Supplementary Information for

Highly Selective Filler-Polymer Gaps *In-situ* Fabricated in Mixed Matrix Membranes for Gas Separation

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1. Materials

Cupric acetate (98%+), 4-fluorobenzoic acid (99%) and 4-bromobenzoic acid (99%) were purchased from Energy Chemical Co. Ltd. (Shanghai, China). 4-Chlorobenzoic acid (99%) and 4-iodobenzoic acid (98%) were purchased from J&K Scientific Co. Ltd. (Beijing, China). Polydimethylsiloxane (PDMS), tetraethyl orthosilicate (TEOS), dibutyltin dilaurate (DBD), n-heptane and polyvinyl alcohol (PVA) (polymerization degree of 1700 and hydrolysis degree of 87-89%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Anhydrous methanol was purchased from Guoyao Chemical Research Institute (Tianjin, China) and the reagent was used without further treatment. N-Vinylformide (NVF, 98%) was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China), and distilled under vacuum before used, then stored at -10 °C. 2,2'-Azobis (2-methylpropionamidine) dihydrochloride (AIBA, 98%) was purchased from Sigma-Aldrich. It was further recrystallized from ethanol and stored at 0 °C. The polysulfone (PSf) ultrafiltration membrane with a mean pore diameter of 20~50 nm was obtained from Shandong Jiuzhang Membrane Technology Co., Ltd. (China), and used after immersing into deionized water for 12 h.

2. Synthesis and characterization of halogen-induced metal polymer (HMP) particles.

A new class of HMP particles were *in-situ* synthesized with reference to the method of solid reaction at low-temperature.^[1] Typically, $Cu^{2+}(CH_3COO^{-})_2$ (0.90 g, 5 mmol) was dissolved in 50 mL deionized water, and 4-fluorobenzoic acid (1.40 g, 10 mmol) was dissolved in 100 mL methanol. Subsequently, the two solutions were

mixed under vigorous stirring. The mixed solution became turbid soon and the suspension was kept under stirring at 30 °C for another 10 h. After that, the suspension was centrifuged and washed with deionized water and methanol (3 times), respectively. Finally, the crystalline particles were obtained (denoted as P_{4-F}), and dried at 80 °C under vacuum for the next test.

The synthetic processes for P_{4-Cl} , P_{4-Br} , and P_{4-I} crystalline particles are similar to P_{4-F} , excepting that different ligand masses were used (1.56 g of 4-chlorobenzoic acid, 2.01 g of 4-bromobenzoic acid, and 2.48 g of 4-iodobenzoic acid, respectively).

The HMP particles were characterized by Fourier transform infrared spectroscopy (FTIR, TENSOR II, Bruker, Germany), powder X-ray diffraction (XRD, D2 Discover, Bruker, Germany), scanning electron microscopy (SEM, Gemini SEM500, ZEISS, Germany), X-ray photoelectron spectrometer (XPS, Thermo Fisher, UK), and the contact angle analyzer (Drop Shape Analyzer 100, KRUSS GmbH Co., Hamburg, Germany).

3. Fabrication of MPSf and HMP/MPSf membranes.

A highly permeable and hydrophilic interface layer was firstly fabricated by coating PDMS and PVA on the PSf support layer in sequence (denoted as MPSf membrane), based on our previous work with a slight change.^[2-3] The synthetic procedures are similar, excepting that the different PDMS concentration of 0.4 wt% and different PVA concentration of 0.025 wt%. PDMS coated on the PSf support layer is used to improve surface uniformity, and PVA coated on the PDMS layer is to improve membrane hydrophilicity. The affinity between two coating layers depends

not only on the relationship between hydrophilicity and hydrophobicity, but also on the factor like interaction.^[4] The PVA used in this work is type 1700, and the degree of alcoholysis is about 89%. This means that PVA has abundant -OH groups, which can form hydrogen bond with Si–O bonds in PDMS during coating.^[4] The SEM cross-sectional image of MPSf membrane (See Figure 2) shows no delamination between the PDMS and PVA layers.

