

## Supporting Information

### **Tunable monovalent cation separation in polymeric carbon nitride membranes via multivalent ions**

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## Experimental Section

**Fabrication of PCN membranes.** A piece of copper foil (2.5 cm × 2.5 cm) was ultrasonic cleaned with acetone and anhydrous ethanol successively and dried with nitrogen. 68 mg of cyanuric chloride monomer and the copper foil were sealed in a quartz tube (inner diameter, 30 mm; length, 15 cm) in the glovebox (the content of oxygen and water is below 0.1 ppm). Then the quartz tube was transferred to an electric furnace, the temperature was increased to 300 °C in 30 mins and kept for 12 hours under argon gas. When the furnace was cooled down to room temperature naturally, the copper foil with PCN membranes was obtained. The copper foil was then transferred to a FeCl<sub>3</sub> solution (10 wt% in water) to etch the copper, after 12 hours, PCN membranes float on the surface of the solution. Then the membranes were washed with deionized water for several times. Finally, the PCN membranes can be transferred onto different substrates, such as SiN<sub>x</sub>/Si, SiO<sub>2</sub>/Si wafers and TEM grids.

**Membrane Characterization.** SEM imaging of PCN membranes on silicon chips was carried out on an ultrahigh resolution field-emission SEM (Hitachi-SU8220). UV-vis spectra were measured with a Hitachi U-3900H UV-vis-near infrared spectrophotometer. A PCN membrane was transferred onto a quartz support for the measurement, and the absorbance of the corresponding cyanuric chloride monomer (1 μM, ethanol) was measured in solution in quartz cuvettes. The membrane was soaked in salt solutions e.g. KCl or KCl-LaCl<sub>3</sub> over 1h to achieve the absorption spectra, and then was washed thoroughly in deionized water. Raman spectroscopy (Zetasizer Nano ZS, λ=514nm) was used for the characterization of the membrane property. The crystal structure of the PCN powder was determined by X-ray diffraction experiments (D/MAX-TTRIII, CBO). PCN powder was collected from the fabricated membrane in a centrifugation, washing and drying process. Zeta potentials

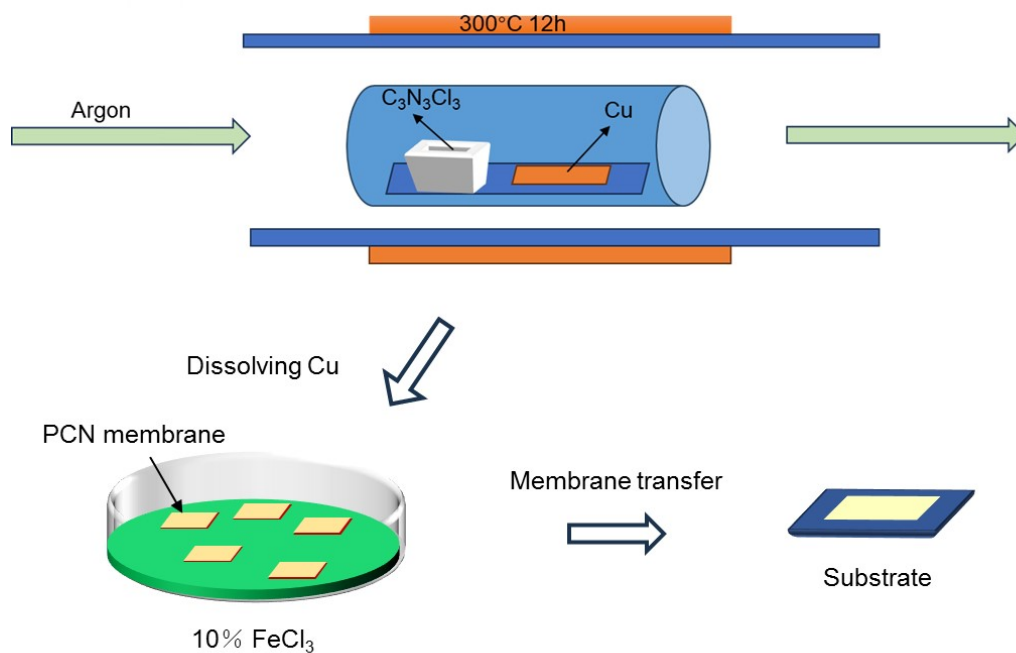
were carried out using a Zetasizer Nano ZS instrument. The PCN powder was dissolved via sonication in ethanol with concentrations of 10 ppm, 1 ppm and 0.1 ppm, respectively. Every experiment was repeated over three times to calculate the mean value. Pore size of the PCN powder was determined by BET (Brunauer, Emmett and Teller) surface area characterization using Autochem II 2920 instrument. The PCN powder (>20 mg) was placed in a centrifuge tube for carbon dioxide adsorption test, and the porosity distribution was further analyzed by CO<sub>2</sub>-DFT.

