

Supporting Information for

Enantioselective Recognition and Separation of Racemic 1-Phenylethanol by a Pair of 2D Chiral Coordination Polymers

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Experimental Section

General Remarks. 1,4-Bis(imidazol-1-yl-methyl)benzene (bix) was prepared according to the reported method.¹ All of the other chemicals were commercially available and used without further purification. Elemental analyses of C, H and N were determined by Elementar Vario EL elemental analyzer. The IR spectra were recorded in the 4000~400 cm⁻¹ region using KBr pellets and a Bruker EQUINOX 55 spectrometer. The solid state CD spectra were recorded on a J-810 spectropolarimeter (Jasco, Japan). TG analysis was performed on a Netzsch TG 209 instrument under nitrogen atmosphere with a heating rate of 10 °C/min. Chiral high performance liquid chromatography (HPLC) analysis was performed on a Shimadzu LC-20A HPLC system at a UV detection wavelength of 254 nm. Powder X-ray diffraction measurements were performed on D8 ADVANCE X-Ray Diffractometer.

Preparation of Cd(*l*-cps)₂·(H₂O)₆: CdO (3.2 g, 24.9 mmol) was added to a hot solution of (-)-camphor-10-sulfonic acid [H(*l*-cps)] (10.5 g, 45.2 mmol) in water (55

°C), the solution was stirred at 55 °C for 3 h. Then the surplus CdO was filtered off, and the filtrate was concentrated under vacuum until white crystals appeared. The solution was kept at -18 °C for 24 h. The product was obtained as colorless crystals, which were collected by filtration, washed with small amount of methanol, and dried with P₂O₅ for one week. Yield, 1.5 g, 10 % based on H(*l*-cps). Anal. Calcd for CdC₂₀H₄₂O₁₄S₂: C, 35.17; H, 6.20%; Found: C, 35.17; H, 6.11%.

Cd(*d*-cps)₂·(H₂O)₆: This compound was prepared by a similar procedure to that of Cd(*l*-cps)₂·(H₂O)₆ except using (+)-camphor-10-sulfonic acid [H(*d*-cps)] instead of H(*l*-cps). Yield, 2.5 g, 33% based on H(*d*-cps). Anal. Calcd for CdC₂₀H₄₂O₁₄S₂: C, 35.17; H, 6.20%; Found: C, 35.17; H, 6.54%.

{[Cd₂(*l*-cps)₄(bix)₄]·(CH₂Cl₂)₂(EtOH)(H₂O)}_n (*l*-1): A solution of bix (0.107 g, 0.45 mmol) in CH₂Cl₂ (10 mL) was layered with an ethanol solution (8 mL) of Cd(*l*-cps)₂·(H₂O)₆ (0.154 g, 0.225 mmol), with CH₂Cl₂/EtOH (10 mL, 1:1) between two layers. Needle-shaped colorless crystals formed within one week. The crystals were collected by filtration, washed with ether and dried in air. Yield, 0.127 g, 83% based on Cd(*l*-cps)₂·(H₂O)₆. Anal. Calcd for Cd₂C₉₇H₁₁₈O₁₆N₁₆S₄Cl₂ [Cd₂(*l*-cps)₄(bix)₄(CH₂Cl₂)]: N, 10.24; C, 53.25; H, 5.44%; Found: N, 10.14; C, 53.04; H, 5.88%. IR (KBr): 3635 (w), 3395 (br), 3128 (s), 3114 (s), 2957 (vs), 1733 (vs), 1606 (m), 1520 (vs), 1449 (s), 1403 (w), 1363 (w), 1284 (m), 1169 (s), 1107 (m), 1086 (s), 1039 (s), 934 (m), 805 (w), 789 (w), 736 (m), 661 (m) cm⁻¹.

{[Cd₂(*d*-cps)₄(bix)₄]·(CH₂Cl₂)₂(EtOH)(H₂O)}_n (*d*-1): This compound was prepared by a similar procedure to that of *l*-1 except using Cd(*d*-cps)₂·(H₂O)₆ instead

of $\text{Cd}(l\text{-cps})_2 \cdot (\text{H}_2\text{O})_6$. Yield, 0.130 g, 85% based on $\text{Cd}(d\text{-cps})_2 \cdot (\text{H}_2\text{O})_6$. Anal. Calcd for $\text{Cd}_2\text{C}_{97}\text{H}_{118}\text{O}_{16}\text{N}_{16}\text{S}_4\text{Cl}_2$ [$\text{Cd}_2(d\text{-cps})_4(\text{bix})_4(\text{CH}_2\text{Cl}_2)$]: N, 10.24; C, 53.25; H, 5.44%; Found: N, 10.16; C, 53.01; H, 5.716%. IR (KBr): 3635 (w), 3394 (br), 3128 (s), 3115 (s), 2957 (vs), 1734 (vs), 1606 (m), 1520 (vs), 1449 (s), 1403 (w), 1363 (w), 1284 (m), 1168 (s), 1107 (m), 1087 (s), 1039 (s), 934 (m), 805 (m), 789 (w), 763 (m), 660 (m) cm^{-1} .

$\{[\text{Cd}_2(l\text{-cps})_4(\text{bix})_4] \cdot (\text{PEA})_4\}_n$ (*l*-2): *l*-1 (15 mg) was dissolved in a mixture of CHCl_3 and racemic 1-phenylethanol (PEA, 5.2 mL, 1:1) under heating (40 °C). The resulting solution was evaporated slowly at room temperature. Colorless block-shaped crystals were obtained after one week. Yield, 6.2 mg, 40% based on *l*-1. Anal. Calcd for $\text{Cd}_2\text{C}_{112}\text{H}_{132}\text{N}_{16}\text{O}_{18}\text{S}_4$: N, 9.56; C, 57.40; H, 5.68%; Found: N, 9.56; C, 57.35; H, 5.87%. IR (KBr): 3635 (w), 3395 (br), 3128 (m), 2957 (s), 1945 (w), 1734 (vs), 1606 (w), 1521 (s), 1449 (s), 1403 (w), 1363 (w), 1284 (m), 1168 (s), 1107 (s), 1087 (s), 1039 (s), 934 (m), 825 (w), 789 (w), 737(m), 661 (m), 619 (m) cm^{-1} .

