Supporting information

Anisotropic Assembly of a Side Chain Liquid Crystal Polymer Containing Sulfoalkoxy Groups for Anhydrous Proton Conduction

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Materials

All commercially-available starting materials, reagents and solvents were used as supplied and were obtained from TCI, Acros and Chengdu Changzheng. All reactions were carried out using a dry nitrogen atmosphere. The ^{1}H nuclear magnetic resonance (NMR) spectra were measured by using a Bruker AV II-400 spectrometer. The Fourier transform infrared (FT-IR) spectra were obtained with the use of a NEXUS 670 FTIR spectrometer. Differential scanning calorimetry (DSC) measurements were performed by a TA modulated Netzsch DSC 204 F1. Thermogravimetric analyses (TGA) were carried out by a TA instrument Netzsch TGA 209C. The scanning of DSC and TGA were both with a rate of 10^oC min^{-1} under nitrogen or air. Cross-polarizing optical microscopies of thin samples, sandwiched between two glass slides, were observed using a Weitu XPL-30TF polarizing optical microscope (POM) equipped with a WT-3000 hot-stage. The molecular weights of the polymers were determined on a gel permeation chromatography (GPC) systems with Tosoh HLC-8320 high-speed liquid chromatograph system using THF as an eluent at 40 ℃ at a flow rate of 0.6 mL min^{-1} with two TSK gel Super HM-H column (6 × 150 mm). Elemental analyses were done by using a Euro EA3000 CHNS/O Elemental Analyzer. A JEOL JSM-6510LV Scanning Electron Microscope with 15kV electron source was used to investigate the film structure. Electrochemical Impedance Spectroscopy (EIS) were recorded on electrochemical workstation consisted of an EG&G Princeton Applied Research (PAR) potentiostat/galvanostat model 273A and PAR lock-in-amplifier model 5210 connected to a PC running electrochemical impedance software. X-Ray diffraction (XRD) analyses were conducted on a Bruker AXS D8 Discovery diffractometer equipped with a Hi-Star 2D detector, using Cu-Kα radiation filtered by cross-coupled Göbel mirrors at 40 kV and 40 mA. Sample's temperature was controlled by an Anton Parr hot-stage.

Synthesis

The synthetic procedure is presented in Scheme 1. Compound **1** and **2** were prepared according to the procedure described previously [1-2]. The ^{1}H and ^{13}C NMR spectra of this compound were found to be in accordance with the literature.


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Synthesis of compound 3

Triethylamine (1.5ml, 10.35mmol) was added into a light-resistant flask containing **2** (2.4g, 6.9mmol) in dichloromethane (20ml). The solution was stirred at room temperature for 20min. **1** (excess) dissolved in dichloromethane (5ml) was added into the solution by dropwise in an ice bath. The mixture was stirred at room temperature for 5h. After the reaction, the mixture was concentrated *in vacuo*. The residue was crystallized from methanol for twice, and then purified by flash column chromatography (silica) using dichloromethane as an eluent. A white solid (3.22g) was obtained in 75% yield. Phase transition temperature: C 102 S_A 155 N 178 I (C stands for crystal phase, S_A stands for smetic A phase, N stands for nematic phase and I stands for isotropic phase). ^{1}H NMR (400 MHz CDC1$_3$) 8.15(d, 2H, Ph), 7.59(d, 2H, Ar), 7.57(d, 2H, Ar), 7.23(d, 2H, Ar), 6.98(d, 2H, Ar), 6.91(d, 2H, Ph), 6.40(d, 1H, C$\underline{H}_2$=CHMe), 6.13(m, 1H, CH$_2$=C$\underline{H}$Me), 5.82(d, 1H, C$\underline{H}_2$=CHMe), 4.21(m, 2H, MeOC$\underline{H}_2$), 4.01(m, 4H, MeOC$\underline{H}_2$), 3.44(m, 2H, C$\underline{H}_2$Br), 1.75~1.24(m, 16H, C$\underline{H}_2$C$\underline{H}_2$). FT-IR(KBr)υ: 2932, 2861, 1725, 1623, 1606, 1510, 1498, 1470, 1392, 1288, 1213, 1165, 1070, 997, 882, 841 cm^{-1}. ^{13}C NMR (67.5MHz, CDCl$_3$) 25.3, 25.6, 25.7, 27.9, 28.6, 29.0, 29.1, 32.7, 33.8, 64.5, 67.8, 68.0, 114.3, 114.8, 122.0, 127.4, 127.7, 128.1, 128.6, 130.6, 132.3, 132.9, 138.5, 150.0, 154.6, 158.6, 166.4. Elemental analysis calcd (%) for C$_{34}$H$_{39}$O$_6$Br requires C, 65.49; H, 6.30; Found: C, 65.51; H, 6.31.

