

Supplementary Information

Assembling covalent organic framework membranes via phase switching for ultrafast molecular transport

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1. Materials and Methods

Reagents, Solvents and Materials

1,3,5-triformyl phloroglucinol (TFP), 1,3,5-triformylbenzene (TFB), 1,4-phenylenediamine (PDA) and methylene blue (MeB) were purchased from HEOWNS chemicals Co., Ltd. 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (TTA), acetic acid, N, N-Dimethylacetamide (DMAC), o-dichlorobenzene (DCB) and n-butanol (BuOH) were purchased from Meryer Chemical Technology Co., Ltd. Alcian blue (AB), Congo red (CR) protoporphyrin IX, (PPh-IX), methyl blue (MB), and orange G (OG) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Indium tin oxide (ITO) coated glasses support were purchased from Luoyang Guluo Glass Co., Ltd. PTFE substrates were provided by Haining Chuangwei Filter Equipment Company Co. Ltd. All chemicals were used as received without further processing. Milli-Q water purification system was used to prepare Deionized water (DI water).

Methods

Phase switching strategy using two-steps procedure

Pre-assembly step in liquid phase toward pristine membranes

For the fabrication of ≈ 150 nm ultrathin membranes, TFP (2.10 mg, 0.01 mmol), 1,3,5-triformylbenzene (TFB, 1.62 mg, 0.01 mmol), PDA (1.62 mg, 0.015 mmol), TTA (3.54 mg, 0.01 mmol) were dissolved in separate vials in DMAc. DMAc was chosen in this step due to high solubility of amine and aldehyde monomers in DMAc which reduces reaction volumes (TFP ≈ 23 mg/ml, PDA ≈ 25 mg/ml and TTA ≈ 17 mg/ml) and relatively high boiling point of DMAc, which wins sufficient evaporation time for the completion of the polymerization at this step. Next, the mixed solution containing TFP/PDA, TFP/TTA or TFB/PDA was poured on Indium Tin Oxide (ITO) coated disk; the solvents were evaporated at 60 °C to obtain pristine membranes. For the fabrication of thicker membranes, the concentration of monomers was increased keeping the same molar ratio.

Assembly step in vapor phase toward COF membranes

The pristine membranes from the pre-assembly step were placed on top of a glass bottle in a Teflon lined autoclave. Solvents (oDCB, BuOH) and catalyst (AcOH) in a volumetric ratio of 1:1:0.1

were poured on bottom of the Teflon vessel, at least 5 cm below the membrane surface. The whole assembly was heated at 145 °C for 18 h to obtain COF membranes. Free- standing COF membranes were obtained by etching ITO layer through dilute HCl.

Solvothermal strategy

The pristine membrane from the pre-assembly step was also treated in the liquid phase containing oDCB, BuOH and AcOH in a volumetric ratio of 1:1:0.1, and heated at 145 °C for 18 h. Free-standing COF membranes were obtained by etching ITO layer through dilute HCl.

Characterization

The Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max 2500v/pc equipment in the range of 3-35°. The membranes were etched and mounted on the XRD holder for characterization. The XRD simulations of all COF membranes were carried out using Reflex module of Materials Studio (MS) software. High resolution transmission electron microscopy (HTEM) (Tecnai G2 F20) was employed to obtain high resolution diffraction pattern of samples. The membranes were crushed in ethanol and drop casted on Ultrathin Carbon Film on Lacey Formvar/Carbon Films (Beijing Zhongjingkeyi Technology Co.,Ltd. BZ11032a) TEM grids. The Fourier transform infrared (FT-IR) spectra were recorded at a arrange from 500-4000 cm⁻¹ on a BRUKER Vertex 70 spectrometer. Scanning Electron Microscopy (SEM) images were observed by field emission scanning electron microscope (Nanosem 430). N₂ adsorption/desorption isotherms were recorded on PS2-1055-B gas adsorption analyzers at 77 K using a liquid nitrogen bath. Several membranes were first fabricated and then grinded for porosity evaluation. All the membrane samples were degassed at 120 °C for 6 h under vacuum before N₂ analysis. For X-ray photoelectron spectroscopy (XPS) characterizations, the membranes were directly mounted on holders and characterized.

