Science Advances
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Supplementary Materials for

Facile manufacture of porous organic framework membranes for precombustion CO_2 capture

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Published 21 September 2018, *Sci. Adv.* **4**, eaau1698 (2018)
DOI: 10.1126/sciadv.aau1698

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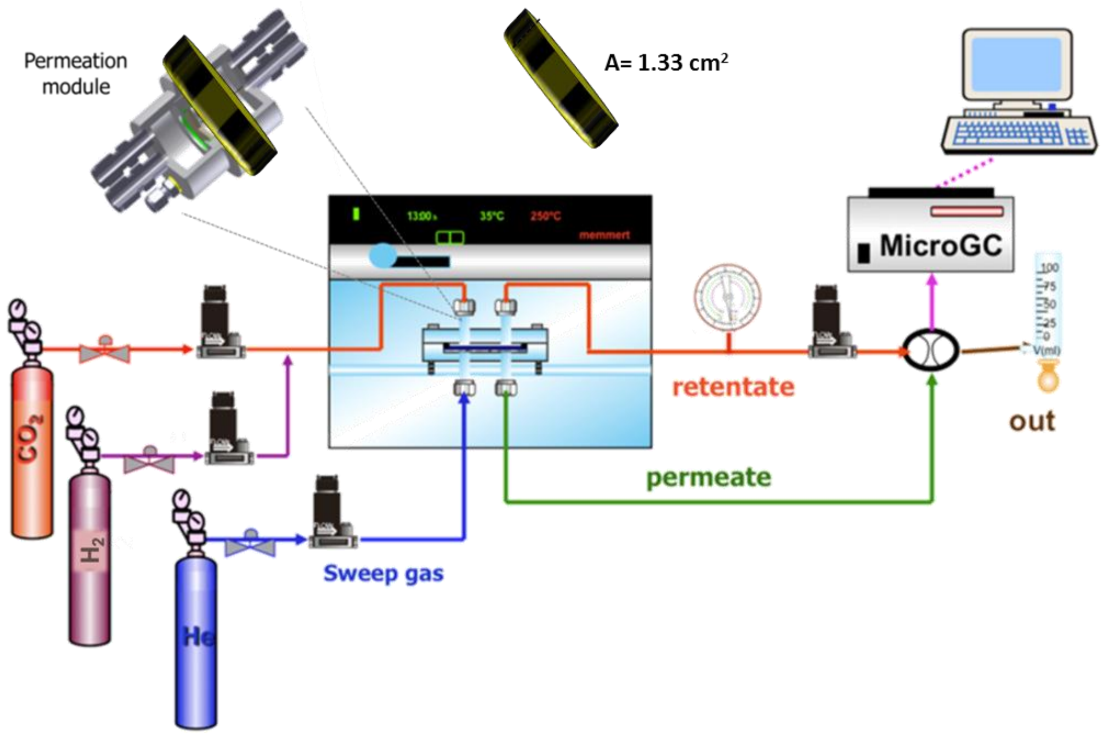

Scheme S1. Diagram of gas permeation apparatus used in this work.

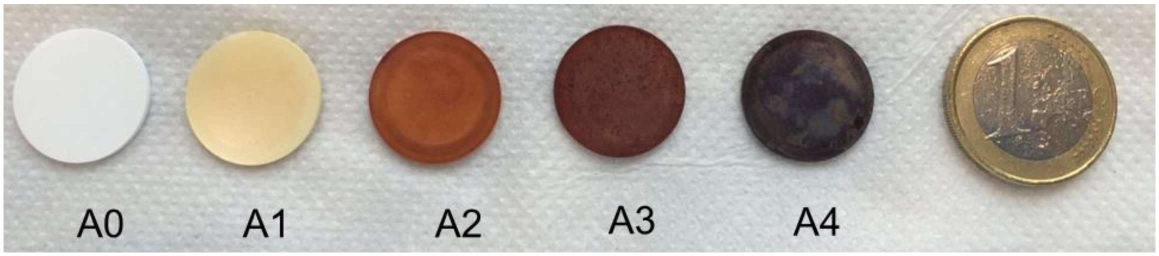

Fig. S1. Digital photo of the prepared membranes under four different conditions.

