Electronic Supplementary Information

Microporous polymeric composite membranes with advanced film properties: Pore intercalation yields excellent CO2 separation performance

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Materials, preparation and experimental methods

All 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. Tension tests were conducted with a TA instruments model Q800 dynamic mechanical analyzer (DMA). 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. ^{1}H (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.

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. A one-sided sample stacked on a Na-22 positron source deposited on a W substrate (with a thin 13 μm foil of Kapton to separate the source from the sample) was used. The sample stack was 3-5 layers to ensure that no positrons penetrate through the stack. Including the backscattered positrons from the W substrate we estimate that ~65% of the positrons emitted from the source stop in the samples so any fitted positronium intensities quoted herein could be increased by a factor of 1/0.65 = 1.54. PALs spectra were fit either using four discrete lifetimes (two short positron lifetimes and two positronium (Ps) lifetimes). In addition, the pore size distributions in Figure 3 of the article were fit directly from the spectra using the La Place inversion continuum program.

Pure gas permeation test

Pure gas permeation tests were performed using a custom-built isochoric (constant volume) permeation system that we have utilized in previous studies.[1] The films were sealed directly in a stainless steel membrane cell using a Viton® perflouroelastomer O-ring on the upstream side, and a piece of office paper on top of a 2 micron mesh porous stainless steel filter on the downstream side. The sample was outgassed for at least 12 hours at low vacuum (~0.01 torr) prior to experiments. The entire setup is housed inside an environmental chamber (Tenney T10) maintained at 40°C. The relevant gases (CO_2, O_2, CH_4, H_2 and N_2) were introduced one at a time at 2 bar upstream and 1 bar downstream. The gas was allowed to permeate into a fixed volume, isolated downstream chamber where the rate of pressure increase was monitored using MKS Baratron 628D vacuum transducers.

The method for determing film thickness was based on the sample hardness. The brittle PIM-1 was measured using a standard laboratory micrometer. However, softer samples (those containing MEEP80) can be easily deformed by the standard micrometer. Therefore, for these samples we utilized a Mitutoyo VL-50A low force gauge which has probe force of 0.01 N.

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% CO_2, 20 mol% N_2, and balance Ar on a dry basis. 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 28 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

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

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

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

Synthesis of PIM-1

PIM-1 was synthesized by the experimental method reported by Budd et al. 3,3,3`,3`-tetramethyl-1-1``-spirobisindane-5,5`,6,6`-tetrol (12.4 mmol, 4.1 g) and 2,3,5,6-tetra-fluorophthalonitrile (12.4 mmol, 2.4 g) were dissolved in dry dimethylformamide (DMF) (120 mL). K_2CO_3 was added in the solution and the reaction was stirred at 65^{o}C for three days. Water (130 mL) was added after cooling the reaction mixture and the product was separated by filtration. Further purification was performed by reprecipitation from $CHCl_3$ solution with MeOH and a bright yellow solid product was produced (5.12 g, yield 92 %) after thermal activation at 120 ^{o}C.

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 tetrahydofuran (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^{o}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^{o}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^{o}C (69.7 g, 79% yield).

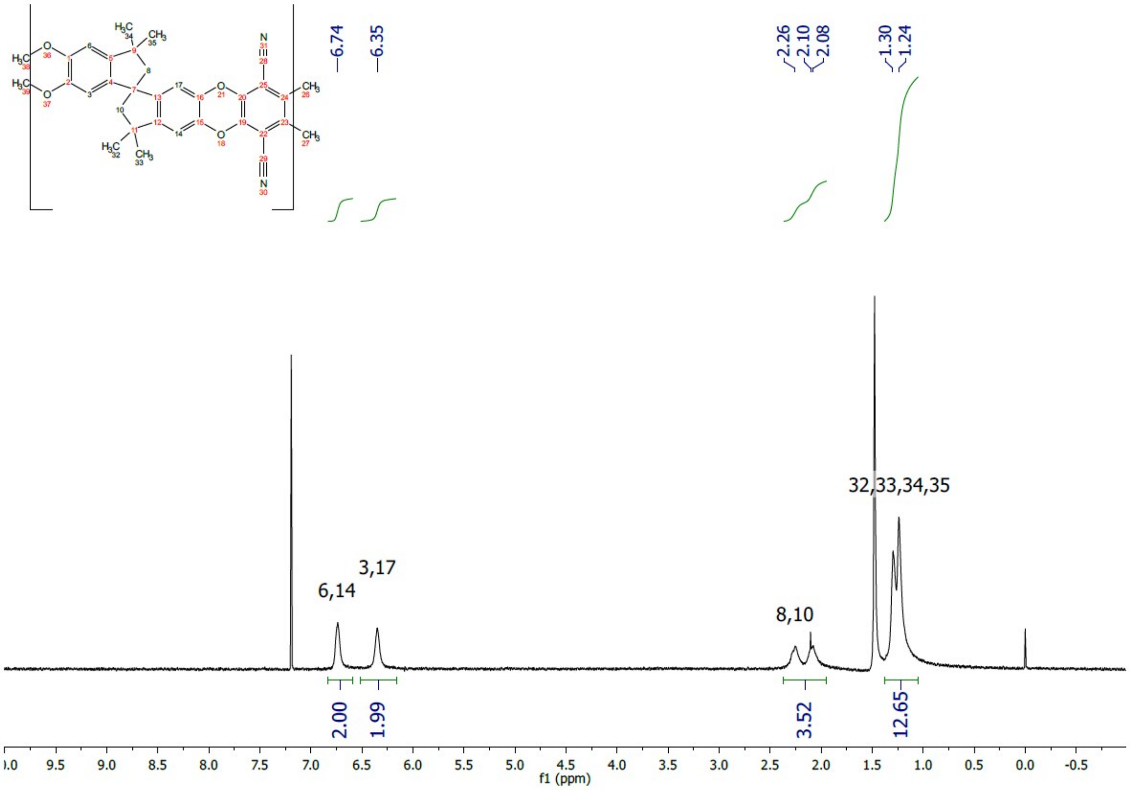


Figure S1. ^{1}H (300 MHz) NMR spectrum of PIM-1.

Figure S2. N_2 adsorption/desorption isotherms collected at 77K and pore size distribution for PIM-1 calculated by non-local density functional theory (NLDFT) model.

