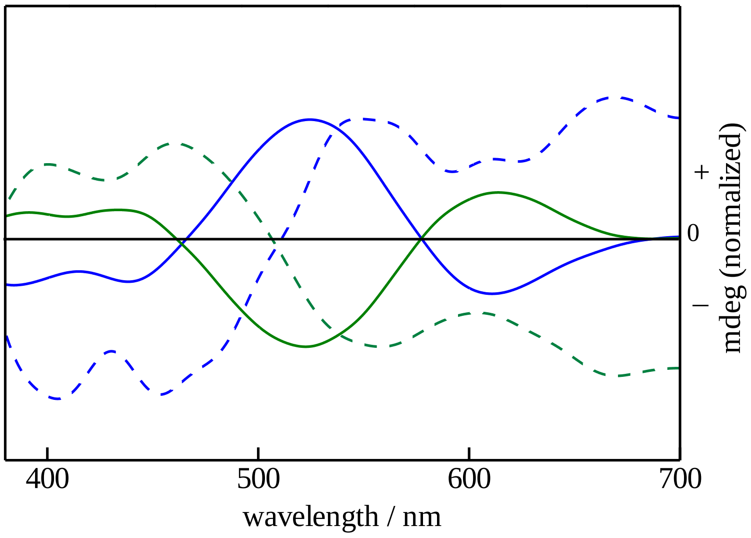

Figure S4. CD spectra of Na[Co(D-ebp)] (blue dashed line), Na[Co(L-ebp)] (green dotted line), D$_3$-**1**$_\mathrm{I}$ (blue dashed line), and L$_3$-**1**$_\mathrm{I}$ (green solid line) in the solid state. The CD intensity was normalized at the band approximately 500-550 nm.

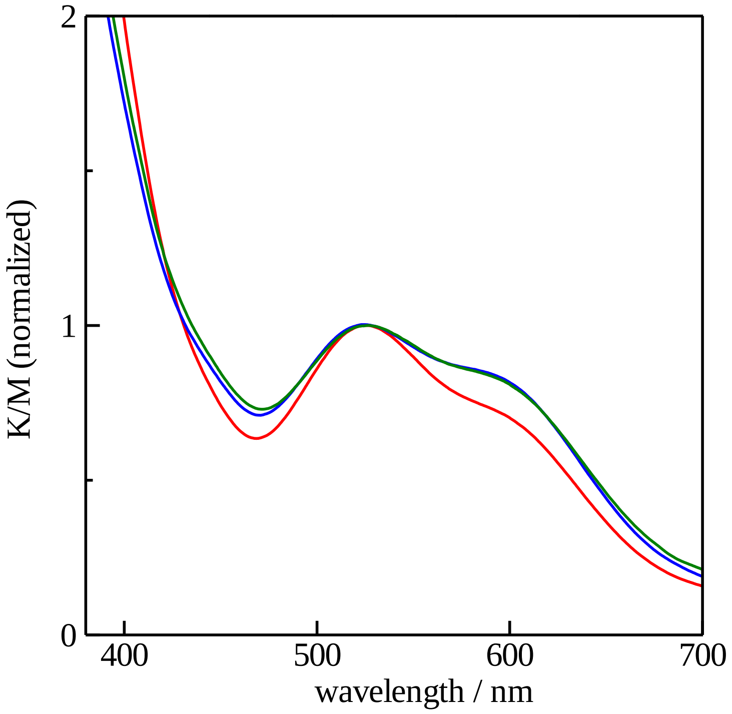

Figure S5. Diffuse reflection spectra of D3-**1**I (blue), L3-**1**I (green), and D3L3-**2**I (red). The reflection intensity was normalized at the absorption band approximately 500-550 nm.

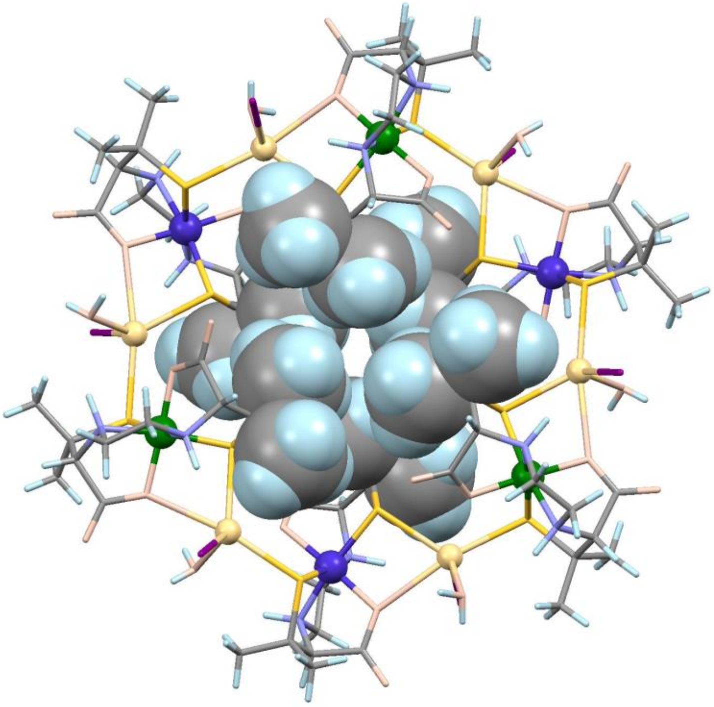

Figure S6. A perspective view of D3L3-**2$_{\mathbf{I}}$**. The methyl groups occupying the central cavity were illustrated as a space-filling model. Colour code: Cd, beige; I, purple; Co, blue for $[\mathrm{Co}(\text{D-ebp})]^{-}$ unit and green for $[\mathrm{Co}(\text{L-ebp})]^{-}$ unit; S, yellow; O, pink; N, pale blue; C, grey. H, sky blue.

