PIM-1 Mixed Matrix Membranes for Gas Separations using Cost-Effective Hypercrosslinked Nanoparticle Fillers

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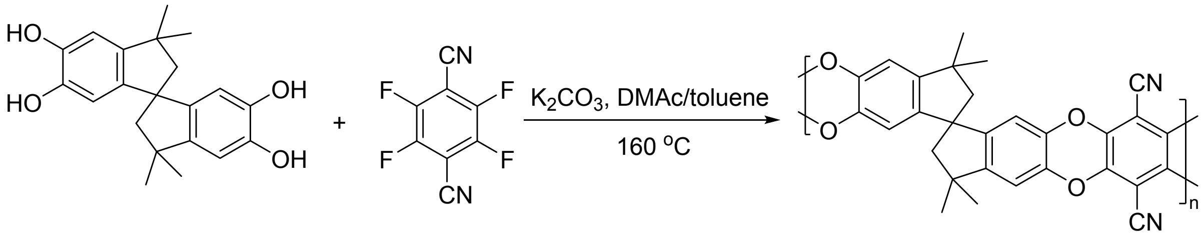
SUPPORTING INFORMATION

1. Synthesis of PIM-1 (Scheme S1):

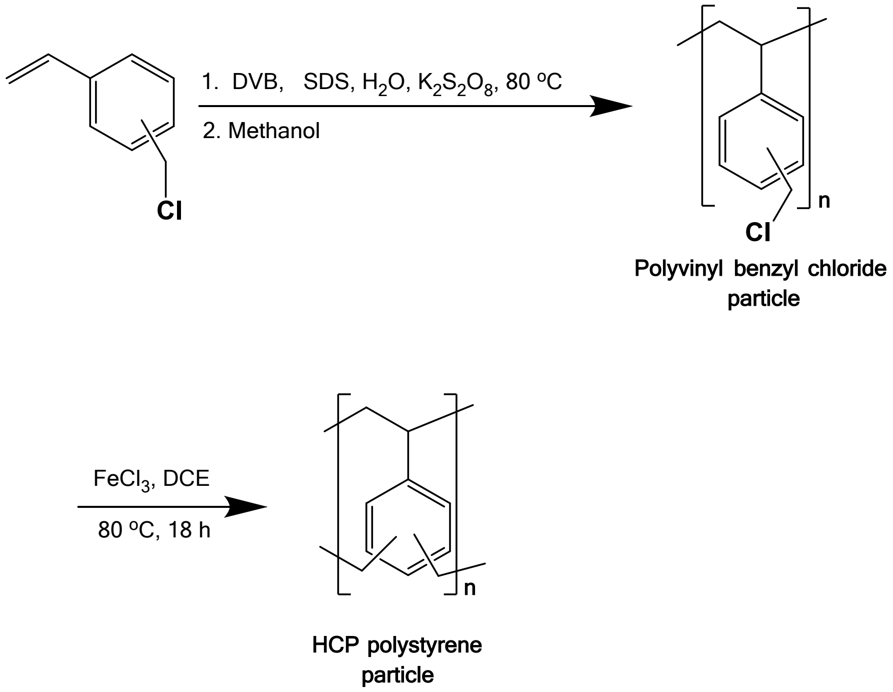
To a dry 500 mL round bottom flask equipped with a Dean−Stark trap and mechanical stirrer, 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (17.288 g, 0.05 mol) and dicyanotetrafluorobenzene (10.005 g, 0.05 mol), anhydrous K_2CO_3 (20.73 g, 0.15 mol), DMAc (100 mL), and toluene (50 mL) were added under an inert atmosphere of nitrogen. The reaction temperature was set to 160 °C and carried out for a total of 45 min (15 min used to obtain equilibrium) under reflux. At the end of the reaction, when stirring was stopped, the highly viscous solution was immediately poured into methanol (500 mL). Following this, it was dissolved in chloroform (500 mL) and reprecipitated from methanol (2 L). The product was refluxed for 15 hours in deionized water, washed with acetone and then dried at 110 °C for 2 days. This gave 19.9 g (81% yield) of PIM-1. GPC (in chloroform): M_w = 144000 g mol^{-1}, and M_w/M_n = 2.9. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.75 (2H, s), 6.35 (2H, s), 2.26−2.09 (4H, dd), 1.40−1.10 (broad, 12H). Anal. Calc. for $C_{29}H_{20}N_2O_4$ (wt %): C, 75.64; H, 4.37; N, 6.08. Found: C, 74.14; H, 4.18; N, 5.9.



Scheme S1. Synthesis of PIM-1.

2. Synthesis of HCP polystyrene (Scheme S2):

Nanoparticles of HCP Polystyrene were synthesised as described previously.[1]



Scheme S2. Synthesis of HCP polystyrene nanoparticles.

Synthesis of polyvinyl benzyl chloride particle: 0.45 g (5.6 wt% based on vinylbenzyl chloride) sodium dodecyl sulphate was dissolved in distilled water (80 mL) and added to a 500 mL three-necked round bottom flask. Then the inhibitor freed co-monomer mixture (vinylbenzyl chloride, 8 g, p-divinylbenzene, 2 wt%, 0.20 g) was added and pre-emulsified using a mechanical stirrer at 400 rpm under N_2 for 30 minutes. An aqueous solution of potassium persulphate (1 wt% based on vinylbenzyl chloride, 0.082 g in 2 mL) was added to the above mixture at 80 °C, and the emulsion polymerization was carried using a mechanical stirrer at 400 rpm under N_2 for 5 hours. The emulsions were broken by drop-wise addition into stirring methanol (200 mL), and then the white nanoparticles were isolated by centrifugation and washed three times with distilled water, methanol, and diethyl ether, followed by drying for 24 hours at 60 °C. The white nanoparticle product was characterized by dynamic light scattering. (See Figure S1).

