

## Supporting Information

### **A hybrid ZIF-8/ZIF-62 glass membrane for gas separation**

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# 1. Experimental procedures

## 1.1 Materials

All chemicals were commercially available without further purification.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.99%, Sigma-Aldrich), imidazole (Im, 99.5%, Sigma-Aldrich), benzimidazole (Bim, 99%, Sigma-Aldrich), 2-methylimidazole (Hmim, 99%, Sigma-Aldrich), N,N-dimethylformamide (DMF, 99.5%, Sinopharm Chemical Reagent Co., Ltd), methanol (99.5%, Sinopharm Chemical Reagent Co., Ltd). Porous  $\alpha\text{-Al}_2\text{O}_3$  disks (18 mm in diameter, 1.0 mm in thickness, and 70 nm particles on the top layer) were purchased from Fraunhofer Institute IKTS, Germany.

## 1.2 Synthesis of ZIF-62 powder

A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.1 M), Im (1.35 M), and Bim (0.15 M) was dissolved in DMF and stirred for 15 min to obtain a homogeneous solution.<sup>1</sup> Then the solution was transferred to Teflon-lined stainless-steel autoclaves and heated in an oven at 130 °C for 96 h. The product was collected by centrifugation, washed with clean DMF thoroughly and dried at 100 °C for 24h.

## 1.3 Synthesis of ZIF-8 powder

ZIF-8 nanoparticles were synthesized according to our previously reported method.<sup>2</sup> A methanol solution (60 mL) of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.879 g) was quickly added to another methanol solution (60 mL) of Hmim (1.776 g), and the mixture solution was stirred at room temperature for 1 h. The product was collected by centrifugation, washed with clean methanol thoroughly and dried at 100 °C for 24h.

## 1.4 Synthesis of $(\text{ZIF-8})_x(\text{ZIF-62})_{1-x}$ hybrid crystals and glasses

A series of hybrid crystals with different doping amounts of ZIF-8 had been prepared, which were named  $(\text{ZIF-8})_x(\text{ZIF-62})_{1-x}$ , where x was the mass percentage of ZIF-8. Specifically, a mixture of ZIF-8 and ZIF-62 at a certain mass ratio was dispersed in deionized water and ball-milled with a 7 mm stainless steel ball at 25 Hz for 5 min. The obtained hybrid sample was obtained by centrifugation and dried at 80 °C.

Subsequently, the hybrid ZIF-8/ZIF-62 crystal was heated in a tube furnace with argon atmosphere protection, at a rate of 10°C/min to 500°C and kept for 10 min, and finally cooled naturally to room temperature.<sup>3</sup> The obtained hybrid glasses were named  $a_g[(\text{ZIF-8})_x(\text{ZIF-62})_{1-x}]$ .

### **1.5 Synthesis of ZIF-8/ZIF-62 hybrid membrane via post-synthetic ligand exchange approach**

Post-synthetic ligand exchange approach was employed for preparing the mixed-phase ZIF-8/ZIF-62 polycrystalline membrane. First, the ZIF-62 polycrystalline membrane was prepared by in situ growth method at room temperature. A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , imidazole and benzimidazole with molar ratio of 1:13.5:1.5 was dissolved in DMF and stirred for 15 min. The precursor solution was then transferred to a glass container with  $\alpha\text{-Al}_2\text{O}_3$  support in advance, reacted at room temperature for 12h for fabricating ZIF-62 polycrystalline membrane. To prepare ZIF-8/ZIF-62 hybrid membrane, the ZIF-62 membrane was subsequently immersed in the DMF solution containing Hmim (8 M) ligand of ZIF-8 to react at 50 °C for 2 h. Finally, the resultant ZIF-8/ZIF-62 polycrystalline membrane was heated at 500 °C for 30 min in a tube furnace filled with Ar atmosphere.

### **1.6 Synthesis of ZIF-8/ZIF-62 hybrid membrane via in-situ solvothermal method**

A DMF solution containing  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Im, Bim and Hmim was prepared according to the optimal formula, i.e., Zn:L: Hmim: DMF molar ratio of 1:5:8:208, where L=im+bim and im: bim is 5:1. The precursor solution was transferred to a Teflon-lined stainless-steel autoclave in which the  $\alpha\text{-Al}_2\text{O}_3$  support was placed horizontally in advance, and then heated at 50 °C for 2 h. The obtained ZIF-8/ZIF-62 polycrystalline membrane was then heated at 500 °C for 30 min in a tube furnace filled with Ar atmosphere to achieve the corresponding hybrid glass membrane.

