Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Covalent organic frameworks embedded in polystyrene membranes for ion sieving

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Materials & Methods

Materials

Tetra-(4-aminophenyl)-methane was purchased from Jilin Chinese Academy of Sciences- Yanshen Technology Co., Ltd .Terephthalaldehyde (>99%), polystyrene (PS, MW ≈ 260000), 1,4-dioxane (99.8%), CH_3COOH (99.8%) were purchased from J&K Scientific Shanghai. KCl (>99.5%), NaCl (>99.5%), LiCl (>99.5%), and $MgCl_2$ (>99.5%) were purchased from Sigma-Aldrich. CCl_4 (99.5%) was purchased from Beijing InnoChem Science & Technology Co., Ltd. All the above chemicals were used without further purification. All deionized water used in the experiments was produced by the Milli-Q ultrapure water system.

Methods

Preparation of COF-300 particles

In order to obtain COF-300 with homogeneous scale and rounded shape, we improved the temperature, reaction time, and tetra-(4-aminophenyl)-methane content in the synthesis step. In the experiment, 36.0 mg of Tetra-(4-aminophenyl)-methane and 60.0 mg of terephthalaldehyde were added to the reaction kettle, 1, 4-dioxane was shaken and dissolved, and then a bright yellow solution was obtained after both were fully dissolved. It is worth noting that the acetic acid solution must be added with sufficient stirring. After completing the above dissolution, the kettle was loaded and the reaction was carried out at 120°C for 3 days. After the reaction, COF-300 was purified and dried using 1,4-dioxane and tetrahydrofuran to obtain a yellow powder.

Preparation of COF-300/PS membrane

In order to obtain a complete dense PS membrane without defects, we chose polystyrene with a molecular weight of 260,000 as the substrate membrane preparation material. In the experiment, PS was fully dissolved with CCl_4, where the doping amount of PS was 3 wt% and the doping amount of COF-300 was 0.2 wt%. Specifically, the total weight of the casting solution was 20 g, then the added PS was 600 mg, COF-300 was 40 mg, and CCl_4 was 19.36 g. The membranes were prepared by the slide cast method, where 1 mL of the casting solution was measured and placed on one end of the slide, and the membrane was evenly scraped twice using a scraper, different thicknesses of the composite membrane can be obtained by setting the height of scraper. It is worth mentioning that the slides of scraper on the casting solution should be horizontal, preventing the flow casting solution. After two-hour drying in a closed environment, the casting solution becomes dense due to the volatilization of CCl_4. It is worth noting that the ultrasound was used after the casting solution was completely spread in order to obtain uniformly arranged COF -300/PS membrane. The sonication time was set at 3 min, and afterwards the slide was left at room temperature and covered to prevent airborne particles from falling on the surface of the membrane. During this process, CCl_4 generally evaporated out after two hours. The membrane was automatically removed from the slide by placing it in DI water.

Characterizations

COF-300 particles and COF-300/PS membrane surface morphology were observed by field emission scanning electron microscopy (SEM, Hitachi S-4800). COF-300 EDS elemental determination was observed by field emission projection electron microscopy (TEM, EDS FEI-TALOS-F200X), powder polycrystalline X-ray diffraction (XRD, Model X'pert3), BET multilayer adsorption (BET, Quantachrome ASiQwin).

Ion transport behavior on COF-300/PS membrane

The ion transport of COF-300/PS membranes was measured by a picoammeter (Keithley 6430) using Ag/AgCl electrodes by 0.1 M KCl, 0.1 M NaCl, 0.1 M LiCl, 0.1 M $MgCl_2$ respectively. The current measurement at constant voltage was performed with the same device as the *I-V* test. The voltage was set to 0.1 V and the scan time was 200 S. In addition, ion transmembrane transport for solution mixed with 0.1 M KCl, 0.1 M NaCl, 0.1 M LiCl, and 0.1 M $MgCl_2$ was also performed in the above apparatus. Under magnetic stirring for 3 days, the solution at DI water (18.2 MΩ) side was measured for ion concentration. The ion concentration detection of the post-diffusion solution was determined by inductively coupled plasma emission spectrometry (ICP, Varian 710-OES), and the four elements of Li, Na, K, and Mg were determined in the post-diffusion solution, respectively.

Contact angle measurement on COF-300/PS membrane

The contact angle (CA) measured by OCA25 contact angle meter (Dataphysics, Germany) at room temperature. The area of the membrane and the single injection volume were adjusted before the test, and multiple measurements were performed on the same membrane to reduce errors. Before the test, the membranes were washed several times with deionized water, then blown dry by N_2 and laid flat on glass plate. The droplet volume was set to 0.2 ml/s at medium speed, and five measurements were taken at different locations on each membrane.

