

SUPPORTING INFORMATION

Superhydrophobic Hexamethylene Diisocyanate (HMDI) Modified Hydrolyzed Polymers of Intrinsic Microporosity (PIM-1) Electrospun Ultrafine Fibrous Membrane for Adsorption of Organic Compounds and Oil-Water Separation

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1. Characterization of PIM-1 and hydrolyzed PIM-1 powders

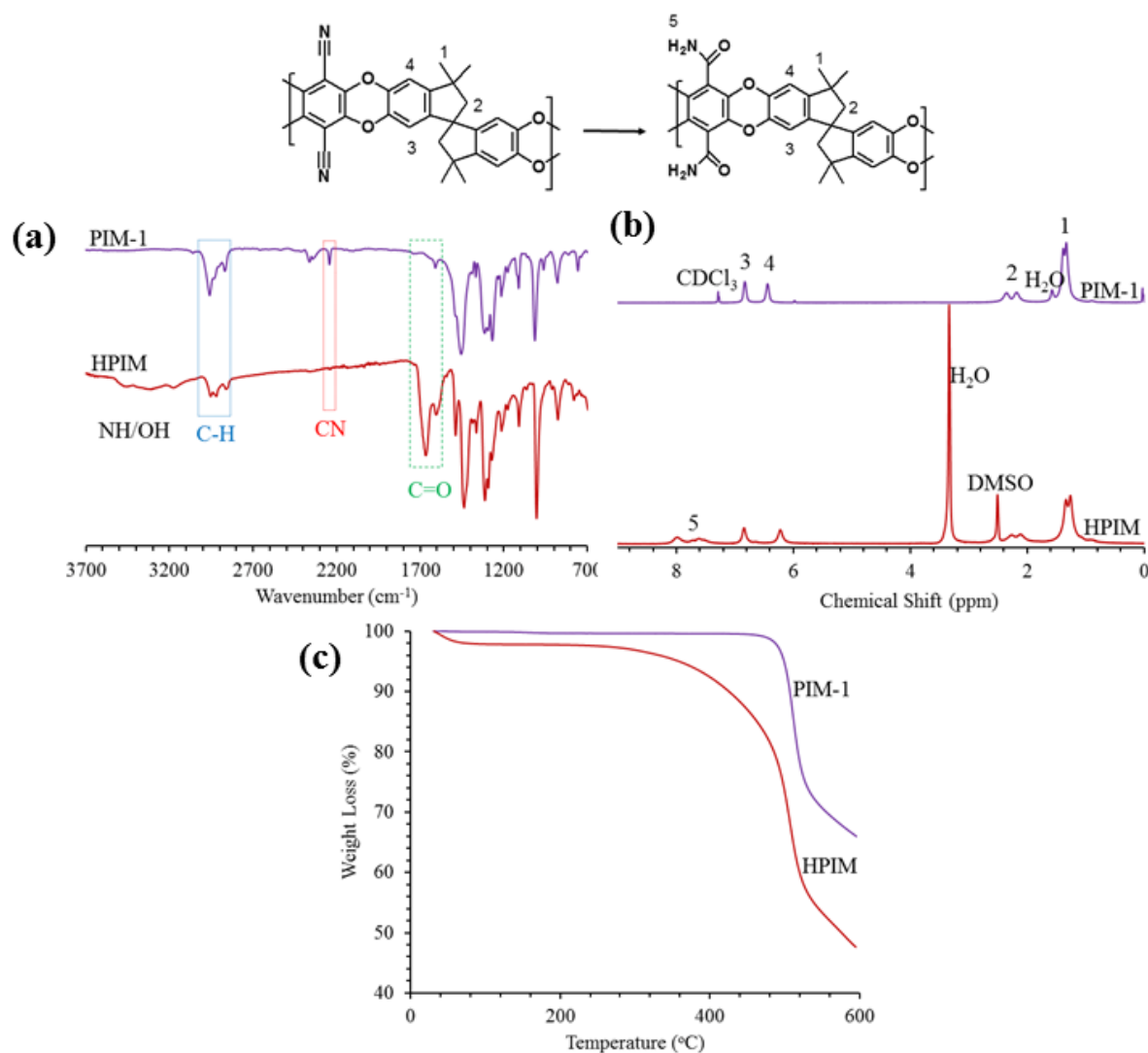


Figure S1. (a) ATR-IR spectra, (b) ^1H -NMR spectra, (c) TGA curves of PIM-1 and hydrolyzed PIM-1.