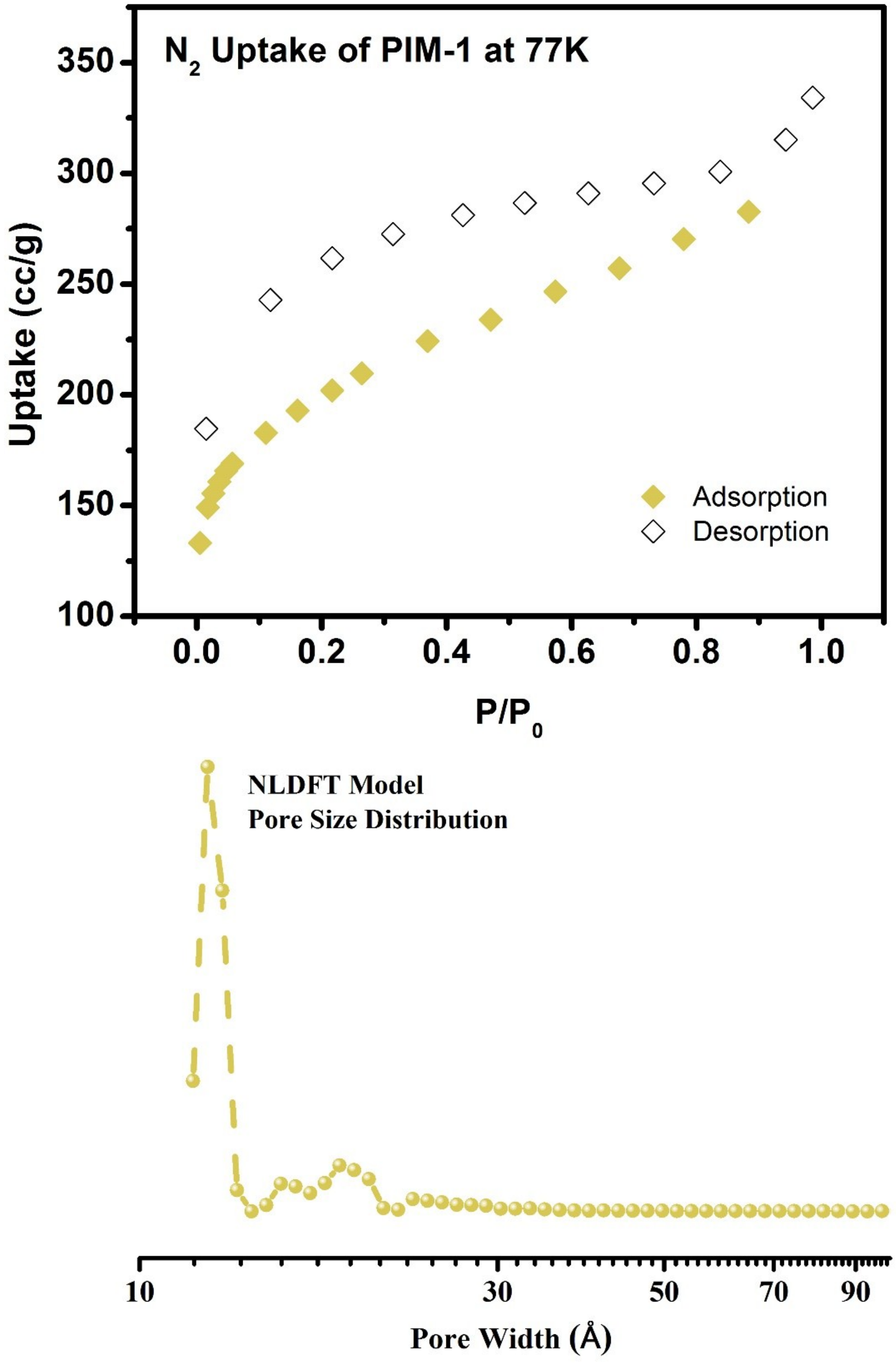


Figure S3. ^{1}H (600 MHz) (top) and 31P (bottom) NMR spectra of MEEP80. Peak labels for ^{1}H NMR as follows: allylphenol and methoxyphenol aromatics (1); methoxyphenol methyl (2); allylphenol allyl (3) and (4); DEG ethylenes (5); DEG methyl (6). 31P NMR shows characteristics of heterogeneous polyphosphazene with three peaks representing P(DEG)2, P(Ar)2, and P(DEG)(AR), where Ar = allylphenol and methoxyphenol.

