Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Locking of Phase-Transition in MOF ZIF-7: Improved Selectivity in Mixed-Matrix Membranes for O_2/N_2 Separation

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Table of Contents

1. Experimental Procedures 2
   - 1.1. Materials 2
   - 1.2. Synthesis of ZIF-7 nanocrystals 2
   - 1.3. Fabrication of composite membranes 2
   - 1.4. Characterization 3
   - 1.5. Gas sorption measurements 3
   - 1.6. Simulation methods 3
   - 1.7. Gas permeation 3
2. Figure and Tables 4
3. Author Contributions 12
4. References 12

1. Experimental Procedures

1.1. Materials

All reagents and solvents were used without further purification. The 4, 4'-oxydianiline (ODA), 4, 4′-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA), 3,3′-diaminobenzophenone (BPDA), 3, 3′, 4, 4′-benzophenonetetracarboxylic acid dianhydride (BTDA), Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%), and benzimidazole (BzIM, 98%) were obtained from Sigma-Aldrich. N, N-dimethylformamide (DMF, 99.9%), N, N-dimethylacetamide (DMAc, 99.9%), ethanol (99.9%) *n*-heptane (99.9%) and methanol (99.9%) were supplied from Sinopharm Chemical Reagent Co., Ltd. The gases (CO_2, O_2 and N_2) for the permeation and adsorption tests with purity of 99.999% were all supplied by Nanjing Tianze gas Co., Ltd. The water used in all experiments was treated by the Millipore Milli-Q purification system.

1.2. Synthesis of ZIF-7 nanocrystals

ZIF-7 nanocrystals were synthesized following the reported procedure [1]. Briefly, a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (2.5 mmol) in 25 mL of DMF is rapidly poured into a solution of BzIM (5 mmol) in 25 mL of methanol quickly. The mixture slowly became turbid and continued stirred for 6 h at room temperature (~25 °C). The as-synthesized ZIF-7 nanocrystals were collected by centrifugation (10000 rpm, 8 min), followed by washing with fresh methanol. Finally, the zeolitic imidazolate framework crystals were purified and activated using the method described elsewhere [1].

1.3. Fabrication of composite membranes

Polydimethylsiloxane (PDMS) composite membrane: Fully activated ZIF-7 nanocrystals were dispersed in *n*-heptane by applying sonication and vigorous agitation. To this mixture, PDMS oligomer and crosslinker (Momentive RTV 615) were added and then further agitated until the solution is homogenized. Prior to the membrane casting, the solution was sonicated for 30 min to remove any gas bubble. The dope solution prepared was poured in a Teflon® dish and the solvent was evaporated at room temperature. Then, the nascent membrane was solidified by crosslinking PDMS oligomers at 80 °C for 24 h. Finally, the membrane was further vacuum-dried at 150 °C for a week. The PDMS MMMs with 15 wt%, 30 wt% and 40 wt% ZIF-7 loadings were made.

Polysulfone (PSF) composite membrane: PSF (Solvay Polymers) mixed-matrix membranes were fabricated by the solution casting technique. After the activated dispersing ZIF-7 nanocrystals in anhydrous chloroform by applying sonication and vigorous agitation, the PSF was added. The ZIF-7-PSF solution was prepared by the standard 'priming' technique, which can be seen elsewhere [2]. The mixture was further agitated at room temperature until the solution is homogenized. A nascent film was cast with the solution on a glass plate using a "doctor's knife", the glass plate was covered with a glass cover to slow the evaporation of solvent, allowing for a film with a uniform thickness without curling. Finally, the membrane was further dried at 150 °C for a week in a vacuum oven to remove residual solvent and moisture. The weight ratio of ZIF-7-PSF in the resulting MMMs were adjusted to 15/85 and 40/60.

Pebax®1657 composite membrane: The Pebax®1657 (Arkema) membranes were synthesized by the procedure described in the previous work [2]. A certain amount of ZIF-7 were dispersed in water/ethanol (3/7 by weight) mixture, and the Pebax was dissolved after two hours by refluxing the mixture in an oil bath at 80 °C under N_2 protection. The Pebax solution and the ZIF-7 dispersion were directly mixed without any pretreatment, and then sonicated for 10 min, followed by stirring at room temperature. The dope solution finally prepared was poured in a Teflon® dish and the solvent was evaporated at room temperature and dried in a vacuum oven at 100 °C for a week. The filler loading in mixed-matrix membrane were 15 wt% and 40 wt%.