ATR-IR spectra of PIM-1 and hydrolyzed PIM-1 are depicted in Figure S1(a). PIM-1 shows characteristic nitrile (CN) stretches at 2240 cm^{-1} along with aromatic and aliphatic C-H stretches around 3000 cm^{-1} for. After hydrolysis the relative intensity of nitrile is reduced and new bands appeared in the region $3000\text{--}3500\text{ cm}^{-1}$ along with a carbonyl peak at $\sim 1700\text{ cm}^{-1}$ that indicates amide structure and it also shows no significant carboxylic acid structure. ^1H -NMR spectra of PIM-1 and HPIM are displayed in Figure S1(b) showing four different proton

environments for PIM-1. In addition, HPIM shows amide proton signals in the region 7.5 to 8.2 ppm and no more peaks appeared around 14 ppm showing no carboxylic acid protons. Thus, we have obtained fully hydrolyzed PIM-1 which has dominantly amide functionality. Thermal properties of PIM-1 and HPIM are studied using thermogravimetric analysis technique that shows both PIM-1 and HPIM are thermally stable. Although PIM-1 starts degrading at 450 °C (Figure S1c), HPIM shows slight weight loss below 100 °C due to the residuals and polymer start degrading around 250 °C indicating functional group degradation. The results are in good agreement with previous studies and indicates complete hydrolysis of PIM-1.¹⁻⁴

2. Optimization of the membrane production

To optimize the process of membrane production, crosslinking stage has been investigated comprehensively by using several observations. First, spinning solution has been stirred in room temperature for a couple of days and no significant precipitation has been observed (Figure S2a). Then, this solution has been heated up to 100 °C for a couple of hours that showed no sign of crosslinking. Further stirrings for a couple of days at this temperature caused slight precipitation (Figure S2a). As a result, we have determined that the crosslinking reaction between HPIM and HMDI can barely start with the help of heat in the solution. In addition, drying method of the fibers has also been examined. Two pieces of HMDI/HPIM-FM were dried at room temperature for overnight and at 150 °C for 2h to distinguish the effect of the drying method. Both samples became insoluble and they displayed different visual characteristics (Figure S2b). In addition, the infrared spectrum of the sample which is dried in high temperature has indicated more completed reaction. The carbonyl peaks turned into one single peaks that indicates the formation of urethane linkage at 150 °C spectrum unlike room temperature spectrum. Therefore, it was concluded that high temperature not only helps to remove DMF from membrane but also catalyze the crosslinking reaction which can be seen in

Figure S3. It was found that the membrane dried at different temperatures have similar fiber diameter distributions. SEM images of both samples are also provided in Figure S4.