Synthesis of HCP polystyrene particle: The precursor nanoparticles of polyvinylbenzyl chloride (2.5 g) were swollen in 40 mL dry dichloroethane (DCE) under inert atmosphere for 3 hours. A suspension of $FeCl_3$ (2.61 g) in DCE (40 mL) was added to the nanoparticle suspension, which was then heated at 80 °C for 18 hours. The resulting hypercrosslinked products were filtered and washed three times with distilled water, methanol, and diethyl ether followed by soxhlet extraction in methanol for 24 hours, finally, drying for 24 hours at 60 °C.

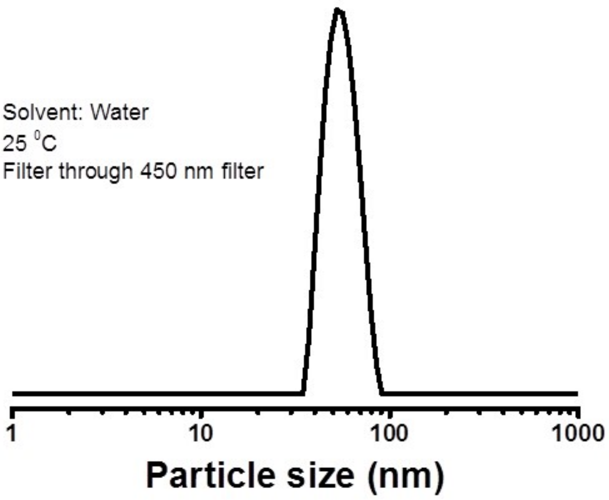


Figure S1. Particle size distribution from dynamic light scattering (DLS) of precursor polyvinyl chloride particle re-dispersed in water. R_H = 55.28 nm, Std Dev = 10.28 nm.

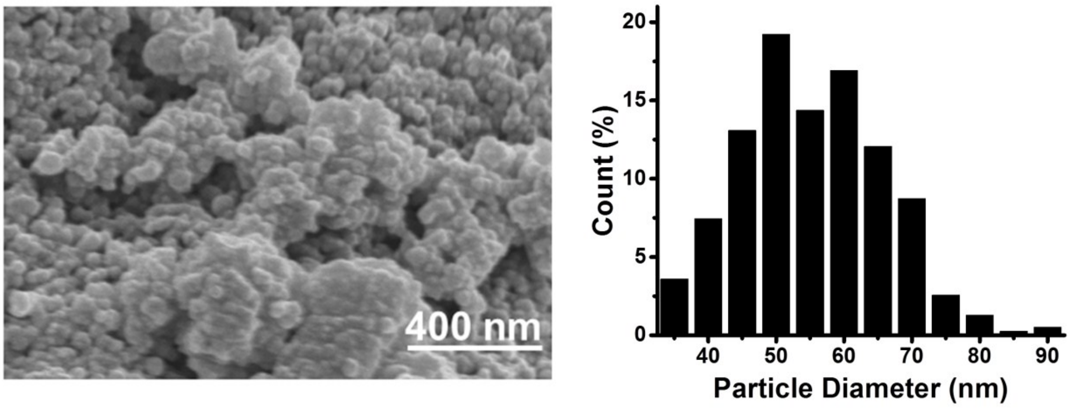


Figure S2. Left: SEM images for HCP polystyrene**.** Right: Histogram showing distribution of HCP Polystyrene (calculated on 390 particle).

3. Preparation of MMMs:

Weight percentage of filler in all MMMs prepared was calculated as,

$$\text{Wt\% of filler in MMMs} = 100\ x \frac{wt.\ of\ filler}{wt.\ of\ filler + wt.\ of\ PIM - 1}$$

Ten thickness measurements were made for each membrane sample with a digital micrometer.

Preparation from chloroform: MMMs of PIM-1 with HCP polystyrene in $CHCl_3$ were prepared in three different proportions (4.76 wt%, 9.1 wt% and 16.67 wt% of HCP polystyrene). For preparation of MMMs containing 16.67 wt% of HCP polystyrene, a suspension of filler (0.06 g) in 5 mL $CHCl_3$ was stirred for 12 hours at ambient temperature, followed by sonication for 30 minutes in an ultrasonic bath type sonicator at ambient temperature. A $CHCl_3$ solution of PIM-1 (0.3 g in 5 mL $CHCl_3$) was added to the suspension and stirred for 20 hours. The resulting solution was sonicated for 20 minutes in an ultrasonic bath type sonicator at ambient temperature before being poured into a 9 cm glass petri dish. The membrane was allowed to form by slow solvent evaporation for 24-36 hours in a closed environment. The formed membranes were then kept in a desiccator under vacuum until used for characterization.

Preparation from DCM: MMMs of PIM-1 with HCP polystyrene in DCM were prepared in three different proportions (5.7 wt%, 16.67 wt% and 21.3 wt% of HCP polystyrene). For preparation of MMMs containing 16.67 wt% of HCP polystyrene, a suspension of filler (0.108 g) in 10 mL DCM was sonicated for 30-40 minutes in an ultrasonic bath type sonicator at ambient temperature. A DCM solution of PIM-1 (0.525 g in 10 mL DCM) was added to the suspension and stirred for 20 hours. The resulting solution was sonicated for 5-10 minutes in an ultrasonic bath type sonicator at ambient temperature before being poured into a mould. The mould was made up of an 8 cm Teflon ring. The membrane was allowed to form by slow, solvent evaporation for 24-36 hours in a closed environment.