Synthesis of P1

P1 was synthesized with the procedure described for brominated polyacrylates[3]. Polymerization of the monomer **3** (2g, 3.22mmol) was carried out in dioxane (10ml) with
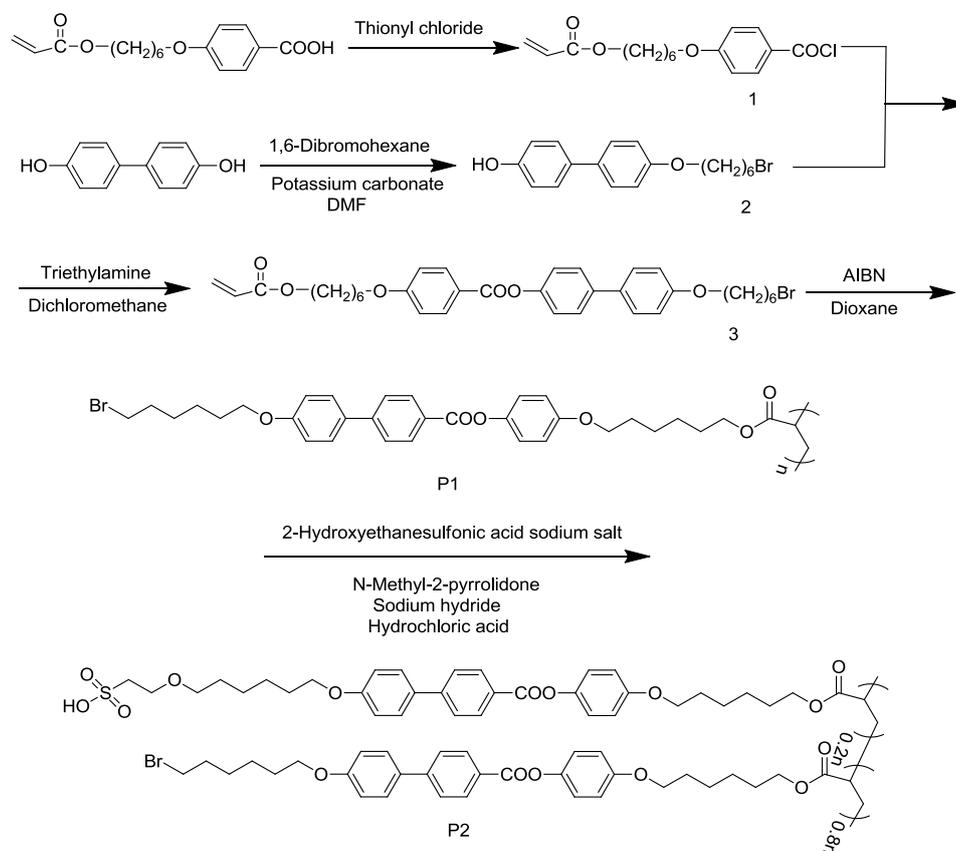