$\{[\text{Cd}_2(d\text{-cps})_4(\text{bix})_4] \cdot (\text{PEA})_4\}_n$ (*d*-2): This compound was prepared by a similar procedure to that of *l*-2 except using *d*-1 instead of *l*-1. Yield, 5.9 mg, 37% based on *d*-1. Anal. Calcd for $\text{Cd}_2\text{C}_{112}\text{H}_{132}\text{O}_{18}\text{S}_4$: N, 9.56; C, 57.40; H, 5.68%; Found: N, 9.59; C, 56.94; H, 5.91%. IR (KBr): 3635 (w), 3393 (br), 3128 (m), 2957 (s), 1945 (w), 1734 (vs), 1606 (w), 1520 (s), 1449 (s), 1403(w), 1363 (w), 1284 (m), 1169 (s), 1108 (s), 1087 (s), 1039 (s), 935 (m), 825 (w), 789 (w), 737 (m), 661 (m), 618 (m) cm^{-1} .

X-Ray Crystallography. The single-crystal data for $\text{Cd}(l\text{-cps})_2 \cdot 6\text{H}_2\text{O}$, *l*-1, *d*-1, *l*-2, *d*-2 were collected on Agilent Technologies Gemini A Ultra system, with $\text{Cu}/\text{K}\alpha$

radiation ($\lambda = 1.54178 \text{ \AA}$). All empirical absorption corrections were applied using the SCALE3 ABSPACK program.² The structures were solved by direct method and refined by full-matrix least-squares analysis on F^2 using the SHELX97 program package. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs.³ In *l*-**1** and *d*-**1**, highly disordered ethanol and lattice water molecules were restrained using DFIX, SADI, ISOR instructions. One of imidazol ring of bix ligand and cps^- anion bonded to Cd2 in *l*-**2** and *d*-**2** exhibit orientational disorder over two sets of positions, resulting in the disordered PEA bonded to disordered cps^- anion. Fortunately, two structures of *l*-**2** and *d*-**2** can be satisfactorily modeled with the positional disorder and were treated with FVAR, and the disordered components have been refined with corresponding occupancies (0.603(5) and 0.397(5) for *l*-**2**, and 0.621(6) and 0.379(6) for *d*-**2**). All of the disordered parts were restrained using FLAT, DFIX, SADI, ISOR, DELU, and SIMU instructions to make the displacement parameters more reasonable. Crystallographic data and details of refinements are listed in Table S1, and selected bond distances and angles for are listed in Table S2.

Table S1 Crystal Data and Structural Refinements for Cd(*l*-cps)₂·6H₂O, *l*-1, *l*-2, *d*-1 and *d*-2

	Cd(<i>l</i> -cps) ₂ ·6H ₂ O	<i>l</i> -1	<i>l</i> -2
Formula	C ₂₀ H ₄₂ O ₁₄ S ₂ Cd	C ₁₀₀ H ₁₂₈ N ₁₆ O ₁₈ S ₄ Cl ₄ Cd ₂	C ₁₂₈ H ₁₅₆ N ₁₆ O ₂₀ S ₄ Cd ₂
Fw.	683.06	2337.02	2591.73
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	11.6515(3)	10.3574(2)	10.6881(4)
<i>b</i> (Å)	7.1578(2)	14.2352(2)	18.3271(7)
<i>c</i> (Å)	17.3543(4)	19.0283(3)	18.4365(9)
α (°)	90	93.0020(10)	63.639(4)
β (°)	94.349(2)	98.9740(10)	88.776(3)
γ (°)	90	107.7390(10)	83.366(3)
<i>V</i> (Å ³)	1443.17(6)	2624.50(8)	3212.4(2)
<i>Z</i>	2	1	1
<i>D</i> _c (g·cm ⁻³)	1.572	1.479	1.340
Reflections	6120	69350	25410
/ unique	3470	17092	13061
<i>R</i> _{int}	0.0482	0.1044	0.0375
GOF on <i>F</i> ²	1.014	1.019	1.045
<i>R</i> ₁ [[<i>I</i> > 2σ (<i>I</i>)] ^a	0.0406,	0.0531	0.0771
<i>wR</i> ₂ [[<i>I</i> > 2σ (<i>I</i>)] ^a	0.0928	0.1392	0.2012
flack parameter	0.003(11)	0.027(5)	0.028(14)
	<i>d</i> -1	<i>d</i> -2	
Formula	C ₁₀₀ H ₁₂₈ N ₁₆ O ₁₈ S ₄ Cl ₄ Cd ₂	C ₁₂₈ H ₁₅₆ N ₁₆ O ₂₀ S ₄ Cd ₂	
Fw.	2337.02	2591.73	
Crystal system	Triclinic	Triclinic	
Space group	<i>P</i> 1	<i>P</i> 1	
<i>a</i> (Å)	10.3479(2)	10.7036(3)	
<i>b</i> (Å)	14.2287(2)	18.3229(4)	
<i>c</i> (Å)	19.0288(2)	18.4237(5)	

