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Supporting information

Metal-Organic Framework Membranes Fabricated via Reactive Seeding

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1. Experimental details

(1) Membrane preparation

Alumina powders (particle size of ~400 nm) were uniaxially pressed at 200 MPa to prepare green disks with diameters of 22 mm and thicknesses of 2 mm. The green disks were then sintered at 1200 ºC for 2 h to form the porous supports. Normal pore size of the support was ca. 110 nm and the porosity was about 35 %. One side of the support was polished by SiC sandpaper and washed in deionized water before being used for the growth of MOF membrane.

The MIL-53 membrane was prepared on alumina support by the RS method. A typical synthesis procedure contained two processes. Seed growth: 0.36 g H_2BDC (98%, Sigma-Aldrich) and 25 g deionized water was mixed and stirred vigorously several minutes. An alumina support was placed vertically in a Teflon lined stainless steel autoclave with the mixture solution. The autoclave was heated at 220 ºC for 12h in the oven, and then cooled to room temperature. The support (with MIL-53 seed on the surface) was washed with deionized water and dried at 100 ºC for 12 h. Secondary growth: the seeded support was placed into the precursor solutions, with a composition of 0.82 g $Al(NO_3)_3{\cdot}9H_2O$ (98%, Sigma-Aldrich), 0.18g H_2BDC and 25 g deionized water. Again, the autoclave including the seeded support and precursor solutions was heated at 220 ºC for 12 h. After cooling, the membrane was washed with deionized water and dried at 100 ºC for 12 h.

To confirm that the synthesis of MIL-53 seeds can be achieved by employing alumina, direct hydrothermal reaction of alumina powders (1g) with H_2BDC (1g) in an autoclave at 220 ºC for 12 h was conducted. The produced powder samples were washed with deionized water, and then dried at 100 ºC for 12 h.

(2) Characterization techniques

The crystal phases of samples were determined by X-ray diffraction (XRD) with Cu Ka radiation (Bruker, model D8 Advance). Diffraction patterns were collected at room temperature in the range of $5° \leq 2\theta \leq 50°$ with a step width of 0.05° and scan rate of 0.2 s step^{-1}.

Morphologies of membranes and support were examined by scanning electron microscopy (SEM) (FEI, model QUANTA-2000). The working parameters of the SEM are as follows: high voltage (HV) 25-30 kV, work distance (WD) 8-10 mm and Spot 3.0.

FT-IR spectra were recorded by spectrophotometer (AVATAR-FT-IR-360, Thermo Nicolet, USA) in the range of 4000 to 400 cm^{-1}, using the KBr disk technique. Thirty two scans were accumulated with a resolution of 4 cm^{-1} for each spectrum.

Single gas permeation experiments were performed on the permeation setup shown in Fig. S1. The permeation of small gas molecules (H_2, CH_4, N_2, and CO_2) was measured at room temperature (25 ^{o}C) through MIL-53 membranes or supports. The feed side was regulated at different pressures and the permeate side was open to atmosphere. The permeated gas flow rate was measured by a soap film flowmeter.

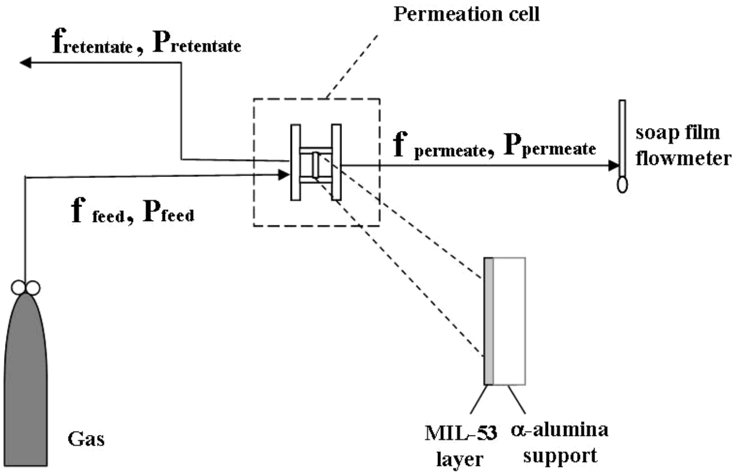

Fig. S1 Schematic diagram of the single gas separation experimental apparatus.

