

Electronic Supplementary Information

***In situ* bottom-up growth of metal-organic frameworks in crosslinked
poly(ethylene oxide) layer with ultrahigh loading and superior
uniform distribution**

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1. Characterization of ZIF-8(x)-based mixed matrix membranes prepared using the *in situ* growth approach

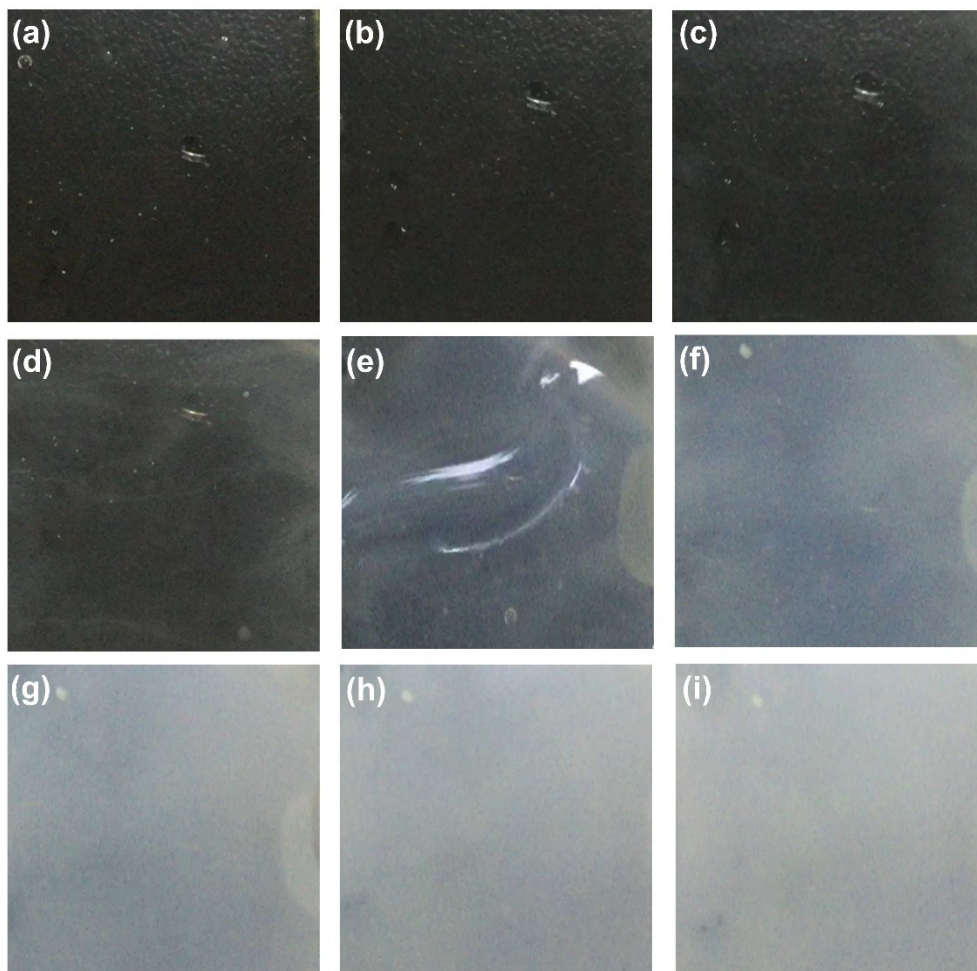


Figure S1. Photographs of ZIF-8(x)-based mixed matrix membranes prepared via free-radical polymerization at 65 °C for 2 h, and then immersed in water at room temperature for different periods of time, (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5, (g) 6, (h) 7, and (i) 8 min.