We conducted controlled experiments by using single ligand of ZIF-8 or ZIF-62. All operations are consistent with the above-mentioned ZIF-8/ZIF-62 membrane preparation, except for changing the solution to Zn:Hmim:DMF molar ratio of 1:8:208 or Zn:L:DMF (L=im+bim, im:bim=5:1) molar ratio of 1:5:208, respectively.

### **1.7 Characterizations**

Powder X-ray diffraction (PXRD) patterns were carried out on a Bruker D8 ADVANCE X-ray diffractometer (accelerating voltage: 40 kV, current: 40 mA) using a Cu K $\alpha$  radiation source with a 2 $\theta$  range between 5° and 40°. Thermogravimetric analysis (TGA) was performed on NETZSCH STA 2500 at a heating rate of 10 °C/min from 50 to 700 °C under nitrogen atmosphere. Differential scanning calorimeter (DSC) curve was obtained on NETZSCH DSC 214 instrument. Fourier transformed infrared spectroscopy (FTIR) was carried out on a VERTEX 70 (Bruker). A Nova Nano SEM 450 scanning electron microscope (SEM) instrument was used to characterize the sample

morphology at an accelerating voltage of 5 kV. The gas adsorption isotherms were measured on a Micromeritics 3Flex Surface Characterization Analyzer. Prior to gas measurement, all the samples were degassed at 80 °C for 48 h under dynamic vacuum. Proton NMR (<sup>1</sup>H NMR) spectroscopy was performed on Magnet System 500/54 Ascend. The sample was dissolved in a mixture of DMSO-D6 (500 μL) and DCl (36.5 %)/D<sub>2</sub>O (100 μL).

### 1.8 Gas permeation experiments

The gas separation performances of glass membranes were measured by the Wicke-Kallenbach method. Single gas or equimolar gas mixture was used as feed gas, and helium was used as sweep gas. A gas chromatography (Agilent 7890B) is used to measure the concentration of the gas on the permeate side.

The gas permeance was determined by Eq. (1):

$$P_i = \frac{N_i}{A \cdot \Delta P_i} \text{ (Eq. 1)}$$

where  $P_i$  (mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>) is the gas permeance,  $N_i$  (mol s<sup>-1</sup>) is the molar flow rate of component  $i$ ,  $\Delta p_i$  (Pa) is the transmembrane pressure difference, and  $A$  (m<sup>2</sup>) represents the effective membrane area.

The ideal selectivity was determined by Eq. (2):

$$S_{ij} = \frac{P_i}{P_j} \text{ (Eq. 2)}$$

where  $P_i$  and  $P_j$  represent the permeance of component  $i$  and component  $j$ , respectively.

### 1.9 Calculation of the gas adsorption isotherms

All the C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> isotherms were fitted using Dual-site Langmuir (DSL) model (Eq. 3):

$$q = q_1 \frac{b_1 p}{1 + b_1 p} + q_2 \frac{b_2 p}{1 + b_2 p} \text{ (Eq. 3)}$$

where  $q_1$  and  $q_2$  are the adsorbed amount per mass of adsorbent (mmol g<sup>-1</sup>) for each site,  $p$  is the pressure of the bulk gas at equilibrium (kPa),  $b_1$  and  $b_2$  are the affinity coefficients of each site (kPa<sup>-1</sup>).

The IAST selectivity  $S_{ads}$  was determined by Eq. (4):

$$S_{ads} = \frac{q_i \times p_j}{q_j \times p_i} \text{ (Eq. 4)}$$

where  $q_i$  and  $q_j$  are the adsorbed amount per mass of adsorbent of component  $i$  and  $j$ ,  $p_i$  and  $p_j$  are the pressure of the bulk gas at equilibrium of component  $i$  and  $j$  in the bulk.

