

Supporting information for:

Mixed Matrix Membranes from a Microporous Polymer Blend and Nano-sized Metal-Organic Frameworks with Exceptional CO₂/N₂ Separation Performance

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Materials, preparation and experimental methods

Dimethylformamide (DMF) used in the synthesis of UiO-66-NH₂ was purchased from Sigma Aldrich and dried over 4 Å molecular sieves. All other chemicals were purchased from Sigma Aldrich and were used without any further purification. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 thermal analysis system. Tensile tests were conducted with a TA instruments model Q800 dynamic mechanical analyzer (DMA) in controlled force mode with 1 N/min ramp rate at 25°C. Differential scanning calorimetry (DSC) was performed using a TA Instruments Q2000. Surface area measurements were collected using a gas sorption analyzer (Nova) from Quantachrome. Scanning electron microscopy (SEM) was performed using an FEI Quanta 600 scanning electron microscope under high vacuum with 20 keV acceleration. Energy-dispersive X-ray spectroscopy (EDX) was performed using an Oxford Inca Energy 350 X-act energy dispersive X-ray system attached to the SEM. ¹H (300 MHz) NMR spectrum was recorded on a Bruker AVANCE III 300 spectrometer. Fourier transform infra-red (FT-IR) spectra were collected using a Bruker Vertex 70. X-ray powder diffraction (PXRD) patterns were collected using a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu K α , (λ = 1.5406 Å) with a scan speed of 0.30 sec/step from 3.0 to 45° at a step size of 0.02°. The data were analyzed using the EVA program from the Bruker Powder Analysis Software package. The simulated powder patterns were calculated using Materials Studio based on single crystal diffraction data of corresponding MOFs. Transmission electron microscopy (TEM) images used to determine size distributions of MOF crystallites were collected on an FEI Morgagni 268 operated at 80 kV with an AMT side mount CCD camera system. Elemental microanalysis of MOFs was performed by the University of Illinois Urbana-Champaign Microanalysis Laboratory with an Exeter Analytical CE440 for CHN analysis; a Thermo

Scientific *Orin* Ion Selective Electrode for Cl analysis; and a PerkinElmer 2000DV ICP-OES for metal analysis.

Positron annihilation lifetime spectroscopy

A conventional fast timing positron annihilation lifetime spectroscopy (PALS) spectrometer at the University of Michigan was used to acquire spectra on a sample in vacuum to avoid any positronium annihilation with air in these relatively large polymer voids. Beginning with a base blend of 25% MEEP80 in PIM-1 three membranes with 10%, 20%, and 30% by weight fraction of MOF UiO-66-NH₂ were cast as nominally 80 μm thick films that arrived as mainly broken flakes ~5-15 mm on a side. The source sample “sandwich” configuration is as follows: a mm thick Cu plate has 4-5 of the larger flakes piled in its center; the Kapton sealed (a thin 13 μm foil of Kapton to separate the source from the sample) ²²NaCl (positron) source is laid on top with the source (~2-3 mm spot) directly over the membrane pile; another pile of 4-5 flakes are piled over the source followed by another Cu plate; the entire assembly is wrapped in Al foil to keep it together; the foil wrapped assembly is placed in a pancake-shaped vacuum container that fits between the PALS detectors. This geometry should stop at least ~70% of the positrons in the target membrane with the rest stopping equally in Kapton or Cu (neither of which produces positronium, Ps). Using this configuration we have acquired PALS spectra on the base blend (0% MOF) and the three MOF weight fractions.

The neat UiO-66-NH₂ MOF powder was synthesized and shipped to Michigan in a sealed container. PALS data was acquired on this sample using a well-type powder holder that is 5 mm in diameter, 2.2 mm deep and has ²²NaCl source deposited in a 2 mm diameter spot on the bottom of the well. The source is covered with a 13 μm Kapton thin film so the powder is not contaminated. Enough MOF was supplied to entirely fill the sample well. Some of the “clumps” of grains were broken down with a spatula to make for an easier fit into the 5 mm diameter well. About 60% of the source positrons are expected to stop in the powder sample compared to ~70% for the membranes piled on both sides of the Kapton sealed source. A metal cover was placed

over this and clipped into place. This assembly fits into a pancake-shaped vacuum chamber and the chamber was pumped under rough vacuum for some 6 hours before beginning data acquisition. Three days of PALS data were acquired at vacuum and then chamber was backfilled with 30 psi of He buffer gas.

Mixed gas permeation test

The permeances and selectivities of mixed gas testing were determined using a custom-built isobaric (constant pressure) gas permeation system. The feed gas composition was 20 mol% CO₂, 20 mol% N₂, and 60% dry Ar. Ultra-high purity Argon was used as the sweep gas. A flat sheet membrane was loaded in a circular permeation cell. The flow rate was controlled at 10 ml/min for the feed gas and 3.65 ml/min for the sweep gas by mass flow controllers. The feed and sweep gas were introduced counter-currently into the permeation cell. The pressure was maintained at 131 kPa and 128 kPa for the feed and sweep sides, respectively, measured with a pressure transducer (Honeywell). The permeate flow rate was measured using a mass flow meter. The gas composition of the retentate and permeate streams were measured using a gas chromatograph (Perkin Elmer ARNEL Clarus 500). In these measurements, the permeance, (P/l) , of a particular gas species, i , is defined as

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{A\Delta p_i} \quad (1)$$

where P is permeability, l is membrane thickness, Q is the flux across the membrane, A is the membrane surface area, and Δp is the partial pressure difference across the membrane.

Selectivity, α of gas species i with respect to species j is

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (2)$$

Mixed gas permeation tests at different temperatures

The mixed matrix membrane containing 10 wt% UiO-66-NH₂ in the total membrane was tested at 22 °C, 35 °C, and 45 °C. The feed gas was the simulated flue gas containing 14 mol% CO₂ and

86 mol% N₂. Ultra-high purity Argon was used as the sweep gas. A flat sheet membrane was loaded in a circular permeation cell. The flow rate was controlled at 80 ml/min for the feed gas and 60 ml/min for the sweep gas by mass flow controllers. The feed and sweep gas were introduced counter-currently into the permeation cell. The pressure was maintained at 1.5 atm and 1.2 atm for the feed and sweep sides, respectively. From these results, the activation energies for CO₂ and N₂ were calculated using an Arrhenius equation.

$$P = P_o e^{\frac{-E_a}{RT}}$$

Where P_o is the pre-exponential factor of permeation, R is the ideal gas constant (8.314 kJ/mol·K), T is the temperature (K), and E_a is the activation energy of permeation (kJ/mol). The activation energies for each gas were determined from the slope of the linear-fit from the measured permeabilities for the three different temperatures (Tables S4, S5, Figure S19).

Mixed gas permeation tests at different pressures

The mixed matrix membrane containing 10 wt% UiO-66-NH₂ in the total membrane was tested at feed side pressure of 1.5 atm, 2.5 atm and 3.5 atm, respectively, at 22 °C. The feed gas was the simulated flue gas containing 14 mol% CO₂ and 86 mol% N₂. Ultra-high purity Argon was used as the sweep gas. A flat sheet membrane was loaded in a circular permeation cell. The flow rate was controlled at 80 ml/min for the feed gas and 60 ml/min for the sweep gas by mass flow controllers. The feed and sweep gas were introduced counter-currently into the permeation cell. The sweep side pressure was maintained at 1.2 atm.

Humidified gas permeation tests

The mixed matrix membrane containing 10 wt% UiO-66-NH₂ in the total membrane was tested at 22°C with feed gas 95% saturated with water vapor. The feed gas was humidified by bubbling it through a stainless steel vessel filled with distilled water. The relative humidity was measured by an in-line probe hygrometer (HMT 330 series, Vaisala), which indicated 95.3% RH. The simulated flue gas containing 14 mol% CO₂ and 86 mol% N₂ was used as the feed gas. Ultra-high purity Argon was used as the sweep gas. The pressures was maintained at 1.5 atm and 1.2 atm for the feed and sweep side, respectively. The CO₂ permeability was 2623 Barrer and CO₂/N₂ selectivity was 37. Although the CO₂ permeability was much lower than in the dry test, the performance has exceeded the 2008 Robeson Upper Bound.¹

Synthesis of PIM-1

PIM-1 was synthesized by the experimental method reported by Budd et al.² 3,3,3',3'-tetramethyl-1,1''-spirobisindane-5,5',6,6'-tetrol (26.48 mmol, 9.02 g) and 2,3,5,6-tetrafluorophthalonitrile (26.48 mmol, 5.31 g) were dissolved in dry dimethylformamide (DMF) (120 mL). K₂CO₃ was added in the solution and the reaction was stirred at 58°C for 40 hr. Water (200 mL) was added after cooling the reaction mixture and the product was separated by filtration. Further purification was performed by reprecipitation from CHCl₃ solution with MeOH and a bright yellow solid product was produced after thermal activation at 120°C.