The pervaporation performance of MIL-53 membrane was measured on a homemade apparatus (Fig. S2). The feed solution was continuously circulated from a feed tank through the side of the membrane module using a variable speed feed pump.

The feed speed was maintained at 15 L·h^{-1}. Vacuum on the permeate side was maintained at about 200 Pa and was monitored by a digital vacuum gauge. The permeated vapor was collected in liquid nitrogen traps. Before pervaporation, the membranes were immersed in the feed solution for 3h. At the beginning of the PV process, the mass transfer equilibrium was established after about 2h, and PV performance was considered to be stable. At steady state, the weight of the permeated component collected in the cold trap was measured to calculate the total flux, *J*.

$$J = \frac{W}{At} \tag{S1}$$

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

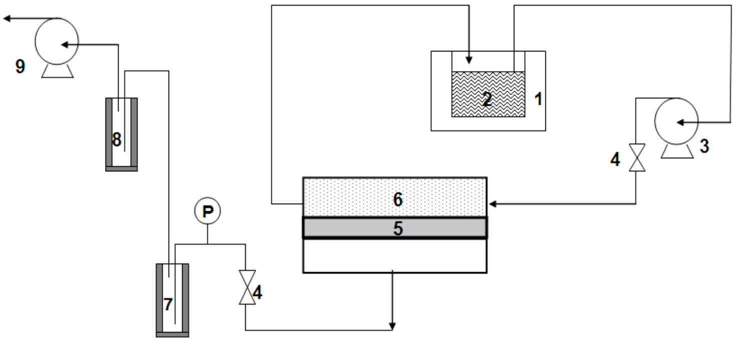

Fig. S2 The pervaporation setup: 1. water bath, 2. feed, 3. circulation pump, 4. stop valve, 5. membrane, 6. membrane module, 7. collecting trap (liquid N_2), 8. trap (liquid N_2), 9. vacuum pump.

The water content in the feed and permeated samples were analyzed by gas chromatography (GC-2014, SHIMADZU, Japan) equipped with a thermal conductivity detector, using a Φ 3 mm × 2 m stainless steel column packed with porapak Q and helium as the carrier gas.

The permselectivity of MIL-53 membranes is expressed by a separation factor, which is defined as α

$$\alpha = \frac{w_{water}^{P} / (1 - w_{water}^{P})}{w_{water}^{F} / (1 - w_{water}^{F})} \quad \text{(S2)}$$

Where w_{water}^{F} and w_{water}^{P} refer to the weight fractions of water in the feed and permeated samples, respectively.

2. IR spectra of MIL-53 crystals

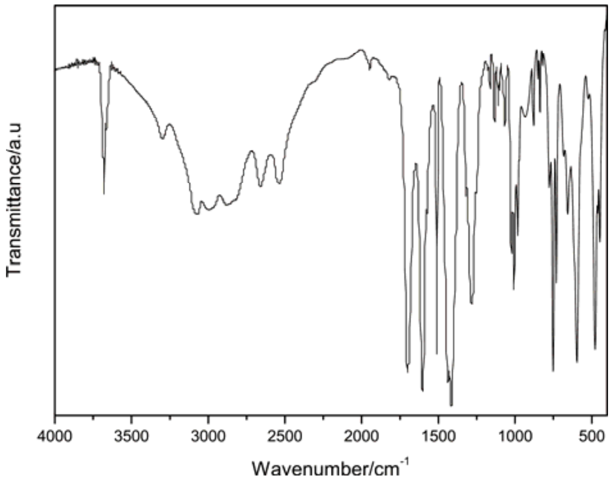

Fig. S3 IR spectra of MIL-53 crystals obtained from the bottom of the autoclave after membrane synthesis.

