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Supporting Information for

A hybrid zeolitic imidazolate framework membrane by mixed-linker synthesis for efficient CO_2 capture

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1. Experimental details:

Materials:

Cobalt(II) nitrate hexahydrate (99%, J&K Scientific Ltd.), 2-methylimidazole (mIM, 99%, J&K Scientific Ltd.), benzimidazole (bIM, 99%, Aladdin Chemistry Co. Ltd.), *N*,*N*-dimethylformamide (DMF, ≥99.5%, Sinopharm Chemical Reagent Co. Ltd.), vinyltrimethoxysilane (CH_2=CHSi(OCH_3)$_3$, ≥97.5%, J&K Scientific Ltd.), sodium hydroxide (NaOH, ≥96%, Beijing Chemical Works), sodium periodate ($NaIO_4$, ≥99.5%, Tianjin Fuchen Chemical Reagents Factory), potassium permanganate ($KMnO_4$, Beijing Yongjia Boyuan Trading Co. Ltd.), potassium carbonate (K_2CO_3, ≥99%, Beijing Chemical Works). Porous α-Al_2O_3 disks, (Angtai Electronic Ceramics Co. Ltd.) 30 mm in diameter, 3 mm in thickness, were used as supports.

Modification of the support surface:

Porous α-Al_2O_3 disks were selected as the supports of membranes with the most probable pore size of ca. 160 nm and about 35% porosity. One side of the support was polished using 2000 grit SiC sandpaper to obtain a smoother surface for membrane growth, ultrasonically cleaned using abundant deionized water to clean off the impurities.[1,2] Then the α-Al_2O_3 discs were soaked in saturated NaOH solution for 24 h to get rid of the oil of support surfaces and also increase the concentration of free hydroxyl groups.[3] After that the supports were ultrasonically dealt with abundant deionized water, then dried at 100 °C for 1 h.[4] The supports were then exposed to the vinyltrimethoxysilane (CH_2=CH Si(OCH_3)$_3$ for 20 h, followed by rinsing with deionized water and drying. The terminating vinyl group of the vinyltrimethoxysilane self-assembled organic monolayer (SAM) was oxidized by immersing the supports into an aqueous solution (20 ml) of 0.002 g $KMnO_4$, 0.084 g $NaIO_4$ and 0.007 g K_2CO_3 according to the methods in literature.[5-7] After 20 h the supports were removed from the oxidation solution, rinsed with water and dried.

Synthesis of ZIF-9-67 hybrid membrane:

To prepare the precursor solution for the growth of ZIF-9-67 hybrid membrane, a solid mixture of benzimidazole (0.23 g, 2 mmol) and 2-methylimidazole (0.16 g, 2 mmol) was dissolved in 30 ml of *N, N*-dimethylformamide (DMF) (solution I) and $Co(NO_3)_2$•$6H_2O$ (0.64 g) was dissolved in 30 ml of DMF (solution II). The solutions I and II were mixed for 20 minutes under stirring vigorously. Meanwhile, the support with the unpolished side coated using teflon tape was placed in a 100 ml autoclave. The growth solutions were then transferred into the autoclave, in which the support was placed vertically in the autoclave with the help of teflon tape. The growth solutions were heated up to 135 °C. After crystallization at 135 °C with a period of 36 hours, the autoclave was slowly cooled down to room temperature with a cooling rate of 25 °C/h inside the oven. The sample was thoroughly washed with abundant DMF and methanol respectively. Then the ZIF-9-67 hybrid

membrane was dried in a vacuum convective oven at 80 °C for 3 hours. After that, membrane was prepared by rubbing the surface of the support with dry ZIF-9-67 seeds until the surface abrupt particles were removed.[8] Then the sample was treated by the methanol cleaning, ultrasonic, and vacuum drying.