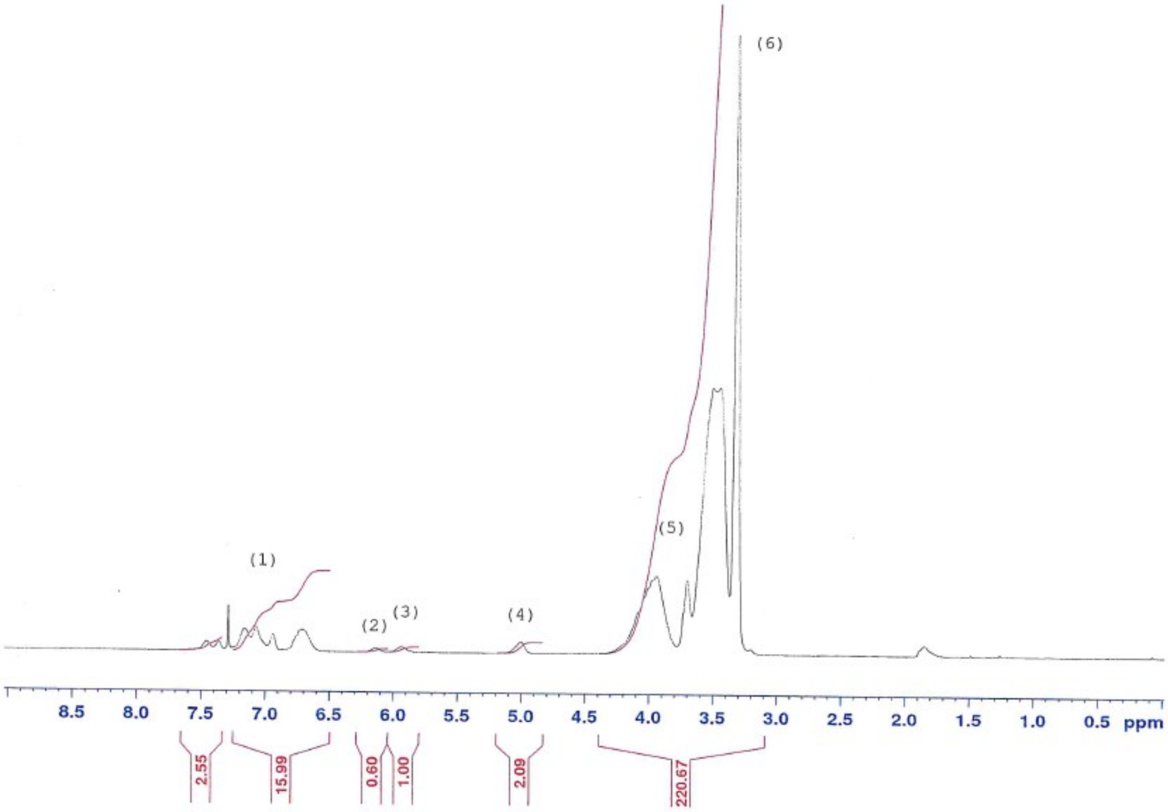


Figure S4. Thermogravimetric analysis (TGA) of polymers and blend membranes.

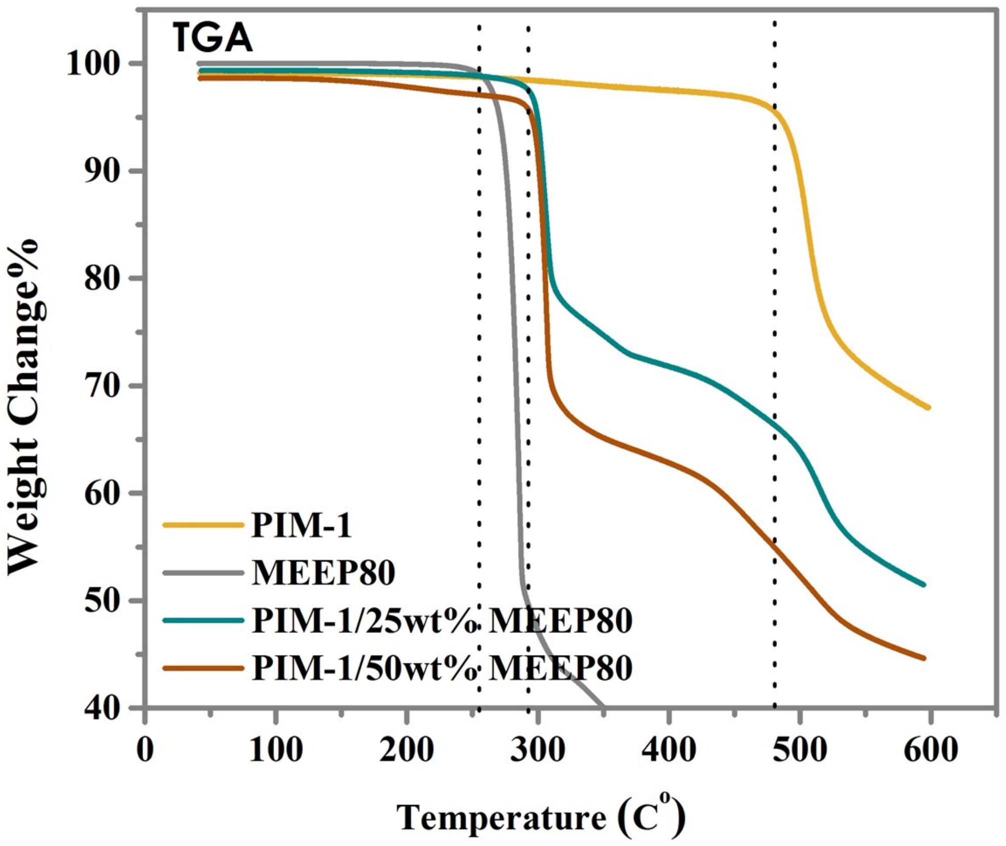


Figure S5. Cross-sectional SEM images of PIM-1/25 wt% MEEP80.

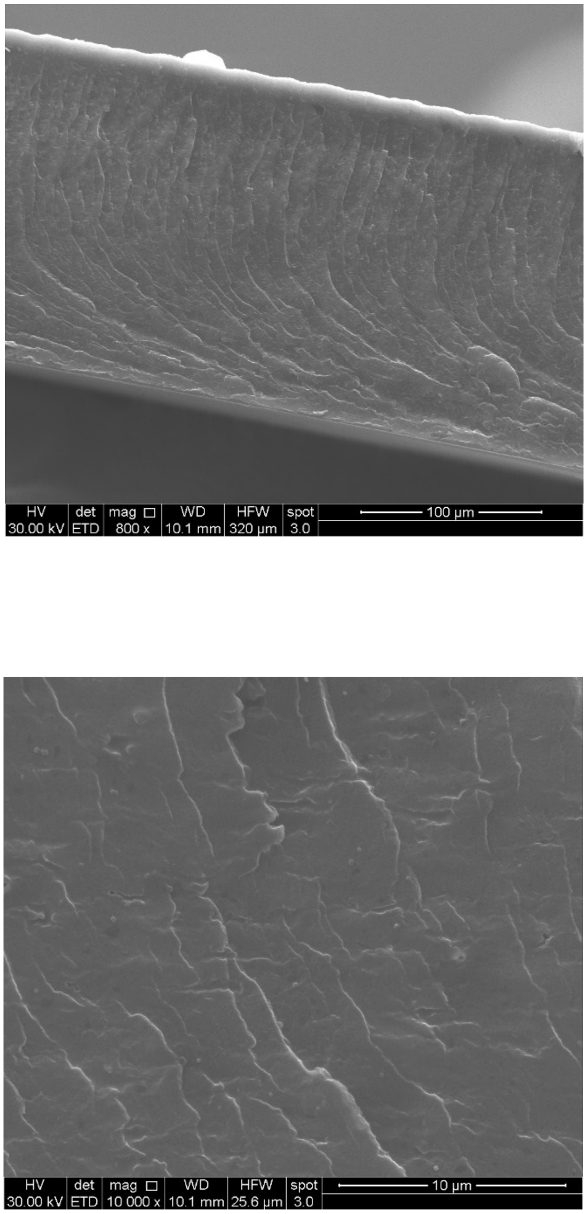


Figure S6. Cross-sectional SEM images of PIM-1/50 wt% MEEP80.

