Front. Chem. Sci. Eng.

https://doi.org/10.1007/s11705-017-1690-7

COMMUNICATION

Tetrazole tethered polymers for alkaline anion exchange membranes

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Electronic Supplementary Material

Materials

1-(2-(dimethylamino)ethyl)-1H-tetrazole-5-thiol (DMAT) was purchased from J&K chemicals Ltd. and was used without further purification. Benzyl bromide, sodium sulfate, sodium chloride, sodium hydroxide, potassium carbonate, acetone, dichloromethane, NMP, diethyl ether, chloroform, n-hexane, were purchased from Shanghai Sino Pham Chemical Reagent Co. Ltd. (China). Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with an intrinsic viscosity of 0.57 dl/g in chloroform at 25 °C was obtained from Tianwei Membrane Company (Shandong, China). N-bromosuccinimide (NBS), 2,2'-azobis(2-methylpropionitrile) (AIBN) were purchased from Energy Chemical Co. Ltd.(Shanghai, China) and were used without further purification.

Synthesis of 2-(5-(benzylthio)-1H-tetrazol-1-yl)-N,N-dimethylethanamine (BTTDMEA)

In 150 mL bottom flask, 5.19 g (30 mmol) of 1-(2-(dimethylamino)ethyl)-1H-tetrazole-5-thiol and 6.21 g (45 mmol) of K_2CO_3 were added in 80 mL of acetone. Benzyl bromide (7.695 g, 45 mmol) was all at once added in the above mixture. After stirring the above mixture at 70 °C for 5 h, the acetone was removed at reduced pressure and then the reactants were cooled at room temperature. It was extracted three times by using ethyl acetate (3 × 50 mL) after dissolution in

100 mL of water. The organic solutions were washed three times by water and then by brine solution. The combined organic solutions were dried over magnesium sulfate anhydrous and the ethyl acetate was removed at reduced pressure. The oily as-product was purified by silica gel column chromatography using dichloromethane and methanol as developing solvents to afford the title compound. Yield: 38%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46–7.20 (m, 5H), 4.51 (s, 2H), 4.19 (t, *J* = 6.5 Hz, 2H), 2.66 (t, *J* = 6.5 Hz, 2H), 2.21 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.66, 135.79, 129.05, 128.82, 128.10, 57.60, 45.45, 45.37, 38.16.

Bromination of poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO)

Brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) of different bromination degree were prepared through free radical bromination and the procedure is described as follows: to a stirred solution of PPO (12 g, 100 mmol) in chlorobenzene (100 mL) was added N-bromosuccinimide (NBS) (7.3 g, 40 mmol) and 2,2-azobis(2-methylpropionitrile) (0.5 g). The reaction mixture was heated at 135 °C for 3 h. After cooling to room temperature, the reaction mixture was poured into excess ethanol to form light brown precipitate and then dissolve the precipitate in chloroform (120 mL) followed by precipitation in ethanol. The obtained polymer was dried at 40 °C for 48 h to get BPPO of 26% bromination (BPP-26) as indicated by NMR. The BPPO of 36%, 21% and 17% grafting ratio of bromobenzyl (-CH_2Br) were prepared as described above by changing the amount of NBS.

Synthesis of tetrazole tethered Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with quaternary ammonium groups (t-QBTTPPO)

0.867 g (3.3 mmol) of 2-(5-(benzylthio)-1H-tetrazol-1-yl)-N,N-dimethylethanamine (BTTDMEA) was dropwise added to a solution of 2 g (2.99 mmol) BPPO-26 in 25 mL of NMP into 50 mL bottom flask. The mixture was stirred at room temperature for 12 h and then poured in toluene to precipitate the product. The precipitate was washed several times with hexane and then diethyl ether anhydrous. The obtained solid was dried in vacuum oven at 40 °C for 48 h. The polymer obtained is a 25% substituted as determined from ^{1}H NMR integration ratio of methylene protons. t-QBTTPPO-15, t-QBTTPO-20 and t-QBTTPPO-30 were prepared by using BPPO-17, BPPO-21, and BPPO-36 and the above described procedure, respectively.

Synthesis of quaternized Poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO)

The synthesis of QPPO follows the procedure described in reported work[1] and modified as follows. To 2 g of BPPO dissolved in 30 mL of NMP, was added trimethylamine aqueous solution (TMA, 1.5 equiv). After stirring the above mixture for 24 h at room temperature, the obtained mixture was precipitate in toluene and then washed several times with hexane and ether. The crude product was then dried in vacuum oven at 35 °C for 24 h.