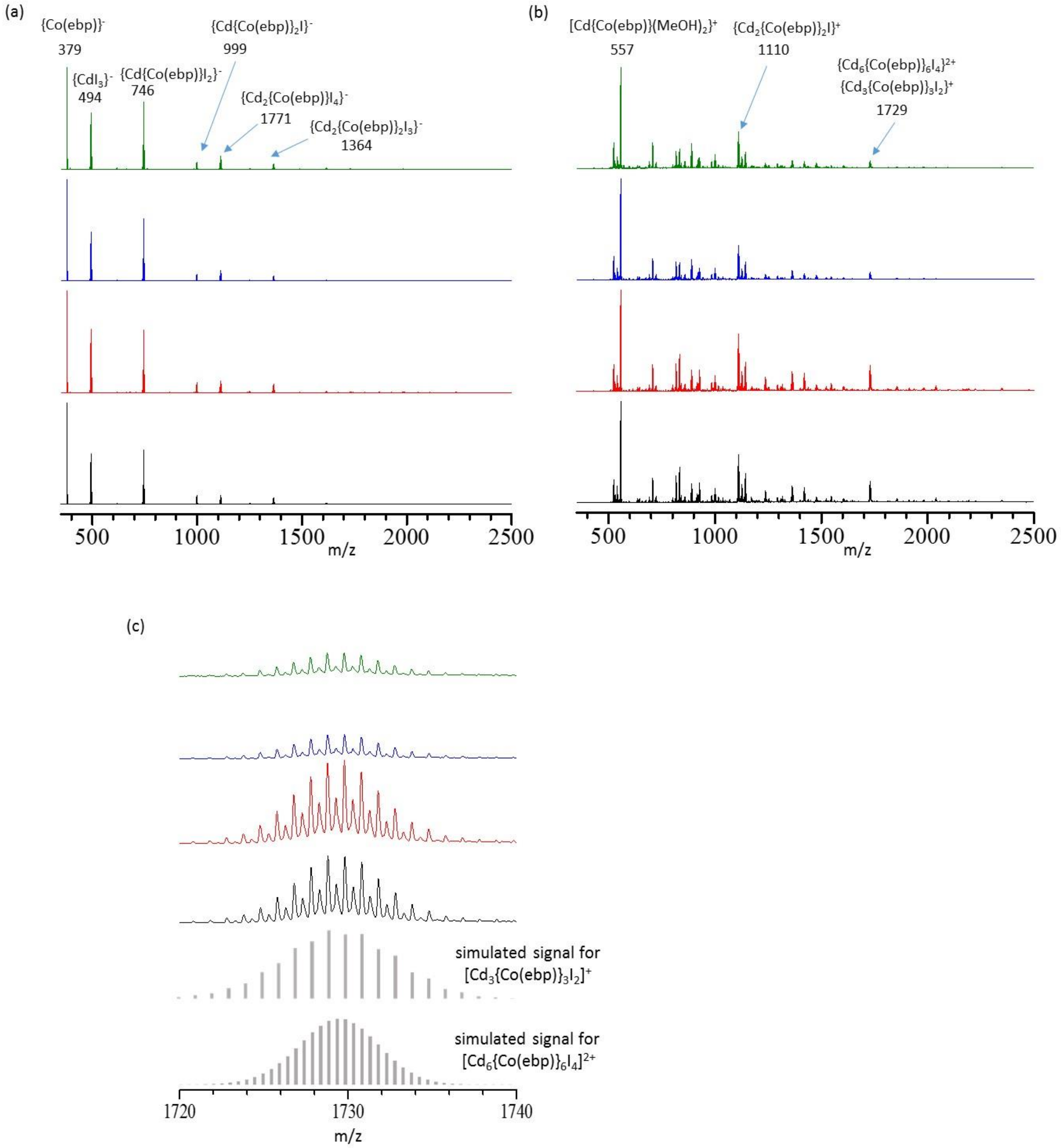

Figure S7. ESI-mass spectra of D$_3$-**1**$_\text{I}$ (green), L$_3$-**1**$_\text{I}$ (blue), D$_3$L$_3$-**2**$_\text{I}$ (red), and a mixture of D$_3$-**1**$_\text{I}$ and L$_3$-**1**$_\text{I}$ (black) in H_2O/MeOH. (a) The entire spectra measured in negative mode and (b) positive mode. (c) The isotope pattern of the signal at *m*/*z* = 1729 observed in the positive mode with the simulated patterns.

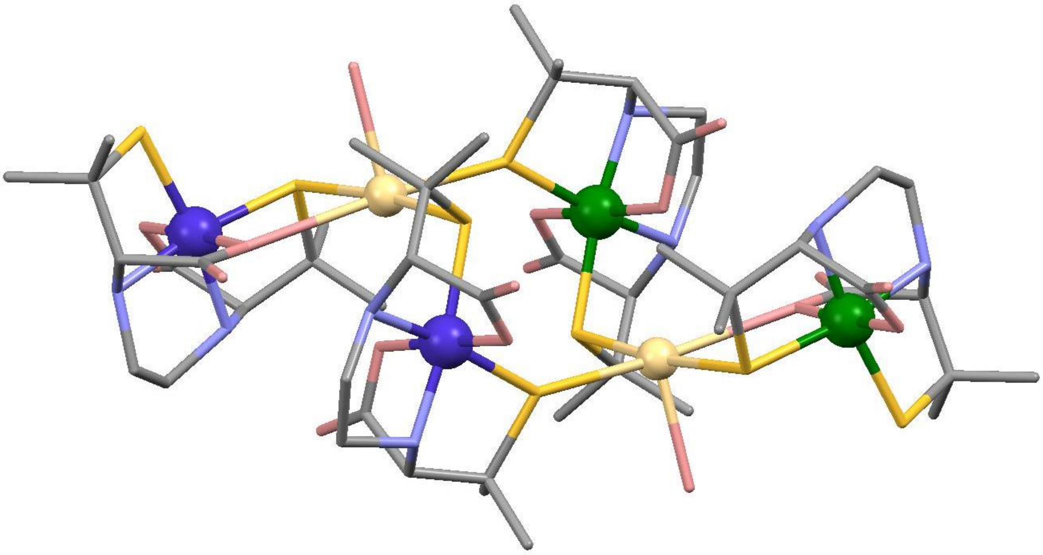

Figure S8. A perspective view of D$_2$L$_2$-**3**. Colour code: Cd, beige; Co, blue for [Co(D-ebp)]$^-$ unit and green for [Co(L-ebp)]$^-$ unit; S, yellow; O, pink; N, pale blue; C, grey. H atoms are omitted for clarity.

