Electronic Supplementary Information (ESI)

High performance MIL-101(Cr)@6FDA-mPD and MOF-199@6FDA-mPD mixed-matrix membranes for CO_2/CH_4 separation

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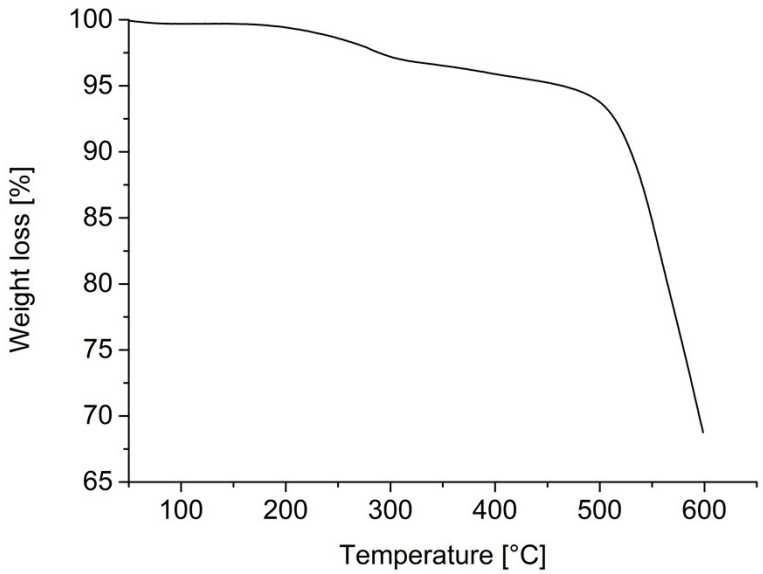

Fig. S1 Thermogravimetric analysis (TGA) curve of pure 6FDA-mPD under nitrogen at a heating flow of 5 K/min.

Table S1 Elemental analysis of MOF-199 and MIL-101(Cr) [a]

	MOF-199 $[Cu_3(btc)_2(H_2O)_2]$ [b]		MIL-101(Cr) $[Cr_3(O)(OH)(bdc)_3(H_2O)_2]\cdot DMF$ [c]	
Atom	calculated	experimental	calculated	experimental
C	33.73	35.10	41.03	40.66
H	1.57	1.84	3.06	2.95
N	0	0	1.77	1.52

[a] We note that CHN analyses of MOFs are often ambiguous due to the solvent which can partly remain in the pores during sample preparation or at least water vapor which can be adsorbed from air during sample storage and handling for the analysis.
[b] MOF-199: The aqua ligands are weakly bound to the Cu atoms with elongated Cu···O bond distances due to the inherent Jahn-Teller distortion at the Cu(II) atom. Upon drying and sample preparation part of the initially three aqua ligands (one at each Cu atom) will be removed.
[c] MIL-101(Cr): The solvent DMF was used for washing and is obviously partly retained and not removed when the sample was then finally dried at room temperature.

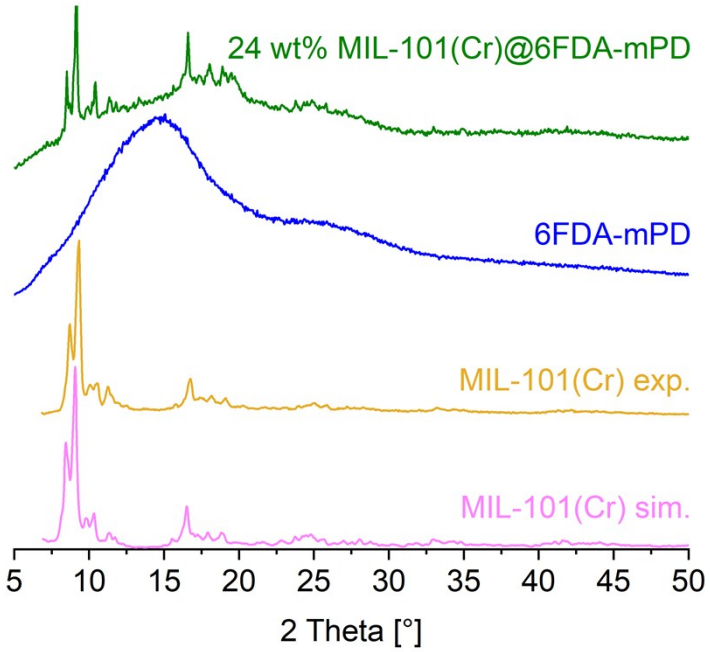

Fig. S2 X-ray powder diffraction pattern of MIL-101 (Cr), 6FDA-mPD polyimide and a mixed matrix membrane of 6FDA-mPD with 24 wt% loading of MIL-101 (Cr).