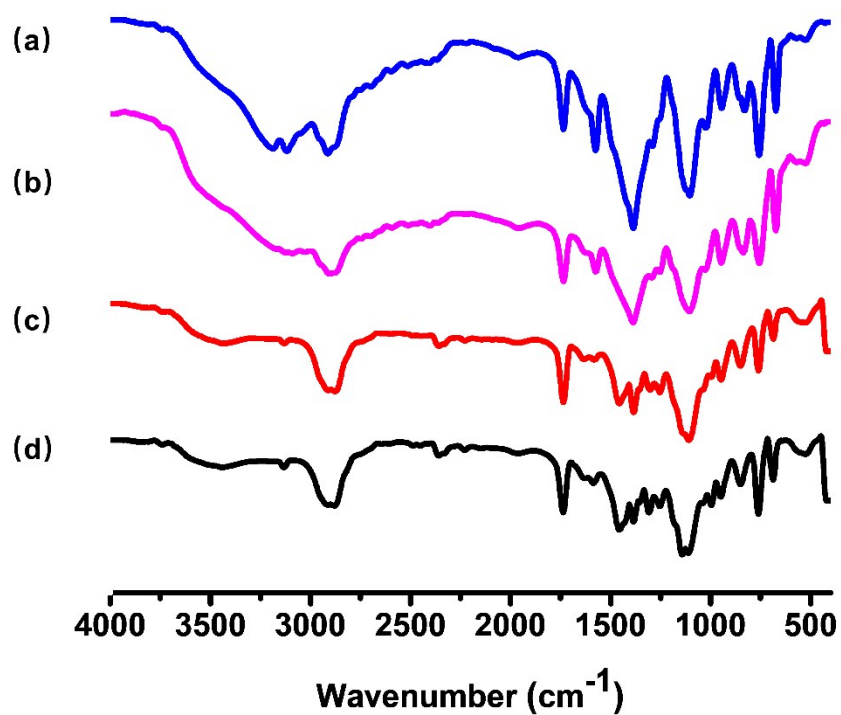


Figure S2. FTIR spectra of ZIF-8(600) (a) and ZIF-8(800) (b) based mixed-matrix membranes prepared without thermal and solvent treatments. FTIR spectra of ZIF-8(600) (c) and ZIF-8(800) (d) based MMMs prepared with thermal treatment at 120 °C for 5 h and water treatment at room temperature for 30 min.

2. Characterizations of ZIF-8 nanoparticles

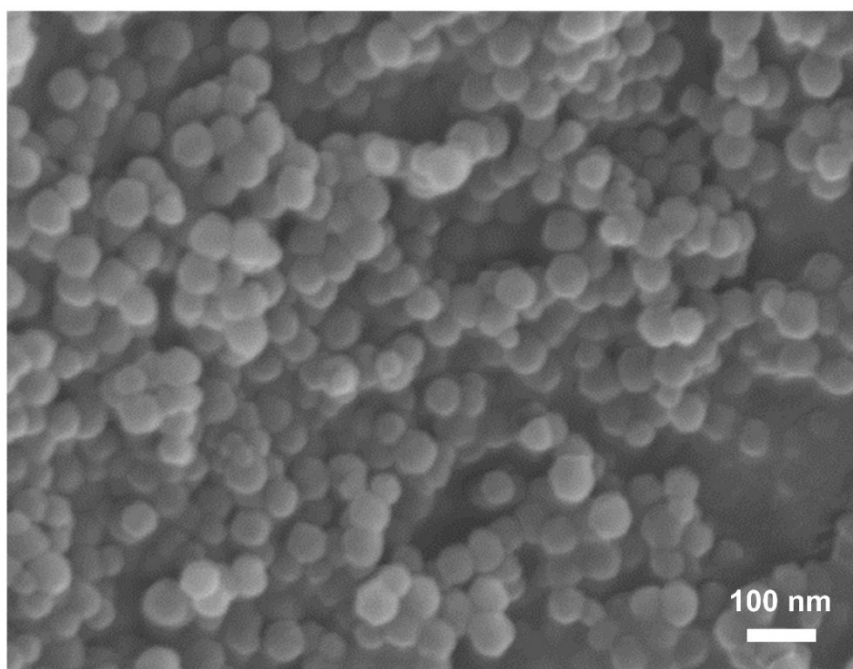


Figure S3. Scanning electron microscopy image of ZIF-8 nanoparticles.

