ARTICLE

Supporting Information

Thin film nanocomposite membranes of superglassy PIM-1 and amine-functionalised 2D fillers for gas separation

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1. Supplementary figures

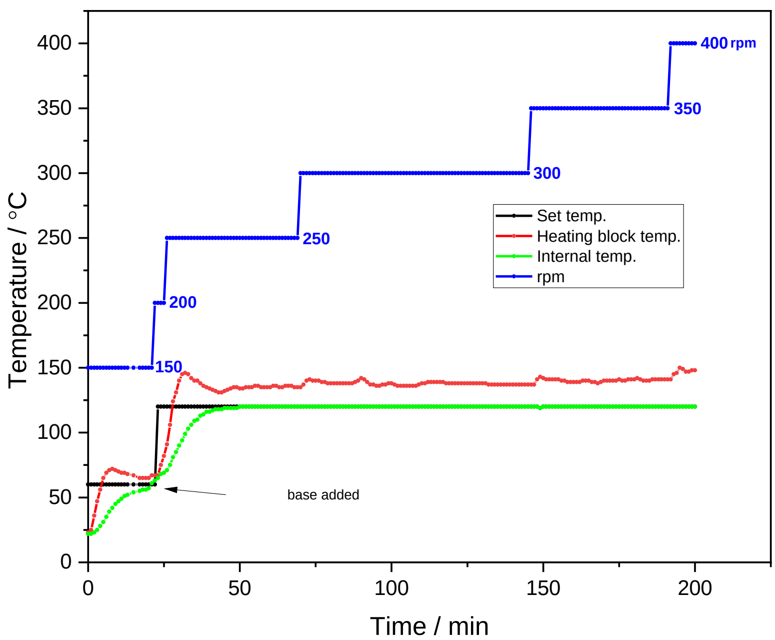

Fig. S1 PIM-1 polymerization temperature and stirring conditions.

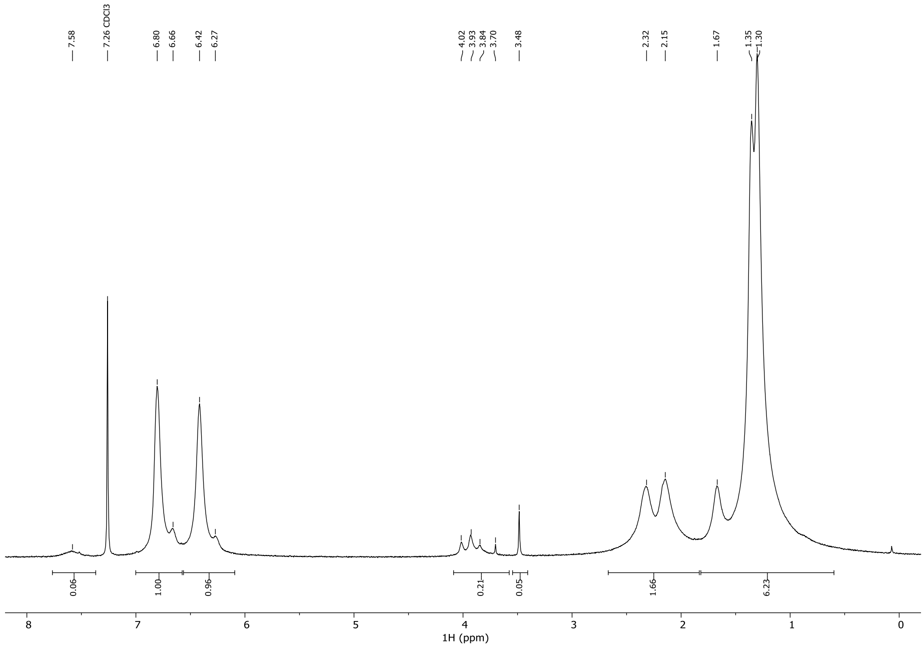

Fig. S2. ^{1}H NMR spectrum of PIM-1 polymer.