S-Scheme 1 Synthetic pathway of the sulfonic side-chain liquid crystal polymer.
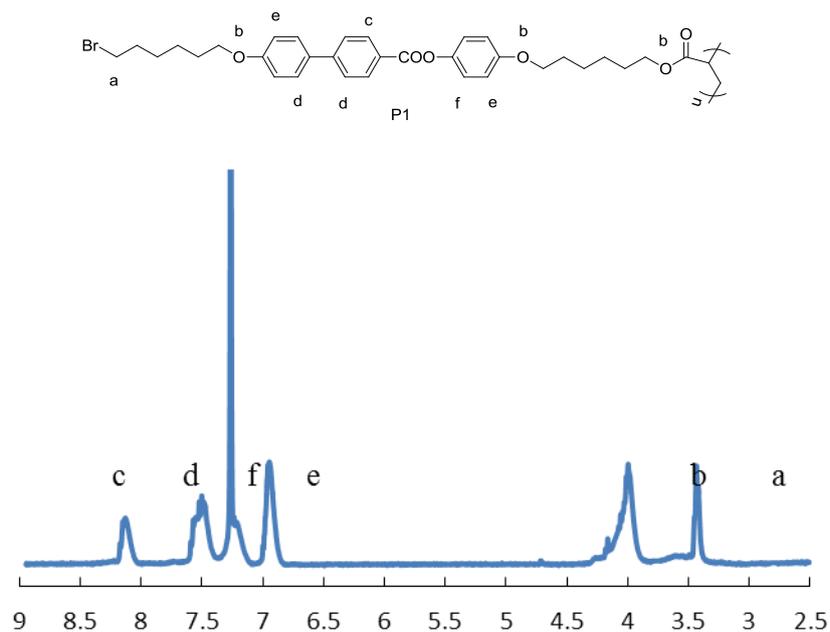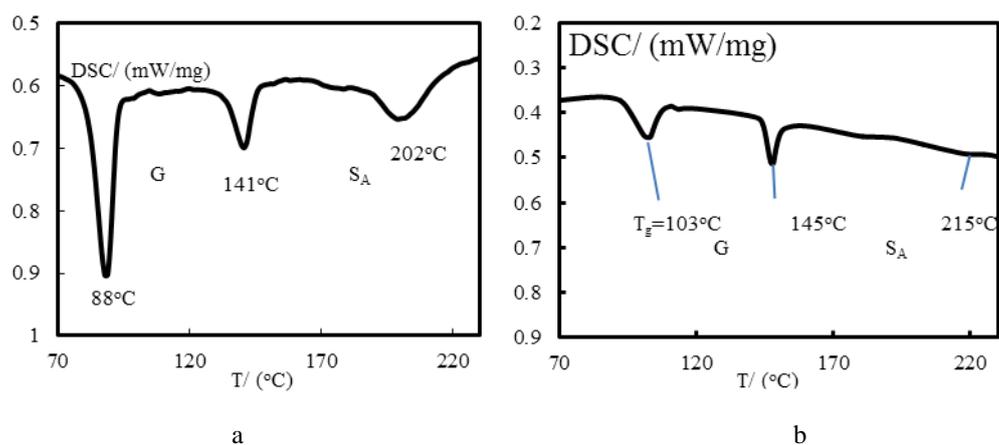
S-Figure 1 ^{1}H NMR spectrum of **P1** in CDCl$_3$.

