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Thin supported MOF based mixed matrix membranes of Pebax® 1657 for biogas upgrade

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Synthesis of MOF nanoparticles

ZIF-8. This synthesis was performed following a recipe based on a MeOH-water mixture [1] as solvent. 0.47 g of zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$, >98%, Sigma Aldrich) was dissolved in 10 mL of methanol (MeOH, HPLC grade, Sharlau) and 10 mL of water. Besides, 1.0 g of 2-methylimidazole (mIm, $C_4H_6N_2$, >99%, Sigma Aldrich), was dissolved in 10 mL of MeOH, and the two solutions were mixed and stirred for 2 h. The final product was collected by centrifugation at 10,000 rpm, washed once with MeOH, and dried at 110 ^{0}C overnight.

UiO-66[2]: 0.40 g of zirconium (IV) chloride ($ZrCl_4$, ≥99.5%, Sigma-Aldrich) was dissolved in 100 mL of N,N-dimethylformamide (DMF, 99.8%, Sigma–Aldrich) at room temperature with the help of a ultrasound bath, before the addition of 0.28 g of benzene-1,4-dicarboxylic acid (BDC, 98%, Sigma-Aldrich) and 0.13 mL of distilled water. The obtained solution was later transferred into a stainless steel teflon-lined autoclave for a solvothermal process in a pre-heated oven at 120 °C for 24 h. After cooling to room temperature, the colloidal suspension was centrifuged at 10,000 rpm and the precipitated solid was rinsed three times with fresh DMF, followed by washing three times more with the same amount of MeOH. Finally, the MOF was activated in a furnace at 300 °C for 3 h, with a heating rate of 15 $°C·min^{-1}$.

MIL-101(Cr): 0.5 g of chromium(III) chloride hexahydrate ($CrCl_3·6H_2O$, 96%, Sigma-Aldrich) and 0.45 g of terephthalic acid (98%, Sigma–Aldrich) were dissolved in 26 mL of distilled water [3]. After mixing, the solution was maintained for 30 min at 180 °C in a microwave oven. The solid was separated by centrifugation at 10,000 rpm and washed with water. Then, the synthesized MOF was activated with DMF at 120 °C overnight and thereafter with MeOH for 12 h under reflux. Finally, the MIL-101(Cr) powder was dried at 100 °C overnight.

ZIF-7/8 core-shells. The ZIF-7/8 core-shells were prepared *via* post-synthetic modification of the above explained ZIF-8 nanoparticles[4]. An initial amount of benzimidazole (bIm, Sigma Aldrich) was added to DMF at 65 °C to obtain a concentration of 13 g/L. Once dissolved, ZIF-8 was added to the solution (3.3 g/L), which was stirred for 24 h. The solid was then collected by centrifugation at 10,000 rpm, washed three times with MeOH and dried at 110 °C overnight.

Membrane characterization

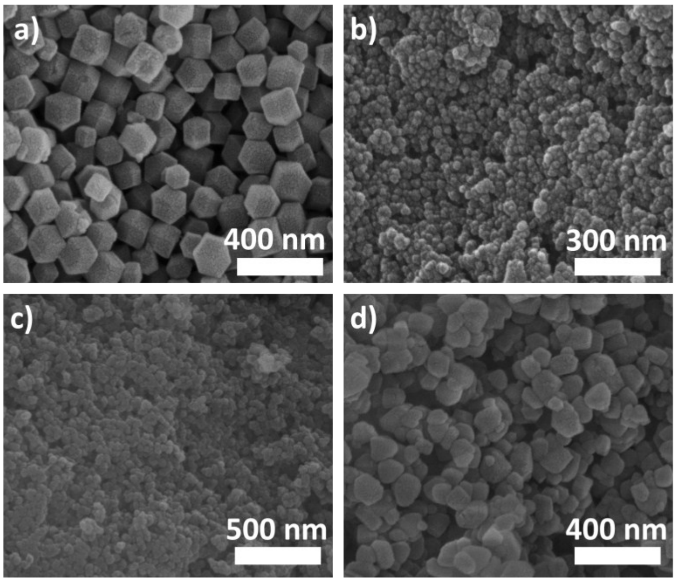


Fig. S1. SEM images of ZIF-8 (a), MIL-101(Cr) (b), UiO-66 (c) and ZIF-7/8 core-shell particles (d)

