Supporting Information

Homochiral Metal–Organic Framework Membranes Synthesized Using a Nonstochastic Chiral Bias for Enhanced Enantioselective Separation

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1. Materials

$Co(CH_3COO)_2{\cdot}4H_2O$ was purchased from by Boer Chemical Reagents CO., Ltd. (Shanghai, China). 2,5-pyridinedicarboxylic acid, dimethyl pyridine-2,5-dicarboxylate, acetonitrile (ACN), α-Al_2O_3, trifluoroacetic acid (TFA), ibuprofen, flurbiprofen, lactic acid and naftopidil were purchased from by Aladdin Reagent Co., Ltd. (Shanghai, China). KBr and Ethanol (EtOH) were purchased from by Meryer Reagents CO., Ltd. (Shanghai, China). Polyaniline (PANI, $M_w \approx 5 \times 10^4$) was purchased from by Sigma-Aldrich CO., Ltd. (USA). Trifluoroacetic acid was purchased from by Energy Chemical Reagents CO., Ltd. (Anhui, China). All reagents were used as received without further purification.

2. Synthetic Procedures

2.1 Synthesis of (*P*)-CoMOF crystals

As a typical preparation procedure, a mixture of dimethyl pyridine-2,5-dicarboxylate (0.5 mmol) and $Co(CH_3COO)_2{\cdot}4H_2O$ (0.5 mmol) was suspended in 8 mL deionized water and sealed in a 20 mL Teflon-lined autoclave. The pH of the solution is 3.6. Upon heating at 180 ^oC for three days, the autoclave was slowly cooled to room temperature. The red crystals were collected, washed with deionized water and vacuum dried (0.091 g, yield 66 %).

2.2 Synthesis of (*M*)-CoMOF crystals

As a typical preparation procedure, a mixture of 2,5-pyridinedicarboxylic acid (0.5 mmol) and $Co(CH_3COO)_2{\cdot}4H_2O$ (0.5 mmol) was suspended in 8 mL HCl (0.03 mol L^{-1}) and sealed in a 20 mL Teflon-lined autoclave. The pH of the solution is 2.4. Upon heating at 180 ^oC for three days, the autoclave was slowly cooled to room temperature. The red crystals were collected, washed with deionized water and vacuum dried (0.083 g, yield 60 %).

2.3 Preparation and pretreatment of α-Al_2O_3 substrate

Use a powder press to press at a pressure of 15 MPa for 5 minutes to obtain an alumina matrix blank with a thickness of about 3 mm and a diameter of 18 mm. Subsequently, the compacted alumina billet was put into a high-temperature tube furnace and sintered at 1000 ^oC for 12 hours in an air atmosphere to obtain a porous alumina matrix. The sintered alumina substrate was polished with 2000-grit sandpaper to make the surface smooth, then rinsed several times with distilled water and absolute ethanol to remove dust, and finally dried in an oven at 80 ^oC for later use. Then, PANI was used to chemically modify the surface of the homemade porous alumina.

2.4 Synthesis of (*P*)-CoMOF membrane

The homochiral (*P*)-CoMOF membrane was prepared on PANI-Al_2O_3 support by the in-situ growth method. Briefly, dimethyl pyridine-2,5-dicarboxylate (0.25 mmol), $Co(CH_3COO)_2{\cdot}4H_2O$ (0.25 mmol), and deionized water (10 mL) were mixed and stirred vigorously for 12 h. A PANI-Al_2O_3 support was placed, with the PANI-surface up, in a Teflon lined stainless steel autoclave (25 mL) with the solution mixture. The autoclave was heated at 180 ^oC for 6 h in an oven and then cooled down to room temperature. After cooling, the membrane was washed with deionized water and vacuum dried at 80 ^oC for 6 h.

2.5 Stability test of the membrane in solvent.

The synthesized MOF membranes were immersed in common solvents (water, ethanol, acetonitrile and *n*-hexane) for 10 days. After being taken out, the membranes were dried at 80oC for 12h and then subjected to XRD analysis.

3. Methods

3.1 Characterization

The powder X-ray diffraction (PXRD) patterns of all materials were collected on a Bruker D8 Advance instrument with Cu-Kα radiation operating at 40 kV and 40 mA, and recorded from 5^o to 60^o (2θ) at a scan rate of 0.3 time/step. Scanning Electron Microscopy (SEM) were performed on Carl Zeiss Gemini SEM 300 with 5 kV and Hitachi S-4800 SEM with 10 kV. The ultraviolet-visible (UV-Vis) spectra was performed with a Shimadzu UV-2700 spectrometer. The circular dichroism (CD) measurements were performed using a MOS-500 Spectrometer. The samples of 2 mg and KBr of 150 mg are fully ground evenly, and the solid samples are tested with the special mold matching with the instrument. The spectra were recorded from 200 to 800 nm with a path length of 1.0 nm.

3.2 Measurement of Membrane Chiral Selectivity

The chiral transport through the membrane was performed in a diffusion cell where the membrane was placed in the middle of the cell. The effective area of the membrane was 0.79 cm^2. 200 mL of racemic solution in ACN, and fresh ACN, were added as the feed solution and permeate side, respectively. The racemic compound was allowed to diffuse through the membrane due to the concentration gradient. In this work, racemic ibuprofen/flurbiprofen was dissolved in fresh ACN to prepare feed solutions of different concentration (0.005 mol L^{-1}, 0.01 mol L^{-1} 0.03 mol L^{-1} and 0.05 mol L^{-1}). The separation process was allowed to proceed for 12 h and 1 mL of permeate was collected every 2 h. The collected permeates were sent for HPLC analysis.

The concentrations of the enantiomers were analyzed with a high-performance liquid chromatography (HPLC) system (Agilent 1200 Series) equipped with a diode array detector (DAD) and an autosampler. Chromatographic separations were performed at 25 °C using a CHIRALPAK AD-RH column (5 µm, 4.6 mm × 250 mm). The analyses were performed by a UV detector at 254 nm using a mobile phase consisting of 50 % ACN, 50 % TFA aqueous solution at a flow rate of 0.5 mL·min^{-1}. The injected sample volume was 3 µL.

3.3 Calculation of enantioselectivity and flux

The results of chiral separation were expressed by enantiomeric excess (*ee*) value. The *ee* value was calculated using the areas of each enantiomer, A_R (*R*-enantiomer) and A_S (*S*-enantiomer) by the equation below:

$$ee \text{ value } (\%) = \frac{[AR - AS]}{AR + AS} \times 100\%$$

The permeation flux of the (*P*)-CoMOF membrane can be written as

$$flux = \frac{n}{A \cdot t}$$

where *n* is the permeated *R*- or *S*-ibuprofen (mol), *A* and *t* refer to the effective membrane area (m^2) and the permeation time (h), respectively. The final fluxes were obtained by plotting concentration over time, followed by deriving an exponential equation with R^2 value greater than 0.999.

3.4 Binding of (*P*)-CoMOF with *R*- or *S*-ibuprofen containing compounds

At first, the crystals of (*P*)-CoMOF were treated at 100 ºC under vacuum for 8 h. After this, (*P*)-CoMOF (10 mg) was mixed with chiral ibuprofen in ACN. The mixture was left undisturbed at room temperature for 12 h. Prior to adding the (*P*)-CoMOF, the initial guest concentrations were 0.001 - 0.02 mol L^{-1}. Changes in guest concentrations upon addition of hosts were recorded by HPLC. In consideration of the formation of a host-guest complex, the formation constant (K_f) can be represented by drawing analogy with the Langmuir adsorption model as

$$BS + G \underset{k_{de}}{\overset{k_{ad}}{\rightleftharpoons}} BS{\cdot}G$$

$$K_f = \frac{k_{ad}}{k_{de}} = \frac{[BS{\cdot}G]}{[BS][G]}$$

where BS, G, [BS], [G], [BS·G], k_{ad} and k_{de} represent the binding sites, guest molecules, concentration of the binding sites, concentration of the guest molecules, concentration of the guest molecules bound to the binding sites, forward adsorption reaction constant, and backward desorption reaction constant, respectively.

The change in free energy of the system was determined from the relation,

$$\Delta rGm(T) = -RT \cdot \ln K$$

where *R* stands for the universal gas constant, *T* for the temperature and *K* for the equilibrium constant.

4. Supplementary Figures

Table S1. Crystallographic data for compounds 1, 2 and 3.

Compound	1	2	3
Formula	$C_7H_9CoNO_7$	$C_7H_9CoNO_7$	$C_7H_9CoNO_7$
Formula weight	278.08	278.08	278.08
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a / Å	7.3443 (10)	7.3239 (3)	7.3222 (3)
b / Å	9.3985 (10)	9.3929 (4)	9.3874 (5)
c / Å	13.9551 (2)	13.7799 (6)	13.7738 (6)
Volume / Å^3	963.26 (2)	947.96 (8)	946.76 (8)
Z	4	4	4
2θ range	11.35 to 153.71	11.40 to 160.52	5.25 to 62.99
Reflections collected	9279	32018	23410
Independent reflections	1973	2006	3153
R_{int}	0.0732	0.0511	0.0376
R_{sigma}	0.0493	0.0230	0.0170
GOF on F^2	1.042	1.099	1.125
R_1/wR_2[a] ($I > 2\sigma(I)$)	0.0425 / 0.1053	0.0263 / 0.0674	0.0171 / 0.0410
R_1/wR_2[a] (all data)	0.0446 / 0.1067	0.0263 / 0.0674	0.0178 / 0.0413
Flack parameter	-0.029 (5)	-0.006 (2)	-0.001 (4)

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

*The disordered guest molecules were calculated by the PLATON/SQUEEZE program combined with the charge conservation, elemental analyses and thermogravimetric analyses.

Single-crystal X-ray analysis shows that the compound is a 2-D layer coordination polymer which possesses two types of helical chains. Co(II) displays a distorted octahedral coordination environment with one nitrogen atom (N1) and three oxygen atoms (O1, O3, O4) from three dimethyl pyridine-2,5-dicarboxylate ligands, and other two oxygen atoms (O5, O6) from two water molecules, there is one guest water molecule (O7) in the compound. The compound is stable in air and insoluble in water and common organic solvents. The compound crystallizes in the chiral space group $P2_12_12_1$. Each carboxylate of the dimethyl pyridine-2,5-dicarboxylate ligands bridges two Co(II) ions in *syn-anti* coordination mode to form infinite right-hand helical –Co–PDC–Co– chains. The diameter of the spiral channel is about 7.532 Å. The two coordinated water molecules and two coordinated carboxylate oxygen atoms form intralayer H-bonds with an O5…O1 distance of 2.662 Å and an O6…O3 distance of 2.605 Å. One coordinated water molecule and the uncoordinated carboxylate oxygen atom of an adjacent layer form an interlayer H-bond with an O5…O2 distance of 2.680 Å. The guest water molecule and one coordinated water form an H-bond with an O7…O6 distance of 2.620 Å.

