**Electronic Supplementary Information**

# Simple and universal synthesis of sulfonated porous organic polymers with high proton conductivity

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# Section 1. Experiment

## Materials and methods

Tetraphenylmethane (TPM), triphenylene (TP), biphenyl (BP), benzene (B), formaldehyde dimethyl acetal, chlorosulfonic acid, anhydrous Iron (III) chloride, 1,2-dichloroethane, dichloromethane, acetone, and methanol were obtained from TCI, Wako, and Sigma-Aldrich. Field emission scanning electron microscope was performed on HITACHI Miniscope TM3030. Energy-dispersive X-ray spectroscopy (EDS) mapping was measured by TM3030Plus miniscope. The X-ray photoelectron spectroscopy (XPS) measurement was implemented on a DLD spectrometer (Kratos Axis-Ultra; Kratos Analytical Ltd). Nitrogen sorption isotherms were measured at 77 K by BELSORP-max. Water uptake were measured by performed by using a Micrometrics ASAP2050 analyzer. Fourier transforms Infrared (FT IR) spectra were measured from 650 to 4000 $cm^{-1}$ on FT IR spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.). Powder X-ray diffraction (PXRD) data were recorded on fully automatic horizontal multipurpose X-ray diffractometer (Rigaku Smartlab) from 2θ = 1.5° up to 30° with 0.02° increment. Thermogravimetric analysis (TGA) was implemented on TG-DTA 2010 SA (NETZSCH) Japan under nitrogen flow at 10°C $min^{-1}$.

## Section 2. Fourier transforms Infrared spectra

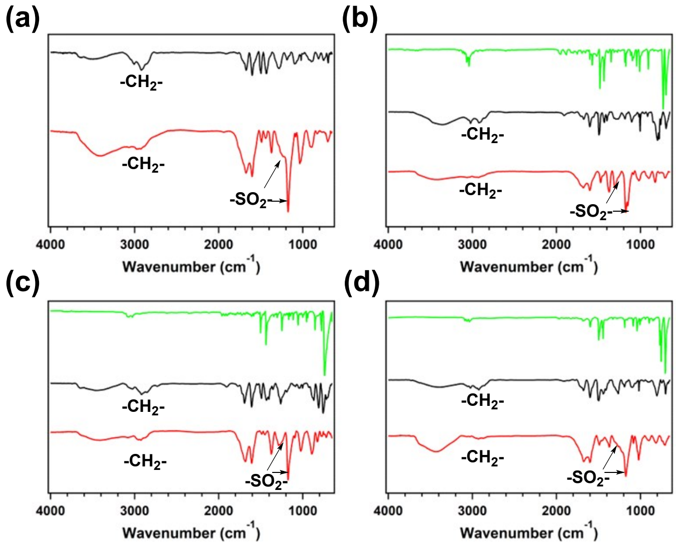


**Fig. S1.** FT IR spectra of (a) POP-B (black curve) and S-POP-B (red curve); (b) BP (green curve), POP-BP (black curve), and S-POP-BP (red curve); (c) TP (green curve), POP-TP (black curve), and S-POP-TP (red curve); (d) TPM (green curve), POP-TPM (black curve), and S-POP-TPM (red curve).