Secondary growth was performed using the same gel composition used for the first synthesis. The seeded support was vertically placed in a Teflon lined steel autoclave containing the synthesis gel and heated in an oven at 135 °C for another 36 h.[1] The resulting membrane was taken out and rinsed with fresh DMF and methanol at least three times to remove any solvent on the surface, and then immersed in 30ml fresh methanol for another 24 h to exchange the solvent occluded in the channels. The sample was dealt with new methanol solution for 5 days. After that the membrane was dried at 70 °C for 48 h.[9]

Characterization of ZIF-9-67 hybrid membrane:

XRD analysis of the membranes and powder samples was carried out on a SHIMADZU XRD-6000 X-ray diffractometer in reflection mode using Cu Kα radiation (λ = 1.5406 Å). The 2θ range from 5° to 60° was scanned with a step size of 0.05°. Thermogravimetric and decomposition analyses were performed on a TGA/DSC 1/1100 SF instrument. Solution ^{1}H NMR measurements were carried out using a Brücker 600 MHz spectrometer by digesting crystals using d4-acetic acid (C_3DCO_2D) as the solvent. Nitrogen physisorption was measured at 77 K on an Autosorb-iQ-MP (Quantachrome Instruments) automated gas sorption analyzer. Prior to adsorption experiments, the samples were first degassed at 423 K for 200 minutes and further at 473 K for 400 minutes. The membrane morphologies were observed via scanning electron micrographs (SEM) (FEI, a XL-30 ESEM-FEG microscope, US), where gold-coated specimens were used to increase the conductivity and the measurements were operated under 10-20 kV acceleration voltage.[4] The membrane was first simply broken and cleaned in air flow to remove dust.[10]

Permeation measurements:

For the single gas permeation, the supported ZIF-9-67 hybrid membranes were sealed in a permeation module with silicone O-rings. The feed gases were fed to the top side of the membrane, and sweep gas was fed on the permeate side to keep the concentration of permeating gas low providing a driving force for permeation. Before the gas permeation measurements, the as-synthesized ZIF-9-67 hybrid membrane was on-stream activated at 150 °C for 5 hours.[11] During our measurements, exactitude manometers and temperature transducers were used to control the pressure and temperature, respectively. The downstream side was contacted with the atmosphere (~0.1 MPa), and the pressure at the feed side was controlled with the exactitude manometer. The effective area of the ZIF-9-67 hybrid membrane was estimated to be around 3.14 cm^2. The permeation experiments were carried out for five single gases (H_2, N_2, CO, CH_4 and CO_2) in this study. The permeation rates of these gases were

recorded using the bubble flower. The ideal selectivities of CO_2 with respect to H_2, N_2, CO and CH_4 were calculated as the ratio of their permeances.[4] Each measurement was repeated three times, and the averaged values were adopted.

