Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information

A Novel Poly(2,6-dimethyl-1,4-phenylene oxide) with Trifunctional Ammonium Moieties for Alkaline Anion Exchange Membranes

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Experimental Section

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was supplied by the Institute of Chemical Engineering of Beijing (China). Dimethylamine solution (33%), formaldehyde solution (37%), phenol, N,N-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), methanol, cesium carbonate (Cs_2CO_3), iodomethane and 4-fluorobenzoyl chloride were used as purchased.

Synthesis of 2,4,6-tri(dimethylaminomethyl)-phenol (TDAP), 4-dimethylaminomethyl-2,6-dimethylphenol (MDAP) and 2, 6-di(dimethylaminomethyl)-4-methyl-phenol (DDAP)

The 2,4,6-tri(dimethylaminomethyl)-phenol (TDAP) was synthesized from phenol, dimethylamine solution (33%) and formaldehyde solution (37%) according to the method in the literature.[S1] Yield: 76%.

The 4-dimethylaminomethyl-2,6-dimethylphenol (MDAP) was synthesized from 2.6-dimethylpheno1, dimethylamine solution (33%) and paraformaldehyde according to the method in the literature.[S2] Yield: 85%.

The 2, 6-di(dimethylaminomethyl)-4-methyl-phenol (DDAP) was synthesized from p-Cresol, dimethylamine solution (33%) and formaldehyde solution (37%) according to the method in the literature.[S3] Yield: 48%.

Synthesis of 4-fluorobenzoylated PPO (PPO-BzF)

The degree of substitution (DS_x, the number of 4-fluorobenzoyl groups/repeat units) was controlled by adjusting the amount of 4-fluorobenzoyl chloride. A typical synthetic procedure of PPO-BIm as follows: 2.4 g of PPO was dissolved in 40 ml of 1, 2-dichloroethane at the ambient temperature. A complex of 4-fluorobenzoyl chloride (11 mmol, 1.30 mL) and anhydrous $AlCl_3$ (12.1 mmol, 1.61 g) in 15 ml of 1,2-dichloroethane was added slowly to the solution and stirred for 6 h at 60 ^oC. Then the reaction mixture was cooled to room temperature and added to methanol to precipitate the product. After filtration and washing with methanol, the polymer was dissolved in chloroform and reprecipitated in methanol. The precipitate was collected and dried in a vacuum oven at 60 ^oC. The white powder (yield 98%) was obtained with a degree of substitution value of 50%, determined by ^1H NMR.

Synthesis of TDAP functionalized PPO (PPO-TA), MDAP functionalized PPO (PPO-MA) and DDAP functionalized PPO (PPO-DA)

In a typical procedure to prepare PPO-TA, 0.9 g of PPO-BzF (DS_x= 0.5, 2.5 mmol of F group), TDAP (1 g, 3.75 mmol), Cs_2CO_3 (1.6 g, 5 mmol) and 30 ml of DMAc were added into a 100 mL three-neck flask. The mixture slowly heated to 110 ^oC. N_2 gas was bubbled through the reaction mixture to facilitate the removal of water while the reaction mixture was kept at 110 °C for 10 h. Then the reaction mixture was cooled to room temperature and poured into a large excess of methanol to precipitate the product. After filtration and washing thoroughly with water and ethanol several times, the precipitate was collected and dried under vacuum at 60 °C for 24 h.

A similar procedure was employed to prepare PPO-MA and PPO-DA.

Synthesis of PPO with trifunctional ammonium moieties (PPO-TQA), difunctional ammonium moieties (PPO-DQA) and monofunctional ammonium moieties (PPO-MQA), and fabrication of the polymer membranes

PPO-TA was dissolved in DMAc and then iodomethane (3 equiv) was added. The mixture was stirred at room temperature for 24 h and then poured into stirred ethyl ether. The precipitate was filtered off and washed with ethyl ether three times prior to being dried under vacuum to produce the PPO-TQA.

A similar procedure was employed to prepare PPO-MQA and PPO-DQA.

The PPO-TQA was dissolved in DMAc to form a 10% solution. The solution was cast onto a glass dish and dried at 80 °C for 12 h to form a membrane. Then the membrane was vacuum-dried at 100 °C for 24 h. After the resultant membrane was immersed in 1 M NaOH at room temperature for 24 h, it was washed thoroughly and immersed in deionized water for 24 h to remove residual NaOH and stored in a closed vessel filled with deionized water. Thickness of membranes: 40 ± 5 μm.

Characterization

NMR spectra were recorded on a Bruker AVANCE II spectrometer with TMS as an internal standard. Thermal analysis was carried out on NETZSCH STA 449F3 thermogravimetric analyzer (TGA). Samples were heated from 50 to 600 °C at a heating rate of 10 °C /min under a nitrogen flow.

Tensile measurements of fully humidified membranes were carried out using a dynamic mechanical analyzer (DMA Q800, TA Instruments from America) in controlled force mode using a stretch rate of 0.50 N/min at room temperature. The cross sectional area of the samples is about 0.45 mm^2. Stress-strain curves were recorded and tensile modulus was determined from the slope of the initial, linear portion of the stress-strain curve.

Small-angle X-ray scattering (SAXS) was measured for the dry membranes (Cl^-) experiments. The SAXS measurements on the samples were carried out on a Bruker Nanostar SAXS instrument with CuKα radiation (wavelength = 0.154nm) at room temperature. The SAXS intensity profiles were output as the plots of the scattering intensity versus (I) the scattering vector (q). The SAXS profiles were corrected for the background scattering.