The IR spectra of the crystals obtained from the bottom of the autoclave after membrane synthesis is in good agreement with the MIL-53 spectra data reported in the literature [1]. The vibrational bands in the usual region of 1400-1700 cm^{-1} refer to the carboxylic function. [2] The absorption bands located at 1604 and 1503 cm^{-1} are assigned to -CO_2 asymmetric stretchings, whereas the bands at 1435 and 1414 cm^{-1} are assigned to -CO_2 symmetric stretchings. These values are consistent with the presence of CO_2^- groups that are coordinated to aluminum. The absorption peak at 1669 cm^{-1} is attributed to free BDC acid molecules, which are encapsulated within the pores of the structure in their protonated form (-CO_2H). The vibrational bands in the region 3600-3500 cm^{-1} correspond to the stretching modes of water. These results further confirmed that the membrane was indeed MIL-53.

S1 T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Ferey, *Chem. Eur. J.*, 2004, **10**, 1373.

S2 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, 1986.

3. *In situ* growth of MIL-53 membrane

$Al(NO_3)_3 \cdot 9H_2O$ (98%, Sigma-Aldrich), 1,4-benzenedicarboxylic acid (H_2BDC, 98%, Aldrich) and deionized water were used as the starting materials for in-situ growth of the MIL-53 membrane. The molar composition of the initial solution was 1Al (0.8226g): 0.5BDC (0.1801g): $640H_2O$ (25g). The synthesized mother liquid was placed in a Teflon lined stainless steel autoclave. A polished alumina support was placed vertically in the autoclave with the help of a Teflon holder. Then, the autoclave heated at 170 ºC and 220 ºC for 72h. After the autoclave was cooled to room temperature, the membrane was washed with deionized water and dried at 100 ºC for 12h.

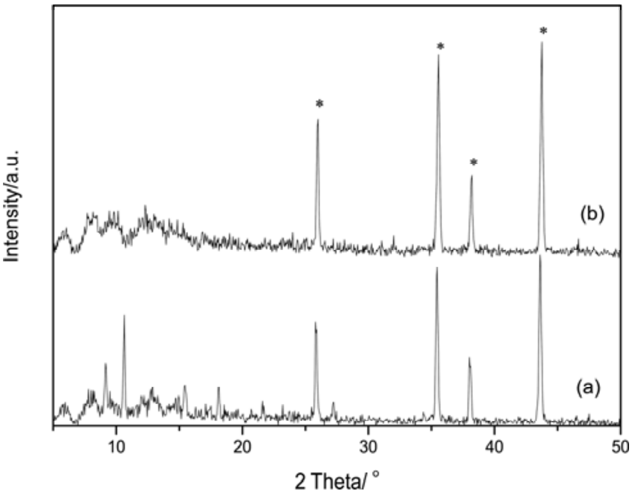

Fig. S4 XRD patterns of the MIL-53 membranes synthesized by the *in situ* hydrothermal method at (a) 170 ºC and (b) 220 ºC,*from alumina support.

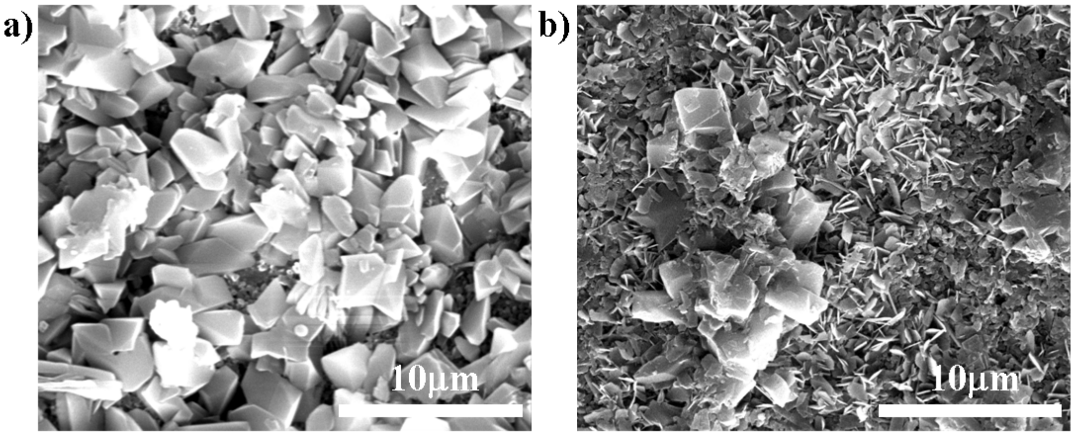

Fig. S5 SEM images of MIL-53 membranes by the *in situ* hydrothermal method at (a) 170 ºC and (b) 220 ºC.