## 2. Supplementary Figures and Tables

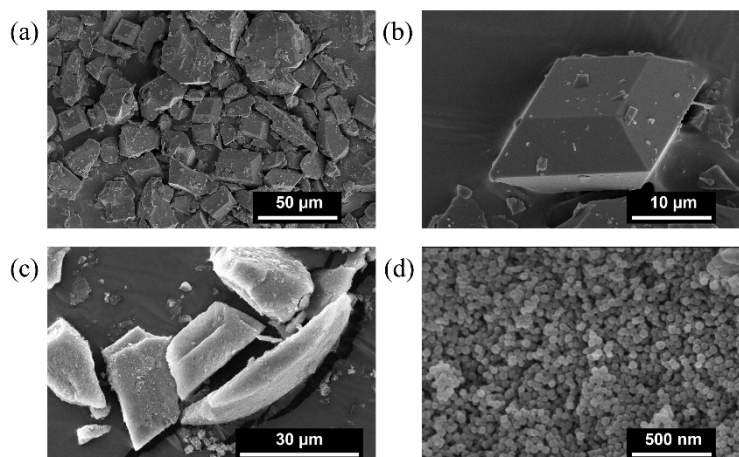


Fig. S1 SEM images of (a, b) ZIF-62 and (c, d) ZIF-8.

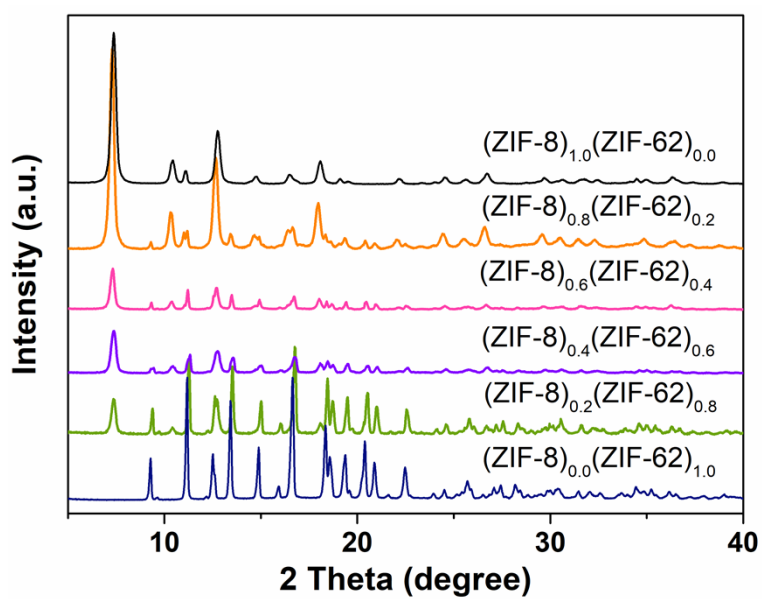


Fig. S2 PXRD patterns of (ZIF-8)<sub>x</sub>(ZIF-62)<sub>1-x</sub> samples.

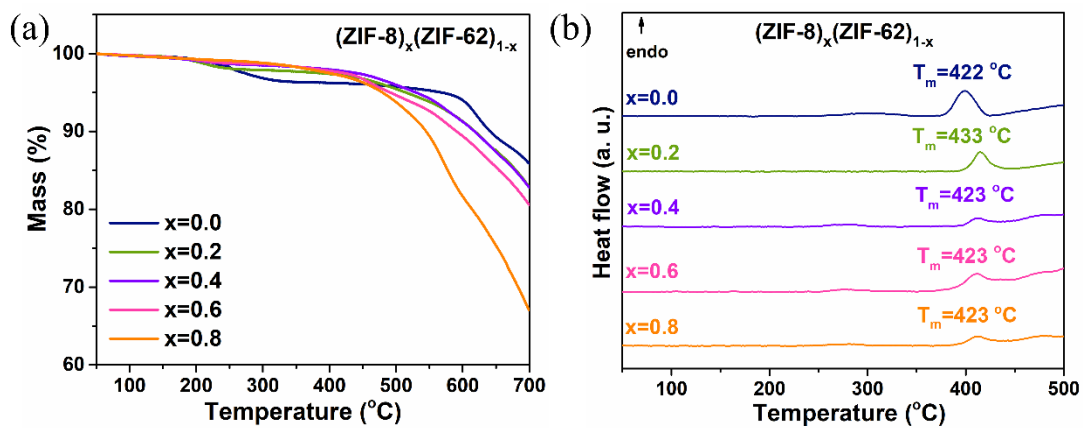


Fig. S3 (a) TG and (b) DSC curves of  $(\text{ZIF-8})_x(\text{ZIF-62})_{1-x}$  samples.

