Supporting Information

Synthesis of homochiral zeolitic imidazolate frameworks *via* solvent-assisted linker exchange for enantioselective sensing and separation

Chao Zhuo, Fei Wang* and Jian Zhang*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian 350002, Fuzhou, PR China.

E_mail: zhj@fjirsm.ac.cn, wangfei04@fjirsm.ac.cn

Materials and methods

All materials were commercially available in analytical grade and used without further purification.

^{1}H NMR spectra were recorded with an AVANCE Ⅲ (400 MHz) spectrometer. IR spectra were recorded with a VERTEX70 FT-IR spectrophotometer. UV-Vis spectra were recorded with a Lambda 950 spectrophotometer. Powder X-ray diffractograms (PXRDs) were recorded on a MiniFlex Ⅱ powder X-ray diffractometer. The elemental analysis results were obtained by a vario MICRO elemental analyser. Thermogravimetric analyses (TGA) (N_2 atmosphere, heating rate of 10 ^{o}C/min) were carried out with a NETZSCH STA 449F3 TGA apparatus. The liquid and solid-state CD spectra were recorded using Biologic Science Instruments at 25 ^{o}C.

Preparation of S(R)-OH-bim

S(R)-OH-bim was synthesized according to previous report.[1]

Preparation of ZIF-78

Crystal sample of ZIF-78 was synthesized according to previous report.[2]

Preparation of S(R)-ZIF-78h through SALE

1.62 g (10 mmol) S-OH-bim was dissolved in 40 mL n-butyl alcohol to obtain 0.25 M stock solution. And 100 mg as-synthesized ZIF-78 was placed in a 13 mL sealed glass bottle along with 5 mL stock solution above. Then it was allowed to reaction at 120 ^{o}C for 7 days, but the solution need to be replaced with fresh stock solution every 24 hours. The solid sample was washed and collected as S-ZIF-78h in approximately 80% yield. R-ZIF-78h was prepared in the same way except for R-OH-bim replacing S-OH-bim.

CD measurement of D(L)-proline with S-ZIF-78h

D(L)-proline standard aqueous solutions were prepared in concentration of 0.07M. Then they were mixed in a volume ratio of 4:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:4. Once the CD signals of those mixed samples were recorded, 0.1mg S-ZIF-78h was added into 2mL of them each, following by another measurement in 10 seconds. All the quantities used here were according to condition optimization.

Elemental analysis

ZIF-78 structure formula: Zn(2-nim)(5-nbim), molecule formula: $ZnC_{10}H_6N_6O_4$, calculated: C 35.37%, H 1.78%, N 24.75%, found: 34.23%, H 2.21%, N 23.52%.

S-ZIF-78h Structure formula: $Zn(2\text{-nim})(5\text{-nbim})_{0.743}(S\text{-OH-bim})_{0.257}$, molecule formula: $ZnC_{10.514}H_{7.285}N_{5.743}O_{3.743}$, calculated: C 37.21%, H 2.16%, N 23.70%, found: C 37.57%, H 2.68%, N 22.26%.

