

## Supporting information for

### **Poly(arylene ether sulfone) crosslinked networks with pillar[5]arene units grafted by multiple long-chain quaternary ammonium salts for anion exchange membranes**

Jinwu Peng,<sup>a</sup> Minhui Liang,<sup>a</sup> Zhenchao Liu,<sup>a</sup> Peng Wang,<sup>a</sup> Chengying Shi,<sup>a</sup> Wei Hu,<sup>b</sup> and Baijun Liu<sup>\*</sup>

<sup>a</sup> *Key Laboratory of High Performance Plastics, Ministry of Education. National & Local Joint Engineering Laboratory for Synthesis Technology of High Performance Polymer. College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R. China.*

<sup>b</sup> *Key Laboratory of Polyoxometalate Science of the Ministry of Education, Faculty of chemistry, Northeast Normal University, 5268 Renmin Street, Changchun 130024, P.R. China.*

*\*E-mail address: [liubj@jlu.edu.cn](mailto:liubj@jlu.edu.cn)*

## Experimental

### Materials

4,4'-Biphenol (BPL, 95%), 4,4'-difluorodiphenyl sulfone (FPS, 95%), tetramethylbisphenol A (TMBA, 98%), *N*-bromosuccinimide (98%), diammonium cerium(IV) nitrate (98%), Boron tribromide (BBr<sub>3</sub>), 1,6-dibromohexane (98%), diethylene glycol bis(3-aminopropyl) ether (DGBAE) and sodium hexafluorophosphate (95%) were obtained from Energy Chemical and used as received. Pillar[5]arene was synthesized according to a previous report.<sup>1</sup>

### Syntheses of pillar[4]arene[1]quinone and pillar[5]arene-containing bisphenol monomer

An aqueous solution of (NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>] (2.19 g, 4.00 mmol) was added dropwise into the solution of pillar[5]arenes (3.00 g, 4.00 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) in a 250 mL round-bottom flask. When the mixture was stirred at room temperature for 4 h, the organic solvent was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After being filtered and evaporated, the concentrated crude product was purified by chromatography on silica gel (petroleum ether/acetone, v/v 1: 2) to obtain oxblood red pillar[4]arene[1]quinone (0.98 g) in 34% yield.

The solution of pillar[4]arene[1]quinone (0.98 g, 1.36 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was stirred in a 50 mL round-bottom flask while a cold aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (4.73 g, 27.2 mmol) was added. After 24 h, the color of mixture turned to milk white at room temperature. The water layer was extracted by CH<sub>2</sub>Cl<sub>2</sub> for three times (50 mL × 3), and the collection was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After being filtered and evaporated under vacuum, bifunctional pillar[5]arene (BFP-OH) (0.96 g) was obtained as a white solid in 98% yield, which was pure enough using a bisphenol monomer.

FT-IR  $\nu$  (cm<sup>-1</sup>): 3365 (-OH), 2999-2848 (-CH<sub>3</sub>,-CH<sub>2</sub>-), 1459 (-OCH<sub>3</sub>), and 1207 (C-O). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): 7.07 (s, 2H), 6.79 (s, 2H), 6.73 (s, 2H), 6.49 (s, 2H), 6.48 (s, 2H), 3.73 (s, 6H), 3.66 (s, 12H), 3.63 (s, 6H), 3.58 (s, 6H), and 3.56 (s, 4H).

### Synthesis of poly(arylene ether sulfone)s containing pillar[5]arenes (PES-P5-X-OCH<sub>3</sub>)

As a typical procedure, the synthesis of PES-P5-X-OCH<sub>3</sub> was described as follows, where X was the molar ratio of BFP-OH to FPS. In this example, X was designed to 12. BPL (1.4524 g, 7.8 mmol), FPS (2.5425 g, 10 mmol), TMBA (0.2844 g, 1 mmol), BFP-OH (0.8675 g, 1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (1.6585 g, 12 mmol), DMSO (15 mL) and toluene (7 mL) were introduced into a 100 mL round-bottomed flask equipped with a Dean-Stark apparatus, a mechanical stirrer, a condenser, and a gas vent. The mixture was stirred at 145 °C for 4 h under nitrogen, and the temperature was slowly raised to 180 °C for another 20 h. The viscous solution was poured into water to form precipitate. Afterward product was washed by water and ethanol for three times, respectively. After being dried in vacuum at 60 °C, the PES-P5-12-OCH<sub>3</sub> was achieved in 95% yield.

FT-IR  $\nu$  (cm<sup>-1</sup>): 3054-2832 (-CH<sub>3</sub>, -CH<sub>2</sub>-), 1594, 1482 (C=C), 1101 (O=S=O), 1014 (Ar-O-Ar), and 847 (Ar-H). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>)  $\delta$  (ppm): 7.93-7.83 (m, 4H), 7.58 (d, 3.12H, 6.4Hz), 7.12-7.06 (m, 7.12H), 6.97 (s, 0.4H), 6.91-6.86 (m, 0.88H), 6.77-6.49 (s, 1.2H), 3.76 (m, 2.88H), 3.40 (d, 1.2H), 2.06 (s, 1.2H), and 1.68 (s, 0.6H).

