

## Supporting Information for

# Self-crosslinking for dimensionally stable and solvent-resistant quaternary phosphonium based hydroxide exchange membranes

Shuang Gu, Rui Cai and Yushan Yan\*

### 1. Experimental Methods

**Synthesis of chloromethylated polysulfone (CMPSf186):** 3.39 g (113 mmol) paraformaldehyde and 12.3 g (113 mmol) trimethylchlorosilane were added into a PSf solution (5 g or 11.3 mmol PSf in 250 ml chloroform), followed by dropwise addition of 0.589 g (2.26 mmol) stannic chloride. The mixture was kept at 50 °C for 72 hrs. Subsequently the reaction mixture was poured into ethanol (95%) to precipitate chloromethylated polysulfone (CMPSf). The CMPSf precipitate was filtrated, well washed by ethanol, and dried in vacuum at room temperature for 12 hrs. The CMPSf obtained had a 186% (<sup>1</sup>H NMR) of degree of chloromethylation (DC). DC was defined as the average numbers (in percentage) of chloromethyl group onto one PSf-repeat unit in CMPSf.

**Preparation of self-crosslinked TPQPOH (SCL-TPQPOH) HEMs:** The quaternary phosphorization and self-crosslinking were achieved by a simple one-step method. 0.533 g CMPSf186 (1.86 mmol chloromethyl group, -CH<sub>2</sub>Cl, or CM) was first dissolved in 10 ml N-methyl-2-pyrrolidone (NMP), and then a certain amount of tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) was added and dissolved into NMP. The NMP solution was poured onto a Petri dish and covered by a Petri dish lid, followed by heating at 80 °C for 48 hrs, and then the Petri dish was removed and the temperature was lowered to 30 °C to slowly evaporate solvent for 1 to 2 weeks to obtain SCL-TPQPOH membrane. The SCL-TPQPOH membrane was obtained by treating SCL-TPQPOH in 2 M KOH at room temperature for 48 hrs, followed by thorough washing and immersion in deionized water for 48 hrs to remove residual KOH.

The amount of TTMPP added to the 0.533 g CMPSf186 (i.e., the ratio of TTMPP to CM, or TTMPP:CM) is the key to prepare SCL-TPQPOH with controlled degree of self crosslinking. When the TTMPP:CM ratio exactly equals 1, i.e., 0.991 g or 1.86 mmol TTMPP is added, the uncrosslinked TPQPOH186 is prepared as described in our previous works<sup>1,2</sup>. However, when the TTMPP:CM ratio is less than 1 (i.e., CM is in excess), the CM reacts first with TTMPP to form quaternary phosphonium groups preferentially owing to the much higher reactivity of quaternary phosphorization<sup>1</sup>. Then, the residual CM will react with the quaternary phosphonium groups just formed, leading to the SCL-TPQPOHs. Here, 0.941 g or 1.77 mmol TTMPP (TTMPP:CM = 0.95) formed SCL-TPQPOH5.3%. 5.3% is the degree of crosslinking, or DCL. It is defined as the average percentage of the quaternary phosphonium group (containing three trimethoxyl benzene rings) that crosslinked with the chloromethyl groups. Similarly, 0.891 g or 1.67 mmol TTMPP or TTMPP:CM = 0.90, leads to SCL-TPQPOH11%, 0.793 g or 1.49 mmol TTMPP, or TTMPP:CM = 0.80 for SCL-TPQPOH25%, and 0.594 g or 1.12 mmol TTMPP, or TTMPP:CM = 0.60 for SCL-TPQPOH67%.

**<sup>1</sup>H NMR spectroscopy:** A Varian Inova 500 was used as the spectrometer at a resonance frequency of 500.059 MHz to obtain high-resolution <sup>1</sup>H NMR spectra. For the spectra of TTMPP or uncrosslinked TPQPOH, a dilute solution (~5 mg) was prepared directly in deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>, 0.7 ml) containing small amount of tetramethylsilane (TMS) as the internal standard. For the spectra of SCL-TPQPOHs, owing to the excellent solvent resistance, larger amount (~50 mg) of SCL-TPQPOHs was immersed in 0.7 ml DMSO-d<sub>6</sub> at 40 °C for one month to increase the polymer concentration, so as to obtain clear and reliable <sup>1</sup>H NMR signals.