Polyimides (PI) composite membrane: The ZIF-7 nanofiller was uniformly dispersed in DMAc and the dispersion was transferred to the poly(amic acid) solution prepared at 10 wt% solids from the two monomers by the standard protocol of dissolving at room temperature the ODA first followed by addition of the 6FDA/BPDA (1/1 wt%) or BTDA.[3] The unhybridized poly(amic acid) solutions were first stirred for 24 h before proceeding further. The resulting ZIF-7-poly(amic acid) solution was stirred for 12 h to ensure a homogeneity. Doped mixture solutions were cast as films onto a solid Teflon® plate using a doctor blade to obtain ~50 μm thick films after thermal curing. The dense films were first dried at 50 °C for 48 h, followed by vacuum-drying at 250 °C for 24 h. The filler loading in mixed-matrix membranes was 15 wt%.

1.4. Characterization

Morphologies of the as-prepared ZIF nanoparticles and membrane samples were all characterized by scanning electron microscope (SEM, S–4800, Hitachi, Japan). The membrane samples were fractured in liquid nitrogen and subsequent sputter-coated of palladium. X-ray diffraction (XRD) patterns of all samples were collected on a Rigaku Smartlab TM 9 KW powder diffractometer at 40 kV, 100 mA for Cu-Kα, (λ = 1.542 Å). To determine the presence of solvents in the ZIF-7-polymer composites, solid-state (SS) ^{13}C cross-polarization-magic angle spinning (CP-MAS) NMR was performed on a Bruker Avance III 600 spectrometer equipped with a 14.1 T wide-bore magnet using a 4 mm MAS probe. Thermogravimetry coupled mass spectrogram (TG-MS) analysis of samples using a NETZSCH STA 449 machine interfaced to a Micromass Quattro Micro Mass Spectrometer. The samples (∼10 mg) were heated from 30 to 800 °C at a scanning rate of 10 °C/min under a flow of N_2, the evolved products were introduced directly into the MS unit via a silica capillary. The glass transition temperature (T_g) for each membrane was determined using a differential scanning calorimeter (NETZSCH DSC 204 F1 Phoenix) under nitrogen at a heating and cooling rate of 1 K/min in a temperature range of − 150–400 °C.

1.5. Gas sorption measurements

High-pressure adsorption isotherms of CO_2, O_2 and N_2 on ZIF-7 nanocrystals and membrane samples were recorded on a Belsorp-HP adsorption apparatus at 308 K, and the pressures was up 1000 kPa. Prior to the test, ZIF nanocrystals and membrane samples were activated at 150 ^{o}C under a vacuum (10^{-5} torr) for 24 h, respectively. At each point, an equilibration time of at least 500 s was used. For all membranes, the O_2 and N_2 sorption isotherms exhibit linear pressure dependence, are often described by the Henry's law linear isotherm equation [4]:

$$C = k_D p \tag{S1}$$

where k_D (cm^3 (STP) cm^{-3} (membrane) cmHg^{-1}) is the Henry's solubility coefficient, C (cm^3 (STP)/cm^3) is the concentration for adsorbed component, p (cmHg) is the adsorbate gas pressure at equilibrium. The solution coefficient (S) of single-gas in membrane sample can be expressed as:

$$S = \frac{C}{p} \tag{S2}$$

In addition, based on the solution-diffusion mechanism in polymer-based membrane, the diffusion coefficient (*D*) was calculated from the relationship between the permeability (*P*) and solution coefficient (*S*) as shown below.

$$D = \frac{P}{S} \tag{S3}$$

1.6. Simulation methods

The single-component isotherms of CO_2 and O_2 on different ZIF-7 structures were determined from Grand Canonical Monte Carlo (GCMC) simulations using the universal force field (UFF) and charge equilibration (QEq) algorithm [5]. Crystal structure of ZIF-7-I (CCDC602541) were taken from the data available in the Cambridge Crystallographic Data Centre. Crystal structure of ZIF-7-II were supported by Redfern et al [6]. Typically, single component CO_2 and O_2 adsorption were simulated on at 25 ^{o}C over the pressure range of 0-1000 kPa.

