

Electronic Supplementary Information (ESI)

Designing superhydrophobic surfaces with SAMs modification on hierarchical ZIF-8/polymer hybrid membranes for efficient bioalcohol pervaporation

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1. Experimental section

1.1 Materials.

Zn(NO₃)₂•6H₂O (99.0%) and 2-methylimidazole (99.0%) was purchased from Aldrich. PDMS with a viscosity of 2550 Pa•s was purchased from China Bluestar Chengrand Chemical Co. Ltd. (China). Tetraethyl silicate (TEOS), methanol and *n*-butanol were obtained from Beijing Chemical Company (China). Dibutyltin dilaurate, *n*-heptane and *n*-butanol were supplied by Tianjin Fuchen Chemical Reagents Company (China). (Tridecafluorooctyl)triethoxysilane was obtained from Degussa (Germany). Flat sheet polysulfone (PSf) ultrafiltration (UF) membranes with a nominal molecular weight cutoff of 20,000 were supplied by Sepro Membranes. In our experiments, all reagents were of analytical grade and were used without further purification.

1.2 Preparation of ZIF-8 nanoparticles.

ZIF-8 nanoparticles were synthesized according to Cravillon et al.¹ As shown in Fig. S1, ESI[†], a solution of Zn(NO₃)₂•6H₂O in 70 ml methanol was rapidly poured into a solution of 2-methylimidazole (Hmim) in 70 ml methanol under stirring at room temperature. After 1 h, the nanoparticles were separated from the mother liquid by centrifugation and washed by methanol. The as-synthesized ZIF-8 nanoparticles were curing for removal of the solvent at 40 °C for 12 h.

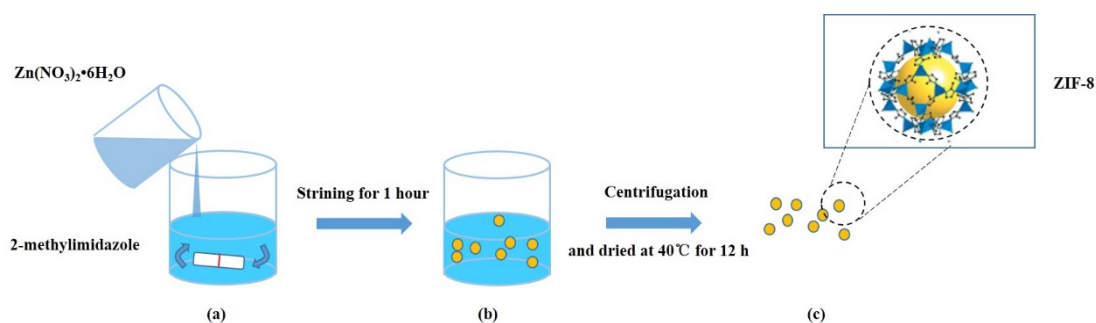


Fig. S1 The schematic diagram describing the preparation of the ZIF-8 nanoparticles