**Transmembrane ion transport.** Focused ion beam (FEI Inc., Nova200 NanoLab) was used to drill an aperture of 10 μm in diameter in the freestanding SiN<sub>x</sub>/Si substrate. Then, the target PCN membrane was transferred on the aperture forming a PCN/SiN<sub>x</sub>/Si chip. Next, the chip was mounted in a Teflon disk and sandwiched between two reservoirs (Figure S5 in the Supporting Information). A pair of Ag/AgCl electrodes was used to apply voltage bias. The electrochemical measurements were carried out on a Keithley 2634B source meter (Keithley Instruments) to obtain the voltage-current data, which can be used to analyze the ionic conductance and ion selectivity. Concentration gradient driven ion sieving measurements were performed in a diffusion model with two cells defined as feed and permeate compartments consisting salt solution and deionized water. Ion transport from the feed side to the permeate side was driven by the osmotic pressure difference. Ion flux ( $J$ , mol m<sup>-2</sup> h<sup>-1</sup>) was calculated from the concentration change in the permeate side ( $\Delta C$ , 1 mol L<sup>-1</sup>), reservoir volume ( $V$ , ~7.6 ml), time ( $\Delta t$ , h) and the area of the aperture ( $A$ , 7.85×10<sup>-11</sup> m<sup>2</sup>) according to equation:

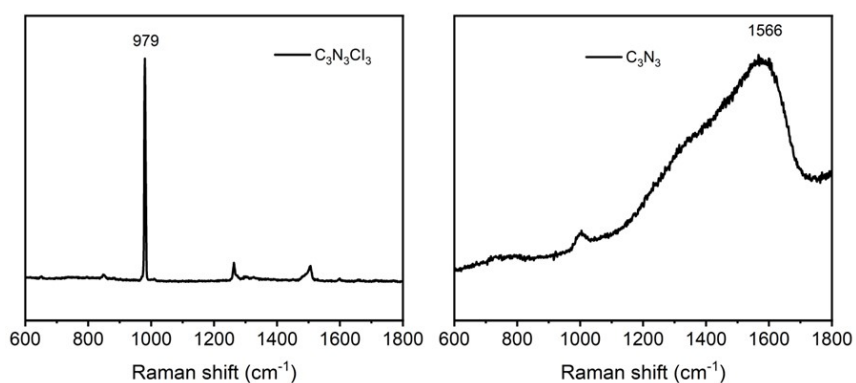
$$J = \frac{\Delta C \cdot V}{A \Delta t}$$

The cation concentration in the permeate side was detected by inductively couple plasma-optical emission spectrometry (ICP-oes, 710-ES Varian).