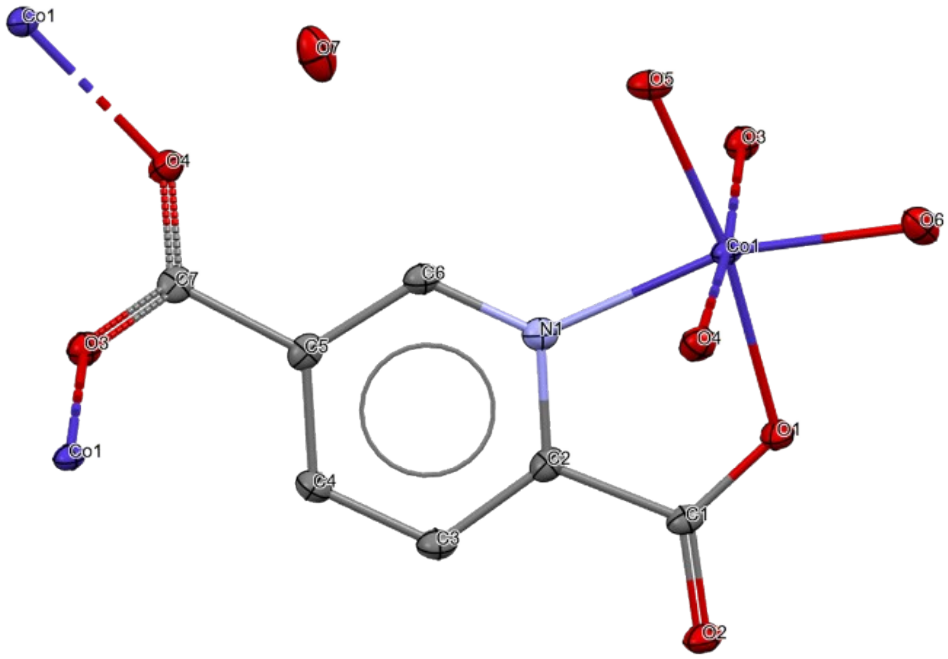


Fig. S1. Thermal ellipsoid plot (50%) showing an asymmetric unit of (*P*)-CoMOF.

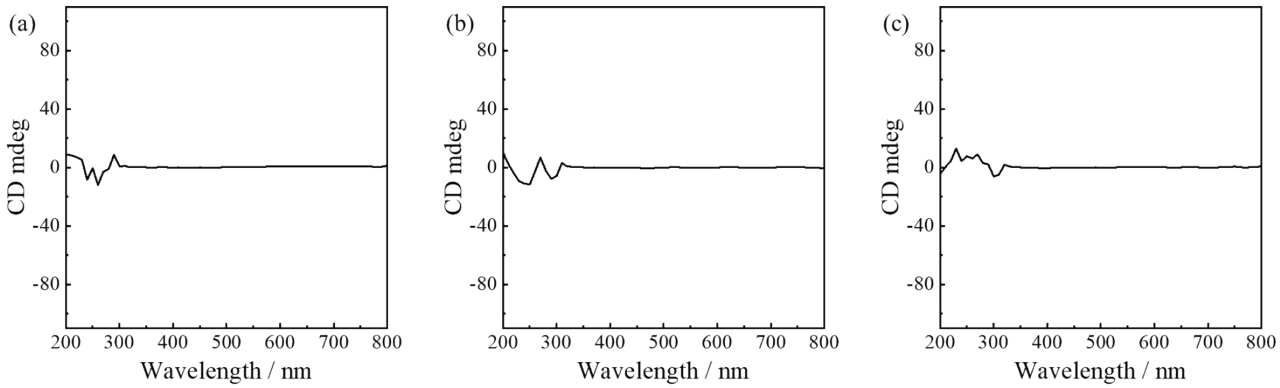
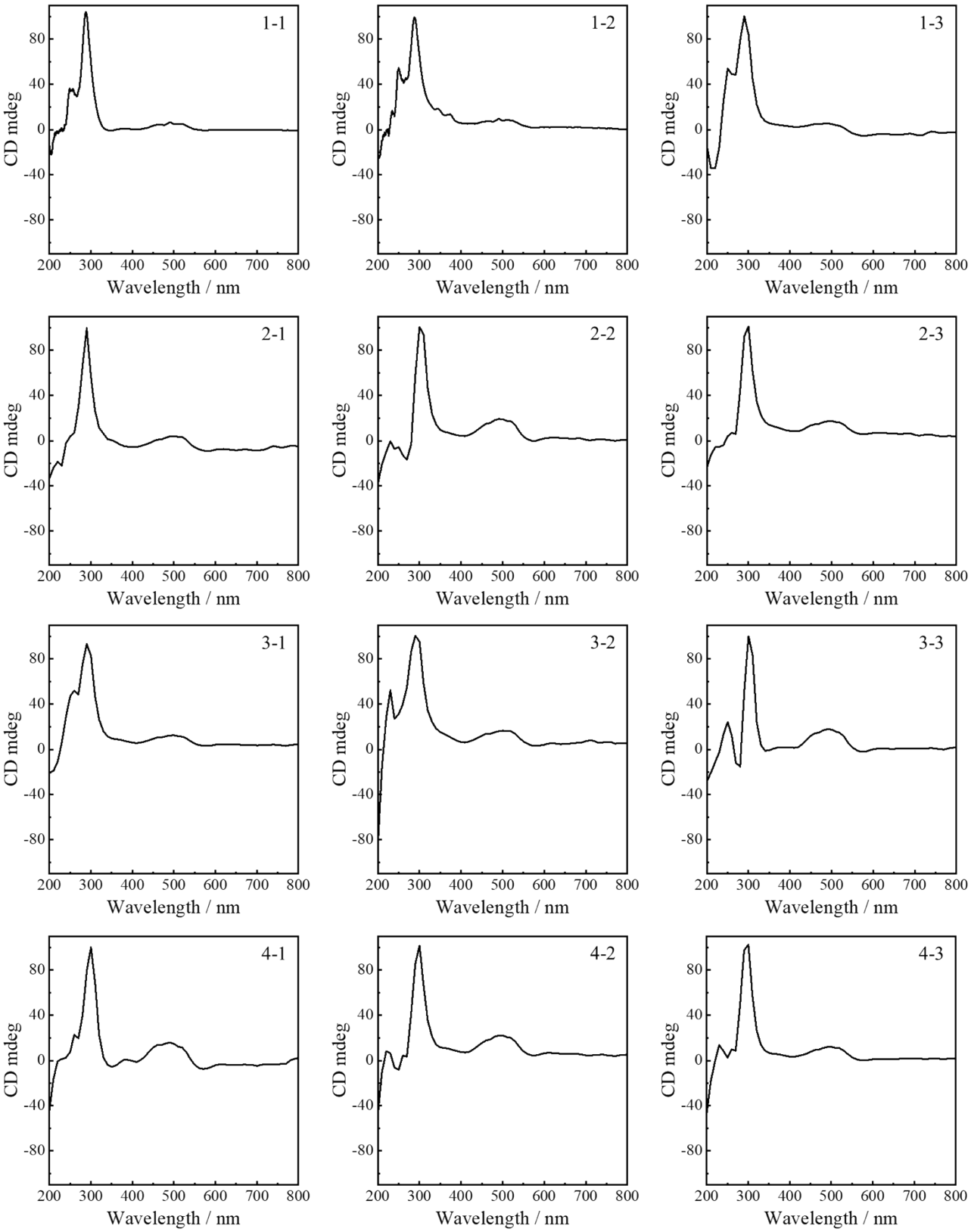


Fig. S2. CD spectra of $Co(CH_3COO)_2{\cdot}4H_2O$ (a), dimethyl pyridine-2,5-dicarboxylate (b) and precursor (c).


