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Electronic Supplementary Information (ESI)

Self-aggregating cationic-chains enable alkaline stable ion-conducting channel for anion-exchange membrane fuel cells

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Content

1. ^{1}H NMR spectroscopic characterization

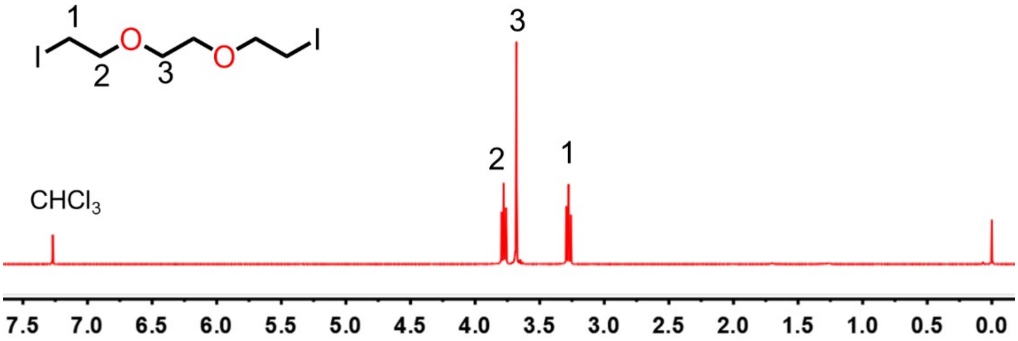

Fig. S1 ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of 1, 2-bis (2-iodoethoxy)ethane.

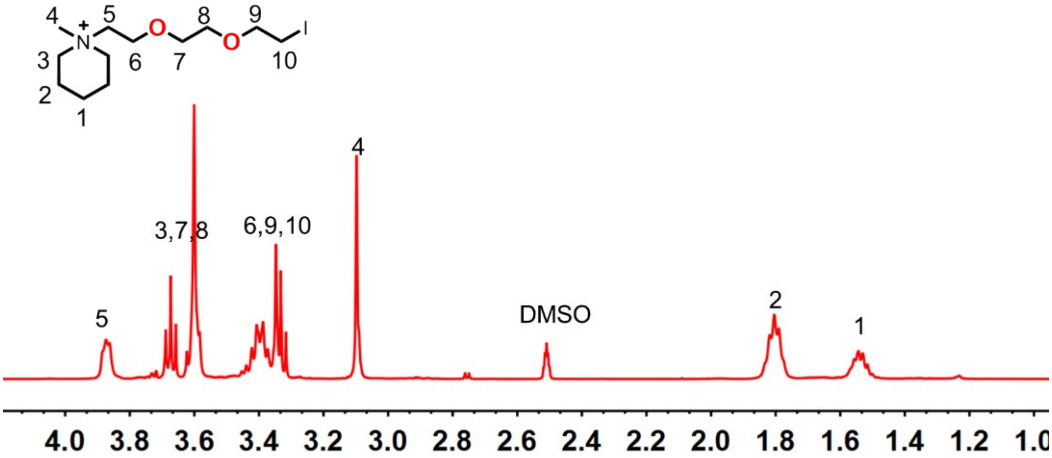

Fig. S2 ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d_6) of OIMP.

