Electronic Supplemental Information

Homochiral porous coordination polymer of Eu^{III} for metal ion sensing

and enantioselective adsorption

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1. Materials and methods.

1.1. General methods

All the reagents were of analytical grade and obtained from commercial sources without further purification. Enantiopure ligand (S)-5-(((1-carboxy-3methylbutyl)amino)methyl)-isophthalic acid (H_{3L}) was prepared according to our reported procedure.¹ IR spectrum (KBr pellet) was recorded in the range 400–4000 cm⁻¹ on a Nicolet NEXUS 470 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was performed on a STA 409 PC thermal analyzer under air using a heat rate of 5 °C·min⁻¹. X-ray diffraction (PXRD) patterns were recorded on a RIGAKU-DMAX2500 X-ray diffractometer with Cu-Ka radiation. The luminescence spectra for the solid and suspension samples were determined at room temperature on a Hitachi F-4500 fluorophotometer with a xenon arc lamp as light source. Solid-state circular dichroism (CD) spectrum (KBr pellet) was recorded at room temperature on a MOS-450 spectrometer. Electronic absorption spectra were recorded on a Unico-2102 UV-Vis spectrometer.

1.2. Synthesis of crystals 1

A mixture of H_3L (7.7 mg, 0.025 mmol), EuCl₃·6H₂O (9.2 mg, 0.025 mmol), CH₃CN (2 mL) and deionized H_2O (0.5 mL) was stirred for 30 min at room temperature, and then was sealed into a 25 mL Teflon-lined stainless autoclave. The autoclave was heated at 120 °C for 72 h. After the mixture was cooled to room temperature at a rate of 5 °C·h⁻¹, colourless prismatic crystals of {[Eu₂(HL)₂(H₂O)₆]2Cl·2H₂O}·*n*(solvent) (1) were obtained, washed with distilled water and dried in air, resulting in 50% yield (14.6 mg). The synthesis of 1 was repeated several times in order to collect sufficient amounts of material. IR (KBr, cm⁻¹): 416 (s), 2957 (w), 1661 (w), 1607 (s), 1450 (m), 1386 (s), 1346 (s), 775 (m), 708 (s).

2. Characterization

2.1. Solid-state circular dichroism spectrum



Fig. S1 solid-state circular dichroism spectrum of 1.

2.2 Single crystal X-ray diffraction

Single-crystal data of **1** were collected on a RIGAKU SUPERNOVA CCD diffractometer with a graphite crystal and incident beam monochromator at 173 K using Mo-K*a* radiation ($\lambda = 0.71073$ Å). Raw data collection and reduction were done using CrysAlisPro.² Empirical absorption correction was performed using spherical harmonics, implemented in a SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods and intrinsic phasing, and then refined on F^2 full-matrix least-squares using the Olex2 and SHELXTL program packages.^{3–5} Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. The H atoms attached to C were generated geometrically while the H atoms attached to O and N were located from different Fourier maps and treated as idealized contributions. For structure of **1**, highly disordered solvent molecules are present, the SQUEEZE command has been employed to account for the corresponding electron density.⁶ Crystal data and structure refinement for **1** are listed in Table S1, and selected bond lengths and angles are listed in Table S2. CCDC 2092762 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

1				
formula	$C_{30}H_{50}Cl_2Eu_2N_2O_{20}$			
М	1133.54			
Т (К)	173(2)			
Crystal system	Trigonal			
Space group	P321			
<i>a</i> (Å)	19.4078(10)			
<i>b</i> (Å)	19.4078(10)			
<i>c</i> (Å)	23.1536(2) 90 90			
<i>α/</i> °				
<i>6/</i> °				
<i>γ/</i> °	120			
V (ų)	7552.69(10)			
Z	6			
D _c (g cm ⁻³)	1.495			
Goodness of fit (GOF)	1.072			
Flack parameter	0.05(2)			
R_1 , w R_2 (I>2 σ (I))	0.0295, 0.0680			
Largest difference in peak and hole	1.119, -0.716			

Table S1 Crystal data and structure refinement for 1

Table S2 Selected bond lengths (Å) and angles (°) for 1.