Anion exchange membrane preparation

1 g of polymer (**t-**QBTTPPO or QPPO) was dissolved in 15 mL of NMP followed by solution casting on glass plate. The solvent was evaporated at 60 °C for 12 h. The membrane was peered off the glass plate, immersed in water for 24 h and then in 2 mol/L NaCl to convert the Br^- ions into Cl^- ions. To convert the Cl^- ions into OH^-, the membranes were dipped into 2 mol/L NaOH for 3 days by changing the solution every 12 h to ensure the complete conversion. The ion exchange, water uptake, ion conductivities, morphology and mechanical and thermal properties of **t-**QBTTPPO membranes were measured and calculated by using the method described below.

Characterization

NMR spectra were recorded on a Bruker AVANCEII spectrometer with TMS as an internal standard. Atomic force microscopy (AFM) images in tapping mode were recorded by a Veeco diinnova SPM, using micro-fabricated cantilevers with a force constant of approximately 20 N /m. Thermal behavior 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 membranes were carried out using a dynamic mechanical analyzer (DMA Q800) in controlled force mode using a stretch rate of 0.50 N/min at room temperature. Stress-strain curves were recorded.

Water uptake and swelling ratio

The prepared AEM in OH^- and Cl^- form with a know weight and dimension (1 × 4 cm) was immersed in deionized water at room temperature for 24 h. After that, the sample was taken out

and excess water on the surface was rinsed with a tissue paper and immediately measured the length and weight of the hydrated membrane. The water uptake (WU) and swelling ratio ratio (SR) were calculated from the equation 1 and 2, respectively.

$$WU = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

where W_w and W_d were defined as the mass of the sample in hydrated and dehydrated conditions separately.

$$Swelling\ ratio(\%) = \frac{L_w - L_d}{L_d} \times 100\% \quad (2)$$

L_w and L_d were defined as the length of the sample in hydrated and dehydrated conditions separately.

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

$$\lambda = \frac{Water\ uptake}{18 \times IEC} \times 1000 \quad (3)$$

Ion exchange capacity

IEC of the prepared AEMs was measured by the conventional Mohr method. The membrane samples in Cl^- form were immersed in aqueous Na_2SO_4 (0.5 mol/L) solution and then the Cl^- ions released from membranes were titrated with aqueous $AgNO_3$ solution (0.1 mol/L) using K_2CrO_4 as an indicator. The IEC was calculated from the following equation:

$$IEC(\text{mmol/g}) = \frac{V_{Ag^+}(\text{mL}) \times 0.1(\text{mol/L})}{W_{Cl^-}(\text{g})} \quad (4)$$

V_{Ag^+} was the amount of $AgNO_3$ solution consumed while titration and W_{Cl^-} was the mass of the sample in Cl^- form.

Hydroxide Conductivity

Hydroxide conductivity of synthesized AEMs was measured by conventional impedance spectroscopy using four-point probe technique employing an Autolab PGSTAT 30 (Eco Chemie, Netherland) in galvanostatic mode and with an a.c. current amplitude of 0.1 mA and a frequency range of 1 MHz to 100 Hz. Bode plots were used to determine the frequency region over which the magnitude of the impedance was constant. Afterwards, the ionic resistance was obtained from the associated Nyquist plot. A sample of AEM was set into a Teflon cell and the membrane was in contact with 2 current collecting electrodes and two potential sensing electrodes. Then, the cell was quickly immersed in deionized water and sealed to minimize the contamination of membranes by atmospheric carbon dioxide. The sample was equilibrated at a certain temperature for at least 30 min before measurement. The ionic conductivity (σ) was calculated as follows:

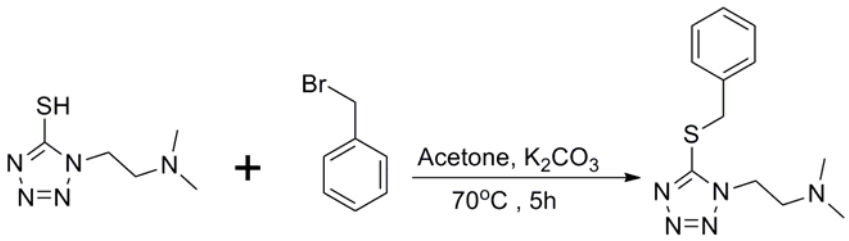
$$\sigma = \frac{L}{dwR} \tag{5}$$

where L is the distance between two sensing electrodes, d and w are the thickness and width (1 cm) of AEM, R is the membrane resistance.