### Demethylation of poly(arylene ether sulfone)s containing pillar[5]arenes (PES-P5-X-OH)

The demethylation of PES-P5-X-OCH<sub>3</sub> was conducted via BBr<sub>3</sub> in mild condition. The PES-P5-12-OCH<sub>3</sub> (0.5 g) and dry CHCl<sub>3</sub> (30 mL) was introduced into 100 mL three-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer and a gas vent. BBr<sub>3</sub> (0.759 g, 3.03 mmol) was slowly added in the mixture at -30 °C under nitrogen. The white polymer slowly precipitated from solution with reaction elevating to room temperature. After 24 h, the product was obtained via pouring mixture into ethanol and washed by a large amount of ethanol and dried under vacuum at 80 °C for 24 h with 95% yield. The products of demethylation are termed as PES-P5-X-OH, where the "OH" represents the phenolic hydroxyl group.

FT-IR  $\nu$  (cm<sup>-1</sup>): 3435 (-OH), 3054-2832 (-CH<sub>3</sub>, -CH<sub>2</sub>-), 1594, 1482 (C=C), 1101 (O=S=O), 1014 (Ar-O-Ar), and 847 (Ar-H). <sup>1</sup>H NMR (400 MHz; DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 8.53-8.39 (s, 0.96H), 7.94 (s, 4H), 7.72 (s, 3.12H), 7.16 (s, 7.12H), 7.06 (s, 0.4H), 6.87 (s, 0.88H), 6.65-6.47 (s, 1.2H), 3.48 (s, 1.2H), 1.93 (s, 1.2H), and 1.62 (s, 0.6H).

### Grafting reaction of poly(arylene ether sulfone)s containing pillar[5]arenes (g-PES-P5-X)

The (6-bromohexyl)trimethylammonium hexafluorophosphate (BTAMH) was synthesized according to the

literature<sup>2</sup> and exchanged ion by sodium hexafluorophosphate.<sup>3</sup> Taking PES-P5-12-OH for example, the PES-P5-X-OH grafted by BTAMH was carried out as follows: PES-P5-12-OH (0.5 g), BTAMH (0.768 g, 2.09 mmol), K<sub>2</sub>CO<sub>3</sub> (0.168 g, 1.22 mmol), KI (20 mg, 0.12 mmol) and NMP (10 mL) were added in 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a thermometer and a gas vent. The mixture was stirred for 36 h at 100 °C under nitrogen and poured into a large amount of ethanol to precipitate the product, followed by washing for three times and drying under vacuum at 80 °C with 88% yield. The products are termed as g-PES-P5-X, where the “g” represents the graft.

FT-IR  $\nu$  (cm<sup>-1</sup>): 3054-2864 (-CH<sub>3</sub>, -CH<sub>2</sub>-), 1586, 1411 (C=C), 1110 (O=S=O), 1014 (Ar-O-Ar), and 847 (Ar-H). <sup>1</sup>H NMR (400 MHz; DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 7.94 (s, 4H), 7.73 (s, 4H), 7.17 (s, 8.32H), 7.05 (s, 0.4H), 6.87 (s, 0.88H), 4.03 (t, 0.96H, *J*=7.2 Hz), 3.44 (m, 0.6H), 3.27-2.96 (m, 11.2H), 1.93-1.12 (m, 9.48H).

#### **Benzylic bromination of graft poly(arylene ether sulfone)s containing pillar[5]arenes (Br-g-PES-P5-X)**

The g-PES-P5-12 (0.5 g), NBS (0.048 g, 0.027 mmol), 1,1,2,2-tetrachloroethane (10 mL) were added into 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a thermometer and a gas vent. The mixture was stirred for 6 h at 80 °C, and then was poured into ethanol. Precipitate was washed three times and dried under vacuum at 80 °C with 90% yield. The products are termed as Br-g-PES-P5-X, where the “Br” represents the bromination.

FT-IR  $\nu$  (cm<sup>-1</sup>): 3063-2872 (-CH<sub>3</sub>, -CH<sub>2</sub>-), 1586-1411 (C=C), 1101 (O=S=O), 1006 (Ar-O-Ar), 847 (Ar-H), and 641 (C-Br). <sup>1</sup>H NMR (400 MHz; DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 7.94 (s, 4H), 7.73 (s, 4H), 7.17 (s, 8.32H), 7.05 (s, 0.4H), 6.87 (s, 0.88H), 4.51 (s, 0.24H), 4.04 (t, 0.96H, *J*=7.2 Hz), 3.44 (m, 0.6H), 3.27-2.96 (m, 11.2H), and 1.93-1.12 (m, 9.48H).

#### **Membrane preparation and anion exchange of PES-P5-X**

The Br-g-PES-P5-X (0.5 g) was dissolved in DMSO (10 mL) at 0 °C. D-GBAE (15 mg, 0.068 mmol) was added into the mixture and stirred for 30 min. The above solution was cast onto a leveled glass plate, and dried at 80 °C for 48 h to get the transparent and flexible crosslinked membrane (Fig. S8). The OH<sup>-</sup> form membranes were obtained by immersing the membranes in ammonium chloride saturated solution at 100 °C for 48h and 1 M KOH at room temperature for 48 h. The crosslinked membranes are termed as PES-P5-X, where X is 12, 10, 7, respectively.