azobisisobutyronitrile (AINB, 5mol%) at 70°C for 8h. After cooling, the polymer solution was poured into ethyl acetate. The precipitate was washed with ethyl acetate and methanol. A white solid (1.60g) was obtained in 80% yield. Phase transition temperature: G 141 S$_A$ 202 I (G stands for glassy state). ^{1}H NMR (400 MHz CDCl$_3$) 8.15(2H, Ph), 7.55(4H, Ar), 7.23(2H, Ar), 6.94(4H, Ar/Ph), 4.05(6H, MeOC$\underline{H}_2$), 3.44(2H, C$\underline{H}_2$Br), 1.75~1.24(m, 18H, C$\underline{H}_2$C$\underline{H}_2$); FT-IR(KBr)υ：2931, 2856, 1732, 1605, 1508, 1498, 1471, 1393, 1288, 1213, 1165, 1070, 997, 883, 841 cm^{-1}. M$_W$=1.0 ×10^4 g/mol, M$_N$=5.5×10^3 g/mol, M$_W$/M$_N$ =1.82.

Synthesis of P2

2-Hydroxyethanesulfonic acid sodium salt (0.28g, 1.93mmol) and sodium hydride (0.05g, 2.08mmol) were added into a flask containing N-methyl-2-pyrrolidone (5ml) in an ice bath. The solution was stirred for 30min. Then **P1** (1g, 1.61mmol) was added into the solution. The mixture was stirred at room temperature for 24h. After that, hydrochloric acid (1mol/L) was added into the solution by dropwise until PH<7. The solution was stirred for about 1h and then poured into methanol. The precipitate was washed with water, methanol and ethyl acetate in turns. A white solid (0.97g) was obtained. Phase transition temperature: G 145 S$_A$ 215 I. ^{1}H NMR (400 MHz CDCl$_3$) 8.13(2H, Ph), 7.49(4H, Ar), 7.23(2H, Ar), 6.94(4H, Ar/Ph), 4.05(6.6H, MeOC$\underline{H}_2$), 3.40(1.7H, C$\underline{H}_2$Br), 2.85(0.3H, C$\underline{H}_2$SO$_3$H), 1.75~1.24(m, 18H, C$\underline{H}_2$C$\underline{H}_2$); FT-IR(KBr)υ：2931, 2856, 1732, 1605, 1510, 1498, 1471, 1393, 1288, 1213, 1165, 1070, 1032(SO$_3$H), 997, 885, 843 cm^{-1}. M$_W$=1.0×10^4 g/mol, M$_N$=6.5×10^3 g/mol, M$_W$/M$_N$ =1.54.

A new peak at 2.85 ppm appeared in the ^{1}H NMR spectrum of **P2,** indicting presence of alkyl protons linked to the sulfur atom[8-9] in the side chains. The degree of functionalization was determined from ^{1}H NMR analysis by comparing the signal intensity of the alkyl protons adjacent to the sulfur atom at 2.85 ppm with that of the alkyl protons adjacent to the bromine atom at 3.4

ppm. The determined degree of functionalization was about 20%.

S-Figure 2 ^{1}H NMR spectrum of **P2** in CDCl$_3$. A new peak appeared at 2.85 ppm marked by (*).

IR spectra of **P1** and **P2** were shown in S-Fig 3. In the IR spectrum of **P2**, a new band with a peak at 1032cm^{-1} appeared. It was attributed to the symmetric stretching of O=S=O[4-7], indicating the successful post polymerization etherification.

S-Figure 3 IR spectra of **P1** and **P2**.