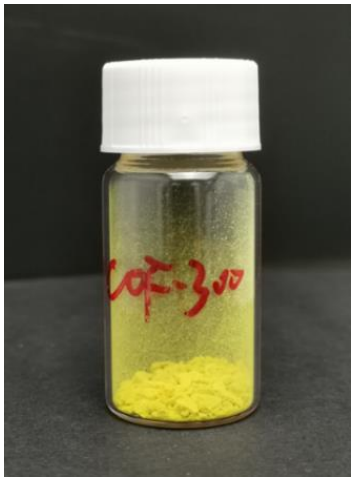

Fig S1. The prepared COF-300 powders with bright yellow color.

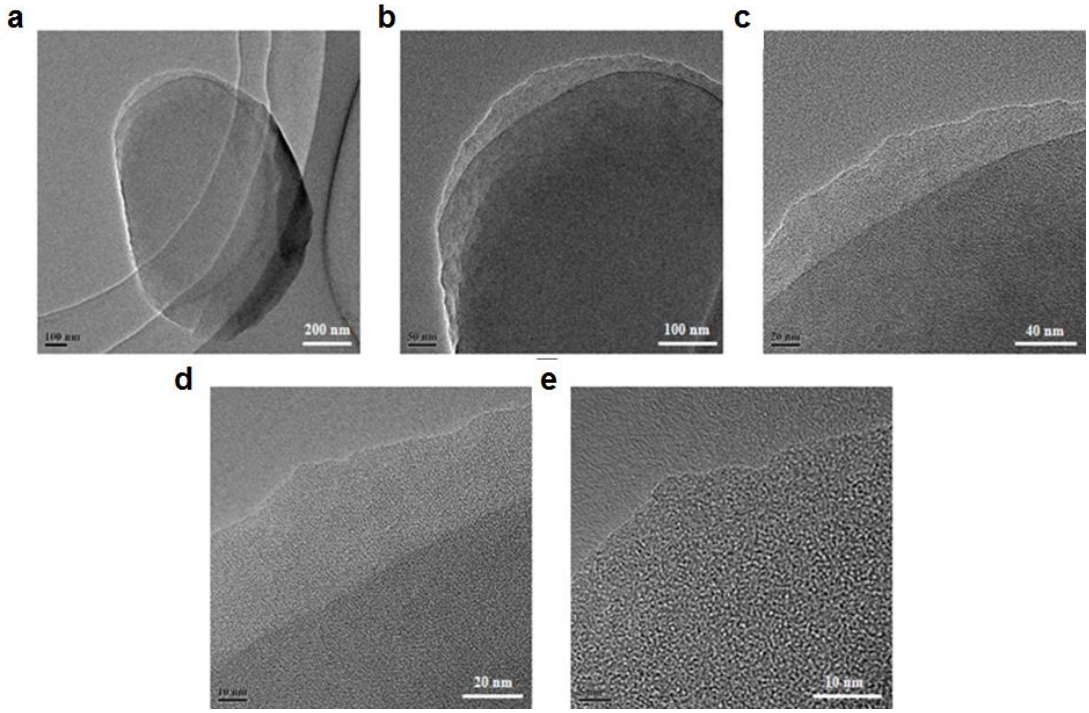

Fig S2. The transmission electron microscope (TEM) images (a-e) show the nanostructure of the COF-300.

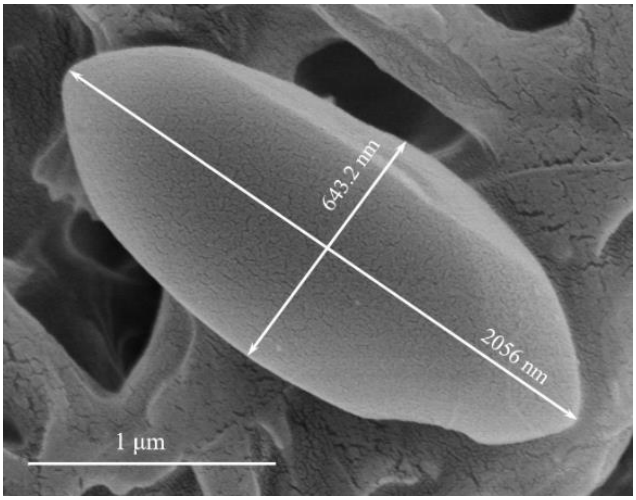

Fig S3. The Scanning electron microscope (SEM) image showed that COF-300 had a smooth surface and a regular three-dimensional rice-like shape.