1-1
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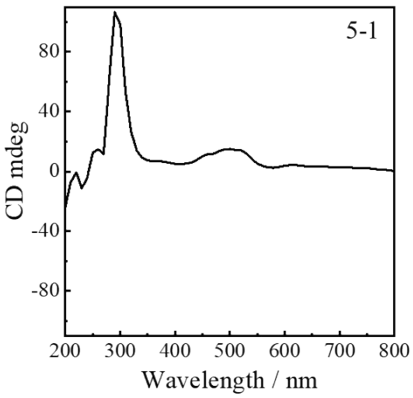
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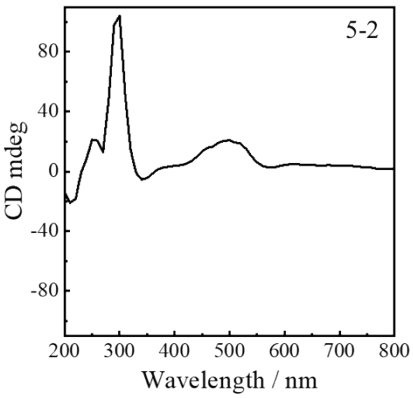
Wavelength / nm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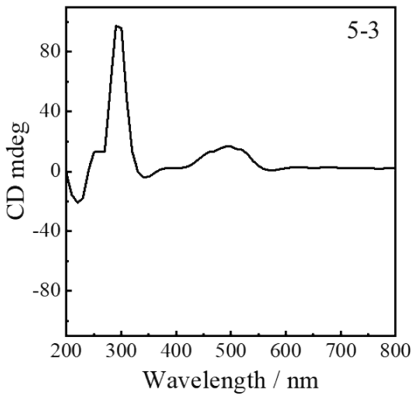
Wavelength / nm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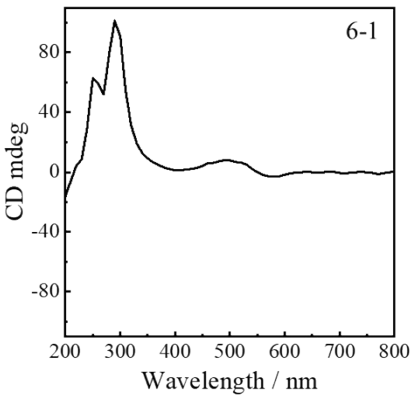
Wavelength / nm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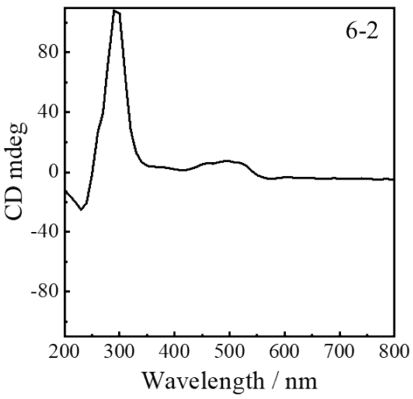
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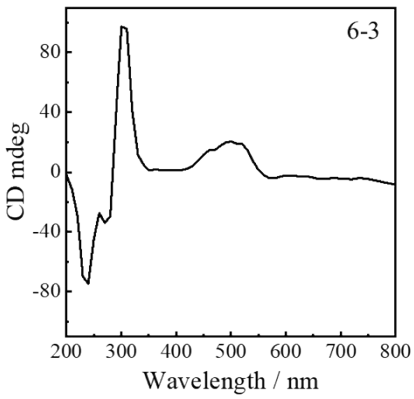
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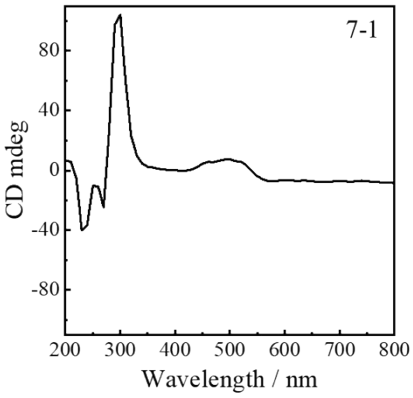
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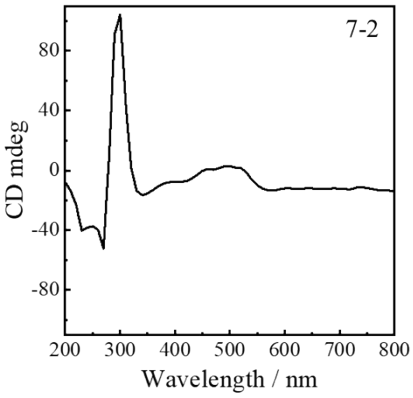
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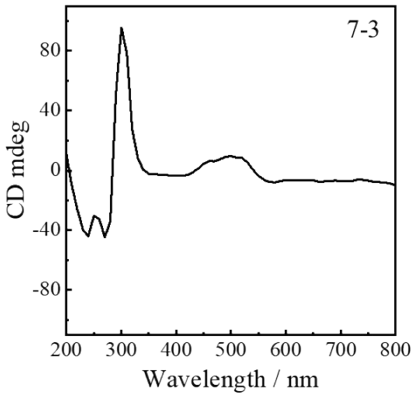
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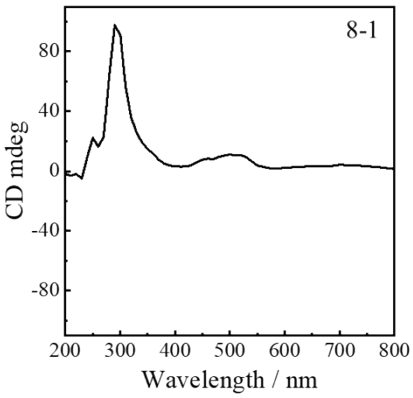
Wavelength / nm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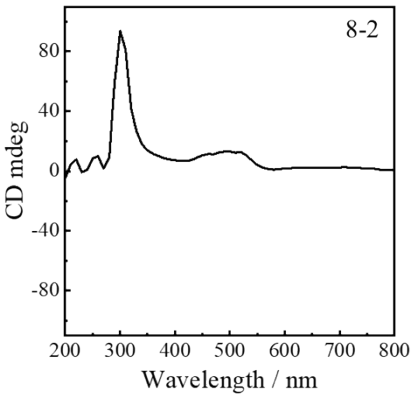
Wavelength / nm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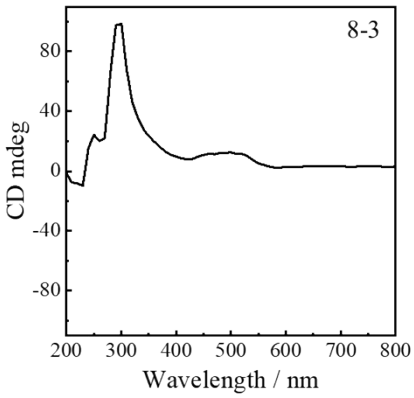
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Wavelength / nm

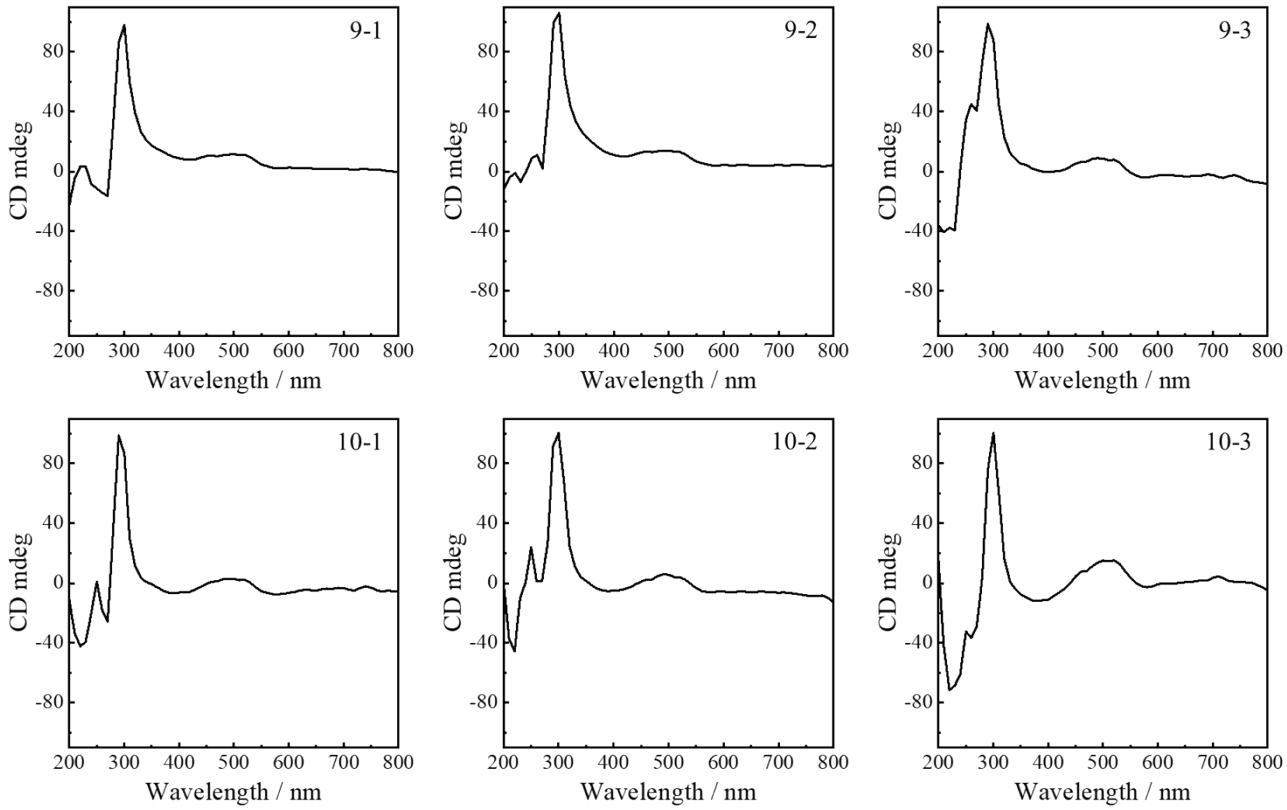


Fig. S3. CD spectra of 10 parallel synthesized bulk samples and three randomly selected samples.

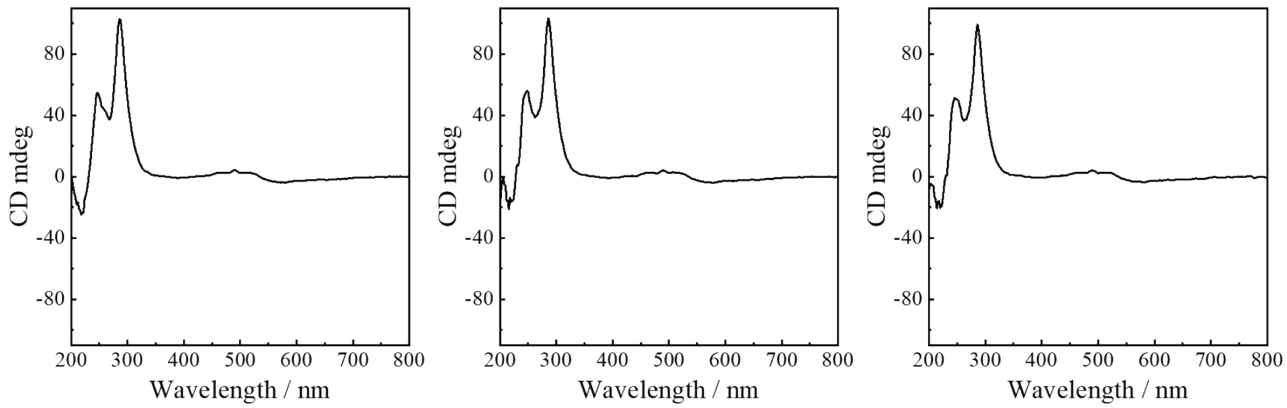
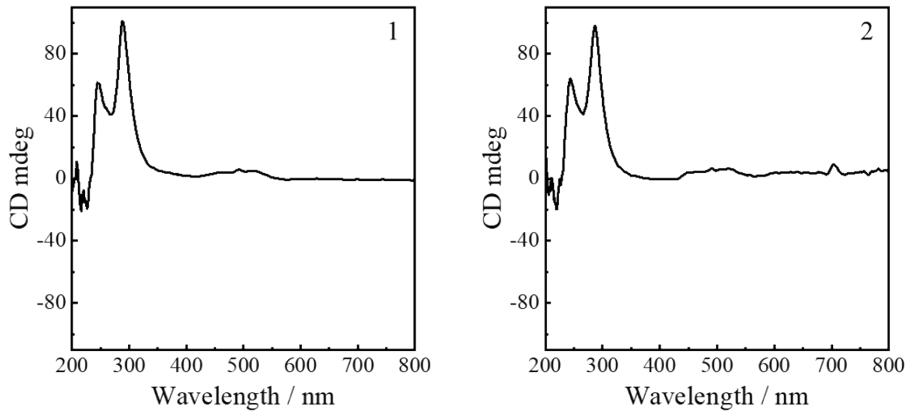


Fig. S4. CD spectra of (*P*)-CoMOF layers in three different regions of the same membrane.