As shown in Figs S4 and S5, the nucleation density at the support surface was not high enough to provide a continuous membrane. The separation performances of these discontinuous membranes are almost similar to that of the porous supports.

4. Single gas permeation

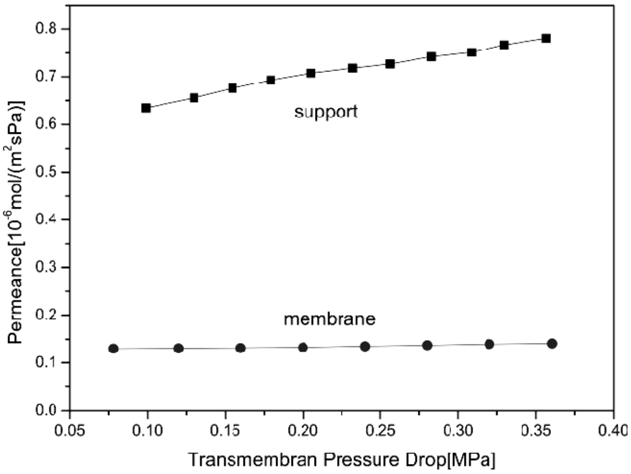

Fig. S6 Permeance of nitrogen through alumina support and MIL-53 membrane at different trans-membrane pressure drops.

The permeance of the support increases with increasing trans-membrane pressure drop. This indicates that the gas transport through the support includes both Knudsen diffusion and viscous flow. The permeance of MIL-53 membrane is almost independent of the trans-membrane pressure drop, implying that the MIL-53 membrane has no macroporous defects.

5. Pervaporation performance

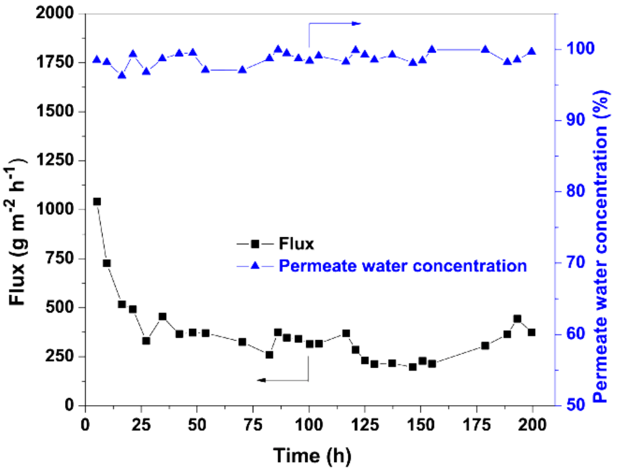

Fig 7. Pervaporation performances of the MIL-53 membrane as a function of operating time. Pervaporation conditions: 93 wt % EAC aqueous solution at 60 ºC.

Table S1. PV results of the MIL-53 membrane (60 ºC).

Feed type	Separation factor	Flux (kg·m^{-2}·h^{-1})
7% water and 93% ethanol	1	5.6
7% water and 93% t-butanol	1.2	3.1
7% water and 93% ethyl acetate	1317	0.5

As shown in Table S1, we observe that MIL-53 membrane is extremely selective for removal of water from ethyl acetate solutions by PV. However, for ethanol/water solutions and t-butanol/water solutions, the MIL-53 membrane has no separation capability. The high selectivity of the MIL-53 membrane is mainly attributed to two effects: the molecular size effect and the preferential adsorption of water molecules. The kinetic diameter of the bigger liquid molecule, EAC (ca. 5.2 Å), is smaller than the pore size of MIL-53 (7.3×7.7 Å). Therefore, the high performance could not be attributed to the molecular sieving effect only. Another reasonable explanation is that the hydroxyl groups (which exist on the surface of MIL-53 membrane) can form hydrogen bonds with H_2O. Thus, H_2O may more easily enter into the membrane pores than EAC molecules. Furthermore, the ethanol (ca. 4.3 Å) and t-butanol (ca. 5.02 Å) have smaller molecular size than that of EAC, and have many hydroxyl groups, so the MIL-53 membrane has shows no separation performance for the water/ethanol and water/t-butanol mixtures.

