Electronic Supplementary Information

Ionic liquid modified MOFs incorporated mixed matrix membrane by metal site anchoring for gas separation

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1. Experimental details

1.1 Materials

The polysulfone (PSf) ultrafiltration membrane with a mean pore diameter of 8-15 nm was obtained from Collaborative Innovation Center for membrane separation and water treatment Of Zhejiang Province. PDMS was purchased from Jinan Xingfeilong Chemical Co. Ltd. N, N-Dimethylformamide (DMF, 99.5 %), n-Hexane (97 %), ethanol (EtOH, 99.7 %) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. Tannic acid (TA, AR), tetraethyl orthosilicate (TEOS, AR), HCl (36 %), formic acid (98 %) were purchased from Sinopharm Chemical Reagent Co. Ltd. Polyvinylpyrrolidone (PVP, K30, molecular weight: 58000 Da), polyvinyl alcohol (PVA, degree of hydrolysis: 98%~99%), di-tin butyl dilaurate (DBTDL, 95 %), 1,3,5-benzenetricarboxylic acid (H_3BTC, 99 %), Zirconium Oxychloride Octahydrate ($ZrOCl_2 \cdot 8H_2O$, 99 %), Bromoacetic acid (98 %), 1-Methylimidazole (99 %) were obtained from Aladdin Reagent Co. Ltd. Pebax®1657 (containing 60 wt% polyethylene oxide (PEO) segment and 40 wt% polyamide (PA) segment) was purchased from Arkema. Pure CO_2 and N_2 were supplied by Hangzhou Jingong Special Gases Co. Ltd. Deionized (DI) water was produced through a self-made RO-EDI system. All reagents do not require further purification.

1.2 Synthesis of MOF-808(Zr) by solvent thermal process

$ZrOCl_2 \cdot 8H_2O$ (3.3 g) and H_3BTC (0.7 g) were dissolved in 300 mL DMF/formic acid mixture (v/v=1:1), placed in a 500 mL round-bottomed flask, connected with a condensing tube, vacuumed inside the flask and filled with N_2 protection. The round-bottomed flask was heated at 130 ℃ for 48 h, and then centrifuge washed with DMF and EtOH after cooling. The sediment was dried in vacuum at 60 ℃ to obtain MOF-808(Zr).

1.3 Synthesis of [mim]Br@MOF-808(Zr) by metal site anchoring

Some amount of MOF-808(Zr) was dispersed in 80 mL HCl solution, heated at 90 ℃ for 12 h under stirring conditions, centrifuged and dried under vacuum to obtain the

pre-treated MOF-808(Zr). Bromoacetic acid was dissolved in 50 mL EtOH, 0.1 g of pre-treated MOF-808(Zr) was added to it, and the reaction was continued at 80 ℃ for 24 h under stirring conditions, the excess substance was removed by washing and re-dispersed in 50 mL EtOH. Then 0.55 mL 1-methylimidazole was added and reacted at 80 ℃ for 12 h, [mim]Br@MOF-808(Zr) was obtained by centrifugation.

1.4 Preparation of MMMs by solvent evaporation and spin coating

The [mim]Br@MOF-808(Zr)/Pebax MMMs were prepared on multi-modified PSf substrate by solvent evaporation method, as shown in Fig. S3. In order to coat an ultra-thin selective layer without defects on porous substrate, PDMS was used as the interlayer to prevent the Pebax layer from penetrating into the pores of the porous substrate. A mixture of n-hexane: PDMS: TEOS: DBTDL was prepared in a ratio of 950:50:5:1. After cross-linking at room temperature, the mixture was spin-coated on the surface of PSf (M0) membrane, denoted by M1. The interface adhesion between the Pebax selective layer and the PDMS interlayer was enhanced by pretreatment technology based on hydrophilic modification of PDMS surface. After the membrane was irradiated by UV lamp for 3 h (M2-U), it was immersed in PVP/TA solution (TA and PVP dissolved in 500ml DI) for 3.5 h, and gently washed with DI to remove free TA and PVP on the surface of the membrane, and dried in oven at 60 ℃, denoted by M2. Finally, 0.1wt% PVA solution was coated on the surface of the membrane by spin coating to complete the hydrophilic modification of the membrane (M3).