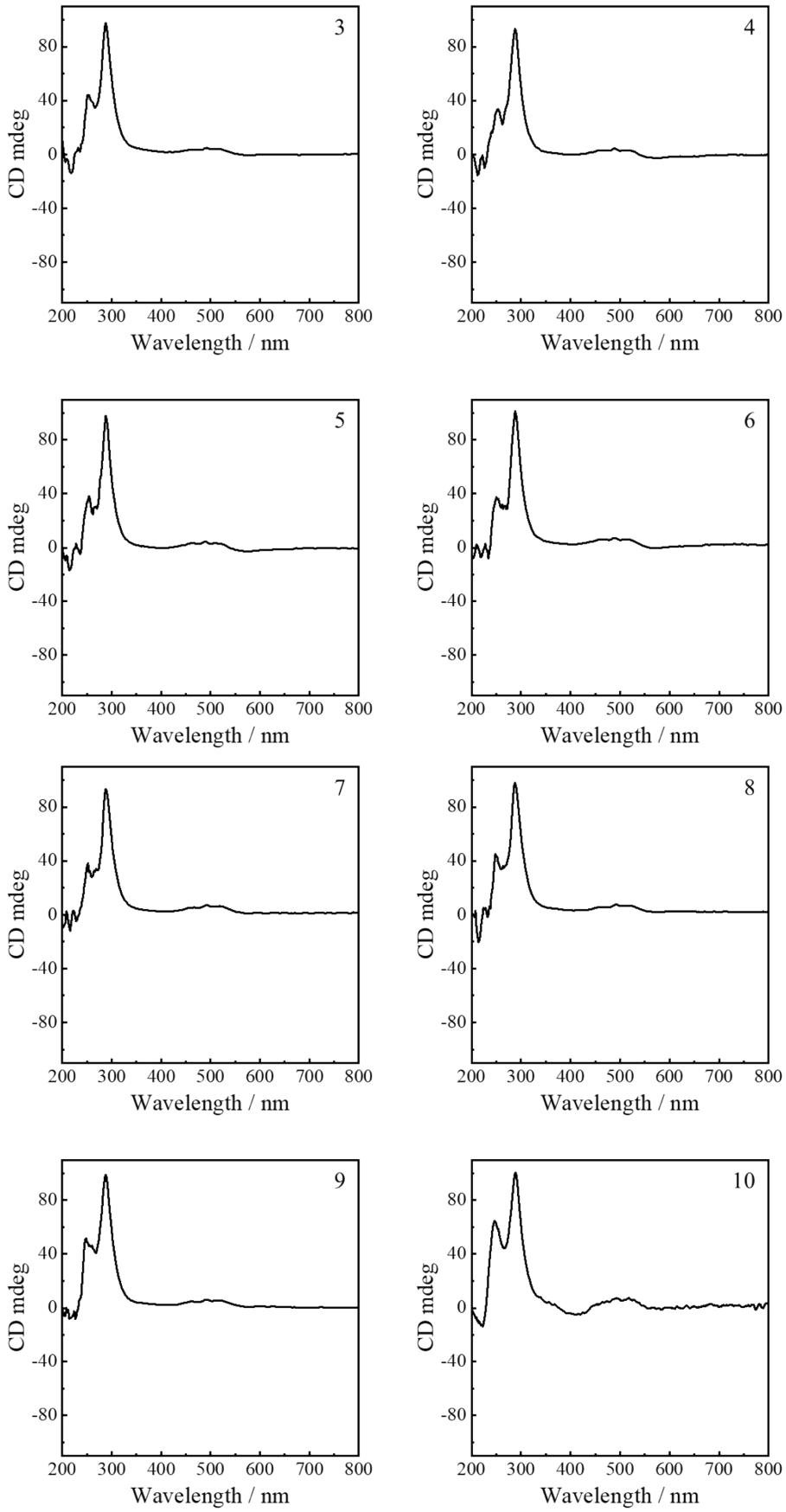


Fig. S5. CD spectra of ten different batches of membranes.

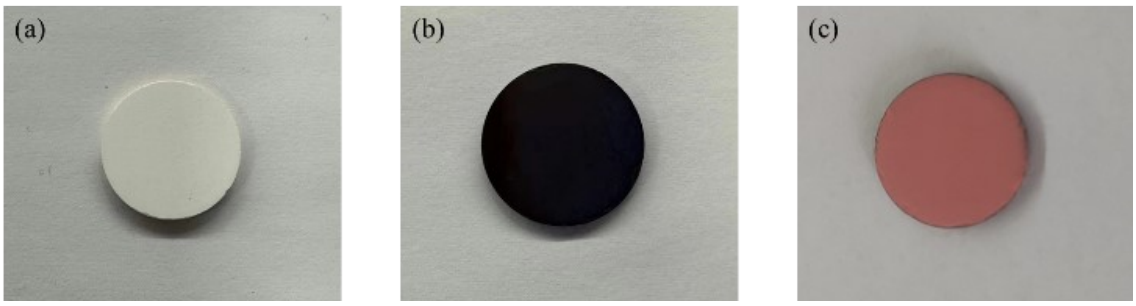


Fig. S6. Photographs of Al_2O_3 support (a), PANI-Al_2O_3 substrate (b) and (*P*)-CoMOF membrane (c).

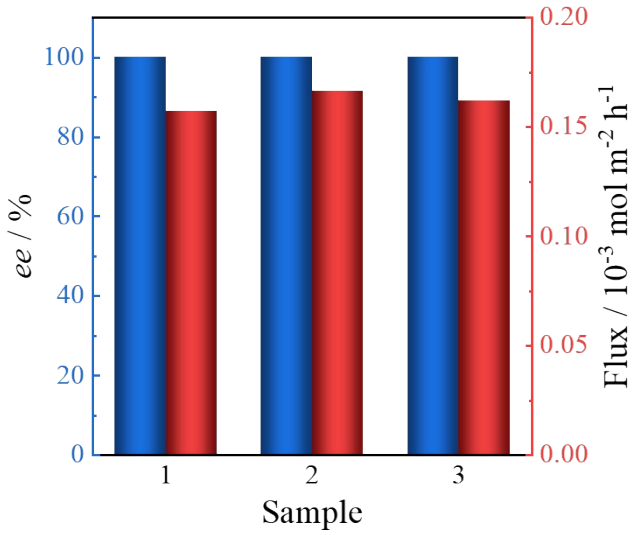


Fig. S7. *ee* and flux values of racemic ibuprofen solutions resolved for 2 h by three membranes from different batches.

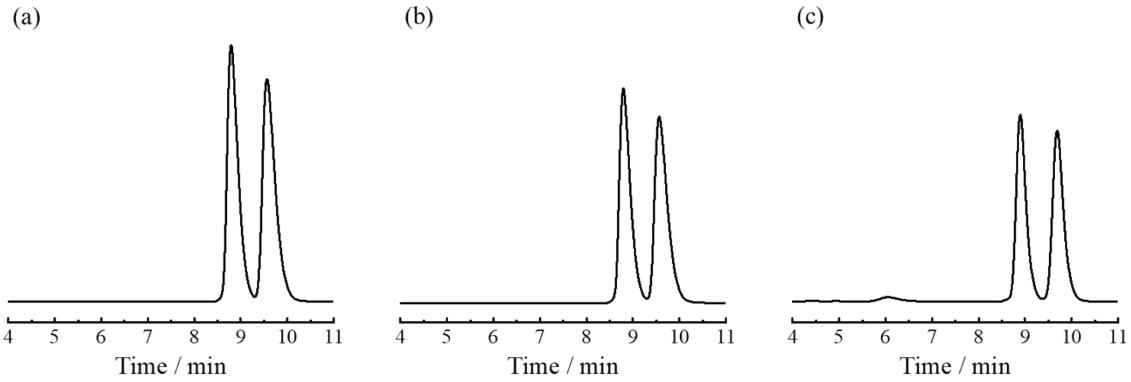


Fig. S8. HPLC chromatograms of racemic ibuprofen solution (a) and its passage through Al_2O_3 support (b) and PANI-Al_2O_3 substrate (c) for 2 h.

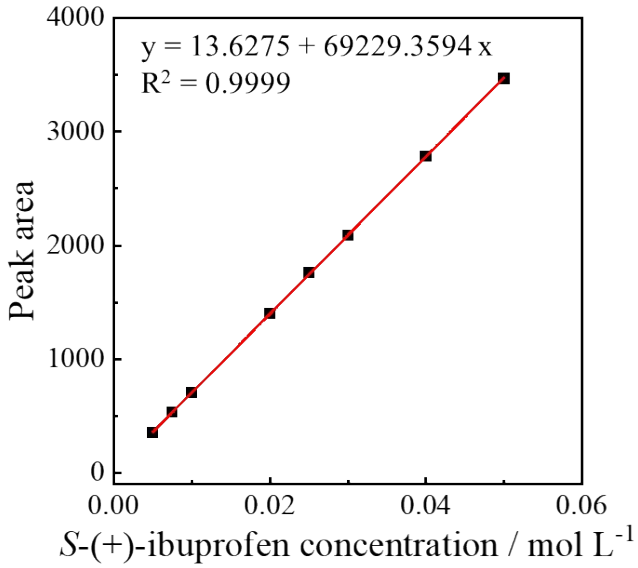
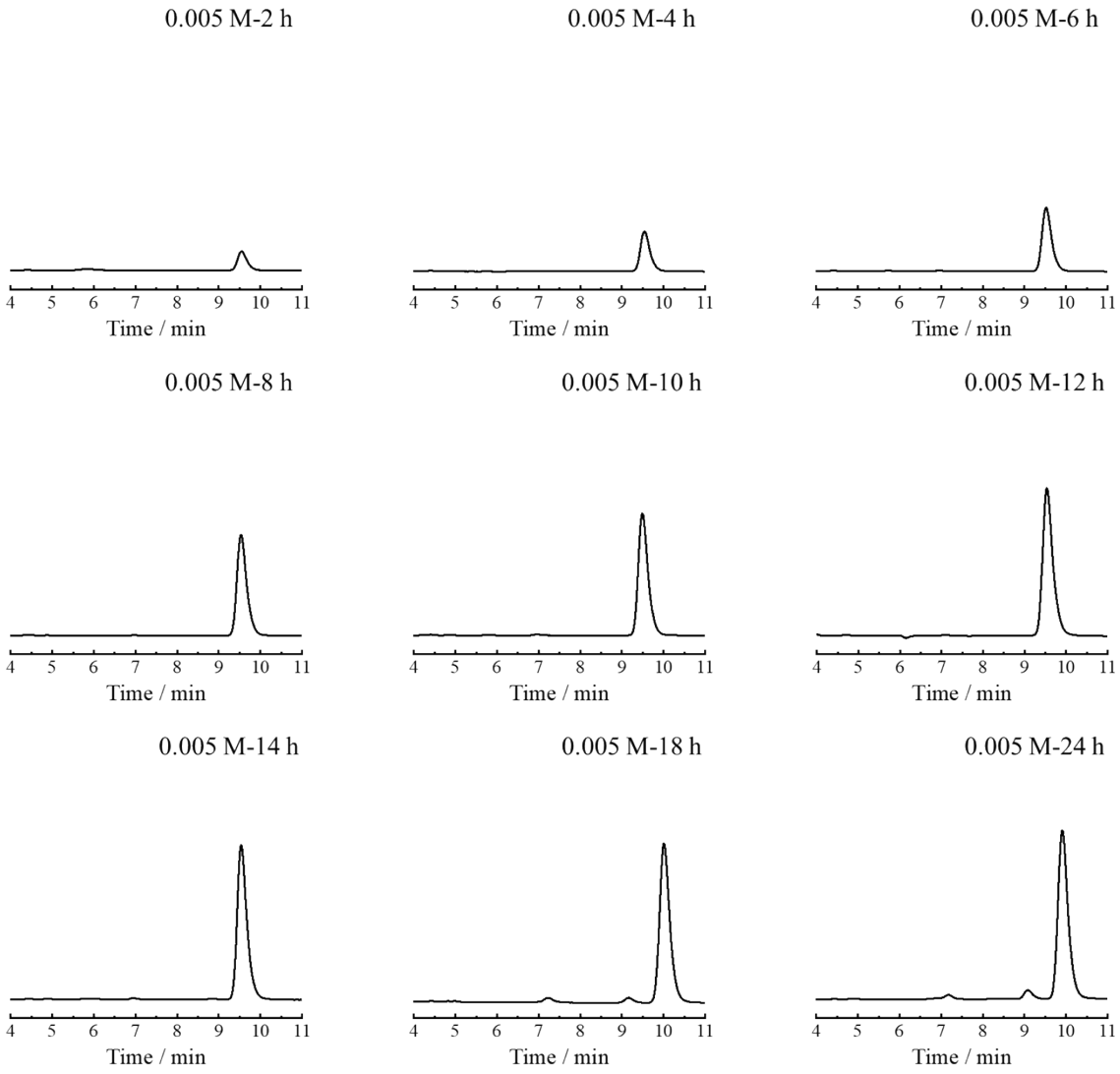


