

## Supplementary Information

# Ultramicroporous Crosslinked Polyxanthene-Poly(biphenyl piperidinium)-based Anion Exchange Membranes for Water Electrolyzers Operating under Highly Alkaline Conditions

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## Experimental

### Materials

4'-bromo-2,2,2-trifluoroacetophenone, 5-bromo-1-pentene, 9-borabicyclo[3.3.1]nonane dimer (9BBN), biphenyl, *N*-methyl-4-piperidone, methanesulfonic acid (MSA), trifluoromethanesulfonic acid (TFSA), trifluoroacetic acid (TFA), dichloromethane (DCM), tetrahydrofuran (THF), tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>), iodomethane (CH<sub>3</sub>I) were purchased from Anhui senrise technologies Co., Ltd. and used as received. *N*-methyl pyrrolidone (NMP), potassium hydroxide (KOH), sodium hydroxide (NaOH) were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. and used without further purification. 3,3,3',3'-Tetramethyl-1,1'-spirobiindane-6,6'-dihydroxy (SBI) and poly(biphenyl piperidine) (PBP) were synthesized according to literature methods [1,2].

### Characterization

<sup>1</sup>H NMR spectra were recorded on an AVANCE III 400 MHz spectrometer (Bruker, Karlsruhe, Germany) using deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) or deuterated methylene chloride (CD<sub>2</sub>Cl<sub>2</sub>) as the solvents. Gel permeation chromatography (GPC) was performed on a PL-50 GPC apparatus (Agilent Technologies, USA) using dimethylformamide (DMF) as the eluent at a flow rate of 1.0 mL min<sup>-1</sup>. FT-IR spectra were recorded on a Cary 660 FT-IR spectrometer (Agilent Technologies, USA) in attenuated total reflection (ATR) mode. Thermal gravimetric analysis (TGA) was carried out on a Q55 TGA (TA Instruments, USA) at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. Dynamic mechanical analysis (DMA) was conducted on a DMA 850 apparatus (TA Instruments, USA) at a heating rate of 5 °C min<sup>-1</sup> in tension mode with a frequency of 1 Hz under nitrogen. Tensile properties were measured on a Zwick/Roell Z1.0 universal material testing machine (ZwickRoell GmbH&Co.KG, Germany) with a constant displacement rate of 2 mm min<sup>-1</sup> in parallel for five

repetitions. Gas sorption isotherms were measured on a Micromeritics 3Flex Surface Characterization Analyzer at 77 K for N<sub>2</sub> and 273 K for CO<sub>2</sub>. Surface areas and pore size distributions were calculated using multipoint Brunauer-Emmet-Teller (BET) and density functional theory (DFT) methods, respectively. Small angle X-ray scattering (SAXS) was collected in the  $q$ -range of 0.3-6.0 nm<sup>-1</sup> using a Bruker Nanostar instrument. Atomic force microscopy (AFM) phase diagrams were obtained on a Bruker Dimension Icon instrument using a silicon-based n-type cantilever in the tapping mode. The polymer solution (1 mg/mL) was dipped on the mica flakes and drying under vacuum at 80 °C before AFM measurement. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 microscope operating at 200 kV.

### **Ion exchange capacity (IEC)**

The experimental IECs of AEMs in Cl<sup>-</sup> form were determined by Mohr titration. First, the membranes were exchanged to Cl<sup>-</sup> and heated at 80 °C under vacuum to a constant weight (recorded as  $W_{dry}$ ). Then, the membranes were immersed in 25 mL of 0.2 M NaNO<sub>3</sub> aqueous solution for 24 h. Finally, an AgNO<sub>3</sub> aqueous solution (0.01 M) was used to titrate the replaced Cl<sup>-</sup>, using K<sub>2</sub>CrO<sub>4</sub> as the indicator. The volume of AgNO<sub>3</sub> consumed was noted as  $V_{AgNO_3}$ . The IEC values were calculated from the dry mass of the membrane and the amount AgNO<sub>3</sub> consumed in titration, and calculated according to the following equation.

