Electronic Supplementary Information (ESI)

Controllable ion transport induced by pH gradient in thermally crosslinked submicrochannel heterogeneous membrane

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1. Synthesis and characterization of VBTPA

Bis(4-bromophenyl) aniline (2.00 g, 4.96 mmol), 4-vinylphenylboric acid (1.84 g, 12.40 mmol), $Pd(PPh_3)_4$ (0.40 g, 0.35 mmol), potassium carbonate (50 mL, 2 mol/L aqueous solution) were added into a 500 mL double-necked flask, and then 150 mL THF was added while stirring and heated to 100 °C under nitrogen atmosphere. After refluxing for 48 h, the mixture was cooled to room temperature and filtered, the precipitate was eluted with ethyl acetate. The filtrate was extracted with water and ethyl acetate, then the combined organic layer was dried with anhydrous sodium sulfate. After removal of the solvent by rotary evaporation, the crude material was purified by column chromatography on silica gel (n-hexane) to give VBTPA. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.59–7.44 (m, 12H), 7.33–7.27 (m, 2H), 7.19 (d, 6H), 7.07 (t, 1H), 6.76 (dd, 2H), 5.79 (d, 2H), 5.28 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 147.61, 147.18, 140.12, 136.59, 136.33, 135.02, 129.52, 127.79, 126.84, 124.86, 124.31, 123.40, 113.79; MS (ESI, m/z) $[M+H]^+$ calcd for $C_{34}H_{27}N$: 449.2143, found: 450.2218.

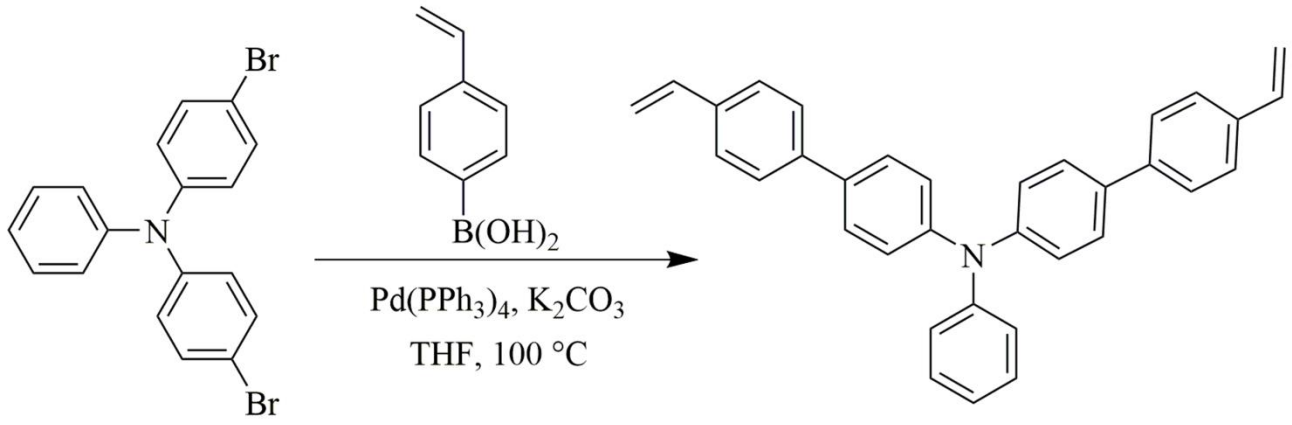

Fig. S1 The synthesis route of VBTPA.