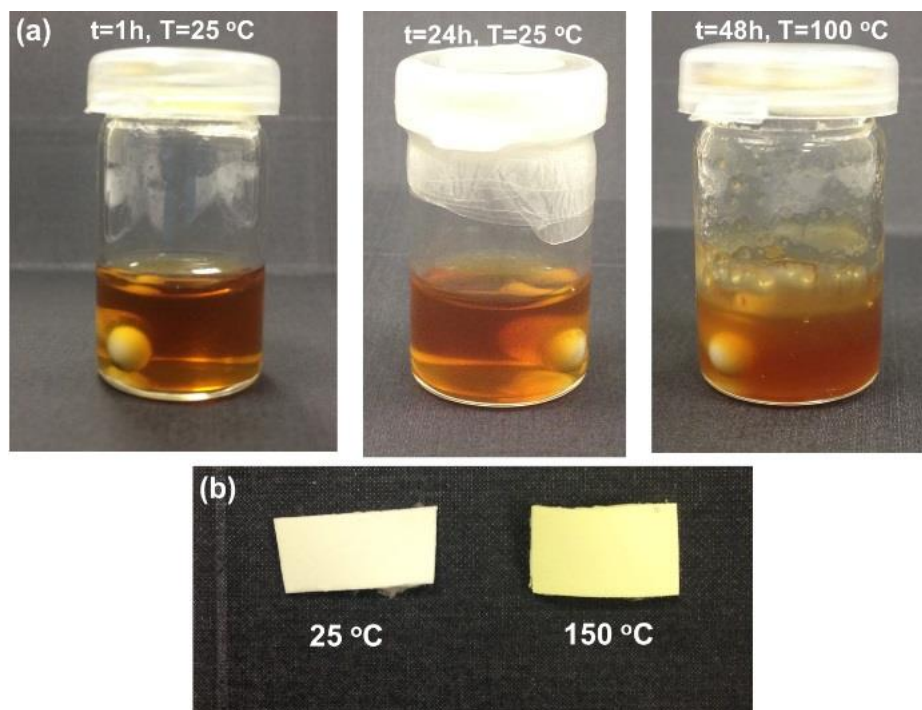


Figure S2: Digital images of (a) the mixture of HMDI/HPIM spinning solutions at different temperatures and times, (b) fibrous membrane of HMDI/HPIM dried at different temperatures.

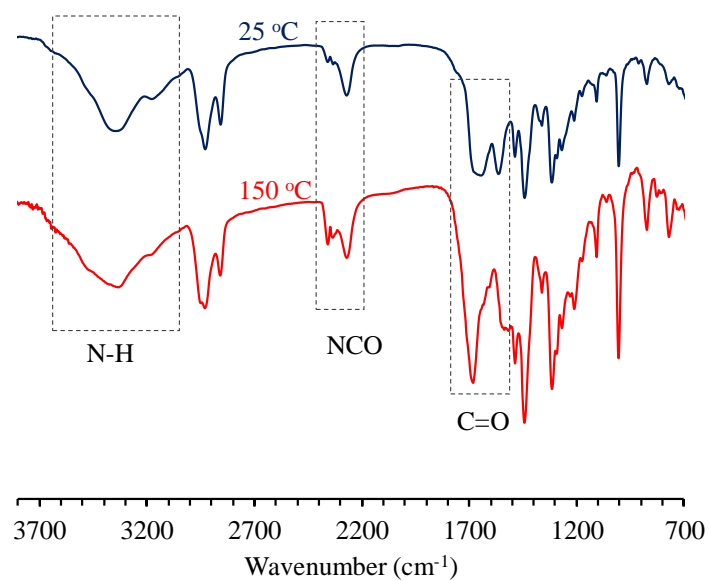


Figure S3: Infrared Spectra of HMDI/HPIM-FMs dried at room temperature (25 °C) and 150 °C.

