SUPPORTING INFORMATION

Hierarchically Structured Conducting Polymer Hydrogels with Enhanced Stretchability and Conductivity via Freeze-Casting and Salting-Out with Oxidant Salts

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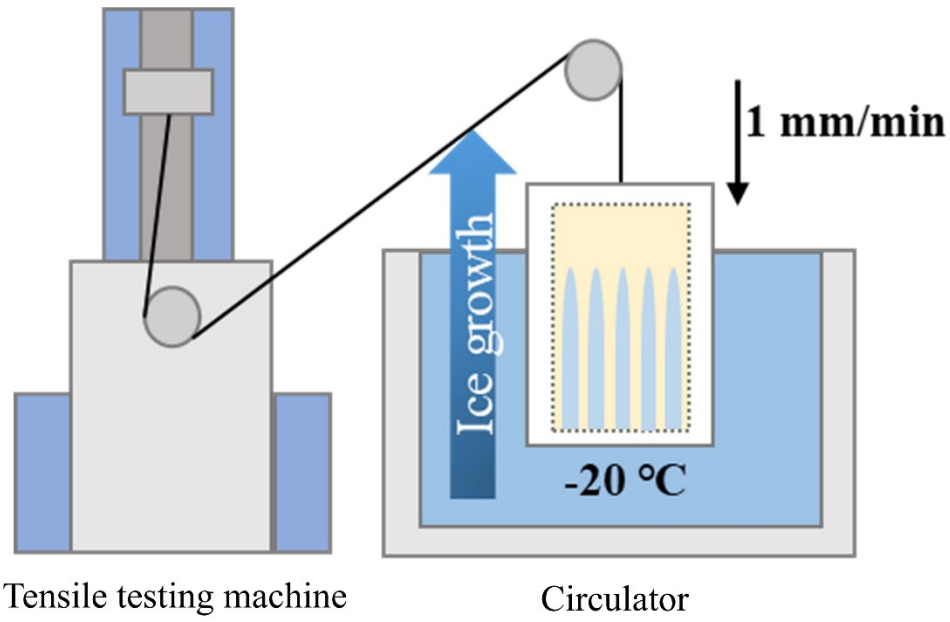

Figure S1. Schematic diagram of directional freezing device.

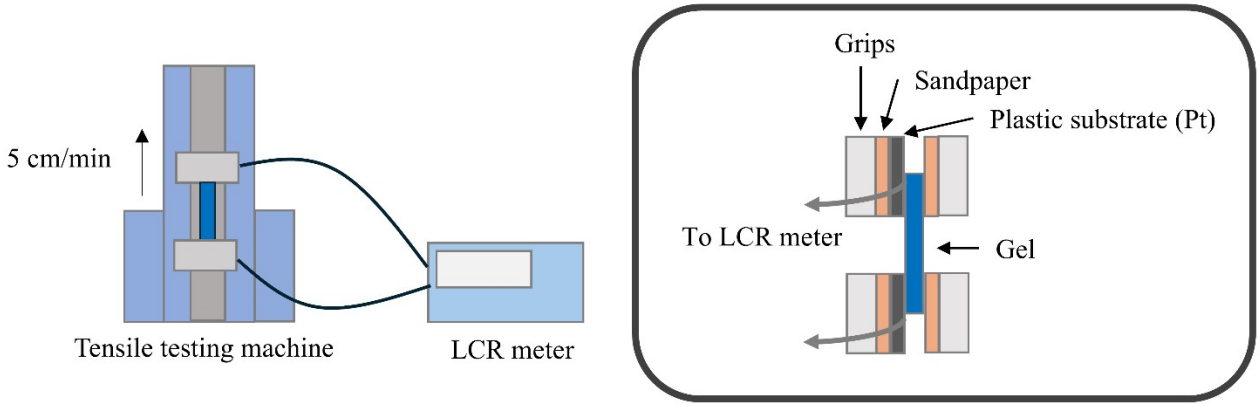

Figure S2. Schematic diagram of impedance measurement during elongation.