1.7. Gas permeation

The single-gas (O_2 or N_2) permeation experiments were conducted using the constant-volume variable-pressure method (Figure S1) [7]. The permeate flux was measured by monitoring the pressure increase of collected permeate gas in a closed volume using a pressure transducer. A home-made permeation cell with effective membrane area of 18 cm^2 was used for all tests. The feed pressure and temperature in the permeation module were 2 bar and 308 K, respectively. Prior to the test, residual gas present in the membranes and the pipeline were removed by vacuum pump. In addition, to guarantee the reliability of testing, three membrane samples fabricated under the same condition were used for permeation, and the results were averaged as the final data with deviation. The gas permeability is calculated based on the following equation:

$$P = \frac{VL}{A} \frac{T_0}{p_f p_0 T} \left(\frac{dp}{dt}\right) \tag{S4}$$

where *L* is the thickness of selective layer (cm), measured with a digital micrometer (Mitutoyo, Japan), *V* is the permeate volume (cm^3), *A* is the effective area of the membrane (cm^2), p_f is the feed pressure (cmHg), p_0 is the pressure at standard state (76 cmHg), *T* is the absolute operating temperature (K), T_0 is the temperature at standard state (273.15 K), dp/dt is the rate of pressure increase in the permeate volume at the steady state (cmHg/s). The unit of the permeability (*P*) is commonly expressed as Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)). The ideal selectivity of membrane was calculated by the following equation:

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{S5}$$

2. Figure and Tables

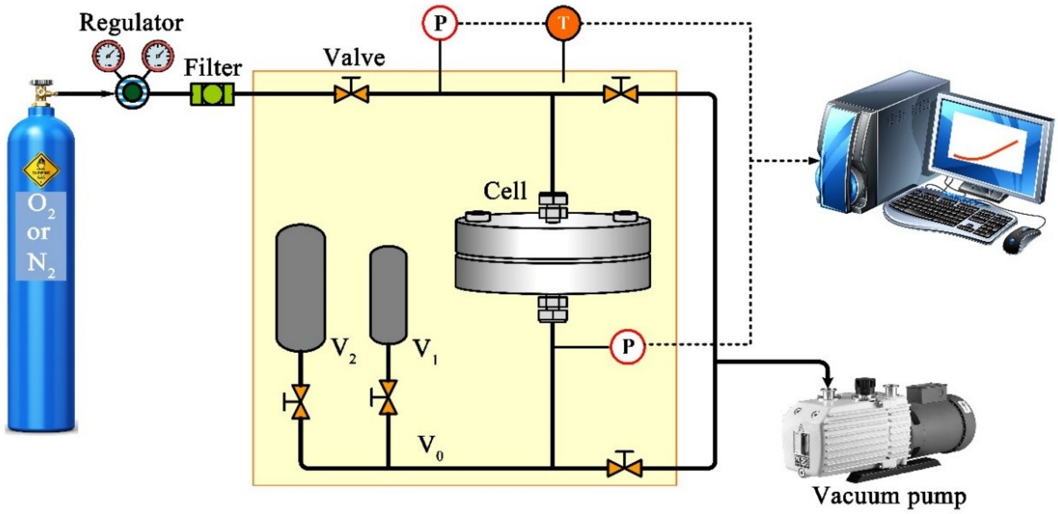

Figure S1. Schematic diagram of pure gas permeation apparatus. P: pressure transducer; T: temperature controller; V_0, V_1 and V_2: volume of tube, gas cylinder 1 and 2 respectively; The parts within the flavous box are in a temperature-controlled chamber.

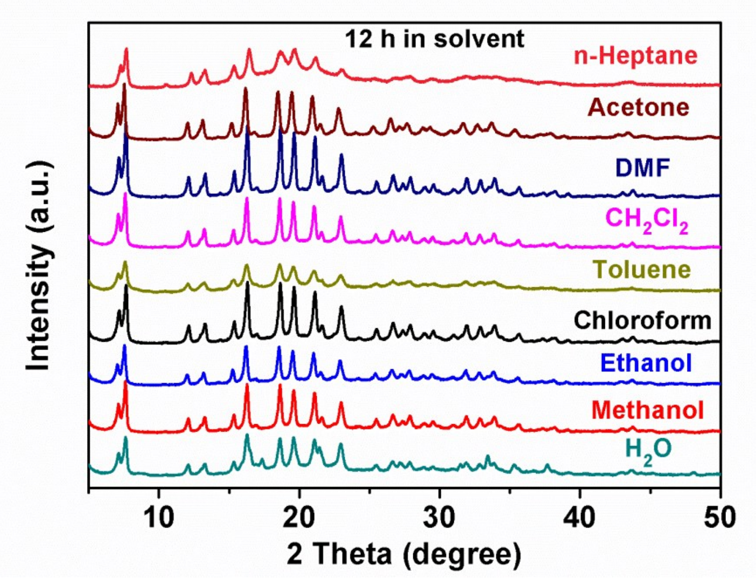

Figure S2. The XRD patterns of ZIF-7-II nanocrystals immersed in various solvents at room temperature for 12 h.

