Electronic Supplementary Material (ESI) for Nanoscale Advances.

Porous Hydrogen-Bonded Organic Membrane for High-Performance Molecular Separation

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1. Materials and Instrumentation

1.1 Materials and chemicals

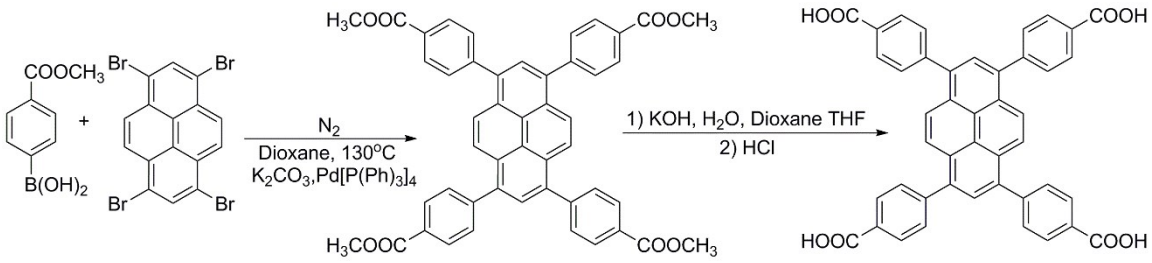
Unless otherwise mentioned, all reagents and solvents were purchased from commercial sources and used as received without further purification. 4-(methoxycarbonyl)phenyl)boronic acid (98%) and 1,3,6,8-terabronopyrene (98%) were obtained by Energy Chemical company. Palladium tetrakis(triphenylphosphine) with 9.2% Palladium ($Pd(PPh_3)_4$) was bought from Tansoole company. N,N'-dimethylformamide (DMF), ethanol (EtOH), acetone, hydrochloric acid (HCl), tetrahydrofuran (THF), 1,4-dioxane, potassium hydroxide (KOH), potassium carbonate (K_2CO_3), and n-hexane (>99.5%) were purchased by Sinopharm Chemical Reagent Co. Ltd (China). Polyethersulfone (PES) macrofiltration membrane with average pore size of 22 μm were purchased from Titan Co. Ltd China. Piperazine (PIP, 99%), 1,3,5-benzenetricarbonyl trichloride (TMC, 98%), and all dyes (methyl blue, rhodamine B, Congo red, calcein and coomassie brilliant blue) were purchased from Shanghai Aladdin Reagent Co., Ltd. The deionized water was obtained by Ulupure equipment.

1.2. Instrumentations

PXRD was performed on Rikagu Miniflex 600 Benchtop X-ray diffraction instrument. SEM was performed on JSM6700-F Field Emission Scanning Electron Microscope and Phenom Pharos Scanning Electron Microscope. The N_2 gas isotherms of the samples were measured using ASAP 2460 from Micromeritics Co. Ltd. UV-Vis absorbance of liquid samples were collected at room temperature on a Shimadzu UV-2550 spectrophotometer. Diffuse reflectance infrared Fourier transform spectroscopy (FTIR-DRIFTS) over the samples were performed on a Nicolet 6700 spectrometer. The Zeta potential was obtained by the BI-200SM Laser Particle Size and Zeta Potential Analyser. The membrane separation equipment was purchased from Nanjing Hope Analytical Equipment Co. Ltd (China). The salt concentration was measured with an ion chromatography on 863 compact autosampler and 850 chromatographic column from Metrohm Herisau Switzerland (China).

2. Experimental section

2.1. Ligand Synthesis



Scheme S1. Synthetic routine of the H_4TBAPy ligand.

Synthesis of 1,3,6,8-tetrakis(4-(methoxycarbonyl)phenyl) pyrene.

A mixture of (4-(methoxycarbonyl)phenyl)boronic acid (5 g, 32.9 mmol), 1,3,6,8-tetrabromopyrene (2.85 g, 5.5 mmol), palladium tetrakis(triphenylphosphine) (0.1 g 0.09 mmol), and potassium carbonate (6 g, 44 mmol) in dry dioxane (100 mL) was stirred under the protection of N_2 for 72 h at 130 °C. The reaction mixture was poured into a solution of ice water and concentrated hydrochloric acid (v/v = 3:1). The organic phase was extracted with chloroform, and the combined extraction was dried over magnesium sulfate. After filtration, the solvent was removed under vacuum to give 3.44 g (4.6mmol) 1,3,6,8-tetrakis(4-(methoxycarbonyl)phenyl)pyrene (yield: 84%).

Synthesis of 1,3,6,8-Tetrakis(benzoic acid)pyrene (H_4TBAPy) Ligand.

1 g (17.8 mmol, 12 equiv) KOH was added to a suspension of 1 g (1.465 mmol) of 1,3,6,8-tetrakis(4-(methoxycarbonyl)phenyl)pyrene in 100 mL of THF/dioxane/H_2O (v/v = 5:2:2), and the mixture was stirred under reflux at 85 °C for 12 hours. The solvent was removed under vacuum, and then 100 mL H_2O was added to the residue. The mixture (yellow clear solution) was stirred at room temperature for 2 h. The pH value was adjusted to 2 using concentrated HCl. The resultant yellow solids were collected by filtration and washed with water several times. After drying under vacuum, 0.88 g (1.29mmol) product was obtained with a yield of 97%. ^{1}H-NMR (DMSO-d6): δ 7.86(d, 8H), 8.08(s, 2H), 8.17(d, 8H), 8.21(s, 4H), 13.14 (s, 4H).

2.2. Synthesis of Nano-PFC-1

H_4TBAPy (10 mg, 0.015 mmol) was dissolved in 1.5 mL of DMF to which 10 mL H_2O was added and stirred for 5 minutes. Then 8.3 mL of EtOH was added to the mixture. The products were separated via centrifugation at 12000 rpm for 15 minutes and further purified with EtOH and acetone for several times.