### **Characterization and measurements**

#### **1. Nuclear magnetic resonance (NMR)**

The moderate amount copolymers were dissolved in 0.6 mL CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> and characterized by Bruker Avance III 400 MHz spectrometer.

#### **2. Fourier-transform infrared spectrometer (FTIR)**

Powder samples were mixed with spectral pure potassium bromide, pressed into sheets and characterized by fourier-transform infrared spectrometer (Nicolet Impact 410). The membranes could be tested directly in surface scattering modes.

#### **3. Gel Permeation Chromatography (GPC)**

The samples were dilute to 3-5 mg mL<sup>-1</sup> in 5 mL HPLC grade *N,N*-Dimethylformamide. The GPC (Agilent Technologies PL-GPC-220) was calibrated by standard polystyrene sample. After baseline stabilization, the samples were automatically injected into the machine and eluted by HPLC grade *N,N*-Dimethylformamide with a flow rate of 1.0 mL min<sup>-1</sup>.

#### **4. Mechanical properties**

The membranes were cut into strip form of 50 mm × 5 mm, every samples were prepared for three strips to

eliminate error. Shimadzu AG-I machine at a speed of 2 mm min<sup>-1</sup> was applied to pull the strips in wet state at room temperature.

#### 5. Thermal analysis

Thermogravimetric analyzer (Pyris 1 TGA) was employed to investigate the thermal stability of polymer. The sample (4-6 mg) was carefully placed in a crucible and heated up from 80 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup>.

#### 6. Water uptake and swelling ratio

The wet weight ( $W_w$ ) and wet length ( $L_w$ ) of membranes in form of OH<sup>-</sup> were measured firstly, after the samples were soaked in setting temperature for 24 h in 100% humidity under nitrogen protection. The wet membranes were flattened by glass plate and dried in vacuum at 90 °C for 24 h, and the dry weight ( $W_d$ ) and dry length ( $L_d$ ) were achieved. The water uptake (WU) and swelling ratio (SR) were calculated as follows:

$$(1) \quad WU(\%) = [(W_w - W_d)/W_d] \times 100\%$$

$$(2) \quad SR(\%) = [(L_w - L_d)/L_d] \times 100\%$$

#### 7. Ion conductivity

The conductivity was measured via four-electrode ac impedance method in a polytetrafluoroethylene test chamber. The distance between adjacent electrodes was  $L$  (cm). The membranes (4 cm × 1 cm) in OH<sup>-</sup> form with cross-sectional area of  $S$  (cm<sup>2</sup>) were tested in aqueous solution from 20 °C to 80 °C under nitrogen protection. The resistance of the sample ( $R$  kΩ) was obtained. Ion conductivity ( $\sigma$  mS cm<sup>-1</sup>) was calculated as follows:

$$(3) \quad \sigma = \frac{L}{RS}$$

#### 8. Ion exchange capacity

The ion exchange capacities of membranes were measured via back titration method. The membranes in OH<sup>-</sup> form whose weight was  $m_{dry}$  (g) in dry state, were immersed in HCl ( $n_1$  mmol) for 24 h. After that, the HCl solution was titrated by NaOH solution until neutral. The consumption of NaOH recorded as  $n_2$  mmol. IEC (mmol g<sup>-1</sup>) values were calculated using the following formula:

$$(4) \quad IEC = \frac{n_1 - n_2}{m_{dry}}$$

#### 9. Transmission electron microscopy (TEM)

The membranes with thickness of 4-5 mm in the form of Br<sup>-</sup> were cut into slice of 60 nm thickness via a microtome. After being soaked in 1 M H<sub>2</sub>WO<sub>3</sub>, the slice was collected on copper grids and the test was operated on JEM-2100 electron microscope.

#### 10. Small-angle X-ray scattering (SAXS)

The membranes in Br<sup>-</sup> form were with thickness of about 0.1 mm were measured in SAXSessmc AntonPaar equipped with Cu Ka source. The measures were carried out under vacuum at room temperature.

#### 11. Single cell performance

The catalyst ink mixing Pt/C catalyst, a 5 wt% polyelectrolyte solution, deionized water, and ethanol, was sprayed on the membrane to form 5×5 cm effective area and the load was ensured 0.5 mg cm<sup>-2</sup>. The two sides of

membrane were hot pressured with two carbon papers as gas diffusion layer. The test of single cell performance was operated on Fuel Cell Test System (Arbin Instrument Corp.), under the 100% humidity and different temperature, with hydrogen ( $0.3 \text{ L min}^{-1}$ ) and oxygen ( $0.15 \text{ L min}^{-1}$ ) flowing through anode and cathode.

