

Electronic Supplementary Information

for

A mechanically strong and tough anion exchange membrane engineered with non-covalent modalities

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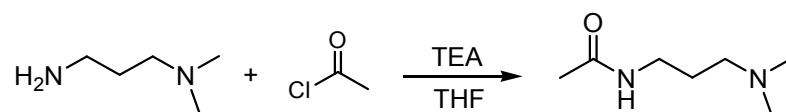
1. Experimental Section

1.1 Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was kindly supplied by Saudi Basic Industries Corporation. N-bromosuccinimide (NBS) was purchased from Aladdin Industrial Corporation and used without further purification. 2,2'-Azobisisobutyronitrile (AIBN, Sinopharm Chemical Reagent Co., Ltd.) was recrystallized from ethanol and carefully stored in the refrigerator. N-methyl-2-pyrrolidone (NMP) was purchased from Sinopharm Chemical Reagent Co., Ltd and purified by distillation under reduced pressure over phosphorus pentoxide and stored over 4-Å molecular sieves. N,N-dimethyl-1,3-propanediamine, N,N,N'-trimethyl-1,3-propanediamine, N,N-dimethyl-1-hexanamine and acetyl chloride were purchased from J&K Chemicals and used without any purification. Unless otherwise noted, the other chemicals were purchased from Sinopharm Chemical Reagent and used as received. Bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-Br) was synthesized according to our previous reported method.^[S1]

1.2 Syntheses of amide-containing tertiary amine

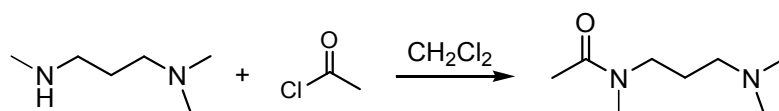
1.2.1 Synthesis of N-[3-(dimethylamino)propyl]acetamide



To a solution of N,N-dimethyl-1,3-propanediamine (2.00 g, 19.57 mmol) and Et₃N (3.4 mL, 24.47 mmol) in dry THF (10 mL), placed in ice-water bath under nitrogen atmosphere, acetyl chloride (1.92 g, 24.27 mmol) in dry THF (20 mL) was added dropwise with a dropping funnel. After stirring at about 0 °C for 30 min, the mixture was stirred for 12 h at room temperature. The reaction mixture was filtered to remove the triethylammonium chloride, then concentrated under reduced pressure to provide the crude product. A yellowish liquid with the yield of 75% was obtained by a chromatography on silica gel using DCM/MeOH (7/1, v/v) as eluent. ¹H NMR (600

MHz, CDCl₃): δ 1.72 (quint, $J = 6.6$ Hz, 2H), 1.96 (s, 3H), 2.33 (s, 6H), 2.50 (t, $J = 6.6$ Hz, 2H), 3.33 (quart, $J = 6.0$ Hz, 2H), 6.91 ppm (s, 1H). HR-MS (ESI) calcd for C₇H₁₆N₂O [2M+Na]⁺: 311.2423, found: 311.0936.

1.2.2 Synthesis of N-[3-(dimethylamino)propyl]-N'-methylacetamide



To a solution of N,N,N'-trimethyl-1,3-propanediamine (1.0 g, 8.61 mmol) and 2 mL dry CH₂Cl₂ (2.0 mL), placed in ice-water bath under nitrogen atmosphere, acetyl chloride (0.81 g, 10.33 mmol) in dry CH₂Cl₂ (10 mL) was added dropwise with a dropping funnel. After stirring at about 0 °C for 30 min, the mixture was stirred for 12 h at room temperature, and then quenched with potassium carbonate water solution (50% w/w). The mixture was further extracted with CH₂Cl₂, and the organic layer was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to provide the target molecule (60%) as a yellow oil which was purified by chromatography on silica gel using DCM/MeOH (8/1, v/v) as eluent. ¹H NMR (300 MHz, CDCl₃): δ 1.72 (quint, $J = 5.4$ Hz, 2H), 2.08 (s, 1.5 H), 2.12 (s, 1.5 H), 2.22 (s, 3H), 2.25 (s, 3H), 2.32-2.26 (m, 2H), 2.91 (s, 1.5 H), 3.00 (s, 1.5 H), 3.34 (t, $J = 5.7$ Hz, 1H), 3.40 ppm (t, $J = 5.7$ Hz, 1H). HR-MS (ESI) calcd for C₈H₁₈N₂O [2M+Na]⁺: 339.2736, found: 339.1015.