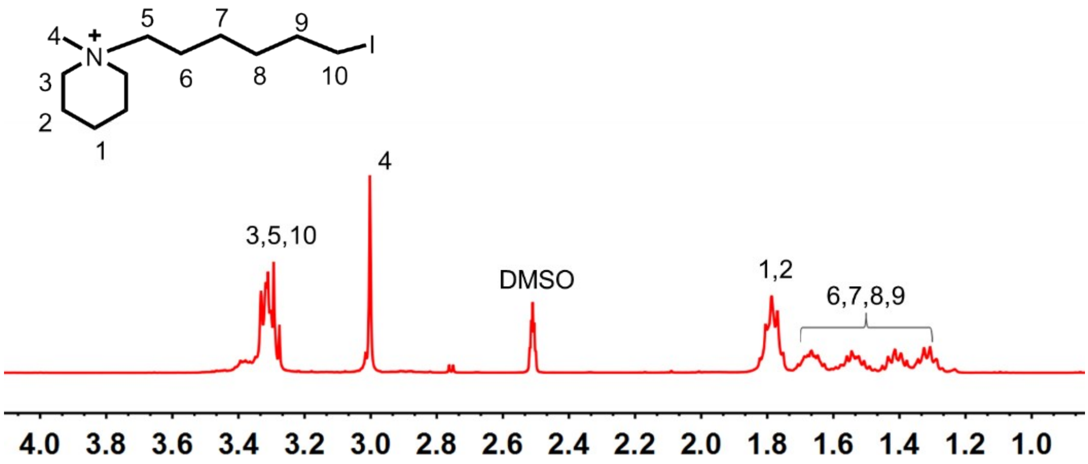

Fig. S3 ^{1}H NMR spectra (400 MHz, 298 K, DMSO-d$_6$) of IMP.

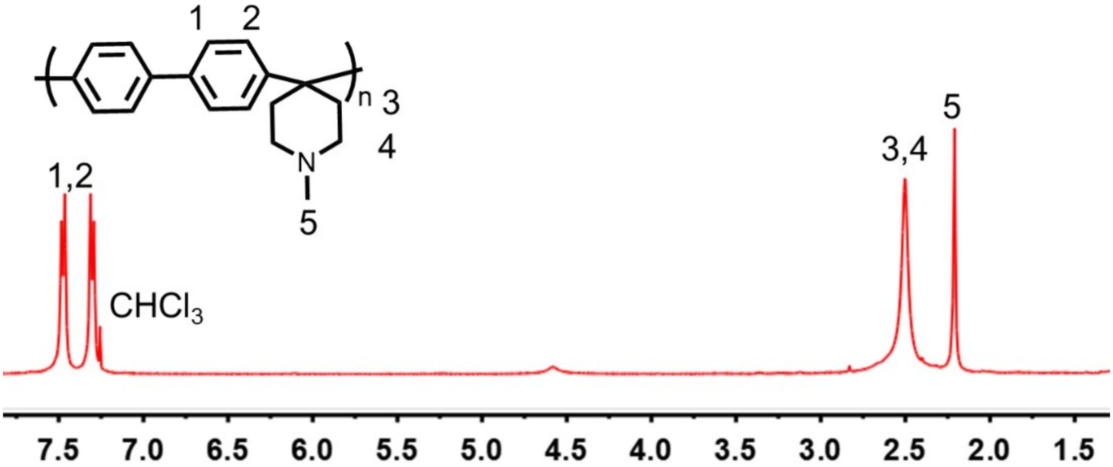

Fig. S4 ^{1}H NMR spectra (400 MHz, 298 K, CDCl$_3$) of PBP

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2. Experimental details

2.1 Characterization.

^{1}H NMR spectra were recorded at 400 MHz on a Bruker 510 instrument using $CDCl_3$ or DMSO-d_6 or D_2O as the solvent and tetramethylsilane (TMS) as the shift reference. Atomic Force Microscope (AFM) analysis was conducted in tapping mode using a Veeco dinnova SPM equipped with a vibrating probe. For transmission electron microscopy (TEM), the AEM was firstly stained with iodide anions. The dried sample was then sectioned into ~60 nm thick slices using a LEICA UC6+UC7 ultra microtome and then coated on a Cu grid. The TEM images were collected on a JEM 2100F field emission transmission electron microscope (JEOL Ltd., Akishima, Tokyo, Japan) operated at an accelerating voltage of 200 kV. A discovery DMA 800 dynamic mechanical analyzer (TA Instruments Co., USA) was used to record key mechanical properties, including tensile strength (TS) and elongation at break (E_b). Thermogravimetric analysis (Discovery TGA Q5000IR, TA Instruments, USA) was employed to investigate the thermal stability of the as-prepared AEMs. The resultant thermograms were recorded at a heating rate of 10 °C min^{-1} under a N_2 atmosphere. Small-angle X-ray scattering (SAXS) data were recorded on an Anton Paar Saxesess mc^2 instrument equipped with an Osmic microfocus Cu Ka source and a parallel beam optic.