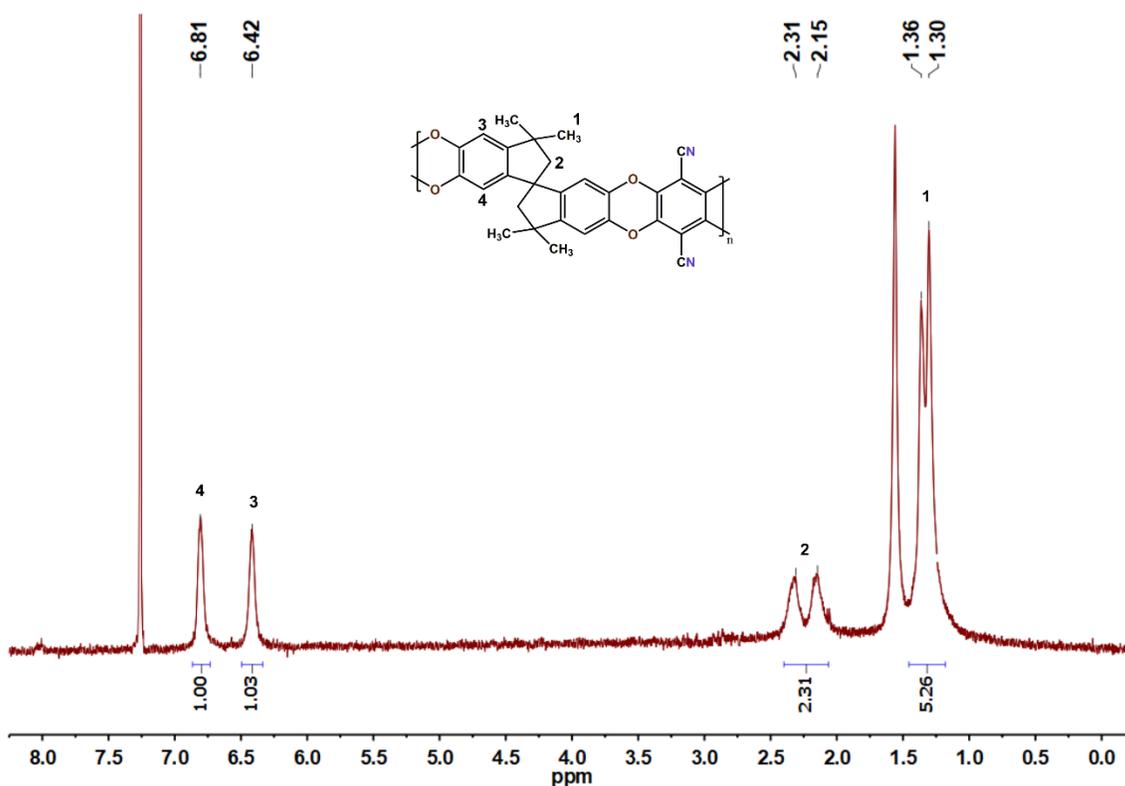


Figure S1. ¹H (400 MHz) NMR spectrum of PIM-1. In chloroform (7.26) residual water (1.56)

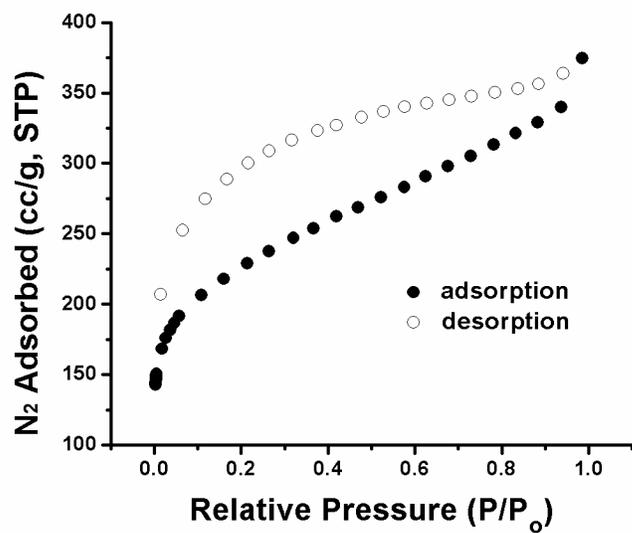


Figure S2. N₂ isotherm of PIM-1 collected at 77 K. Calculated BET surface area is 813 m²/g.

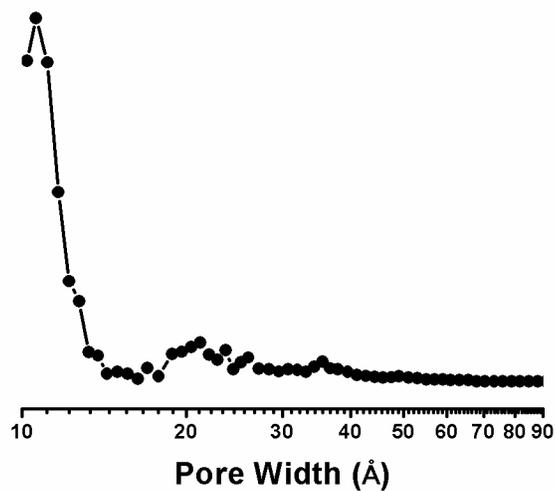


Figure S3. Pore size distribution for PIM-1 calculated by non-local density functional theory (NLDFT) mode.

Synthesis of MEEP80

Poly(dichlorophosphazene) (~40 g) was dissolved in 600 mL anhydrous toluene under an argon atmosphere. Once dissolved, the polymer was precipitated by the addition of 1.5 L hexanes and the supernatant was reduced to dryness to determine the mass of polymer by the difference. The purified poly(dichlorophosphazene) (35.4 g) was re-dissolved in 600 mL anhydrous toluene under argon. In a separate flask, 4-methoxyphenol (10.8 g, 87.3 mmol) and 2-allylphenol (4.09, 30.5 mmol) were dissolved in ~1 L anhydrous tetrahydrofuran (THF) under argon. NaH (60 %, 4.38 g, 110 mmol) was carefully added to the flask and the reaction was allowed to stir for 14 hrs. The polymer solution was poured into the phenoxide solution and the reaction stirred for 24 hrs. In a separate flask, 2-(2-methoxyethoxy)ethanol (120 g, 1.00 mol) was slowly added to a mixture of NaH (60 %, 34.7 g, 0.950 mol) in ~1 L anhydrous THF. The reaction was allowed to stir for 18 hrs. The alkoxide reaction solution was added to the polymer via cannula, and the reaction was allowed to stir at room temperature for 24 hrs. The crude polymer was precipitated with the addition of 4 L hexanes, and then re-dissolved in 1 L THF. The polymer was precipitated with 3 L hexanes and then dried in a vacuum oven at 50°C overnight before being added to 1.5 L H₂O. HCl (3 M) was used to neutralize, and then the mixture was heated to 70°C. The polymer was collected by centrifugation and dissolved in 1 L THF. The solution was centrifuged and decanted into 4 L hexanes to precipitate the purified polymer, which was collected and dried in a vacuum oven at 50°C (69.7 g, 79% yield).