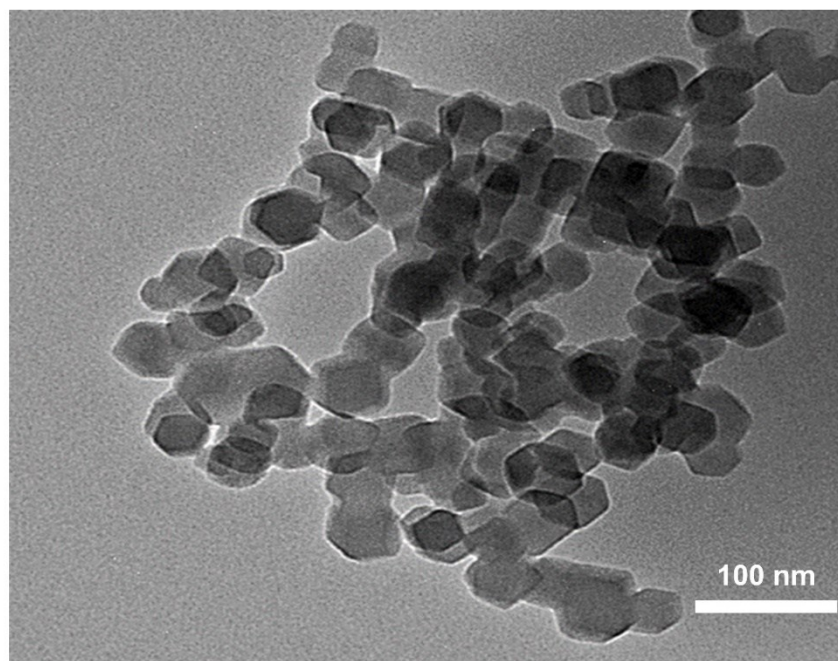


Figure S4. Transmission electron microscopy image of ZIF-8 nanoparticles

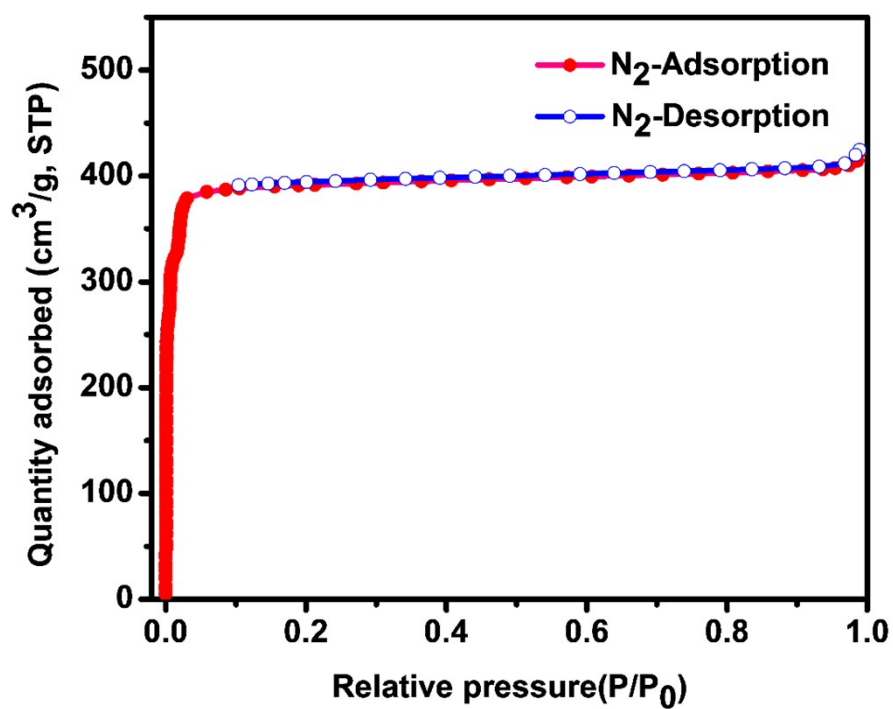


Figure S5. Nitrogen adsorption/desorption isotherms of the ZIF-8 nanoparticles at 77 K.