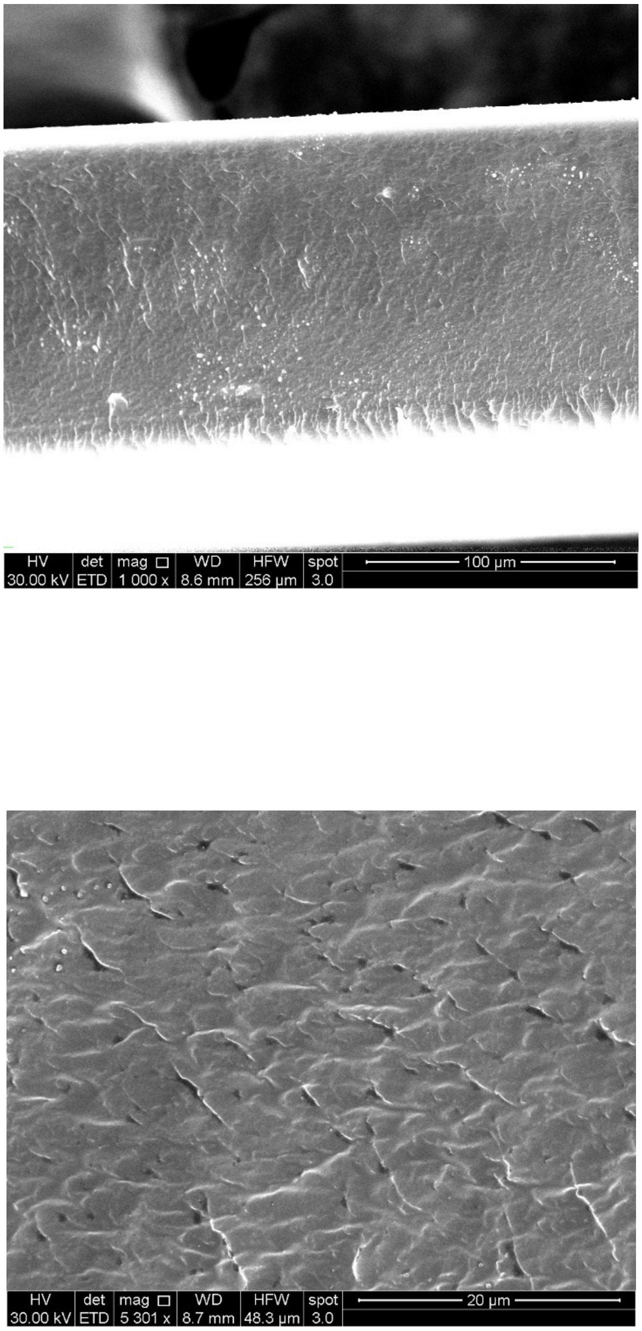


Figure S7. Cross-sectional EDX mapping of images of PIM-1/25 wt% MEEP80 for phosphorous (green), carbon (purple), nitrogen (yellow), oxygen (green).