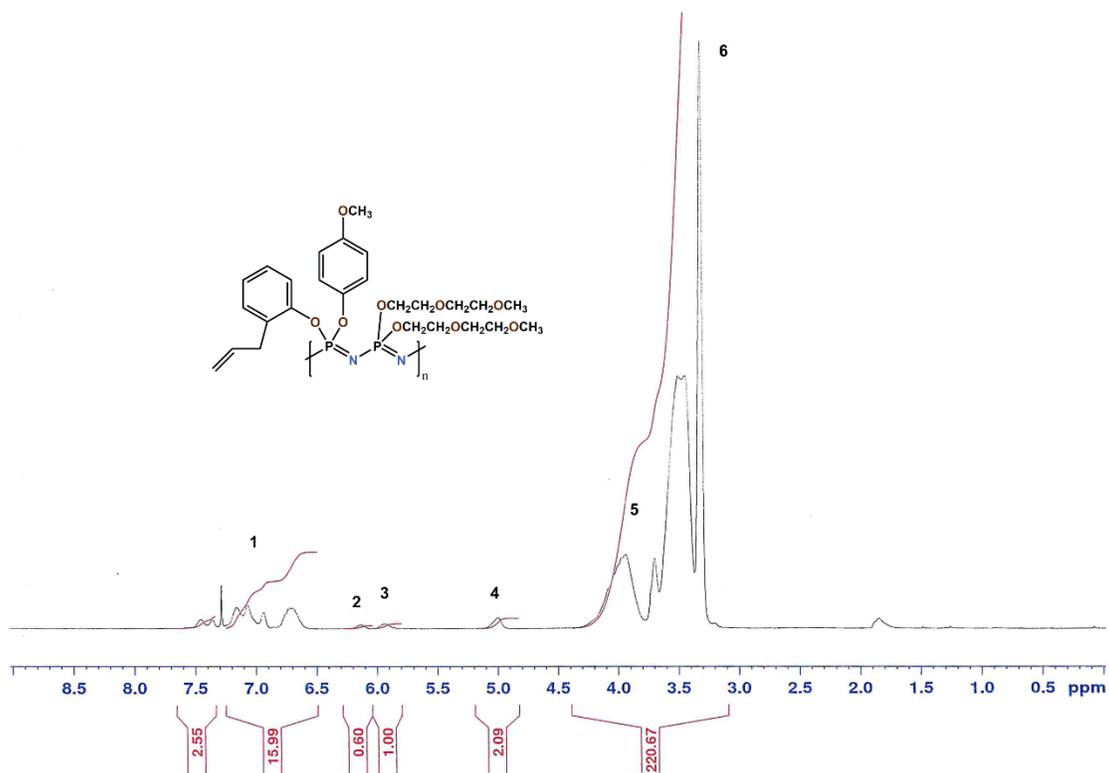
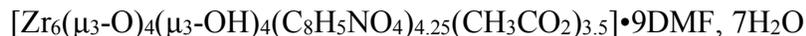


Figure S4. ¹H (600 MHz) NMR spectra of MEEP80. Peak labels for ¹H NMR as follows: allylphenol and methoxyphenol aromatics (1); methoxyphenol methyl (2); allylphenol allyl (3) and (4); DEG ethylenes (5); DEG methyl (6).

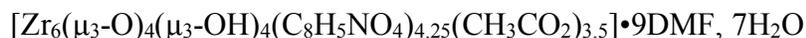
Synthesis of UiO-66-NH₂



A 0.05 M solution of 2-aminoterephthalic acid (H₂-BDC-NH₂) in DMF was prepared by sonicating a mixture of H₂-BDC-NH₂ (181.15 mg, 1 mmol) and DMF (20 mL) until complete dissolution. A 0.4 M solution of Zr(OⁿPr)₄ (Zirconium propoxide) in CH₃COOH was prepared by mixing Zr(OⁿPr)₄ 70 wt. % in n-propanol (4 mL, 4.176 g, 8.92 mmol) with CH₃COOH (18.31 mL). We note that it was crucial to prepare the Zr(OⁿPr)₄ solution immediately before use and while still clear. To ten separate 40 mL Pyrex vials were added in sequence DMF (20 mL), CH₃COOH (1 mL), 0.05 M H₂-BDC-NH₂ solution (2 mL), and 0.4 M Zr(OⁿPr)₄ solution (2 mL). The vials were tightly capped and heated at 65 °C for 7 h in an isothermal oven to yield turbid pale yellow suspensions. The suspensions were centrifuged at 10000 rpm for 2 min to obtain yellow precipitate. The precipitates from ten vials were combined and washed with fresh DMF (20 mL, 4x) and used for characterization and membrane fabrication. In the case of membrane fabrication, MOFs would also undergo solvent exchange with chloroform (20 mL, 4x) and ¹H NMR was used to confirm that DMF was fully removed.

Elemental composition of UiO-66-NH₂

A combination of ¹H NMR, elemental analysis, and TGA were used to determine the composition of synthesized UiO-66-NH₂. As-synthesized crystals (~100 mg) were washed with dry DMF 3x to remove unreacted starting materials. Crystals were then dried under vacuum in a Schlenk line fitted with a liquid N₂ cold trap for 3 hours. The dried crystals were then split into three separate batches: ~10 mg for ¹H NMR, ~25 mg for TGA, and ~65 mg for EA. For ¹H NMR analysis, crystals were digested with 0.1 M K₃PO₄ in D₂O. ¹H NMR spectrum (Figure SX) of dissolved crystals indicate 29% of NH₂-BDC linkers is replaced with acetates (two acetates per missing linker) and also shows the presence of approximately 2 DMF molecules per linker[Zr₆(μ₃-O)₄(μ₃-OH)₄(C₈H₅NO₄)_{4.25}(CH₃CO₂)_{3.5}]•9DMF, xH₂O. The remaining water (x=7) was then determined by a combination of TGA (Figure S6) and EA and the resulting formula was found to be in good agreement with EA:



Anal. calcd. (%): C, 33.59; H, 4.67; N, 7.63; Zr, 22.51; Found (%): C, 33.53; H, 4.11; N, 7.23; Zr, 22.43.

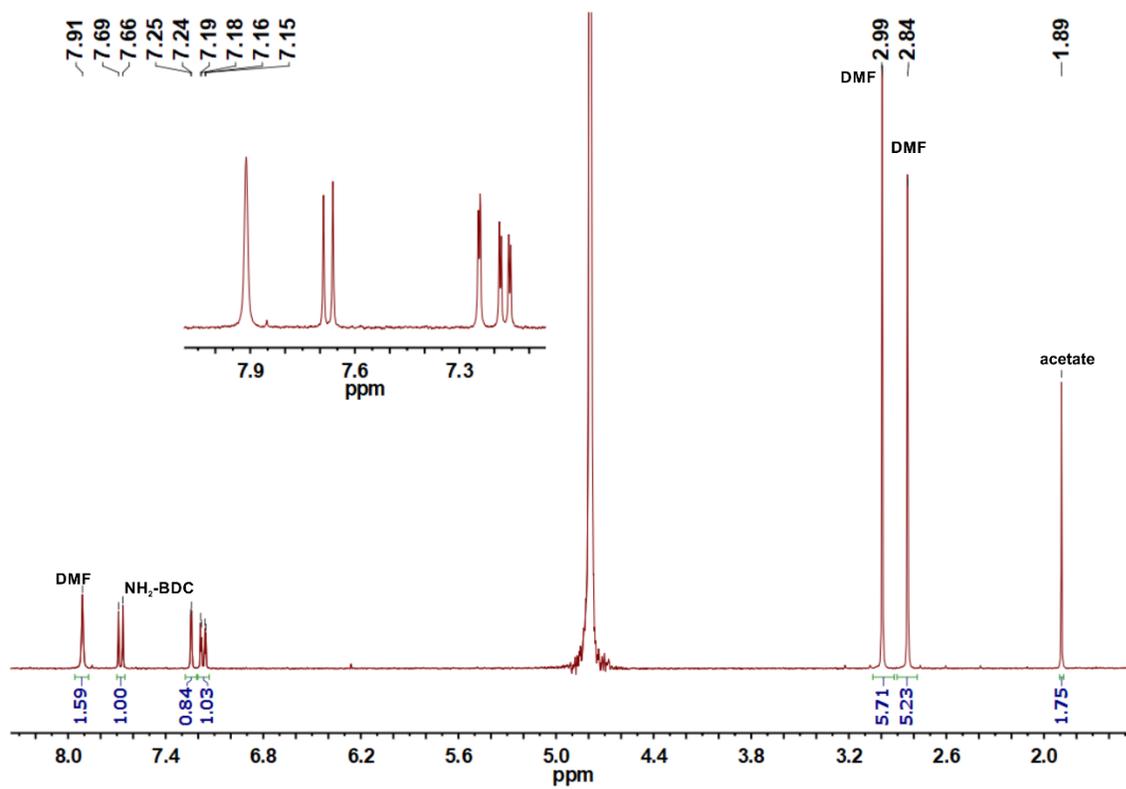


Figure S5. ¹H (400 MHz) NMR spectrum of dissolved UiO-66-NH₂. In basic (0.1 M K₃PO₄) D₂O (4.79 ppm).