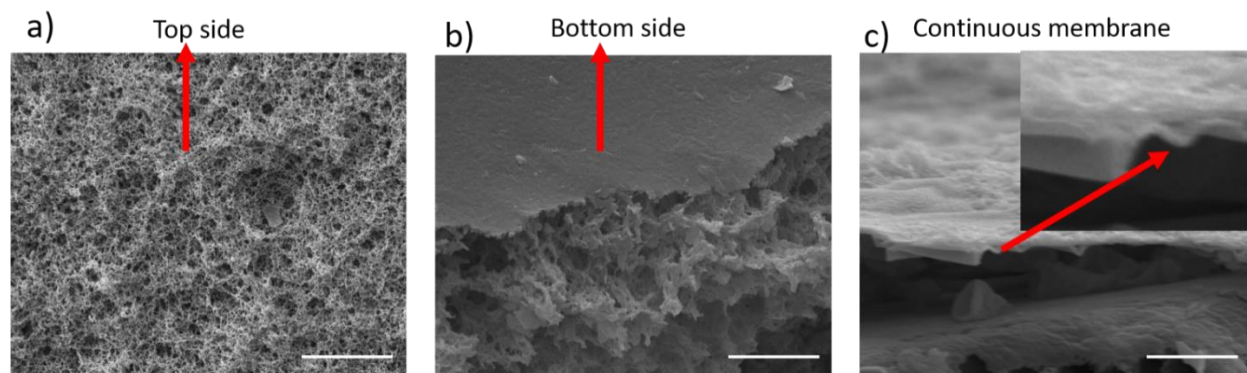
Performance evaluation

Molecular transport experiments

A lab made dead-end filtration cell (active area of 4.1 cm²), equipped with magnetic stirrer and nitrogen flow for pressure maintenance, was used for molecular transport. DI water was used for water transport while reagent grade organic solvents were used for organic solvent nanofiltration

experiments. All dyes except (PPH-IX, dissolved in ethanol)) were dissolved in water for molecular separation. The concentration of dyes ranged from 50-1000 ppm. The permeance was stabilized by using an initial pressure of 3.5 bar. To make sure that the COF membranes do not act as adsorbent¹, the first 10 ml permeate of each test was discarded and then the concentration in the permeate was calculated at different intervals (10ml each for 20 cycles). Similarly, the permeance was also recorded at different pressures ranging from 0.5-3.5 bar. Long term water permeance was obtained by recording data at various intervals at 1 bar. Similarly, the performance was evaluated at various cycles of operation. After each cycle, the membrane was washed with water before next cycle.

