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Sorption-enhanced mixed-gas transport in amine functionalized polymers of intrinsic microporosity (PIMs)

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1. Sample information, materials, and methods

Gas purity and suppliers. Pure- and mixed-gas permeation and sorption tests were performed using ultrahigh purity gases purchased from Airgas: H_2 (UHP300, 99.999%), CH_4 (UHP300, 99.99%), N_2 (UHP300, 99.999%), and CO_2 (UHP300, 99.999%).

Pure-gas permeation. Pure-gas permeation tests were performed at 35 °C and 1 atm using an automated constant-volume, variable-pressure system purchased from Maxwell Robotics. The temperature in the cell was maintained with a water bath using a Thermo Fisher SC150L water circulator. Polymer films of approximately 25 mm^2 in area were placed over a hole on a brass disk, and the edges of the film were attached to the disk using Devcon 5 min Epoxy. Samples were loaded into a stainless steel cell and tightly sealed with two concentric o-rings. At the beginning of a permeation test, the samples were de-gassed for 8 h under vacuum to remove environmental moisture or residual atmospheric gases. When switching between gases, the sample cell was flushed with helium and de-gassed under vacuum for at least 1 h. After conducting pure-gas tests at 1 atm, high-pressure CO_2 tests were performed up to fugacities of 29 atm. For each pressure point, samples were held for 0.5 h to ensure all samples had identical CO_2 exposure and sufficient time to reach steady state.

Table S1. Thickness (l), aging time (t), and treatment conditions for samples tested in mixtures.

Polymer	l (μm)	t (days)	treatment 1 d after casting
PIM-1 (fresh)	58.0 ± 0.9	1	MeOH 24 h, 130 °C 12 h
PIM-1 (381 d)	43.8 ± 0.9	381	MeOH 24 h, 130 °C 12 h
PIM-NH$_2$ (fresh)	49 ± 2	1	MeOH 24 h, 130 °C 12 h
PIM-NH$_2$ (290 d)	51 ± 2	290	MeOH 24 h, 130 °C 12 h
PIM-NH$_2$ (448 d)	67.2 ± 0.9	448	MeOH 24 h, 130 °C 12 h
PIM-NH$_2$ (cond.)	82 ± 1	433	MeOH 24 h, 130 °C 12 h followed by a pure-gas CO_2 conditioning test up to 31 atm
PIM-*t*-BOC	70 ± 9	351	MeOH 24 h, 130 °C 12 h
PIM-deBOC(acid)	65.0 ± 0.6	339	MeOH 24 h, 130 °C 12 h
PIM-deBOC(thermal)	83 ± 2	343	MeOH 24 h, 130 °C 12 h
PIM-1 (402 d)	46 ± 1	402	130 °C 12 h (labeled as "untreated")
PIM-COOH (330 d)	34.2 ± 0.8	330	130 °C 12 h (labeled as "untreated")

Table S2. Critical temperature for gases considered in this work[1].

Gas	T_c (K)
H_2	33.2
N_2	126.2
CH_4	190.5
CO_2	304.1

2. Physical aging upper bound

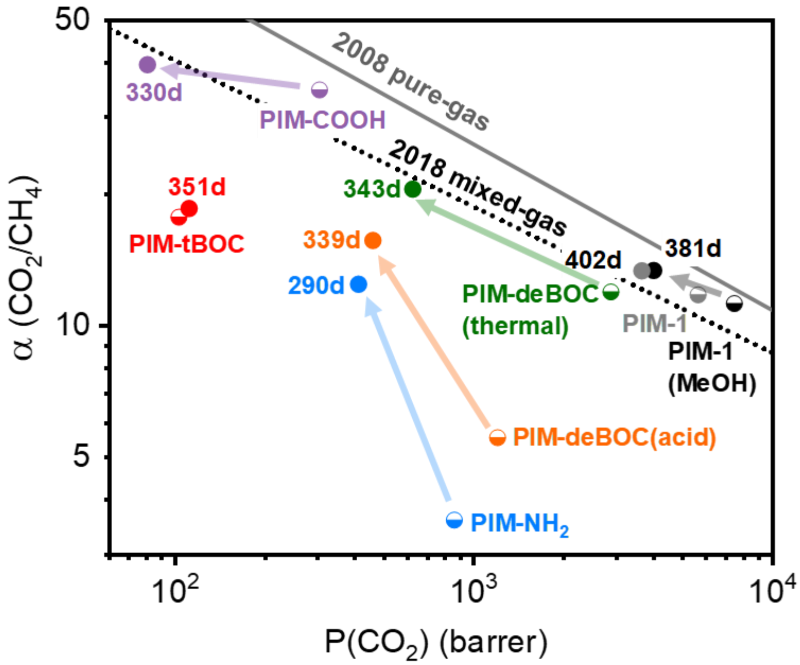

Fig. S1. Upper bound performance for freshly treated films (half-filled symbols) and aged films (filled symbols) tested at 1 atm and 35 °C for CO_2/CH_4 separation. The 2008 pure-gas upper bound[2] and 2018 mixed-gas upper bound[3] are shown for reference.

3. Variable-pressure mixed-gas permeation

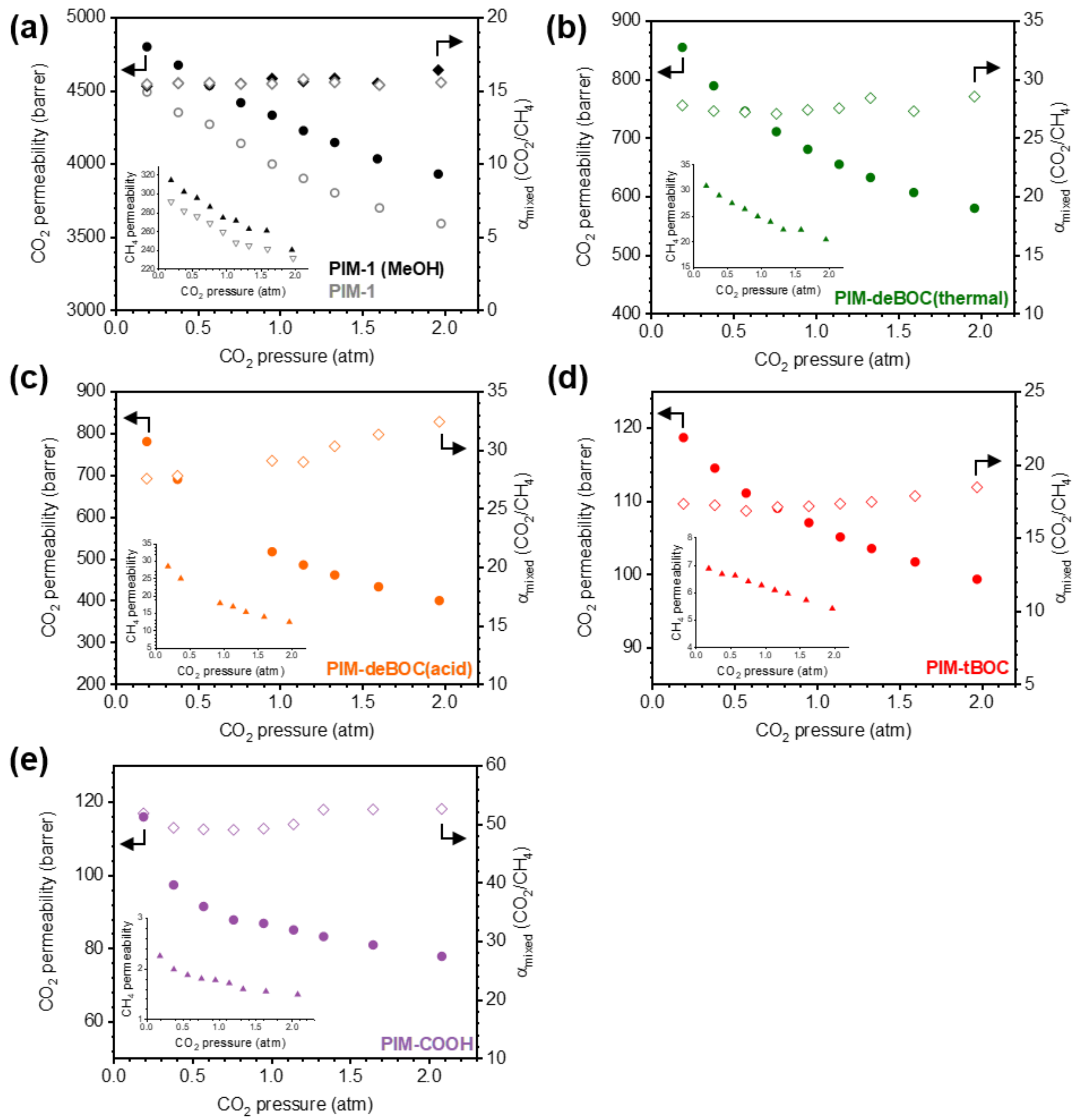

Fig. S2. CO_2 mixed-gas permeabilities (filled circles) and CO_2/CH_4 selectivities (open diamonds) for incremental CO_2 compositions ranging from 10% to 90% CO_2 tested at a total pressure of approximately 2 atm for (a) treated and untreated PIM-1 (381d and 330d aged, respectively), (b) PIM-deBOC(thermal), (c) PIM-deBOC(acid), (d) PIM-*t*-BOC, and (e) PIM-COOH. Insets correspond to mixed-gas CH_4 mixed-gas permeabilities (filled triangles) for incremental CO_2 compositions. Generally, mixed-gas tests were performed at a total pressure of 2 ± 0.2 atm.