Fig. S9. Linear curve of HPLC in various *S*-(+)-ibuprofen concentration.



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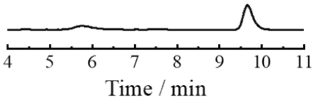

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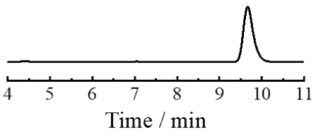
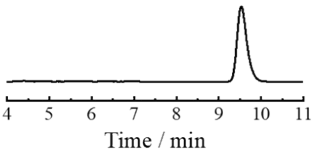
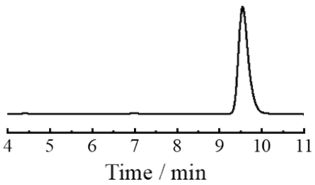


0.01 M-6 h



0.01 M-8 h



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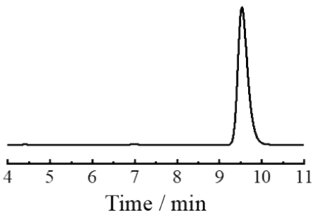
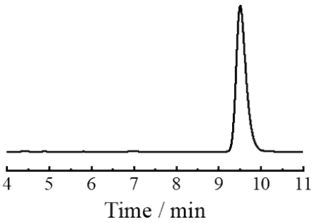
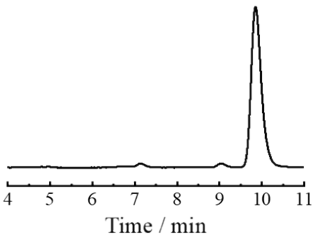


