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"Single nickel source" in situ fabrication of a stable homochiral MOF membrane with chiral resolution properties[†]

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A homochiral MOF membrane was successfully and facilely synthesized using an in situ growth method, which had the advantages of cheap raw materials, simple operation and high thermal stability. A diol isomer mixture was used to test the separation efficiency of the membrane at different temperatures and pressures.

Nowadays considerable attention is being paid to chiral resolution on account of significant differences in biological and pharmacological properties of the isomers of chiral compounds.¹ One has the desired affect while the other may be inert or even harmful.² The optical resolution of racemic mixtures is possible through various separation techniques, including thin layer chromatography (TLC), gas chromatography (GC), high performance liquid chromatography (HPLC), etc.³ However, all of these methods suffer from drawbacks such as small separation amounts per run, batch processing and high cost.

As an alternative method, membrane separation offers great promise owing to incomparable preponderance over traditional methods with advantages such as low-energy consumption, large processing capacity, and a continuous mode of operation. Some liquid and polymer membranes have been reported for the optical resolution of chiral isomers.⁴ Liquid membranes have demonstrated reasonably good permeability and enantioselectivity, but they have inferior durability and stability.⁵ Likewise, polymer membranes also have some disadvantages, such as a flexible skeleton and poor thermal stability, which restrict their application in the field of chiral separation. Zeolites and mesoporous membranes have attracted intense interest due to their well-defined porosity and stability in engineering applications such as gas or liquid separations, membrane reactors and chemical sensors, etc.⁶ However, it is very difficult to synthesize these materials with chiral structures,

which is the core of chiral separation. Therefore, exploring new types of membranes for application in chiral resolution is of critical importance.

Recently, metal-organic frameworks (MOFs) have emerged as a unique class of porous materials, which are very promising for a variety of applications, including chemical separation, gas storage, catalysis, sensing and drug delivery.⁷ MOFs are typically synthesized by assembling metal ions with organic ligands in appropriate solvents.8 They have crystalline structures, large internal surface areas and uniform cavities. It is worth mentioning that the design and modification of MOFs at the molecular level can be generally achieved through tuning or controlling their pore size and shape.9 Similarly, membranes made from specific MOFs are expected to offer unique opportunities with a potential to achieve superior performance, which not only extends the application of MOFs, but may also provide a solution for many engineering challenges. The ability to rationally tune the structure of the materials may create unique interactions with guest molecules and thus achieve unusual chemicophysical properties in separation or catalysis. Chiral separation by inorganic membranes is still a challenging task, but it could be potentially achieved by MOF membranes since a chiral pore structure in MOF can be relatively easily prepared by selecting the chiral ligand with expected length and functional groups.

 $Ni_2(L-asp)_2(bipy)$ is a chiral MOF with neutral chiral Ni(L-asp) layers connected by 4,4'-bipyridine(bipy) linkers to afford a pillared structure. It has a 1D corrugated channel (about 3.8 imes4.7 Å) lined with the chiral carbon atoms of L-aspartic acid (L-asp) ligands (Fig. S1, ESI⁺).¹⁰ This homochiral MOF possesses the following advantages: (i) it is thermally stable in air, which is very important for separation applications as the structure can be retained up to 300 °C; (ii) L-asp is a low cost, commercially available raw material, and can be obtained by catalysed enzymatic reaction. Theoretically, the pore size and functionality of the carrier material are crucial to membrane-based separations, and therefore usually the first consideration in selecting the material for a special separation. We believe that this homochiral MOF membrane can meet the requirements of practical chiral separation.

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Fig. 1 Schematic diagram of homochiral MOF membrane preparation by *in situ* growth on nickel nets.

Several reliable techniques have been innovated for synthesis of MOF membranes and films.¹¹ *In situ* and secondary growth are two main synthetic strategies.¹² We focus on the first method due to the simple steps involved in preparation. Some previous research studies focused on using organic linkers to support the growth of MOFs on a substrate, which is limited to functional surfaces.¹³ Microwave-heating approaches have also been developed for bulk materials and are now being extended to films.¹⁴ Slow diffusion of reactants was recently applied for the fabrication of ZIF-8 films on flexible porous nylon membranes.¹⁵ However, these approaches require additional laborious processing steps therefore it is highly desirable to fabricate a simpler but efficient process for assembling MOF membranes.

In this work, we followed a method of "single metal source" to facilely prepare a homochiral MOF membrane on a nickel net. The nickel net played two important roles in the synthesis process: as the only nickel source added to the reaction system and as a substrate to support the membrane. As shown in Fig. 1, the nickel net substrate was placed horizontally in a Teflon-lined autoclave, and it reacted with the organic ligands in a solution of suitable concentration. The Ni₂(μ -asp)₂(bipy) crystals first grow around the wires of the nickel net, then they continue to intergrow as time passes (Fig S9, ESI[†]). As the nickel net is the only metal source in the reaction system, which is different from our previous "twin copper source" work,¹⁶ the growth process stops after a layer of the crystal film is formed, which makes the final membrane thinner and defect free.