**Conductivity measurements:** The conductivity measurements were carried out by using a typical ex-situ four-electrode AC impedance method (20 °C, in along-membrane direction, under immersed deionized water). The detailed information for the conductivity measurement and solubility test can be found in the Supporting Information in our previous work<sup>1</sup>. Other methods such as swelling ratio, water uptake, and thermal analysis used here were described in detail in our another previous work<sup>3</sup>.

## 2. Full names of the abbreviated HEMs

P(MDMXDA-COE)-QAOH: Poly((1-methylcyclooct-4-enyl)methylene, N,N-dimethyl, *p*-xylene diammonium hydroxide *co* cyclooctene)

P(TMM-DCPD)-QAOH: Poly(N,N,N-trimethyl-1-(2-methylbicyclo[2.2.1]hept-5-en-2-yl)methylene ammonium hydroxide *co* dicyclopentyladiene)

GA-PVA/chitosan-QAOH: Glutaraldehyde crosslinked quaternized poly(vinyl alcohol/chitosan) hydroxide

GA-PVA/TMAPS-QAOH: Glutaraldehyde crosslinked poly(vinyl alcohol)/quaternized 3-(trimethylammonium) propyl-functionalized silica) hydroxide

GA-PVA-EPTMA-QAOH: Glutaraldehyde crosslinked poly(vinyl alcohol)-(2,3-epoxypropyl)trimethylammonium hydroxide

GA-chitosan-QAOH: Glutaraldehyde crosslinked quaternized chitosan hydroxide

CPPO-BPPO-QAOH: Crosslinked chloroacetylated poly(2,6-dimethyl-1,4,-phenylene oxide)-bromomethylated poly(2,6-dimethyl-1,4,-phenylene oxide) trimethyl quaternary ammonium hydroxide

EDA-CPP-QAOH: Ethylenediamine crosslinked/quaternized chlorinated polypropylene hydroxide

Dabco/TEA-PECH-QAOH: Diazabicyclooctan crosslinked/(triethylamine)quaternized polyepichlorohydrin hydroxide

TMDAs/TMA-PSf-QAOH: N,N,N',N'-tetramethyl methylene (or ethylene, or propylene, or butylene, or hexylene) (-1,3- or -1,4-, or -1,6-)diamines crosslinked/(trimethylamine)quaternized polysulfone hydroxide

TMEDA/BE-PSf-QAOH: N,N,N',N'-tetramethylethylenediamine/bromoethane quaternized polysulfone hydroxide

4EP-6FPSf-QAOH: Tetraphenylethane glycidyl ether crosslinked quaternized hexafluorinated polysulfone hydroxide

TEOS/EPh-PPO-QAOH: Tetraethoxysilane/monophenyltriethoxysilane crosslinked quaternized poly(2,6-dimethyl-1,4,-phenylene oxide) hydroxide

TEOS/EPh-P(VBC- $\gamma$ -MPS)-QAOH: Tetraethoxysilane/monophenyltriethoxysilane crosslinked quaternized poly(vinylbenzyl chloride- $\gamma$ -methacryloxypropyl trimethoxyl silane) hydroxide

HDT-Dabco/AO-P(ECH-AGE)-QAOH: 1,6-Hexanedithiol crosslinked diazabicyclooctan/1-azabicyclo-[2,2,2]-octane quaternized poly(epichlorohydrin-allyl glycidyl ether) hydroxide

PEI-QAOH: Quaternized polyetherimide hydroxide

PPESK-QAOH: Quaternized poly(phthazinone ether sulfone ketone) hydroxide

PEK-C-QAOH: Quaternized polyetherketone-cardo hydroxide

FEP-g-QAOH: Quaternized vinylbenzyl chloride-radiation-grafted poly(hexafluoropropylene-co-tetrafluoroethylene) hydroxide