## Section 3. Energy-dispersive X-ray spectroscopy mapping images

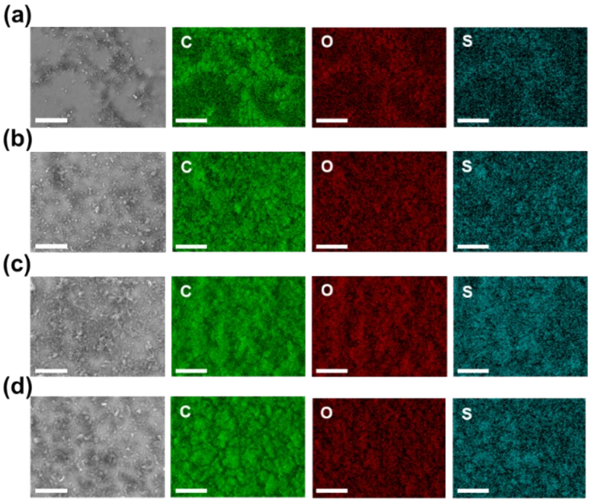


**Fig. S2**. EDS mapping images of (a) S-POP-B, (b) S-POP-BP, (c) S-POP-TP, and (d) S-POP-TPM (Scale bar: 25 μm).

## Section 4. Thermogravimetric analysis curves

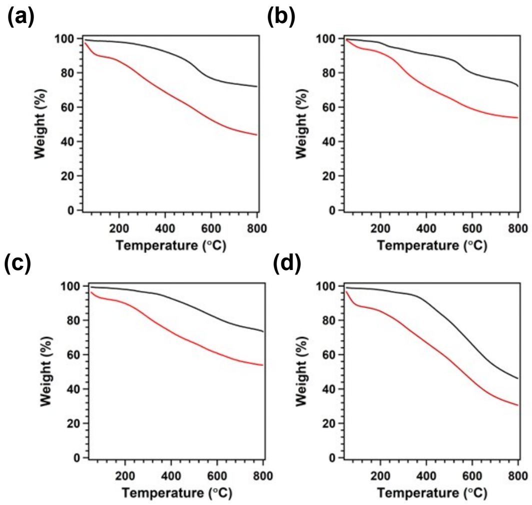


**Fig. S3.** TGA curves of (a) POP-B (black curve) and S-POP-B (red curve); (b) POP-BP (black curve) and S-POP-BP (red curve); (c) POP-TP (black curve) and S-POP-TP (red curve); (d) POP-TPM (black curve) and S-POP-TPM (red curve).

## Section 5. Field emission scanning electron microscope images

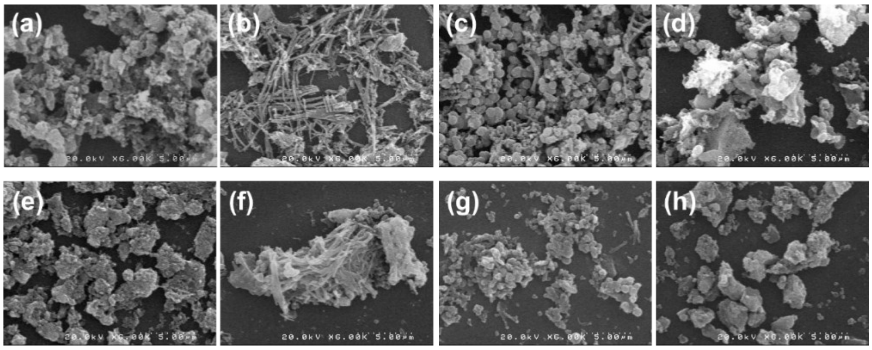

**Fig. S4.** FE SEM images of (a) POP-B, (b) POP-BP, (c) POP-TP, (d) POP-TPM, (e1) S-POP-B, (f) S-POP-BP, (g) S-POP-TP, and (h) S-POP-TPM.

## Section 6. Powder X-ray diffraction patterns

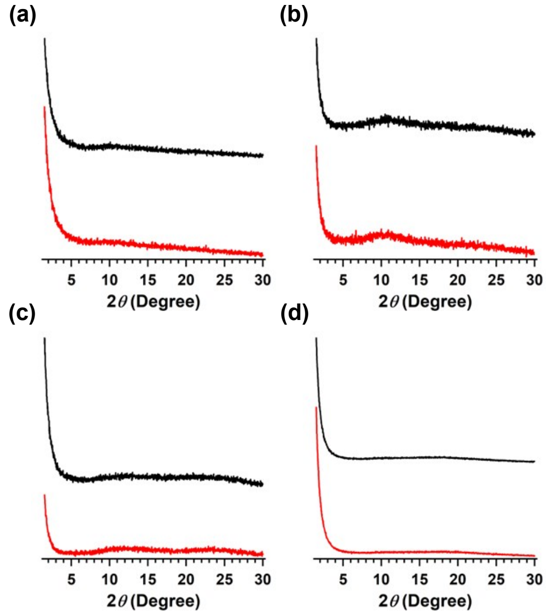


**Fig. S5.** PXRD patterns of POP-B (black curve) and S-POP-B (red curve). (b) POP-BP (black curve) and S-POP-BP (red curve); (c) POP-TP (black curve) and S-POP-TP (red curve); (d) POP-TPM (black curve) and S-POP-TPM (red curve).

