

Supporting Information

“Single nickel source” in-situ Fabrication of Stable Homochiral MOF Membrane with Chiral Resolution Property

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1. Experimental

Materials: All reagents and solvents were used as received from commercial suppliers without further purification. A nickel substrate was obtained by pressing three nickel nets (180 mesh, State No. 540 Equipment Co., Xinxiang, China) together mechanically. A nickel support cut into circular wafers (20 mm in diameter) was washed with ethanol for 30 min and then five times using water under ultrasound to clean the surface and then placed in an oven at 100°C at least for 5 hours for drying.

Preparing of Ni₂(L-asp)₂(bipy) homochiral membranes on nickel nets: nickel nets acts as the nickel precursor, which reacts with L-asp (L-aspartic acid, NH₂CH(COOH)CH₂COOH) and bipy (4,4'-bipyridine) ligands to produce a chiral membrane. 0.1g (0.75mmol) of L-asp was dispersed in a mixture containing 2mL of methanol (62.4mmol) and 0.2mL of water (11.1mmol). To this solution, 0.0586g of bipy (0.375mmol) was added and stirred for 1 hour. A nickel net and the final mixture of the composition: 1.0L-asp: 0.5bipy: 15H₂O: 83CH₃OH was sealed into a Teflon-lined stainless autoclave and heated at 150°C for 48 hours. The membranes were taken out, washed with CH₃OH and H₂O, and dried at 80°C. Then the membranes were activated at 150°C oven for 10 hours. The activated membranes were characterized by XRD and SEM, and their chiral isomers-separation properties were determined.

2. Characterization

The mother solution after the reaction was determined by Perkin-Elmer Optima 3300 DV ICP spectrometer to prove that nickel ions can be released under solvothermal synthesis condition. The result shows that there are still a little amount of nickel ions (0.40~0.45%) in the solution after reaction.

The crystalline structures of Ni₂(L-asp)₂bipy membranes were determined by X-ray Diffraction (XRD) measurements using a SHIMAZU LabX XRD-6000 X-ray-Diffract Meter with Cu Ka radiation ($\lambda = 1.5418 \text{ \AA}$).

The seed crystals and membrane were characterized by analytical scanning electron microscope (JEOS JSM-6510A).

As-synthesized MOFs membranes were activated by heating at 150°C in ovens for at least 10 hours. Then the crystalline structures of activated membranes were determined by X-ray Diffraction (XRD) measurements.

Thermogravimetric analysis was performed using a SHIMAZU DTG-60 thermal analyzer system at the heating rate of 5 °C min⁻¹ to 700 °C. Samples were placed in an alumina pan.

CO₂ sorption isotherms measurements were carried on a Micro Meritics Tristar II 3020 surface area analyzer at 195K.

The mixtures content in the feed and permeated samples were analyzed by gas chromatography (GC-2010, SHIMADZU, Japan) equipped with a thermal conductivity detector, using a CP-Chirasil-Dex CB column and Nitrogen as the carrier gas. The permselectivity of Ni₂(L-asp)₂bipy membranes is expressed by enantiomeric excess, which is defined as *ee*.

$$ee = \frac{R - S}{R + S} \times 100$$

The Ni₂(L-asp)₂bipy membrane pretreated as described above was sealed in the cell and the separation tests were performed. Schematic showing diols isomers separation process was described in Figure S5. The feed speed was maintained at 1.2 L·h⁻¹. The permeated vapor was

collected in liquid nitrogen traps. Before pervaporation, the membranes were immersed in the feed solution for 3h. The weight of the permeated component collected in the cold trap was measured to calculate the total flux, J .

$$J = \frac{W}{AT}$$

Where, W is the total mass permeated during the experiment time interval, T and A are the operating time and effective membrane area, respectively.

