Electronic Supplementary Information (ESI)

Highly efficient CO_2 capture by mixed matrix membranes containing three-dimensional covalent organic framework fillers

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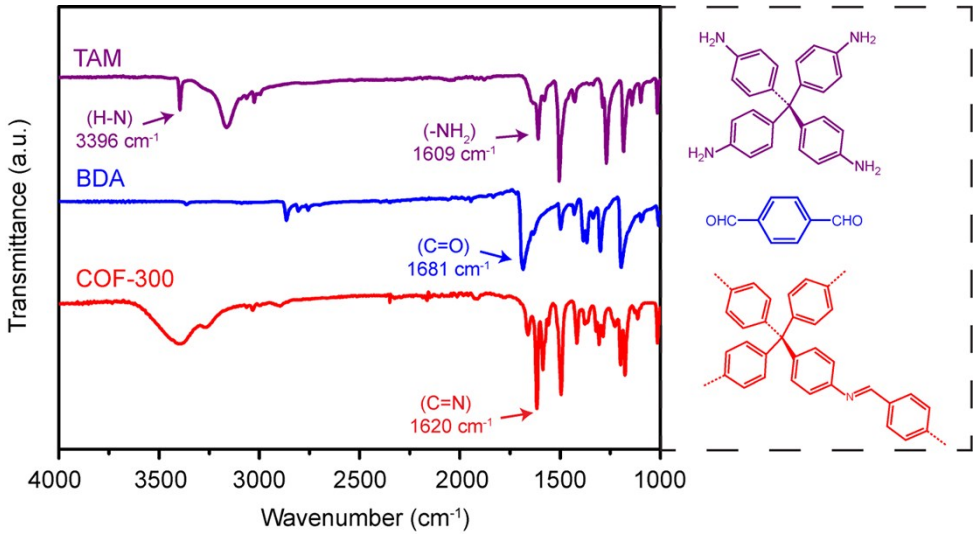

Fig. S1. FTIR spectra of COF-300 and its monomers.

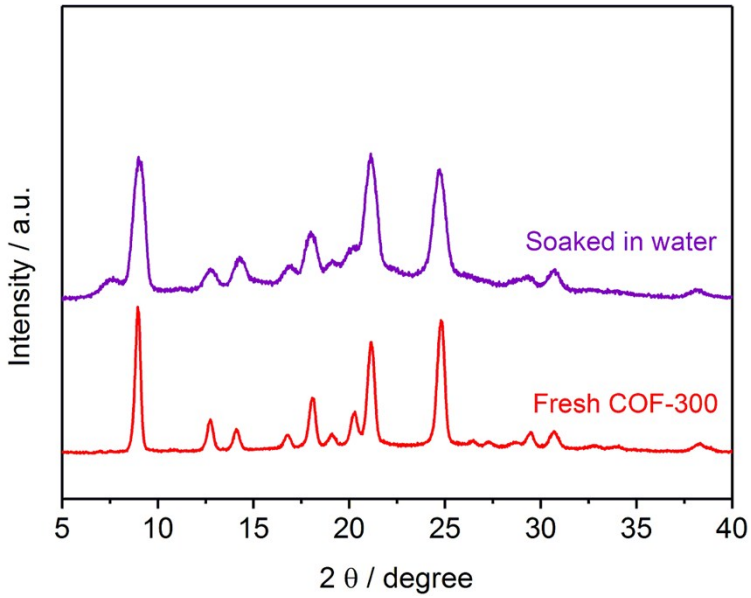

Fig. S2. PXRD patterns of fresh COF-300 and COF-300 soaked in water at room temperature for 3 days.

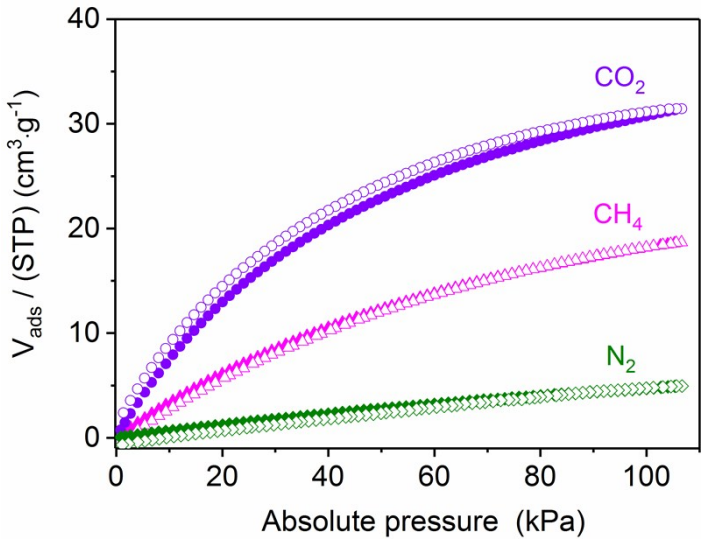

Fig. S3. CO_2, CH_4, and N_2 sorption isotherms of COF-300 measured at 273 K.

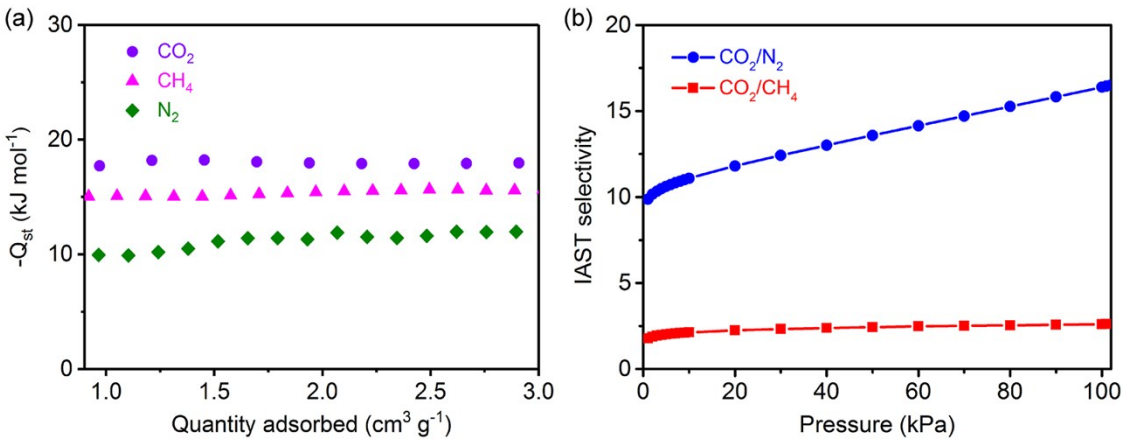

Fig. S4. (a) The isosteric heat of adsorption (Q_{st}) for CO_2, CH_4 and N_2 of COF-300. (b) The ideal adsorption solution theory (IAST) selectivity of COF-300 for the equal molar mixtures of CO_2/CH_4 or CO_2/N_2 at 298K and 1 bar.