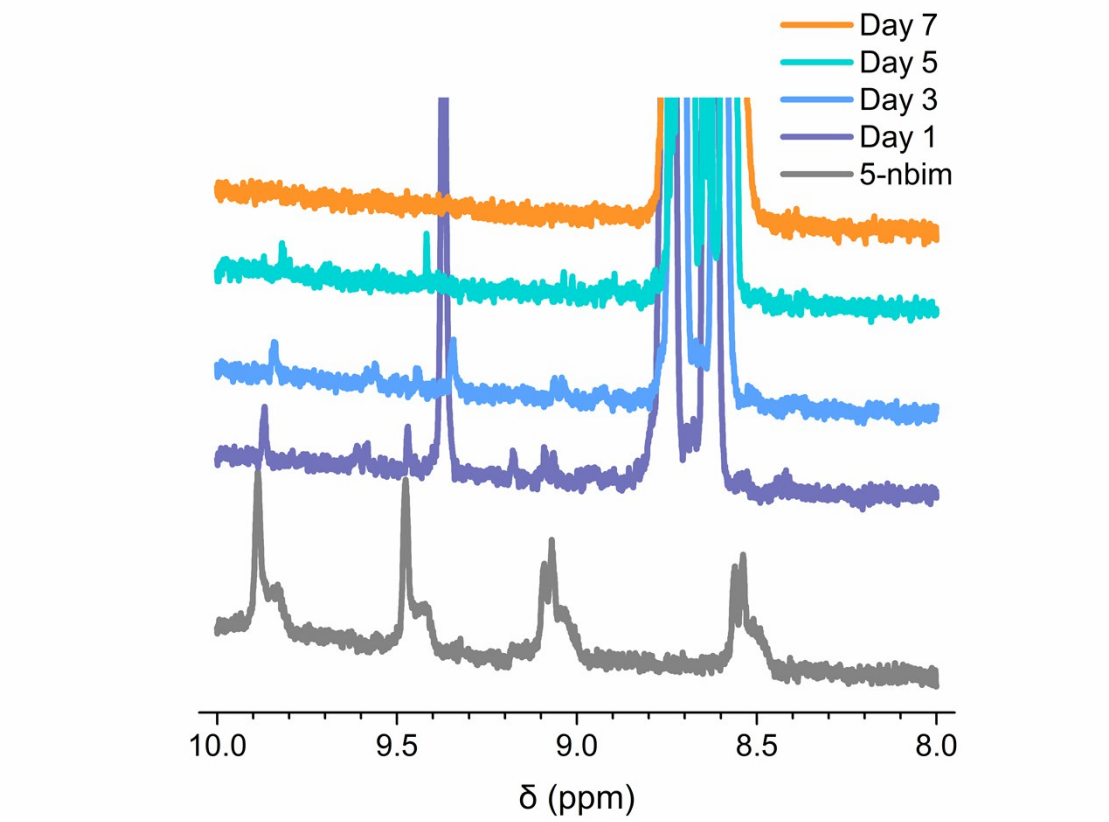

Fig. S1 ^{1}H NMR spectra (d-TFA) of 5-nbim in n-butanol solution and solutions replaced at different day.