Hydroxide conductivity

The ionic conductivities of the membranes were measured using the commonly encountered four-point probe technique. The impedance was recorded using an Autolab PGSTAT 30 (Eco Chemie, Netherland) at galvanostatic mode with a current amplitude of 0.1 mA over frequencies ranging from 1 MHz to 50 Hz. Bode plots were used to determine the frequency region over which the the magnitude of the impedance was constant, and the ionic resistance was then obtained from the associated Nyquist plot (Fig. S10). The membrane being studied was set into a

Teflon cell where it was in contact with 2 current collecting electrodes and 2 potential sensing electrodes (the distance between the potential sensing electrodes was 1 cm). The cell was completely immersed in deionized water and the impedance spectrum was collected. This was done quickly to minimize the potential error caused by reaction of the hydroxide ions in the membrane with dissolved carbon dioxide (resulting in the formation of carbonate/bicarbonate anions and reduced membrane conductivity). The ionic conductivity was calculated according to the following equation:

$$\sigma = \frac{L}{RWd} \qquad (1)$$

where R is the obtained membrane resistance, L is the distance between potential-sensing electrodes (here 1 cm), and W and d are the width (here 1 cm) and thickness of the membrane, respectively.

Ion exchange capacity (IEC)

IEC was measured using standard back titration methods. The membranes in OH^- form were immersed in 100 mL of 0.1 M HCl standard solution for 24 h. The solutions were then titrated with a standardized NaOH solution using phenolphthalein as an indicator. The IEC value was calculated using the equation:

$$IEC = \frac{V_{0,NaOH}\, C_{NaOH} - V_{x,NaOH} C_{NaOH}}{m_{dry}} \qquad (2)$$

where $V_{0,NaOH}$ and $V_{x,NaOH}$ are the volume of the NaOH consumed in the titration without and with membranes, respectively, C_{NaOH} is the mole concentration of the standardized NaOH solution, and m_{dry} is the mass of the dry membranes. Three replicates were conducted for each sample.

Water uptake and swelling ratio

The water uptake values were determined for all the membranes in their OH^- forms. The membranes were dried in a vacuum oven at 80 °C to obtain a constant dry weight. The dry membrane samples were soaked in the deionized water at a given temperature for 24 h. The hydrated polymer membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. The water uptake values of membranes were calculated according to

$$\text{Water uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (3)$$

Where W_{dry} and W_{wet} are the weight of the dry and water-swollen membranes, respectively.

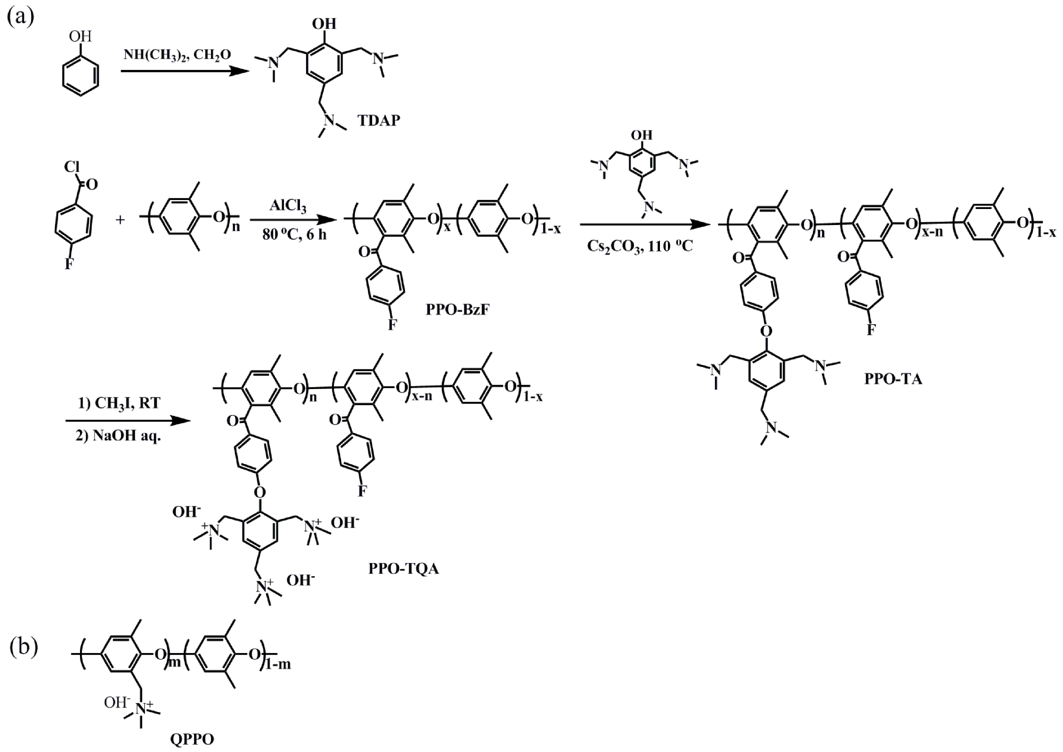
The number of absorbed water molecules per ammonium group (λ) was calculated according to

$$\lambda = \frac{\text{Water uptake}}{18 \times \text{IEC}} \times 1000 \qquad (4)$$

The swelling ratio was characterized by linear expansion ratio, which was determined by the difference between wet and dry dimensions in the length or thickness direction of a membrane sample. The swelling ratio was calculated from

$$\text{Swelling ratio（\%} = \frac{l_{wet} - l_{dry}}{l_{dry}} \times 100 \qquad (5)$$

Where l_{wet} and l_{dry} are the dimensions of wet and dry membranes, respectively.



Scheme S1 (a) Synthesis of TDAP, PPO-BzF, PPO-TA and PPO-TQA; (b) Chemical structure of QPPO for the contrast experiment.