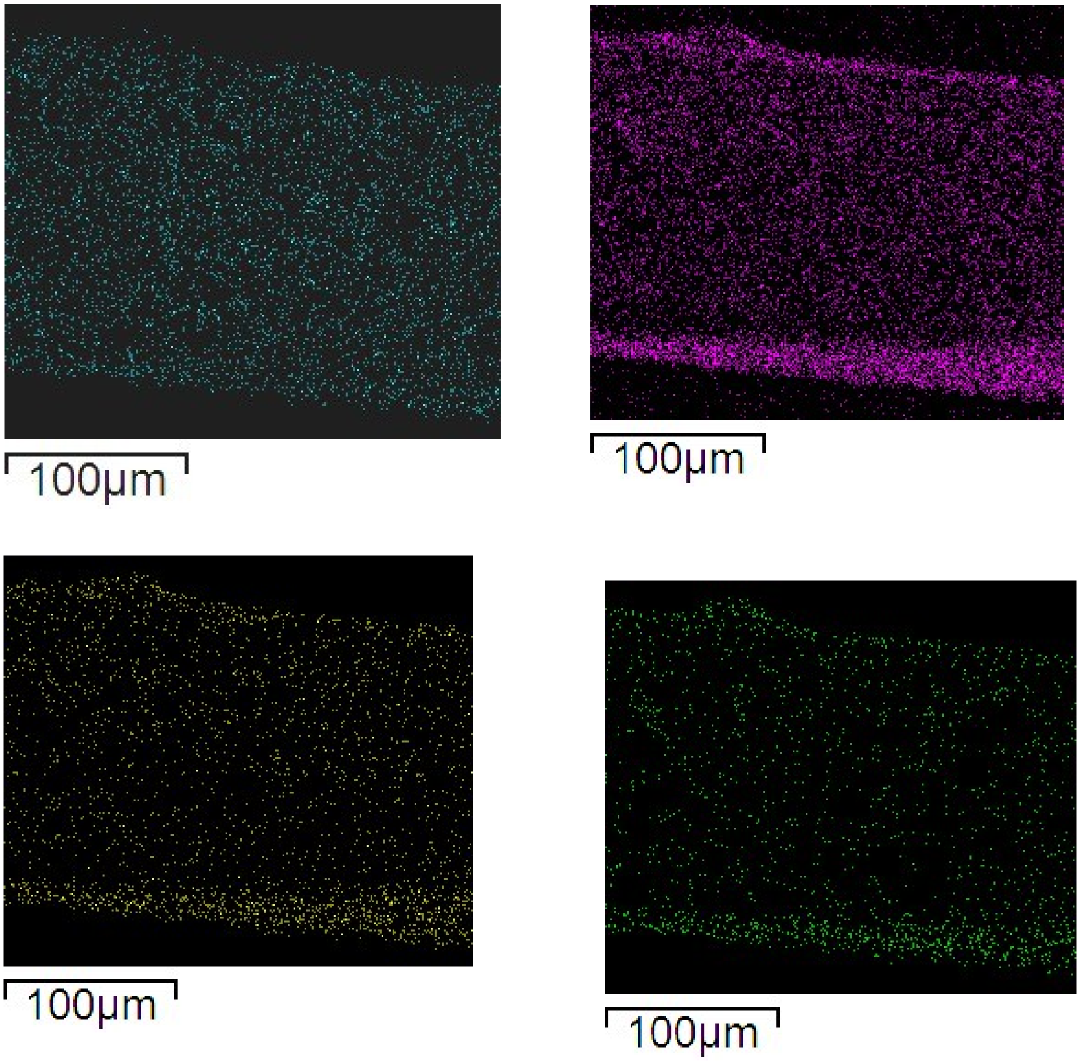


Figure S8. Cross-sectional EDX mapping of images of PIM-1/50 wt% MEEP80 for phosphorous (green), carbon (orange), oxygen (grey), nitrogen (yellow).

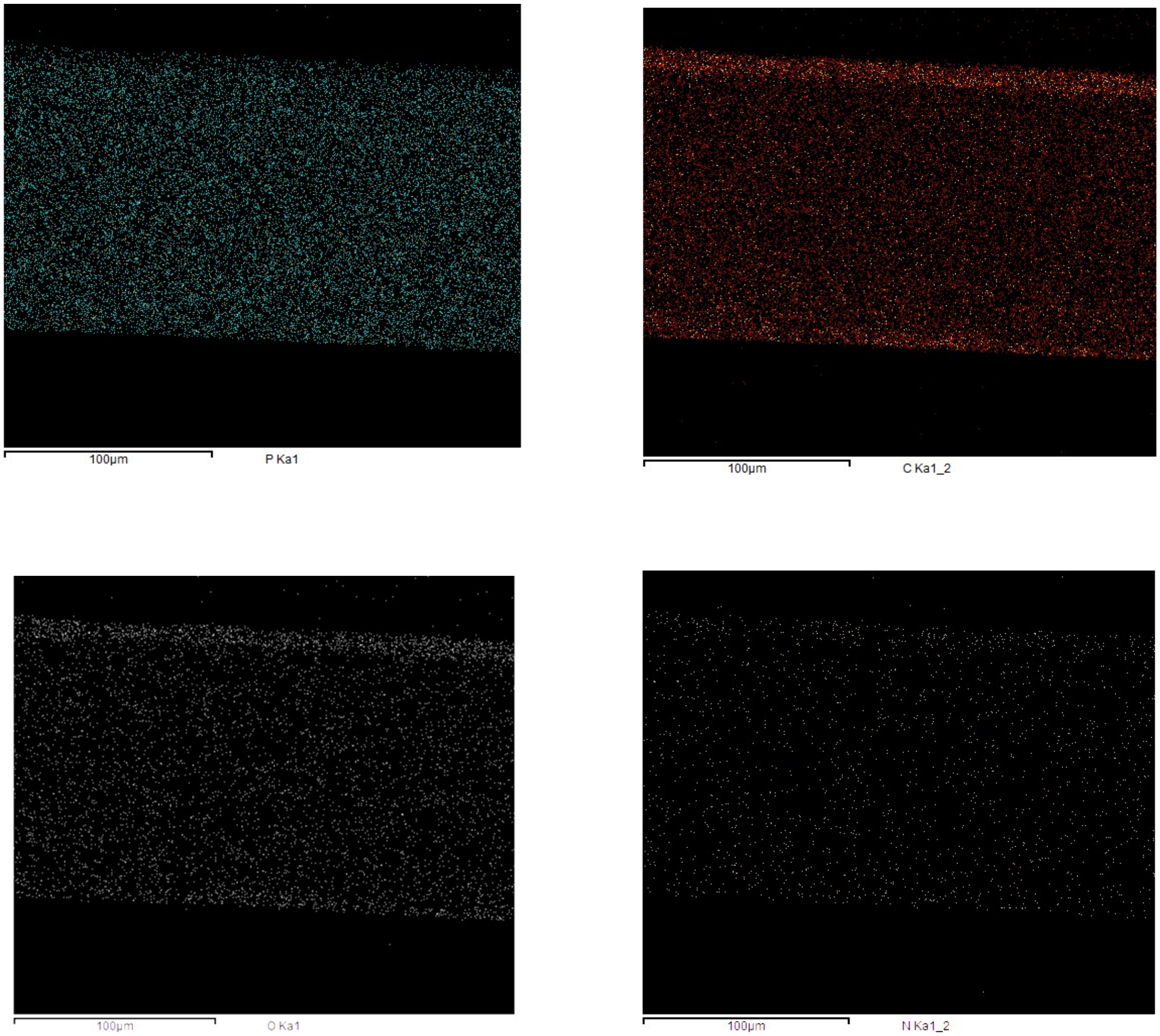


Figure S9. FT-IR spectra (1600-400 cm^{-1}) of polymers and blend membranes.