S-Figure 4 DSC measurements of **P1** (a) and **P2** (b) at heating rate of $10^{\circ}C$ min^{-1} under a nitrogen atmosphere.
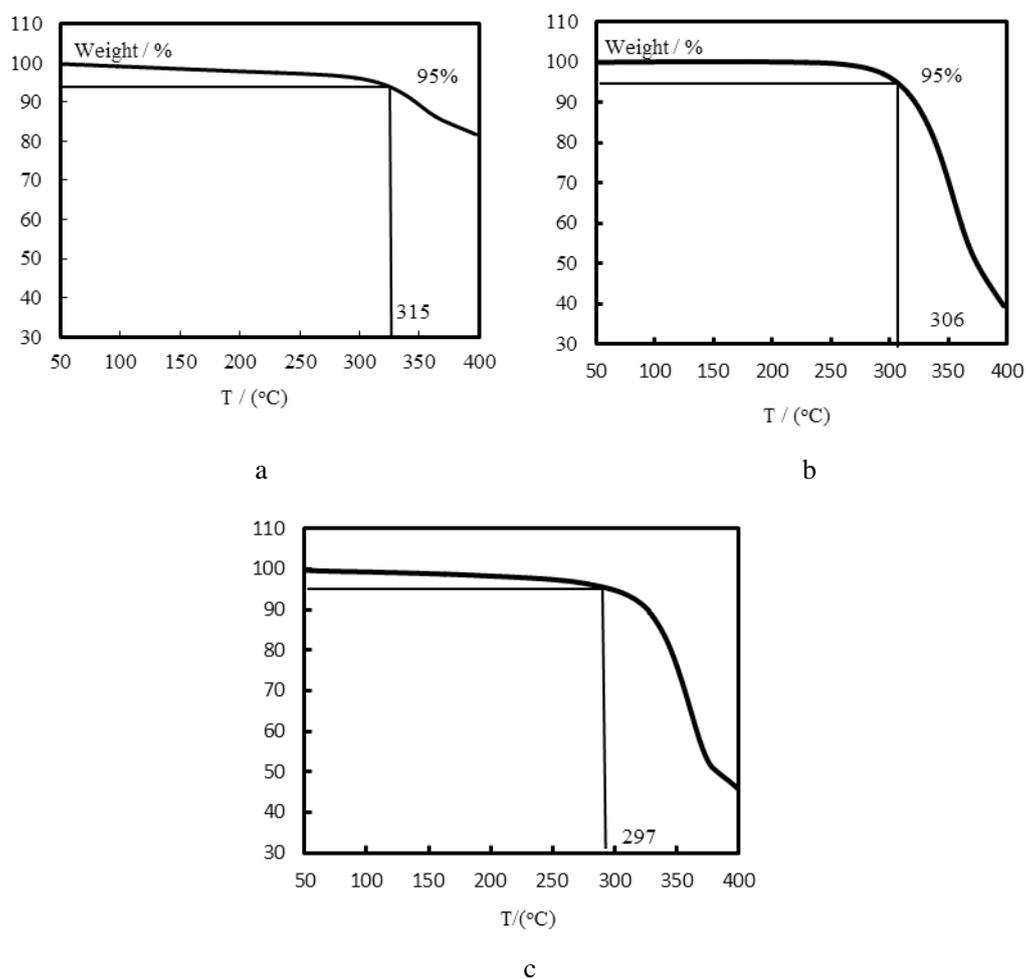
S-Figure 5 TGA of (a) **P1** and (b) **P2** at heating rate of 10 $^{\circ}C$ min^{-1} under a nitrogen atmosphere and (c) **P2** at

heating rate of 10 $^{\circ}C$ min^{-1} under an air atmosphere.

a   b
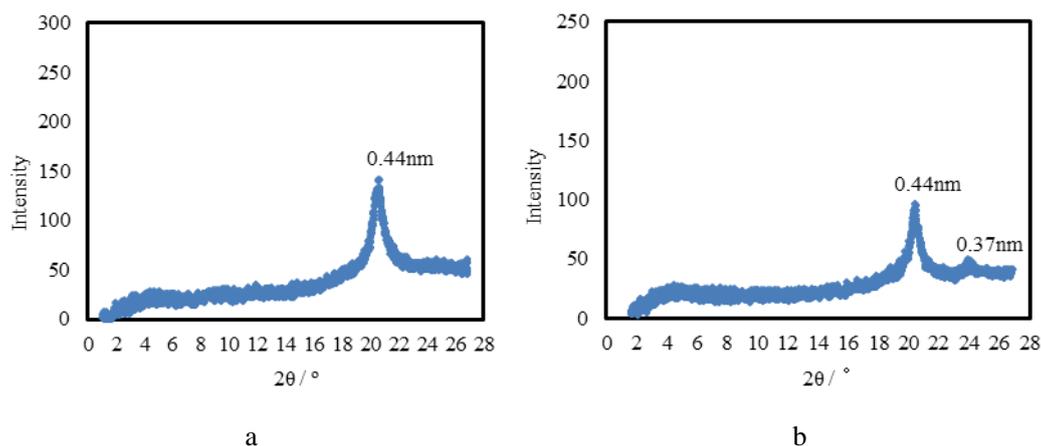
S-Figure 6 X-ray diffraction patterns for (a) **P1** at 150°C and (b) **P2** at 155°C. The XRD patterns for **P1** and **P2** recorded at room temperature after cooling the samples from the S_A phases are identical to those recorded at temperatures within the S_A phases.

Oxidative Stability of P2

The chemical oxidative stability of **P2** was evaluated in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80℃. Residue after treatment with hot Fenton's reagent for 1hr and 10 hr were 95wt% and 88wt%, respectively.