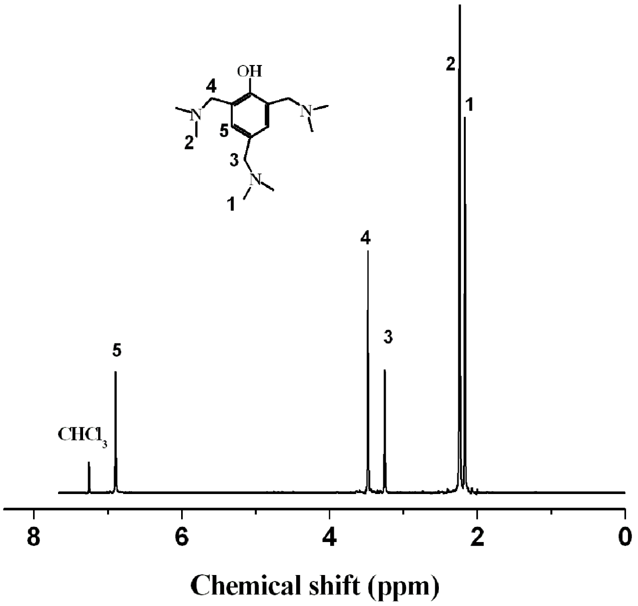


Fig. S1 ^{1}H NMR spectrum of TDAP in $CDCl_3$.

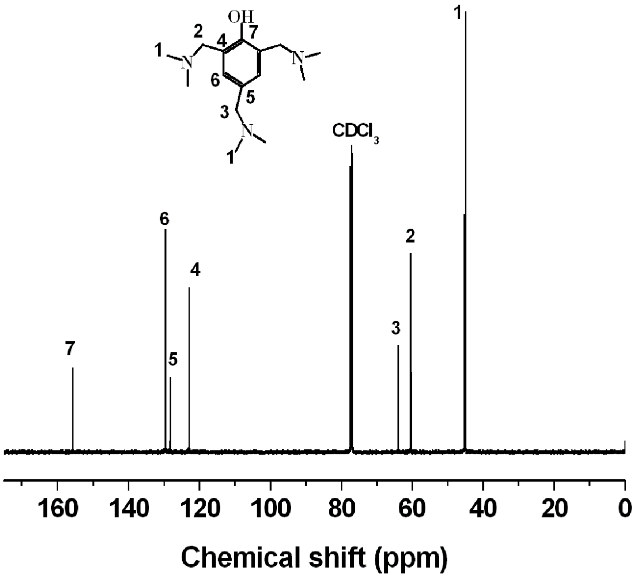


Fig. S2 ^{13}C NMR spectrum of TDAP in $CDCl_3$.

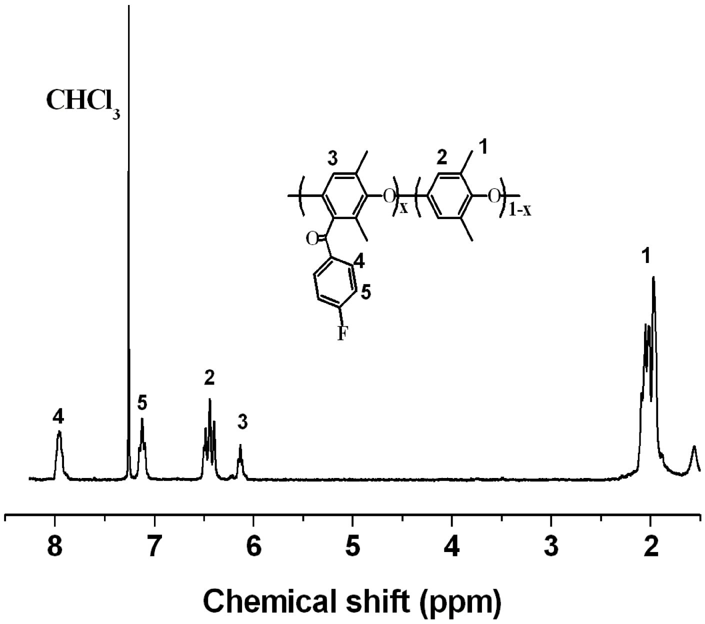


Fig. S3 ^{1}H NMR spectrum of PPO-BzF (DS$_x$=0.38) in CDCl$_3$.

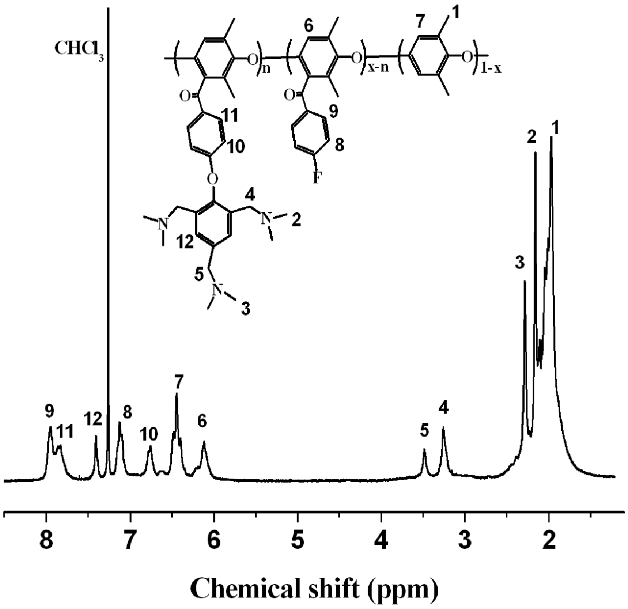


Fig. S4 ^{1}H NMR spectrum of PPO-TA-2 in CDCl$_3$.