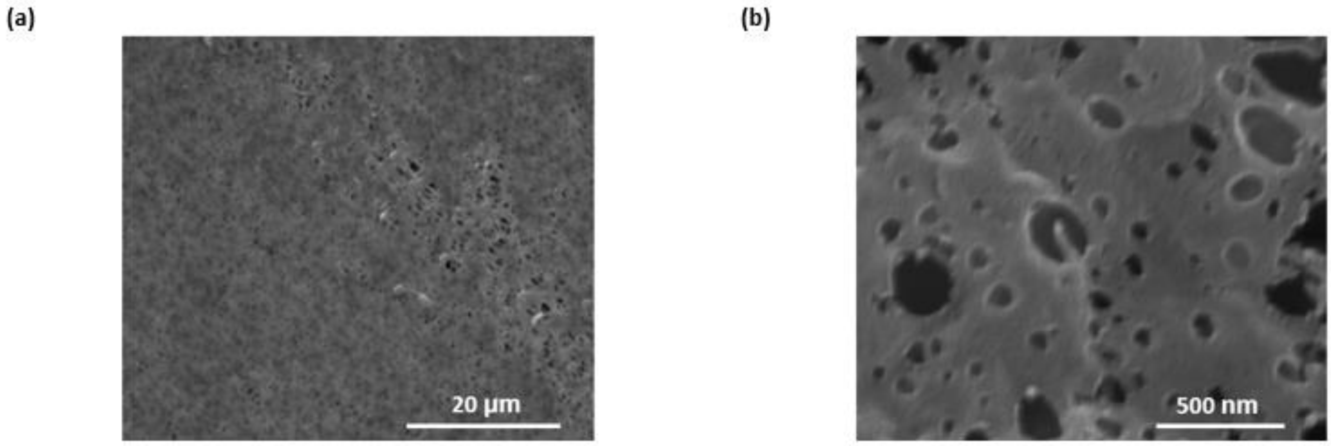

Fig. S3 (a) and (b) show the porosity of the surface of PAN supports at low and high magnifications, respectively. From the images acquired, the average pore size and surface porosity are 45.6 nm and 11.7 %, respectively.

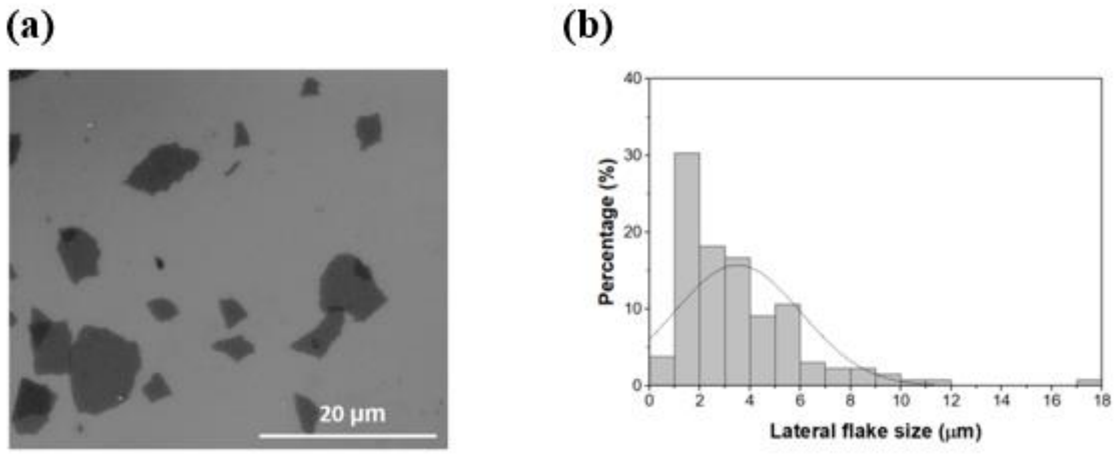

Fig. S4 (a) SEM image of graphene flakes used in this study and (b) analysis of the lateral flake size. The histogram was fitted using the normal function as shown in the black line. The sizes of 132 flakes from multiple SEM images were measured using ImageJ®.