$$IEC (mmol g^{-1}) = \frac{0.01 \times V_{AgNO_3}}{W_{dry}}$$

### **Water uptake (WU) and swelling ratio (SR)**

AEMs (1 × 4 cm) were immersed in DI water at 30, 60 and 80 °C for 8 h. Then, the surface water of the membranes was wiped with a tissue, and the weight ( $W_{wet}$ ) and length ( $L_{wet}$ ) of the membranes were measured. Afterwards, the membranes were dried under vacuum for 24 h at 80 °C, and the weight ( $W_{dry}$ ) and length ( $L_{dry}$ ) of the dry membranes were also recorded. The following equations were used to determine the WU and SR:

$$WU (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \%$$

$$SR (\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \%$$

### Gel fraction

Gel fraction was evaluated using a solvent extraction method. A dry membrane sample was weighted ( $W_a$ ) and immersed in NMP at 80 °C for 12 h to dissolve the soluble component. The insoluble component was taken out and dried under vacuum at 150 °C for 12 h to remove the residual solvent. The weight ( $W_b$ ) of the dry insoluble polymer membrane was measured. The following equation was used to determine gel fraction (GF):

$$GF (\%) = \frac{W_b}{W_a} \times 100 \%$$

### Density and fractional free volume

Membrane density was recorded using a density balance (Sartorius YDK03 Density Determination Kit) with an accuracy of 0.1 mg, with isooctane as the medium solvent. Before testing, all membranes were dried in vacuum condition at 100 °C for 12 h. Fractional free volume ( $FFV$ ) was calculated as follows:

$$FFV = 1 - \frac{1.3\rho V_w}{M}$$

where  $M$  is the molar mass ( $\text{g mol}^{-1}$ ) of the repeat unit,  $V_w$  represents the van der Waals volume calculated by a literature method [3].

### Gas permeability

$\text{H}_2$  and  $\text{O}_2$  permeability was tested at 35 °C under a upstream pressure of 2 and 5 bar by constant-volume/variable-pressure time-lag method [4]. The downstream pressure was recorded by an Inficon transducer ranging from 0 to 100 torr. Gas permeability ( $P$ ) was measured using the following equation [5]:

$$P = D \times S = 10^{10} \times \frac{V_d \times l}{P_{up} \times T \times A \times R} \times \frac{d_p}{d_t}$$

where  $P$  is the permeability (Barrer),  $V_d$  is the calibrated permeate volume ( $\text{cm}^3$ ),  $l$  is the membrane thickness (cm),  $P_{up}$  is the upstream pressure (cmHg),  $A$  is the effective membrane area ( $\text{cm}^2$ ),  $T$  is the operating temperature (K),  $R$  is the gas constant ( $[\text{cm}^3 \text{ cmHg (STP)}]/[\text{cm}^3\text{K}]$ ) and  $d_p/d_t$  is the steady-state downstream pressure increase rate (cmHg/s).

### **Ion conductivity**

The ohmic resistance was tested on an electrochemical impedance spectroscopy (CHI760E workstation) in DI water from 30 to 80 °C at 10 mV and 10-10<sup>5</sup> Hz using a four-point probe method. At given temperatures, each membrane was equilibrated at least 30 min before recording the impedance. The OH<sup>-</sup> and Cl<sup>-</sup> conductivities can be calculated according to the following equation:

$$\sigma \text{ (mS cm}^{-1}\text{)} = \frac{L}{RWT}$$

where  $L$  (1 cm) is the distance between the two inner platinum wires,  $R$  is the resistance of the membrane in  $\Omega$ , and  $W$  and  $T$  are the width and the thickness of the membrane in cm, respectively.

### **Chemical stability**

The membranes were soaked in 6 M NaOH aqueous solutions at 80 °C for 40 days. The alkaline stability of the membranes was evaluated by comparing the changes in OH<sup>-</sup> conductivity, chemical structure, and mechanical property.

### **Anion exchange membrane water electrolyzers (AEMWE)**

Membrane electrode assembly (MEA) was fabricated by the catalyst-coated substrate method using Ni foam anode and Ni-based ternary cathode (EHYDRO<sup>®</sup>Coral, Ningbo Sino-Tech Hydrogen Membrane Technology Co., Ltd, China). The membrane was sandwiched between the cathode and anode. The electrolysis cell was made up of stainless steel flow field plates and rubber gaskets. The power is supplied with commercial battery testing equipment (CT-4008-5V10A-

FA, NEWARE Technology Limited, China). Before the first polarization curve, the cell was conditioned at  $12.5 \text{ mA cm}^{-2}$  for 30 min. During the testing, the temperatures were 40-80 °C, the flow rates of the electrolyte were 16-48  $\text{mL min}^{-1}$ , and the circulating alkaline concentrations were 1-10 M. The polarization curves were measured in a galvanostatic mode at  $12.5\text{-}3000 \text{ mA cm}^{-2}$ . Finally, the *in-situ* durability was evaluated at a constant current density of  $0.5 \text{ A cm}^{-2}$  at 80 °C and a KOH concentration of 6 M.

