Supplementary Information

Chiral induction in boron imidazolate frameworks: the construction of cage-based absolute helices

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Contents

Section 1. Experiment and Characterization

1.1 Chemicals

KBH $(bim)_3$ was synthesized according to the reported literature.[1-3] Unless otherwise specified, other reagents were purchased from commercial channels and used without further purification.

1.2 Physical characteristics

Powder X-ray diffraction (PXRD) data were collected on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) with a step size of 0.02° over the 2θ range of 5-40° at room temperature. Thermogravimetric analyses (TGA) were carried out with a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 K/min under a N_2 atmosphere. Fourier transform infrared (FT-IR) spectra (KBr pellets) were taken on an ABB Bomem MB102 spectrometer over a range 400-4000 cm^{-1}. The UV-vis diffuse reflection data was recorded on a Perkin Elmer Lamda-950 UV spectrophotometer at room temperature by using a powder sample with $BaSO_4$ as a standard (100 % reflectance), which is scanned at 200-600 nm. Degassed the sample at 100°C under vacuum and then gas adsorption was measured on the Micromeritics ASAP 2020 surface area and pore size analyzer. The CO_2 adsorption isotherm measured the surface area at 195 K, and the CO_2 adsorption isotherm was measured at 273 and 298 K using Micrometrics ASAP 2010. The CD spectrum was recorded on a JASCO J-815 spectrometer using a solid tablet method with KBr as the background.

1.3 Experimental part

Synthesis of **BIF-109-Zn**:

A mixture of KBH$(bim)_3$ (0.060 g, 0.15 mmol), 4,4'-diphenyl ether dicarboxylic acid (0.020g, 0.08mmol), $Zn(NO_3)_2 \cdot 6H2O$ (0.029g, 0.10 mmol), DMF (1 mL), ethanol (2 mL), and 3-amino-1-propanol (1 mL) was sealed in a 25 mL vial, then heated at 80 °C for 3 days, and then cooled to room temperature. The colorless block crystals were collected and air-dried (69% yield based on $Zn(NO_3)_2 \cdot 6H_2O$).

The synthesis of compounds **BIF-109-Zn (P)** using D-alanine, **BIF-109-Zn (M)** using L-alanine was similar with that of **BIF-109-Zn**, except that D-alanine (0.022 g, 0.024 mmol) or L-alanine (0.019 g, 0.021 mmol) was added as chiral inducing agents. In addition, we also selected different types of inducers in the same ratio, such as (+)-Cinchonine, L-leucine, L-malic acid, L-leucine, L-serine, etc. However, only (+)-Cinchonine induced very small powdery crystals, and none of the others grew crystals.

Synthesis of **BIF-110-Zn**:

A mixture of KBH$(bim)_3$ (0.060 g, 0.15 mmol), 4,4'-carbonyldibenzoic acid (0.036g, 0.13mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.029g, 0.10 mmol), DMF (1 mL), methanol (2 mL),

and 3-amino-1-propanol (1 mL) was sealed in a 25 mL vial, then heated at 80 °C for 3 days, and then cooled to room temperature. The colorless block crystals were collected and air-dried (45% yield based on $Zn(NO_3)_2 \cdot 6H_2O$).

Determination of the standard curve of the CD spectrum:
The solutions of R-1- and S-1-phenylethanol in ethanol solvent with same concentrations (3×10^{-3}mol/L) and same volume (5mL) were placed in the cell, respectively, and the CD signals were recorded in Fig.S5.

Section 2. Structure description

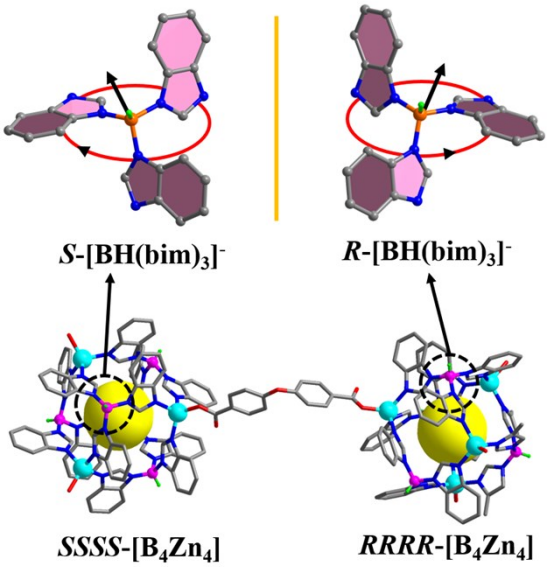

Fig. S1 The enantiomeric building blocks of **BIF-109-Zn**.

