

Layer-by-Layer Assembly of Polymer of Intrinsic Microporosity: Targeting the CO₂/N₂ Separation Problem

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Electronic Supplementary Information

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1. Materials and Methods

5,5',6,6'-Tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) (Sigma-Aldrich Co., St. Louis, MO.), tetrafluoroterephthalonitrile (TFTPN) (Sigma-Aldrich Co., St. Louis, MO), 4-dimethylaminopyridine (DMAP) (Sigma-Aldrich Co., St. Louis, MO), trimethylamine solution in EtOH (~4.2 M) (Sigma-Aldrich Co., St. Louis, MO), poly(diallyldimethylammonium chloride) (PDDA) (M_w = 100-200 kDa, 20 wt% in water, Sigma-Aldrich Co., St. Louis, MO), poly(4-vinylbenzyl chloride) (PVBC) (M_w = 39500, M_n = 22500, Polymer Source Inc., Montreal, Canada), poly[1-(trimethylsilyl)-1-propyne] (PTMSP) (Gelest, Inc., Morrisville, PA), *n*-octadecyltrichlorosilane (OTS, Gelest, Inc., Morrisville, PA), branched poly(ethylenimine) (*b*-PEI) (M_w = 70,000, 30% W/V aqueous solution, Polysciences Inc., Warrington, PA) and anhydrous potassium carbonate were used as received. House-deionized water was purified by using a Millipore Milli-Q-filtering system containing one carbon and two ion-exchange stages. Experimental methods that were used for (1) layer-by-layer assembly of polyelectrolyte membranes (PEMs) on PTMSP and surface modified silicon wafers (Si-wafer), (2) measuring film thicknesses by ellipsometry and AFM and (3) quantifying gas permeabilities of polyelectrolyte membranes PEMs were similar to those previously reported.¹⁻³ Gas permeabilities of the PEMs were measured *via* a custom-built constant volume-variable pressure apparatus.¹ Ellipsometry measurements were done using a VASE ellipsometer (J.A. Woollam Co., Inc., Lincoln, NE), equipped with variable wavelengths from 250-1700 nm and an angle of incidence from 15°-90°. A λ value of 632.8 nm and an incidence angle of 70° were used for all measurements. Film thicknesses were determined using the CAUCHY model and software supplied by the manufacturer. This software uses the thickness and refractive index of the native oxide layer of silicon as well as the refractive index of the silicon substrate in determining the starting point for the calculation of the thickness and refractive indices of the organic layers. The refractive indices that were used in determining the thickness of an *n*-octadecyltrichlorosilane (OTS)-modified layer, the branched poly(ethylenimine) layer, and the polyelectrolyte multilayers were 1.46, 1.41 and

1.41, respectively. Such values are commonly found for soft materials like organic polymers. All AFM measurements were done using a tapping mode atomic force microscopy (Solver Next, Multimode SPM, NT MDT America Inc., Santa Clara, CA) and were examined at a minimum of three different locations along the surface. For each sample, $5 \times 5 \mu\text{m}^2$ size images were obtained. Film thicknesses were also determined via AFM analysis by scratching the surface of OTS-modified silicon wafers bearing the layer-by-layer assembled films with a razor blade to remove the surfactant assembly, and measuring step heights. Surface morphology of layer-by-layer assembled PEMs on PTMSP were examined by using Zeiss 1550VP a high resolution (2 nm) variable pressure field emission scanning electron microscopy (FESEM). Before the analysis the polymer films were coated by using Iridium (Ir). FT-IR analysis of powder polymer samples were recorded using the Thermo Scientific Nicolet iS10 spectrometer with the attenuated total reflection (ATR) mode. Analysis of the molecular weight of PIM-1 and its molecular weight distribution were measured by using gel permeation chromatography (GPC). Tetrahydrofuran (THF) was used as an eluent with a flow rate of 1.0 mL/min at ambient temperature and narrow dispersity polystyrenes were used as calibration standards.

2. Supports

The PTMSP supports were prepared using a casting technique.⁴ A typical casting apparatus consisted of a Pyrex glass square (8 in \times 8 in \times 1/8 in), an aluminum centering ring seal, 160 ISO flange size (Kurt J. Lesker Co., Allentown, PA), and five (2.10 in o.d. \times 1.64 in i.d. \times 0.010 in) stainless steel washers (Boker's, Inc., Allentown, PA). The Pyrex glass square, ring seal, and five washers were cleaned with chloroform, methanol, and acetone, with the aid of Kimwipes. The ring seal was then adhered to the glass square using a 5% toluene solution (HPLC grade) of PTMSP which acted as a "glue". The steel washers were then placed, symmetrically, within the ring seal/glass square casting unit. A PTMSP/toluene casting solution (ca. 480 mg/30 mL) was then poured into the ring seal and covered with 15 large pieces of filter paper (Whatman qualitative circles, 18.5 cm) in order to keep the casting unit

dust-free and to avoid the solvent from evaporating too fast. The toluene was allowed to evaporate for at least 24 h, leaving a PTMSP film across the steel washers and glass square. A surgical blade (S/P Surgical Blades, Baxter Diagnostics) was then used to cut out the individual washers. Deionized water (ca. 30 mL) was poured into the ring seal to help separate the washers. The PTMSP cast films were then dried by placing them between several large filter papers for at least 24 h in the laboratory ambient temperature. The resulting membranes, having a typical thickness of ca. 30 μm , were placed in antistatic bags for at least 15 min prior to use for composite membrane fabrication.