### **Synthesis of PX-SBI-Br**

4'-bromo-2,2,2-trifluoroacetophenone (3.04 g, 12 mmol), SBI (3.08 g, 10 mmol), and DCM (12 mL) were charged into a 50 mL one-necked flask, and stirred at room temperature for 10 min. TFSA (9.6 mL) was added dropwise to the solution, and stirred for 48 h. The resultant gel was precipitated in methanol, and the solid was filtered and washed three times with a mixture of methanol and water (1:1). The obtained powder was dried under vacuum at 100 °C for 12 h (5.0 g, yield: 95 %).

### **Synthesis of PX-SBI-5CBr**

9BBN (0.98 g, 4 mmol), 5-bromo-1-pentene (0.60 g, 4 mmol), and THF (20 mL) were added in a 120 mL pressure flask with a stir bar. The reaction was heated at 60 °C for 8 h. PX-SBI-Br (1.05 g, 2 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.07 g, 0.06 mmol), KOH (0.19 g, 3.4 mmol), DI water (2 mL), and THF (20 mL) were added to the pressure flask under anaerobic treatment, and the mixture was stirred at 70 °C for 16 h. After cooling to room temperature, the solution was precipitated into methanol. The resulting solid was filtered and washed three times with a mixture of methanol and water (1:1). The polymer was purified by Soxhlet extraction with methanol and freeze-dried under vacuum (1.1 g, yield: 92 %).

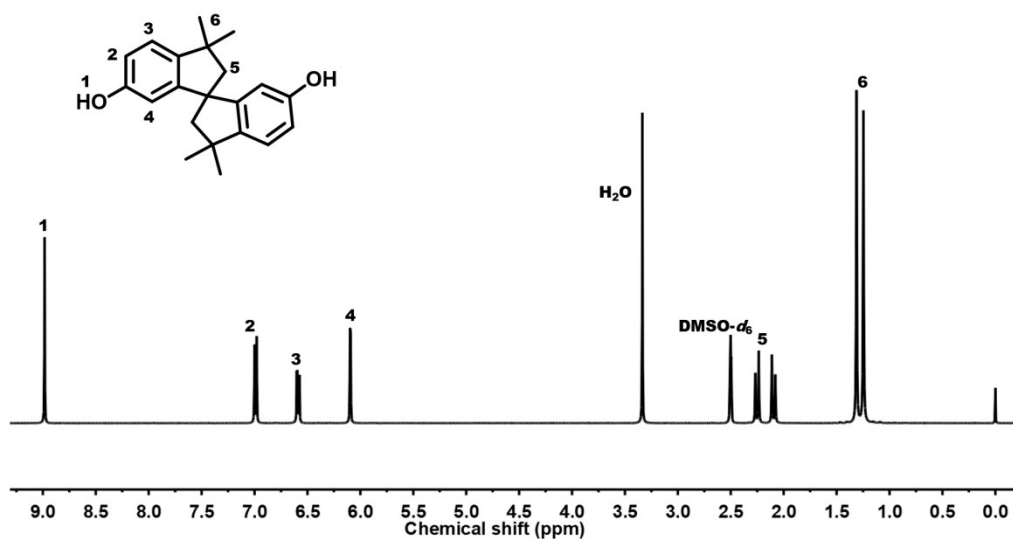
### **Synthesis of QPBP-PX-x**

The procedure for QPBP-PX-5% was shown below. PBP (0.125 g, 0.5 mmol) and PX-SBI-5CBr (0.0149 g, 0.025 mmol) were separately dissolved in 15 mL of NMP, and the two solutions were subsequently mixed. The resulting solution was heated at 80 °C for 48 h to performance the cross-linking reaction. After cooling to room