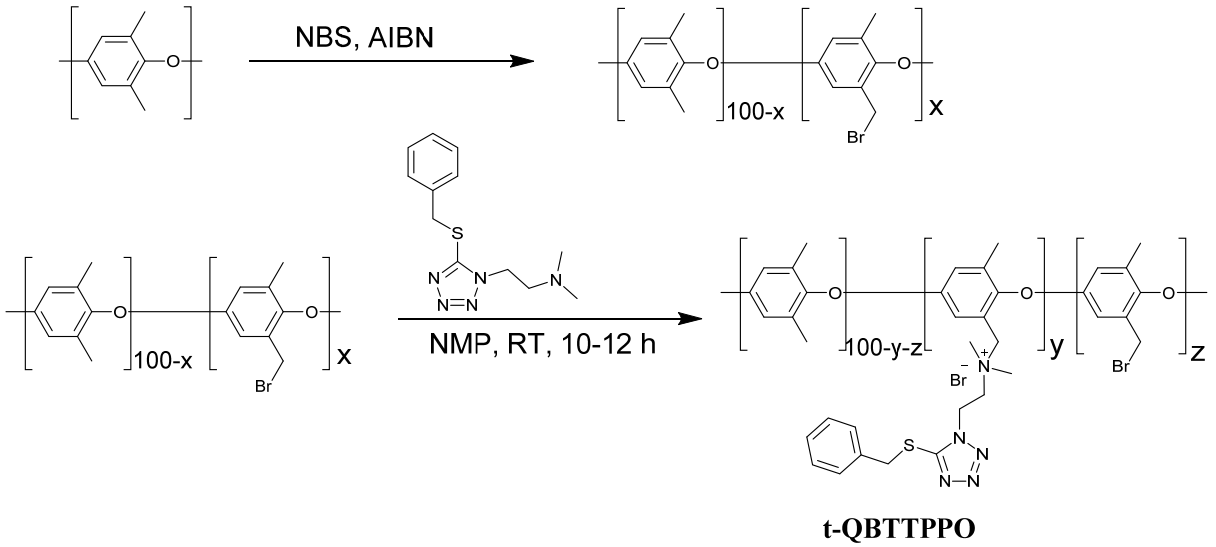
The activation energy of hydroxide ion conductivity was calculated from the following equation based on the Nernst–Einstein equation and Arrhenius plot:

$$\sigma_{\mathrm{T}} = \sigma_0 \mathrm{EXP}(-\frac{E_{\mathrm{a}}}{\mathrm{R}T}) \tag{6}$$

where σ_{T}, σ_0, E_{a}, R and T represent the final and initial hydroxide conductivity, activation energy, gas constant and temperature.



Scheme S1 Synthesis of BTTDMEA



Scheme S2 Synthesis of t-QBTTPPO polymers

Table S1 IEC and WU of tQTTPPO and QPPO membranes

Samples	SD (%)	Thickness (μm)	IEC[a]* (meq·g^{-1})	IEC[b]* (meq·g^{-1})	IEC [c]* (meq·g^{-1})	WU* (%)	λ*	σ_{OH}^{-1} (mS·cm^{-1})
t-QBTTPPO-15	15	63	0.91	0.86	0.62	5.9	5.28	6.72
t-QBTTPPO-20	20	60	1.12	1.05	0.91	9.4	5.73	10.6
t-QBTTPPO-25	25	66	1.30	1.20	1.11	12.1	6.11	14.7
t-QBTTPPO-30	30	64	1.43	1.31	1.32	16.7	6.72	23.18
QPPO-25	25	104	1.65	1.46	1.49	48.7	18.15	12.9

[a)] Theoretical, [b)] Calculated from ^{1}H NMR, [c)] Experimental by titration method, * In OH^- form