**Table S1** Molecular weights of the polymers

<b>Polymers</b>	<b>Mn (kDa)</b>	<b>Mw (kDa)</b>	<b>PDI (Mw/Mn)</b>
PES-P5-12-OCH <sub>3</sub>	108.6	228.1	2.1
PES-P5-10-OCH <sub>3</sub>	124.3	236.2	1.9
PES-P5-7-OCH <sub>3</sub>	142.8	314.2	2.2

**Table S2** Mechanical properties of the AEMs

<b>Membrane</b>	<b>Tensile strength (MPa)</b>	<b>Elongation at break (%)</b>	<b>Young's modulus (MPa)</b>
PES-P5-12	27.7	15.0	671
PES-P5-10	30.2	16.3	717
PES-P5-7	36.5	15.3	896

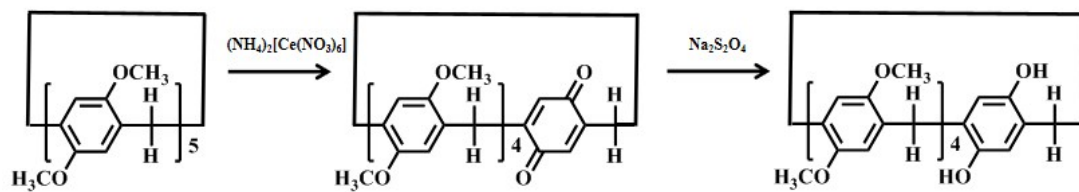
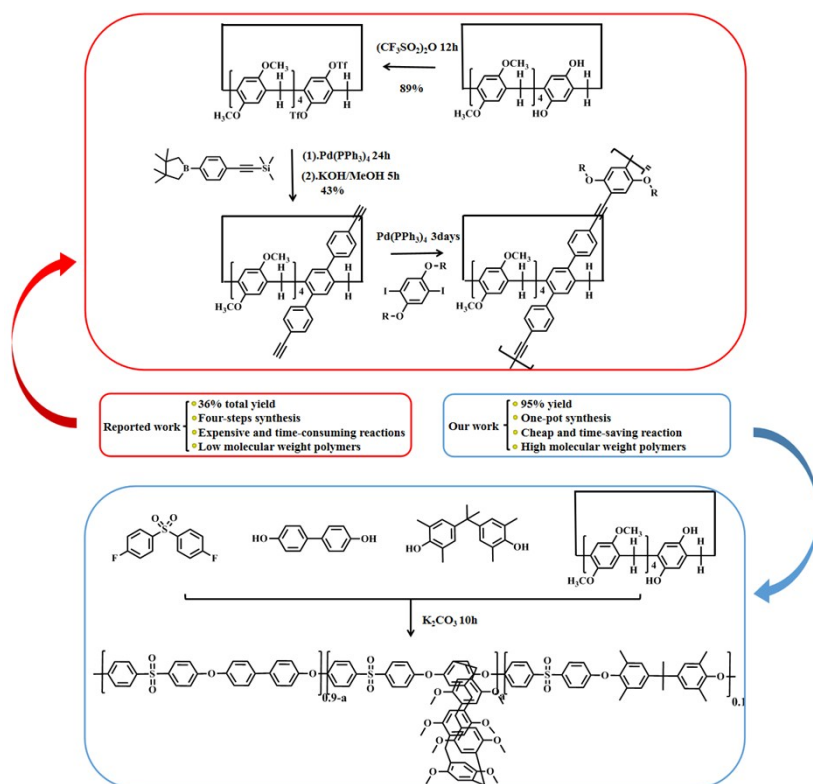
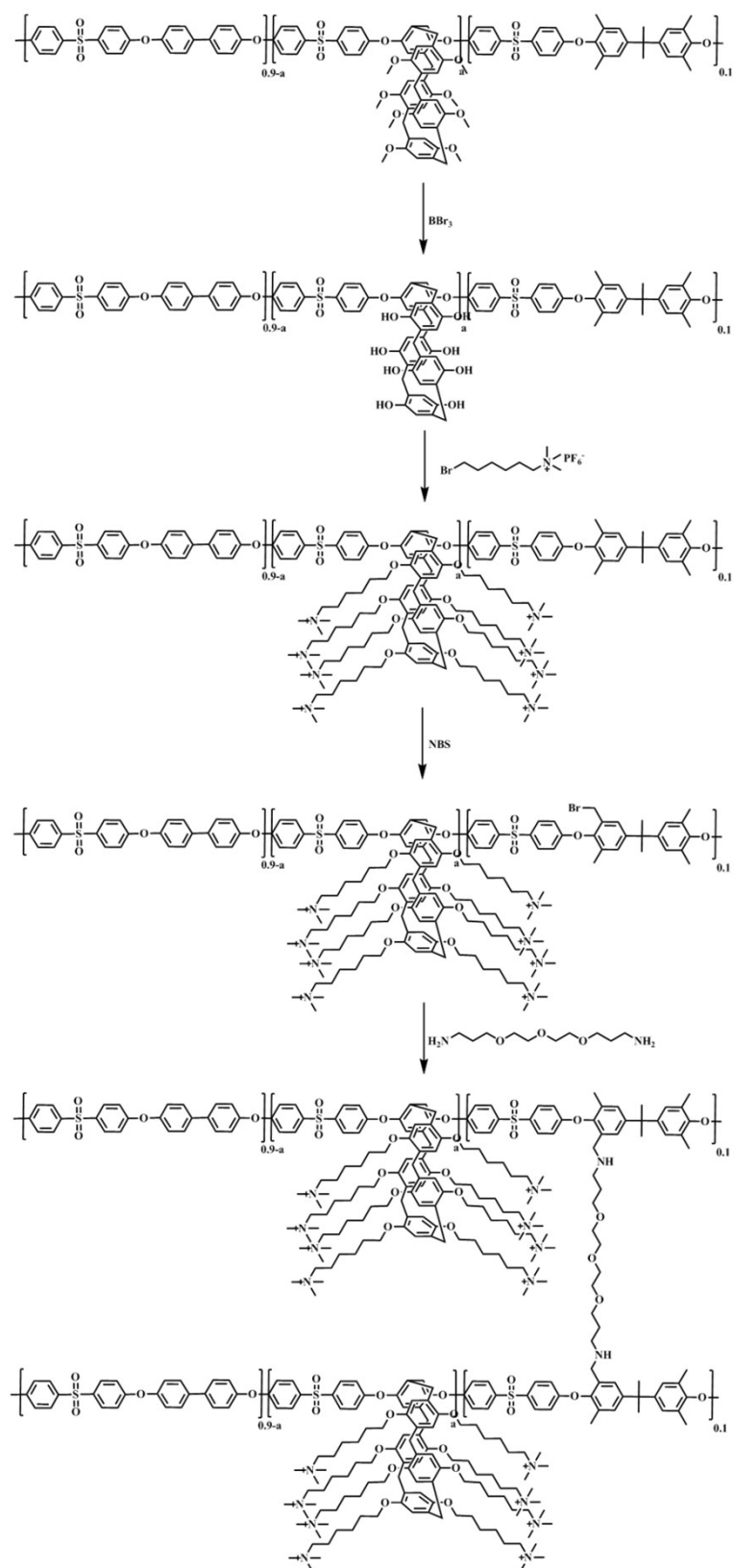