α (°)	93.0720(10)	63.578(2)
β (°)	98.9160(10)	88.824(2)
γ (°)	107.7140(10)	83.348(2)
V (Å ³)	2621.50(7)	3212.10(14)
Z	1	1
D_c (g·cm ⁻³)	1.480	1.340
Reflections	70895	58203
/ unique	18104	20024
R_{int}	0.0874	0.0690
GOF on F^2	1.020	1.028
R_1 [$I > 2\sigma(I)$] ^a	0.0477	0.0823
wR_2 [$I > 2\sigma(I)$] ^a	0.1244	0.2132
flack parameter	0.015(4)	0.068(12)

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

Table S2 Selected bond distances (Å) and angles (°)

Cd(<i>l</i>-cps)₂·6H₂O					
Cd(1)-O(5W)	2.247(4)	Cd(1)-O(6W)	2.264(4)	Cd(1)-O(2W)	2.268(7)
Cd(1)-O(3W)	2.276(7)	Cd(1)-O(1W)	2.278(6)	Cd(1)-O(4W)	2.298(7)
O(5W)-Cd(1)-O(6W)	176.83(19)	O(5W)-Cd(1)-O(2W)	91.5(3)	O(6W)-Cd(1)-O(2W)	87.4(3)
O(5W)-Cd(1)-O(3W)	89.4(2)	O(6W)-Cd(1)-O(3W)	93.3(3)	O(2W)-Cd(1)-O(3W)	82.0(3)
O(5W)-Cd(1)-O(1W)	90.2(2)	O(6W)-Cd(1)-O(1W)	87.0(2)	O(2W)-Cd(1)-O(1W)	96.83(13)
O(3W)-Cd(1)-O(1W)	178.7(3)	O(5W)-Cd(1)-O(4W)	86.1(3)	O(6W)-Cd(1)-O(4W)	95.1(3)
O(2W)-Cd(1)-O(4W)	177.3(3)	O(3W)-Cd(1)-O(4W)	96.87(13)	O(1W)-Cd(1)-O(4W)	84.3(3)
<i>l</i>-1					
Cd(1)-N(13)	2.302(5)	Cd(1)-N(9)	2.305(5)	Cd(1)-N(1)	2.308(5)
Cd(1)-N(5)	2.340(5)	Cd(1)-O(1)	2.389(4)	Cd(1)-O(5)	2.403(4)
Cd(2)-N(3)	2.296(5)	Cd(2)-N(11)#1	2.311(5)	Cd(2)-N(7)#2	2.312(5)
Cd(2)-N(15)#3	2.326(5)	Cd(2)-O(13)	2.374(4)	Cd(2)-O(9)	2.428(4)
N(13)-Cd(1)-N(9)	178.74(18)	N(13)-Cd(1)-N(1)	94.66(17)	N(9)-Cd(1)-N(1)	86.57(17)
N(13)-Cd(1)-N(5)	83.76(17)	N(9)-Cd(1)-N(5)	95.03(17)	N(1)-Cd(1)-N(5)	176.40(19)
N(13)-Cd(1)-O(1)	91.48(16)	N(9)-Cd(1)-O(1)	88.33(16)	N(1)-Cd(1)-O(1)	87.34(16)
N(5)-Cd(1)-O(1)	95.92(16)	N(13)-Cd(1)-O(5)	92.99(16)	N(9)-Cd(1)-O(5)	87.38(16)
N(1)-Cd(1)-O(5)	83.68(17)	N(5)-Cd(1)-O(5)	93.17(17)	O(1)-Cd(1)-O(5)	170.26(16)
N(3)-Cd(2)-N(11)#1	96.25(17)	N(3)-Cd(2)-N(7)#2	174.00(19)	N(11)#1-Cd(2)-N(7)#2	84.87(17)

N(3)-Cd(2)-N(15)#3	85.89(17)	N(11)#1-Cd(2)-N(15)#3	177.67(19)	N(7)#2-Cd(2)-N(15)#3	92.91(17)
N(3)-Cd(2)-O(13)	83.50(17)	N(11)#1-Cd(2)-O(13)	83.00(16)	N(7)#2-Cd(2)-O(13)	90.79(17)
N(15)#3-Cd(2)-O(13)	96.36(16)	N(3)-Cd(2)-O(9)	84.30(16)	N(11)#1-Cd(2)-O(9)	87.48(16)
N(7)#2-Cd(2)-O(9)	101.65(16)	N(15)#3-Cd(2)-O(9)	93.65(16)	O(13)-Cd(2)-O(9)	163.60(15)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z+1; #2 x,y,z+1; #3 x-1,y,z