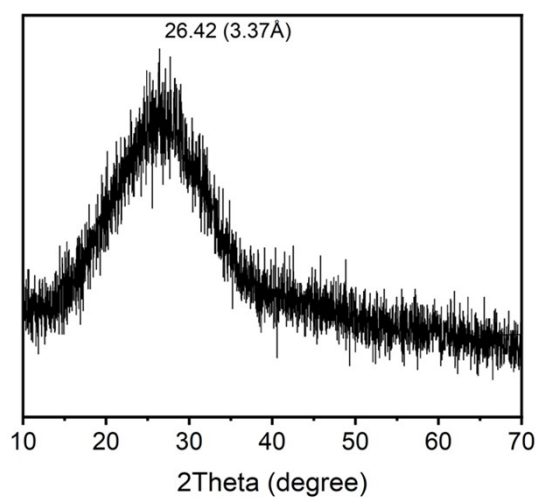
## Graphics



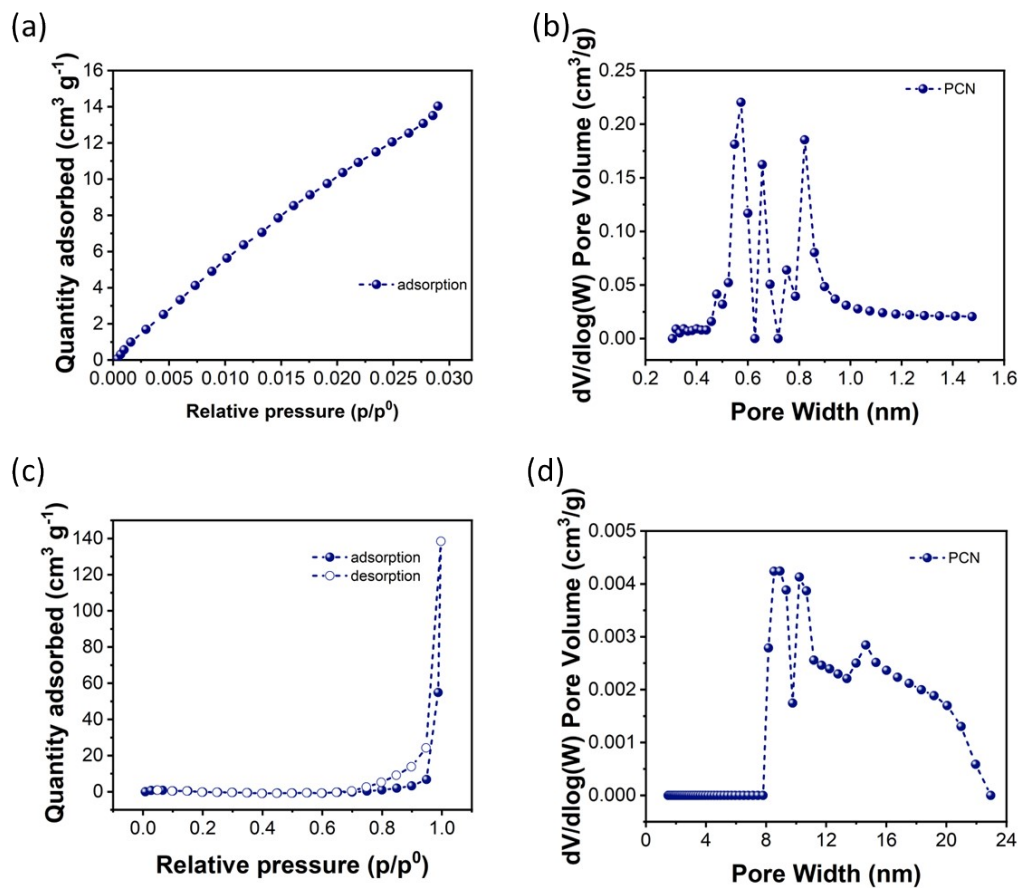
**Fig. S1** Scheme of synthesis and transfer process of the PCN membrane.