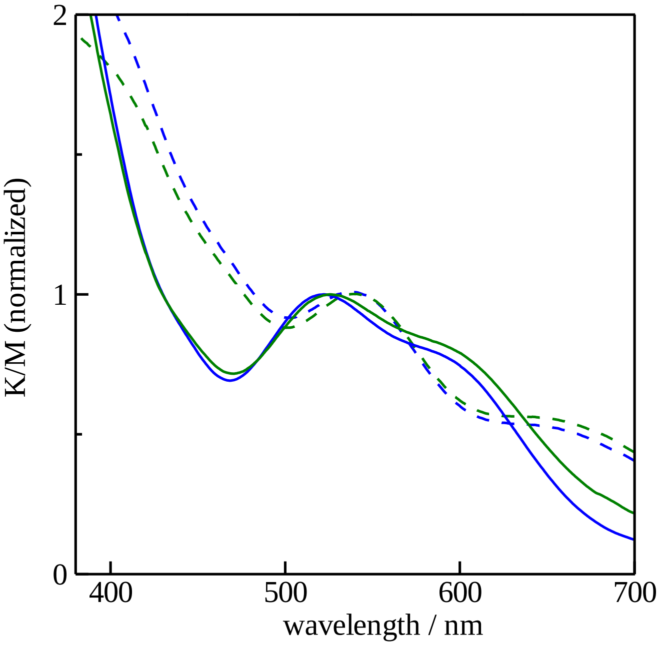

Figure S9. Diffuse reflection spectra of Na[Co(D-ebp)] (blue dashed line), Na[Co(L-ebp)] (green dashed line), D3-**1**$_{\mathbf{Br}}$ (blue solid line), and L3-**1**$_{\mathbf{Br}}$ (green solid line) in the solid state. The reflection intensity was normalized at the absorption band approximately 500-550 nm.

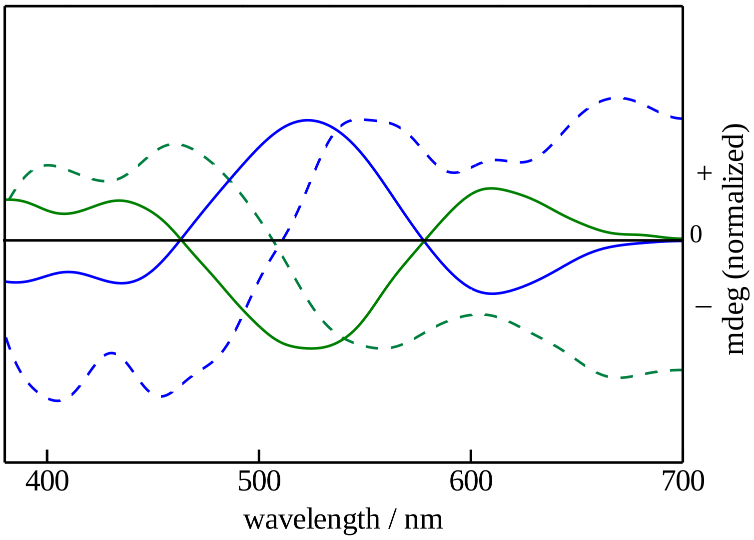

Figure S10. CD spectra of Na[Co(D-ebp)] (blue dashed line), Na[Co(L-ebp)] (green dashed line), D3-**1**$_{\mathbf{Br}}$ (blue solid line), and L3-**1**$_{\mathbf{Br}}$ (green solid line) in the solid state. The CD intensity was normalized at the absorption band approximately 500-550 nm.