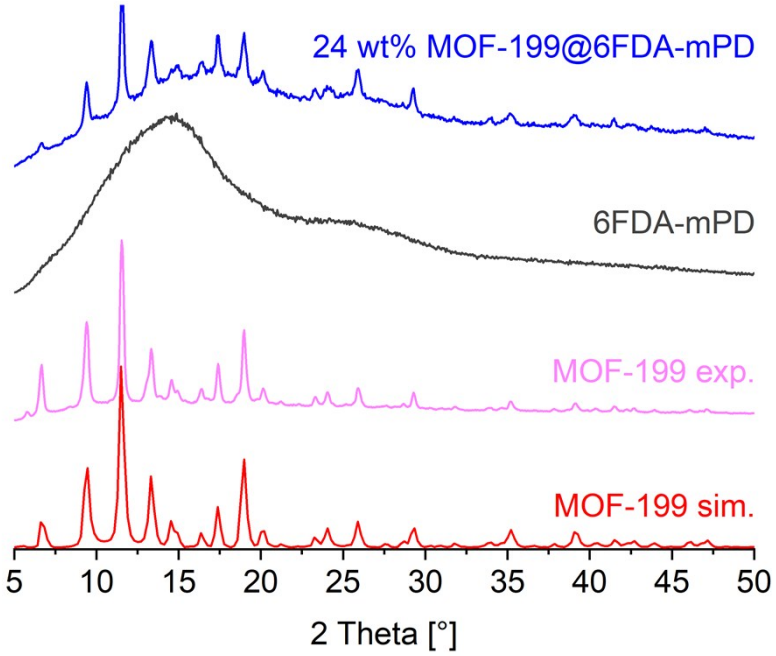

Fig. S3 X-ray powder diffraction pattern of MOF-199, 6FDA-mPD polyimide and a mixed matrix membrane of 6FDA-mPD with 24 wt% loading of MOF-199.

We measured the N_2-77 K sorption isotherms of MIL-101(Cr) @6FDA-mPD and MOF-199@6FDA-mPD to possibly verify the preserved porosity of the MOF filler.