1.3 Syntheses of the anion exchange ionomers

1.3.1 Synthesis of PPO-SA

A 50 mL round bottomed flask equipped with a magnetic stirrer was charged with 0.80 g (5.5 mmol benzylic bromide) PPO-Br-30 (brominated PPO with the degree of bromination of 30%) and NMP (10 mL). The mixture was stirred at room temperature until a homogeneous solution was formed, then N-[3-(dimethylamino)propyl]acetamide (0.38 g, 2.64 mmol) was added and the reaction mixture was warmed at 50 °C during 24 h under stirring. After cooling to the room temperature, the mixture was added dropwise to diethyl ether to precipitate the

product. After washed thoroughly with diethyl ether and dried under vacuum, the product (PPO-SA) was obtained as a light brown powder (1.21 g, yield: 98%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 1.82 (s, 3.92H), 2.03-2.07 (m, 15.83H), 2.99-3.09 (m, 9.63H), 4.36 (s, 2H), 6.52-6.56 (m, 4.64H), 6.94-7.05 (m, 1.94H), 8.02 ppm (s, 0.89H).

1.3.2 Synthesis of PPO-TA

A 50 mL round bottomed flask equipped with a magnetic stirrer was charged with 0.80 g (5.5 mmol benzylic bromide) PPO-Br-30 and 10 mL NMP. The mixture was stirred at room temperature until a homogeneous solution was formed, then N-[3-(dimethylamino)propyl]-N'-methylacetamide (0.42 g, 2.64 mmol) was added and the reaction mixture was warmed at 50 °C during 24 h under stirring. After cooling to the room temperature, the mixture was added dropwise to diethyl ether to precipitate the product. After washed thoroughly with diethyl ether and dried under vacuum, the product (PPO-TA) was obtained as a light brown powder (1.05 g, yield: 95%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 1.99-2.06(m, 24.09H), 2.96-3.02(m, 10.09H), 3.29 (m, 1.70 H), 4.39 (s, 2H), 6.54 (s, 5.24H), 6.94 ppm (s, 1.53H).

1.3.3 Synthesis of PPO-HE

A 50 mL round bottomed flask equipped with a magnetic stirrer was charged with 0.80 g (5.5 mmol benzylic bromide) PPO-Br-30 and 10 mL NMP. The mixture was stirred at room temperature until a homogeneous solution was formed, then N, N-dimethyl-1-hexanamine (0.34 g, 2.64 mmol) was added and the reaction mixture was warmed at 50 °C during 24 h under stirring. After cooling to the room temperature, the mixture was added dropwise to diethyl ether to precipitate the product. After washed thoroughly with diethyl ether and dried under vacuum, the product (PPO-HE) was obtained as a light brown powder (1.05 g, yield: 91%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 0.84 (s, 4.06H), 1.27 (s, 7.75H), 2.03 (m, 17.39H), 3.01 (s, 6.98H), 4.37 (s, 2H), 6.54 (s, 5.15H), 7.00 ppm (s, 1.62 H).

1.4 Membrane Preparation

The membranes with the counterion of bromide were prepared by solution casting from NMP solution. A solution of the dried ionomer powders in NMP with a concentration of 8-10 wt% was filtered and then casted onto a glass plate, and dried at 80 °C for overnight, and followed by an additional further drying in vacuum oven for another 12 h at 80 °C. The resultant membrane was soaked in deionized water and peeled off the glass to obtain the anion exchange membrane with the counter ion of Br⁻ form. The membrane's thickness was in the range of 30-50 μm. The chloride and hydroxide form membranes were obtained by exchanging the bromide form membrane in 2 M aqueous NaCl or 1 M aqueous NaOH for 24 h followed by fresh 2 M NaCl (aq) or 1 M NaOH for another 24 h, then thoroughly rinsed with deionized water to remove excess salt.