The materials and membranes were characterized by gas sorption analysis, scanning electron microscopy and IR spectroscopy.

4. Gas sorption analysis

Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Samples were degassed offline at 60 °C for 12 hours under vacuum (10^{-5} bar) before analysis, followed by degassing on the analysis port under vacuum, also at 60 °C. Nitrogen adsorption/desorption isotherms for PIM-1and HCP polystyrene are shown in **Figure S2**.

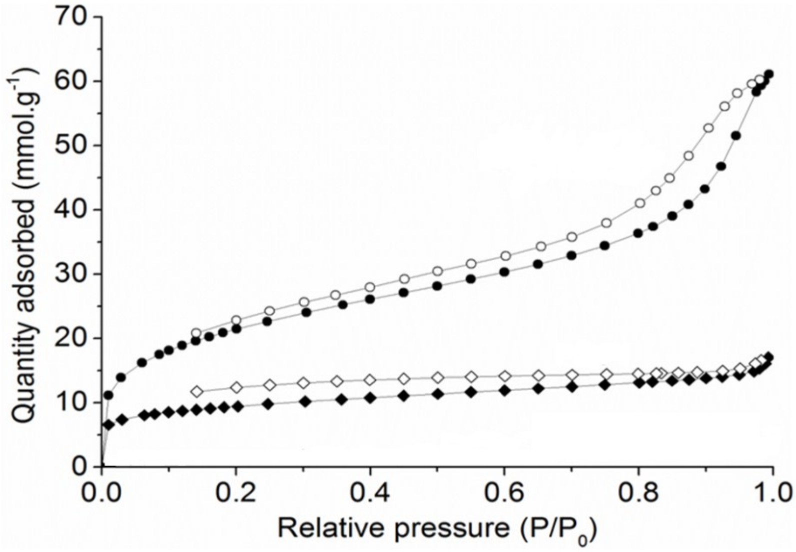


Figure S3. Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K for PIM-1 (🕘,✵) and HCP polystyrene (●,O).

5. Visual appearance of mixed matrix membranes and homogenity test by IR spectroscopic method

PIM-1/Hypercrosslinked Polystyrene membranes are opaque, due to the presence of secondary phase or filler phase. The opacity becomes more conspicuous as concentration of filler is increased.

The relative uniformity of filler distribution across the membrane was checked by recording transmission IR spectra using a Bruker Tensor 27 platereading FT-IR. Multiple data were collected at various different points (as shown in Figure S3 and Figure S4). The area under the peak at the stretching frequency of –CN (2200-2260 cm^{-1}) was calculated from each of these collected spectra and the highest value was normalized to 100. The area under the peak at 2245 cm^{-1} was considered as an indication of relative quantity and distribution of PIM-1 and filler particle. Though each membrane was found to be evenly thick, a small variation in thickness of the membrane may cause some distortion in the contour-map plot.

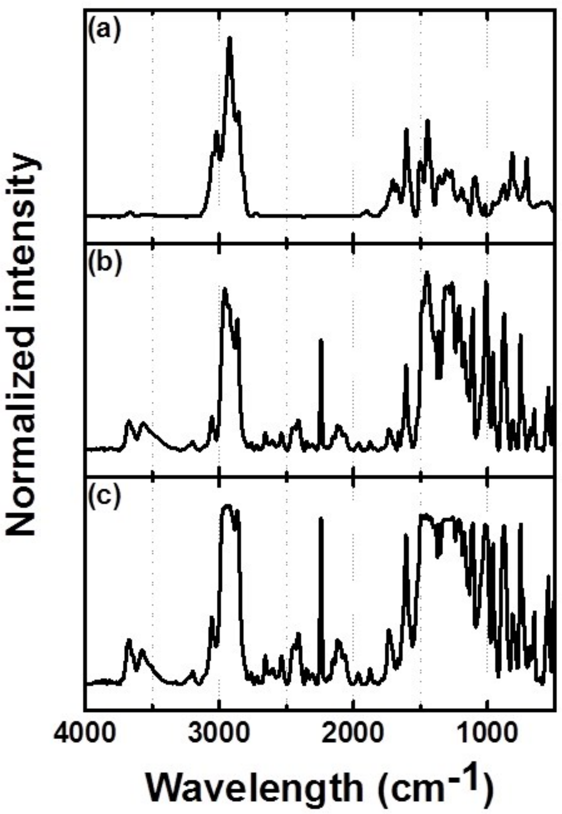


Figure S4. Transmission IR spectra; (a) HCP polystyrene, (b) PIM-1, (c) representative transmission IR spectrum of PIM-1/HCP polystyrene membrane.