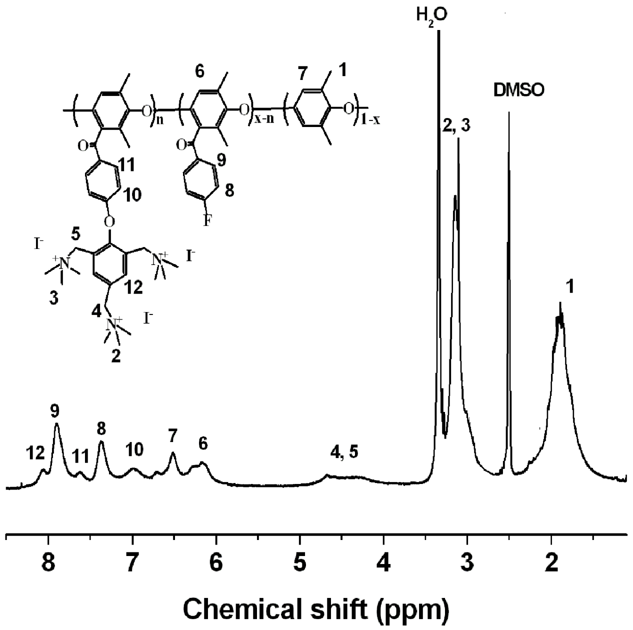


Fig. S5 ^{1}H NMR spectrum of PPO-TQA-3 in I$^-$ form in DMSO-d$_6$.

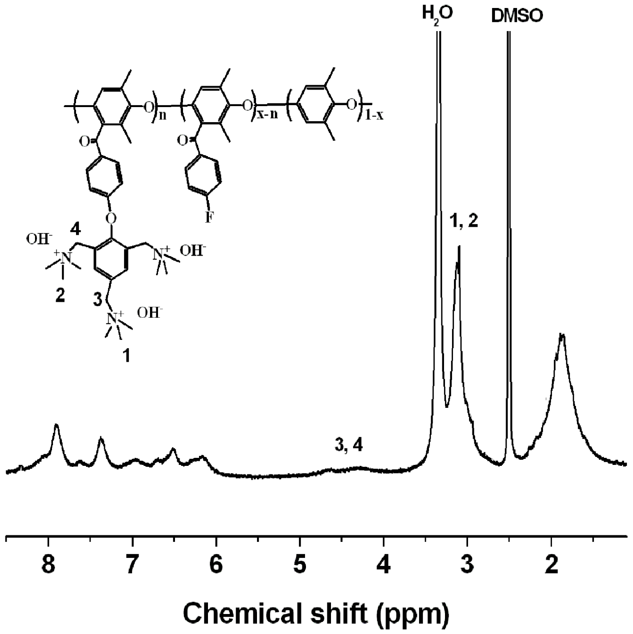


Fig. S6 ^{1}H NMR spectrum of PPO-TQA-3 in OH$^-$ form in DMSO-d$_6$.

Table S1. Selected data of the synthesis of PPO-TQA.

Sample	DS$_x$^{a}	Conversion^b (%)	DS$_n$^{c}	IEC$_{th}$^{d} (meq/g)	IEC$_{ex}$^{e} (meq/g)
PPO-TQA-1	0.29	17.2	0.05	0.87	0.84
PPO-TQA-2	0.38	18.4	0.07	1.10	1.06
PPO-TQA-3	0.50	22.0	0.11	1.51	1.50

[a] Number of side chains per repeating polymer unit. [b] Calculated from ^{1}H NMR. [c] Number of highly quaternized side chains per repeating polymer unit. [d] Calculated from ^{1}H NMR spectra. [e] Determined by titration.

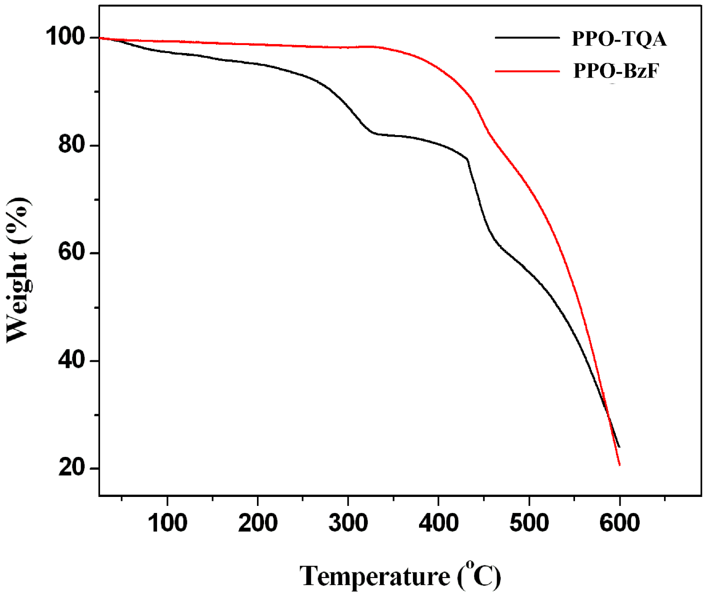


Fig. S7 TGA curves for PPO-BzF and PPO-TQA under N_2 atmosphere.

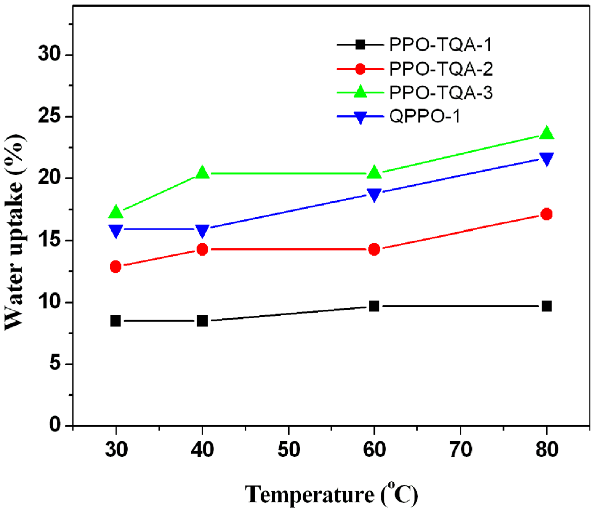


Fig. S8 Water uptake of PPO-TQA and QPPO membranes as a function of temperature in water.