2FPDPS-QAOH: Quaternized difluorinated poly(diphenyl sulfone) hydroxide

### 3. Tables

**Table S1.** Degrees of crosslinking (DCLs) of SCL-TPQPOHs.

| SCL-TPQPOH                  | $R_{\text{TTMPP:CM}}^a$ | $R_{\text{CM:QPOH}}^b$ | $\text{DCL}_t^c$ | $\text{DCL}_m^d$ |
|-----------------------------|-------------------------|------------------------|------------------|------------------|
| SCL-TPQPOH-25% <sup>e</sup> | 0.80                    | 0.25                   | 25%              | 22%              |
| SCL-TPQPOH-67% <sup>e</sup> | 0.60                    | 0.67                   | 67%              | 69%              |

<sup>a</sup>  $R_{\text{TTMPP:CM}}$ , molar ratio of the added tertiary phosphonium (TTMPP) to the initial chloromethyl group (CM) of CMPSf. <sup>b</sup>  $R_{\text{CM:QPOH}}$ , molar ratio of the residual chloromethyl group (CM) to formed quaternary phosphonium group (QPOH) after quaternary-phosphorylation. <sup>c</sup>  $\text{DCL}_t$ , theoretical degree of crosslinking, assuming all of the residual chloromethyl groups completely crosslinked with quaternary phosphonium groups. <sup>d</sup>  $\text{DCL}_m$ , measured degree of crosslinking from <sup>1</sup>H NMR spectra,  $\text{DCL}_m = 6A(\text{H}^c)/[A(\text{H}^u)+2A(\text{H}^c)] \times 100\%$ . <sup>e</sup> CMPSf186 as the polymer precursor.

**Table S2.** Solubility<sup>a</sup> of TPQPOH and SCL-TPQPOH.

| Solvent                      | Boiling point (°C) | TPQPOH (20 °C) | SCL-TPQPOH <sup>b</sup> (20–80 °C) |
|------------------------------|--------------------|----------------|------------------------------------|
| Acetone                      | 58                 | +              | –                                  |
| Methanol                     | 65                 | +              | –                                  |
| Ethanol                      | 78                 | +              | –                                  |
| n-Propanol                   | 97                 | +              | –                                  |
| N,N-Dimethylformamide (DMF)  | 153                | +              | –                                  |
| Dimethylacetamide (DMAc)     | 166                | +              | –                                  |
| Dimethyl sulfoxide (DMSO)    | 189                | +              | –                                  |
| N-Methyl-2-pyrrolidone (NMP) | 204                | +              | –                                  |

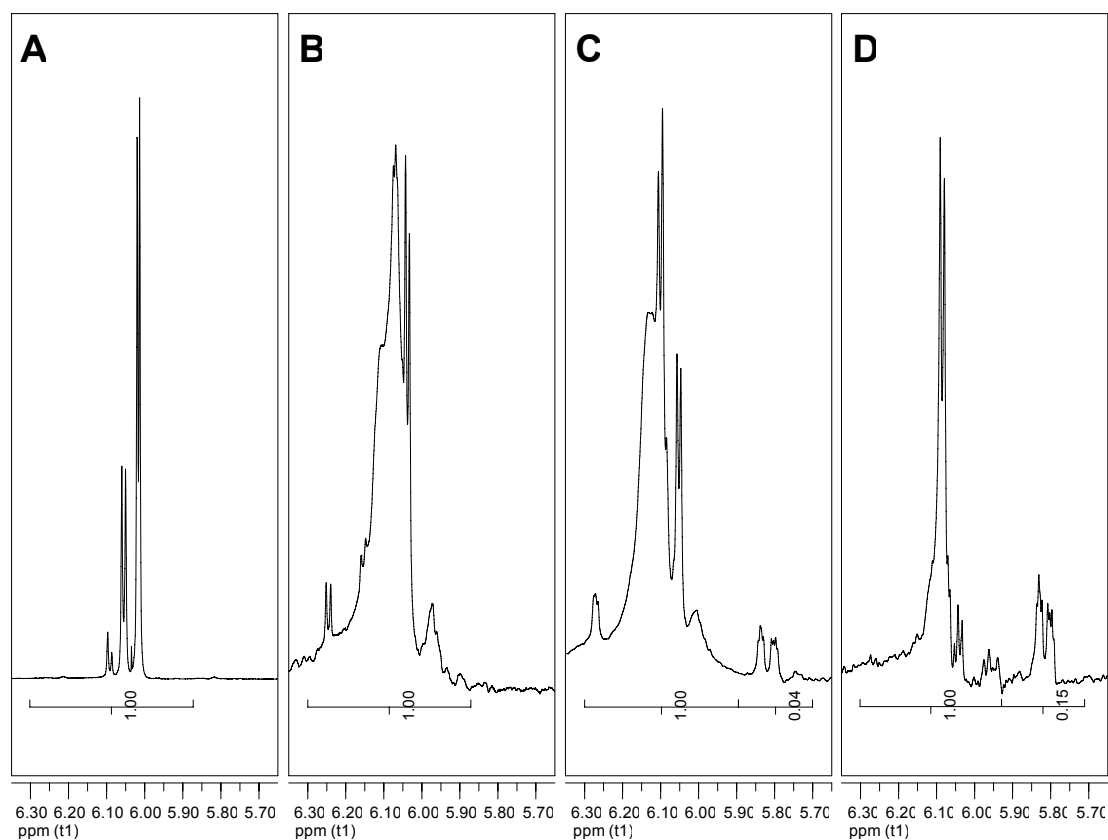
<sup>a</sup> +: Soluble, -: Insoluble. <sup>b</sup> DCL of SCL-TPQPOH: 5.3%–67%.