2.3. Gas Sorption Measurements of Nano-PFC-1.

The N_2 isotherms were measured using ASAP 2460 from Micromeritics Co. Ltd. The as-prepared sample was washed with acetone for 3 times. Then the sample was allowed to soak in acetone for 48 h with the supernatant being replaced by fresh acetone several times during the process to exchange and remove nonvolatile solvates (DMF). After removal of acetone by centrifugation, the samples were activated under vacuum at room temperature, and then dried again in the "outgas" function of instruments at 90 °C for 6 hours prior to gas adsorption. The N_2 isotherm measurements were performed at 77 K to a pressure of 1 bar.

2.4. Preparation of HOF Membranes.

The polyamide composite nanofiltration membrane was prepared by interfacial polymerization. The PES substrate was soaked overnight to remove the glycerin in its pore. The Nano-PFC-1 particles were dispersed in the aqueous phase of PIP with the concentration of 0, 0.1, 0.2, and 0.4 mg/mL, respectively. PIP solution (0.35 w/v%, 10 mL) was dropwisely added to the PES substrate and try to keep the well-dispersed nano-PFC-1 evenly distributed on the PES surface. After standing at room temperature for 15 min, the excess solution was removed, and the membrane was dried under a ventilated environment for 25 min. Then the surface of the membrane was immersed in TMC-n-hexane solution (0.20 w/v%,10mL). The organic solution was removed after 1 min reaction, and the excess organic phase was removed. Subsequently, the membrane was placed in an oven at 70 °C for 10 min and then stored in DI water for use and characterization. TFC, HOF-TFN-1, HOF-TFN-2 and HOF-TFN-4 membranes were prepared by using the above-mentioned method but without addition of PFC-1 for TFC and different amount of Nano-PFC-1 for HOF-TFN-1 (0.1 mg/mL), HOF-TFN-2 (0.2 mg/mL) and HOF-TFN-4 (0.4 mg/mL).

2.5. Gas Sorption Measurements of HOF Membranes.

The HOF membranes were soaked in H_2O for 72 h, and dried under vacuum at 80°C for 7 h. Then the samples were dried again in the "outgas" function of instruments at 80 °C for 10 h prior to gas adsorption.

2.6 Water permeation measurement of HOF membranes

The water permeability of TFC and HOF membranes synthesized in this work were evaluated via a cross-flow filtration apparatus. Typically, to make the system stable, membrane area (9.6 cm^2) were pre-pressurized for 30 min. Afterward, pure water fluxes were recorded.

2.7 Dye separation procedures of HOF membranes

The dye separation of TFC and HOF membranes synthesized in this work were evaluated via a cross-flow filtration apparatus. Dye (methyl blue, rhodamine B, Congo red, calcein and coomassie brilliant blue, 0.25 $mmol \cdot L^{-1}$) retention were tested separately at room temperature. Herein, the concentration of dye was measured with an UV−vis spectrophotometer.

3. SEM photos of HOF membranes

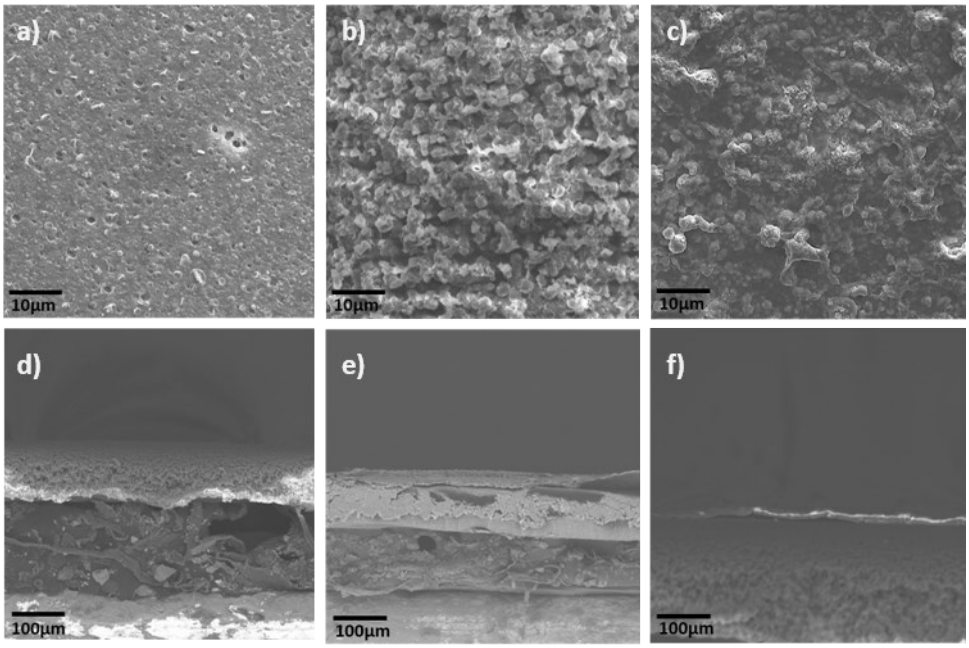


Figure S1. SEM images in both top-view and cross-sectional view of (a, d) HOF-TFN-1, (b, e) HOF-TFN-2, and (c, f) HOF-TFN-4.