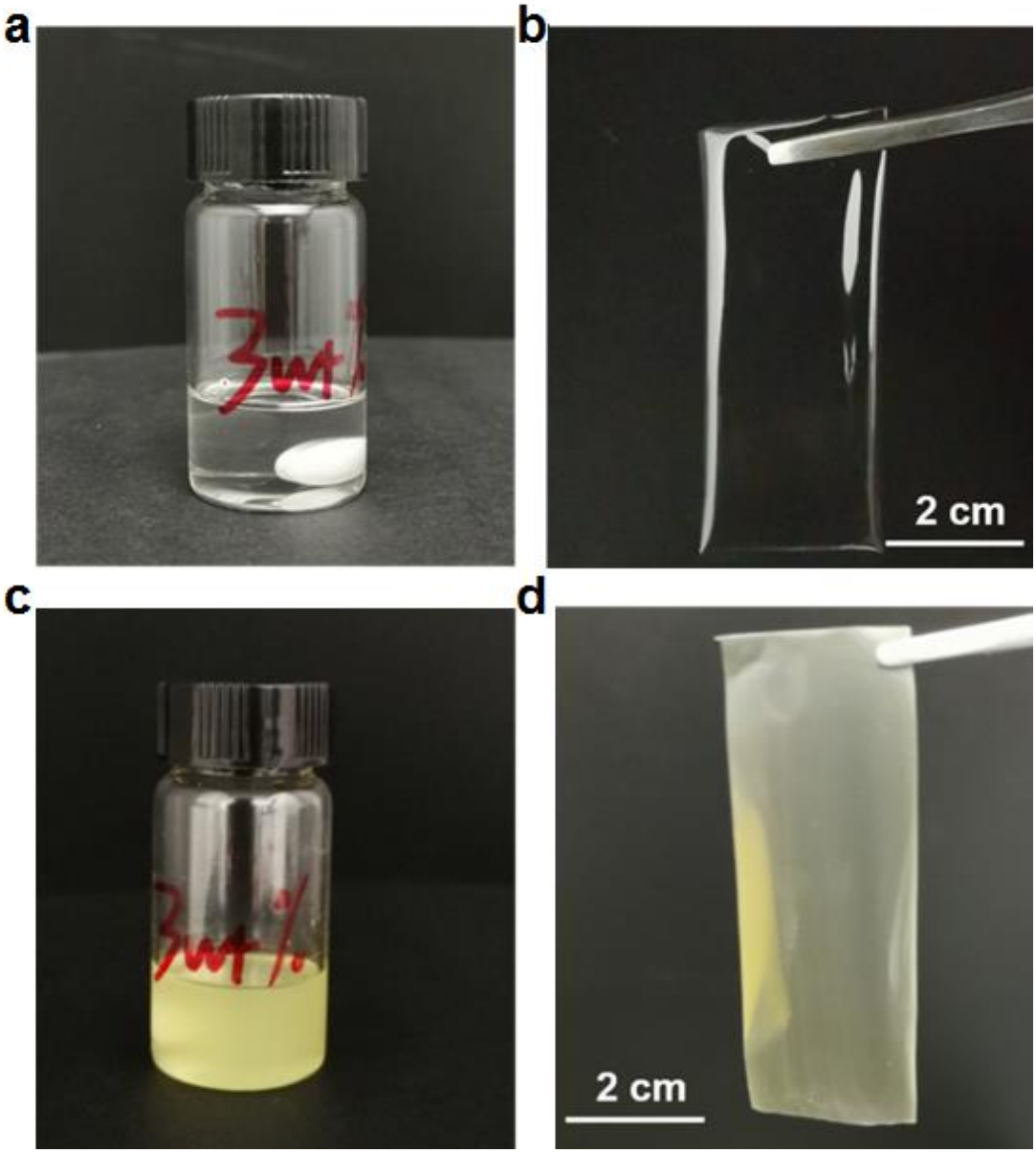

Fig S4. (a) Polystyrene was dissolved in CCl_4 to obtain a colorless PS/CCl_4 solution. (b) Transparent PS membrane prepared by the casting method. (c) PS/COF-300 membrane was prepared by the casting solution. (d) Light yellow COF membrane prepared by casting method.