1.3 Preparation of ZIF-8/PDMS hybrid membrane.

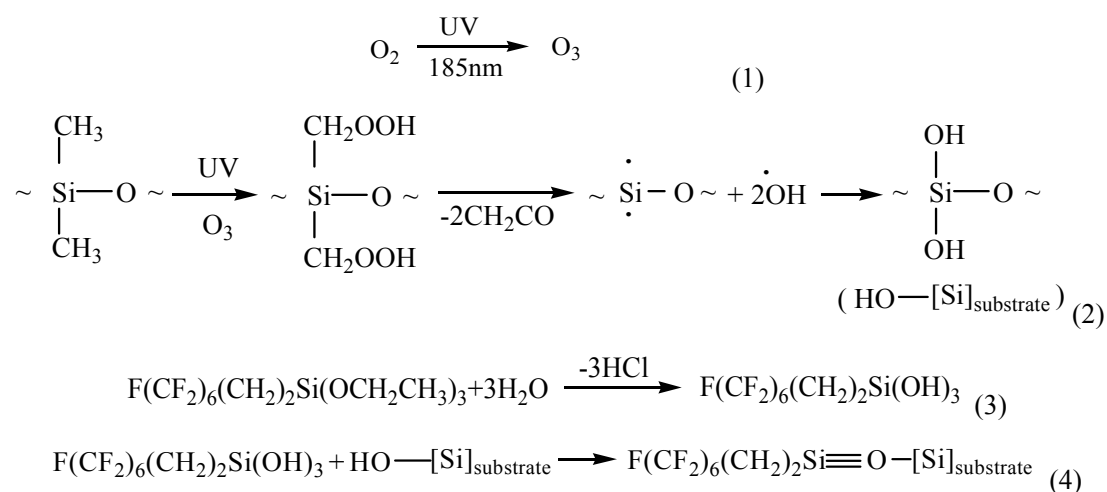
The ZIF-8 nanoparticles were re-dispersed in *n*-heptane using a sonicator for 30 min. The PDMS, TEOS and dibutyltin dilaurate were added into this solution to give the weight composition: $W_{\text{ZIF-8}}: W_{n\text{-heptane}}: W_{\text{PDMS}}: W_{\text{TEOS}}: W_{\text{dibutyltin dilaurate}} = 5:100:10:1:0.05$. This mixture was dramatically stirred for 30 min and then sonicated for 30 min. Air bubbles trapped in the polymer solution were removed by degassing at 100 Pa for 3 min. Before coating, the PSf substrate was pre-wetting by pure water to fill up the pores.² The ZIF-8/polymer solution was dip-coated on the surface of the PSf support for 1 min. Following removal of the solvent at room temperature for 12 h and subsequent curing in the oven at 80 °C for 12 h, the ZIF-8/PDMS composite membrane was finally fabricated (Fig. 1(a)). As a comparison, a PDMS membrane without ZIF-8 particles was also prepared by the same method.

1.4 SAMs-Modified ZIF-8/PDMS Membrane.

The SAMs-modified membranes were fabricated by depositing $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ onto ZIF-8/PDMS substrates prepared by exposing ZIF-8/PDMS films to UVO equipment (Beijing Institute of Opto-Electronic

Technology, China) for 60 min (Fig. 1).³ The UV intensity on the sample surface was 4 mW/cm² at $\lambda = 254$ nm, based on measurement by a UV power meter (Photoelectric Instrument Factory of Beijing Normal University). Ozone was generated in situ from atmospheric oxygen during UV exposure. The CF₃(CF₂)₅CH₂CH₂Si(OCH₂CH₃)₃ in ethanol solution (1.0 wt %) was hydrolyzed by the addition of a threefold molar excess of water at room temperature. After UVO treatment, the oxidized ZIF-8/PDMS membranes (hereafter known as ZIF-8/PDMS^{OH}) were immediately treated with the mixture of hydrolyzed silane solution and were allowed to react for 1 h at room temperature. The adsorbed SF molecules react with the silanol groups present on ZIF-8/PDMS^{OH} to yield terminal –CF₃ groups (the resulting membrane is referred as ZIF-8/PDMS^{CF₃}). After removal from the solution, the membranes were washed with ethanol and then vacuum-dried at 40 °C for 1 h.

The reactions involved in the modification of PDMS by UV radiation (at 185 and 254 nm in air) and the fabrication of SAMs are presented below: ⁴



Scheme S1

1.5 Membrane Characterization.

XRD (X-ray diffraction) patterns were recorded on Rigaku D/MAX 2500/PC (using Cu K α radiation, $\lambda = 0.154$ nm at 40 kV and 200 mA). Contact angles of water on the membranes were measured by using a contact angle analyzer (DSA 100, Germany). Prior to measurements, water were applied as droplets onto the membrane surfaces. The average value of 10 measurements at different positions of the sample was adopted as the CA value. The membrane surfaces were observed under a scanning electron microscope (Hitachi-S4300, Japan), and AFM images were acquired on a Pico ScanTM 2500 (USA) to characterize their morphology. Chemical compositions of the membranes were analyzed using an EDX spectrometer.

