Supplementary Information for:

Synthesis of amine-functionalized ZIF-8 with 3-amino-1,2,4triazole by postsynthetic modification for efficient CO₂-selective adsorbents and beyond

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List of Supplementary Information

1. Experimental Section

1.1 Synthesis of ZIF8-A via a direct solvothermal synthesis method.

1.2 Fabrication of a dense polymer membrane and mixed matrix membranes (MMMs).

1.3 Theory and evaluation of gas sorption isotherms.

- 1.4 Theory and evaluation of gas separations.
- 2. Supporting Figures & Tables
- 3. References

1. Experimental Section

1.1 Synthesis of ZIF8-A via a direct solvothermal synthesis method.

A direct solvothermal method was applied for the synthesis of ZIF8-A using a methanol solution containing a mixture of mim and Atz as mixed ligands and $Zn(NO_3)_2 \cdot 6H_2O$ as a metal ion. The mole ratio between metal and ligand was retained as 1:8 for all reactions. The mole ratios of the prepared ligand mixture between mim and Atz were 2/8, 4/6, 6/4, and 8/2 (mim/Atz). The same reaction procedure used for the synthesis of ZIF-8 was applied. In brief, the ligand mixture solution in 10 mL methanol was rapidly poured into $Zn(NO_3)_2 \cdot 6H_2O$ (0.29 g, 0.97 mmol) solution in 10 mL methanol and then the prepared reaction solution was stirred for 2 h at 30 °C. The precipitates were separated from the reaction solution by centrifugation and rinsed with methanol. The centrifugation and rinsing steps were repeated three times. Thereafter, the obtained resultants were dried in an oven at 70 °C for 3 days under reduced pressure for activation.

1.2 Fabrication of a dense polymer membrane and mixed matrix membranes (MMMs).

Polysulfone (PSF) pellets were dried at 100 °C under vacuum overnight to remove any residual solvent and 0.16 g of PSF was dissolved in NMP (1.8 mL) by stirring for 12 h. For fabrication of MMMs, the ZIF-8 or ZIF8-A particles (0.04 mg) were dispersed in NMP (1.8 mL) by two-step sonication using water bath-type sonicator for 30 min and then horn-type sonicator for 3 min, sequentially. To prepare the mixture, the PSF solution was immediately poured into the well-dispersed ZIF suspension. The prepared PSF solution or PSF-ZIF solution mixture was placed on the clean glass plate to fabricate the nonporous dense membranes by a knife-casting method. Thereafter the nascent films were dried at 120 °C under vacuum for 12 h. The fabricated films were peeled off from the glass plate and then dried at 120 °C under vacuum

for 12 h. The applied membrane size was the average thickness and area of ca. 20 μ m and ca. 1.5 cm², respectively.

1.3 Theory and evaluation of gas sorption isotherms.

The sorption isotherms of gas penetrants in microporous materials with a finite number of adsorption sites were described by the Langmuir mode sorption model as follows:¹

$$C_i = \frac{C'_{H,i}b_i p_i}{1 + b_i p_i} \tag{S1}$$

where C_i is the concentration of penetrant *i* in microporous molecular sieves, p_i is the partial pressure of penetrant *i* at equilibrium, $C_{H,i}$ ' is the Langmuir capacity constant (mmol g⁻¹) and b_i is the Langmuir affinity constant (atm⁻¹). All samples were dried at 35 °C under vacuum for 12 h before each measurement and various gas penetrants including CO₂, N₂, CH₄, C₃H₆, and C₃H₈ were tested. The calculated Langmuir parameters of ZIF-8 for C₃H₆ and C₃H₈ were almost identical with the values reported by Zhang *et al.*, supporting the reliability of our sorption data (Tables S2). Unfortunately, the Langmuir model parameters for CO₂, N₂, and CH₄ were not available in their work.² The Langmuir sorption capacity, $C_{H,i}$ ' for N₂, CH₄, C₃H₆ and C₃H₈ decreased monotonically with increasing the Atz conversion due to a reduction in the number of Langmuir adsorption sites while that for CO₂ increased with increasing Atz conversion up to 61% conversion due to enhanced chemisorptions with uncoordinated primary and secondary amines (Tables 1 and S2).