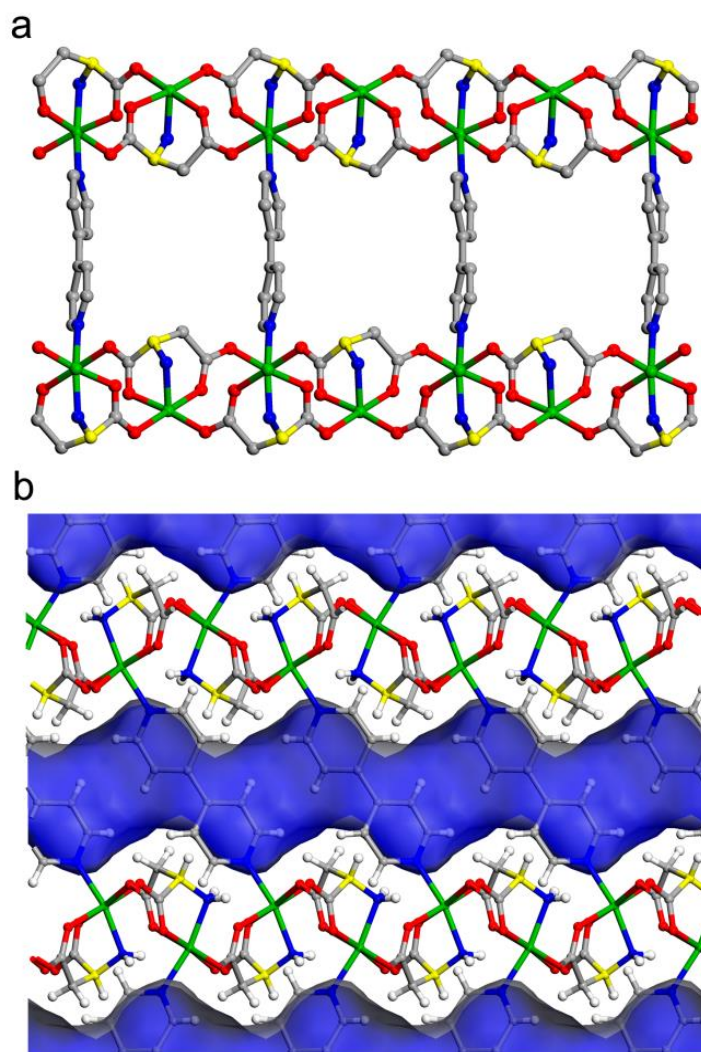


Figure S1. The crystal structure of $\text{Ni}_2(\text{L-asp})_2(\text{bipy})$: a) 3D framework formed by bipy supporting the $\text{Ni}(\text{L-asp})$ layers viewed along the $[010]$ direction and b) 1D corrugated channels viewed along the $[001]$ direction. Color Code: Ni: green, C: gray (chiral centers yellow), N: blue, O: red, H: white.

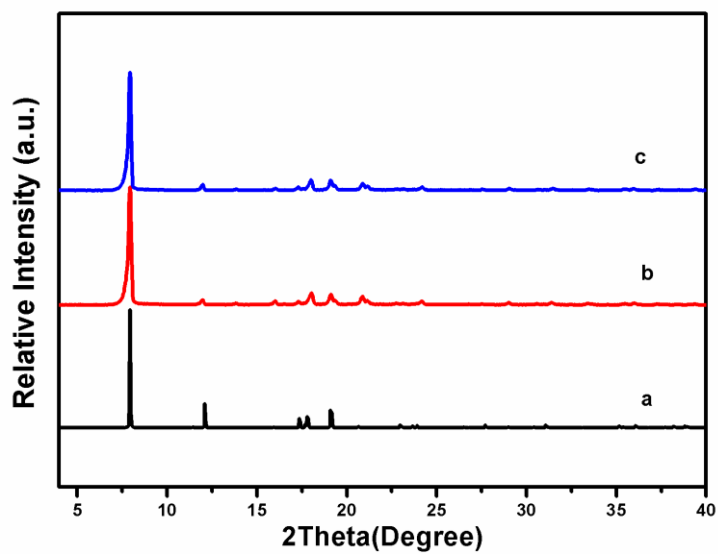


Figure S2. X-ray diffraction patterns of a) simulated $\text{Ni}_2(\text{L-asp})_2(\text{bipy})$ material; b) as-synthesized $\text{Ni}_2(\text{L-asp})_2(\text{bipy})$ membranes; c) activated $\text{Ni}_2(\text{L-asp})_2(\text{bipy})$ membranes.

