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Supporting information

Zinc-Substituted ZIF-67 Nanocrystals and Polycrystalline Membranes for Propylene/Propane Separation†

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1. Materials and Methods:

Chemicals: In order to synthesize ZIF-67 and zinc-substituted ZIF-67 nanocrystals, as well as corresponding polycrystalline membranes, both cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) were supplied from Sigma-Aldrich and used as the metal precursor. The organic ligand 2-methylimidazole (MeIm) was also obtained from Sigma-Aldrich. Analytical grade methanol was supplied from Sinopharm Chemical Reagent Co., Ltd. Above chemicals were all used as received without further purification. The water used in all experiments was treated by the Millipore Milli-Q purification system.

Preparation of porous α-Al_2O_3 supports: Disk-shaped α-Al_2O_3 supports (2 mm thickness and 22 mm diameter) were home-made from high purity alumina powder (Baikowski, CR-6). The green discs were formed by pressing the alumina powder in a stainless steel mold. After sintering at 1200 ^oC for 2 h, the alumina discs contain pores with nominal pore size around 250 nm and total porosity around 40%. One side of the substrate was polished by sandpapers (grid #1200), followed by cleaning with water and drying at 200 ^oC for 12 h.

Preparation of ZIF-67 and zinc-substituted ZIF-67 nanocrystals: ZIF-67 nanocrystals were prepared following our previous aqueous procedures published elsewhere.[S1] In a typical synthesis, 0.717 g of $Co(NO_3)_2 \cdot 6H_2O$ and 10.118 g of MeIm were separately dissolved in two beakers filled with 5 and 35 mL DI water, respectively. Subsequently, cobalt solution was rapidly poured into the MeIm solution for agitation at room temperature (~25 ^oC) for 6 h. The composition of the synthesis solution is 1Co: 50MeIm: 900H_2O. After syntheses, the obtained dark-purple precipitate was collected by centrifugation, washed with DI water and methanol for three cycles, and finally vacuum dried in 60 ^{o}C oven for overnight.

Zn-substituted ZIF-67 and pure zinc analogue (ZIF-8) nanocrystals were synthesized following the same synthesis procedure but using zinc nitrate hexahydrate (Zn $(NO_3)_2{\cdot}6H_2O$) as a zinc source to substitute Co ions by Zn ions. The composition of the synthesis solution is fixed as 1metal (Co+Zn): 50 Hmim: 900 H_2O. The obtained products were also purified and activated by the above same procedures.

Deposition of ZIF seeds: Above synthesized ZIF nanocrystals, served as seeds, were deposited on the polished side of the substrates by the slip-coating method.[S2] Schematic description of this process is shown in Fig. S1. Firstly, the alumina discs were half-immersed in the above-prepared seed suspension (0.5 wt% in methanol solution) for about 20 s, and then carefully slid away and held vertically until dried. In order to obtain the satisfied coverage of ZIF seeds, the slip-coating procedure was repeated.

Preparation of ZIF membranes by secondary growth: For synthesis of ZIF-67 membrane, the seeded support was placed vertically in a 50 mL spawn bottle, which was filled with a secondary synthesis solution with composition of 1Co: 45MeIm: 3000H_2O. The synthesis was carried out at 30 ^{o}C for 6 h. After synthesis the discs was taken out, rinsed three times by water and methanol, and then immersed in 30 mL fresh methanol for another 24 h. Finally, the as-synthesized membranes were activated under saturated-vapor condition for 2 days.[S3]

For the synthesis of Zn-substituted ZIF-67 membrane, above same synthesis procedures were implemented with the exception of partially or fully replacing Co precursor by Zn precursor. The composition of the secondary growth solution was fixed as 1metal (Co+Zn): 45MeIm: 3000H_2O.

Finally, the obtained membranes were also washed and activated like above procedures.