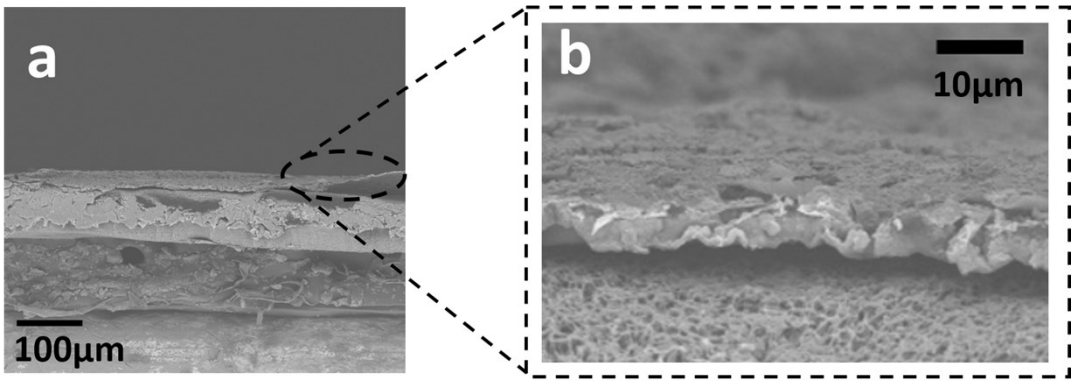


Figure S2. SEM image in cross-sectional view of HOF membrane that shows the thickness is about 7 μm.

4. Water contact of Nano-PFC-1 and HOF membranes

Table S1. Contact angle of water on Nano-PFC-1, PES, TFC, and HOF membranes.

	Water contact angle		Water contact angle
Nano-PFC-1	62.05°	**HOF-TFN-1**	49.93°
PES	43.55°	**HOF-TFN-2**	53.64°
TFC	45.03°	**HOF-TFN-3**	61.72°

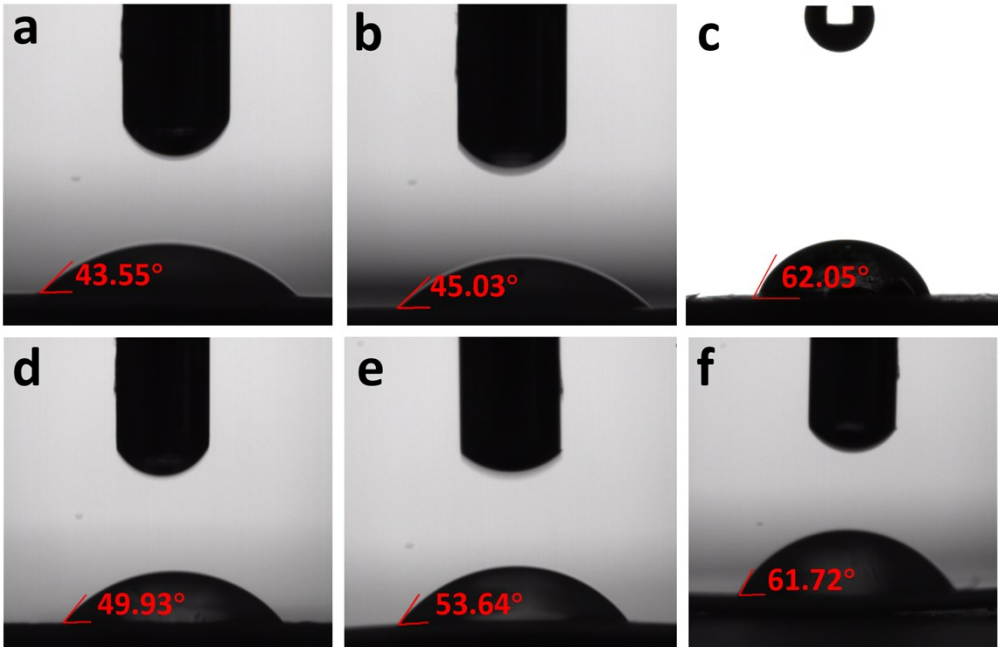


Figure S3. Contact angle of water on (a) PES, (b) TFC, (c) Nano-PFC-1, (d) HOF-TFN-1, (e) HOF-TFN-2, and (f) HOF-TFN-4.

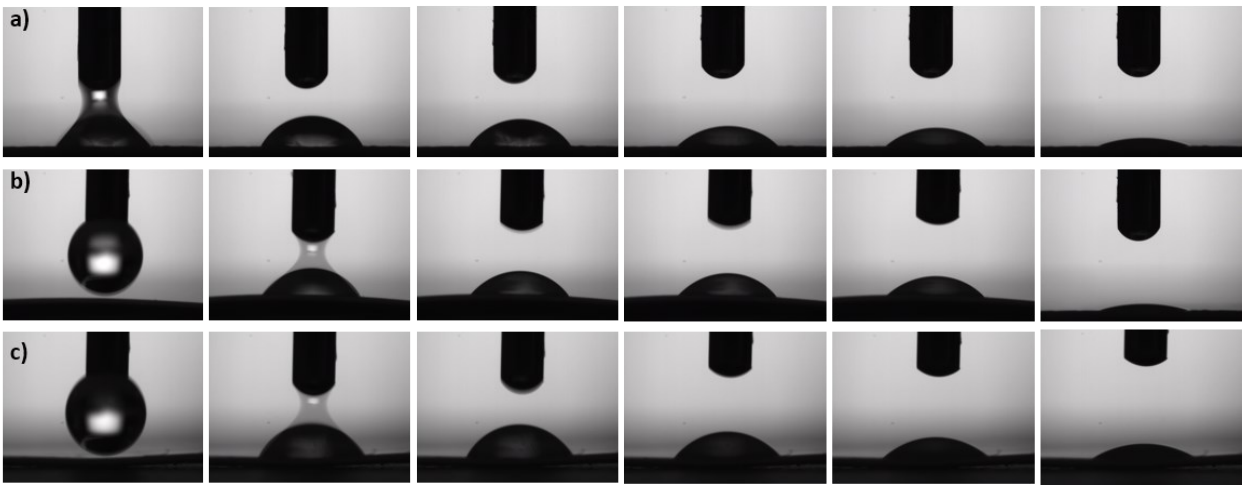


Figure S4. Optical images showing the dynamic spreading and permeating behaviours of a water droplet on the (a) HOF-TFN-1, (b) HOF-TFN-2, and (c) HOF-TFN-4.