1.5 Characterization and measurements

1.5.1 General characterization

NMR spectra were recorded on an Agilent 600 MHz spectrometer or Bruker 300 MHz using CDCl₃, or DMSO-*d*₆ as solvents and chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane (TMS). Thermo gravimetric analysis (TGA) was recorded on a TA instrument (Q500) at a heating rate of 10 °C/min from 30 to 800 °C under nitrogen atmosphere. Tensile measurements were obtained for samples (40 mm long, 10 mm wide and about 40 μm thick) equilibrated at the environment of 25 °C and 30% relative humidity for over 24 h, and tensile measurements were performed using a MTS CMT4304 electromechanical universal testing machine at a speed of 5 mm/min under the environment of 25 °C and 30% RH. Small-angle X-ray scattering (SAXS) measurements were performed using a SAXSess (Anton Paar) equipped with Kratky block-collimation system. The scattering pattern was recorded on an imaging plate (IP) with a pixel size of 42.3 × 42.3 μm², which extended to the high-angle range (the *q* range covered by the IP was from 0.06 to 29 nm⁻¹).

1.5.2 Water uptake and Swelling ratio

Water uptake (WU) and in-plane swelling ratio (SR) was measured after drying the membrane in the vacuum at 80 °C for 12 h. The dried membranes were soaked in the deionized water and weighed on an analytical balance at different temperature (from 30 °C to 80 °C) every 12 h. Water uptake was calculated by the following equation:

$$WU = \frac{m_{hyd} - m_{dry}}{m_{dry}}$$

where m_{dry} is the mass of the dry membrane; m_{hyd} is the hydrated membrane mass after immersed in the deionized water at the different temperatures.

The swelling ratio was characterized by the liner expansion ratio which is calculated between the dry and hydrated dimensions of the membrane via the following equation:

$$SR = \frac{L_{hyd} - L_{dry}}{L_{dry}}$$

where the L_{dry} and L_{hyd} are the lengths of the membrane in its dry and hydrated states respectively.

1.5.3 Chloride conductivity

In order to alleviate the interference of CO₂ in the atmosphere, the conductivities in this article were all reported as chloride conductivity. The chloride conductivity was obtained in a frequency range from 1 Hz to 1 MHz using a CH Instruments CHI 600E by a four-point probe ac impedance method. The samples (3 cm in length and 1 cm in width) were measured in 100% relative humidity (RH) at different temperatures, and the hydroxide conductivity (σ) was calculated by the following equation:

$$\sigma = \frac{L}{R \cdot w \cdot d}$$

where R is the membrane resistance, L is the distance between potential-sensing electrodes, w and d refer to the width and thickness of the membrane, respectively. The conductivity were tested by two or three samples and the results were averaged.

1.5.4 Alkaline Stability

The alkaline stability of the obtained AEMs was evaluated by the changes of chloride conductivity after soaking the membrane in 1 M NaOH aqueous solution at 60 °C for 1, 2 and 3 days.

1.5.5 Membrane electrode assembly and single cell performance

A catalyst-loaded carbon paper ($0.8 \text{ mg}\cdot\text{cm}^{-2}$ Pt, Johnson Matthey Co.), which uses as the anode/cathode electrodes and diffusion layer, was prepared by spraying by the mixture of Pt (40% Johnson Matthey Co.) and ionomer solution (fumion®, 1 wt% in 1-propanol and deionized water, v/v = 10/1). The membrane electrode assembly (MEA) was prepared by sandwiching the PPO-SA membrane between the anode and cathode electrodes with the effective electrode area was 4 cm^2 . H_2 - O_2 fuel cell tests were conducted by using a fuel cell testing system G20 (Greenlight, Canada) with humidifier temperatures of 55 and 55 °C for H_2 and O_2 , respectively. The flow rate of O_2 and H_2 is $100 \text{ mL}\cdot\text{cm}^{-1}$.

