

Supporting Information

Hydrophilic flexible di-piperidine crosslinked membranes with highly-effective ionic channels for water electrolysis

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1. Instruments and test characterizations

1.1 Structure

¹H NMR: The polymers PTP, PTP-C and PTP-N and the crosslinker QABIEP and QABBrPP were analyzed by hydrogen NMR spectroscopy, using Avance III spectrometer (Bruker, 400 MHz).

FTIR: The membrane materials were analyzed by Fourier Transform Infrared Spectroscopy (FTIR, Varian CP-3800) to prove the success of click crosslinking.

1.2 Gel fraction

The prepared crosslinked membranes were dried at 80 °C for 24 h and the weights were recorded, then the dried membranes were immersed in DMSO and ultrasonicated for 2 h and 4 h. Finally, the membranes were dried and the weights were recorded. The gel fraction was calculated as follows.

$$\frac{W_1 - W_2}{W_1} \times 100\% \quad (2)$$

Where W_1 is the original dry weight of the membranes and W_2 is the dry weight after ultrasound.

1.3 Gel permeation chromatography (GPC)

GPC was performed on a SIL-20AXR (SHIMADZU) to determine the weight-average molar masses (M_w), using N,N-Dimethylformamide (chromatographic purity) with a flow rate of 1.0 mL min⁻¹

1.4 Morphology

Surface and cross-section of the dry AEMs in the Br⁻ form were observed by scanning electron microscope (SEM, Tescan, MAIA3 XMU). Microphase separation structure of the dry AEMs in the Br⁻ form were detected by atomic force microscope (AFM, DMFASTSCAN2-SYS).

1.5 Ionic exchange capacity (IEC)

The ion exchange capacities of membranes were measured by Mohr back titration. Typically, the crosslinked membranes in Br⁻ form were immersed in 0.01 M (C₁) 50 mL (V₁) HCl solution for 48 h. Then, the newly prepared 0.01 M (C₂) NaOH solution was used for back titration, When the titrated solution is neutral, record the lye volume (V₂). Finally, we need to dry the membranes and weigh them. The IEC of the membrane samples were calculated by the following formula.

$$IEC = \frac{C_1V_1 - C_2V_2}{m_{dry}} \quad (3)$$

1.6 Water uptake (WU) and swelling ratio (SR)

The OH⁻ form crosslinked membrane was soaked in deionized water at 30 °C to 80 °C for 72 h. Hereafter, the wet weight (m_{wet}) and wet length (L_{wet}) at each temperature were measured. Finally, the AEMs were dried and tested the dry weight (m_{dry}) and dry length (L_{dry}). The WU and SR of the AEMs can be calculated by the follow formulas.

$$WU(\%) = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\% \quad (4)$$

$$SR(\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \quad (5)$$

The hydration number is, defined as the number of water molecules contained in each polymer unit, was calculated as:

$$\lambda = \frac{WU \times 10}{SR \times 18} \quad (6)$$

1.7 Hydroxide conductivity

The hydroxide conductivity of AEMs were measured by Zahner IM6EX

electrochemical workstation with four electrode modes. Ohmic resistance (R) was recorded by electrochemical impedance spectroscopy (EIS) in the frequency range of 100 MHz to 100 KHz. Furthermore, The OH^- conductivity of the membranes can be calculated by the following formula.

$$\sigma = \frac{l}{RS} \quad (7)$$

Where L is the thickness of AEMs, R is the measured resistance and S is the contact area of AEMs.

1.8 Thermal stability and mechanical properties

In a nitrogen atmosphere, the TG209C thermogravimetric analysis (TGA) instrument was used to test the quality change of the membranes during the process from 30 °C to 800 °C, and the heating rate was controlled to 10 °C·min⁻¹. Changes in TGA curve was used for evaluating the thermal stability of the sample.

The tensile strength and elongation at break of the Br⁻ form membranes were detected by the MTS Model E43 tensile machine, where the tensile speed is 5 mm/min and the gauge length is 10.00 mm at room temperature.