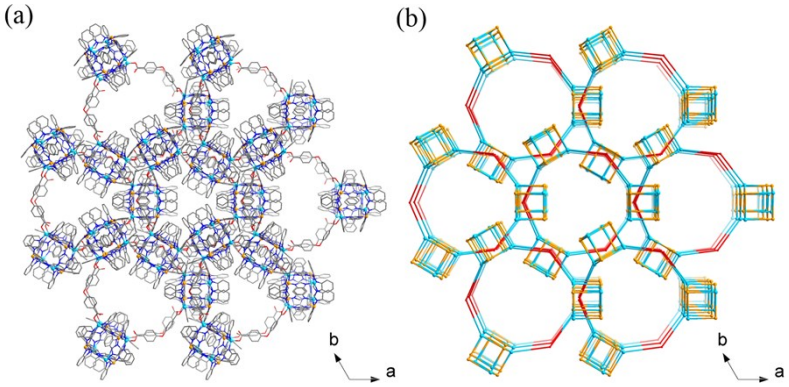

Fig. S2 The packing of helices in **BIF-109-Zn** in *ab* plane.

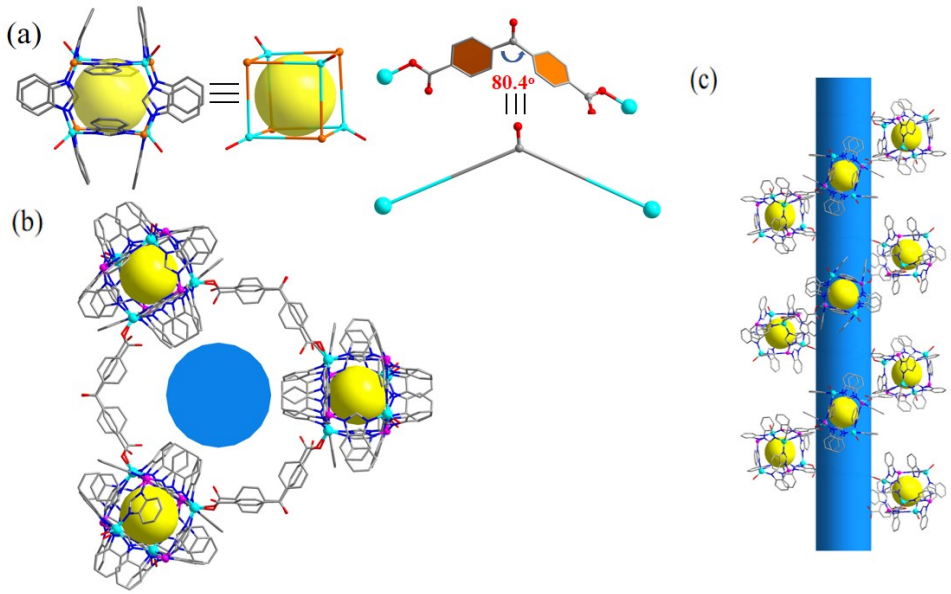

Fig. S3 Views of **BIF-110-Zn** (a) the building blocks of cubic cage BIF-26-Zn and 4,4'-carbonyldibenzoic acid linker in **BIF-110-Zn**; (b) the helical channel along *c* axis; (c) big right-handed helix.