1.6 Pervaporation Experiments.

The pervaporation performance of the membrane was evaluated using a pervaporation apparatus fabricated in our laboratory.⁵ The selected *n*-butanol concentration in the feed solution was 3 wt%. The experiments were conducted at a feed temperature of 60 °C. The downstream pressure was maintained at around 100 Pa. The pervaporation performance was measured three times by using three membranes under the same fabrication and modification conditions; the average of the three trials was used as a data point. The permeate vapor was trapped in liquid nitrogen and subsequently analyzed by gas chromatography (GC-14C, Shimadzu, Japan). The permeate flux (J) was determined according to the following equation:

$$J = \frac{W}{At} \quad (1)$$

Where W is the weight of the liquid collected in the cold traps, A is the effective area of the membrane, and t is the certain time for the pervaporation.

The selectivity of the composite membranes is expressed as a separation factor α , which is defined as

$$\alpha = \frac{(1 - Y_w) / Y_w}{(1 - X_w) / X_w} \quad (2)$$

Where the Y_w and X_w are the weight ratios water in the permeation and feed sides, respectively.

2. EDX analytical results of the top surface of the membranes

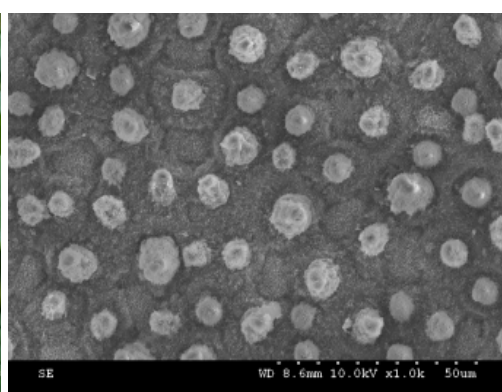
Table S1 EDX analytical results of the top surface of the membranes

	PDMS	PDMS ^{CF3}	ZIF-8/PDMS	ZIF-8/PDMS ^{CF3}
C	37.43	34.25	26.68	23.61
O	28.91	31.41	21.24	25.41
Si	33.65	32.48	27.36	26.25
Zn	-	-	08.98	06.27
N	-	-	15.74	14.58
F	-	1.87	-	3.88

3. Morphology of ZIF-8 particles and PDMS^{CF3} membrane



(a)



(b)