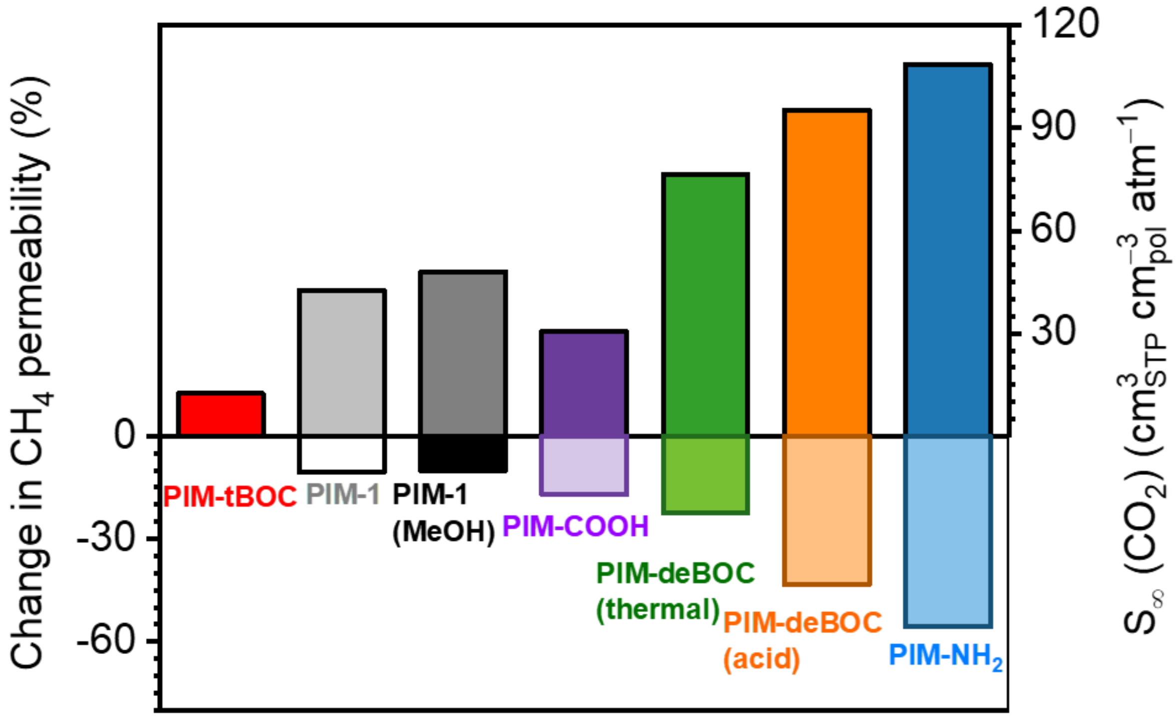

Fig. S3 Percent decrease in mixed-gas vs pure-gas CH_4 permeability measured at a CO_2 partial pressure of 1.2 atm compared to pure-gas sorption at infinite dilution for the aged PIM-1 derivatives considered in this study. No significant change was observed for PIM-tBOC.

4. Other mixtures (CO_2/N_2, H_2/N_2, and H_2/CH_4)

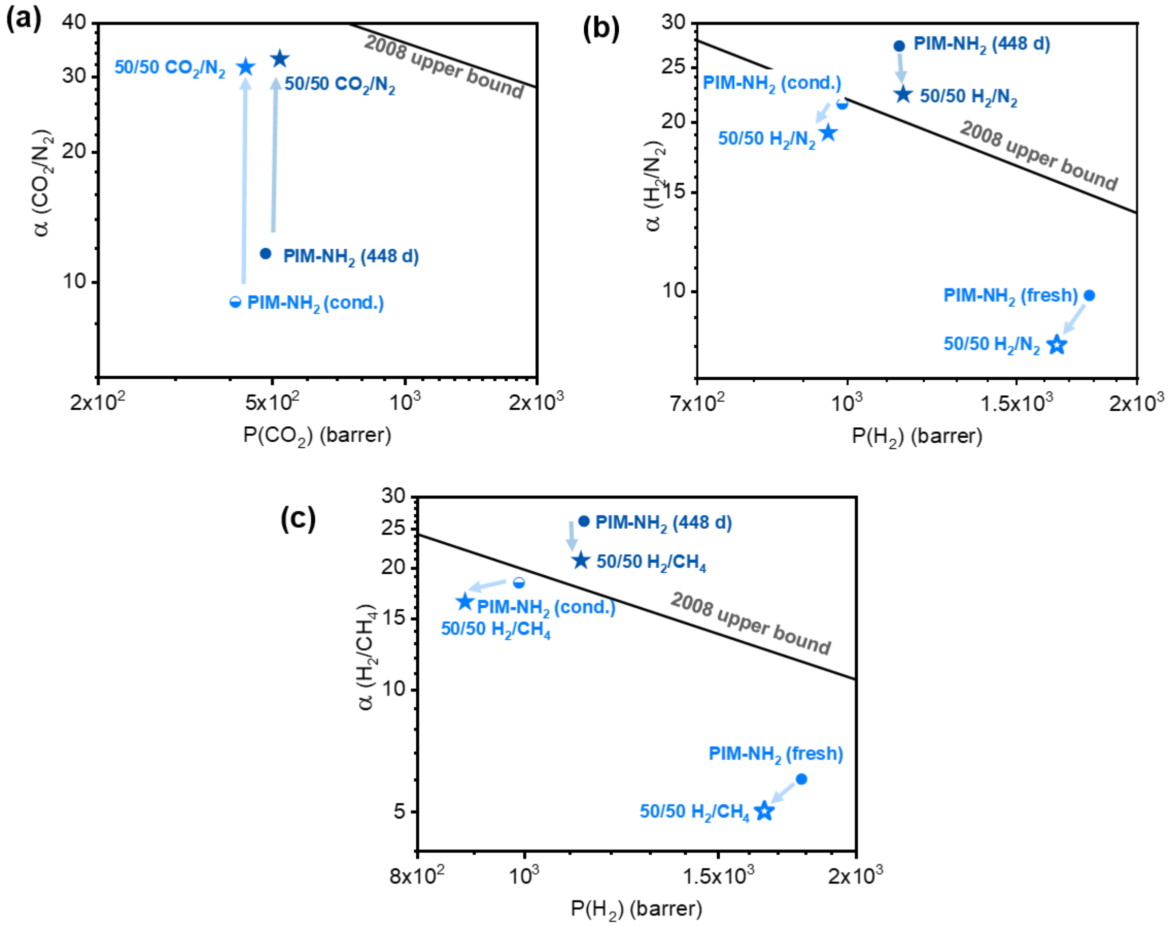

Fig. S4. (a) CO_2/N_2, (b) H_2/N_2, and (c) H_2/CH_4 upper bound plots for aged PIM-NH_2 (448 d) and an aged PIM-NH_2 sample previously conditioned at high CO_2 pressure (PIM-NH_2 (cond.)). Circles indicate pure-gas data and stars indicate mixed-gas data for the relevant mixture measured at 35 °C and 1 atm (pure-gas) and 2 atm total pressure (mixed-gas). H_2/CH_4 and H_2/N_2 plots include data for a freshly methanol treated PIM-NH_2 film.

