Electronic Supplementary Information (ESI)

Synthesis of trinity metal-organic framework membranes for CO_2 capture

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1. Experimental detail:

1.1 Materials:

Benzene-1,3,5-tricarboxylate (BTC, 98%) and 2-Methylimidazole (98%) were purchased from Hangzhou Banghua chemical Co., Ltd., China. $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ in A.R. grade were purchased from Changzheng Chemical Reagent Co., China. Ethanol, methanol, cyclohexane and hydrochloric acid were purchased as analytical reagents from Sinopharm Chemical Reagent Co., Ltd., China. Polydimethysiloxane (PDMS), ethyl silicate and dibutyl tin dilaurate were obtained from Shanghai SSS reagent Co., Ltd., China. And water used in this study was obtained from a self-made RO-EDI system, in which ion concentration was analyzed by IRIS Intrepid ICP and Metrohm 861 Compact IC and controlled to meet the experimental requirement of $\sigma \leq 0.5$ μS cm^{-1}.

1.2 Synthesis of the MOF crystals:

The $Cu_3(BTC)_2$ powders was synthesized by solvothermal, the solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.875 g) in 12 ml water and the H_3BTC (benzene-1,3,5-tricarboxylate) (0.42 g) in 12 ml ethanol was mixed and transferred into a Teflon-lined autoclave to allow crystal growth at 110 °C for 18 h. After crystallization, the $Cu_3(BTC)_2$ powders was isolated by centrifugation and then dried at 80 °C in vacuum.

1.3 Coated the hollow fiber by PDMS/MOFs:

The mixed PDMS/$Cu_3(BTC)_2$ solution was first prepared. The PDMS (0.5 g), cross-linking agent (0.5 g), catalyst (0.25 g) and $Cu_3(BTC)_2$ powders (0.1 g) were dissolved in 25.0 g of cyclohexane for 10 min. After the solution was prepared, the HFM was placed vertically upright at 80 °C atmosphere, the solution was uniformly coated on the HFM surface and then stood for 5 minutes to dry and crosslink (Fig. S1 ESI†). After several times, the membrane was upside down and coated to obtain a uniform coated membrane. The prepared membrane was heated at 80 °C for 24 h to crosslink completely. For comparison, pure PDMS layer was also coated on the HFM, the pure

PDMS layer solution was similar to the mixed PDMS/$Cu_3(BTC)_2$ solution, except lack of the MOF crystals.