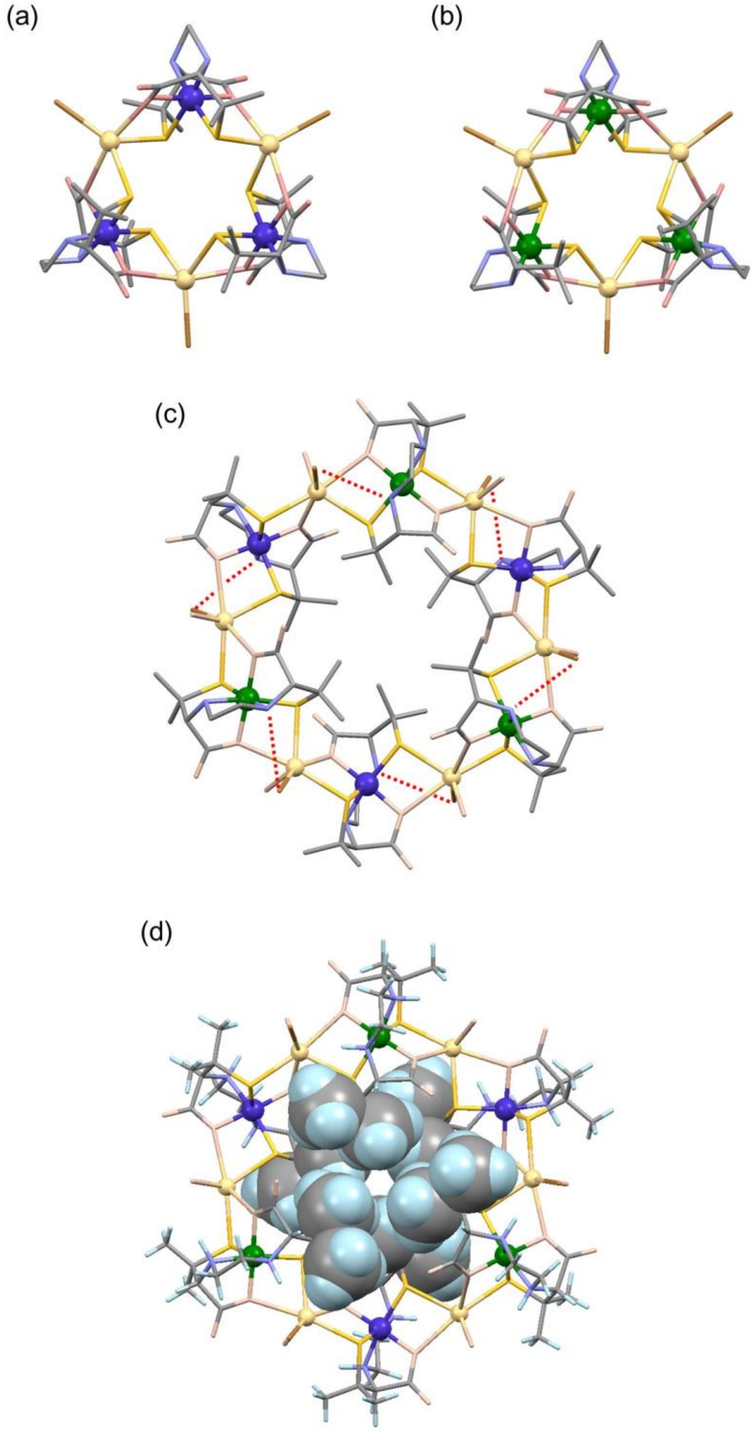

Figure S11. Perspective views of (a) D$_3$-**1**$_{\mathbf{Br}}$, (b) L$_3$-**1**$_{\mathbf{Br}}$, and (c,d) D$_3$L$_3$-**2**$_{\mathbf{Br}}$. The methyl groups occupying the central cavity were illustrated as a space-filling model for (d). Colour code: Cd, beige; Br, brown; Co, blue for [Co(D-ebp)]$^-$ unit and green for [Co(L-ebp)]$^-$ unit; S, yellow; O, pink; N, pale blue; C, grey. H atoms are omitted for clarity for (a)-(c). Red dashed lines indicate NH···I hydrogen bonds.

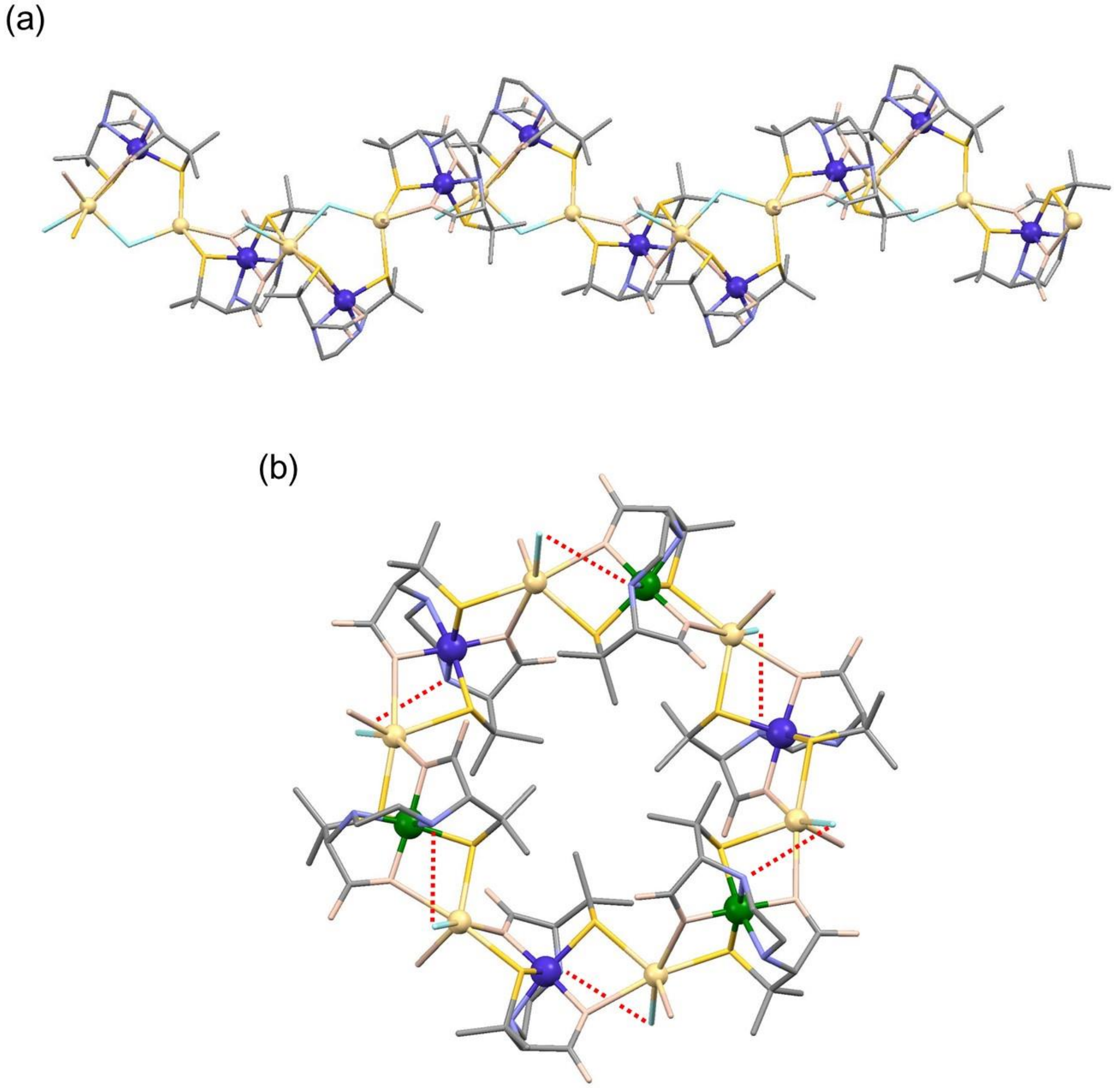

Figure S12. Perspective views of (a) [CdCl{Co(D-ebp)}]$_n$ and (b) D$_3$L$_3$-**2**$_{\mathbf{Cl}}$. Colour code: Cd, beige; Cl, sky blue; Co, blue for [Co(D-ebp)]$^-$ unit and green for [Co(L-ebp)]$^-$ unit; S, yellow; O, pink; N, pale blue; C, grey. Red dashed lines indicate NH···I hydrogen bonds.

