

## Supporting Information for

### Strategy to Construct Alkali Stable Anion Exchange Membranes

#### Bearing Ammonium Groups via Flexible Spacers

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#### Experimental Section

##### Materials

Poly (2, 6-dimethyl-1, 4-phenyleneoxide) (PPO) was purchased from Polyxlyenol Singapore Pte. Ltd. (Singapore). Bis(pinacolato)diboron ( $B_2Pin_2$ , 98%), 1-bromo-3-phenylpropane (BrPP, 97%) and tetrakis(triphenylphosphine)palladium(0) ( $Pd(PPh_3)_4$ , 99%) were obtained from Energy Chemicals (Shanghai, P.R. China). 4,4-Di-tert-butyl bipyridine (dtbpy, 98%) was purchased from Aladdin Industrial Corporation (Shanghai, P.R. China). Octane (96%) and (1,5-cyclooctadiene)(methoxy)iridium(I) dimer ( $[Ir(OMe)(COD)]_2$ , 96%) was obtained from Macklin Biochemical Co., Ltd. (Shanghai, P.R. China). N-methyl-2-pyrrolidone (NMP) was bought from Guangfu Fine Chemical Research Institute (Tianjin, P.R. China). Trimethylamine alcohol solution (TMA, 33wt %) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P.R. China). Bromine, toluene, hexane, ethyl acetate (EtOAc), chlorobenzene, methanol and anhydrous potassium carbonate ( $K_2CO_3$ ) were

purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P.R. China). Silica gel (200-300 mesh) was obtained from Yantai Chemical Industry Research Institute (Shandong, P.R. China). All chemicals otherwise stated were of analytical pure and utilized as received without any further purification.

### **Bromination of PPO (BPPO)**

PPO (10g) was dissolved in chlorobenzene (100ml) in round-bottomed flask fitted with a reflux condenser. Bromine (13.3g, 83.1 mmol) diluted with 50 ml of chlorobenzene was slowly added under vigorous stirring. The solution was heated in a 40 °C oil bath overnight. After cooling to room temperature, crude BPPO was obtained by precipitating the resulting solution in methanol. It was further purified by precipitation from chlorobenzene into methanol. It should be noted that HCl gas will be generated in this process and special attention shall be paid.

### **Synthesis of borylated 1-bromo-3-phenylpropane (BBrPP)**

The synthesis of BBrPP is based on the Ir-catalyzed C-H borylation reaction. The following presents a representative procedure.  $B_2Pin_2$  (7.98g, 31.4 mmol),  $[Ir(OMe)(COD)]_2$  (0.31g, 0.47 mmol, 1.5mol% based on the amount of 1-bromo-3-phenylpropane) and dtbpy (0.25g, 0.93 mol, 3mol% based on the amount of 1-bromo-3-phenylpropane) were quickly weighed and placed in a three-necked, round-bottomed flask equipped with a magnetic stirrer. The flask fitted with a reflux condenser was then filled and flushed with  $N_2$ . Liquid compounds, 1-bromo-3-phenylpropane (BrPP, 4.8 ml, 31.6 mmol) and n-octane (60 ml) were added under  $N_2$ . The resulting mixture was heated and stirred in a 100 °C oil bath for 16h under  $N_2$ .

After cooling to room temperature, the reaction solution was filtered through a short plug of silica gel to remove the catalyst. The filtrate was concentrated using a rotatory evaporator. The crude product was purified by silica gel column chromatography (eluting solution: EtOAc/ Hexane=1:8). The obtained products were characterized and stored to perform the intended Suzuki coupling reaction in the following steps.

### **Suzuki coupling of BBrPP with BPPO (gPPO)**

The synthesis of gPPO, i.e. grafting BBrPP onto BPPO backbone is fulfilled via a Suzuki coupling reaction. BPPO (0.74g, 3.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.21g, 0.18 mmol) and K<sub>2</sub>CO<sub>3</sub>(2.22g, 16.1 mmol) was quickly weighed and placed in a three-necked, round-bottomed flask. The flask fitted with a magnetic stirrer and a reflux condenser was then sealed. Evacuate the flask and backfill it with Ar. Repeat the evacuation and backfilling procedure three times. Degassed liquid compounds, BBrPP (1.75 g, 5.38 mmol), toluene (30 ml) and deionized water (2 ml) were sequentially added via syringe through the septum under Ar. The resulting mixture was further evacuated and backfilled with Ar three times. Remove the flask from the vacuum line and stir it in a 90 °C oil bath for 48 h. After cooling to room temperature, the mixture was concentrated using a rotatory evaporator, precipitated in a large amount of methanol and filtered. The solid product was washed with methanol and water. Purification of the resulting polymer was fulfilled by precipitation from NMP into methanol. Finally, the polymer product was completely dried in a 60 °C oven.