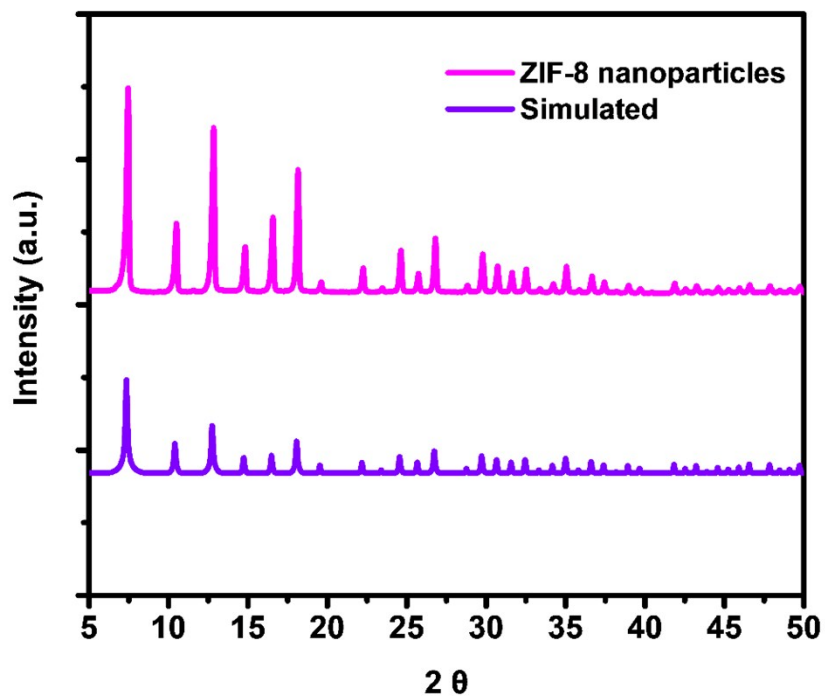


Figure S6. X-ray diffraction patterns of ZIF-8 nanoparticles.

3. Preparation of ZIF-8 hybrid membranes using the conventional solution casting

approach

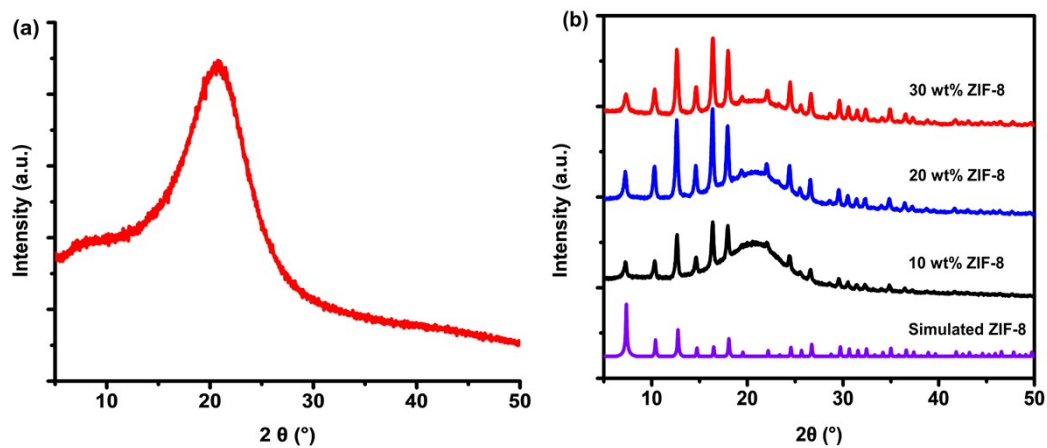


Figure S7. X-ray diffraction patterns of PEO containing polymer membrane (a), and ZIF-8 containing hybrid membranes with different ZIF-8 loadings (b).

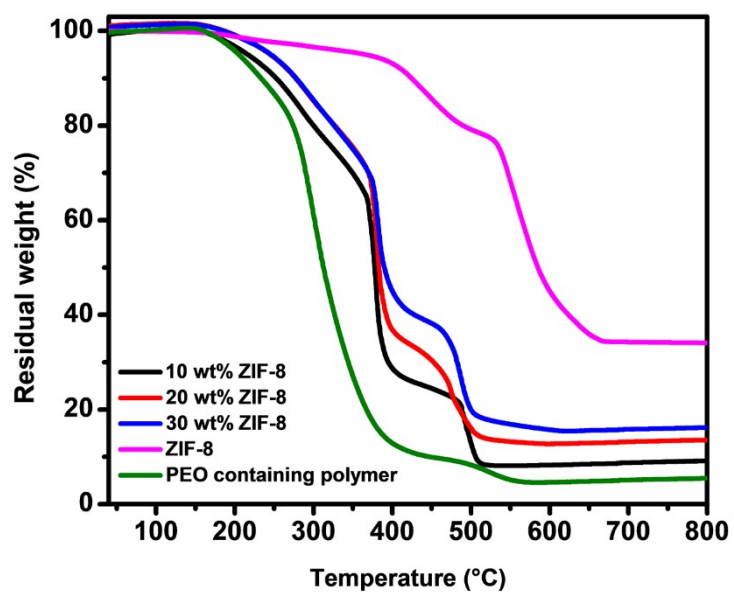


Figure S8. Thermal gravimetric analysis of pristine PEO containing polymer, as well as ZIF-8 and ZIF-8 hybrid membranes containing 10, 20, and 30 wt% ZIF-8 nanoparticles.