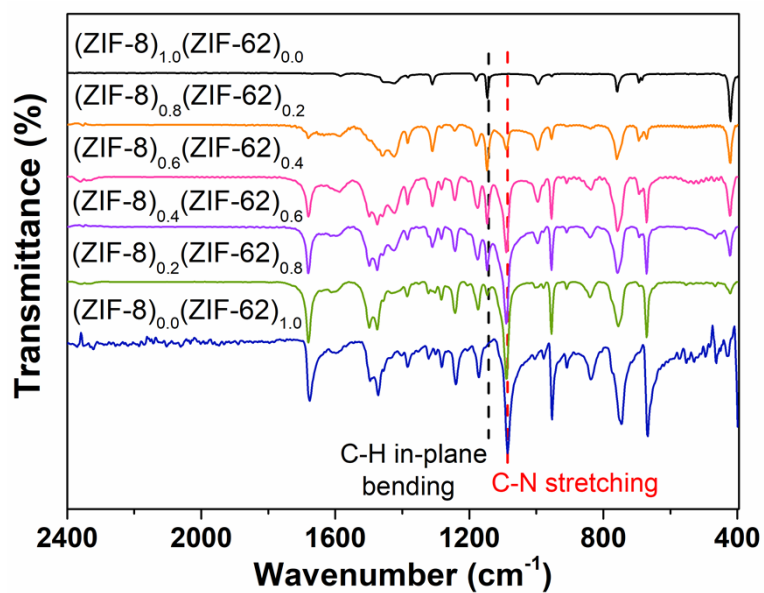


Fig. S4 FTIR spectra of  $(\text{ZIF-8})_x(\text{ZIF-62})_{1-x}$  samples.

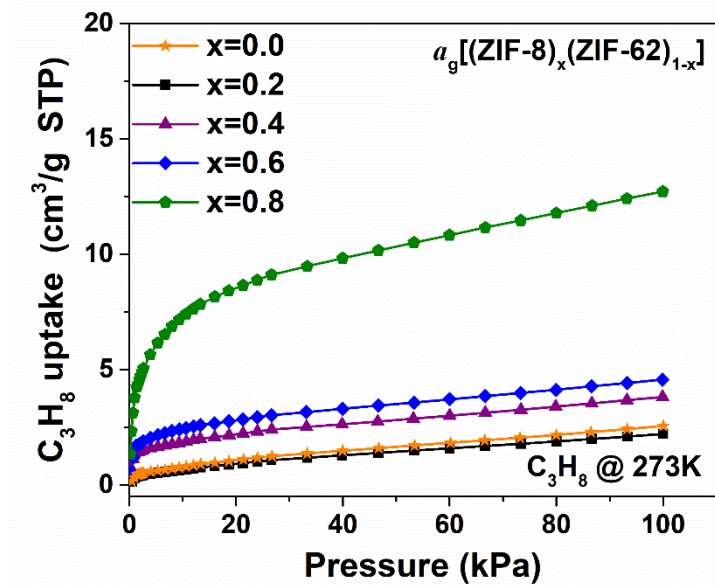


Fig. S5  $C_3H_8$  adsorption isotherms of  $a_g[(ZIF-8)_x(ZIF-62)_{1-x}]$  samples at 273K.