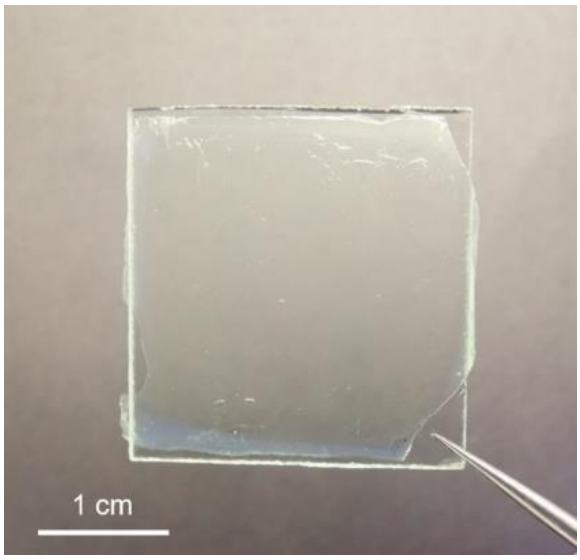

Fig S5. Pictures of slides after volatilization of COF-300/PS/CCl_4.

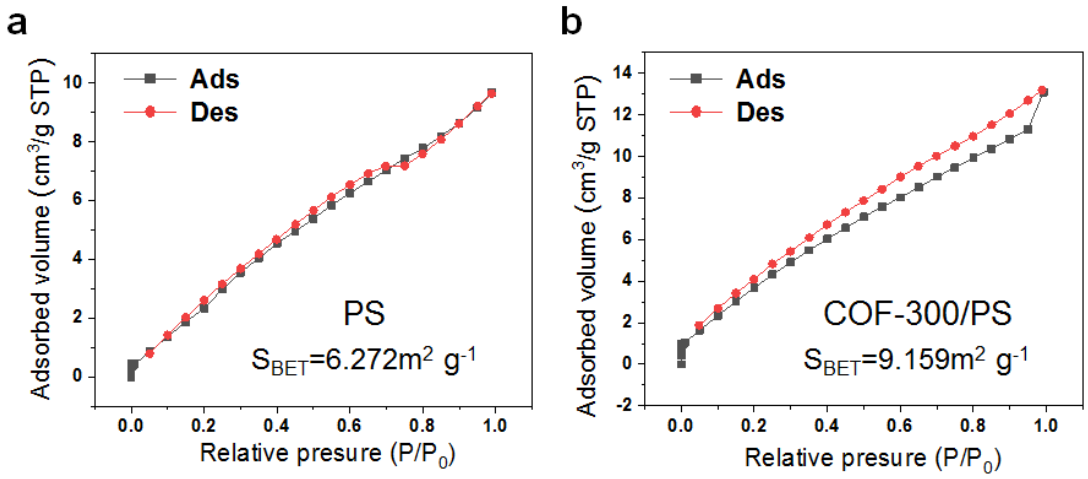

Fig S6. N_2 adsorption (black symbols) and desorption (red symbols) isotherm of (a) PS membrane (b) 0.3 wt% COF-300/PS membrane measured at 77.35 K.

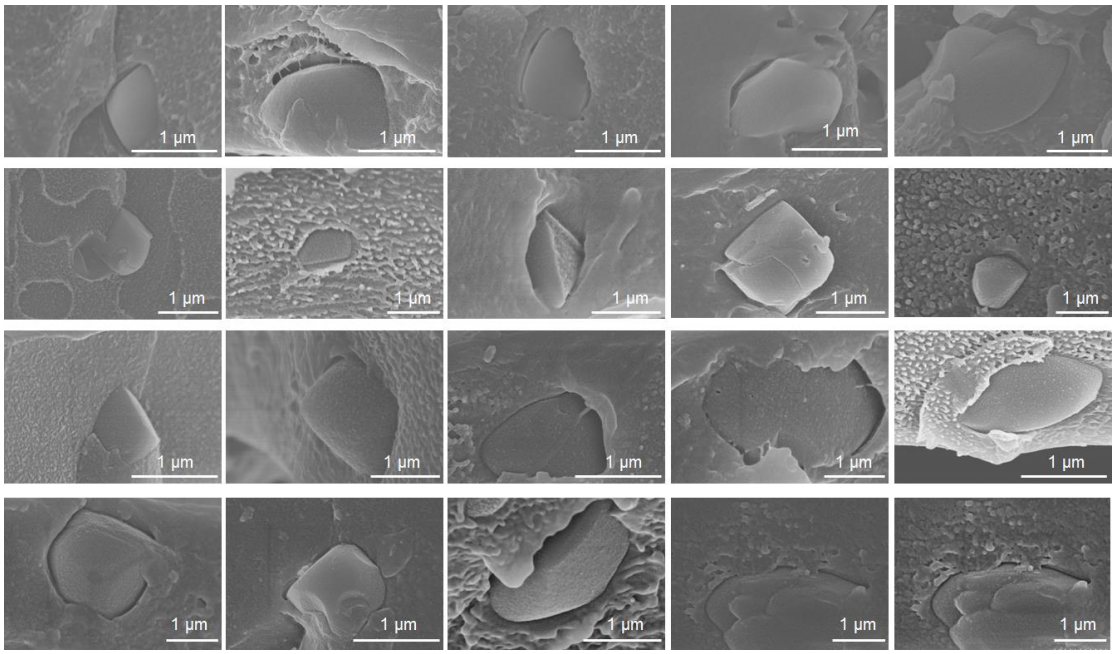

Fig S7.SEM images of COFs in COF-300/PS membrane after ultrasound.

