Supporting Information

# Micro-block versus random quaternized poly(arylene ether sulfone) with a highly dense quaternization units for anion exchange membrane

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# ADDED EXPERIMENTAL SECTION

# Materials

1-Methyl-4-piperidone, iodomethane, bromobutane and 1-bromooctane were obtained from the Energy Chemical Co. Bis(4-fluorophenyl)sulfone and were purchased from the Sinopharm Chemical Reagent Co. Ltd. Phenol, Toluene, H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, methanol, acetone, diethyl ether and dimethylacetamide were purchased from the Beijing Chemical Works. Bromohexane was purchased form TCI (Shanghai) Development Co., Ltd. Sulfolane was obtained from the Aladdin Industrial Corporation.

Synthesis of tri-tetraphenyl bis-phenol (TTP-OH) monomer

Tri-tetraphenyl bis-phenol was synthesized according to our published synthetic pathway via nucleophilic reaction <sup>1,2</sup>. Overall, the main route is illustrated as shown in Scheme 1. In the first step, 4.5 g (12.8 mmol) of 4,4'- (diphenylmethylene)diphenol, 16.23 g (63.8 mmol) of Bis(4-fluorophenyl)sulfone, 2.12 g (15.3 mmol) K<sub>2</sub>CO<sub>3</sub>, 54 mL of sulfolane and 15 mL of toluene were added into a 100 mL three-necked round-bottomed flask with a Dean–Stark trap and argon flow. The mixture was stirred and refluxed at 150 °C for 3 h, and then the temperature was gradually raised to 190 °C for an additional 8 h. The solution was cooled to room temperature and transferred into deionized water to yield a crude product. Afterwards, the difluorinated monomer (i) was purified over a silica gel column chromatography (CHCl<sub>3</sub>: ethyl acetate, 20: 1, v: v) with a yield of 93%.

In the second step, the tri-tetraphenyl dimethoxyl monomer (ii) was prepared in a similar way. 3.5 g (4.1 mmol) of monomer (i), 3.08 g (8.4 mmol) of 4-((4-methoxyphenyl)diphenylmethyl)phenol, 0.70 g (5.0 mmol) K<sub>2</sub>CO<sub>3</sub>, 15 mL of sulfolane and 10 mL of toluene were charged into a 50 mL three-necked round-bottomed flask with a Dean–Stark trap and argon flow. The mixture was also stirred and refluxed at 150 °C for 3 h, and then the reaction temperature was gradually heated to 190 °C for approximate 8-10 h. The crude product was precipitated into

deionized water and washed with boiling water several times. Then the tri-tetraphenyl dimethoxyl monomer (ii) was also purified over a silica gel column chromatography (CHCl<sub>3</sub>: ethyl acetate, 20: 1, v: v) with a yield of 76%.

In the third step, a common demethylation was performed to obtain the end-product, TTP-OH. A solution of dimethoxyl monomer (ii) (4 g, 2.6 mmol) dissolved in 40 mL of  $CH_2Cl_2$  was cooled to 0 °C. And then 1.5 mL of BBr<sub>3</sub> dissolved in 5 mL of  $CH_2Cl_2$  was added dropwise into the solution, while the mixture turned yellow immediately and kept stirring overnight. The resulting solution was poured into ice water to precipitate. The obtained white product was washed with deionized water and subsequently dried in vacuum (TTP-OH, yield: 98%).



Scheme S1. Synthetic pathway for tri-tetraphenyl bis-phenol (TTP-OH) monomer.

Synthesis of the PES-containing single tetraphenyl group (STP-n-PES)

A typical polycondensation procedure to prepare STP-n-PES is illustrated in Scheme S1. STP-OH (3 g, 8.5 mmol), bis(4-hydroxyphenyl) sulfone (3.20 g, 12.8 mmol) and bis(4-fluorophenyl)sulfone (6.11 g, 21.3 mmol), K<sub>2</sub>CO<sub>3</sub> (3.53 g, 25.6 mmol), 29 mL sulfolane and 18 mL of toluene were charged into a 100 mL three-necked round-bottomed flask equipped with a mechanical agitator and nitrogen inlet. Then, the mixture was refluxed at 150 °C for 3 h to remove the generated water. After toluene was evaporated, the system was heated to 210 °C along with an entire evaporation of toluene. After an approximate reaction time of 6 h, the high viscous solution was precipitated in 1 L of deionized water. The resulting product was subsequently washed several times with boiling deionized water and hot ethanol. After drying under vacuum at 60 °C, STP-40-PES was obtained with the yield of 96%.