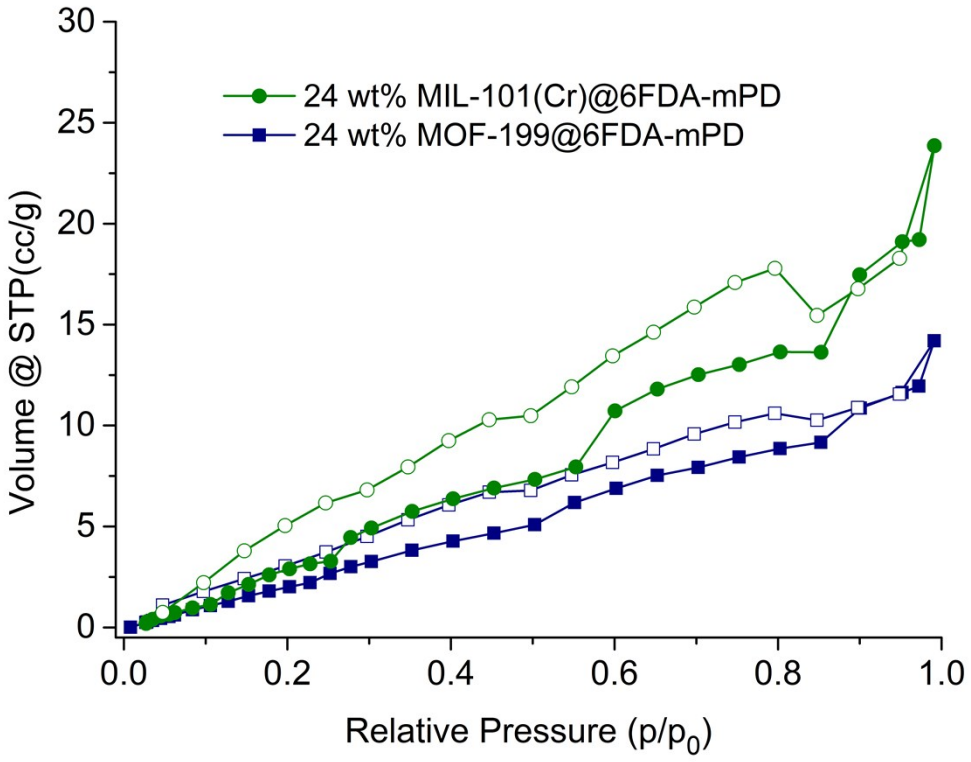

Fig. S4 N_2-sorption isotherm of 24 wt% MIL-101(Cr) @6FDA-mPD and 24 wt% MOF-199@6FDA-mPD at 77K.

Due to the low temperature it is kinetically not possible for the N_2 molecules to diffuse in the necessary time or time limit through the dense polymer part of the membrane into the MOF. Thus, the isotherm corresponds to a nonporous sample (Matrimid). This confirms our earlier experience with other MMMs based, for example, on polysulfone where we had also (unsuccessfully) attempted to confirm the porosity of the embedded MOF through gas sorption measurements.