l-2

Cd(1)-N(13)	2.282(10)	Cd(1)-N(1)	2.285(9)	Cd(1)-N(9)	2.288(11)
Cd(1)-N(5)	2.316(13)	Cd(1)-O(1)	2.391(8)	Cd(1)-O(5)	2.420(9)
Cd(2)-N(11)#2	2.299(10)	Cd(2)-N(15)#3	2.307(10)	Cd(2)-N(7')#4	2.362(6)
Cd(2)-N(7)#4	2.362(6)	Cd(2)-O(9)	2.369(10)		
N(13)-Cd(1)-N(1)	83.4(4)	N(13)-Cd(1)-N(9)	179.2(4)	N(1)-Cd(1)-N(9)	95.9(4)
N(13)-Cd(1)-N(5)	95.4(4)	N(1)-Cd(1)-N(5)	178.2(5)	N(9)-Cd(1)-N(5)	85.3(4)
N(13)-Cd(1)-O(1)	92.3(3)	N(1)-Cd(1)-O(1)	86.8(4)	N(9)-Cd(1)-O(1)	88.1(4)
N(5)-Cd(1)-O(1)	91.9(4)	N(13)-Cd(1)-O(5)	86.7(4)	N(1)-Cd(1)-O(5)	91.8(4)
N(9)-Cd(1)-O(5)	92.8(4)	N(5)-Cd(1)-O(5)	89.5(4)	O(1)-Cd(1)-O(5)	178.4(5)
N(3)-Cd(2)-N(11)#2	88.5(4)	N(3)-Cd(2)-N(15)#3	91.4(4)	N(11)#2-Cd(2)-N(15)#3	178.4(4)
N(3)-Cd(2)-N(7')#4	173.4(4)	N(11)#2-Cd(2)-N(7')#4	95.5(3)	N(15)#3-Cd(2)-N(7')#4	84.8(4)
N(3)-Cd(2)-N(7)#4	173.4(4)	N(11)#2-Cd(2)-N(7)#4	95.5(3)	N(15)#3-Cd(2)-N(7)#4	84.8(4)
N(7')#4-Cd(2)-N(7)#4	0.0(6)	N(3)-Cd(2)-O(9)	83.9(4)	N(11)#2-Cd(2)-O(9)	94.2(4)
N(15)#3-Cd(2)-O(9)	87.4(4)	N(7')#4-Cd(2)-O(9)	90.6(4)	N(7)#4-Cd(2)-O(9)	90.6(4)
N(3)-Cd(2)-O(13')	89.8(4)	N(11)#2-Cd(2)-O(13')	94.4(5)	N(15)#3-Cd(2)-O(13')	83.9(5)
N(7')#4-Cd(2)-O(13')	95.1(4)	N(7)#4-Cd(2)-O(13')	95.1(4)	O(9)-Cd(2)-O(13')	169.1(6)
N(3)-Cd(2)-O(13)	104.7(3)	N(11)#2-Cd(2)-O(13)	88.6(3)	N(15)#3-Cd(2)-O(13)	89.8(4)
N(7')#4-Cd(2)-O(13)	80.7(3)	N(7)#4-Cd(2)-O(13)	80.7(3)	O(9)-Cd(2)-O(13)	171.0(4)
O(13')-Cd(2)-O(13)	16.1(4)				

Symmetry transformations used to generate equivalent atoms:

#2 x-1,y,z; #3 x+1,y-1,z; #4 x,y-1,z

d-1

Cd(1)-N(13)	2.302(4)	Cd(1)-N(1)	2.306(5)	Cd(1)-N(9)	2.307(4)
Cd(1)-N(5)	2.333(5)	Cd(1)-O(1)	2.388(4)	Cd(1)-O(5)	2.412(4)
Cd(2)-N(3)	2.295(5)	Cd(2)-N(7)#1	2.311(5)	Cd(2)-N(11)#2	2.319(4)
Cd(2)-N(15)#3	2.324(4)	Cd(2)-O(13)	2.380(4)	Cd(2)-O(9)	2.423(3)
N(13)-Cd(1)-N(1)	94.39(16)	N(13)-Cd(1)-N(9)	178.89(17)	N(1)-Cd(1)-N(9)	86.68(16)
N(13)-Cd(1)-N(5)	83.84(16)	N(1)-Cd(1)-N(5)	176.39(18)	N(9)-Cd(1)-N(5)	95.11(16)
N(13)-Cd(1)-O(1)	91.52(15)	N(1)-Cd(1)-O(1)	87.27(15)	N(9)-Cd(1)-O(1)	88.23(15)
N(5)-Cd(1)-O(1)	95.92(16)	N(13)-Cd(1)-O(5)	93.10(14)	N(1)-Cd(1)-O(5)	83.53(15)
N(9)-Cd(1)-O(5)	87.32(14)	N(5)-Cd(1)-O(5)	93.41(16)	O(1)-Cd(1)-O(5)	169.99(14)
N(3)-Cd(2)-N(7)#1	174.21(18)	N(3)-Cd(2)-N(11)#2	96.47(15)	N(7)#1-Cd(2)-N(11)#2	84.81(15)
N(3)-Cd(2)-N(15)#3	85.82(16)	N(7)#1-Cd(2)-N(15)#3	92.83(16)	N(11)#2-Cd(2)-N(15)#3	177.58(17)
N(3)-Cd(2)-O(13)	83.62(15)	N(7)#1-Cd(2)-O(13)	90.95(15)	N(11)#2-Cd(2)-O(13)	83.12(15)
N(15)#3-Cd(2)-O(13)	96.40(15)	N(3)-Cd(2)-O(9)	83.89(15)	N(7)#1-Cd(2)-O(9)	101.83(15)
N(11)#2-Cd(2)-O(9)	87.34(14)	N(15)#3-Cd(2)-O(9)	93.68(14)	O(13)-Cd(2)-O(9)	163.31(13)

Symmetry transformations used to generate equivalent atoms:

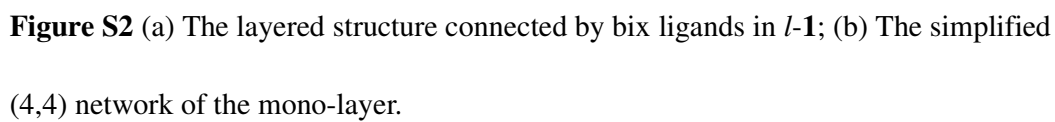
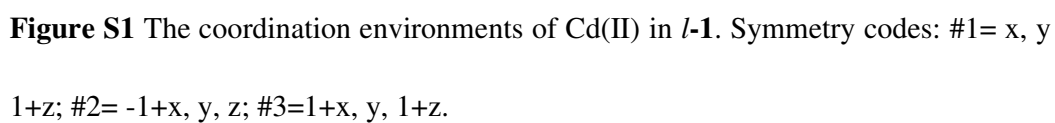
#1 x,y,z-1; #2 x-1,y,z-1; #3 x+1,y,z; #4 x,y,z+1; #5 x+1,y,z+1; #6 x-1,y,z