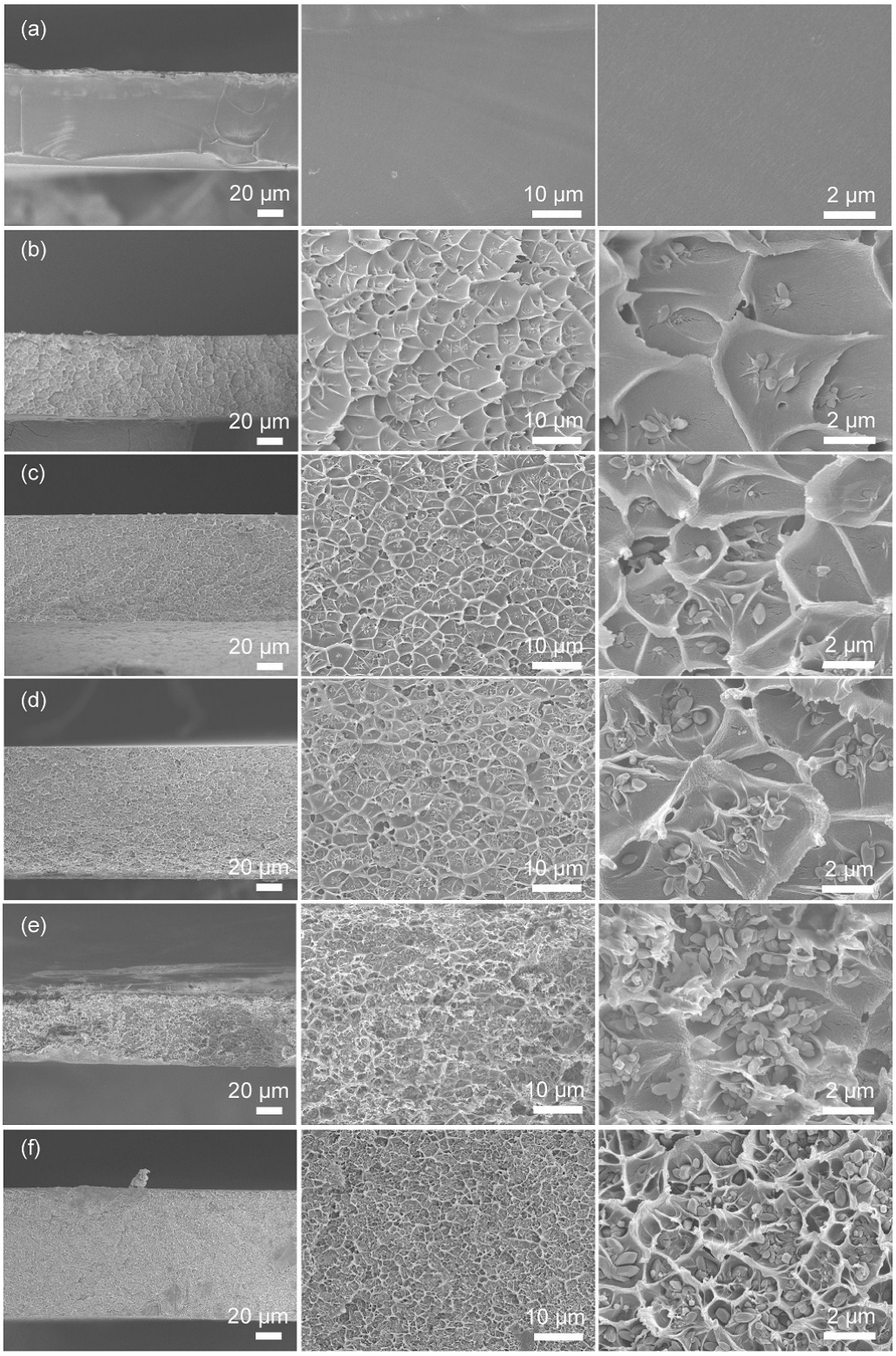

Fig. S5. Cross-sectional FESEM images of COF-300/6FDA-DAM MMMs containing (a) 0 wt%, (b) 2 wt%, (c) 5 wt%, (d) 7 wt%, (e) 10 wt% and (f) 15 wt% COF-300 fillers at different magnifications.

