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Supporting Information

Aromatic Porous Polymer Network Membranes for Organic Solvent

Nanofiltration under Extreme Conditions

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1. General Information.

1,4-diacetylbenzene, 1,3-diacetyl-benzene and 1,3,5-triacetylbenzene were purchased from TCI America. Methanesulfonic acid (MSA) was purchased from Oakwood Chemical. All dye molecules were purchased from TCI or Sigma-Aldrich. All purchased starting materials were used without further purification. Field-emission scanning electron microscopic (SEM) images were collected using the FEI Quanta 600 FE-SEM at 20 kV. Film samples were taped on double side carbon tape and were coated with iridium prior tests. Atomic Force Microscopy (AFM) images were collected with a Bruker Dimension S4 Icon AFM in tapping mode and processed by NanoScope Analysis. In order to measure the thickness of film, a scratch was made on the surface of film to expose the silicon wafer. N₂ adsorption data were collected from activated samples using the Micrometrics ASAP 2020 at 77 K from 0-1 bar. The porosity data including Brunauer-Emmett–Teller (BET) surface area were calculated by density functional theory (DFT) method. The ideal pore size of PPN membranes were calculated based on ideal scheme in Chem3D. Thermogravimetric analysis (TGA) was carried on with a TA Q500 thermogravimetric analyzer from 30-900 °C at a heating rate of 20 °C min⁻¹ under N₂ atmosphere. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by ZnSe attenuated total reflection with a Shimadzu IRAffinity-1S spectrometer. Powder X-ray diffraction (PXRD) was obtained with a Bruker D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$ Å) at 40 kV and 40 mA. Solid-state C¹³ nuclear magnetic resonance (NMR) data were obtained using Bruker Advance-400 Solids NMR spectrometer. Membrane samples were ground into powder and purified by soxhlet extraction using ethanol before TGA, FT-IR and solid-state NMR tests. UV-Vis absorption spectra were recorded with a Shimadzu UV-2600 UV-Vis spectrophotometer. Contact angles were measured using a CAM 200 Optical Goniometer. A drop

size of 10 μ L was used to apply the test liquids. Dimension of dye molecules indicated by Van der Waals diameters were calculated by Marvinsketch.

2. Methods

Fabrication of PPN thin film. The monomer (1,4-diacetylbenzene, 1,3-diacetylbenzene or 1,3,5triacetylbenzene) was dissolved in MSA at 50 °C to form a 15 mg/mL solution. The solution was drop casted onto a micro cover glass and sandwiched by another micro cover glass, followed by heating at 110 °C for 24 h. After the reaction was completed, the micro cover glasses were separated and PPN film was adhered to one of glass pieces. A pressure-sensitive tape was used to tape off the film from the glass surface (Figure S1). The tape was then soaked in THF where the polyacrylate adhesive was dissolved and PPN thin film was released into THF, and subsequently transferred onto a silicon wafer by using a pipette, and rinsed with THF for further tests.



Figure S1. Transfer a PPN thin film from glass substrate onto a silica wafer.

Fabrication of PPN membranes for OSN. The monomer (90 mg) was dissolved in MSA (1 mL) at 50 °C to form the reaction solution. The solution was drop casted onto a 6×6 inches glass substrate and sandwiched by another piece of glass with the same size. These glass substrates were pre-treated by spray-coating a thin layer of PTFE to prevent undesired adhesion of the membrane onto the glass. Two pieces of 200 µm-thick micro cover glass slides were placed in between (Figure 1b). The sandwiched system was heated at 110 °C for 24 h. After the reaction, the freestanding PPN membrane was detached from the glass substrate and soaked in methanol for 45 min. It was then taken out and soaked in another batch of clean methanol. After repeating for twice, the

membrane was either used directly for subsequent experiments, or preserved by soaking in PEG 600/methanol solution (weight ratio = 1:1) overnight and dry in the air for long-term storage.