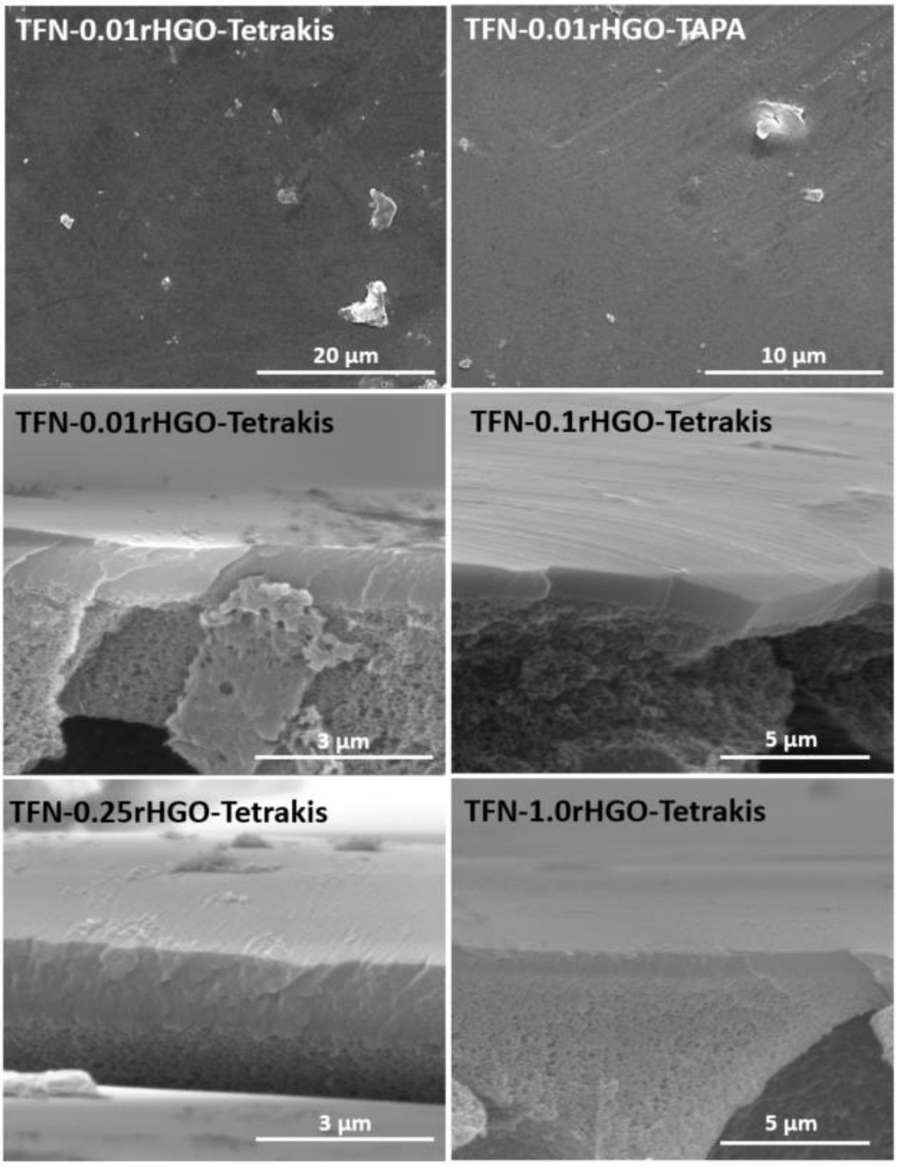

Fig. S5 (a) Representative SEM images of the surface and cross-sections of membranes prepared in this study.