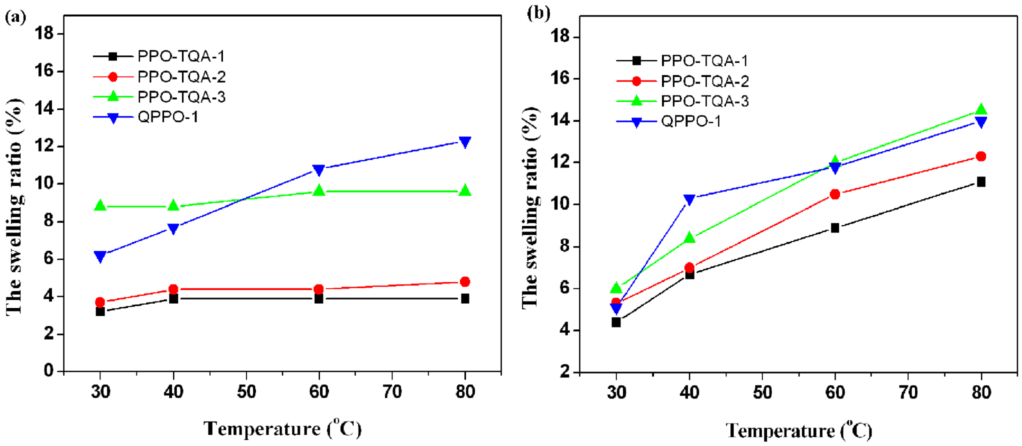


Fig. S9 The swelling ratio in the length (a) or thickness (b) direction of PPO-TQA and QPPO membranes as a function of temperature in water.

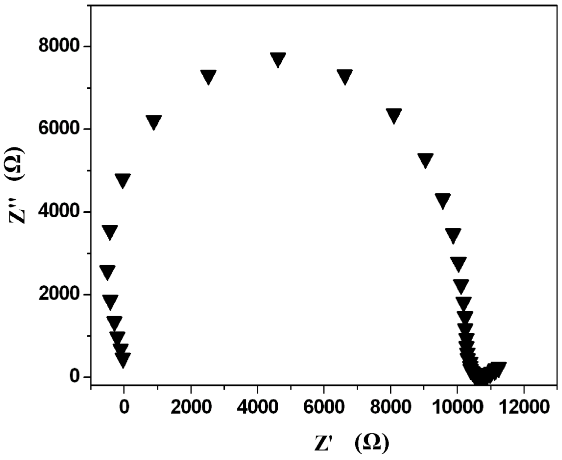


Fig. S10 A representative Nyquist plot of Z″ vs. Z′ from AC impedance spectroscopy measurements of PPO-TQA-1 membrane at 30 °C.

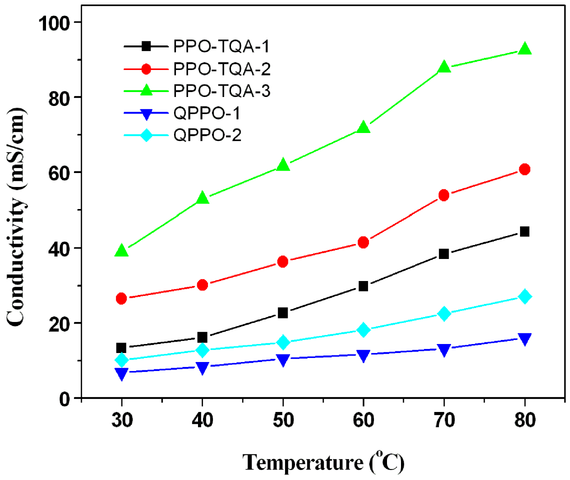


Fig. S11 Temperature-dependent hydroxide conductivity of PPO-TQA and QPPO membranes.