Measurements of Proton Conductivities

Proton conductivities were measured by the electrochemical impedance spectroscopy (EIS) technique previously reported for ion conduction measurements[10] (shown in S-Figure 7. frequency range: 0.1Hz~100KHz，applied voltage: 10mV). The anisotropic samples were prepared as follows: the **P2** sample was melted at 220 °C on a glass slide and then annealed at the same temperature for 10 min. The isotropic liquid of **P2** was cooled to 155 °C and held for 10 min. Afterwards, the sample film was sheared using another glass slide having the same temperature and then quenched by air.

Proton conductivities (σ) can be obtained from the following equation:

$$\sigma = d/(R_b A)$$

where R_b, d and A are the bulk resistance, the sample thickness, and the interface area of the ITO glass and **P2**, respectively. In Our work, $d=0.014cm$, and $A =0.08cm^2$. Proton conductivities were practically calculated to be the product of $1/R_b$ (Ω^{-1}) times cell constants (cm^{-1}), which were calibrated with KCl aqueous solution (0.1 $mol\ L^{-1}$) as a standard conductive solution. The impedance data (Z) were modeled as a two RC circuits connecting in series (R: resistance, C: capacitance) and were divided into imaginary (Z") and real (Z') [11]. Representative examples of impedance spectrum exhibited in the cell A at 180 °C was shown in S-Figure 8 (X-axis: Z', Y-axis:-Z"). The cell C did not exhibit the RC circuits in the liquid crystal phase, which may mean protons cannot be transported along the direction perpendicular to the macroscopically orientated layers. The bulk resistance R_b was obtained from the intercept of the left semi-circle on the Z' axis. All the data were collected over a temperature range from S_A phase to isotropic state to investigate the proton conductiveperformance of the materials (shown in Fig. 2). We also measured the proton conductive ability of polymer **P1** as a control and **P1** did not exhibit the RC circuits.
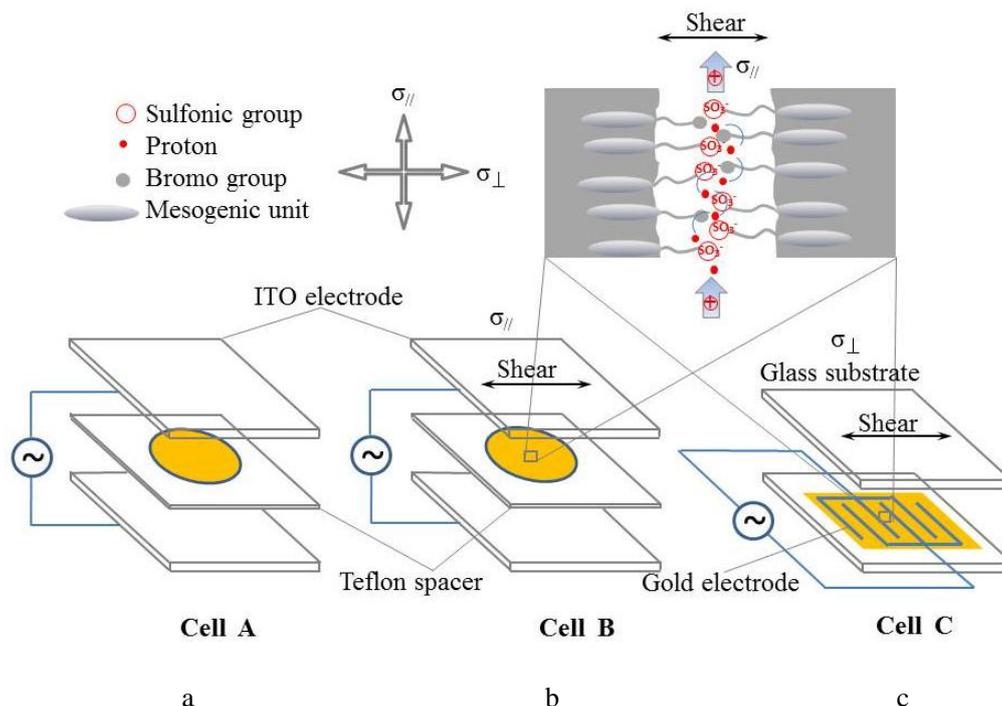
S-Figure 7 Schematic illustration of conduction measurement setups for **P2**: (a) random oriented state, (b) shearing direction perpendicular to the electrode pair and (c) shearing direction parallel to the electrode pair.
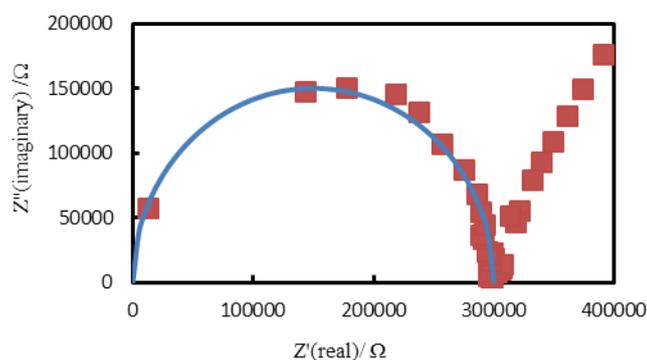