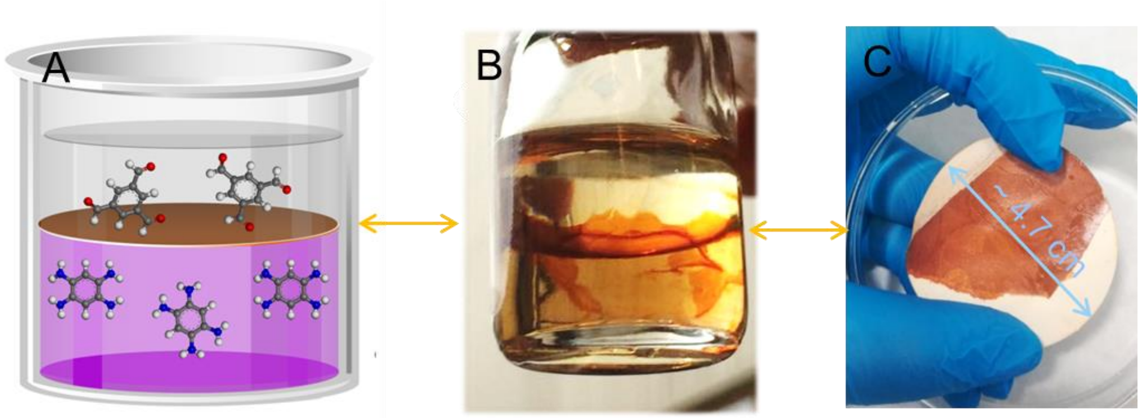

Fig. S2. Description of freestanding BILP-101x film synthesis process and resulting films. (**A**) synthesis process of BILP-101x film. (**B**) Photograph of the film formed at the water-benzene interface, and (**C**), the film supported on a nylon substrate. The diameter of nylon support is 4.7 cm.

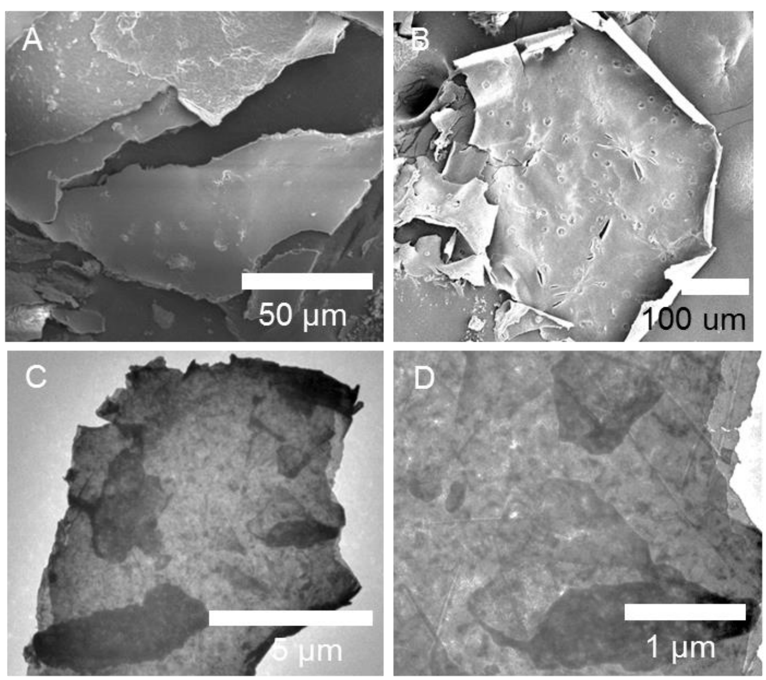

Fig. S3. Morphology of the prepared BILP-101x film. (**A** and **B**) are low resolution SEM images of the films. (**C** and **D**) are low resolution TEM images.

