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An easy and low-cost method of embedding chiral molecules in metal-organic framework for enantioseparation

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1. Materials and Instrumentation

All the reagents and solvents were commercially available and used as received. Powder X-ray diffraction patterns (PXRD) were measured by using a Rikagu Miniflex 600 Benchtop X-ray diffraction instrument. N_2 sorption measurements were conducted on a Micrometritics ASAP 2460 system from Micromeritics Co. Ltd. All the samples underwent solvent exchange with acetone and activation at 100 ℃ for 12 h before N_2 sorption measurements. ^{1}H NMR spectra were collected on AVANCE III Bruker Biospin spectrometer, operating at 400 MHz. MOF samples (around 8mg) were ultrasonically dissolved in KOH/D_2O solution before collecting their ^{1}H NMR spectra.[1] The morphologies of MOF nanoparticles were studied using scanning electron microscope (SEM) working at 10 KV. The solid-state CD spectra were recorded using Biologic Science Instruments at 25 ℃. The enantiomeric excess values (ee%) were determined with a Alliance HPLC system (Waters Corporation, Milford, USA). It consists of a 20-A pumps and a variable-wavelength ultraviolet detector. Data acquisition and processing were performed on an Empower system. The injection volume and the flow rate were 10 µl and 1 ml/min, respectively. The wavelength of ultraviolet detection was 254 nm.

2. Synthesis of MOFs

2.1 Preparation of MOF-808

MOF-808 has been synthesized by solvothermal reaction using a slightly modified procedure of previous reports.[2] First, H_3BDC (105 mg) was ultrasonically dissolved in DMF (22.5 ml) and placed in a Teflon-lined stainless-steel autoclave, then $ZrOCl_2{\cdot}8H_2O$ (385 mg) and formic acid (12.5 ml) were mixed into the solution by ultrasonic for fifteen minutes. The mixture was finally reacted under 130 ℃ for two days. After cooling to room temperature, the precipitated white powder was collected by centrifugation, washed several times with fresh DMF and soaked in DMF and acetone for three days, respectively. The acetone of MOF-808 was removed by evacuating under room temperature.

2.2 Preparation of MOF-808-His, MOF-808-Tar and MOF-808-Glu

MOF-808-His was synthesized according to a modified method from previous reports.[3] The preparing process mainly consisted the reaction of MOF-808 with L-Histidine (93.75mg/ml) in the aqueous solution at 85 ℃. After 12 h, the obtained samples were washed with hot water for five times. And then the synthesized samples were soaked in water for two days, during which the solvent was removed and replaced with fresh water for six times. Next, the solids were isolated by filtration and washed with fresh acetone for three times, followed by immersing the sample in acetone for additional two days, during which the solvent was replaced by fresh acetone foe six times. Finally, the acetone of MOF-808-His was removed by evacuation under room temperature. For comparison, Treated MOF-808-1 was prepared through the same procedures but without L-Histidine in the solution.

MOF-808-Tar and MOF-808-Glu were prepared as follows: the dry powder of MOF-808 was added in the aqueous solution of L-sodium tartrate (100mg/ml) or L-sodium glutamate (100mg/ml) at first. After reacted under 60 ℃ in the oven for about 24 h, the synthesized samples were filtered out and washed with fresh water for several times. And then samples were soaked in water for two days, during which the supernatant was removed and replaced with fresh water for six times. After that, the solids were isolated by filtration and washed with fresh acetone three times, followed by immersing samples in acetone for additional two days, during which the solvent was replaced by fresh acetone six times. Finally, the acetone of MOF-808-His was removed by evacuation under room temperature. For comparison, Treated MOF-808-2 was prepared through the same procedures but without L-sodium tartrate/ L-sodium glutamate in the solution.

3. Enantioselective separation study

3.1 Enantioseparation in solution

About 20 mg activated samples (MOF-808, MOF-808-His, MOF-808-Tar and MOF-808-Glu) were soaked in the dichloromethane solution of racemic 1-phenyl-1,2-ethanediol (60 mg/mL) to adsorb guest molecules. Three days later, the soaked samples were filtered and slightly washed with fresh dichloromethane for three times. Then the samples were dried for several hours at room temperature and immersed in 1 mL fresh dichloromethane for another three days to desorb guest molecules inside MOF pores. Finally, the desorbed guest molecules were dissolved in 95:5 of n-hexane : iso-propanol solution, and the ee value of the encapsulated enantiomers was determined by HPLC.[4]

About 30 mg activated samples (MOF-808, MOF-808-His, MOF-808-Tar and MOF-808-Glu) were soaked in methanol solution of racemic 1-(4-bromophenyl) ethanamine (0.01 ml/5mL) to adsorb guest molecules and filtered out after two hours. Then the samples were successively washed with fresh methanol once and THF three times to extract the encapsulated enantiomers inside MOF pores. To the combined elution, two drops of Et_3N and one drop of BzCl were added, and the mixture was stirred for two hours until all the 1-(4-bromophenyl) ethanamine had been transformed into the corresponding benzoylation compounds. Then 10 ml Et_2O was added for dilution and the mixture was then washed two times with aqueous HCl, saturated NaCl solution, respectively. Next, the solution was dried with anhydrous Na_2SO_4 for several hours. Finally, the clear solution was evacuated to remove the solvent and the residual was dissolved in 1 mL 95:5 of n-hexane: iso-propanol solution. The ee value of the extracted enantiomers was determined by HPLC.[5]

3.2 Enantioselective separation with solid phase extraction (SPE)

As displayed in Figure 4b, about 120 mg activated samples of MOF-808, MOF-808-His, MOF-808-Tar and MOF-808-Glu were ultrasonically dispersed in 1 mL elution (95:5 of n-hexane: iso-propanol). Then the mixture was transferred to a 1 mL syringe with the end of the syringe blocked by cotton in advance. After slightly flushing the device several times with elution, 0.01 mol/L racemic 1-phenylethanol in elution (0.5ml) was dropt wisely and added into the device slowly. Meanwhile, the solution, flowing out from the bottom of syringe, was continuously collected by 0.5 ml centrifuge tubes and tested by HPLC to determine the ee value of the extracted enantiomers.

4. Results of Scanning electron microscopy (SEM)

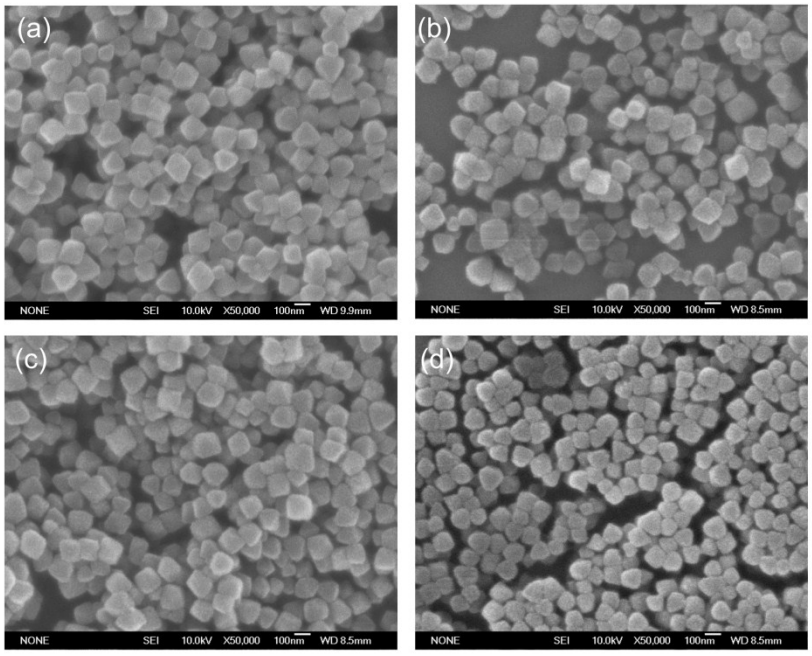


Fig. S1 The SEM images of as synthesized MOF-808 (a), MOF-808-His (b), MOF-808-Tar (c) and MOF-808-Glu (d) nanoparticles.