2. The results of TGA, DSC, ^{1}H NMR and N_2 physisorption measurments

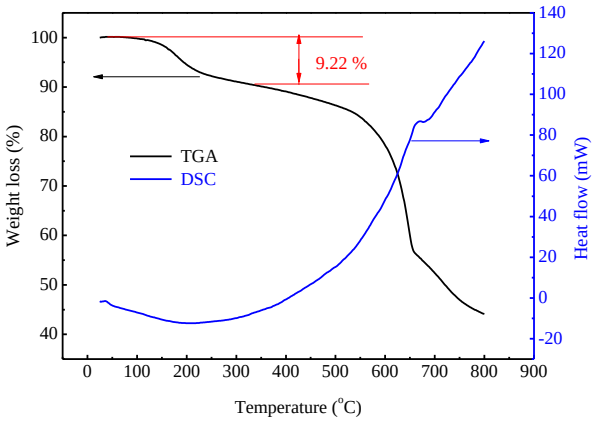

Fig. S1 TGA and DSC plots of ZIF-9-67 hybrid

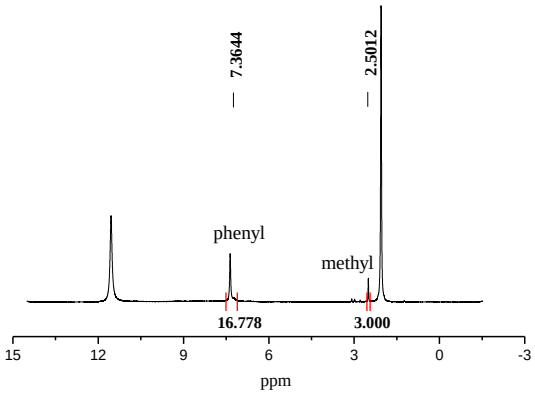

Fig. S2 ^{1}H NMR of ZIF-9-67 hybrid

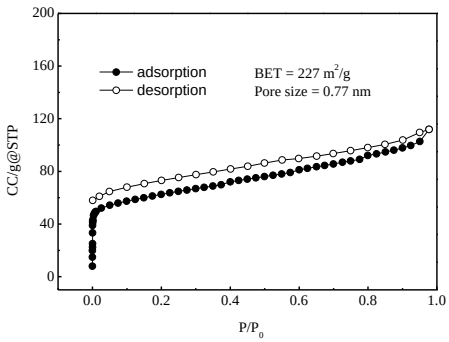

Fig. S3 N_2 adsorption at 77 K for ZIF-9-67 hybrid

Thermogravimetric and decomposition analyses as well as solution ^{1}H NMR measurements were performed to determine decomposition temperature and the ligand fraction in hybrid materials, respectively. This porous

network releases its free molecules and DMF guests in the temperature range of 25 °C to 350 °C, forming its solvent-free phase, which is thermally stable up to 550 °C (Fig. S1). The ratio of bIM and mIM is about 4:1 in the ZIF-9-67 hybrid membrane (Fig. S2). This is different from the initial proportion of these two linkers due to their different solubilities in reaction solution. The permanent microporous feature was studied by N_2 adsorption measurements at 77 K (Fig. S3). The BET surface area and pore size are estimated to be 227 m^2/g and 0.77 nm, respectively.

3. N_2 permeances measured at the room temperature and different trans-membrane pressure drops

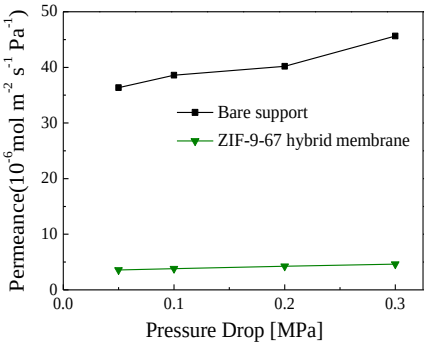

Fig. S4 N_2 permeances measured at the room temperature and different trans-membrane pressure drops (the upper curve is for the bare support and the lower one for the ZIF-9-67 hybrid membrane).

4. SEM images of pure ZIF-9 and pure ZIF-67 membranes on α-Al_2O_3

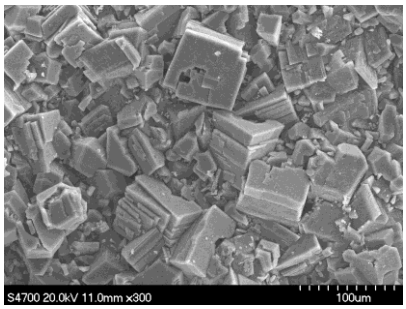

Fig. S5 Top view scanning electron micrographs (SEM) image of ZIF-9 membrane synthesized on α-Al_2O_3.

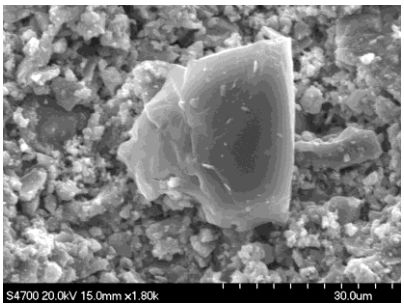

Fig. S6 Top view scanning electron micrographs (SEM) image of ZIF-67 membrane synthesized on α-Al_2O_3.