Characterization: Field emission scanning electronic microscope (SEM) pictures were taken by FEI Quanta 600 FEG, using an acceleration voltage of 5 kV. In order to analyze the distribution of metal ions in the cross-sectional membrane, energy dispersive X-ray spectrometer (EDX) and line scanning analyses were operated with 20 keV of acceleration voltage and 9 mm of working distance. The mean particle size of the product was determined by manual measurement of about 300 crystals in SEM picture.[S4] Transmission electron microscopy (TEM)/EDX was carried out by a FEI-Titan ST electron microscope operated at 300 kV. X-ray diffraction (XRD) patterns were collected on a Rigaku Smartlab TM 9 KW powder diffractometer at 40 kV, 40 mA with Cu Kα (λ = 1.542 Å) radiation to verify the phase purity of as-synthesized ZIF nanocrystals and membranes. Thermal gravimetric analysis (TGA) measurements were performed on a Netzsch STA 449 F1 Jupiter thermoanalyzer. For this purpose, ca. 10 mg samples were filled into an alumina crucible and heated in a continuous-flow of nitrogen gas with a ramp rate of 5 °C/min from 50 up to 700 °C. Nitrogen physisorption isotherms were measured at 77 K on an automatic volumetric adsorption apparatus (Micromertics ASAP 2420). The samples were filled into glass ampoules and outgassed in high vacuum at 423 K for 12 h before the start of the sorption measurements. Diffuse-reflectance UV-Visible (UV-Vis) spectra were recorded on a Varian CARY-500 spectrophotometer equipped with a diffuse reflectance accessory in the wave length range of 200~800 nm. The metal compositions of pure ZIF-67 and Zn-substituted ZIF-67 nanocrystals were determined by inductively coupled plasma (ICP) atomic emission spectroscopy on Varian Vista AX CD system.

Gas permeation: All permeation measurements were performed by the Wicke-Kallenbach technique, as shown in Fig. S3. Same total pressure was applied to both sides of the permeation cell, and was approximately equal to the atmosphere pressure. The feed side was fed with propylene/propane mixture at a total volumetric flow rate of 100 mL/min. At the permeate side, helium was used as sweep gas. The flow rate was set to 100 mL/min to ensure that the concentration of the most permeable species at the permeate side will not exceed 5%. The compositions of the feed and the permeate streams were measured by an on-line gas chromatography (Agilent 7890A). To guarantee the reliability of testing, three membrane samples fabricated from different batches were used for gas permeation. The permeation results were averaged as the final data with deviations. At each permeation condition the system was stabilized for at least 4 h and the measurement was repeated for at least three times.

The membrane permeance, F_i, is defined as

$$F_i = \frac{N_i}{A \times \Delta P_i}, \qquad (1)$$

where N_i is the permeation rate of component i (mol/s), ΔP_i is the partial pressure difference of component i (Pa) across the membrane, and A is the membrane area (m^2).

Ideal selectivity is defined as the ratio of the permeances measured at single-component. For binary mixtures, the separation factor ($\alpha_{i,j}$) for component i over component j is defined as

$$\alpha_{i,j} = \frac{y_i / y_j}{x_i / x_j}, \qquad (2)$$

where x_i and x_j are the molar fractions of components i and j in the feed stream, respectively, and y_i and y_j are the molar fractions of components i and j in the permeate stream, respectively.

Adsorption kinetics measurement for propane and propylene. Prior to the tests, the synthesized pure ZIF-67 or Zn-substituted ZIF-67 nanocrystals (~0.35 g) were outgassed in high vacuum at 423 K for 12 h. Gas adsorption were measured by a volumetric method using a home-built adsorption system. Helium was then used to calibrate the volume of adsorption cell with sorbent at 30 °C. The pressure change was collected in every 1 second using a MKS transducer and Labview® software. Adsorption kinetics profiles (M_t/M_∞ vs. time) of propane and propylene on pure ZIF-67, Zn50-ZIF-67, Zn90-ZIF-67 and pure ZIF-8 are shown in Fig. 4a. The M_∞ values of all samples are listed in Table S3. The diffusivity of both propane and propylene in all samples were estimated by fitting the uptake data with a simplified solution given by Kaerger and Ruthven for short times:

$$\frac{M_t}{M_\infty} = \frac{6}{\sqrt{\pi}}\sqrt{\frac{Dt}{r^2}} \qquad (3)$$

Where D is the Fickian diffusivity, and r is the radius of the crystal. M_t is the mass adsorbed at time t, and M_∞ is the mass adsorbed at infinite time.

2. Figures and Tables:

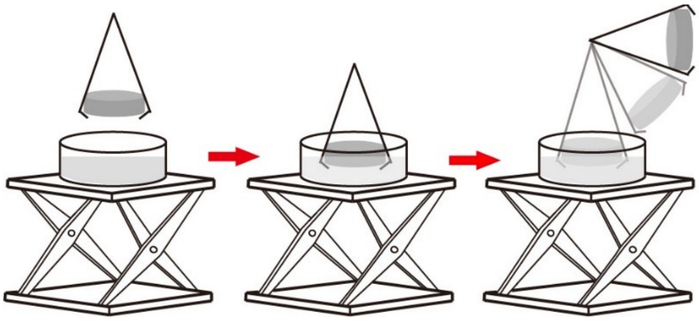

Fig. S1. Schematic description of the slip-coating process for depositing ZIF seeds on one-side of the alumina discs.