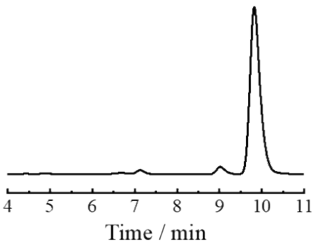
0.01 M-12 h



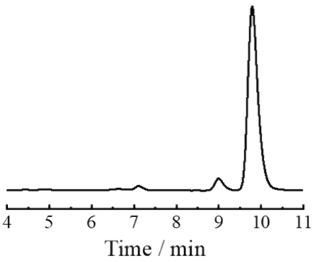
0.01 M-14 h



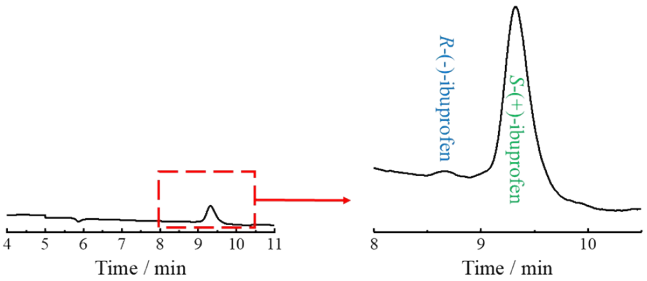
0.01 M-18 h



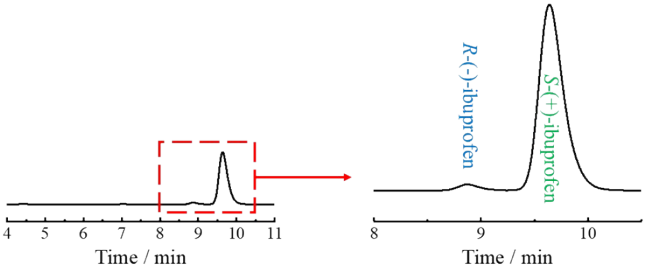
0.01 M-24 h

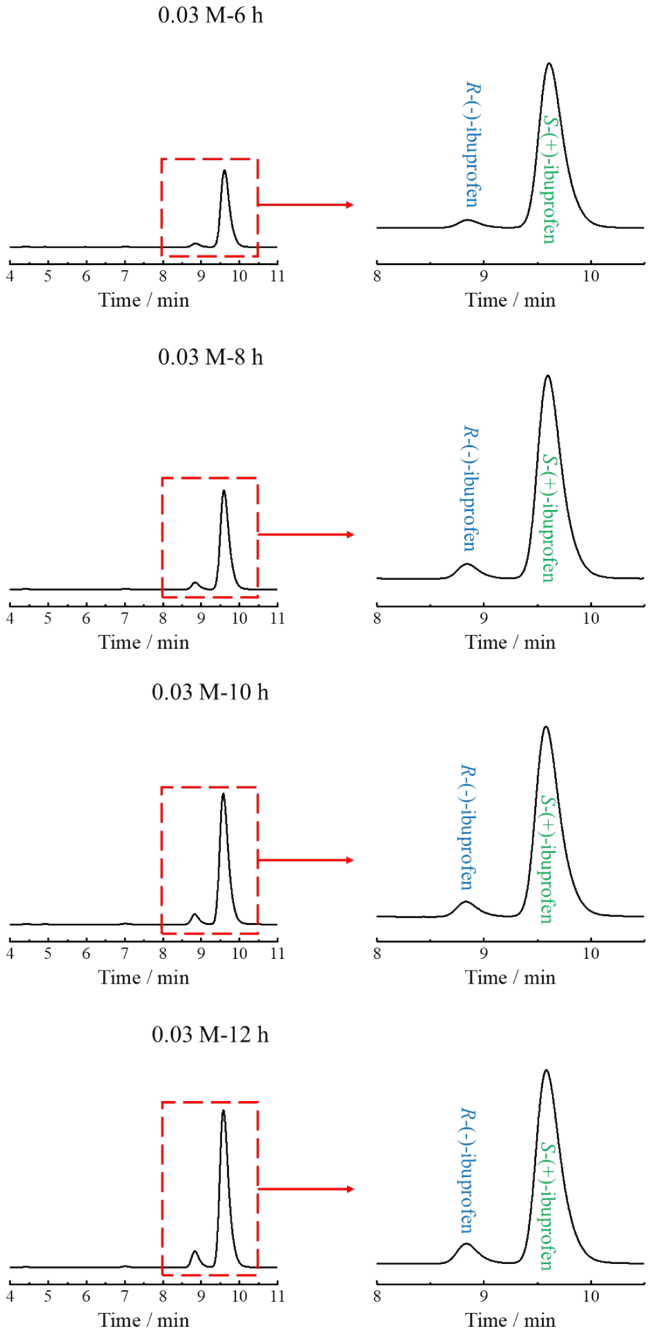


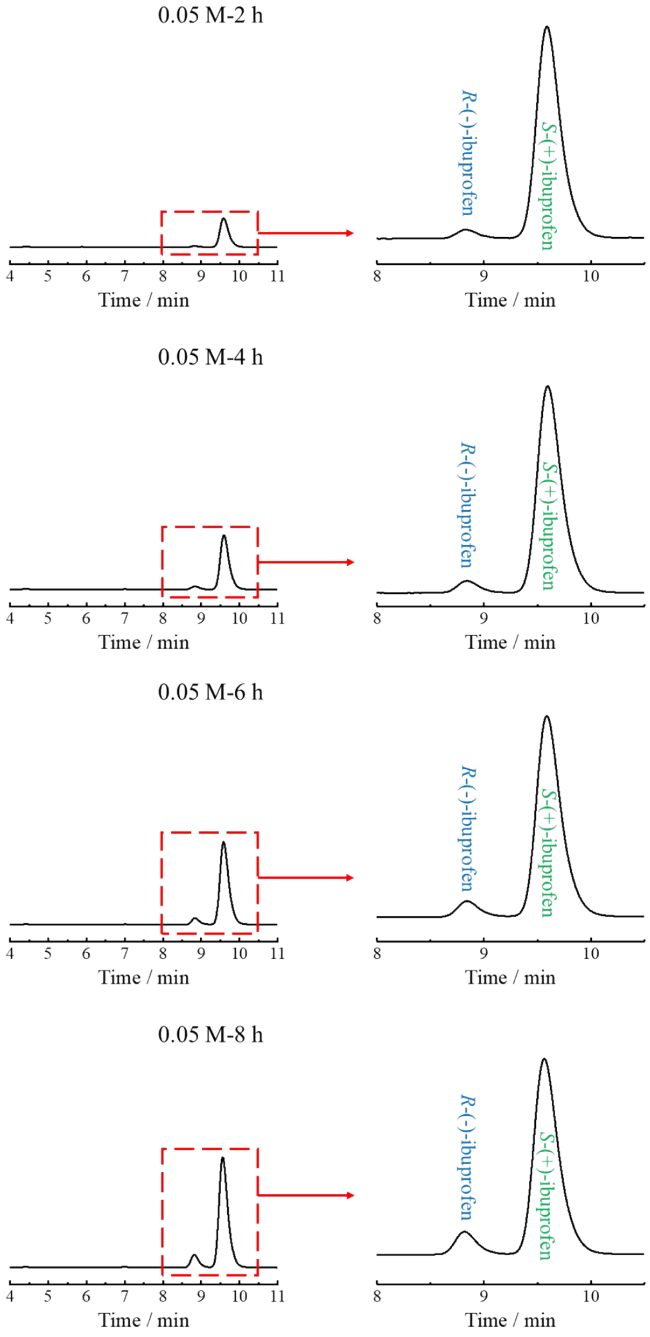
0.03 M-2 h



0.03 M-4 h




0.03 M-6 h
R-(-)-ibuprofen
S-(+)-ibuprofen
4 5 6 7 8 9 10 11
Time / min
8 9 10
Time / min
0.03 M-8 h
R-(-)-ibuprofen
S-(+)-ibuprofen
4 5 6 7 8 9 10 11
Time / min
8 9 10
Time / min
0.03 M-10 h
R-(-)-ibuprofen
S-(+)-ibuprofen
4 5 6 7 8 9 10 11
Time / min
8 9 10
Time / min
0.03 M-12 h
R-(-)-ibuprofen
S-(+)-ibuprofen
4 5 6 7 8 9 10 11
Time / min
8 9 10
Time / min


0.05 M-2 h
R-(-)-ibuprofen
S-(+)-ibuprofen
4 5 6 7 8 9 10 11
8 9 10
Time / min
0.05 M-4 h
R-(-)-ibuprofen
S-(+)-ibuprofen
4 5 6 7 8 9 10 11
8 9 10
Time / min
0.05 M-6 h
R-(-)-ibuprofen
S-(+)-ibuprofen
4 5 6 7 8 9 10 11
8 9 10
Time / min
0.05 M-8 h
R-(-)-ibuprofen
S-(+)-ibuprofen
4 5 6 7 8 9 10 11
8 9 10
Time / min

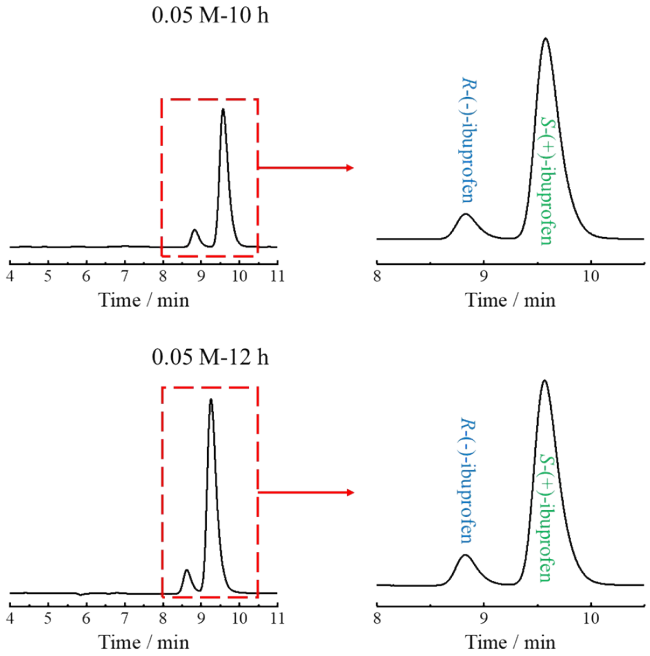


Fig. S10. HPLC chromatograms of chiral resolution results of racemic ibuprofen feed solutions at different concentrations.

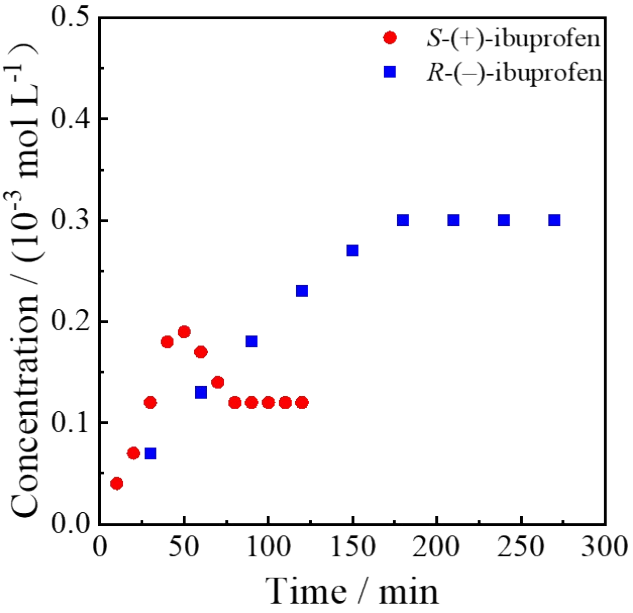


Fig. S11. The adsorption amount of (*P*)-CoMOF adsorbing *S*-(+)-ibuprofen (red) and *R*-(–)-ibuprofen (blue) respectively changes with time.

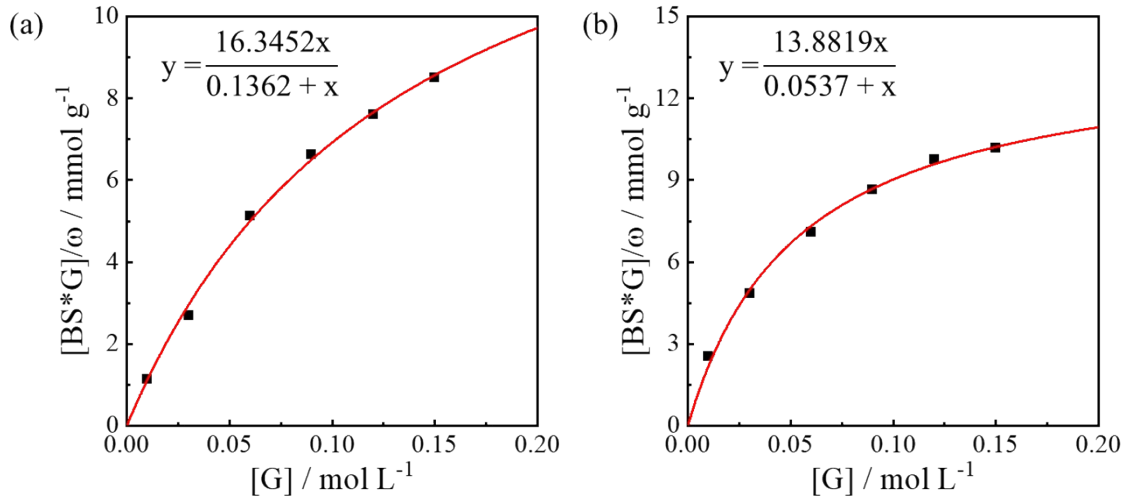


Fig. S12. Binding of host solid (*P*)-CoMOF with *S*-(+)-ibuprofen (a) and *R*-(–)-ibuprofen (b).

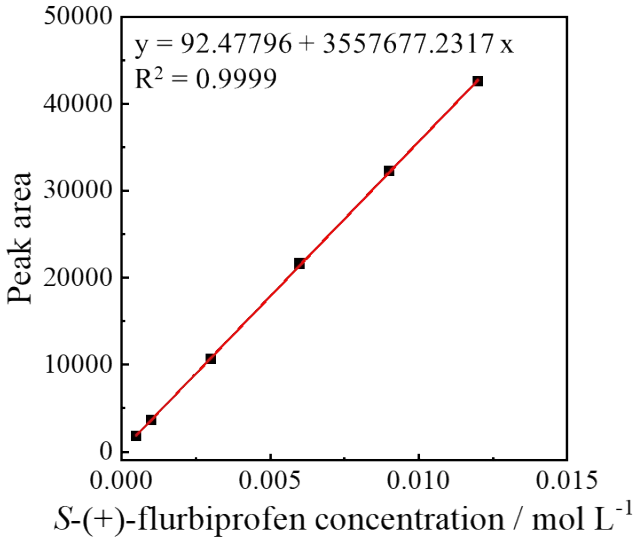
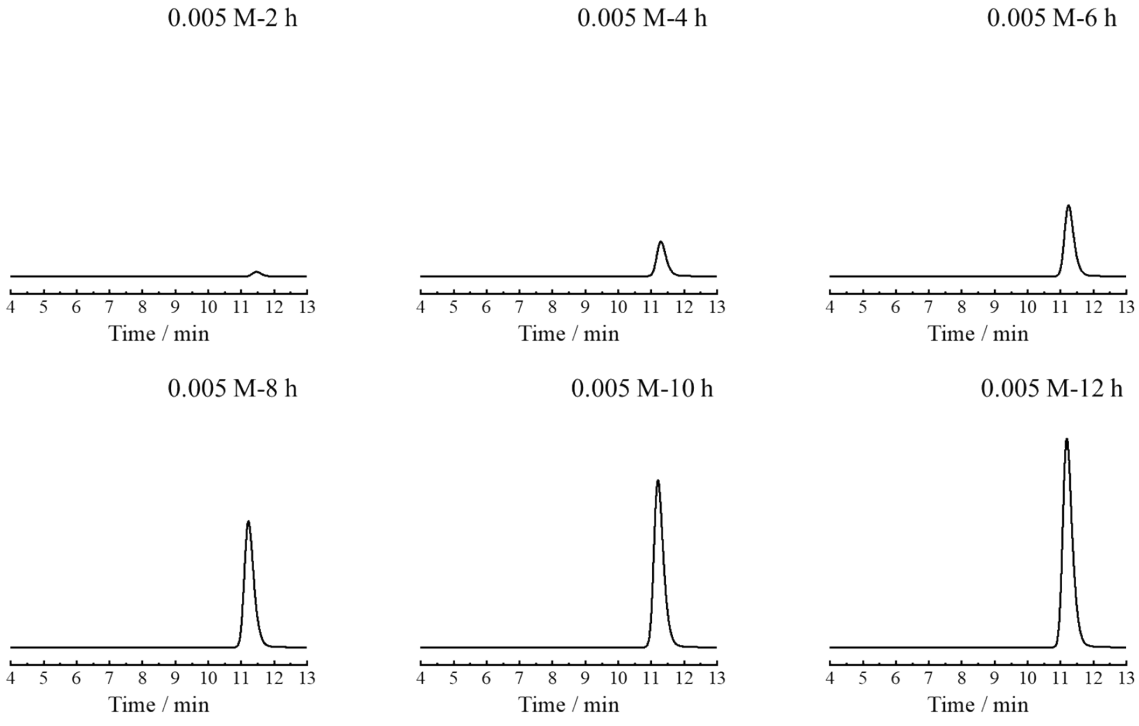
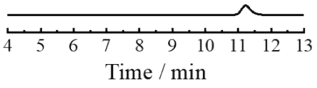


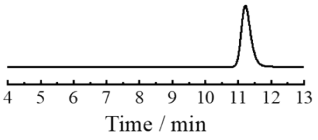
Fig. S13. Linear curve of HPLC in various *S*-(+)-flurbiprofen concentration.