SEM images with EDX mapping

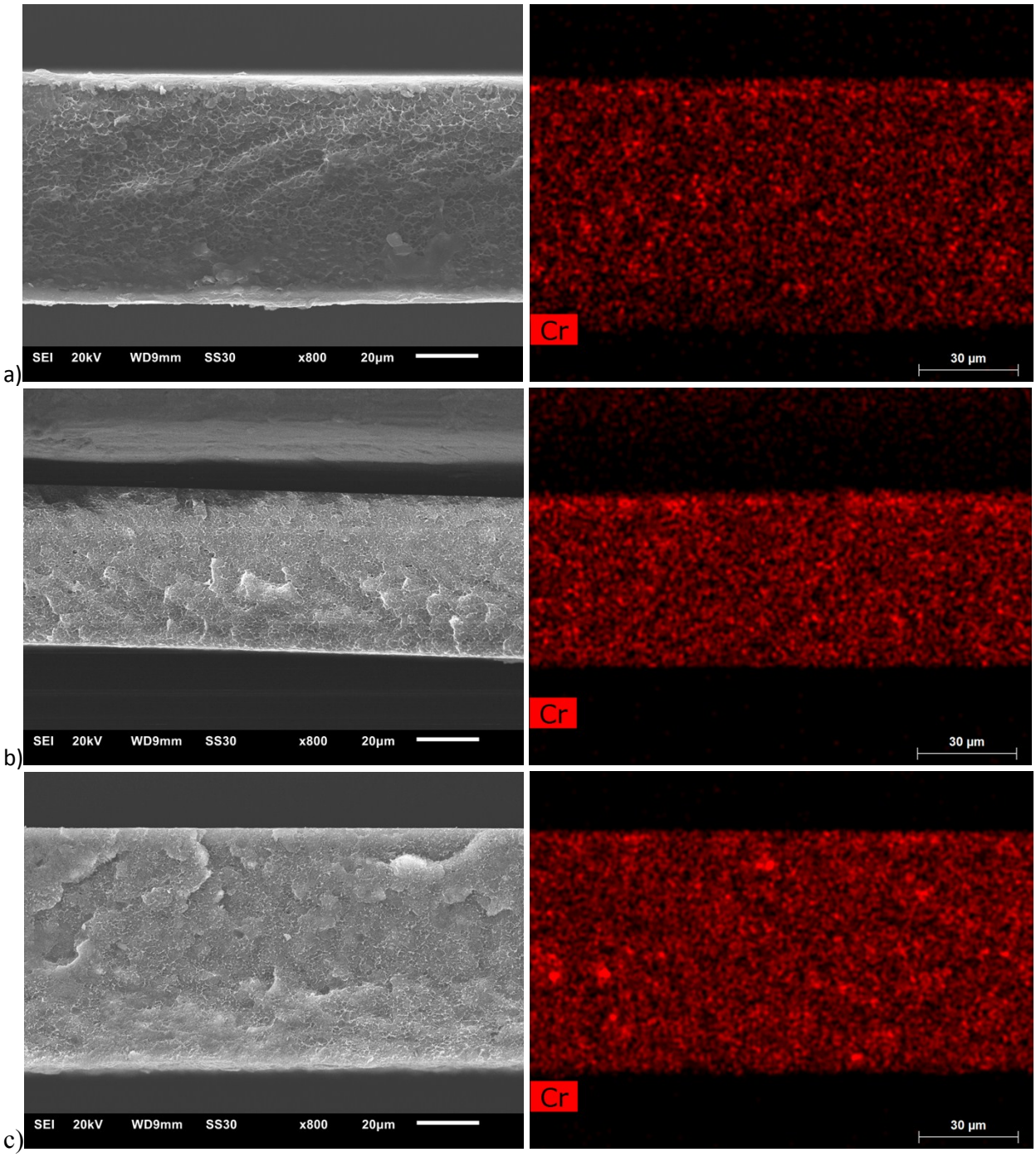

Fig. S5 SEM images combined with SEM/EDX mapping of chromium for cross sections of MMMs of MIL101(Cr)@6FDA-mPD with different loadings of MIL-101(Cr). a) 8 wt% MOF; b) 16 wt% MOF; c) 24 wt% MOF.

