Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

Enhanced Propylene/propane Separation Performance on Metal-Organic Frameworks Membranes through Blocking Defects and Hindering Framework Flexibility by Silicone Rubber Coating

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1. Materials and methods

Materials: Zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%) and 2-methylimidazole (Hmim, 98%) were purchased from Sigma-Aldrich. Polydimethylsiloxane (PDMS) was provided by GE Toshinba Silicones Co., Ltd., Japan. Methanol, toluene, n-heptane, ethanol and chloroform were all supplied from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals were used without further purification. Poly(1-trimethylsilyl-1-propyne) (PTMSP) was purchased from ABCR GmbH, Germany. Pebax®2533 was purchased from Arkema Inc., France. Polymers of intrinsic microporosity (PIM-1) was synthesized following the procedures by Budd's group.[1] Gases (propylene, propane and helium) used for permeation measurements were all supplied by Nanjing Tianze group Co., Ltd., China.

Preparation of ZIF-8 polycrystalline membranes: ZIF-8 polycrystalline membranes were fabricated according to our reported seeded-secondary growth method on homemade α-alumina discs.[2] Firstly, the ZIF-8 seeds were prepared by the rapid aqueous-synthesis method at room temperature. In a typical synthesis, a solution of 1.17 g (3.95 mmol) of zinc nitrate in 8 mL deionized (DI) water and another solution of 22.70 g (276.50 mmol) of 2-methylimidazole in 80 mL DI water were mixed by vigorously stirring for 5 min at room temperature (22 ^{o}C). The resulting ZIF-8 nanocrystals were separated by centrifugation, followed by washing with DI water twice and finally re-dispersing in fresh methanol as seeding solution (0.1 wt%).

Seeding procedure was conducted by slip-coating process of above seeding solution on the α-alumina discs. The detailed steps for preparing α-alumina discs and seeding procedures can be found elsewhere.[3] Subsequently, the seeded support was then exposed to the secondary synthesis solution at 30 ^{o}C for 10 h to allow further secondary growth of seeds to occur. The synthesis solution was prepared by mixing 0.11 g $Zn(NO_3)_2{\cdot}6H_2O$ and 2.27 g 2-methylimidazole as well as 40 mL DI water. After synthesis, the as-synthesized membranes were carefully washed with copious amounts of water at room temperature. Finally, the ZIF-8 polycrystalline membranes were immersed in fresh methanol for 2 days to complete the solvent-exchange process, and followed by the drying at 60 ^{o}C for 24 h.

Preparation of ZIF-8/PDMS composite membranes: ZIF-8/PDMS composite membranes were prepared by spreading a few drops of the PDMS solution on the surface of the above mentioned ZIF-8 polycrystalline membrane using a pipette, followed by the vacuum-drying at 80 ^{o}C for 24 h. PDMS solution with different concentrations were prepared by dissolving precursor with a ratio of part A to part B of 10:1 in n-heptane under vigorous agitation at room temperature for 3 h.[4] The concentration of PDMS solution was mainly fixed as 10 wt.% unless otherwise specified.

In order to examine the role of PDMS coating of ZIF-8/PDMS composite membrane on C_3H_6/C_3H_8 separation performance, another two membranes were also fabricated. One sample is ZIF-8 polycrystalline membrane covered with a pre-cured PDMS thin layer. The PDMS solution (10 wt.%) were spread on the glass slides and then solidified at 80 ^{o}C for 24 h under vacuum. This pre-cured PDMS thin layer were peeled off and then covered on the surface of ZIF-8 polycrystalline membrane, followed by the gas-permeation experiment. Another sample is one composite membrane derived from the coating of PDMS layer on the α-alumina support. This composite membrane was prepared by spreading a few drops of the PDMS solution (10 wt.%) on the surface of the α-alumina support using a pipette, followed by the vacuum-drying at 80 ^{o}C for 24 h. In order to avoid the penetration of PDMS solution into the α-alumina support, the α-alumina support was immersed with DI water prior to the coating.

Preparation of ZIF-8/PTMSP, ZIF-8/PEBAX2533, ZIF-8/PIM-1 composite membranes: The preparation procedures of these three composite membranes were similar to above ZIF-8/PDMS composite membrane, only with the exception of coating solution. The PTMSP solution (2 wt.%) was prepared by dissolving 0.1 g

PTMSP into 5.6 mL toluene with mechanical stirring for 3 h at room temperature. The PEBAX solution (3 wt.%) was prepared by dissolving 0.1 g PEBAX 2533 in 4.5 mL ethanol under stirring at 70 ^{o}C for 3 h. The PIM-1 solution (2 wt.%) was prepared by dissolving 0.1 g PIM-1 into 2.5 mL chloroform with mechanical stirring for 3 h at room temperature. After coating of the solution, all composite membrane were vacuum-dried at 60 ^{o}C for 24 h.