Table S1. Detailed results for ICP measurements of all samples

Co/Zn ratio in synthesis solution	Metal content in samples	Denoted name of sample
Pure Co	24.9% Co	ZIF-67
7:3	17.9% Co and 7.4% Zn	Zn30-ZIF-67
5:5	12.8% Co and 12.6% Zn	Zn50-ZIF-67
3:7	7.4% Co and 17.7% Zn	Zn70-ZIF-67
1:9	2.5% Co and 22.7% Zn	Zn90-ZIF-67
Pure Zn	24.7% Zn	ZIF-8

Table S2: N_2 adsorption results of all samples

Sample	$D_{H\text{-}K}$ (Å)	S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	V_{micro} (cm^3/g)
ZIF-67	3.5	1135	1172	0.42
Zn30-ZIF-67	3.5	1201	1254	0.43
Zn50-ZIF-67	3.5	1281	1317	0.47
Zn70-ZIF-67	3.6	1279	1316	0.43
Zn90-ZIF-67	3.5	1235	1287	0.42
ZIF-8	3.5	1179	1214	0.41

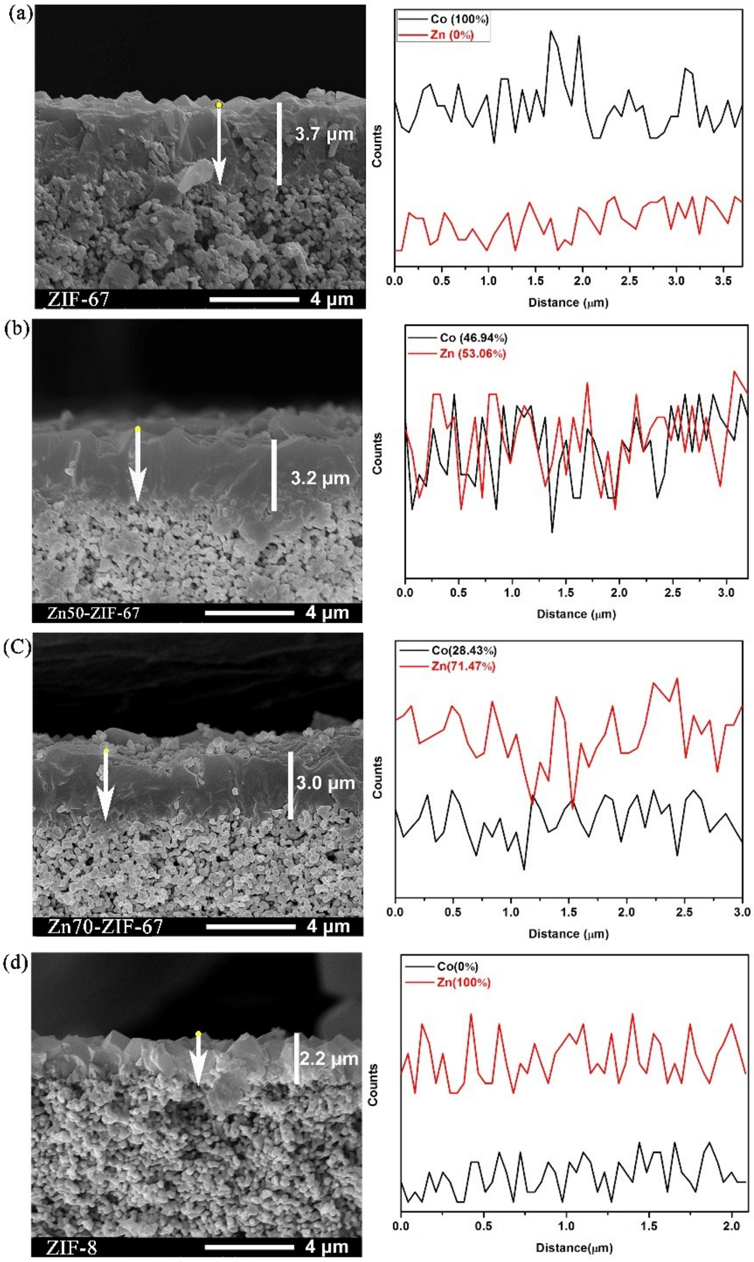

Fig. S2. Cross-section SEM images and EDX profiles of the as-synthesized ZIF membranes: (a) ZIF-67, (b) Zn50-ZIF-67, (c) Zn70-ZIF-67, and (d) ZIF-8. The white solid line and arrow marked in the SEM pictures indicate the EDX analysis area and direction, respectively.