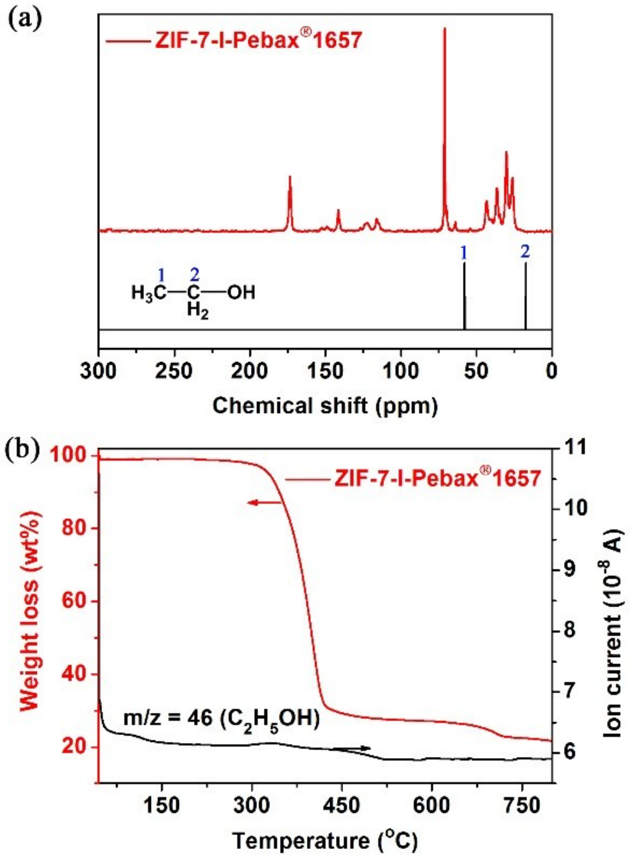

Figure S3. (a) Solid-state ^{13}C CP-MAS NMR spectra and (b) TGA and ion current traces of ZIF-7-I-Pebax composites.