Characterization: X-ray diffraction (XRD) patterns of membranes were collected at room temperature on a Rigaku Smartlab TM 9 KW powder diffractometer using CuKα radiation (λ = 1.54059 Å) at 40 kV and 40 mA. Morphologies of the surfaces and cross-sections of membranes were all characterized by scanning electron microscope (SEM, S4800, Hitachi, Japan). The cross-sections of membranes were prepared by freeze-fracture after immersion in liquid nitrogen for several minutes. Prior to the SEM observations, all membranes were coated with gold in vacuum to increase their conductivity. In order to analyze the distribution of elements in the cross-sectional membrane, energy dispersive X-ray spectrometer (EDX) analyses were operated with 20 keV of acceleration voltage and 9 mm of working distance. Differential scanning calorimetry (DSC) measurement was conducted on Seiko DSC6200 under nitrogen atmosphere from –170 to 25 ^{o}C. The cooling and heating rate was maintained at 10 ^{o}C/min.

Laser scan confocal microscope (LSCM) measurements on pristine ZIF-8 polycrystalline membrane and ZIF-8/PDMS composite membrane were conducted to evaluate the inter-crystalline defects inside the membranes.[5] The membrane was mounted on a home-made permeance cell. The membrane side was contacted to pure methanol, and the support side was saturated with the methanol solution containing CdTe quantum dots (~2.8 nm) for a period of 2 days. Afterwards, the membranes were removed and washed with copious amount of fresh methanol, dried by blowing N_2 gas, and kept at room temperature for 12 h. The LSCM images were obtained from a Leica TCS SP5 with the wavelength of 488 nm.

Roughness measurement was performed with a hand-held surface roughness tester (Time group, TR200). The measurement technique consists of the displacement of a pick-up (diamond stylus), placed in contact with the surface, along a straight line trajectory and at constant velocity.[6] The pick-up copies the surface roughness through vertical displacements, which are converted in an inductive phase-sensitive rectified analog signal. This signal, proportional to the vertical displacement, is then recorded in a plotting device.

Hydrophobic properties of the ZIF-8 polycrystalline membrane and ZIF-8/PDMS composite membrane were characterized by measuring the static water contact angle of the surfaces with a contact angle meter (DropMeter A-100P) through sessile drop method. Membranes placed on the glass sample plate and fixed with tape. The water droplets used for the measurements were 1 μL in volume. Contact angles were measured at five different positions of each sample and then averaged.

Gas permeation: Mixed-gas (propylene/propane, 1:1) permeation experiments were conducted through Wicke-Kallenbach (W-K) technique,[7] as shown in Figure S1. At the feed side, the total volumetric flow rate of the propylene/propane mixture was set to 70 mL/min. Helium was used as sweep gas for the permeate stream (atmospheric). The total pressure difference was controlled by increasing the upstream pressure through a back-pressure controller at the retentate side. The permeating temperature was maintained at 35 °C. The compositions of the steady state feed, retentate, and permeate were all tested by gas chromatography (Agilent 7890A). At each permeation condition the system was stabilized for at least 4 h and the measurement was repeated for at least three times. In addition, the parallel membranes were prepared in exactly the same manner to guarantee the reliability of testing.

The permeance of gas through the membrane, F_i, is defined as：

$$F_i = \frac{N_i}{A \times \Delta P_i} \tag{1}$$

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

The separation factor ($\alpha_{i,j}$) for component i over component j is defined as:

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

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.

Hydrothermal stability tests: The hydrothermal stability of pristine ZIF-8 polycrystalline membrane and ZIF-8/PDMS composite membrane was examined by immersing membranes into 40mL DI water at room temperature and monitoring its morphology and structure evolution by SEM and XRD, respectively. Prior to the hydrothermal stability measurement, mixed-gas permeation experiments of the ZIF-8/PDMS composite membranes were conducted. The membranes were taken out and washed with abundant methanol, then immersed in fresh methanol for 12 h, followed by drying under ambient conditions at for 12 h. After the hydrothermal stability experiments, mixed-gas permeation experiments of the ZIF-8/PDMS composite membranes were conducted again.