The Pebax particles were dissolved in 7:3 (w/w) EtOH/water solvent under continuous stirring at 80 °C, the [mim]Br@MOF-808(Zr) particles of different quality were added and dispersed by stirring to obtain [mim]Br@MOF-808(Zr)/Pebax casting solution. The modified membrane was fixed in the plate frame, the casting solution was added, solvent evaporated at room temperature, and vacuum dried at 50 °C to obtain [mim]Br@MOF-808(Zr)/Pebax MMMs (M4).

1.5 Characterization

The surface and cross-sectional morphology of the membranes were characterized

by scanning electron microscopy (SEM, Hitachi, Japan). The surface functional groups of the membranes were analyzed by Fourier transform infrared spectroscopy (FTIR, iS50, Thermo Fisher Nicolet, USA). The content of elements in the material was analyzed by Inductively Coupled Plasma (ICP-MS: Agilent 7800). The crystal morphology of MOF-808(Zr) was studied by X-ray diffraction (XRD, X'Pert PRO, PNAlytical, Holland). The X-ray photoelectron spectroscopy (XPS, PHI5300, Thermo, USA) analyses were performed with a Thermo Scientific K-Alpha instrument using a monochromated Al-Kα X-ray source. The contact angle (CA) measurements were conducted with the sessile drop method using contact angle meter (OCA50AF, Dataphysics, Germany).

1.6 Evaluation of gas permeability

Gas permeation properties were tested using a constant volume/variable pressure method at specific pressure and 25 °C. The membrane was placed in a stainless-steel module containing two separable parts (effective area = 7.0686 cm^2), and a rubber O-ring was applied in the module to seal the equipment. The penetration volume flow rate of gases is measured by a soap bubble flowmeter. Before testing each gas, both sides of the membranes were swept and the equipment was stabilized for sufficient time to avoid errors. In order to ensure the stability of the data, each gas penetration should be sampled 5 times. The permeability and selectivity of the MMMs in the stable state are calculated by the following formula:

$$J = \frac{Q}{\Delta p \cdot A} \cdot \frac{T_0}{T} \tag{1}$$

$$P_A = \frac{J_A}{l} \tag{2}$$

$$\alpha_{A/B} = \frac{J_A}{J_B} \tag{3}$$

where J is the gas permeability in unit of GPU (1 GPU=10^{-6}·cm^3·(STP)/(cm^2·s·cmHg)), Q is the Gas flow rate measured by soap bubble flowmeters (cm^3/s), Δp is the transmembrane pressure difference (cmHg), A is the area of the membrane with an

effective membrane area of 7.0686 cm^2, and T is the operating temperature (K), T_0 = 273.15 K (standard state temperature). P is the gas permeability coefficient (1 Barrer = 10^{-10}·cm^3·(STP)·cm/(cm^2·s·cmHg)), l is the membrane thickness (cm). α is the ideal selectivity. To verify reproducible results, some permeability measurements were performed with 3 different membranes and the mean values are reported in this paper.

The permeation data for each membrane were collected from at least three distinct samples from different batches, and the permeation test was repeated at least three times for each sample to ensure the accuracy of the data.