### **Preparation of alkali anion exchange membrane (gQAPPO)**

The alkali anion exchange membrane (gQAPPO) was prepared by sequential

gPPO amination and alkali exchange treatment. The synthesized polymer, gPPO was dissolved in NMP and reacted with excess amount of NMe<sub>3</sub> alcohol solution at room temperature. The resulting solution was cast on a clean glass plate and heated at 80 °C to allow the full evaporation of organic solvents. From the glass plate, the fabricated membrane was peeled off and stored in deionized water. Alkali anion exchange membrane (gQAPPO) was obtained by ion exchange treatment in NaOH aqueous solution (1 mol/L) at room temperature for 24h. Similar ion exchange treatment allows the fabrication gQAPPO anion exchange membrane with different counter-ions.

### **Characterization methods**

#### *Nuclear Magnetic Resonance (NMR)*

NMR measurements were conducted on a Bruker Ascend™ 400M spectrometer.

#### *Ion exchange capacity (IEC) titration*

IEC value was measured by the Mohr method. Typically, the membrane samples (in Cl<sup>-</sup>/Br<sup>-</sup> form) were immersed in aqueous Na<sub>2</sub>SO<sub>4</sub> solution (0.3 mol/L). The Cl<sup>-</sup>/Br<sup>-</sup> ions released from the membranes were titrated with aqueous AgNO<sub>3</sub> solution ( $C_{AgNO_3}$ =0.01 mol/L) using K<sub>2</sub>CrO<sub>4</sub> as an indicator. The IEC values were calculated from the amount of AgNO<sub>3</sub> consumed ( $V_{AgNO_3}$ ) and the weight of dry membrane samples ( $m_{dry}$ ).

$$IEC(\text{mmol/g}) = \frac{V_{AgNO_3} \times C_{AgNO_3}}{m_{dry}} \quad (S1)$$

#### *Ionic conductivity ( $\sigma$ )*

Measurement of ionic conductivity was conducted on the four-point probe

technique (Autolab® PGSTAT 30) using galvanostatic mode with an a.c. current amplitude of 0.1 mA and a frequency range of 1 MHz-100 Hz. Bode plots were used to determine the frequency region over which the magnitude of impedance was constant. Ionic resistance was then obtained from the associated Nyquist plot. The membrane sample being studied was set into a Teflon cell where it was in contact with two current collecting electrodes and two potential sensing electrodes (the distance between electrodes was 1cm). 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. The ionic conductivity was calculated according to the following equation.

$$\sigma = \frac{L}{RWd} \quad (S2)$$

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

#### *Water uptake and linear expansion ratio measurement*

Membrane samples (4 cm × 1 cm, in OH<sup>-</sup> form) were immersed in deionized water for 48 h. The swelled membrane samples were taken out and the surface of samples was quickly wiped with tissue paper with weight and length recorded. The weight and length of the dry membrane samples were also measured. Water uptake (WU) of membranes was calculated as follows.

$$WU = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (S3)$$

Where  $W_{\text{wet}}$  is the weight of swelled membrane samples and  $W_{\text{dry}}$  is the weight of dry membrane samples. Linear expansion ratio (LER) was calculated in a similar way.

$$\text{LER} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (\text{S4})$$

Where  $L_{\text{wet}}$  is the length of swelled membrane samples and  $L_{\text{dry}}$  is the length of dry membrane samples.

To investigate the impact of temperature on the membrane water uptake and swelling ratio, the wet membrane samples were immersed in hot water with predetermined temperature and equilibrated for 4 h. The wet weight of the membrane samples were then obtained and water uptake as well as swelling ratio were calculated.