## Section 7. Pore size distribution profiles

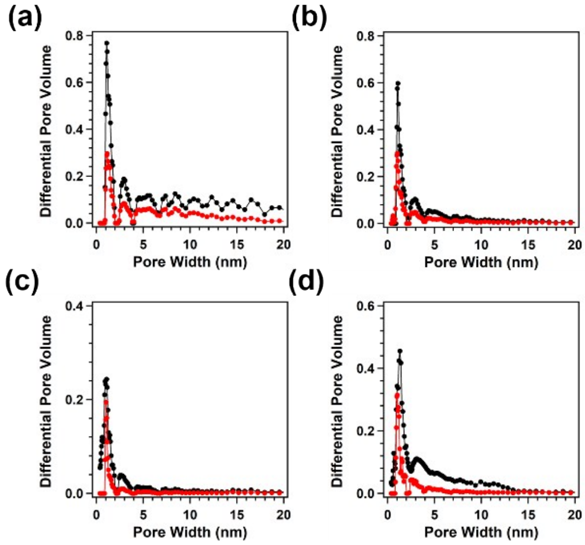


**Fig. S6.** Pore size distribution profile of (a) POP-B and S-POP-B, (b) POP-BP and S-POP-BP, (c) POP-TP and S-POP-TP, (d) POP-TPM and S-POP-TPM measured at 77 K (black curves for POP and red curves for S-POP).

## Section 8. Water vapor absorption curves

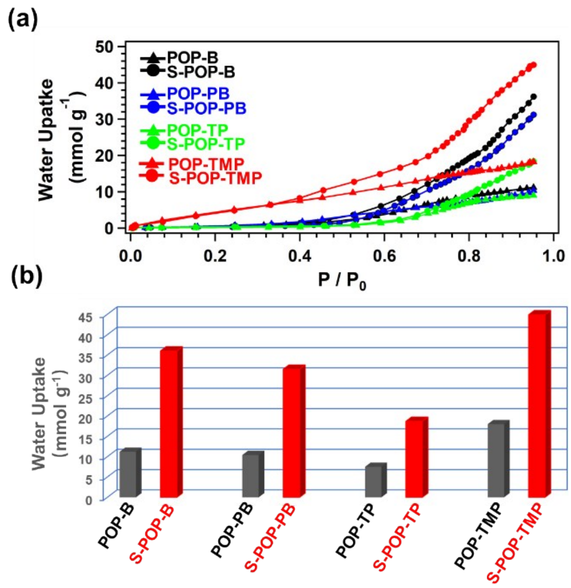


**Fig. S7.** (a) Water vapor absorption curves of POPs and S-POPs measured at 298 K. (b) Comparison of water uptake of POPs and S-POPs.

## Section 9. Nyquist plots of S-POPs recorded at 25 ºC and different relative humidity

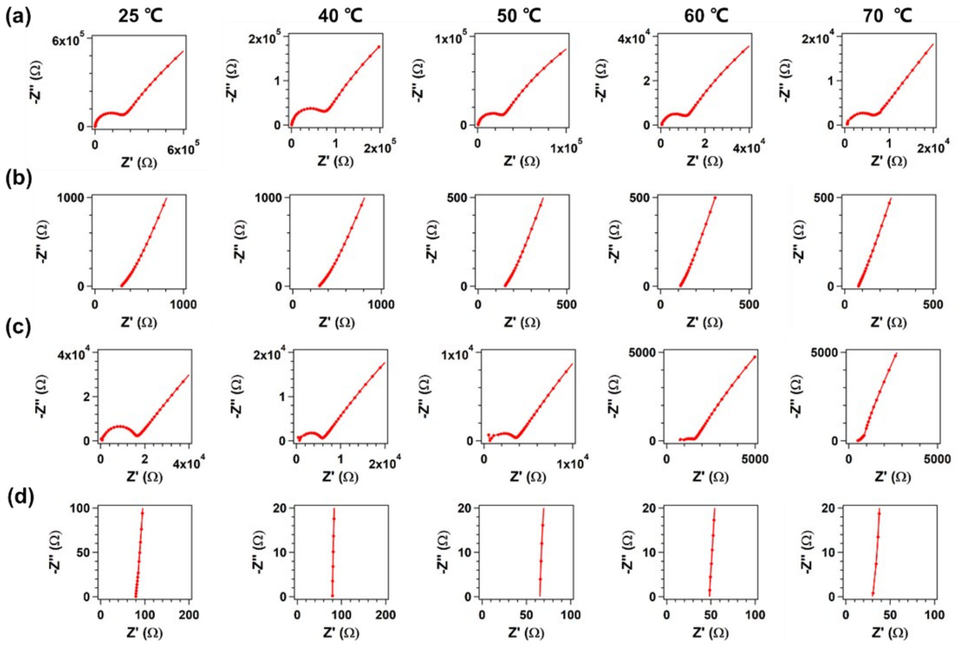


**Fig. S8.** Nyquist plots of (a) S-POP-B, (b) S-POP-BP, (c) S-POP-TP, and (d) S-POP-TPM recorded at 25 ºC and different relative humidity.