Secondly, the HMP particles were *in-situ* formed on the interface layer. A ligand solution (60 mmol/L) (4-fluorobenzoic acid, 4-chlorobenzoic acid, 4-bromo-benzoic acid, and 4-iodide benzoic acid, respectively) was prepared, and the solution was coated on the MPSf membrane using a 300 µm scraping knife to form a uniform ligand layer (ligand/MPSf membrane). Then, the membrane was dried at 30 °C and 40% RH for at least 8 h. Next, in order to facilitate the complete reaction between the halogen benzoic acid in the membrane and copper acetate, the ligand/MPSf membrane was putted into an aqueous solution with excessive copper acetate to *insitu* form HMP particles on the membrane surface. After the reaction, remove and clean the residual copper acetate with water on the surface membrane, followed by drying the membranes at 30 °C and 40% RH for 24 h. The formed membranes were represented by HMP/MPSf membrane, denoted as HMP(F)/MPSf membrane, HMP(C1)/MPSf membrane, HMP(Br)/MPSf membrane and HMP(I)/MPSf membrane, respectively.

4. Fabrication of PVAm/MPSf and PVAm-HMP/MPSf MMMs.

Polyvinylamine (PVAm) was synthesized based on the protocol described in the

previous work.^[5-6] PVAm solution was coated on the HMP/MPSf membrane, and formed the PVAm-HMP/MPSf mixed matrix membranes (MMMs). The formation process of the PVAm-HMP/MPSf MMMs was as follow.

0.3 wt% of PVAm aqueous solution was used to fabricate the MMMs with a wet coating thickness of 300 μ m, followed by drying the membrane at 30 °C and 40% RH for 24 h.

For comparison, PVAm/MPSf membrane was prepared by the same way.

5. Characterization of membranes.

HMP/MPSf membranes were characterized by scanning electron microscopy (SEM, Hitachi S-4800, Japan), atomic force microscope (AFM, Agilent-S5500, USA), X-ray diffractometer (XRD, D8 Discover, Bruker) and the contact angle analyzer (Drop Shape Analyzer 100, KRUSS GmbH Co., Hamburg, Germany). Fourier transform attenuated total reflection infrared spectrum (ATR-FTIR, TENSOR II, Bruker, Germany) and positron annihilation (PALS) experiments based on the method described in the literature^[7-8] were tested for PVAm-HMP/MPSf MMMs. PVAm/MPSf membrane was also characterized by SEM mentioned above.

Gas permeances of the membranes were measured by gas permeance test equipment.^[9] Three individual membranes of every type were tested, and the standard deviations are represented by error bars. Membranes were mounted in a circular stainless-steel cell (effective membrane area = 19.26 cm^2). Dried He served as the downstream sweep gas for pure and mixed gas tests. The downstream sweep gas composition was analyzed using a gas chromatograph equipped with a thermal conductivity detector (HP7890, Porapak N). The downstream pressure in the apparatus was maintained at atmospheric pressure. Permeation experiments were carried out at room temperature, and steady state permeation was assumed to have been reached when the sweep gas flowrate and composition remained unchanged over time. The gas permeability (P) can be calculated by Eq. (S1)^[10]:

$$P = R \times l \tag{S1}$$

Where *P* is the gas permeability (in units of barrer, 1 barrer= 10^{-10} cm³(STP) cm·cm⁻ ²·s⁻¹·cmHg⁻¹= 3.35×10^{-16} mol m·m⁻²·s⁻¹·Pa⁻¹), *R* is the gas permeance (in units of GPU, 1 GPU= 10^{-6} cm³(STP)·cm⁻²·s⁻¹·cmHg⁻¹) = 3.35×10^{-10} mol·m⁻²·s⁻¹·Pa⁻¹), and *l* is the thickness of selective layer (in units of μ m).

6. Supporting tables and figures



Figure S1. Morphology analysis of P_{4-F} , P_{4-Cl} , P_{4-Br} and P_{4-I} .



