Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Chirality from substitution: enantiomer separation via a modified metal-organic framework

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Contents:

Section A. Materials and methods

All the reagents in this work were used as received without further purification. $Zn(NO_3)_2 \cdot 4H_2O$ was purchased from Merck KGaA. 2-methylimidazole (HMeIM), D-histidine, (±)-alanine, and (±)-glutamic acid were purchased from J&K Scientific Company. MeOH, EtOH, DMF, and HNO_3 were obtained from Sinopharm Chemical Reagent Co. Ltd. De-ionized water was used.

Powder X-ray diffraction (PXRD) patterns of the samples were analyzed with monochromatized Cu-Kα (λ = 1.54178 Å) incident radiation by a Shimadzu XRD-6000 instrument operating at 40 kV voltage and 50 mA current. The FT-IR spectra were recorded from KBr pellets in the range 400-4000 cm^{-1} on Nicolet 170 SXFT/IR spectrometer. The UV-vis spectra of the leaching test were examined on a TU-1901 spectrophotometer in the wavelength range of 200-600 nm. The N 1 s and O 1 s core level binding energies (BEs) of the samples were analyzed by PHI5300 X-ray photoelectron spectroscopy (XPS). ^1H solid-state NMR spectroscopy was implemented through AVANCE III 600 Nuclear magnetic resonance spectrometer. Elemental analyses (C, H and N) were conducted on Perkin-Elmer 2400CHN elemental analyzer. Zn content was determined by a PLASMA-SPEC (I) ICP atomic emission spectrometer. The solid state UV-vis spectrum was conducted with a Varian Cary 500 UV-vis-NIR spectrometer. N_2 isotherm was measured using a Quantachrome CorporationAutosorb-iQ2-MPautomatic volumetric instrument. The measurement of chiral optical properties was implemented through the Bio-LogicMOS-450Circular Dichroism Spectrometer.

Section B. Experimental section

Synthetic method of D-his-ZIF-8.

D-his-ZIF-8 was synthesized via a one-pot method. D-histidine (1.29 mmol, 0.200 g) was first dissolved in water (15 mL) followed by addition of methanol (MeOH, 85 mL) into the solution. Then, $Zn(NO_3)_2•4H_2O$ (2.80 mmol, 0.734 g) and 2-methylimidazole (HMeIM) (9.87 mmol, 0.811 g) was separately dissolved in the D-histidine $MeOH/H_2O$ mixtures. Subsequently, the mixture of $Zn(NO_3)_2•4H_2O$ and D-histidine was gradually added into the mixture of HMeIM and D-histidine. Upon stirring at room temperature for 24 h, the crude product was collected by centrifugation and extensively washed with large amounts of water and MeOH consecutively.

Synthetic method of ZIF-8.

$Zn(NO_3)_2·4H_2O$ (1.33 mmol, 0.351 g), HMeIM (2.44 mmol, 0.206 g) were dissolved with the DMF (15 mL) respectively. $Zn(NO_3)_2$ solution were gradually added to HMeIM, then adding 3 drops of HNO_3. The mixed solution was transferred to the 25 mL glass vial, and heated at 120 °C for 24 h. The product was washed with DMF several times, and ZIF-8 crystals were obtained.

Procedure for chiral separation

The racemic amino acid ((±)-alanine or (±)-glutamic acid, 6 mg) was dissolved in $EtOH/H_2O$ (3:1, 20 mL) mixture, and then ZIF-8 or D-his-ZIF-8 (1 g) was added. The mixture was first stirred for 30 min to realize evenly dispersed, and further stand at room temperature for 24 h. Then the solution was collected from the mixture via centrifugation and further filtrated through a 200-nm filter membrane. The resulting liquid was analyzed by circular dichroism spectrometer and chiral chromatographic column, from which the enantiomeric excess (ee) value was obtained.