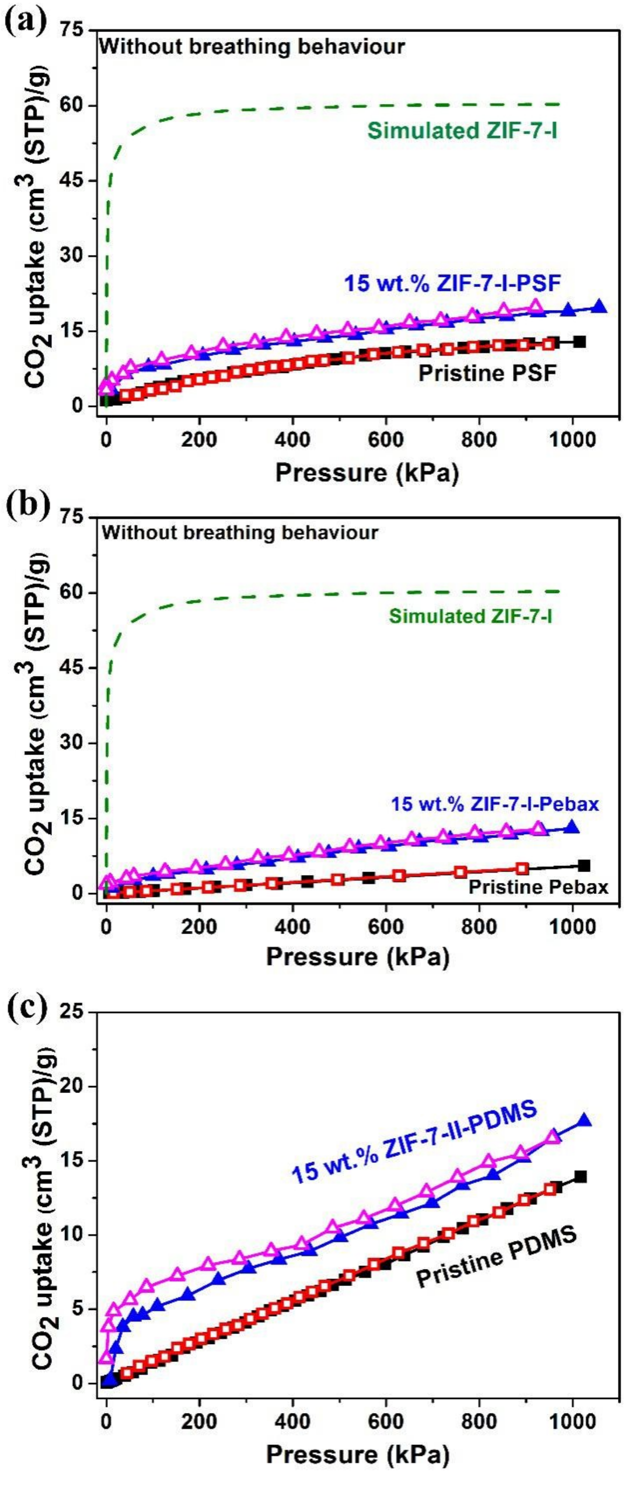

Figure S4. CO_2 adsorption properties of pristine polymer and 15 wt% ZIF-7-polymer composites derived from (a) PSF, (b) Pebax®1657 and (c) PDMS. Closed and open symbols represent adsorption and desorption branches, respectively. The dashed line is the GCMC adsorption of the ZIF-7-I phase.

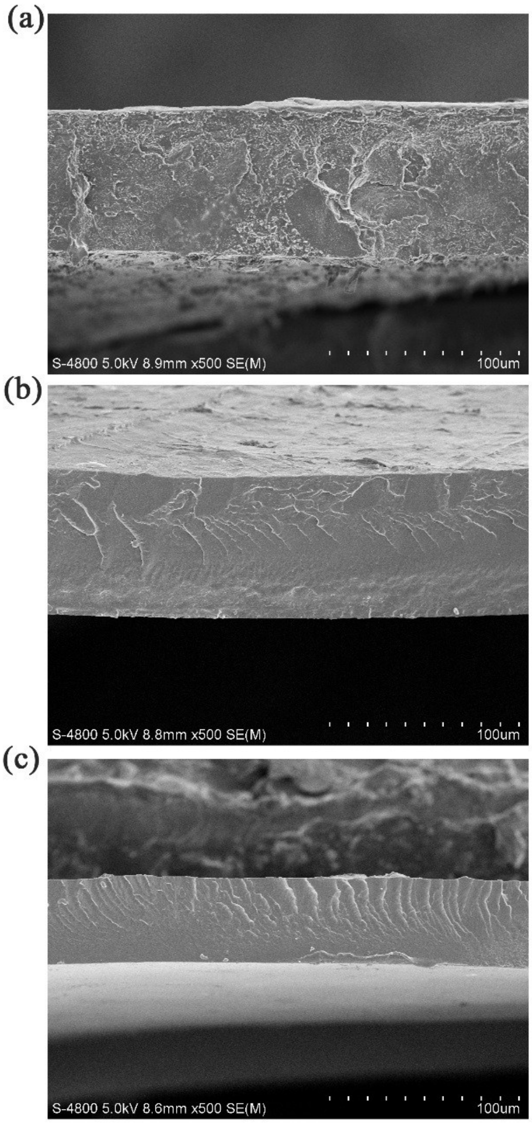

Figure S5. SEM images of cross-sections of 15 wt% ZIF-7-based MMMs: (a) ZIF-7-I in PSF; (b) ZIF-7-I in Pebax®1657 and (c) ZIF-7-II in PDMS.

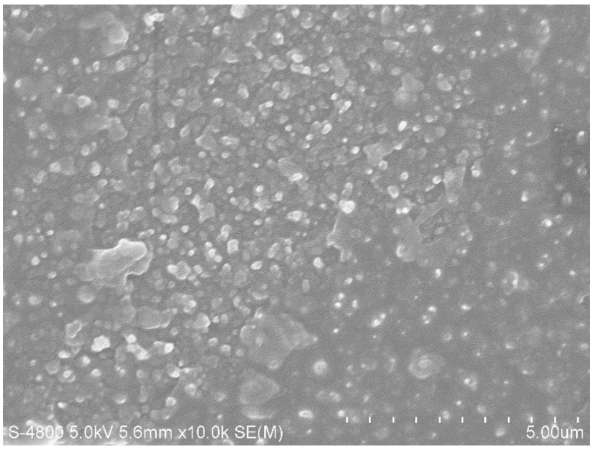

Figure S6. Typical cross-sectional SEM image of 15 wt.% ZIF-7-I-PSF membrane with obvious signs of microscale phase segregation or aggregates.