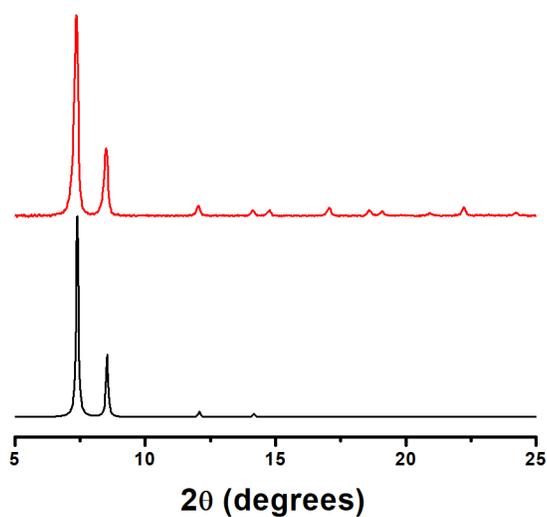


Figure S6. Powder X-ray diffraction patterns for simulated (black) and DMF-washed (red) UiO-66-NH₂.

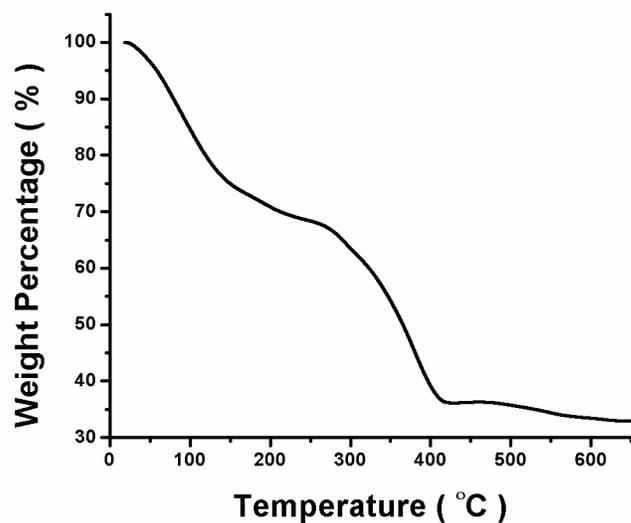


Figure S7. TGA of DMF washed UiO-66-NH₂ (ramp rate of 1°C/min). TGA data was correlated with EA data. The major weight loss of 33.1% between r.t. and 275°C corresponds to the loss of 9 DMF and 7 H₂O (calcd. 32.2%). Individual weight loss steps could not be differentiated due to a lack of a clear plateau between them.

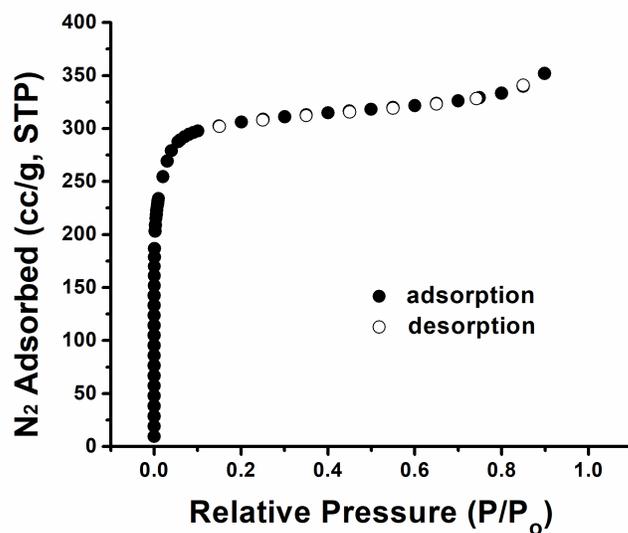


Figure S8. N₂ isotherm at 77 K of UiO-66-NH₂ on a Micromeritics 3Flex instrument. The calculated BET surface area is 1205±9 m²/g. In this case, the material was activated using the following protocol: as-synthesized crystals were washed with DMF (3x) followed by drying with a Schlenk line fitted with a liquid N₂ cold trap for two hours. The MOF sample was then evacuated on a Micromeritics Smart VacPrep 100°C for 21 hours to obtain 29.2 mg of activated sample.

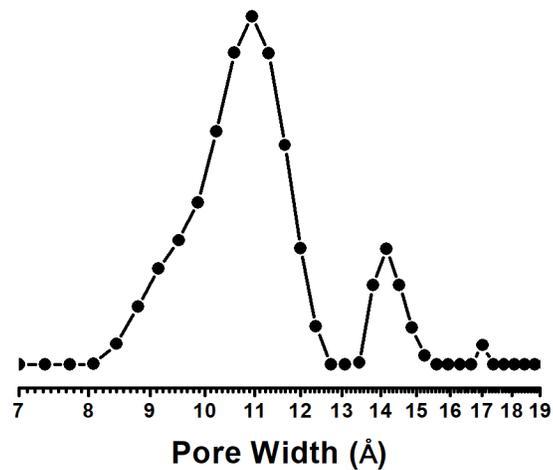


Figure S9. Pore size distribution for UiO-66-NH₂ calculated from N₂ isotherm shown in Figure S8 by non-local density functional theory (NLDFT) mode.

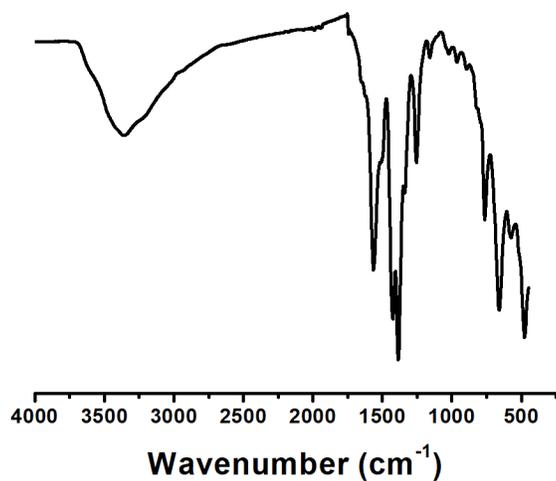


Figure S10. FT-IR spectrum for neat UiO-66-NH₂. FT-IR analysis was performed on dry powder after N₂ isotherm.

Synthesis of mixed matrix membranes

The dried PIM-1 was dissolved in chloroform to form a 4% stock solution and then filtered through a 1.0 μm PTFE filter. Chloroform suspensions of UiO-66-NH₂ of various concentrations were sonicated to prevent particle aggregation. The UiO-66-NH₂ suspension and MEEP80 were then added into the filtered PIM-1 solution. The total concentration of MEEP80 and PIM-1 in chloroform was maintained at 2.0 wt% in all cases (with 25 wt% MEEP80 in PIM-1). The resulting mixed matrix dope solution was mixed on a rolling mixer overnight and then sonicated prior to casting onto a clean petri PTFE dish in a glove bag pre-saturated with chloroform. The film was left in the glove bag overnight at ambient temperature to allow the solvent to evaporate slowly. The obtained membranes were further dried at 70 °C under vacuum prior to gas permeation measurements and structural characterization. Mixed matrix membranes were formed with loadings of Zr-MOF particles varying from 10% to 30 wt% determined by the mass ratio of MOF and total weights (MOF+polymer). Masses of MOF and polymer added to casting suspensions were used to determine final MOF loading because there was no washing or other procedure used which could remove nonvolatile material from the membranes after casting. Pure PIM-1 or PIM-1/MEEP80 dense films were prepared by casting the polymer solution under the similar procedure.