3. Table and Figures

Table S1. Properties of the PPO-SA, PPO-TA and PPO-HE membranes

Sample	IEC ^a (mmol·g ⁻¹)	WU ^b (%)	λ^c	SR ^b (%)	Conductivity ^d (mS·cm ⁻¹)	Mechanical properties ^e	
						Tensile Strength (MPa)	Elongation at Break (%)
PPO-SA	1.78	31.3	9.7	3.6	10.1	32.1	101
PPO-TA	1.76	43.7	13.8	7.1	11.2	27.3	19.5
PPO-HE	1.83	13.2	4.0	2.2	4.5	29.7	11.1

^a Calculated from ¹H NMR spectra; ^b measured at room temperature with the counterion of chloride in liquid water; ^c the hydration number (number of absorbed water molecules per cationic group) at 30 °C; ^d the conductivity at 50 °C in the Cl⁻ forms; ^e measured at the environment of 25 °C and 30% relative humidity.

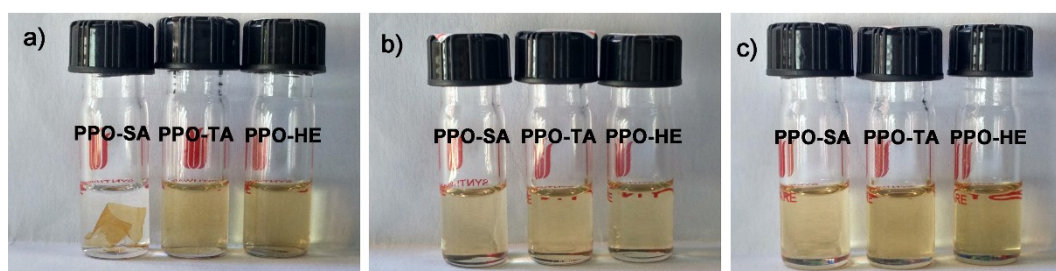


Fig. S1 Solubility test of as-prepared membranes with the concentration of 5 wt% (50 mg in 1 mL solvents) in different solvents: a) in acetonitrile; b) in N,N-dimethylformamide; c) in N-methyl-2-pyrrolidone. From the solubility results, we can see that PPO-SA membrane containing a second amide was insoluble in acetonitrile, while PPO-TA and PPO-HE were readily soluble in acetonitrile (Fig. S1a), indicating the existence of a substantial crosslinking in the PPO-SA membrane. Moreover, all of the three membranes were readily soluble in polar aprotic solvents with hydrogen bond-interrupting characteristics, such as DMF and NMP (Fig. S1b and Fig. S1c), further demonstrates that the crosslinking of PPO-SA with non-covalent nature.

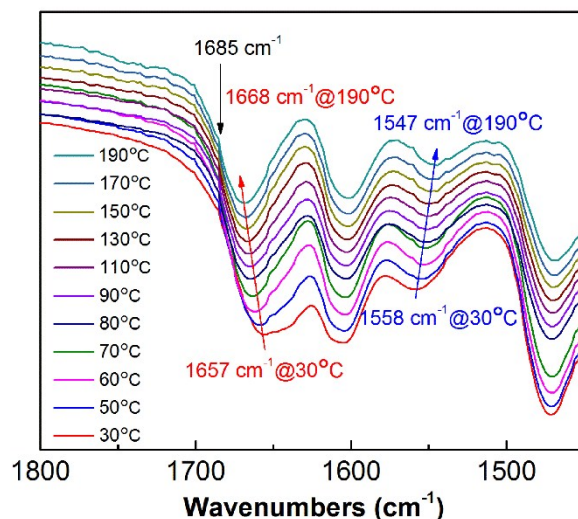


Fig. S2 FT-IR spectra of the PPO-SA membrane in the amide I and II regions recorded as a function of increasing temperatures in the range 1800-1450 cm^{-1} .