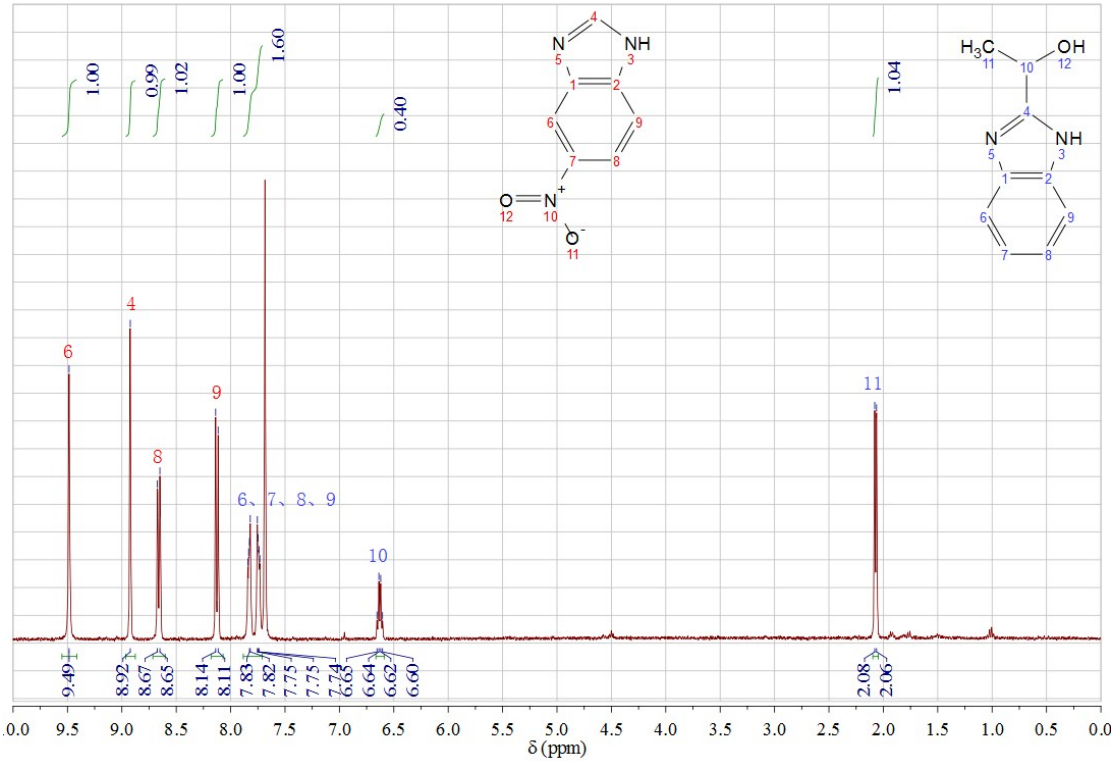

Fig. S2 ^{1}H NMR spectra (d-TFA) of S-ZIF-78h in detail.

$$\text{Exchange Ratio} = \frac{\frac{1.04}{3}}{1+\frac{1.04}{3}} * 100\% = 25.7\%$$

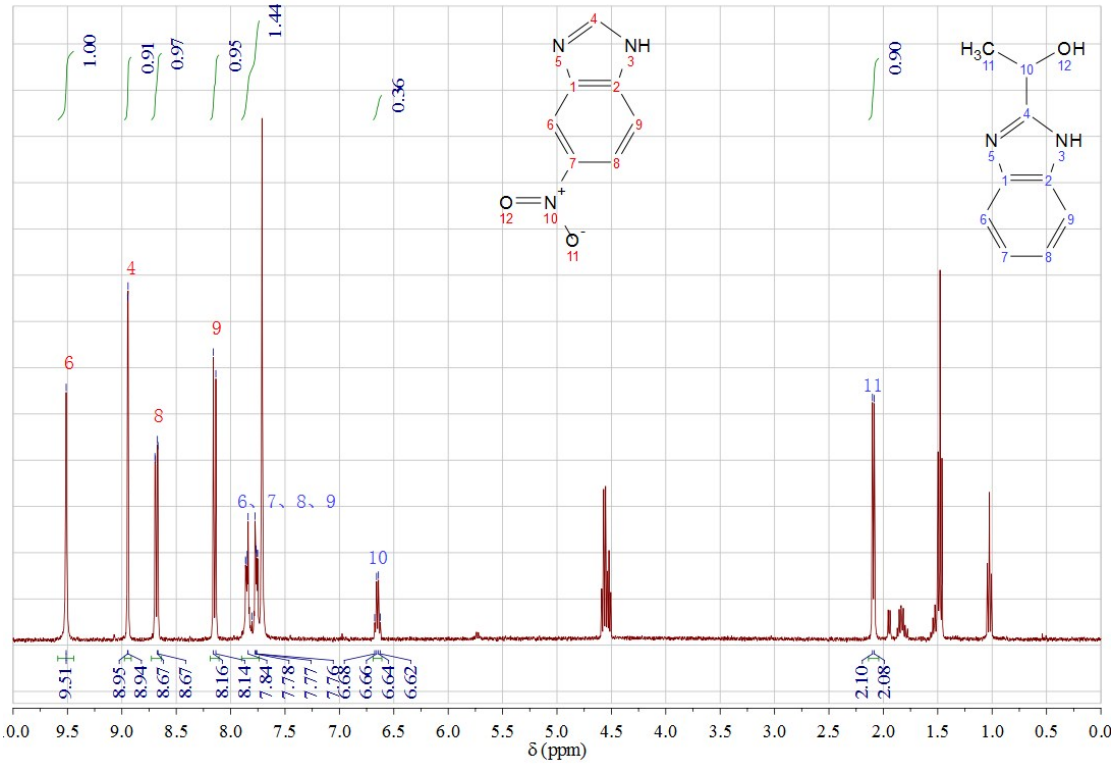

Fig. S3 ^{1}H NMR spectra (d-TFA) of R-ZIF-78h in detail.