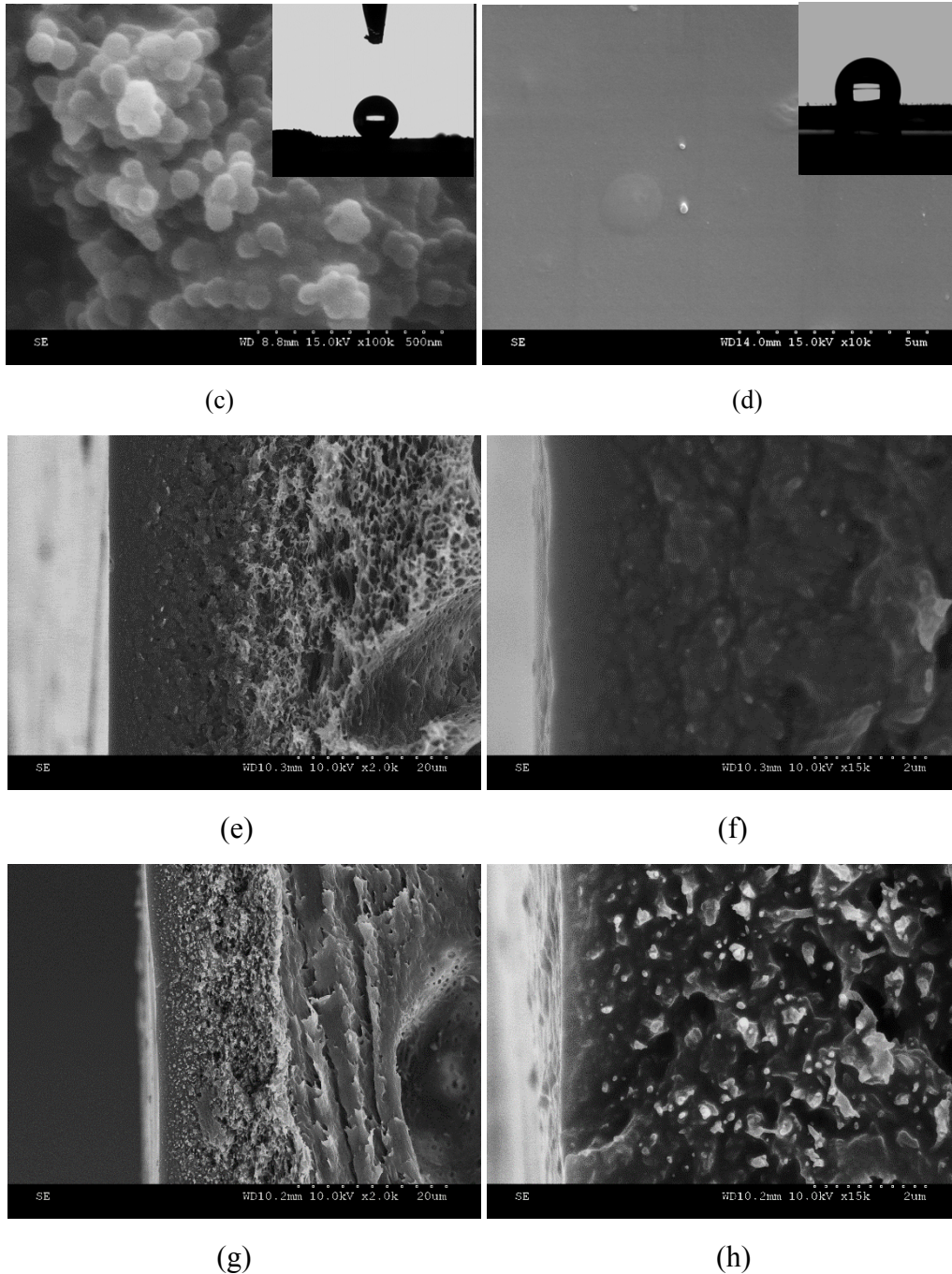


Fig. S2 (a) Photograph of lotus leaf; SEM images of the surface of (b) lotus leaf ($\times 1$ K), (c) ZIF-8 particles ($\times 100$ K), (d) PDMS^{CF3} membrane ($\times 10$ K); SEM images of the cross section of (e) PDMS^{CF3} membrane ($\times 2$ K), (f) PDMS^{CF3} membrane ($\times 15$ K), (g) ZIF-8/PDMS^{CF3} membrane ($\times 2$ K), (h) ZIF-8/PDMS^{CF3} membrane ($\times 15$ K); Inset: water contact angle images of (c) ZIF-8 particles, (CA = 151.6⁰); (d) PDMS^{CF3} membrane, (CA = 108.4⁰)