5. Ion chromatography (IC) study

The signals of formate ions in the solution of MOF-808 after PSEm and treated MOF-808 were tested through a Metrohm 883 IC instrument based on an anion analyzing method. The test and calculation results of all the MOF samples were summarized in Table S1.

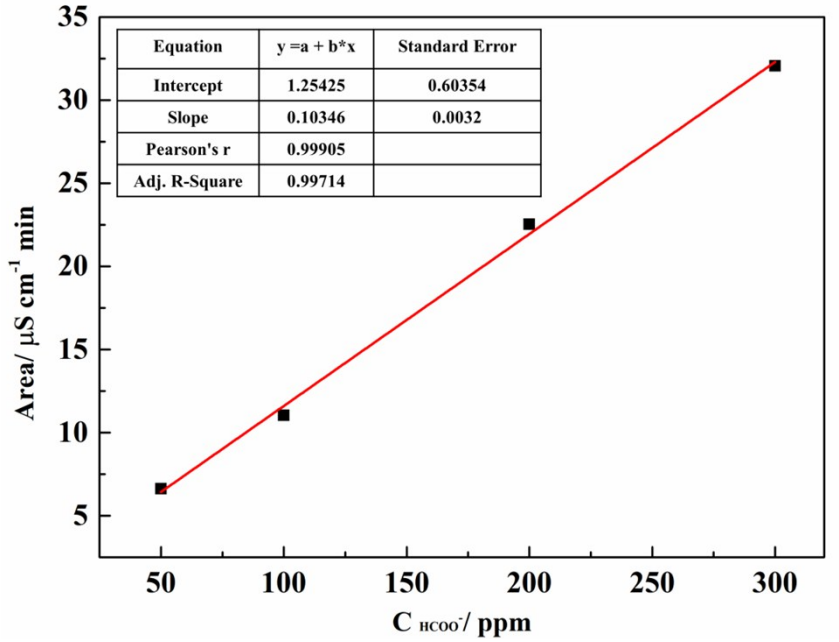


Fig. S2 The calibration curve for concentration of $HCOO^-$ ($CHCOO^-$).

Table S1 The testing results of ion chromatography for all samples.

Sample name	Area (µS cm^{-1} min)	$CHCOO^-$ (ppm)
Treated MOF-808-1	3.2027	18.832
Treated MOF-808-2	2.7035	14.008
MOF-808-His	24.6259	225.893
MOF-808-Tar	15.0805	133.635
MOF-808-Glu	14.7410	130.353

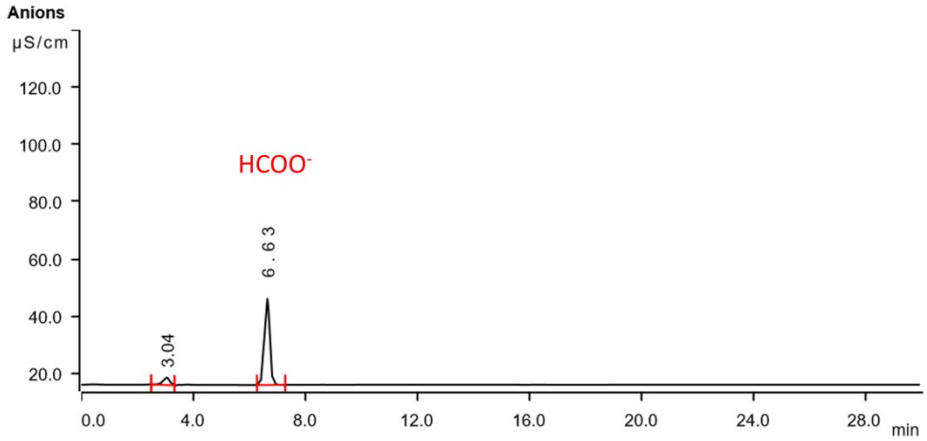


Fig. S3 The IC spectrum of formate ions in the aqueous solution ($CHCOO^-$=50ppm).

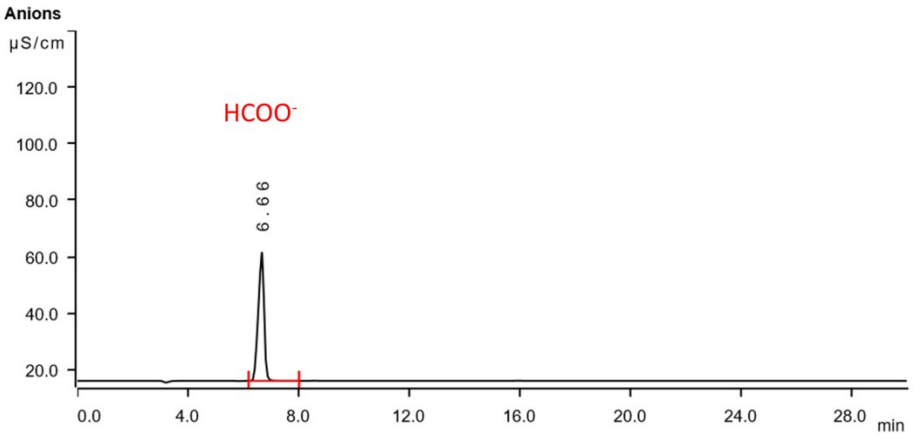


Fig. S4 The IC spectrum of formate ions in the aqueous solution ($CHCOO^-$=100ppm).

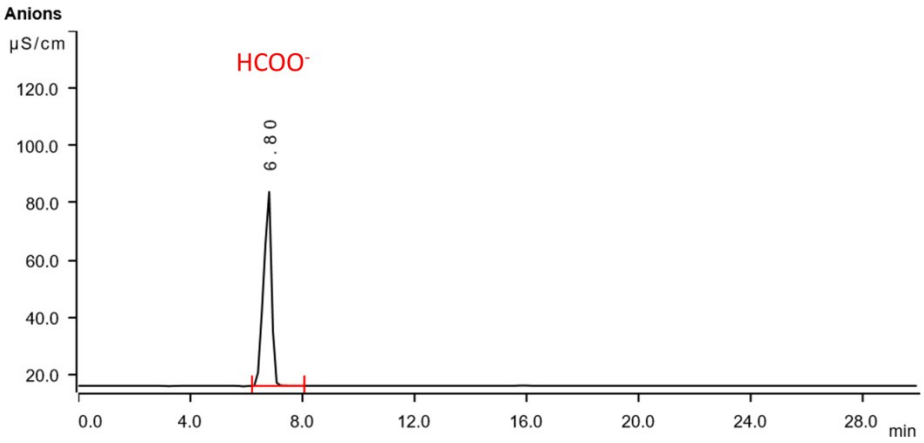


Fig. S5 The IC spectrum of formate ions in the aqueous solution ($CHCOO^-$=200ppm).