1.9 Alkaline stability

Typically, the crosslinked membranes were immersed into 2 M NaOH solution for 2350 h at 80 °C. The alkaline stabilities of membranes were evaluated by ionic conductivity, IEC and FTIR, respectively.

1.10 Monomer solution preparation

The membrane electrode assemblies were composed with two sheets of gas diffusion layers (GDLs) and a catalyst-coated membrane (CCM). The catalyst slurry was prepared using 5 wt% polymers solution and 1 mg/mL of Pt/C catalyst (Johnson Matthey, 60 %) as cathode. 5 wt% polymers solution and 1 mg/mL of IrO₂ (Macklin, Ir>84.5%) catalyst is used as anode, where the ratio of catalyst to ionomer solution was 4:1(wt%). In detail, IPA and water (25:1 v/v) were added to catalyst to prepared 1 mg/mL catalyst solutions. Polymer was dissolved respectively in methanol and filtered using a 0.45 μm filter to produce 5 wt% ionomer solutions. Then, the mixed and homogeneous ionomer slurry was sprayed on the surface of the membranes using

Ultrasonic Electrostatic Spraying Apparatus to prepared the CCM. Finally, The CCM were immersed in 1 M NaOH for 12 h and then washed perfectly by deionized water for later using.

1.11 Water electrolysis

Anion exchange membrane water electrolysis experiments were performed in an alkaline electrolyzer (MEA: 4 cm²) with 1.0 mg cm⁻² IrO₂ anode catalyst and 1.0 mg cm⁻² 60 % Pt/C cathode catalyst at 80 °C. 1 M KOH solution was circulated by a set of peristaltic pumps with 80 mL min⁻¹. Electrochemical impedance spectra (*EIS*) (Zahner, Germany) were performed at 1.8 V and 1Hz-100kHz to analyze the R_{ohm} and R_{ct} of the AEMWEs for crosslinked membranes PTP-N-QAX and PTP-C-QAX. The *EIS* results were finally fitted by ZSimpWin software. Constant voltage tests and polarization curves were performed by an electrochemical workstation (Wuhan LANHE). Durability tests are performed at a constant current of 500 mA cm⁻² and 60 °C.

1.12 Molecular dynamics simulation and Gaussian simulation

Polymer unit model was constructed by Materials Studio 2019 and was run by molecular dynamics calculation and analysis. When performing the geometry optimization, we choose the COMPASS II force field and the Smart algorithm. After geometry optimization, Chain spacing of crosslinked polymer backbones was measured by distance tool.

Gaussian (G09W) was adopted to conduct density functional theory (DFT) calculations with Becke's three-parameter hybrid method using the Lee-Yang-Parr correlation functional (B3LYP). Geometric optimization and calculation at the 3-21G level, after that, the electrostatic potential (ESP) was obtained.

2. Supplementary results and data

2.1 Supplementary Figure

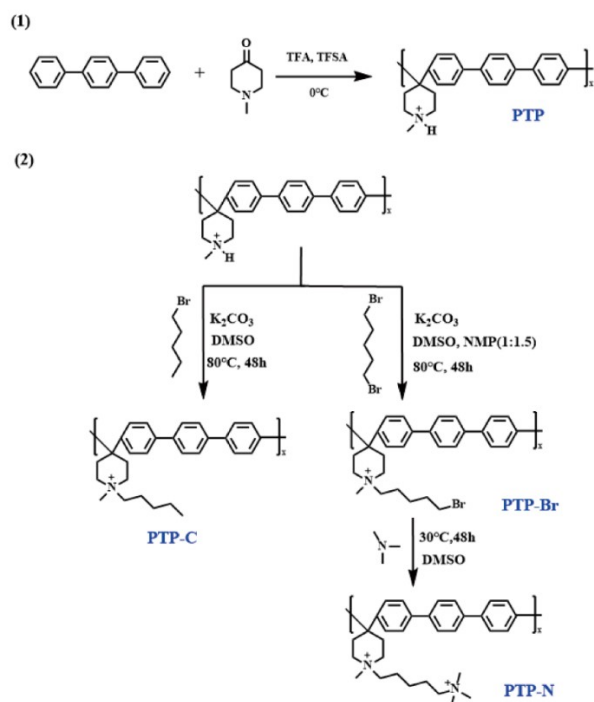


Fig. S1. Synthesis route of backbone PTP and polymers PTP-N and PTP-C.