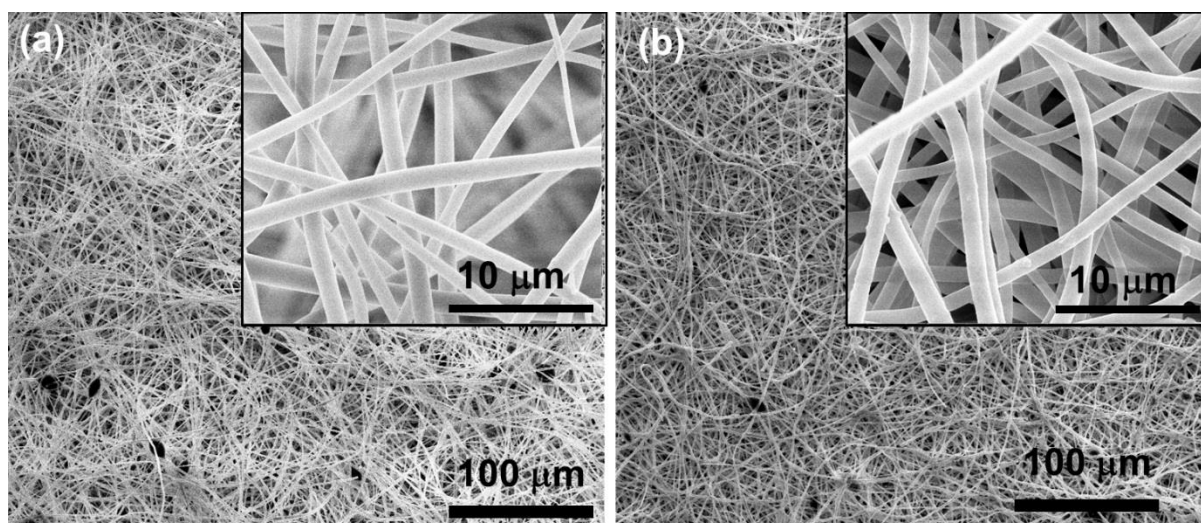


Figure S4: SEM images of HMDI/HPIM-FMs (a) dried at room temperature, (b) dried at 150 °C and inset pictures are the higher magnifications of the images.

3. Organic and oil adsorption experiment

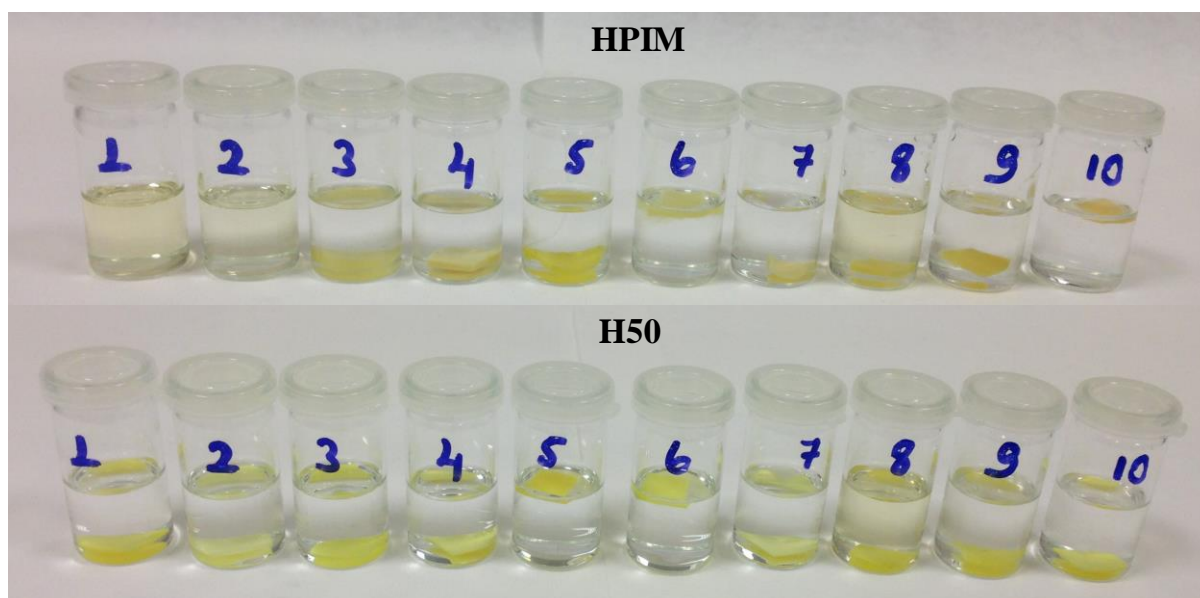


Figure S5. Weight based adsorption capacities of HPIM and H50 on different organic compounds (1) DMSO, (2) DMF, (3) Toluene, (4) Hexane, (5) DCM, (6) Chloroform, (7) Methanol, (8) Olive oil, (9) Pump oil and (10) silicone oil.

Table S1: Organic solvent and oils used for adsorption experiments and the weights of membranes before and after adsorption.