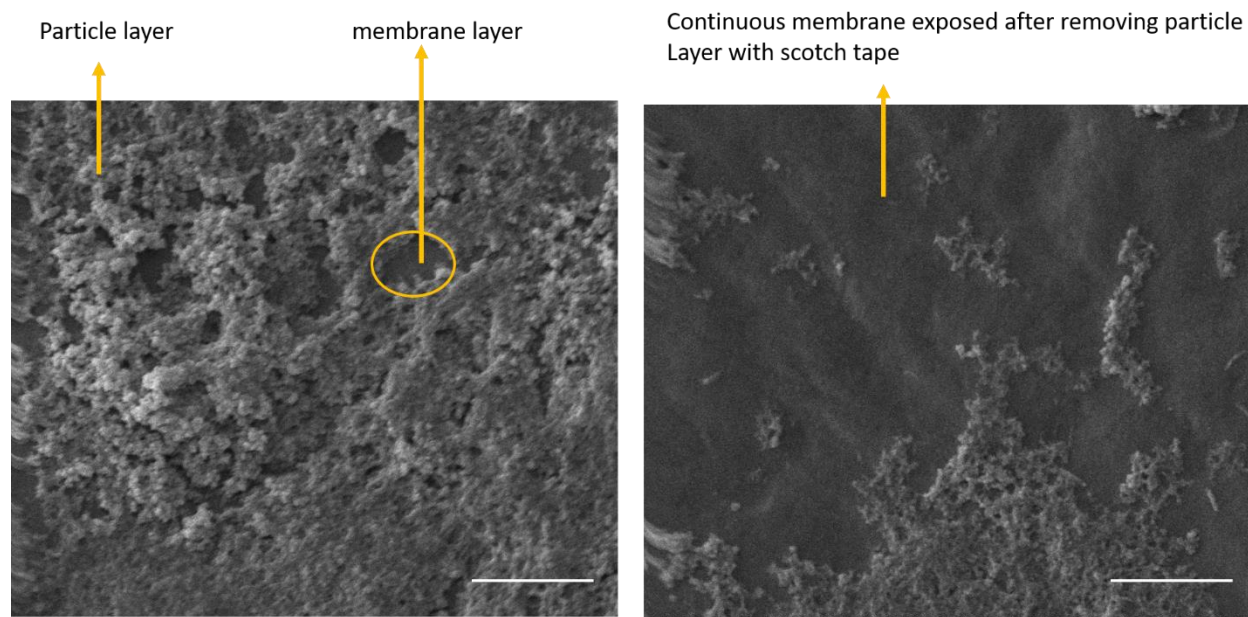
2. Supplementary Figures



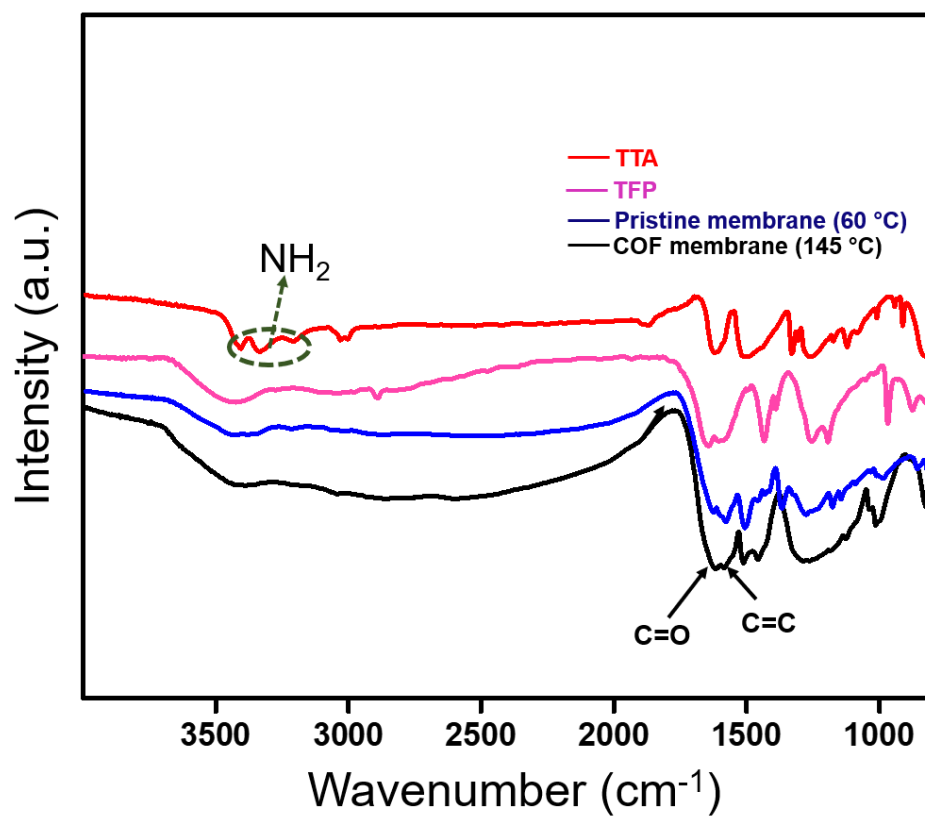
Supplementary Fig. 1. SEM image of thick membranes showing (a) the top and (b) bottom surface of COF membranes. (c) represents the ultra-thin membranes obtained after removing the top layer through adhesive tape. Scale bar, (a) 50 μm , (b, c) 1 μm .



