## **Supporting Information**

## Highly Selective Proton Conductive Networks based on Chain-end Functionalized Polymers with Perfluorosulfonate Side Groups

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**Characterization**. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a Bruker AM-300 spectrometer instrument with tetramethylsilane as internal reference. Gel permeation chromatography (GPC) measurements were performed on a Viscotek Model 302 triple detector system equipped with refractive index, light scattering and viscometer detectors. DMF containing 0.02 M LiBr was used as the eluent at a flow rate 1.0 mL/min, and the column temperature was set at 45 °C. FTIR spectra were recorded on a Varian Digilab FTS-800 spectrometer. The thermal transition data were obtained by a TA Instruments Q100 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min. Thermo-gravimetric analysis (TGA) measurements were performed on a TA instruments model 2950 at a heating rate of 20 °C/min under N<sub>2</sub> from room temperature up to a maximum of 750 °C. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-1200 EX II TEM equipment. For TEM measurement, the membranes were stained by a saturated lead acetate solution, washed with water and dried under vacuum at 40 °C for 24 h. The stained membranes were embedded in epoxy resin and sectioned to yield 100 nm thickness using a microtome, and then placed on copper grids.

The tensile stress-strain properties of the cross-linked membranes and Nafion 117 were tested on Instron model 4411 universal testing machine using ASTM D 882-02 method. The wet films were examined immediately after the membranes being soaked in liquid water for 4 hours. Membranes II and III showed elongations at break of 59.5% and 56.25% respectively at dry state, and 48.6% and 43.7% respectively at wet state. Moduluses of II and III are  $6.9 \times 10^8$  and  $7.6 \times 10^8$  Pa at dry state and  $9.4 \times 10^7$  and  $9.8 \times 10^7$  at wet state.



Figure S1. NMR spectrum of the P(VDF-PFSVE) with t-Boc protected amino end-groups.



Figure S2. NMR spectrum of the P(VDF-PFSVE) with amine end-groups.



*Figure S3.* FTIR spectra of P(VDF-PFSVE) and the cross-linked membranes.



Figure S4. TEM images of the cross-linked membranes and Nafion.



*Figure S5.* Humidity dependence of proton conductivity of the cross-linked membranes and Nafion 117.