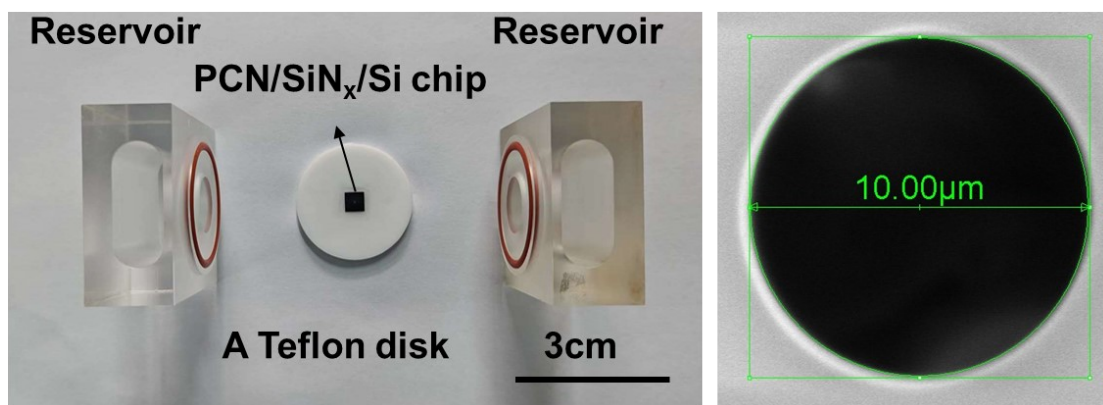
**Fig. S2** Raman spectra of  $C_3N_3Cl_3$  monomer and poly  $C_3N_3$  membrane.



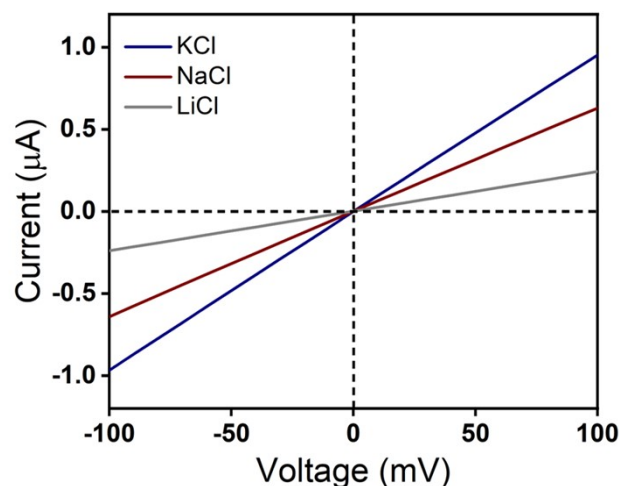
**Fig. S3** XRD spectrum verifies the crystallinity of  $C_3N_3$ .



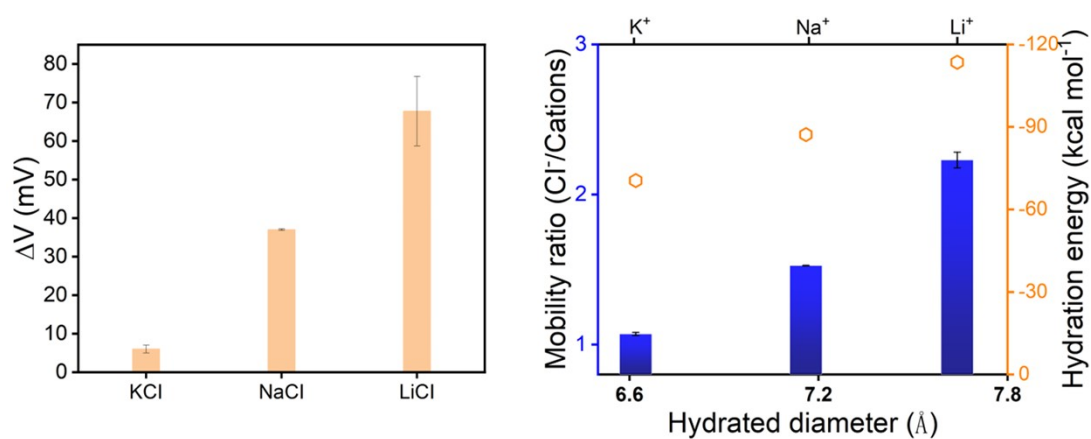
**Fig. S4** Carbon dioxide and nitrogen sorption analysis on PCN membrane. (a) Low-pressure  $\text{CO}_2$  sorption (273 K, 1 bar) and (b) pore size distribution obtained by DFT. (c)  $\text{N}_2$  sorption (77.3 K, 1 bar) and (d) pore size distribution obtained by DFT.