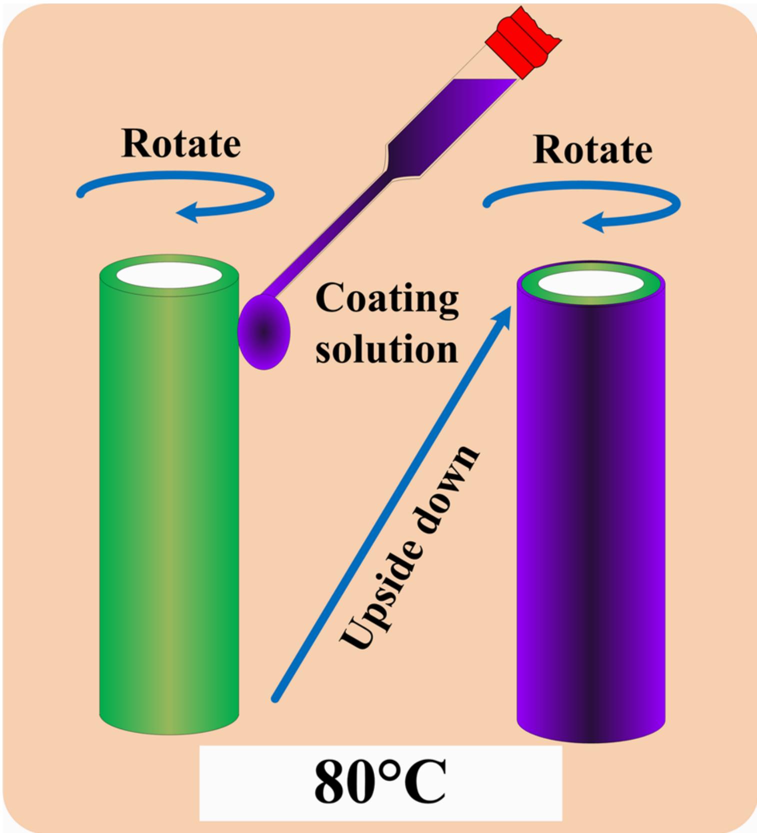


Figure S1. Schematic diagram of coated the PDMS/MOFs or PDMS on HFM.

***1.4 Synthesis of trinity MOF membranes*:**

The mixed solution of $Cu_3(NO_3)_2 \cdot 3H_2O$ (0.875 g) in 12 ml water and H_3BTC (0.42 g) in 12 ml ethanol was poured into the teflon-lined autoclave, the coated membrane were vertically soaked in the solution by a self-made Teflon holder. Then the Teflon-lined autoclave was transferred into an oven to allow crystal growth at 110 °C for 18 h. After crystallization, the membrane was washed by ethanol for several times and dried at room temperature.

***1.5 Characterization*:**

The scanning electron microscope (SEM) (TM-1000, Hitachi, Japan) was used to observe morphology of the membranes. To minimize charging, the ion sputter coater

(E-1045, Hitachi, Japan) was used to coat the specimens by a thin layer of platinum. The chemical properties were analyzed by Fourier transform infrared spectrometer (Nicolet 6700, Thermo Scientific, USA). The X-ray diffraction (XRD) patterns were recorded with PNAlytical X' Pert PRO X-ray diffractometer with CuKa radiation at 40 kV and 40 mA.

1.6 Permeation measurements:

The prepared membranes were used for gas permeation experiments. The membranes were sealed in a permeation module with epoxy glue. The diameter of the membrane was measured by scanning electron microscope. The feed gases (H_2 (0.289 nm), CO_2 (0.33 nm), and N_2 (0.364 nm)) were fed to the shell side of the membrane. Before the measurement, the tube was rinsed by the measured gases. The data was read and recorded until the system was run stable. The permeation side was contacted with the atmosphere (~0.1 MPa), and the pressure at the feed side was controlled with the exactitude manometer. The permeance for the gas is defined as:

$$P_i = \frac{N_i}{S \times \Delta P}$$

where *Ni* is the permeation fluxes of component i (mol/s), ΔP and S are the transmembrane pressure (Pa) and effective area (m^2), respectively. The ideal separation factor (α_{ij}) is calculated by follow equation:

$$\alpha_{ij} = \frac{P_i}{P_j}$$

2. Results and discussions

2.1 Characterization:

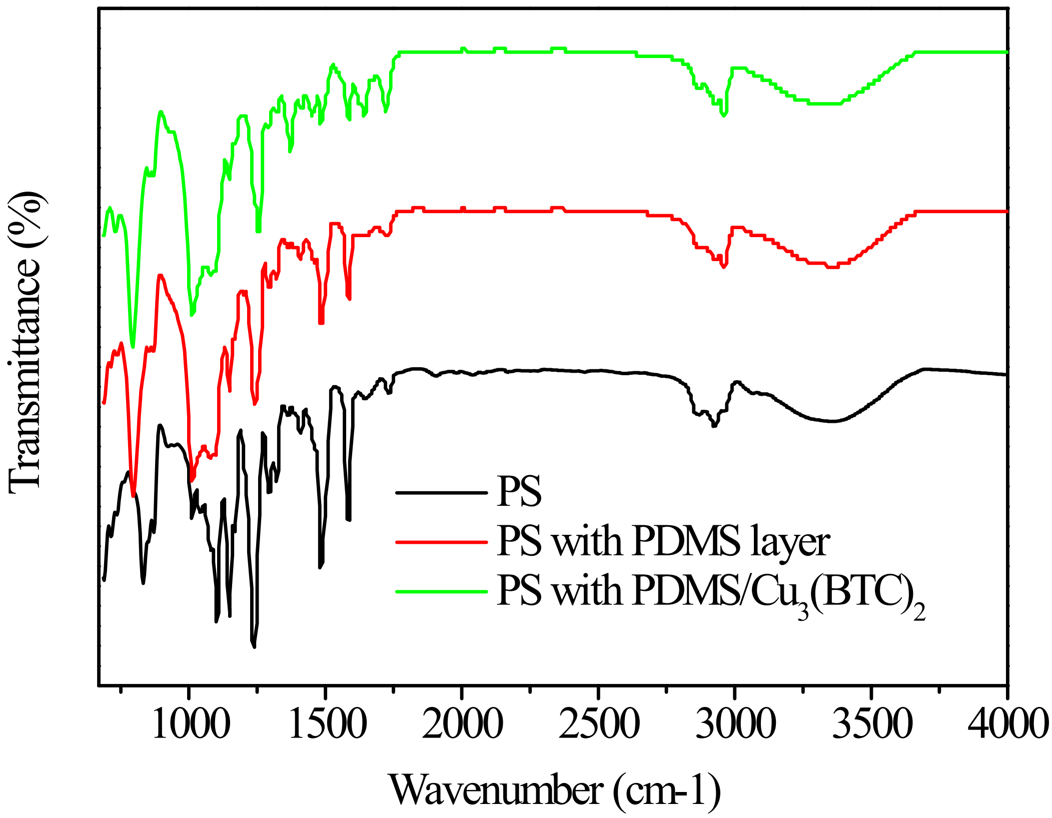


Figure S2. The FTIR spectra of the original PSf HFM, PSf HFM with PDMS layer and PSf HFM with PDMS/ $Cu_3(BTC)_2$ mixed layer.