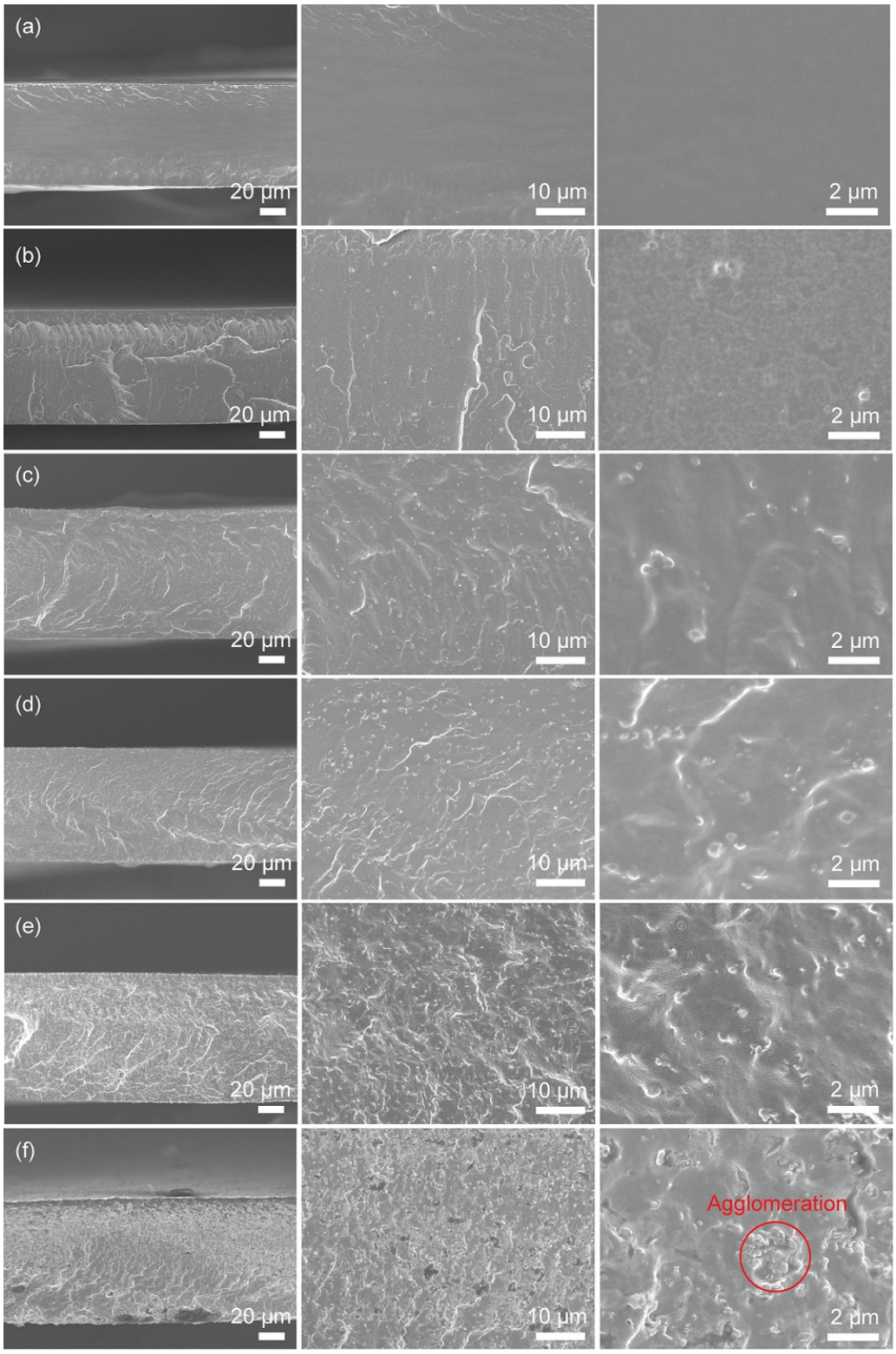

Fig. S6. Cross-sectional FESEM images of COF-300/Pebax MMMs containing (a) 0 wt%, (b) 2 wt%, (c) 5 wt%, (d) 7 wt%, (e) 10 wt% and (f) 15 wt% COF-300 fillers at different magnifications.

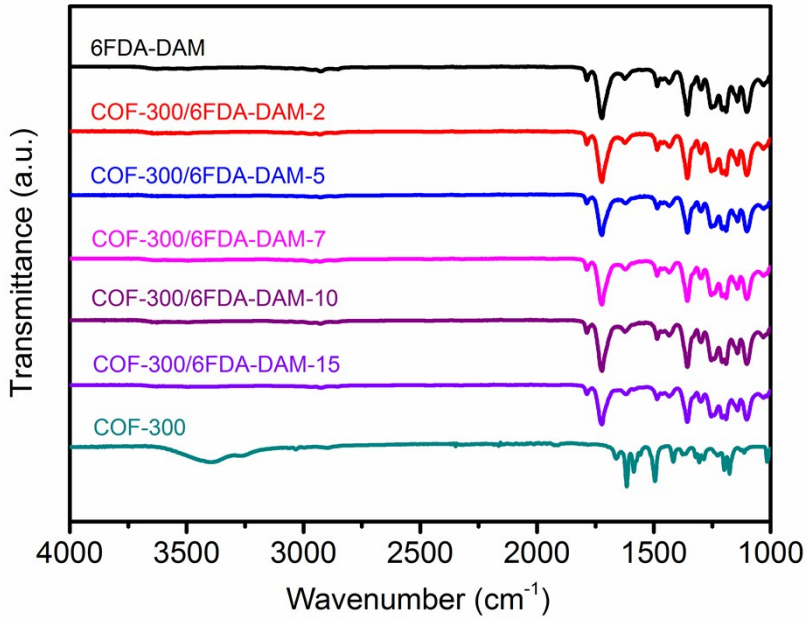

Fig. S7. FTIR spectra of COF-300/6FDA-DAM series MMMs.

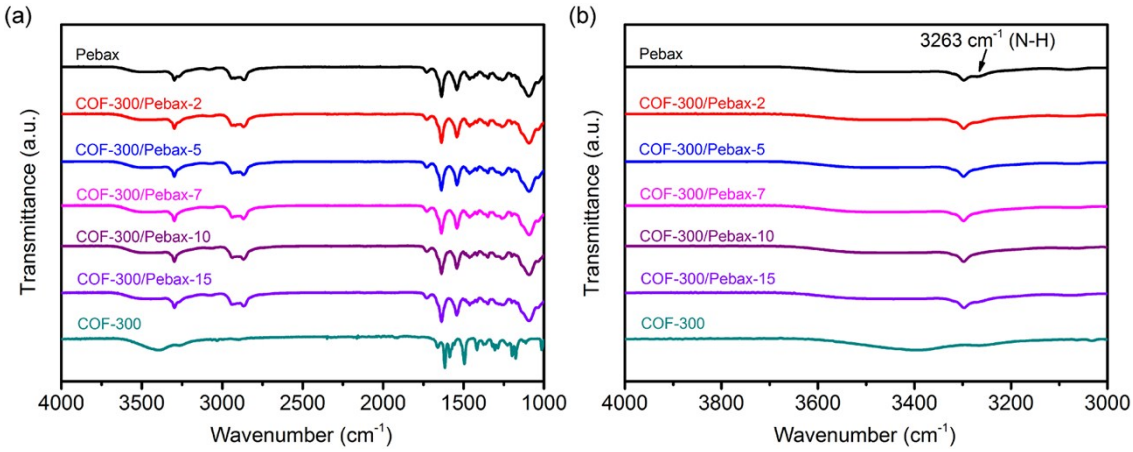

Fig. S8. FTIR spectra of COF-300/Pebax series MMMs.

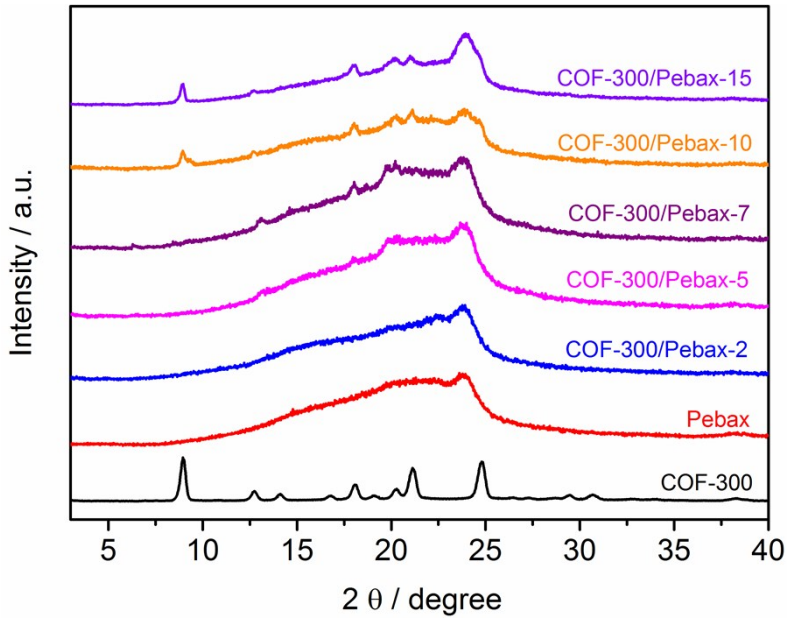

Fig. S9. XRD patterns of COF-300 and COF-300/Pebax series MMMs.