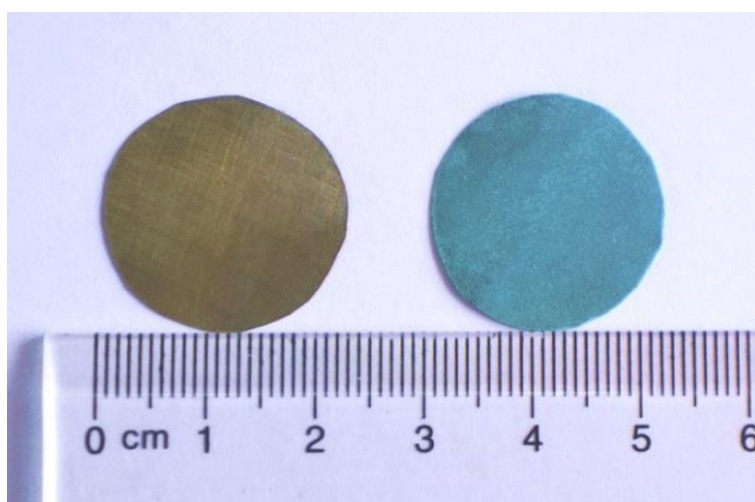


Figure S3. Photographs of nickel net substrate (left) and homochiral $\text{Ni}_2(\text{L-asp})_2(\text{bipy})$ membrane (right).

To further verify the quality of the membranes, single-gas permeation experiments were performed. The permeation of small gas molecule (N_2) was measured at room temperature ($25\text{ }^\circ\text{C}$) through the $Ni_2(L\text{-asp})_2\text{bipy}$ membrane. The feed side was regulated at different pressures and the permeate side was open to atmosphere. The penetrated gas flow rate was measured by a soap film flow meter. The result is shown in Figure S4.

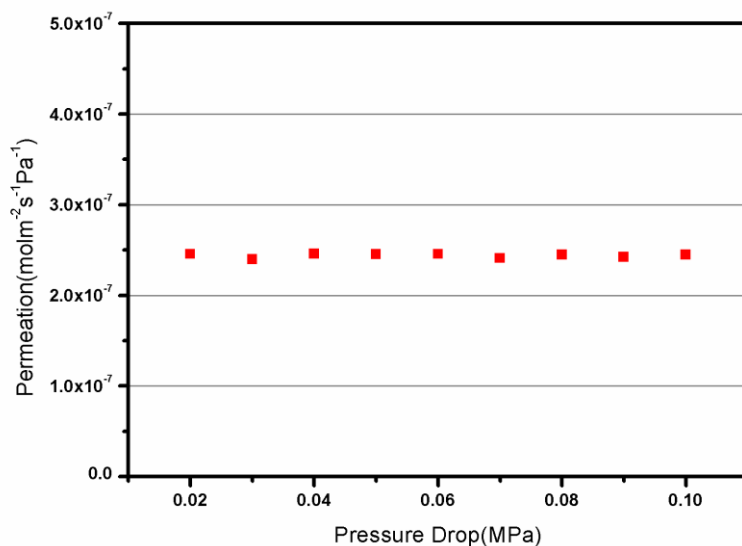


Figure S4. Permeance of N_2 through homochiral $Ni_2(L\text{-asp})_2(\text{bipy})$ membrane at different trans-membrane pressure drops.