3. Layer-by-Layer Depositions

The OTS-modified silicon wafers and the PTMSP supports that were used were further modified by depositing an adsorbed monolayer of *b*-PEI by immersing them in a 0.1 % aqueous solution of *b*-PEI containing 0.1 M NaCl (pH 10.0) for 15 min. The surface modification of the silicon wafers by OTS was carried out using procedures similar to those previously reported.^{3,4} Typically, for multilayer depositions on the silicon wafers, the substrate was immersed in 200 mL of an aqueous solution of PIM-CO₂Na (i.e. polymer **1**) (10 mM repeat unit, 0.1 M NaCl) for 15 min without stirring, and then washed by immersing twice in 200 mL of deionized water for 5 min, each time without stirring, followed by air-drying in a clean room. The substrate was then immersed in 200 mL of an aqueous solution of PDDA (15 mM repeat unit, 0.1 M NaCl) for 15 min. The next washing procedure was same as used for polymer **1**. In the case of the PTMSP supports, the LbL depositions were carried out using an automated Histo-Tek SL Slide Stainer (Sakura, USA), equipped with glass inserts and (i) 600 mL of deionized water, (ii) 600 mL of a 10 mM aqueous solutions of polymer **1** containing 0.1 M NaCl and (iii) 600 mL of an aqueous solution of PDDA containing 0.1 M NaCl. All membranes were allowed to dry in a desiccator (containing dry CaSO₄, Drierite, Mesh 8, Macron Fine Chemicals, USA) for 72 h after the depositions were completed prior to gas permeation measurements. Similar layer-by-layer deposition methods were used for polymer **1** (10 mM repeat unit, 0.1 M NaCl) when combined with polymer **2** (15 mM repeat

unit, 0.1 M NaCl) system and for polymer **1** (10 mM repeat unit, 0.1 M NaCl) being combined with polymer **3** (15 mM repeat unit, 0.1 M NaCl) system.

4. Gas Permeation Measurements

Gas permeation measurements were done using a home-built stainless steel permeation apparatus. The gases studied were H₂ (Ultra High Purity, water < 3 ppm, Messer Griesheim Industries, Inc., Malvern, PA), CO₂ (Ultra Pure, water < 3 ppm, Praxair, Inc., Danbury, CT) and N₂ (Prepurified grade, water < 3 ppm, Praxair, Inc., Danbury, CT). Prior to gas permeation measurements, all membranes were allowed to dry in a desiccator for 72 h after the LbL deposition. During such time, the approximate room temperature was 22 ± 2 °C. Typically, a membrane to be measured was placed in the permeation cell between two Viton rubber O-rings (3.45 cm i.d., Scientific Instrument Services, Inc.) with a support screen (4.70 cm, Millipore Corp.) and held securely with a quick flange clamp (Scientific Instrument Services, Inc.). Membranes were always placed in the cell in such way that the polyelectrolyte multilayers faced the high pressure side of the pressure gradient. When a feed pressure of less than 1 atm was used, a vacuum pump (model N8203ANP, KNF Neuberger, Trenton, NJ) on the feed side was adjusted in such a way that a desired pressure could be achieved. Once the vacuum pumping and gas feed reach equilibrium, the vacuum pressure can be maintained constant. The pressure gradient that was applied across each membrane was 40 psi. Before each measurement, the pressure on the permeate side was reduced to less than 1.5 Torr, while the feed side (upstream) pressure was maintained constant (40 psi). The increase of pressure on the permeate side (downstream) was monitored using a pressure transducer (626C Baratron Capacitance Manometer, MKS Instrument, Inc., MA) under steady state and isothermal conditions. The following equations was used to calculate the permeance values P/l .⁵

$$p_t = p_0 + (dp/dt)_0 \cdot t + \frac{RT \cdot A}{V_p \cdot V_m} \cdot \frac{p_f \cdot P}{l} \left(t - \frac{l^2}{6D} \right) \quad (1)$$

$$\frac{P}{l} = \frac{V_p \cdot V_m}{RT \cdot A \cdot p_f} \left(\frac{dp}{dt} \right) \quad (2)$$