Figure S1 ^{1}H NMR spectrum of BTTDMEA

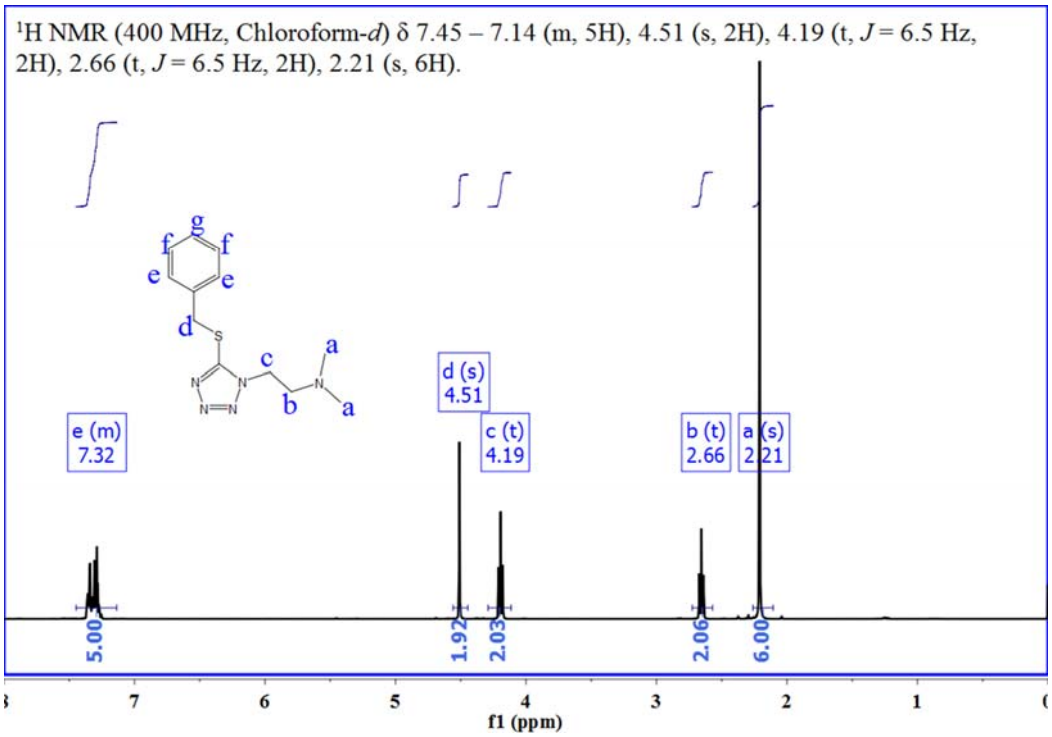


Figure S2 ^{13}C NMR spectrum of BTTDMEA

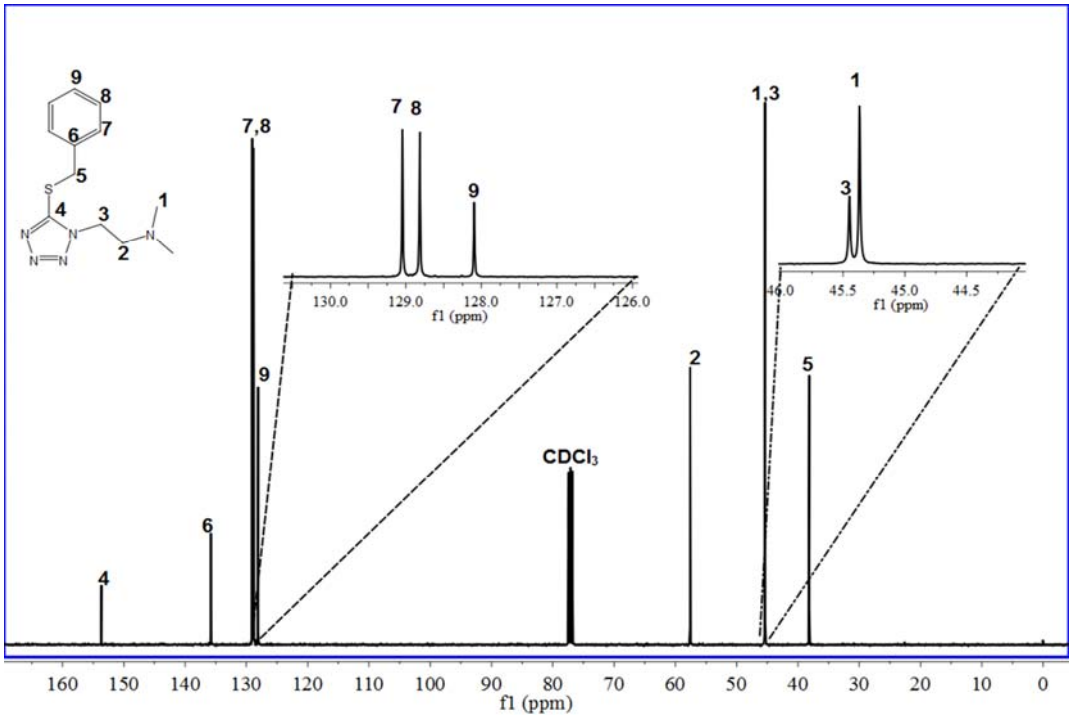