Figure S2. (A) FTIR spectra of cupric acetate, halogen benzoic acid and HMP particles; (B) XPS wide-scan spectra of HMP particles. The FTIR characteristic peaks are at 1228 cm⁻¹ (C-F), 764 cm⁻¹ (C-Cl), 530 cm⁻¹ (C-Br), and 522 cm⁻¹ (C-I). The adsorption peaks at 1593 cm⁻¹ and 1539 cm⁻¹, are attributed to the C=O conjugated with the aromatic ring and C=C. With the variation of stretching vibration peak of C=O belonging to halogen benzoic acid at 1676 cm⁻¹, Cu²⁺ ions in the HMP particles were coordinated with carboxyl groups belongs to the bridging bidentate ligand.^[11] The XPS peaks at 687.2 eV, 201.2 eV, 71 eV, and 620.8 eV are corresponding to F1s, Cl2p, Br3d, and I3d, respectively. Furthermore, the chemical compositions were calculated (Table S1).



Figure S3. PXRD patterns of P_{4-F} , P_{4-Cl} , P_{4-Br} , and P_{4-I} . Although the ligand structures of HMP particles (P_{4-F} , P_{4-Cl} , P_{4-Br} and P_{4-I}) are similar, the differences in electronegativity and ligand size for halogen atoms have an effect on the HMP structures, which leads to XRD pattern variations.



Figure S4. Water contact angles of P_{4-F} , P_{4-Cl} , P_{4-Br} and P_{4-I} particles.



Figure S5. XRD patterns of HMP particles after immersing into the deionized water, acid and alkali solutions at 30 °C for 24 h. When the pH is lower than 2, the ligands of the HMP particles tend to establish dynamic ionization equilibrium and exist as molecules in the solution rather than metal-ligand complexes,^[12] which possibly destroys the HMP structure. When the pH is higher than 12, the Cu²⁺ ions of the HMP particles with strong hydrolysis effect tends to form Cu(OH)₂ precipitation in the solution.^[13]



Figure S6. ATR-FTIR spectra of the MPSf membrane and PVAm-HMP/MPSf MMMs.



Figure S7. SEM cross-sectional image of PVAm/MPSf membrane.



Figure S8 Representation of the transport model of CO₂ and N₂ molecules in the gaps.



Figure S9. (A) Mixed CO₂ permeance of MPSf membrane and PVAm/MPSf membranes; (B) Mixed CO₂ permeance of HMP/MPSf membranes and PVAm-HMP/MPSf MMMs. CO₂/N₂ mixed gas (15/85 by volume), 298K.

Power	Composition (At. %)				
	Cu 2P ³	F/Cl/Br/I			
P _{4-F}	2.79	3.24			
P _{4-Cl}	6.67	8.89			
P _{4-Br}	3.99	4.88			
P _{4-I}	4.19	4.94			

Table S1 Chemical compositions of the HMP particles

Samples	$\tau_3(ns)$	I ₃ (%)	$ au_4(ns)$	I ₄ (%)	R ₃ (nm)	R ₄ (nm)	Pore size
PVAm film	1.44	14.97	/	/	0.23	/	/
PVAm-HMP(F) film	0.86	6.80	3.30	16.02	0.14	0.38	0.76
PVAm-HMP(Cl) film	1.15	7.14	3.47	15.82	0.19	0.42	0.84
PVAm-HMP(Br) film	0.98	7.78	4.56	18.00	0.16	0.45	0.90
PVAm-HMP(I) film	1.58	3.74	8.25	16.00	0.24	0.60	1.20

 Table S2 Pore size of the gaps in the PVAm-HMP/MPSf MMMs obtained by

positron annihilation spectrum (PALS) [7,8,14-16]

Uniformly distributed PVAm and PVAm-HMP films were prepared into a block of 1 cm × 1 cm with a thickness of about 1 mm. Five samples were clamped on both sides of the ²²Na source to form a typical "sandwich" geometry. All the PALS were analyzed by a finite-term lifetime analysis method using a PATFIT program.^[7] Tao et al ^[8] correlated the positron annihilation lifetime with the pore radius (R_3 and R_4 in the Table), and obtained the pore radius based on the derivation of Schrodinger's equation. The hypothesis based on Tao et al. is reasonable for polymers with flexible chains or relatively stiff chains.^[14] The pore characteristics and physicochemical properties of the gaps formed between PVAm and HMP particles are similar to those of the hypothesis proposed by Tao et al., therefore, the pore radius acquired is credible. However, PVAm with a large amount of amino groups and strong intermolecular interactions has a sufficiently strong rigid structure and is used to as dense membrane materials,^[15-16] therefore, the pore radius is not credible. PVAm-HMP(F) film is the sample that PVAm-HMP(F) selective layer formed on PVA/PDMS film; PVAm-HMP(Cl) film is the sample that PVAm-HMP(Cl) selective layer formed on PVA/PDMS film; PVAm-HMP(Br) film is the sample that PVAm-HMP(Br) selective layer formed on PVA/PDMS film; and PVAm-HMP(I) film is the sample that PVAm-HMP(I) selective layer formed on PVA/PDMS film.