Section 3. CD, PXRD, TGA， UV spectra characterization

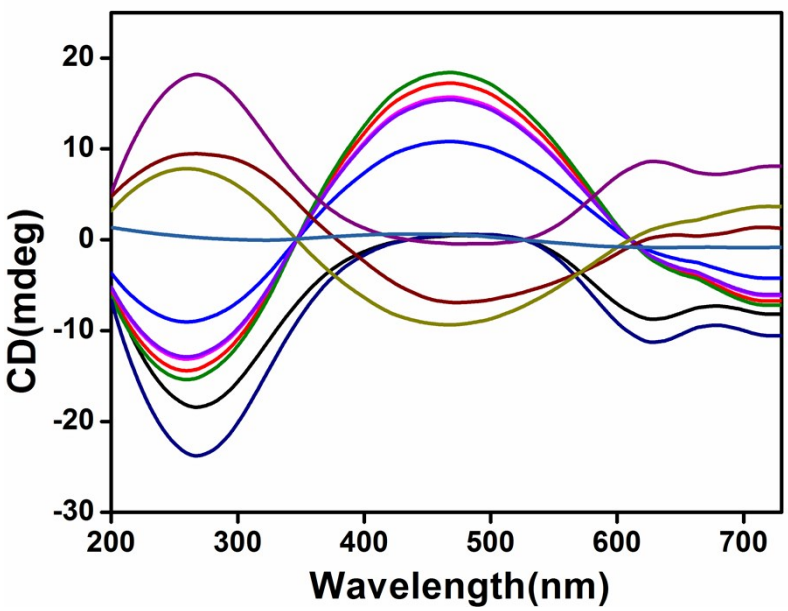

Fig. S4 Solid-state CD spectra of **BIF-109-Zn.**

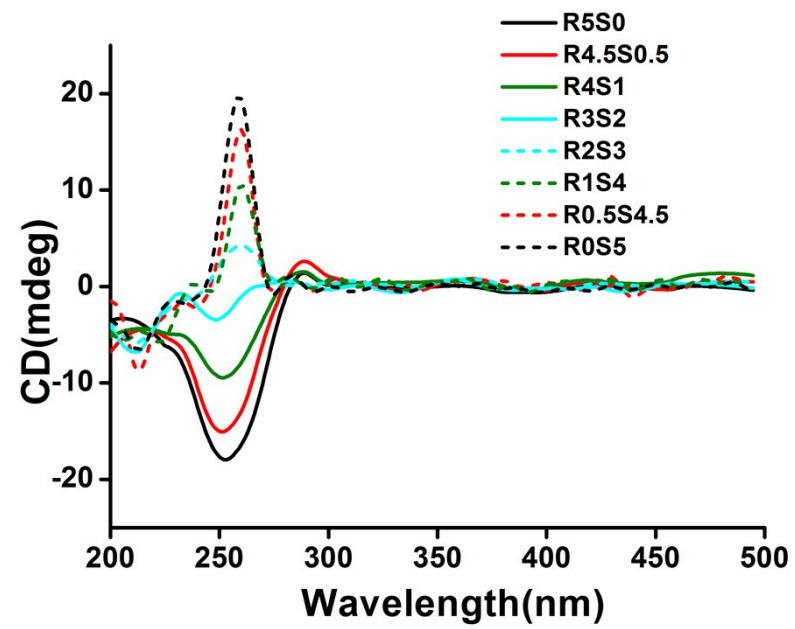

Fig. S5 CD spectra of mixed *R*-1- and *S*-1-phenylethanol solution in different volume ratio.

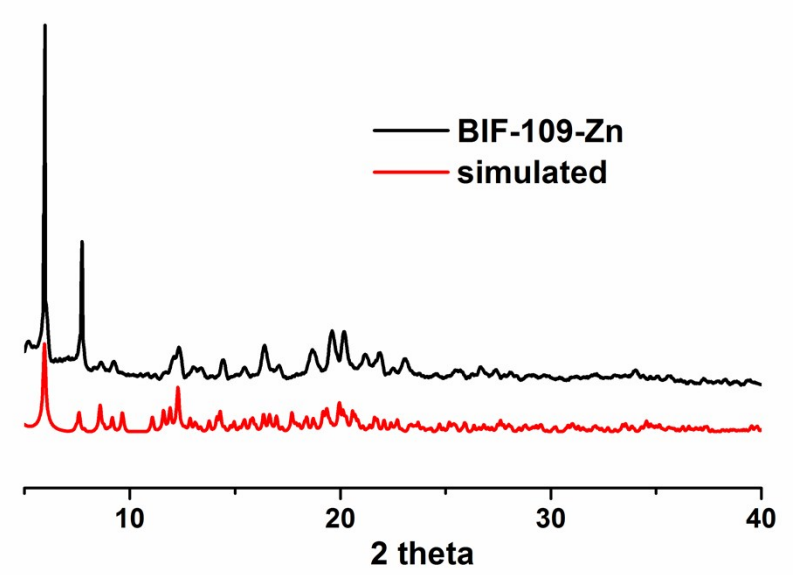

Fig. S6 Experimental and calculated Powder X-ray diffraction (PXRD) patterns for **BIF-109-Zn.**