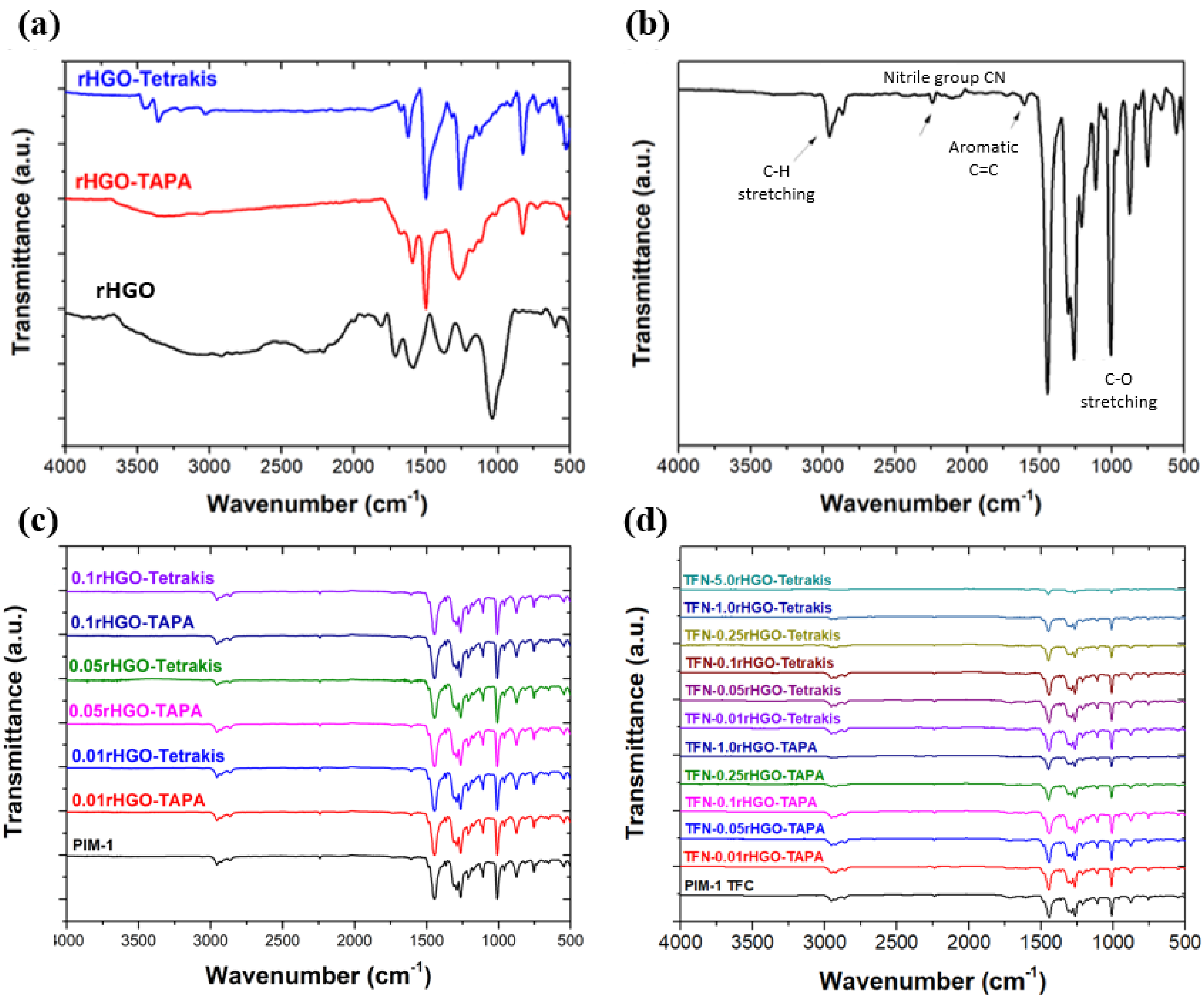

Fig. S6 (a) FTIR spectra of rHGO, rHGO-TAPA and rHGO-Tetrakis and (b) freestanding PIM-1 membrane, (c) MMMs and (d) TFC PIM-1 and TFN membranes.

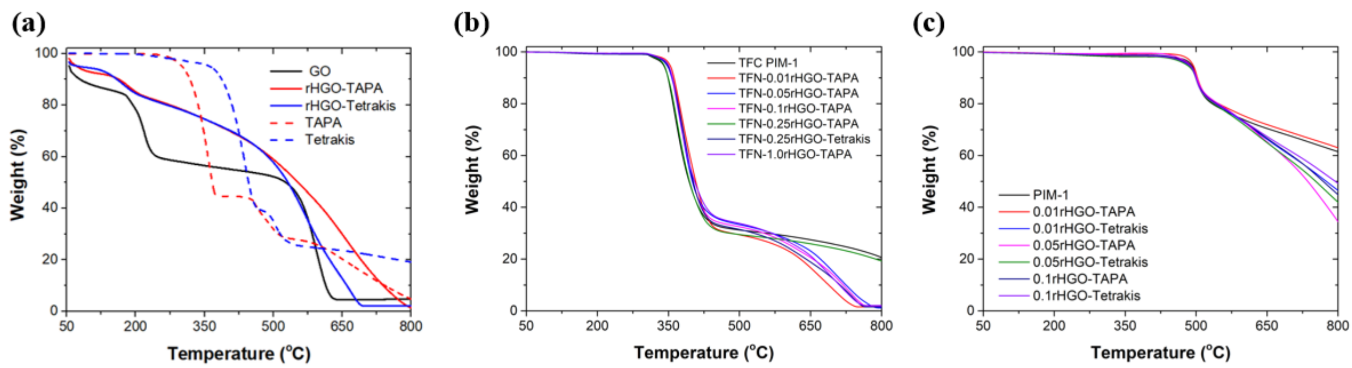

Fig. S7 TGA curves of (a) GO, rHGO-TAPA and rHGO-Tetrakis, TAPA (as received) and Tetrakis (as received), (b) TFC PIM-1 and TFN membranes, and (c) MMMs. These measurements were conducted under a nitrogen atmosphere and a heating rate of 10 °C min^{-1}.

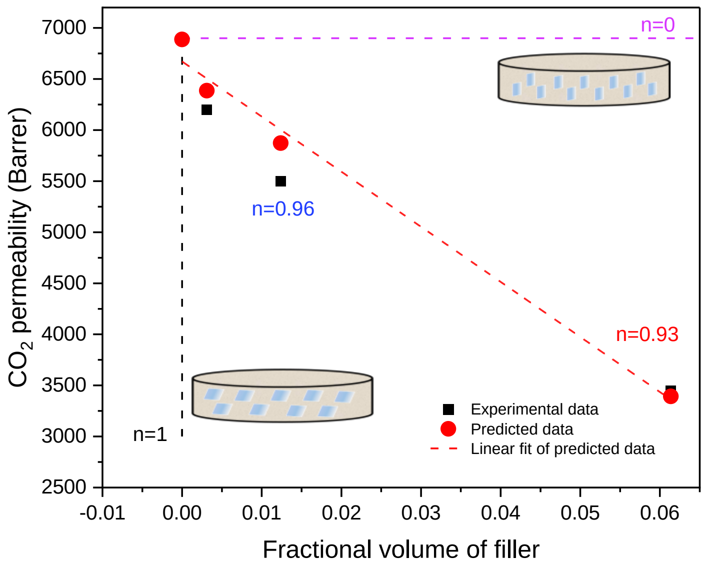

Fig. S8 Predicted CO_2 permeability vs. fractional volume of filler loading based on Maxwell equation. When n=0 the permeation through the membranes is parallel, if n=1 the permeation through laminate shape nanosheets.