5. N_2 isotherm of HOF membrane

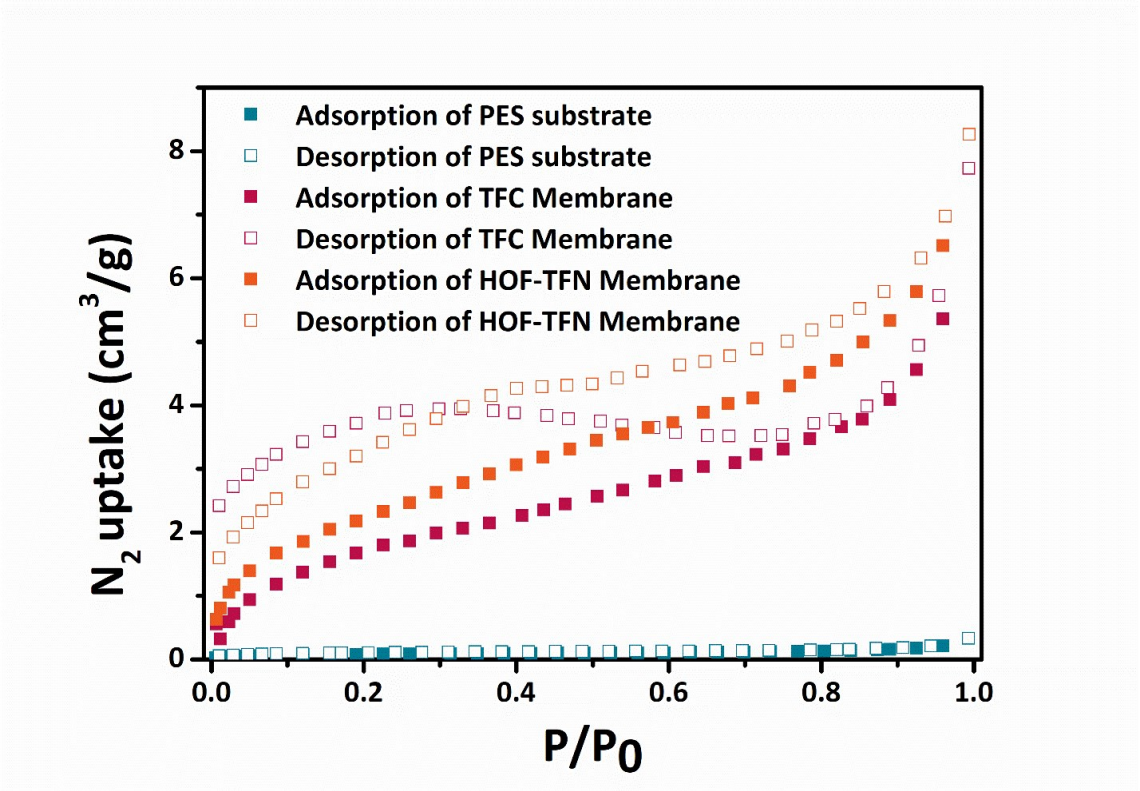


Figure S5. N_2 adsorption at 77K of PES substrate, TFC membrane, HOF-TFN-2 membrane.

6. FTIR-DRIFTS of Nano-PFC-1 and HOF membrane.

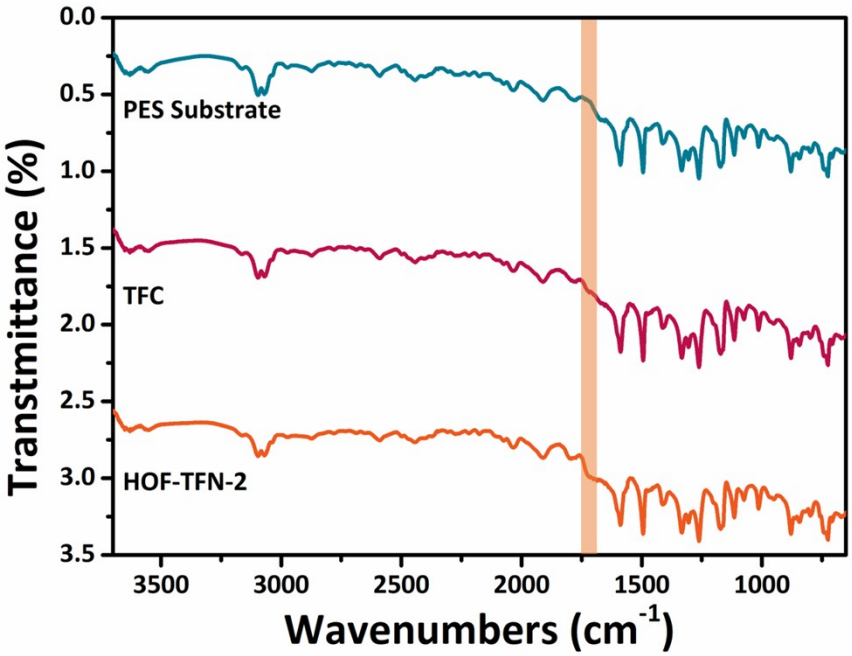


Figure S6. FTIR spectra curves of PES substrate, TFC, and HOF-TFN-2.

