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Decorated traditional cellulose with nanoscale chiral metal-organic frameworks for enhanced enantioselective capture

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Index

1. Materials and Instrumentation

Microcrystalline cellulose was purchased from Sinopharm Group Chemical Reagent Co. Ltd. $Cu(OAc)_2 \cdot H_2O$ was obtained from Aladdin Instrument Corporation. Succinic anhydride, *L*-malic acid, 4, 4'-bipyridine, 2-methylimidazole and (±)-1-(1-naphthyl)ethanol were supplied by Macklin Biochemistry Technology Co. Ltd. (Shanghai, China). All the solvents were purchased from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Ultrapure water was produced using the Milli-Q system (Millipore, Bedford, MA, USA).

Scanning electron microscopy (SEM) was carried out on a S-4300 instrument (Hitachi, Japan). The energy dispersive X-ray (EDS) analysis was recorded on a JSM-700F instrument (Hitachi, Japan). Infrared absorption spectra were obtained from a Nicolet 6700 infrared Fourier transform spectrometer (Bruker, Germany). Powder X-ray diffraction (PXRD) data were collected on X-ray diffractometer with Cu target (45 kV, 40 mA) (Thermo Fisher, USA). Thermogravimetric analysis (TGA) was measured on STA 409 PC thermogravimetric analysis (Netzsch, Germany). High performance liquid chromatography (HPLC) analysis was performed on Agilent 1260 series system with a G1314A model multiple wavelength UV–Vis detector (Agilent, USA) with Chiral column Chiralpak OD-H (4.6*250 mm, 5 μm). Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was conducted on an ICPE-9820 equipment (Shimadzu, Japan).

2. Synthesis of the nanosized CuLBH functionlized carboxylated cellulose (CC-CuLBH) composite

2.1 Preparation of carboxylated cellulose

The preparation of carboxylated cellulose (CC) was referred to the reported reference.[1] Briefly, 1 g microcrystalline cellulose (MC) was added into a 50 mL flask with 15 mL N, N-dimethyl acetamide (DMF). Then, 5 g butanedioic anhydride was added into the solution under stirring. After that, the system was heated to 100 ^{o}C for 24 h under nitrogen. After cooled to room temperature, the obtained product was

filtered and washed with DMF, water, ethanol and acetone for 3 times in turn. Finally the CC obtained was dried overnight at 60 ^{o}C in a vacuum condition.

2.2 Preparation of CC-CuLBH

$Cu(OAc)_2 \cdot H_2O$ (0.9 g) and carboxylated cellulose (1.0 g) were added into a 100 mL flask with 60 mL of methanol/water (v/v, 1:1), and the solution was stirred at 100 ^{o}C for 6 h under nitrogen atmosphere. After the supernatant was removed by hot filtration, *L*-malic acid (0.42 g, 3 mmol), 4, 4'-bipyridine (0.23 g, 3 mmol) and 30 mL methanol/water (1:1, v/v) were added. The reaction was conducted at 100 ^{o}C for 24 h under nitrogen protection. After cooled to room temperature, the product was filtered, washed with water and methanol, respectively. Finally, CC-CuLBH was obtained by dried overnight at 60 ^{o}C in vacuum.

The composite CC-CuLBH consists of CuLBH and CC. The quality of CuLBH in CC-CuLBH was determined as follows. Firstly, the maximum adsorption amount of CC for copper irons was investigated. Then, a low proportion of *L*-malic acid and 4, 4'-bipyridine relative to regular molar ratio of Cu^{2+} was added to avoid the self-nucleation of CuLBH in the preparation process of CC-CuLBH. The quality of CuLBH in CC-CuLBH was finally determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The process can now be reformulated with more detail as follows.