The X-ray diffraction (XRD) patterns of the as-synthesized Ni₂(L-asp)₂(bipy) membrane and activated membrane correspond well with the simulated one (Fig. S2, ESI[†]), which indicates that highly crystalline crystals grow on the substrate without orientation, and the membrane maintains permanent porosity after removal of guest molecules. The surface of the membrane was observed using both optical and scanning electron microscopy (SEM). Fig. 2a illustrates the optical micrograph of the nickel net supported MOF membrane, which clearly indicates that the nickel net acts as a homogeneous support allowing the continuous formation of the Ni₂(L-asp)₂(bipy) membrane over a larger area through this simple method. The morphology of the membrane was observed more in detail using SEM. From the top-view, it was observed that the membrane was defect-free and 20–30 μ m crystals merged tightly (Fig. 2b and c). From the cross-sectional view, it can be seen that the membrane has a thickness of 10-20 μm and crystals connect with the threads of the nickel net compactly and uniformly (Fig. 2d). The relatively low thickness of the membrane enables the chiral membrane to have a relatively large flow. Meanwhile, in the cross section SEM picture we can observe that the surface of the nickel mesh exposed in the bottom part had



Fig. 2 (a) Leica picture of the surface of the Ni₂(L-asp)₂(bipy) membrane. SEM pictures of the surface of (b) the Ni₂(L-asp)₂(bipy) membrane and (c) details of the densely packed crystallites. (d) A cross-section SEM picture of the Ni₂(L-asp)₂(bipy) membrane.

been corroded, which further confirmed that the membrane is synthesized by the nickel net as the nickel source, ensuring a strong adhesion between the membrane and the substrate.

The MOF membranes were subjected to the nitrogen permeance test at different transmembrane pressure drops to assess the integrity. The permeance of the membrane is independent of the transmembrane pressure drop, implying that the membrane has no macroporous defects, while the carriers are not able to hold the pressure (Fig. S4, ESI[†]).

A good match of size and shape between the guest molecule and the host channel is important. A chiral molecule (\pm) -2-methyl-2,4pentanediol was used to test the chiral resolution of Ni₂(1-asp)₂bipy membranes. Enantioselective separation measurements on the homochiral MOF membranes were performed using a home-built pervaporation apparatus (Fig. S5, ESI⁺). The membrane sample was mounted in a stainless steel membrane cell with the MOF layer on the feed side, while the pervaporation apparatus was heated using a silicone oil bath and a heating belt with controllable temperature. The contents of the two chiral isomers in the permeation samples were determined by gas chromatography (GC) measurements, and pure (R)-2-methyl-2,4-pentanediol was used to confirm the sequence of peaks. Before the separation of chiral isomers, the MOF membrane was activated at 150 °C for at least 10 hours, and the TGA curves indicate that all guest molecules had been removed after the activation process (Fig. S6, ESI⁺). Upon passing racemic mixtures through the membrane, the permeate concentrations and flux data of isomers at varied temperatures were calculated and are shown in Tables S1 and S2 (ESI⁺). The higher penetration amount of R diols through the membrane is largely attributed to our assumption that there is a geometry-dependent interaction between the chiral channel and the optical isomer guests, so it is easier for R-diols to enter into the membrane pores than S-diols.¹⁰

To investigate the influence of permeation temperature on the separation and thermal stability of the membrane, the operating temperature was increased from 25 to 200 °C under 0.1 MPa (Fig. 3). The permeance of (*R*)-2-methyl-2,4-pentanediol increased from 526 g m⁻² h⁻¹ to 1047 g m⁻² h⁻¹, while that of



Fig. 3 Comparison of the ee values for racemic diol mixtures at different temperatures and pressures.

(S)-2-methyl-2,4-pentanediol only slightly increased from 406 g m⁻² h⁻¹ to 533 g m⁻² h⁻¹. Thus the resulting ee value reached 32.5% at 200 °C, which is close to the boiling point of 2-methyl-2,4pentanediol (197 °C). This phenomenon can be explained by an adsorption-diffusion model (Fig. S7, ESI⁺). Since both R and S enantiomers can pass through the channel of the Ni₂(L-asp)₂(bipy) membrane due to their smaller kinetic diameters, S enantiomers adsorbed in the homochiral MOF pores block the diffusion of the more highly mobile R enantiomers with a matching configuration of the channel structure. As the temperature is increased, less S enantiomers are adsorbed and R enantiomers can now diffuse in the resulting free volume. So the selectivity of the membrane is improved as the temperature increases, and similar results have been obtained for the separation of C8 alkylaromatics on MOF materials and gas purification on zeolitic imidazolate framework (ZIF) membranes.¹⁷ Meanwhile, due to the kinetic energy of the molecules increasing with the rising temperature, the diffusion of the two isomers is accelerated, which results in the enhancement of the flux. The membrane can function at 200 °C for 12 hours continuously with similar separation performances (Fig. S11, ESI⁺), and is reusable, which indicates that the MOF membrane has a high thermal stability. Furthermore, when the pressure drop increases from 0.1 to 0.2 MPa, the permeation results reveal that the flux of isomers becomes larger, while the ee values decline slightly (Fig. S8, ESI^+).

As far as we know, very few studies have been reported to date on MOF membranes for chiral resolution. Fischer and co-workers reported a MOF thin film with a "selective adsorption" of chiral molecules.¹⁸ Jin's group reported a chiral membrane obtained by second-growth, and the resolution process was carried out by a "side-by-side diffusion cell" and gave the best ee value of 33% at the lowest concentration.¹⁹ Here, our fairly stable homochiral membranes were used to separate pure racemic mixtures by a practical technology of the "pervaporation process" under varied conditions and resulted in a comparable ee value of 32.5%.

In summary, a homochiral MOF membrane was successfully synthesized by utilizing a "single nickel source" method, which has the advantages of low cost raw materials and simple operation. The MOF membrane possesses chiral channels and has excellent thermal stability. So it can be applied in the field of chiral resolution. A diol isomer mixture was used to test their separation efficiency. A temperature–pressure-related membrane performance of homochiral MOF membranes was observed for the first time, which could be an important issue in the development of chiral resolution. Due to the advantages of tunable pore size and structural modifications, the high-quality and effective homochiral MOF membranes may find promising applications in different molecular chiral resolutions and chiral membrane catalysis.

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