Recycle experiments

After the chiral separation, the recovered D-his-ZIF-8 was ultrasonic washed with H_2O for five times in order to get rid of the adsorbed amino acids. Then D-his-ZIF-8 was soaked in EtOH overnight, and the solids were separated by centrifugation and dried at 80 °C overnight. Thus-obtained powders were further treated at 120 °C for 3 h under vacuum and then used for the next round of chiral separation.

Section C. Elemental analysis

Table S1. Elemental analysis of D-his-ZIF-8.

Element	Zn	C	H	N
Mass Percentage (%)	26.863	41.880	3.670	24.360
Calculated Data	25.191	41.615	4.601	24.110

Section D. Supplementary Figures S1-S4

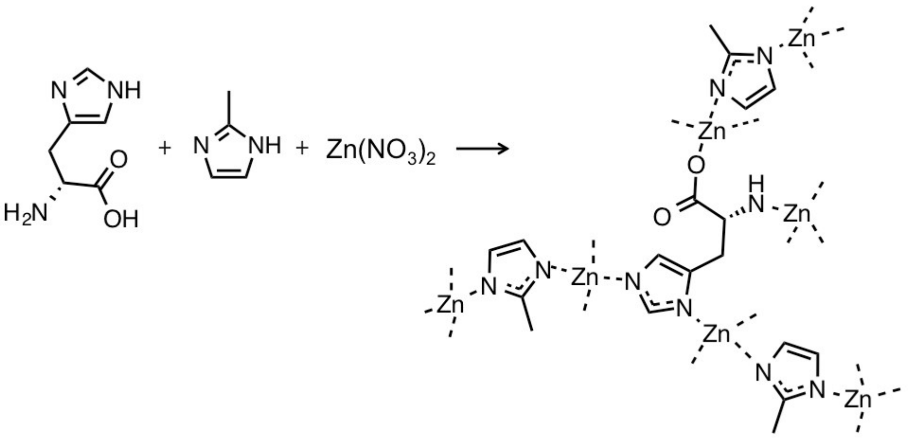

Fig. S1 Formation of D-his-ZIF-8 from the reaction between $Zn(NO_3)_2$, HMeIM and D-histidine.

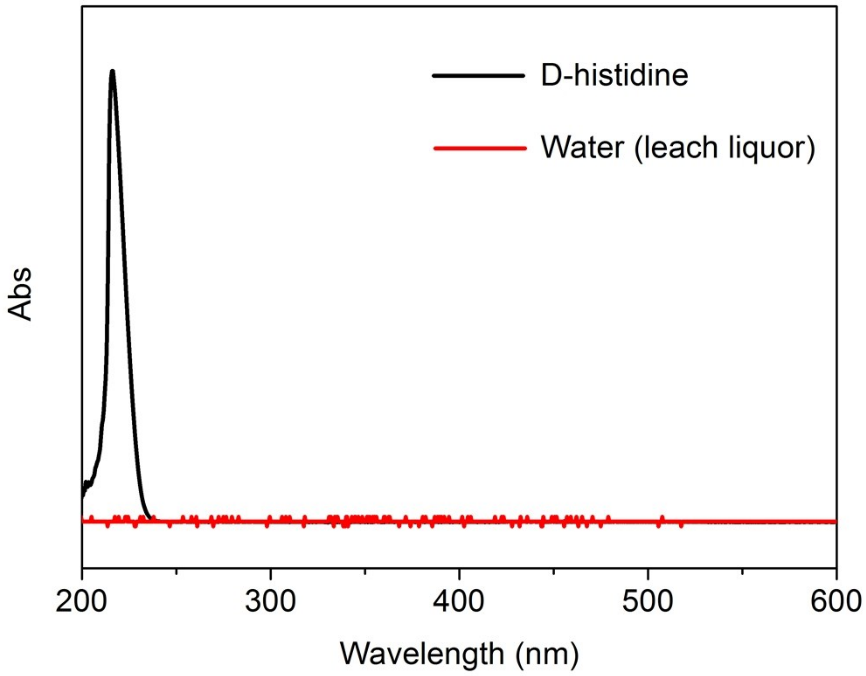

Fig. S2 Liquid-phase UV-vis spectra from leaching test of D-his-ZIF-8 in H_2O.