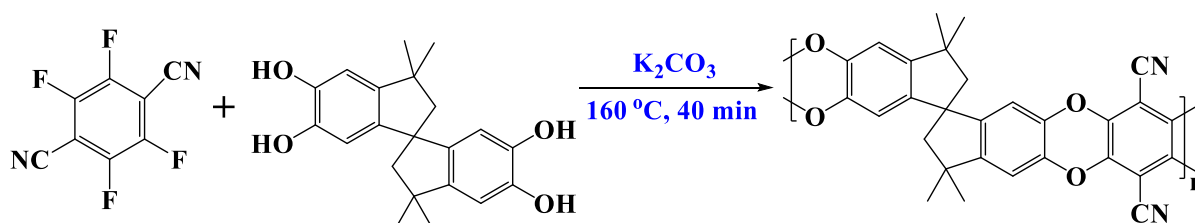
Here P is the permeability coefficient, l the membrane thickness, p_t is the permeate pressure at time t , p_0 the starting pressure, $(dp/dt)_0$ the baseline slope, p_f the feed pressure, R the universal gas constant (8.314×10^{-5} in $\text{m}^3 \cdot \text{bar} / \text{mol} \cdot \text{K}$), T the absolute temperature (298 K), A the exposed membrane area (9.62 cm^2), V_P the permeate volume, V_m the molar volume of the permeating gas (22.41×10^{-3} in m^3 / mol) at standard temperature and pressure (0°C and 1 atm).

The term $p_0 + (dp/dt)_0 \cdot t$ in eq. 1 refers to the starting pressure and the baseline slope is negligible in a well evacuated and sealed system. Rearrangement of the slope dp/dt in eq. 1 gives the eq. 2. dp/dt is the increase in pressure over time and was measured experimentally.

In general, the permeation properties were first measured for H_2 , CO_2 and then for N_2 . To ensure that no damage to the membrane had occurred while these measurements were being made, after the last permeant was investigated, the H_2 permeances were measured again and found to be unchanged.

5. Synthetic Procedures

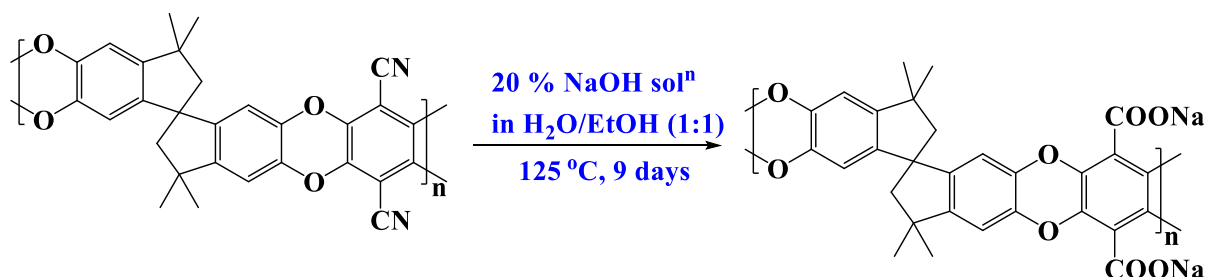
Synthesis of PIM-1.



PIM-1 was synthesized according to the method reported previously.^{6,7} In a typical polymerization reaction, 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) (5 g, 14.68 mmol), tetrafluoroterephthalonitrile (TFTPN) (2.938 g, 14.68 mmol), anhydrous potassium carbonate (6.089 g, 44.06 mmol), dimethylacetamide (DMAc) (30 mL), and toluene (15 mL) were charged into a 250 mL three neck round bottom flask. The reaction mixture was refluxed at 160°C for 40 min under N_2 atmosphere and the viscous solution was poured into methanol for precipitation. The crude polymer was dissolved in chloroform and re-precipitated from methanol. The final polymer was refluxed in deionized

water for 6 h and then dried at 100 °C for 2 days. Conversion = 80%. $M_{n, GPC} = 5600$, $M_{w, GPC} = 8200$, $D = 1.46$. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 6.82 (2H, s), 6.42 (2H, s), 2.32-2.15 (4H, dd), 1.46-1.15 (12 H, broad). Anal. Calcd for $\text{C}_{29}\text{H}_{20}\text{N}_2\text{O}_4$ (wt %): C : 75.64, H : 4.37, N : 6.08; Found : C : 72.04, H : 4.62, N : 5.68.

Synthesis of Polymer 1.



PIM-1 was hydrolysed via alkaline hydrolysis by using highly concentrated sodium hydroxide solution.⁸ PIM-1 (1 g) in powder form was added to 80 mL 20 % NaOH solution (H_2O /ethanol = 1/1, w/w). The reaction mixture was magnetically stirred and refluxed at 125 °C under a N_2 atmosphere. The reaction was run for 9 days to produce a highly carboxylated PIM as its sodium salt. The reaction mixture was then added to a large amount (200 mL) of slightly acidified (using HCl) water (pH = 4~5) and refluxed at 110 °C for 6 h. The solution was then concentrated under reduced pressure and solubilized in small volume of deionized water and dialyzed against deionized water using a Float-A-Lyzer membrane (Spectapor, MWCO 3-5 kDa) for 48 h (changing the dialysate every 12 h). Subsequent lyophilization afforded an orange colored powder (70%) having $^1\text{H-NMR}$ (400 MHz, D_2O , δ , ppm): 6.75 (2H, s), 6.35 (2H, s), 2.26-2.09 (4H, dd), 1.40-1.10 (12H, broad). Anal. Calcd for $\text{C}_{29}\text{H}_{20}\text{O}_4\text{Na}_2 \cdot 3.5 \text{H}_2\text{O}$ (wt %): C : 57.52, H : 4.46, Na : 7.60; Found : C : 57.58, H : 4.96, Na : 7.59.