d-2

Cd(1)-N(9)	2.279(9)	Cd(1)-N(13)	2.282(8)	Cd(1)-N(1)	2.294(8)
Cd(1)-N(5)	2.309(11)	Cd(1)-O(5)	2.408(8)	Cd(1)-O(1)	2.408(7)
Cd(2)-N(11)#2	2.292(8)	Cd(2)-N(15)#3	2.306(9)	Cd(2)-N(7')#4	2.350(5)
Cd(2)-N(7)#4	2.350(5)	Cd(2)-O(9)	2.376(8)	N(9)-Cd(1)-N(13)	178.9(4)
N(9)-Cd(1)-N(1)	95.8(3)	N(13)-Cd(1)-N(1)	83.2(3)	N(9)-Cd(1)-N(5)	85.5(3)
N(13)-Cd(1)-N(5)	95.5(4)	N(1)-Cd(1)-N(5)	178.7(4)	N(9)-Cd(1)-O(5)	93.8(3)
N(13)-Cd(1)-O(5)	86.6(3)	N(1)-Cd(1)-O(5)	91.3(3)	N(5)-Cd(1)-O(5)	88.8(4)
N(9)-Cd(1)-O(1)	87.7(3)	N(13)-Cd(1)-O(1)	92.0(3)	N(1)-Cd(1)-O(1)	87.4(3)
N(5)-Cd(1)-O(1)	92.4(4)	O(5)-Cd(1)-O(1)	178.2(4)	N(3)-Cd(2)-N(11)#2	87.8(3)
N(3)-Cd(2)-N(15)#3	91.4(3)	N(11)#2-Cd(2)-N(15)#3	178.0(4)	N(3)-Cd(2)-N(7')#4	174.4(3)
N(11)#2-Cd(2)-N(7')#4	96.3(3)	N(15)#3-Cd(2)-N(7')#4	84.6(3)	N(3)-Cd(2)-N(7)#4	174.4(3)
N(11)#2-Cd(2)-N(7)#4	96.3(3)	N(15)#3-Cd(2)-N(7)#4	84.6(3)	N(7')#4-Cd(2)-N(7)#4	0.00(9)
N(3)-Cd(2)-O(9)	84.5(4)	N(11)#2-Cd(2)-O(9)	93.8(3)	N(15)#3-Cd(2)-O(9)	87.9(3)
N(7')#4-Cd(2)-O(9)	91.4(3)	N(7)#4-Cd(2)-O(9)	91.4(3)	N(3)-Cd(2)-O(13')	88.4(4)
N(11)#2-Cd(2)-O(13')	93.6(4)	N(15)#3-Cd(2)-O(13')	84.6(4)	N(7')#4-Cd(2)-O(13')	95.2(3)
N(7)#4-Cd(2)-O(13')	95.2(3)	O(9)-Cd(2)-O(13')	169.5(5)	N(3)-Cd(2)-O(13)	103.5(3)
N(11)#2-Cd(2)-O(13)	88.2(3)	N(15)#3-Cd(2)-O(13)	90.2(3)	N(7')#4-Cd(2)-O(13)	80.5(3)
N(7)#4-Cd(2)-O(13)	80.5(3)	O(9)-Cd(2)-O(13)	171.9(3)	O(13')-Cd(2)-O(13)	16.3(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z; #2 x+1,y,z; #3 x-1,y+1,z; #4 x,y+1,z; #5 x-1,y,z; #6 x+1,y-1,z



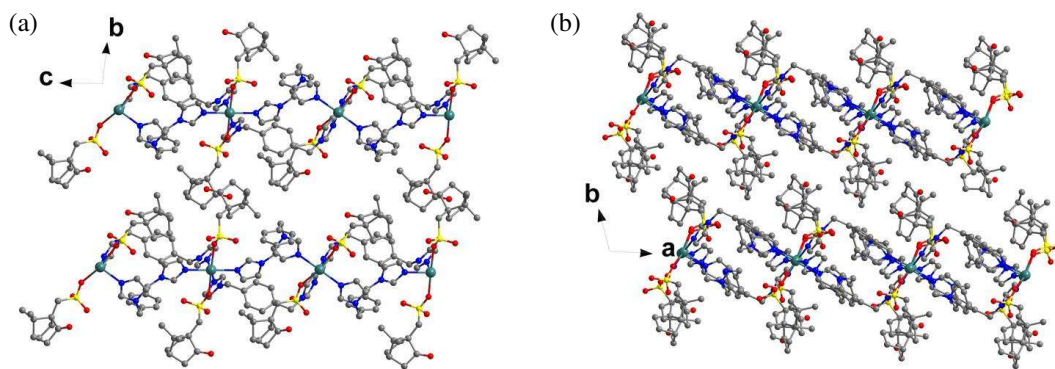


Figure S3 The 3D structures of *l*-1 viewing along the *bc* (a) and *ab* planes (b).

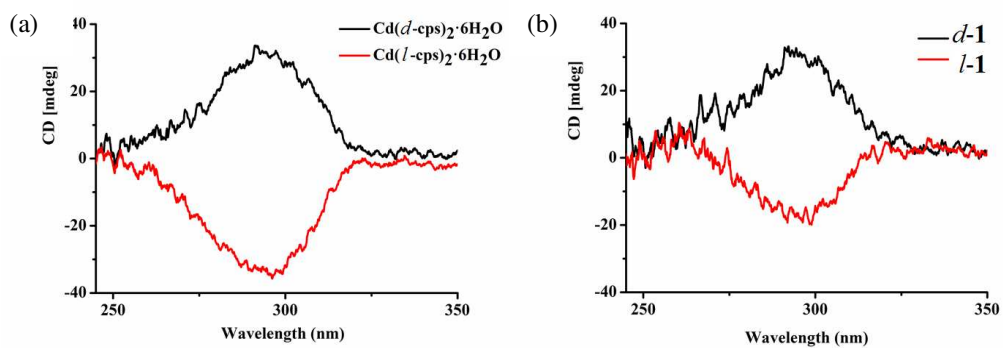


Figure S4. The solid CD spectra of (a) $\text{Cd}(l\text{-cps})_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(d\text{-cps})_2 \cdot 6\text{H}_2\text{O}$, and (b) *l*-1 / *d*-1.