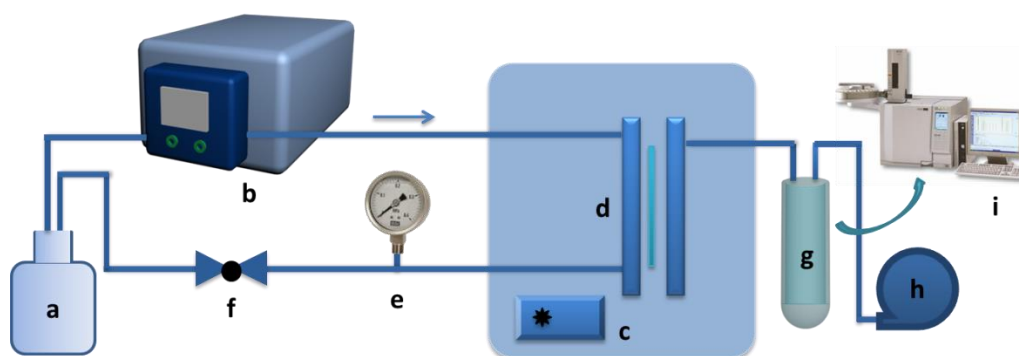


Figure S5. The pervaporation apparatus: a) Feed solution; b) flow controller; c) heating system with temperature controller; d) permeation cell; e) pressure gauge; f) valve; g) container in cold trap; h) vacuum pump; i) GC.

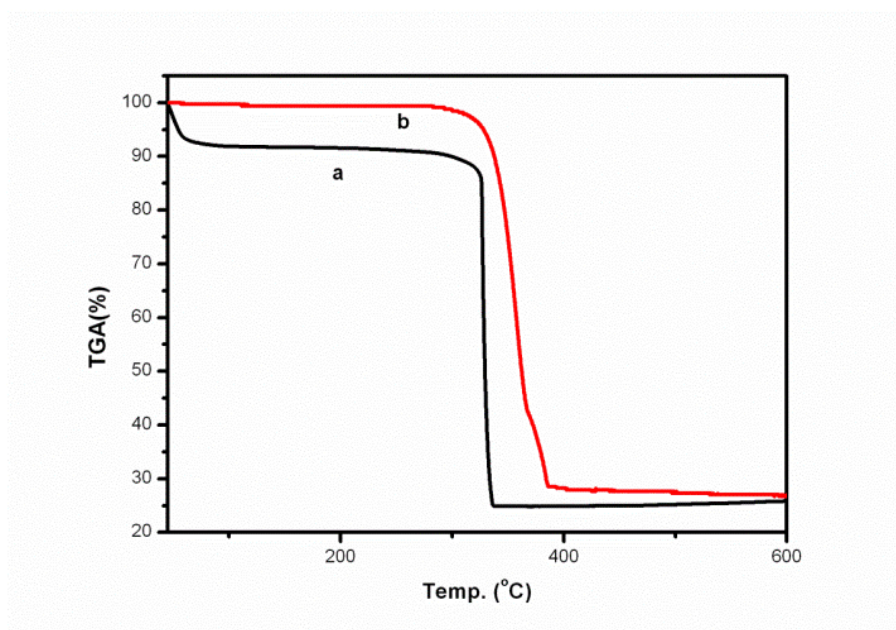


Figure S6. TGA plot of a) powder sample scraped from as-prepared $\text{Ni}_2(\text{L-asp})_2\text{bipy}$ membranes and b) powder sample scraped from activated $\text{Ni}_2(\text{L-asp})_2\text{bipy}$ membranes.