	1		
Eu1–O3A	2.321(6)	01–Eu1–O18	141.0(3)
Eu1–O1	2.322(7)	O4B-Eu1-O18	75.0(3)

Eu1–O4B	2.371(7)	371(7) O3A–Eu1–O2C	
Eu1-018	2.385(7)	01–Eu1–O2C	77.1(3)
Eu1–O2C	2.391(7)	O4B-Eu1-O2C	131.4(3)
Eu1-07	2.418(8)	018–Eu1–O2C	141.5(3)
Eu108	2.528(7)	03A-Eu1-07	142.9(3)
Eu109	2.528(7)	01-Eu1-07	77.5(3)
Eu1-Eu1C	4.3209(8)	04BEu107	138.7(3)
Eu2-015C	2.330(6)	018-Eu1-07	103.9(3)
Eu2-013	2.334(6)	02C-Eu1-07	74.8(3)
Eu2–016E	2.350(6)	O3A-Eu1-O8	142.8(3)
Eu2–O14F	2.376(6)	01–Eu1–O8	74.6(3)
Eu2-011	2.378(6)	01–Eu1–O18	141.0(3)
Eu206	2.402(6)	O4B-Eu1-O18	75.0(3)
Eu2-012	2.527(6)	O3A-Eu1-O2C	78.6(3)
Eu2010	2.534(5)	01–Eu1–O2C	77.1(3)
O4B-Eu1-O8	71.6(3)	015D-Eu2-013	119.8(3)
O18–Eu1-O8	69.9(3)	015D-Eu2-016E	77.3(3)
O2C-Eu1-O8	138.3(3)	013–Eu2–O16E	78.9(3)
07–Eu1–O8	69.6(3)	O15D-Eu2-O14F	78.5(2)

O3A-Eu1-O9	74.7(3) O13–Eu2–O14F		75.9(3)
01–Eu1–O9	140.9(3)	016D-Eu2-014F	129.6(2)
O4B-Eu1-O9	139.7(3)	015D-Eu2-011	139.9(2)
O18-Eu1-O9	71.9(3)	013–Eu2–O11	88.2(3)
O2C-Eu1-O9	71.2(3)	016E-Eu2-011	140.1(2)
07–Eu1–O9	72.6(3)	014F-Eu2-011	81.8(2)
08–Eu1–O9	116.1(3)	08-Eu1-09	116.1(3)
011–Eu2–O6	87.9(2)	08-Eu1-09	116.1(3)
O15D-Eu2-O12	71.8(2)	08-Eu1-09	116.1(3)
013–Eu2–O12	138.9(3)	08-Eu1-09	116.1(3)
O16-Eu2-O12	140.0(3)	O16F-Eu2-O10	71.4(3)
014F-Eu2-012	67.9(2)	014F-Eu2-010	136.7(3)
011–Eu2–O12	68.4(2)	011–Eu2–O10	68.7(2)
06–Eu2–O12	72.1(2)	06–Eu2–O10	71.7(2)
O15D-Eu2-O10	143.5(3)	012–Eu2–O10	123.8(2)
013–Eu2–O10	72.4(3)		

Symmetry code: (A) x - y, -y + 1, -z; (B) -y + 1, x - y, z; (C) y, x, -z; (D) x - y + 1, -y + 1, -z + 1; (E) -y + 1, x - y + 1, z; (F) y, x, -z + 1 for **1**.



Fig. S2 (a) Coordination environment of Eu(III) ions in 1, with hydrogen atoms being omitted for clarity, and (b) view of distorted square antiprism geometry of Eu1 and distorted biaugmented trigonal prism geometry of Eu2.



Fig. S3 two symmetry-related Eu1 or Eu2 atoms being linked into $[Eu_2(COO)_4]$ clusters with a paddlewheel pattern.



Fig. S4 Schematic representation of (3,6)-connected $(4 \cdot 6^2)(4^2 \cdot 6^7 \cdot 8^2 \cdot 10^4)$ topology for **1** with ligand $(HL)^{2-}$ as 3-connected nodes and cluster $[Eu_2(COO)_4]$) as 6-connected nodes.



Fig. S5 (a) The window aperture of the smaller circular channel being reducing to ca. 3.6 Å (represented by blue ball) by coordination water molecules in the channel and the hydrophobic channel (represented by brass ball) of a window aperture ca. 10.0 Å being formed by the isobutyl groups of $(HL)^{2-}$ ligands extending into the larger

hexagonal channel (showing the smaller and wider gaps between isobutyl groups in the hydrophobic channel), (b) cylindrical hydrophilic spaces with a diameter of ca. 7.0 Å and a length of ca. 8.5 Å separated by coordinated water molecules in the smaller circular channel, and (c) view of the lining of the larger hexagonal channel modified by the embedded chiral fragments including N and O active sites, providing a potential environment for enantioselective recognition. Notably, the lining of the larger hexagonal channel is the outer walls of the smaller circular channel.

2.3. Thermal stability, water stability and purity of 1



Fig. S6 TG curves of 1.



Fig. S7 Simulated PXRD pattern using the single crystal data of **1** (a), and PXRD patterns for as-synthesized **1** (b) and sample **1** soaked in water for 24 h (c).

2.4. Photoluminescence measurements



Fig. S8 Solid-state excitation/emission spectra of 1 at room temperature.



Fig. S9 Solid-state excitation/emission spectra of free ligand H₃L at room temperature.