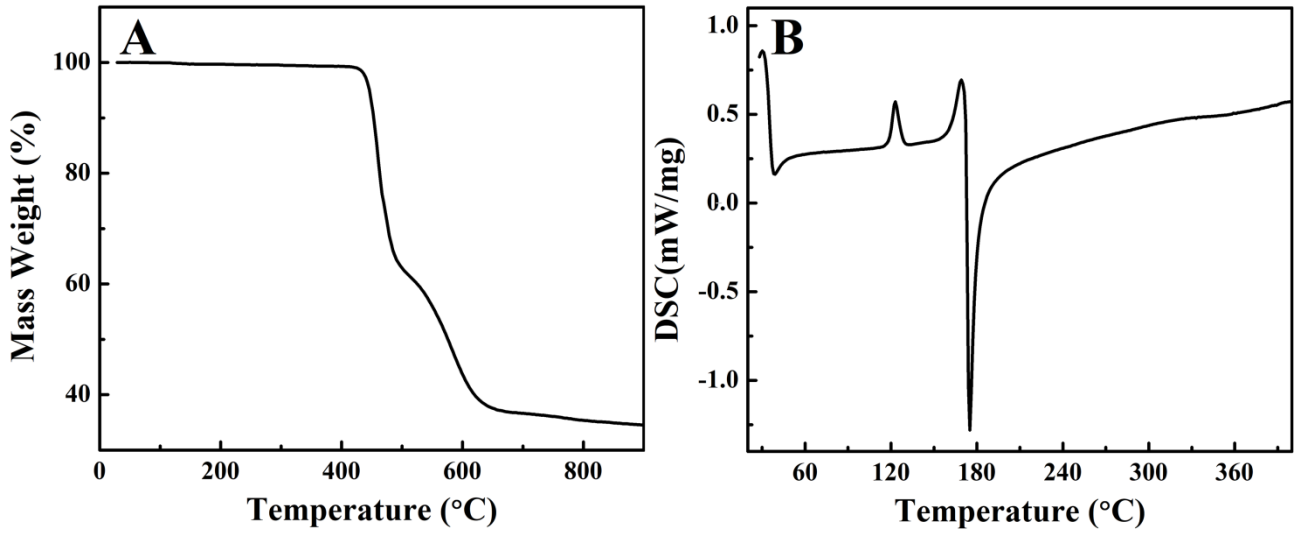

Fig. S2 The thermogravimetric analysis (A) and differential scanning calorimetry analysis (B) of VBTPA.

2. Preparation of the heterogeneous membrane

The VBTPA/AAO heterogeneous membrane was prepared by dropping coating a solution of VBTPA in THF (50 μL, 7.6 mg/mL) onto AAO membrane, after drying at room temperature, the VBTPA/AAO heterogeneous membrane was annealed at 70 °C for 20 min under argon atmosphere, and then cross-linked at 175 °C for 10 h to get the PTPA/AAO heterogeneous membrane.

3. Measurement of the contact angle

A solution of VBTPA in THF (7.6 mg/mL) was spin-coated on the glass at 1000 rpm for 20 s, then the VBTPA/glass film was annealed at 70 °C for 20 min and crosslinked at 175 °C for 10 h under argon atmosphere to get the PTPA/glass film. Using the aqueous solution of pH 3 and pH 11 as the liquid phase, the contact angle was measured with AAO (D≈319 nm) and the PTPA/glass film as the substrates, respectively.

4. TEM characterization of heterogeneous membrane

The PTPA/AAO (D≈319 nm) heterogeneous membrane was immersed in 5 wt% NaOH aqueous solution to fully dissolve AAO template and filtered by PC (D=0.1 μm), then it was washed with deionized water and the filter residue was dispersed in a mixture solution of ethanol and water (1:1). After drying naturally in the air, the test of TEM was performed.

5. The fluorescence staining

The thermally crosslinked PTPA/AAO heterogeneous membrane was immersed in acid solution (pH 3) and base solution (pH 11) for 4 h, respectively. Then it was rinsed with deionized water for 3 min and stored in deionized water for 5 min. After blowing dry, lissamine rhodamine B (100 μL, 0.1 mM) was drop-coated on the PTPA side for 15 min. Then, it was rinsed thoroughly with deionized water and observed with inverted fluorescent microscopic imaging system.

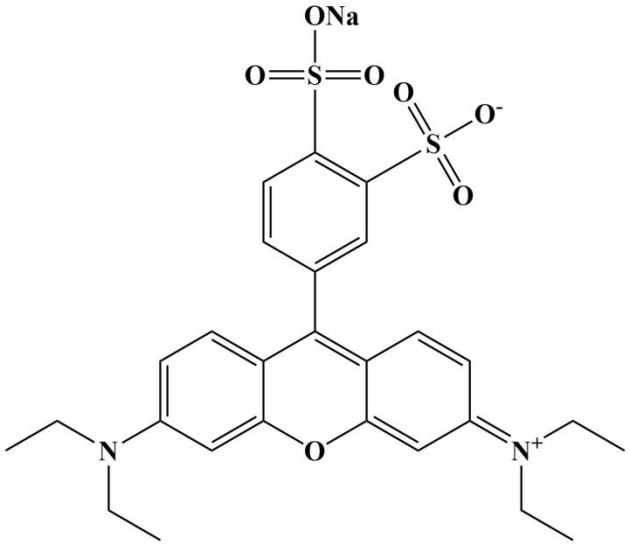

Fig. S3 The structural formula of lissamine rhodamine B dye.