2. Results and Discussions

2.1 Characterization:

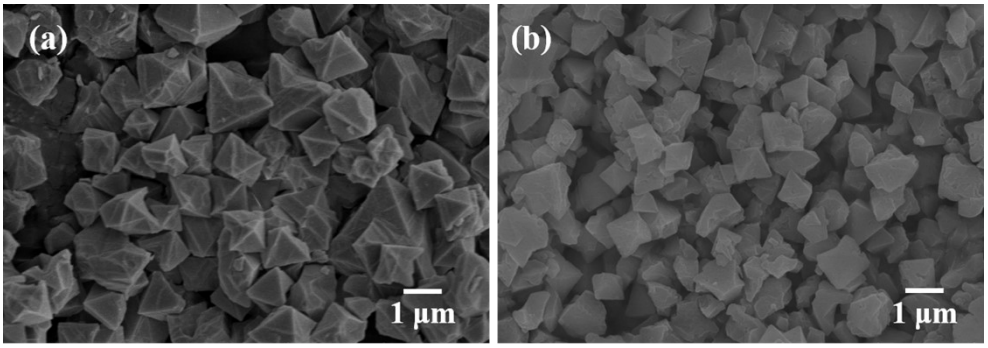

Fig. S1 SEM images of (a) MOF-808(Zr) and (b) [mim]Br@MOF-808(Zr).

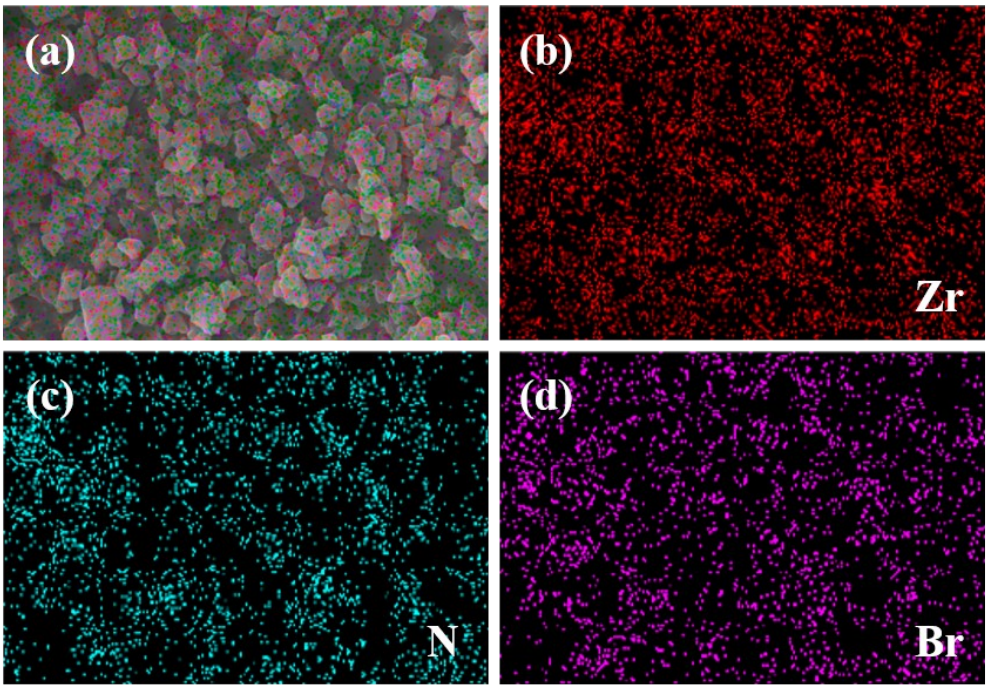

Fig. S2 (a) Elemental maps of [mim]Br@MOF-808(Zr), (b) Zr, (c) N and (d) Br signal elemental maps of the [mim]Br@MOF-808(Zr) particle.

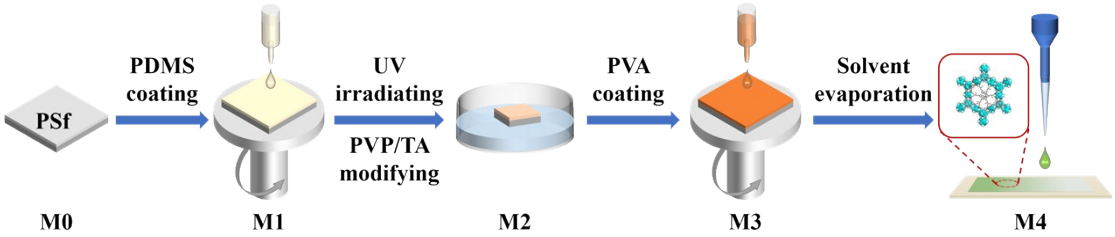

Fig. S3 Schematic of preparation of [mim]Br@MOF-808(Zr)/Pebax MMMs.