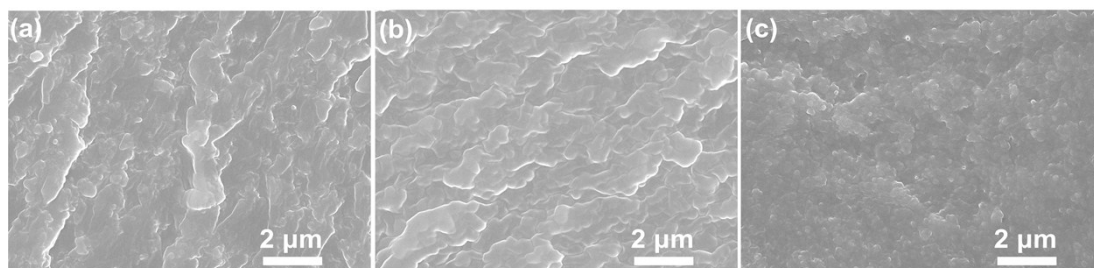


Figure S9. Scanning electron microscopy images of the ZIF-8 hybrid membranes containing different loadings of ZIF-8 nanoparticles, (a) 10, (b) 20, and (c) 30 wt%.

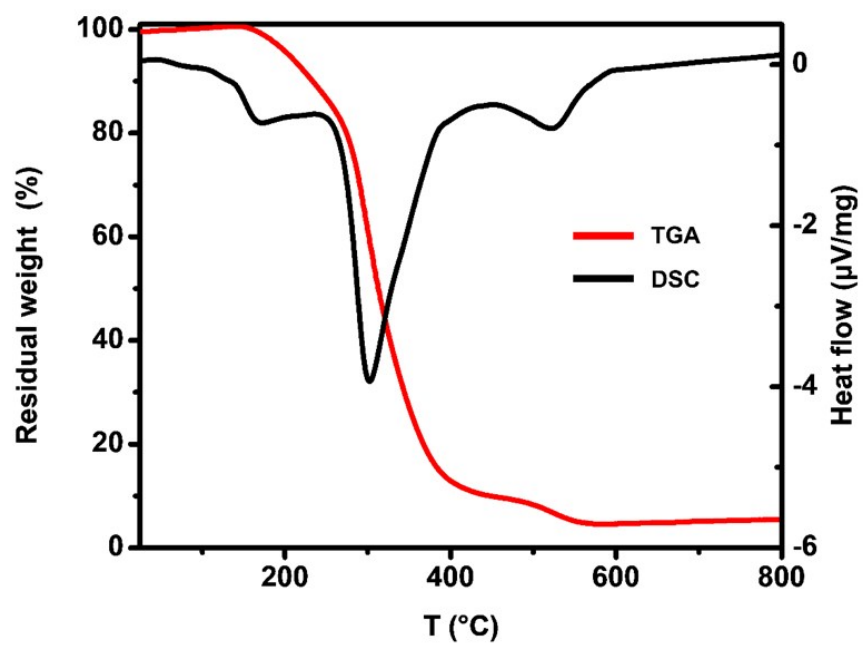


Figure S10. TGA-DSC plots of pristine PEO containing polymer membrane.