$$\text{Exchange Ratio} = \frac{\frac{0.90}{3}}{1+\frac{0.90}{3}} * 100\% = 23.1\%$$

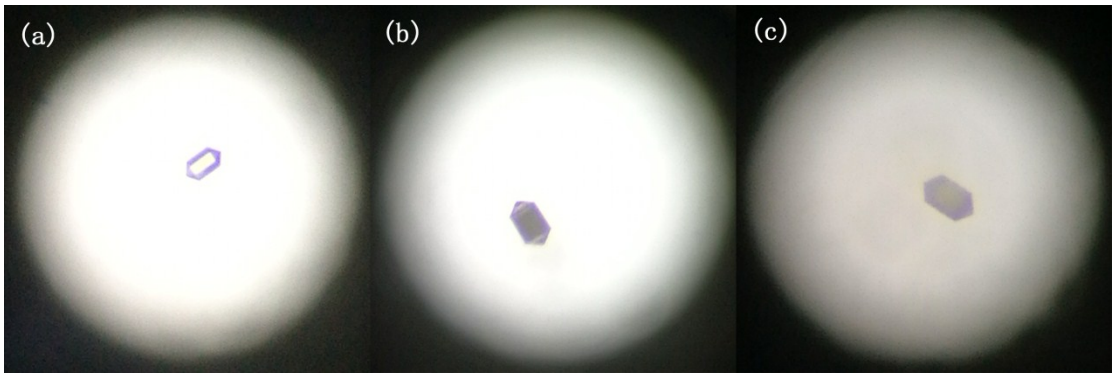

Fig. S4 Photos of (a) ZIF-78, S-ZIF-78h (b) before and (c) after immersed in 0.07M D-proline for 8 hours.