OSN tests of PPN membranes. A piece of PPN membrane was washed thoroughly by methanol and cut by a round cutter with diameter of 4.7 cm. The membrane was transferred into a dead-end solvent-resistant stirred cell (Millipore, effective diameter 4.7 cm) with a Nylon filtration membrane (Whatman, 0.45 μ m pore size) underneath as a cushion (Figure S2). Kalrez solventresistant O-ring (outside diameter 4.7 cm) was placed on the PPN membrane to seal the cell. All experiments were repeated for at least three times. In a typical dye rejection test, dye solution (30 mL, 10 ppm) was charged into the cell as the feed solution. A transmembrane pressure of 1 bar was applied by using compressed nitrogen gas. The feed solution was stirred at 400 rpm to minimize concentration polarization effect close to the membrane. The first 3 mL of permeate was discarded and the following permeate was collected for measurements. After the test, the solution remained in the cell was collected as the retentate. The concentration of feed, permeate, and retentate was measured by UV-vis spectrophotometer. The rejection *R* was calculated using Equation (1), where *C*_f and *C*_p is the concentration of feed and permeate, respectively.

$$R = \left[1 - \left(\frac{c_p}{c_f}\right)\right] \times 100\% \quad (1)$$

In a pure solvent permeance test, 30 mL pure organic solvent (acetonitrile, acetone, methanol, tetrahydrofuran, toluene, dimethylformamide, or isopropanol) was used as the feed. The permeation test was conducted under transmembrane pressure of 1 bar with stirring rate of 400 rpm. The first 3 mL was discarded and the permeation time and solvent volume of the following permeate was recorded. The permeance p of PPN membrane was calculated using Equation (2), where V is solvent volume, A is effective area of membrane, t is time, Δp is TMP.

$$p = \frac{V}{A.t.\Delta p} \quad [unit: L \ m^{-2}h^{-1}bar^{-1}] \qquad (2)$$

The permeability P, which reveals the intrinsic property of materials, of PPN membrane was calculated using Equation (3), where p is permeance and l is thickness of membrane.

 $P = pl \quad [unit: L m^{-2}h^{-1}bar^{-1}m] \quad (3)$



Figure S2. Photographic image of a *p*-PPN membrane performing OSN in a solvent resistant cell. A PPN membrane was placed in the bottom of a dead-end solvent resistant stirred cell. The feed solution in the cell was rose bengal in methanol. Colorless permeate was collected in a 20 mL vail. The tube on top of cell connected with a N_2 cylinder to add a transmembrane pressure.

3. AFM Analysis

Atomic Force Microscopy (AFM) images were recorded with a Bruker Dimension S4 Icon AFM in tapping mode and processed by NanoScope Analysis. In order to measure the thickness of film, a scratch was made on the surface of the film to expose the underneath silicon wafer. As shown in Figure S3, the thickness of the thin *p*-PPN and *m*-PPN membranes transferred onto silicon wafers was around 200 nm.



Figure S3. Thickness of a, b) p-PPN and c, d) m-PPN thin membranes measured by AFM.



Figure S4. Top-view AFM of a) *p*-PPN and b) *m*-PPN membranes (thick or thin?)

Table S1.	Roughness	of <i>p</i> -PPN,	, <i>m</i> -PPN, <i>tri</i> -PPN	membranes m	easured by AFN	A (thick or thin?	')
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	Rq	Ra
p-PPN	19 nm	15.1 nm
m-PPN	15.9 nm	12.8 nm
tri-PPN	19.1 nm	16.55 nm

4. SEM analysis

Field-emission scanning electron microscopic (SEM) images were collected using the FEI Quanta 600 FE-SEM at 20 kV. Film samples were taped on double side carbon tape and were coated with iridium prior tests. Thickness of the PPN thin membrane can be controlled by turning the concentration of monomer solution. When the concentration was increased (from 15 mg/mL to 30 mg/mL), the thickness of membrane was also increased (from 150 nm to 360 nm, see **Figure S4**).