2.5. Fluorescence-based metal ion sensing

The ground sample 1 (10 mg) was dispersed in an aqueous solution (5 mL, 1.0×10^{-3} M) of $M(NO_3)_x$ (M^{x+} = Ag⁺, K⁺, Na⁺, Pb²⁺, Ca²⁺, Ba²⁺, Mg²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Hg²⁺, Mn²⁺, Ni²⁺, Co²⁺ or Fe³⁺), and ultrasonicated for 30 min at room temperature. The resulted mixtures were used for luminescent measurements. Based on the fluorescence quenching effects, we chose the sample soaked in Cu²⁺ aqueous solution (the Cu²⁺ having little effect on the fluorescence of 1 dispersed in water) and the samples soaked in Ni²⁺, Ag⁺ or Fe³⁺ (the Ni²⁺, Ag⁺ or Fe³⁺ having remarkable quenching effect on the fluorescence of **1** dispersed in water) to further explore the stability of **1** after soaked in the aqueous solutions with a cationic concentration of 10 mM by PXRD measurements. As shown in Fig. S11, the PXRD pattern of the sample soaked in Cu²⁺ aqueous solution is basically agreement with that of as-synthesized 1, indicating that the framework of $\mathbf{1}$ is stable as soaked in Cu²⁺ aqueous solution. As for the samples soaked in Ni²⁺or Fe³⁺ aqueous solutions, there are no obvious peaks in their PXRD spectra, indicating that the framework of 1 was completely decomposed by Ni²⁺or Fe³⁺ and the resulted pale yellow or brown precipitate is amorphous. As for the sample soaked in Ag⁺ aqueous solution, the intensity of most PXRD peaks is extremely weak and even difficult to be distinguished, indicating that the crystallinity of the sample immersed in the aqueous solution of Ag⁺ became significantly worse and even the framework of **1** might be decomposed.



Fig. S10 (a) Emission spectra of 1 in aqueous solutions of various concentrations of Ag⁺ under excitation at 395 nm, (b) Ag⁺ selectivity (I_0/I) of 1 in H₂O, (c) Emission spectra of 1 in aqueous solutions of various concentrations of Fe³⁺ under excitation at 395 nm, and (d) Fe³⁺ selectivity (I_0/I) of 1 in H₂O.



Fig. S11 PXRD patterns for as-synthesized **1** (a), sample **1** soaked in Cu²⁺ aqueous solution (b), sample **1** soaked in Ag⁺ aqueous solution (c), sample **1** soaked in Fe³⁺

aqueous solution (d), and sample **1** soaked in Ni²⁺ aqueous solution (e).

2.6. Enantioselective adsorption investigation

(1) The stability of 1 in CH₃CN, Pham and Phal

The as-synthesized polycrystalline sample **1** (10 mg) was soaked in 5 mL CH₃CN, racemic 1-phenylethanamine (Pham) or racemic 1-phenylethanol (Phal) for 96 h, respectively. After filtration, the sample **1** soaked with Pham or Phal was repeatedly washed with CH₃CN to replace the adsorbed Pham or Phal, and then filtering. All filtered samples were heated at 120 °C under dynamic vacuum for 10 h to remove CH₃CN. The resulted powders were investigated by PXRD, and the results disclosed the structure integrity of the material.



Fig. S12 PXRD patterns of as-synthesized 1 and samples 1 soaked with CH_3CN , Pham or Phal for 96 h (b).



Fig. S13 PXRD patterns of as-synthesized 1 (a) and activated 1 (b).

(2) Optical absorption spectra

All the spectra were recorded in a range of 230-280 nm with a Unico-2102 UV-Vis spectrometer. The strongest absorption peaks of (R)-/(S)-Pham and (R)-/(S)-Phal at 258 nm were used as the monitored wavelength. A serial of acetonitrile solutions of enantiopure (R)-/(S)-Pham and (R)-/(S)-Phal with the concentrations of 1, 2, 3, 4 and 5 mM were prepared to determine the calibration lines, and the solution absorbance at 258 nm showed a typical Lambert-Beer linear correlation with the concentrations. In the adsorption experiment, the activated 1 (10 mg) was soaked in 5 mL acetonitrile solutions of enantiopure (R)- or (S)-Pham and (R)- or (S)-Phal with the concentrations of 10, 20, 30, 40 or 50 mM, respectively. From the absorbance values of the solutions diluted 10 times after adsorption, the equilibrium concentration of adsorbate (C_e) or the concentration at a certain time (C_t) was calculated using the calibration line. The adsorption quantity (q) of (R)- or (S)-Pham and (R)- or (S)-Phal gram of material **1** was then calculated using the equation per

 $q = \frac{\left[C_0 - C_e (or C_t)\right] \times V \times M_s}{m} \qquad [q = \text{adsorption amount (mg g^{-1}), C_0 = the initial concentration of adsorbate (mmol L^{-1}), C_e = the equilibrium concentration of adsorbate (mmol L^{-1}), C_t = the concentration of adsorbate at a certain time (mmol L^{-1}), V = the volume of adsorbate solution used for adsorption, <math>M_s$ = the molar mass of adsorbate (g mmol⁻¹), and m = the quality of activated **1** (g)].