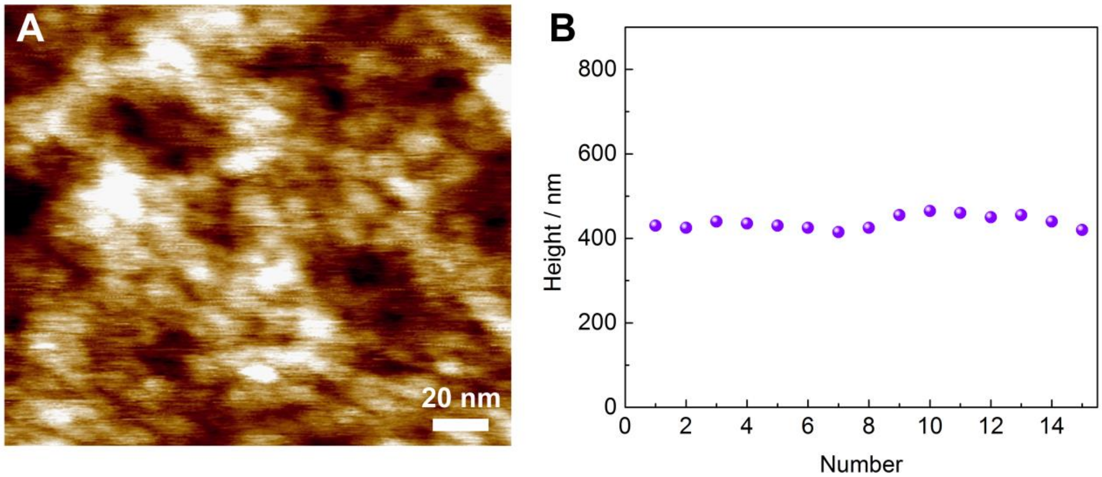

Fig. S4. AFM analysis of the BILP-101x film under A3 conditions. (**A**) AFM image of one piece of BILP-101x film and (**B**) two dimensional (2D) distribution of the height of BILP-101x film used in Fig.1E.

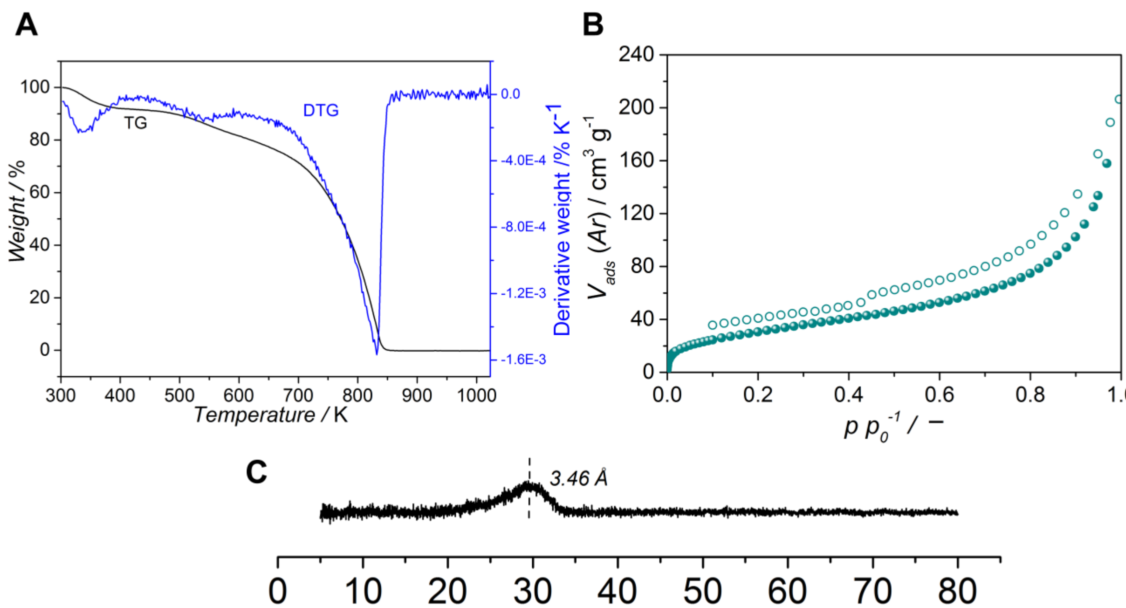

Fig. S5. Characterization of the BILP-101x film prepared under A3 conditions. (**A**) TG and DTG profile of BILP-101x film under air flow (100 mL/ min) at a heating rate of 5 K/ min. (**B**) Argon adsorption isotherms of BILP-101x film at 87 K. (**C**) Powder X-ray diffraction pattern of the free standing BILP-101x film.