**Table S3.** Thermal decomposition temperatures of uncrosslinked TPQPOH and SCL-TPQPOHs. N<sub>2</sub> atmosphere and 10 °C/min heating rate.

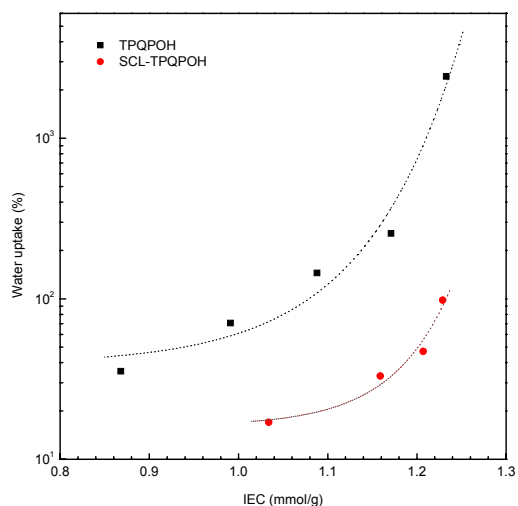
| HEM               |  | $T_{\text{OD}}^a$ (°C) | $T_{\text{FD}}^b$ (°C) |
|-------------------|--|------------------------|------------------------|
| Uncrosslinked HEM | TPQPOH <sup>c</sup> (this work)                | 178                    | 184                    |
|                   | PEI-QAOH <sup>4</sup>                          | 140                    |                        |
|                   | PPESK-QAOH <sup>5</sup>                        | 150                    |                        |
|                   | PEK-C-QAOH <sup>6</sup>                        | ~160                   |                        |
|                   | FEP-g-QAOH <sup>7</sup>                        | 165                    |                        |
|                   | 2FDPS-QAOH <sup>8</sup>                        | 170                    |                        |
| Crosslinked HEM   | SCL-TPQPOH25% <sup>c</sup> (this work)         | 183                    | 192                    |
|                   | SCL-TPQPOH67% <sup>c</sup> (this work)         | 186                    | 203                    |
|                   | TEO/Eph-PPO-QAOH <sup>9</sup> (air atmosphere) | 135–144                |                        |
|                   | TMDAs/TMA-PSf-QAOH <sup>10</sup>               | ~160–170               |                        |

<sup>a</sup>  $T_{\text{OD}}$ , onset decomposition temperature. <sup>b</sup>  $T_{\text{FD}}$ , fastest-weight-loss decomposition temperature. <sup>c</sup> CMPSf186 as the polymer precursor.