Synthesis of the PES-containing bis-tetraphenyl groups (BTP-n-PES)

The original polymer, BTP-25-PES was synthesized as an instance, according to our published protocol<sup>2</sup>. BTP-OH (0.88 mmol), bis(4-hydroxyphenyl) sulfone (3.63 mmol), bis(4-fluorophenyl)sulfone (4.41 mmol), K<sub>2</sub>CO<sub>3</sub> (5.29 mmol), 7.6 mL of sulfolane and 10 mL of toluene were charged into a 100 mL three-necked round-bottomed flask equipped with a mechanical agitator and nitrogen inlet. Then, the mixture was refluxed at 150 °C for 3 h to remove the generated water. After toluene was evaporated, the system was heated to 210 °C for approximately 6-8 h. The viscous solution was poured into deionized water to yield a precipitate. After being pulverized into a powder, the resulting product was washed several times with boiling deionized water and hot ethanol, followed by drying to obtain 3.1 g of BTP-25-PES (yield 98%).



Scheme S2. Synthetic pathway for STP-n-PES and BTP-n-PES via nucleophilic aromatic substitution polycondensation

#### Measurements

<sup>1</sup>H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker 400 MHz instrument with the utilization of DMSO- $d_6$  as the solvent and tetramethylsilane (TMS) as an internal reference.

Fourier transform infrared spectra (FT-IR) of the polymer membranes were recorded by a Thermo Fisher Scientific iS10 spectrometer over the wavenumber range from 400 to 4000 cm<sup>-1</sup>.

Thermogravimetric analysis (TGA) was performed with a Pyris 1 thermogravimetric analyzer (Perkin-Elmer) under a nitrogen atmosphere. All the samples were preheated at 100 °C for a certain period and then heated to 800 °C at a heating rate of 10 °C min<sup>-1</sup>.

Gel permeation chromatography (GPC) analyses were carried out using a Polymer Laboratories PLGPC 220 apparatus. N,N-dimethylformamide (DMF) was used as the eluent at a rate of 1 mL min<sup>-1</sup> to confirm the molecular weights and dispersity indices relative to polystyrene standards.

The mechanical properties of the AEMs were measured at room temperature under wetting conditions for samples cut into 40 mm by 5 mm pieces. The measurement process was carried out using a SHIMADZU AG-I 1 KN with a strain rate of 2 mm min<sup>-1</sup>

Ion exchange capacity (IEC)

IEC values for the membranes were determined by a back-titration method. A patch of completely dried membrane was weighed and immersed in 25 mL of HCl solution with an appropriate concentration for 7 days to fully exchange the hydroxide to the chloride form. The resulting solution was titrated by a calibrated NaOH solution with phenolphthalein as an indicator. The IEC values were calculated by the following formula:

$$IEC(meq g^{-1}) = \frac{V_{HCl} \times C_{HCl} - V_{NaOH} \times C_{NaOH}}{W_{dry}}$$

where  $V_{HCl}$ ,  $C_{HCl}$ ,  $V_{NaOH}$  and  $C_{NaOH}$  are the volumes and concentrations of the HCl and NaOH solutions, respectively, and  $W_{dry}$  is the dry weight of the sample.