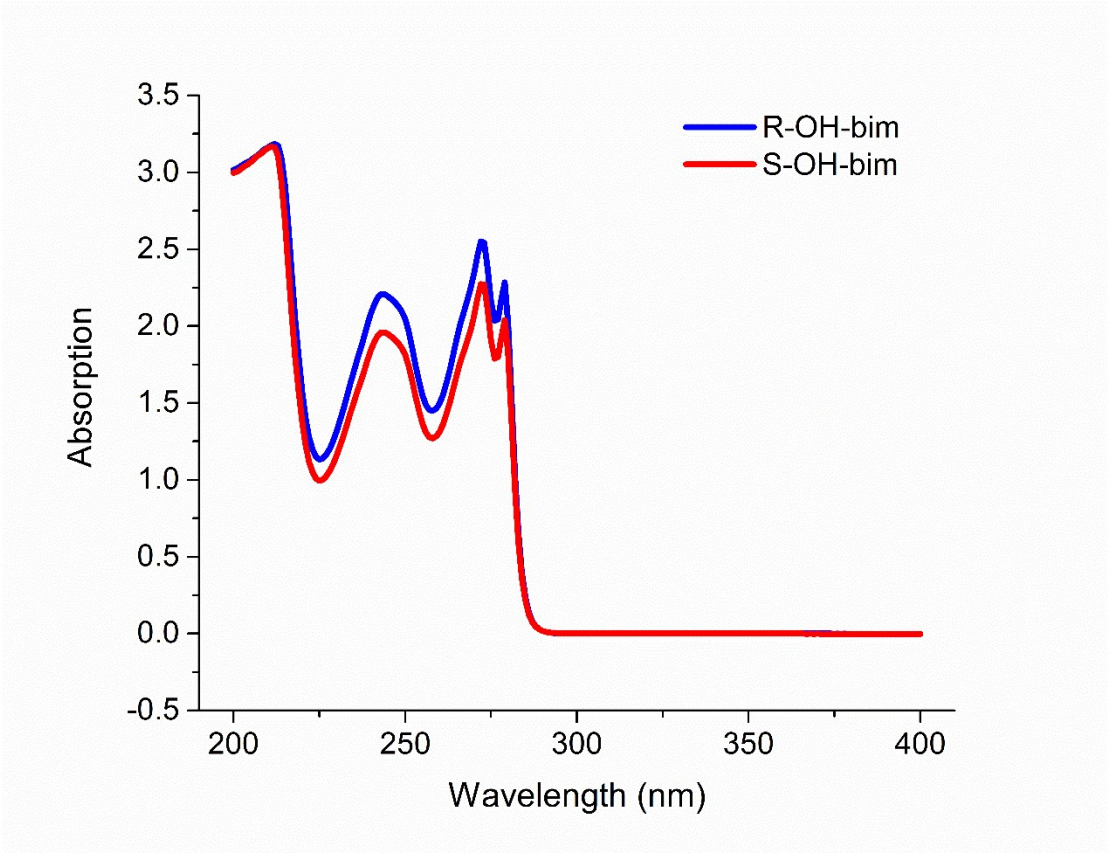

Fig. S5 UV absorption spectra of S(R)-OH-bim in aqueous solution.

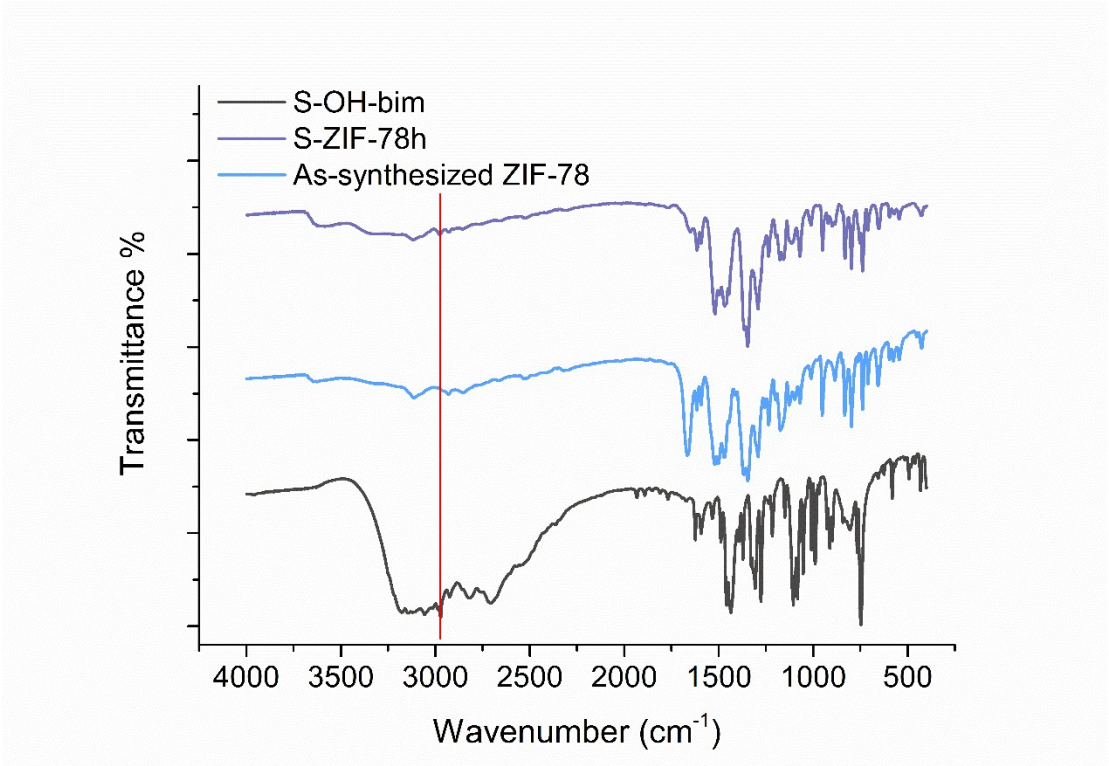

Fig. S6 IR spectra of S-OH-bim, S-ZIF-78h and ZIF-78.

After SALE, S-ZIF-78h shows an extra weak absorption peak at 2975 cm^{-1}, corresponding to C-H stretching vibration of CH_3 which can only be observed in S-OH-bim. It indicated that 5-NO_2-bim

did be replaced by S-OH-bim in a certain ratio.