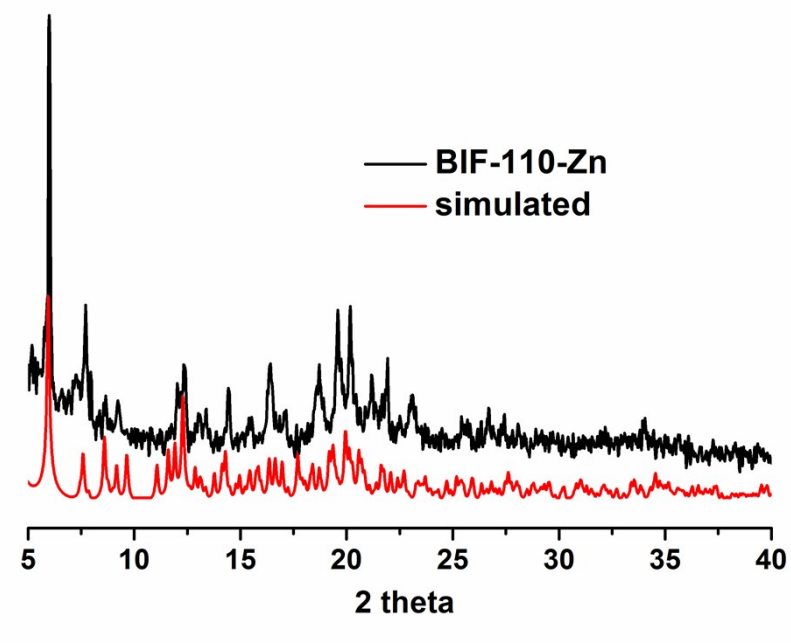

Fig. S7 Experimental and calculated Powder X-ray diffraction (PXRD) patterns for **BIF-110-Zn.**

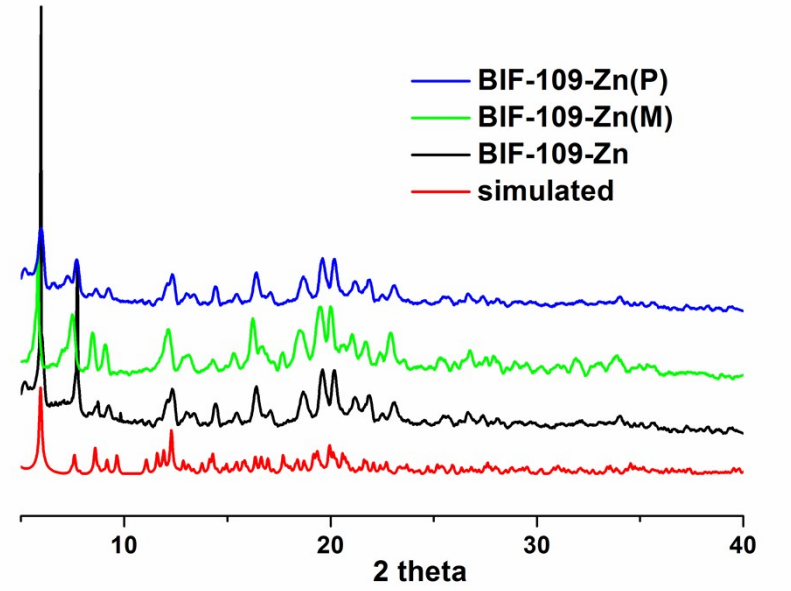

Fig. S8 Experimental and calculated Powder X-ray diffraction (PXRD) patterns for **BIF-109-Zn, BIF-109-Zn(M)** and **BIF-109-Zn(P),** indicating the phase purity of the as-synthesized sample.