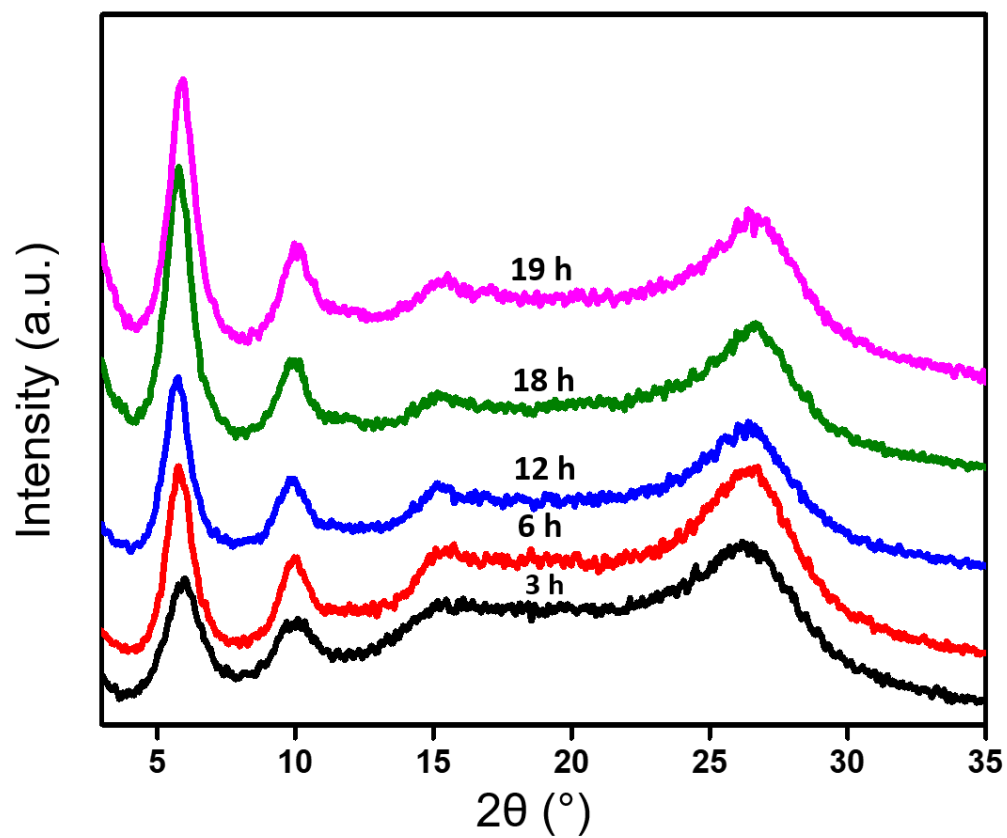
Supplementary Fig. 2. Digital photos of removing the top layer using adhesive tape.



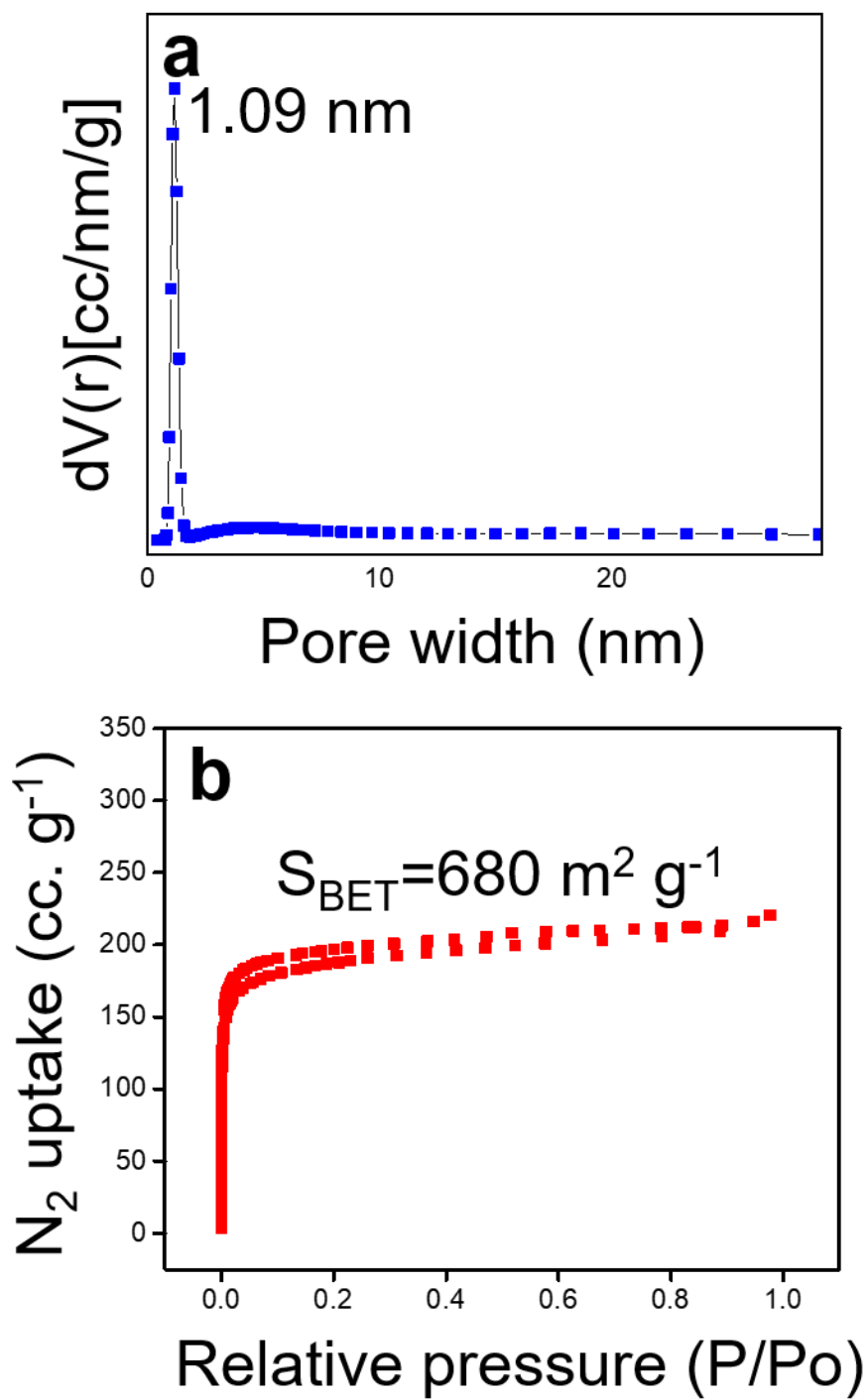
Supplementary Fig. 3. SEM of membranes top and bottom layer; before and after removing the top layer with adhesive tape. (Scale bar, 2 μm).