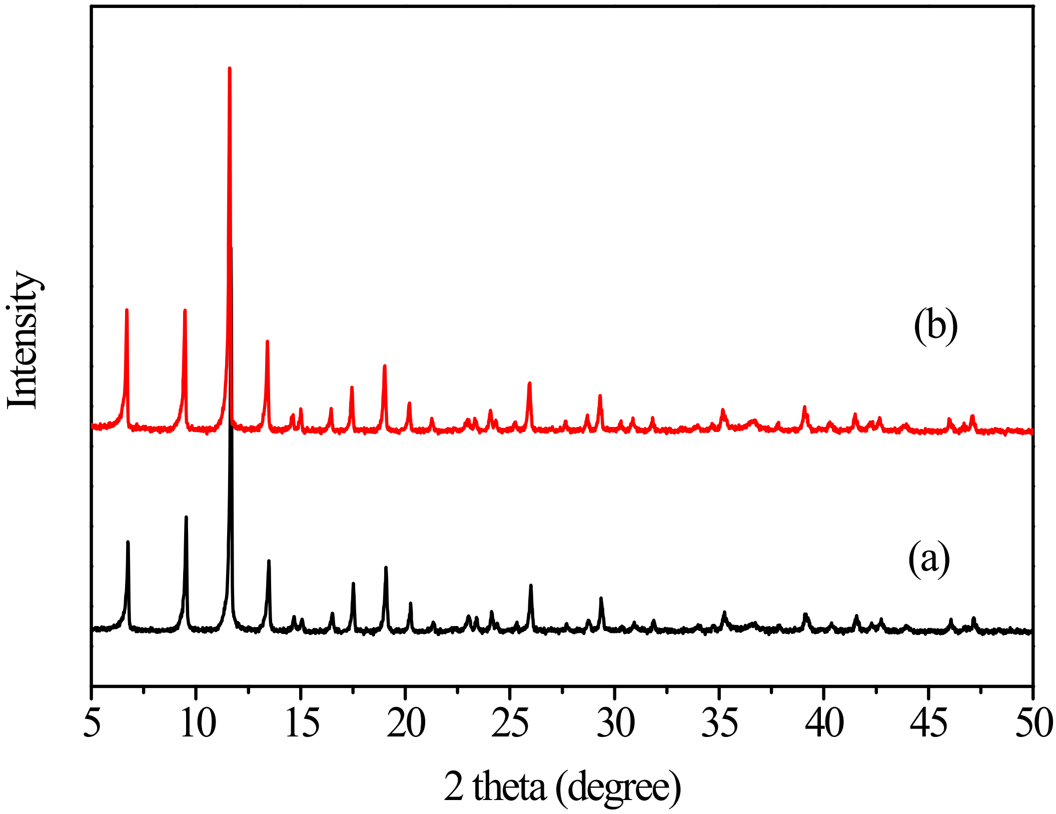


Figure S3. The XRD diffractogram of (a) $Cu_3(BTC)_2$ powder and (b) $Cu_3(BTC)_2$ powder in membrane synthesis solutions.

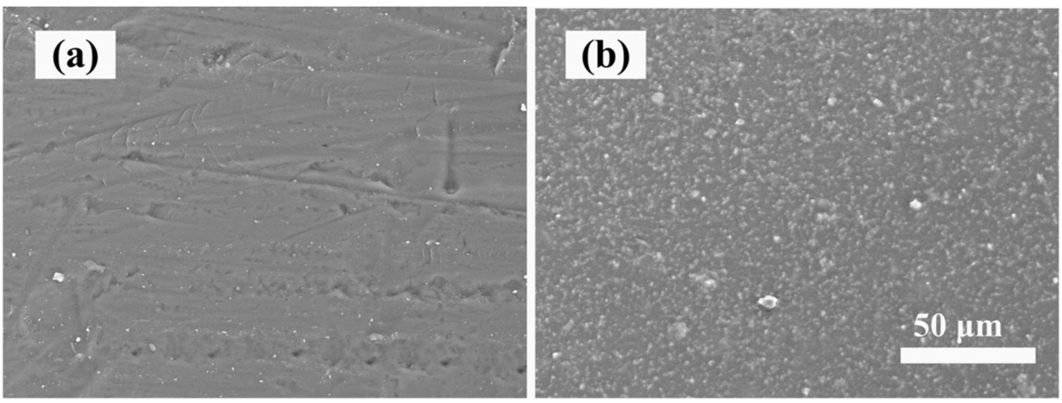
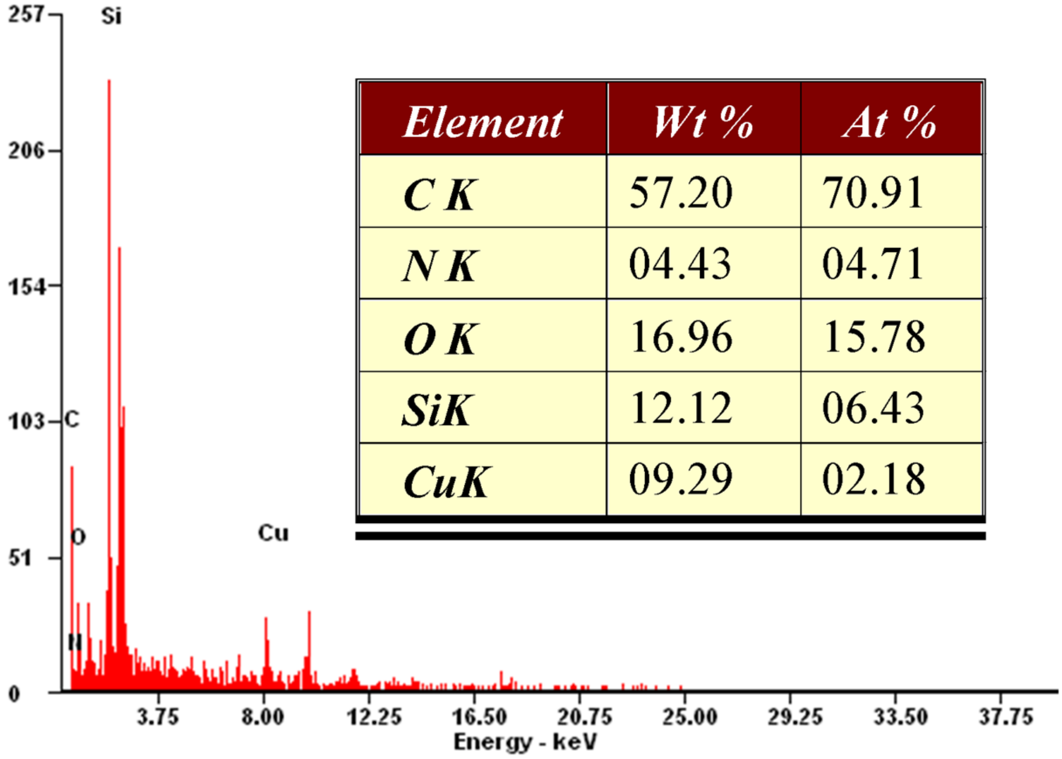