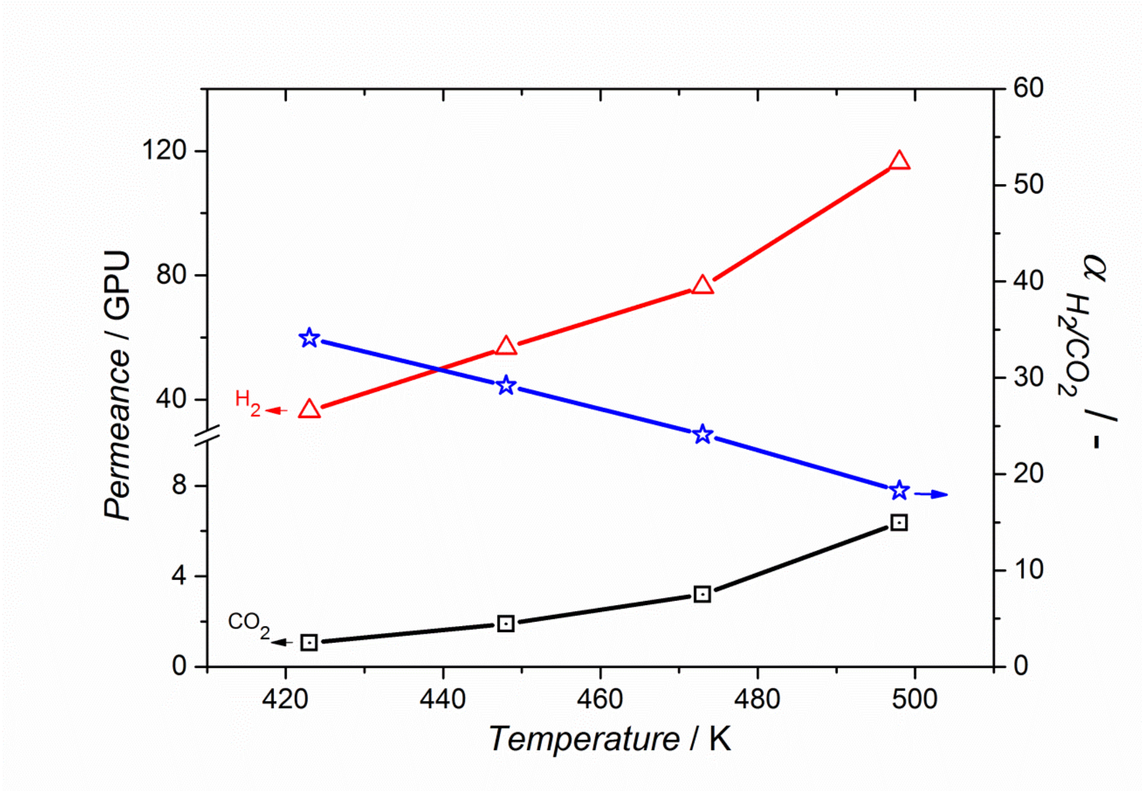

Fig. S6. Effect of the temperature on the membrane separation performance toward H_2/CO_2. H_2/CO_2 feed ratio = 1, sweep gas helium, no absolute pressure difference across the membrane. Results are obtained for sample A3-2.