Figure S5. Cross section SEM image of *tri*-PPN membrane fabricated from 30 mg/mL of 1,3,5-triacetylbenzene solution



Figure S6. Top and cross-section views of a, c) *m*-PPN and b, d) *tri*-PPN membranes for OSN tests. Cross-section view of e) *p*-PPN membrane with high magnification.

The thickness of PPN membranes used for OSN were around 100 μ m, shown in Figure S6 c, d. The surface view showed that no large pin-holes visible under SEM can be found. Under high magnification, cross-section view of PPN membranes still showed symmetric features.

5. Photographic Images



Figure S7. Photographic images of the freestanding a) *m*-PPN and b) *tri*-PPN membranes (4.7 cm in diameter) on top of worded white paper.

6. Contact angle analysis



Figure S8. Contact angle of a) *p*-PPN, b) *m*-PPN, and c) *tri*-PPN membranes.

The contact angles of PPN membranes were in the range of 106.8° to 108.9°, demonstrating the hydrophobic nature of the membranes. These values are similar to typical smooth surfaces composed of aromatic hydrocarbons.

7. FT-IR spectra



Figure S9. Full FTIR spectra of membranes of a) *p*-PPN, b) *m*-PPN, and c) *tri*-PPN.

8. Powder X-ray diffraction tests of PPN membranes



Figure S10. Powder X-ray diffraction of *p*-PPN, *m*-PPN and *tri*-PPN.

9. Porosity and pore size distribution of PPN membranes

Membranes BET surface area		Langmuir surface area	Pore volume	
<i>p</i> -PPN	802 m ² /g	928 m²/g	$0.28 \text{ cm}^{3}/\text{g}$	
<i>m</i> -PPN	734 m ² /g	1071 m ² /g	$0.33 \text{ cm}^{3}/\text{g}$	
tri-PPN	1235 m ² /g	1440 m ² /g	$0.47 \text{ cm}^{3}/\text{g}$	

 Table S2. Porosity of p-PPN, m-PPN, tri-PPN membranes



Figure S11. Pore size distribution of membranes of a) *p*-PPN, b) *m*-PPN, and c) *tri*-PPN, calculated based on DFT method.



Figure S12. Estimated pore size from ideal structure of a) *p*-PPN b) *m*-PPN, and c) *tri*-PPN by Chem3D.

10. Organic solvent nanofiltration performance



Figure S13. UV-vis spectra of feed permeate and retentate of dye molecules before and after OSN by *p*-PPN membranes. a) rose bengal, b) brilliant blue, c) congo red, d) bromothymol blue, e) rhodamine B, f) fluorescein

Dye Molecules	Structure	Molecular weight (g/mol)	Dimension (Å)	Rejection (p-PPN)	Rejection (<i>m</i> -PPN)	Rejection (<i>tri</i> -PPN)
Rose Bengal		1017	14.9 × 14.9	99.2 %	98.1 %	97.3 %
Brilliant Blue	$\begin{array}{c} \vdots \\ \vdots $	820	23.0 × 28.0	99.1 %	98.6 %	98.9 %
Congo Red		697	12.9 × 28.3	99.5 %	99.7 %	99.7 %
Bromothy mol Blue	HO Br HO HO HO Br HO HO HO HO HO HO HO HO HO HO HO HO HO	624	12.0 × 14.8	98.9 %	80.2 %	87.5 %
Rhodamine B	H ₃ C N CF CH ₃ H ₃ C N CH ₃ C CF CH ₃ C CH ₃	479	13.9 × 16.5	47.7 %	80.5 %	40.5 %
Fluorescein	нососон	332	11.8 × 12.4	1.3 %	3.9 %	1.2 %