5. Permeation results for single gases

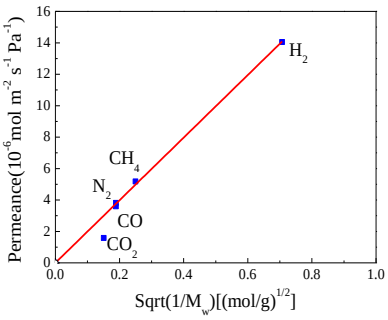

Fig. S7 Permeation results for the five single gases through ZIF-9-67 hybrid membrane at room temperature under a trans-membrane pressure drop of 0.1 MPa.

6. Reproducibility of membranes

To examine the reproducibility of α-Al_2O_3 supported membranes, two additional membranes were synthesized. The corresponding SEM images are shown in Figs. S8 (a) and (b) (denoted by membranes 2 and 3) with the single gas permeation data in Fig. S9. Obviously, the three membranes are very similar to each other if one considers the influence of the fluctuation of room temperature. This indicates that good reproducibility of the membranes is obtained in our synthesis procedure.

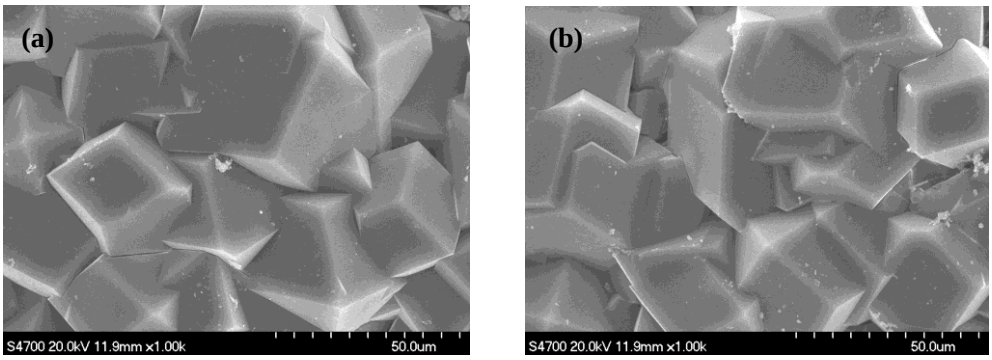

Fig. S8 Top view scanning electron micrographs (SEM) images of ZIF-9-67 hybrid membrane synthesized on α-Al_2O_3: membrane 2 (a), membrane 3 (b).

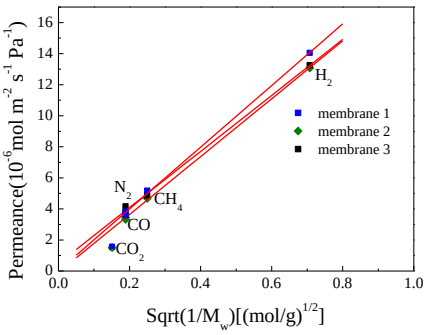

Fig. S9 Single gas permeation data of ZIF-9-67 hybrid membranes.

7. Comparison to other MOF membranes

Table S1 Comparison of the ideal selectivity ($S_{permeance}$) and permeation properties in the obtained ZIF-9-67 hybrid membrane and other MOF membranes.