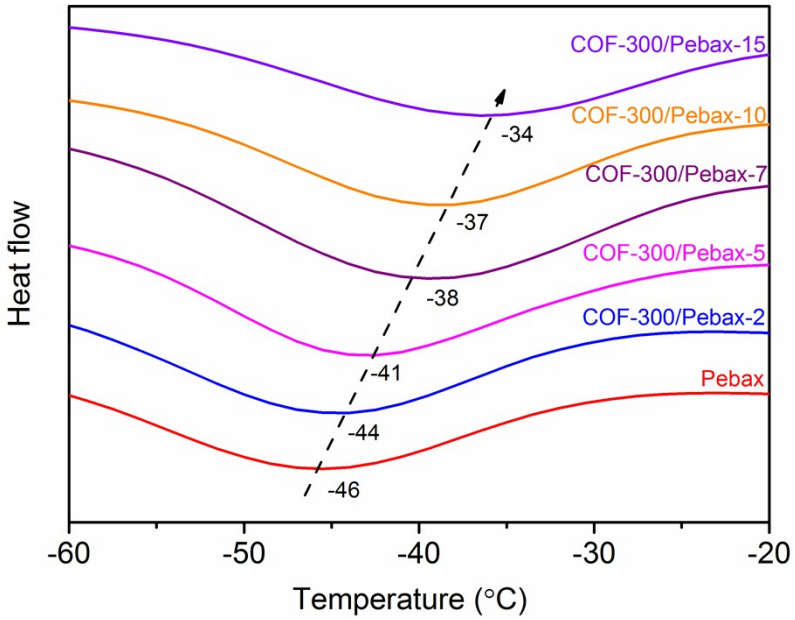

Fig. S10. DSC curves of COF-300/Pebax series MMMs.

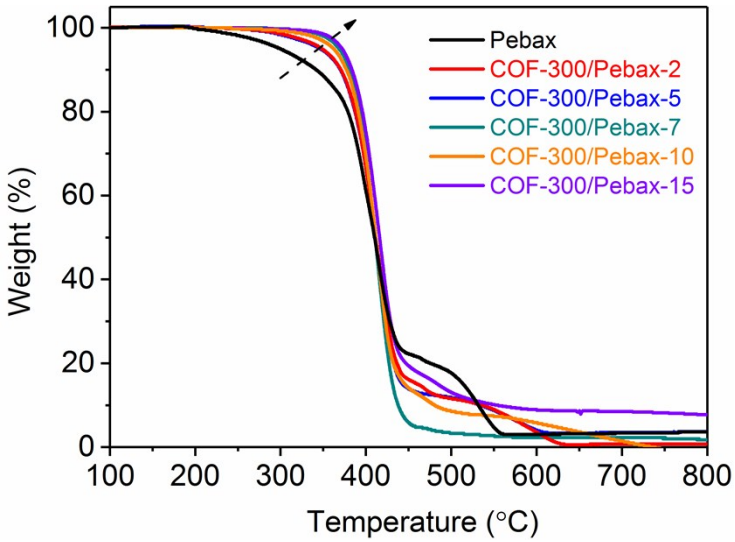

Fig. S11. TGA curves of COF-300/Pebax series MMMs.

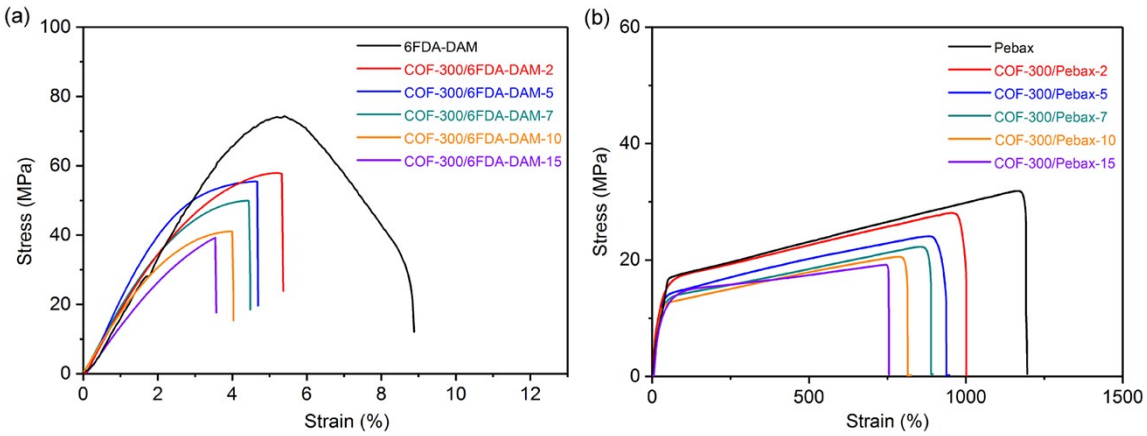

Fig. S12. Stress-strain curves for (a) COF-300/6FDA-DAM series MMMs; (b) COF-300/Pebax series MMMs.

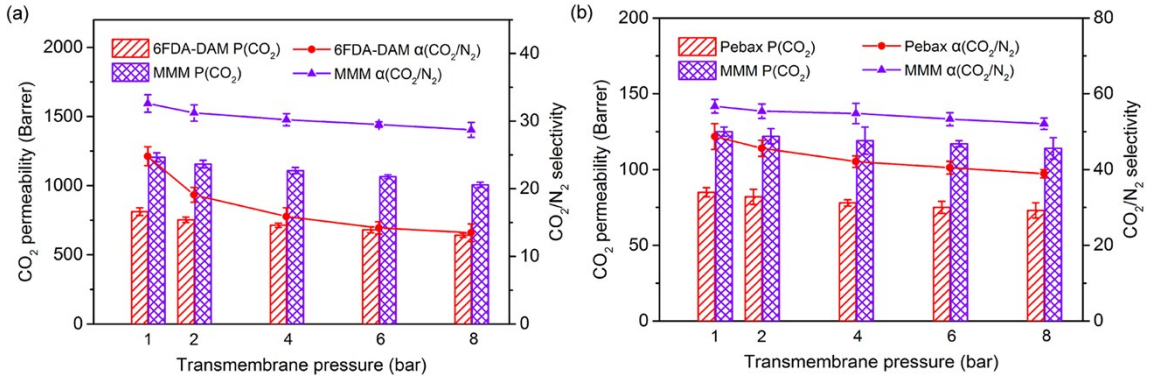

Fig. S13. Transmembrane pressure influence on the CO_2/N_2 separation performance of (a) 6FDA-DAM and (b) Pebax systems.