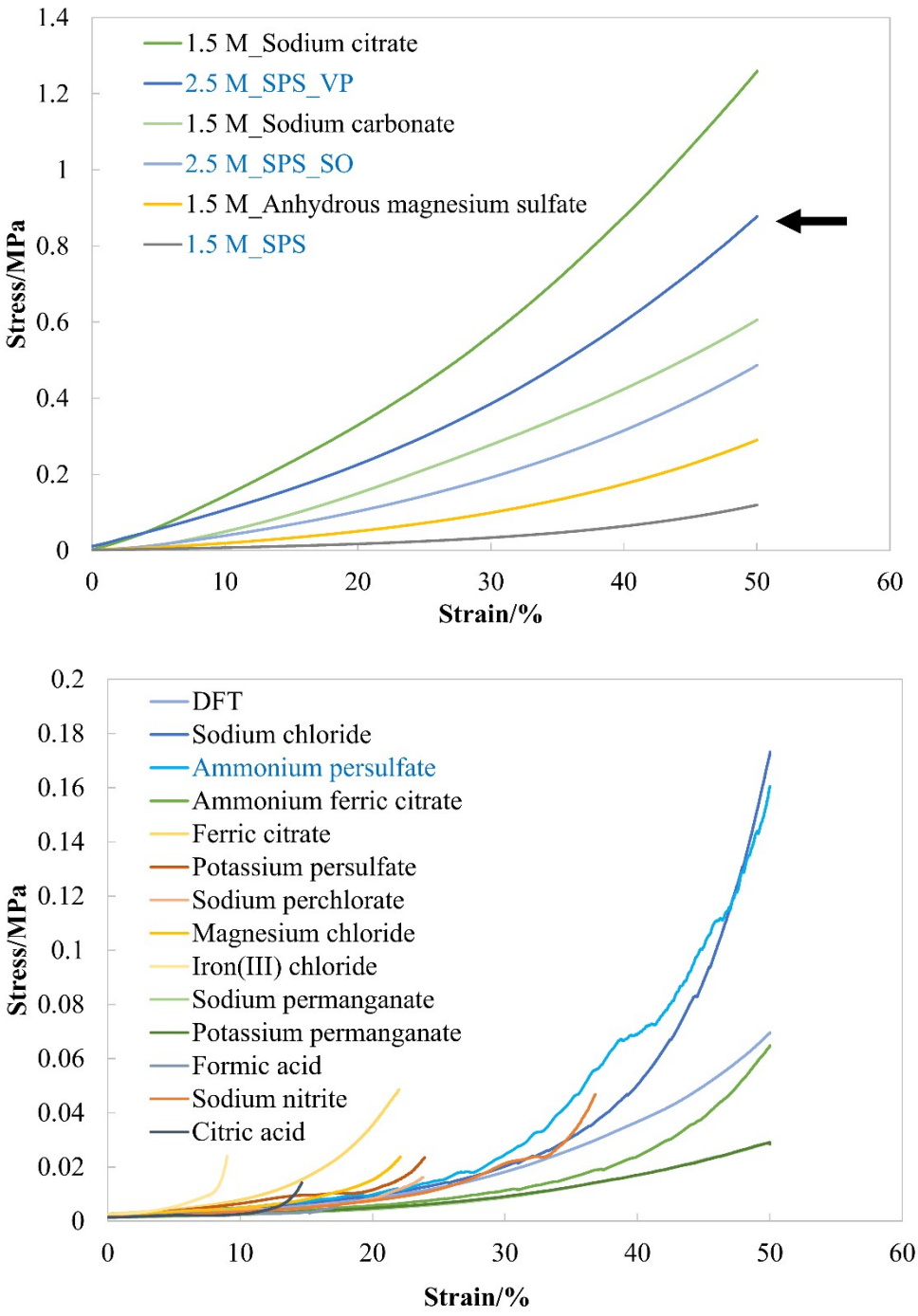

Figure S3. For investigating the capability of salting-out and PEDOT polymerization, the compression test of the gels obtained from salting-out with 20 different reagents was performed. The stress-strain curves are presented (SPS: sodium persulfate, SO: salting-out, VP: vapor-phase polymerization of EDOT, DFT: directional freezing and thawing). The gel made with *p*-toluenesulfonic acid or ferric *p*-toluenesulfonate could not be measured because it could not hold its shape. Reagents for which PEDOT polymerization was confirmed in the gel are highlighted in blue text. The appropriate reagent with both salting-out capability and the ability to polymerize PEDOT is a 2.5 M sodium persulfate aqueous solution.