0.04000 g CC-CuLBH was dissolved in 30 mL of 4% hydrochloric acid/H_2O solution, and diluted to a constant volume of 100.00 mL with H_2O. Then 1.00 mL of this mother liquor was diluted stepwise to another constant volume of 25.00 mL with H_2O. The supernate was gained by filtering and afterwards analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). All tests above were performed in triplicate. The standard curve and regression equation were also established ($I = 3815.92906C + 29.28256$, $R^2 = 0.99996$). The results showed that the average concentration of Cu^{2+} was 0.603 mg L^{-1}. That is to say, in 50 mg of CC-CuLBH, CuLBH was 11.5 mg and CC was 38.5 mg. This proportion was brought into

line with their physical blended in the next step.

2.3 Preparation of [Cu(*L*-mal)(bpy)·H_2O] (CuLBH)

CuLBH was obtained according to previous literature.[2] $Cu(OAc)_2·H_2O$ (0.09 g, 0.45 mmol), *L*-malic acid (0.123 g, 0.9 mmol), 4, 4'-bipyridine (0.069 g, 0.45 mmol), and 9 mL methanol/water (1:1, v/v) were mixed in a 25 mL round bottom flask and stirred for 24 h at 100 °C. Then the mixture was cooled to room temperature, filtrated and washed with water and methanol. The product was activated by methanol for 48 h, and finally dried overnight at 60 °C in a vacuum atmosphere.

2.4 Preparation of [Cu(*L*-mal)(bpy)] (CuLBH) with different sizes (CuLBH-1, CuLBH-2, CuLBH-3, CuLBH-4, CuLBH-5, CuLBH-6, CuLBH-7, CuLBH-8, CuLBH-9)

CuLBH-1, CuLBH-2, CuLBH-3 were prepared by the similar procedure with CuLBH described above. The only difference was the dosage of the reaction solvent. The original amount of 9 mL methanol/water (1:1, v/v) was changed to 18 mL, 45 mL, 90 mL in turn, and the obtained products were denoted as CuLBH-1, CuLBH-2 and CuLBH-3, respectively.

CuLBH with different size in the presence of various concentrations of 2-methylimidazole (2-MI) was synthesized according to the references.[2,3] $Cu(OAc)_2·H_2O$ (0.27 g, 1.35 mmol), *L*-malic acid (0.369 g, 2.7 mmol), 4, 4'-bipyridine (0.207 g, 1.35 mmol) and 27 mL of 2-MI methanol/water (v/v, 1:1) at the concentration of 10 mmol L^{-1}, 20 mmol L^{-1}, 30 mmol L^{-1}, 50 mmol L^{-1}, 100 mmol L^{-1}, 150 mmol L^{-1} were mixed separately in a 50 mL round bottom flask and stirred for 24 h at 100 °C. Then these admixtures were cooled to room temperature, filtrated, washed with water and methanol, respectively. The products were all activated by methanol for 48 h, and finally dried overnight at 60 °C in vacuum. The resulting products were named as CuLBH-4, CuLBH-5, CuLBH-6, CuLBH-7, CuLBH-8, CuLBH-9 in sequence.

3. Typical enantioseparation procedure for (±)-1-(1-naphthyl)ethanol

3.1 Preparation of standard solutions

(±)-1-(1-naphthyl)ethanol standard was dissolved with *n*-hexane to obtain 1.0 mg mL^{-1} reserve solution and stored under 4 ^{o}C. 50 μg mL^{-1} of standard solution was gained by diluted stepwise with the corresponding extraction solvent.

3.2 Typical separation procedure using the CC-CuLBH composite

For extraction of 1-(1-naphthyl)ethanol, racemic solution (50 μg mL^{-1}, 0.5 mL) and six different adsorbents (50 mg), including CC, CuLBH, CuLBH-6, CC/CuLBH (38.5 mg/11.5 mg), CC/CuLBH-6 (38.5 mg/11.5 mg) and CC-CuLBH, were mixed in vials, respectively. These six solutions were all first immersed into an oscillating bath of *n*-hexane (9.5 mL) at room temperature for 24 hours. Then the supernatants were removed. The collected composite-enantiomer complexes were mixed with 1 mL methanol and oscillated at room temperature for 20 hours in order to retrieve the absorbed enantiomers. The eluants were evaporated under a gentle nitrogen stream. Finally, the residues with 1-(1-naphthyl)ethanol enantiomers were redissolved in 500 μL of isopropanol and analyzed by HPLC. They were resolved on Chiralpak OD-H column (4.6 × 250 mm, 5 μm) with *n*-hexane/isopropanol (95:5, v/v) as the mobile phase at a flow rate of 0.1 mL min^{-1} at 25 ^{o}C and 254 nm as the detection wavelength. The enantiomeric excess (*ee*) values were calculated by comparing the ratio of the enantiomers. All tests were performed in triplicate.