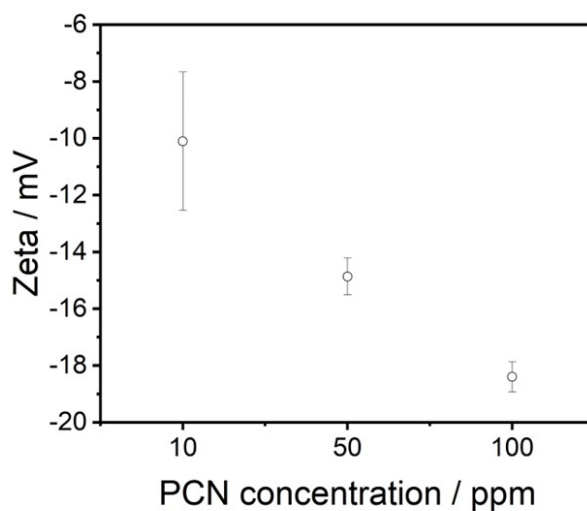
**Fig. S5** Schematic of the experimental device and the SEM of an empty  $\text{SiN}_x$  aperture.



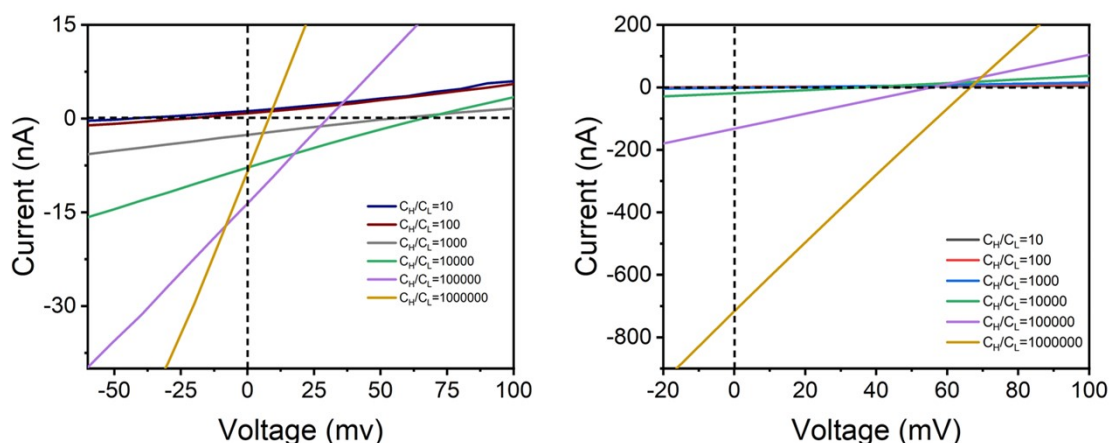
**Fig. S6** Representative current-voltage ( $I$ - $V$ ) curves of KCl, NaCl and LiCl solutions (0.1M) to measure the ionic conductance of PCN membrane.



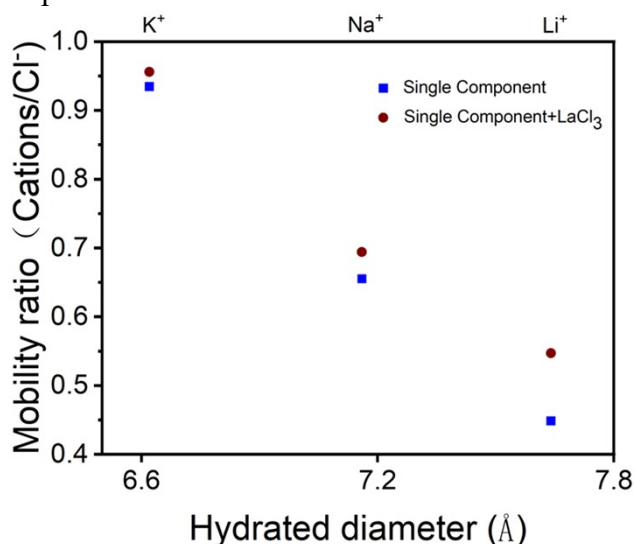
**Fig. S7** Reversal voltages ( $E_m$ ) across the membrane deduced from the representative  $I$ - $V$  curves (Fig. 2b), and mobility ratio  $\mu^-/\mu^+$  as a function of cation hydrated diameter. Open hexagons denote the hydration energy.