Fabrication and characterization of thin film mixed matrix membranes

To demonstrate thin film gas separation properties, we prepared a multi-layer thin-film composite membrane using a 20 wt% UiO-66-NH₂ in 25%MEEP80/75%PIM-1 MMM as a selective layer in the following procedure. First, 1.0 w/w% polydimethylsiloxane (PDMS) in hexane was applied to a proprietary polymeric microporous substrate (5 × 5 cm) using a casting knife with a gap clearance of 50 μm . The PDMS gutter layer has been widely used to prevent solution pore penetration and smoothen substrate surface for the formation defect-free thin films.³ The PDMS coating was then dried in an oven at 100°C for 1 hour. Second, a dilute coating solution containing 2.0 w/w% MMM in chloroform was cast onto the dried PDMS

surface (5×5 cm) using a casting knife with a gap clearance of 100 μm. Finally, the TFC membrane was obtained after drying in a fume hood for 2 hours at 23°C to completely evaporate the solvent. Pure-gas permeance of CO₂ and N₂ across membrane samples were determined using a constant pressure/variable volume apparatus at 23 °C and a pressure drop ($p_f - p_p$) of 1 bar. Pure-gas permeance was calculated using:

$$(P_A/l) = \frac{J_A}{A \cdot (p_f - p_p)} \times \frac{273}{T}$$

where (P_A/l) is the permeance of gas component A, J_A (cm³/s) is steady-state volumetric flow rate of permeate gas, A (cm²) is effective sample area, and T (K) is temperature.⁴ The steady-state volumetric flow was measured using a mass flow meter (Alicat Scientific, AZ, USA). The cross-sectional SEM image shown in **Figure S18** shows that our PDMS gutter layer was made as thin as 200 nm to minimize additional gas transport resistance and that a 2 μm-thick MMM layer was successfully achieved on top of the PDMS gutter layer. The measured pure gas CO₂ permeance of this TFC membrane was 1030 GPU at 23°C, and its CO₂/N₂ ideal selectivity was 21.4, aligned with its bulk film selectivity of 21.9, demonstrating that this membrane is defect-free.

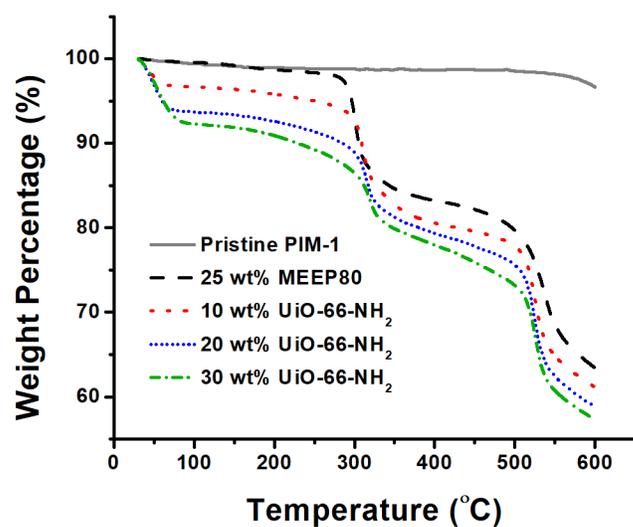


Figure S11. TGA of PIM-1, PIM-1/25 wt% MEEP80 blend, and MMMs with PIM-1/25 wt% MEEP80 blends and varying amounts of UiO-66-NH₂ filler particles.

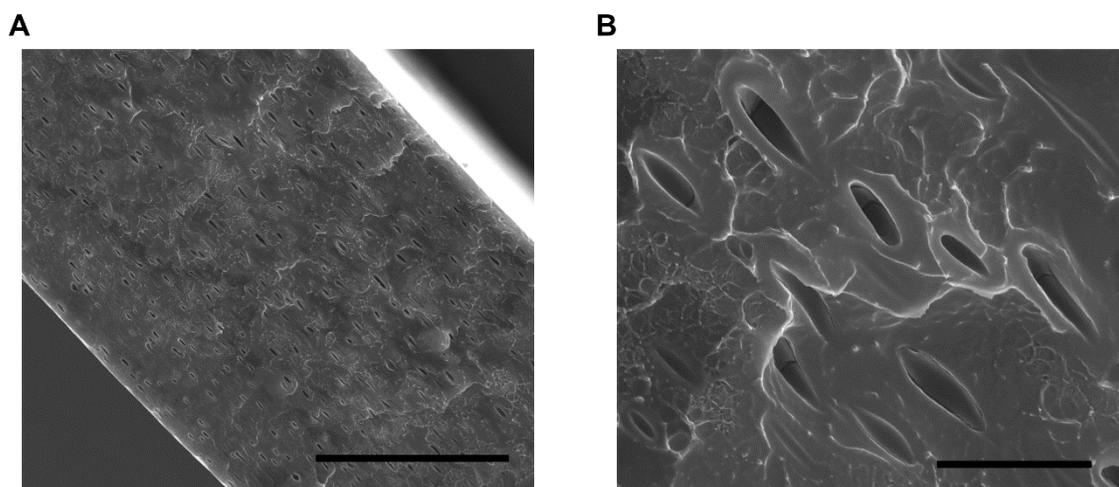


Figure S12. SEM images of PIM-1/25 wt% MEEP80 blend without any MOF, indicating microvoids; (A) Scale bar = 50 μm; (B) Scale bar = 5 μm.

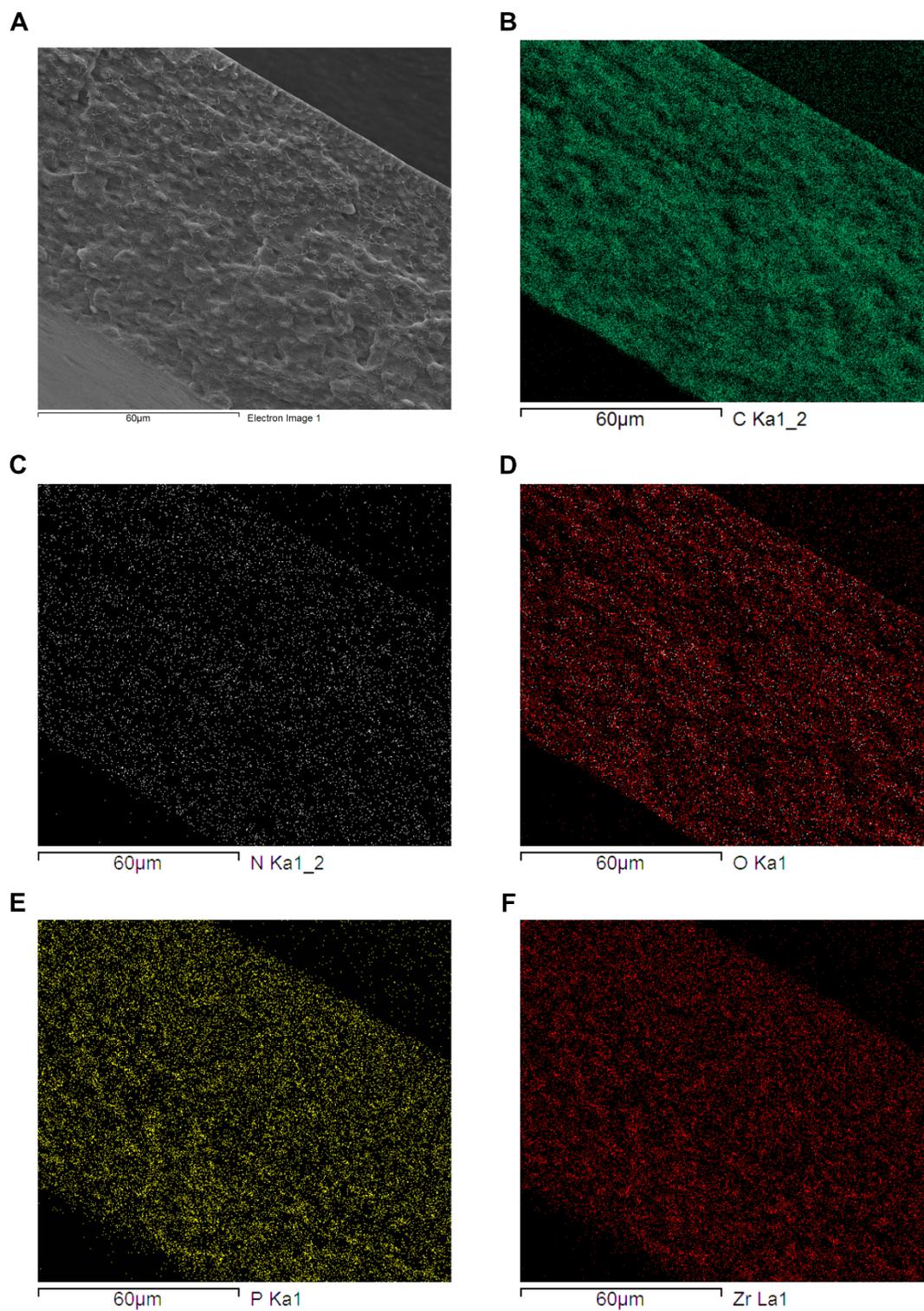


Figure S13. 10 wt% loading blend SEM-EDS; A. SEM of cross section; (B) corresponding EDS mapping of carbon; (C) of nitrogen; (D) of oxygen; (E) of phosphorous; (F) of zirconium.