(3) Enantioseparation capacity measurement.

The activated **1** (10 mg) was soaked in 5 mL acetonitrile solutions of racemic Pham or racemic Phal with a concentration of 50 mM, and then stirred for 30 minutes to mix completely. The mixture was allowed to stand for 48 h to achieve the adsorption equilibrium, and then filtered. Wash off the solution attached to the resulting powder sample with a small amount of methanol, soak in 10 mL methanol for desorption for 48 h. Finally, the supernatant was collected by centrifugation for further analysis of enantioseparation capacity. The enantiomeric excess (ee) values were measured on a 2D nano-LC & UPLC-QTrap-MS system. The column is an OD-H column. Mobile phase is a mixture of N-hexane and isopropanol in a volume ratio of 70:30. The flow rate is 0.3 mL min⁻¹.



Fig. S14 UV-Vis absorption spectra of (R)- and (S)-Pham with different concentrations, and absorbance *versus* concentration calibration lines of (R)-

and (S)-Pham (selected wavelength = 258 nm, concentration range from 1 to 5 mM).



Fig. S15 UV-Vis absorption spectra of (R)- and (S)-Phal with different concentrations, and absorbance *versus* concentration calibration lines of (R)- and (S)-Phal (selected wavelength = 258 nm, concentration range from 1 to 5 mM).



Fig. S16 UV-Vis absorption spectra of (*R*)-Pham (a), (*S*)-Pham (b), (*R*)-Phal (c) and (*S*)-Phal (d) solutions diluted 10 times after adsorption at different initial concentrations. The black, red, blue, pink and green curves represent initial concentrations of 10, 20,



30, 40 and 50 mM, respectively. (V = 5 mL, m (adsorbent) = 10 mg, temperature = 25 °C, contact time = 96 h).

Fig. S17 UV-Vis absorption spectra of (*R*)-Pham (a), (*S*)-Pham (b), (*R*)-Phal (c) and (*S*)-Phal (d) solutions diluted 10 times after adsorption at different contact time. (V = 5 mL, m (adsorbent) = 10 mg, temperature = 25 °C, initial concentration (adsorbate) = 50 mM).



Fig. S18 Curves of Uptake efficiency *versus* contact time for (R)-/(S)-Pham and (R)-/(S)-Phal (V = 5 mL, m (adsorbent) = 10 mg, temperature = 25 °C, initial concentration

(adsorbate) = 50 mM).



Fig. S19 Pseudo-first-order kinetic plot (a) and pseudo-second-order kinetic plot (b) for the adsorption of (*R*)-Pham onto HMOF **1**, and Pseudo-first-order kinetic plot (c) and pseudo-second-order kinetic plot (d) for the adsorption of (*S*)-Pham onto HMOF **1** (V = 5 mL, m (adsorbent) = 10 mg, temperature = 25 °C, initial concentration (adsorbate) = 50 mM).



Fig. S20 Pseudo-first-order kinetic plot (a) and pseudo-second-order kinetic plot (b) for the adsorption of (*R*)-Phal onto HMOF **1**, and Pseudo-first-order kinetic plot (c) and pseudo-second-order kinetic plot (d) for the adsorption of (*S*)-Phal onto HMOF **1** (V = 5 mL, m (adsorbent) = 10 mg, temperature = 25 °C, initial concentration

(adsorbate) = 50 mM).



Fig. S21 HPLC-Mass separation diagram of racemic Phal. Chromatography condition: OD-H; mobile phase, N-hexane/isopropanol = 70:30; flow rate, 0.3 mL min⁻¹; injection volume, 5 μ L.

	Pseudo-First-Order Kinetic			Pseudo-Second-Order Kinetic			
	q _{e,exp}	$q_{ m e,cal}$	<i>k</i> ₁	R ²	$q_{ m e,cal}$	k ₂	R ²
(<i>R</i>)-Pham	74.2	91.9	0.127	0.979	93.4	1.04 × 10 ⁻³	0.735
(S)-Pham	114.3	158	0.156	0.968	130	1.32 × 10 ⁻³	0.919
(<i>R</i>)-Phal	101.0	144.5	0.154	0.952	-296	4.03 × 10 ⁻⁵	-0.0516
(S)-Phal	153.8	378.8	0.306	0.917	-184	1.27 × 10 ⁻⁴	-0.0232

Table S3 Kinetic parameters for adsorption of (R)-/(S)-Pham and (R)-/(S)-Phal

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