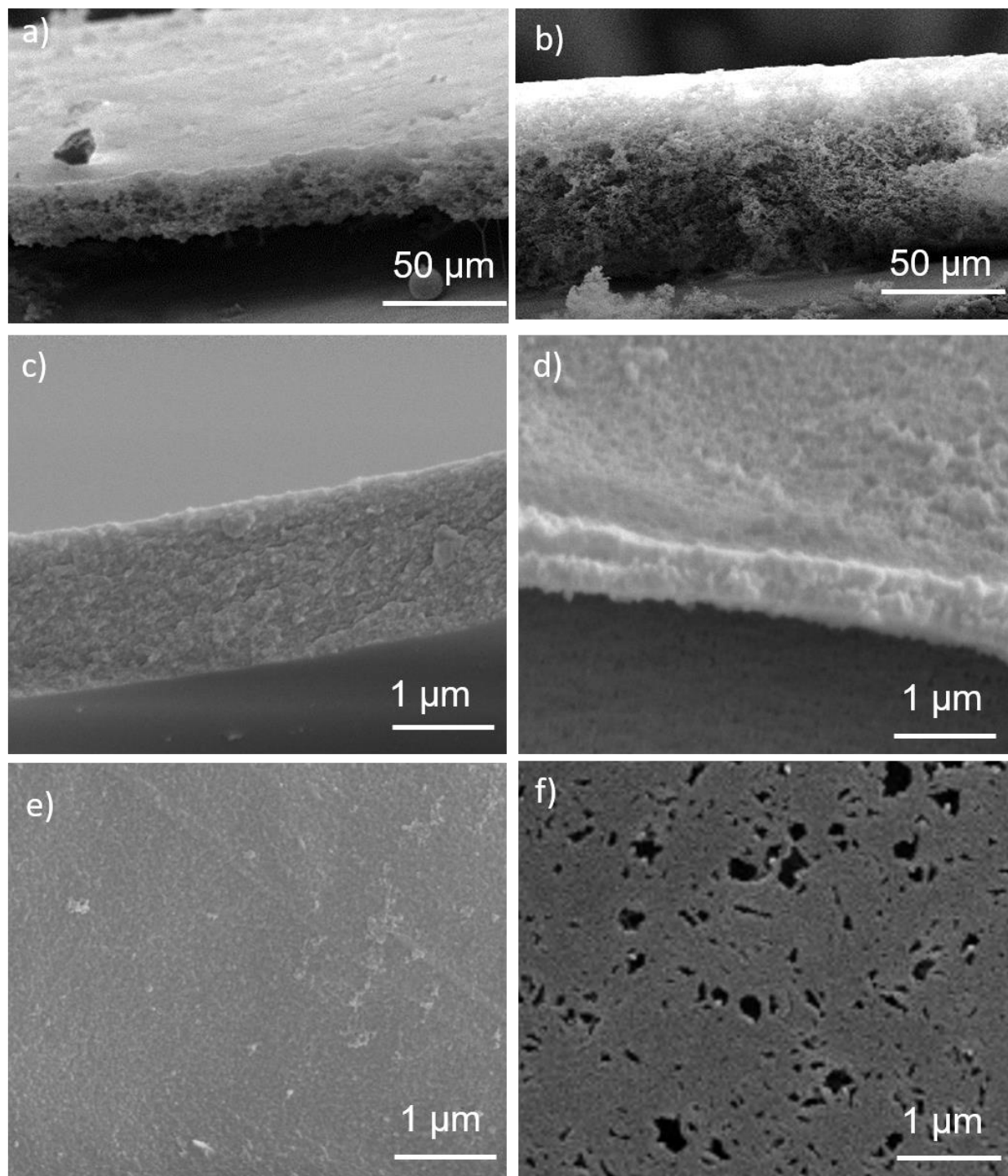
Supplementary Fig. 4. FT-IR of the TFP and TTA monomers, TFP-TTA pristine and COF membrane.