#### *Small angle X-ray scattering (SAXS) measurement*

The membranes were irradiated by X-ray ( $\text{CuK}\alpha$ ,  $\lambda=0.154$  nm). The scattering intensity is collected by a multi-wire proportional chamber detector (Rigaku, D/max 2500, Japan). Each scattering pattern was recorded for 1800s at ambient temperature. Scattering vectors ( $q$ ) were calculated from the scattering angles ( $\theta$ ) using ( $q=4\pi \sin(2\theta)/\lambda$ ), where  $\lambda$  and  $2\theta$  are the incident wavelength and total scattering angle, respectively.

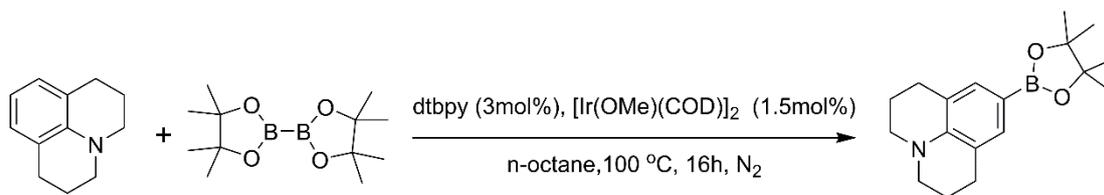


Fig. S1 Schematic for the Iridium catalyzed Miyaura borylation reaction of commercial compounds, julolidine (CAS No.:479-59-4). Steric hindrance is employed to control location of substitutes.

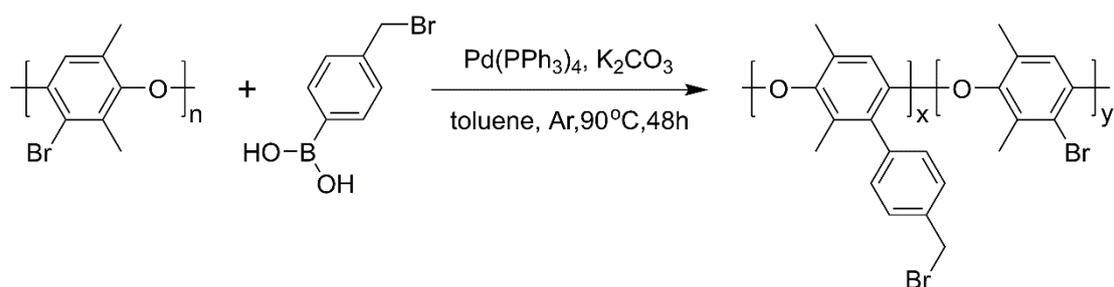


Fig. S2 Schematic for the Pd catalyzed Suzuki coupling reactions involving commercialized boronic acid (CAS No.:68162-47-0) as a tool to tune spacer length.