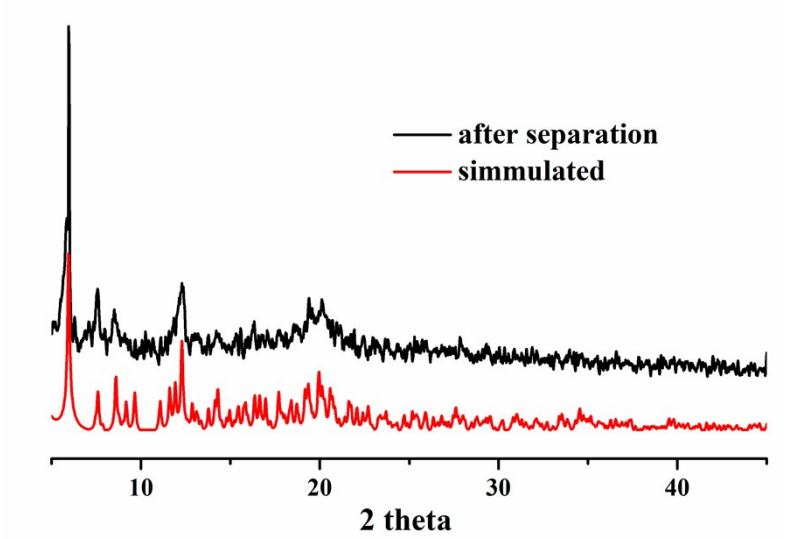

Fig. S9 PXRD patterns of simulated and after enantioselective separation of **BIF-109-Zn(M)**.

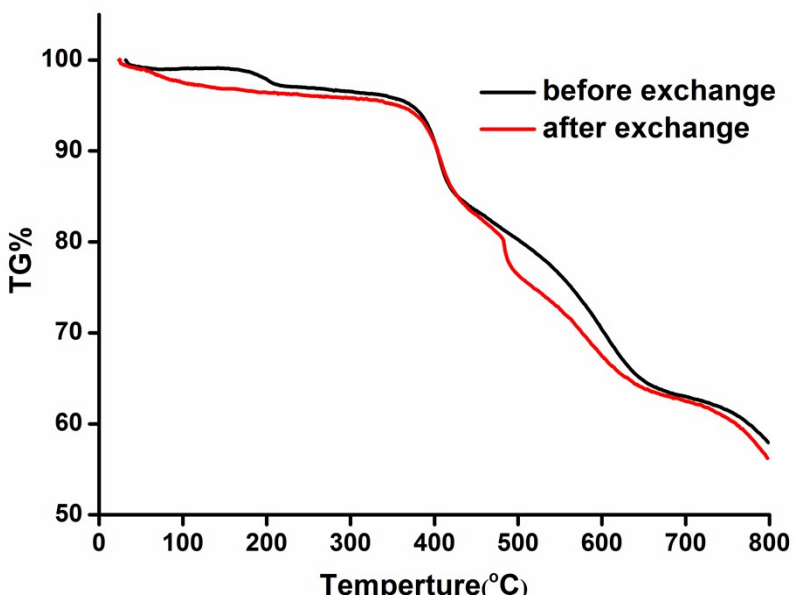

Fig. S10 TGA curves of the as-synthesized and activated (MeOH exchanged) samples for BIF-109-Zn.