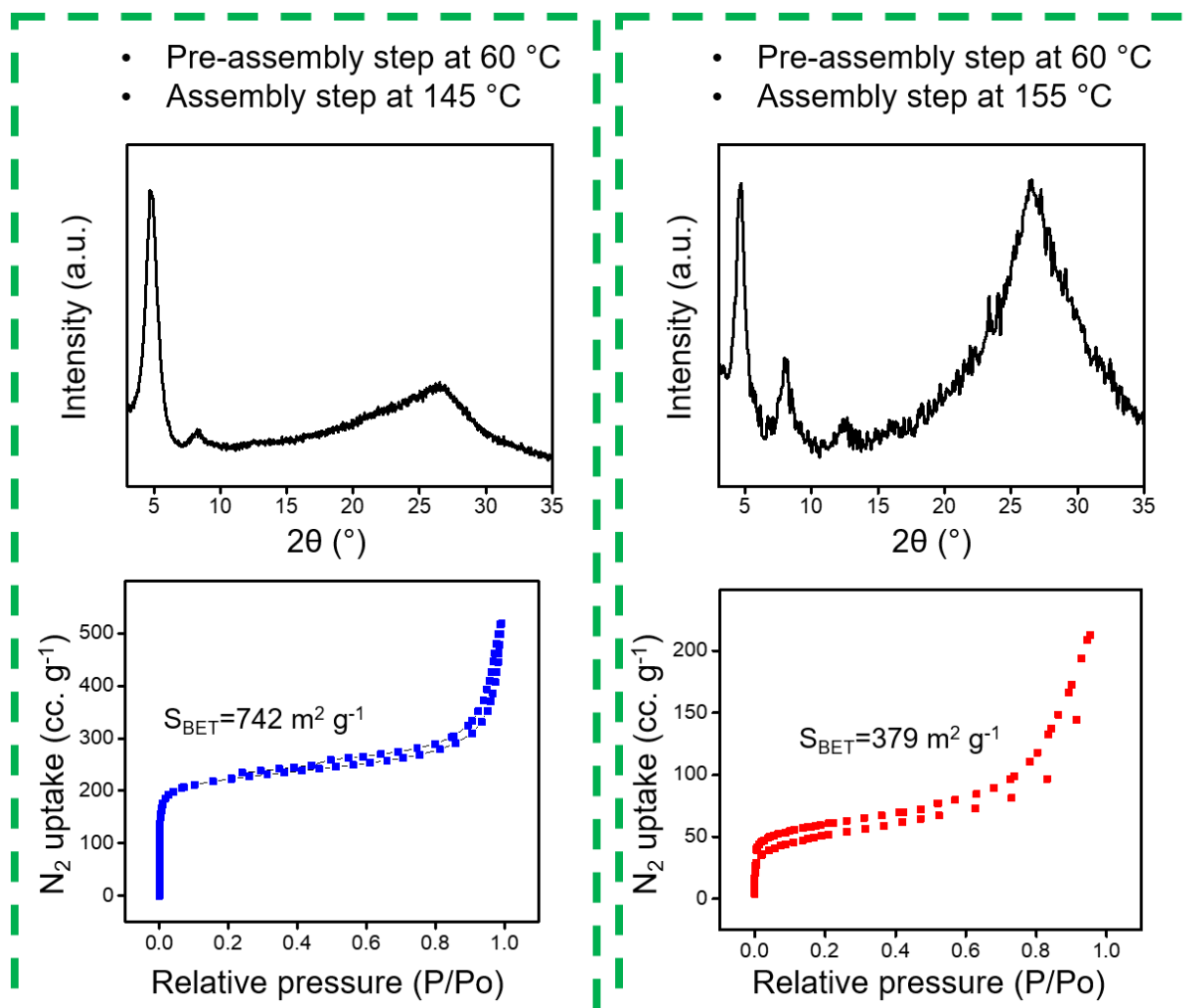
Supplementary Fig. 5. Time dependent XRD of TFP-TTA membranes at different time intervals. The intensity of peak at lower 2θ value increases with time and remains similar after 18 h.