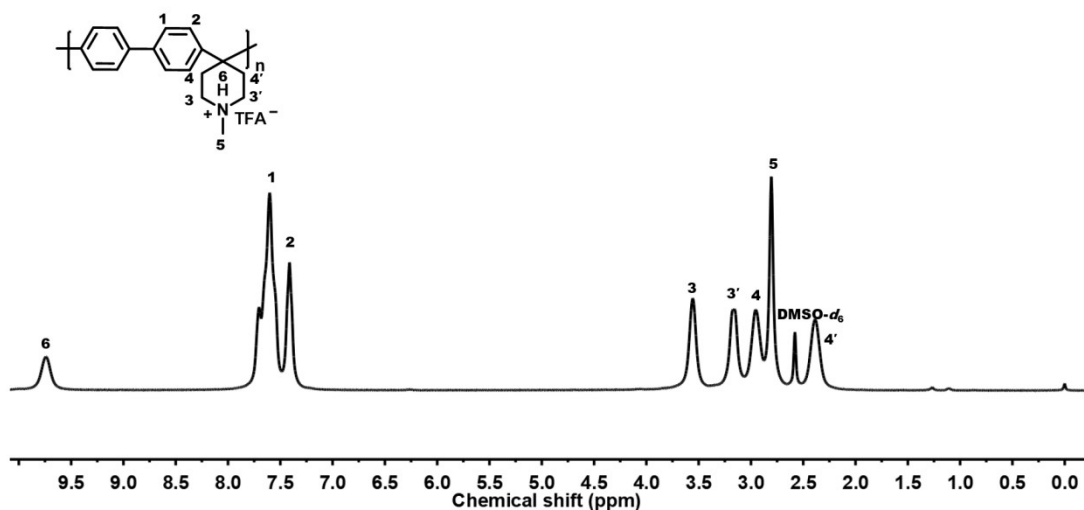
temperature, CH<sub>3</sub>I (0.710 g, 5 mmol) was added to completely quaternize the rest piperidine. The reaction mixture was then stirred at 50 °C for 24 h. Then, the polymer solution was poured into ethyl acetate, and yellowish-brown solid was obtained. It should be noted that the precipitated polymer exhibited significantly different solubility before and after vacuum drying. The undried polymers remained soluble in NMP. However, once dried, the polymers can not be dissolved any more. It is hypothesized that this discrepancy arised from the solvation by the residue solvents within the polymer before drying. Finally, the solid was collected by filtration and then dissolved in NMP for preservation. QPBP-PX-10% and QPBP-PX-15% were prepared according to a similar procedure, with the mole ratios between PX-SBI-5CBr and PBP being 1:10 and 1.5:10, respectively.

#### **Preparation of QPBP-PX-x crosslinked membranes**

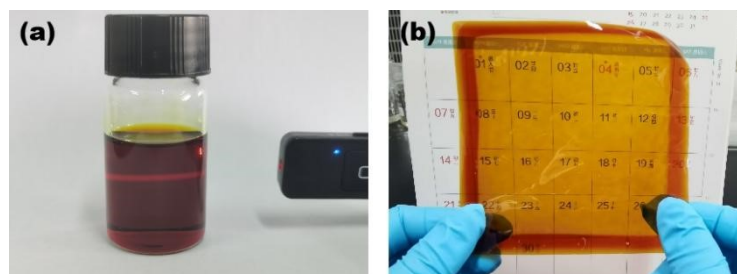
The QPBP-PX-x NMP solutions were filtered through a 1 μm PTFE filter and cast onto clean glass plates. The wet membranes were dried in a conventional oven at 100 °C for 12 h. After cooling, the membranes were peeled off by soaking in DI water and washed three times with DI water. Then, the membranes were immersed in 1 M NaOH or NaCl solution for 48 h to obtain QPBP-PX-x AEMs in OH<sup>-</sup> or Cl<sup>-</sup> form, respectively. The AEMs were washed thoroughly with DI water and stored in DI water before measurements.