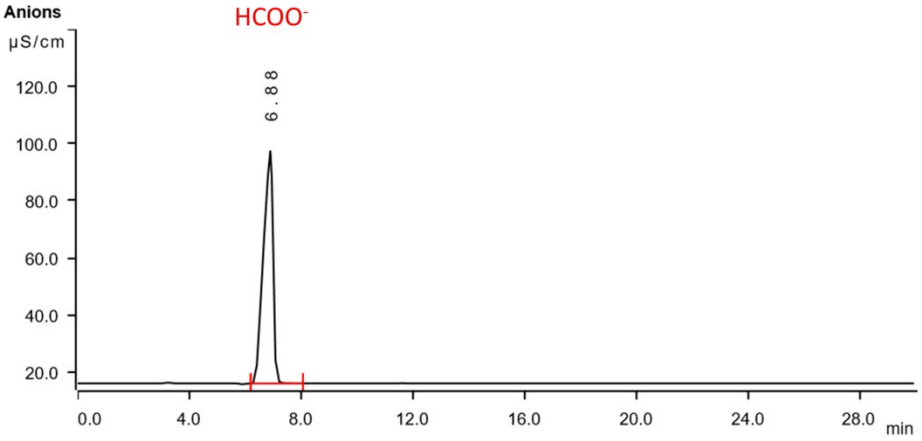


Fig. S6 The IC spectrum of formate ions in the aqueous solution ($CHCOO^-$=300ppm).

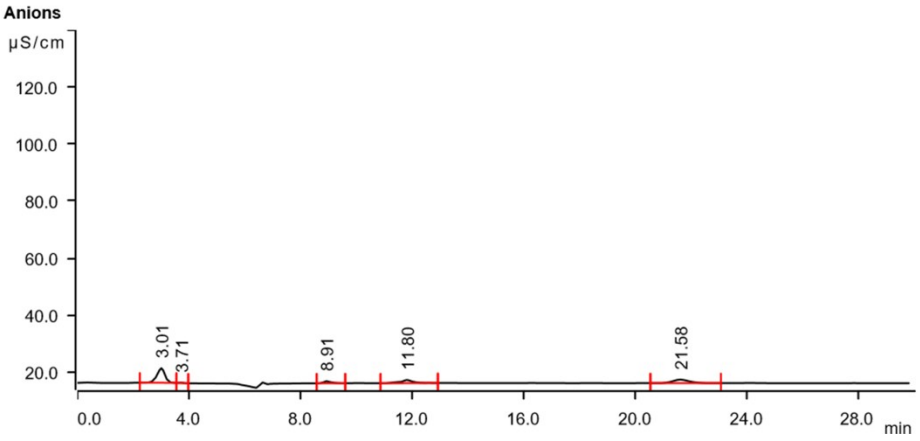


Fig. S7 The IC spectrum of the aqueous solution only containing L-Histidine before PSEm.

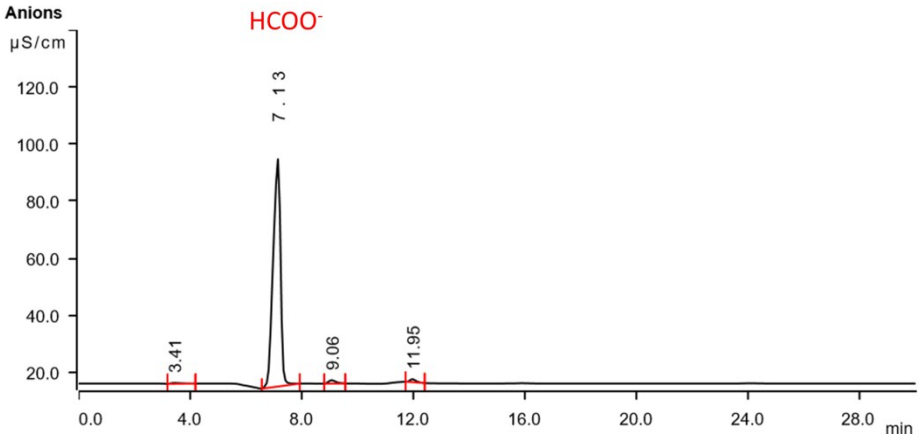


Fig. S8 The IC spectrum of the aqueous solution of MOF-808 after PSEm with L-Histidine (the slight shift of the peak was ascribed to plenty of L-Histidine and formate ions in solution).

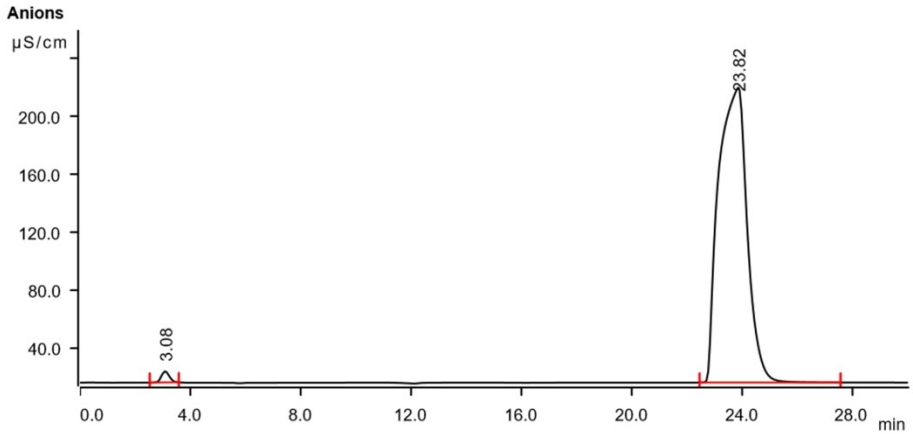


Fig. S9 The IC spectrum of the aqueous solution only containning L-Sodium Tartrate before PSEm.

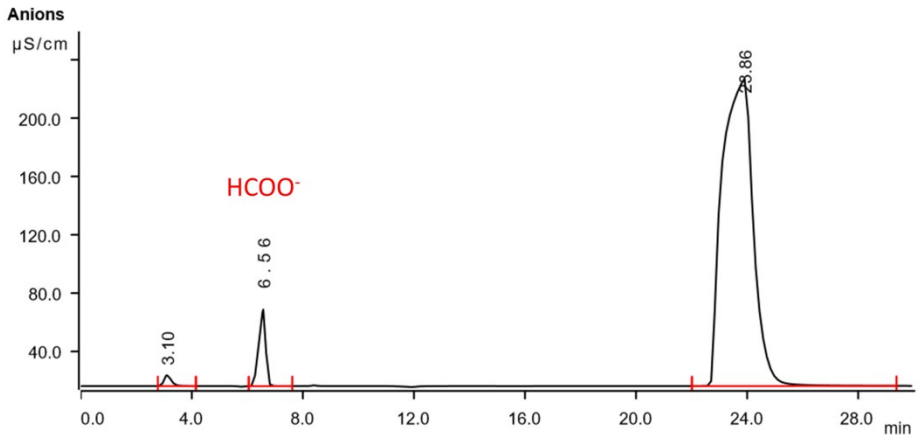


Fig. S10 The IC spectrum of the aqueous solution of MOF-808 after PSEm with L-Sodium Tartrate.