2.2 Water uptake (WU) and swelling ratio (SR) and ion exchange capacity (IEC).

Before the AEM samples (4 cm × 1 cm, in OH^- form) were dried in a vacuum at 60 ^oC for 24 h, the samples were immersed in DI water at given temperatures for 24 h. And then gently wiping away the water from the surfaces with tissue paper, the weight and length of the hydrated samples were measured quickly. The mass and length were then measured (denoted as W_{wet} and L_{wet}). Afterward, WU and SR of the membranes were calculated as follows:

$$water\ uptake(wt\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

$$swell\ ratio(wt\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\%$$

where W_{dry} and L_{dry} are the weight and length of the dried samples, respectively, and W_{wet} and L_{wet} are weight and length of hydrated samples. The IEC of each AEM was measured using the Mohr titration method. A dried AEM sample (weight was recorded W_{dry}) was immersed in NaCl aqueous solution (1 mol L^{-1}) for 24 h at room temperature. Then, the sample was washed with DI water. Afterward, the sample was immersed in aqueous Na_2SO_4 (0.5 mol L^{-1}) for 24 h to exchange the Cl^- anions with SO_4^{2-}. Finally, the collected solution was titrated with a standardized aqueous $AgNO_3$ (C_{AgNO_3}= 0.01 mol L^{-1}) solution using K_2CrO_4 as the colorimetric indicator. The volume of the consumed $AgNO_3$ was recorded as V_{AgNO3}, and the IEC value can be calculated from the following equation:

$$IEC(mmol/g) = (V_{AgNO_3} \times C_{AgNO_3})/W_{dry}$$

2.3 Hydroxide conductivity.

The conductivity of each AEM was measured using impedance spectroscopy with a standard four-point probe technique and an Auto lab Zahner Zennium E (Germany) in galvanostatic mode. An AEM sample (OH^- form) was placed into a Teflon cell where it was in contact with two current collecting electrodes and two potential sensing electrodes. Then the cell was immediately immersed in DI water. And the electrochemical impedance spectrum was collected at a given temperature. The test was conducted in galvanostatic mode with an AC current amplitude of 0.01 mA and a frequencies range of 1 MHz to 100 Hz. The conductivity can be calculated according to the following equation:

$$\sigma = \frac{L}{RWd}$$

where L is the distance between two potential-sensing electrodes (1 cm), R is the ohmic resistance of the membrane, W and d are the width and thickness of the sample at the corresponding temperature, respectively.

2.4 Alkaline stability.

The AEMs were immersed in aqueous 2M aq. NaOH at 80 °C for controlled periods of time. After thorough washing with DI water (to remove the excess sodium hydroxide), the OH^- conductivity of the AEMs was measured at 30 °C.

2.5 H_2/O_2 single fuel cell.

The membrane electrode assembly (MEA) was prepared according to our previous work.[1, 2] Quaternized poly(2,6-dimethyl-1,4-phenyleneoxide) with terminal vinyl pendants (VBQPPO) was firstly dissolved in methanol. Then the solution was then added into a suspension of catalyst (cathode: Pt/C, for anode: PtRu/C, both 60 *wt%* metal content), to prepare the ink (20 wt% ionomer and 80 *wt%* catalyst). The resulting catalyst inks were inkjet printed onto a carbon paper (Toray TGP-H-060) to fabricate the gas diffusion electrodes (GDEs). The metal loading in both anode and cathode was controlled at 0.5 mg cm^{-2}, and the electrode area was 12.25 cm^2. The prepared GDE and AEM were then converted to OH^- form by immersing in 1M aq. NaOH for 12 h and followed by thorough washing with deionized water. Finally, the AEM to be tested was sandwiched between two GDE to obtain the membrane electrode assembly (MEA). Single-cell H_2/O_2 AEMFC was galvanostatically tested using an 890E Multi Range fuel cell test station (Scribner Associates, USA) in a galvanic mode at 70 °C with a flow rate of 1 L min^{-1} (both H_2 and O_2 supplied, 100% RH, without backpressure on both sides). The cell voltage and power density at each current density were recorded after the power output stabilized. The longer-term durability test was conducted at 70 °C with a flow rate of 0.5 L min^{-1}(100%RH). The operating voltages were recorded as a function of time with the cell held at 0.4 A cm^{-2} current density. In situ electrochemical impedance spectroscopy (EIS) analysis were conducted with H_2/O_2 feed at 1 L min^{-1} (70 °C, with frequency range of 1Hz to 10 kHz, at a constant current of 1000 mA.).