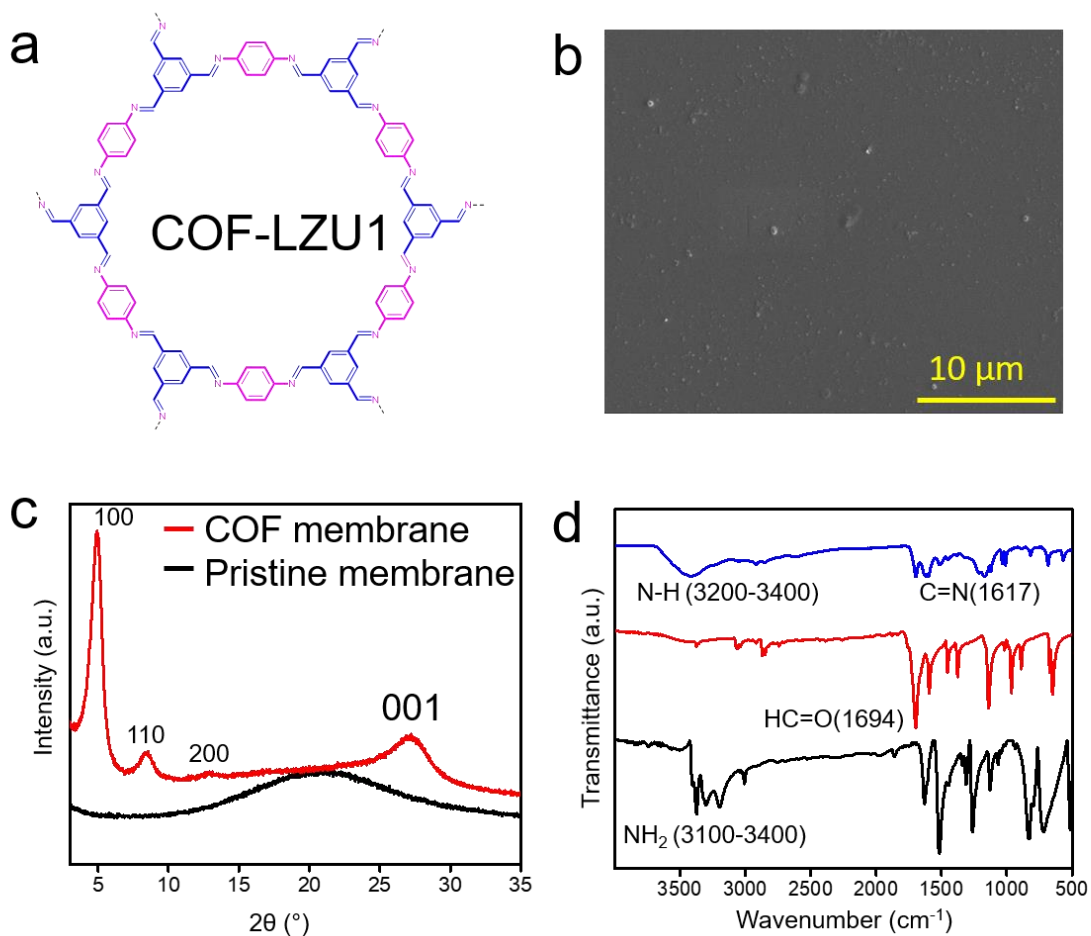
Supplementary Fig. 6. BET of TFP-TTA membrane showing pore size (a) and surface area (b).