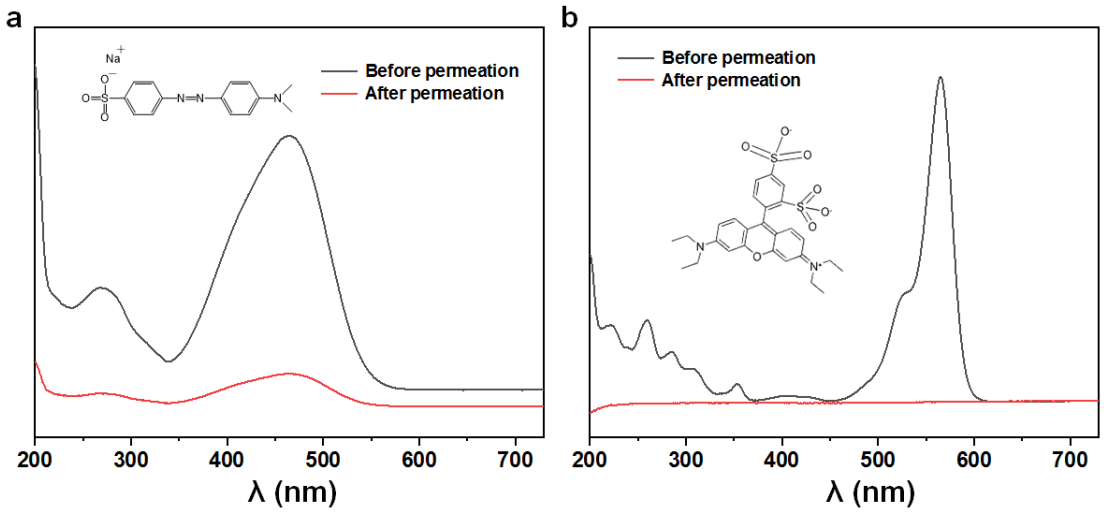

Fig S8. Dye partition transport experiments. (a) UV spectrum of methyl orange (3.4×4.9×13.6 $Å^3$); (b), UV spectrum of sulfonated rhodamine (10.5×10.7×12.5 $Å^3$).

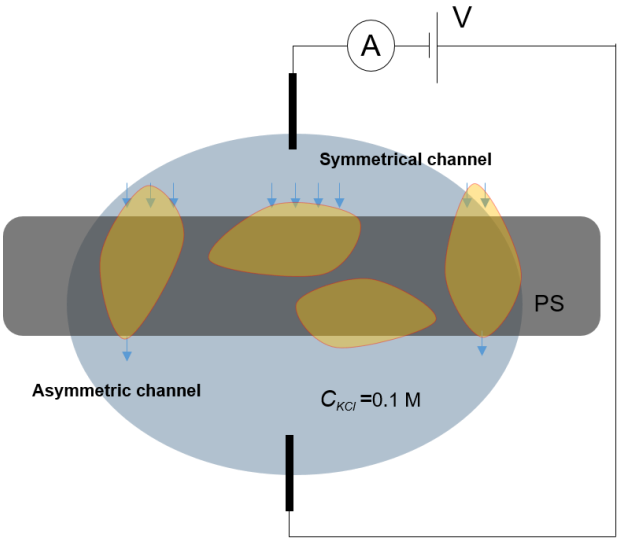

Fig S9. Schematic diagram of *I-V* measurement of COF-300/PS membrane.