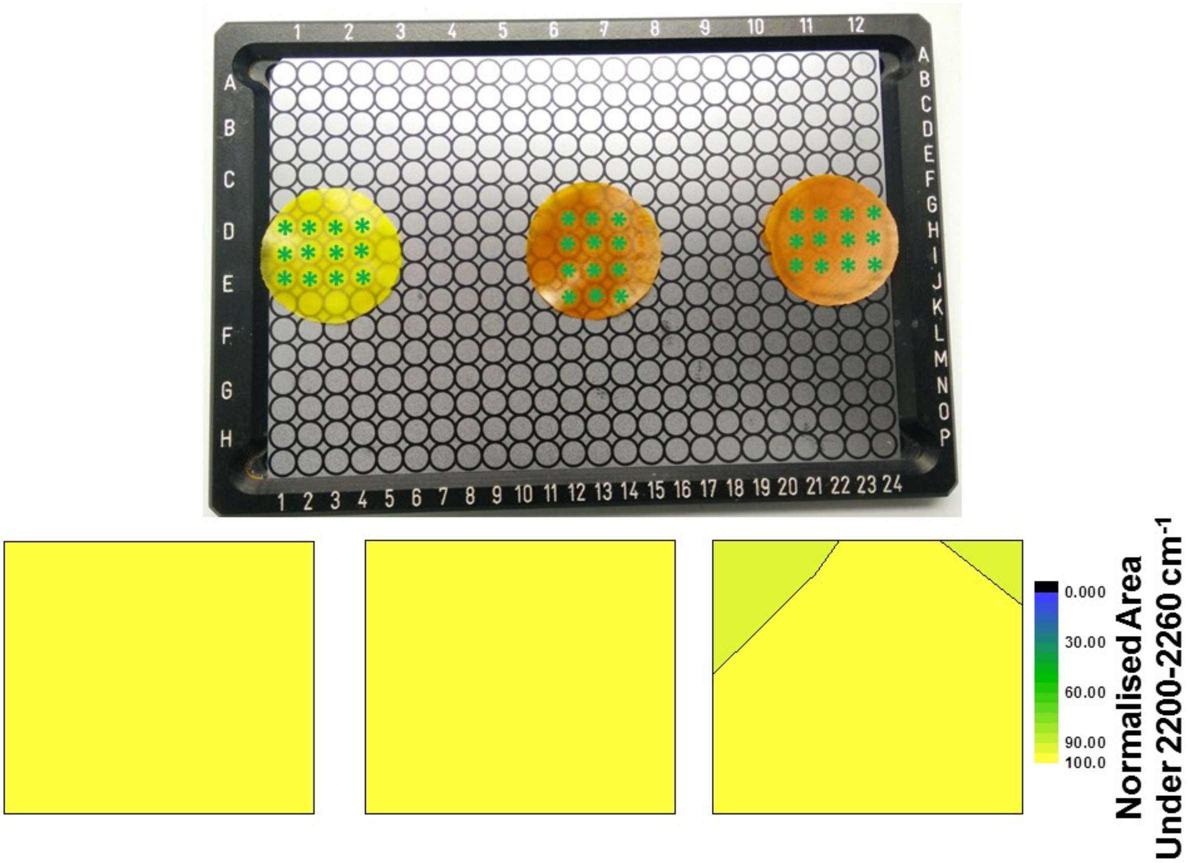


Figure S5. Photographs of mixed matrix membranes prepared from DCM; from left to right: PIM-1/HCP polystyrene (filler wt% 5.7%, 16.67%, 21.3%) where each circular pattern underneath the membrane represents an individual data collection point for IR area mapping experiments. Bottom, contour plot summarizing IR mapping data; from left to right: PIM-1/HCP polystyrene (filler wt% 5.7%, 16.67%, 21.3%). "*" marked positions indicate the data points (IR spectra) which were used to construct the contour plot.