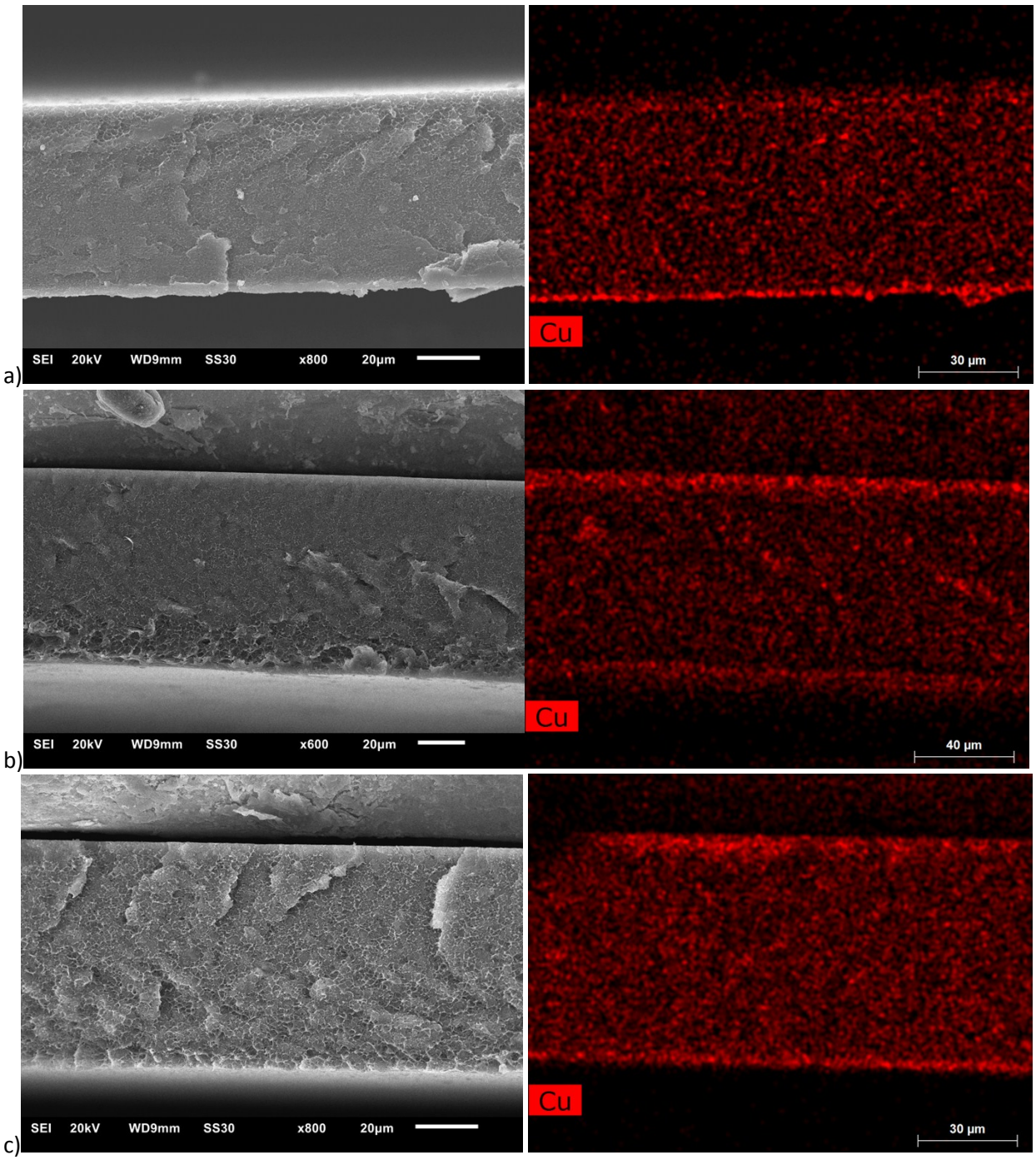

Fig. S6 SEM images combined with SEM/EDX mapping of copper for cross sections of MMMs of MOF-199@6FDA-mPD with different loadings of MOF-199. a) 8 wt% MOF; b) 16 wt% MOF; c) 24 wt% MOF. Note, that for some EDX images copper is detected outside of the membrane cross section, due to reflections from the sample holder which is made of brass.

Maxwell model[1,2,3,4]

The Maxwell model requires no assumption and leads to no conclusion about the gas selectivity of the MMMs. The Maxwell model is solely based on permeability (P) and filler volume fraction (ϕ with weight percentage and density) as given in eq. (S1)-(S3). With the Maxwell model it is possible to predict gas permeation through a dense composite membrane. For spherical particles the permeability of the composite membrane P_{eff} can be estimated as follows:

$$P_{eff} = P_c \times \frac{P_d + 2P_c - 2\phi_d \times (P_c - P_d)}{P_d + 2P_c + \phi_d \times (P_c - P_d)} \quad \text{(S1)}$$

Where, P_c is the continuous phase permeability, P_d is the dispersed phase permeability and ϕ_d is the volume fraction of the filler.

With equation S2 one can calculate the filler volume fraction in the dispersed phase:

$$\phi_d = \frac{w_d / \rho_d}{\frac{w_c}{\rho_c} + \frac{w_d}{\rho_d}} \quad \text{(S2)}$$

With w_d and w_c as the weight percentages, ρ_d and ρ_c as the densities of the filler and the polymer.

In cases where the filler exhibits a distinctly higher permeability than the continuous phase ($P_d >> P_c$) equation (S1) can be simplified as follows, which then corresponds to "Maxwell model ∞":

$$P_d >> P_c; \quad \frac{P_{eff}}{P_c} = \frac{1 + 2\phi_d}{1 - \phi_d} \quad \text{(S3)}$$

This limiting equation (S3) is also given as equation (1) in the main manuscript.
For MOF-199 (HKUST-1) pure MOF membranes were already fabricated and measured several times for their CO_2 and CH_4 permeance.[5]
The experimental CO_2 permeance of roughly 2000×10^{-10} mol m^{-2} s^{-1} Pa^{-1} with a membrane thickness of about 10 µm translates into a CO_2 permeability of about 6000 Barrer = P_d in eq. (S1).
For CH_4 a permeability of about 1000 was measured (permeance ≈ 300×10^{-10} mol m^{-2} s^{-1} Pa^{-1}).
CO_2 permeability of pure 6FDA-mPD, P_c = 10 Barrer.
For MIL-101(Cr), to our best knowledge, no pure MOF membrane was ever produced. But considering that the pore sizes of MIL-101(Cr) are even larger than those of MOF-199 we would expect a similar result.

Table S2 CO_2/CH_4 (50/50 mixture) permeation results on Mixed MIL-101(Cr)@6FDA-mPD membranes. Values are the average and standard deviation of at least two different membrane samples.

Membrane				
MIL-101(Cr) loading [wt%]	Membrane thickness [µm]	P (CO_2) [Barrer]	P (CH_4) [Barrer]	α (CO_2/CH_4)
0	44 – 110	9.9 ± 0.4[b]	0.19 ± 0.01[b]	54 ± 6
8	47 – 55	13.8 ± 0.1[a]	0.26 ± 0.00[a]	53 ± 1
16	61 – 74	29 ± 1[b]	0.51 ± 0.04[b]	54 ± 7
24	81 – 85	49.6 ± 0.2[a]	1.00 ± 0.02[a]	50 ± 1

[a] experiments performed at 35 °C and ΔP = 2 bar total feed pressure; [b] experiments performed at 25 °C and ΔP = 3 bar total feed pressure.