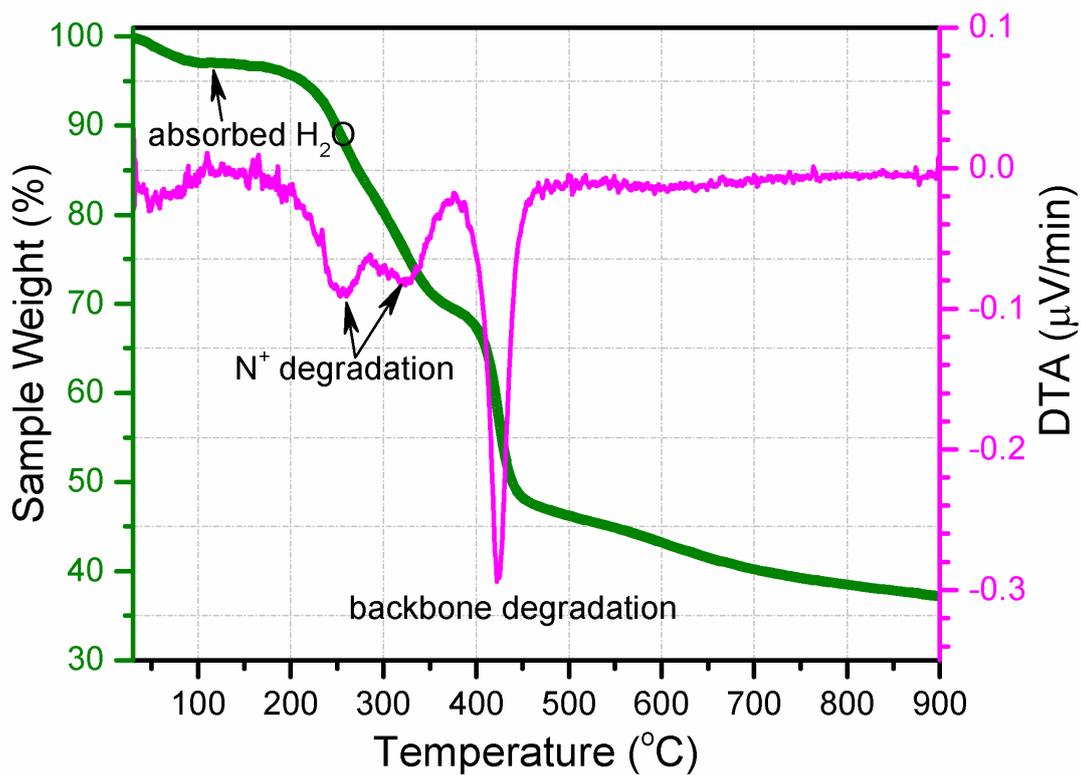


Fig. S3 Thermal gravimetric analysis of gQAPPO membrane (IEC: 1.78 mmol/g) under nitrogen with a heating rate of 10 °C/min.

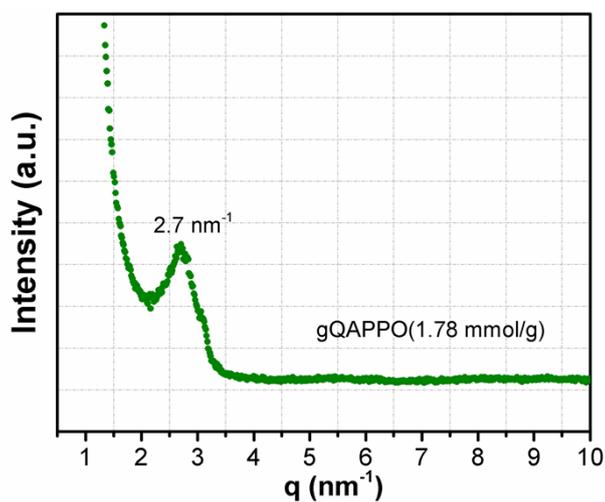


Fig. S4 Small angle X-ray scattering (SAXS) spectrum of gQAPPO membrane (IEC: 1.78 mmol/g)

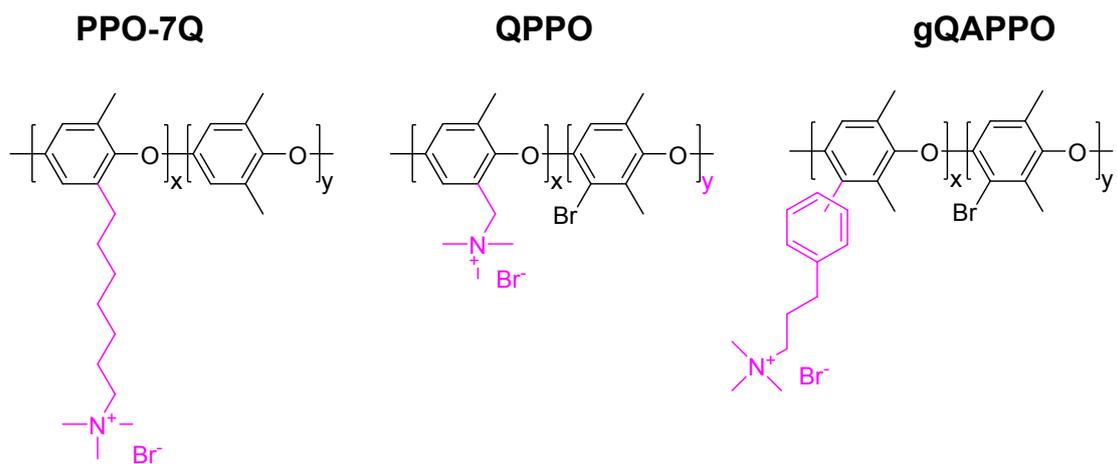


Fig. S5 The chemical structure of PPO-7Q, QPPO and the as prepared gQAPPO.

Table S1 Expansion ratio of gQAPPO membrane (1.43 mmol/g) in water at varied temperatures

Temperature (°C)	30	40	50	60	70	80
Expansion Ratio (%)	13.42	13.95	14.63	15.91	16.07	16.06