5. Pure-gas sorption

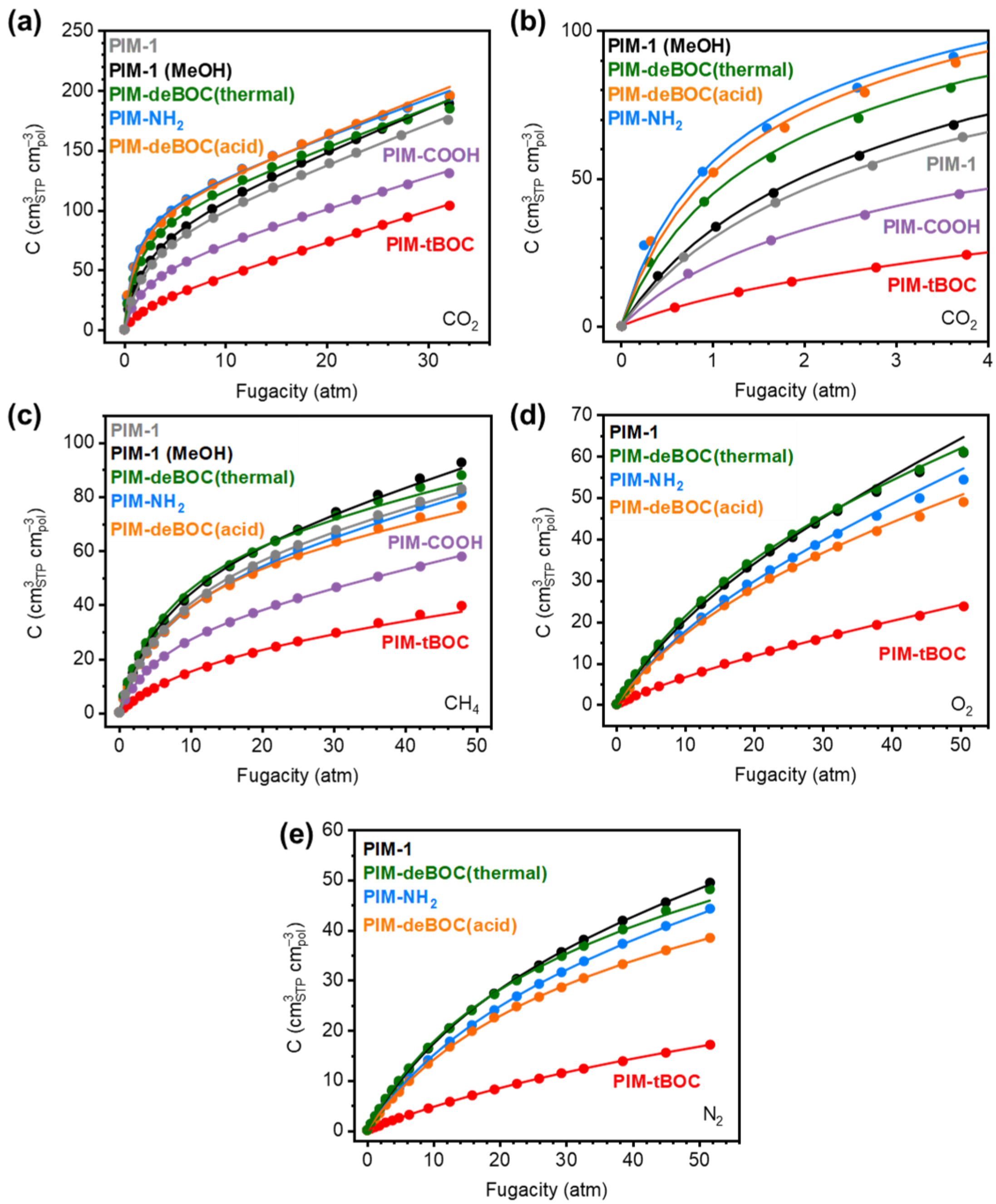

Fig. S5. (a and b) CO_2, (c) CH_4, (d) O_2, and (e) N_2 sorption isotherms and dual-mode sorption fitting for methanol treated PIM-1, PIM-deBOC(thermal), PIM-NH_2, PIM-deBOC(acid) and PIM-*t*-BOC, measured at 35 °C. Reference CO_2 and CH_4 isotherms for untreated PIM-1 and PIM-COOH are also included in (a), (b), and (c)[4].

Table S3. Dual mode sorption (DMS) model parameters and S_{∞} values calculated for all samples.

Parameter[a]	Gas	PIM-1[b]	PIM-NH_2	PIM-*t*-BOC	PIM-deBOC (thermal)	PIM-deBOC (acid)	PIM-1[c, 4]	PIM-COOH[d, 4]
$\boldsymbol{b}$ (atm^{-1})	N_2	0.042	0.039	0.017	0.044	0.038	0.041	0.041
	O_2	0.054	0.054	0.042	0.046	0.047	-	-
	CH_4	0.142	0.147	0.076	0.146	0.137	0.130	0.157
	CO_2	0.518	1.006	0.427	0.768	0.895	0.491	0.516
$\boldsymbol{k_D}$ (cm^3_{STP} cm^{-3}_{pol} atm^{-1})	N_2	0.32	0.29	0.10	0.19	0.16	0.24	0.24
	O_2	0.46	0.42	0.17	0.30	0.26	-	-
	CH_4	0.75	0.68	0.33	0.52	0.48	0.61	0.57
	CO_2	3.5	3.1	2.6	3.1	3.2	3.2	2.6
$\boldsymbol{C'_H}$ (cm^3_{STP} cm^{-3}_{pol})	N_2	48.1	43.4	25.6	52.2	45.8	46.0	26.5
	O_2	36.4	31.0	11.0	51.3	38.1	-	-
	CH_4	62.4	54.3	27.3	68.5	59.7	60.9	34.8
	CO_2	86.0	104.9	23.2	95.7	102.9	80.4	54.2
$\boldsymbol{S^{\infty}}$ (cm^3_{STP} cm^{-3}_{pol} atm^{-1})	N_2	2.32	1.97	0.525	2.46	1.88	2.13	1.34
	O_2	2.43	2.10	0.629	2.65	2.06	-	-
	CH_4	9.64	8.65	2.41	10.5	8.64	8.54	6.05
	CO_2	48.0	109	12.5	76.6	95.3	42.7	30.5

[a]DMS parameters were calculated by constraining the slope of the $\ln(k_D)$ versus critical temperature (T_c) trend to equal the slope of $\ln(S_{10atm})$ versus T_c[5].
[b]PIM-1 film soaked in methanol for 24 h then vacuum-dried at 130 °C for 12 h.
[c]PIM-1 film vacuum-dried at 130 °C for 12 h, as reported elsewhere[4].
[d]PIM-COOH film vacuum-dried at 130 °C for 12 h, as reported elsewhere[4].

6. Mixed-gas sorption predictions

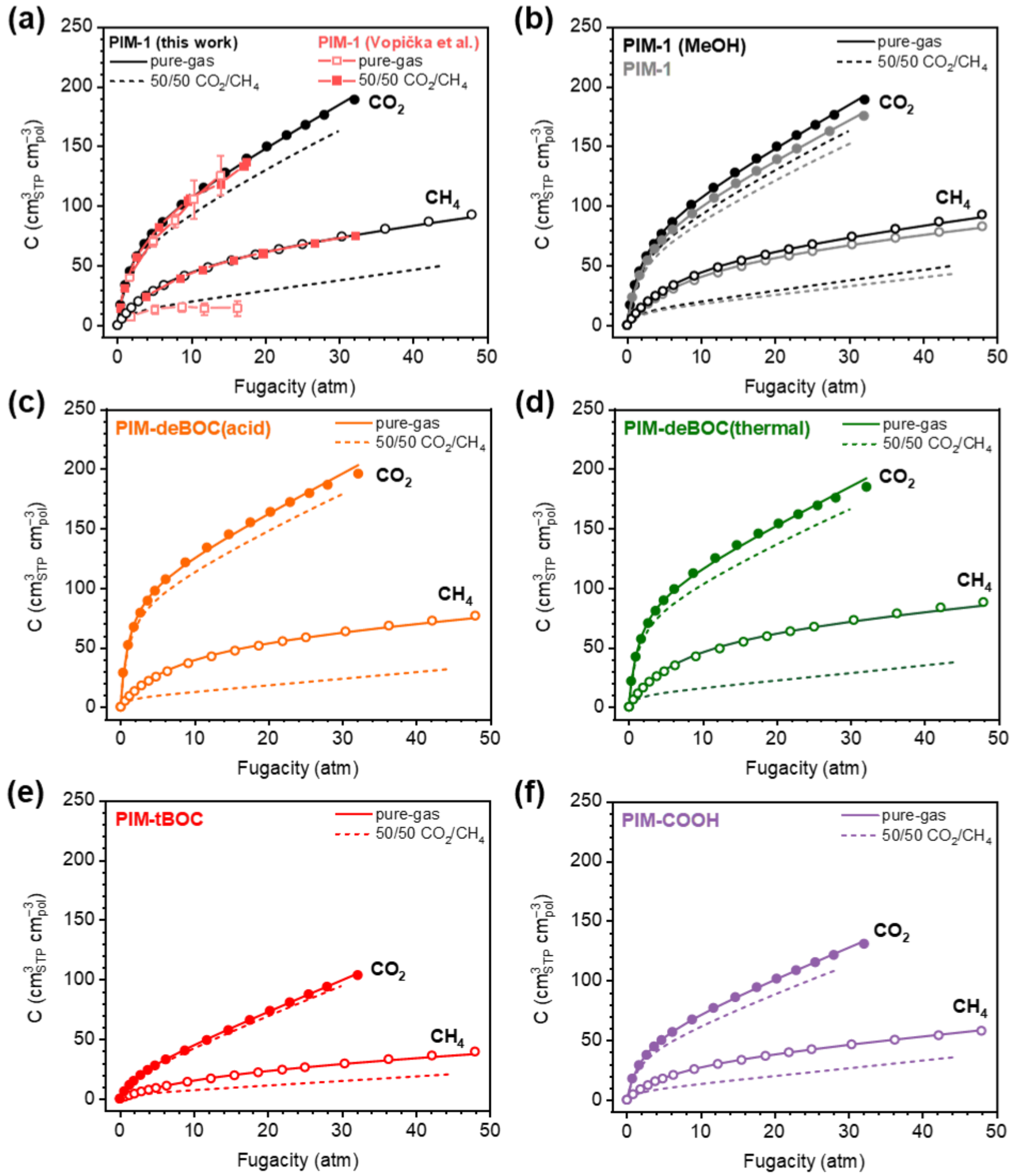

Fig. S6. Pure-gas CO_2 and CH_4 experimental sorption isotherms, represented as filled and open symbols, respectively. Pure-gas DMS model fittings (solid lines), and mixed-gas CO_2 and CH_4 sorption predictions (dashed lines) for (a) methanol treated PIM-1, (b) methanol treated and untreated PIM-1, (c) PIM-deBOC(acid), (d) PIM-deBOC(thermal), (e) PIM-*t*-BOC, and (f) PIM-COOH. Fig. S6a includes experimental pure- and 50/50 CO_2/CH_4 mixed-gas data previously reported for PIM-1 by Vopička et al.[6]