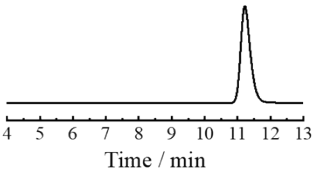
0.01 M-2 h



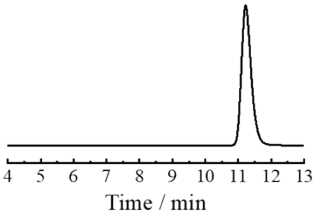
0.01 M-4 h



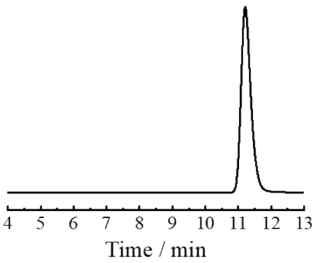
0.01 M-6 h



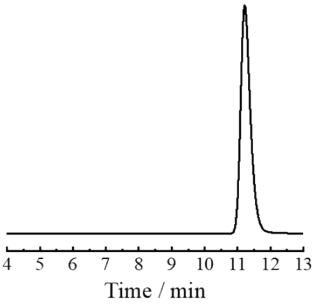
0.01 M-8 h



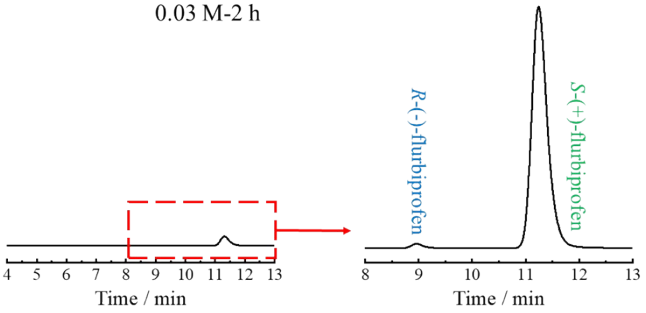
0.01 M-10 h



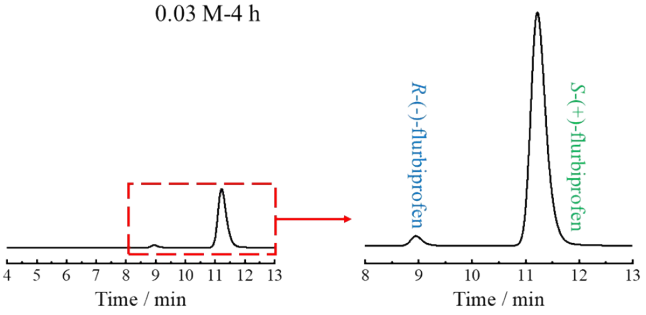
0.01 M-12 h

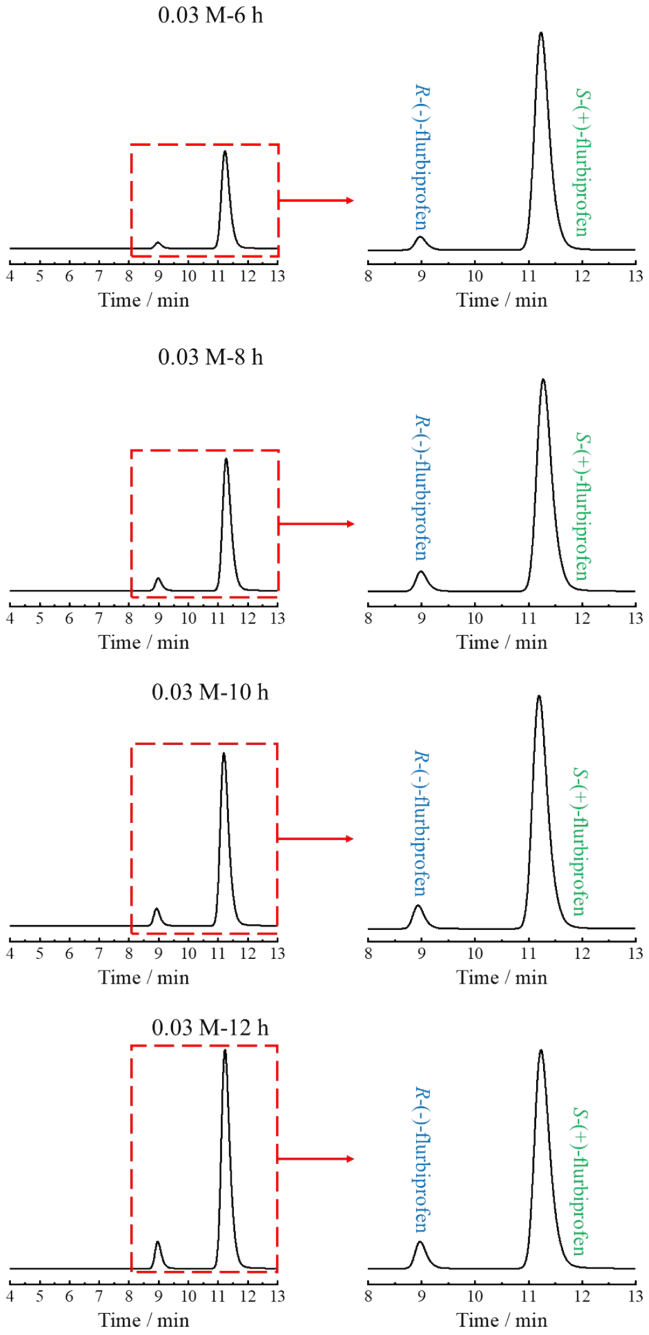


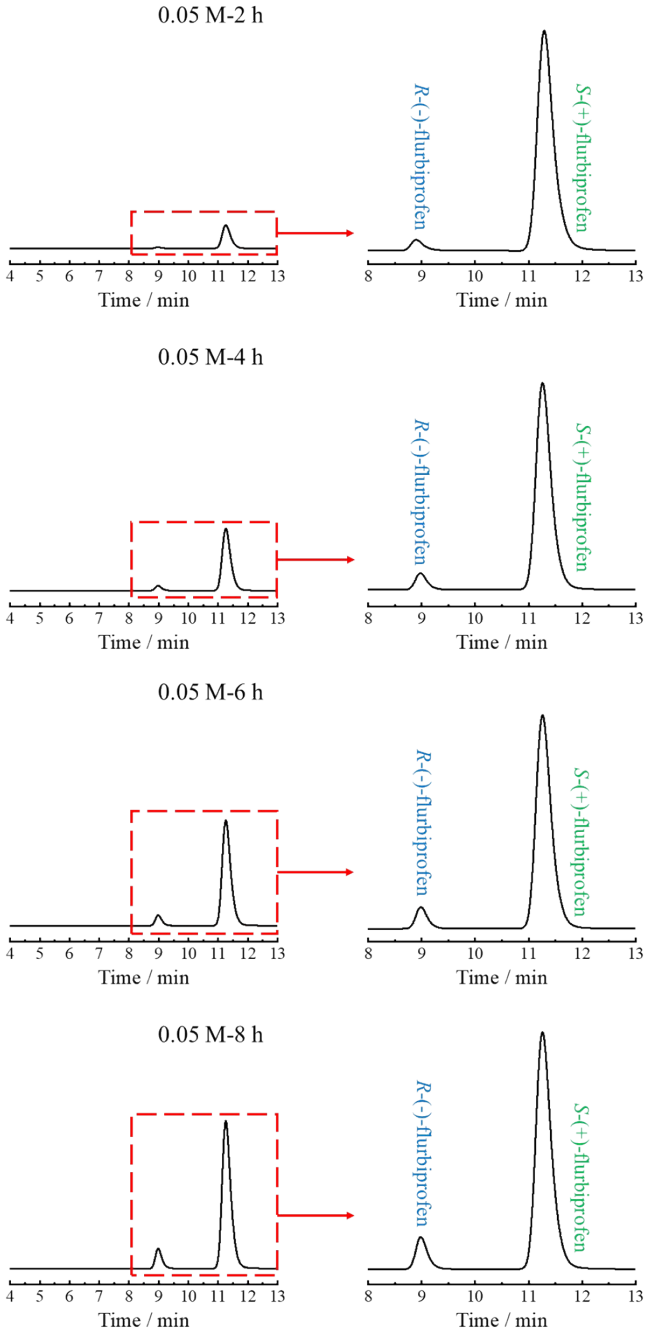
0.03 M-2 h



0.03 M-4 h




0.03 M-6 h
R-(-)-flurbiprofen
S-(+)-flurbiprofen
Time / min
0.03 M-8 h
R-(-)-flurbiprofen
S-(+)-flurbiprofen
Time / min
0.03 M-10 h
R-(-)-flurbiprofen
S-(+)-flurbiprofen
Time / min
0.03 M-12 h
R-(-)-flurbiprofen
S-(+)-flurbiprofen
Time / min


0.05 M-2 h
R-(-)-flurbiprofen
S-(+)-flurbiprofen
Time / min
0.05 M-4 h
R-(-)-flurbiprofen
S-(+)-flurbiprofen
Time / min
0.05 M-6 h
R-(-)-flurbiprofen
S-(+)-flurbiprofen
Time / min
0.05 M-8 h
R-(-)-flurbiprofen
S-(+)-flurbiprofen
Time / min

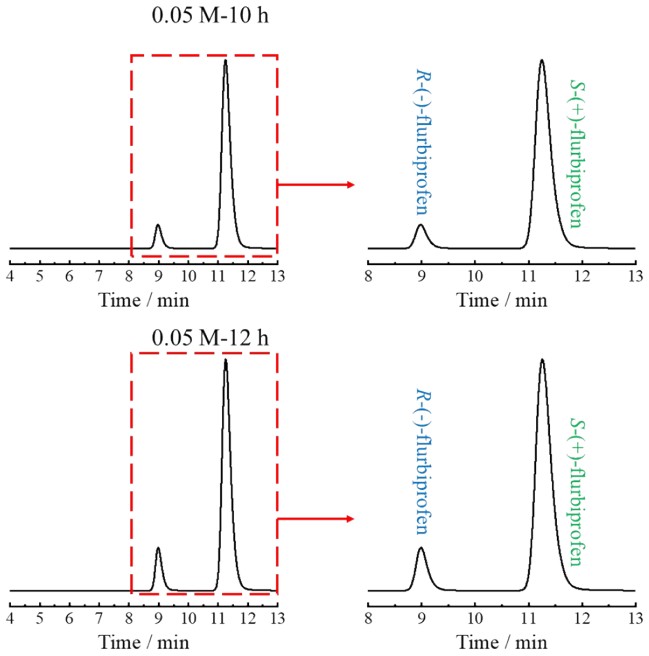


Fig. S14. HPLC chromatograms of chiral resolution results of racemic flurbiprofen feed solutions at different concentrations.