2. Figures and Tables:

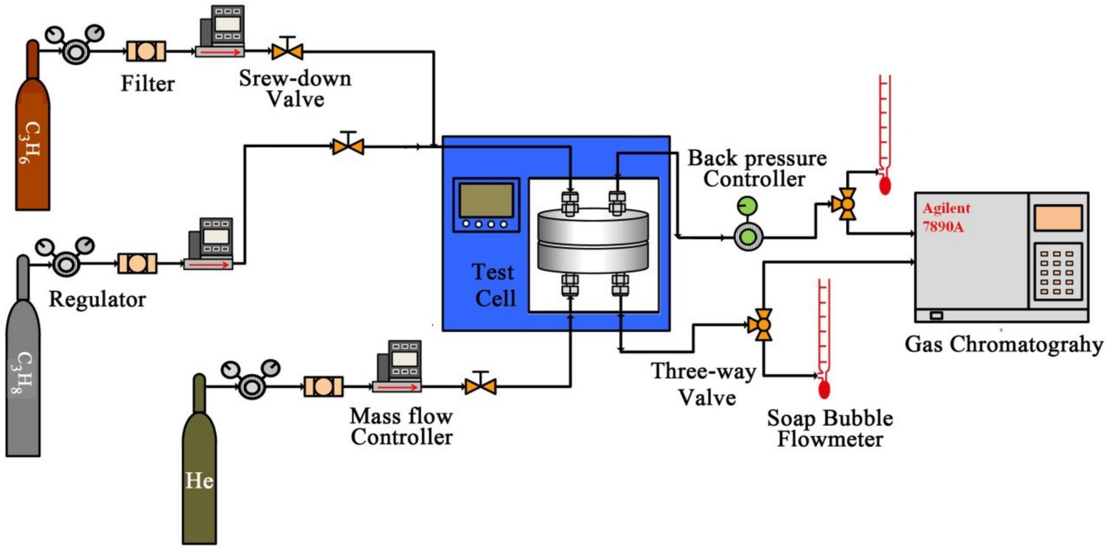

Figure S1. Schematic diagram of the set-up for gas permeation measurements.

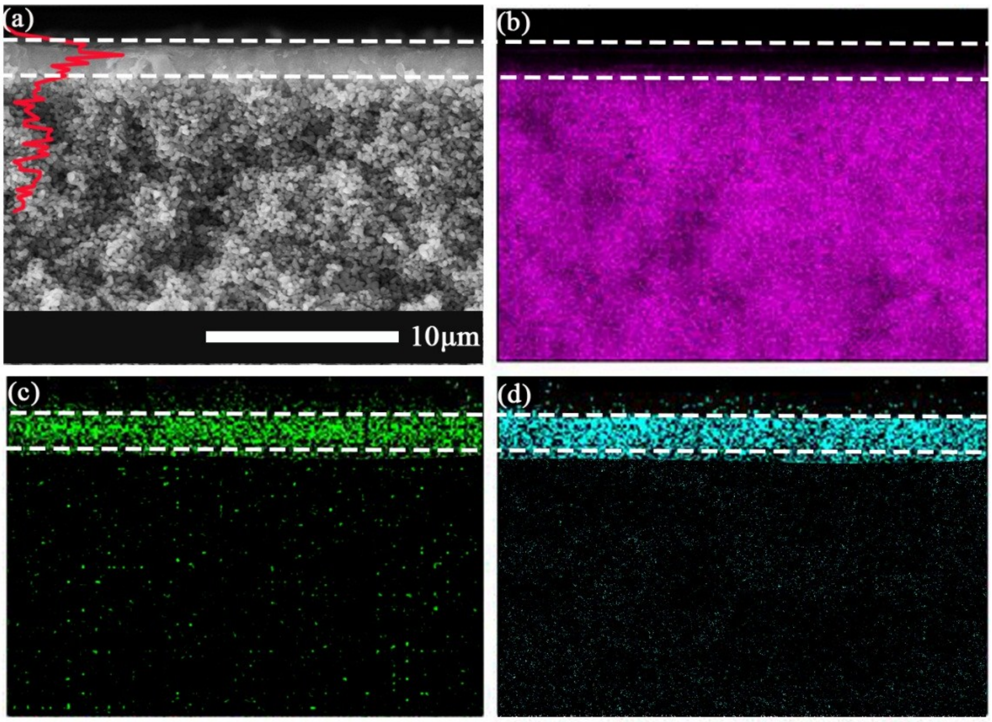

Figure S2. (a) Cross-sectional SEM image and EDX spectra of (b) Al element, (c) Zn element, (d) Si element on the ZIF-8/PDMS composite membrane M2. The red line in (a) is the EDX vertical line scan for Si element.