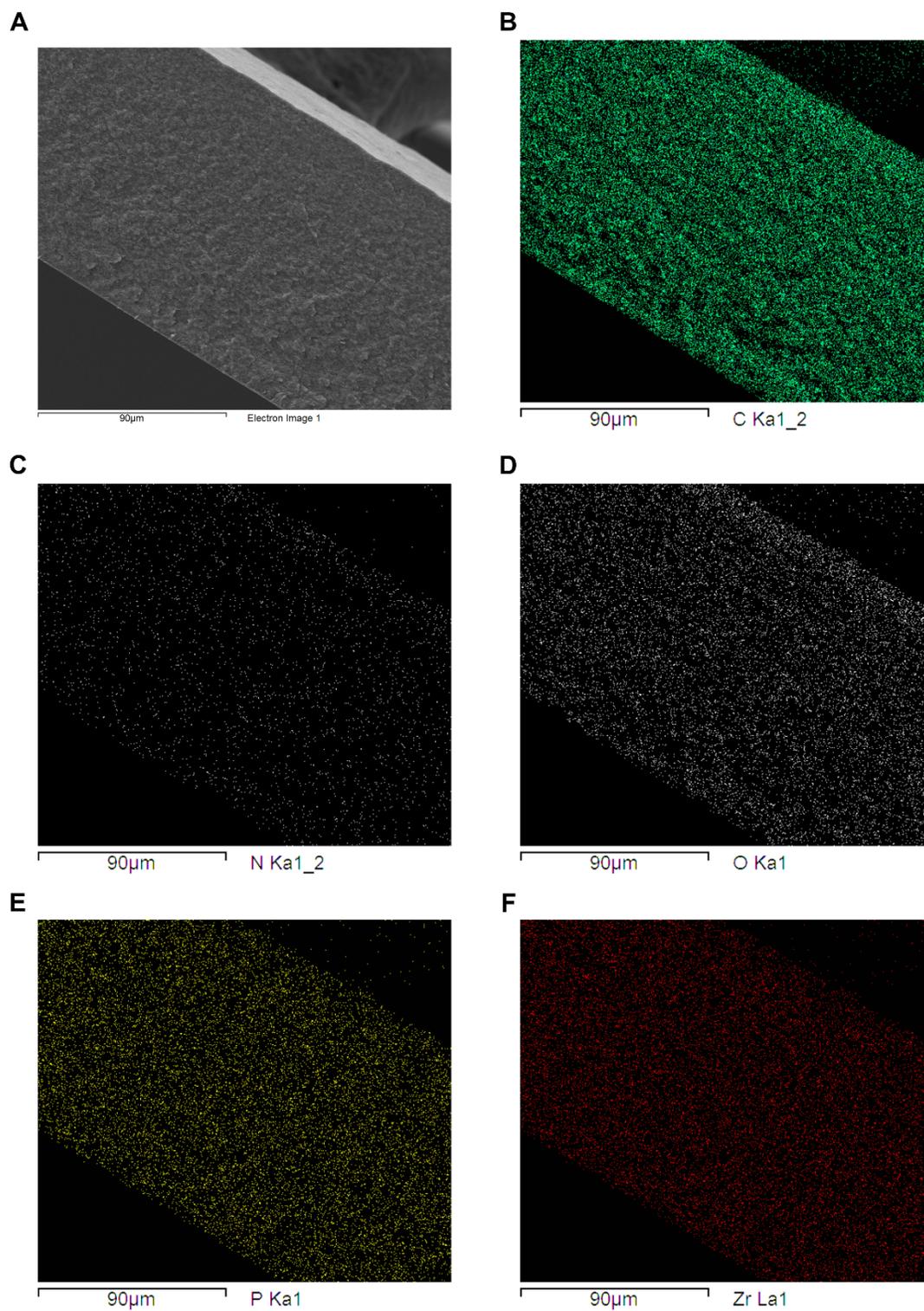


Figure S14. 20 wt% loading blend SEM-EDS; A. SEM of cross section; (B) corresponding EDS mapping of carbon; (C) of nitrogen; (D) of oxygen; (E) of phosphorous; (F) of zirconium.

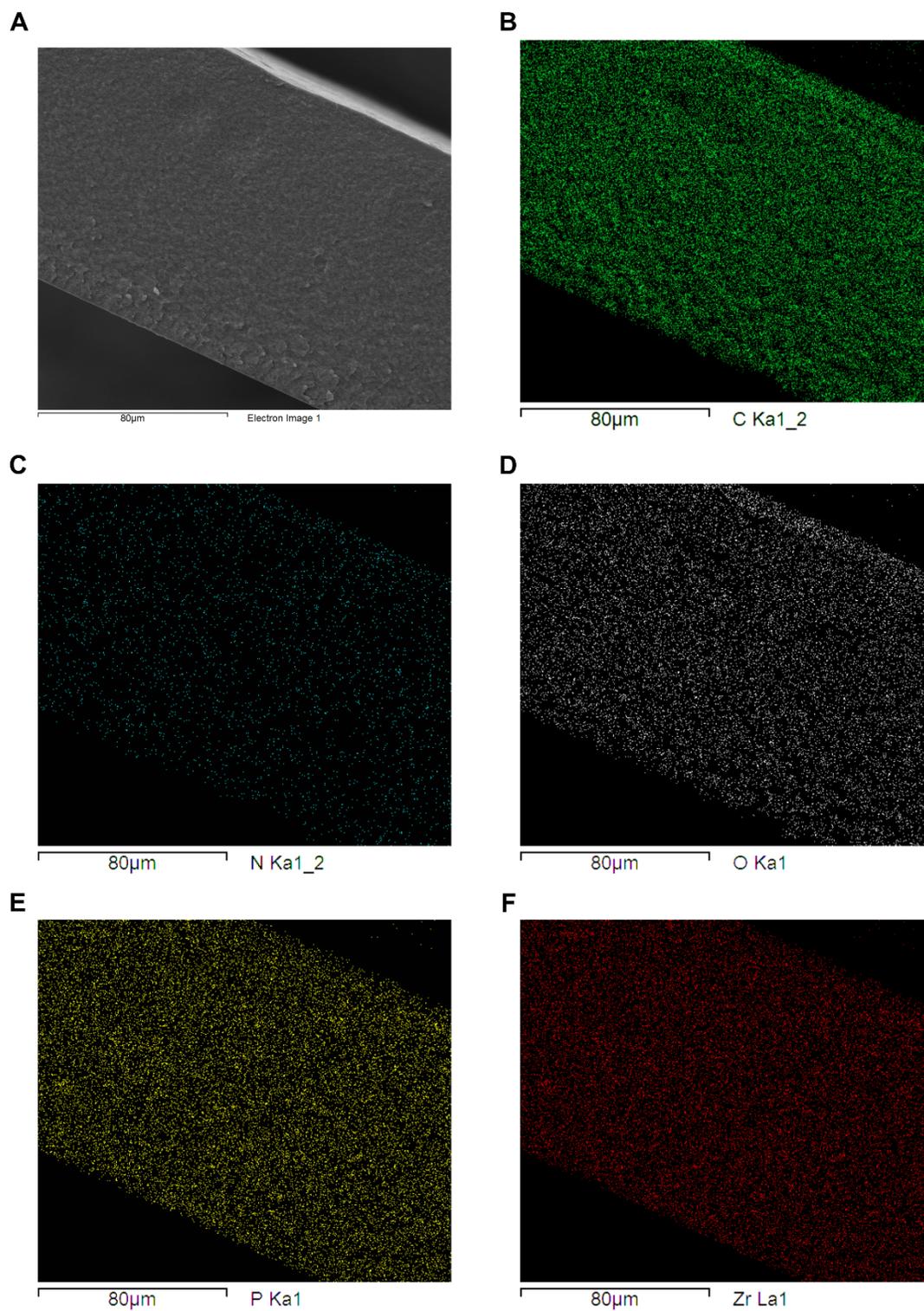


Figure S15. 30 wt% loading blend SEM-EDS; A. SEM of cross section; (B) corresponding EDS mapping of carbon; (C) of nitrogen; (D) of oxygen; (E) of phosphorous; (F) of zirconium.