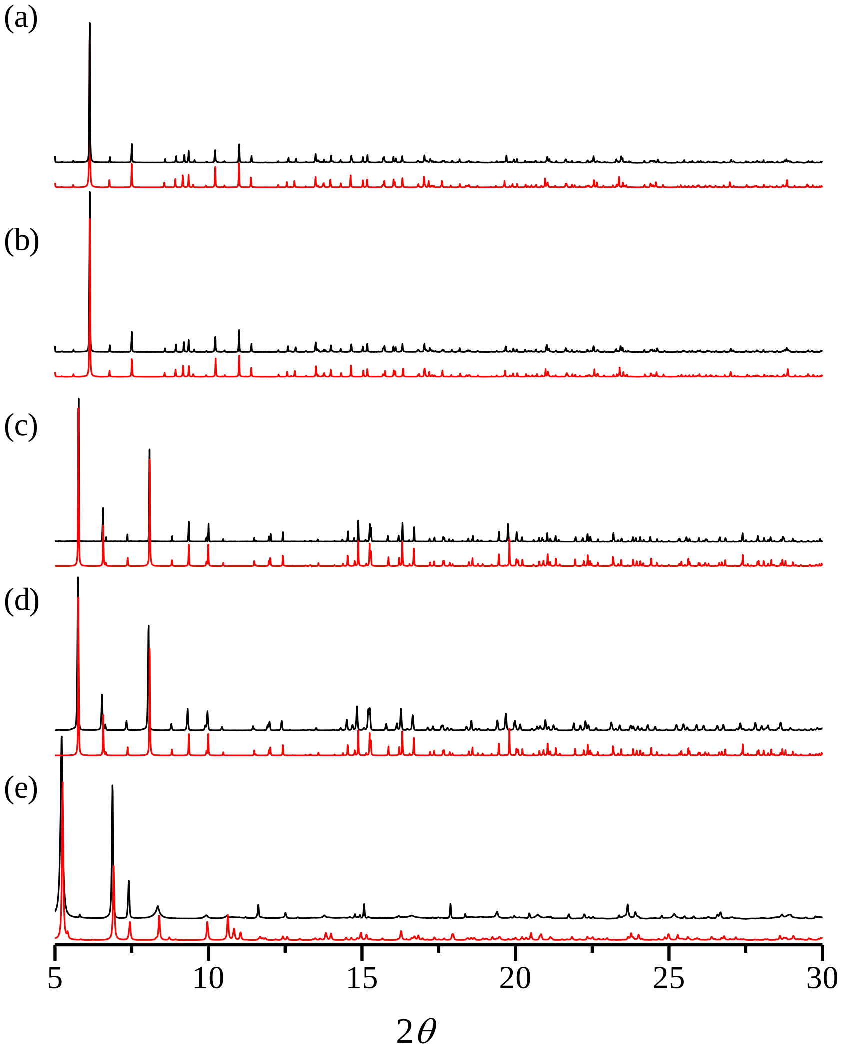

Figure S13. Observed (black) and calculated (red) PXRD patterns of (a) D3-**1**I, (b) L3-**1**I, (c) D3L3-**2**I prepared from the reaction of Na[Co(D-ebp)], Na[Co(L-ebp)], and CdI_2, (d) D3L3-**2**I prepared from the reaction of D3-**1**I, L3-**1**I, and NaI, and (e) D2L2-**3** [λ = 1.000 Å, 200 K].

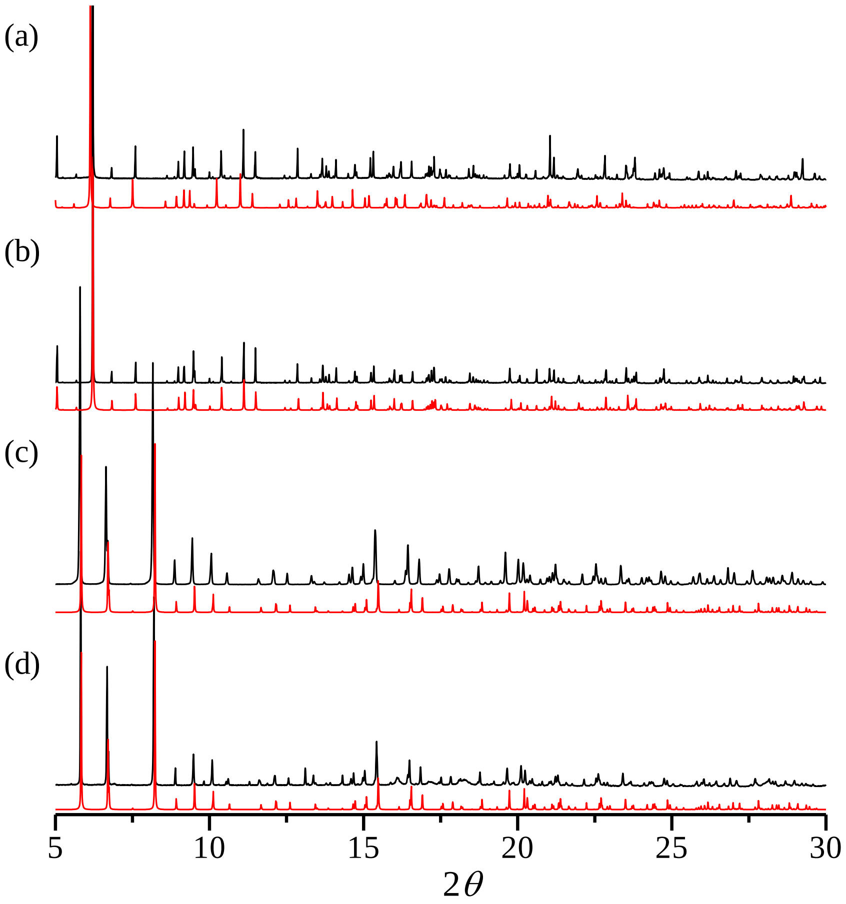

Figure S14. Observed (black) and calculated (red) PXRD patterns of (a) D3-**1**Br, (b) L3-**1**Br, (c) D3L3-**2**Br prepared from the reaction of Na[Co(D-ebp)], Na[Co(L-ebp)], and $CdBr_2$, and (d) D3L3-**2**Br prepared from the reaction of D3-**1**Br, L3-**1**Br, and NaBr. [$\lambda = 1.000$ Å].