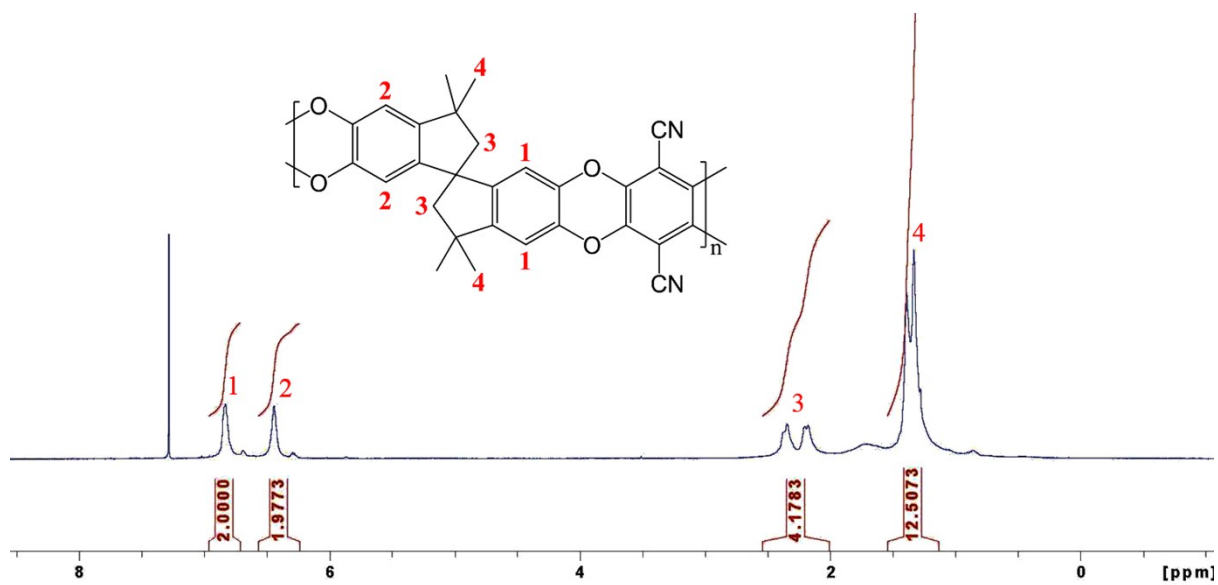


Figure S1. ¹H NMR spectrum of PIM-1.

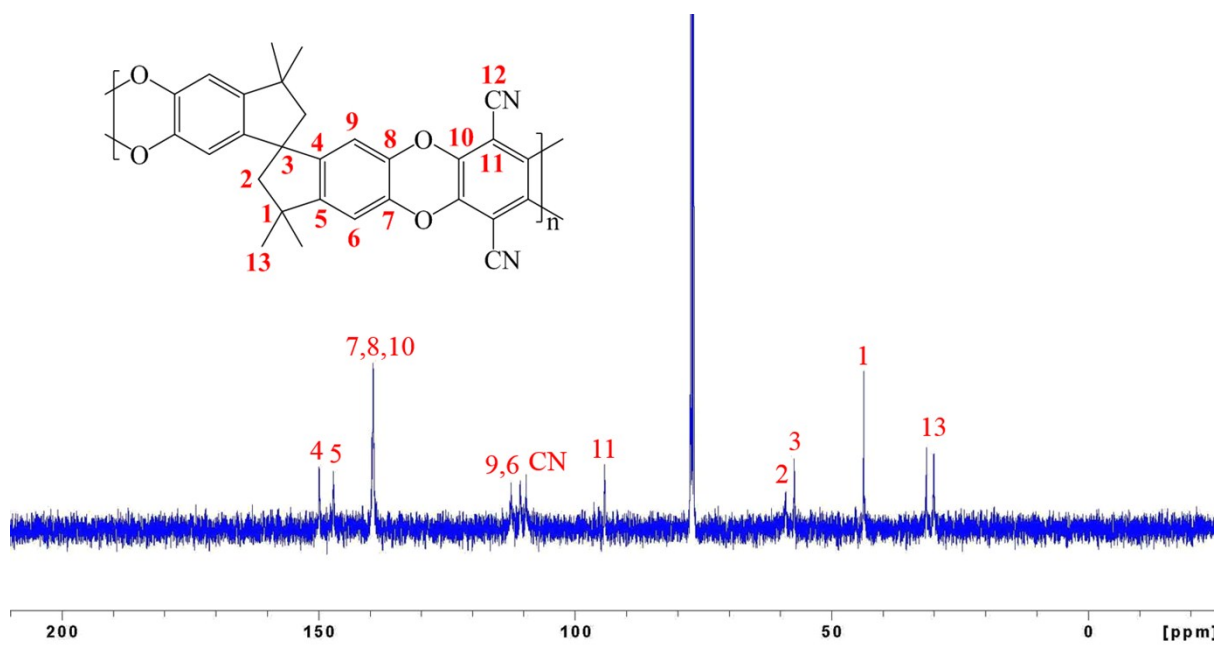


Figure S2. ¹³C NMR spectrum of PIM-1 in CDCl₃.