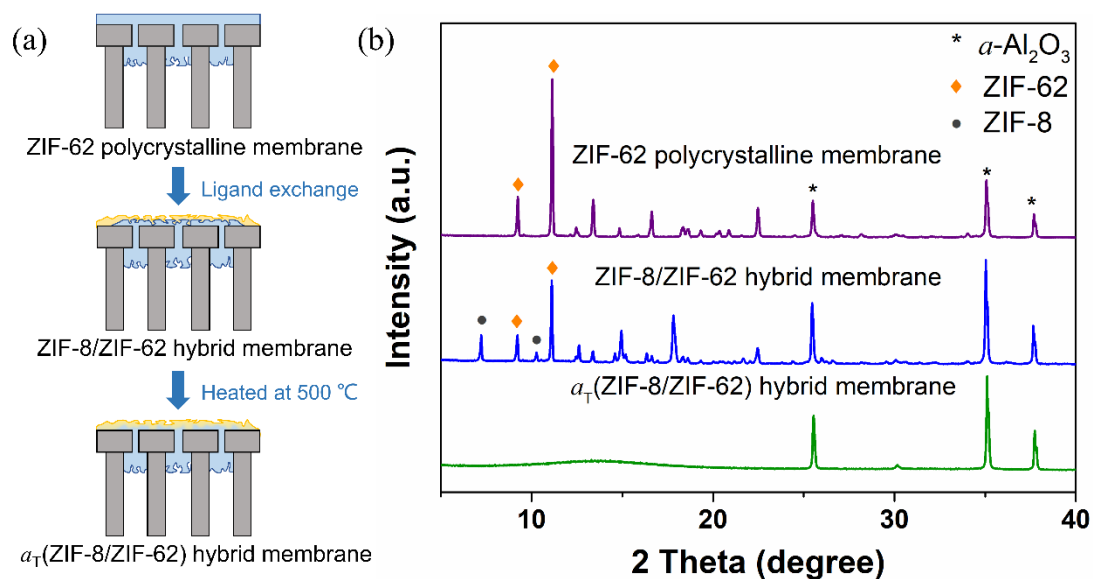
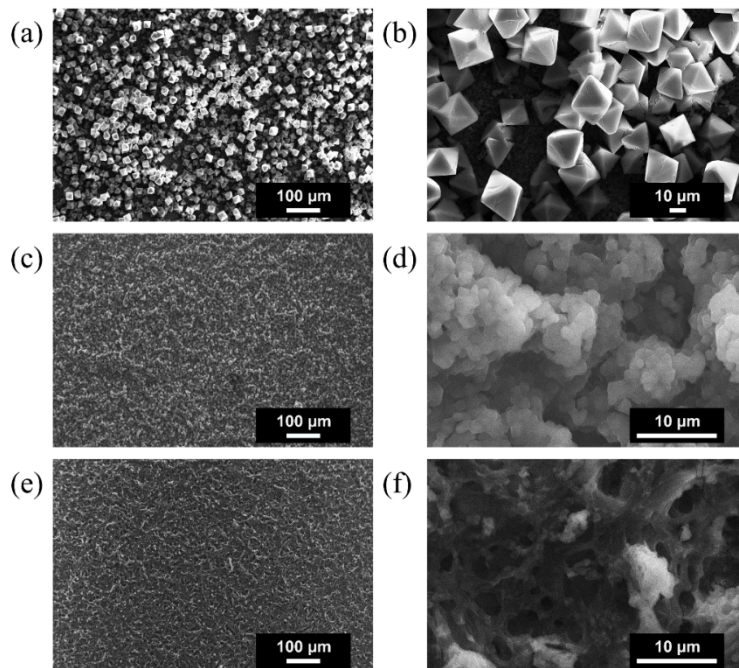
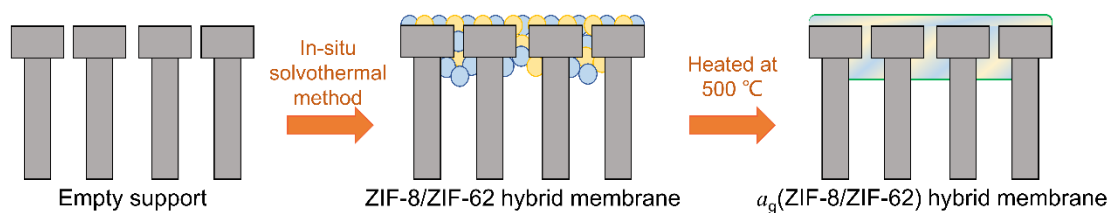


Fig. S6 (a) Schematic diagram of the preparation of hybrid ZIF-8/ZIF-62 glass membrane. (b) XRD patterns of membranes obtained from different treatment processes, the ZIF-62 polycrystalline membrane (purple), the ZIF-8/ZIF-62 hybrid membrane via post-synthetic ligand exchange (blue) and  $a_T$ (ZIF-8/ZIF-62) hybrid membrane after heat-treatment process (green), which  $a_T$ MOF means temperature-induced amorphization.