Figure S4. Outer surface SEM images of (a) PSf HFM and (b) PSf HFM with PDMS layer.



Element	Wt %	At %
C K	57.20	70.91
N K	04.43	04.71
O K	16.96	15.78
SiK	12.12	06.43
CuK	09.29	02.18

Figure S5. EDS spectra of PDMS/$Cu_3(BTC)_2$ layer in the trinity membrane. The position is shown in Figure 2d.

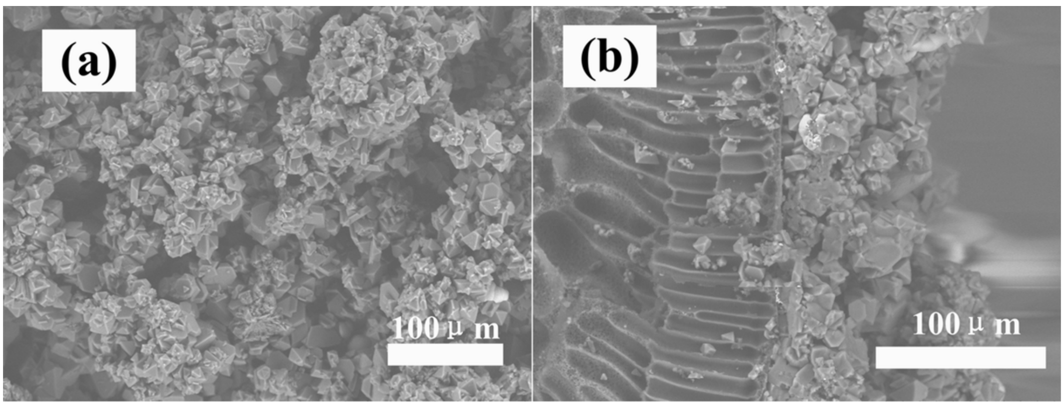


Figure S6. Outer surface and cross-section SEM images of the $Cu_3(BTC)_2$ supported by PSf HFM.