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4. Table S1, Figure S1-S9

Table S1 Compared with other reported methods for the sample preparation and enantioselective capture.

Material	Sample preparation	Enantioselective capture	*ee* value (%)	Ref.
$[Zn_2(L\text{-}Phe)_2(bpe)_2]_n$	solvothermal condition	alanine	50%	[1]
		leucine	25%	
SiO_2-CuLBH	in situ synthesis	phenyl methyl sulfoxide	31%	[2]
MGO-CuLBH	one-step method	propranolol hydrochloride	98%	[3]
MGO–ZnBND	one-step method	2,2'-furoin	85%	[4]
		benzoin	66%	
MGO-ZnCB	one-step method	1, 1'-bi-2-naphthol	74.8%	[5]
		2, 2'-furoin	57.4%	
N-rGO/CD-Cu-CMC	self-assembly synthesis	Tryptophan	/	[6]
Cellulose	Cu^{2+} adsorption	/	/	[7]

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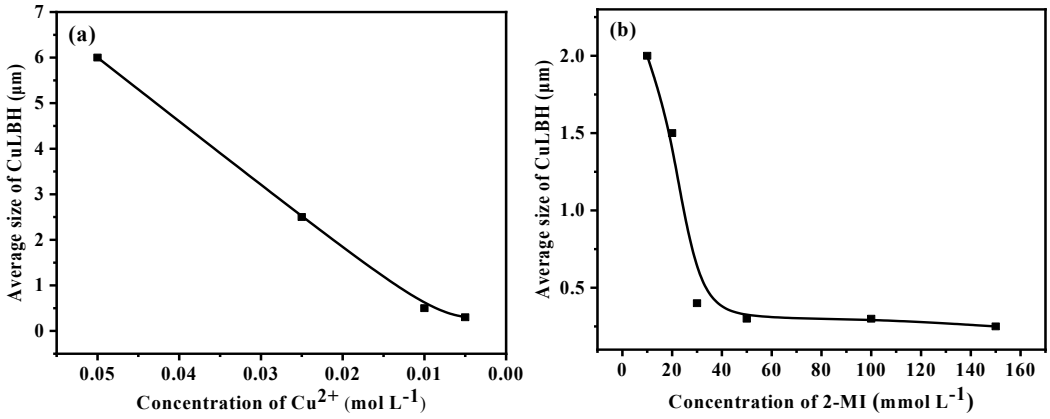


Figure S1 (a) The plot of Cu^{2+} concentration versus the average size of CuLBH crystals; (b) The plot of 2-methylimidazole (2-MI) concentration versus the average size of CuLBH crystals.