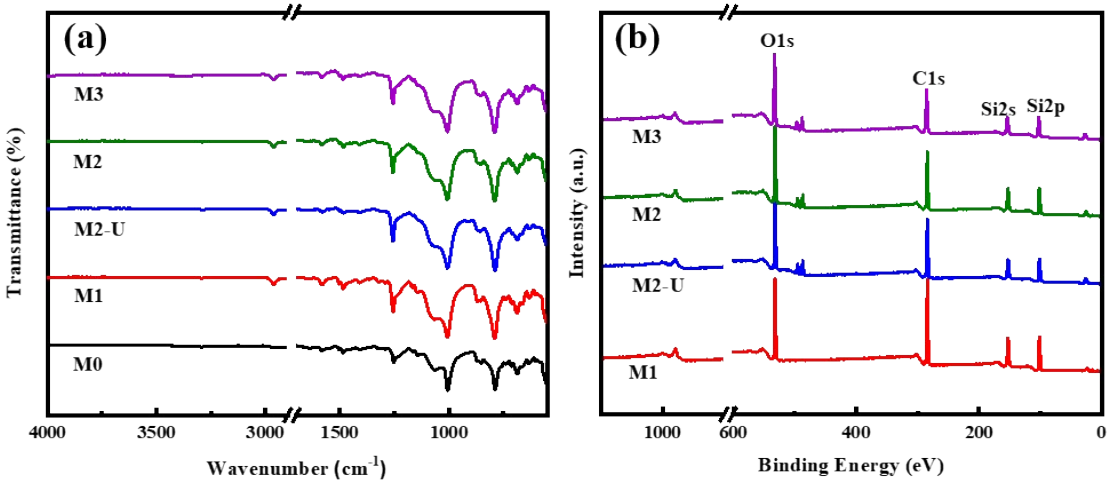

Fig. S4 (a) FT-IR, (b) XPS spectra of interlayer at different modification stages (M1~M3).

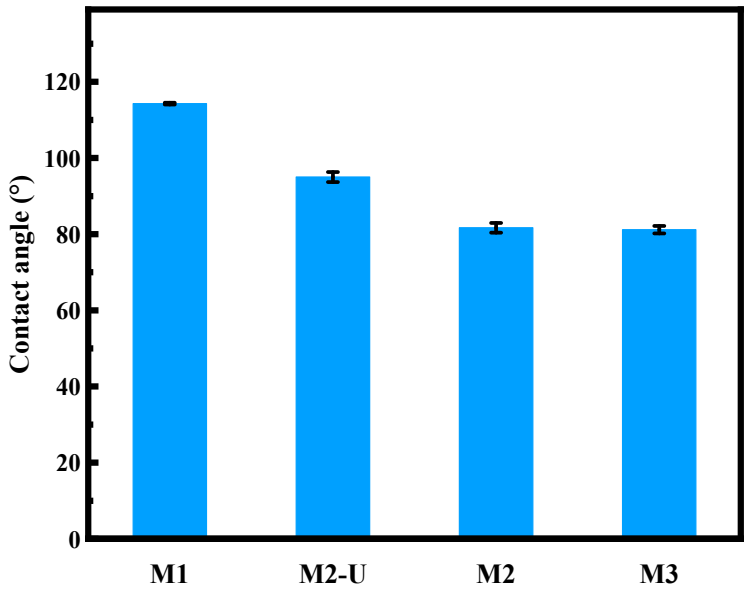

Fig. S5 Contact angle of interlayer at different modification stages (M1~M3).