Table S3 CO_2/CH_4 (50/50 mixture) permeation results on MOF-199@6FDA-mPD membranes.

Membrane				
MOF-199 loading [wt%]	Membrane thickness [µm]	P (CO_2) [Barrer]	P (CH_4) [Barrer]	α (CO_2/CH_4)
0	44 – 110	9.9 ± 0.4[b]	0.19 ± 0.01[b]	54 ± 6
8	77 – 82	11.4 ± 0.3[b]	0.17 ± 0.01[b]	67 ± 6
16	99 – 102	20.2 ± 0.9[b]	0.27 ± 0.01[b]	73 ± 6
24	80 – 87	28.3 ± 0.4[a]	0.32 ± 0.01[a]	89 ± 4

Values are the average and standard deviation of at least two different membrane samples. [a] experiments performed at 35 °C and ΔP=2 bar total feed pressure; [b] experiments performed at 25 °C and ΔP=3 bar total feed pressure.

Table S4 Glass transition temperatures (T_g) for pure 6FDA-mPD and different weight percentages of MIL-101Cr and MOF-199@6FDA-mPD MMMs.

Material	**T_g [K]**	
6FDA-mPD	300	± 2
8wt% MIL-101Cr@6FDA-mPD MMM	303	± 2
16wt% MIL-101Cr@6FDA-mPD MMM	299	± 4
24wt% MIL-101Cr@6FDA-mPD MMM	302	± 1
8wt% MOF-199@6FDA-mPD MMM	297	± 2
16wt% MOF-199@6FDA-mPD MMM	292	± 1
24wt% MOF-199@6FDA-mPD MMM	294	± 2

Table S5 Gas (CO_2/CH_4) permeation data of mixed-matrix membranes with MOFs from literature.

Polymer[a]	MOF	MOF (wt%)	P (CO_2)[b] [Barrer]	P (CH_4)[b] [Barrer]	S [c] (CO_2/CH_4)	Ref.
Matrimid 5218	MOF-5	*0*	9	0.22	41.7	6
		10	11.1	0.22	51	
		20	13.8	0.34	40.5	
		30	20.2	0.45	44.7	
PSF	Cu-BTC	*0*	6.5	0.3	17	7
		5	7.7	0.3	22	
		10	7.9	1.3	7	
Matrimid 5218	Cu-BPY-HFS	*0*	7.29	0.21	34.7	8
		10	7.81	0.24	31.9	
		20	9.88	0.36	27.6	
		30	10.36	0.38	25.4	
		40	15.06	0.59	25.6	
Matrimid 5218	ZIF-8	*0*	9.52	0.24	39.8	9
		20	9.03	0.18	51.1	
		30	14.23	0.38	38.2	
		40	24.55	0.89	27.8	
		50	4.72	0.05	124.9	
		60	8.08	0.1	80.8	
Matrimid	ZIF-90	*0*	7.8	–	35.5	10
		15	12.5	–	35.6	
6FDA-DAM	ZIF-90B	*0*	400	–	17	
		15	680	–	26	
6FDA-DAM	ZIF-90A	*15*	800	–	27	
PSF	ZIF-8	*16*	12.1	–	19.8*	11
PSF	ZIF-8/S1C	*16*	8.5	–	19.6*	
PSF	HKUST-1	*16*	8.8	–	15.7*	
PSF	HKUST-1/S1C	*16*	8.9	–	22.4*	
PSF	S1C	*16*	9.6	–	20.9*	
PSF	NH_2-MIL-53(Al)	*0*	4.7	0.2	23.5*	12
		8	4.7	0.13	29.3*	
		16	5	0.13	33.0*	
		25	5.4	0.1	46.0*	
		40	10.3	0.64	16.7*	
6FDA-ODA	UiO-66	*0*	14.4	0.33	44.1	13
		25	50.4	1.1	46.1	
6FDA-ODA	NH_2-UiO-66	*25*	13.7	0.27	51.6	
6FDA-ODA	MOF-199	*25*	21.8	0.43	51.2	
6FDA-ODA	NH_2-MOF-199	*25*	26.6	0.45	59.6	