Figure S4. The frozen body of 10 % PVA aqueous solution after directional freezing: DF gel (left). The 10 % PVA hydrogel after salting-out phase separation with 2.5 M sodium persulfate aqueous solution: DF-SO gel (right).

Table S1. Sample sizes after directional freezing and salting-out.

	DF gel	DF-SO gel
Length/cm	8.61	6.89
Width/cm	5.18	4.06
Thickness/cm	0.300	0.2167
Volume/cm^3	13.4	6.06

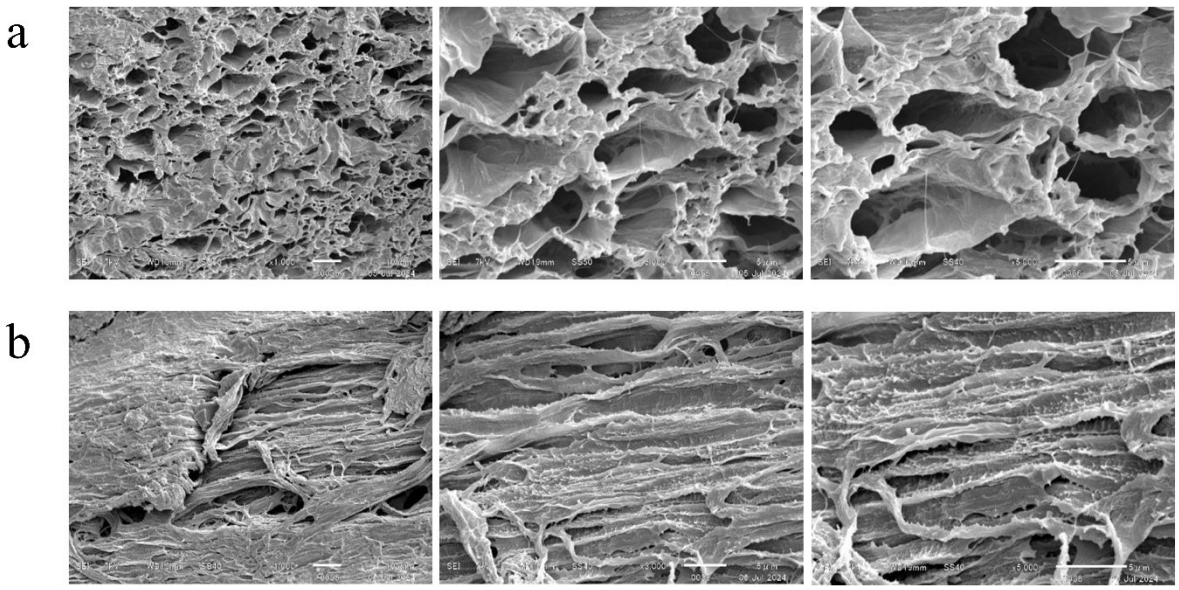

Figure S5. SEM images of hydrogels after salting-out, (a) cut perpendicular (⊥) to the freezing direction and (b) cut parallel (//) to the freezing direction.