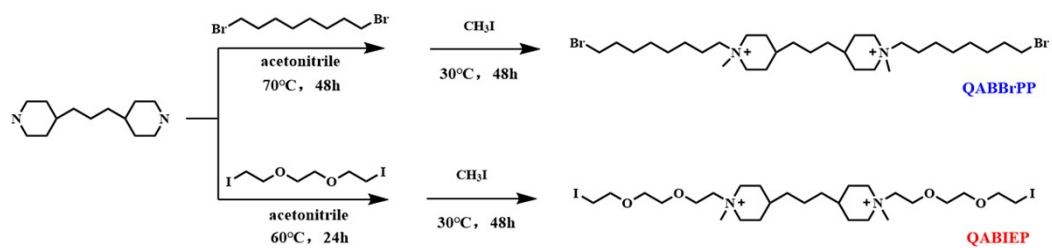


Fig. S2. Synthesis route of QABBrPP and QABIEP

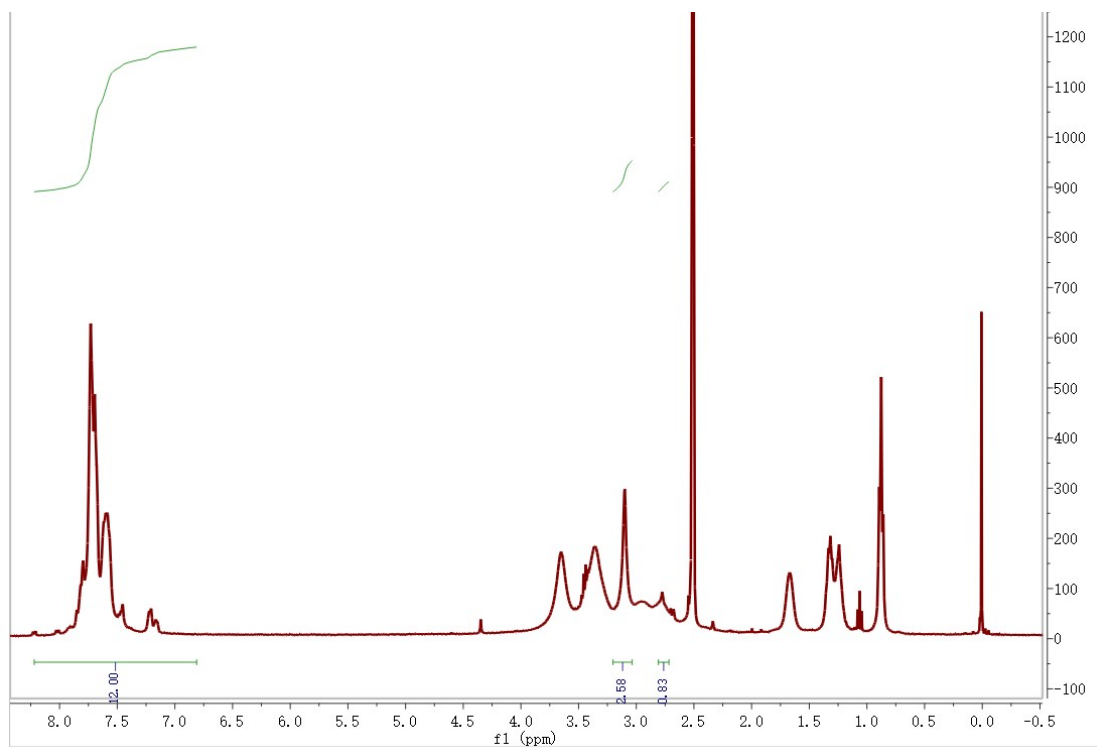


Fig. S3. 1-bromopentane graft ratio of ^1H NMR in polymer PTP-C.