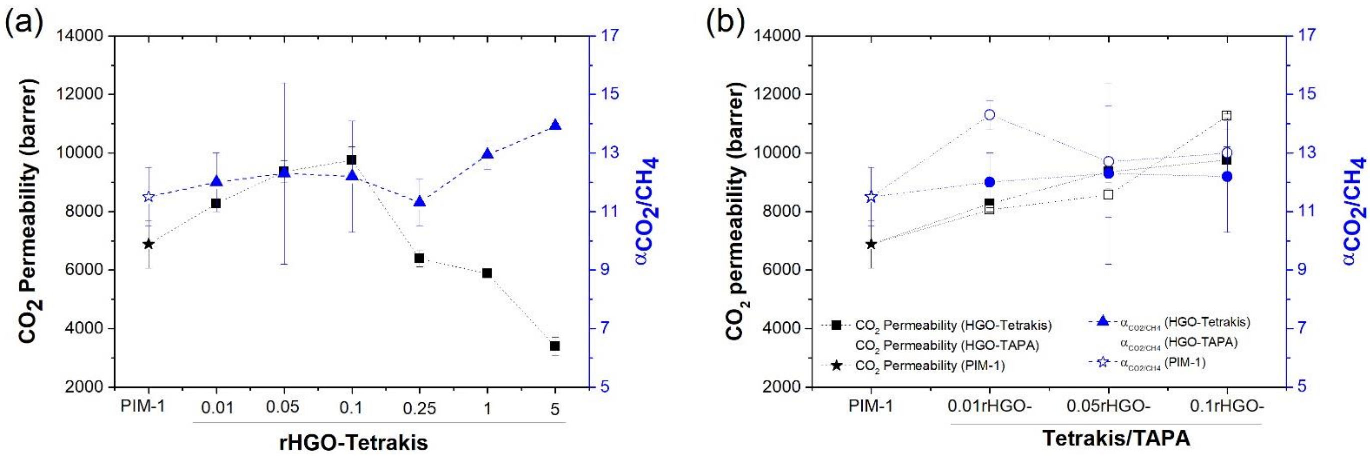

Fig. S9: (a) Effect of rHGO-Tetrakis filler loading on the CO_2 permeability and CO_2/CH_4 selectivity of pristine PIM-1 membranes and rHGO-Tetrakis/PIM-1 MMMs: ■ CO_2 permeability and ▲CO_2/CH_4 selectivity of rHGO-Tetrakis/PIM-1 MMMs, and (b) comparison of gas separation performance of PIM-1 and MMMs with rHGO-TAPA or rHGO-Tetrakis incorporated into the PIM-1 polymeric matrix: ★ CO_2 permeability and ☆ CO_2/CH_4 selectivity of PIM-1, ■ CO_2 permeability of rHGO-Tetrakis/PIM-1 MMMs, □ CO_2 permeability of rHGO-TAPA/PIM-1 MMMs, ● CO_2/CH_4 selectivity of rHGO-Tetrakis/PIM-1 MMMs, and ○ CO_2/CH_4 selectivity of rHGO-TAPA/PIM-1 MMMs. At least two membranes of each type were tested and the error bars correspond to the standard deviation. Membranes were tested using a 50/50 vol. % CO2 and CH4 binary mixture, at 25 °C under a transmembrane pressure of approximately 1 bar. (Dashed lines are used for guide purposes only.