1.4 Theory and evaluation of gas separations.

The separation performance of gas separation membranes is evaluated by two important transport parameters: permeability and permselectivity. Permeability is defined as the flux of gas penetrants through membranes normalized by a given pressure and a membrane thickness;

$$P_i = \frac{N_i \times l}{p_2 - p_1} \tag{S2}$$

where P_i and N_i are the permeability and the flux of gas *i*, respectively. *l* is a thickness of the membrane, and p_1 and p_2 are the pressure of downstream and upstream, respectively. A common unit for permeability is Barrer, and it can be defined as follows.

$$1 Barrer = 10^{-10} \frac{cm^3 (STP) cm}{cm^2 s cmHg}$$
(S3)

The gas transport in dense polymeric membranes is preceded by the solution-diffusion mechanism. Permeability can be expressed by the product of diffusivity (D_i) for a kinetic factor and solubility (S_i) for a thermodynamic factor.

$$P_i = D_i \times S_i \tag{S4}$$

The apparent diffusivity (D) was determined by the time-lag method as follows;

$$D = \frac{l^2}{6\theta} \tag{S5}$$

where *l* is the thickness of the membrane, θ is the diffusion time-lag. For single gas separations, the ideal selectivity, *so-called* permselectivity ($\alpha_{i/j}$) is simply defined as the ratio of the permeability of fast gas penetrant *i* over that of slow gas penetrant *j*. Also, the permselectivity can be expressed as a product of diffusivity selectivity and solubility selectivity as follows.

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i}{D_j} \times \frac{S_i}{S_j}$$
(S6)

The single gas C_3H_6/C_3H_8 separation performance of the pristine PSF membrane and the ZIF-8 or ZIF8-A containing MMMs was evaluated using a constant volume-variable permeation system at 2 atm and 35 °C (Table S4). Note that the ZIF nanoparticles in all MMMs used in this work were well dispersed and exhibited good adhesion with PSF matrices (Fig. S4B – D).

The C₃H₆ permeability and the C₃H₆/C₃H₈ selectivity of the pristine PSF membrane were 0.038 Barrer and 9.5, respectively (Table S4). The PSF/ZIF-8 MMM showed substantially enhanced C₃H₆ permeability (i.e., 0.11 Barrer) due to the free diffusion through ZIF-8 pores and also improved C₃H₆/C₃H₈ selectivity (i.e., 14.2) due to the molecular sieving effect of ZIF-8. Our previous study also demonstrated that both 6FDA-DAM/ZIF-8 and 6FDA-DAM/ZIF-67 MMMs displayed substantially enhanced C₃H₆ permeability and C₃H₆/C₃H₈ selectivity compared to those of the pristine 6FDA-DAM polymeric membrane.¹ The PSF/ZIF8-A-37% MMM, however, exhibited decreases in both C₃H₆ permeability and C₃H₆/C₃H₈ selectivity compared to those of the PSF/ZIF-8 counterpart. In addition, the PSF/ZIF-8-74% MMM further reduced both C₃H₆ permeability and C₃H₆/C₃H₈ selectivity (Table S4 and Fig. 5). It suggests that the gate size of ZIF-8 decreased with increasing Atz conversion.

Table S5 shows the diffusivity and solubility parameters of both C_3H_6 and C_3H_8 for PSF and the ZIF-8 or ZIF8-A containing MMMs. It should be noted that the diffusivity of C_3H_6 for the PSF/ZIF-8 MMM substantially increased compared to that for the PSF membrane (i.e., 0.70 vs. 1.72 cm²/sec) due to the free diffusion through the pores of ZIF-8. Also, the C_3H_6/C_3H_8 diffusivity selectivity of the PSF/ZIF-8 MMM was enhanced compared to that of PSF (i.e., 13.2 vs. 9.0) due to the size sieving effect of ZIF-8. The PSF/ZIF8-A MMMs, however, exhibited a continuous reduction in C_3H_6 diffusivity with increasing the Atz conversion compared to that of PSF/ZIF-8 MMM. Also, the PSF/ZIF8-A37% MMM exhibited a decrease in the diffusivity selectivity (i.e., 11.0), and the PSF/ZIF8-74% MMM showed an even further reduction in the diffusivity selectivity (i.e., 9.8), although these C_3H_6/C_3H_8 diffusivity selectivities are still higher than that of the pristine PSF membrane. It suggested that the replacement of mim with Atz in ZIF-8 induced reduction in its gate size. Meanwhile, all the membranes used in this work exhibited the C_3H_6/C_3H_8 solubility selectivity of unity due to the similar boiling points of them (i.e., $T_{b,C3H6}$: -47.6 °C and $T_{b,C3H8}$: -42.1 °C).³



2. Supporting Figures & Tables

Fig. S1 (A) ¹H NMR spectra of ZIF-8 and ZIF8-A prepared by a direct synthesis method with different ligand ratios between Atz and mim ranging from 0/10 to 10/0. (B) The plot for Atz in solution vs. Atz in framework contents for the synthesis of ZIF8-A and resultants from the reaction, respectively.