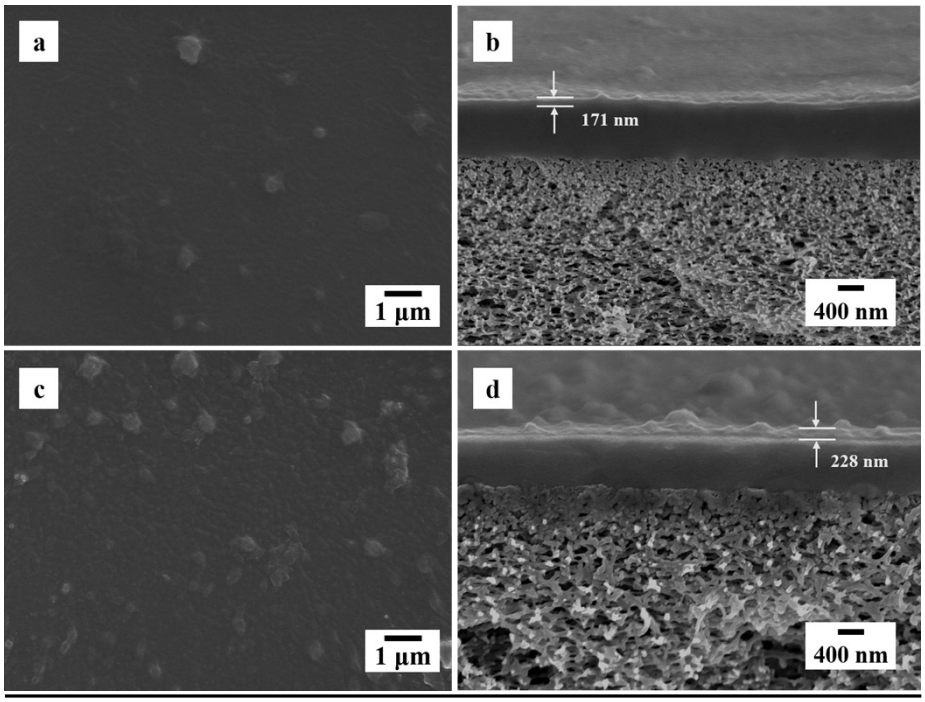

Fig. S6 Surface and cross-sectional SEM images of MMMs under different [mim]Br@MOF-808(Zr) loadings: (a,b) 2.5 wt%, (c,d) 10 wt%.

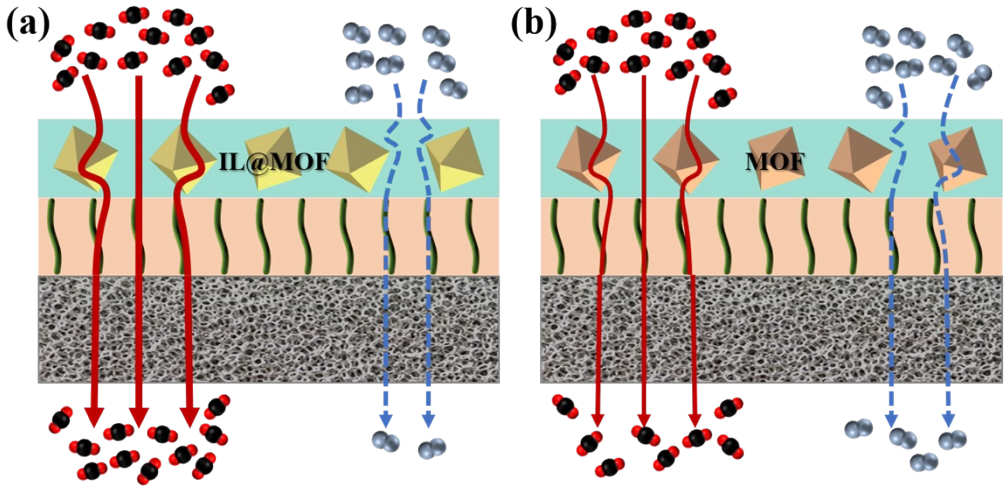

Fig. S7 The transport mechanism of CO_2 and N_2 moleculesacross: (a) [mim]Br@MOF-808(Zr)/Pebax MMM, (b) MOF-808(Zr)/Pebax MMMs.