6. The universality of the RS method

(1) *In situ* growth of the membrane

A solution was prepared by completely dissolving 0.1185 g 1,3,5-benzenetricarboxylic acid (H_3BTC) and 0.741 g $Al(NO_3)_3 \cdot 9H_2O$ in 30 ml deionized water. Then the solution was transferred into a Teflon-lined autoclave in which the support was placed on the bottom facing downward. Afterward, the autoclave was heated in an oven at 210 °C for 24 h. After crystallization, the synthesized MIL-96 membrane was washed, dried, and last calcined in air at 200 °C for 5 h.

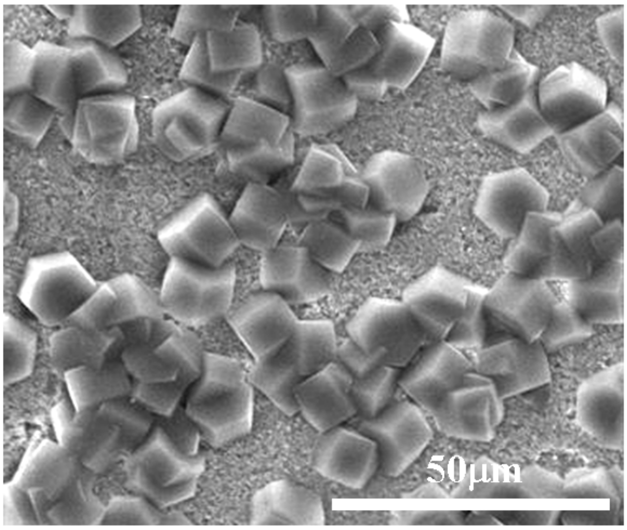

Fig. S8 SEM images of MIL-96 membrane by the *in situ* hydrothermal method.

From Fig. S8, the nucleation density at the support surface was not high enough to provide a continuous membrane.

(2) The growth of the membrane via RS method

A 0.01mol L^{-1} aqueous solution of H_3BTC was transferred it to a Teflon-lined autoclave containing the support on the bottom. After hydrothermal treatment at 210 °C for 12 h, we removed the support and rinsed it with deionized water, and dried it in air. For secondary growth, 30mL deionized water was added into a solid mixture of 0.1185 g H_3BTC and 0.741 g $Al(NO_3)_3 \cdot 9H_2O$ with stirring. This clear solution was transferred into a Teflon autoclave in which a seeded support was placed. Afterwards, the autoclave was heated in an oven at 210 °C for 24 h. After crystallization, the synthesized MIL-96 membrane was washed, dried, and last calcined in air at 200 °C for 5 h. The XRD patterns of the MIL-96 are shown in Fig. S9. It can be found that the as-prepared membranes exhibit pure MIL-96 phase.

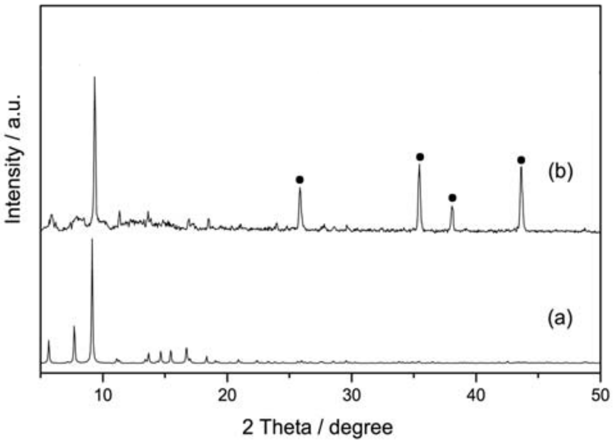

Fig. S9. XRD patterns of simulated MIL-96 crystal (a), and MIL-96 membrane prepared by RS method on the α-Al_2O_3 support (b). Black dots denote the reflections of α-Al_2O_3.