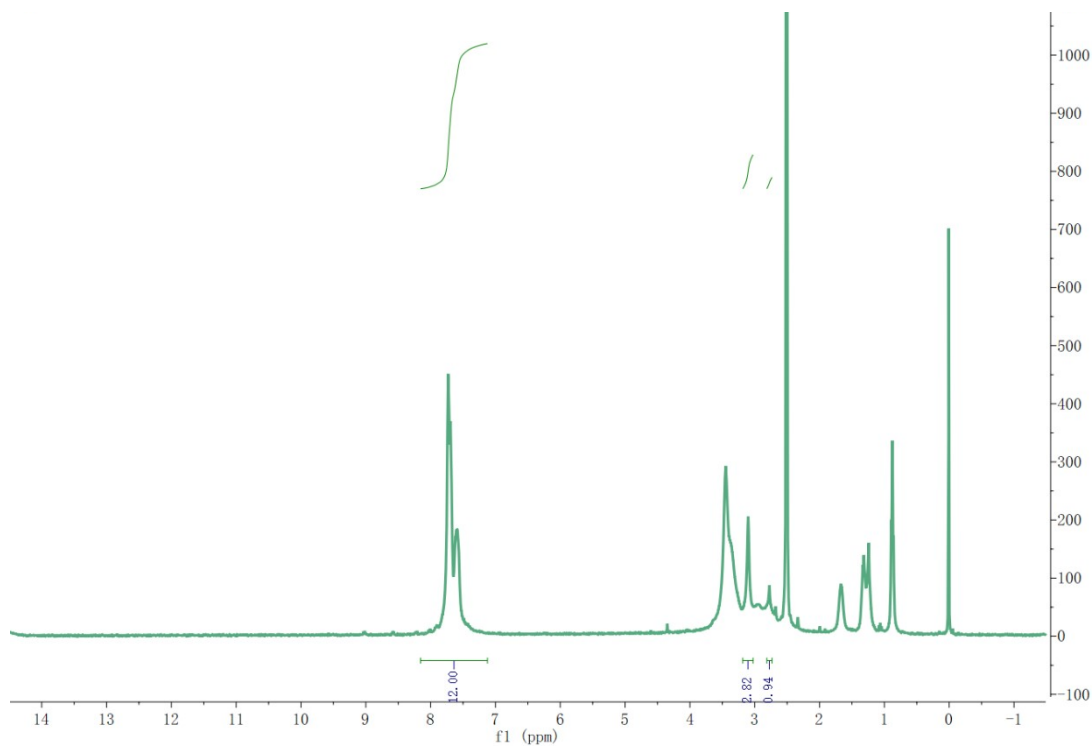


Fig. S4. 1,5-dibromopentane graft ratio of ^1H NMR in polymer PTP-N.

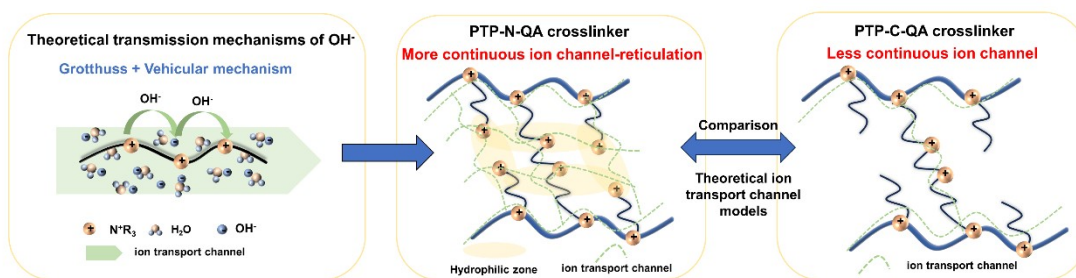


Fig. S5. Theoretical transport of ions analysis of polymers.