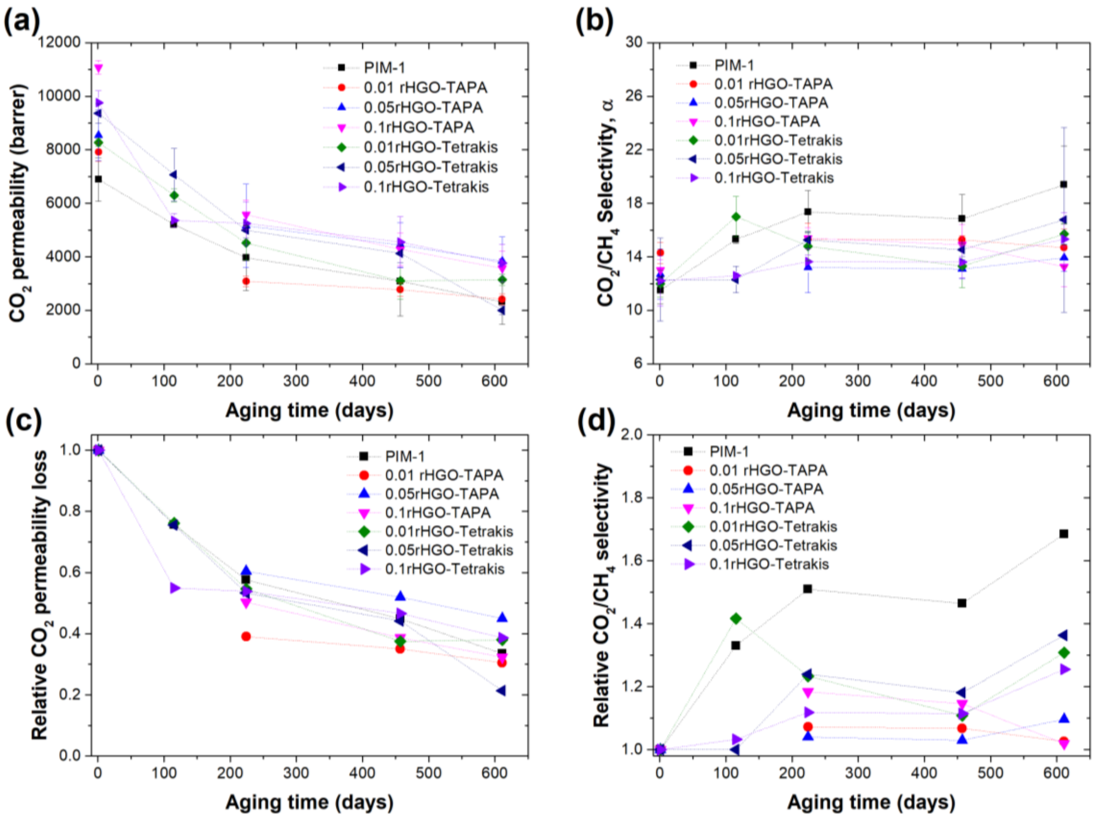

Fig. S10 (a) CO_2 permeability, (b) CO_2/CH_4 selectivity, (c) relative CO_2 permeability and (d) relative CO_2/CH_4 selectivity of rHGO-Tetrakis/PIM-1 and rHGO-TAPA/PIM-1 MMMs. Membranes were tested over a period of 611 days. At least two membranes of each type were tested and the error bars correspond to the standard deviation. Membranes were tested using a 50/50 vol. % CO_2 and CH_4 binary mixture, at 25 °C under a transmembrane pressure of approximately 1 bar. (Dashed lines are used for guide purposes only.

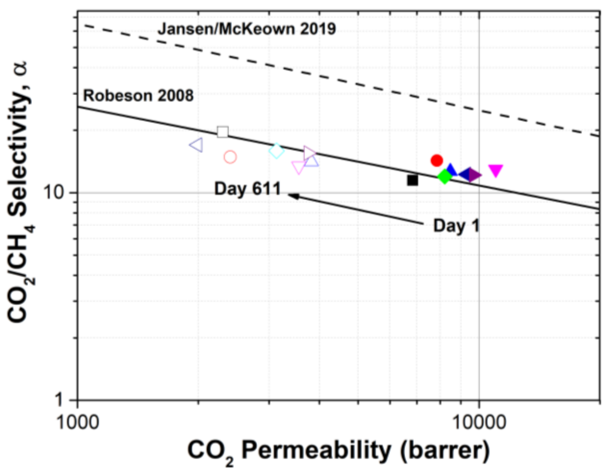

Fig. S11 Comparison of the membrane performance of freestanding PIM-1 and rHGO-Tetrakis/PIM-1 MMMs for CO_2/CH_4 separation with the 2008 Roberson and 2019 Jansen/McKeown upper-bounds. Membranes were tested using a binary CO_2 and CH_4 mixture with equal vol. %. Membranes were tested at 25 °C under a transmembrane pressure of 1 bar. Fill and empty symbols represent the performance at day 1 and day 611, respectively. (■ □ – PIM-1, ●O – 0.01rHGO-TAPA, ▲△– 0.05rHGO-TAPA, ▼▽- 0.1rHGO-TAPA, ◆◇ – 0.01rHGO-Tetrakis, ◀◁- 0.05rHGO-Tetrakis, ▶▷ - 0.1rHGO-Tetrakis).

2. Supplementary tables

Table S1 Gas separation performance of TFN membranes with rHGO-Tetrakis as filler. Results were obtained from pure gas measurements at room temperature and a feed pressure of 2.4 barg. The effective membrane re is 2.1 cm^2. Samples were stored at ambient conditions.