4. Morphologies of PDMS, PDMS^{CF3}, ZIF-8/PDMS and ZIF-8/PDMS^{CF3} membranes

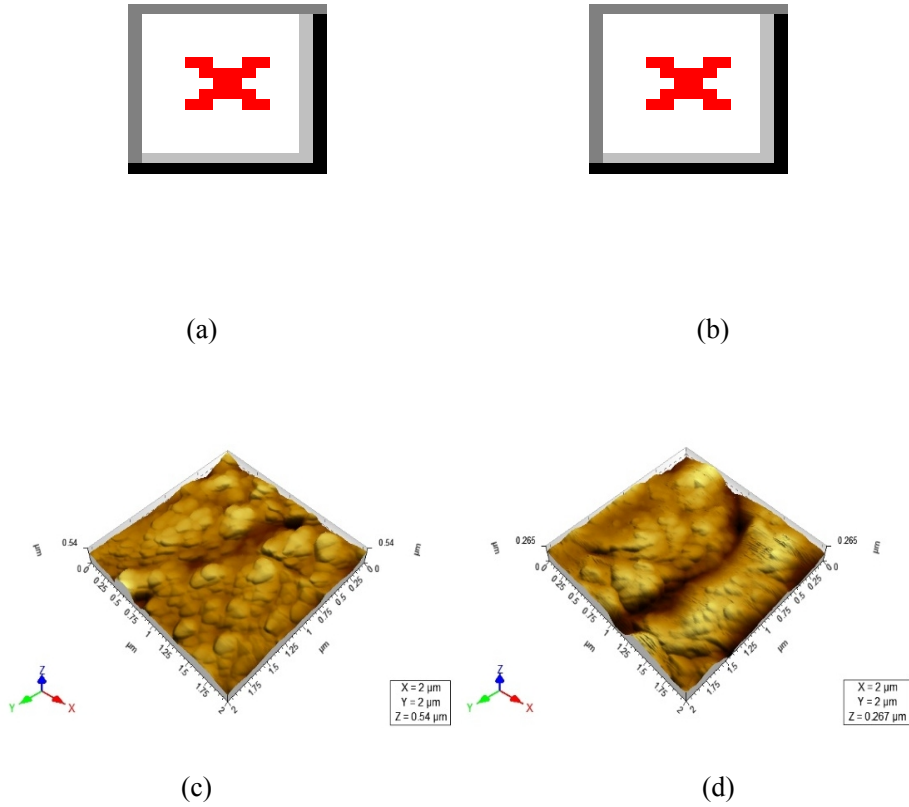


Fig. S3 Tapping mode 3D AFM images of membranes ($2\ \mu\text{m}\times 2\ \mu\text{m}$). (a) PDMS membrane ($R_a = 2.43\ \text{nm}$); (b) $\text{PDMS}^{\text{CF}_3}$ membrane ($R_a = 2.40\ \text{nm}$); (c) ZIF-8/PDMS membrane ($R_a = 57.2\ \text{nm}$); (d) ZIF-8/ $\text{PDMS}^{\text{CF}_3}$ membrane ($R_a = 42.8\ \text{nm}$).

Table S2 R_a values of different membranes

Membrane	$2\ \mu\text{m}\times 2\ \mu\text{m}$	$5\ \mu\text{m}\times 5\ \mu\text{m}$	$10\ \mu\text{m}\times 10\ \mu\text{m}$	$20\ \mu\text{m}\times 20\ \mu\text{m}$
PDMS	$2.43\ \text{nm}\pm 0.03\text{nm}$	$6.17\ \text{nm}\pm 0.03\text{nm}$	$11\ \text{nm}\pm 0.03\text{nm}$	$42.3\ \text{nm}\pm 1\text{nm}$
$\text{PDMS}^{\text{CF}_3}$	$2.40\ \text{nm}\pm 0.03\text{nm}$	$3.32\ \text{nm}\pm 0.05\text{nm}$	$10.1\ \text{nm}\pm 0.03\text{nm}$	$23.3\ \text{nm}\pm 1\text{nm}$
ZIF-8/PDMS	$57.2\ \text{nm}\pm 1\text{nm}$	$140\ \text{nm}\pm 3\text{nm}$	$179\ \text{nm}\pm 3\text{nm}$	$295\ \text{nm}\pm 5\text{nm}$
ZIF-8/ $\text{PDMS}^{\text{CF}_3}$	$42.8\ \text{nm}\pm 1\text{nm}$	$77.8\ \text{nm}\pm 1\text{nm}$	$137\ \text{nm}\pm 3\text{nm}$	$234\ \text{nm}\pm 5\text{nm}$