Polymer[a]	MOF	MOF (wt%)	P (CO_2)[b] [Barrer]	P (CH_4)[b] [Barrer]	S [c] (CO_2/CH_4)	Ref.
6FDA-ODA	UiO-67	*25*	20.8	1.4	15	12
Matrimid 5218	MIL-53	*0*	6.2	0.2	28.5*	14
		15	6.7	0.71	8.5*	
	MIL-53-NH_2	*15*	9.2	4.4	2.1*	
Ultem 1000	MIL-53	*0*	1.46	0.037	31.6*	
		15	1.77	0.041	42.8*	
	MIL-53-NH_2	*15*	3	0.083	36.1*	
6FDA/ODA-DAM (1:1)	MIL-53	*0*	54.1	2.3	23.6	
		20	61.5	4.8	13	
	MIL-53-NH_2	*10*	51.2	1.8	31.8	
		20	52.6	3.4	13.1	
		22	50	4.8	12.5	
6FDA/ODA-DAM (1:4)	MIL-53	*0*	130	6.4	23.6	
		25	123	6.9	19.1	
	MIL-53-NH_2	*10*	112	4.5	23.5	
		15	113	4	28.5	
		20	115	8.2	14.3	
PSF	MIL-101(Cr)	*0*	5.6	0.33	16.9	15
		7.5	15.2	0.64	23.9	
		14	22.3	0.93	24	
		19	32	1.26	25.3	
		24	36.2	1.64	22.2	
PES	C15A1	*0.25*	3.01	0.16	18.72	16
	C15A2	*0.25*	9.77	0.29	33.49	
PPO	Cu-BTC	*40*	113.7	3.49	33.5	17
Matrimid	Fe-BTC	*30*	13.5	0.45	30	18
Pebax-2553	ZIF-8	*35*	1287	143	9	19
6FDA-durene	ZIF-8	*33.5*	1552	140	11.06	20
Matrimid	SMBA@CNT	*10*	4.1	0.043	97	21
Cellulose acetate	Ni_2(dobdc)	*23*	3.78	–	30.3*	22
Matrimid		*23*	9.31	–	29.5*	
6FDA-DAT		*15*	63.9	–	51.9*	
6FDA-DAM:DAT		*18*	220	–	30.5*	
6FDA-DAM		*23*	715	–	14.5*	
6FDA-durene		*21*	1035	–	12.3*	

Polymer[a]	MOF	MOF (wt-%)	P (CO_2)[b] [Barrer]	P (CH_4)[b] [Barrer]	S [c] (CO_2/CH_4)	Ref.

6FDA-DAM	ZIF-11	*0*	20.6	-	32.7	23
		10	109.7	-	31.3	
		20	257.5	-	31.0	
		30	73.1	-	30.4	
6FDA-DAM	3D-COF	*0*	540	-	25.5	24
		10	850	-	29.0	
		15	1280	-	27.1	
Pebax-1657	Fe-BTC	*30*	402.7	-	21.5	25
Pebax-1657	Ni_2(L-asp)$_2$bipy	*20*	120.2	-	37.1	26
	Ni_2(L-asp)$_2$pz	*20*	89.7	-	23.1	
PVDF	Cu-BTC	*0*	0.915	0.043	21.3	27
		5	1.067	0.043	24.8	
		10	2.002	0.048	41.7	
		15	3.206	0.080	40.1	
PMP	Cu-BTC	*0*	76.1	5.0	15.2	28
		5	88.3	5.2	17.1	
		10	102.5	5.3	19.2	
		15	124.4	5.5	22.7	
		20	143.8	5.9	24.3	

[a] PVAC: poly(vinylacetate); PSF: polysulfone; 6FDA: 6FDA: 2,2-bis(3,4-carboxyphenyl) hexafluoro-propane dianhydride, DAM: diaminomesitylene, ODA: 4,4'-oxydianiline; DAT: diamino toluene; PVDF: poly(vinylidene fluoride)
[b] gas permeability
[c] all are ideal selectivities except those marked with (*) which correspond to 50/50 % CO_2/CH_4 mixed gas selectivities
MOF-199 = Cu-BTC

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