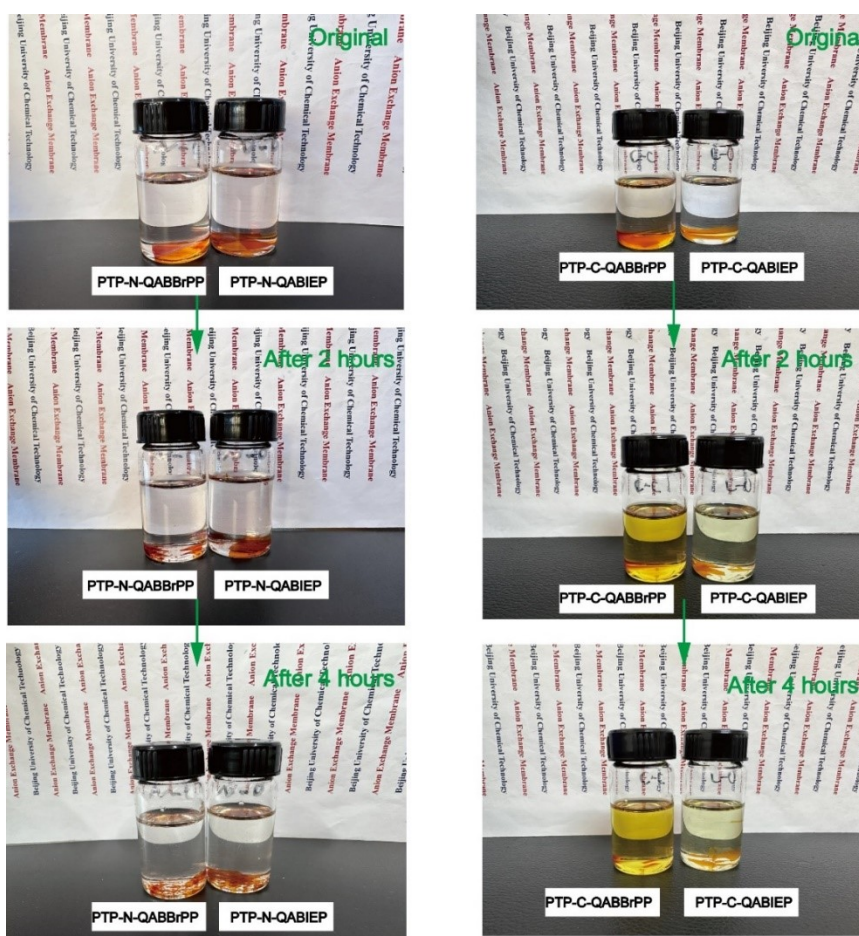


Fig. S6. The picture of gel fraction for crosslinked membranes PTP-N-QABrPP, PTP-N-QABIEP, PTP-C-QABrPP and PTP-C-QABIEP.