5. XRD spectra of ZIF-8, PDMS, PDMS^{CF3}, ZIF-8/PDMS and ZIF-8/PDMS^{CF3} membrane

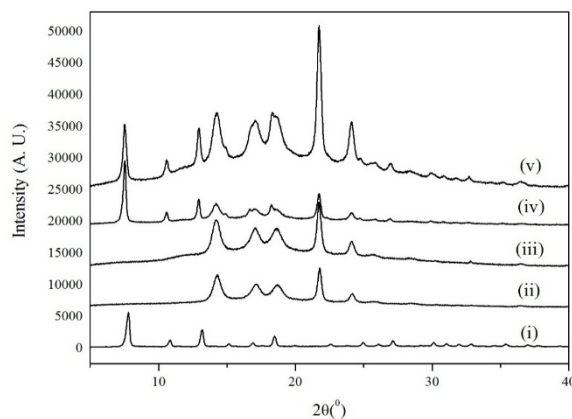


Fig. S4 XRD spectra of (i) ZIF-8; (ii) PDMS; (iii) PDMS^{CF3}; (iv) ZIF-8/PDMS; (v) ZIF-8/PDMS^{CF3}

6. Pervaporation performance of various membranes for the separation of 3 wt% *n*-butanol/water mixtures

Table S3. Pervaporation performance of various membranes for the separation of 3 wt% *n*-

butanol/water mixture

Membrane	Total flux (g/m ² •h)	<i>n</i> -butanol flux(g/m ² •h)	Water flux(g/m ² •h)	Separation factor (α)	<i>n</i> -butanol in permeate (wt%)
PDMS	1065	312	753	13.4	29.30
PDMS ^{CF3}	1049	394	655	19.4	37.52
ZIF-8/PDMS	1459	940	519	58.4	64.40
ZIF-8/PDMS ^{CF3}	1339	969	370	84.8	72.39

(Experimental conditions: feed of 3 wt% *n*-butanol at 60 °C)

7. Effect of ZIF-8 loading on the CA and PV performance of the ZIF-8/PDMS^{CF3} membranes

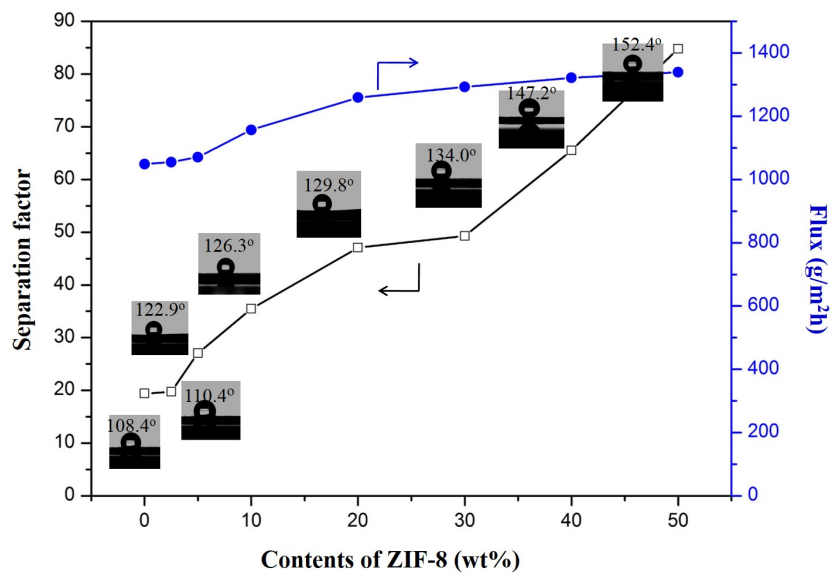


Fig. S5 Effect of ZIF-8 loading on the CA and PV performance of the ZIF-8/PDMS^{CF3} membranes (Experimental conditions: feed of 3 wt% n-butanol at 60 °C)