			1				
Samples	Pure	Pure CO ₂ permeability (barrer)			Mixed CO ₂ permeability (barrer)		
	1.1 bar	1.5 bar	3 bar	1.1 bar	1.5 bar	3 bar	
PVAm	110	99	86	111	98	90	
PVAm-HMP(F)	520	497	495	511	492	461	
PVAm-HMP(Cl)	771	758	747	871	838	804	
PVAm-HMP(Br)	811	800	793	939	914	899	
PVAm-HMP(I)	995	991	969	1022	1013	978	

Table S3 Pure and mixed CO_2 permeabilities of PVAm and PVAm-HMP selective

layers at different pressure

Membrane	CO ₂ Permeance (GPU)	CO ₂ /N ₂ Selectivity	Symbols in Figure 5	Ref.
MXene (0.15 wt%)/Pebax	21	72.5	•	[17]
ZIF-8@GO/PEDM	9.5	58.2		[18]
SP ₅ -Tf ₂ N-ME (5 wt%)/PSf membrane	7.19	44.9		[19]
Si (3%)/PC	24.4	38		[20]
Uio-66-COOH (50 wt%)/Pebax	240	50		[21]
ZIF-7 (30 wt%)/Pebax	300	48		[21]
All-silica ZSM-58	870	44		[22]
PAN-r-PEGMA67	51	65		[23]
$Ms_1P_{0.6}$	2700	20		[24]
$Ms_2P_{0.4}$	770	5		[24]
PtP-3	167	77.2		[25]
BUPP/PSf	1295	91	_	[26]
AMT/PSf	820	120	•	[27]
COF-PVAm/PSf	1168	68.3		[28]
HKUST-1-IL-CS	2244	5.51	<	[29]
4A-PTMSP	1251	7.06	*	[29]
СНА	2418	25.1		[30]
Y-type	627	31.2		[31]
PVAm-HMP(F)/MPSf	1897	69	*	This work
PVAm-HMP(Cl)/MPSf	2535	14.52	*	This work
PVAm-HMP(Br)/MPSf	2971	7.21	*	This work
PVAm-HMP(I)/MPSf	3418	3.3	*	This work

Table S4. Comparison of CO_2/N_2 separation performance

References

- [1] P. Stachová, D. Valigura, M. Koman, M. Melník, M. Korabik, J. Mroziński, and T. Glowiak, *Polyhedron*, 2004, 23, 1303-1308.
- [2] Y. Gao, Z. Qiao, S. Zhao, Z. Wang, and J. Wang, J. Mater. Chem. A, 2018, 11, 3151-3161.
- [3] Z. Qiao, S. Zhao, M. Sheng, J. Wang, S. Wang, Z. Wang, C. Zhong, and M. D. Guiver, *Nat. Mater.*, 2019, 18, 163-168.
- [4] B. Wang, Z. Qiao, J. Xu, J. Wang, X. Liu, S. Zhao, Z. Wang, and M. D. Guiver, *Adv. Mater.*, 2020, 1907701.
- [5] S. Zhao, Z. Wang, Z. Qiao, X. Wei, C. Zhang, J. Wang, and S. Wang, J. Mater. Chem. A, 2013, 1, 246-249.
- [6] J. Liao, Z. Wang, C. Gao, M. Wang, K. Yan, X. Xie, S. Zhao, J. Wang, and S. Wang, J. Mater. Chem. A, 2015, 3, 16746-16761.
- [7] R. Xia, X. Cao, M. Gao, P. Zhang, M. Zeng, B. Wang, and L. Wei, *Phys. Chem. Chem. Phys.*, 2017, **19**, 3616-3626.
- [8] S. J. Tao, J. Chem. Phys., 1972, 56, 5499-5510.
- [9] X. Yu, Z. Wang, Z. Wei, S. Yuan, J. Zhao, J. Wang, and S. Wang, J. Membr. Sci., 2010, 362, 265-278.
- [10] X. Cao, H. Xu, S. Dong, J. Xu, Z. Qiao, S. Zhao, J. Wang, and Z. Wang, J. Membr. Sci., 2020, 601, 117882.
- [11] R. Świsłocka, M. Kalinowska, W. Ferenc, J. Sarzyński, and W. Lewandowski, Cent. Eur. J. Chem., 2012, 10, 1095-1105.
- [12] W. Zhang, A. Bu, Q. Ji, L. Min, S. Zhao, Y. Wang, and J. Chen, ACS Appl.