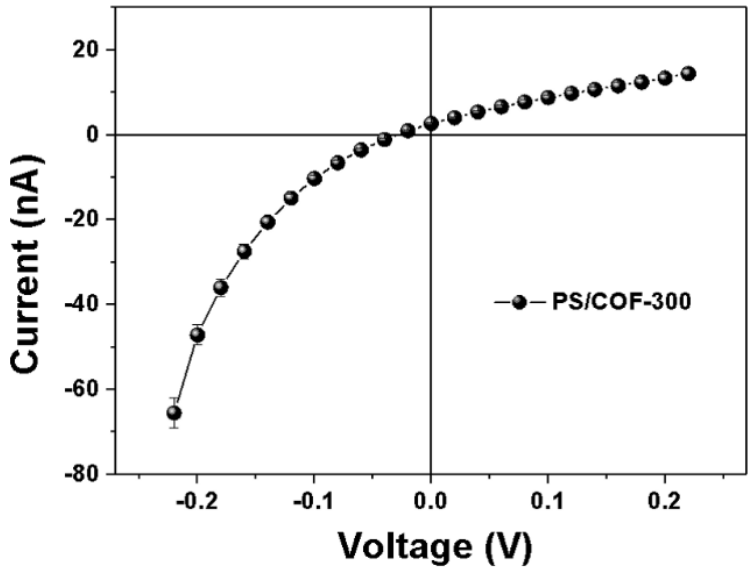

Fig S10. Ion transport of 0.1 M KCl through COF-300/PS membranes.

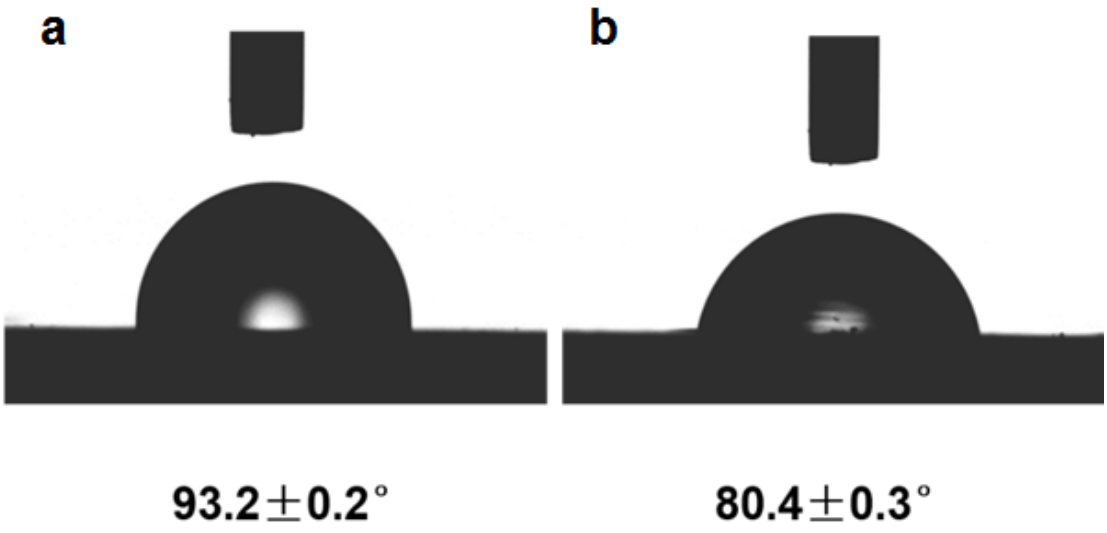

Fig S11. Surface contact angle image of (a) PS and (b) COF-300 doped PS membrane.