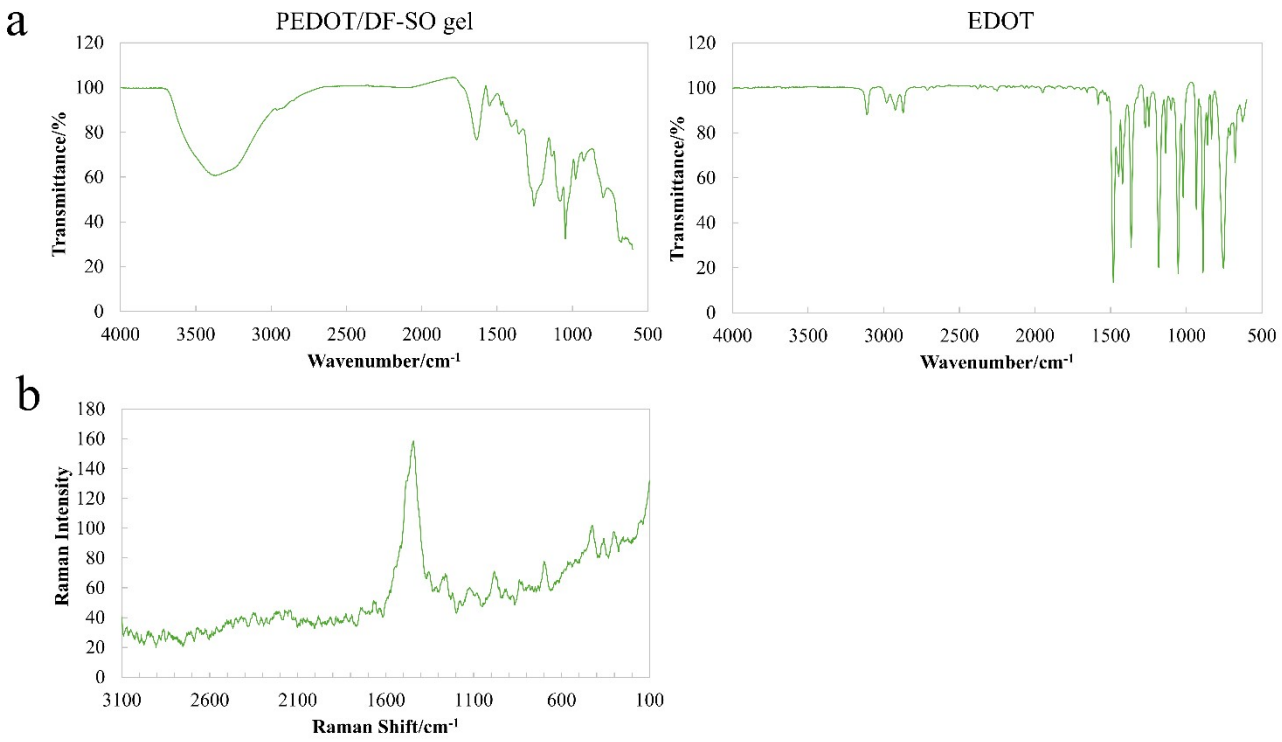

Figure S6. (a) Fourier-transform infrared (IR) spectroscopy with attenuated total reflection (ATR) of the PEDOT/DF-SO gel and EDOT. (b) Raman spectrum of the PEDOT/DF-SO gel.

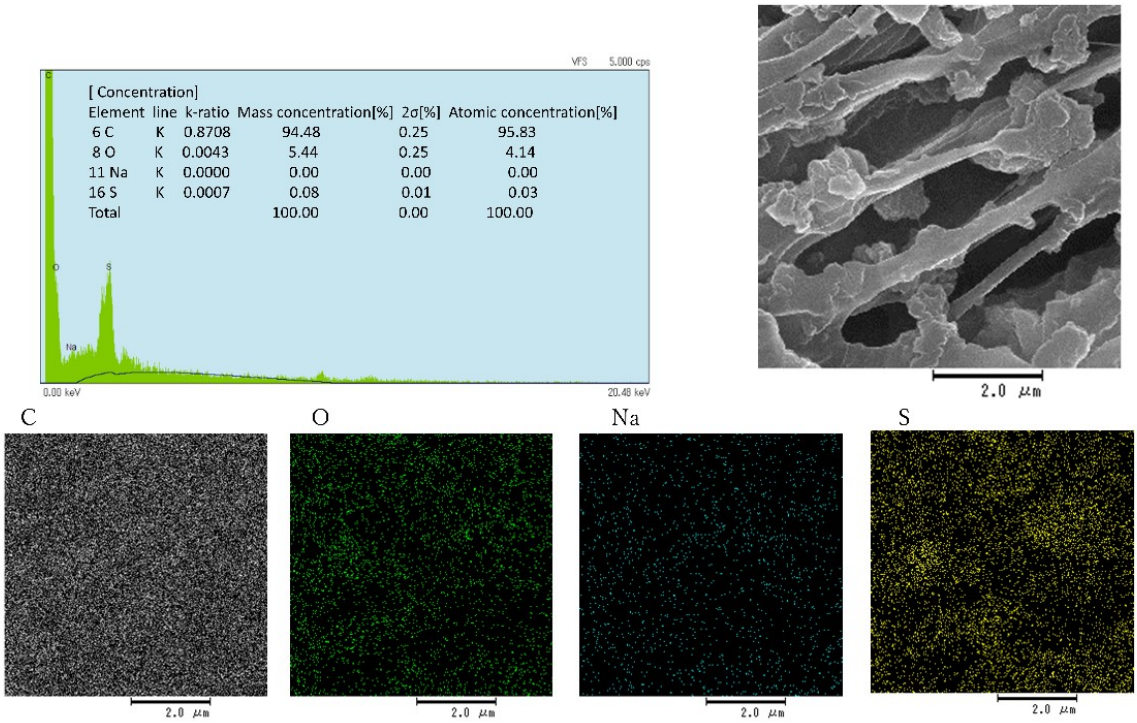

Figure S7. Elemental concentrations in the PEDOT/DF-SO gel were determined by energy-dispersive X-ray spectroscopy (EDX) analysis.