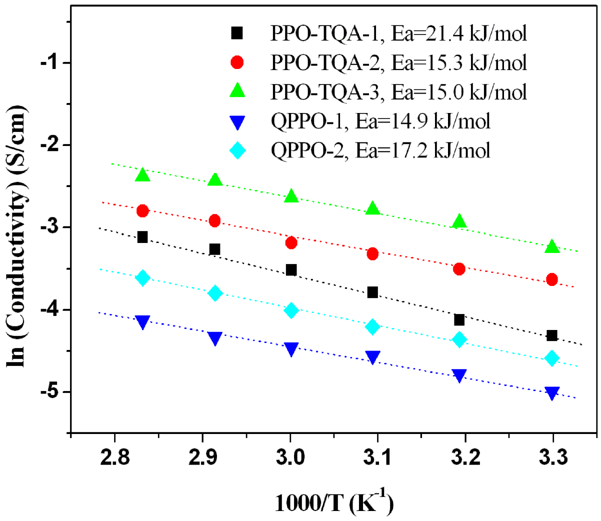


Fig. S12 Arrhenius plots of the PPO-TQA and PPO membranes

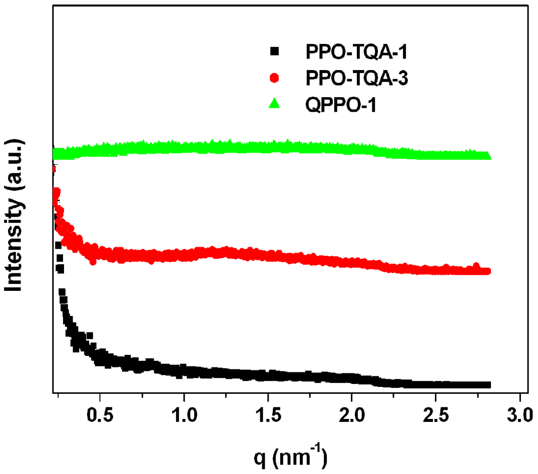
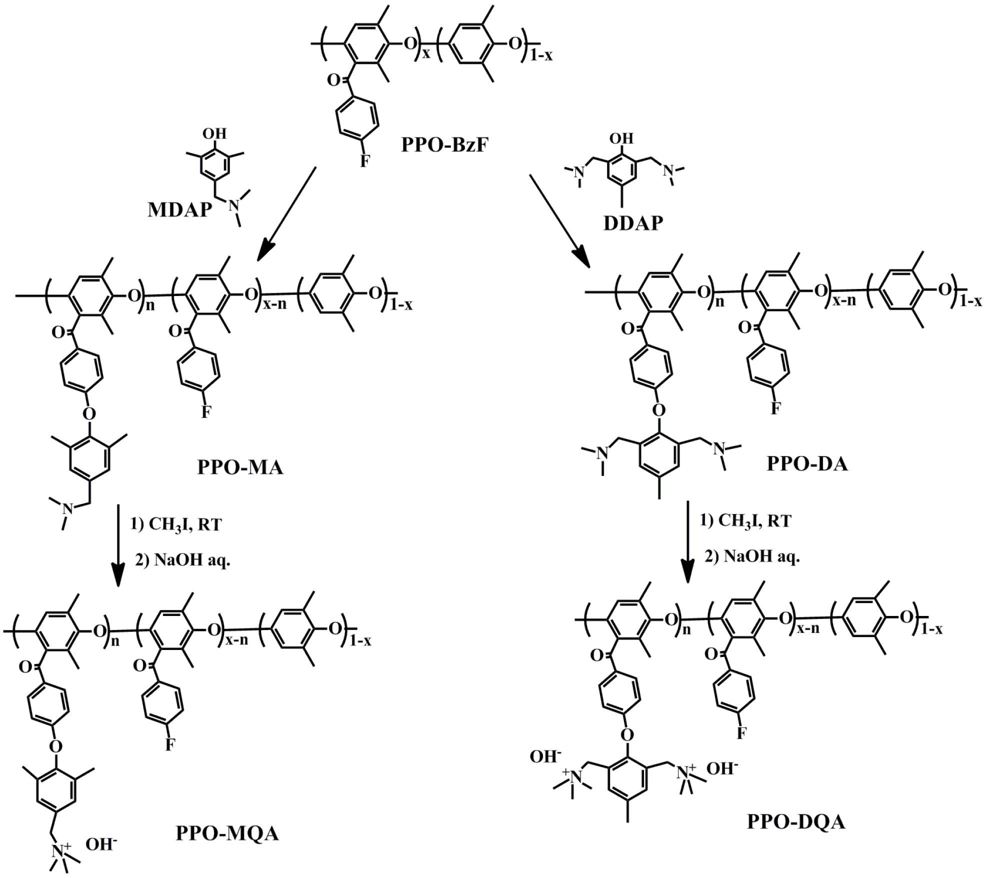


Fig. S13 SAXS patterns of PPO-TQA and QPPO membranes



Scheme S2 Synthesis of PPO-MQA and PPO-DQA for the contrast experiments.