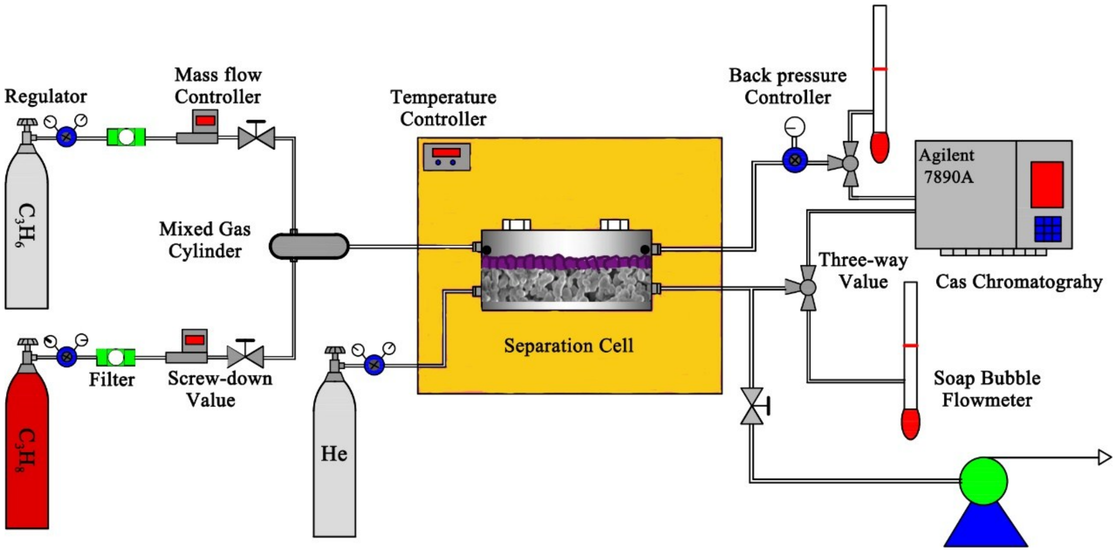

Fig. S3. Schematic diagram of gas permeation set-up by Wicke-Kallenbach technique.

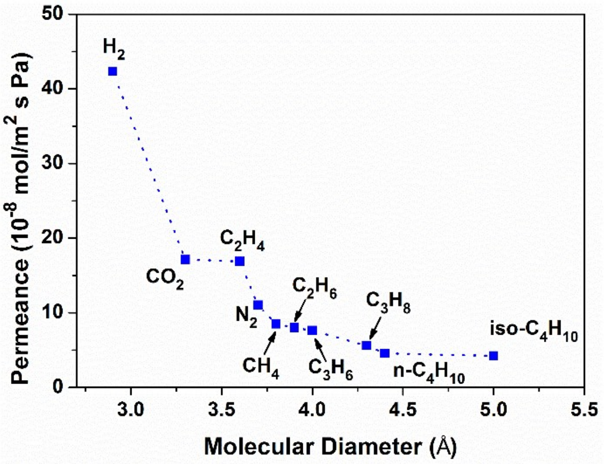

Fig. S4. Single-gas permeation results through pure ZIF-67 polycrystalline membrane.

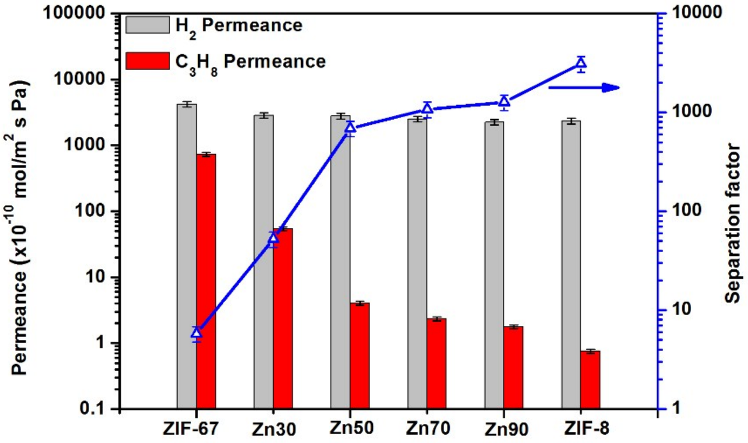

Fig. S5. Mixed-gas permeation results of H_2/C_3H_8 on ZIF-67 polycrystalline membranes with various amount of substituted zinc ions.