**Fig. S1** <sup>1</sup>H NMR spectra of SBI

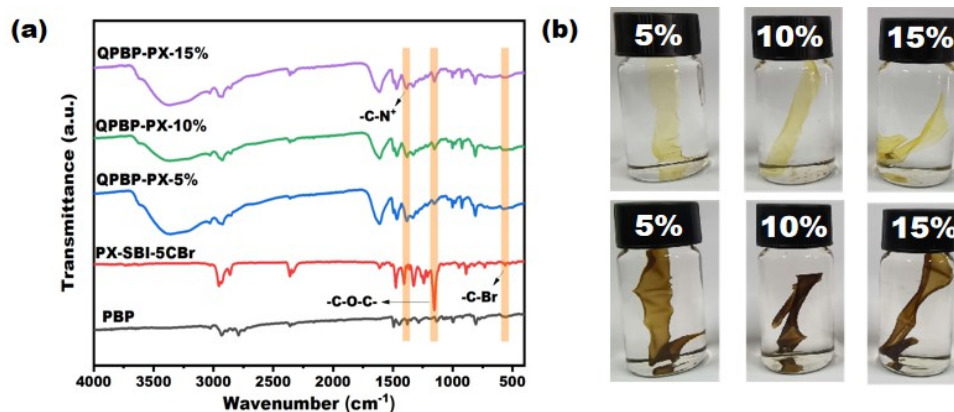


**Fig. S2** <sup>1</sup>H NMR spectra of PBP (The solvent was DMSO-*d*<sub>6</sub> containing 3–6 vol% of TFA)

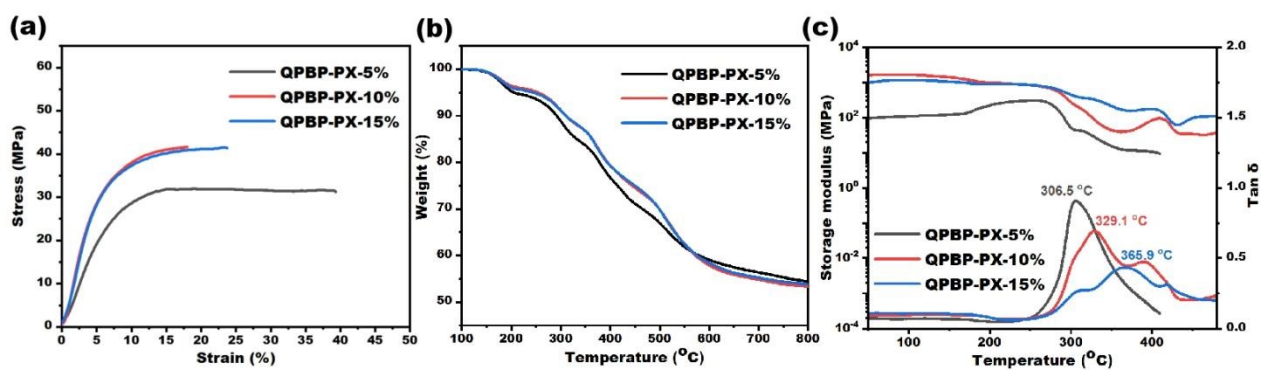


**Fig. S3** (a) The colloidal solution and (b) membrane images of QBP-PX-15%





**Fig. S4** (a) FT-IR spectra of PBP, PX-SBI-5CBr, and QPBP-PX-x; (b) images of QPBP-PX-x crosslinked membranes immersing in NMP at room temperature (top) and 80 °C for 8 h (bottom)



**Fig. S5** (a) stress-strain, (b) TGA, and (c) DMA curves of QPBP-PX-5%, QPBP-PX-10%, and QPBP-PX-15%

**Table S1.** H<sub>2</sub> and O<sub>2</sub> permeability of QPBP-PX-5%, QPBP-PX-10%, QPBP-PX-15%, and commercial PiperION in OH<sup>-</sup> form

AEM	H <sub>2</sub> permeability (barrer)		O <sub>2</sub> permeability (barrer)	
	2 bar	5 bar	2 bar	5 bar
QPBP-PX-5%	4.38	3.84	0.28	0.22
QPBP-PX-10%	9.83	9.14	0.69	0.65
QPBP-PX-15%	16.3	16.15	1.50	1.49
PiperION	24.4	26.5	3.38	3.29

**Table S2.** Mechanical properties of QPBP-PX-5%, QBPBPX-10%, and QPBP-PX-15%

Polymer	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)
QPBP-PX-5%	31.2 ± 3.2	0.158 ± 0.054	39.1 ± 3.2
QPBP-PX-10%	41.6 ± 2.3	0.186 ± 0.066	18.3 ± 1.2
QPBP-PX-15%	41.4 ± 3.6	0.304 ± 0.012	24.6 ± 2.1

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