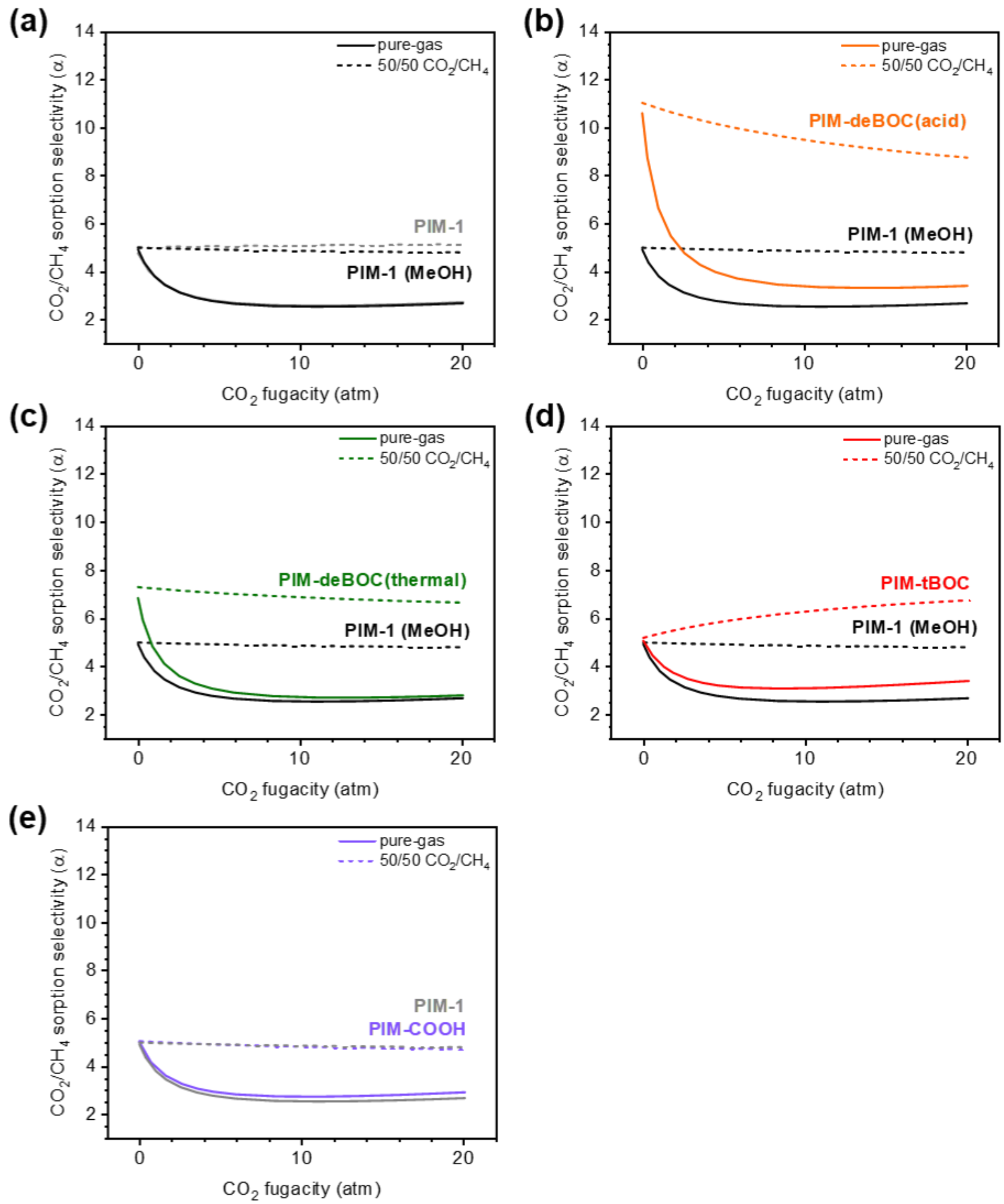

Fig. S7. Pure-gas (solid lines) and 50/50 mixed-gas (dashed lines) CO_2/CH_4 sorption selectivities for (a) methanol treated and untreated PIM-1, (b) PIM-deBOC(acid), (c) PIM-deBOC(thermal), (d) PIM-*t*-BOC, and (e) PIM-COOH.

Table S4. Pure- and mixed-gas diffusion and sorption selectivities for aged samples determined at CO_2 partial fugacities of 1 atm.

Polymer	Diffusion selectivity (α_D)[a]		Sorption selectivity (α_S)	
	α_D^{pure}	α_D^{mixed}	α_S^{pure} [b]	α_S^{mixed} [c]
PIM-1 (MeOH, 381 d)	3.5 ± 0.3	3.2 ± 0.2	3.8 ± 0.1	5.0 ± 0.2
PIM-1 (402 d)	3.6 ± 0.2	3.1 ± 0.2	3.8 ± 0.2	5.0 ± 0.2
PIM-NH$_2$ (290 d)	1.8 ± 0.2	2.5 ± 0.2	7.1 ± 0.3	11.9 ± 0.5
PIM-deBOC(acid)	2.4 ± 0.1	2.7 ± 0.2	6.6 ± 0.1	10.8 ± 0.2
PIM-deBOC(thermal)	4.4 ± 0.4	3.8 ± 0.3	4.6 ± 0.2	7.2 ± 0.3
PIM-tBOC	4.5 ± 0.9	3.2 ± 0.6	4.1 ± 0.2	5.4 ± 0.3
PIM-COOH (330 d)	9.8 ± 0.8	9.8 ± 0.8	4.0 ± 0.1	5.0 ± 0.2

[a]Calculated using the sorption–diffusion model and pure-gas sorption values or predicted mixed-gas sorption values.
[b]Calculated from DMS curves calculated with best-fit (i.e., unconstrained) parameters.
[c]Calculated from mixed-gas DMS curves predicted with constrained DMS parameters.