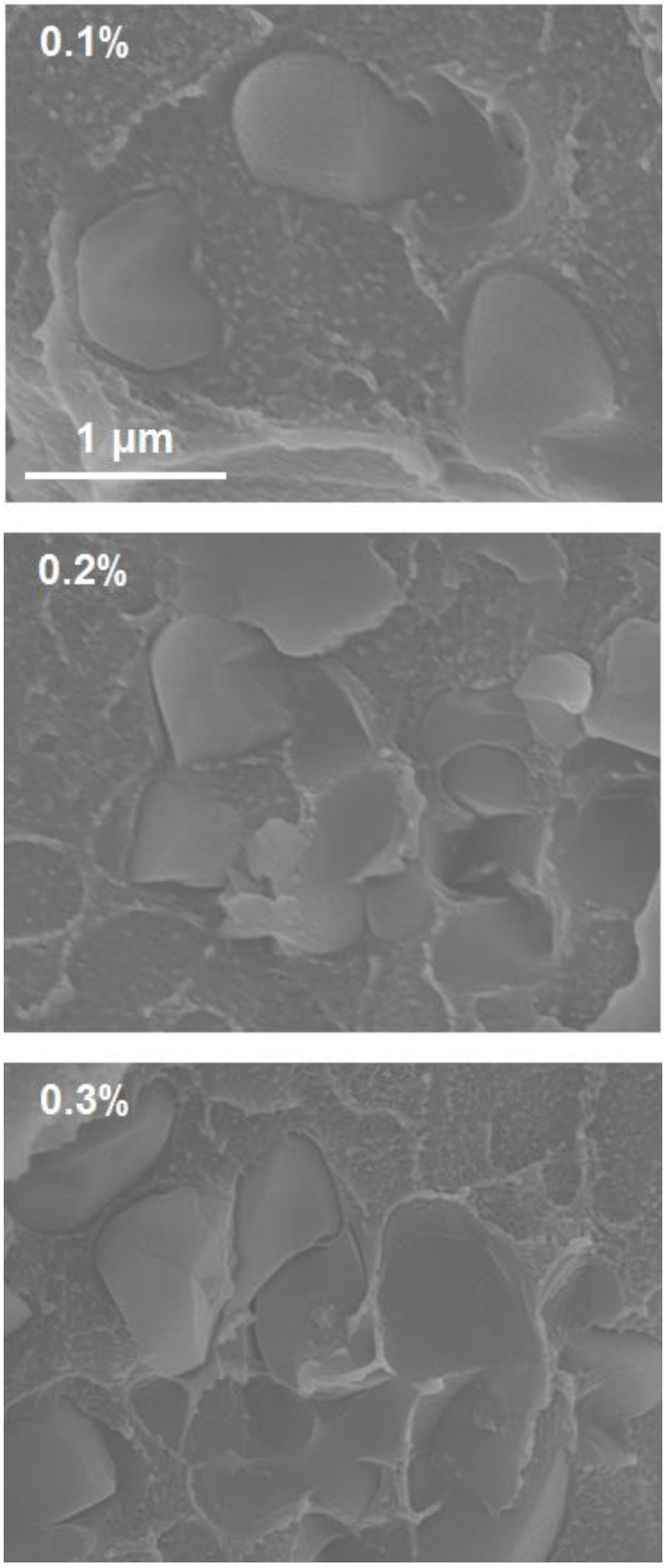

Fig S12. The SEM images of COF-300/PS membranes with different COF-300 doping quantity (0.1, 0.2, 0.3 wt%).