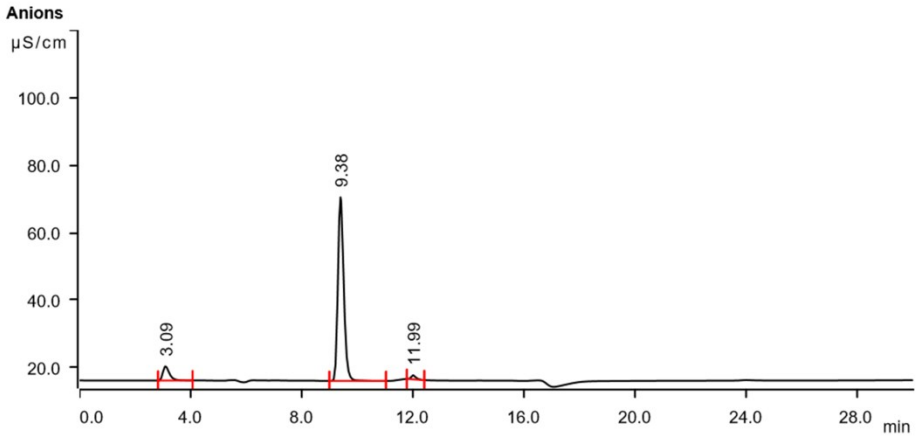


Fig. S11 The IC spectrum of the aqueous solution only containning L-Sodium Glutamate before PSEm.

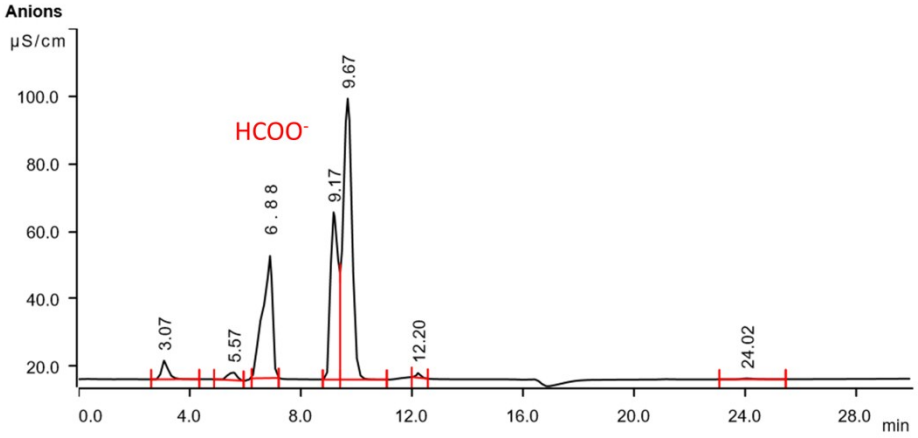


Fig. S12 The IC spectrum of the aqueous solution of MOF-808 after PSEm with L-Sodium Glutamate.

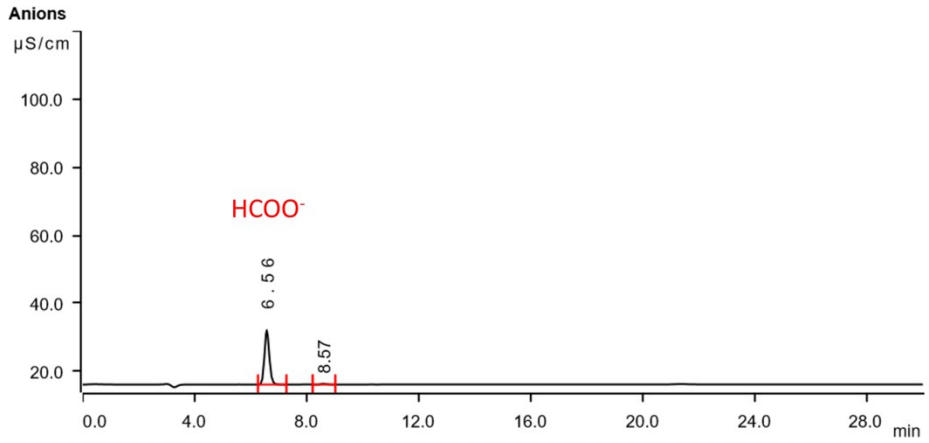


Fig. S13 The IC spectrum of the aqueous solution of Treated MOF-808-1.

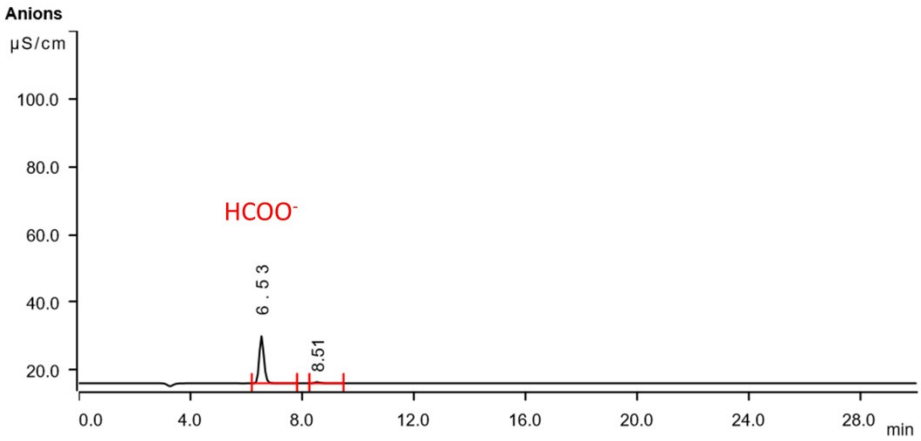


Fig. S14 The IC spectrum of the aqueous solution of Treated MOF-808-2.

6. ^{1}H NMR spectra of digested MOFs

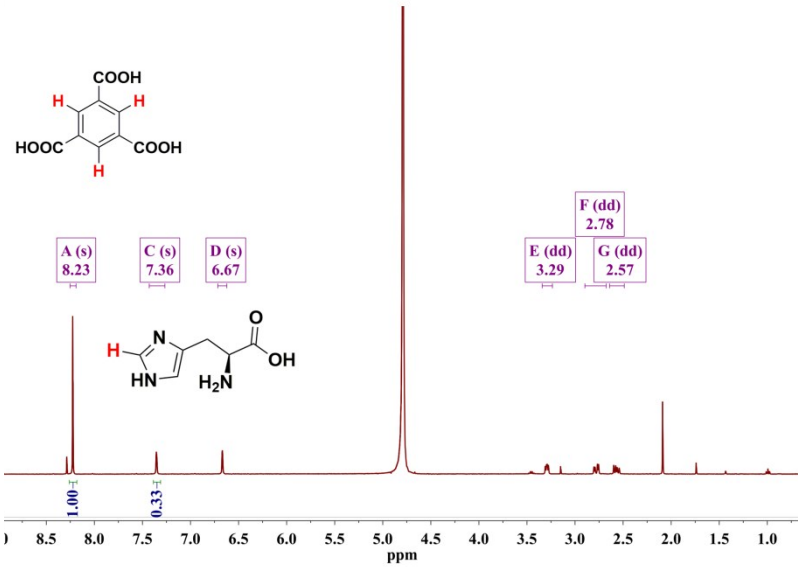


Fig. S15 ^{1}H NMR spectrum of alkaline-digested MOF-808-His.