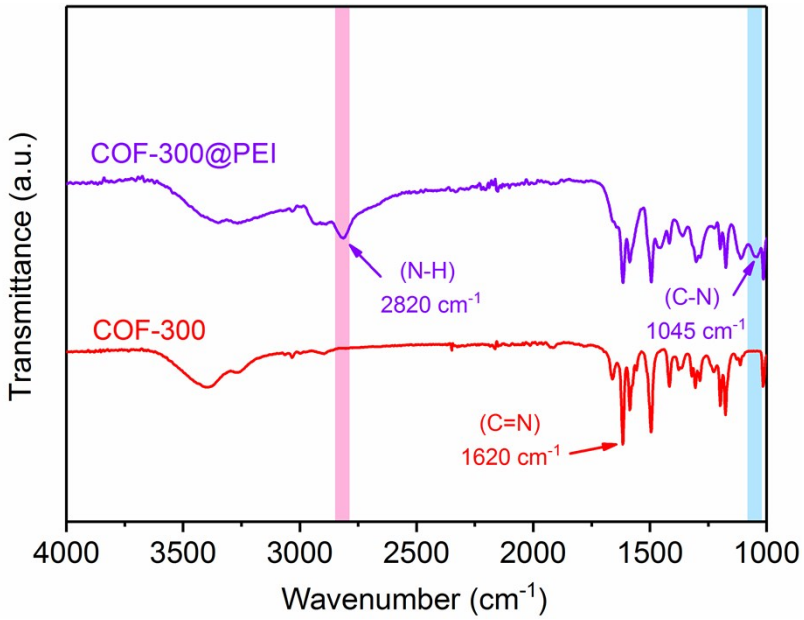

Fig. S14. FTIR spectra of COF-300 and COF@PEI.

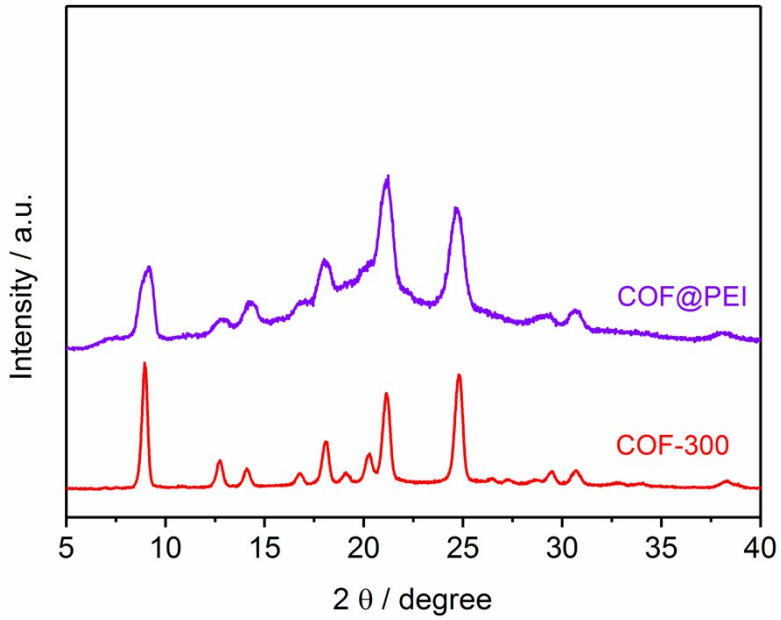

Fig. S15. PXRD patterns of COF-300 and COF@PEI.

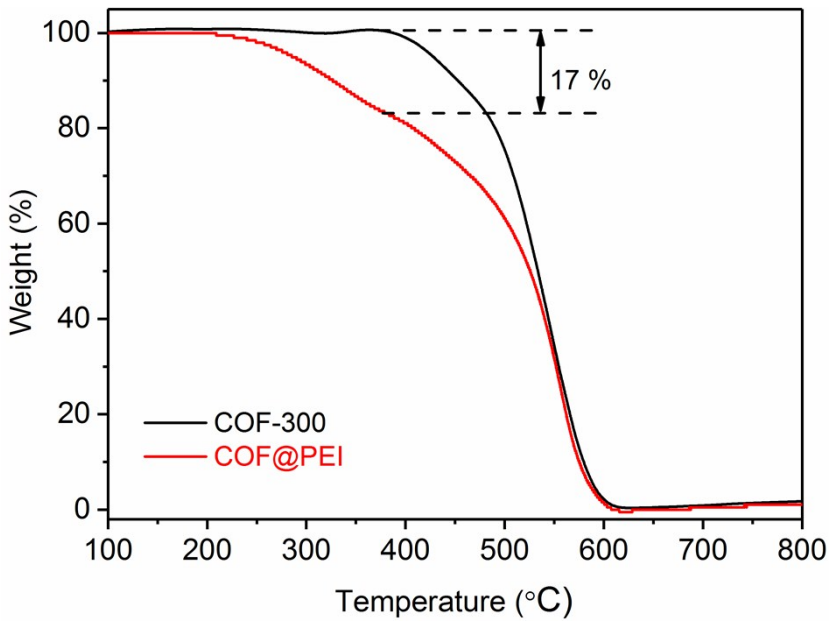

Fig. S16. TGA curves of COF-300 and COF@PEI.

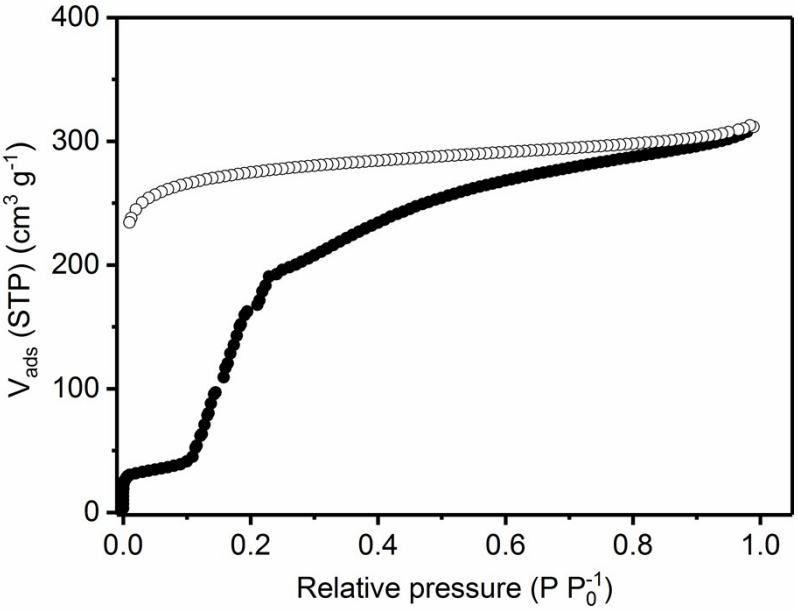

Fig. S17. N_2 sorption isotherm (77 K) of COF@PEI (adsorption: solid symbols; desorption: empty symbols).