As shown in Fig. S10, the MIL-96 membrane obtained by the RS method consisted of well-intergrown grains fully covering the entire substrate surface. The membrane layer is well bonded with the support, and the thickness of the membrane is about 10 μm.

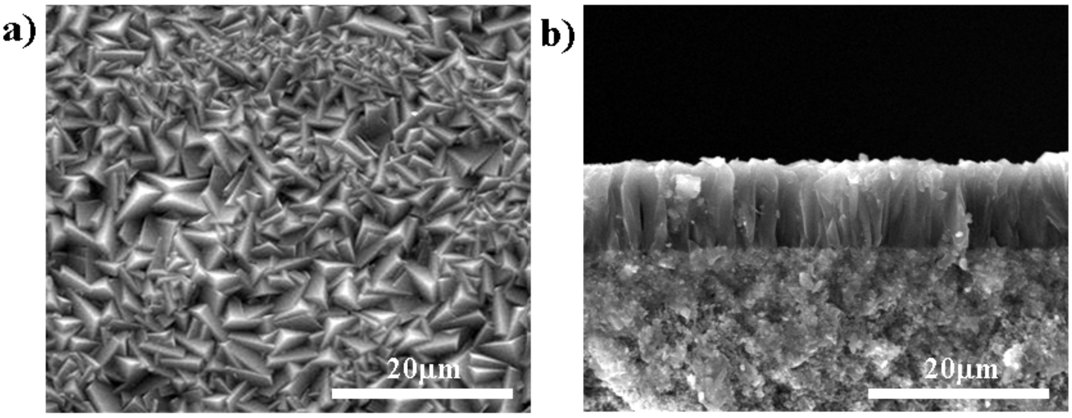

Fig. S10 SEM images of MIL-96 membrane produced by the RS method, (a) surface and (b) cross section.

(3) Single gas permeation

The permeation of N_2 molecules was conducted at room temperature through MIL-96 membranes and supports. Fig. S11 shows the permeance of N_2 through the membrane and the support at different trans-membrane pressure drops. The permeance of the MIL-96 membrane is largely independent of the transmembrane pressure drop, implying that the MIL-96 membrane contained a negligible amount of macroporous defects.

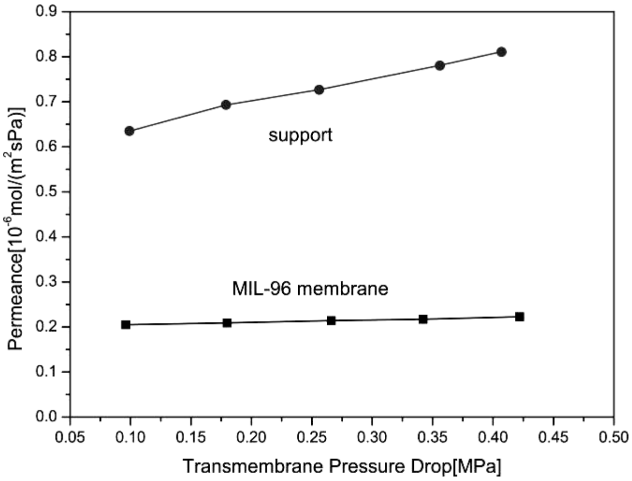

Fig. S11 Permeance of nitrogen through alumina support and MIL-96 membrane at different trans-membrane pressure drops.

(4) Pervaporation performance

In the dehydration of ester/water mixtures, the MIL-96 membrane also exhibited excellent pervaporation performance (see Table S2), especially in the dehydration of ethyl acetate/water mixture at 4.0 wt.% water in feed with a flux of 70 g m^{-2} h^{-1} and a separation factor larger than 1279.

Table S2 Pervaporation dehydration results of MIL-96 membranes (60 ºC)

Feed mixture(A/B)	Separation factor	Flux ($g \cdot m^{-2} \cdot h^{-1}$)
5.6 wt.% water and 94.4 wt.% ethanol	6	125
9.3 wt.% water and 90.7 wt.% t-Butanol	16	81
4.4 wt.% water and 95.6 wt.% Ethyl acetate	1279	70