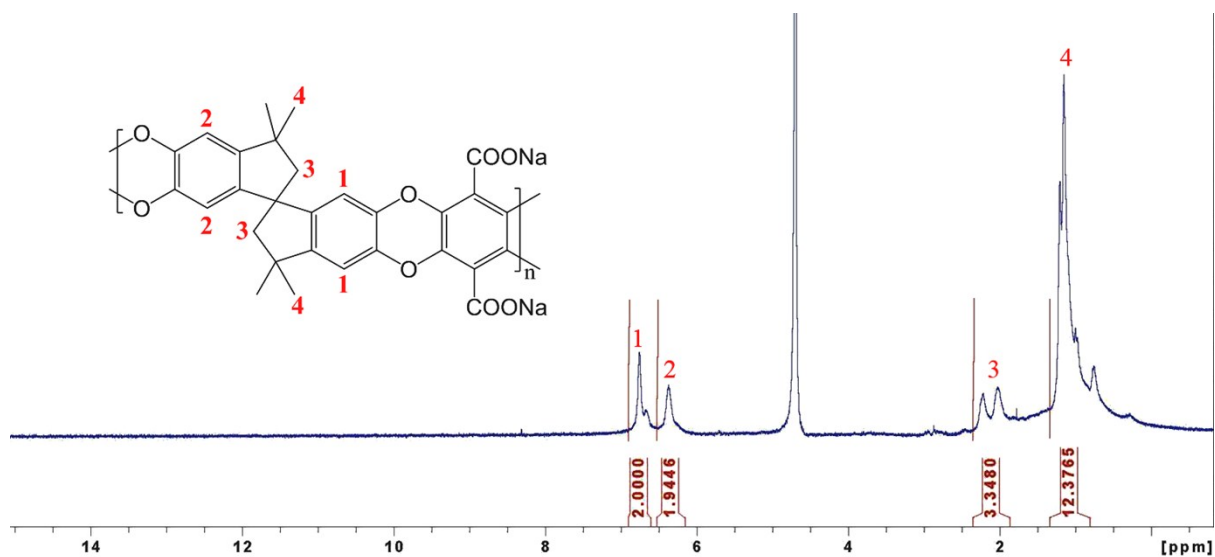


Figure S3. ¹H NMR spectrum of PIM-CO₂Na i.e. polymer 1.

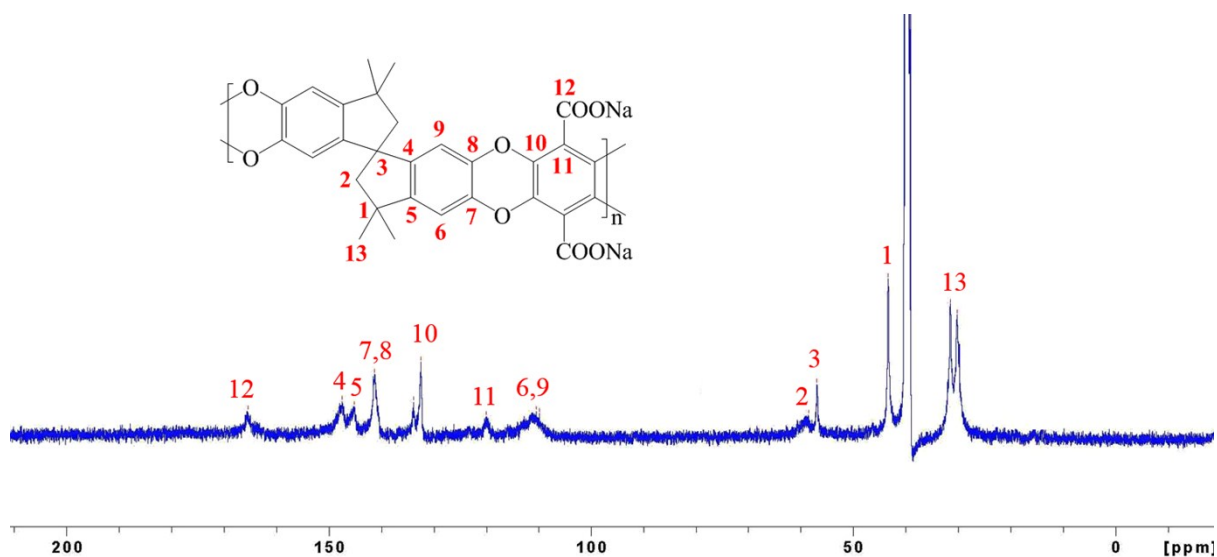


Figure S4. ¹³C NMR spectrum of PIM-CO₂Na i.e. polymer 1 in d⁶-DMSO.