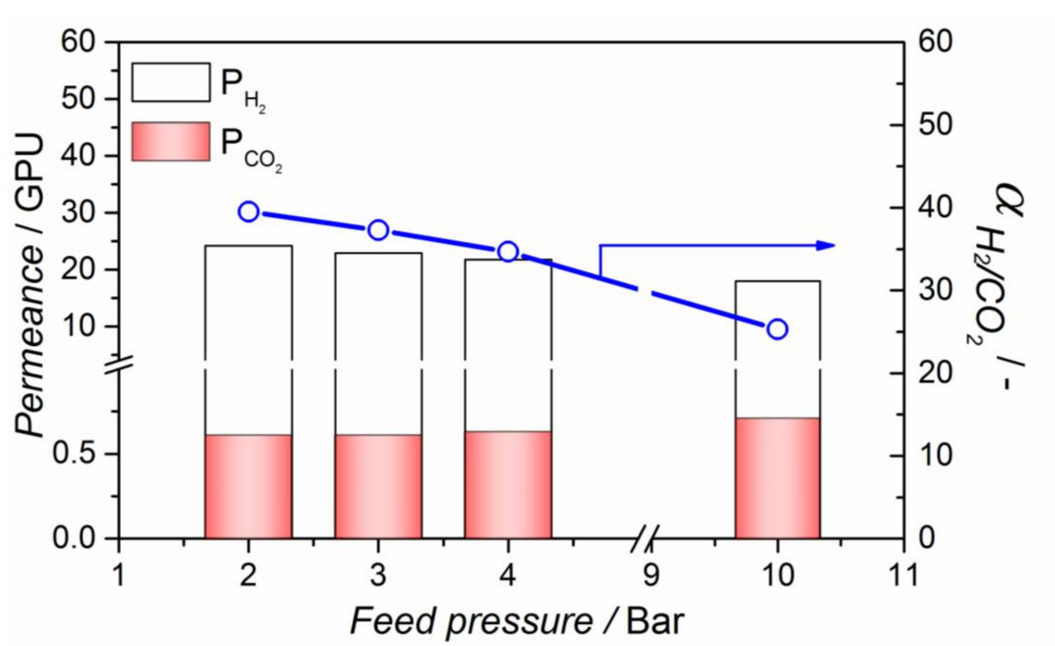

Fig. S7. Effect of pressure on the membrane performance toward H_2/CO_2. H_2/CO_2 feed ratio = 1, sweep gas helium. Results are obtained for sample A3-1 under 423 K.

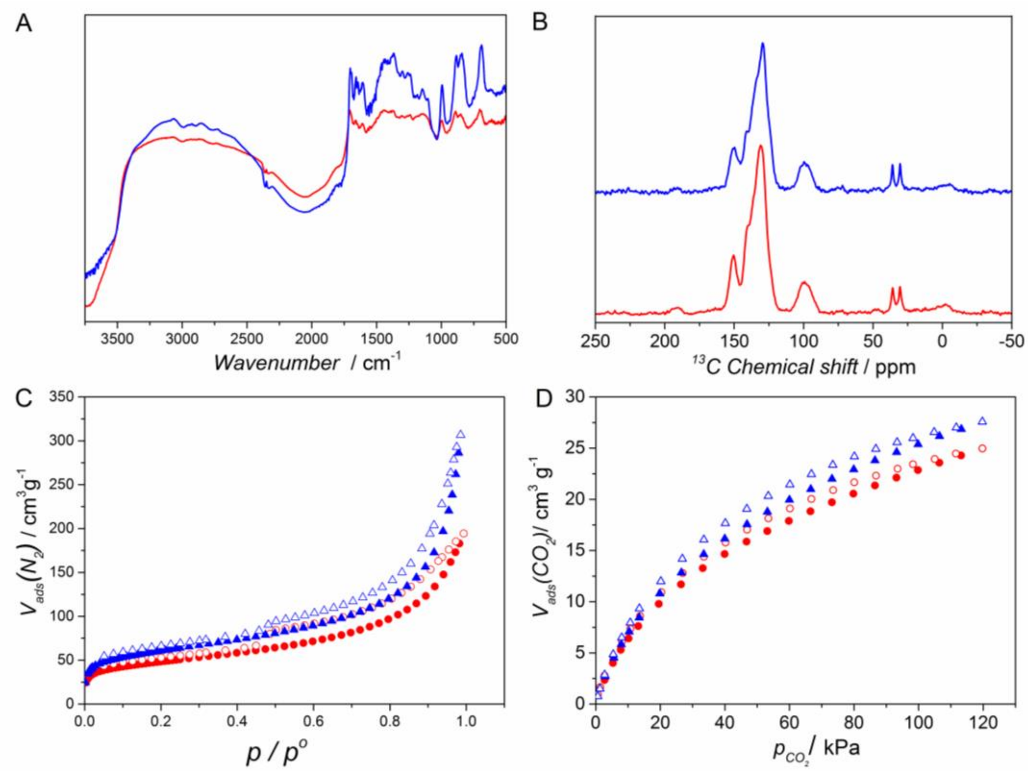

Fig. S8. Characterization of the BILP-101x film prepared under A1 and A2 conditions. (**A** and **B**) DRIFT-IR and ^{13}C CP/MAS spectra of films. (**C** and **D**) N_2 and CO_2 adsorption (solid symbols) and desorption (open symbols) isotherms of the films at 77 and 298 K, respectively. Red and blue corresponds to samples A1 and A2, respectively.