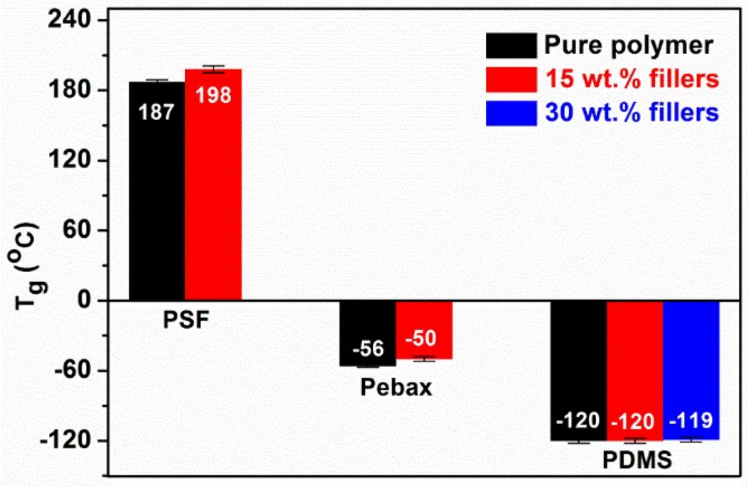

Figure S7. The glass transition temperature (T_g) values of ZIF-7-based MMMs.

Table S1. Pure component O_2 and N_2 permeation properties of membranes measured at 2 bar upstream pressure and 35 °C.

Membranes	Permeability (Barrer)		Selectivity O_2/N_2
	O_2	N_2	
Pristine PSF	0.6	0.19	3.2
15% ZIF-7-I-PSF	0.53±0.05	0.06±0.005	8.9±0.3
Pristine Pebax®1657	3.9	1.4	2.8
15% ZIF-7-I-Pebax®1657	5.5±0.4	1.1±0.1	5±0.2
Pristine PDMS	373	196	1.9
15% ZIF-7-II-PDMS	273±15	144±10	1.9±0.4
30% ZIF-7-II-PDMS	199±13	105±9	1.9±0.5

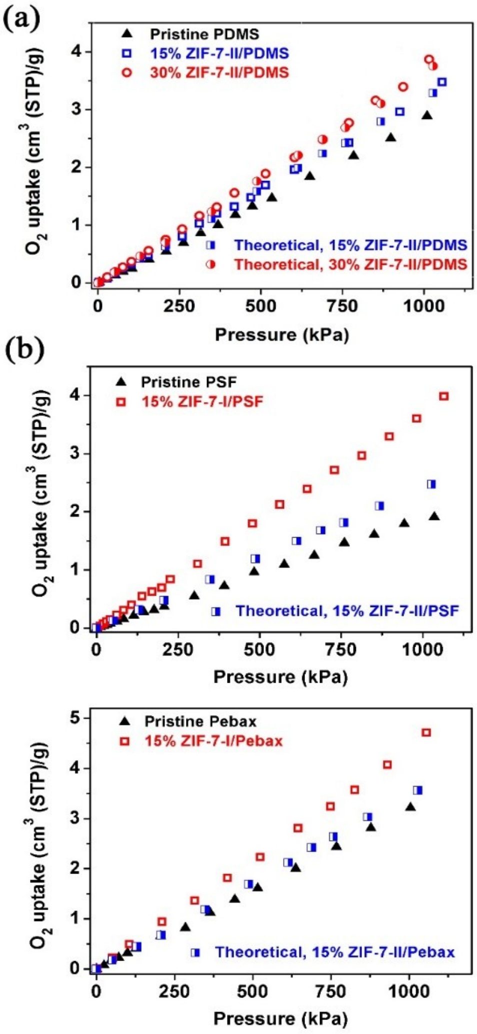

Figure S8. O_2 adsorption properties of pure polymer and mixed-matrix membranes containing ZIF-7 nanocrystals: ZIF-7-II-PDMS, ZIF-7-I-PSF and ZIF-7-I-Pebax®1657. Filled symbols represent the neat polymer membranes, open symbols represent the ZIF-7 loaded MMMs, and right-half-filled squares refer to the theoretical O_2 uptake of mixed-matrix membranes when all ZIF-7-II in membranes are available for O_2 adsorption.