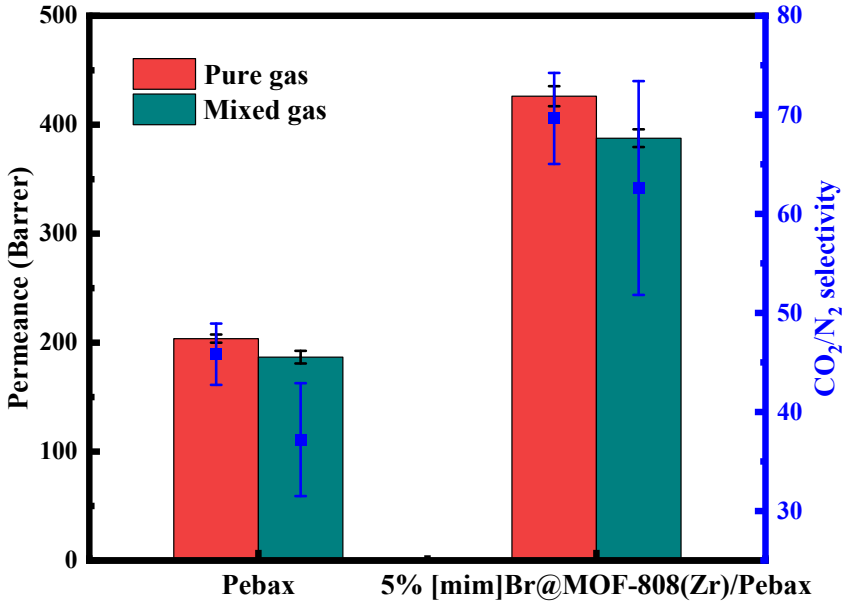

Fig. S8 Pure gas and mixed gas separation performance of the 5% [mim]Br@MOF-808(Zr)/Pebax MMMs (25 ℃, 2 bar).

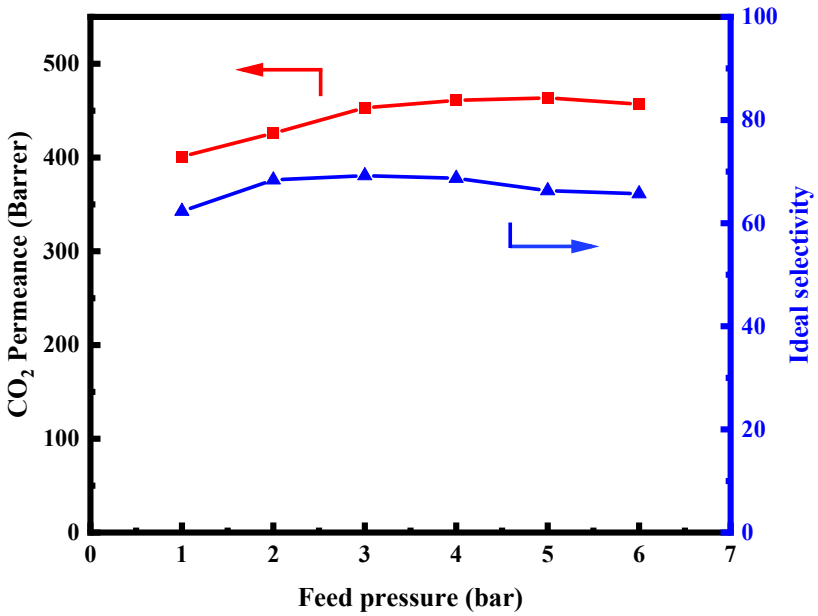

Fig. S9 Performance of the [mim]Br@MOF-808(Zr)/Pebax MMM with 5 wt% fillers loading under varied pressures (25 ℃).