Table S1. Separation performance of propylene/propane mixture on 12 ZIF-8 membranes before and after PDMS coating with a feeding pressure of 1 bar at 35 °C.

Membranes	Original ZIF-8 membrane			After PDMS coating		
	Permeance (10^{-10} mol m^{-2} s^{-1} Pa^{-1})		Separation factor	Permeance (10^{-10} mol m^{-2} s^{-1} Pa^{-1})		Separation factor
	Propylene	Propane		Propylene	Propane	
M3	295.2	7.2	41	242.1	2.6	93
M4	268.6	7.1	38	225.4	2.7	85
M5	496.8	364	1	189.5	4.7	40
M6	284.2	101.5	3	172.8	3.2	54
M7	750.9	616.1	1	240.8	10.6	23
M8	189.2	21.0	9	154.0	2.0	77
M9	254.8	5.5	46	217.3	2.1	104
M10	506.8	323.5	1	217.0	7.4	29
M11	226.7	21.7	10	188.6	2.3	82
M12	181.4	19.1	10	138.6	1.8	77
M13	189.2	85.9	2	149.8	3.3	45
M14	208.6	54.6	4	182.5	2.9	63

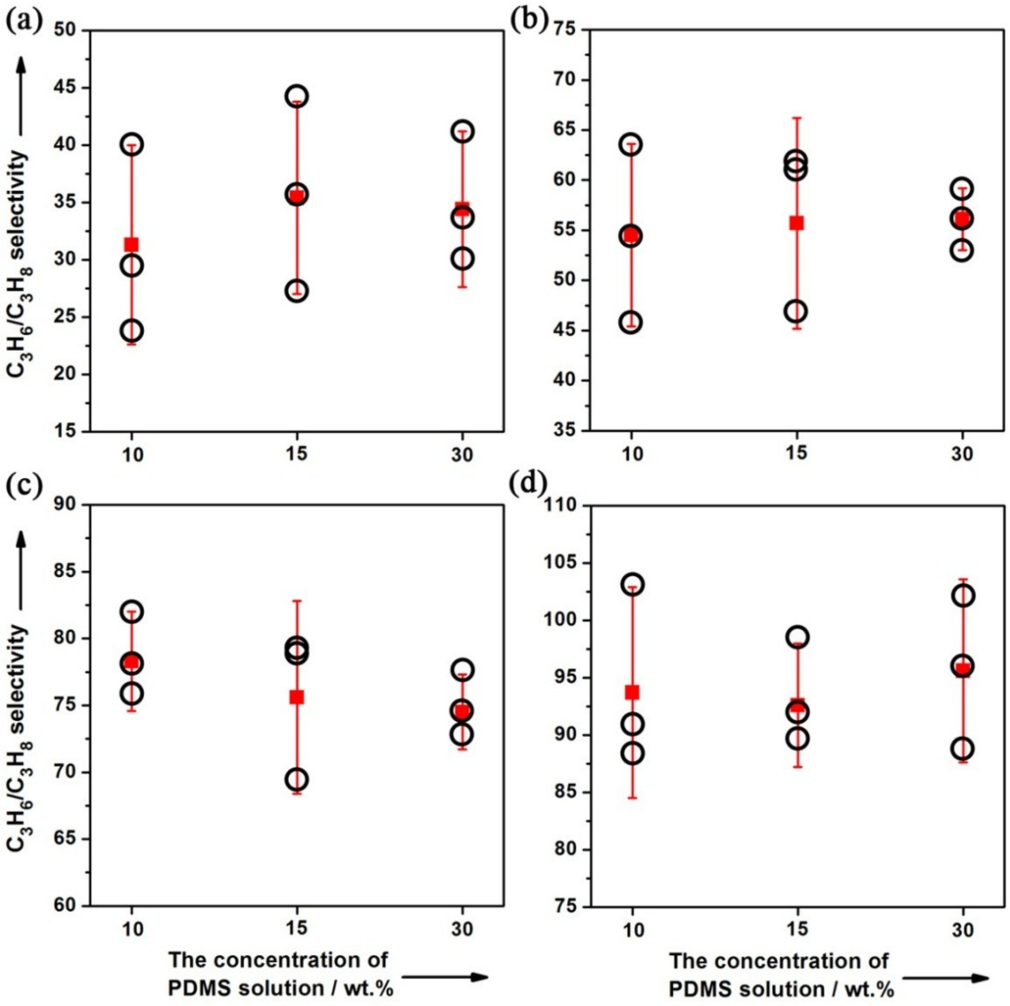

Figure S3. Scatterplot of propylene/propane selectivities on ZIF-8 polycrystalline membranes coated with PDMS layer as a function of the concentration of PDMS solution (10~30 wt.%). The original selectivities of ZIF-8 membranes were (a) ~1; (b) ~3; (c) ~9; (d) ~40. The red line with symbols shows the average selectivity and dispersion of selectivity of the membranes derived from different original selectivity.