Mater. Inter., 2019, 11, 33931-33940.

- [13]M. Liu, M. A. Little, K. E. Jelfs, J. T. A. Jones, M. Schmidtmann, S. Y. Chong, T. Hasell, and A. I. Cooper, *J. Am. Chem. Soc.*, 2014, **136**, 7583–7586.
- [14] C. Nagel, E. Schmidtke, K. Günther-Schade, D. Hofmann, D. Fritsch, and T. Strunskus, F. Faupel, *Macromolecules*, 2000, **33**, 2242-2248.
- [15] Y. Chen, L. Zhao, B. Wang, P. Dutta, and Ho W. S. Winston, J. Membr. Sci., 2016, 497, 21-28.
- [16] Z. Qiao, Z. Wang, C. Zhang, S. Yuan, Y. Zhu, J. Wang, and S. Wang, AIChE J., 2013, 59, 215-228.
- [17] G. Liu, L. Cheng, G. Chen, F. Liang, G. Liu, and W. Jin, Chem-Asian J., 2019.
- [18] B. Chen, C. Wan, X. Kang, M. Chen, C. Zhang, Y. Bai, and L. Dong, Sep. Purif. Technol., 2019, 223,113-122.
- [19] N. N. R. Ahmad, C. P. Leo, and A. L. Ahmad, *Micropor. Mesopor. Mater.*, 2019, 283, 64-72.
- [20] A. Idris, Z. Man, and A. S. Maulud, J. Appl. Poly. Sci., 2017, 134, 45310.
- [21] P. D. Sutrisna, J. Hou, M. Y. Zulkifli, H. Li, Y. Zhang, W. Liang, D. M. D'Alessandro, and V. Chen, J. Mater. Chem. A, 2018, 6, 918-931.
- [22] E. Hayakawa, and S. Himeno, Micropor. Mesopor. Mater., 2020, 291, 109695.
- [23] M. Karunakaran, M. Kumar, R. Shevate, F. H. Akhtar, and K-V. Peinemann, *Polymers*, 2017, 9, 219.
- [24] K. Xie, Q. Fu, P. A. Webley, and G. G. Qiao, Angew. Chem. Int. Ed., 2018, 57, 8597-8602.
- [25] C. H. Park, J. H. Lee, J. P. Jung, W. Lee, D. Y. Ryu, and J. H. Kim, Angew.

Chem. Int. Ed., 2019, 58, 1143-1147.

- [26] R. Xu, Z. Wang, M. Wang, Z. Qiao, and J. Wang, J. Membr. Sci., 2019, 573, 455-464.
- [27] Z. Qiao, S. Zhao, J. Wang, S. Wang, Z. Wang, and M. D. Guiver, Angew. Chem. Int. Ed., 2016, 55, 9321-9325.
- [28] X. Cao, Z. Wang, Z. Qiao, S. Zhao, and J. Wang, ACS Appl. Mater. Inter., 2019, 11, 5306.
- [29] A. F. Barquin, C. C. Coterillo, M. E. Benavides, J. Zuniga, and A. Irabien, *Chem. Eng. Technol.*, 2017, 40, 997-1007.
- [30] E. Jang,; S. Hong; E. Kim, N. Choi, S. J. Cho, J. Choi, J. Membr. Sci., 2018, 549, 46–59.
- [31] T. L. Chew, Y. F. Yeong, C.i D. Ho, and A. L. Ahmad, *Ind. Eng. Chem. Res.*, 2019, 58, 729-735.