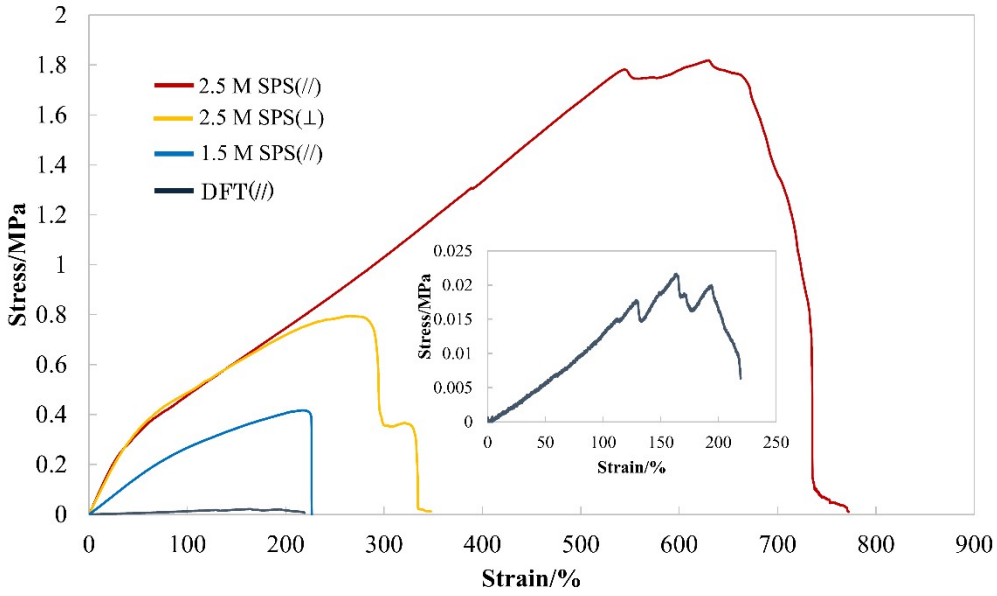

Figure S8. The results of the tensile tests for the DF-SO gels. In DF-SO gel (//), increasing the SPS concentration to the saturation point around 2.5 M improved the fracture strain of the resulting hydrogel (from 378 ± 137 % at 1.5 M to 855 ± 96 % at 2.5 M).