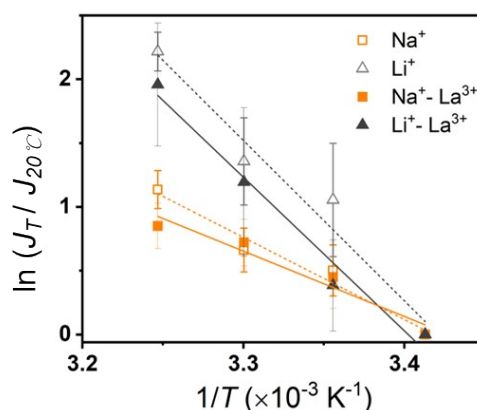
**Fig. S8** Zeta potential of PCN powder suspension in different concentrations (0.01 M KCl was used as electrolyte solution).



**Fig. S9** Current-voltage curves of a PCN membrane recorded in different salt gradients of from 10 to  $10^6$  for KCl (left) and  $\text{LaCl}_3$  (right), respectively. The low concentration was fixed at  $1 \mu\text{M}$ . The charge inversion was more easily for multivalent  $\text{La}^{3+}$  compared with monovalent  $\text{K}^+$ .

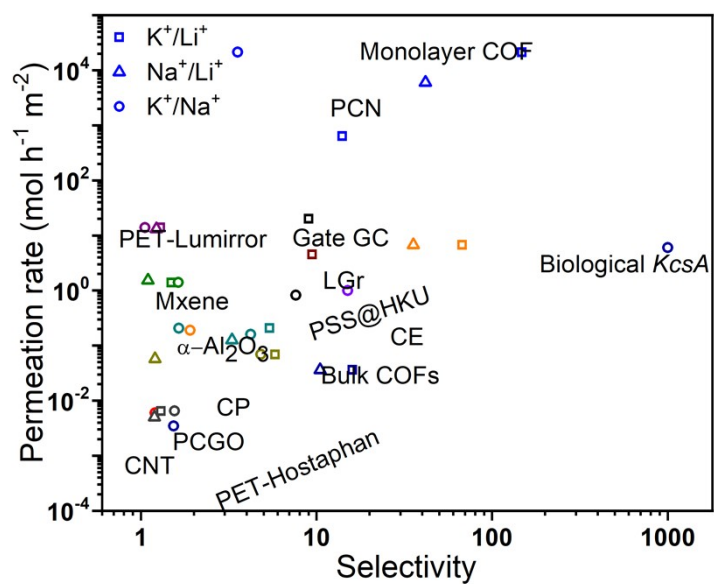


**Fig. S10** Differences in mobility ratio between individual component and adding  $\text{LaCl}_3$  salt ( $0.01 \text{ M}$ ).



**Fig. S11** Arrhenius plot for Na and Li and in the presence of La ions transport through the PCN membrane. The value of  $E_a(\text{Na}^+)$  and  $E_a(\text{Li}^+)$  decline from  $12.8 \text{ kcal mol}^{-1}$  to

10.2 kcal mol<sup>-1</sup>, and from 24.9 kcal mol<sup>-1</sup> to 23.9 kcal mol<sup>-1</sup>, respectively, in the presence of La<sup>3+</sup>.



**Fig. S12** Compared with the reported membrane separation performance