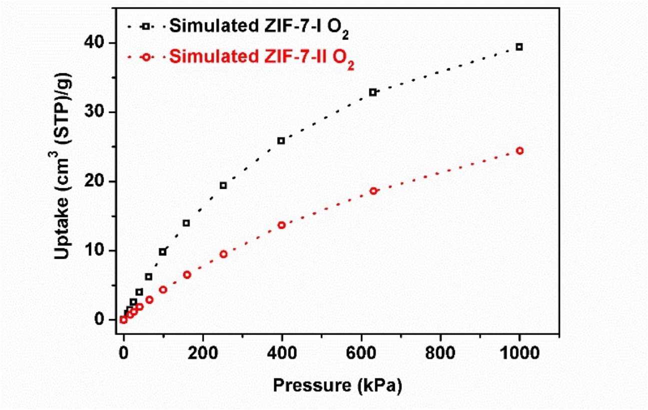

Figure S9. The simulated O_2 adsorption isotherms of ZIF-7-I and ZIF-7-II at 25 °C.

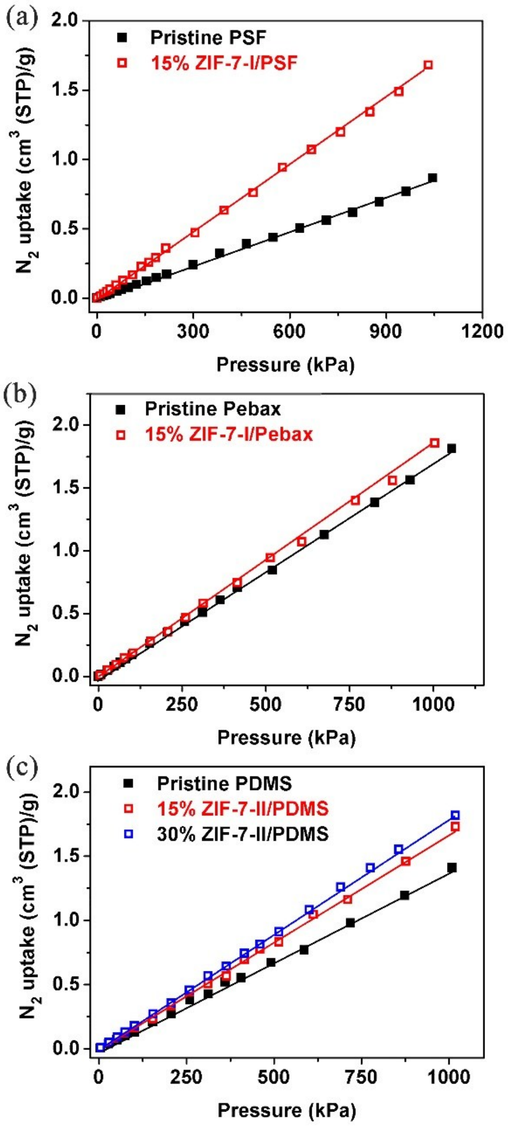

Figure S10. N_2 adsorption properties of pure polymer membranes and mixed-matrix membranes and measured at 35 °C.

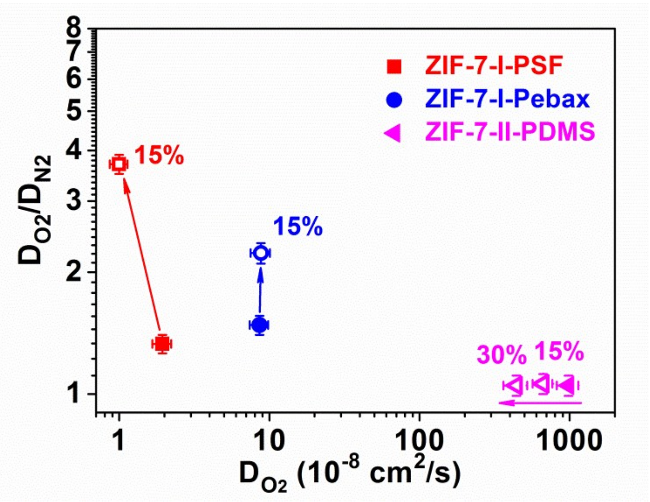

Figure S11. Gas diffusion properties of membranes (ZIF-7-I-PSF, ZIF-7-I-Pebax®1657 and ZIF-7-II-PDMS), filled symbols represent the neat polymer membranes, open symbols represent the ZIF-7 loaded MMMs.