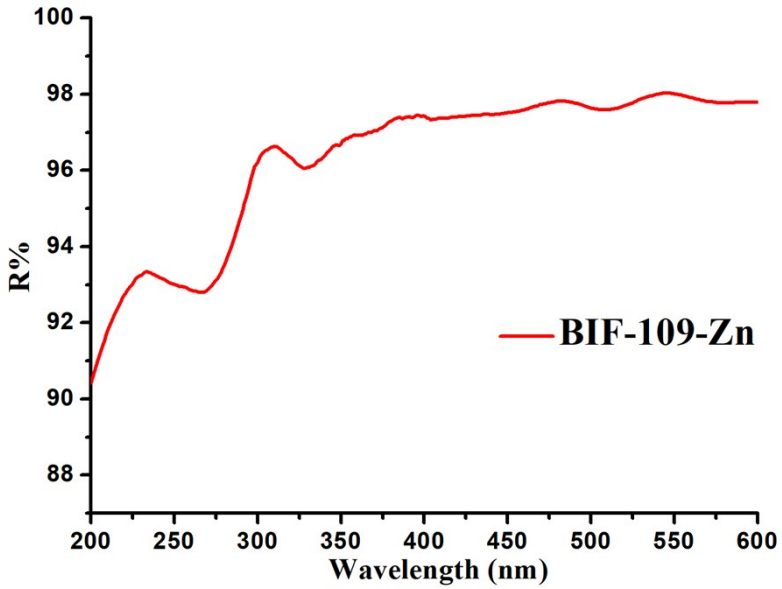

Fig. S11 UV spectra of **BIF-109-Zn.**

Section 4. Gas sorption and separation studies

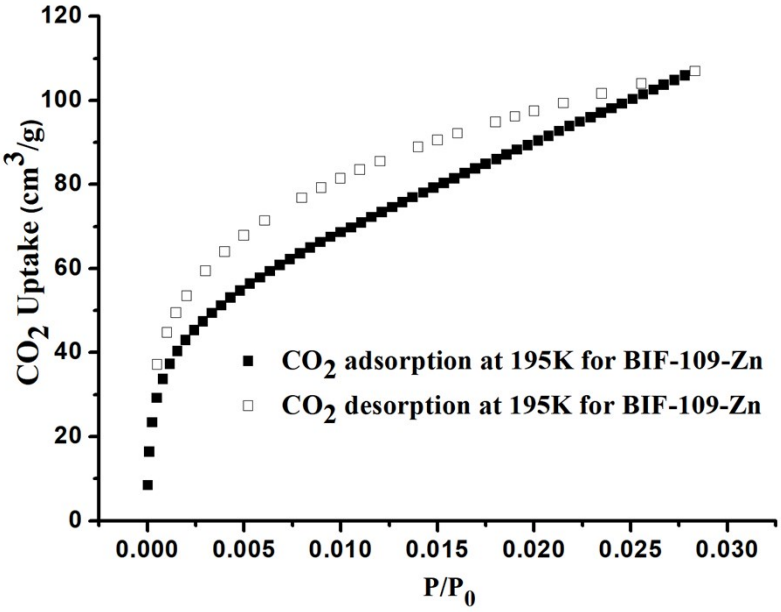

Fig. S12 CO_2 sorption isotherms of **BIF-109-Zn** at 195K. Adsorption: closed symbols; desorption: open symbols, respectively.

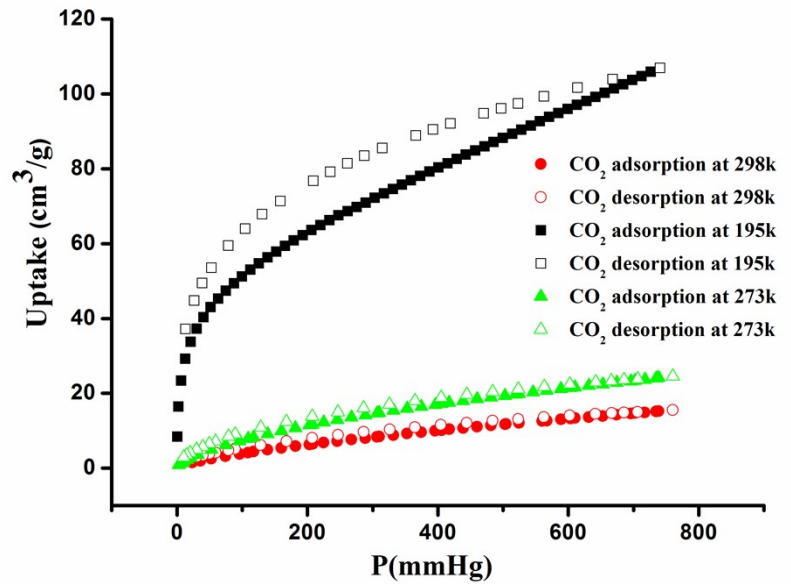

Fig. S13 CO_2 sorption isotherms of **BIF-109-Zn** at 195K,273K and 298K.

Section 5. Chemical Stability

Experimental procedure for the chemical stability of BIF-109-Zn powder: Suspend 20 mg of BIF-109-Zn in different pH solutions for 1 day. Then the sample powder was collected by natural drying and compared with PRXD.