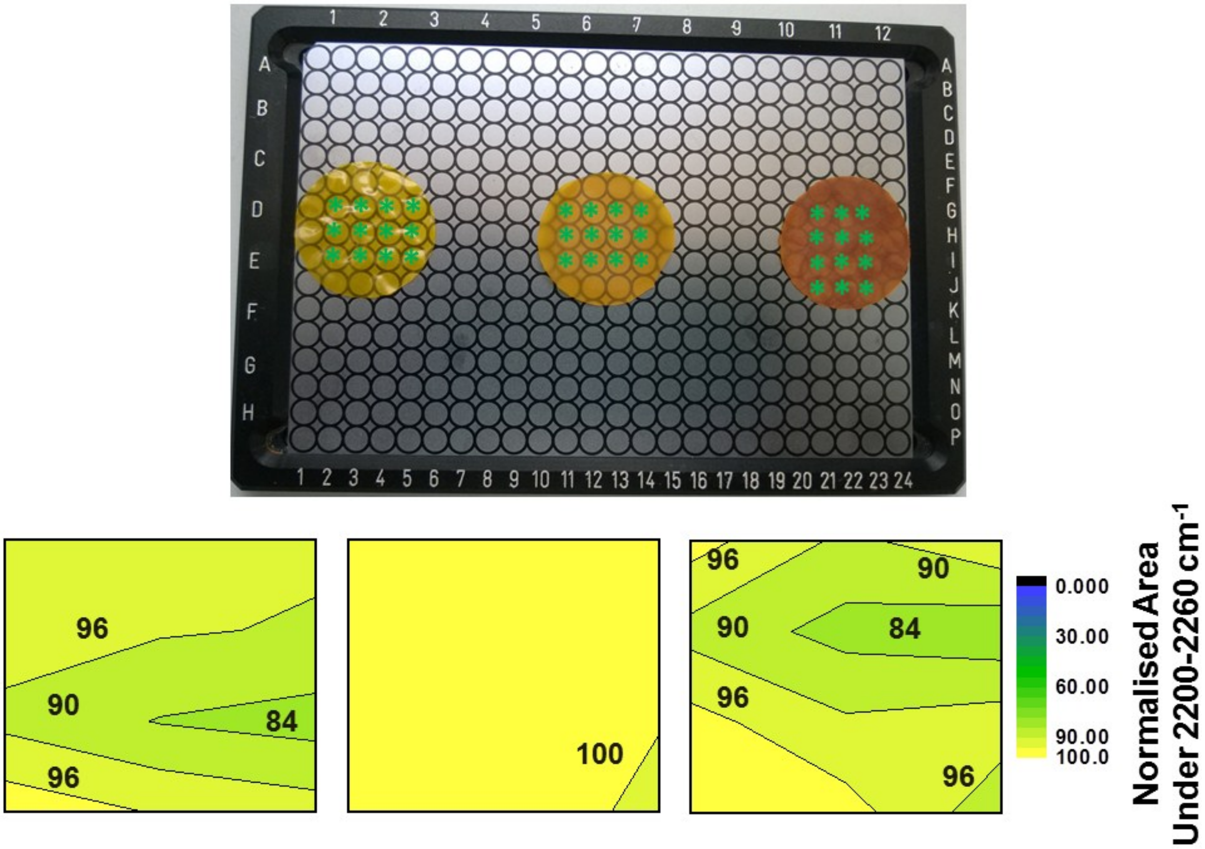


Figure S6. Photographs of mixed matrix membranes prepared from chloroform; from left to right: PIM-1/HCP polystyrene (filler wt% 4.76%, 9.1%, 16.67%) where each circular pattern underneath the membrane represents an individual data collection point for IR area mapping experiments. Bottom, contour plot summarizing IR mapping data; from left to right: PIM-1/HCP polystyrene (filler wt% 4.76%, 9.1%, 16.67%). "*" marked positions indicate the data points (IR spectra) which were used to construct the contour plot.

6. Scanning Electron Microscopy (SEM)

The membrane morphology was studied by scanning electron microscopy (SEM) using a Hitachi S-4800 Field-Emission Scanning Electron Microscope with Energy Dispersive X-Ray (EDX) detector and cold cathode electron source. The membrane cross section was prepared via freeze fracturing using liquid nitrogen. The sample was then coated with gold via sputtering using an Emitech coater.

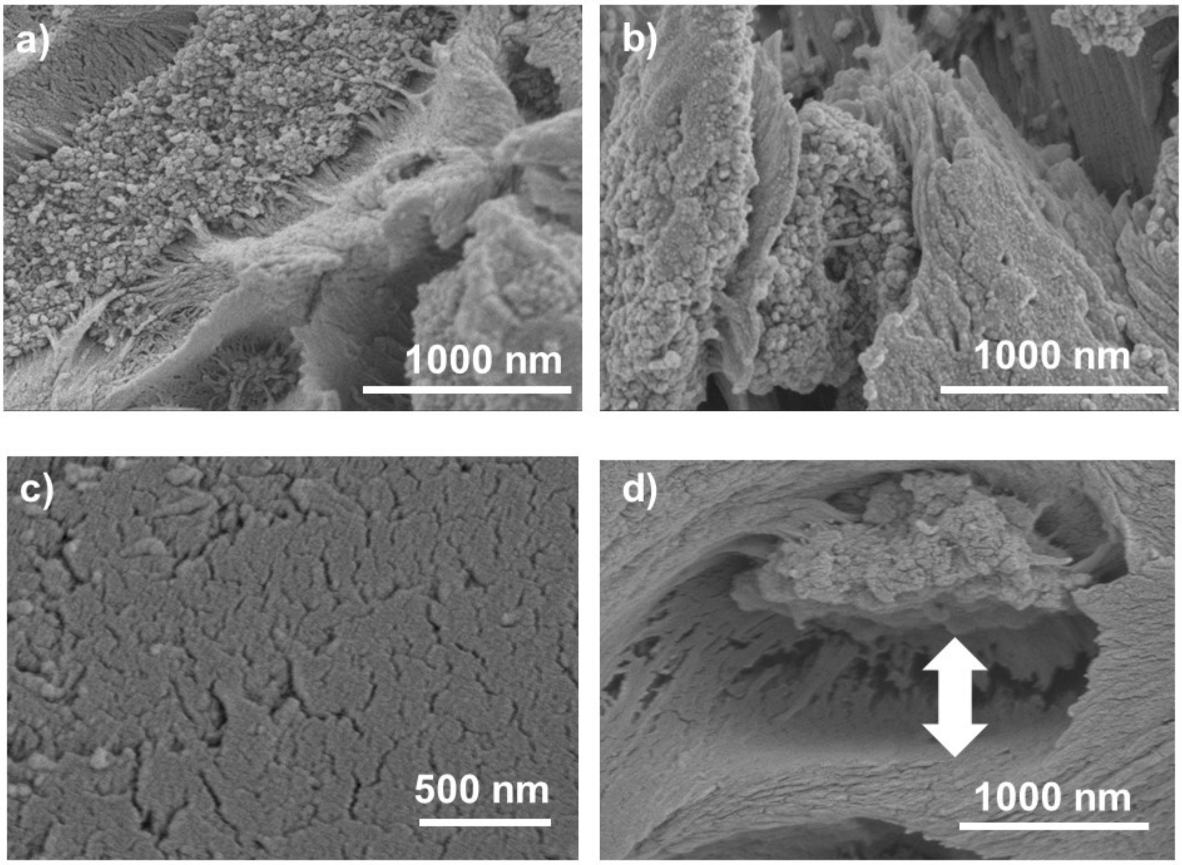


Figure S7: SEM of (a) PIM-1/HCP polystyrene cast from dichloromethane and (b) chloroform. (c) SEM of pure PIM-1 membrane. (d) SEM of HCP polystyrene (non emulsion synthesis) filler embedded in PIM-1 matrix. The arrow indicates larger PIM-1/particle interfacial defect.