Membrane	Dm (μm)	T (°C)	Permeance ($\times10^{-8}$ mol•m^{-2}•s^{-1}•Pa^{-1})					Ideal Separation factor				Ref.
			H_2	N_2	CO	CH_4	CO_2	H_2/CO_2	N_2/CO_2	CO/CO_2	CH_4/CO_2	
Cu-BTC	60	25	127	27.6	-	16.3	28.1	4.52	0.98	-	0.58	12
	25	25	200	50	-	80	50	4	1	-	1.6	13
	25	25	74.8	20.3	-	25.7	14.8	5.05	1.37	-	1.74	14
	-	25	139	27.4	-	17.5	16	8.68	1.71	-	1.09	15
	25	25	-	53.8	-	67.6	41.2	-	1.31	-	1.64	4
	13	40	7.25	1.01	-	1.25	0.55	13.18	1.84	-	2.27	16
MOF-5	25	25	285	80.0	-	103	66.7	4.27	1.20	-	1.54	17
	85	25	132	40.0	-	56.7	33.3	3.96	1.20	-	1.70	
	40	25	80	30	-	39	25	3.2	1.20	-	1.56	18
ZIF-7	1.5	200	7.40	1.1	-	1.18	1.1	6.73	1	-	1.07	19
	1.5	220	4.55	0.22	-	0.31	0.35	13	0.63	-	0.89	10
	40	25	6.04	0.52	-	0.48	1.33	4.54	0.39	-	0.36	20
ZIF-8	9	20	-	-	-	242	1690	-	-	-	0.14	8
	5	20	-	-	-	472	2430	-	-	-	0.19	
	20	25	17.3	1.49	-	1.33	4.45	3.89	0.33	-	0.30	21
	2.5	25	36.0	8.96	-	7.84	14	2.57	0.64	-	0.56	22
	6	25	54.7	21.9	-	20.2	1.7	32.2	12.9	-	11.9	23
	2	25	5730	370	-	-	336	17.05	1.1	-	-	24
ZIF-22	40	50	20.2	2.84	-	3.02	2.38	8.49	1.19	-	1.27	25
ZIF-69	50	25	6.50	-	1.10	1.85	2.5	2.6	-	0.44	0.74	9
	40	25	-	1.06	0.82	0.86	2.36	-	0.46	0.34	0.37	26
ZIF-78	4	25	11.1	1.91	-	1.73	1	11.07	1.91	-	1.73	2
ZIF-90	20	200	25.0	1.98	-	1.57	3.48	7.18	0.57	-	0.45	27

As-prepared ZIF-90	20	225	30.8	-	-	1.90	4.10	7.51	-	-	0.46	28
APTES-functionalized ZIF-90	20	225	29.6	-	-	0.37	1.37	21.6	-	-	0.27	
As-prepared ZIF-90	20	200	25.0	2.12	-	1.64	3.42	7.30	0.62	-	0.48	29
Imine-functionalized ZIF-90	20	200	21.2	1.28	-	1.09	1.35	15.7	0.95	-	0.81	
ZIF-95	30	325	246	22.8	-	16.1	7.04	34.9	3.23	-	2.28	11
IRMOF-3	10	25	152	41.8	-	64.9	62.4	2.44	0.67	-	1.04	30
IRMOF-3-AM6	10	25	117	31.1	-	64.9	24.3	4.81	1.28	-	2.67	
MIL-53	8	25	49.4	13.6	-	16.4	11.0	4.49	1.24	-	1.49	31
NH_2-MIL-53(Al)	15	15	267	13.7	-	14.4	9.8	27.3	1.40	-	1.47	32
MIL-96	6	25	98.2	26.5	-	33.8	21.4	4.59	1.24	-	1.58	33
$Co_3(HCOO)_6$	11	25	-	-	-	41.5	225	-	-	-	0.18	34
MMOF	20	25	1.21	0.34	-	-	0.34	3.57	1	-	-	1
Ni-MOF-74	25	25	1270	420	-	440	140	9.10	3.00	-	3.14	35
SIM-1	25	30	8.19	3.28	-	3.16	3.61	2.27	0.91	-	0.88	36
ZIF mix-linker	35	25	1405	381	359	517	158	8.89	2.41	2.27	3.27	This study

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