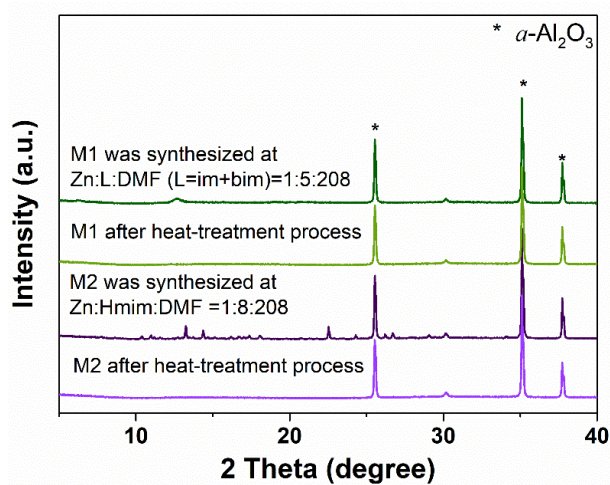




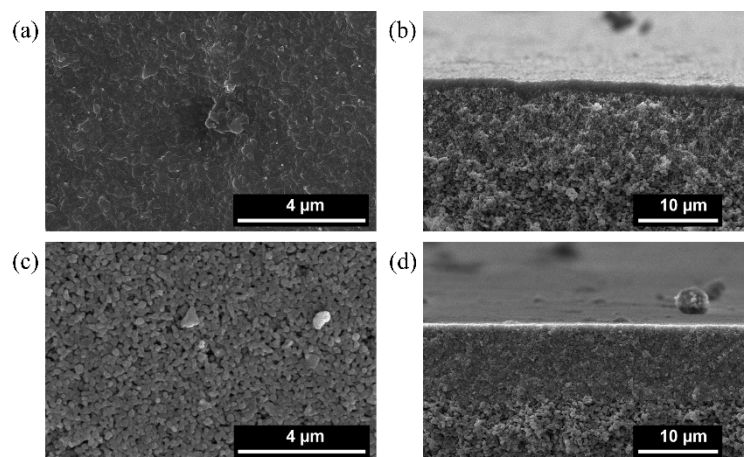
**Fig. S7** SEM images of (a, b) the ZIF-62 polycrystalline membrane, (c, d) the ZIF-8/ZIF-62 hybrid membrane synthesized via post-synthetic ligand exchange approach, and (e, f) the  $a_T$ (ZIF-8/ZIF-62) hybrid membrane after heat-treatment process.



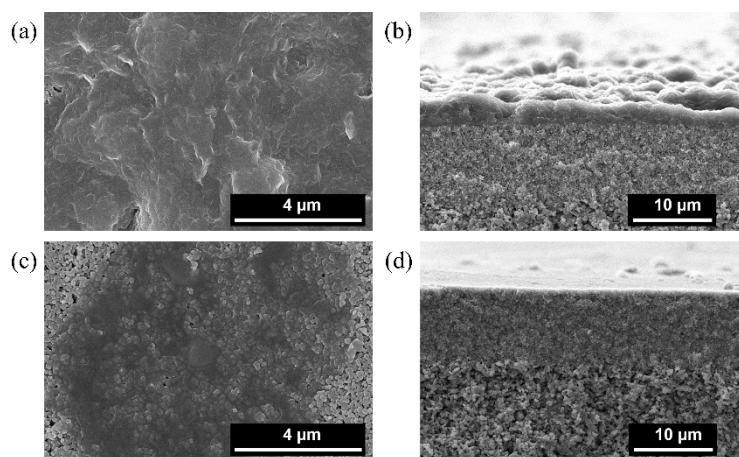
**Fig. S8** Schematic diagram of the preparation of  $a_g$ (ZIF-8/ZIF-62) hybrid membrane, which  $a_g$ MOF means amorphization upon melt-quenching.



**Fig. S9** XRD pattern of the membranes obtained by using single ligand of ZIF-8 or ZIF-62.



**Fig. S10** SEM images of the membrane via in-situ solvothermal process at Zn:Hmim:DMF=1:8:208. Top view and cross-sectional SEM images of (a, b) the membrane, and (c, d) after heat-treatment process.