7. Single gas permeation measurements

The permeability measurement using pure gases (CO_2 and N_2) was carried out by the standard variable volume method[2] as shown in Fig. S7 at upstream gas pressure of 2 atm and at ambient temperature (~ 298 K), while maintaining the permeate side at the atmospheric pressure. Membrane samples (2.5 cm in diameter) after removing from the vacuum desiccator were immediately mounted in the permeation cell. The gas permeability was calculated using the following equation:

$$P = \frac{N \cdot l}{(p_1 - p_2)}$$

where P is the permeability coefficient expressed in Barrer, N is the steady-state penetrant flux ($cm^3\ cm^{-2}\ sec^{-1}$), p_1 and p_2 are the feed and permeate side pressures (cm Hg), while l is the membrane thickness (cm). Ten thickness measurements were made for each membrane sample with a digital micrometre (Mitutoyo).

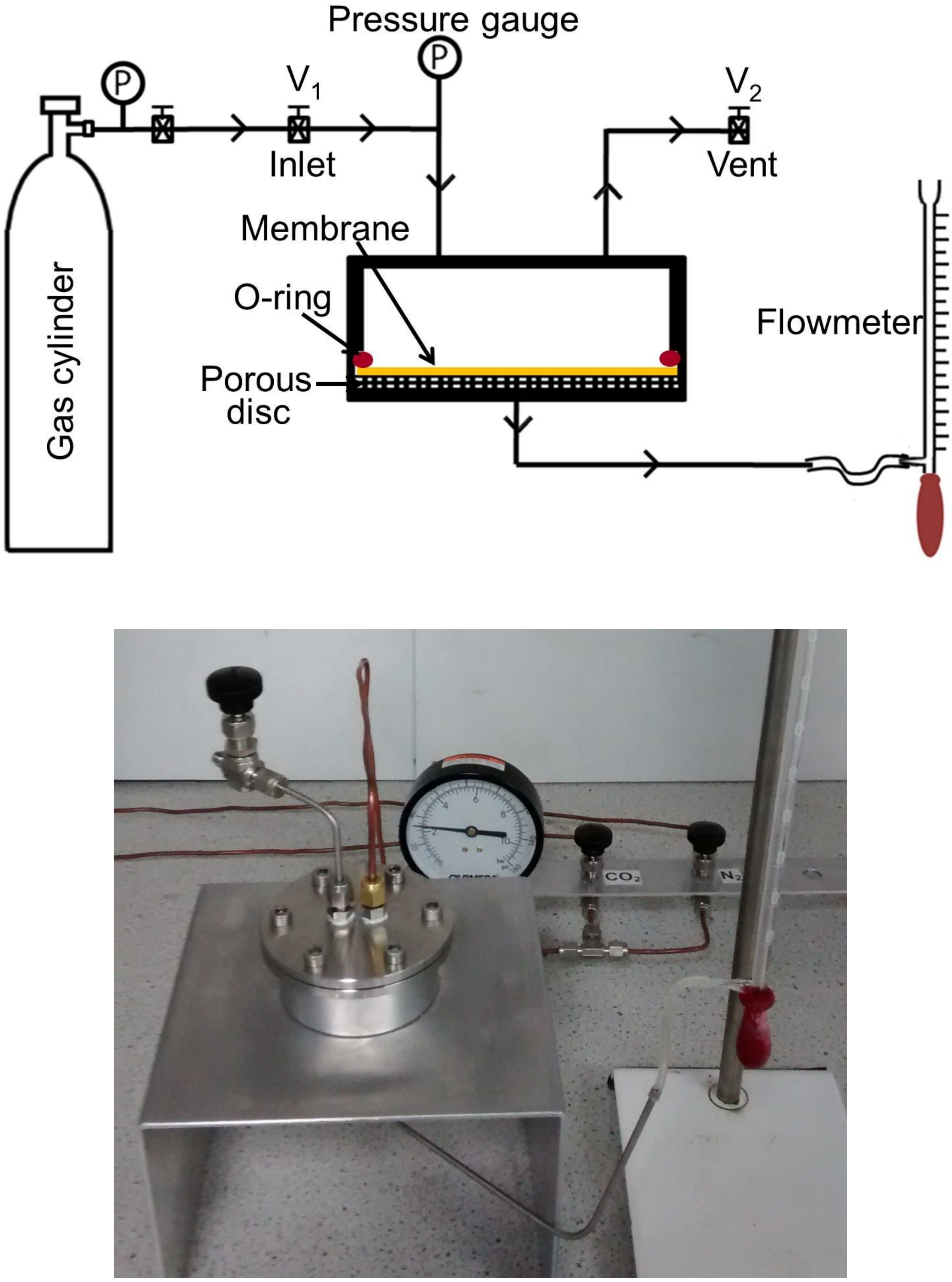


Figure S8: Schematic and photograph of gas permeation equipment.

Table S1. Single gas permeation data for PIM-1/HCP polystyrene MMMs. *P* is permeability coefficient (Barrer*). Membrane cast from chloroform solution on a 9 cm glass petri dish.