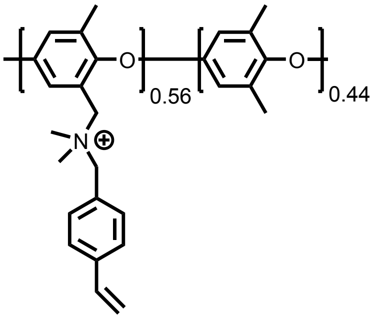

Fig. S5 The chemical structure of the VBQPPO ionomer

3. The general properties of the prepared membranes.

AEM	IEC^{a} (mmol g^{-1})	$\sigma_{OH^{-}}{}^{b}$ (mS cm^{-1})	Water uptake^{b} (wt%)	Swelling Ratio^{b}(%)	TS^{c} (MPa)	E$_{b}$^{c} (%)
O-PDQA-1	1.33	23.2	25.9	5.5	20.8	6.9
PDQA-1	1.30	20.8	22.2	4.2	12.7	2.8
O-PDQA-2	1.62	33.0	34.6	9.0	12.1	12.5
PDQA-2	1.59	28.2	28.6	7.9	14.3	9.3
O-PDQA-3	1.93	61.1	46.2	12.5	7.4	19.7
PDQA-3	1.98	49.1	37.4	9.6	6.8	11.8

Table S1 A summary of the general properties of the prepared AEMs

a. Ion exchange capacities (IECs) were obtained by Mohr titration method.

b. The OH^- conductivities, water uptakes, swell ratios were all measured with AEMs in the OH^- forms at 30 °C.

c. Tensile strength (TS, MPa) and elongation at break (E_b, %) of the AEMs were measured in their hydrated state at room temperature.

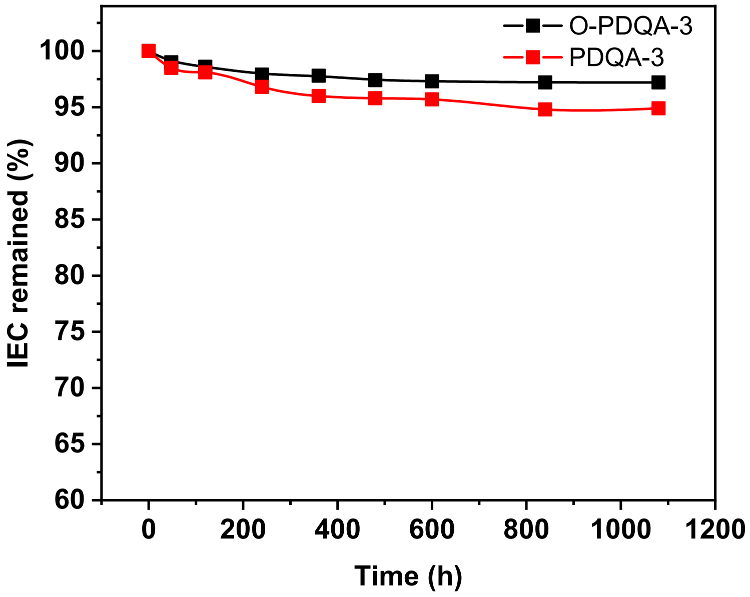

Fig. S6 IEC retention of the O-PDQA and PDQA membranes when immersed at 80 °C in 2 M aq. NaOH for different time intervals.