Table S2. Separation performance of propylene/propane mixtures on ZIF-8/PDMS composite membranes as a function of feeding upstream pressures.

Membrane	Upstream pressure (kPa)	Permeance (10^{-10} mol m^{-2} s^{-1} Pa^{-1})		Separation factor
		Propylene	Propane	
M15	100	189.2	2.0	95
	400	171.2	1.7	101
	700	157.4	1.5	105
M16	100	219.1	2.6	84
	400	197.6	2.3	86
	700	176.0	2.0	88
M17	100	230.5	2.6	87
	400	205.3	2.3	89
	700	172.1	1.9	91

Table S3. Glass transition temperature (T_g) for pure PDMS and ZIF-8/PDMS mixed matrix membranes blending with different loadings of ZIF-8 fillers.

Membrane samples	T_g (^oC)
Pure PDMS	-123
ZIF-8/PDMS 5 wt.%	-123
ZIF-8/PDMS 10 wt.%	-122
ZIF-8/PDMS 20 wt.%	-121

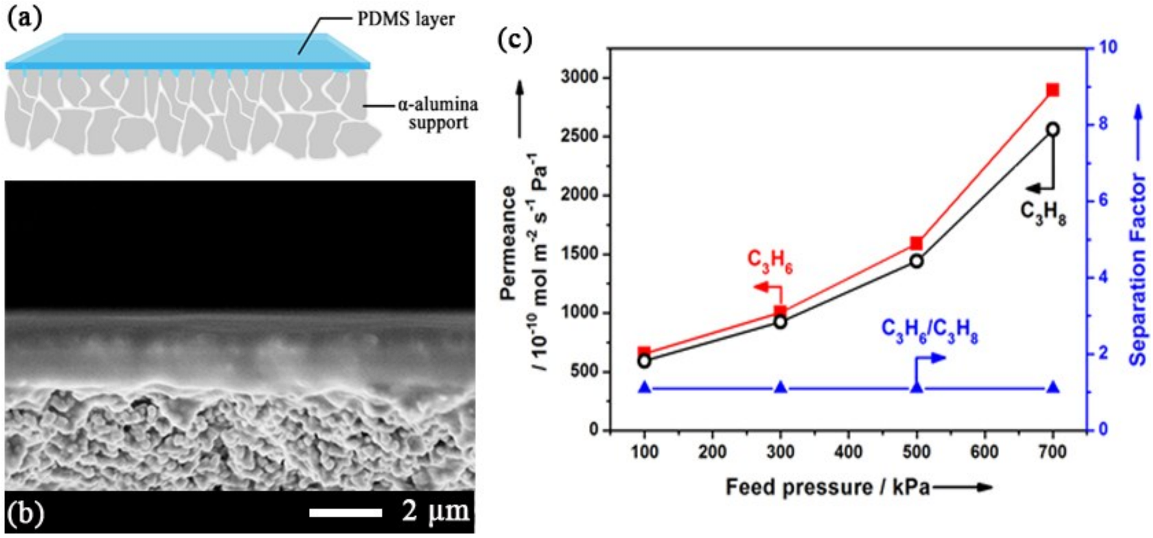

Figure S4. (a) Schematic description of PDMS/α-alumina membrane; (b) cross-sectional SEM image of the PDMS/α-alumina composite membrane; (c) separation performance of propylene/propane mixture on the PDMS/α-alumina composite membrane as a function of feeding upstream pressures.