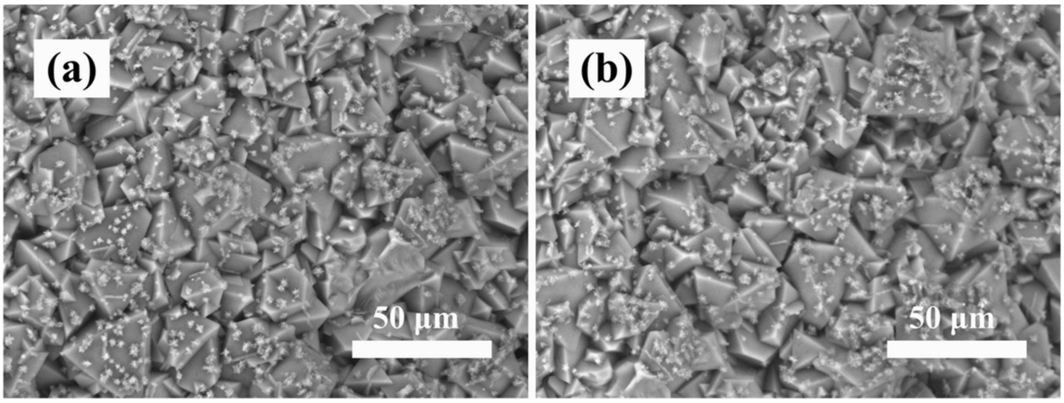


Figure S7. SEM images of $Cu_3(BTC)_2$/PSf HFM: (a) membrane 2, (b) membrane 3.

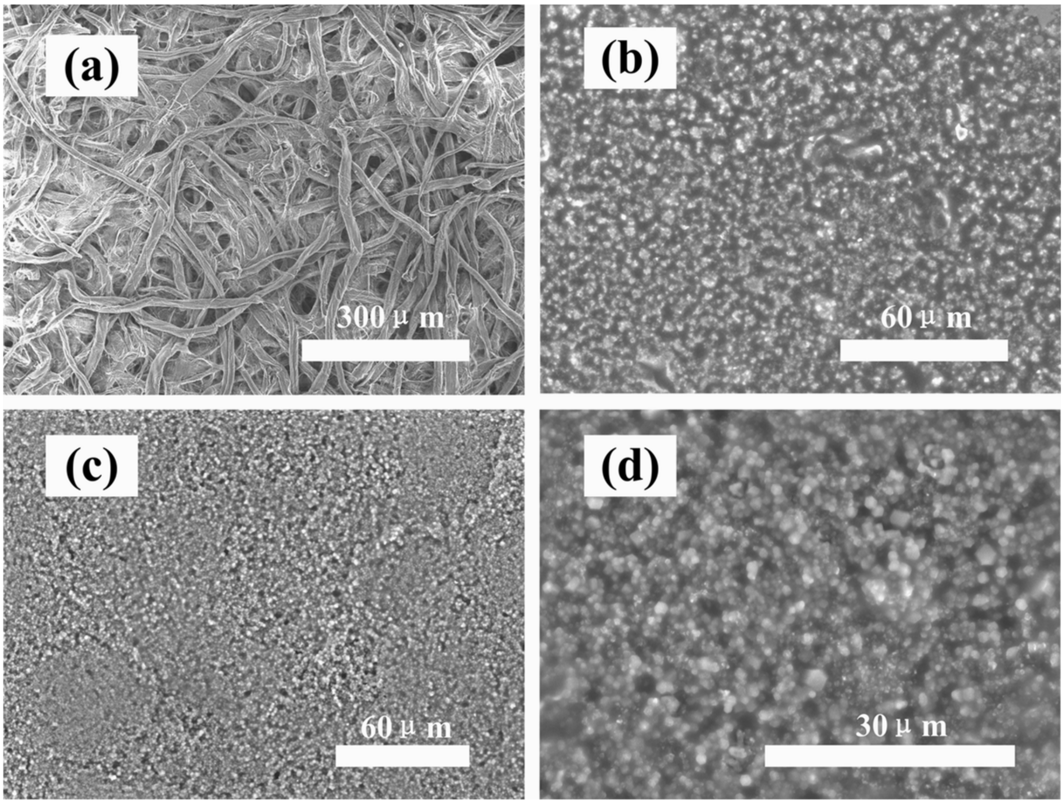


Figure S8. SEM images of the trinity ZIF-8 membrane with filter paper as substrate: (a) filter paper, (b) filter paper with PDMS/ ZIF-8 layer, (c) and (d) trinity ZIF-8 membrane.*

*The synthesis method of trinity ZIF-8 membrane with filter paper as substrate is similar to the of trinity $Cu_3(BTC)_2$ membrane with PSf HFM as substrate except the filter paper lies on glass pane in coated process.