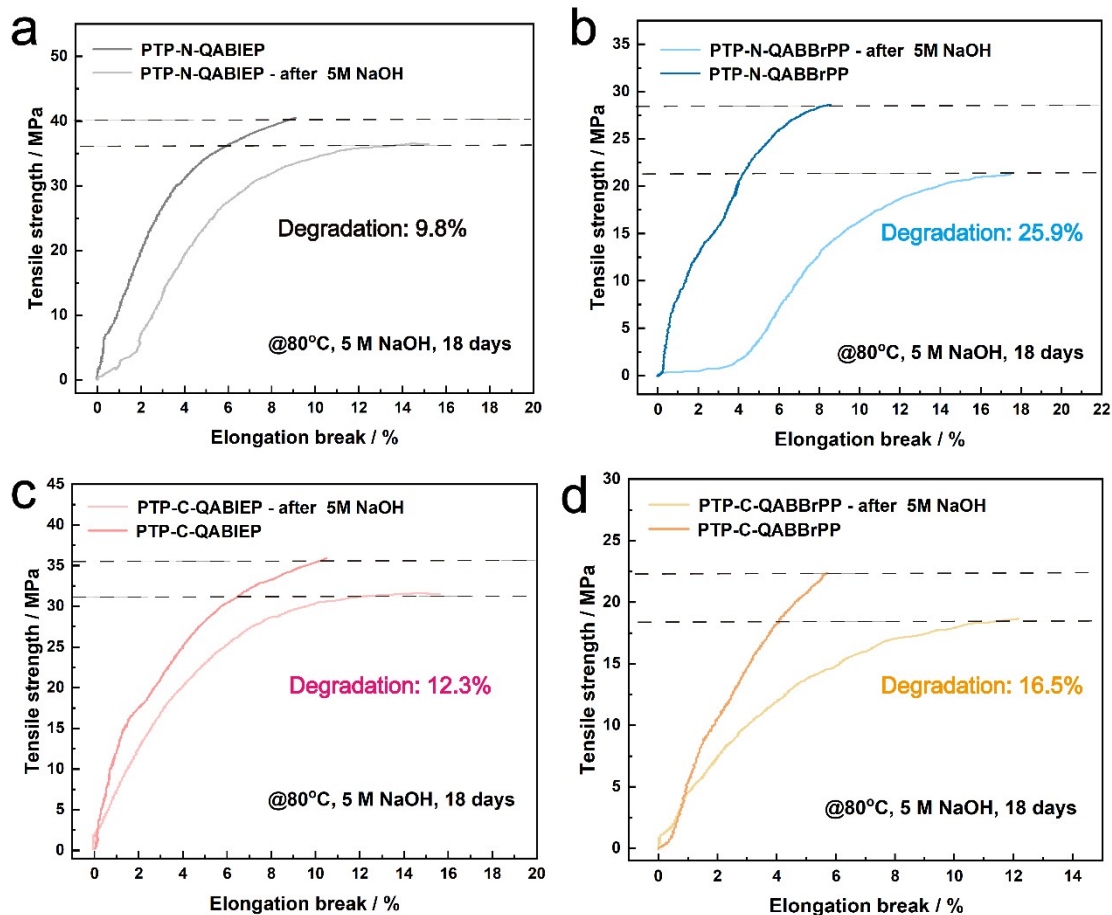


Fig. S7. The mechanical properties of crosslinked membranes PTP-N-QABBrPP, PTP-N-QABIEP, PTP-C-QABBrPP and PTP-C-QABIEP after stabilization in 5 M NaOH for 18 days, at 80°C.

2.2 Supplementary Table

Tab. S1. OH⁻ conductivity, WU, SR, IEC and λ of PTP-N-QAX and PTP-C-QAX crosslinked membranes.

Membrane	Gel fraction (%)	IEC ^a (mmol/g)	OH ⁻ conductivity (mS/cm)		WU (%)		SR (%)		λ ^a
			30°C	80°C	30°C	80°C	30°C	80°C	
PTP-N-QABIEP	80	2.38	26.0	151.7	56.4	118.4	9.8	20.2	3.2
PTP-N-QABBrPP	78	2.25	19.2	123.0	37.1	92.3	7.4	16.0	2.8
PTP-C-QABIEP	75	2.02	10.9	84.3	24.2	65.5	5.2	12.5	2.6
PTP-C-QABBrPP	70	1.97	6.7	60.3	20.7	48.0	4.9	10.1	2.3

^a is at 30°C

Tab. S2. The change of IEC of PTP-N-QAX and PTP-C-QAX crosslinked membranes after alkaline stability. Water electrolysis performance in 1 M KOH concentration and pure water.

Membrane	IEC ^a (mmol/g)	R _{ohm} ^b (Ω cm ²)		R _{ct} ^b (Ω cm ²)		LSV ^c (A cm ⁻²)	
		1M KOH	Pure water	1M KOH	Pure water	1M KOH	Pure water
PTP-N-QABIEP	2.02	0.136	0.162	0.051	0.239	2.14	0.600
PTP-N-QABBrPP	1.76	0.138	0.165	0.096	0.292	1.68	0.428
PTP-C-QABIEP	1.66	0.176	0.252	0.238	0.366	0.760	0.186
PTP-C-QABBrPP	1.40	0.217	0.254	0.274	0.449	0.540	0.125

a: the change of IEC after 2000h alkaline stability; b: at 1.8V, 1 Hz-100 kHz and 60°C; c: at 2.2V and 60°C