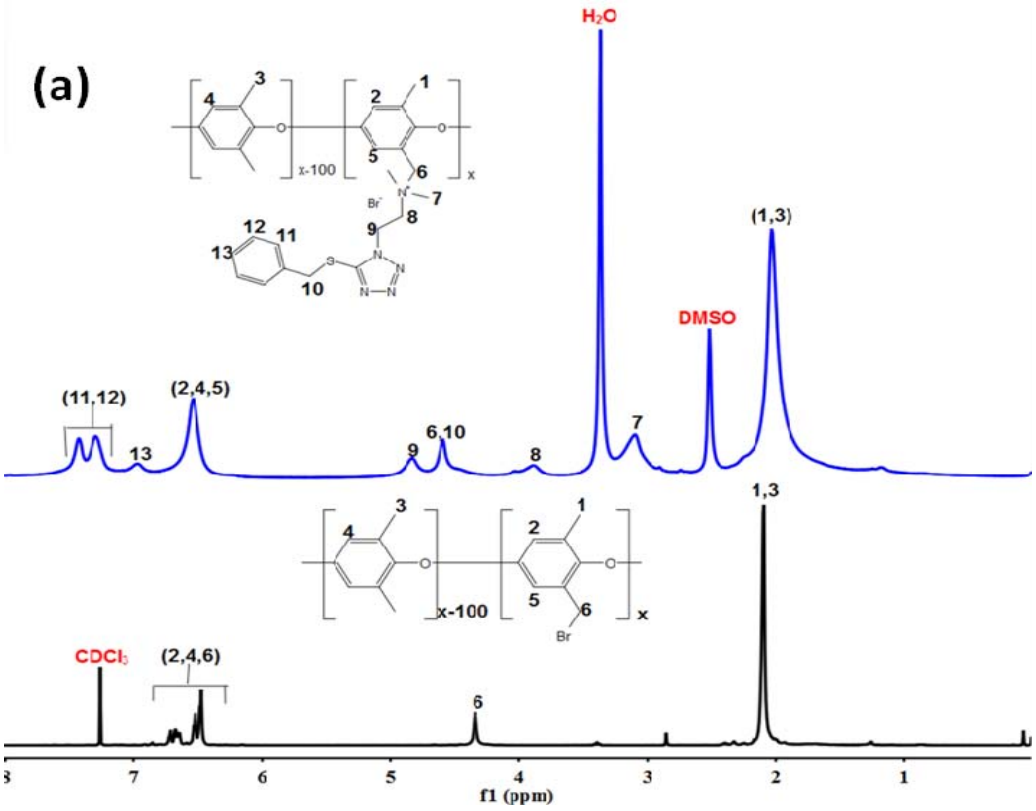


Figure S3 ^{1}H NMR spectrum of; a) t-QBTTPPO-30 in DMSO-d6 and BPPO-42 in $CDCl_3$, b) QPPO-23