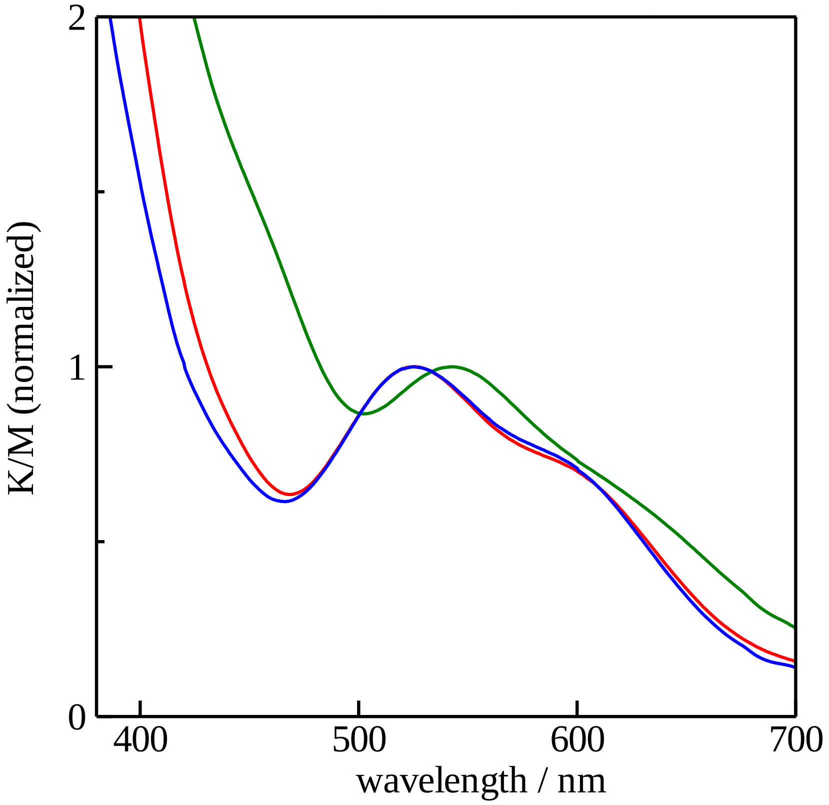

Figure S15. Diffuse reflection spectra of D_3L_3-**2**$_{\mathbf{I}}$ (red), D_2L_3-**3** (green), and D_3L_3-**2**$_{\mathbf{Br}}$ (blue). The reflection intensity was normalized at the absorption band approximately 500-550 nm.

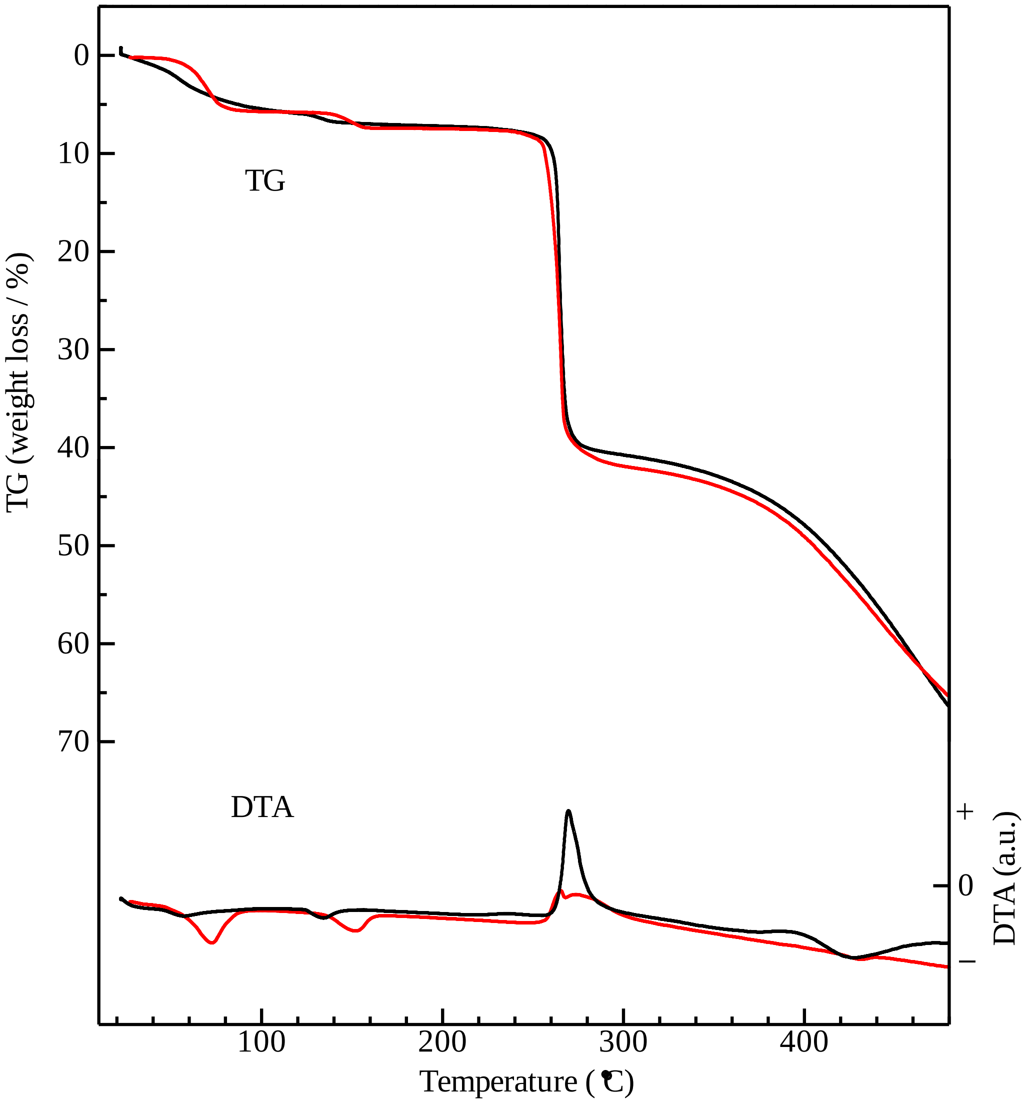

Figure S16. TG/DTA data for D3-**1**I (black) and D3L3-**2**I (red).