Table S1 Elemental analysis before and after [mim]Br@MOF-808(Zr) washing.

	Zr (%)	Br (%)
Before washing	29.99	4.13
After washing	29.98	4.13

Table S2 Element content of interlayer in different modification stages (M1-M3).

	C (%)	O (%)	Si (%)	C/Si	O/Si
M1	51.43	24.15	24.42	2.1061	0.9889
M2-U	50.24	27.26	22.5	2.2329	1.2116
M2	46.91	29.19	23.9	1.9628	1.221
M3	46.62	32.34	21.04	2.2158	1.5371

2.2 Gas separation performance comparison

Table S3 Separation performance of interlayer at different modification stages (M1-M3).

	CO_2 permeance (GPU)	**CO_2/N_2 selectivity**
M1	2677	10.45
M2	2149	9.53
M3	1193	11.37

Table S4 Comparison of the performance of [mim]Br@MOF-808/Pebax MMMs with the literature in this field.

Filler	Matrix	Condition	CO_2 permeance (Barrer)	CO_2/N_2 selectivity	Refs.
UTSA-16	PTO	30 ℃ 1 bar	184	38	[S1]
SUM-9	Pebax 2533	35 ℃ 6 bar	539	24.69	[S2]
MIL-178(Fe)	Pebax 3533	35 ℃ 3 bar	165	16	[S3]
C_5mimBF_4@ZIF-67	[C_5mim][BF_4] /Pebax 1657	30 ℃ 2 bar	408	97.2	[S4]
UiO-66-NM@PEG	Pebax 1657	25 ℃ 1 bar	307.4	31.4	[S5]
ZIF-94	Pebax 1657	35 ℃ 3 bar	174	25.6	[S6]
ZIF-67-L	Pebax 1657	30 ℃ 2 bar	91.6	51.8	[S7]
ZIF-7/COK-1745(S)	Pebax 1657	25 ℃ 1.2 bar	64.2	183.4	[S8]
ZIF-94	Pebax 1657	35 ℃ 3 bar	152	46	[S9]
[EMIM][OAc]/CuBTC	Pebax 1657	35 ℃ 1 bar	335	176	[S10]
ZIF-8 @NH_2-MIL-125	Pebax 1657	35 ℃ 4 bar	156.7	52.2	[S11]
UiO-66@IL	Pebax 1657	25 ℃ 10 bar	143	61.11	[S12]
PEI-ZIF-62	Pebax 1657	25 ℃ 10 bar	58	83	[S13]
ZIF-90@C_3N_4	Pebax 1657	25 ℃ 2 bar	110.5	84.4	[S14]

NH_2-ZIF-8	Pebax 1657	25 ℃ 1 bar	121.9	96.6	[S15]
PEI@ZIF-8	Pebax 1657	25 ℃ 2 bar	177	72	[S16]
CuBDC-ns@MoS_2	Pebax 1657	35 ℃ 4 bar	123	69	[S17]
UiO-66 PLs	Pebax 1657	25 ℃ 1 bar	113	41.2	[S18]
ZnO@ZIF-8 HNT	Pebax 1657	25 ℃ 5 bar	147	68	[S19]
UiO-66	Pebax 1657	35 ℃ 1.5 bar	114.14	198	[S20]
Cu-BTC-SC	Pebax 1657	25 ℃ 1.5 bar	557.34	63.1	[S21]
MWCNTs@ZIF-8	Pebax 1657	35 ℃ 5 bar	186.3	61.3	[S22]
[Bmim][PF_6]@ZIF-8	Pebax 1657	25 ℃ 2 bar	117	84.5	[S23]
NOTT-300	Pebax 1657	25 ℃ 10 bar	395	61.2	[S24]
[mim]Br@MOF-808(Zr)	Pebax 1657	25 ℃ 2 bar	426.17	69.63	This work

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