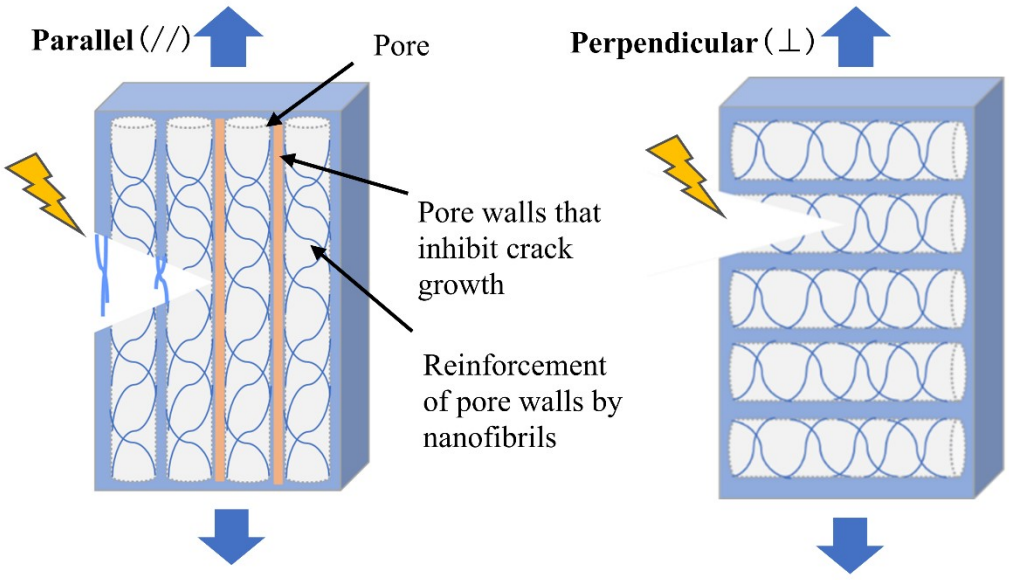

Figure S9. A schematic representation of the hierarchical structure of the PEDOT/DF-SO gel under elongation. When the hydrogel is stretched parallel (//) to the freezing direction, it resiliently withstands even when cracks occur. When the hydrogel is stretched perpendicular (⊥) to the freezing direction, the fracture propagates along the pore walls.

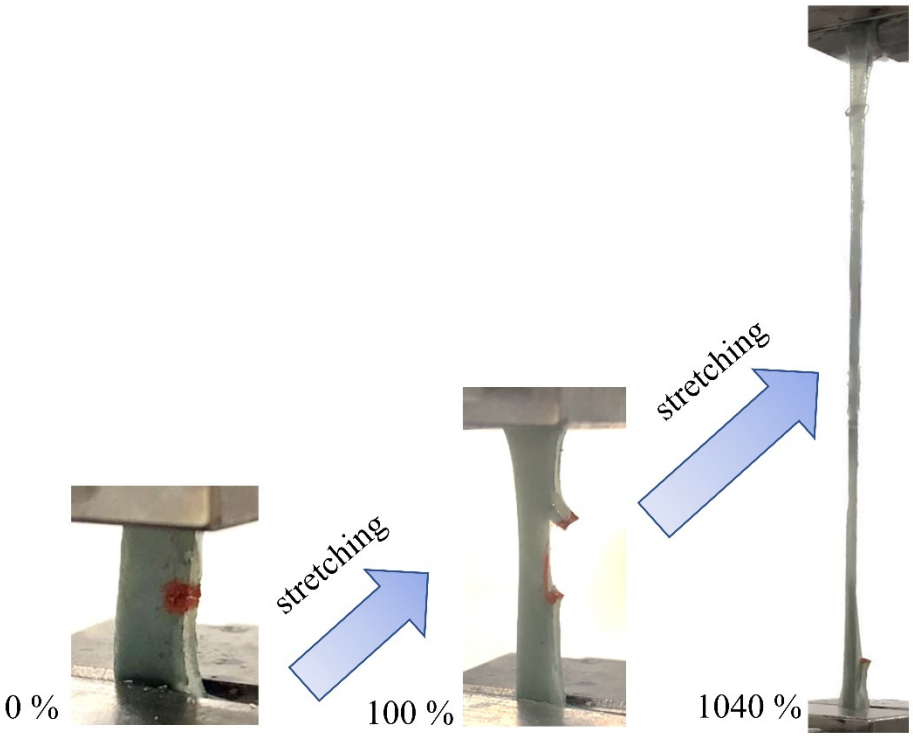

Figure S10. Photographic images during the tensile test with a 1 mm notch inserted.