2.2 Comment on gas permeation:

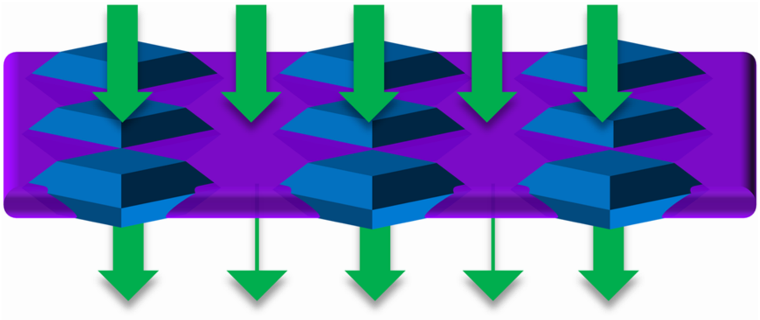


Figure S9. Proposed scheme for gas transportation paths through the membranes at larger size $Cu_3(BTC)_2$ crystals loadings

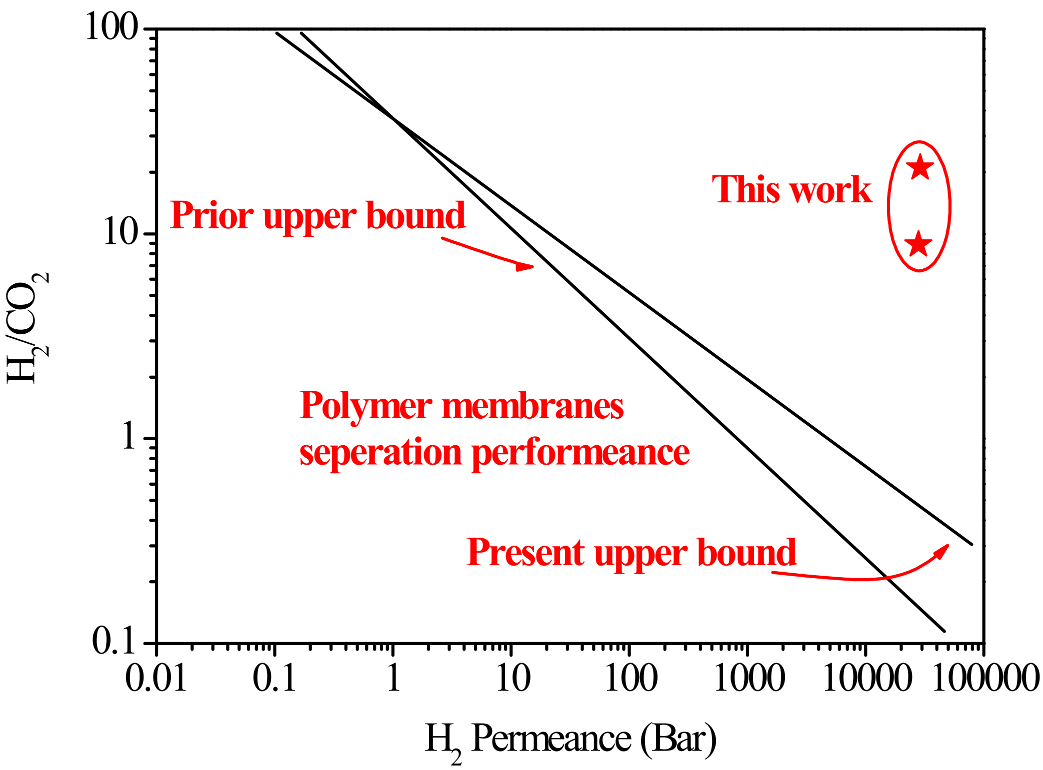


Figure S10. H_2/CO_2 separation performance of the prepared membranes. The Robeson upper bounds for polymer performance are shown.[1]*