S-Figure 8 Impedance spectrum for **P2** in cell A at 180 °C.

The activation energy for the proton conduction of **P2** in the S_A phase was estimated from the Arrhenius plots of the conductivities.

$$ln\sigma = lnA - E_a/RT$$

where σ, A, R and T are the proton conductivity, pre-exponential factor, molar gas constant and temperature, respectively.

The slopes of in the plots of the cell A and B are almost the same and the activation energies are estimated as 100 *KJ/mol*.

a

b
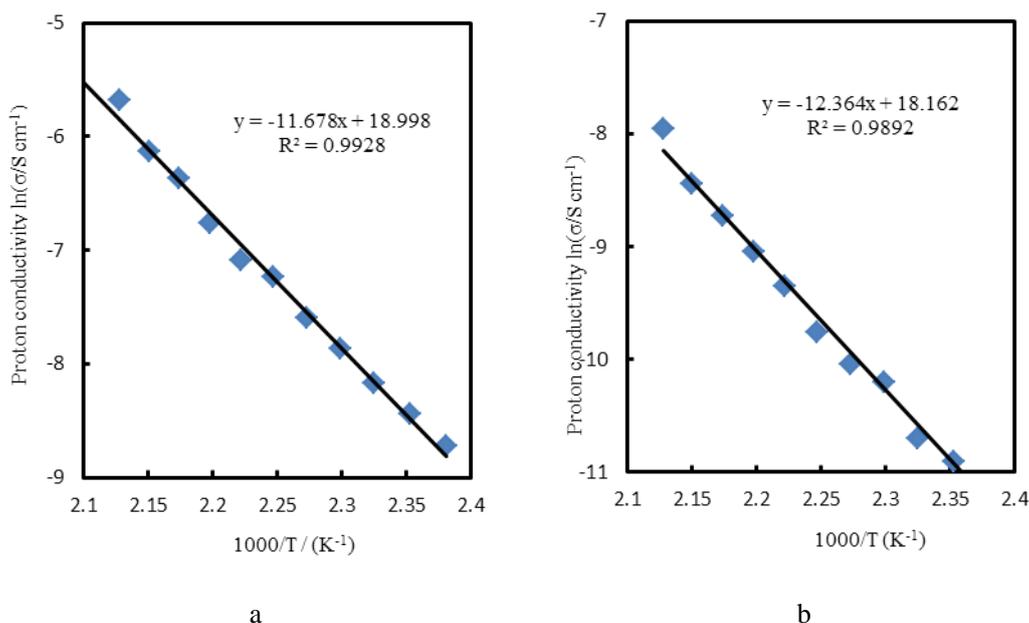
S-Figure 9 Arrhenius fitting of anhydrous proton conductivities for (a) sheared and (b) unaligned **P2** in the S_A phase.

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