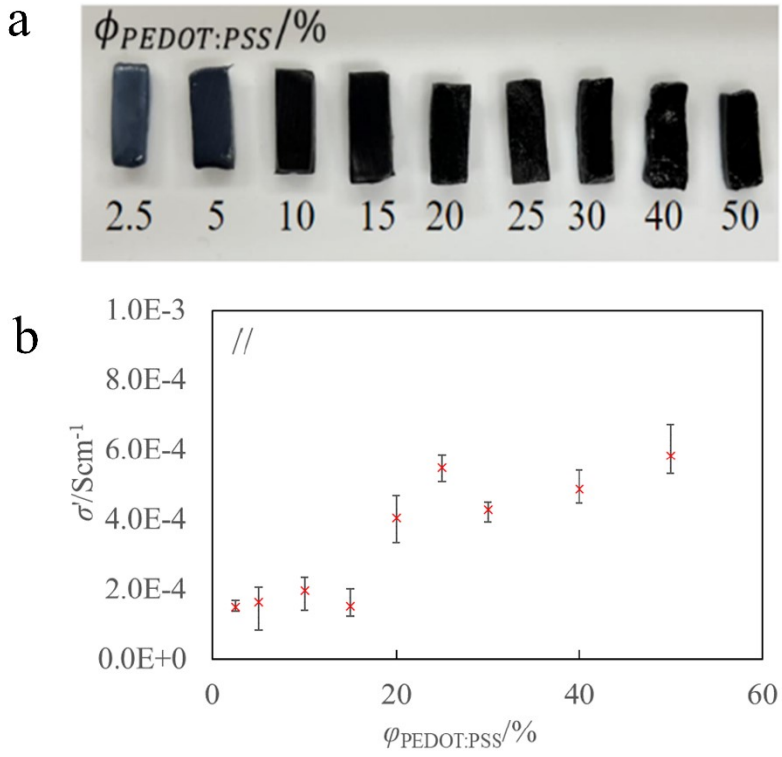

Figure S11. A hydrogel was prepared by mixing Clevios™ PH 1000 (a PEDOT:PSS aqueous dispersion) with a PVA aqueous solution at various ratios, followed by directional freezing, salting-out in a 1.5 M trisodium citrate aqueous solution, and deionization with distilled water. (a) The photographic image of the hydrogels with changing PH 1000 content. In the content exceeded 50 %, gelation did not occur. (b) PH 1000 content dependence of conductivity measured by the four-point probe method with the Loresta-GP, manufactured by Mitsubishi Chemical Analytech.

Table S2. Conductivity of DF-SO gel and PEDOT/DF-SO gel measured by LCR meter.

	Conductivity/S cm^{-1}
DF-SO gel (ion)	$(1.7 \pm 0.49) \times 10^{-2}$
PEDOT/DF-SO gel (ion＋electron)	$(2.6 \pm 0.55) \times 10^{-2}$

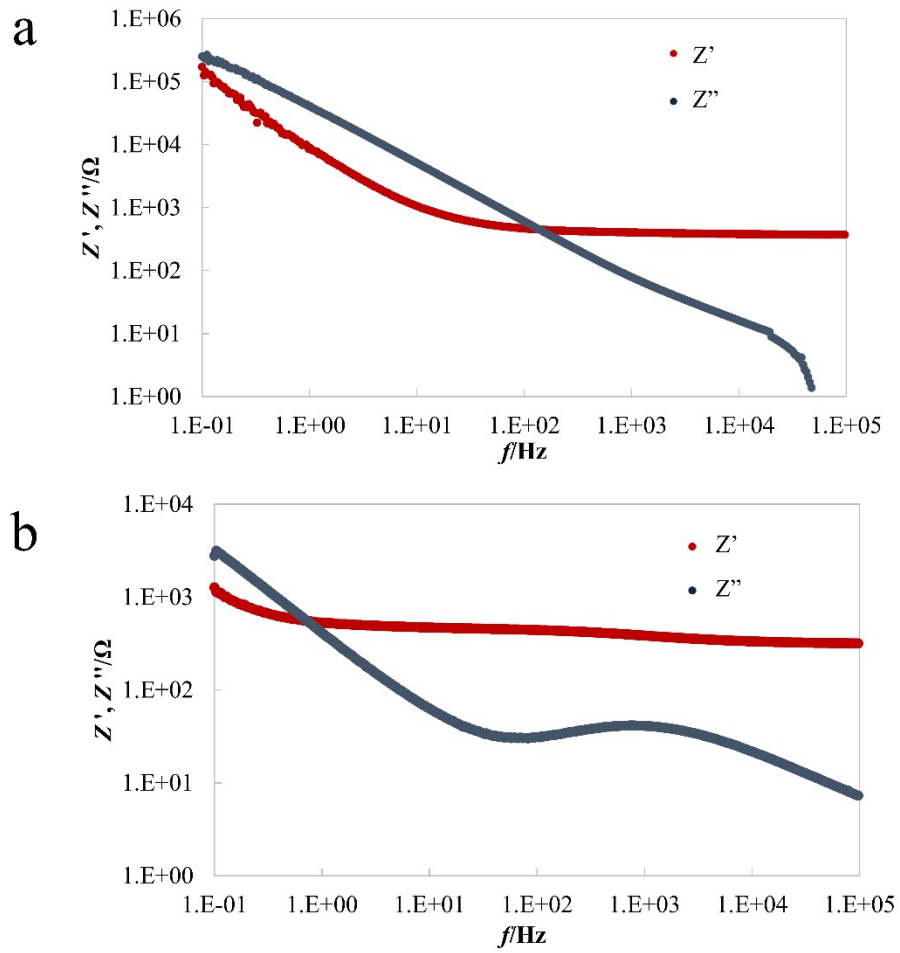

Figure S12. AC impedance spectra of (a) DF-SO gel and (b) PEDOT/DF-SO gel (*f*: frequency, *Z′*: real part, *Z″*: imaginary part).