**Fig. S11** SEM images of the membrane via in-situ solvothermal process at Zn:L:DMF (L=im+bim)=1:5:208. Top view and cross-sectional SEM images of (a, b) the resultant membrane and (c, d) after heat-treatment process.

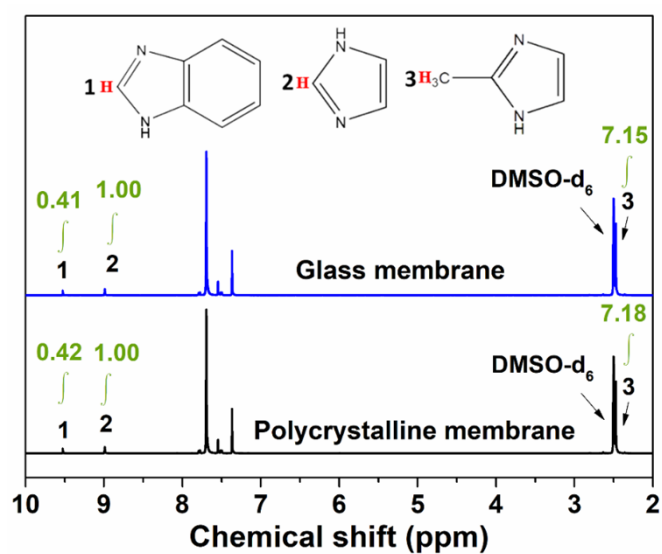


Fig. S12  $^1\text{H}$  NMR spectra of polycrystalline and glassy ZIF-8/ZIF-62 hybrid membranes.

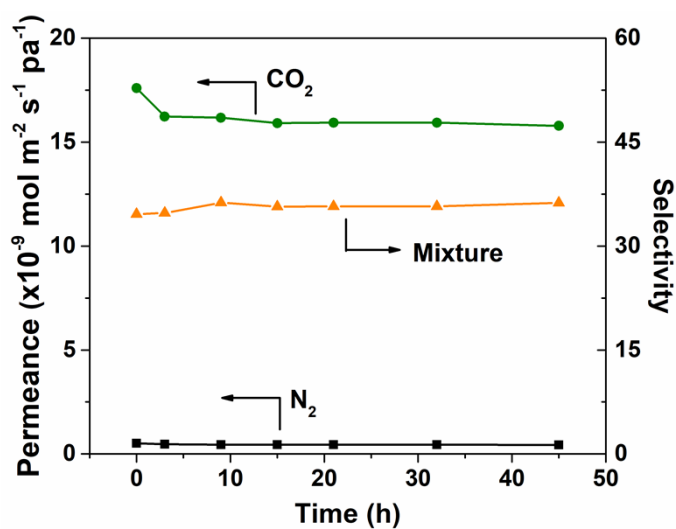


Fig. S13 Long-term stability of the hybrid glass membrane for  $\text{CO}_2/\text{N}_2$  separation.

**Table S1** The gas separation performances of hybrid ZIF-8/ZIF-62 glass membranes for equimolar  $\text{CO}_2/\text{CH}_4$  and  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  mixtures.

Membrane	$\text{CO}_2$ permeance ( $\times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ )	$\text{CO}_2/\text{CH}_4$ separation factor	$\text{C}_3\text{H}_6$ permeance ( $\times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ )	$\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation factor
M1	6.5	29.9	0.09	18.7
M2	11.7	25.2	0.13	12.9
M3	35.9	19	0.67	10

### 3. References

- 1 Y. Wang, H. Jin, Q. Ma, K. Mo, H. Mao, A. Feldhoff, X. Cao, Y. Li, F. Pan and Z. Jiang, *Angew. Chem. Int. Ed.*, 2020, **59**, 4365-4369.
- 2 H. Jin, Y. Li, X. Liu, Y. Ban, Y. Peng, W. Jiao and W. Yang, *Chem. Eng. Sci.*, 2015, **124**, 170-178.
- 3 L. Longley, S. M. Collins, S. Li, G. J. Smales, I. Erucar, A. Qiao, J. Hou, C. M. Doherty, A. W. Thornton, A. J. Hill, X. Yu, N. J. Terrill, A. J. Smith, S. M. Cohen, P. A. Midgley, D. A. Keen, S. G. Telfer and T. D. Bennett, *Chem. Sci.*, 2019, **10**, 3592-3601.