Supporting information

Chiral template induced homochiral MOFs built from achiral components: SHG enhancement and enantioselective sensing of chiral alkamines by ion-exchange

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General information. All reagents were commercially purchased and used without any further purification. The TGA measurements were performed on a STA449C instrument heated from 40 to 1000 °C under a nitrogen atmosphere at a heating rate of 10°C/min. Powder X-ray diffraction was recorded on a PANalytical X`pert PRO Xray Diffraction using Cu-K α radiation in the 20 range of 5–50°. The Fourier transform infrared spectra using KBr pellets were collected on a VERTEX70 FT-IR spectrophotometer in the range of 4000–400 cm⁻¹. Elemental analyses (C, H, and N) were measured with an Elemental Vairo EL III Analyzer. Li⁺ was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Ultima 2 analyzer (Jobin Yvon). Powder SHG measurement on the sample was performed on a modified Kurtz-NLO system using 1.064 µm laser radiations.

Synthesis of {[L-HAPA]4[Cd₈(OBA)₁₀]} (1L) and {[D-HAPA]4[Cd₈(OBA)₁₀]} (1D). A mixture of Cd(NO₃)₂·4H₂O (0.50 mmol, 154.20 mg), 4,4'-oxybisbenzoic acid (H₂OBA, 1.0 mmol, 258.23 mg) and L- or D-2-amino-1-propanol (0.2 mmol, 15.02 mg) was sealed in a 20 mL of Teflon-lined stainless steel vessel with 10 mL ethanol. The mixture was heated to 150°C in 4 hours and kept this temperature for 3 days. Then the reaction system was cooled slowly to room temperature during another 2 days. The colorless transparent prismatic crystals of 1L and 1D were collected, washed with ethanol and dried in air (yield 89% for 1L and 87% for 1D based on Cd(NO₃)₂·4H₂O). Elemental analysis calcd. (%) for C₁₅₂H₁₃₂N₄O₅₄Cd₈ (3777.72): C 48.32, H 3.52, N 1.48, O 22.87; found for 1L: C 48.87, H 3.66, N 1.42, O 22.80, found for 1D: C 48.67, H 3.63, N 1.48, O 22.90. IR (KBr, cm⁻¹) for 1L: 3431s, 3282w, 3062w, 2968w, 1598vs, 1525vs, 1510vs, 1398vs, 1301w, 1247vs, 1166s, 1095w, 1047w, 1010w, 883s, 858w, 777vs, 696s, 655sw, 540w, 424w. The IR spectrum of 1D is similar to that of 1L.

Single-crystal X-ray Diffraction Study. Single-crystal X-ray diffraction data were collected on a Rigaku Diffractometer with a Mercury CCD area detector (Mo K α : $\lambda = 0.71073$ Å) at room temperature. Crystal Clear software was used for data reduction and empirical absorption correction.¹ These structures were solved by direct methods using SHELXTL and refined by full-matrix least-squares on F^2 using SHELX-97 program.² Metal atoms in each compound were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were

positioned geometrically. Because the unit cell of **1L** and **1D** is very huge, when the SQUEEZE routine of PLATON was applied to remove contributions to scattering from highly disordered solvent molecules, the software procedure cannot run. The alert A: "VERY LARGE Solvent Accessible VOID(S) in Structure!" cannot be refined. Crystallographic data and other pertinent information for **1** are summarized in Table S1. CCDC numbers for **1L** and **1D** is 1056921 and 1056922, respectively.

IR Spectroscopy. The IR spectrum of **1L** and **1D** shows the characteristic bands of the carboxylic groups in the usual region at 1398 cm⁻¹ for symmetric vibrations and at 1533 cm⁻¹ for asymmetric vibrations (Fig. S9). The absence of strong absorption associated with the carboxyl group at around 1707 cm⁻¹ indicates that the carboxylic acid ligands are completely deprotonated.

Second Harmonic Generation (SHG) Measurements. Powder SHG measurement on the sample was performed on a modified Kurtz-NLO system using 1.064 μ m laser radiation.³ The SHG signal was collected and focused into a fiber optic bundle. The output of the fiber optic bundle was coupled to the entrance slit of a spectrometer and detected using a CCD detector. The sample was placed in the mould for SHG measurement, and the thickness of the sample is about 0.2 mm. A powdered KDP sample was used as a reference to assume the second-order NLO effect. All the samples and KDP were ground and sieved into distinct particle size ranges (100–150 μ m).