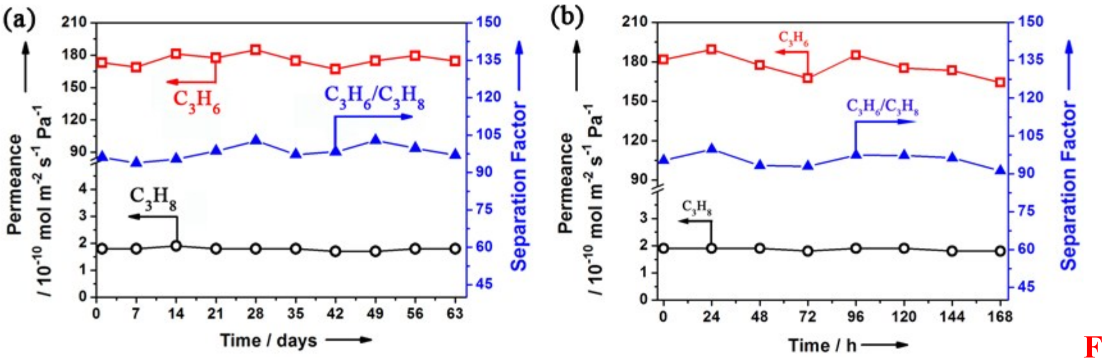

Figure S5. Long-term stability tests for propylene/propane separation on ZIF-8/PDMS composite membrane M3 under (a) dried-state and (b) humidified-state feeding mixtures. The permeating temperature is 35 °C, and the total pressure difference across the membrane is 6 bar.

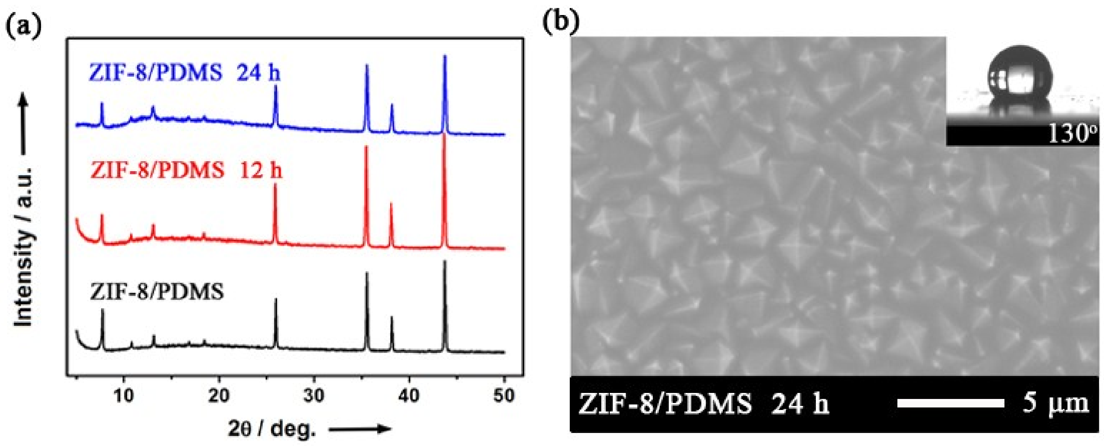

Figure S6. (a) XRD patterns of the ZIF-8/PDMS composite membrane M16 as a function of the immersion time, (b) top-view SEM picture of the ZIF-8/PDMS composite membrane M16 immersed in water for 24 h. The inset image in (b) shows the static contact angle and water droplet profile of the membrane.