7. Pure and mixed-gas plasticization

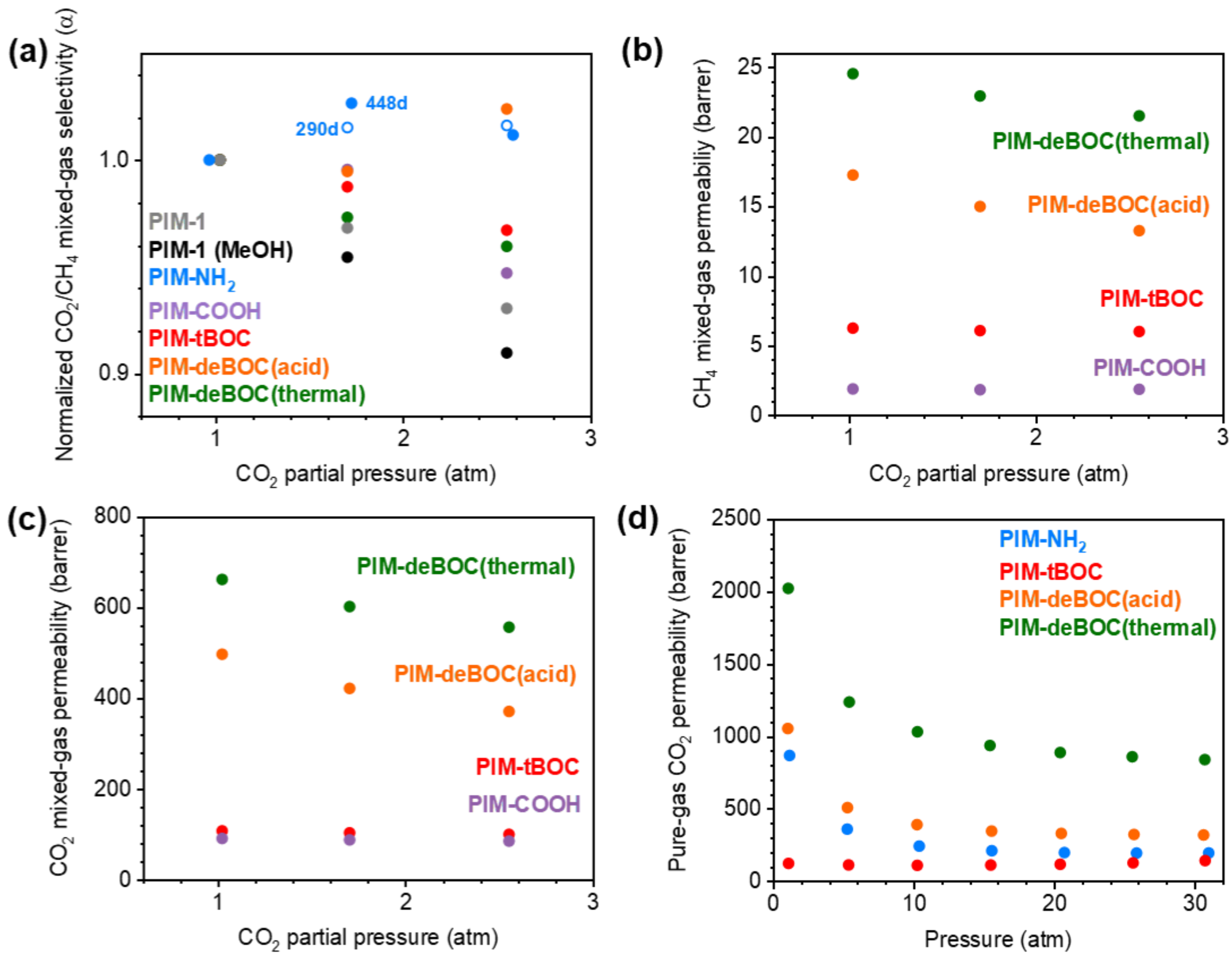

Fig. S8 (a) Normalized CO_2/CH_4 mixed-gas selectivities. Filled and open blue circles indicate data for PIM-NH_2 (448d) and PIM-NH_2 (290d), respectively. (b) CH_4 mixed-gas permeabilities, and (c) CO_2 mixed-gas permeabilities for PIMs considered in this work. Mixed-gas measurements were performed with 50/50 CO_2/CH_4 compositions at 35 °C. (d) Pure-gas CO_2 permeability for fresh PIM-NH_2, PIM-t-BOC, PIM-deBOC(acid), and PIM-deBOC(thermal) tested at 35 °C.

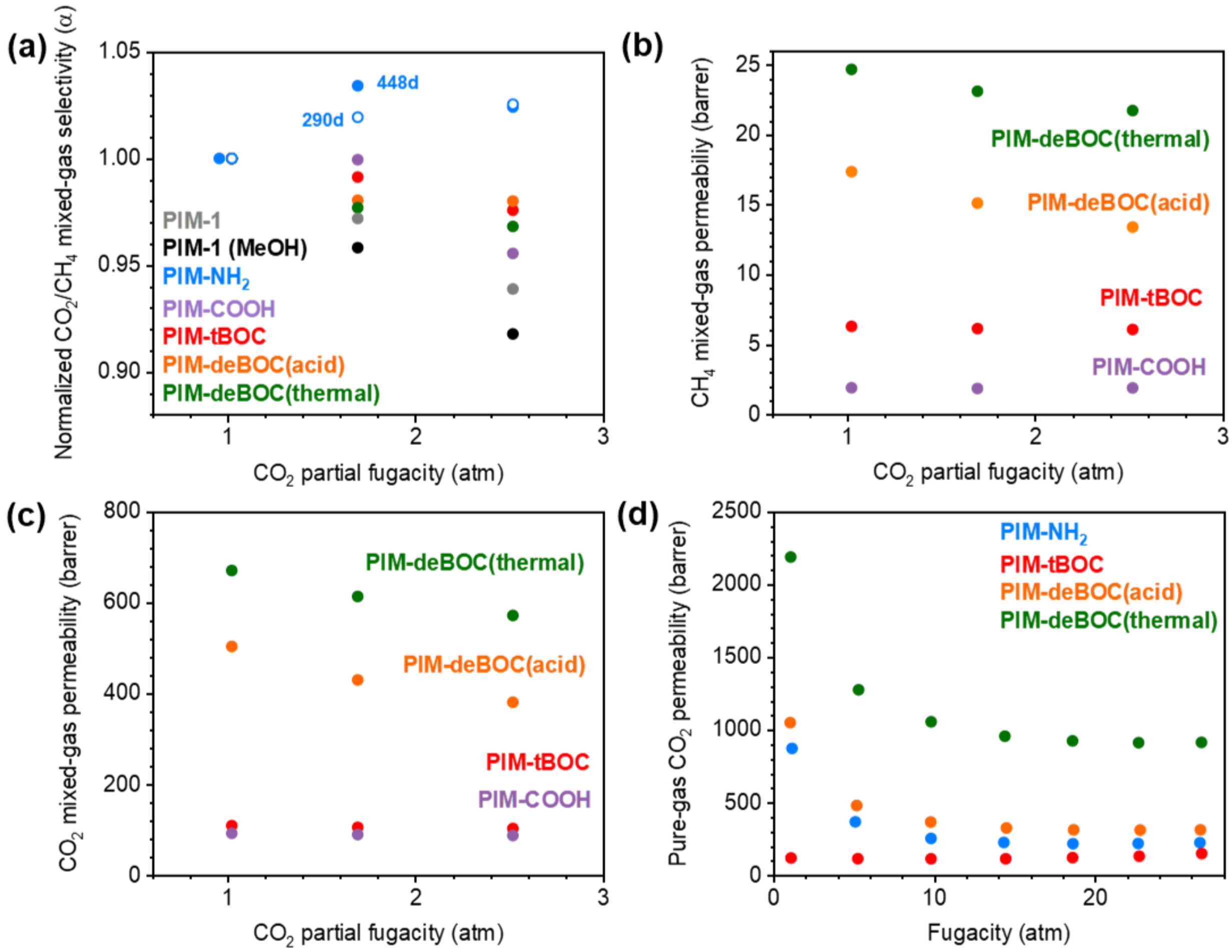

Fig. S9. *Fugacity-based:* (a) Normalized CO_2/CH_4 mixed-gas selectivities. Filled and open blue circles indicate data for PIM-NH_2 (448d) and PIM-NH_2 (290d), respectively. (b) CH_4 mixed-gas permeabilities, and (c) CO_2 mixed-gas permeabilities for PIMs considered in this work. Mixed-gas measurements were performed with 50/50 CO_2/CH_4 compositions at 35 °C. (d) Pure-gas CO_2 permeability for fresh PIM-NH_2, PIM-t-BOC, PIM-deBOC(acid), and PIM-deBOC(thermal) tested at 35 °C.