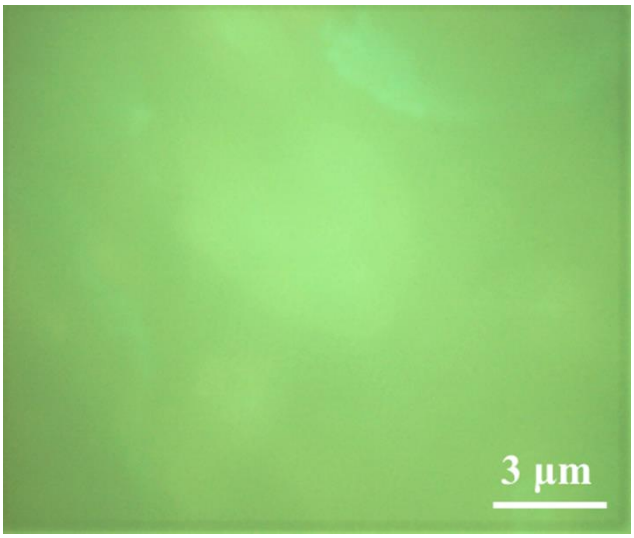

Fig. S4 The fluorescence image of PTPA/AAO heterogeneous membrane on PTPA side without staining.

6. Electrochemical test

In order to study the ion transport property of PTPA/AAO heterogeneous membrane, a two-compartment electrochemical cell was used in this experiment (Fig. 1). A pair of Ag|AgCl electrodes (CH Instrument Inc.) were placed on both sides of the membrane to apply a trans-membrane potential. The PTPA/AAO heterogeneous membrane was fixed in the joint of two compartment to separate KCl electrolyte solution. The pH was adjusted by 0.1 M HCl and 0.1 M KOH. The PTPA side was facing reference electrode (RE) and the AAO side always faced the working electrode (WE). The voltage from -2 V to +2 V with a scanning rate of 100 mV/s was applied to record the I-V curve of the ion current.

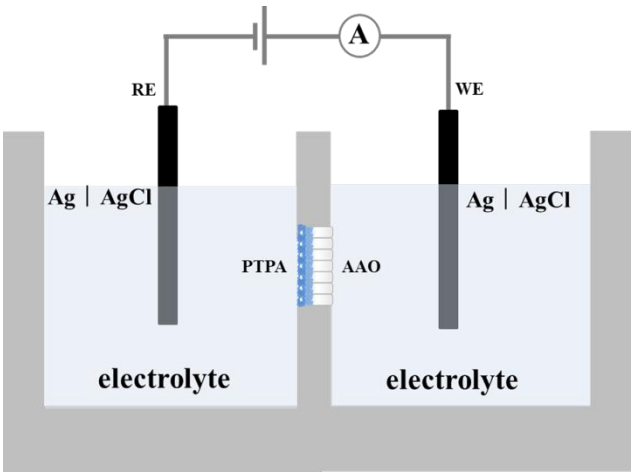

Fig. S5 The schematic diagram of electrochemical test about the submicrochannel heterogeneous membrane.

7. I-V curve of the heterogeneous membrane at symmetric pH condition

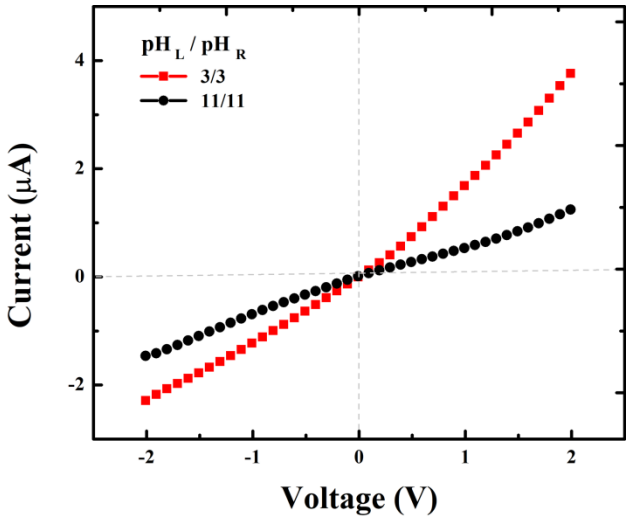

Fig. S6 The I-V curve of the thermally crosslinked heterogeneous membrane for 10 h on the AAO channels with 319 nm pore diameter at symmetric pH condition.