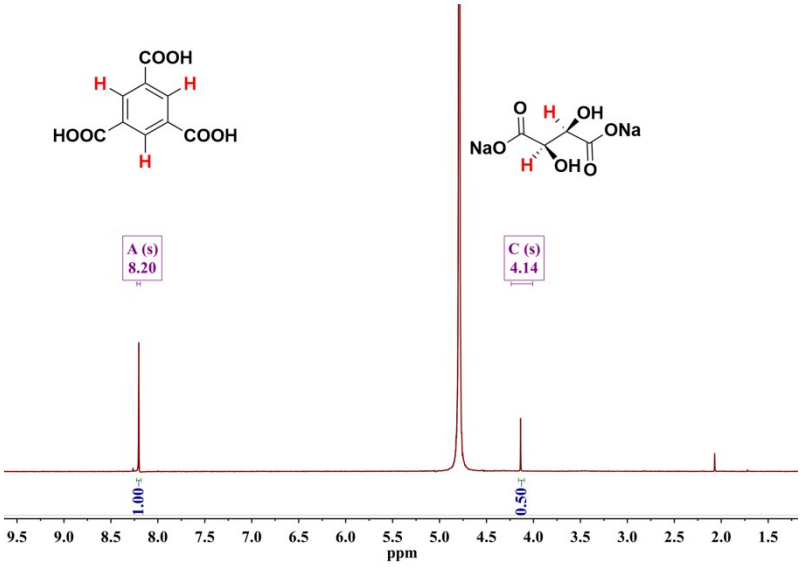


Fig. S16 ^{1}H NMR spectrum of alkaline-digested MOF-808-Tar.

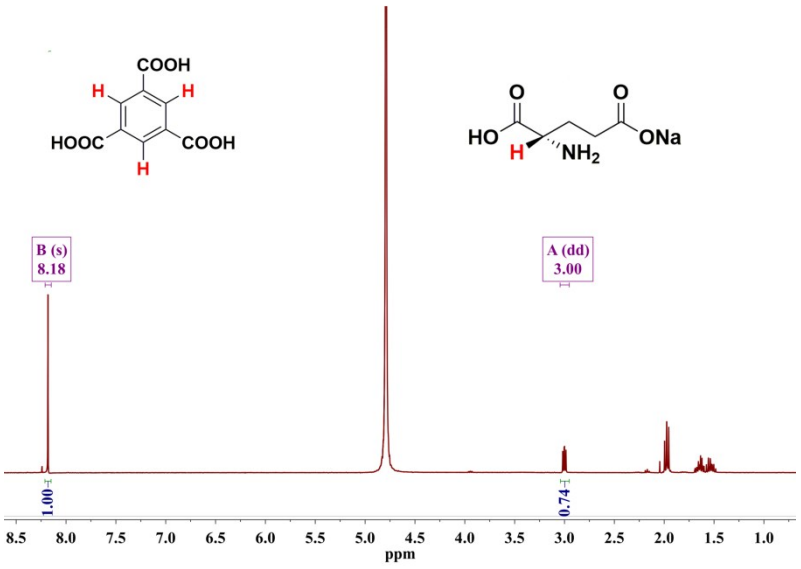


Fig. S17 ^{1}H NMR spectrum of alkaline-digested MOF-808-Glu.

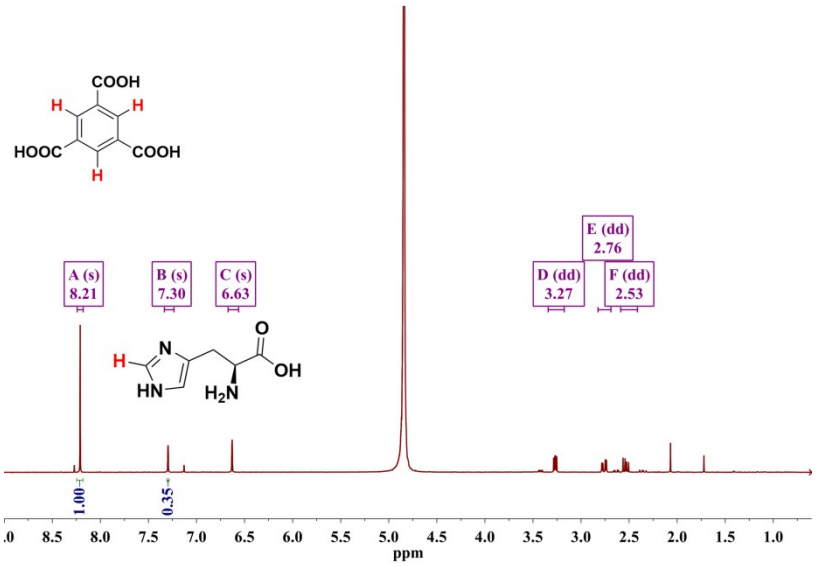


Fig. S18 ^{1}H NMR spectrum of alkaline-digested MOF-808-His after separation of 1-phenyl-1,2-ethanediol.

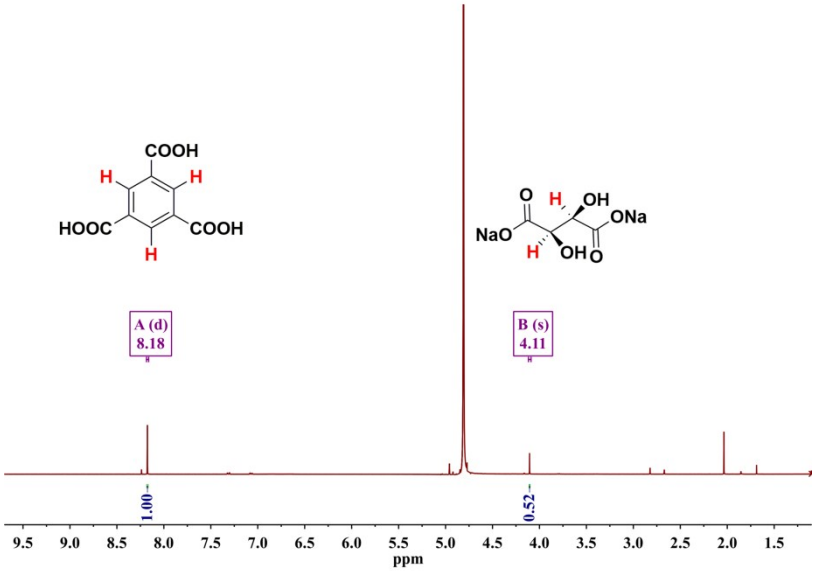


Fig. S19 ^{1}H NMR spectrum of alkaline-digested MOF-808-Tar after separation of 1-(4-bromophenyl)ethanamine.