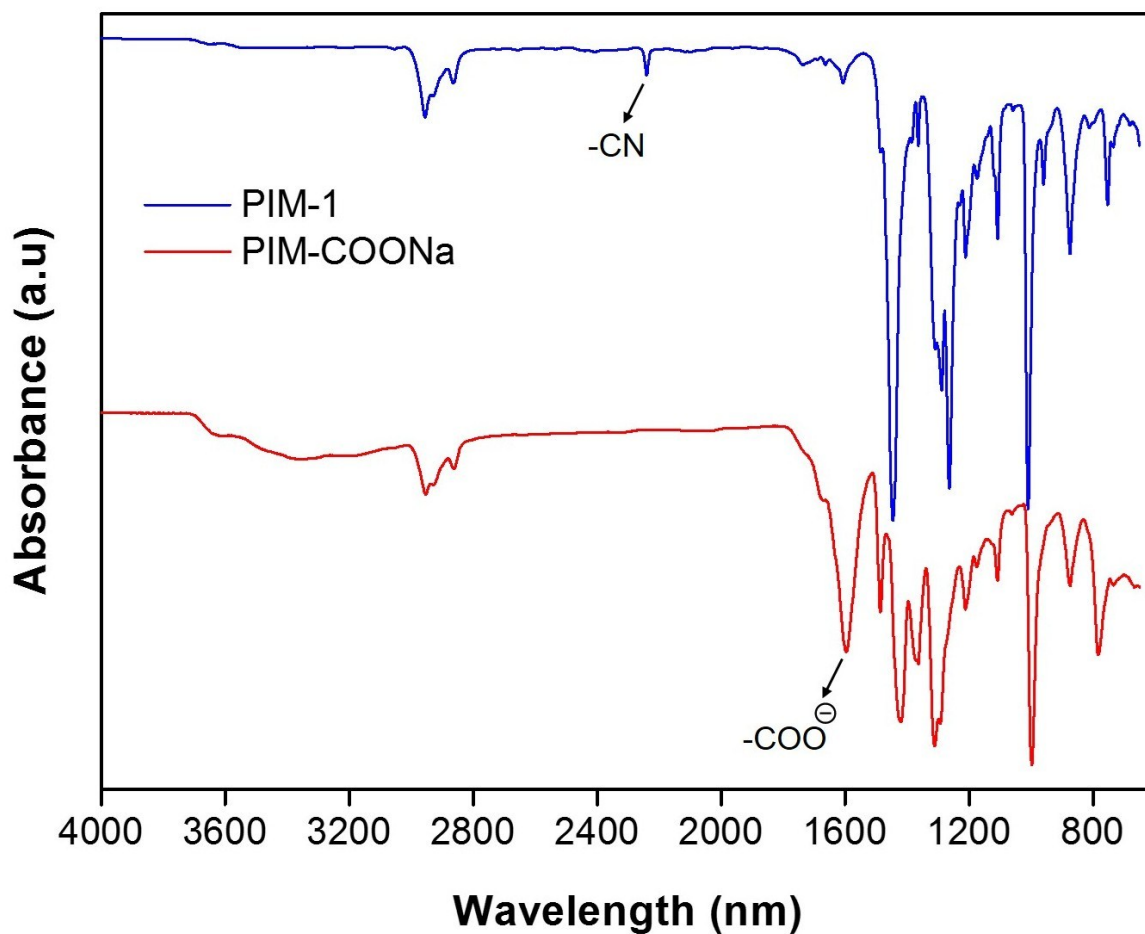
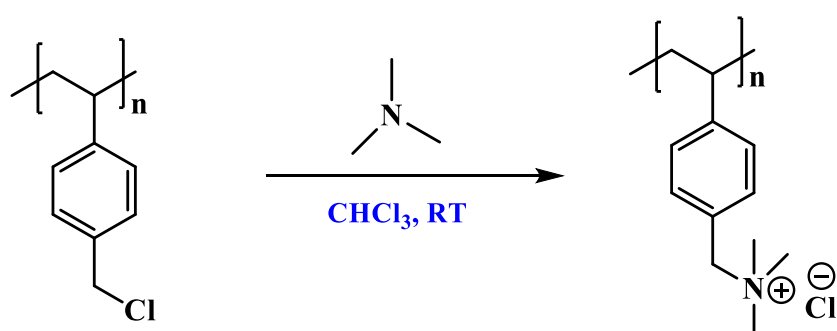


Figure S5. FT-IR spectra of PIM-1 and its hydrolysed carboxylate Na⁺ salt (1).