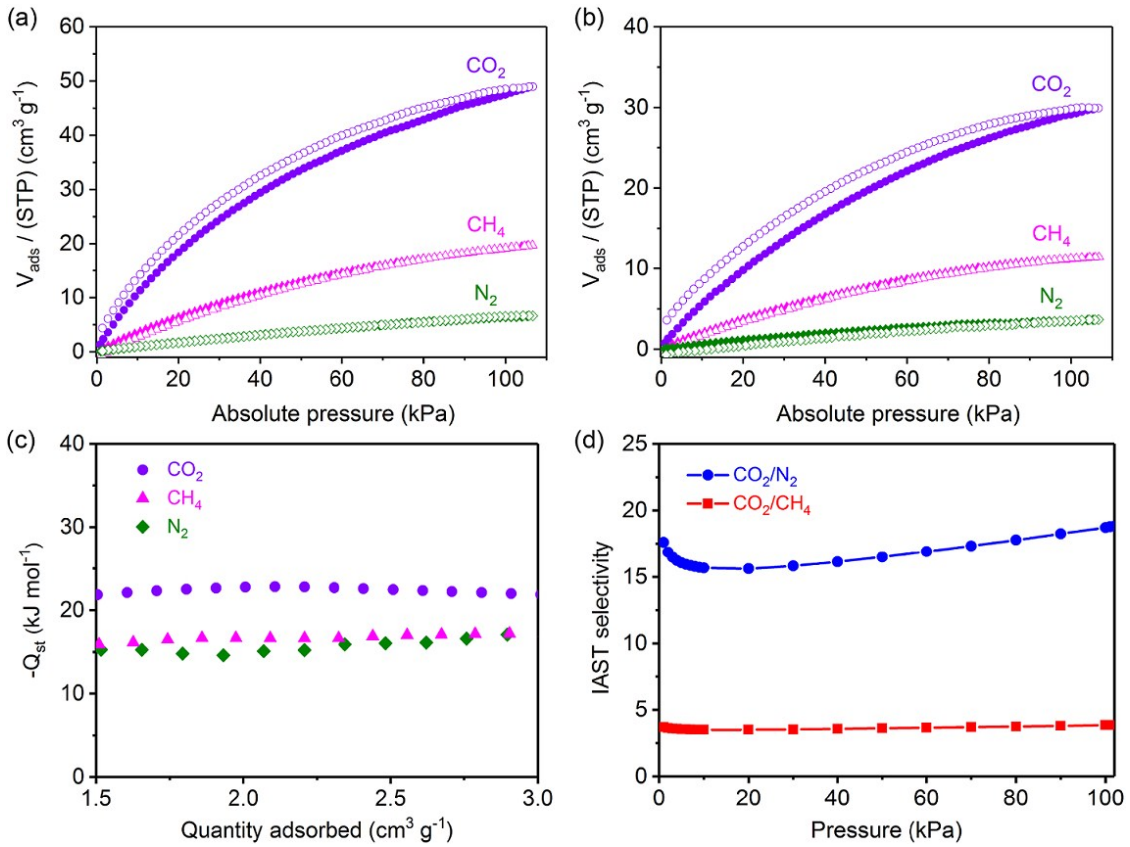

Fig. S18. CO_2, CH_4 and N_2 sorption isotherms of COF@PEI measured at (a) 273 K and (b) 298 K. (c) The isosteric heat of adsorption (Q_{st}) for CO_2, CH_4 and N_2 of COF@PEI. (b) The ideal adsorption solution theory (IAST) selectivity of COF@PEI for CO_2/CH_4 or CO_2/N_2 equal molar mixtures at 298 K and 1 bar.

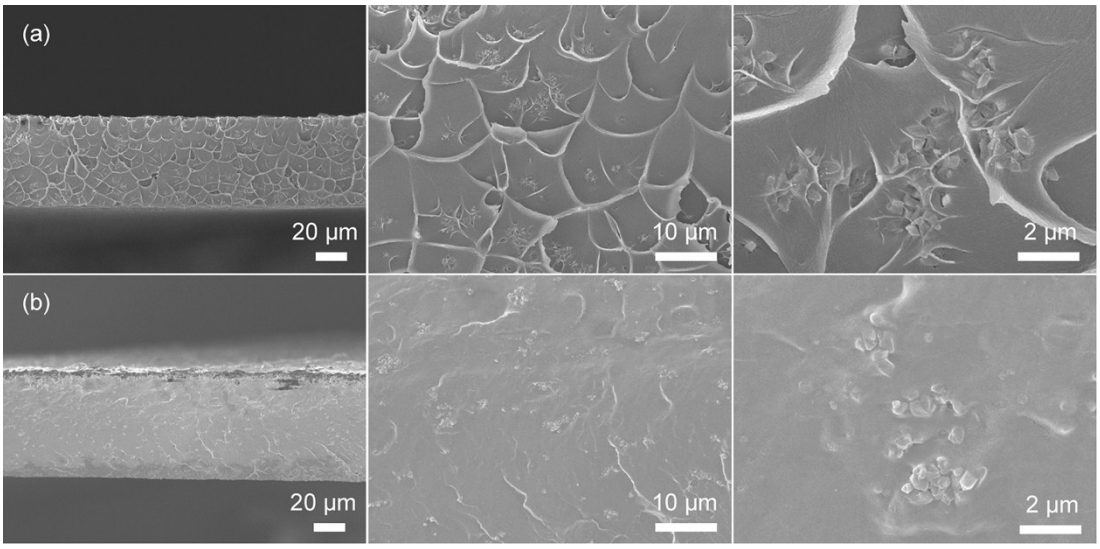

Fig. S19. Cross-sectional FESEM images of (a) COF@PEI/6FDA-DAM-7 and (b) COF@PEI/Pebax-10 MMMs at different magnifications.