Table S1. Summary of membrane preparation conditions. * Two samples were prepared under A3 conditions, marked in the text as A3-1, A3-2 for distinction.

Membranes	Interfacial polymerization (IP) conditions			
	Aqueous amine phase [wt.%]	Aldehyde in benzene phase [wt.%]	IP time (min)	layers
A1	0.3	0.1	60	1
A2	0.75	0.25	60	1
A3*	1.5	0.5	60	1
A4	1.5	0.5	60	2

Table S2. Summary of membrane separation performance tested for H_2/CO_2. The membranes were tested at 423 K using an equimolar H_2/CO_2 mixture. The data were obtained for different membranes under varied feed pressure conditions. Permeate side at atmospheric pressure with helium as sweep gas.

Membrane	Sample A1			
PH_2 [GPU]	PN_2 [GPU]	PCO_2 [GPU]	Selectivity [H_2/CO_2-]	Selectivity [H_2/N_2-]
18397	5508	5298	3.5	3.3

Membrane	Sample A2			
Feed pressure [bar]	2	3	4	10
PH_2 [GPU]	23.5	22.8	22.7	20.8
PCO_2 [GPU]	2.43	2.40	2.47	2.40
Selectivity [H_2/CO_2-]	9.7	9.5	9.2	8.7

Membrane	Sample A3-1			
Feed pressure [bar]	2	3	4	10
PH_2 [GPU]	24.2	22.9	21.8	18.0
PCO_2 [GPU]	0.61	0.61	0.63	0.71
Selectivity [H_2/CO_2-]	39.7	37.5	34.6	25.4

Membrane	Sample A4		
Feed pressure [bar]	2	3	4
PH_2 [GPU]	14.7	13.7	13.0
PCO_2 [GPU]	0.68	0.67	0.68
Selectivity [H_2/CO_2-]	21.6	20.4	19.1

Single gas permeation tests indicate that Sample A1 shows a characteristics of Knudsen diffusion, therefore a mixed-gas test was not performed. For A4 membrane, another layer was grown on top of the first layer (See details in experimental section). As expected, the H_2 permeance decreased due to the thicker layer. For A1, A2 and A3 membranes, the CO_2 permeance decreased with increasing monomer concentration, reflecting the formation of more dense membranes. DRIFT-IR and ^{13}C CP/MAS spectra of films confirm a similar composition (Fig. S8A and B). Interestingly, the relative intensity of aldehyde groups (~ 1700 cm^{-1}) compared to the -C=N- (~1610 cm^{-1}) in the imidazole ring in A1 and A2 samples is higher than that in sample A3 (Fig. 2A), indicating more missing links exist in their structures which explains the lower selectivity for sample A1 and A2. This is further supported by the higher porosity of samples A1 and A2 (Fig. S8C) compared to sample A3 (Fig. 2C). Overall, the membrane prepared under A3 conditions exhibits the best performance. Thus, we mainly focus on the discussion of A3 membrane in the main text. Only A2 and A3-1 membrane were further tested for H_2/N_2 separation.

Table S3. Summary of membrane separation performance tested for H_2/N_2. The membranes were tested at 423 K using an equimolar H_2/N_2 mixture. The data were obtained for different membranes under several feed pressure conditions. Permeate side at atmospheric pressure with helium as sweep gas.