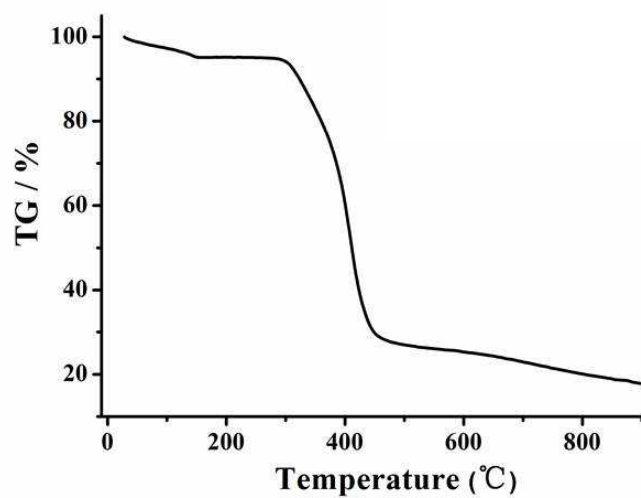


Figure S5. The TGA curve for *l*-1.

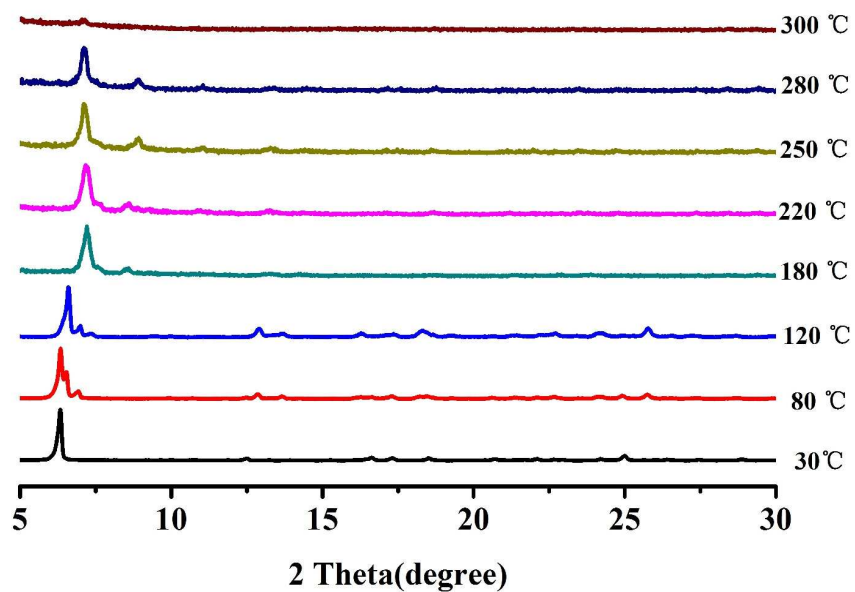


Figure S6. Variable-temperature PXRD for *l*-1. The position of the peak at 6.7° moved to higher degree with the increase of temperature.

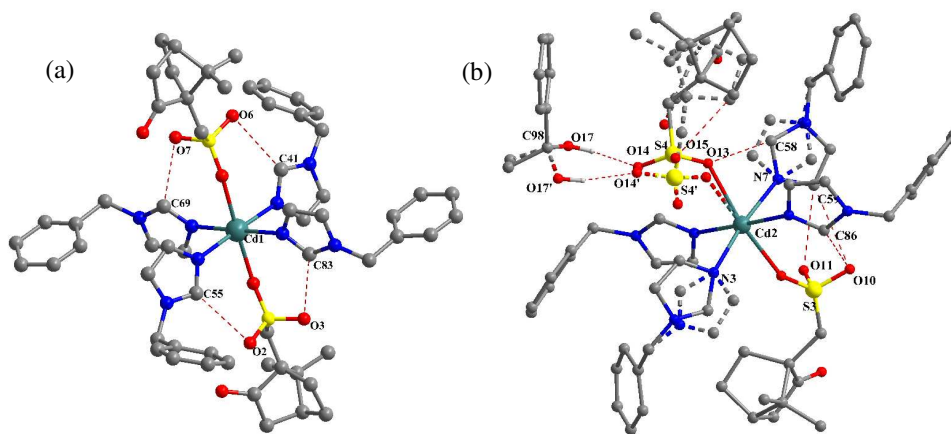


Figure S7 The ordered (a) and disordered (b) *l*-cps[−] anions in *l*-2 (the disordered parts are drawn as dotted lines).

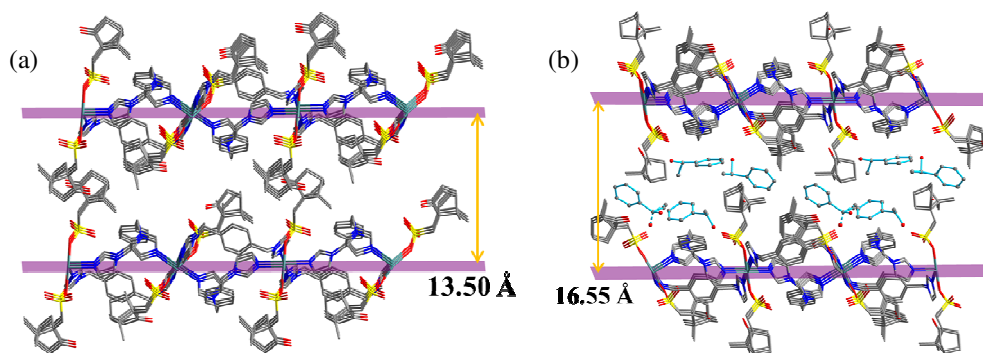


Figure S8 The structures of *l*-1 (left) and *l*-2 (right), showing that the distance between the adjacent layers is extended from 13.50 Å in *l*-1 to 16.55 Å in *l*-2 due to inserting PEA molecules within the interlayer.