Fig. S1 Synthesis route of DP5-OH.



Scheme. S1 Different synthetic route of pillar[5]arenes polymers.



**Fig. S2** Synthesis route of pillar[5]arenes-containing crosslinked networks.

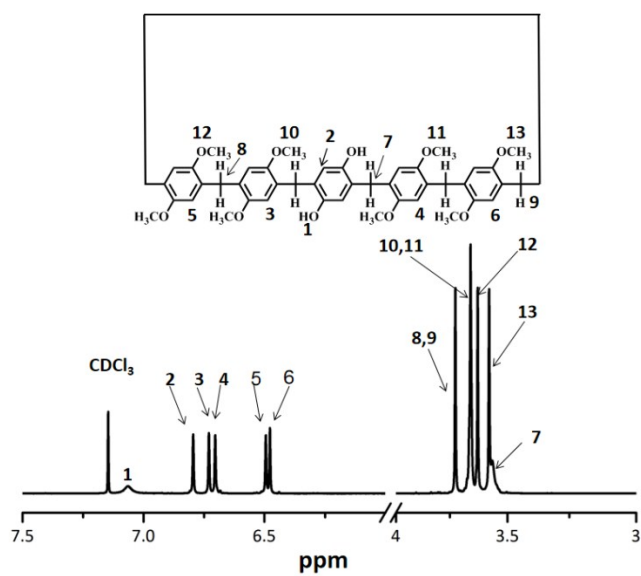


Fig. S3 <sup>1</sup>H NMR spectrum of DP5-OH.

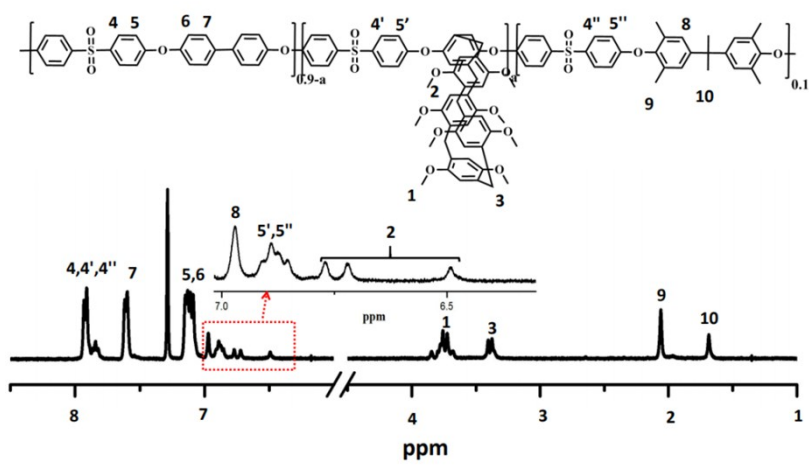


Fig. S4 <sup>1</sup>H NMR spectrum of PES-P5-12-OCH<sub>3</sub>.