4. Characterization of ZIF-7(x)-based mixed matrix membranes prepared using the *in-situ* growth approach

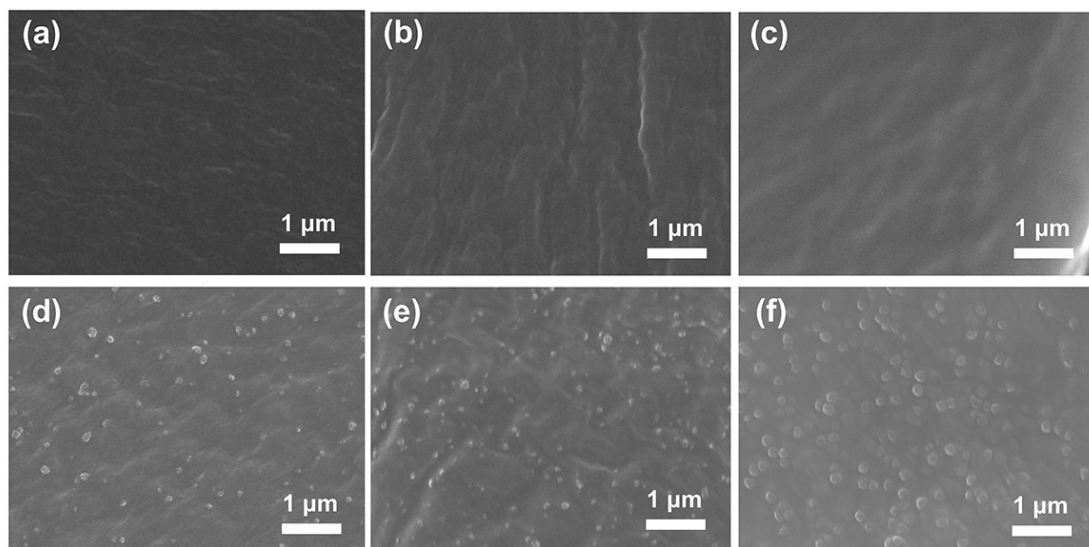


Figure S11. Scanning electron microscopy images of cross-section ZIF-7(x)-based mixed matrix membranes without solvent treatment (a-c), and with DMF/methanol (v/v=1:1) treatment at room temperature for 1 h (d-f). The ZIF-7 precursors were 300 mg $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 300 mg benzimidazole (a, d), 400 mg $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 400 mg benzimidazole (b, e), and 500 mg $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 500 mg benzimidazole (c, f).