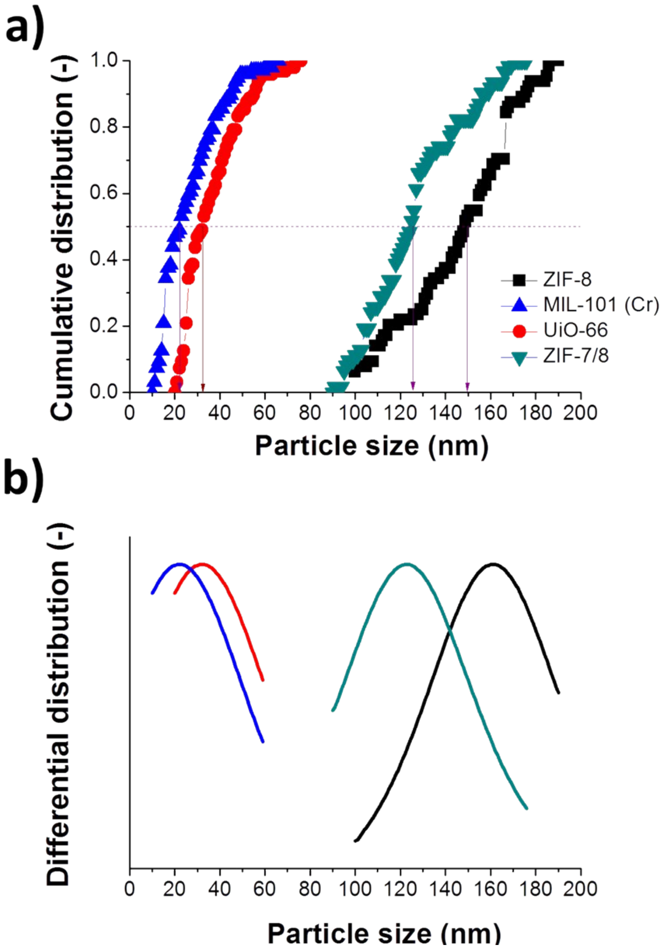


Fig. S2. Cumulative (a) and differential (b) particle size distribution of the ZIF-8, MIL-101(Cr), UiO-66 and ZIF-7/8 core-shells samples.

Table S1. Median particle sizes of the different MOFs used as filler according to the calculation of Fig. S2a.

MOF	**ZIF-8**	**MIL 101 (Cr)**	**UiO-66**	**ZIF-7/8**
Average particle size (nm)	150±60	25±19	33±13	124±22
Mode (nm)	161	22	32	123