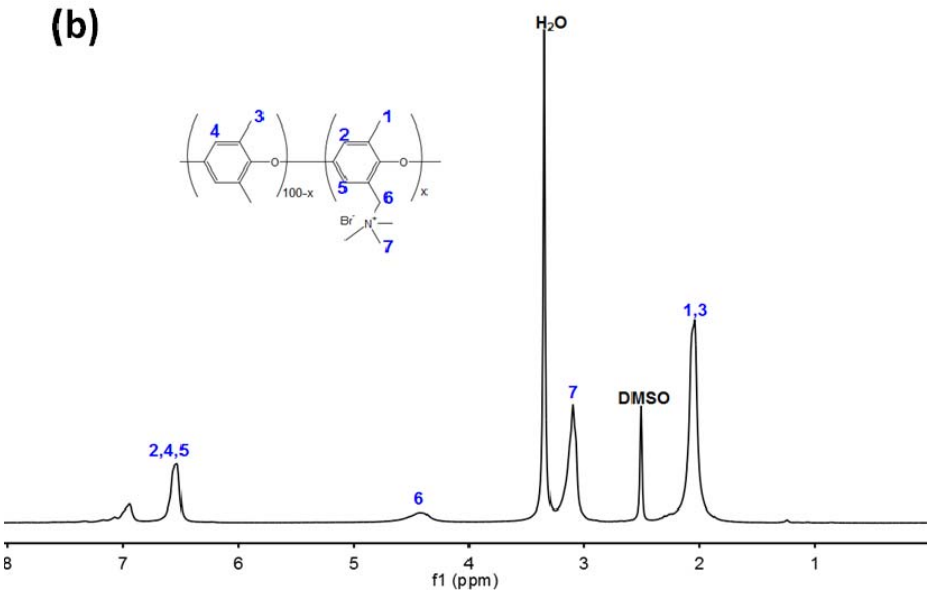


Figure S4 AFM tapping phase images of; t-QBTTPPO-30 and QPPO-25

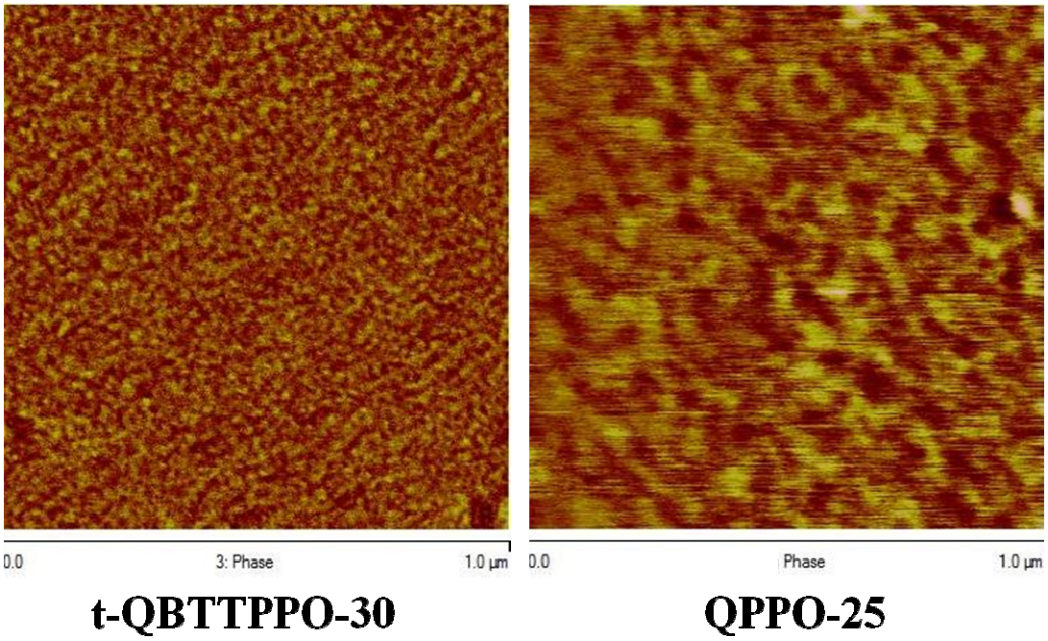


Figure S5 SAXS profiles of t-QBTTPPO-30 membrane.