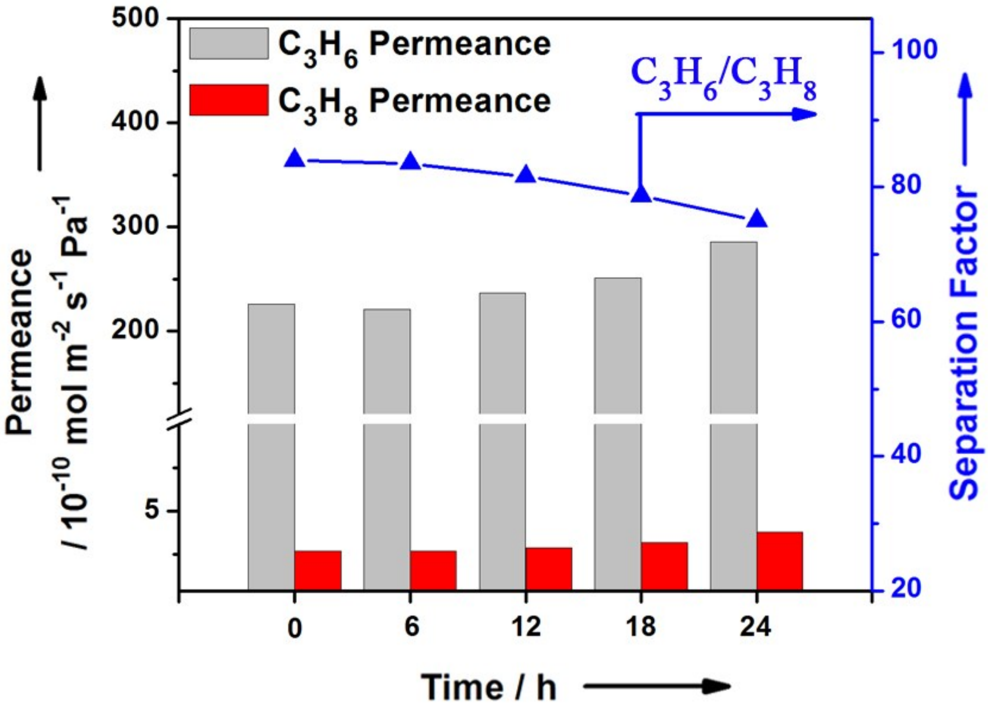

Figure S7. Separation performance on ZIF-8/PDMS composite membrane M16 as a function of immersing time.

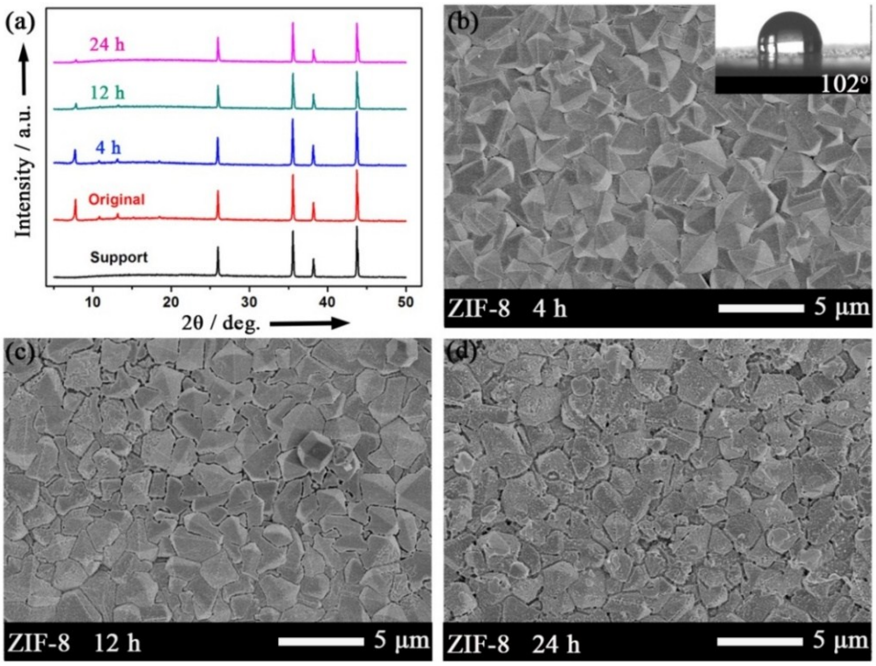

Figure S8. (a) XRD patterns of ZIF-8 polycrystalline membranes immersed in water as a function of immersion time; and top-view SEM pictures of the ZIF-8 polycrystalline membrane immersed in water for (b) 4 h, (c) 12 h, (d) 24 h. The inset image in part b shows the static contact angle and water droplet profile of the membrane immersed for 4 h.

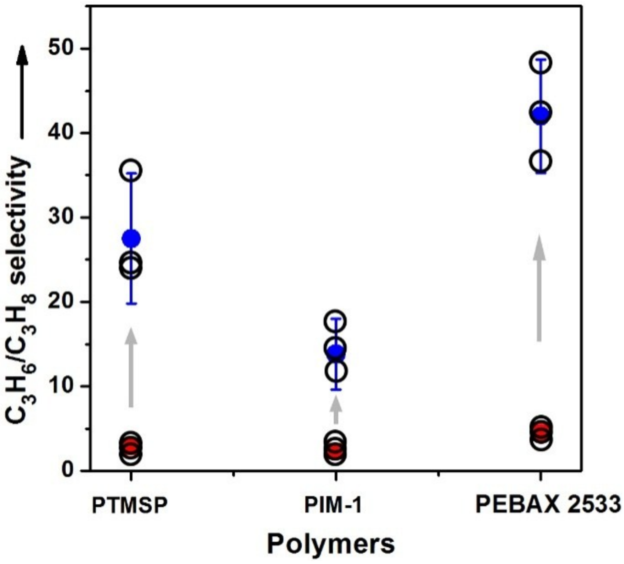

Figure S9. Scatterplot of improved propylene/propane selectivities on ZIF-8 polycrystalline membranes with PTMSP (2 wt.%), PIM-1 (3 wt.%) and PEBAX 2533 (3 wt.%) coatings. The gas-permeation was conducted with a feeding pressure of 1 bar at 35 °C.