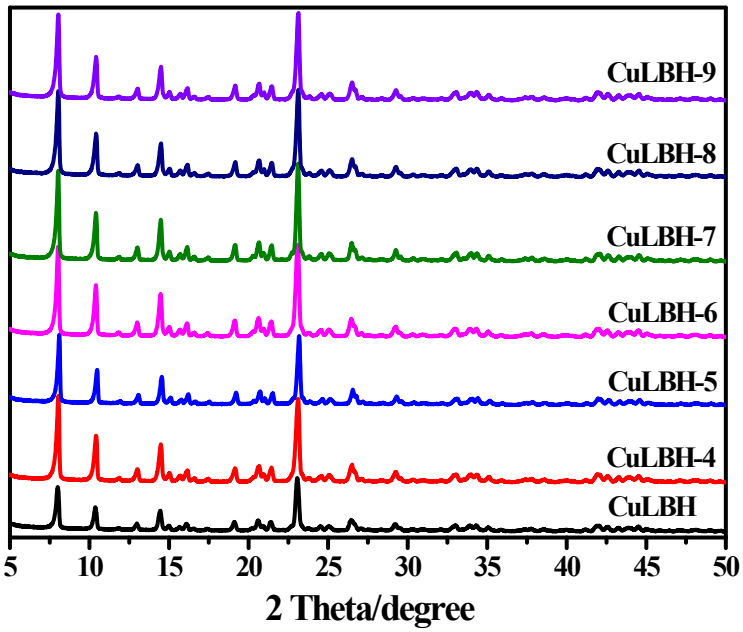


Figure S2 Comparison of PXRD images for CuLBH without and with regulation by 2-MI.

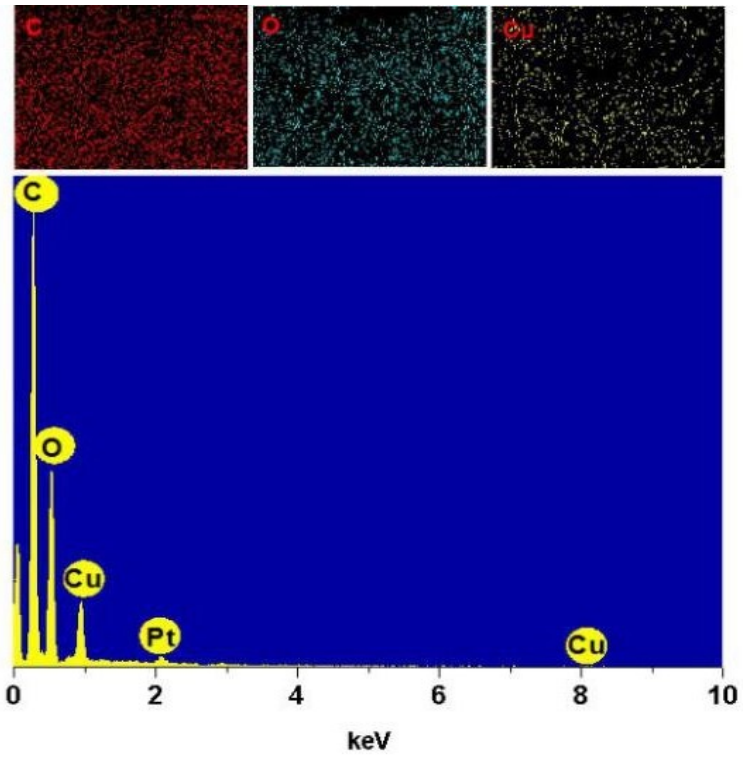


Figure S3 The energy dispersive X-ray (EDS) result of CC-CuLBH.

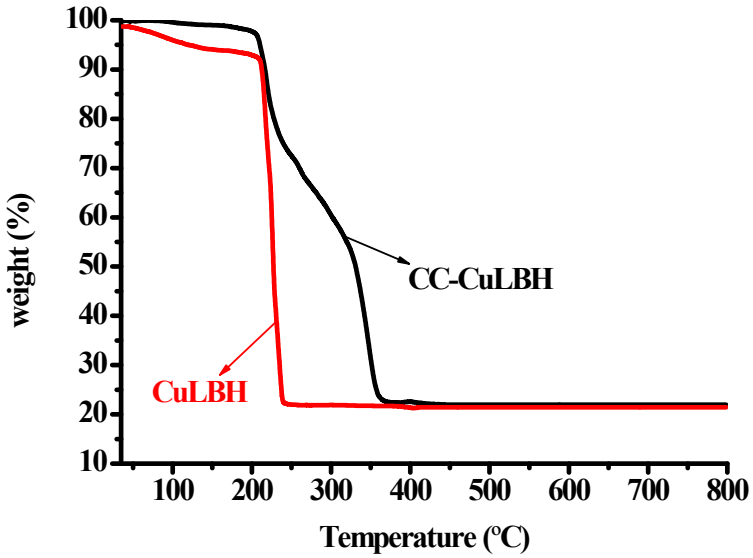


Figure S4 The thermogravimetric curves of CC and CuLBH.