Table S3. Kinetic uptake M_∞ values and calculated diffusion coefficients of propylene and propane in ZIF samples.

Samples	M_∞ (mL/g)		D ($\times 10^{-13}$ cm^2/s)		D_{C3H6}/D_{C3H8}
	C_3H_6	C_3H_8	C_3H_6	C_3H_8	
ZIF-67	95.08	84.65	12.2±2.1	11.1±2.0	1.10±0.4
Zn50-ZIF-67	75.16	88.54	6.22±1.2	5.37±1.0	1.16±0.5
Zn90-ZIF-67	82.44	81.42	2.41±0.6	2.01±0.6	1.20±0.5
ZIF-8	81.31	88.13	1.18±0.4	0.95±0.3	1.23±0.6

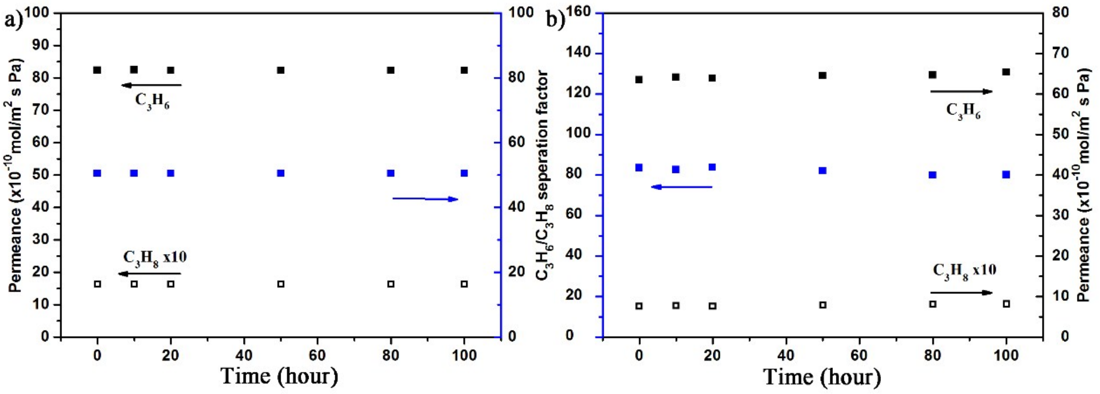

Fig. S6. On-stream propylene/propane separation performances on (a) Zn90-ZIF-67 membrane and (b) ZIF-8 membrane at room temperature for 100 h.

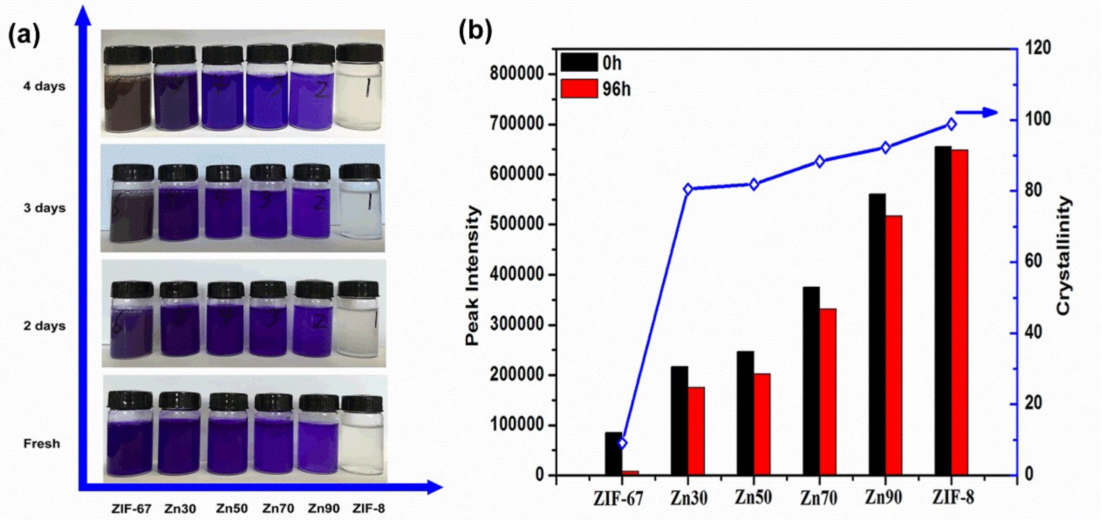

Fig. S7. (a) Photographic pictures of all samples immersed in water (0.6 wt.%) at room temperature for 0~4 days, and (b) comparison of relative XRD crystallinity of all nanocrystals between as-synthesized and immersed in water for 4 days.