7. Zeta potential of Nano-PFC-1

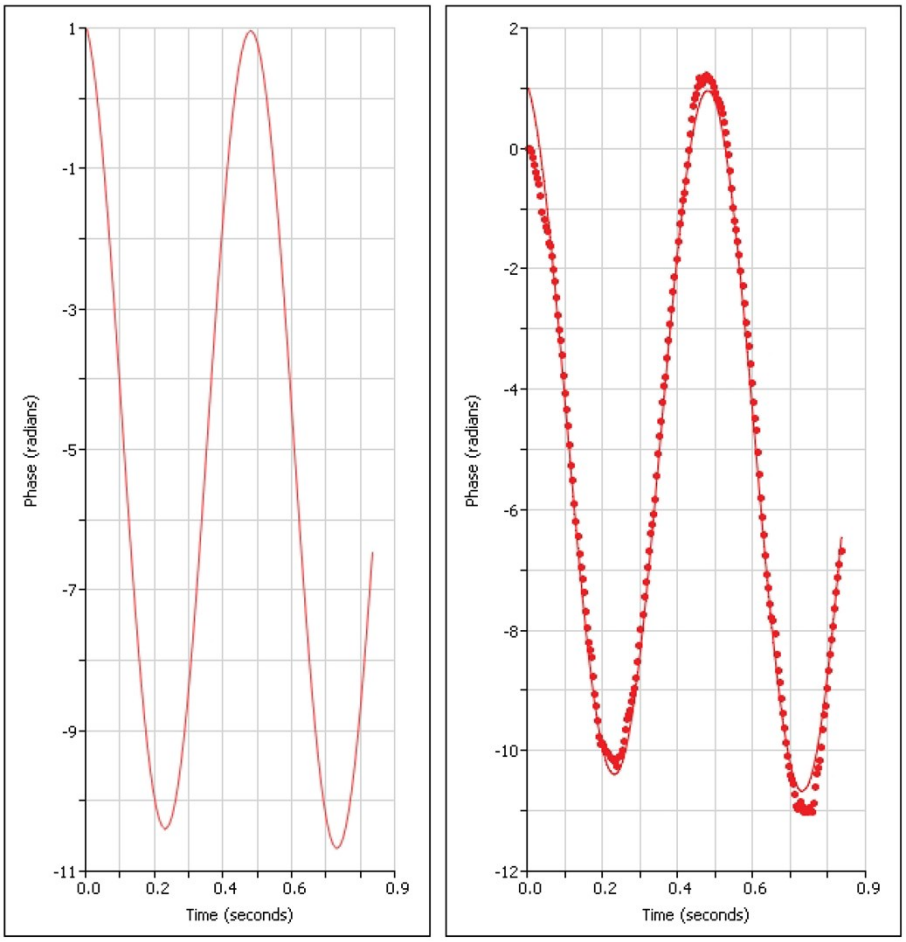


Figure S7. Zeta potential of Nano-PFC-1.

8. PXRD patterns of HOF-TFN membrane.

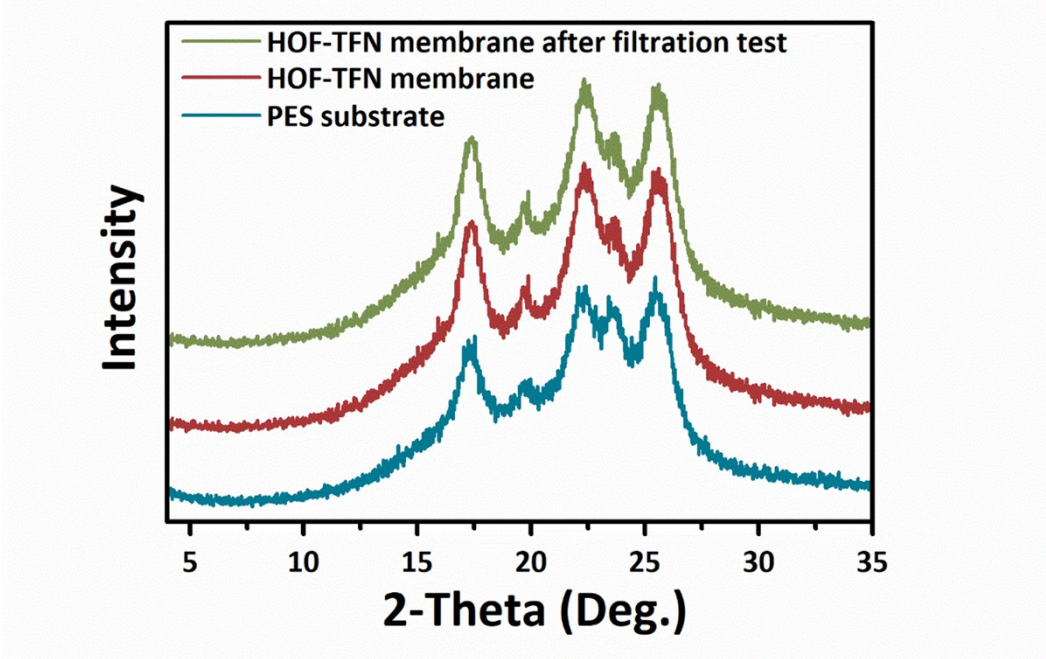


Figure S8. PXRD of PES substrate, HOF-TFN membrane after interfacial polymerization process and HOF-TFN membrane after filtration test.