Membrane Name	Filler loading (wt.%)	Aging times (days)	Permeance (GPU)		CO_2/CH_4 ideal selectivity
			CO_2	CH_4	
PIM-1	-	1	1583 ± 400	190 ± 78	9.2 ± 2.0
		66	669	29	23.4
		360	432 ± 4	35 ± 2	12.3 ±0.7
TFN-0.01rHGO-Tetrakis	0.01	1	1709 ± 199	204 ± 30	8.4 ± 1.0
		38	1128 ± 245	210 ± 59	5.5 ± 0.4
		66	306 ± 14	31 ± 1	9.8 ± 1.0
TFN-0.05rHGO-Tetrakis	0.05	1	2417 ± 732	319 ± 110	7.7 ± 0.4
		10	2063 ± 191	217 ± 18	9.5 ± 0.1
		45	1337	141	9.5
		66	656	212	3.1
TFN-0.1rHGO-Tetrakis	0.1	1	3200 ± 842	388 ± 81	8.3 ± 1.0
		45	1755	161	10.9
		66	1416	102	13.9
		360	234	57	4.2
TFN-0.25rHGO-Tetrakis	0.25	1	1265 ± 70	126 ± 13	10.1 ± 0.5
		66	1092 ± 108	131 ± 39	9.4 ± 3.6
TFN-1.0rHGO-Tetrakis	1	1	1187 ± 728	133 ± 90	12.6 ± 3.0
		43	675	49	13.8
TFN-5.0rHGO-Tetrakis	5	1	821 ± 72	63 ± 0.5	13.2 ± 1.0

1 GPU=10^{-6} cm^3[STP] cm^{-2} s^{-1} $cmHg^{-1}$

Table S2 Gas separation performance of TFN membranes with rHGO-TAPA as filler over 1 year. Results were obtained from pure gas measurements at room temperature and a feed pressure of 2.4 barg. The effective membrane area is 2.1 cm^2. Samples were stored at ambient conditions.

Membrane Name	Filler loading (wt.%)	Aging time (days)	Permeance (GPU)		CO_2/CH_4 ideal selectivity
			CO_2	CH_4	
PIM-1	-	1	1583 ± 400	190 ± 78	9.2 ± 2.0
		66	669	29	23.4
		360	432 ± 4	35 ± 2	12.3 ±0.7
TFN-0.01rHGO-TAPA	0.01	1	2580 ± 244	270 ± 26	9.6
		28	2560 ± 239	538 ± 121	4.9 ± 0.7
		365	637 ± 95	57 ± 5	11.4± 3.0
TFN-0.05rHGO-TAPA	0.05	1	2984 ± 194	409 ± 16	7.3 ± 1.0
		28	1287 ± 396	93 ± 35	14.3 ± 1.1
		45	491	33	14.9
		365	493	49	10.1
TFN-0.1rHGO-TAPA	0.1	1	3351 ± 662	481 ± 74	7.0 ± 0.4
		45	1932	126	15.3
		365	604 ± 34	50 ± 11	12.7 ± 2.0
TFN-0.25rHGO-TAPA	0.25	1	3058 ± 16	335 ± 22	9.2 ± 0.6
		28	2315	505	4.6
		365	696 ± 12	51 ± 1	14.0 ± 0.1
TFN-1.0rHGO-TAPA	1	1	1050 ± 70	79 ± 7	13.3 ± 0.3
		365	846 ± 37	67 ± 7	12.8 ± 2.0

1 GPU=10^{-6} cm^3[STP] cm^{-2} s^{-1} cmHg^{-1}

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Table S3 Performance of PIM-1 and rHGO-Tetrakis/PIM-1 MMMs for CO_2/CH_4 separation. 50:50 vol. % CO_2 and CH_4 binary mixture was used as feed. Tests were conducted at 25 °C under a transmembrane pressure of approximately 1 bar. Membranes were tested over 611 days after their preparation.