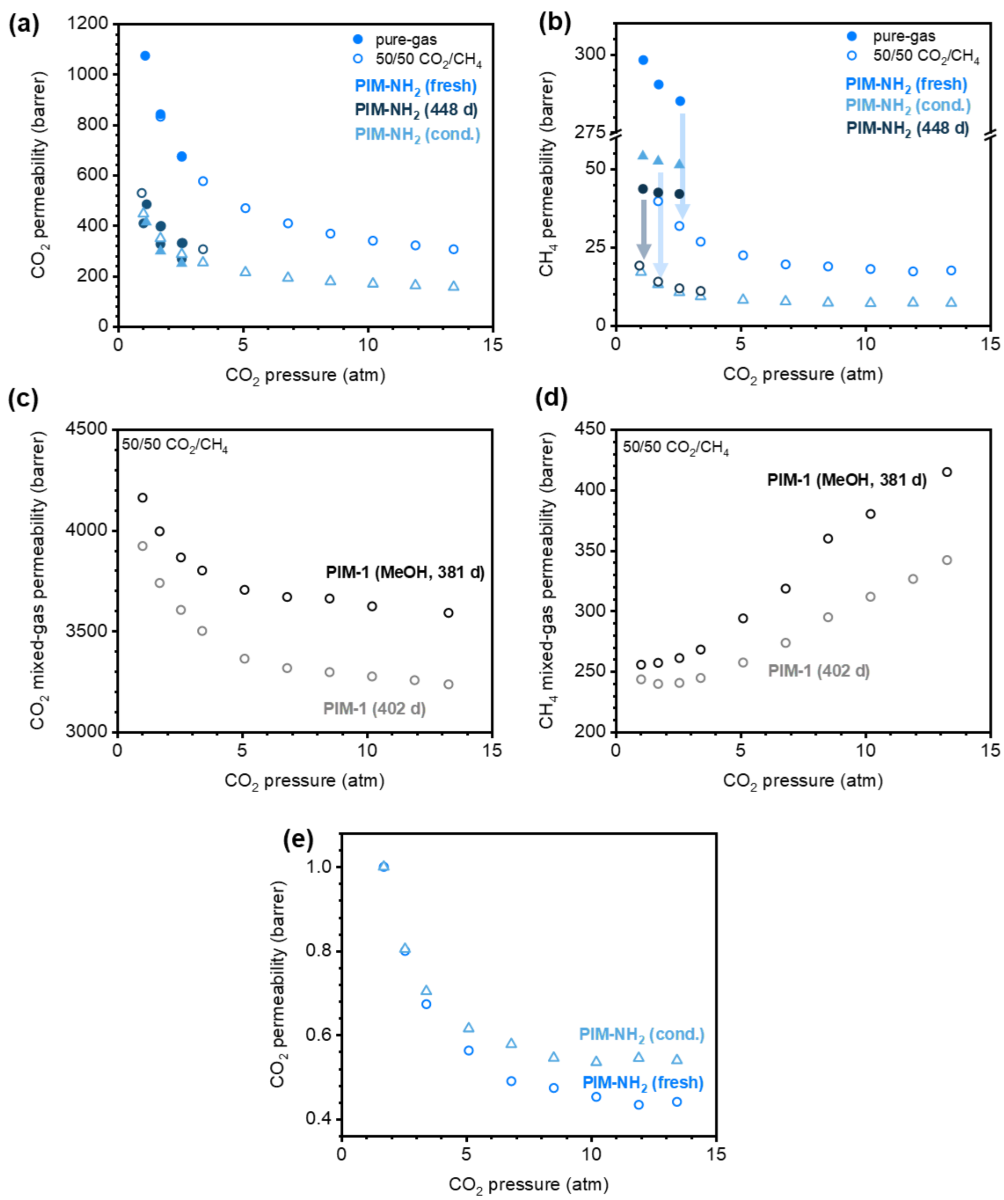

Fig. S10. Pure- (filled circles) and mixed-gas (open circles) (a) CO_2 and (b) CH_4 permeabilities for a PIM-NH_2 (fresh), PIM-NH_2 (448 d), and PIM-NH_2 (cond.). Arrows indicate the reduction in CO_2 or CH_4 permeabilities from pure-gas to mixed-gas tests. Mixed-gas (c) CO_2 and (d) CH_4 permeabilities for methanol treated (black) and untreated (gray) PIM-1 aged for 381 days and 402 days, respectively. (e) Normalized mixed-gas CH_4 permeabilities for PIM-NH_2 (fresh) and PIM-NH_2 (cond.) starting from a CO_2 partial pressure of 1.75 atm. Permeabilities were calculated with respect to pressure.

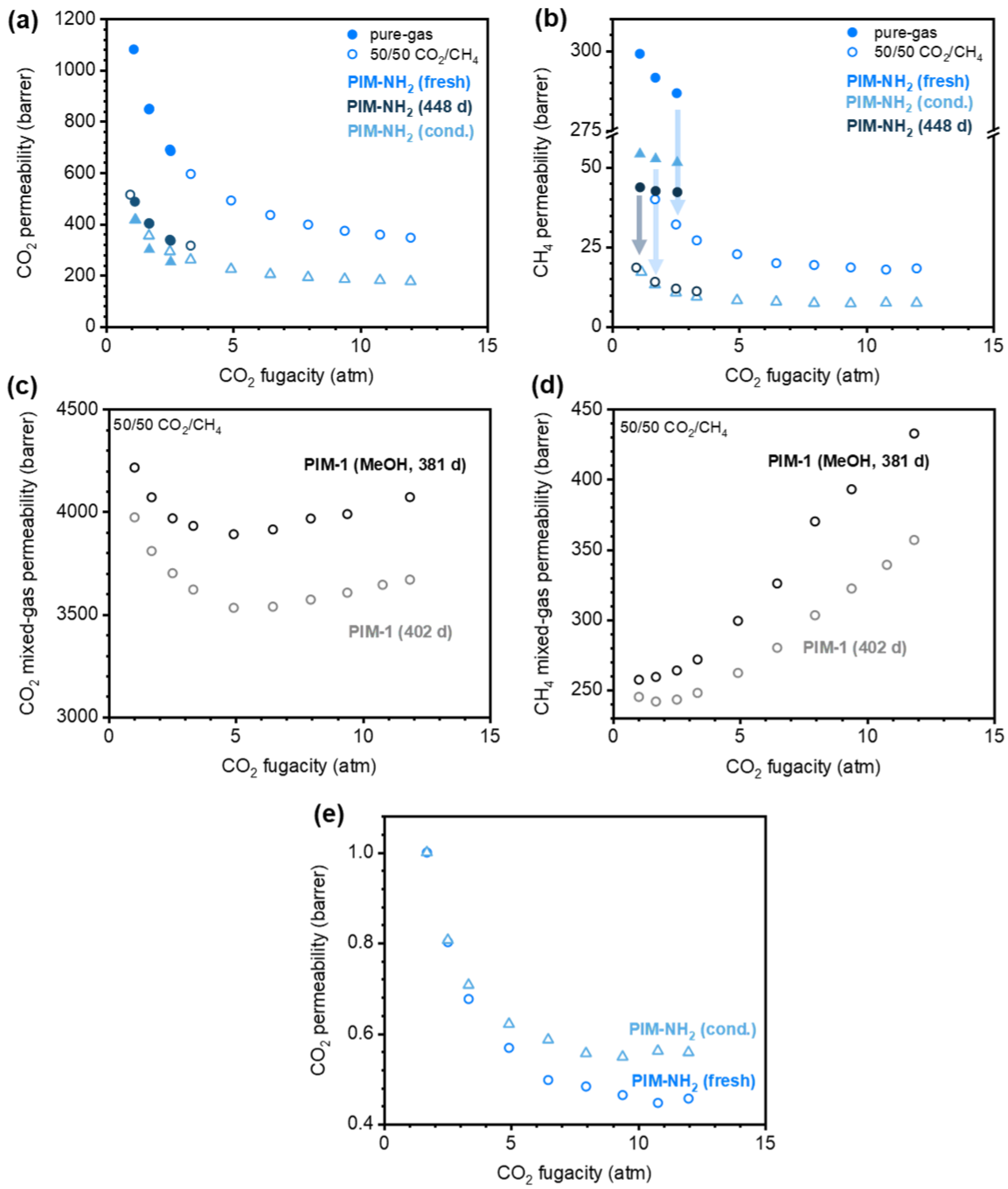

Fig. S11. *Fugacity-based:* Pure- (filled circles) and mixed-gas (open circles) (a) CO_2 and (b) CH_4 permeabilities for a PIM-NH_2 (fresh), PIM-NH_2 (448 d), and PIM-NH_2 (cond.). Arrows indicate the reduction in CO_2 or CH_4 permeabilities from pure-gas to mixed-gas tests. Mixed-gas (c) CO_2 and (d) CH_4 permeabilities for methanol treated (black) and untreated (gray) PIM-1 aged for 381 days and 402 days, respectively. (e) Normalized mixed-gas CH_4 permeabilities for PIM-NH_2 (fresh) and PIM-NH_2 (cond.) starting from a CO_2 partial fugacity of 1.75 atm. Permeabilities were calculated with respect to fugacity.