## Section 10. Nyquist plots of S-POPs recorded at various temperature and 95% relative humidity

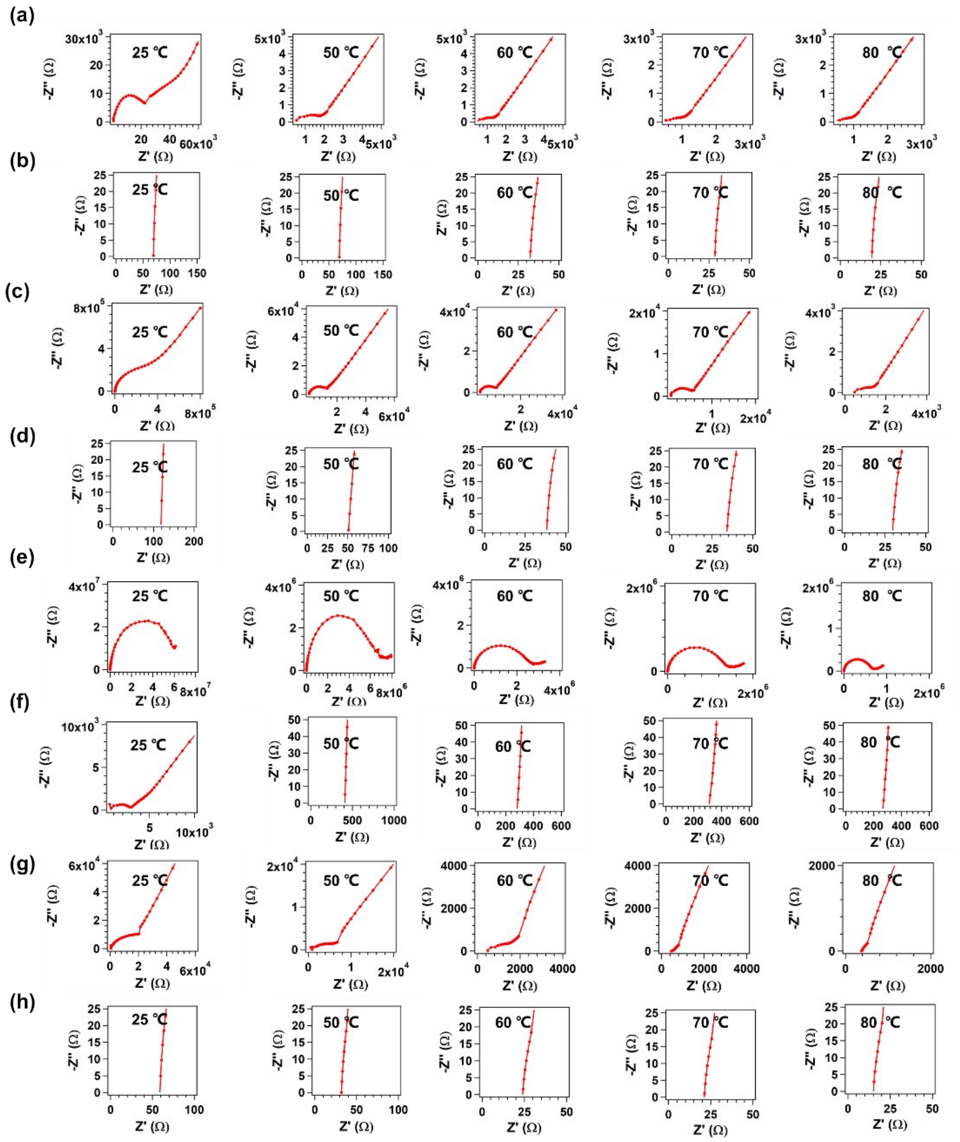


**Fig. S9.** Nyquist plots of (a) POP-B, (b) S-POP-B, (c) POP-BP, (d) S-POP-BP, (e) POP-TP, (f) S-POP-TP, (g) POP-TPM, and (h) S-POP-TPM recorded at various temperature and 95% relative humidity.

## Section 11. Time-dependent proton conduction

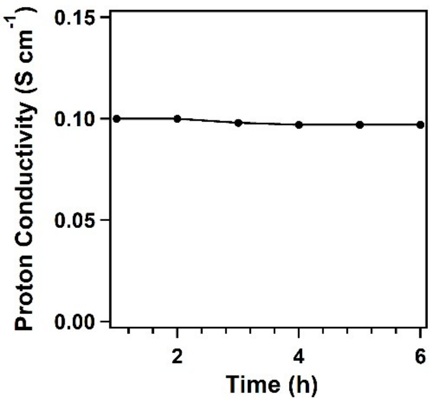


**Fig. S10.** Time dependent proton conduction in S-POP-TPM at 95% RH and 80 °C.