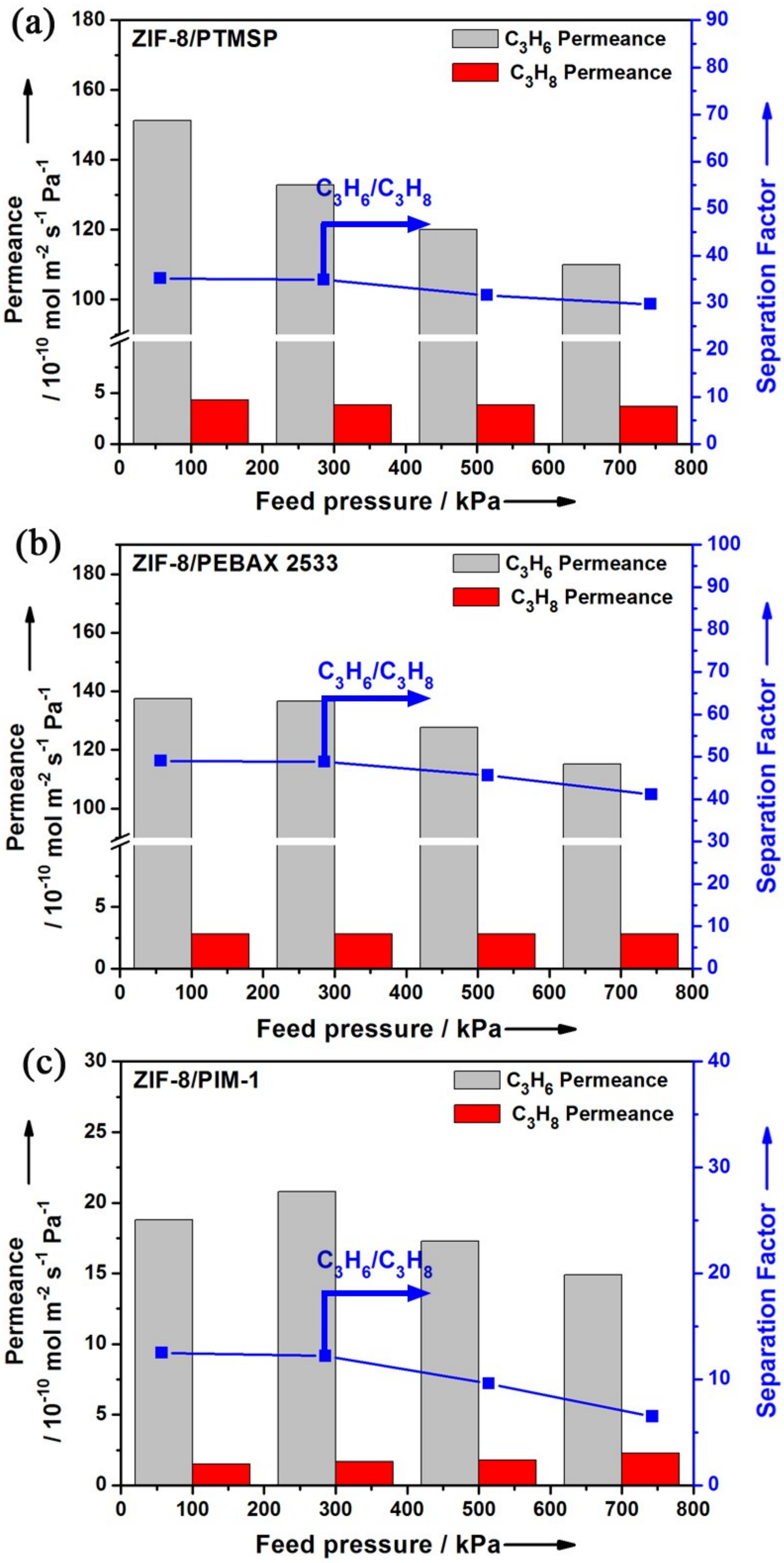

Figure S10. Separation performance of propylene/propane mixtures on (a) ZIF-8/PTMSP; (b) ZIF-8/PEBAX 2533; (c) ZIF-8/PIM-1 composite membranes as a function of feeding upstream pressures.

3. References

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