Supplementary Fig. 7. SEM of TFP-PDA membranes. a) phase-switching strategy, b) solvothermal strategy. Membranes after removing the top layer through adhesive tape, c) phase-switching strategy, d) solvothermal strategy. surface of membranes, e) phase-switching strategy, f) solvothermal strategy.



Supplementary Fig. 8. XRD and BET surface area of TFP-PDA membranes pre-assembled at 60 °C, (left) assembled at 145 °C, (right) assembled at 155 °C.



Supplementary Fig. 9. (a) COF-LZU1 chemical structure, (b) SEM exhibiting large defect-free area of the membrane, (c) XRD of the pristine and COF-LZU1 membranes, (d) FT-IR spectra of 1,4-diaminobenzene (black), 1,3,5-triformylbenzene (red), and COF-LZU1 membrane (blue).

3. Supplementary Tables

Supplementary Table 1. Molecular transport and separation evaluation of TFP-PDA membranes after specified time, prepared at various temperatures.

Time (h)	125 °C		135 °C		145 °C		155 °C	
	Permeance ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	CR rejection (%)	Permeance ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	CR rejection (%)	Permeance ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	CR rejection (%)	Permeance ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	CR rejection (%)
0	800 ±10	55±3	799±12	55±2	798±7	52±2	804±12	54±3
3	759±9	57±4	751±10	59±3	743±6	55±2	712±7	71±3
6	700±11	58±3	633±11	63±3	675±7	63±2	633±8	78±3
9	641±10	61±3	612±12	69±3	581±5	68±1	458±9	80±4
12	613±9	68±2	533±13	76±2	539±5	72±2	399±7	82±2
15	593±7	71±2	475±10	79±3	475±4	86±1	302±8	84±3
16	561±6	73±3	462±9	81±2	434±4	95±2	275±7	89±2
17	552±6	75±2	451±7	82±3	419±2	98±1	209±8	91±3
18	513±5	78±3	444±5	83±2	403±4	99±1	173±9	99±2
19	497±6	82±3	429±6	84±2	389±2	99±1	162±6	99±2
22	463±4	86±1	415±4	85±2	353±2	99±1	148±8	99±3

Supplementary Table 2. Molecular transport and separation evaluation of TFP-TTA membranes after specified time, prepared at various temperatures.

Time (h)	125 °C		135 °C		145 °C		155 °C	
	Permeance ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	CR rejection (%)	Permeance ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	CR rejection (%)	Permeance ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	CR rejection (%)	Permeance ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	CR rejection (%)
0	793 ±12	42±8	793±12	43±7	795±13	43±8	794±12	43±8

3	731±8	47±8	711±10	51±9	699±6	57±2	674±8	64±5
6	682±11	51±6	648±11	54±6	614±6	66±2	588±7	75±4
9	611±9	58±6	598±11	63±5	534±5	70±1	439±7	83±4
12	554±8	62±4	521±12	77±6	500±6	79±2	327±7	88±3
15	515±8	65±4	455±9	81±3	415±4	86±1	271±9	92±4
16	489±7	68±3	437±7	84±3	379±4	90±2	200±8	98±2
17	446±5	75±3	400±6	88±4	338±3	99±1	131±6	99±3
18	405±4	80±3	367±5	92±3	309±3	99±1	102±7	99±2
19	377±4	85±3	351±5	94±3	281±3	99±1	91±5	99±2
22	325±4	90±2	312±4	97±3	218±3	99±1	72±4	99±2

Supplementary Table 3. Molecular transport performance of reported membranes based on COFs.

COF system	Fabrication method	Permeance ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	Reference number
TFP-PDA	Phase-switching	Water=403 Acetonitrile=519	(This work)
TFP-PDA	Solid-vapor IP	Water=411 Acetonitrile=589	²
Tp-Bpy	Liquid-liquid IP	Water=211 Acetonitrile=339	³
M-TpTD	Solvothermal (<i>In-situ</i>)	Water=189 Acetonitrile=278	⁴
COF-LZU1	Solvothermal (<i>In-situ</i>)	Water=76	⁵
COFM	Solvothermal (Exfoliation)	Water= 178 Acetonitrile=280	⁶
TFP-DHF	Liquid-air IP	Water= 90 Acetonitrile=130	⁷

EB-COF:Br	Exfoliation	Water=48	8
GO-CTN	Exfoliation	Water=226	9
COF/PSF	Liquid-Liquid IP	Water=50	10
TpTG _{Cl}	Exfoliation	Water=31	11

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