Adsorbed organic	HPIM Weight (g)		H50 Weight (g)		% Weight gain	
	Before	After	Before	After	HPIM	H50
Silicone oil	0.011	0.27	0.011	0.27	2300	2400
Pump oil	0.008	0.26	0.012	0.17	3200	1300
Sunflower oil	0.005	0.18	0.008	0.13	3400	1500
Methanol	0.007	0.15	0.008	0.10	2000	1200
Chloroform	0.007	0.25	0.010	0.21	3400	2000
DCM	0.006	0.18	0.010	0.17	2800	1600
Hexane	0.011	0.18	0.010	0.08	1500	700
Toluene	0.006	0.15	0.008	0.08	2400	1000
DMF	0.003		0.007	0.10		1400
DMSO	0.006		0.013	0.24		1700

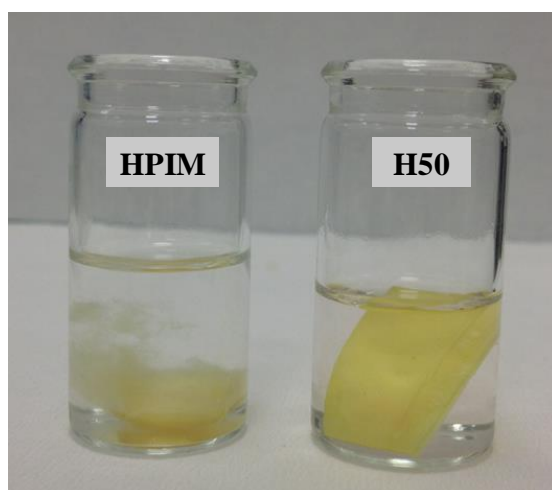


Figure S6. Stability of fibrous membranes in oil HPIM (left) and H50 (right).

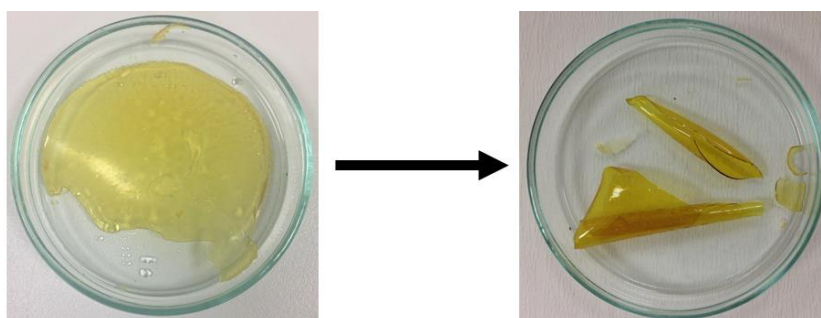


Figure S7: Dense membrane (film) form of HMDI/HPIM-FMs (left) before heat treatment and (right) after heat treatment.

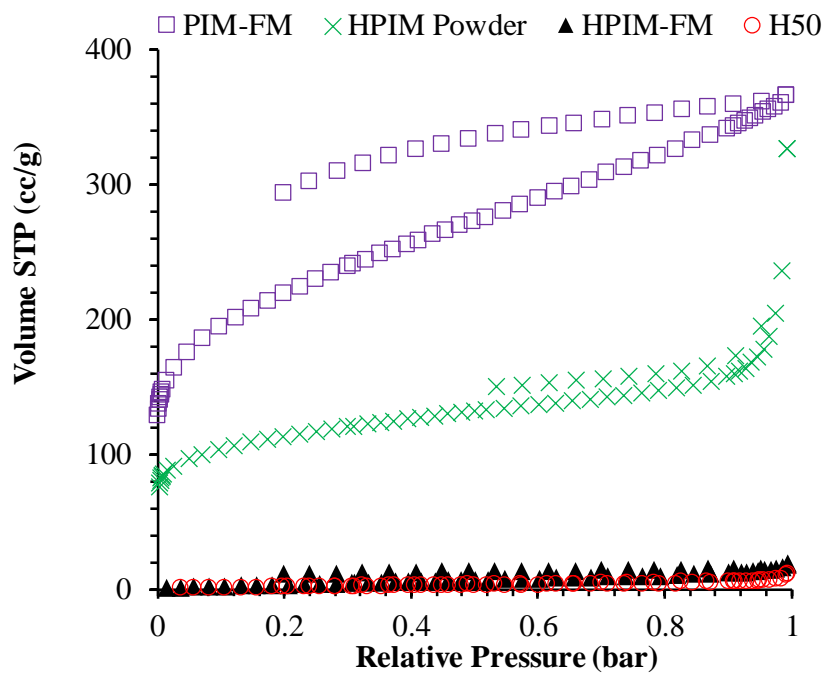


Figure S8: N₂ adsorption/desorption isotherms of samples.