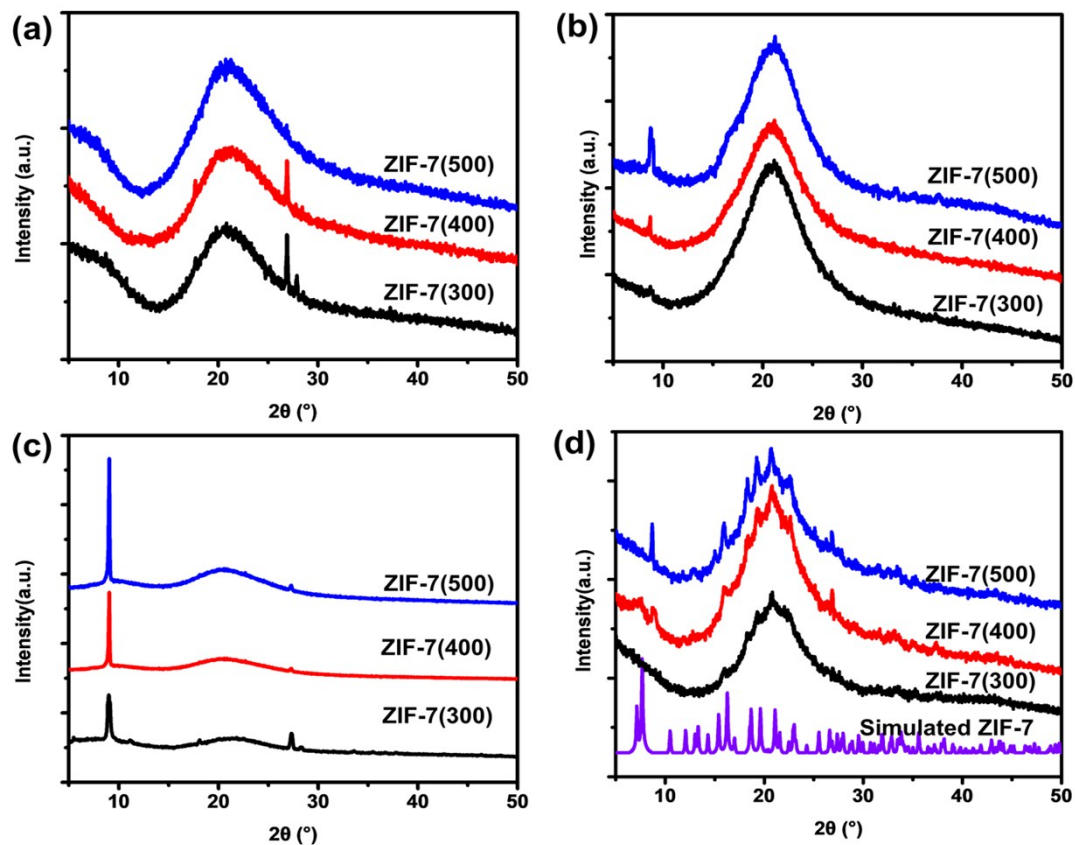


Figure S12. X-ray diffraction patterns of ZIF-7(x)-based mixed matrix membranes without thermal and solvent treatments (a), without thermal treatment but with DMF/methanol (v/v=1:1) treatment at room temperature for 1 h (b), with thermal treatment at 120 °C for 5 h but without solvent treatment (c), with thermal treatment at 120 °C for 5 h and with DMF/methanol (v/v=1:1) treatment at room temperature for 1 h (d).

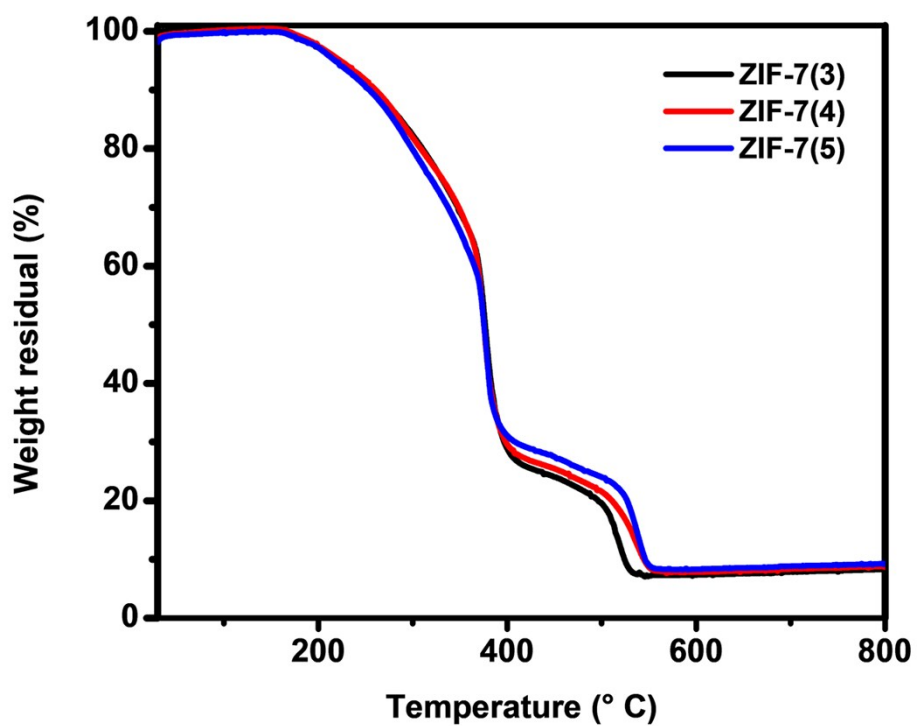


Figure S13. Thermal gravimetric analysis plots of ZIF-7(x)-based mixed matrix membranes prepared using the *in situ* growth approach.

Table S1. The separation performances of ZIF-8(x) and ZIF-7(x) based mixed matrix membranes (MMMs) fabricated from our new strategy in comparison to pristine PEO containing polymer membrane and ZIFs-based MMMs prepared using the conventional solution casting approach using an operational temperature of 35 °C and a feeding pressure of 5 bar.

Membrane	Permeability, barrer			Selectivity	
	CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
Pristine PEO containing polymer	423.6	29.2	12.8	14.5	33.0
ZIF-8 (10 wt%) ^a	510.1	50.0	17.3	10.2	29.5
ZIF-8 (20 wt%) ^a	641.4	66.8	24.6	9.6	26.1
ZIF-8 (30 wt%) ^a	706.5	76.8	28.5	9.2	24.8
ZIF-8(200) ^b	70.3	6.2	3.0	11.3	23.6
ZIF-8(400) ^b	39.5	5.0	2.8	7.9	14.3
ZIF-8(600) ^b	26.7	4.8	2.7	5.6	10.0
ZIF-8(800) ^b	30.4	4.9	2.5	6.3	12.1
ZIF-8(200) ^c	564.3	50.4	16.9	11.2	33.3
ZIF-8(400) ^c	732.6	58.6	22.1	12.5	33.1
ZIF-8(600) ^c	909.7	71.1	27.9	12.8	32.6
ZIF-8(800) ^c	946.3	102.9	33.0	9.2	28.5
ZIF-8(200) ^d	603.6	49.9	21.0	12.1	28.7
ZIF-8(400) ^d	715.0	63.3	25.3	11.3	28.3
ZIF-8(600) ^d	843.2	80.6	30.4	10.5	27.7
ZIF-8(800) ^d	910.8	102.3	36.1	8.9	25.2
ZIF-7(300) ^e	23.6	5.6	2.7	4.2	8.7