9. The Tyndall effect of the aqueous suspension containing Nano-PFC-1 and PIP.

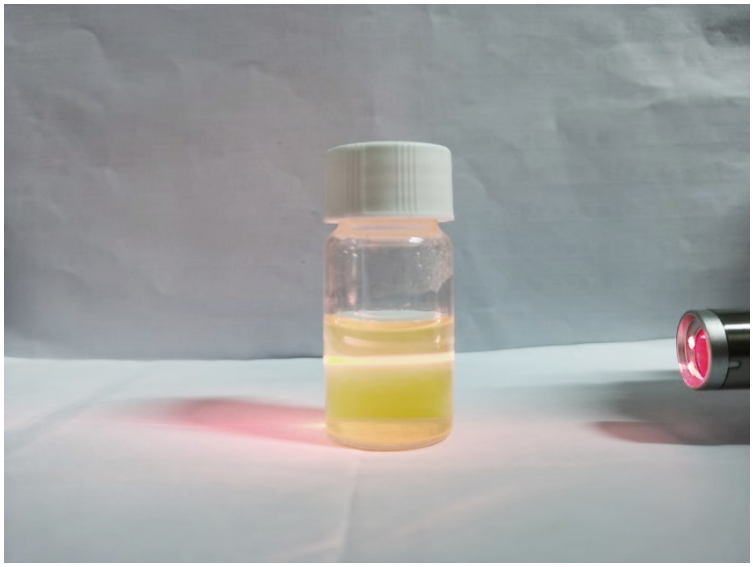


Figure S9. Photo images of the Tyndall effect of aqueous PIP suspension containing Nano-PFC-1

10. Optical photographs of HOF-TFN membrane.

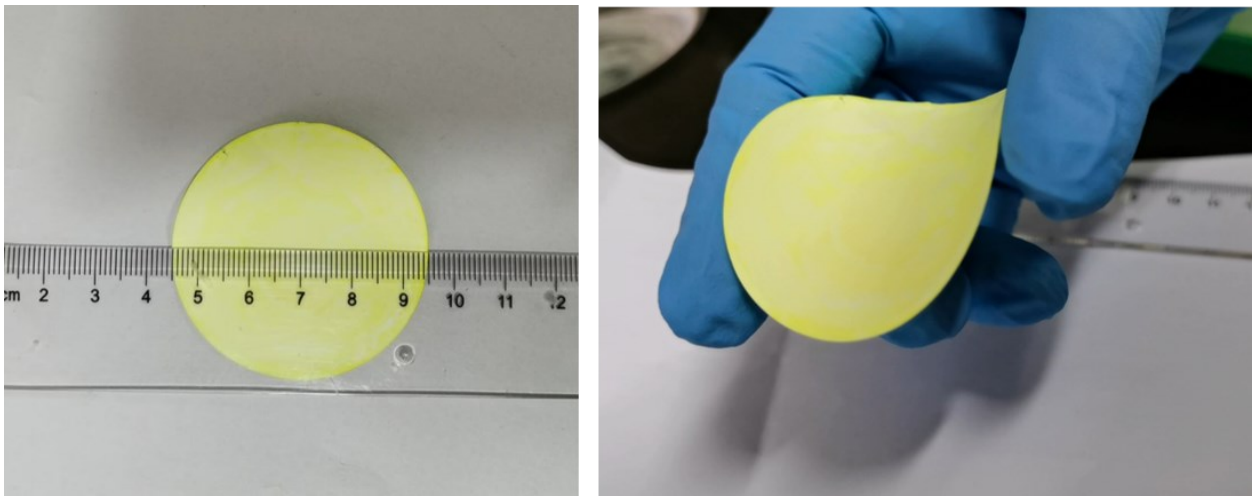


Figure S10. Digital photo of HOF membrane

11. The water permeation and separation performance of HOF membranes

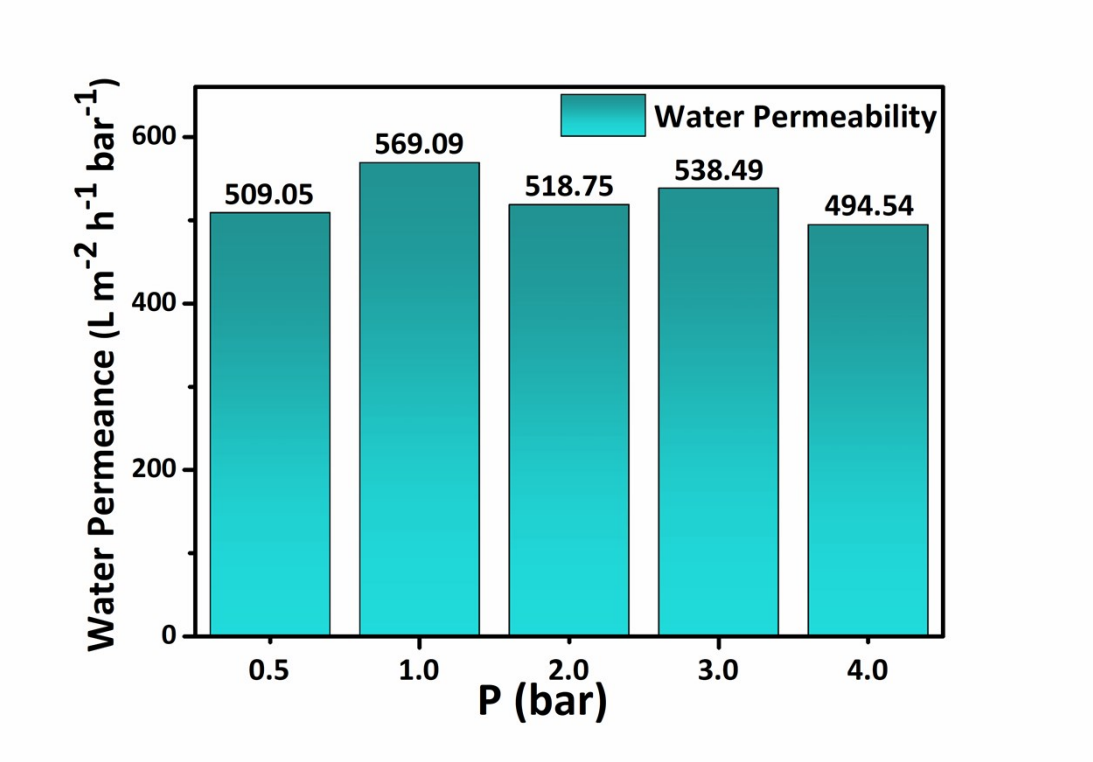


Figure S11. Water flux under different pressure of HOF-TFN-2.