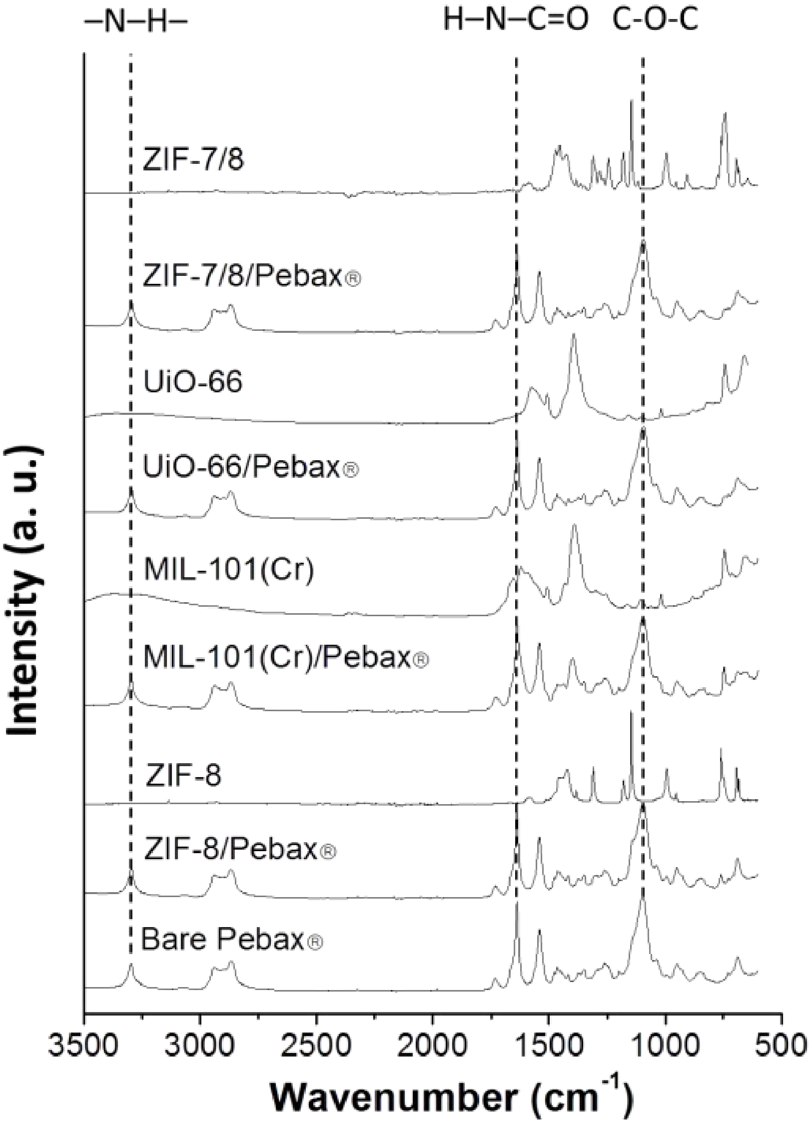


Fig. S3. FTIR spectra of Pebax® 1657 MMMs and MOF powders.

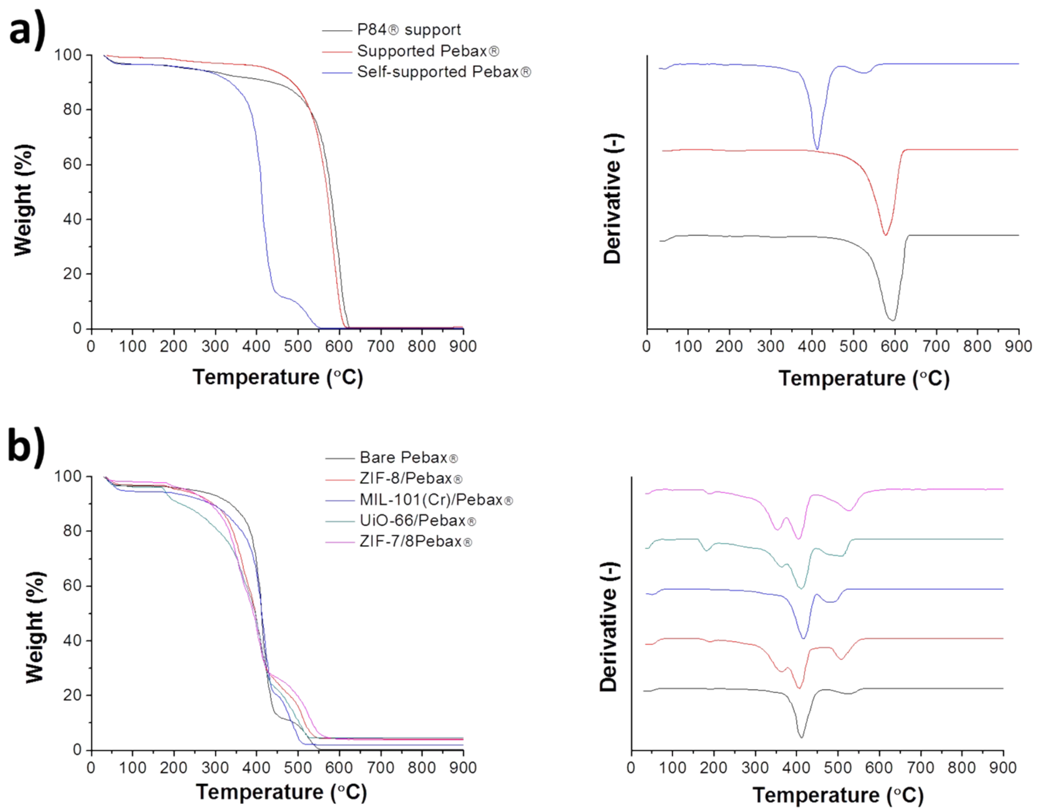


Fig. S4. TGA curves and derivatives in flowing air of pristine Pebax® 1657 membranes together with P84® support (a), and Pebax® 1657 MMMs (b).