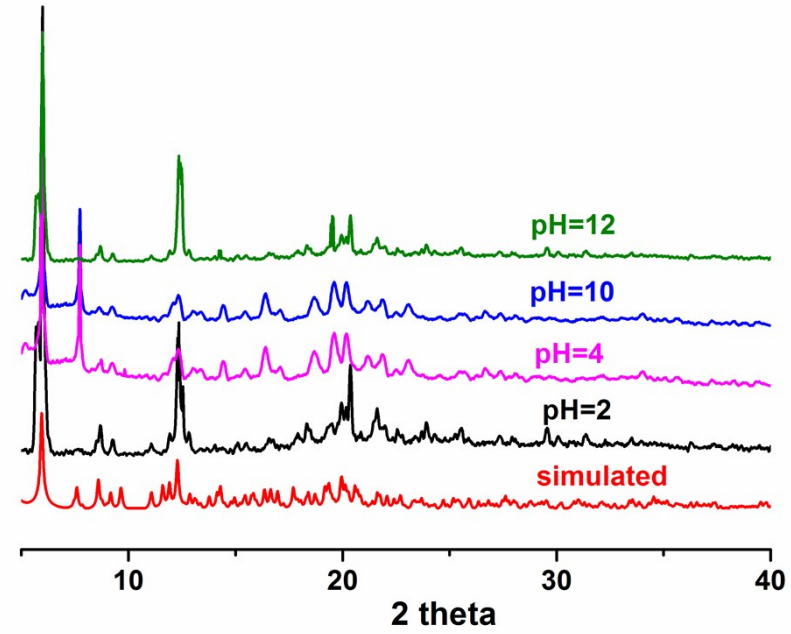

Fig. S14 The acid-base stability of **BIF-109-Zn** in different pH.

Section 6. FT-IR Spectra

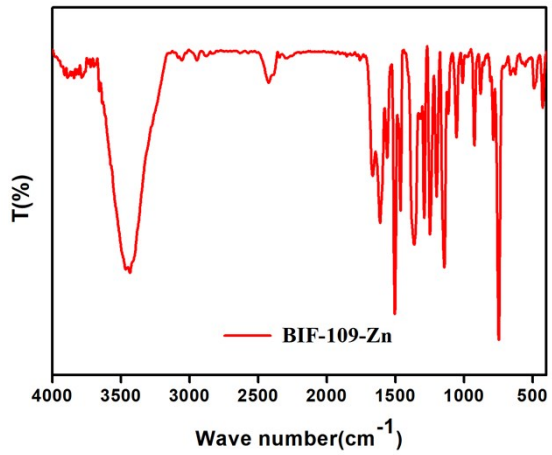

Fig. S15 IR spectra of **BIF-109-Zn.**

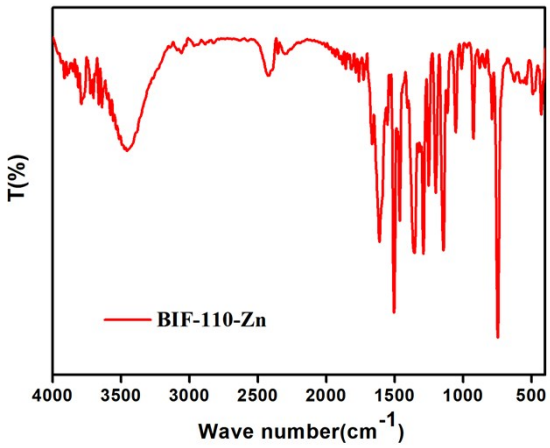

Fig. S16 IR spectra of **BIF-110-Zn.**

Section 7. Enantioselective separation experiments

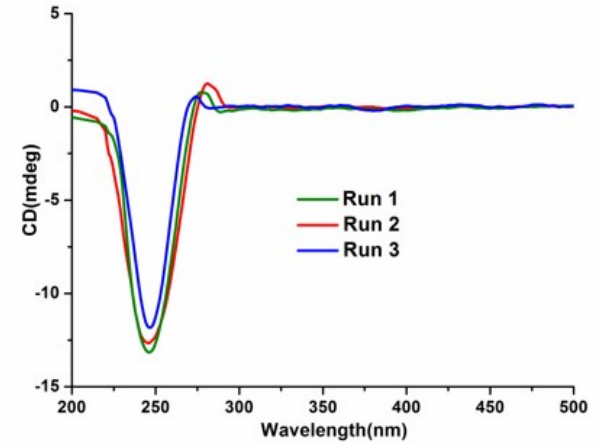

Fig. S17 The cycling curves of **BIF-110-Zn** for enantioselective separation of racemic mixtures of 1-phenylethanol in ethanol solutions.