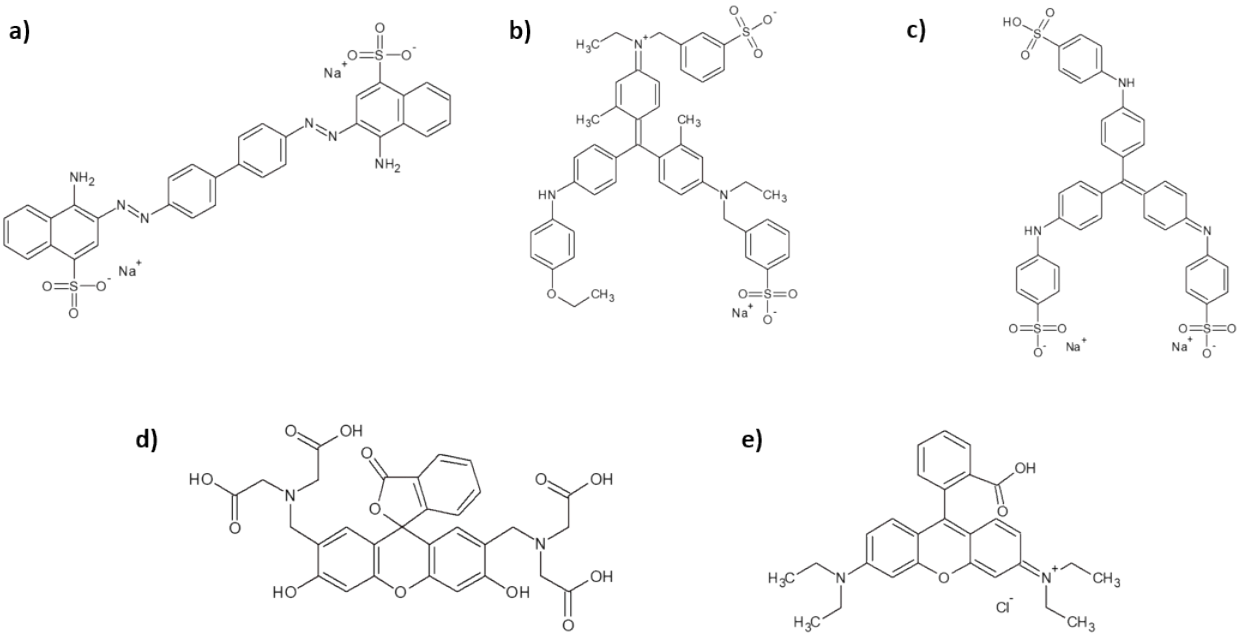


Figure S12. Chemical structure of dyes. (a) Congo red, (b) coomassie brilliant blue, (c) methyl blue, (d) calcein, (e) rhodamine B .

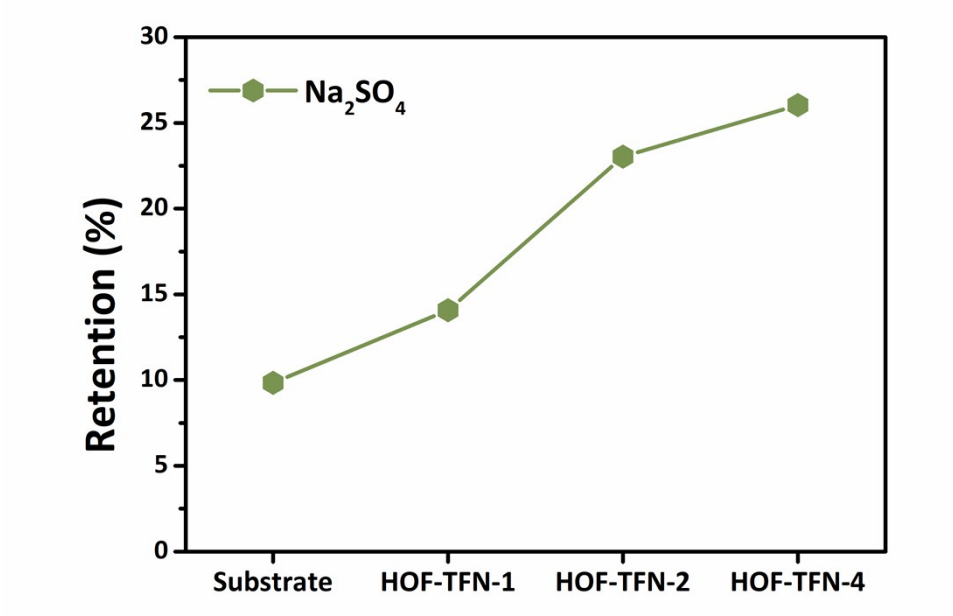


Figure S13. The separation performance of the HOF membranes for divalent salts (SO_4^{2-}).