Membrane	Sample A2			
Feed pressure [bar]	2	3	4	10
PH_2 [GPU]	20.7	20.2	19.7	17.7
PN_2 [GPU]	0.46	0.46	0.46	0.52
Selectivity [H_2/N_2-]	45.0	43.5	42.8	34.0

Membrane	Sample A3-1			
Feed pressure [bar]	2	3	4	10
PH_2 [GPU]	20.8	20.3	20.2	18.0
PN_2 [GPU]	0.24	0.22	0.22	0.24
Selectivity [H_2/N_2-]	86.7	92.3	91.8	75.0

Table S4. Membrane performance of typical PIM, TR polymer, PBI, and BILP presented in Fig. 3A. The membrane thickness was assumed to be 1μm when converting the permeability to permeance.

Membrane material		Performance		Operation conditions			Reference
		P_{H2} (GPU)	H_2/CO_2 *selectivity* (-)	Type of analysis	*T* (K)	*Feed Pressure* *P* (bar)	
PIMs	PIM-EA-TB	7760	1.09	Single gas	298	1	(7)
		7310	1.43	Single gas			
		6155	1.29	Single gas/aged 24h			
	PIM-SBI-TB	2200	0.76	Single gas			
	TPIM-1	2666	1.72	Single gas	298	2	(35)
	TPIM-2	655	1.51	"			
	CoPI-TB-1	249	1.6	Single gas	308	1	(36)
	CoPI-TB-2	403	1.9	"			
	CoPI-TB-3	371	1.9	"			
	CoPI-TB-4	667	2.8	"			
	CoPI-TB-5	334	1.5	"			
	CoPI-TB-6	472	1.4	"			
TR Polymer	TR-1	1200	0.65	Single gas	298	1	(*6, 37*)
	TR-6	6000	1.2	"			
	*m*PBO	206	6.2	Single gas	483	-	(38)
	*p*PBO,	305	3.8	"			
	6*f*PBO	505	3.5	"			
	PHBOA(8:2)	1.8	8.4	Single gas	308	10	(39)
	PBOA(8:2)	3.4	5.4	"			
	PBOA(5:5)	4.2	5.6	"			
	PHBOA(8:2)	26.8	8	Single gas	483		
	PBOA(8:2)	22.3	6	"			
	PBOA(5:5)	26.9	6.5	"			
PBI		0.09	9	Single gas	293	3.4	(*40, 41*)
		13	20	Mixed gas	433		
		11	3	"	623		
		3.7	8.6	Single gas	308	3.5	(42)
		2.9	7.1	Mixed gas	308	7	(30)
		75	8.6	"	453	"	
		30	3.8	Mixed gas	423	5	(43)
		2.9	7.9	Single gas	373	5-8	(44)
		5.5	12.8	"	473		
		8.7	21.7	"	573		
		22.9	27.3	"	673		
		27	16	Single gas	423	8	(45)
Porous organic polymer (POPs) membranes	CMPs	406	1.8	Single gas	303	0.1~0.3	(*46*)
		666	1.5	"	"	"	
		364	1.8	"	"	"	
		258	4	"	"	"	
BILP-101x (400 nm)	Fresh A3-1	24.2	39.5	Mixed gas	423	2	This work
	Fresh A3-2	30.1	31.6	"		1	
	A3-2 [a]	36.4	34.2	Dry gas mixture			
	A3-2 [b]	25.6	37.6	Wet gas mixture			
BILP-101x (assumed 1 μm thickness)	A3-1	9.7	39.5	Mixed gas	423	2	
	A3-2	12.0	31.6	"		1	
	A3-2 [a]	14.6	34.2	Dry gas mixture			
	A3-2 [b]	10.2	37.6	Wet gas mixture			

a and b correspond to A3-2 sample measured after ~800 h on stream under alternating dry gas and wet gas conditions.

Table S5. Membrane performance of some pure COF membranes for H_2/N_2 separation. The membrane thickness was assumed to be 1μm when converting the permeability to permeance.

Membrane material		Performance		Operation conditions			Reference
		P_{H2} (GPU)	H_2/N_2 *selectivity* (-)	Type of analysis	*T* (K)	*Feed Pressure P* (bar)	
COFs	COF-1 nanosheets	990	3.3	Single gas	303	2	(*13*)
		666	4.2	"			
		560	4.1	"			
	COF-320	6685	3.5	Single gas	RT	2	(*47*)