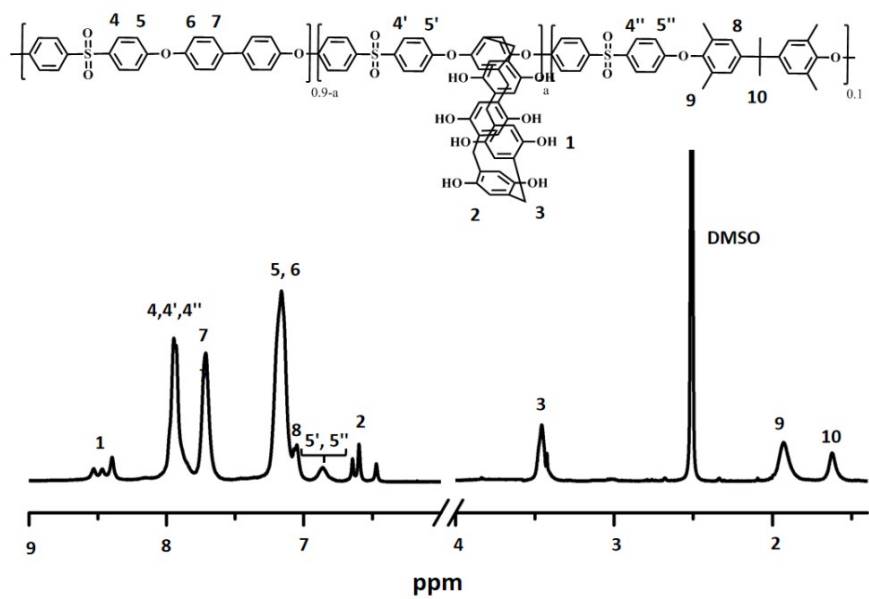


Fig.S5  $^1\text{H}$  NMR spectrum of PES-P5-12-OH.

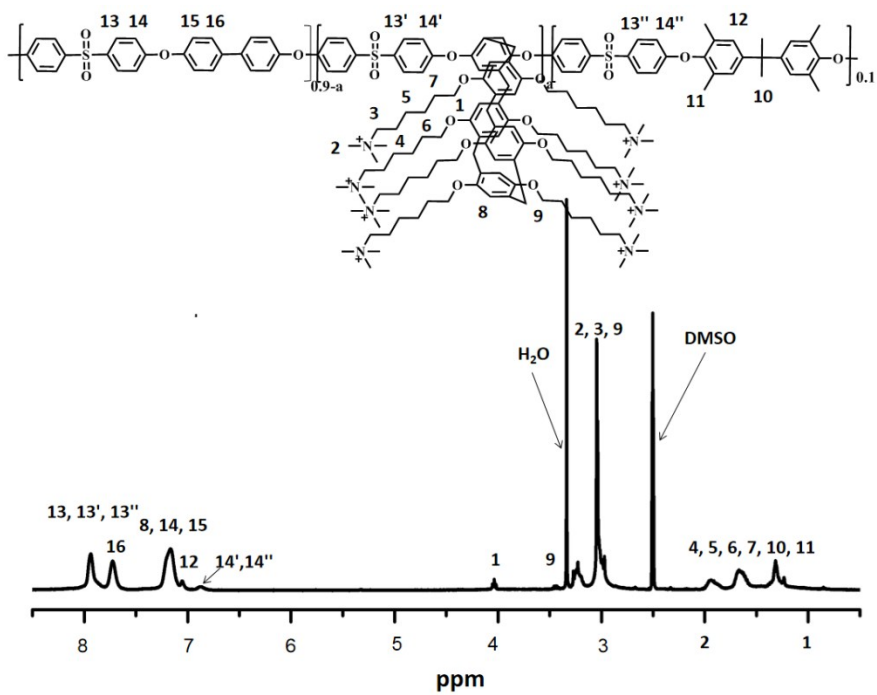


Fig. S6  $^1\text{H}$ NMR spectrum of g-PES-P5-12.

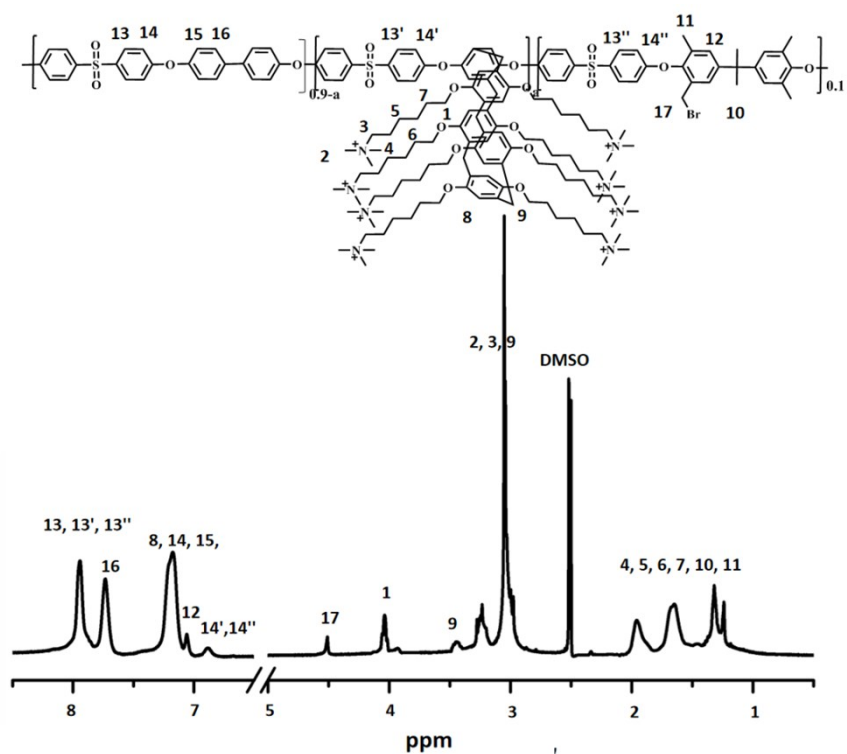


Fig. S7 <sup>1</sup>H NMR spectrum of Br-g-PES-P5-12.