1 Barrer = 3.348×10^{-16} mol m / (m^2 s Pa). There the m is the thickness of the membrane.

* The H_2 permeances of the polymer membranes mostly less than 20000 Bar, and few

membranes separation factors are greater than 10.[1] The prepared membranes thickness used for calculated is the thickness of coated layer and the MOF layer. The thickness of the coated layer and MOF layer is about 5 μm and 20 μm. The permeances of the HFM with PDMS/$Cu_3(BTC)_2$ layer membrane and trinity membrane as high as 28090 and 28972 Bar, respectively. For N_2/CO_2 separation, the polymer membrane usually has a higher CO_2 permeance than N_2 due to the CO_2-selective solubility. But here we have obtained a membrane with high permeance of N_2. This may be the results of the Knudsen diffusion and the N_2-selective diffusivity because CO_2 has a stronger bonding force with $Cu_3(BTC)_2$ than N_2 and H_2.

Table. S1 Comparison of the separation performances of the prepared membrane in this study with other membranes from the literature.

Reference	Membrane	T (°C)	Permeance 10^{-8} mol/(m^2·s·Pa)			Ideal Separation factor	
			H_2	N_2	CO_2	H_2/CO_2	N_2/CO_2
2	ZIF-7	200	7.40	1.1	1.1	6.73	1
3	ZIF-7	220	4.55	0.22	0.35	13	0.63
4	ZIF-7	25	6.04	0.52	1.33	4.54	0.39
5	ZIF-8	25	17.3	1.49	4.45	3.89	0.33
6	ZIF-8	25	36.0	8.96	14	2.57	0.64
7	ZIF-8	25	54.7	21.9	1.7	32.2	12.9
8	ZIF-8	25	5730	370	336	17.05	1.1
9	ZIF-8	25	65.2	8.02	13.5	5.60	0.69
10	ZIF-22	50	20.2	2.84	2.38	8.49	1.19
11	ZIF-69	25	6.50		2.5	2.6	
12	ZIF-69	25		1.06	2.36		0.46
13	ZIF-78	25	11.1	1.91	1	11.07	1.91
14	ZIF-90	200	25.0	1.98	3.48	7.18	0.57

15	ZIF-90	225	30.8		4.10	7.51	
15	APTES-functionalized ZIF-90	225	29.6		1.37	21.6	
16	ZIF-90	200	25.0	2.12	3.42	7.30	0.62
16	Imine-functionaliz ZIF-90	200	21.2	1.28	1.35	15.7	0.95
17	ZIF-90	35	19.4	3.10	10.8	1.8	0.29
18	ZIF-95	325	246	22.8	7.04	34.9	3.23
19	IRMOF-3	25	152	41.8	62.4	2.44	0.67
19	IRMOF-3-AM6	25	117	31.1	24.3	4.81	1.28
20	MIL-53	25	49.4	13.6	11.0	4.49	1.24
21	NH-MIL-53(Al)	15	267	13.7	9.8	27.3	1.40
22	MIL-96	25	98.2	26.5	21.4	4.59	1.24
23	MMOF	25	1.21	0.34	0.34	3.57	1
24	Ni-MOF-74	25	1270	420	140	9.10	3.00
25	SIM-1	30	8.19	3.28	3.61	2.27	0.91
26	ZIF mix-linker	25	1405	381	158	8.89	2.41
27	MOF-5	25	285	80.0	66.7	4.27	1.20
27	MOF-5	25	132	40.0	33.3	3.96	1.20
28	MOF-5	25	80	30	25	3.2	1.20
29	Cu-BTC	25	127	27.6	28.1	4.52	0.98
30	Cu-BTC	25	200	50	50	4	1
31	Cu-BTC	25	74.8	20.3	14.8	5.05	1.37
32	Cu-BTC	25	139	27.4	16	8.68	1.71
33	Cu-BTC	25		53.8	41.2		1.31
34	Cu-BTC	40	7.25	1.01	0.55	13.18	1.84
35	Cu-BTC	25	18	4.3	4.1	4.4	1.05
This work	MMMs	25	188.1	67.0	21.2	8.85	3.16
	Trinity membrane	25	48.5	16.7	2.3	21.03	7.23

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