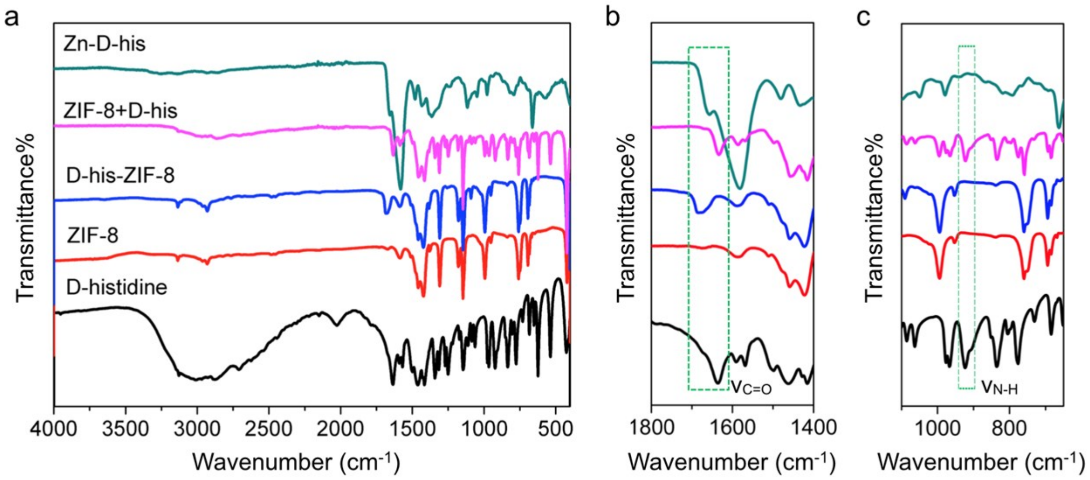

Fig. S3 FT-IR spectra of D-histidine (black), ZIF-8 (red), D-his-ZIF-8 (blue), ZIF-8+D-his (pink) and Zn-D-his (cyan). (b-c) Enlarged views of the FT-IR spectra with the wavenumber range b) from 1800 to 1400 cm^{-1} and c) from 1100 to 650 cm^{-1}.