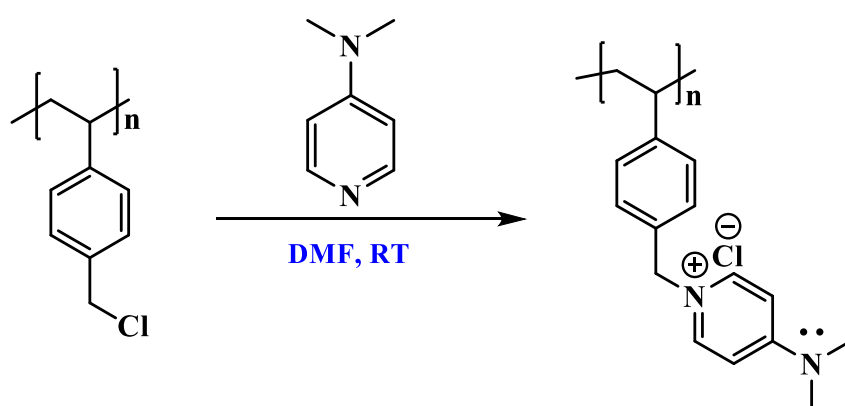
Synthesis of Polymer 2.



Polymer **2** was synthesized according to the procedure reported previously.⁹ In a two neck 50 mL round bottom flask 5.5 mL of an ethanolic solution of trimethylamine (20.3 mmol) was added to a 15 mL of a chloroform solution containing 1 g of poly(4-vinylbenzyl chloride) (6.75 mmol) (M_w 39500, M_n 22500, Polymer Source Inc., Montreal, Canada). The reaction mixture was stirred in sealed flask under an argon atmosphere for 24 h. All volatiles were then

removed under reduced pressure at 45 °C (10 Torr) and the resulting polymer was dissolved in 10 mL of deionized H₂O. This solution was then dialyzed against deionized water using Spectrapor membrane (MWCO 3.5-5 KDa) for 72 h (changing the dialysate every 24 h) and the product isolated by freeze drying. The final product, **2**, was obtained in 85% yield as a colorless solid having ¹H-NMR (D₂O, δ, ppm): 7.18 (2H, brs); 6.68 (2H, brs); 4.38 (2H, brs); 2.99 (9H, s); 1.20-2.30 (3H, brm).

Synthesis of Polymer 3.



Polymer **3** was synthesized according to a method reported previously.¹ A polymer solution was prepared by dissolving poly(4-vinylbenzyl chloride) (0.5 g, 3.4 mmol) in 8 mL of dimethylformamide (DMF) in a two neck 50 mL round bottomed flask. Then 4 mL of a DMF solution containing 4-dimethylaminopyridine (DMAP) (1.246 g, 10.2 mmol) were added. The reaction mixture was then stirred in a sealed flask under a nitrogen atmosphere for 24 h at room temperature. The product mixture was poured into 40 mL of diethyl ether to precipitate the polymer and washed with diethyl ether several times. The final purification was done by dissolving the polymer in 10 mL of deionized water and dialyzing against deionized water using Spectrapor membrane (MWCO 3.5-5 KDa) for 72 h (changing the dialysate every 24 h). Subsequent lyophilisation afforded a 91% yield of polymer **3** as a pale yellow solid having ¹H NMR (400 MHz, D₂O): δ 8.3-5.9 (8H, brm), 5.7-4.9 (2H, brs), 3.3-2.4 (4H, brs), 2.4-3.2 (6H, brs), 0.8-2.2 (3H, brm).