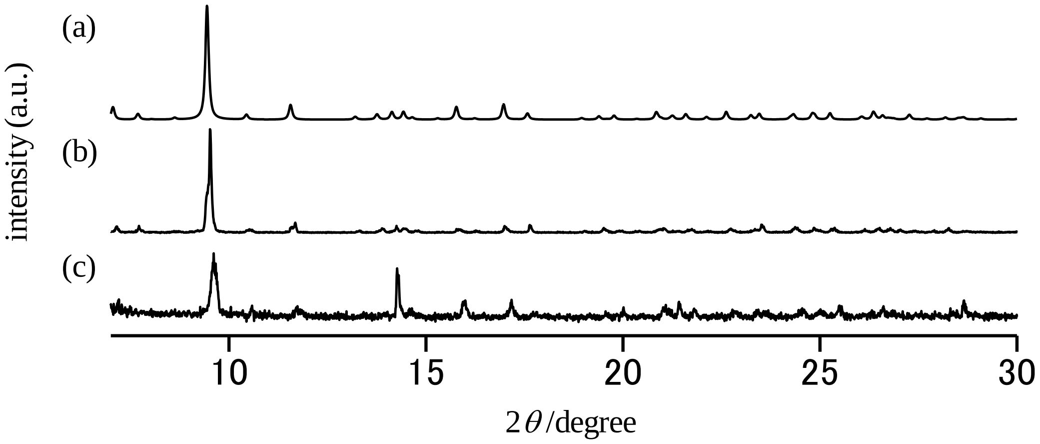

Figure S17. (a) Simulated and (b) observed PXRD patterns of D$_3$-**1**$_\mathrm{I}$ kept at room temperature for more than 1 year and (c) heated at 100 °C for 1 hour [λ = 1.540 Å, room temperature].

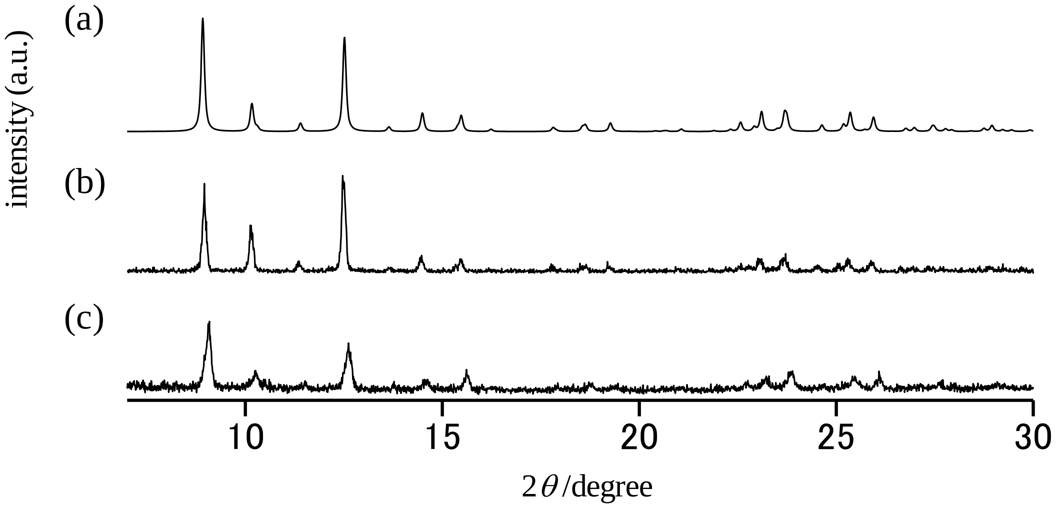

Figure S18. (a) Simulated and (b) observed PXRD patterns of D$_3$L$_3$-**2**$_\mathrm{I}$ kept at room temperature for more than 1 year and (c) heated at 100 °C for 1 hour [λ = 1.540 Å, room temperature].

Table S1. Crystallographic data for D$_3$-**1**$_\mathbf{I}$, L$_3$-**1**$_\mathbf{I}$, and D$_3$L$_3$-**2**$_\mathbf{I}$.

	[Cd$_3${Co(D-ebp)}$_3$I$_3$]·9H$_2$O (D$_3$-**1**$_\mathbf{I}$)	[Cd$_3${Co(L-ebp)}$_3$I$_3$]·9H$_2$O (L$_3$-**1**$_\mathbf{I}$)	[Cd$_6$(H$_2$O)$_6${Co(D-ebp)}$_3${Co(L-ebp)}$_3$I$_6$]·12H$_2$O (D$_3$L$_3$-**2**$_\mathbf{I}$)
Formula	$C_{36}H_{60}Cd_3Co_3I_3N_6O_{21}S_6$	$C_{36}H_{60}Cd_3Co_3I_3N_6O_{21}S_6$	$C_{72}H_{156}Cd_6Co_6I_6N_{12}O_{42}S_{12}$
Colour, form	purple, block	purple, block	purple, hexagonal plate
M	1999.95	1999.95	4036.18
Crystal system	orthorhombic	orthorhombic	trigonal
Space group	$C222_1$	$C222_1$	R-3
a /Å	11.2294(7)	11.2149(7)	34.458(5)
b /Å	25.0427(15)	25.0212(15)	34.458(5)
c /Å	22.9742(16)	22.9649(16)	9.1227(6)
α /°	90	90	90
β /°	90	90	90
γ /°	90	90	120
V /Å^3	6460.7(7)	6444.2(7)	9381(3)
Z	4	4	3
T /K	200(2)	200(2)	200(2)
F(000)	3864	3864	5904
ρ_{calcd} /g cm^{-3}	2.056	2.061	2.143
μ(Mo Kα) /mm^{-1}	3.418	3.427	3.532
Crystal size /mm^3	0.10×0.07×0.02	0.10×0.05×0.03	0.10×0.10×0.03
Limiting indices	$-14 \leq h \leq 14$, $-31 \leq k \leq 32$, $-29 \leq l \leq 29$	$-14 \leq h \leq 12$, $-32 \leq k \leq 32$, $-29 \leq l \leq 29$	$-44 \leq h \leq 44$, $-44 \leq k \leq 44$, $-11 \leq l \leq 11$
R_1[a] (I>2σ(I))	0.036	0.031	0.021
wR_2[b] (all data)	0.081	0.075	0.049
GOF	1.060	1.069	1.140
Flack parameter	0.030(6)	0.011(5)	–
CCDC No.	1879438	1879439	1879440

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

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

Table S2. Crystallographic data for D$_2$L$_2$-**3**.