Number	Filler concentration (wt %)	Thickness (µm) As cast, Ethanol treated	Age (Days)	$P(CO_2)$		$P(N_2)$	
				As Cast	Ethanol treated	As Cast	Ethanol treated
1	**0 (PIM-1)**	**41 (± 3.5), 59 (± 3)**	**0**	2660	8221	119	548
			15	-	6748	-	384
			30	-	5830	-	275
			45	2252	4809	99	215
			60	2039	-	92	-
			90	-	3292	-	136
			150	1225	2767	57	112
2	**4.76**	**48 (± 2), 67 (± 4)**	**0**	4313	10125	218	828
			15	-	9636	-	618
			30	-	8362	-	462
			45	2386	7159	108	339
			60	2357	-	108	-
			90	-	4921	-	231
			150	1857	4774	83	216
3	**9.1**	**53 (± 2.5), 71 (± 2.5)**	**0**	4700	12496	243	1055
			15	-	11731	-	804
			30	-	11339	-	670
			45	2427	10221	111	530
			60	2395	-	110	-
			90	-	6272	-	335
			150	2043	5296	93	257
4	**16.67**	**96 (± 6), 117 (± 5.5)**	**0**	10040	19086	587	1652
			15	-	17572	-	1376
			30	-	15169	-	895
			45	4994	13910	270	804
			60	4891	-	264	-
			90	-	10529	-	546
			150	4165	9972	191	492

*1 Barrer = 10^{-10} cm^3 (STP)cm cm^{-2} s^{-1} $cmHg^{-1}$

Table S2. Single gas permeation data for PIM-1/HCP polystyrene MMMs. *P* is permeability coefficient (Barrer*). Membrane cast from DCM solution on a 8 cm Teflon mould.

Number	**Filler concentration (wt %)**	**Thickness (μm) As cast, Ethanol treated**	**Age (Days)**	$P(CO_2)$		$P(N_2)$	
				As Cast	**Ethanol treated**	**As Cast**	**Ethanol treated**
1	**0 (PIM-1)**	**24 (± 1.5), 59 (± 3)**	**0**	2258	8221[I]	94	548[I]
			15	-	6748[I]	-	384[I]
			30	-	5830[I]	-	275[I]
			45	1832	4809[I]	78	215[I]
			60	1591	-	65	-
			90	-	3292[I]	-	136[I]
			150	1109	2767[I]	45	112[I]
2	**5.7**	**73 (± 3.5), 79 (± 5.5)**	**0**	4690	12081	266	961
			15	-	10174	-	703
			30	-	9446	-	609
			45	4118	8737	211	473
			60	4093	-	207	-
			90	-	6647	-	347
			150	3616	6050	183	314
3	**16.67**	**119 (± 6), 125 (± 5.5)**	**0**	5103	15913	338	1443
			15	-	13254		1104
			30	-	12963		938
			45	4623	12010	298	751
			60	-	-	-	-
			90	-	9072	-	518
			150	-	8369	-	477
4	**21.3**	**153 (± 7.5), 157 (± 8)**	**0**	6331	20394	449	2109
			15	-	17002	-	1600
			30	-	15852	-	1267
			45	6174	14707	428	1084
			60	5855	-	406	-
			90	-	12799	-	882
			150	5060	12256	316	831

*1 Barrer = 10^{-10} cm^3 (STP)cm cm^{-2} s^{-1} cmHg^{-1}

[I] Ethanol treated data“ is as same as “ethanol treated data“, in Table S1. It is often assumed that an alcohol (e.g., ethanol) treatment washes away residual casting solvent (DCM and chloroform in this case) and provides similar condition. Hence, a separate set of data were not measured.