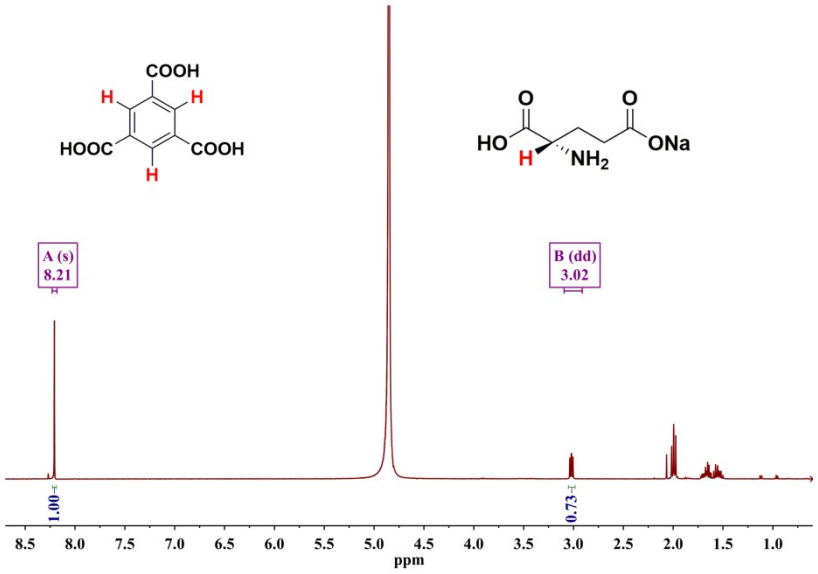
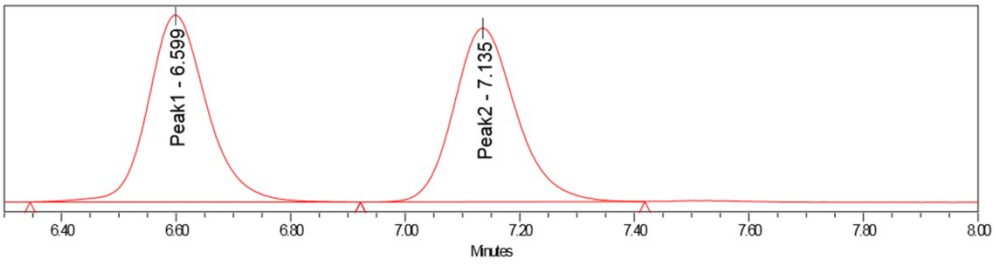


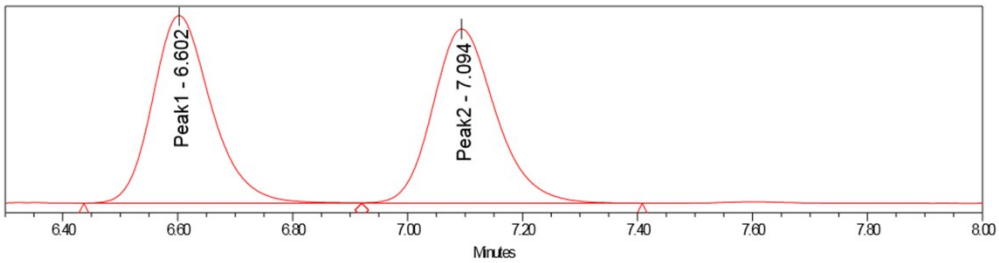
Fig. S20 ^{1}H NMR spectrum of alkaline-digested MOF-808-Glu after separation of 1-phenylethanol.

7. HPLC chromatograms of enantioseparation



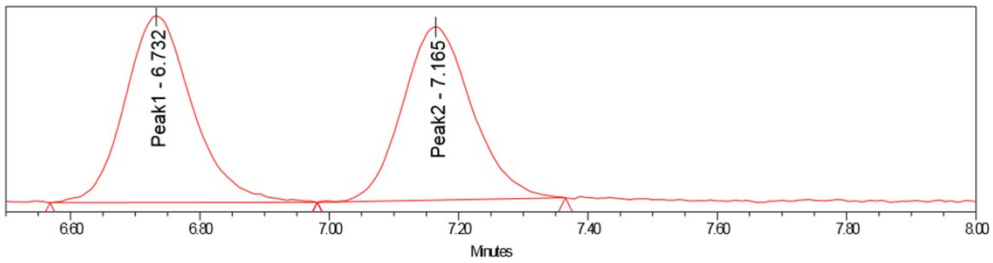
	Retention time / min	Area	% Area
Peak 1	6.599	154478	50.38
Peak 1	7.135	152151	49.62

Fig. S21 HPLC chromatogram of racemic 1-phenylethanol after separation by MOF-808.



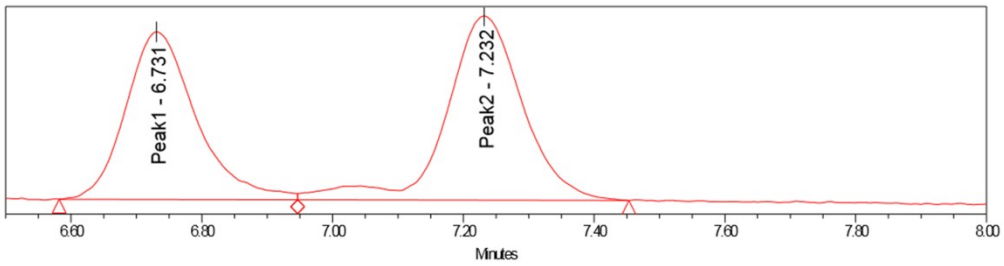
	Retention time / min	Area	% Area
Peak 1	6.602	175288	50.13
Peak 1	7.094	174365	49.87

Fig. S22 HPLC chromatogram of racemic 1-phenylethanol after separation by MOF-808-His.



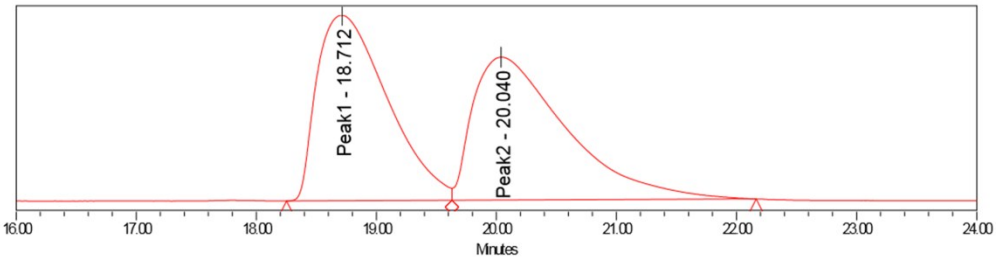
	Retention time / min	Area	% Area
Peak 1	6.732	8934	51.21
Peak 1	7.165	8512	48.79

Fig. S23 HPLC chromatogram of racemic 1-phenylethanol after separation by MOF-808-Tar.