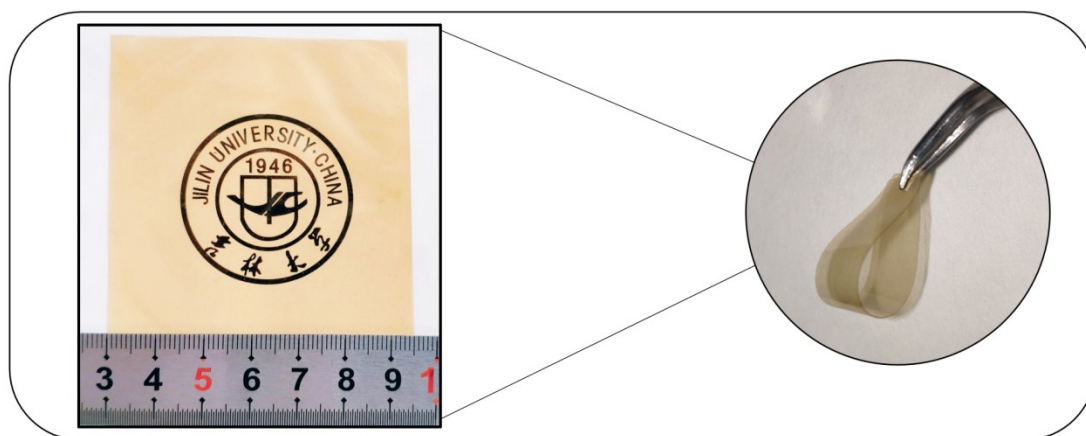


Fig. S8 Photos of transparent and flexible pillar[5]arenes-based AEMs

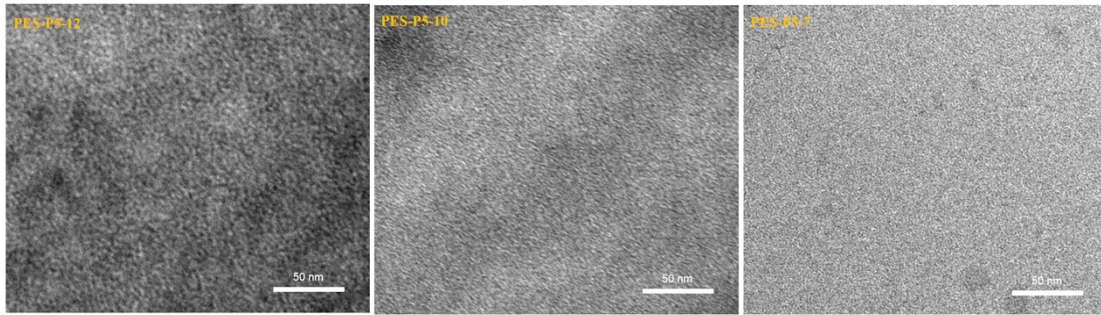


Fig. S9 TEM images of PES-P5-12, PES-P5-10 and PES-P5-7 (from left to right).