Fig. S2 TGA curves of ZIF-8, ZIF8-A15%, ZIF8-A37%, ZIF8-A61%, and ZIF8-A74%, measured under N_2 atmosphere at a flow rate of 10 °C/min.



Fig. S3 (A) N_2 adsorption (close)/desorption (open) isotherms and (B) pore-size distribution for ZIF-8 and ZIF8-A with different Atz conversions.

Entry	Modification method	Measurement condition	CO ₂ uptake (mmol g ⁻¹)	CO_2 uptake (cm ³ g ⁻¹)	Ref.
ZIF-8		308K, 2 bar	0.99	12.5	this work
ZIF8-A15%	PSM of ZIF-8 with HAtz	308K, 2 bar	1.95	24.6	this work
ZIF8-A37%	PSM of ZIF-8 with HAtz	308K, 2 bar	2.23	28.1	this work
ZIF8-A61%	PSM of ZIF-8 with HAtz	308K, 2 bar	2.51	31.6	this work
ZIF8-A74%	PSM of ZIF-8 with HAtz	308K, 2 bar	1.03	13.0	this work
ZIF-67		273K, 1 atm		28.7	5
ZIF-68		273K, 0.08 MPa	2.60		6
ZIF-69		273K, 0.08 MPa	2.70		6
ZIF-7		303K, 100kPa	2.25		7
ZIF-78		298K, 1 atm		51	8
ZIF-79		298K, 1 atm		34	8
ZIF-8		308K, 2 bar	1.00		2
ZIF-81		298K, 1 atm		39	8
ZIF-82		298K, 1 atm		51	8
ZIF-93		298K, 1 atm	1.7		9
ZIF-94		298K, 1 atm	2.4		9
ZIF-8-NH ₂ ^a	Modification of	298K, 5 bar	3.10		10
$ZIF-8-(NH_2)_2^a$	ZIF-8 structure with simulation	298K, 5 bar	4.50		10
ED-ZIF-8 ^b	PSM of ZIF-8 with Ethylene Diamine	308K, 2.5 bar	1.48		11
ZIF-8-90- (50)	In situ substitution of ZIF-8 with 2- amBzIm	308.15K, 200 kPa	2.50		12
ZIF-7-NH ₂ (70)	In situ substitution of ZIF-7 with 2-	308K, 250 kPa		32	4

Table S1. Summary of the CO_2 uptake capacity for state-of-the-art ZIFs and modified ZIFs.

	amBzIm				
Zn40-ZIF-67	Zn-doping on ZIF-67	273K, 1 atm		26.6	5
ZIF-7/8 (10 % bIm)	PSM of ZIF-8 with bIm	273K, 100 kPa	1.5		13
ZIF-7/8 (44% bIm)	PSM of ZIF-8 with bIm	273K, 100 kPa	2.5		13
Zn/Co-ZIF	Mix with Zn and Co salt with 2- mim	273K, 1 bar		34.16	14
LeZIF8- NO ₂ Im _{168h} ^c	Solvent-assisted ligand exchange with NO ₂ Im	273K, 900 mmHg		76	15
LeZIF8- SHBzIm _{72h} ^d	Solvent-assisted ligand exchange with SHBzIm	273K, 900 mmHg		77	15
LeZIF8- NH ₂ BzIm _{168h} ^e	Solvent-assisted ligand exchange with NH ₂ BzIm	273K, 900 mmHg		38.5	15
LeZIF8- PhIm _{168h} ^f	Solvent-assisted ligand exchange with PhIm	273K, 900 mmHg		43	15

^a The value was derived from the theoretical calculation.

^b The mim linker of ZIF-8 was replaced partially by Ethylene Diamine (ED).

^c Mixed ligands of NO₂Im and mim were present in a mole ratio of 66.6:33.4 in the Ligand exchanged (Le) ZIF-8.