Membrane Name	Filler Loading (wt.%)	Membrane effective area (cm^2)	Average thickness (μm)	Aging day	Permeability (barrer)		CO_2/CH_4 Selectivity
					CO_2	CH_4	
PIM-1	0	0.22/0.34/0.20/ 0.26	82/60/98/80	1	6887 ± 815	611 ± 122	11.5 ± 1.0
				115	5205 ± 10	340±8	15.3 ± 0.3
				224	3966 ± 1227	236 ± 88	17.4 ± 1.6
				457	3090 ± 1306	192 ± 96	16.8 ± 1.8
				611	2309 ± 824	129 ± 68	19.4 ± 2.9
0.01rHGO-Tetrakis	0.01	0.13/0.25/0.30/ 0.29	67/76/60/62	1	8271 ± 146	683 ± 64	12.0 ± 1.0
				115	6299 ± 240	371 ± 19	17.0 ± 1.5
				224	4518 ± 635	307 ± 48	14.8 ± 1.1
				457	3101 ± 684	230 ± 27	13.3 ± 1.6
				611	3142 ± 207	201 ± 21	15.7 ± 0.8
0.05rHGO-Tetrakis	0.05	0.31/0.29/0.30/ 0.36	81/84/80/71	1	9361 ± 374	827 ± 265	12.3 ± 3.1
				115	7069 ± 985	588 ± 130	12.3 ± 1.0
				224	4989 ± 287	327 ± 14	15.3 ± 0.6
				457	4132 ± 339	284 ± 17	14.5 ± 0.5
				611	1999 ± 173	148 ± 71	16.8 ± 6.9
0.1rHGO-Tetrakis	0.1	0.23/0.21/0.31/ 0.37	70/73/71/67	1	9760 ± 449	816 ± 117	12.2 ± 1.9
				115	5364 ± 250	425 ±27	12.6 ± 0.2
				224	5253 ± 807	387 ± 70	13.7 ± 0.5
				457	4553 ± 948	341 ± 90	13.6 ± 1.2
				611	3770 ± 701	257 ± 84	15.3 ± 2.0
0.25rHGO-Tetrakis	0.25	0.40/0.36	78±2/95±2	1	6386 ± 281	569 ± 65	11.3 ± 0.8
				115	4803 ± 223	341 ± 24	14.2 ± 1.7
1.0rHGO-Tetrakis	1	0.20/0.48	89±3/112±1	1	5873 ± 107	459 ± 46	12.9 ± 0.5
				115	4199 ± 450	250 ± 40	16.9 ± 0.9
5.0rHGO-Tetrakis	5	0.32/0.36	89±4/89±4	1	3393 ± 315	244 ± 22	13.9 ± 0.1

1 barrer=10^{-10} cm^3[STP] cm $cm^{-2}.s^{-1}$ $cmHg^{-1}$

Table S4 Fresh membrane performance results of PIM-1 and PIM-1/Functionalised GO-TAPA MMMs. Performance of PIM-1 and rHGO-Tetrakis/PIM-1 MMMs for CO_2/CH_4 separation. 50:50 vol. % CO_2 and CH_4 binary mixture was used as feed. Tests were conducted at 25 ^oC under a transmembrane pressure of approximately 2 bar. Membranes were tested over 611 days after their preparation.

Membrane Name	Filler Loading (wt.%)	Membrane effective area (cm^2)	Average thickness (μm)	Aging day	Permeability (barrer)		CO_2/CH_4 Selectivity
					CO_2	CH_4	
PIM-1	0	0.22/0.34/0.20/ 0.26	82/60/98/80	1	6887 ± 815	611 ± 122	11.5 ± 1.0
				115	5205 ± 10	340±8	15.3 ± 0.3
				224	3966 ± 1227	236 ± 88	17.4 ± 1.6
				457	3090 ± 1306	192 ± 96	16.8 ± 1.8
				611	2309 ± 824	129 ± 68	19.4 ± 2.9
0.01rHGO-TAPA	0.01	0.31/0.32/0.25/ 0.25	99/90/81/96	1	7915 ± 344	554 ± 42	14.3 ± 0.8
				224	3090 ± 201	202 ± 15	15.3 ± 1.2
				457	2773 ± 251	182 ± 16	15.3 ± 0.3
				611	2413 ± 200	165 ± 8	14.7 ± 1.4
0.05rHGO-TAPA	0.05	0.27/0.24/0.22/ 0.34	65/82/80/64	1	8540 ± 946	687 ± 126	12.7 ± 1.9
				224	5158 ± 1559	381 ± 68	13.2 1.9
				457	4436 ± 841	343 ± 83	13.1 ± 0.7
				611	3839 ± 907	276 ± 61	13.9 ± 1.0
0.1rHGO-TAPA	0.1	0.30/0.30/0.32	80/84/60	1	11077 ± 261	856 ± 69	13.0 ± 0.8
				224	5574 ± 555	364 ± 51	15.4 ± 0.8
				457	4281 ± 602	292 ± 58	14.9 ± 1.5
				611	3573 ± 639	268 ± 26	13.3 ± 1.5

1 barrer=10^{-10} cm^3[STP] cm cm^{-2}.s^{-1} $cmHg^{-1}$

Table S5. Values of the n parameter for CO_2 and CH_4 of TFN membranes

Membrane Name	***n*** **parameter (CO_2)**	***n*** **parameter (CH_4)**
TFN-1.0rHGO-TAPA	0.975276	0.991068
TFN-0.25rHGO-TAPA	1.00646	1.00719
TFN-0.1rHGO-TAPA	1.00236	1.00206
TFN-0.05rHGO-TAPA	1.00132	1.00116
TFN-0.01rHGO-TAPA	1.00032	1.00042
5.0rHGO-Tetrakis	0.929544	0.967561
1.0rHGO-Tetrakis	0.962381	0.970716
0.25rHGO-Tetrakis	0.987613	0.993869
0.1rHGO-Tetrakis	1.00246	1.00244
0.05rHGO-Tetrakis	1.0018	1.00154
0.01rHGO-Tetrakis	1.00169	1.00181