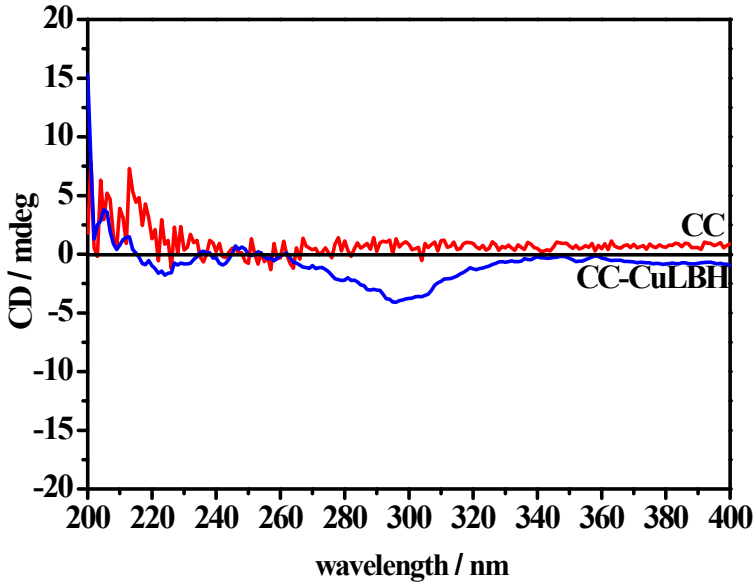
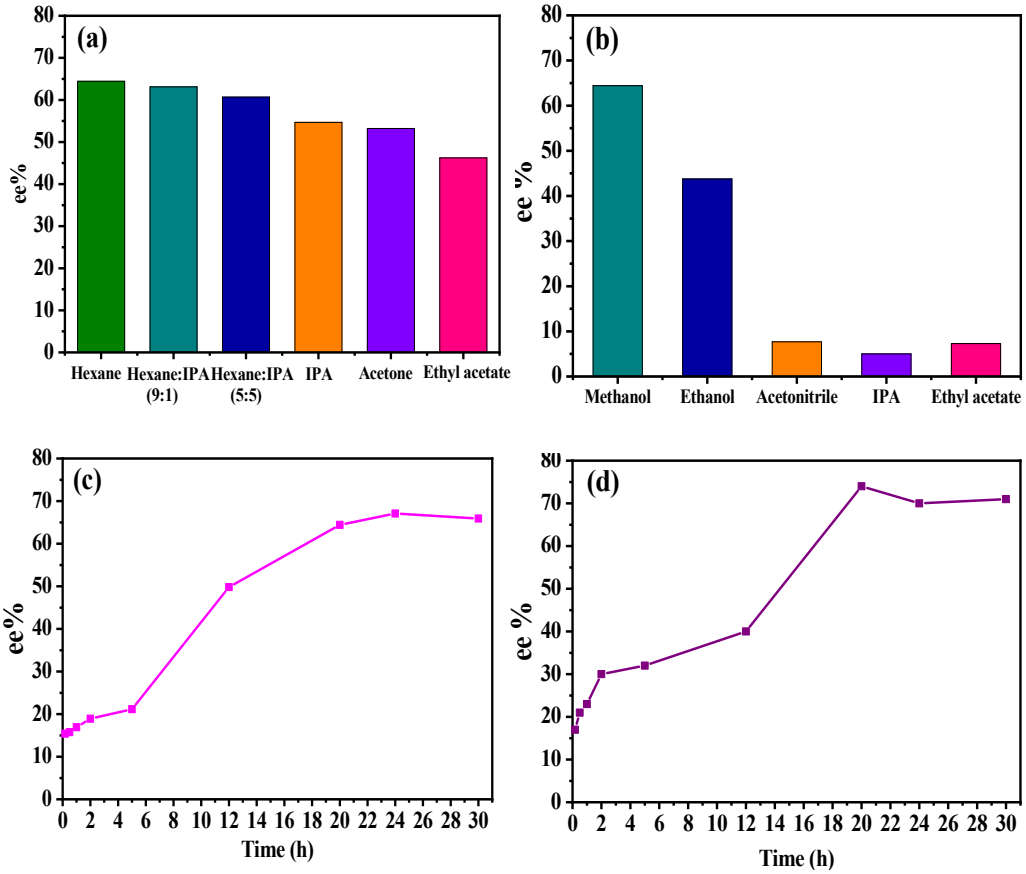