Section 8. Crystal pictures and unit cell parameters

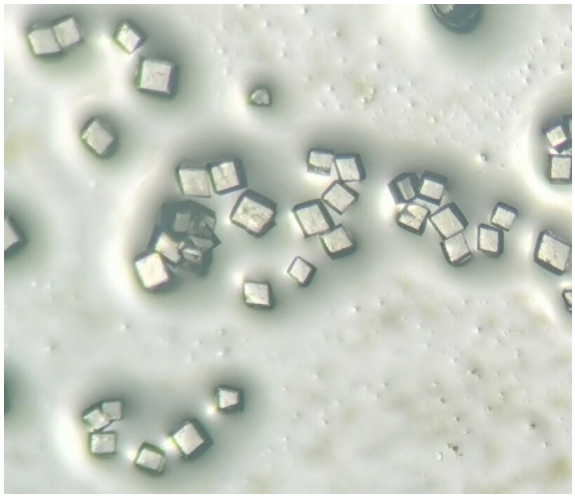

Fig. S18 The picture of **BIF-109-Zn.**

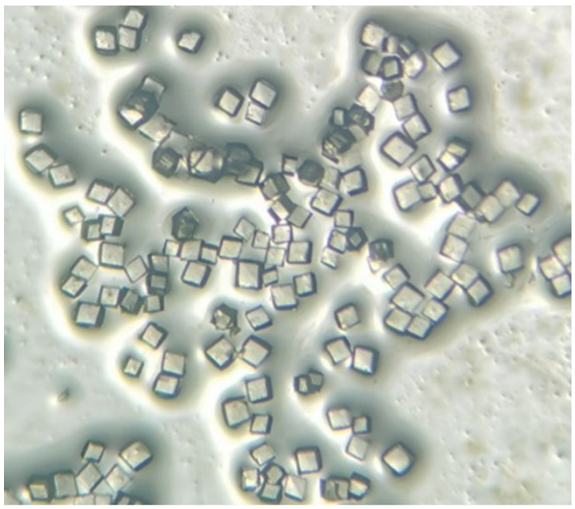

Fig. S19 The picture of **BIF-109-Zn(M).**

Table S1. Crystal data and structure refinement for **BIF-109-Zn**, **BIF-109-Zn(M)** and **BIF-110-Zn.**

Parameter	BIF-109-Zn(M)	BIF-109-Zn	BIF-110-Zn
Empirical formula	$C_{98}H_{76}B_4N_{24}O_7Zn_4$	$C_{588}H_{456}B_{24}N_{144}O_{42}Zn_{24},3(NO_3)$	$C_{99}H_{76}B_4N_{24}O_7Zn_4$
Formula mass	2006.62	12225.78	2018.63
Crystal system	Trigonal	Trigonal	Trigonal
a [Å]	22.9548(3)	23.1589(2)	23.2991(12)
b [Å]	22.9548(3)	23.1589(2)	23.2991(12)
c [Å]	43.2545(7)	43.2658(4)	42.6801(18)

α [°]	90	90	90
β[°]	90	90	90
γ [°]	120	120	120
Volume [Å^3]	19738.3(6)	20096.1(4)	20065.0(2)
Space group	$P3_121$	$P3_221$	$P3_221$
Z	6	1	6
No. of reflections measured	22439	27190	26379
No. of independent reflections	13475	16041	13225
R_{int}	0.0338	0.0296	0.0575
Final R_1 values ($I > 2\sigma(I)$)	0.0779	0.0794	0.0815
Final $wR_2(F^2)$ values (I > 2σ(I))	0.2498	0.2676	0.2788
GOF	1.037	1.031	1.026
Flack	0.008	0.011	0.022

References

1. Hamilton, B. H.; Kelly, K. A.; Malasi, W.; Ziegler, C. J., *Inorg. Chem.* **2003**, 42, 3067-3073.
2. Trofimenko, S., *J. Am. Chem. Soc.* **1967**, 89, 3170-3177.
3. Trofimenko, S., *J. Coord. Chem.* **1972**, 2, 75-77.