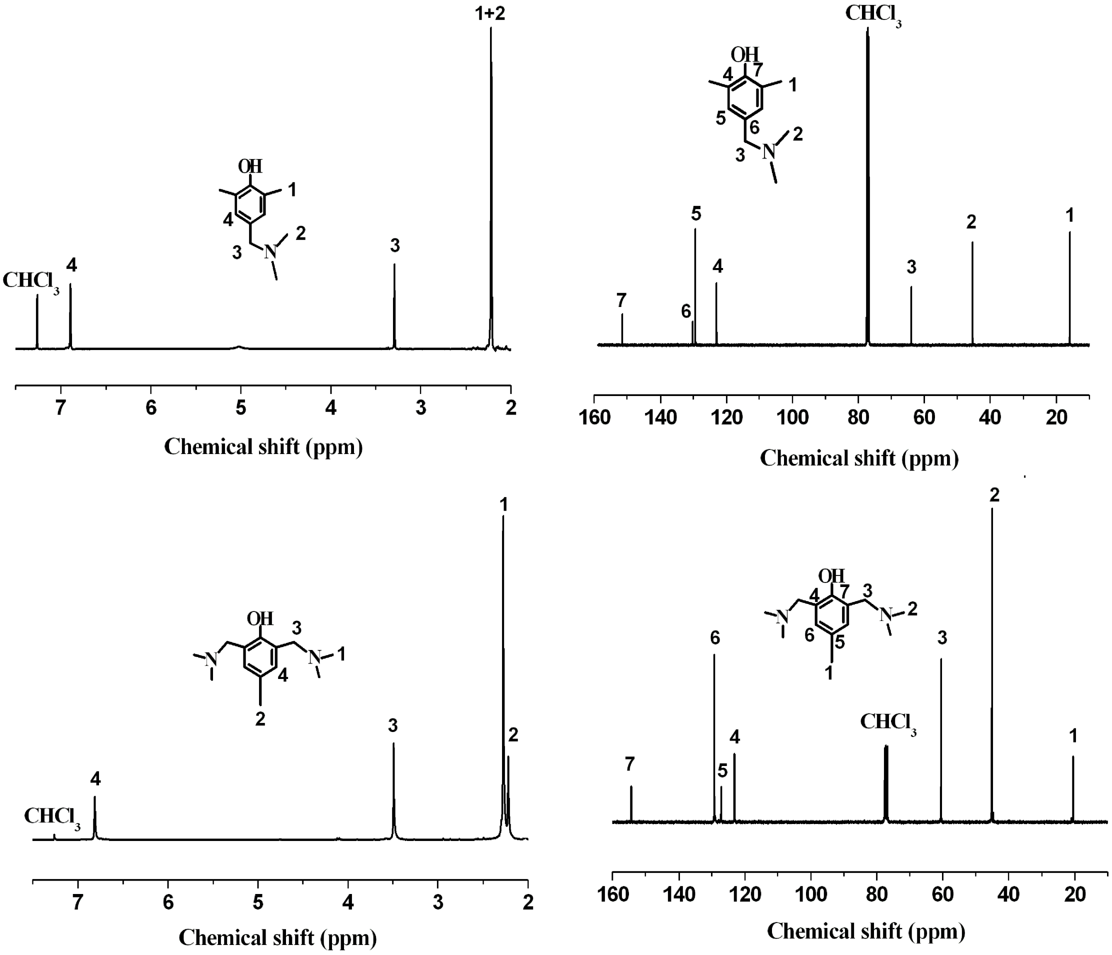


Fig. S14 ^{1}H NMR and ^{13}C NMR spectra of MDAP and DDAP in $CDCl_3$.

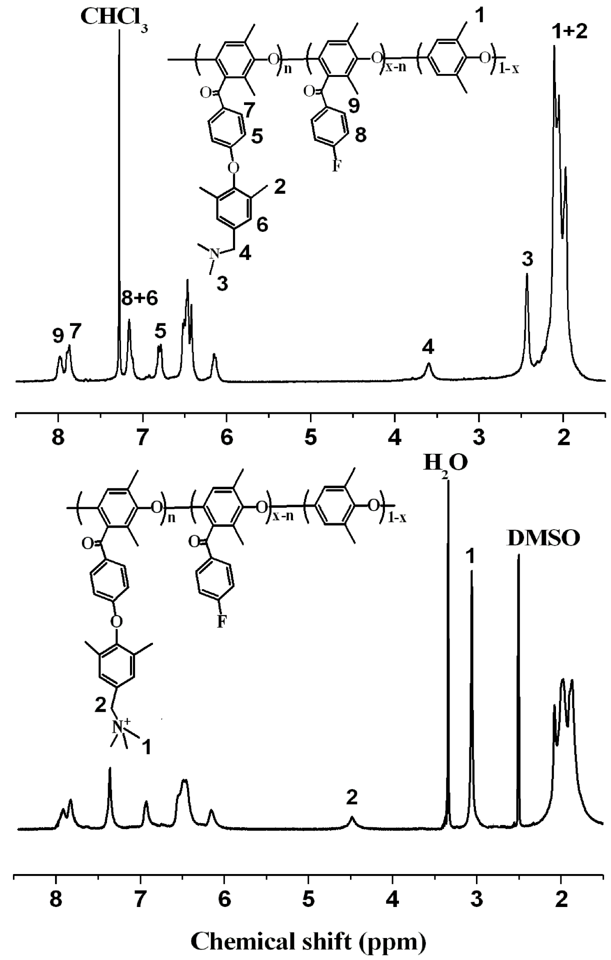


Fig. S15 ^{1}H NMR spectra of PPO-MA and PPO-MQA.

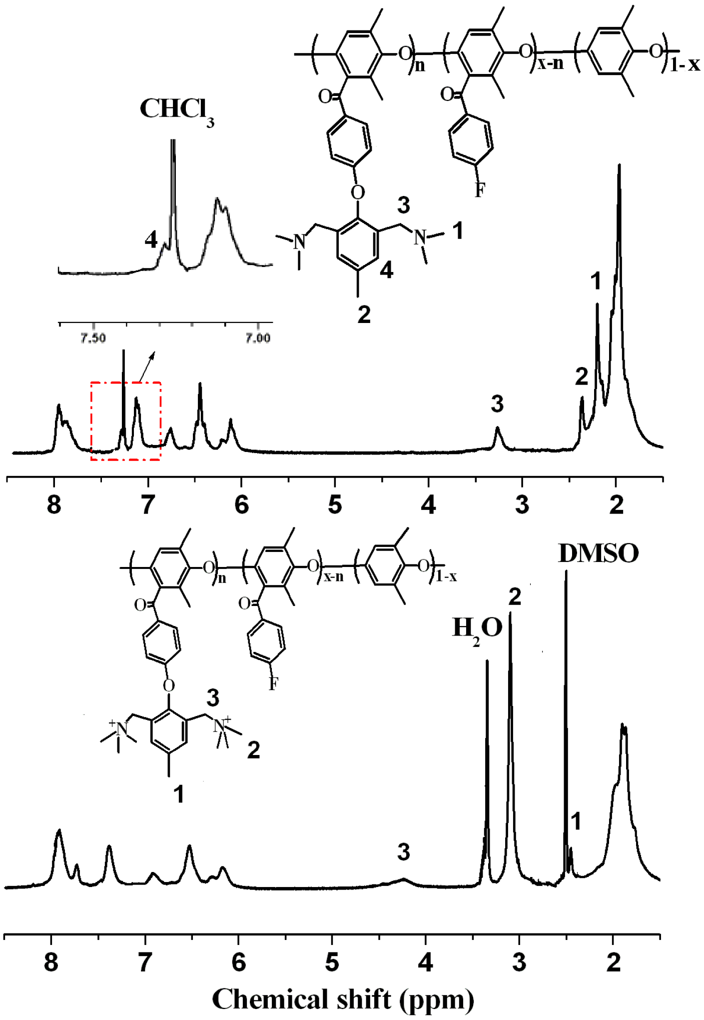


Fig. S16 ^{1}H NMR spectra of PPO-DA and PPO-DQA.