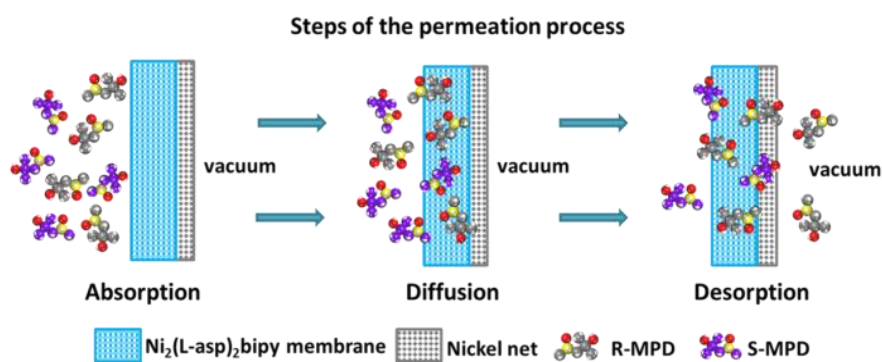


Figure S7. Schematic diagram of process that chiral molecules permeate through the MOF membrane.

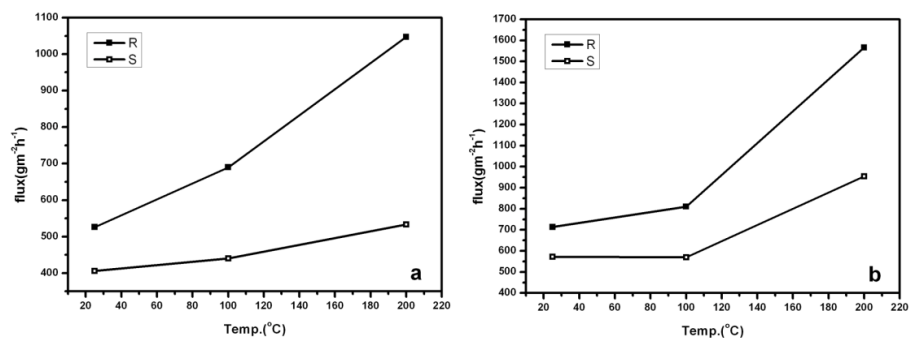


Figure S8. The fluxes of *R* and *S* configuration increase as the rise of test temperatures at the a) 0.1MPa and b) 0.2MPa.

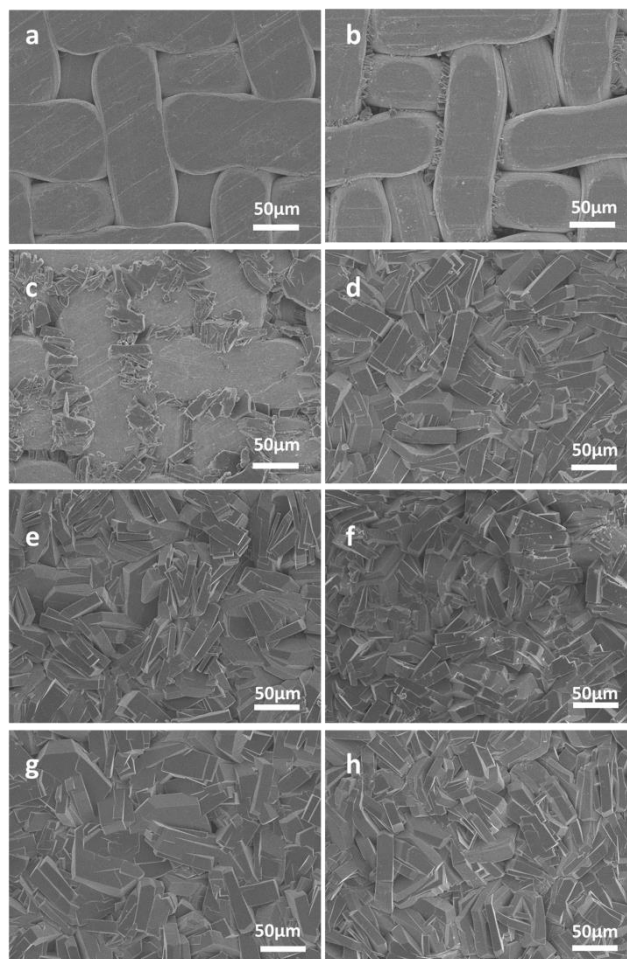


Figure S9. Top view SEM pictures of $\text{Ni}_2(\text{L-asp})_2(\text{bipy})$ membranes grown for a) 1h, b) 2h, c) 3h, d) 4h, e) 5h, f) 6h, g) 8h, h) 12h at 150°C .