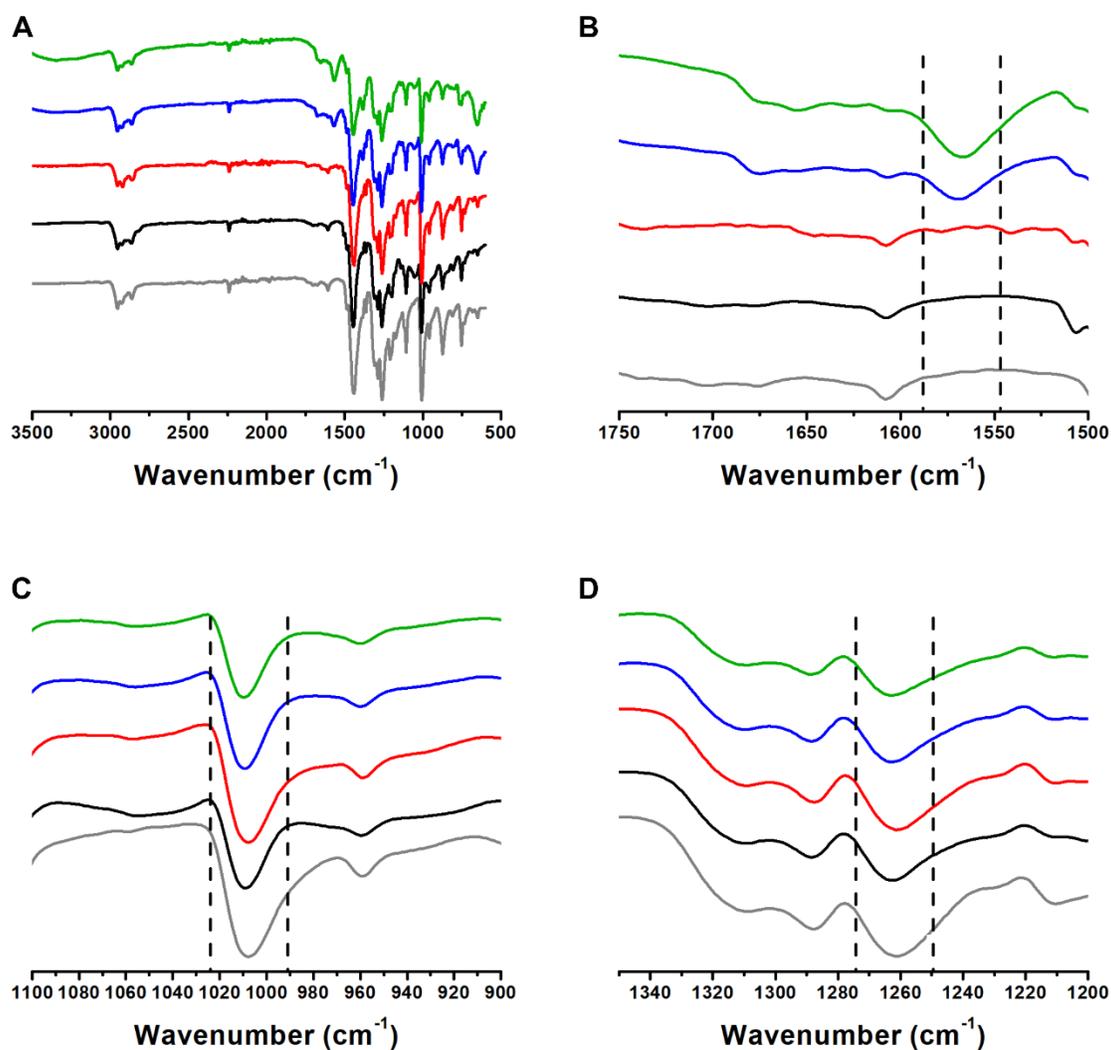


Figure S16. FT-IR spectra of membranes. Pure PIM-1, grey; 75% PIM-1/25% MEEP80 blend, black; Blend with 10% UiO-66-NH₂, red; Blend with 20% UiO-66-NH₂, blue; Blend with 30% UiO-66-NH₂, green. (A) full spectra; (B) 1500-1750 cm⁻¹; (C) 900-1100 cm⁻¹; (D) 1200-1350 cm⁻¹.

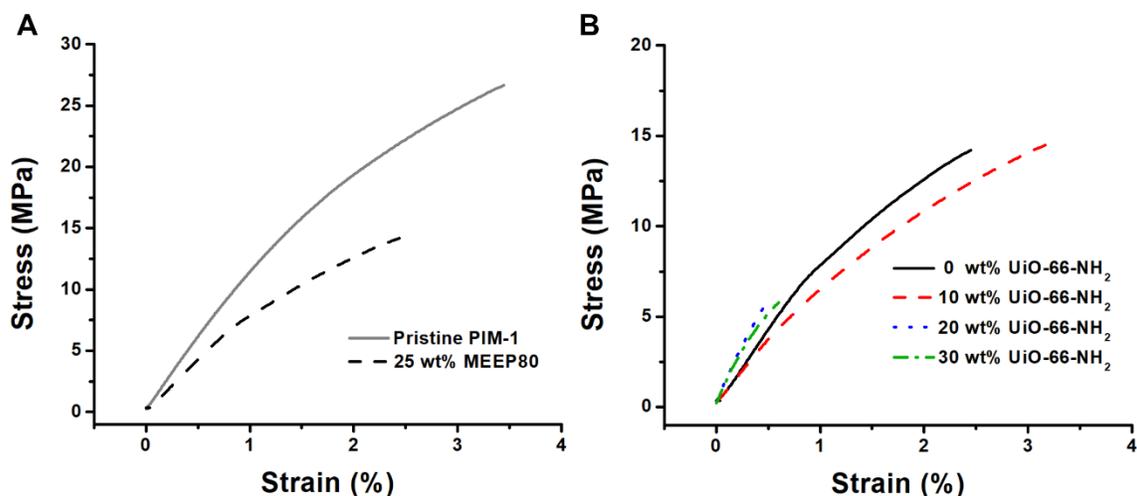


Figure S17. DMA tension tests of membranes (A) PIM-1 and MEEP80 blend; (B) 75%PIM-1/25%MEEP80 blend with varying amounts of UiO-66-NH₂.

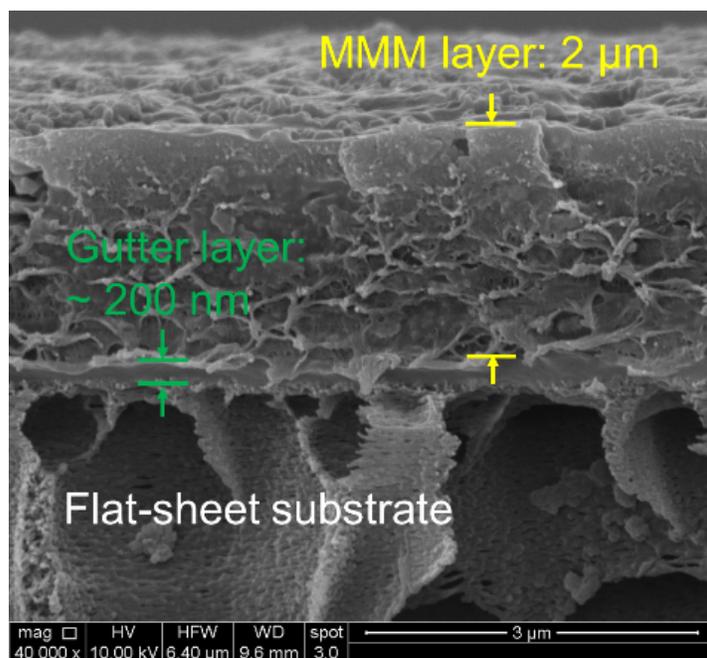


Figure S18 Cross-sectional SEM microstructure of a multi-layer composite membrane composed of a microporous substrate, a PDMS gutter layer and a 20% UiO-66-NH₂ MMM selective layer.