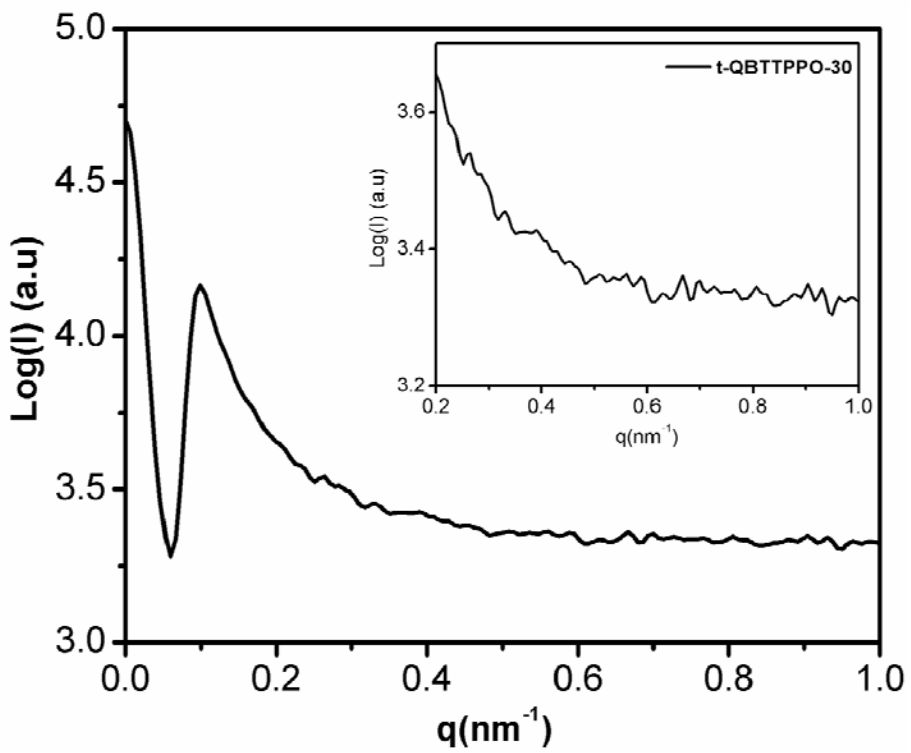
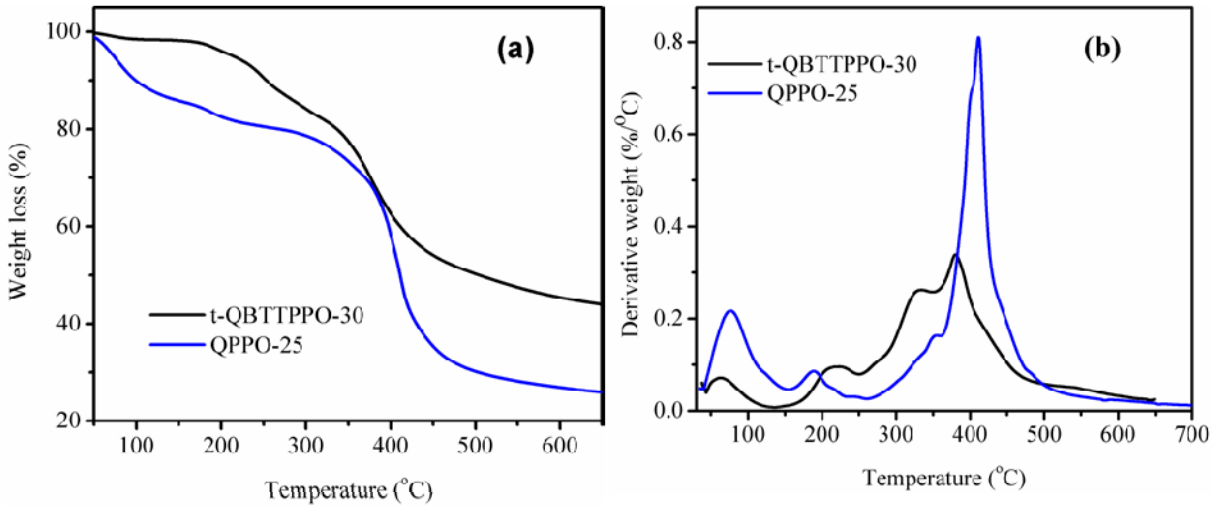


Table S2 Mechanical properties of t-QBTTPPO and QPPO-25 membranes at 25°C under full humidification

Samples	In Cl^- form			In OH^- form		
	Tensile strength	Relaxation modulus	Elongation at break	Tensile strength	Relaxation modulus	Elongation at break
t-QBTTPPO-15	17.5	96	18.1	23.57	349.17	8.75
t-QBTTPPO-20	22.54	130.87	17.22	31.45	616.76	7.21
t-QBTTPPO-25	34.06	170.9	19.92	39.13	780.97	7.5
t-QBTTPPO-30	35.8	192.2	19.7	37.6	830.1	6.95
QPPO-25	17.3	7.39	234.9	8.38	6.5	9.5

Figure S6. TG graph of t-QBTTPPO-30 and QPPO-25; a) weight loss in percentage, b) Derivative weight



References

[1] Y. He, J. Pan, L. Wu, Y. Zhu, X. Ge, J. Ran, Z. Yang, T. Xu, A Novel Methodology to Synthesize Highly Conductive Anion Exchange Membranes, Sci. Rep., 5 (2015) 13417.