Table S3. Summary of dye molecules size and average rejection of PPN membranes

Membrane	Name	Rejection to Brilliant Blue (%)	Permeance of methanol (L m ⁻² h ⁻¹ bar ⁻¹)	Thickness	Permeability (L m ⁻² h ⁻¹ bar ⁻¹ m x 10 ⁻⁷)	Ref
	<i>p</i> -PPN	99.1	4.57	121 µm	5530	
Aromatic PPN	<i>m</i> -PPN	98.6	4.47	118 µm	5593	This work
	tri-PPN	98.6	7.10	102 µm	7242	
	<i>p</i> -CMP	99	22.5	42 nm	9.45	
СМР	<i>m</i> -CMP	97	16.4	45 nm	7.38	1
	o-CMP	85	21	44 nm	9.24	
Polyarylate	PAR-BHF	98	8.0	20 nm	1.6	
	PAR- TTSBI	99.9	6.0	20 nm	1.2	2
	PAR- DHAQ	100	0.6	20 nm	0.12	
	PAR-RES	99.7	0.6	20 nm	0.12	
CD	β-CD	98.6	4.9	95 nm	4.66	3
COF	ТрВру	94	108	2.1 µm	2270	4
	TpAzo	90	188	5.3 μm	9964	

Table S4. Summary of OSN performance of aromatic PPN membranes compared with other state-of-art polymer membranes



Figure S14. Plot of permeance of solvent against a) molecular diameter of solvents, b) combined solvent properties (Hansen solubility parameter x 1/viscosity x 1/(molecular diameter)^2), and c) dielectric constant.^{5, 6}



Figure S15. Flux of a) methanol, b) toluene, and c) THF vs transmembrane pressure relationship of p-PPN membrane.

11. Chemical stability and OSN in harsh conditions



Figure S16. FTIR of pristine *p*-PPN membrane and *p*-PPN membranes treated by extreme conditions for 5 days. The conditions were 18 M H₂SO₄, 14 M NaOH in water/methanol, 0.1 M chromic acid, and 2 M NaBH₄ in methanol.



Figure S17. Surface morphology of and *p*-PPN membranes treated by extreme conditions for 5 days. The conditions are 18 M H₂SO₄, 14 M NaOH in water/methanol, 0.1 M chromic acid, and 2M NaBH₄ in methanol.



Figure S18. The rejection and permeance of congo red in methanol after p-PPN membrane soaking in $18 \text{ M} \text{ H}_2\text{SO}_4$ for 2 days and the rejection and permeance of rose bengal in methanol after p-PPN membrane soaking in 5M MeONa for 2 days.



Figure S19. Long-term OSN test of *p*-PPN membrane filtrating ethanol solutions of a) brilliant blue in the presence of PTSA and b) congo red in the presence of NaOH.

OSN membrane	polymer	MWCO (g/mol)	Solvent / permeance (L m ⁻² h ⁻¹ bar ⁻¹)	Continuous operation	Clean tolerance
PPN membrane	PPN	600	MeOH / 4.6	10 mM NaOH / PTSA in IPA	18 M H ₂ SO ₄ / 5M NaOMe
Puramem® S600	polyimide	600	MeOH / 0.23 ⁷	pH =7	-
Duramem® 500	polyimide	500	MeOH / 1.46 ⁷	pH =7	-
Duramem® 500	polyimide	900	MeOH / 1.56 ⁷	pH =7	-
Solsep® NF 030705	PDMS	500	ACN / 0.2 ⁸	pH = 2-10.5	-
Solsep® NF 090801	PDMS	350	ACN / 0.9 ⁸	-	-
Filmtec [™] NF270	polyamide	200-400	ACN / 11 ⁸	pH = 2-11 *	pH = 1-12 *
Starmem® 240	polyimide	400	Ethanol / <1 ⁹	-	-

Table S5. Summary of OSN performance in harsh condition of aromatic PPN membranes

 compared with commercial membranes

* The performance of Filmtec NF270 was tested in aqueous solution instead of in organic solution.

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