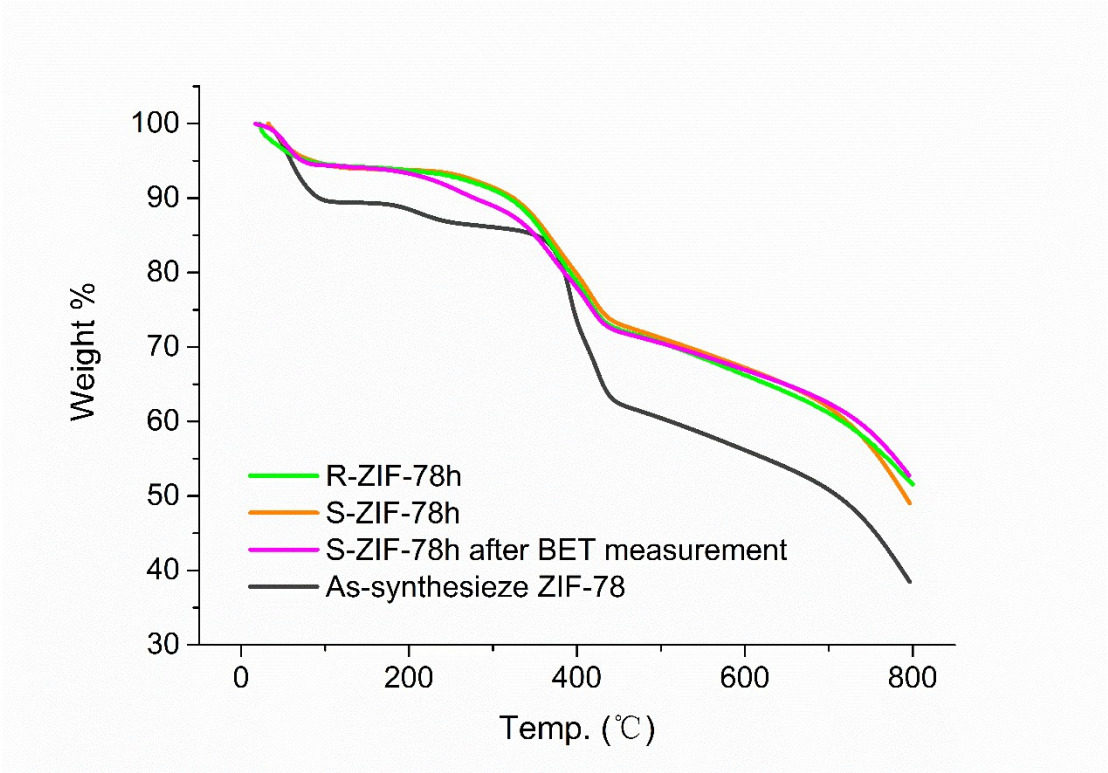

Fig. S7 TGA analysis of S(R)-ZIF-78, S-ZIF-78h after BET measurement and as-synthesized ZIF-78.

After SALE, S(R)-OH-bim becomes less stable than ZIF-78, whose framework collapses at about 330 ^{o}C. The same weight-loss pattern indicates the same framework between S(R)-ZIF-78h and ZIF-78. So is S-ZIF-78h after BET measurement.