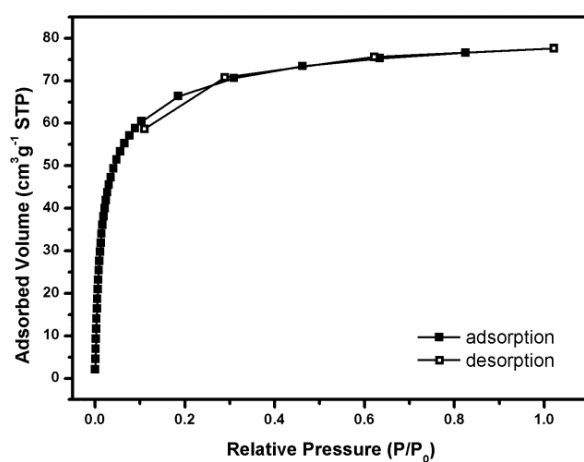


Figure S10. CO₂ sorption isotherm for Ni₂(L-asp)₂(bipy) at 195K, which was used to determine the BET surface area. (BET surface area of Ni₂(L-asp)₂(bipy) calculated with the adsorption data is 276 m²g⁻¹).

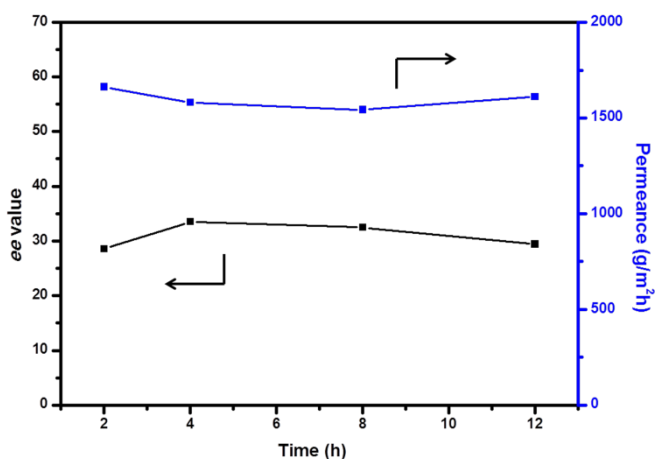


Figure S11. The ee values and permeances results of chiral isomers on the membrane of Ni₂(L-asp)₂(bipy) over time at 200°C and 0.1MPa.

Table S1: Comparison of the *ee* values for the racemic mixtures at different temperatures and pressures.

	25 °C	100 °C	200 °C
2-methyl-2,4-pentanediol ^[a]	12.9	22.2	32.5
2-methyl-2,4-pentanediol ^[b]	10.9	17.4	24.3
2-methyl-2,4-pentanediol ^[c]	-	-	30.8

[a] test pressure: 0.1MPa; [b] test pressure: 0.2MPa; [c] test pressure: 0.1MPa (the membrane was tested after treatment of heating at 200°C for ten days and ultrasound at 40KHz for 1h).

Table S2: Comparison of the permeance (g/m²h) for the racemic mixtures at different temperatures and pressures.

	25 °C	100 °C	200 °C
(<i>R</i>)-2-methyl-2,4-pentanediol ^[a]	526	690	1047
(<i>S</i>)-2-methyl-2,4-pentanediol	406	440	533
(<i>R</i>)-2-methyl-2,4-pentanediol ^[b]	713	810	1566
(<i>S</i>)-2-methyl-2,4-pentanediol	572	570	954

[a] test pressure: 0.1MPa; [b] test pressure: 0.2MPa.