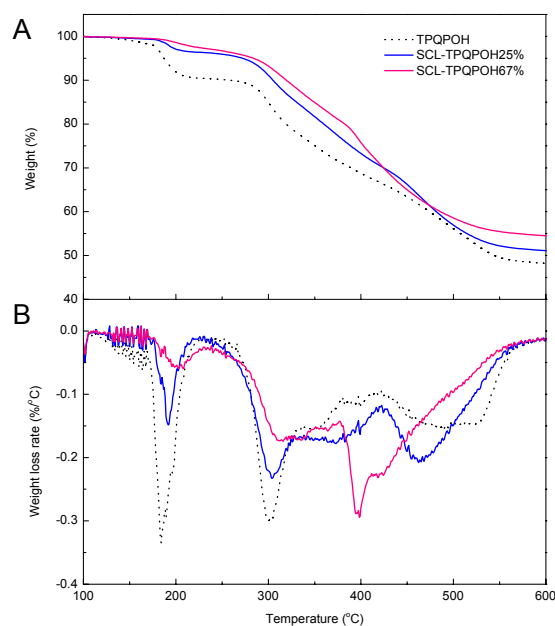
#### 4. Figures



**Figure S1.**  $^1\text{H}$  NMR spectra of TTMPP (A), uncrosslinked TPQPOH (B), SCL-TPQPOH25% (C), and SCL-TPQPOH67% (D). Both TPQPOH and SCL-TPQPOH used the same CMPSf186 as polymer precursor; Deuterated chloroform ( $\text{CDCl}_3$ ) as solvent and tetramethylsilane (TMS) as internal standard. The shown numbers are the relative integral areas for the uncrosslinked trimethoxyl benzene ring aromatic-Hs, H<sup>u</sup>s (from ~5.90 to 6.30 ppm), and the crosslinked trimethoxyl benzene ring aromatic-Hs, H<sup>c</sup>s (from 5.70 to ~5.90 ppm).



**Figure S2.** Water uptake at 60 °C versus IEC of uncrosslinked TPQPOHs (black squares) and SCL-TPQPOHs (red circles). CMPSf186 as the polymer precursor of SCL-TPQPOHs.



**Figure S3.** TGA curves (A) and DTG curves (B) of uncrosslinked TPQPOH (black dot line), SCL-TPQPOH25% (blue solid line), and SCL-TPQPOH67% (pink solid line). CMPSf186 as the polymer precursor of SCL-TPQPOHs. Test conditions: N<sub>2</sub> atmosphere and 10 °C/min heating rate.

#### References

- (1) Gu, S.; Cai, R.; Luo, T.; Chen, Z. W.; Sun, M. W.; Liu, Y.; He, G. H.; Yan, Y. S. *Angew. Chem. Int. Edit.* **2009**, *48*, 6499-6502.
- (2) Gu, S.; Cai, R.; Luo, T.; Jensen, K.; Contreras, C.; Yan, Y. S. *Chemsuschem* **2010**, *3*, 555-558.
- (3) Gu, S.; He, G. H.; Wu, X. M.; Li, C. N.; Liu, H. J.; Lin, C.; Li, X. C. *J. Membrane Sci.* **2006**, *281*, 121-129.
- (4) Wang, G. G.; Weng, Y. M.; Chu, D.; Xie, D.; Chen, R. R. *J. Membrane Sci.* **2009**, *326*, 4-8.
- (5) Fang, J.; Shen, P. K. *J. Membrane Sci.* **2006**, *285*, 317-322.
- (6) Xiong, Y.; Liu, Q. L.; Zeng, Q. H. *J. Power Sources* **2009**, *193*, 541-546.
- (7) Herman, H.; Slade, R. C. T.; Varcoe, J. R. *J. Membrane Sci.* **2003**, *218*, 147-163.
- (8) Wang, J. H.; Zhao, Z.; Gong, F. X.; Li, S. H.; Zhang, S. B. *Macromolecules* **2009**, *42*, 8711-8717.
- (9) Wu, Y. H.; Wu, C. M.; Xu, T. W.; Lin, X. C.; Fu, Y. X. *J. Membrane Sci.* **2009**, *338*, 51-60.
- (10) Park, J. S.; Park, S. H.; Yim, S. D.; Yoon, Y. G.; Lee, W. Y.; Kim, C. S. *J. Power Sources* **2008**, *178*, 620-626.