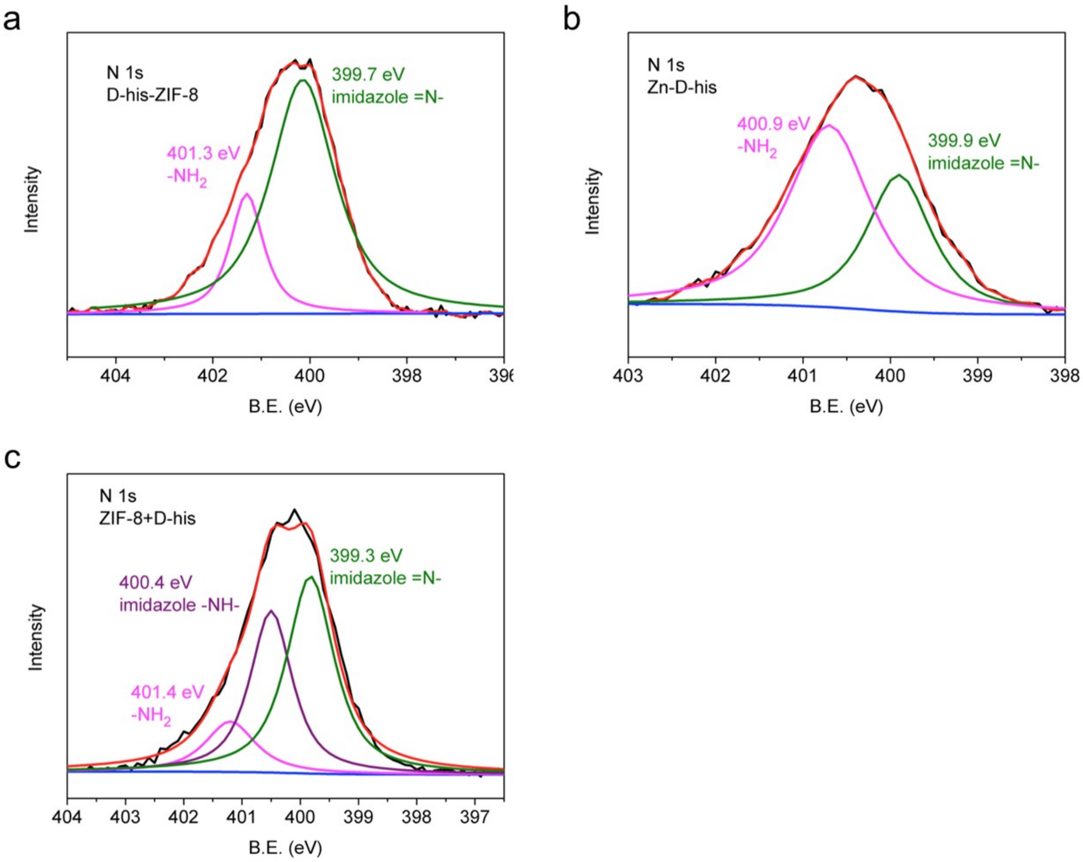

Fig. S4 XPS N 1s spectra of a) D-his-ZIF-8, b) Zn-D-his and c) ZIF-8+D-his.[1-3]