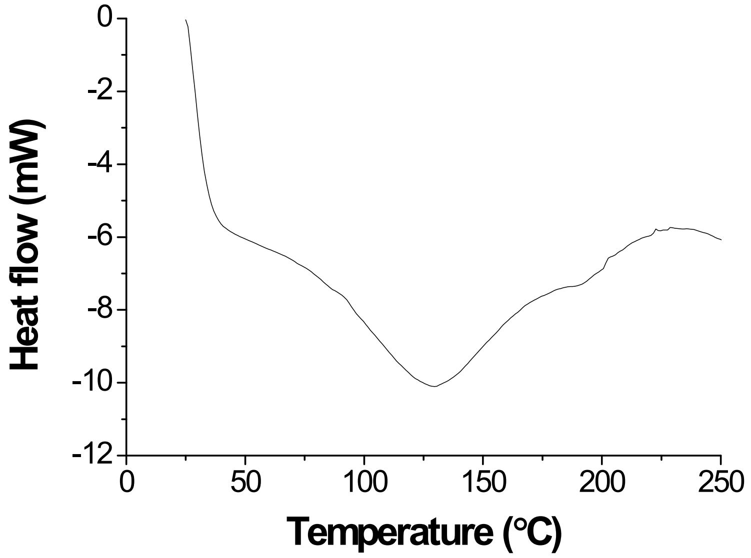
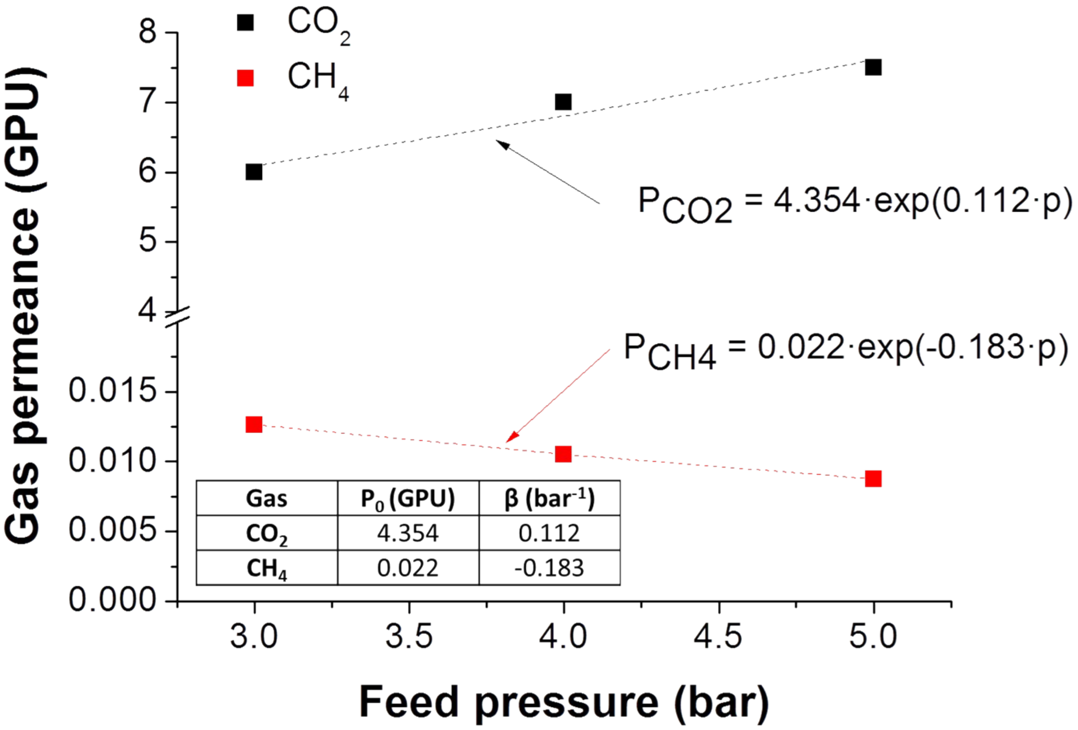


Fig. S5. DSC analysis of a Pebax® 1657 membrane. The analysis was performed in N_2 atmosphere using a heating rate of 10 °C·min^{-1}.

