Supplementary Information

Heterostructured Two-Dimensional Covalent Organic Framework Membranes for Enhanced Ion Separation

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Experimental section

Materials

1,3,5-triformylbenzene (Tb, 95%) was provided by Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. Hydrazine hydrate (Hz, 98%) and *p*phenylenediamine (Pa, 97%) were obtained from Aladdin. The polysulfone*block*-poly(ethylene glycol) (PSF-*b*-PEG) block copolymer with 21 wt% of PEG block was purchased from Nanjing Bangding (the total molecular weight was 79.1 kDa). Silicon wafers with a top layer of silicon dioxide (~1000 nm in thickness) were used as the substrate. Poly(ether sulfone) (PES) membranes (\emptyset = 25 mm, nominal pore diameter = 220 nm) were supplied by JinTeng. Sodium sulfate (99.5%), 1,4-dioxane (99.0%), chloroform (99.5%), acetone (99.5%), ethanol (99.5%), acetic acid (AA, 99.5%) and hydrofluoric acid (HF, 40.0%) were provided from local suppliers. Deionized (DI) water (conductivity < 10 µS cm⁻¹) was used throughout this study. All chemicals and reagents were used with further purification.

Preparation of neat ACOF-1 membranes

ACOF-1 membranes were prepared on silicon wafers under solvothermal condition. Tb (0.096 mmol, 15.6 mg) and Hz (20 μ L) were mixed together in 20 mL of 1,4-dioxane, followed by sonication for 15 min to obtain a homogenous solution. Subsequently, silicon wafers were placed into a Teflon-lined stainless-steel autoclave and AA (500 μ L) was added as the catalyst. The autoclave was sealed and heated at 120°C. After growing of ACOF-1 for 12 h, the autoclave

was cooled down to room temperature and ACOF-1 membranes were washed with 1,4-dioxane and ethanol for several times. Finally, ACOF-1 membranes prepared on silicon wafers were vacuum dried at 90°C for 12 h.

Preparation of neat COF-LZU1 membranes

COF-LZU1 membranes were prepared based on the same procedure of ACOF-1 membranes, except for the replacement of Hz to Pa (0.144 mmol, 15.6 mg) as well as the reaction duration (24 h).

Linker exchange

Pa (0.144 mmol, 15.6 mg) was dissolved in 20 mL of 1, 4-dioxane. After sonication-assisted dispersion, ACOF-1 attached silicon wafers were transferred to a Teflon-lined stainless-steel autoclave, followed by adding AA (500 μ L) as the catalyst. Afterwards, the autoclave was kept in a 120°C oven for designated durations. After being cooled to room temperature, the samples were taken out and washed with 1,4-dioxane and ethanol, and then vacuum dried at 90°C overnight.

Preparation of composite membranes

The composite membranes were prepared by a polymer-assisted transfer method. Firstly, PSF-*b*-PEG in chloroform (2 wt%) was spin-coated on the surface of the membrane after the linker exchange, followed by a selective swelling process in a mixture solvent (20 wt% of acetone and 80 wt% of ethanol) under 70°C for 1 h. After dried at room temperature, the film was delaminated from the silicon wafer after the etch of silicon dioxide layer by 5 wt% HF solution.

Then, the thin film was composited onto PES support to form the composite membrane.

Characterizations

Fourier transform infrared spectroscopy (FTIR) spectra of COF membranes were acquired on a Nicolet 8700 spectrometer under attenuated total reflectance (ATR) model. X-ray diffraction (XRD) patterns of COF membranes were recorded on a SmartLab diffractometer. The scan speed was 0.02° s⁻¹ with 20 angle ranging from 2° to 40°. The thickness of COF membranes on silicon wafers was measured by the spectroscopic ellipsometry (Complete EASEM-2000U, J. A. Woollam) at an incidence angle of 70° with the wavelength ranging from 400 to 999.8 nm. The surface and cross-sectional morphologies of COF membranes were observed by scanning electron microscopy (SEM, Hitachi S-4800) at an accelerating voltage of 5 kV. The elemental composition of COF membranes was characterized by energy dispersive X-ray spectroscopy (EDX) with an operating voltage of 20 kV. The roughness of COF membranes was studied by atomic force microscopy (AFM, XE-100, Park Systems) operating at a noncontact mode. A contact angle goniometer (DropMeter A100, Maist) was used to record the water contact angles (WCAs) of COF membranes.

Separation performance tests

The water permeance and salt rejection rates of COF membranes were tested using a dead-end filtration cell (Amicon 8003, Millipore) under a pressure

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of 3 bar. During the test, the feed was stirred with a speed of 500 rpm to alleviate the concentration polarization. The concentration of inorganic salts was 1000 ppm. Water permeance (L $m^{-2} h^{-1} bar^{-1}$) was calculated by the following equation.

$$Permeance = V / (A t p)$$

where V (L) is the volume of permeated solution, t (h) represents permeating duration, A (m²) is the effective membrane area, and p (bar) is the applied pressure.

Rejection rate (R, %) was calculated by the following equation.

$$R = (1 - C_p / C_f) \times 100\%$$

where C_p and C_f are the concentration of the filtrate and feed, respectively. An electrical conductivity meter (S230-K, Mettler-Toledo) was used to measure the concentrations of inorganic salt solutions.

To demonstrate the separation selectivity toward mono/multivalent ions, the selectivity between Cl⁻ and SO₄²⁻ was evaluated. Based on the rejection rates, separation factors (α) of NaCl to Na₂SO₄ as well as NaCl to MgSO₄ were calculated by the following equation:

$$\alpha = (1 - R_{NaCl}) / (1 - R_{Na2SO4 \text{ or } MgSO4})$$

Molecular weight cut-off as well as pore size distribution were obtained by PEG retention test with different molecular weights (200, 400, 1000, and 2000 Da). The concentration of the PEG solutions was measured by gel permeation chromatography (GPC, Waters 1515). Stokes radius of PEG was calculated by the following equation:

$$r_P = 16.73 \times 10^{-12} \times M_W^{0.557}$$

where r_P is the Stokes radius (m), and M_W represents its average molecular weight.



Fig. S1. Surface SEM images of the COF membranes with linker exchange durations of (a) 3 h, (b) 6 h, (c) 12 h, (d) 24 h, and (e) 48 h.

(a)	(b)	(c)	(d)
200 nm	200 nm	2 <u>00 nm</u>	200 nm
(e)	(f)	(g)	(h)
2 Carl	8 1 3	1.0	0.00
2 <u>00 n</u> m	2 <u>00 n</u> m	200 nm	200 nm

Fig. S2. AFM images of the COF membranes with linker exchange durations

of (a) 0 h, (b) 1 h, (c) 3 h, (d) 6 h, (e) 12 h, (f) 24 h, (g) 36 h, and (h) 48 h.



Fig. S3. (a) Surface and (b) cross-sectional SEM images of the COF-LZU1 membrane.



Fig. S4. Cross-sectional SEM images of the COF membranes with linker exchange durations of (a) 0 h, (b) 1 h, (c) 3 h, (d) 6 h, (e) 12 h, (f) 24 h, (g) 36 h, and (h) 48 h.



Fig. S5. Photographs of the COF membranes with various linker exchange durations.



Fig. S6. (a) Photograph and (b) surface SEM morphology of the composite membrane.



Fig. S7. Chromatograms of the feed and filtrate in PEG retention test.



Fig. S8. Water permeance and Na_2SO_4 rejection rate of the neat COF-LZU1 membrane.



Fig. S9. Separation performances of heterostructured COF membranes with a linker exchange of 3 h. (a) Rejection rates of various salts. (b) Separation factors.