As can be seen in Fig. S2, as the temperature is increased, the amide I band shifted to higher frequency, from 1657 cm^{-1} at $30 \text{ }^\circ\text{C}$ to 1668 cm^{-1} at $190 \text{ }^\circ\text{C}$, accompany with the decrease in intensity, which is the traditional characteristic of hydrogen-bonded carbonyl group with temperature-dependent nature. Moreover, as temperature increases, there is increasing evidence of a shoulder at about 1685 cm^{-1} , attributing to “free” carbonyl groups. In the meantime, with increasing temperature, the amide II band is observed to shift to lower frequency (from 1558 cm^{-1} at $30 \text{ }^\circ\text{C}$ to 1547 cm^{-1} at $190 \text{ }^\circ\text{C}$) and there is also a decrease in the intensity of the band, which is in accordance with the previous research on hydrogen bonding in polyamides.^[S2]

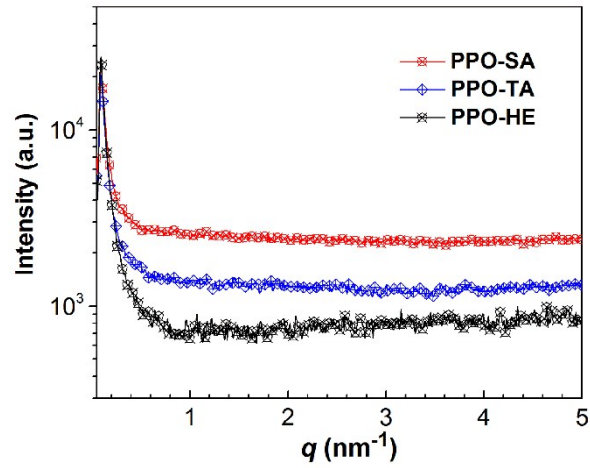


Fig. S3 SAXS profiles of the as-prepared membranes with the counterion of chloride.

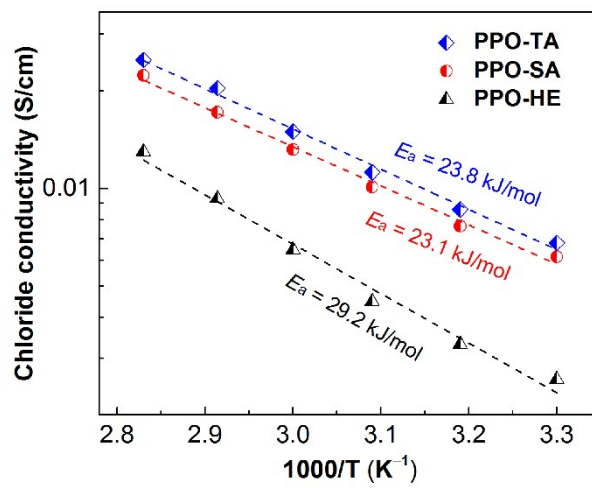


Fig. S4 Arrhenius plots of the as-prepared membranes as a function of temperatures.

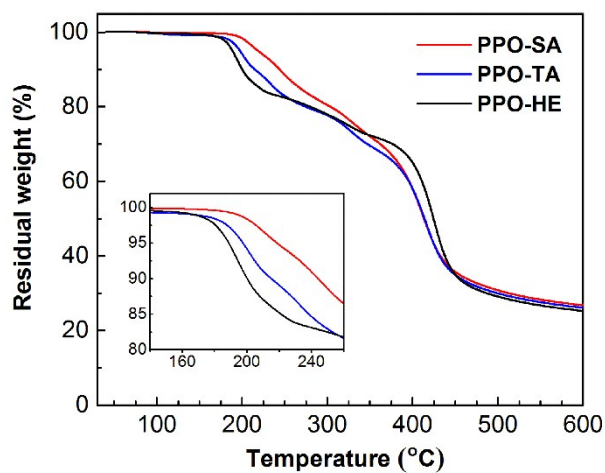


Fig. S5 TGA plots of the as-prepared membranes. The membranes were preheated at 100 °C for 30 min to completely remove the moisture absorbed by the membrane, then renormination.