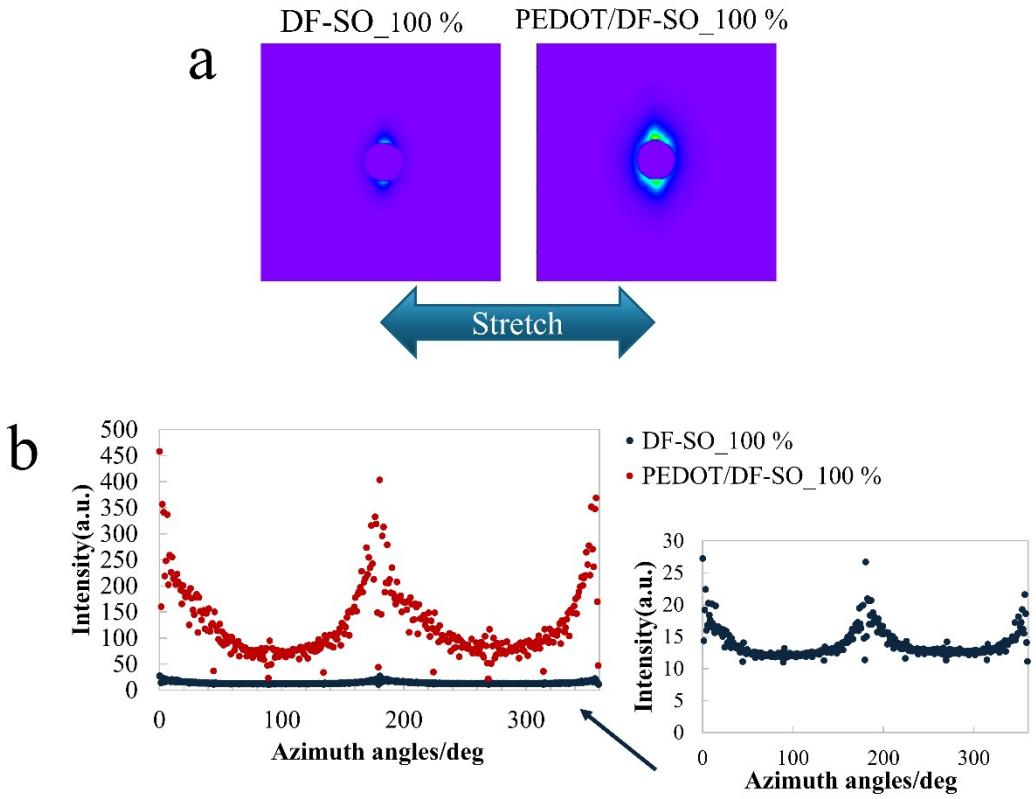

Figure S13. The SAXS results for DF-SO gel and PEDOT/DF-SO gel at 100 % elongation. (a) 2D scattering profiles and (b) azimuth distribution curve.

Video S1.

The video shows the PEDOT/DF-SO gel (//) during the tensile test corresponding to **Figure 3b**. The pulling rate was 5 cm min^{-1}. The playback speed of the video is 16 times faster than the normal rate.

Video S2.

The video shows the LED test when the PEDOT/DF-SO gel was gradually stretched using a tensile-testing machine corresponding to **Figure 5e**. The pulling rate was 5 cm min^{-1}. The playback speed of the video is 5 times faster than the normal rate.

Video S3.

The video shows the strain-sensor test of the PEDOT/DF-SO gel corresponding to **Figure 5f**. For this test, the PEDOT/DF-SO gel was directly clamped with alligator clips connected to an oscilloscope, and the time-dependent voltage of the PEDOT/DF-SO gel was monitored.