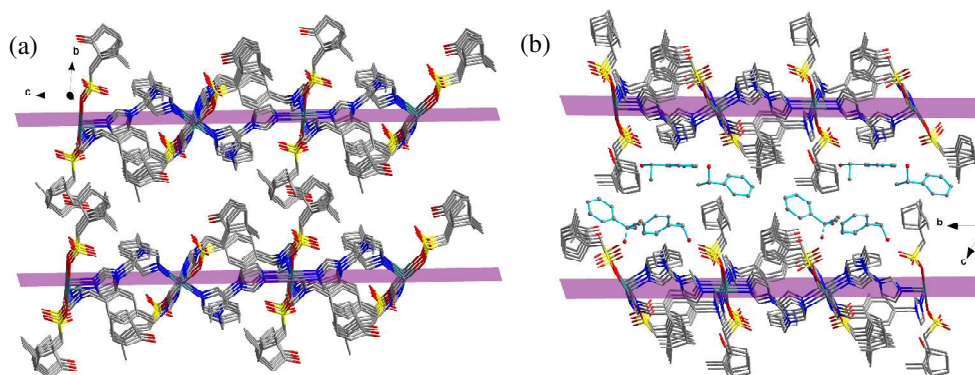
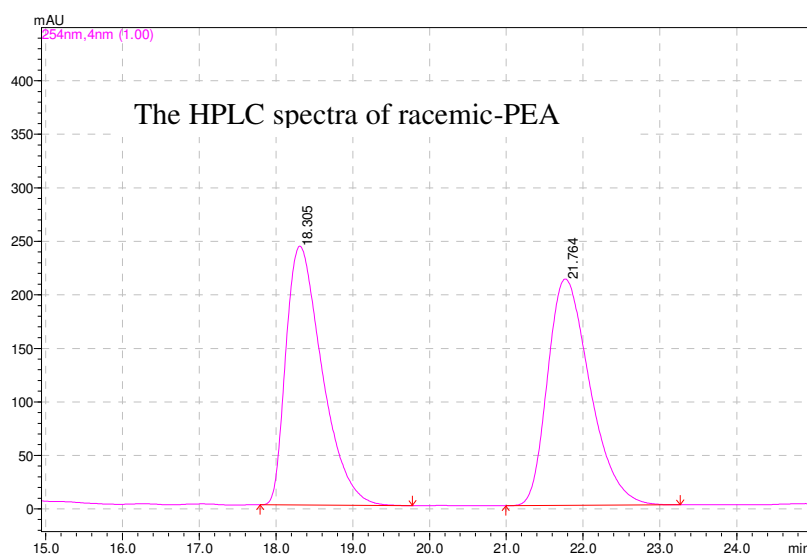


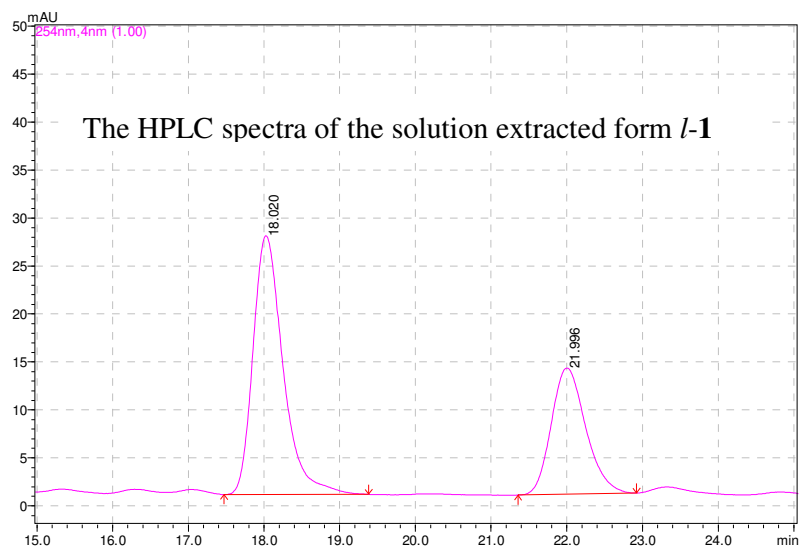
Figure S9 The structures of *d*-1 (a) and *d*-2 (b).