### Water uptake and swelling behavior

Films with a suitable size were fully immersed at a specified temperature for 12 h to guarantee the actual temperature of the membrane. The weight and length were recorded as  $W_{wet}$  and  $L_{wet}$  respectively, after wiping off the visible droplets on the surface of the membrane. Then, the hydrated films were dried completely to measure the weight ( $W_{dry}$ ) and length ( $L_{dry}$ ). The water uptake (WU) was determined as follows:

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

The swelling ratio (SR) was calculated by using the following equation:

$$SR(\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100$$

Conductivity

The hydroxide conductivity ( $\sigma$ ) was recorded using a Princeton Applied Research Model 273A potentiostat (Model 5210 frequency response detector, EG&G GPARC, Princeton, NJ) over a frequency range from 0.1 *Hz* to 100 *kHz*. The samples were fixed onto four-electrode clips and soaked in deionized water. The measurement was carried out for the in-plane direction at temperatures ranging from 20 to 80 °C. The in-plane hydroxide conductivity was calculated by the following equation:

$$\sigma = \frac{L}{R \times S}$$

where *L* (cm) is the distance between the two test electrodes, *R* ( $\Omega$ ) is the resistance obtained from the impedance spectrum and *S* (cm<sup>2</sup>) is the cross-sectional area of the test sample.

## Morphological observation

To measure the atomic force microscopy (AFM) images of the ionomers, the obtained ionomers solution in DMAc (1 wt%) was sprayed onto a pristine mica substrate. After the evaporation of solvent at 60 °C, Atomic force microscopy (AFM) observations were measured in the tapping mode to further observe the microstructural morphology.

Small-angle X-ray scattering (SAXS) measurements were carried out to detect the microphase separation of QAPES-BTP-x using the X-ray beam generated by a Labmate SAXSess mc<sup>2</sup> system ( $\lambda = 0.1542$  nm).

Membrane electrode assembly (MEA) fabrication and fuel cell performance

A catalyst-coated membrane method was adopted to prepare the MEA <sup>2-5</sup>. The catalyst ink was prepared using Pt/C (40 wt%, Johnson Matthey Co.) mixed in a catalyst ionomer solution (5% wt, AS-4, Tokuyama, Japan) with deionized water and isopropanol after ultrasonication. The Pt loading amounts were adjusted to be 0.5 mg cm<sup>-2</sup>, and the ink was sprayed onto both sides of the membranes. The catalyst-coated membrane and carbon paper (HCP120, HESEN, China) were assembled together to complete the MEA. In addition, no hot pressing was carried out.

A  $H_2/O_2$  fuel cell test for QAPES-BTP-x was adapted by using a testing system (Smart2 PEM/DM, WonATech, Korea). After the catalyst-coated membrane being activated at 100 mV until the current density increased to a maximum, the polarization curve was collected in the galvanostatic mode at 60 °C with 100% humid hydrogen and an oxygen flow rate of 200 sccm without back pressure.



**Figure. S1** <sup>1</sup>H NMR spectra for (a) precursor diffuorinated monomer (i), (b) precursor dimethoxyl monomer (ii) and (c) the designed bisphenol monomer TTP-OH in DMSO- $d_{6}$ .



**Figure. S2** TGA profiles for TTP-18.2-PES, TTP-18.2-CMPES and TTP-18.2-QAPES measured at 10 °C min<sup>-1</sup> under nitrogen atmosphere.



Figure. S2 <sup>1</sup>H NMR spectrum of the STP-40-PES, STP-40-CMPES and STP-40-QAPES in DMSO- $d_6$ .



Figure. S2 <sup>1</sup>H NMR spectrum of the TTP-14.3-PES, TTP-14.3-CMPES and TTP-14.3-

QAPES in DMSO-d<sub>6</sub>.



**Figure. S3** <sup>1</sup>H NMR spectra of TTP-22.2-QAPES before and after immersion in 1 M KOH aqueous solution at 80 °C for 10 and 20 d.



**Figure. S4** <sup>1</sup>H NMR spectra of STP-40-QAPES before and after immersion in 1 M KOH aqueous solution at 80 °C for 10 and 20 d.



**Figure. S5** <sup>1</sup>H NMR spectra of TTP-14.3-QAPES before and after immersion in 1 M KOH aqueous solution at 80 °C for 10 and 20 d.



Figure. S6 <sup>1</sup>H NMR spectra of TTP-22.2-QAPES before and after immersion in 1 M

KOH aqueous solution at 80 °C for 10 and 20 d.

# REFERENCE

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