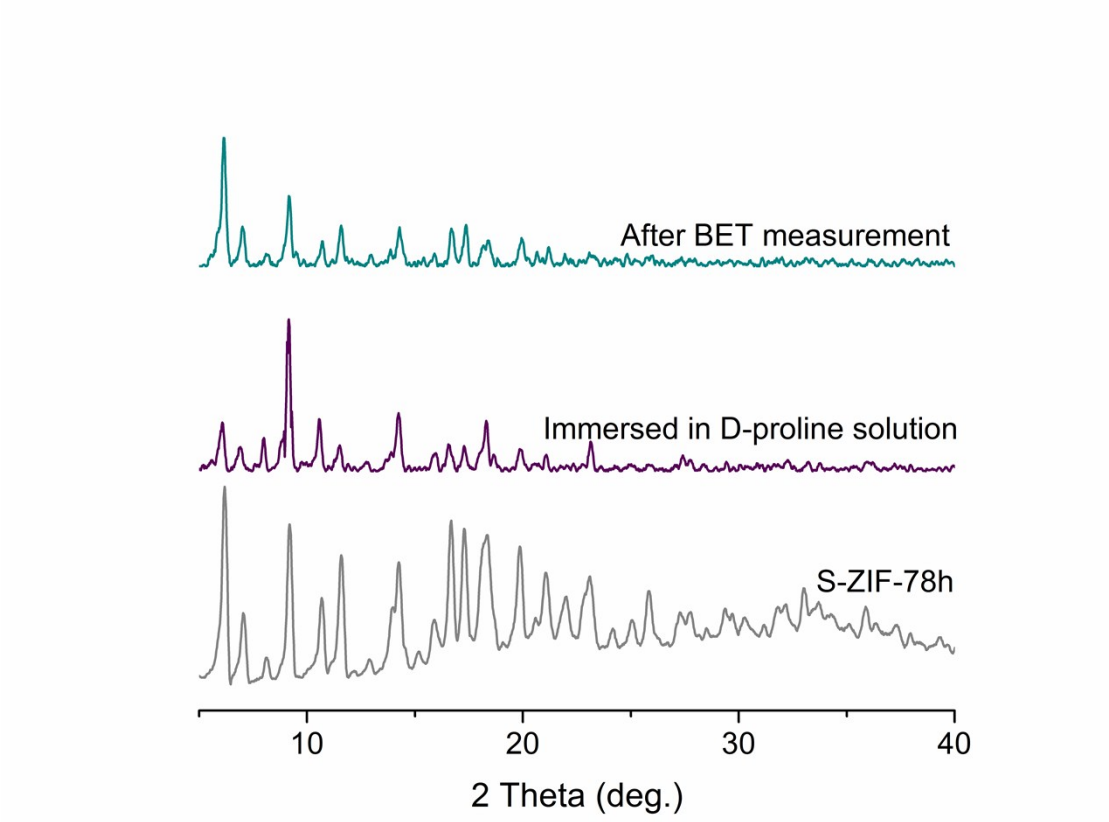

Fig. S8 The powder XRD patterns of S-ZIF-78h, S-ZIF-78h after BET measurement and S-ZIF-78h in 0.07M D-proline for 8 hours.

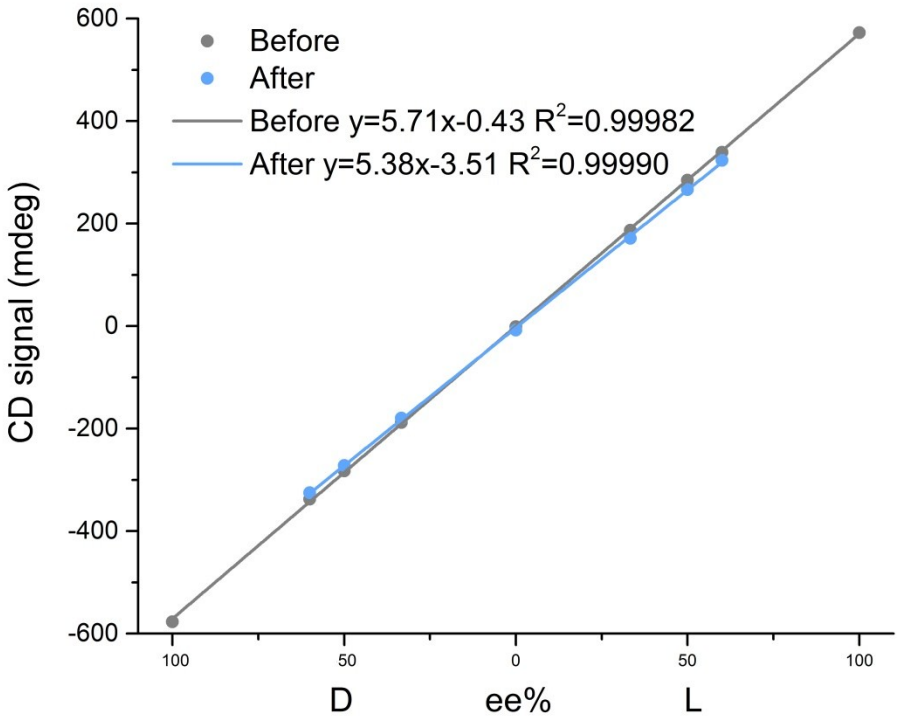

Fig. S9 linear fits of CD signals at 214nm in different ee%.