	$[Cd_2(H_2O)_2\{Co(\text{D-ebp})\}_2\{Co(\text{L-ebp})\}_2]\cdot 8H_2O$ (D$_2$L$_2$-**3**)
Formula	$C_{48}H_{80}Cd_2Co_4N_8O_{26}S_8$
Colour, form	green, block
M	1902.20
Crystal system	monoclinic
Space group	$P2_1/n$
a /Å	14.7082(11)
b /Å	15.4846(12)
c /Å	15.6106(12)
α /°	90
β /°	99.087(7)
γ /°	90
V /Å^3	3510.7(5)
Z	2
T /K	200(2)
F(000)	1928
ρ_{calcd} /g cm^{-3}	1.799
μ(Mo Kα) /mm^{-1}	1.838
Crystal size /mm^3	0.15×0.05×0.03
Limiting indices	$-19 \le h \le 19$, $-20 \le k \le 20$, $-20 \le l \le 19$
R_1^{a} ($I>2\sigma(I)$)	0.059
wR_2^{b} (all data)	0.150
GOF	1.127
CCDC No.	1879441

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

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

Table S3. Crystallographic data for D_3-$\mathbf{1}_{\mathbf{Br}}$, L_3-$\mathbf{1}_{\mathbf{Br}}$, and $\mathrm{D}_3\mathrm{L}_3$-$\mathbf{2}_{\mathbf{Br}}$.

	$[\mathrm{Cd}_3\{\mathrm{Co}(\text{D-ebp})\}_3\mathrm{Br}_3]\cdot 9\mathrm{H}_2\mathrm{O}$ (D_3-$\mathbf{1}_{\mathbf{Br}}$)	$[\mathrm{Cd}_3\{\mathrm{Co}(\text{L-ebp})\}_3\mathrm{Br}_3]\cdot 9\mathrm{H}_2\mathrm{O}$ (L_3-$\mathbf{1}_{\mathbf{Br}}$)	$[\mathrm{Cd}_6(\mathrm{H}_2\mathrm{O})_6\{\mathrm{Co}(\text{D-ebp})\}_3\{\mathrm{Co}(\text{L-ebp})\}_3\mathrm{Br}_6]\cdot 12\mathrm{H}_2\mathrm{O}$ ($\mathrm{D}_3\mathrm{L}_3$-$\mathbf{2}_{\mathbf{Br}}$)
Formula	$\mathrm{C}_{36}\mathrm{H}_{60}\mathrm{Br}_3\mathrm{Cd}_3\mathrm{Co}_3\mathrm{N}_6\mathrm{O}_{21}\mathrm{S}_6$	$\mathrm{C}_{36}\mathrm{H}_{60}\mathrm{Br}_3\mathrm{Cd}_3\mathrm{Co}_3\mathrm{N}_6\mathrm{O}_{21}\mathrm{S}_6$	$\mathrm{C}_{72}\mathrm{H}_{156}\mathrm{Br}_6\mathrm{Cd}_6\mathrm{Co}_6\mathrm{N}_{12}\mathrm{O}_{42}\mathrm{S}_{12}$
Colour, form	purple, block	purple, block	purple, hexagonal plate
M	1858.98	1858.98	3717.95
Crystal system	orthorhombic	orthorhombic	Trigonal
Space group	$C222_1$	$C222_1$	R-3
a /Å	11.0674(9)	11.0409(17)	34.015(13)
b /Å	24.976(2)	24.930(4)	34.015(13)
c /Å	22.7050(18)	22.688(4)	8.9339(18)
α /°	90	90	90
β /°	90	90	90
γ /°	90	90	120
V /Å^3	6276.1(9)	6244.7(17)	8952(7)
Z	4	4	3
T /K	200(2)	200(2)	200(2)
$F(000)$	3648	3648	5472
ρ_{calcd} /g cm^{-3}	1.967	1.977	2.069
$\mu(\text{Mo K}\alpha)$ /mm^{-1}	3.952	3.972	4.156
Crystal size /mm^3	0.20×0.10×0.05	0.10×0.05×0.01	0.10×0.10×0.02
Limiting indices	$-14 \le h \le 14$, $-32 \le k \le 31$, $-29 \le l \le 27$	$-14 \le h \le 14$, $-31 \le k \le 32$, $-29 \le l \le 29$	$-44 \le h \le 38$, $-44 \le k \le 44$, $-10 \le l \le 11$
$R_1{}^{a}$ (I>2σ(I))	0.029	0.060	0.058
$wR_2{}^{b}$ (all data)	0.074	0.100	0.109
GOF	1.046	1.054	1.165
Flack parameter	0.032(5)	0.022(8)	–
CCDC No.	1879442	1879443	1879444

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

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

Table S4. Crystallographic data for [CdCl{Co(D-ebp)}]$_n$ and D$_3$L$_3$-**2**$_{\mathrm{Cl}}$.

	$[Cd_2Cl_2(H_2O)\{Co(\mathrm{D}\text{-}ebp)\}_2]\cdot 14.5H_2O$ ([CdCl{Co(D-ebp)}]$_n$)	$[Cd_6(H_2O)_6\{Co(\mathrm{D}\text{-}ebp)\}_3\{Co(\mathrm{L}\text{-}ebp)\}_3Cl_6]\cdot 12H_2O$ (D$_3$L$_3$-**2**$_{\mathrm{Cl}}$)
Formula	$C_{24}H_{71}Cd_2Cl_2Co_2N_4O_{23.5}S_4$	$C_{72}H_{156}Cd_6Co_6N_{12}O_{42}S_{12}$
Colour, form	purple, block	purple, hexagonal plate
M	1333.64	3717.95
Crystal system	Tetragonal	Trigonal
Space group	$P4_12_12$	R-3
a /Å	17.911(3)	34.015(13)
b /Å	17.911(3)	34.015(13)
c /Å	31.795(3)	8.9339(18)
α /°	90	90
β /°	90	90
γ /°	90	120
V /Å^3	10199(4)	8952(7)
Z	8	3
T /K	200(2)	200(2)
F(000)	5432	5472
ρ_{calcd} /g cm^{-3}	1.737	2.069
μ(Mo Kα) /mm^{-1}	1.806	4.156
Crystal size /mm^3	0.05×0.05×0.02	0.10×0.10×0.02
Limiting indices	$-22 \le h \le 23$, $-23 \le k \le 18$, $-41 \le l \le 41$	$-44 \le h \le 38$, $-44 \le k \le 44$, $-10 \le l \le 11$
R_1[a] ($I > 2\sigma(I)$)	0.045	0.058
wR_2[b] (all data)	0.126	0.109
GOF	1.082	1.165
Flack parameter	0.018(5)	–
CCDC No.	1879445	1879446

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

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