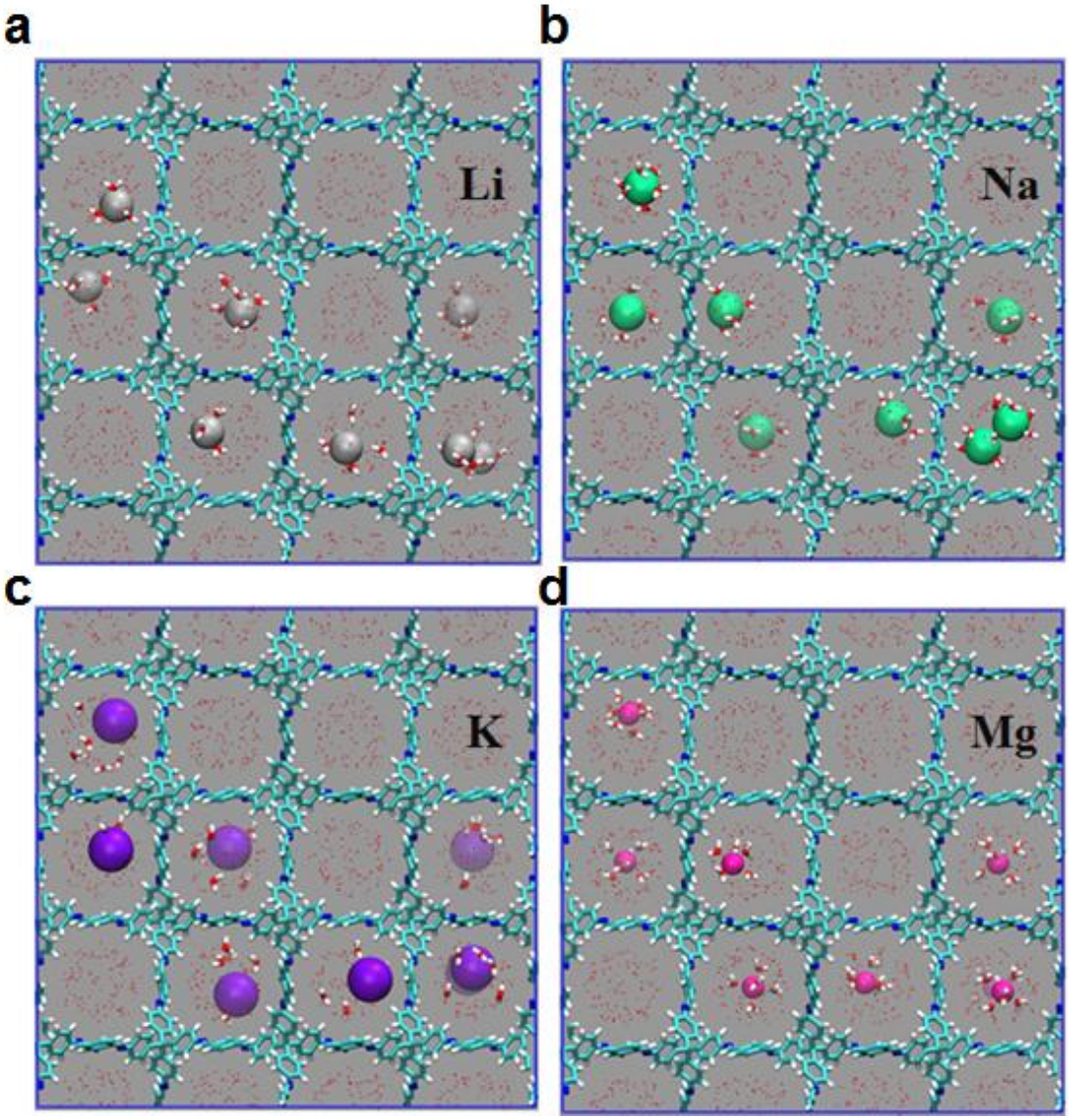

Fig S13. Schematic representation of the transport of different ions (a), Li^+; (b), Na^+; (c), K^+ and (d)Mg^{2+} within the COF channel.

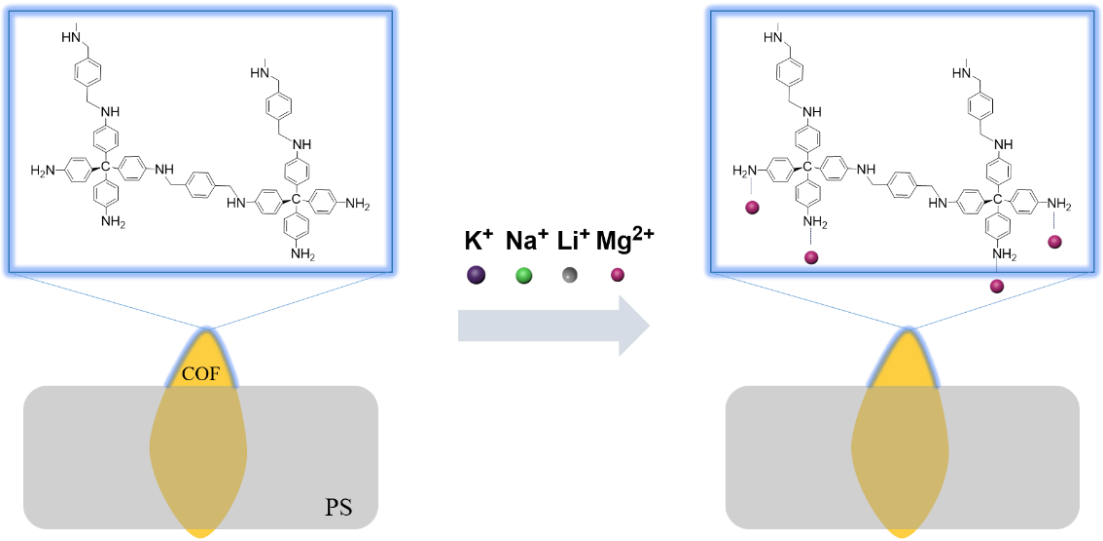

Fig S14. Schematic diagram of surface morphology and functional groups of COF-300/PS membrane.

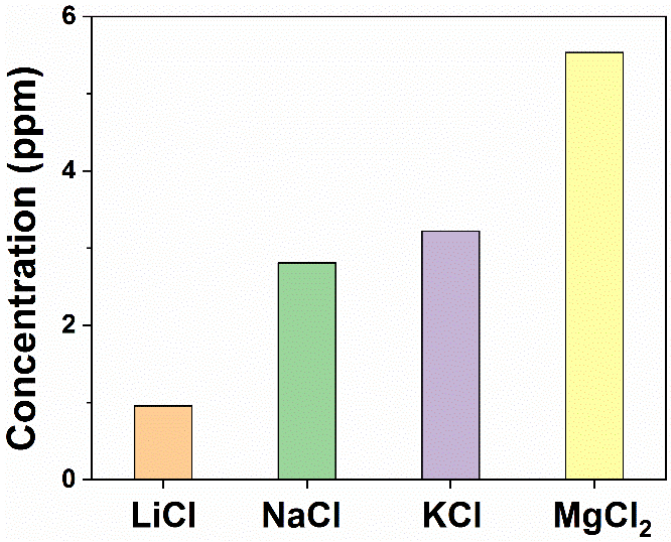

Fig S15. Long-time static diffusion ion transport.