4. Mechanical properties.

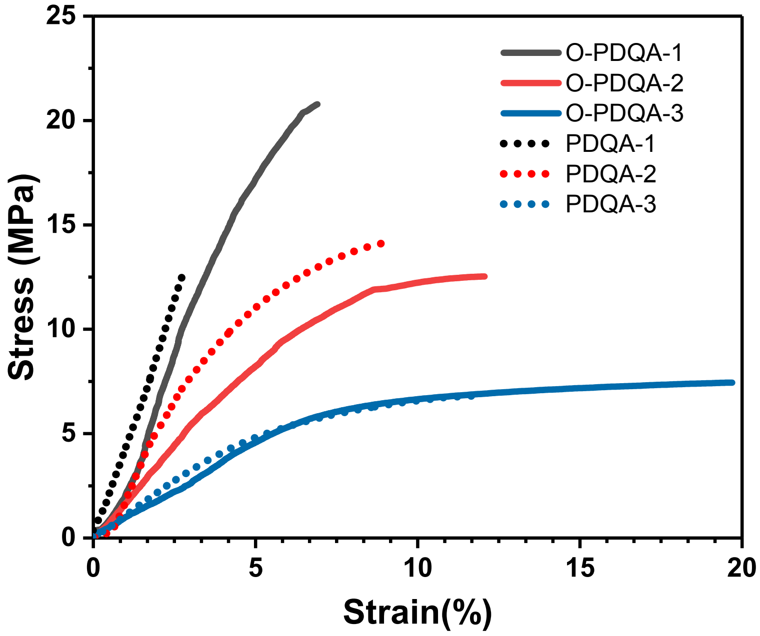

Fig.S7 Tensile mechanical properties (TS, Eb) of the O-PDQA and PDQA AEMs

5. Thermal stability data.

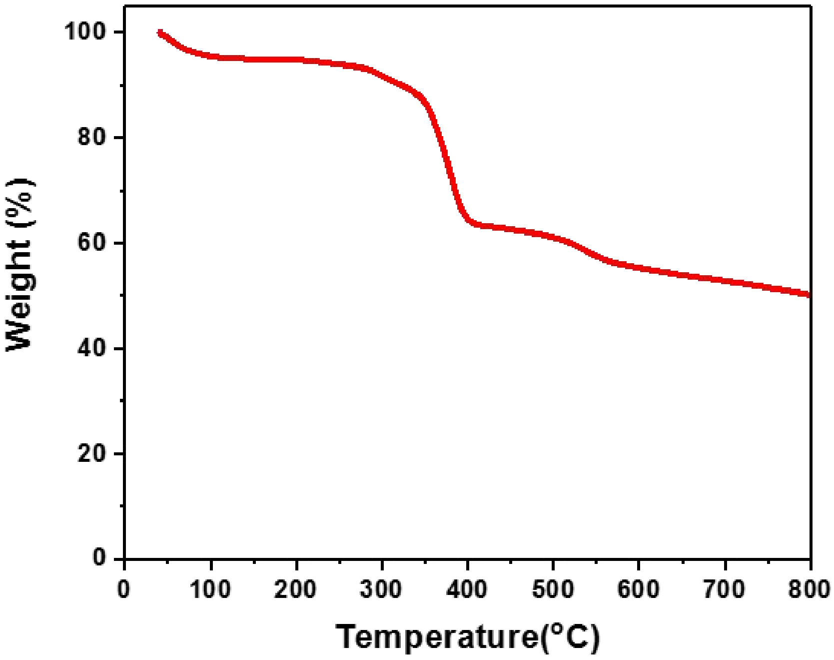

Fig. S8 TGA thermogram of O-PDQA.