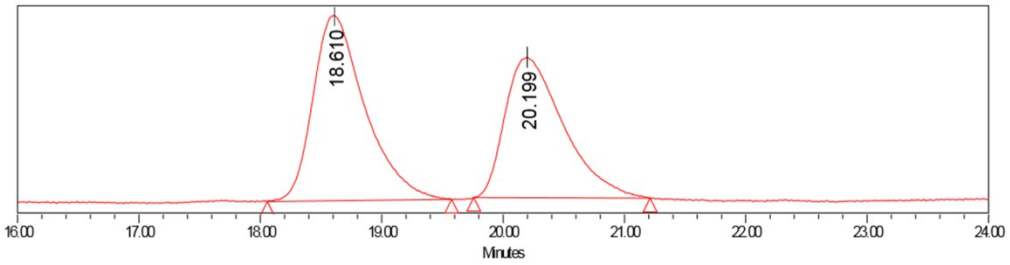
	Retention time / min	Area	% Area
Peak 1	6.731	15176	45.37
Peak 1	7.232	18274	54.63

Fig. S24 HPLC chromatogram of racemic 1-phenylethanol after separation by MOF-808-Glu.



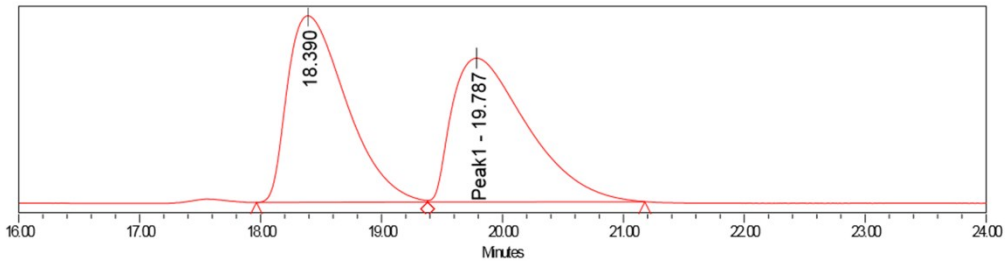
	Retention time / min	Area	% Area
Peak 1	18.712	3414792	49.49
Peak 1	20.040	3484872	50.51

Fig. S25 HPLC chromatogram of racemic 1-phenyl-1,2-ethanediol after separation by MOF-808.



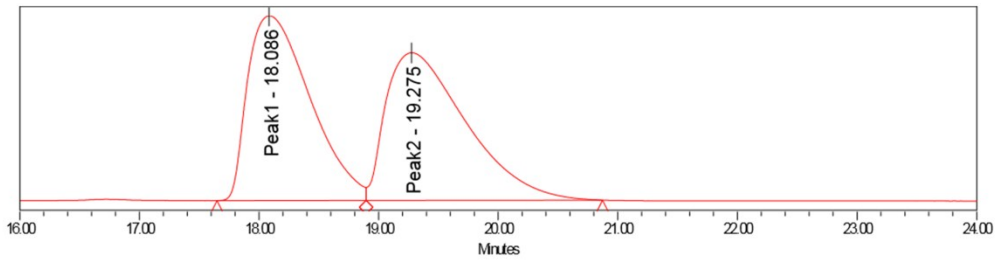
	Retention time / min	Area	% Area
Peak 1	18.610	90818	54.08
Peak 1	20.199	77108	45.92

Fig. S26 HPLC chromatogram of racemic 1-phenyl-1,2-ethanediol after separation by MOF-808-His.



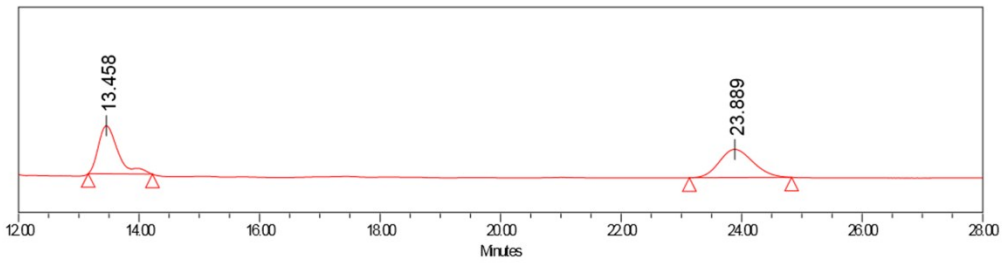
	Retention time / min	Area	% Area
Peak 1	18.390	1380626	50.43
Peak 1	19.787	1356969	49.57

Fig. S27 HPLC chromatogram of racemic 1-phenyl-1,2-ethanediol after separation by MOF-808-Tar.



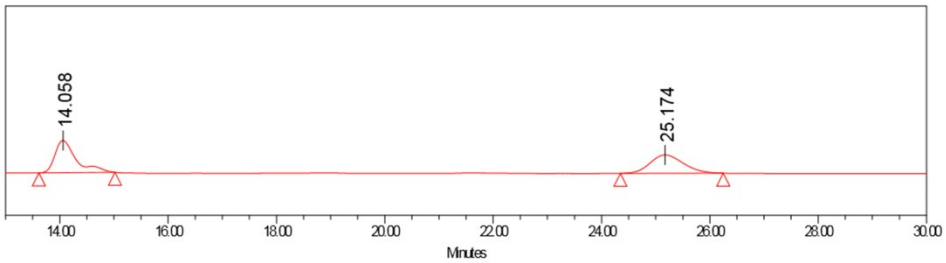
	Retention time / min	Area	% Area
Peak 1	18.086	2862471	49.45
Peak 1	19.275	2916686	50.55

Fig. S28 HPLC chromatogram of racemic 1-phenyl-1,2-ethanediol after separation by MOF-808-Glu.



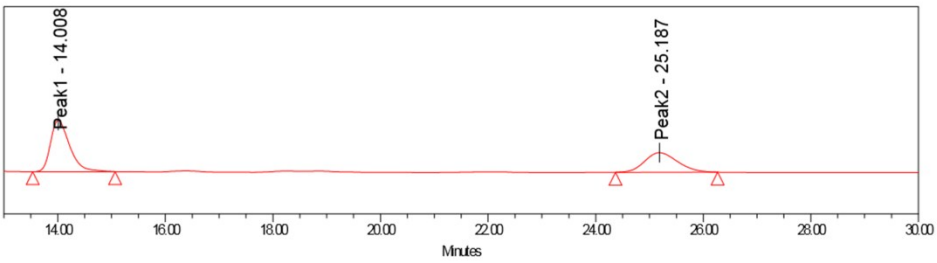
	Retention time / min	Area	% Area
Peak 1	13.458	637463	49.74
Peak 1	23.889	644157	50.26

Fig. S29 HPLC chromatogram of racemic 1-(4-bromophenyl)ethanamine after separation by MOF-808.



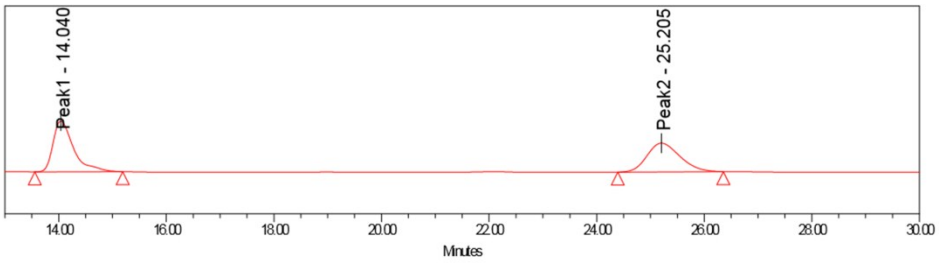
	Retention time / min	Area	% Area
Peak 1	14.058	1046293	53.03
Peak 1	25.174	926880	46.97

Fig. S30 HPLC chromatogram of racemic 1-(4-bromophenyl)ethanamine after separation by MOF-808-His.