General Method for Chiral HPLC Analysis: Racemic 1-phenylethanol (PEA, 1 mL) or 1-phenylpropan-1-ol (PPA, 1 mL) was added to a suspension of *l*-1/*d*-1 (50 mg) in chloroform (1mL). The resulting mixture was sealed at -18 °C for one week. The solid was filtered by the filter paper, and the residual solvent on the solid surface was adsorbed with filter paper for several times, and dried in the air. The included guest molecules in the solid can be readily extracted by chloroform. The contents of *R*- and

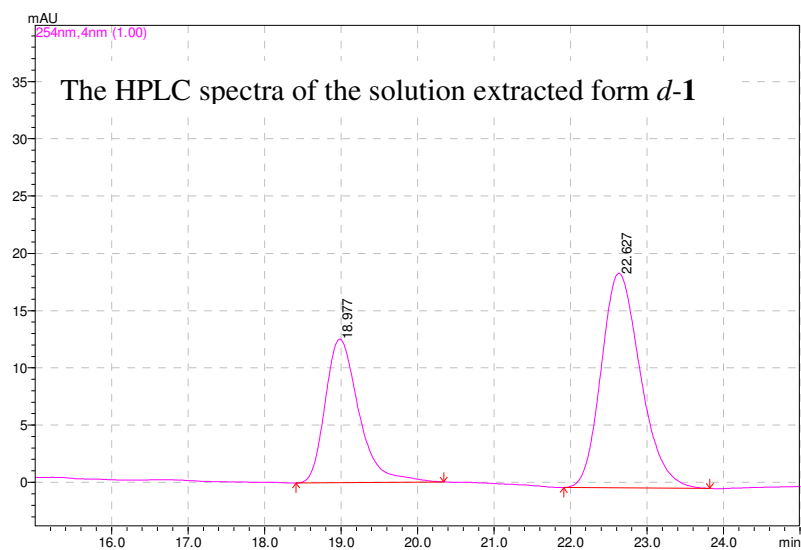
S-enantiomers were determined by chiral HPLC, using Lux Cellulose-1 chiral columns (250 × 4.6 mm, Phenomenex), and a hexane/2-propanol (95:5 for PEA, and 98:2 for PPA, v/v) mixture as the mobile phase, with a flow rate of 0.5 mL/min and a column temperature of 20 °C.



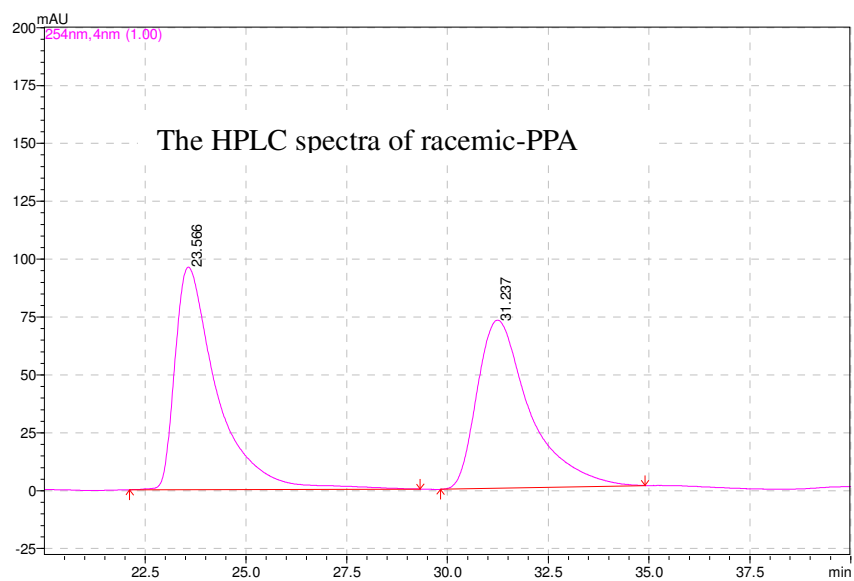
No.	Retention time, min	Area	Area%
1	18.305	7944920.2	49.48
2	21.764	8113271.7	50.52
	Totals	16058191.9	100.00



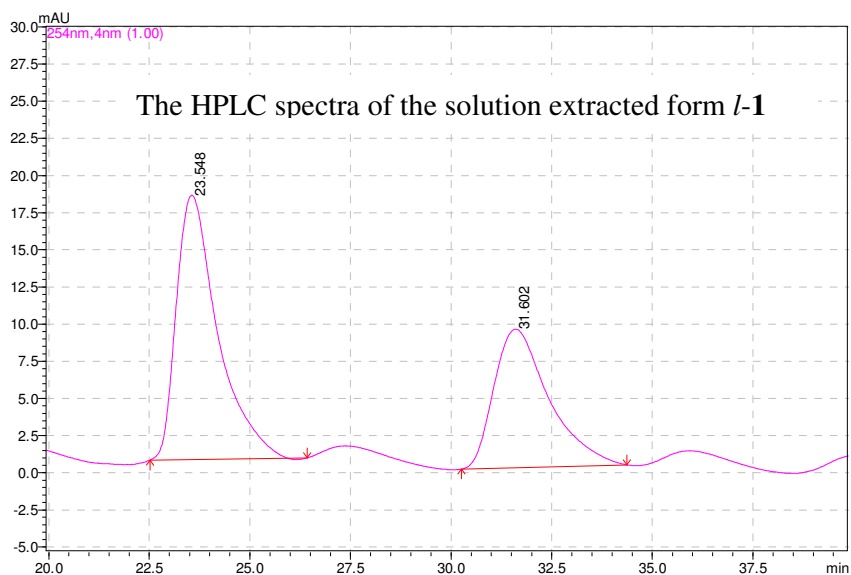
No.	Retention time, min	Area	Area%
1	18.020	743737.3	64.09
2	21.996	416675.9	35.91
	Totals	1160413.2	100.00



No.	Retention time, min	Area	Area%
1	18.977	383009.2	36.41
2	22.627	668965.6	63.59
	Totals	1051974.8	100.00



No.	Retention time, min	Area	Area%
1	23.566	6961430.8	51.40
2	31.237	6583120.1	48.60
	Totals	13544550.9	100.00



No.	Retention time, min	Area	Area%
1	23.548	1270782.2	58.96
2	31.602	884655.0	41.04
	Totals	2155437.2	100.00

Reference:

1. B. F. Hoskins, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.*, 1997, **119**, 2952.
2. G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, 1996.
3. G. M. Sheldrick, SHELXS 97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, 1997.