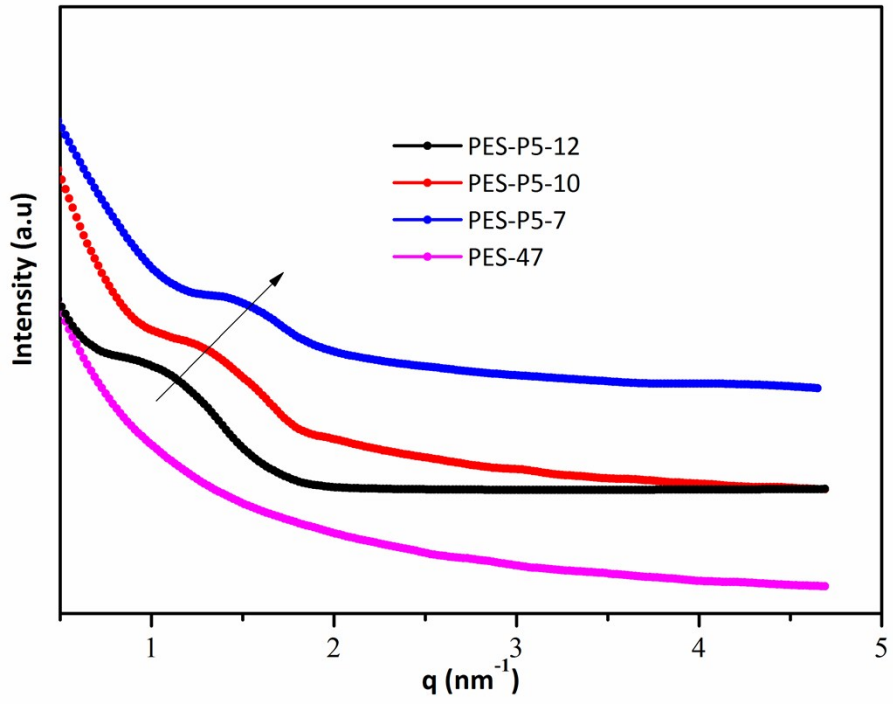
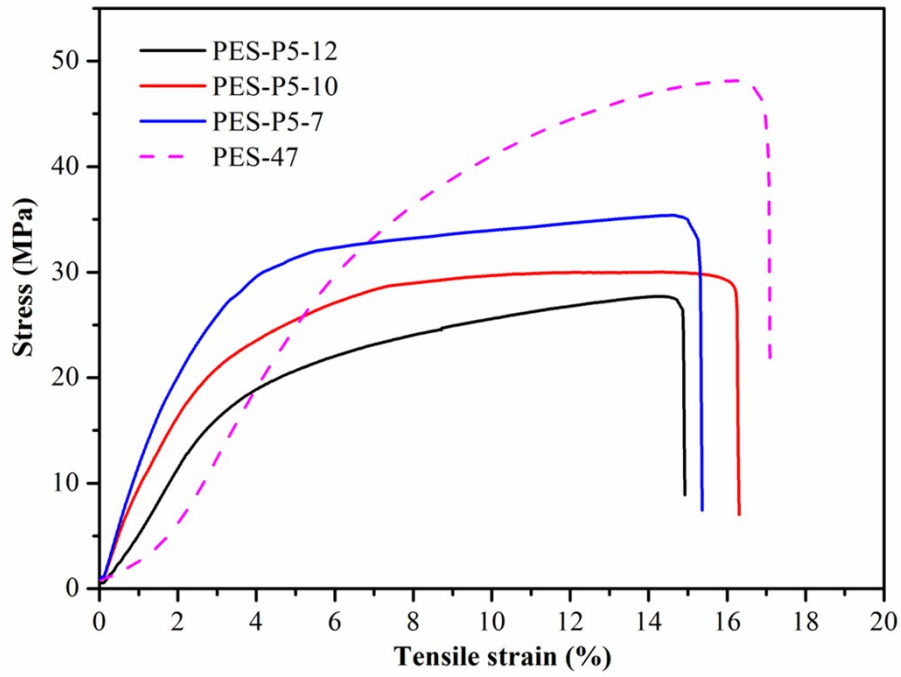
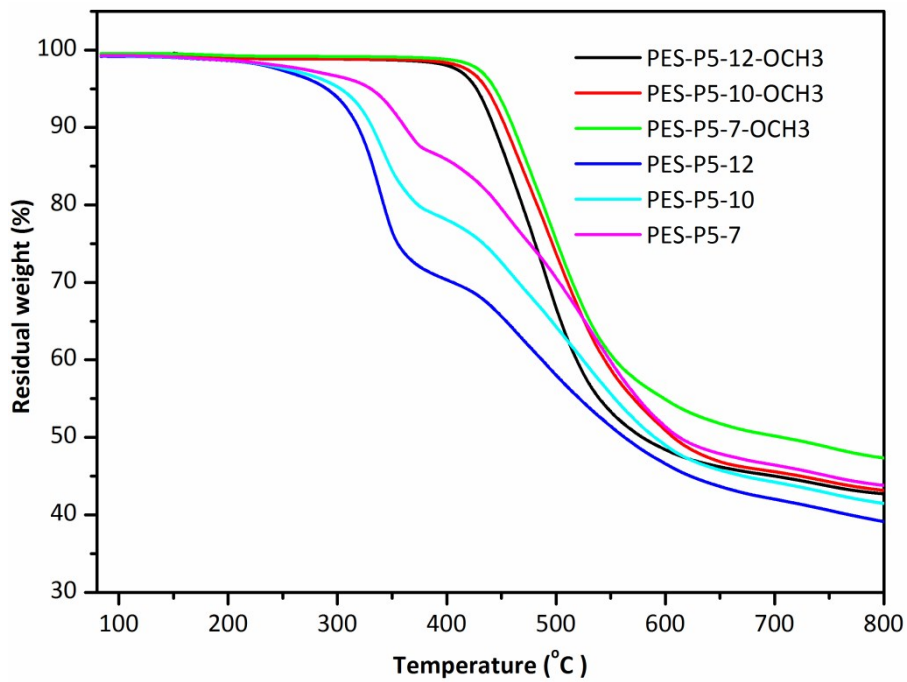


Fig. S10 SAXS profile of the various AEMs.



**Fig. S11** Tensile curves of the membranes.



**Fig. S12** TGA curves of PES-P5-X-OCH<sub>3</sub> and PES-P5-X.

## References

- 1 T. Ogoshi, T. Aoki, K. Kitajima, S. Fujinami, T.-a. Yamagishi, Y. Nakamoto, *Journal of Organic Chemistry* **2011**, *76*, 328.
- 2 C. X. Lin, X. L. Huang, D. Guo, Q. G. Zhang, A. M. Zhu, M. L. Ye, Q. L. Liu, *Journal of Materials Chemistry A* **2016**, *4*, 13938.
- 3 D. J. Strasser, B. J. Graziano, D. M. Knauss, *Journal of Materials Chemistry A* **2017**, *5*, 9627.