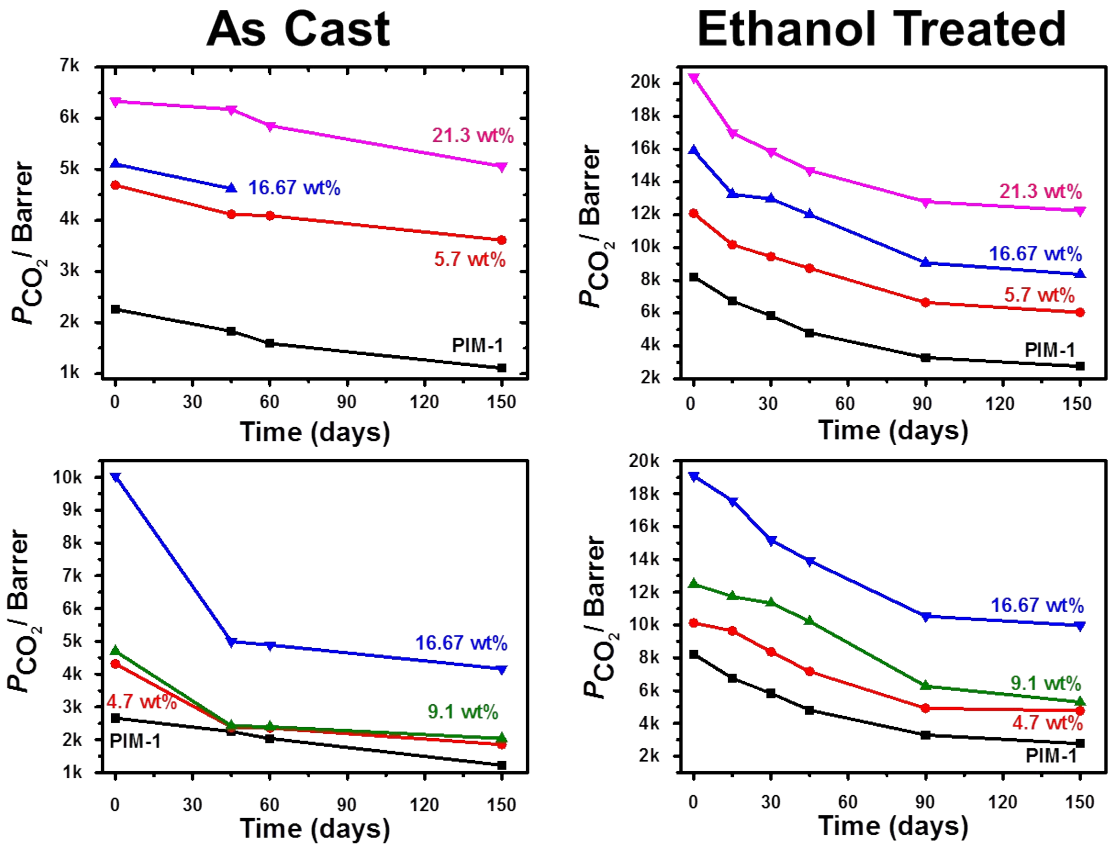


Figure S9. Permeability and aging characteristics of PIM-1 based MMMs with HCP polystyrene as filler. Top: Cast from DCM. Bottom: Cast from chloroform.

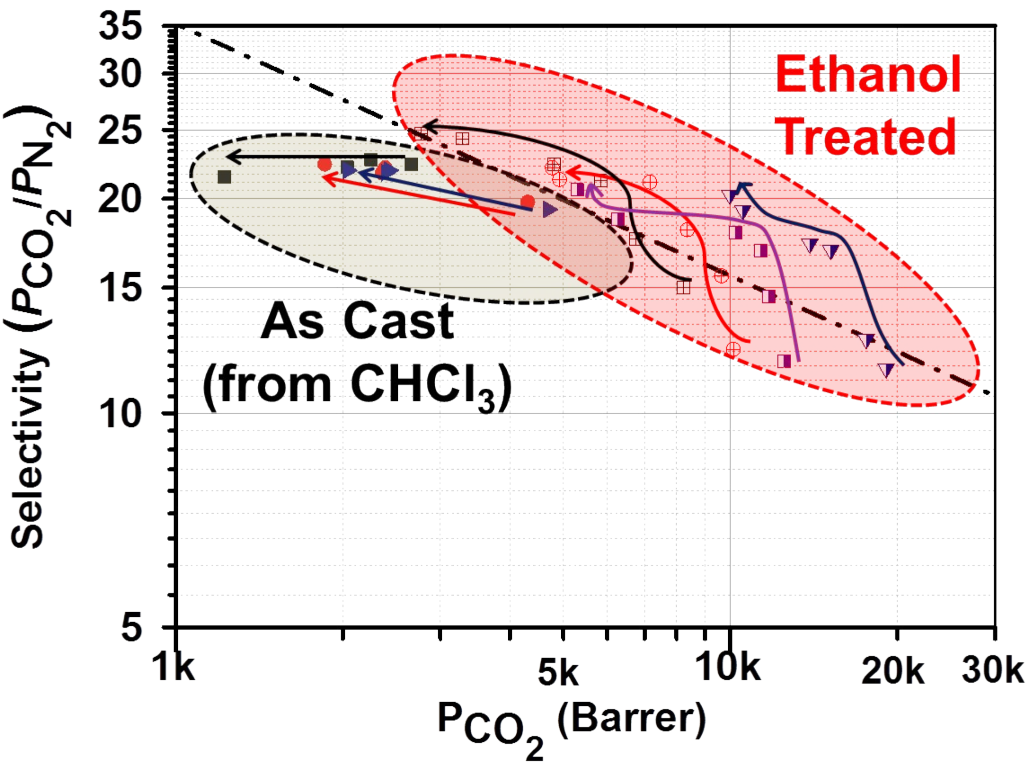


Figure S10 Ideal CO_2/N_2 selectivity versus single gas CO_2 permeability for PIM-1 based MMMs, compared with Robeson's 2008 Upper Bound. The filled squares and squares with the cross represent pure PIM-1 films. (As-cast data: 0 ->45->60->150 days; ethanol treated data: 0->15->30->45->90->150 days). Arrows indicate direction of aging.

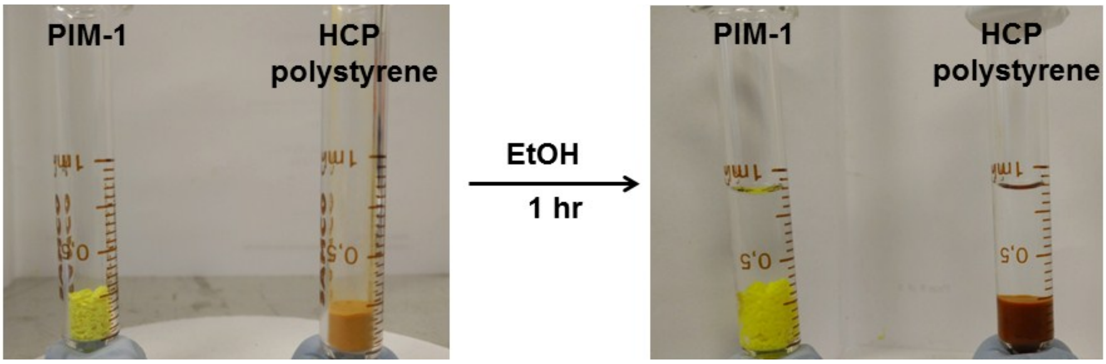


Figure S11. Swelling of PIM-1 in presence of ethanol. Under similar condition, swelling in HCP polystyrene is negligable.

References

1. B. Li, X. Huang, L. Liang and B. Tan, *J, Mat. Chem.*, 2010, **20**, 7444.
2. A. Bhaskar, R. Banerjee and U. Kharul, *J. Mat. Chem. A*, 2014, **2**, 12962.