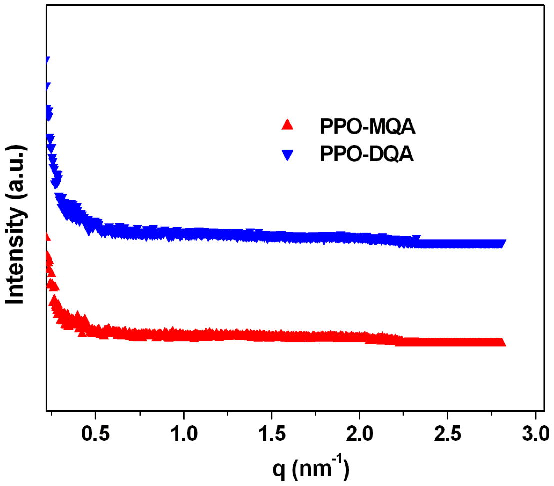


Fig. S17 SAXS patterns of PPO-MQA and PPO-DQA membranes.

Table S2. Mechanical properties of PPO-TQA membranes.

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
PPO-TQA-1	26.3 ± 1.3	437.5 ± 33.2	9.2 ± 0.7
PPO-TQA-2	21.4 ± 0.5	532.3 ± 10.5	7.7 ± 0.2
PPO-TQA-3	12.8 ± 0.8	201.0 ± 14.2	5.4 ± 0.4

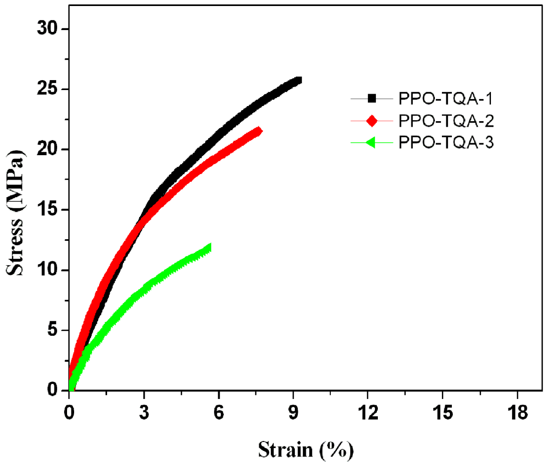


Fig. S18 Stress-strain curves of the fully humidified PPO-TQA membranes at room temperature.

The alkaline stability

The alkaline stability of the carbonyl group was investigated and no change was observed according to the ^{1}H NMR spectra of the samples recorded before and after immersing them in 1 M NaOH at 80 ^{o}C for 10 days (Fig. S19). This result indicates that the carbonyl group is quite stable to the alkaline condition.

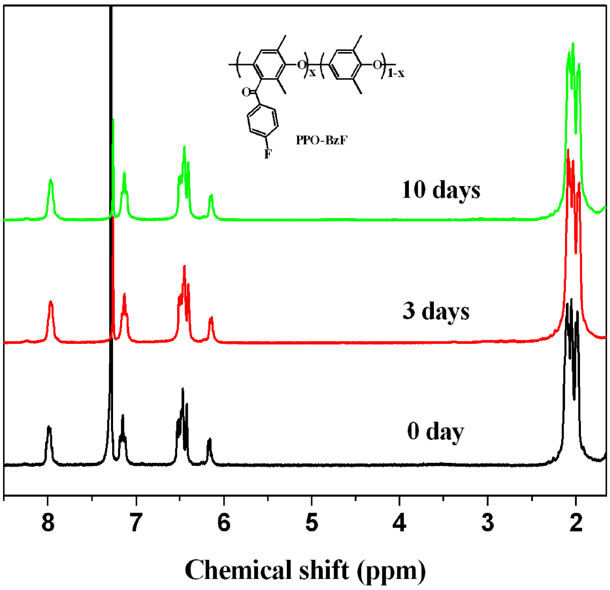


Fig. S19 The alkaline stability of PPO-BzF-1 in 1 M NaOH at 80 ^{o}C.

It has already been demonstrated that the quaternary ammonium groups have a tendency to disintegrate in alkaline solution at high temperature due to the displacement of the ammonium group by OH^- via a direct nucleophilic substitution.[S4] Therefore, both PPO-TQA and QPPO membranes had obvious decline of conductivity due to direct nucleophilic substitution (Fig. S20). The QPPO-1 was broken into small pieces after 3 days in 1 M NaOH at 80 °C. This phenomenon was also observed by Michael A. Hickner et al.[S5] However, the PPO-TQA-3 maintained acceptable properties (conductivity=16.9 mS/cm at 30 °C, tensile strength= 8.1 MPa) after 12 days in 1 M NaOH at 80 °C. The result indicates that the PPO-TQA membrane had better long-term alkaline stability than QPPO.

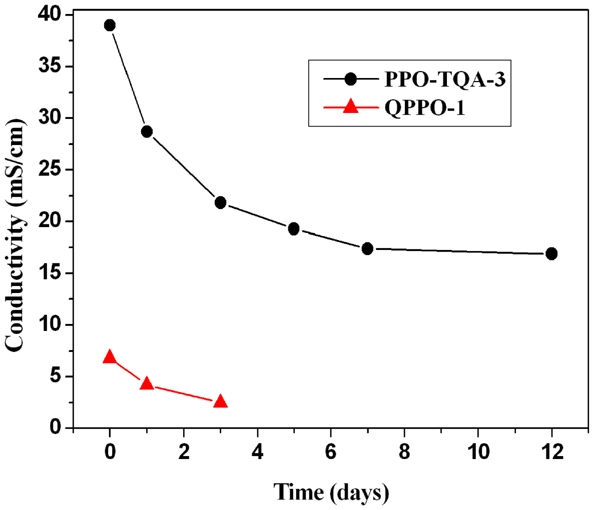


Fig. S20 The alkaline stability of PPO-TQA-3 and QPPO-1 in 1 M NaOH at 80 °C.

References

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