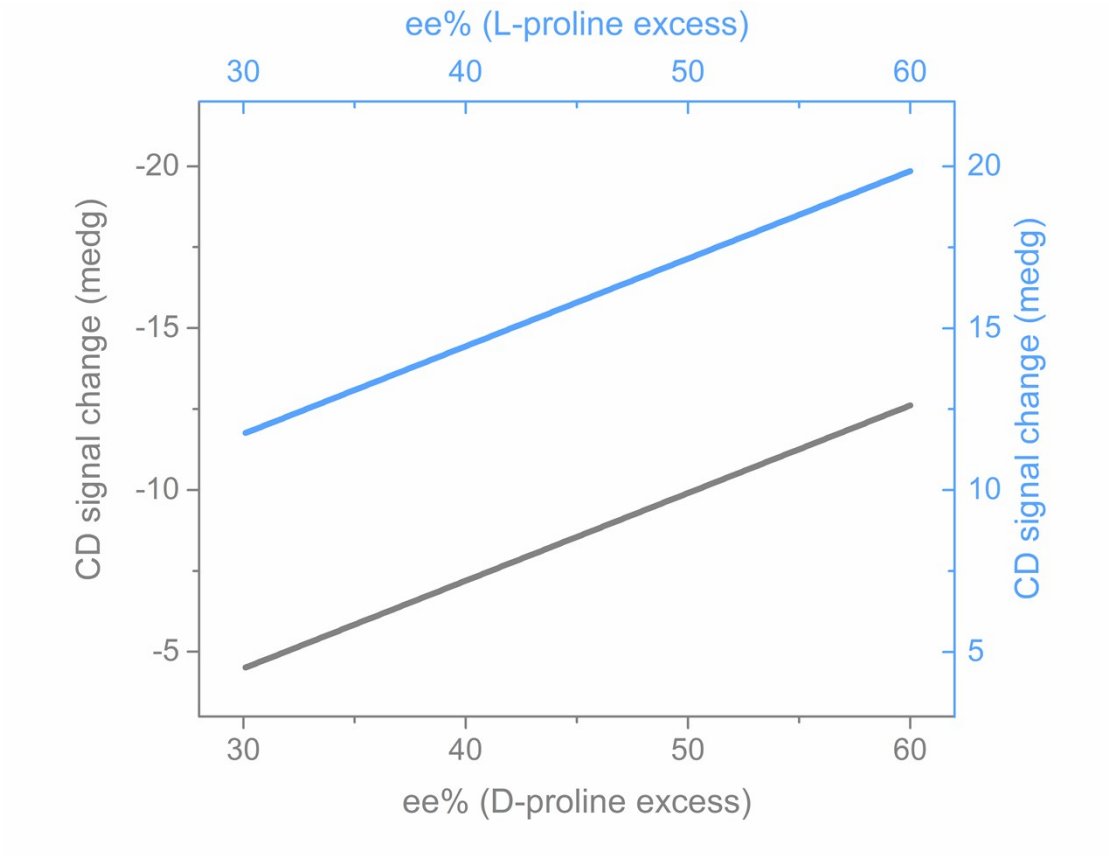

Fig. S10 Absolute value changes of CD signals in defferent ee% according to linear fits.

1 F. Wang, Y. -H.Tang and *J.* Zhang, *Inorg. Chem.,* 2015, **54**, 11064.

2 Y. J. Ban, Y. S. Li, X. L. Liu, Y. Peng and W. S. Yang, *Micro. Meso. Mat.,* 2013, **173**, 29.