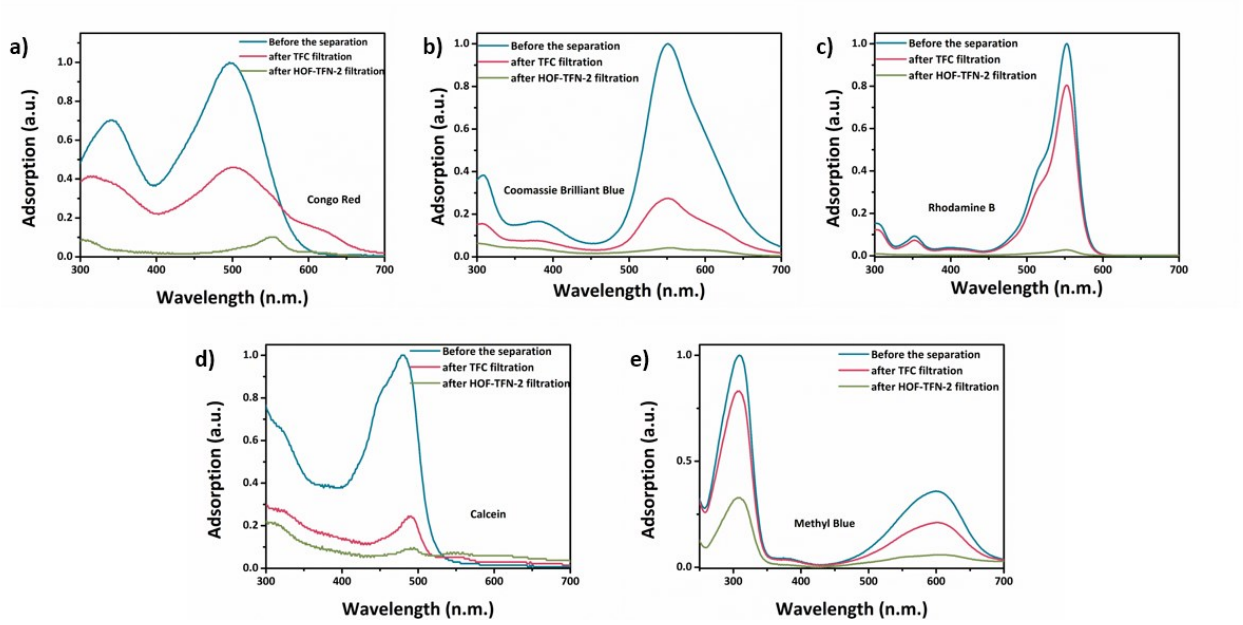


Figure S14. UV spectra of feed and permeate of using TFC and HOF-TFN-2 membranes.

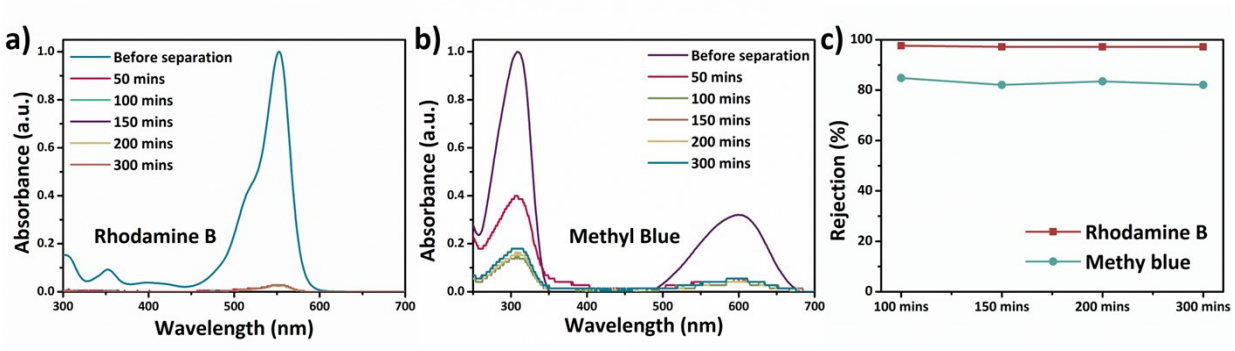


Figure S15. UV-vis spectra and dye separation performance of the HOF-TFN-2 membrane during 300 mins of (a) rhodamine B and (b) methyl blue of the feed and the permeate. (c) Dye separation performance of the HOF-TFN-2 membrane during 300 mins.

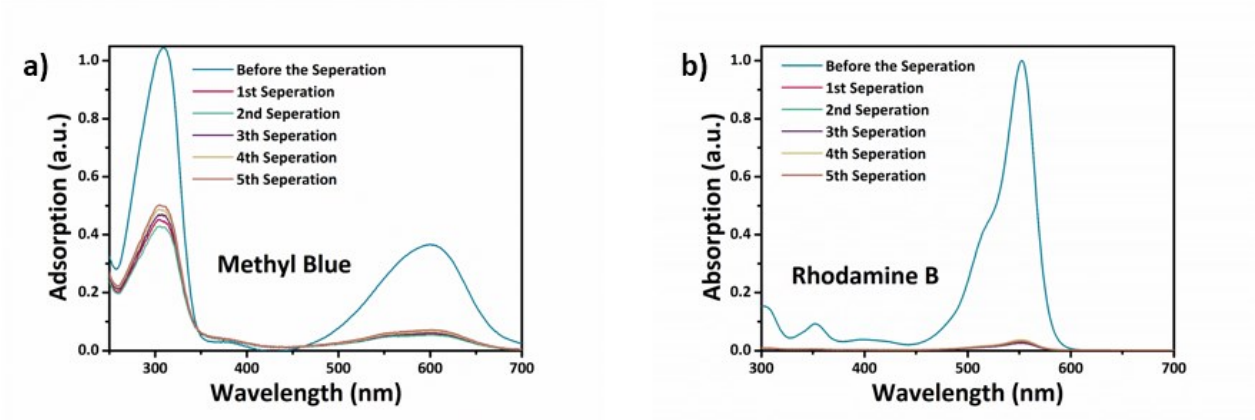


Figure S16. Data of UV spectra of the permeate after each recycled separation procedure using HOF-TFN-2 membrane.