Figure S5 Solid-state CD spectra of CC and CC-CuLBH.



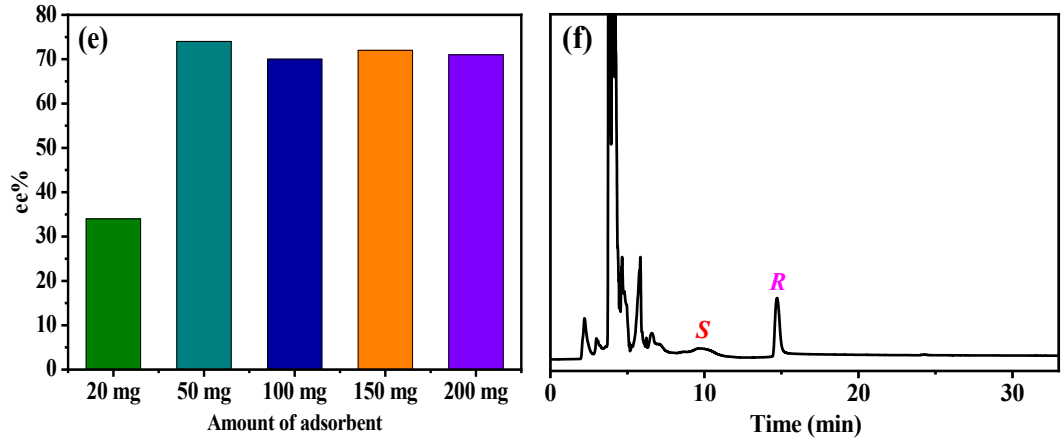


Figure S6 Effects of (a) extraction solvent; (b) eluting solvent; (c) extracting time; (d) elution time; (e) amount of CC-CuLBH on *ee* values of 1-(1-naphthyl)ethanol; (f) Optimization results for 1-(1-naphthyl)ethanol. Condition: Chiralpak OD-H column (4.6 × 250 mm, 5 μm); mobile phase, hexane/isopropanol (95:5, v/v); flow rate, 0.2 mL min^{-1}; detection wavelength, 254 nm; column temperature, 25 °C.

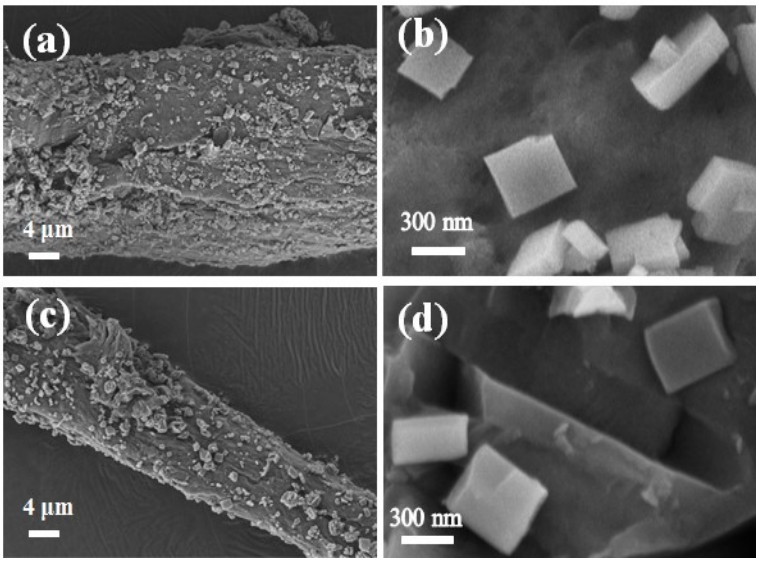


Figure S7 SEM images of CC-CuLBH (a), (b) before the enantioseparation tests (c), (d) after the enantioseparation tests.