8. Reference literature data

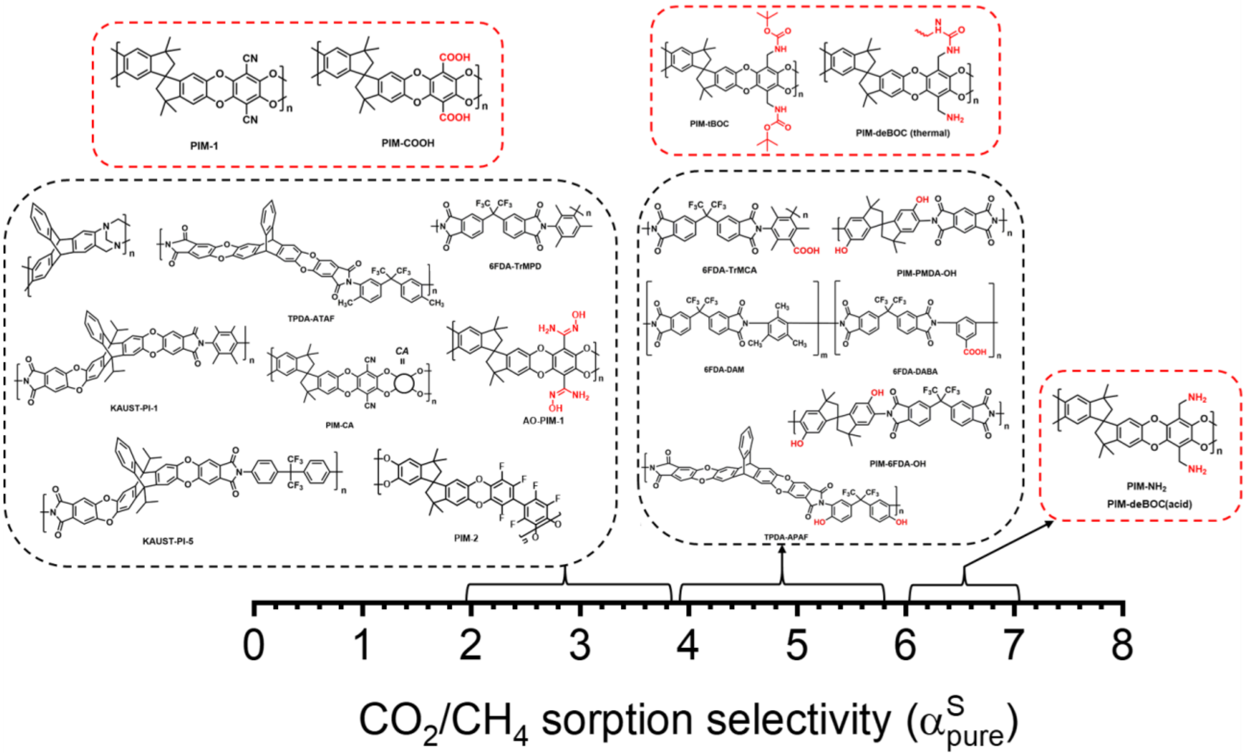

Fig. S12. Pure-gas CO_2/CH_4 sorption selectivity and relevant chemical structures for the samples considered in **Fig. 5a.** Chemical functionality with potential for hydrogen bonding are denoted in red. Polymers from this work are enclosed in red dashed boxes. Structures with sorption and mixed-gas data taken from literature are enclosed in black dotted boxes, including PIM-2[7], PIM-6FDA-OH and PIM-PMDA-OH[8], PIM-Trip-TB[9], 6FDA-DAM:DABA (3:2, 1:1, 1:2)[10], KAUST-PI-1 and KAUST-PI-5[11], TPDA-APAF and TPDA-ATAF[12], 6FDA-TrMPD and 6FDA-TrMCA[13], AO-PIM-1[14,15], PIM-CA (0.5, 1, 2, 3, and 10%)[16], and PIM-1[16–19]. Post-synthetically treated PIM-1 films were also plotted in **Fig. 5**, including PIM-UV (30 min)[20], TOX-PIM-1[19]

Table S5. Reference pure- and mixed-gas permeation data for CO_2/CH_4.

Polymer	T (°C)	P_{Total} (psia)	CO_2/CH_4 Comp.	P_{CH_4} (barrer)	P_{CO_2} (barrer)	$\alpha^{pure}_{CO_2/CH_4}$	$\alpha^{mixed}_{CO_2/CH_4}$	Ref.
P_{Total} = 29 psia								
PIM-2	25	14	pure	203.9	2960.9	14.5	-	7
PIM-2	–	29	35/65	457.2	6229.7	-	13.6	
PIM-Trip-TB	–	15	pure	310.5	4109.2	13.2	-	9

PIM-Trip-TB	–	29	50/50	299.4	3913.7	-	13.1	
PIM-1	30	29	pure	363	4533	12.5	-	21
PIM-1	30	29	30/70	378.5	4391	-	11.6	
PIM-1 (18.8% ZIF-8)	30	29	pure	157	2663	16.9	-	
PIM-1 (18.8% ZIF-8)	30	29	30/70	143	2832	-	19.8	
PIM-Trip-TB	25	14.7	pure	664	8616	12.9	-	22
PIM-Trip-TB	25	29.4	50/50	979	7267	-	7.4	
CoPIM-TB-1	25	14.7	pure	575	7835	13.6	-	
CoPIM-TB-1	25	29.4	50/50	654	6271	-	9.6	
CoPIM-TB-2	25	14.7	pure	448	6767	15.1	-	
CoPIM-TB-2	25	29.4	50/50	536	5818	-	10.9	
C-CoPIM-TB-1	25	14.7	pure	233	5437	23.3	-	
C-CoPIM-TB-1	25	29.4	50/50	264	5241	-	19.9	
C-CoPIM-TB-2	25	14.7	pure	169	4251	25.2	-	
C-CoPIM-TB-2	25	29.4	50/50	184	3931	-	21.4	
CF_3-ROMP	35	14.5	pure	644	6377	9.9	-	23
CF_3-ROMP	35	29	50/50	779	7063	-	9.1	
CF_3-ROMP	35	14.5	pure	1086	8867	8.2	-	
CF_3-ROMP	35	29	50/50	1151	9266	-	8.1	
CF_3-ROMP	35	14.5	pure	2368	13418	5.7	-	
CF_3-ROMP	35	29	50/50	2183	15036	-	6.89	
PIM-MP-TB	35	14.5	pure	26	633	24.4	-	24
PIM-MP-TB	25	29	52.1/47.9	36	766	-	21.3	
PIM-6FDA-OH	35	14.5	pure	9.1	263	28.9	-	8
PIM-6FDA-OH	22	29	50/50	5.3	223	-	42.1	
PIM-PMDA-OH	35	14	pure	7.7	198	25.7	-	
PIM-PMDA-OH	22	29	50/50	3	101	-	33.7	
PIM-TMN-Trip	25	14.6	pure	722	10910	15.1	-	25
PIM-TMN-Trip	25	29.1	60/40	489	11300	-	23.1	
P_{Total} = 43.5 psia								
PIM-2	25	14.5	pure	203.9	2960.9	14.5	-	7
PIM-2	–	43.5	35/65	457.2	5898.6	-	12.9	
PIM-TMN-Trip	25	29.1	pure	735	9773	13.3	-	25
PIM-TMN-Trip	25	43.5	60/40	566	11390	-	20.1	
PIM-EA(H_2)-TB	–	14.5	pure	62.6	1391	22.2	-	26
PIM-EA(H_2)-TB	–	43.5	35/65	70.9	1373.5	-	19.4	
PIM-SBF-1	25	14.5	pure	102	2410	23.6	-	27
PIM-SBF-1	–	43.5	35/65	89.9	2780	-	30.9	
PIM-SBF-5	25	14.5	pure	925	10000	10.8	-	
PIM-SBF-5	–	43.4	35/65	932	11100	-	11.9	
P_{Total} = 58 psia								
6FA-DAM:DABA 3:2	35	24.6	pure	4.2	185.9	44.3	-	10
6FA-DAM:DABA 3:2	35	61.5	50/50	3.3	178.6	-	54.1	

6FDA-DAM:DABA 1:1	35	22.9	pure	2.2	110.9	51.5	-	
6FDA-DAM:DABA 1:1	35	50.5	50/50	1.9	113.3	-	59.6	
6FDA-DAM:DABA 1:2	35	21.3	pure	0.8	41.7	54.2	-	
6FDA-DAM:DABA 1:2	35	52.7	50/50	0.5	43.1	-	86.2	
PIM-2	25	14.5	pure	203.9	2960.9	14.5	-	7
PIM-2	–	58	35/65	465.6	5636.2	-	12.1	
6FDA-mPDA	35	29.4	pure	0.2	14	70	-	28
6FDA-mPDA	35	58	50/50	0.2	14.7	-	67.9	
6FDA-DAP	35	29.4	pure	0.1	11	91.7	-	
6FDA-DAP	35	58	50/50	0.1	10.5	-	93.2	
6FDA-DAR	35	29.4	pure	0.1	8	94.1	-	
6FDA-DAR	35	58	50/50	0.1	7.5	-	94.8	
TDA1-APAF	35	29	pure	0.7	40	54.8	-	29
TDA1-APAF	35	58	50/50	0.55	37	-	67.3	
TDA1-APAF	35	29	pure	0.4	30	75	-	
TDA1-APAF	35	58	50/50	0.3	28	-	87.6	
PIM-1	22	58	pure	393	5147	13.1	-	30
PIM-1	22	53.6	50/50	324	3897	-	12.0	
TOX/PIM-1	22	58	pure	145	3892	26.8	-	
TOX-PIM-1	22	56.6	50/50	28.3	1101	-	38.9	
TPDA-mPDA	35	29.4	pure	11	349	31.7	-	31
TPDA-mPDA	35	59	50/50	9.7	293.5	-	30.3	
TPDA-DAR	35	29.4	pure	4.7	215	46.2	-	
TPDA-DAR	35	58	50/50	3.9	180.4	-	46.7	
AO-PIM-1	35	29	pure	34	1153	33.9	-	14
AO-PIM-1	35	58	50/50	35.5	847	-	23.9	
PIM-1	35	29	pure	362	5919	16.4	-	
PIM-1	35	58	50/50	427	5630	-	13.2	
KAUST-PI-1	35	29	pure	97.5	2329	23.9	-	11
KAUST-PI-1	35	58	50/50	97.5	2409	-	24.7	
KAUST-PI-5	35	29	pure	79.2	1560	19.7	-	
KAUST-PI-5	35	58	50/50	67.3	1431	-	21.2	
TR PIM-6FDA-OH (440°C)	35	29	pure	54	816	15.1	-	32
TR PIM-6FDA-OH (440°C)	35	58	50/50	44	784	-	17.8	
TPDA-APAF 250	35	29	pure	0.9	46	52.9	-	12
TPDA-APAF 250	35	58	50/50	0.6	39	-	60.9	
TPDA-APAF 120	35	29	pure	2.6	99	38.1	-	
TPDA-APAF 120	35	58	50/50	2.1	89	-	42.4	
TPDA-ATAF 250	35	29	pure	3.8	125	32.8	-	
TPDA-ATAF 250	35	58	50/50	3.6	121	-	33.61	
TPDA-ATAF 120	35	29	pure	11	325	29.6	-	
TPDA-ATAF 120	35	58	50/50	10	299	-	29.9	
6FDA-TrMPD (6FDA-DAM)	35	29	pure	23	498	21.6	-	13