ZIF-7(400) ^e	4.2	4.0	2.8	1.0	1.5
ZIF-7(500) ^e	6.3	4.5	2.9	1.4	2.2
ZIF-7(300) ^f	721.3	54.6	17.8	13.2	40.5
ZIF-7(400) ^f	935.6	68.8	23.6	13.6	39.7
ZIF-7(500) ^f	1083.7	85.3	28.1	12.7	38.5

^a ZIF-8 hybrid membranes prepared using the conventional solution casting approach.

^b ZIF-8(x)-based MMMs prepared without thermal and solvent treatments.

^c ZIF-8(x)-based MMMs prepared with thermal treatment at 120 °C for 5 h and water treatment at room temperature for 30 min.

^d ZIF-8(x)-based MMMs prepared with water treatment at room temperature for 30 min but without thermal treatment.

^e ZIF-7(x)-based MMMs prepared without thermal and solvent treatments.

^f ZIF-7(x)-based MMMs prepared with thermal treatment at 120 °C for 5 h and with DMF/methanol (v/v=1:1) treatment at room temperature for 1 h.

Table S2. Solution and diffusion coefficients of CO₂ and CH₄ at a pressure 3 bar and 35 °C for the pristine cross-linked PEO membrane and ZIF-8(x)-based mixed matrix membranes prepared with thermal treatment at 120 °C for 5 h and water treatment at room temperature for 30 min.

Membranes	Solution coefficients		S _{CO₂/SCH₄}	Diffusion coefficients		D _{CO₂/DCH₄}
	× 10 ⁻³ (cm ³ (STP)/ (cm ³ cmHg))			× 10 ⁻⁷ (cm ² /s)		
	CH ₄	CO ₂		CH ₄	CO ₂	
Pristine cross-linked PEO	5.21	50.49	9.69	6.32	8.39	1.33
ZIF-8(200)	9.0	77.51	8.61	5.60	7.28	1.30
ZIF-8(400)	11.49	112.19	9.76	5.10	6.53	1.28
ZIF-8(600)	18.18	186.03	10.23	3.91	4.89	1.25
ZIF-8(800)	27.96	214.10	7.66	3.68	4.42	1.20

Table S3. Solution and diffusion coefficients of CO₂ and N₂ at a pressure 3 bar and 35 °C for the pristine cross-linked PEO membrane and ZIF-8(x)-based mixed matrix membranes prepared with thermal treatment at 120 °C for 5 h and water treatment at room temperature for 30 min.

Membranes	Solution coefficients		S_{CO_2/N_2}	Diffusion coefficients		D_{CO_2}/D_{N_2}
	$\times 10^{-3} \text{ (cm}^3\text{(STP)/ (cm}^3 \text{ cmHg))}$			$\times 10^{-7} \text{ (cm}^2\text{/s)}$		
	N ₂	CO ₂		N ₂	CO ₂	
Pristine cross-linked PEO	2.52	50.49	20.04	5.07	8.39	1.65
ZIF-8(200)	3.74	77.51	20.72	4.52	7.28	1.61
ZIF-8(400)	5.21	112.19	21.53	4.24	6.53	1.54
ZIF-8(600)	8.45	186.03	22.01	3.30	4.89	1.48
ZIF-8(800)	10.96	214.10	19.54	3.01	4.42	1.47

Table S4. Solution and diffusion coefficients of CO₂ at a pressure 3 bar and 35 °C for the ZIF-8(x)-based mixed matrix membranes prepared without thermal and solvent treatments.

Membranes	Solution coefficients × 10 ⁻³ (cm ³ (STP)/ (cm ³ cmHg))	Diffusion coefficients × 10 ⁻⁷ (cm ² /s)
	CO ₂	CO ₂
ZIF-8(200)	61.67	1.14
ZIF-8(400)	74.53	0.53
ZIF-8(600)	92.07	0.29
ZIF-8(800)	233.85	0.13