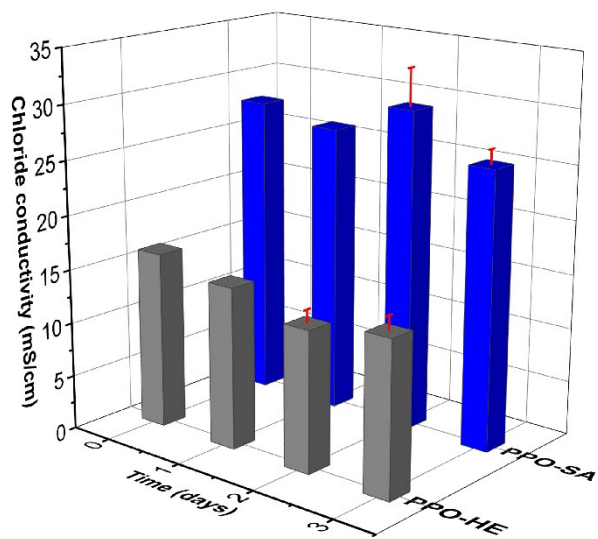


Fig. S6 Residual chloride conductivity of PPO-SA and PPO-HE membranes after aging in 1 M NaOH at 60 °C

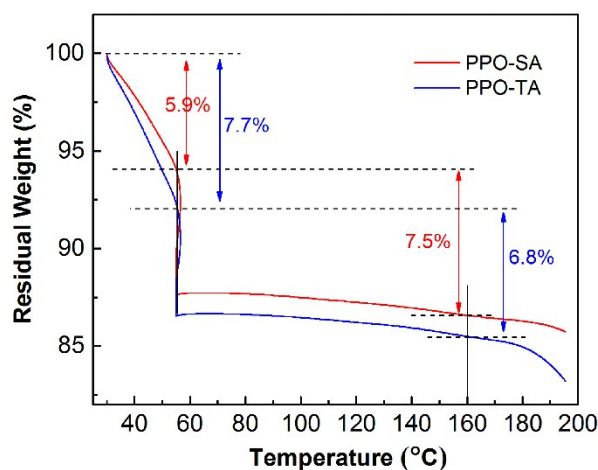


Fig. S7 TGA curves of the PPO-SA and PPO-TA membranes. The membranes were heated from 30 °C to 55 °C with the heating rate of 10 °C/min, maintained at 55 °C for 90 min, then further heated from 55 °C to 195 °C.

As can be seen, the weight loss of PPO-SA (5.9 wt%) was lower than PPO-TA (7.7 wt%) as well as lower weight loss rate, which indicates the PPO-SA with good absorbed water-retention ability. Moreover, although PPO-SA with lower water absorption than PPO-TA, the weight loss from 55 °C to 160 °C (where the membrane can be regarded as loss all of absorbed water at 160 °C) of PPO-SA was 7.5 wt%, in comparison with the PPO-TA of 6.8 wt%, further demonstrating the good water holding capacity of PPO-SA.

4. References

- [S1] J. Wang, H. B. Wei, S. Z. Yang, H. G. Fang, P. Xu and Y. S. Ding, Constructing pendent imidazolium-based poly(phenylene oxide)s for anion exchange membranes using a click reaction, *RSC. Adv.*, **2015**, 5, 93415-93422.
- [S2] D. J. Skrovanek, S. E. Howe, P. C. Painter and M. M. Coleman, Hydrogen bonding in polymers: Infrared temperature studies of an amorphous polyamide, *Macromolecules*, **1985**, 18, 1676-1683.