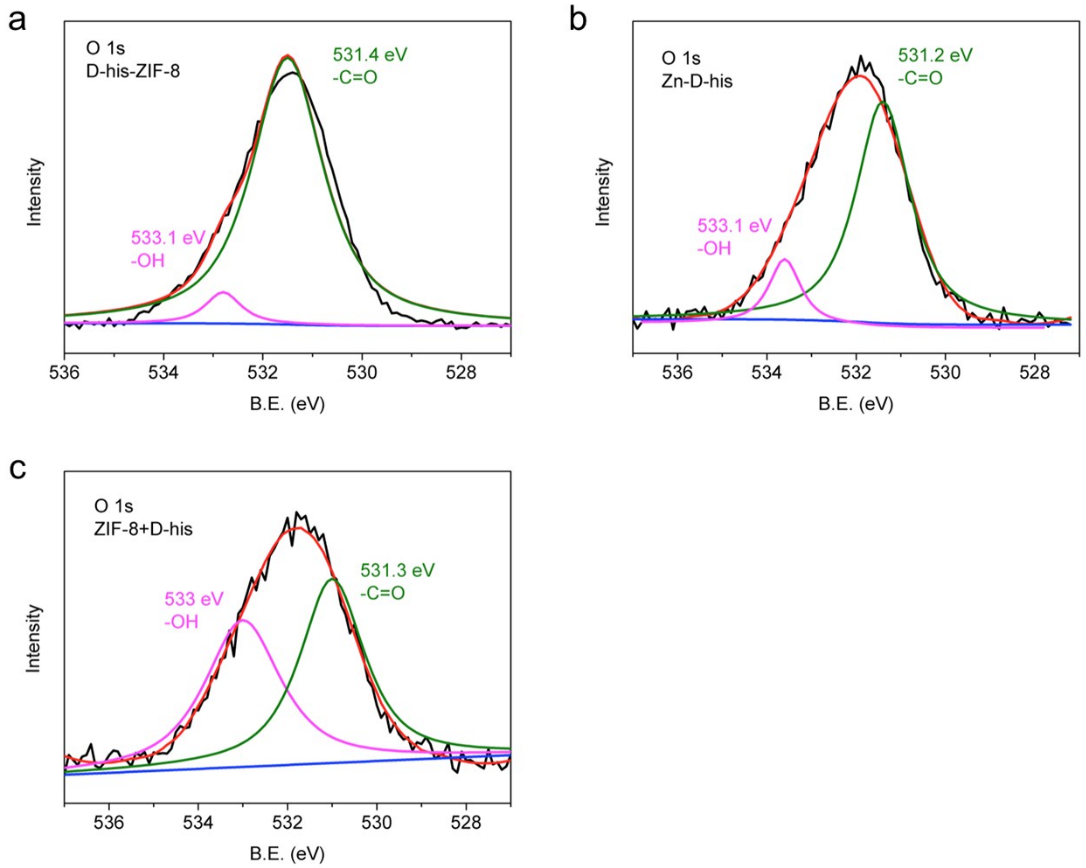

Fig. S5 XPS O 1s spectra of a) D-his-ZIF-8, b) Zn-D-his and c) ZIF-8+D-his.[1-3]

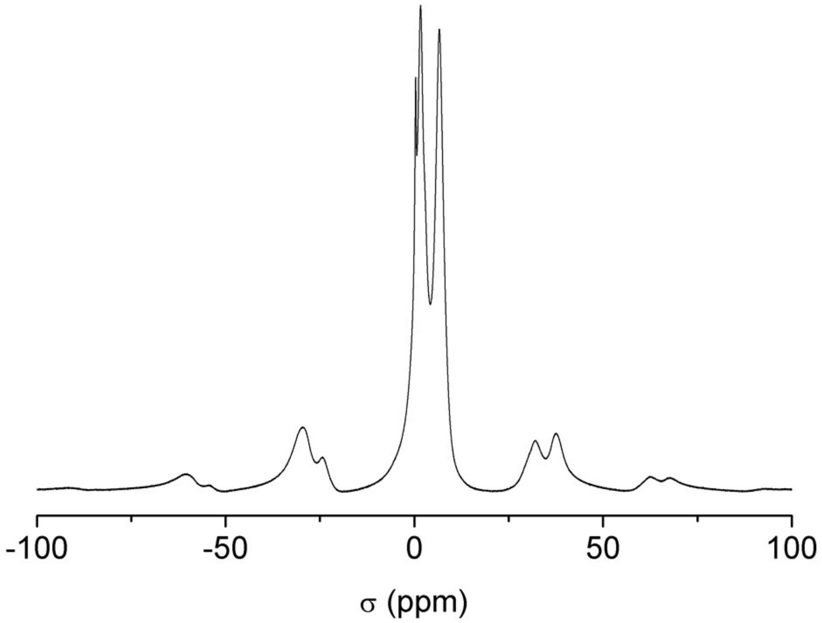

Fig. S6 ^{1}H solid-state NMR spectrum of D-his-ZIF-8.

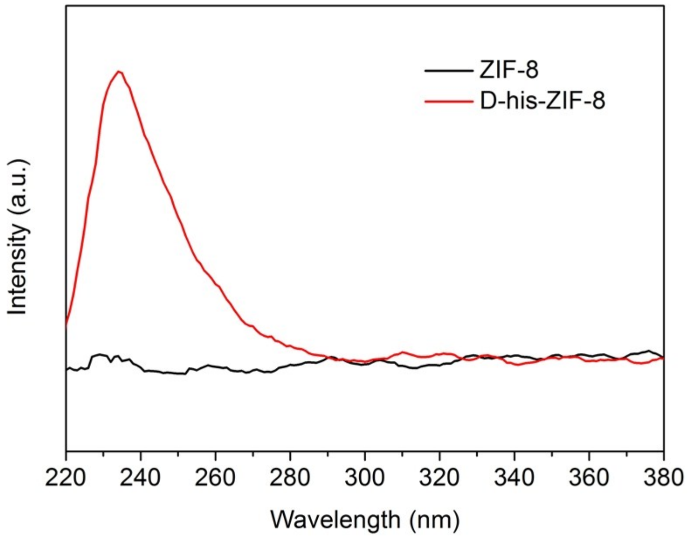

Fig. S7 CD patterns of ZIF-8 (black) and D-his-ZIF-8 (red).