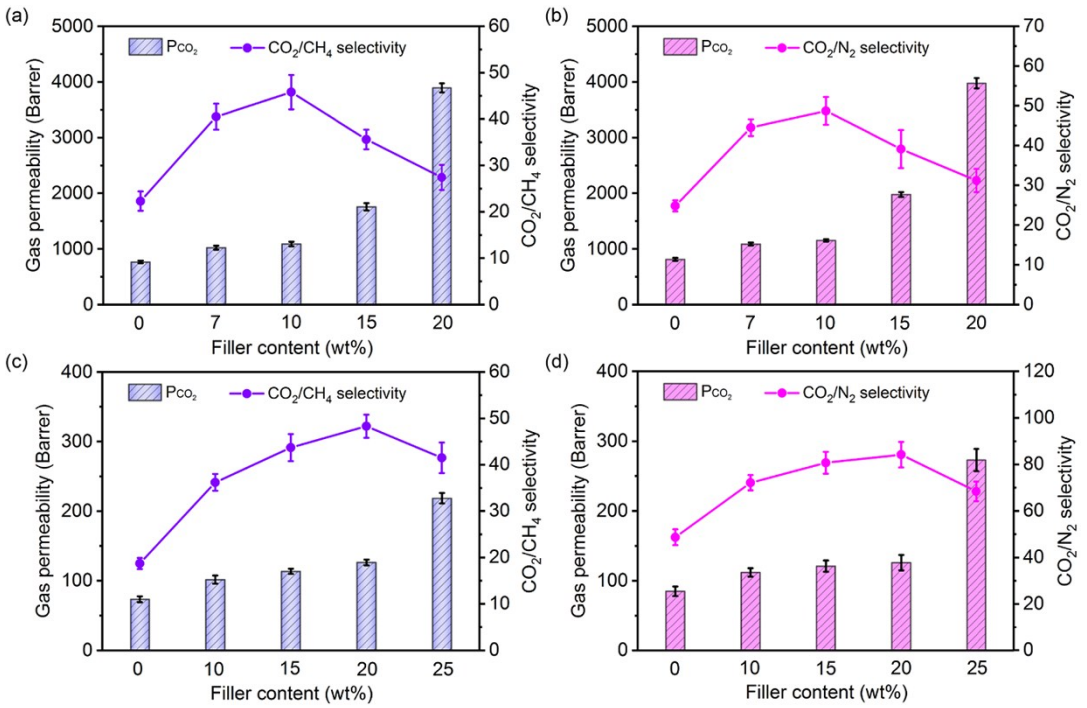

Fig. S20. The effect of COF@PEI filler content on membrane separation performance tested at 25 °C with a transmembrane pressure of 1 bar. (a) CO_2/CH_4 and (b) CO_2/N_2 separation performance of COF@PEI/6FDA-DAM series MMMs. (c) CO_2/CH_4 and (d) CO_2/N_2 separation performance of COF@PEI/Pebax series MMMs.

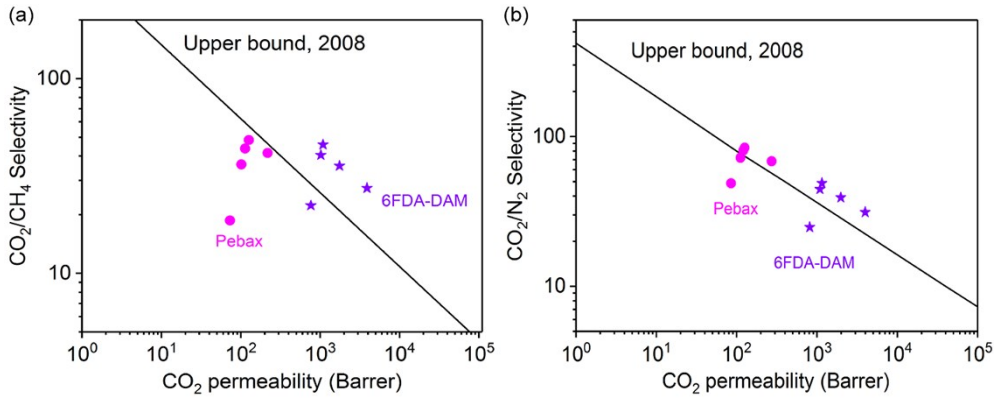

Fig. S21. Robeson upper bound plots for (a) CO_2/CH_4 and (b) CO_2/N_2 of COF@PEI/6FDA-DAM and COF@PEI/Pebax MMMs.

Table S1. Summary of mechanical properties of COF-300/6FDA-DAM and COF-300/Pebax series MMMs.

Membrane	Young's modulus (MPa)	Maximum tensile strength (MPa)	Elongation at break (%)
6FDA-DAM	1.62 ± 0.14	74.1 ± 3.7	8.9 ± 0.7
COF-300/6FDA-DAM-2	1.75 ± 0.12	57.7 ± 2.9	5.4 ± 0.6
COF-300/6FDA-DAM-5	1.83 ± 0.15	55.4 ± 2.1	4.7 ± 0.6
COF-300/6FDA-DAM-7	1.92 ± 0.11	49.9 ± 3.3	4.5 ± 0.3
COF-300/6FDA-DAM-10	1.85 ± 0.14	41.2 ± 1.8	4.0 ± 0.3
COF-300/6FDA-DAM-15	1.12 ± 0.09	39.1 ± 2.2	3.6 ± 0.3
Pebax	3.42 ± 0.43	31.7 ± 3.6	1192 ± 48
COF-300/Pebax-2	4.89 ± 0.57	28.1 ± 2.7	1001 ± 37
COF-300/Pebax-5	6.25 ± 0.62	23.8 ± 3.3	938 ± 35
COF-300/Pebax-7	6.52 ± 0.59	22.1 ± 2.4	886 ± 56
COF-300/Pebax-10	6.98 ± 0.41	20.6 ± 1.5	814 ± 43
COF-300/Pebax-15	4.29 ± 0.36	19.2 ± 2.7	754 ± 39

Table S2. Comparisons of CO_2 capture performance change between 3D COF-based and 2D COF-based MMMs.

Polymer	Filler	Filler type	Filler pore size (Å)	Filler content (wt%)	CO_2 permeability change (%)	Gas selectivity change (%)	References
Ultem	NUS-2	2D	8	20	122	11[a]	1
PIM-1	SNW-1	2D	5	10	106	27[a]	2
Matrimid®	ACOF-1	2D	9.4	16	121	6[a]	3
6FDA-DAM	ACOF-1	2D	9.4	16	0	21[b]	4
PBI-BuI	TpPa-1	2D	18	50	470	-30[a]	5
PBI-BuI	TpBD	2D	24	50	543	15[a]	5
6FDA-DAM	COF-300	3D	4	7	54	36[a]	This work
6FDA-DAM	COF-300	3D	4	7	46	36[a]	This work
Pebax	COF-300	3D	4	10	48	31[b]	This work
Pebax	COF-300	3D	4	10	47	16[b]	This work

[a]: CO_2/CH_4 selectivity; [b]: CO_2/N_2 selectivity.