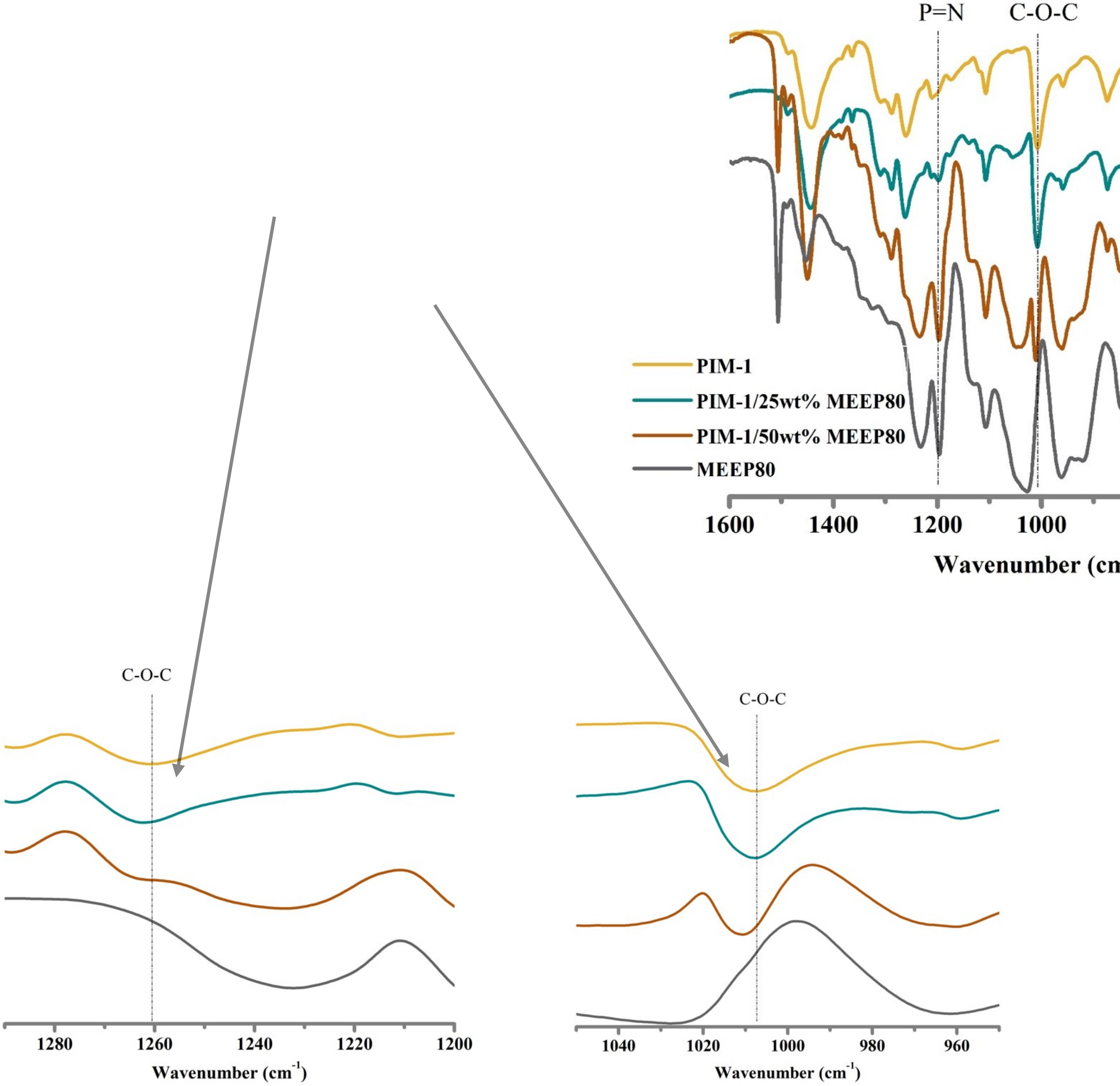


Figure S10. Full FT-IR spectra (4000-400 cm^{-1}) of polymers and blend membranes.

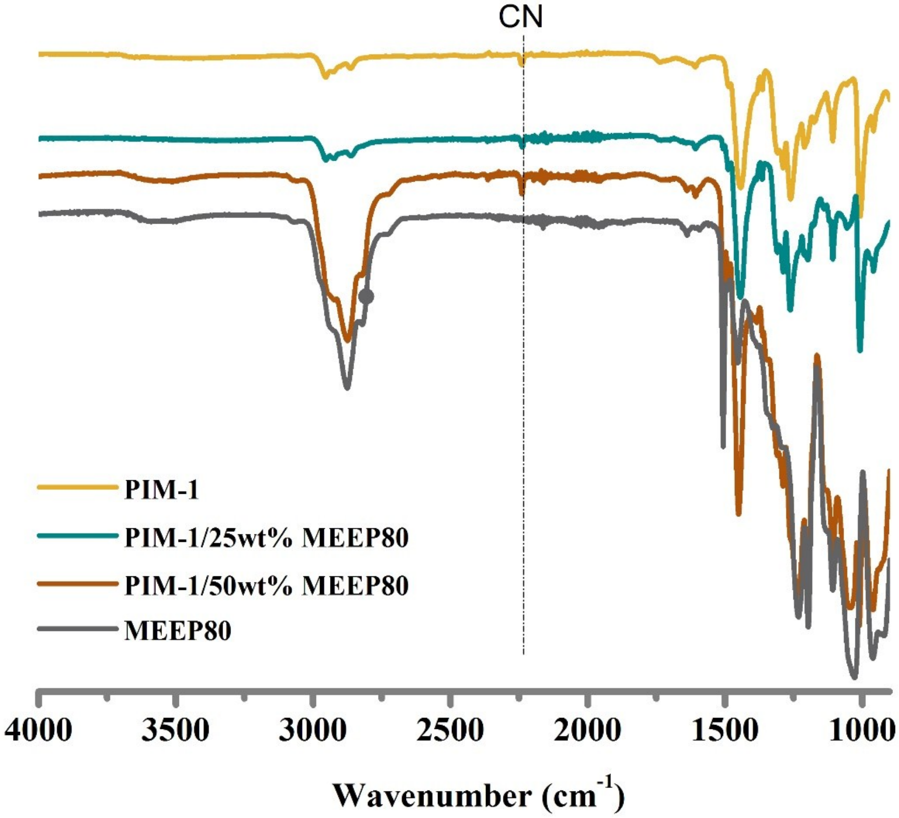


Figure S11. Aging study for PIM-1/50 wt% MEEP80 membrane.