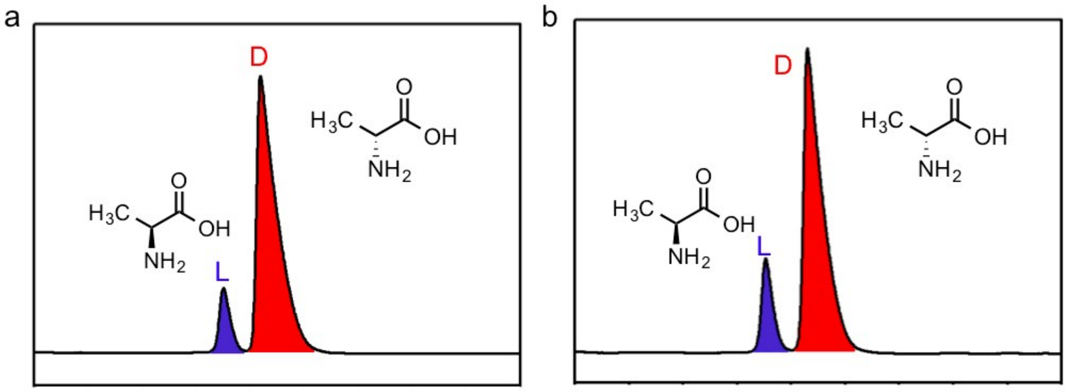

Fig. S8 Chromatogram of alanine separation products using recovered D-his-ZIF-8 as chiral resolving agent in a) the second and b) the third recycle experiments.

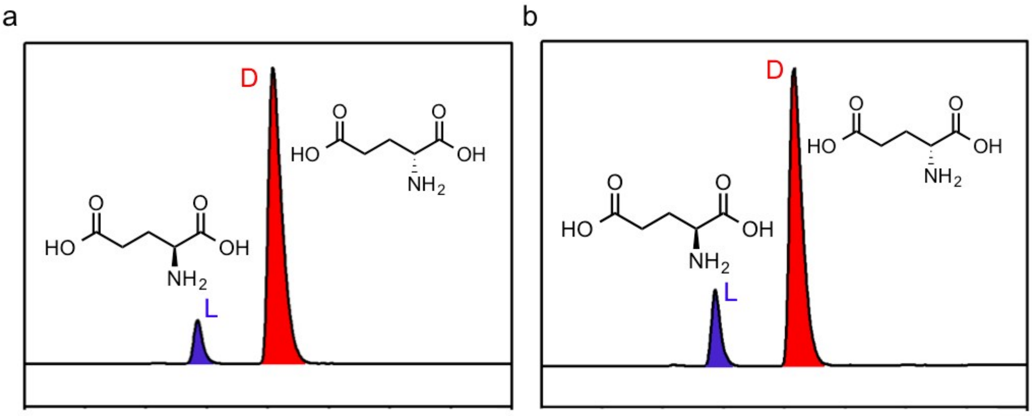

Fig. S9 Chromatogram of glutamic acid separation products using recovered D-his-ZIF-8 as chiral resolving agent in a) the second and b) the third recycle experiments.

Section E. References

1. J. S. Stevens, A. C. d. Luca, M. Pelendritis,G. Terenghi, S. Downesc and S. L. M. Schroeder, *Surf. Interface Anal.*, 2013, **45**, 1238–1246.
2. P. Gerstel, R. C. Hoffmann, P. Lipowsky, L. P. H. Jeurgens, J. Bill and F. Aldinger, *Chem. Mater.*, 2006, **18**, 179−186.
3. F. Tian, A. M. Cerro, A. M. Mosier, H. K. Wayment-Steele, R. S. Shine, A. Park, E. R. Webster, L. E. Johnson, M. S. Johal and L. Benz, *J. Phys. Chem. C*, 2014, **118**, 14449−14456.