Table S3. Experimental and predicted CO_2/CH_4 separation performance of COF-300-based MMMs.

System	Filler content (vol%)	Gas permeability		CO_2/CH_4 selectivity	Predicted CO_2 permeability (Barrer)	Predicted CH_4 permeability (Barrer)	Predicted performance of pure COF-300
		CO_2	CH_4				
COF-300/ 6FDA-DAM	0	767 ± 24	34.5 ± 1.9	22.3 ± 2.1	767*	34.5*	P_{CO_2} = 9830 ± 132 Barrer P_{CH_4} = 125 ± 7 Barrer $\alpha_{(CO_2/CH_4)}$ = 78.6 ± 8.3
	4.0	842 ± 38	36.4 ± 2.5	23.5 ± 1.9	842*	37.9*	
	7.5	972 ± 46	37.1 ± 4.2	26.2 ± 1.4	913	38.3	
	13.2	1185 ± 41	39.2 ± 5.5	30.3 ± 1.5	1037	41.3	
	18.3	2842 ± 76	156.8 ± 12.3	24.6 ± 1.7	1162	44.2	
	26.2	4746 ± 138	390.6 ± 48.4	14.7 ± 1.2	1375	48.9	
COF-300/ Pebax	0	73 ± 4	3.8 ± 0.4	18.7 ± 1.2	73*	3.83*	P_{CO_2} = 8850 ± 178 Barrer P_{CH_4} = 80 ± 3 Barrer $\alpha_{(CO_2/CH_4)}$= 110.6 ± 5.7
	3.4	81 ± 6	4.2 ± 0.3	19.4 ± 0.7	80*	4.18*	
	8.3	86 ± 4	4.0 ± 0.3	21.5 ± 1.1	92	4.72	
	11.5	98 ± 5	4.1 ± 0.5	23.7 ± 1.7	101	5.11	
	16.1	107 ± 6	4.2 ± 0.7	25.5 ± 1.3	114	5.70	
	23.3	327 ± 11	22.3 ± 2.6	14.7 ± 0.8	137	6.75	

*: These values were adopted for Maxwell model calculation and averaged data were used for performance prediction.

Table S4. Experimental and predicted CO_2/N_2 separation performance of COF-300-based MMMs.

System	Filler content (vol%)	Gas permeability		CO_2/N_2 selectivity	Predicted CO_2 permeability (Barrer)	Predicted N_2 permeability (Barrer)	Predicted performance of pure COF-300
		CO_2	N_2				
COF-300/ 6FDA-DAM	0	812 ± 28	31.5 ± 1.2	24.8 ± 1.4	812*	31.5*	P_{CO_2} = 10320 ± 255 Barrer P_{N_2} = 170 ± 8 Barrer $\alpha_{(CO_2/N_2)}$ = 60.7 ± 4.5
	4.0	894 ± 26	33.9 ± 2.3	26.5 ± 1.3	894*	33.9*	
	7.5	1014 ± 53	34.7 ± 3.6	29.2 ± 1.1	967	35.9	
	13.2	1205 ± 32	36.9 ± 4.8	32.6 ± 1.7	1098	39.5	
	18.3	2964 ± 81	125.1 ± 11.4	23.7 ± 1.9	1227	43.0	
	26.2	5133 ± 138	368.2 ± 48.4	13.9 ± 1.6	1454	48.9	
COF-300/ Pebax	0	85 ± 7	1.8 ± 0.2	48.6 ± 3.4	85*	1.75*	P_{CO_2} = 9130 ± 110 Barrer P_{N_2} = 95 ± 4 Barrer $\alpha_{(CO_2/N_2)}$ = 96.1 ± 8.4
	3.4	94 ± 8	1.9 ± 0.2	48.8 ± 2.3	94*	1.92*	
	8.3	103 ± 11	2.0 ± 0.4	51.0 ± 2.1	107	2.20	
	11.5	113 ± 15	2.1 ± 0.3	53.9 ± 3.2	117	2.41	
	16.1	125 ± 14	2.2 ± 0.4	56.6 ± 2.9	132	2.69	
	23.3	359 ± 13	7.9 ± 0.6	45.5 ± 3.6	159	3.23	

*: These values were adopted for Maxwell model calculation and averaged data were used for performance prediction.

Table S5. Experimental CO_2/CH_4 separation performance of COF@PEI-based MMMs.

System	Filler content (vol%)	Gas permeability		CO_2/CH_4 selectivity
		CO_2	CH_4	
COF@PEI/ 6FDA-DAM	0	767 ± 24	34.5 ± 1.9	22.3 ± 2.1
	13.3	1023 ± 37	25.7 ± 3.8	40.5 ± 2.8
	17.0	1089 ± 42	23.5 ± 2.2	45.8 ± 3.7
	24.6	1758 ± 66	49.4 ± 5.7	35.6 ± 2.1
	31.6	3894 ± 83	142.5 ± 11.2	27.4 ± 2.7
COF@PEI/ Pebax	0	73 ± 4	3.8 ± 0.4	18.7 ± 1.2
	15.0	101 ± 5	2.8 ± 0.3	36.2 ± 1.8
	21.8	113 ± 3	2.6 ± 0.2	43.7 ± 2.9
	28.4	126 ± 4	2.6 ± 0.3	48.3 ± 2.5
	34.5	218 ± 7	5.3 ± 0.4	41.5 ± 3.3

Table S6. Experimental CO_2/N_2 separation performance of COF@PEI-based MMMs.

System	Filler content (vol%)	Gas permeability		CO_2/N_2 selectivity
		CO_2	N_2	
COF@PEI/ 6FDA-DAM	0	812 ± 28	31.5 ± 1.2	24.8 ± 1.4
	13.3	1088 ± 26	25.1 ± 2.3	44.5 ± 2.1
	17.0	1154 ± 21	23.7 ± 1.9	48.7 ± 3.5
	24.6	1978 ± 45	50.6 ± 6.3	39.1 ± 4.8
	31.6	3977 ± 92	127.5 ± 9.8	31.2 ± 2.9
COF@PEI/ Pebax	0	85 ± 7	1.75 ± 0.2	48.6 ± 3.4
	15.0	112 ± 6	1.6 ± 0.1	72.1 ± 3.3
	21.8	121 ± 8	1.4 ± 0.2	80.7 ± 4.7
	28.4	126 ± 11	1.5 ± 0.3	84.2 ± 5.5
	34.5	273 ± 16	4.0 ± 0.5	68.4 ± 4.2

References:

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3. H. Fan, A. Mundstock, J. Gu, H. Meng and J. Caro, *J Mater Chem A*, 2018, **6**, 16849–16853.
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