	Retention time / min	Area	% Area
Peak 1	14.008	1524964	60.40
Peak 1	25.187	1000010	39.60

Fig. S31 HPLC chromatogram of racemic 1-(4-bromophenyl)ethanamine after separation by MOF-808-Tar.



	Retention time / min	Area	% Area
Peak 1	14.040	1623184	52.46
Peak 1	25.205	1471086	47.54

Fig. S32 HPLC chromatogram of racemic 1-(4-bromophenyl)ethanamine after separation by MOF-808-Glu.

8. Powder X-ray diffraction (PXRD) patterns before and after enantioseparation

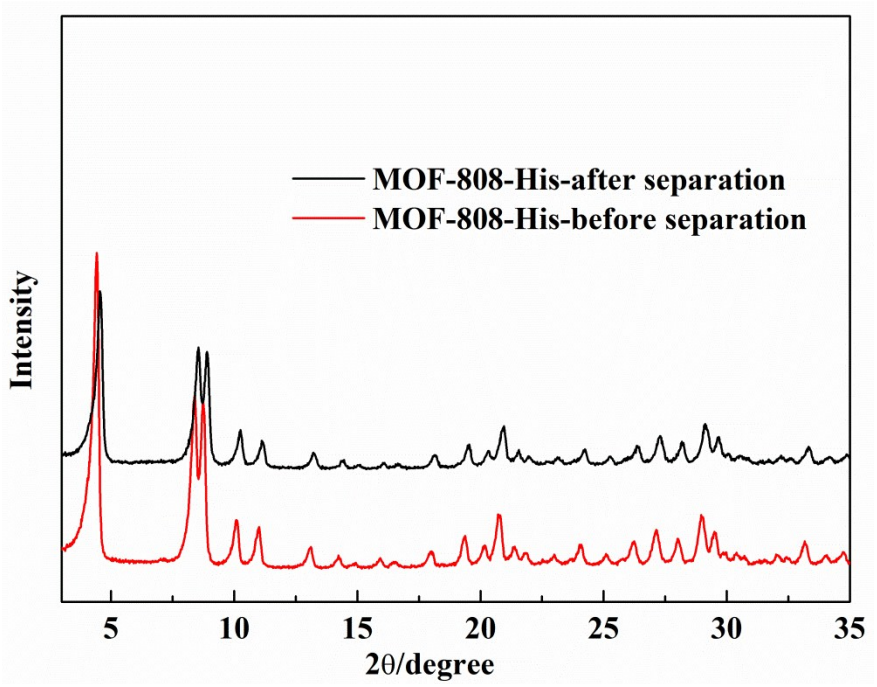


Fig. S33 The PXRD patterns of MOF-808-His before and after enantioseparation of 1-phenyl-1,2-ethanediol.

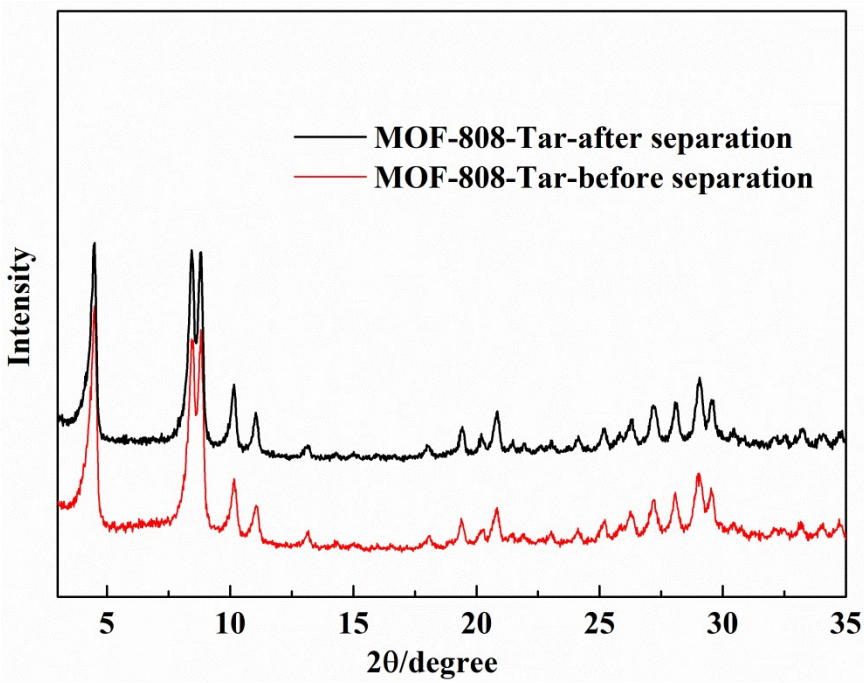


Fig. S34 The PXRD patterns of MOF-808-Tar before and after enantioseparation of 1-(4-bromophenyl)ethanamine.

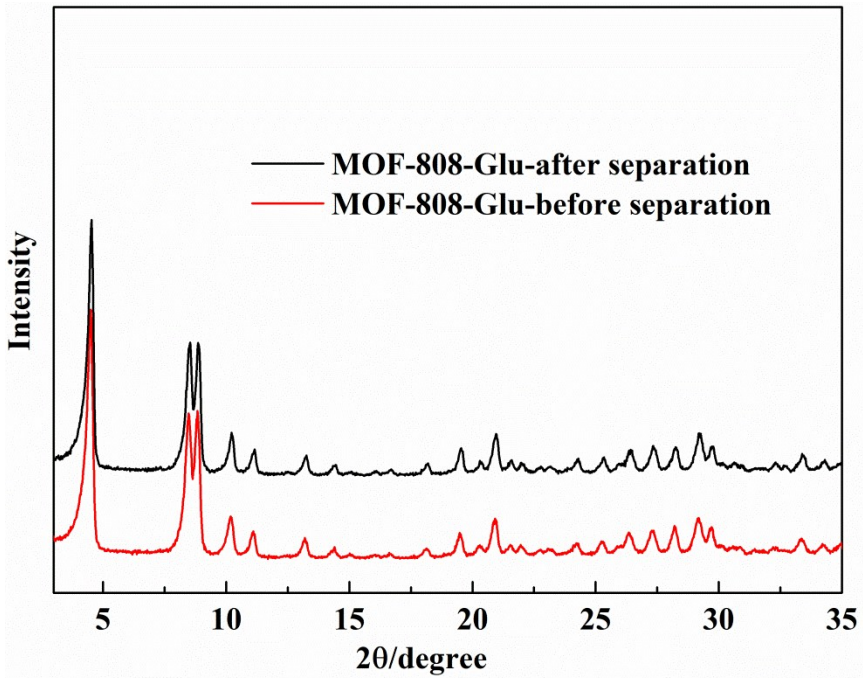


Fig. S35 The PXRD patterns of MOF-808-Glu before and after enantioseparation of 1-phenylethanol.

9. References

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