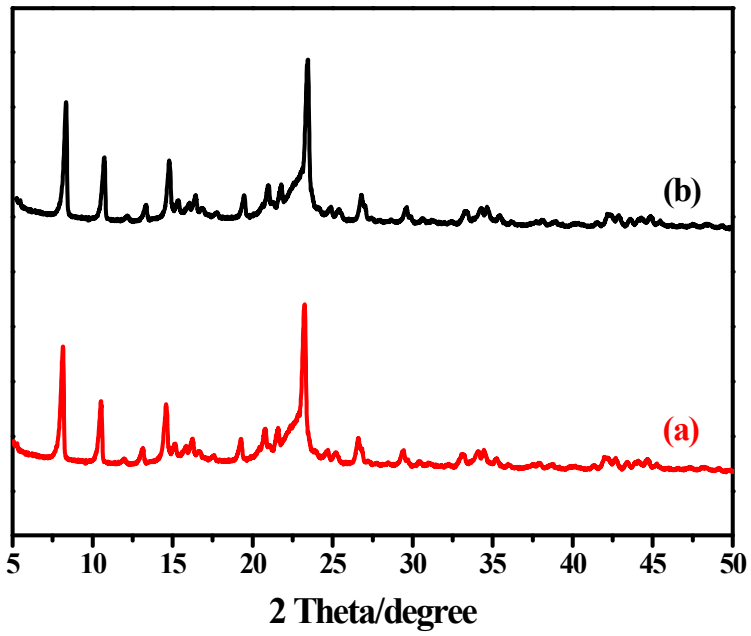
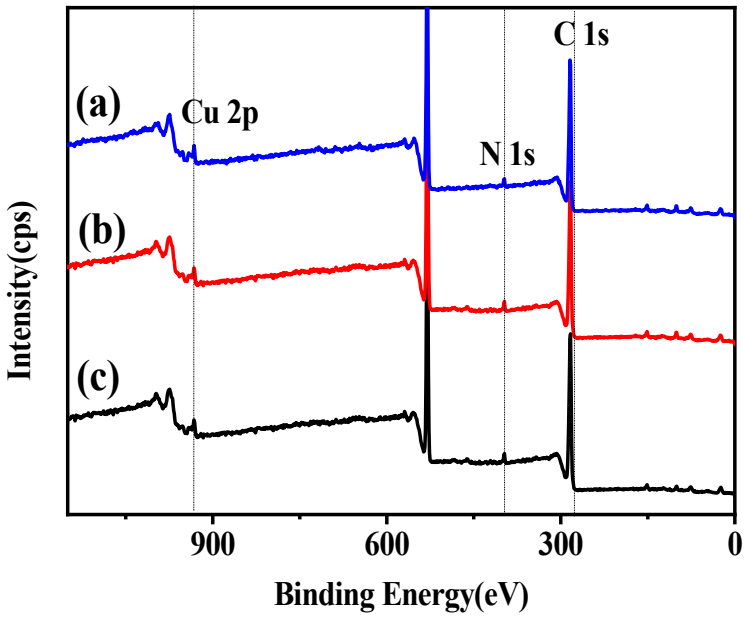


Figure S8 PXRD patterns of CC-CuLBH (a) before the enantioseparation tests (b) after the enantioseparation tests.



Sample Element content (wt %)	C 1s	N 1s	Cu 2p
(a)	92.51	2.42	5.07

(b)	95.15	1.65	3.20
(c)	95.23	1.62	3.15

Figure S9 XPS analysis of (a) CuLBH (b) CC-CuLBH before the enantioseparation tests (c) CC-CuLBH after the enantioseparation tests.