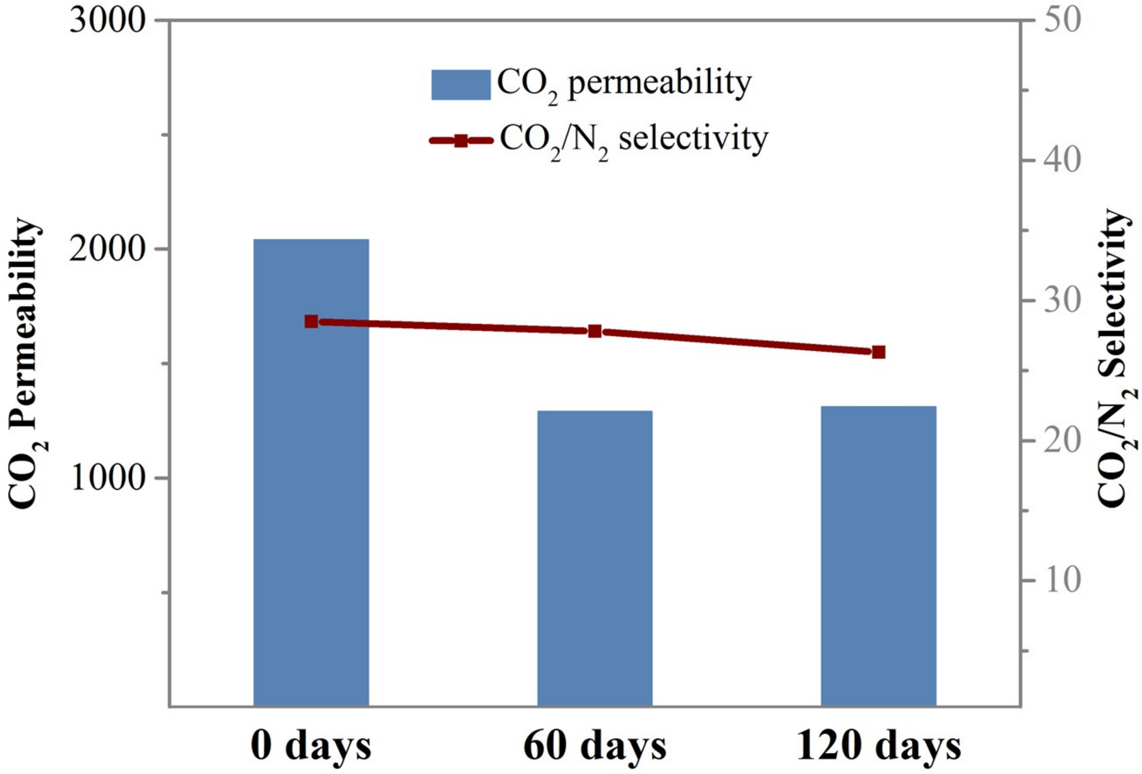
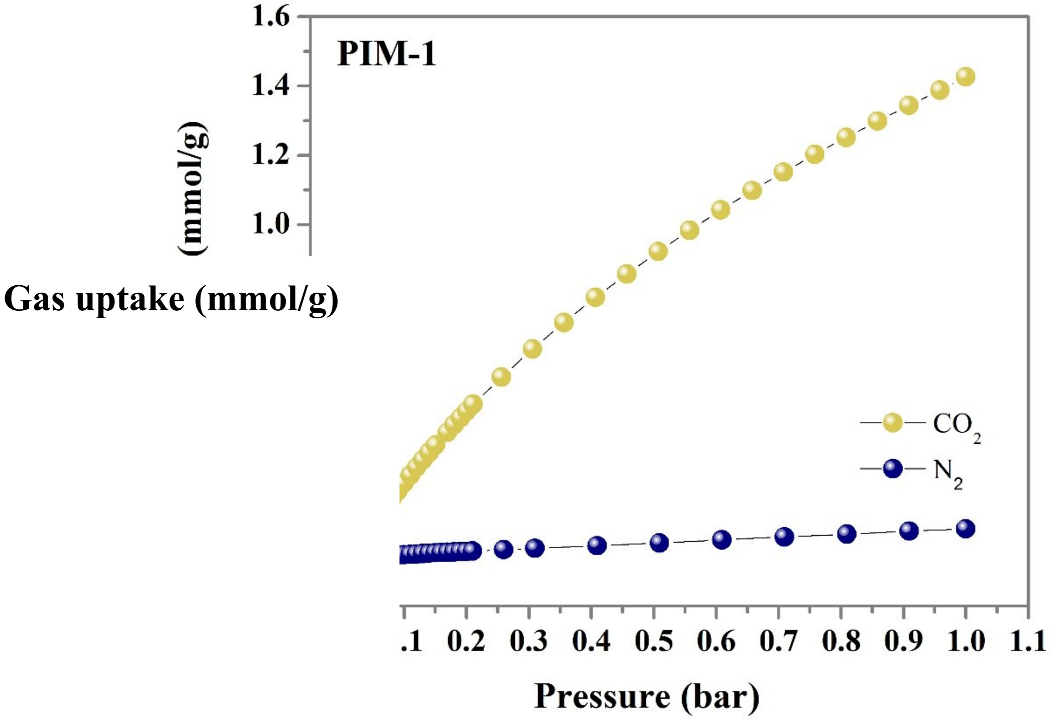


Figure S12: CO_2 (yellow) and N_2 (blue) isotherms of neat PIM-1 at 298K and initial slope calculations.