Gas separation performance

Table S2. Gas separation performance of P84® supports before and after PDMS coating. The testing conditions were 35 °C, 3 bar feed pressure and equimolar CO_2/CH_4 mixture.

Without PDMS			**With PDMS**		
CO_2 permeance (GPU)	**CH_4 permeance (GPU)**	**CO_2/CH_4 selectivity (-)**	**CO_2 permeance (GPU)**	**CH_4 permeance (GPU)**	**CO_2/CH_4 selectivity (-)**
270	256	1.1	55.1	10.0	5.5



Gas	P_0 (GPU)	β (bar^{-1})
CO_2	4.354	0.112
CH_4	0.022	-0.183

Fig. S6. Gas permeance of CO_2 and CH_4 with increasing pressure with numerical exponential fitting. The testing conditions were 35 °C, 3 bar feed pressure and equimolar CO_2/CH_4 mixture.

The CO_2 and CH_4 gas permeances of the Pebax® 16657/P84® supported membranes have been fitted to an exponential tendency according to Equation S1:

$$P = P_0 \cdot \exp(\beta \cdot p) \qquad (Eq. S1)$$

Where P_0 is the permeance coefficient (GPU) at zero feed pressure, p is the feed pressure (bar) and β is a constant (bar^{-1}) characteristic of the penetrant-membrane system at a specified temperature.

Robeson upper-bound adapted

Table S3. Literature review with the values that defined the upper-bound until the present (2018), including membrane thickness, CO_2 permeability in Barrer and CO_2/CH_4 selectivity. The calculated CO_2 permeance in GPU is given.

Polymer	Thickness (µm)	CO_2 permeability (Barrer)	CO_2 permeance (GPU)	α (CO_2/CH_4)	Ref.
PVSH doped polyaniline	20-30	0.029	0.002	2200	5
Polypyrrole 6FDA/PMDA (25/75)-TAB	50-120	120	1.41	47.8	6
Poly(diphenyl acetylene) 3a	30-90	190	3.17	33.4	7
Polyimide PI-5	50-120	290	3.41	31.5	8
Poly(diphenyl acetylene) 3e	50-120	330	3.88	27.5	7
Poly(diphenyl acetylene) 3f	50	678	13.56	20.2	7
Polyimide 6FDA-durene	20-70	958	21.29	24.0	9
6FDA-based polyimide (8)	28	1100	39.28	17.7	10
PTMSP	46	2300	50.00	18.4	11

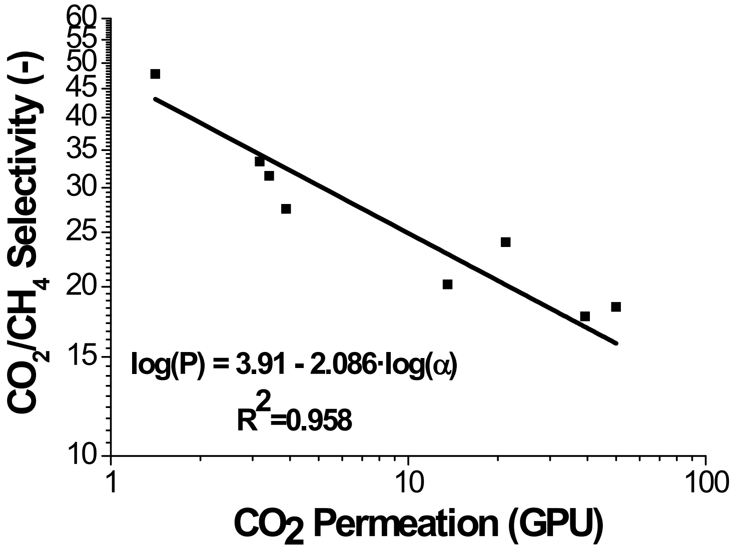


Fig. S7. CO_2/CH_4 bound defined in GPU at 35 ^{0}C. Squares represent the values in GPU of Table S3. The fitting equation of the linear fitting is also given with the R^2 value.

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