6FDA-TrMPD (6FDA-DAM)	35	58	50/50	19.1	448	-	23.4	
6FDA-TrMCA	35	29	pure	3.2	144	45	-	
6FDA-TrMCA	35	60	50/50	2.9	141	-	47.9	
PIM-1	25	29	pure	536	6576	12.3	-	33
PIM-1	25	58	50/50	409	5840	-	14.3	
6FDA-DATRI	35	15	pure	6.2	189	30.5	-	34
6FDA-DATRI	35	58	50/50	-	-	-	28.7	
6FDA-DAT1-OH	35	29	pure	1.4	70	50.0	-	35
6FDA-DAT1-OH	35	58	50/50	1.51	69.5	-	46.0	
6FDA-DAT1	35	29	pure	2.82	102.25	36.3	-	36
6FDA-DAT1	35	58	50/50	2.52	96	-	38.1	
6FDA-DAT2	35	29	pure	5.22	155.75	29.8	-	
6FDA-DAT2	35	58	50/50	4.64	138.75	-	29.9	
PIM-TMN-Trip	25	44	pure	730	10880	14.9	-	25
PIM-TMN-Trip	25	58	60/40	594	10730	-	18.1	
P_{Total} = 58 psia								
cPIM-1/Matrimid (10:90)	35	51	pure	0.6	17.9	32.5	-	37
cPIM-1/Matrimid (10:90)	35	103	50/50	0.5	13.9	-	28.4	
cPIM-1/Matrimid (30:70)	35	51	pure	1.7	48.7	27.9	-	
cPIM-1/Matrimid (30:70)	35	103	50/50	1.8	43.2	-	24.3	
cPIM-1/Matrimid (50:50)	35	51	pure	6.1	145	23.8	-	
cPIM-1/Matrimid (50:50)	35	103	50/50	6.7	131	-	19.6	
cPIM-1/Matrimid (70:30)	35	51	pure	25	486	19.4	-	
cPIM-1/Matrimid (70:30)	35	103	50/50	22.8	417	-	18.3	
cPIM-1/Matrimid (90:10)	35	51	pure	57	982	17.2	-	
cPIM-1/Matrimid (90:10)	35	103	50/50	53.5	905	-	16.9	
PIM-300-2.0d	35	51	pure	73	4000	54.8	-	38
PIM-300-2.0d	35	100	50/50	42.9	2317	-	54.0	
PIM-UV 20min	35	50	pure	62.1	1869	30.1	-	20
PIM-UV 20min	35	100	50/50	61.3	1554	-	25.4	
PIM-UV 30min	35	50	pure	23.1	724	31.3	-	
PIM-UV 30min	35	100	50/50	20.4	724	-	35.5	
PIM-1	22	58.0	pure	397	5135	12.9	-	19
PIM-1	22	116	50/50	298	3020	-	10.1	
TOX-PIM-1	22	58	pure	15.9	1100	69.2	-	
TOX-PIM-1	22	116	50/50	20.4	890	-	43.6	
TOX-PIM-1	22	58	pure	58	1956	33.7	-	
TOX-PIM-1	22	116	50/50	38.2	1390	-	36.4	
Ultem/PIM-1 (90/10)	35	50	pure	0.1	4	32.9	-	39
Ultem/PIM-1 (90/10)	35	100	50/50	0.1	3.4	-	37.4	
cPIM-1/Torlon (10/90)	35	51	pure	-	1.2	39.8	-	40
cPIM-1/Torlon (10/90)	35	102	50/50	-	1.1	-	39.3	
cPIM-1/Torlon (30/70)	35	51	pure	0.1	4.8	34.4	-	

cPIM-1/Torlon (30/70)	35	102	50/50	0.1	4.5	-	34.8	
cPIM-1/Torlon (50/50)	35	51	pure	0.7	21.4	30.6	-	
cPIM-1/Torlon (50/50)	35	102	50/50	0.7	19.5	-	29.9	
AO-PIM-1	35	14	pure	29	980.7	33.8	-	41
AO-PIM-1	35	87	50/50	35	700	-	20	
AO-PIM-1 (9% adamantane)	35	14	pure	82.5	2483.6	30.1	-	
AO-PIM-1 (9% adamantane)	35	87	50/50	73.3	1320	-	18	
PIM-1	30	29	pure	361.7	4521	12.5	-	18
PIM-1	30	96	30/70	359.8	4318	-	12	
PIM-1	35	51.4	pure	198	3127	15.8	-	16
PIM-1	35	102	50/50	228	2708	-	11.9	
PIM-CA-0.5%	35	51	pure	267	4388	16.4	-	
PIM-CA-0.5%	35	102	50/50	304	3993	-	13.1	
PIM-CA-1%	35	51	pure	282	4878	17.3	-	
PIM-CA-1%	35	102	50/50	331	4602	-	13.9	
PIM-CA-2%	35	51	pure	232	4469	19.3	-	
PIM-CA-2%	35	102	50/50	283	4226	-	14.9	
PIM-CA-3%	35	51	pure	204	4139	20.3	-	
PIM-CA-3%	35	102	50/50	257	4031	-	15.7	
PIM-CA-10%	35	51	pure	97	2738	28.2	-	
PIM-CA-10%	35	102	50/50	113	2284	-	20.2	
PIM-1	30	29	pure	363	4521	12.5	-	17
PIM-1	30	96	30/70	377	4336	-	11.5	
PIM-EA(ME_2)-TB	25	29	pure	50	1320	26.4	-	42
PIM-EA(ME_2)-TB	35	88	50/50	118	1626	-	13.8	
PIM-EA(ME_2)-TB (10% PAF-1)	35	44	pure	833	6329	7.6	-	
PIM-EA(ME_2)-TB (10% PAF-1)	35	88	50/50	1085	7237	-	6.7	
PIM-EA(H_2)-TB (10% PAF-1)	35	44	pure	286	4429	15.5	-	
PIM-EA(H_2)-TB (10% PAF-1)	35	88	50/50	511	4842	-	9.5	
6FA-DAM:DABA 3:2	35	55	pure	3.98	166	41.7	-	10
6FA-DAM:DABA 3:2	35	109	50/50	3.3	163	-	49.4	
6FDA-DAM:DABA 1:1	35	52	pure	1.94	102	52.6	-	
6FDA-DAM:DABA 1:1	35	106	50/50	1.9	108	-	56.8	
6FDA-DAM:DABA 1:2	35	50	pure	0.65	37	56.9	-	
6FDA-DAM:DABA 1:2	35	100	50/50	0.45	39	-	86.7	

9. Sorption upper bound at infinite dilution

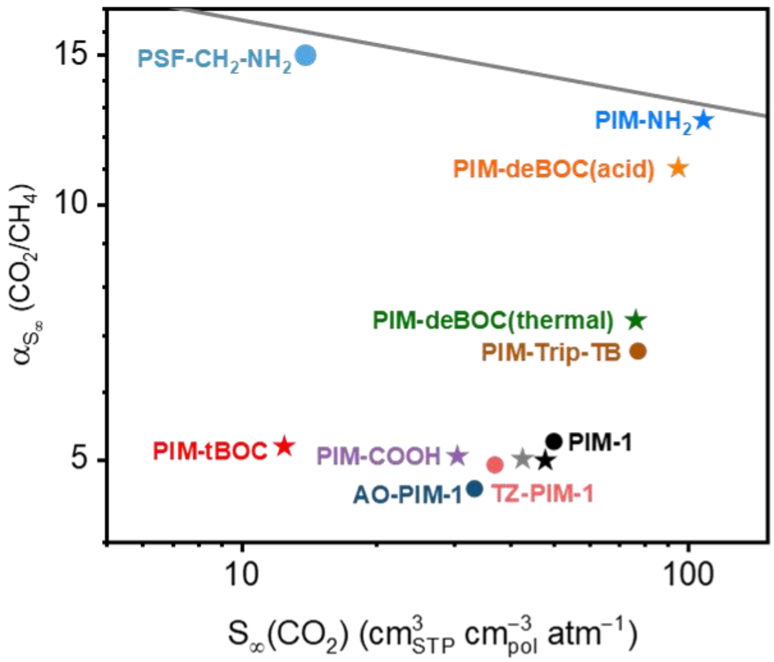

Fig. S13. CO_2/CH_4 2014 pure-gas sorption upper bound[43] at infinite dilution. Plotted data are AO-PIM-1[15] (dark blue circle), TZ-PIM-1[15] (pink circle), PIM-1[6] (black circle), PIM-Trip-TB[9] (brown circle), amine-functionalized polysulfone[44] (light blue circle), methanol treated PIM-1 (gray star), untreated PIM-1 (black star), PIM-NH_2 (light blue star), PIM-deBOC(acid) (orange star), PIM-deBOC(thermal) (green star), PIM-*t*-BOC (red star), and PIM-COOH (purple star). Sorption and CO_2/CH_4 sorption selectivities at infinite dilution were calculated from best-fit DMS modeling of pure-gas sorption data for the six PIM samples included in this work. Literature values for microporous polymers are discussed in work by Genduso et al.[9,45]

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