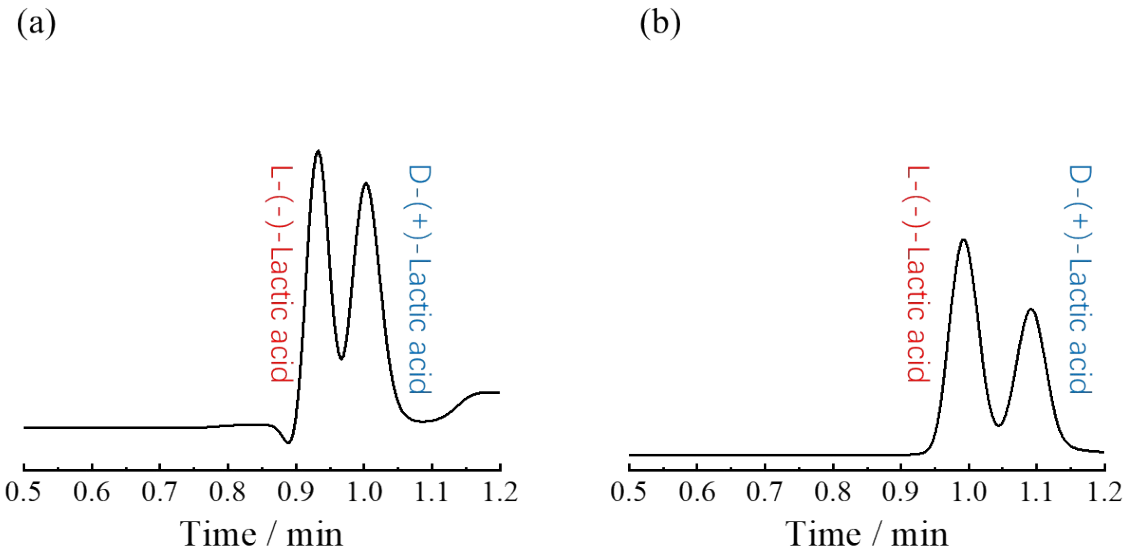


Fig. S15. HPLC chromatograms of racemic lactic acid solution (a) and its passage through (*P*)-CoMOF membrane (b) for 2 h.

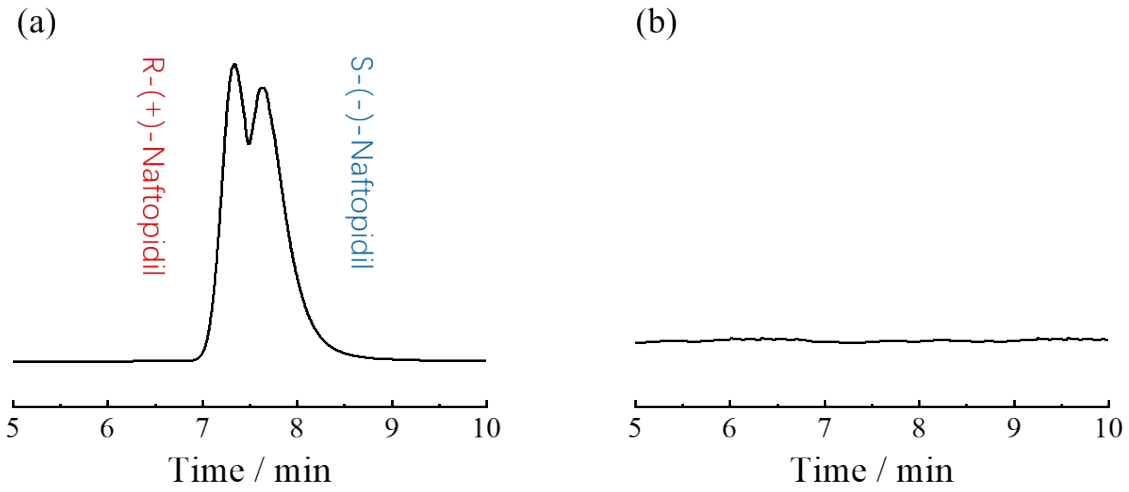


Fig. S16. HPLC chromatograms of racemic naftopidil solution (a) and its passage through (*P*)-CoMOF membrane (b) for 2 h.

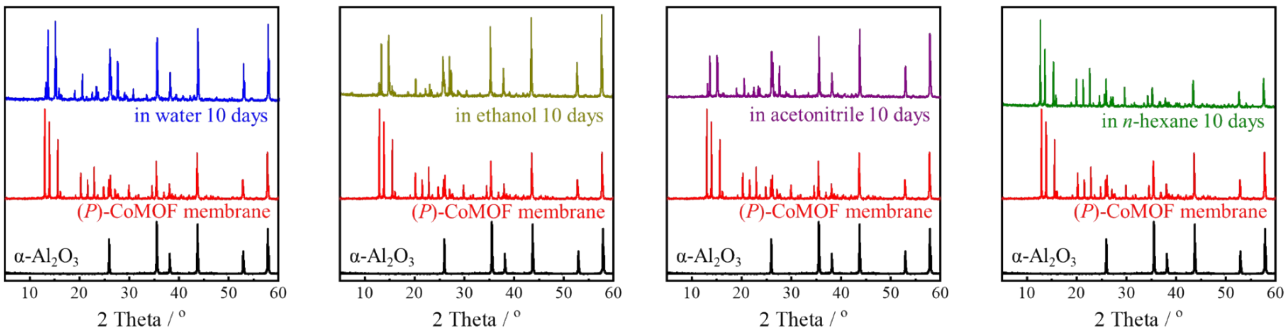


Fig. S17. XRD patterns for the α-Al_2O_3 support (black), (*P*)-CoMOF membrane (red) and (*P*)-CoMOF membranes soaked in water (bule)/ethanol (dark yellow)/acetonitrile (purple)/*n*-hexane (olive green) for 10 days.

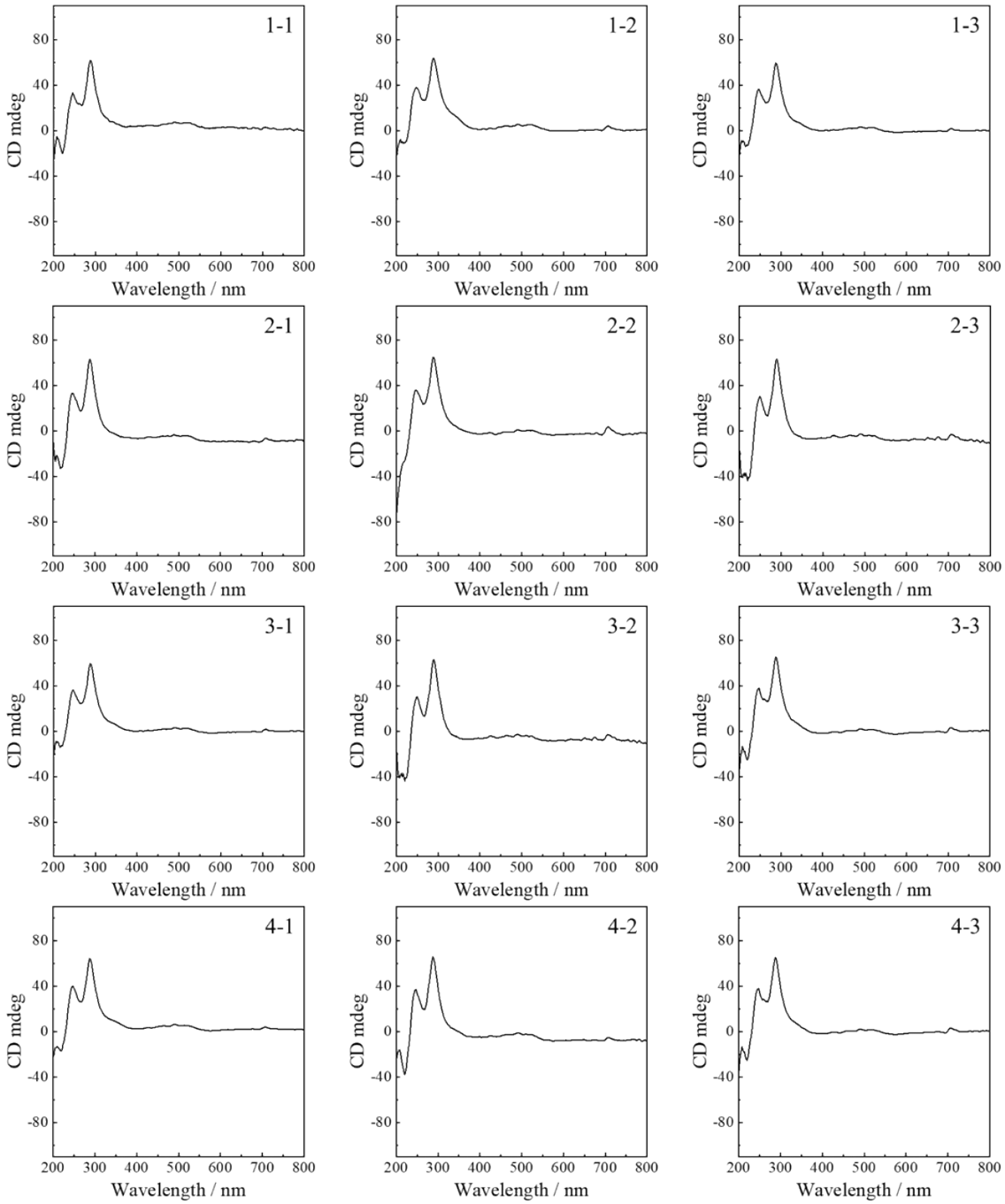


Fig. S18. CD spectra of 4 parallel synthesized batch membrane samples and three randomly selected regions on each membrane.