7. Comparison of the pervaporation performance of various membranes in the separation of *n*-butanol/water mixtures

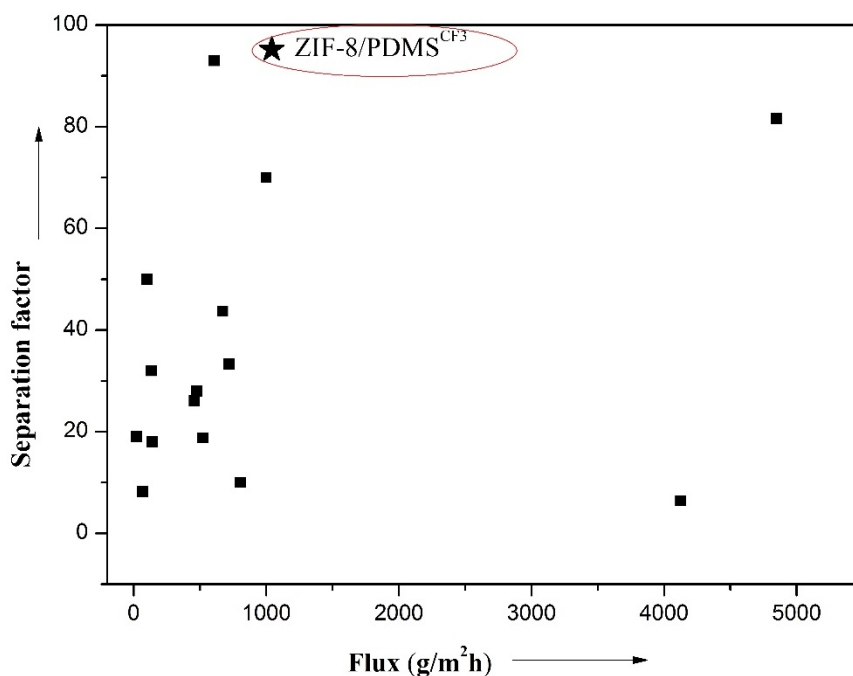


Fig S6. Pervaporation performance of various membranes in the separation of *n*-butanol/water mixtures.

Table S4. Pervaporation performance of various membranes in the separation of *n*-butanol/water mixtures.

Membrane	Feed concentration (wt%)	Feed temperature (°C)	Total flux (g/m ² •h)	Separation factor	Contact angle(°)	Reference
PTMSP	1	70	999	70.0	-	7
PTFE	1	50	805	10	-	8
PEBA	5	23	65.3	8.2	-	9
Ge-ZSM-5	5	30	20	19.0	-	10
PVDF	7.5	50	4126	6.4	-	11
PDMS	2	37	132	32	110	12
PDMS/ceramic composite membrane	1	40	457.4	26.1	-	14
Silicalite/PDMS	1	70	607	93	-	6
Silicalite/PDMS	0.1	65	475	28	-	13
ZSM-5/PEBA	4.3	35	719.3	33.3	-	15
CNT/PEBA	1	37	139	18	-	16
ZIF-71-PEBA	1	37	520.2	18.8	74.1	17
PDMS	1.5	55	670.18	43.72	122.3	18
ZIF-8/PMPS	1	80	5100	36.8	-	19
ZIF-8/PDMS	1	80	4846.2	81.6	136.8	5(d)
ZIF-8/PDMS ^{CF3}	3	60	1339	84.8	152.4	This study
ZIF-8/PDMS ^{CF3}	1	60	1041	95.2	152.4	This study

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