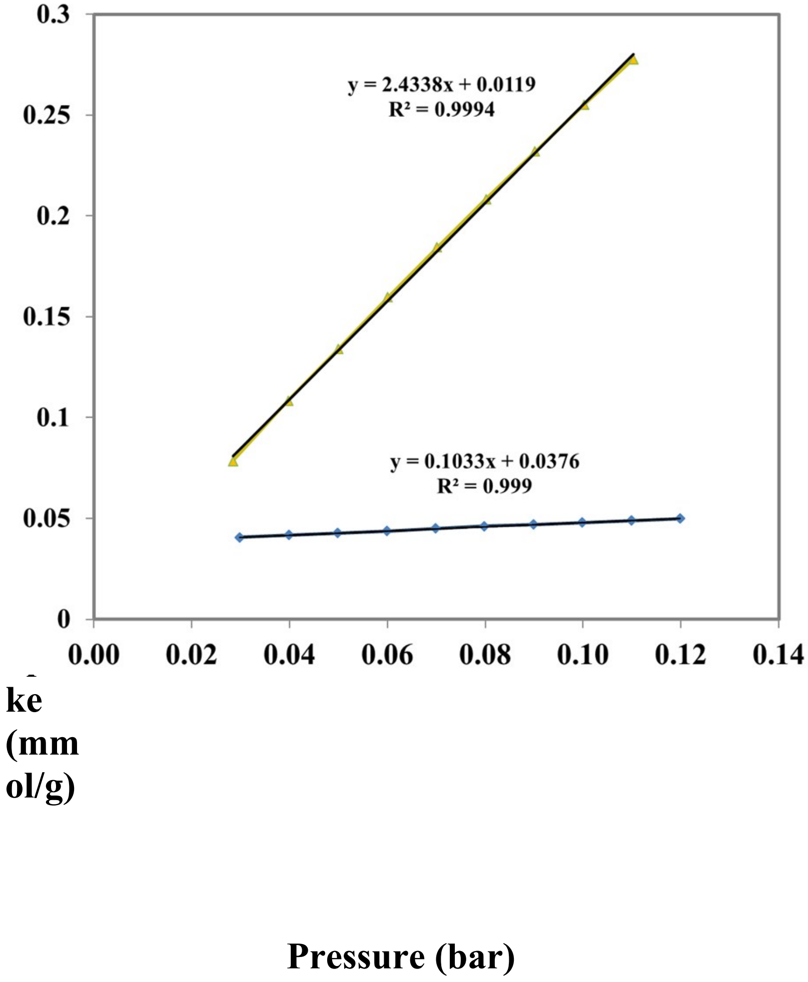


Figure S13: CO_2 (yellow) and N_2 (blue) isotherms of PIM-1/25wt% MEEP80 at 298K and initial slope calculations.[2]

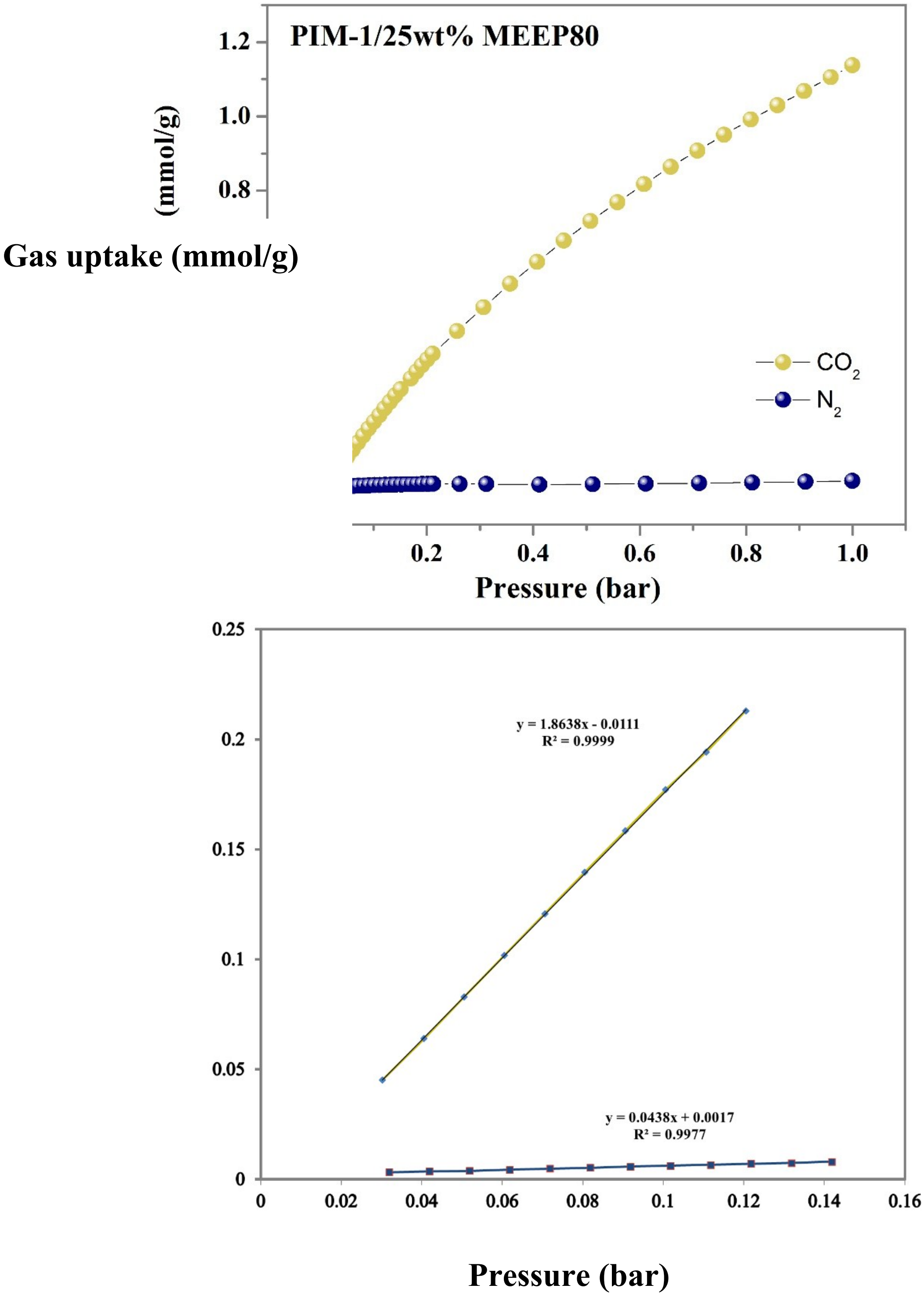


Table S1: Gas permeability and selectivity data for neat PIM-1 and PIM-1/25wt% MEEP-80.

Pure gas permeability (40 ^{o}C, 1 atm)	**CO_2 (barrer)**	**N_2 (barrer)**	**H_2 (barrer)**	**CH_4 (barrer)**	**O_2 (barrer)**
PIM-1	5811	375	2753	644	1028
MEEP-80	350	9	29	19	18
PIM-1/25wt% MEEP-80	2446	117	597	292	274
Pure gas selectivity (40 ^{o}C, 1 atm)	**CO_2/N_2**	**CO_2/H_2**	**CO_2/CH_4**	**O_2/N_2**	
PIM-1	15.5	2.1	9.0	2.7	
PIM-1/25wt% MEEP-80	20.9	4.1	8.4	2.3	

References:

1. Kusuma, V.A., et al., *Ionic liquid compatibility in polyethylene oxide/siloxane ion gel membranes.* Journal of Membrane Science, 2018. **545**: p. 292-300.
2. Sekizkardes, A.K., et al., *An ultra-microporous organic polymer for high performance carbon dioxide capture and separation.* Chemical Communications, 2015. **51**(69): p. 13393-13396.