Recyclability of 1L in the cation exchange process. When sample of L-HPA⁺(*i*)**1L** was immersed in an ethanol solution of Li⁺ ions, the encapsulated L-HPA⁺ ions can be exchanged with Li⁺ ions. The UV-absorption spectra of the solution show that as the immersion time increases, the signals in the region from 250–270 nm corresponding to L-HPA⁺ increase, indicating the release of the encapsulated enantiomers and the possibility of recyclability of **1L** in the cation exchange process (Fig. S10).

Reference

1. *CrystalClear*, version 1.36; Molecular Structure Corp. and Rigaku Corp.: The Woodlands, TX, and Tokyo, Japan, **2000**.

2. G. M. Sheldrick, *SHELXS 97*, *Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany.

3. (a) S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **1968**, *39*, 3798; (b) J.-P. Zou, G. Zhang, C.-H. Huang, G.-C. Guo, *CN Patent* 200710008880.7.



Scheme S1 (a) L-2-amino-1-propanol; (b) L-phenylalaninol; (c) L-phenylglycinol.



Fig. S1 The coordination environments for the Cd(II) ions in **1L** and **1D**. Hydrogen atoms and the labels of carbon atoms are omitted for clarity. (Symmetry codes for **1L**: (A) -x, y-1/2, -z+1; (B) x, y-1, z; (C) x+1, y, z; (D) -x+1, y-1/2, -z+1; (E) x-1, y, z; (F) -x, y+1/2, -z+1; (G) -x+1, y-1/2, -z; (H) -x, y+1/2, -z; (I) -x+1, y+1/2, -z+1; Symmetry codes for 1D: (A) x-1, y, z; (B) -x+2, y+1/2, -z; (C) x-1, y+1, z; (D) -x+3, y-1/2, -z; (E) -x+2, y-1/2, -z+1; (F) -x+2, y-1/2, -z; (G) -x+2, y+1/2, -z+1; (H) -x+3, y+1/2, -z+1; (I) -x+3, y-1/2, -z+1.



Fig. S2 The coordinated modes of OBA²⁻ ligand.



Fig. S3 The solid-state CD spectra for the bulk samples 1L, 1D, HPG⁺@1L, L-HPA⁺@1L and L-HA⁺@1L.



Fig. S4 The PXRD spectra of 1L, Lⁱ⁺@1L, L-HPA⁺@1L, L-HPG⁺@1L and L-HA⁺@1L.



Fig. S5 TGA curves of 1L and 1D.



Fig. S6 The 1D zigzag channels along b axis of in 1.



Fig. S7 Particle size dependence of the SHG intensity for 1L.



Fig. S8 SHG response of **1L**, KDP, Li⁺@**1L** and the inclusion compounds with a roughly equal amount of organic cations (*ca.* 5.9%).







Fig. S9 IR Spectra of 1L, 1D, p-Nitroaniline, L-phenylalaninol, L-phenylglycinol and the inclusion compounds.



Fig. S10 Cation exchange of encapsulated L-HPA⁺ ions by Li⁺ ions in ethanol solution, monitored by time-dependent UV-Vis spectroscopy.

compound	1L	1D
formula	$C_{152}H_{132}N_4O_{54}Cd_8$	$C_{152}H_{132}N_4O_{54}Cd_8$
fw	3777.72	3777.72
cryst syst	Monoclinic	Monoclinic
space group	$P2_{1}$	$P2_1$
<i>a</i> , Å	17.6560(11)	17.754(5)
<i>b</i> , Å	16.2741(18)	16.263(4)
<i>c</i> , Å	26.219(3)	26.250(7)
α, °	90.00	90.00
β, °	90.609(7	90.775(4)
γ, ⁰	90.00	90.00
<i>V</i> , Å ³	7533.1(13)	7575(4)
Ζ	2	2
μ , mm ⁻¹	1.197	1.191
D_{calcd},g cm ⁻³	1.660	1.651
Flack	0.21(3)	0.14(3)
GOF	1.006	1.028
R_1	0.0859	0.0712
wR_2	0.2464	0.2339

Table S1. Crystallographic data and structure refinement details for 1L and 1D.

 ${}^{a}R_{I} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, \ wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}$