^d Mixed ligands of SHBzIM and mim were present in a mole ratio of 12:88 in the Ligand exchanged (Le) ZIF-8.

^e Mixed ligands of NH₂BzIM and mim were present in a mole ratio of 16:84 in the Ligand exchanged (Le) ZIF-8.

^fMixed ligands of PhIM and mim were present in a mole ratio of 10:90 in the Ligand exchanged (Le) ZIF-8.

		ZIF8-	ZIF8-	PSF/ZIF-8	PSF/ZIF8-	PSF/ZIF8-
	ZIF-8	A37%	A74%		A37%	A74%
ZnO wt%	36.1	35.7	35.4	7.1	7.2	7.09
Zn wt%	29.0	28.7	28.4	5.7	5.8	5.7
ZIF-8 wt% loading	N/A	N/A	N/A	19.7	20.2	20.1

 Table S2.
 The actual ZIF-8, ZIF8A-37%, and ZIF8-A74% concentration in each MMM.

Table S3. Langmuir model parameters for C_3H_6 and C_3H_8 in ZIF nanoparticles at 35 °C.

	Langmuir model parameter					
Entry	C_3H_6		C_3H_8		Ref	
	$\frac{C_{H}}{(\text{mmol g}^{-1})}$	b (atm ⁻¹)	C_{H} (mmol g ⁻¹)	b (atm ⁻¹)		
ZIF-8	6.19 ± 0.06	1.97 ± 0.06	5.40 ± 0.09	2.88 ± 0.19	This work	
ZIF8-A37%	4.27 ± 0.09	1.67 ± 0.23	3.47 ± 0.07	1.40 ± 0.07	This work	
ZIF8-A74%	2.98 ± 0.14	1.45 ± 0.08	3.16 ± 0.20	1.08 ± 0.16	This work	
ZIF-8	6.36	1.72	5.65	2.58	2	

Table S4. Single gas permeability and selectivity of PSF, PSF/ZIF-8, PSF/ZIF8-A37%, and PSF/ZIF8-A74% at 2 atm and 35 °C.

Sample	Particle (wt%)	P _{C3H6} (Barrer)	P _{C3H8} (Barrer)	$C_{3}H_{6}/C_{3}H_{8}$ (-)
PSF	0	0.038	0.004	9.5
PSF/ZIF-8	20	0.44	0.031	14.2
PSF/ZIF8-A37%	20	0.29	0.026	11.2
PSF/ZIF8-A74%	20	0.13	0.014	9.5



Fig. S4 (A) FT-IR spectra of PSF/ZIF-8, PSF/ZIF8-A37%, and PSF/ZIF8-A74% MMMs and the cross-sectional FE-SEM images of (B) PSF/ZIF-8, (C) PSF/ZIF8-A37%, and (D) PSF/ZIF8-A74% MMMs. Note that all three MMMs contain the same concentration of ZIF crystallites (20 wt%).

Sample	$D_{\rm C3H6}$	$D_{\rm C3H8}$	$D_{\rm C3H6}/D_{\rm C3H8}$	<i>S</i> _{C3H6}	$S_{\rm C3H8}$	S _{C3H6} /S _{C3H8}
PSF	0.70	0.08	9.0	5.41	4.95	1.1
PSF/ZIF-8	1.72	0.13	13.2	25.8	23.9	1.1
PSF/ZIF8-A37%	1.43	0.13	11.0	20.3	19.8	1.0
PSF/ZIF8-A74%	1.18	0.12	9.8	11.2	11.6	1.0

Table S5. Diffusivity and solubility of propylene and propane for PSF, PSF/ZIF-8, PSF/ZIF8-A37%, and PSF/ZIF8-A74% at 2 atm and 35 °C.

 \overline{D} is the diffusivity (\times 10⁻¹⁰, cm² sec⁻¹).

S is the solubility (\times 10⁻², cm³ (STP) cm⁻³ (MMM) cmHg⁻¹).



Fig. S5 Representative FE-SEM images of (A) ZIF8-A57%, (B) ZIF8-MA17%, and (C) ZIF8-MH13%.



Fig. S6 ¹³C NMR spectra of the ZIF-8, ZIF8-A57%, ZIF8-MA17%, and ZIF8-MH13% (H_2SO_4/CD_3OD (10/90 v/v) solution).

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