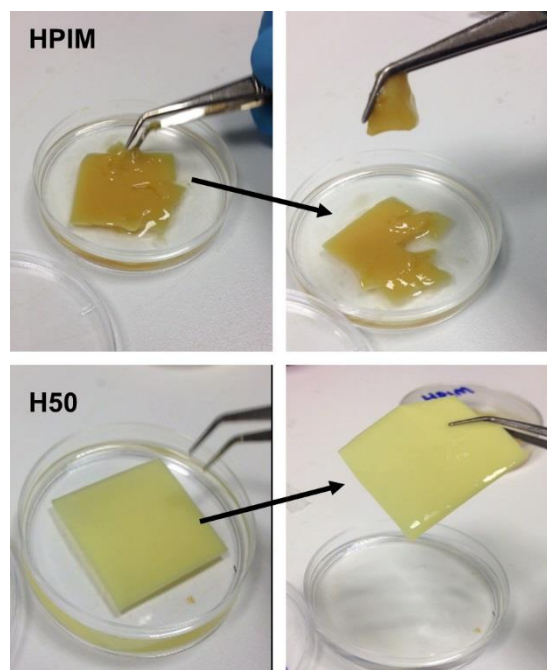


Figure S9: Digital images showing the structural stability of HPIM and H50 after isopropanol adsorption.

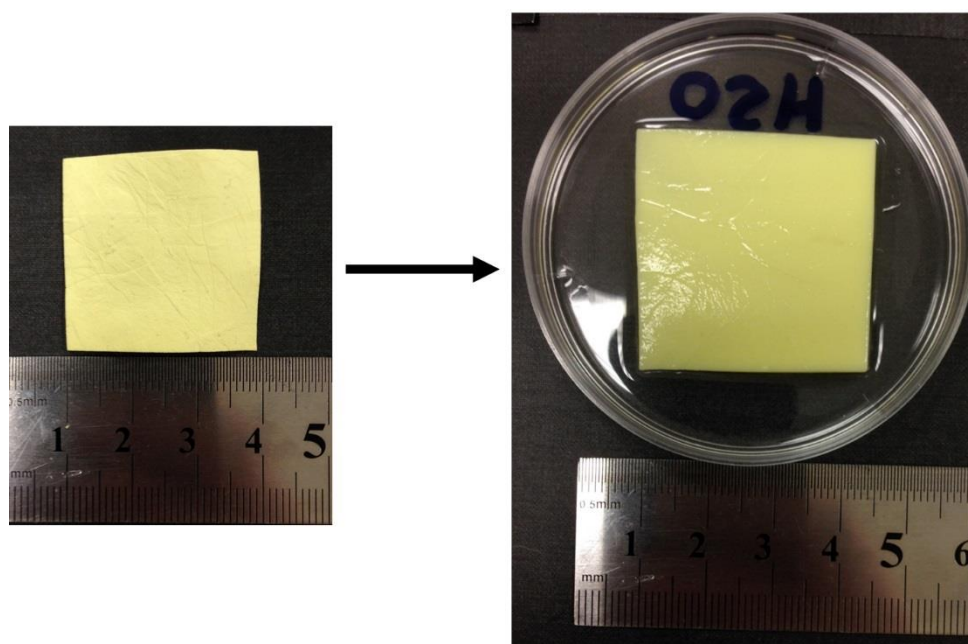


Figure S10: Digital images of H50 showing dimension changes of the membrane (left) before and (right) after isopropanol adsorption.

Table S2: Comparison of adsorption capacities of oil adsorbents based on their form.

Material	Oil uptake (g/g)	Form	Reference
Polypropylene	10-25	fiber/web	[5-6]
Polyvinyl-Alcohol Formaldehyde	14-57	sponge	[7]
Cellulose aerogels	59	aerogel	[8]
Polystyrene	80-130	fiber	[9]
Porous polyimide	57	fiber	[10]
Hydrophobic cotton	12	fiber	[11]
HMDI/HPIM-FMs	13-25	fiber	This work

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