6. PEMs thickness measurement via AFM

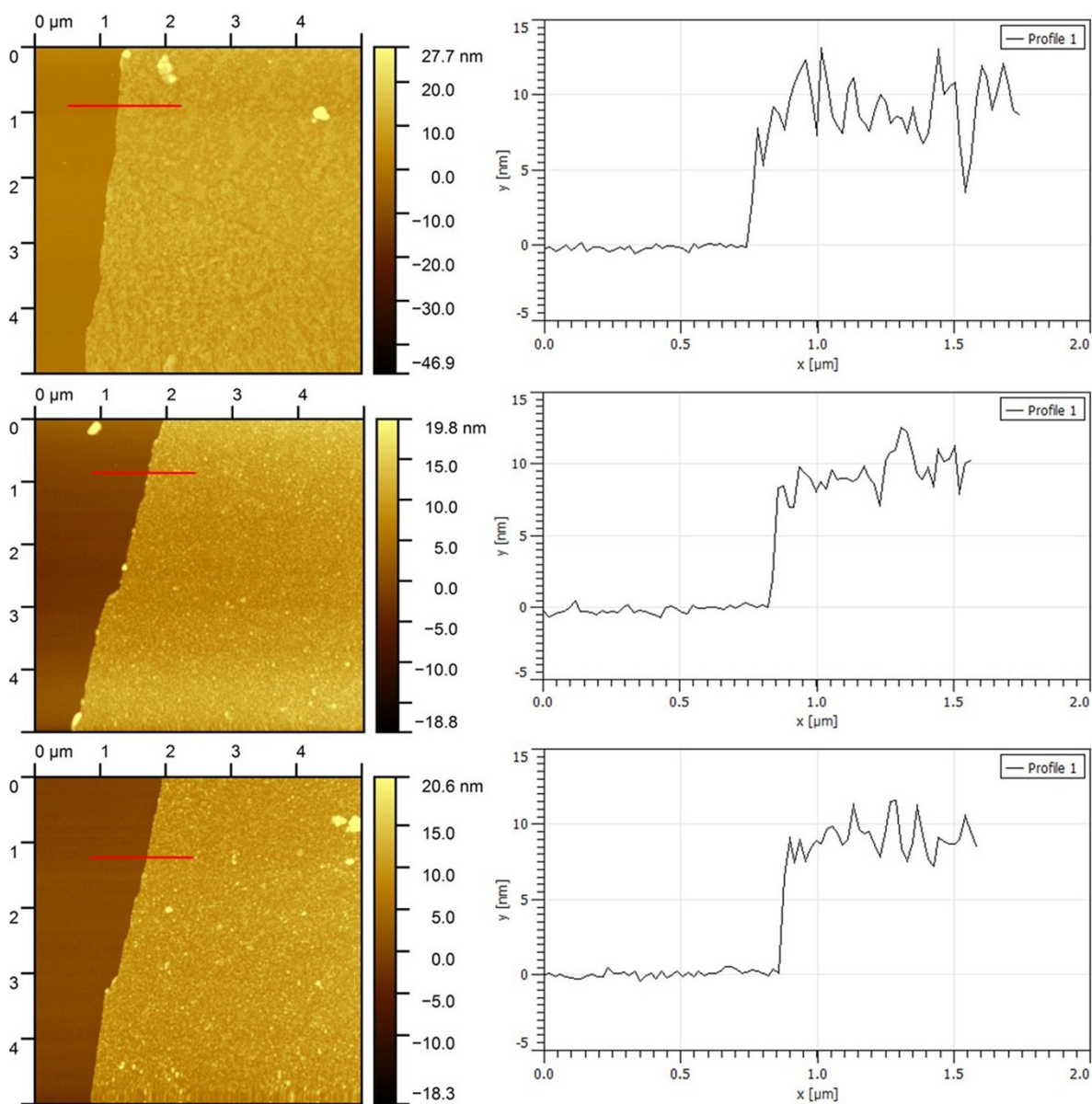


Figure S6. Height image and section profile (AFM, tapping mode, 5 x 5 μm²) showing the film thickness of PEMs: 1/PDDA (top); 1/2 (middle); 1/3 (bottom).

7. Gas Permeances of PEMs

Table S1. Permeances and permeation selectivities for PEMs made from 1/PDDA^a

bilayers (number)	<i>l</i> (nm)	H ₂	CO ₂	N ₂	CO ₂ /N ₂	H ₂ /N ₂
---- ^b	----	940	1900	420	2.2	4.5
1	3	480	910	150	6.1	3.2
		430	870	130	6.7	3.3
2	6	190	130	4.0	33	48
		187	125	3.5	36	53
3	9	170	65	1.05	62	162
		165	63	0.98	64	168
4	12	135	50	0.75	66	180
		130	48	0.71	68	183
5	15	121	40	0.56	72	216
		119	38	0.54	70	220
6	18	105	34	0.47	72	223
		101	32	0.45	71	224
7	21	93	29	0.41	71	227
		91	28	0.40	70	228
8	24	80	25	0.35	71	229
		83	26	0.36	72	228

^aPermeance values (in GPU where 1 GPU = 1 × 10⁻⁶ (cm³/cm²-s-cm Hg) were calculated by dividing the observed flow rate by the area of the membrane (9.36 cm²) at ambient temperature with a pressure gradient of 40 psi. Average values were obtained from 5-10 independent measurements of the same sample; the error in each case was ±5%. Duplicate membranes are reported. ^bPTMSP plus *b*-PEI support.

Table S2. Permeances and permeation selectivities for PEMs made from 1/2^a

bilayers (number)	<i>l</i> (nm)	H ₂	CO ₂	N ₂	CO ₂ /N ₂	H ₂ /N ₂
---- ^b	----	940	1900	420	2.2	4.5
1	4	300	330	30	11	10
		310	350	35	10	9
2	8	166	50	0.64	78	259
		173	51	0.67	76	258
3	12	130	36	0.48	75	271
		136	38	0.51	75	267
4	16	106	28	0.38	74	279
		112	31	0.41	76	273

^{a,b}See footnotes for Table S1.

Table S3. Permeances and permeation selectivities for PEMs made from 1/3^a

bilayers (number)	<i>l</i> (nm)	H ₂	CO ₂	N ₂	CO ₂ /N ₂	H ₂ /N ₂
---- ^b	----	940	1900	420	2.2	4.5
1	4	90	30	1.2	25	75
		100	34	1.4	24	71
2	8	60	8.5	0.12	71	500
		54	8.2	0.11	75	490
3	12	45	6.5	0.089	73	505
		43	6.2	0.085	73	506
4	17	37	5.6	0.073	76	507
		36	5.3	0.071	75	507

^{a,b}See footnotes for Table S1.

8. References

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