Table S2. Gas diffusion and solution coefficients of the membranes at 35 °C.

Membrane	Solution coefficients (10^{-2} cm^3 (STP)/cm^3 cmHg)		S_{O2}/S_{N2}	Diffusion coefficients (10^{-8} cm^2/s)		D_{O2}/D_{N2}
	O_2	N_2		O_2	N_2	
Pristine PSF	0.31	0.13	2.38	1.94	1.46	1.33
15% ZIF-7-I-PSF	0.53	0.22	2.41	1.00	0.27	3.70
Pristine Pebax®1657	0.45	0.26	1.73	8.67	5.38	1.48
15% ZIF-7-I-Pebax®1657	0.63	0.28	2.25	8.73	3.92	2.23
Pristine PDMS	0.38	0.21	1.81	982	933	1.05
15% ZIF-7-II-PDMS	0.41	0.24	1.79	666	626	1.06
30% ZIF-7-II-PDMS	0.45	0.25	1.80	442	420	1.05

Table S3. Pure component O_2 and N_2 permeation properties of membranes measured at 2 bar upstream pressure and 35 °C.

Membranes	Permeability (Barrer)		Selectivity O_2/N_2
	O_2	N_2	
Pristine BTDA-ODA (PI1)	0.30	0.023	13
15% ZIF-7-I-PI1	0.39±0.03	0.022±0.003	17±1.0
Pristine 6FDA/BPDA-ODA (PI2)	1.50	0.15	10
15% ZIF-7-I-PI1	2.9±0.3	0.19±0.1	15±1.0

Table S4. A comparison of separation performance for O_2/N_2 between this work and other published works.

Polymer	Filler	Pressure [bar]	Temperature [^oC]	P_{O2} [Barrer]	P_{N2} [Barrer]	$\alpha_{O2/N2}$	Ref.
6FDA–6FpDA–PDMS	Zeolite L	4	35	10.78	3.64	2.9	[8]
PC	zeolite 4A	3.7	25	1.77	0.2	8.8	[9]
PES	13X	6.9	25	0.5	0.12	4.17	[10]
PES	4A	6.9	25	1.1	0.25	4.4	[10]
PVAc	4A	2.8	35	0.45	0.06	7.3	[11]
Matrimid®5218	4A	-	35	4	0.56	7.2	[12]
Ultem	4A	-	35	0.28	0.022	12.9	[13]
PSF	PVP-sized CMS	1.5	30	6.52	1.08	6.05	[14]
PSF	silica	3.5	35	1.8	0.31	5.6	[15]
X-Pebax	MWNT	10	30	0.22	0.03	7.1	[16]
PIM-1	silica	3.5	23	2330	880	2.7	[17]
6FDA–MDA	OAPS	2	35	3.54	0.62	5.8	[18]
6FDA-6FpDA	PVP coated Al_2O_3	3	30	18	3.6	5	[19]
Matrimid®5218	ZIF-8	2.7	35	5.5	1.1	5	[20]
PSF	MIL-101	3	30	5.7	1	5.7	[21]
PSF	ZIF-8	2.75	35	2.6	0.31	8.3	[22]
6FDA-4MPD/6FDA-DABA	JDF-L1	3.4	35	30	9.5	3.5	[23]
PVDF	SiO_2	-	-	0.36	0.08	4.5	[24]
PIM-1	ZIF-8	1	22	1640	380	4.3	[25]
PSF	NH2-MIL-53	1.1	22	1.6	0.27	5.9	[26]
PVAc	TiO_2	8	30	0.5	0.07	7.1	[27]
PMDA-ODA	SiO_2	-	-	0.34	0.03	11	[28]
Matrimid+TAP	4A	-	-	0.033	0.0018	18	[29]
PI	4A	-	35	0.37	0.03	12.5	[30]
Matrimid®5218	ZSM-5	2	-	1.8	0.17	10.3	[31]

6FDA-6FpDA-8%-DABA	AlPO	4	35	18.5	2.08	8.9	[32]
Matrimid®5218	MOF-5	2	35	4.12	0.52	7.9	[33]
Pebax®2533	ZIF-8	2	25	120	40	3	[34]
PIM-1	ZIF-71	3.5	35	1602	457	3.5	[35]
PI	ZIF-8@PD	-	35	314	73	4.3	[36]
PU	UiO-66	4	25	6.1	1.1	5.5	[37]

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