Table S1: Summary of DMA tension test results for various membranes. All MMMs prepared with MOF used the 75%PIM-1/25%MEEP80 blend.

Membrane	Thickness (μm)	Tensile Strength (MPa)	Failure Strain (%)	Young's Modulus (MPa)
Pristine PIM-1	93.8±3.9	25.3±6.4	3.5±1.1	1090±110
25%MEEP80 Blend	68.8±3.7	15.0±1.4	2.25±0.21	808±69
10% UiO-66-NH ₂	99.33±0.94	15.83±0.74	3.20±0.29	587±74
20% UiO-66-NH ₂	131.0±9.0	5.4±1.6	0.52±0.20	1006±77
30% UiO-66-NH ₂	145±15	5.48±0.85	0.54±0.22	1130±400

Table S2: Mixed gas permeation data for various membranes. All MMMs prepared with MOF used the 75%PIM-1/25%MEEP80 blend.

Membrane	CO₂ Permeability (Barrer)	CO₂/N₂ Selectivity
Pristine PIM-1	7790±560	17.2±2.2
25%MEEP80 Blend	3140±110	25.4±1.0
10% UiO-66-NH ₂	4968±34	22.5±0.4
20% UiO-66-NH ₂	5870±160	21.9±1.0
30% UiO-66-NH ₂	5970±70	22.5±0.4

Table S3: The effect of aging time on mixed gas permeation measurements for PIM-1/MEEP80 and MMMs (In this work, MMM films were stored under ambient conditions between gas transport measurements) and the comparison with the literature.

Membrane	Aging (days)	CO ₂ Permeability (Barrer)	CO ₂ /N ₂ Selectivity
75%PIM/25%MEEP80 blend (this work)	0	3140	25.4
	45	1976	27.2
10% UiO-66-NH ₂ @75%PIM/25%MEEP80 blend (this work)	0	4968	22.5
	96	5020	25.1
	137	5040±130	24.85±0.35
	266	5039	26.1
	306	4905	26.0
20% UiO-66-NH ₂ @75%PIM/25%MEEP80 blend (this work)	0	5870	21.9
	106	4587	26.5
	151	4526	27.2
	268	4635	29.1
	306	4485	29.2
UiO-66-NH ₂ @ PIM-1 ⁵	0	7660	12.0
	105	3100	12.4
	192	2750	13.7
	400	2550	14.2

Table S4: Mixed gas permeation data for variable temperature. All MMMs prepared with MOF used the 75%PIM-1/25%MEEP80 blend.

Membrane	Temperature (°C)	CO ₂ Permeability (Barrer)	CO ₂ /N ₂ Selectivity
10% UiO-66-NH ₂	22	4783	27.1
10% UiO-66-NH ₂	35	4328	23.1
10% UiO-66-NH ₂	45	4127	20.2

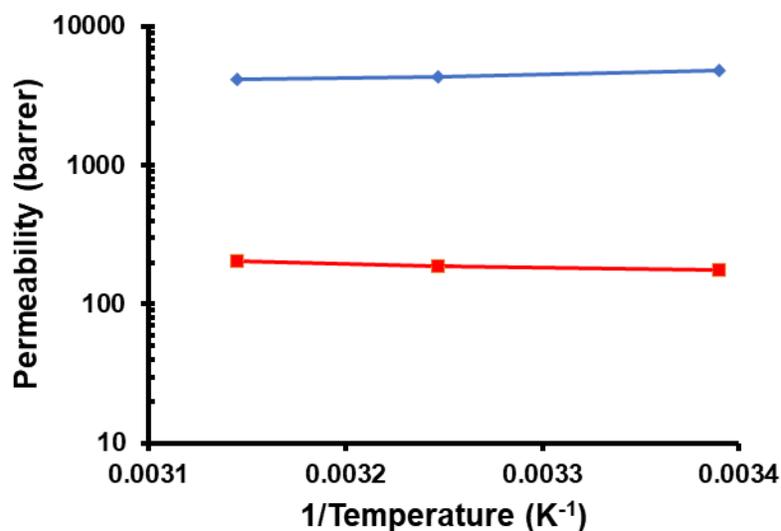


Figure S19: Permeability vs reciprocal temperature at 1.5 atm and 1.2 atm for the feed and sweep side pressures, respectively for a MMM with 10 wt% UiO-66-NH₂ and the 75%PIM-1/25%MEEP80 blend (CO₂, blue; N₂, red).

Table S5: Activation energy of permeation for a MMM with 10 wt% UiO-66-NH₂ and a comparable reference MMM. The MMM from this work was prepared with the 75%PIM-1/25%MEEP80 blend.

Membrane	CO ₂ (kJ/mol)	N ₂ (kJ/mol)
10% UiO-66-NH ₂ @PIM-1/MEEP80 (this work)	-5.16	4.87
10% UiO-66-NH ₂ @PIM-1 ⁶	-3.5	4.6
PIM-1 ⁶	-1.4	4.6

Table S6: Mixed gas permeation data for variable pressure. All MMMs prepared with MOF used the 75%PIM-1/25%MEEP80 blend.

Membrane	Feed Pressure (atm)	CO ₂ Permeability (Barrer)	CO ₂ /N ₂ Selectivity
10% UiO-66-NH ₂	1.5	4783	27.1
10% UiO-66-NH ₂	2.5	4431	27.0
10% UiO-66-NH ₂	3.5	4380	26.7

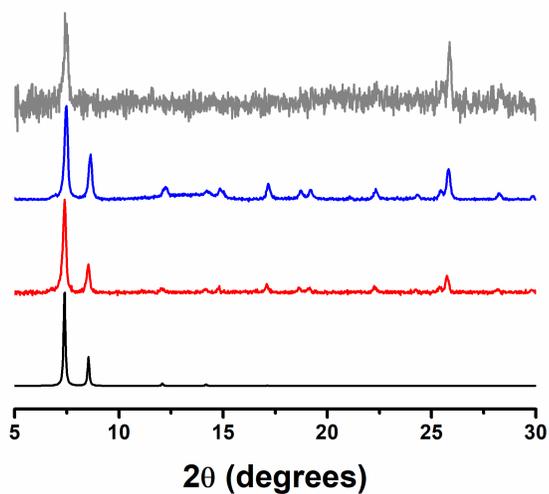


Figure S20. Powder X-ray diffraction patterns for simulated UiO-66-NH₂ (black) and for MMM films of 75%PIM-1/25%MEEP80 blend and 10% (grey), 20% (blue), and 30% UiO-66-NH₂ (red) after aging over 300 days.

Table S7: Gas permeation data for MMMs and selected reference MMMs with PIM-1 and UiO-66-NH₂.

Membrane	Feed Gas	CO ₂ Permeability (Barrer)	CO ₂ /N ₂ Selectivity
10% UiO-66-NH ₂ @PIM-1/MEEP80 (this work)	mixed	4968	22.5
20% UiO-66-NH ₂ @PIM-1/MEEP80 (this work)	mixed	5870	21.9
30% UiO-66-NH ₂ @PIM-1/MEEP80 (this work)	mixed	5970	22.5
5% UiO-66-NH ₂ @PIM-1 ⁶	pure	2952	26.9
10% UiO-66-NH ₂ @PIM-1 ⁶	pure	2869	27.5
20% UiO-66-NH ₂ @PIM-1 ⁶	pure	2210	23.7
30% UiO-66-NH ₂ @PIM-1 ⁶	pure	2005	22.0
40% UiO-66-NH ₂ @PIM-1 ⁶	pure	1727	24.0
20% UiO-66-NH ₂ @PIM-1 ⁵	pure	7660	12.0

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