The relative crystallinity of the samples was quantitatively estimated by calculating the relative XRD peak intensity following expression [S5]:

$$\text{ZIF relative crystallinity} = \frac{the\ peak\ intensity\ of\ (011)\ plane\ at\ 96\ h}{the\ peak\ intensity\ of\ (011)\ plane\ at\ 0\ h} \qquad (4)$$

Table S4. ZIF relative crystallinity as a function of synthesis time.

Sample	XRD peak intensity of (011) plane		Relative crystallinity (%)
	As-synthesized (0 h)	Immersed in water for 4 days	
ZIF-8	655368	648159	98.9
Zn90-ZIF-67	560853	517382	92.3
Zn70-ZIF-67	374782	331307	88.4
Zn50-ZIF-67	246154	201600	81.9
Zn30-ZIF-67	216337	174463	80.6
ZIF-67	84654	7733	9.1

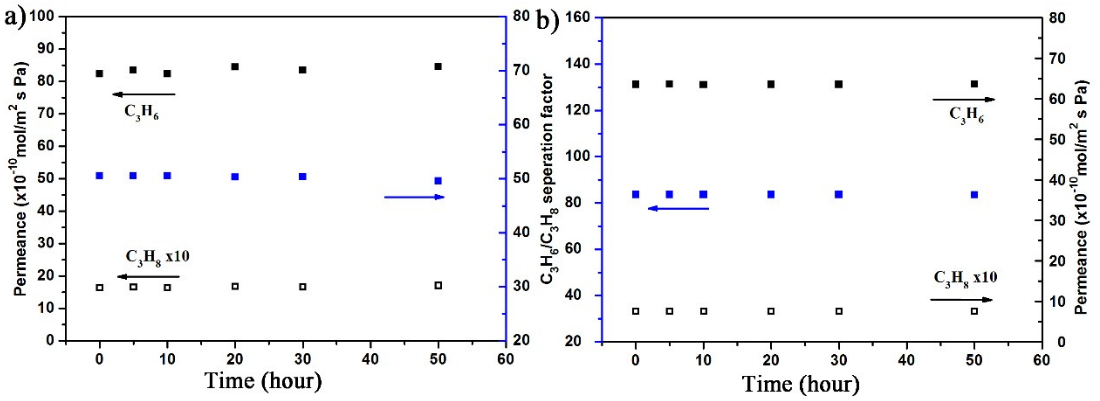

Fig. S8. On-stream separation performances for the humid propylene/propane feeding on (a) Zn90-ZIF-67 membrane and (b) ZIF-8 membrane at room temperature for 50 h.

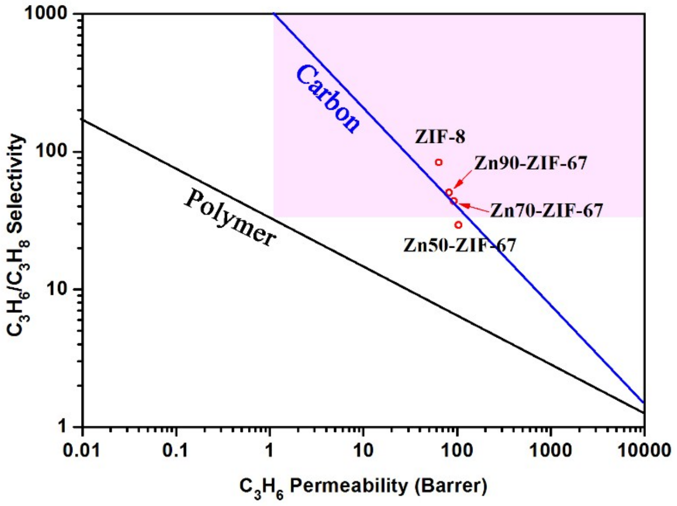

Fig. S9. Comparison of the C_3H_6/C_3H_8 separation performances on the Zn-substituted ZIF-67 polycrystalline membranes with upper bound of polymeric and carbon membranes.

3. Reference

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