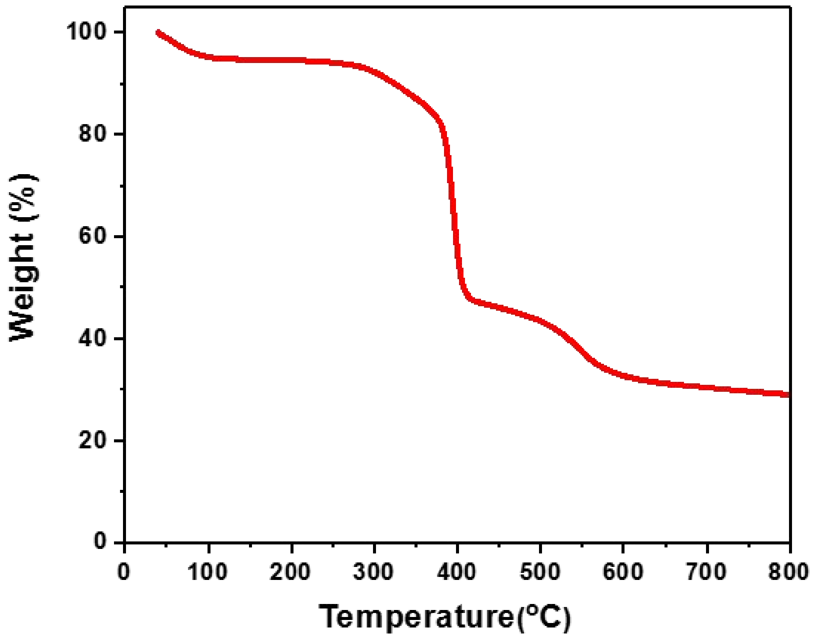

Fig. S9 TGA thermogram of PDQA.

6. EIS test of the fuel cell

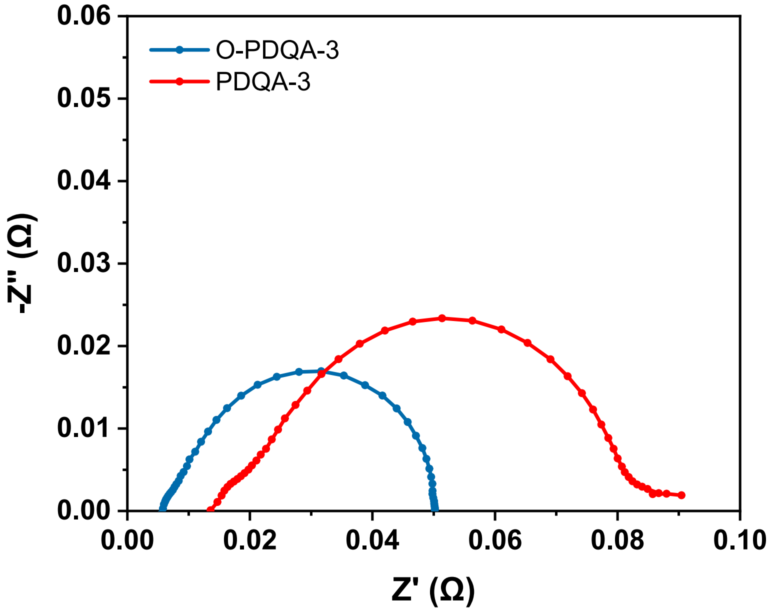

Fig. S10 In situ electrochemical impedance spectroscopy (EIS) analysis of the O-PDQA-3 and PDQA-3 MEAs with H_2/O_2 feed at 1 L min^{-1} (70 °C, at a constant current of 1000 mA)

7. Solubility test of O-PDQA and PDQA polymers

Table S2 The solubility of the O-PDQA and PDQA polymer.

	methanol	ethanol	isopropanol	acetone	$CHCl_2$	DMSO	NMP
O-PDQA	□	□	□	□	□	□	□
PDQA	□	□	□	□	□	□	□

insoluble: - ; soluble: +

8. References for supplementary information.

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2. Y. Zhu, L. Ding, X. Liang, M. A. Shehzad, L. Wang, X. Ge, Y. He, L. Wu, J. R. Varcoe and T. Xu, *Energy Environ. Sci.*, 2018, **11**, 3472-3479.