Supporting Information

Do Acid–Base Interactions Really Improve the Ion Conduction in a Proton Exchange Membrane? — A Study on the Effect of Basic Groups

Yuqian Sui,[#] Yexin Du,[#] Huayuan Hu, Jieshu Qian[*], and Xuan Zhang[*]

(#Yuqian Sui and Yexin Du contribute equally to this work)

Key Laboratory of New Membrane Materials, Ministry of Industry and Information Technology; School of Environmental and Biological Engineering, Nanjing University of Science & Technology, Nanjing 210094, China

Corresponding Author:

J. Qian: qianjieshu@foxmail.com;

X. Zhang: xuanzhang@njust.edu.cn.

Characterization

^1H NMR spectra were recorded on a Bruker AVANCE III spectrometer (500 MHz) using DMSO-d_6 as the solvent. Fourier transform infrared (FTIR) spectra were obtained from a Nicolet IS-10 Fourier transform spectrophotometer equipped DTGS detector. Thermogravimetric analysis (TGA) was measured on a SDT Q600 in N_2 from 120 to 800 ^oC with a heating rate of 10 ^oC/min. Differential scanning calorimetry (DSC) curves of polymers were recorded in N_2 on DSC-823 (Swiss-Mettler Toledo), and the temperature was set in the range of 30-300 ^oC. Number- and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Waters 1515 HPLC system equipped with polystyrene gel columns eluted with *N*,*N*-dimethylformamide (DMF) containing 0.05 M LiBr at a flow rate of 1.0 mL min^{-1} calibrated by standard polystyrene samples. Mechanical properties were analyzed on a Shimazu AGS-100NX with membrane thin films (length, 40 mm; width, 5 mm) under a stretching rate of 2 mm/s. For transmission electron microscopy (TEM) observations, the membrane samples were immersed in 0.5 M lead acetate aqueous for ion exchange of sulfonic acid groups. Then the membranes were washed with deionized water for several times and dried in vacuum oven for 24 h. The stained membranes were embedded in epoxy resin, sectioned to 70 nm thicknesses with Power-Tome-XL, and placed on copper grids. Images were taken on a Hitachi H-7650 with an accelerating voltage of 80 kV.

Water Uptake (WU) measurements. WU was measured by keeping the membranes in thermo-controlled humid equipment under various relative humidity conditions at 80 °C for 2 h. The samples were then removed from the chamber and quickly weighed. WU was calculated using Eq. (S-1).

$$\mathrm{WU} = (W_1 - W_0)/W_0 \times 100\% \tag{S-1}$$

where W_1 and W_0 refer to weights of the membrane samples at wet and dry condition.

Dimensional Change (DC). The dimensional change was measured by putting the membranes in a thermo-controlled humid equipment for at least 2 h at 80 °C under different relative humidity conditions. The dimensional change in membrane thickness direction (Δt_c) and the plane direction (Δl_c) were calculated using Eqs. (S-2) and (S-3).

$$\Delta t_c = (t - t_s)/t_s \tag{S-2}$$

$$\Delta l_c = (l - l_s)/l_s \tag{S-3}$$

where t_s and l_s refer to the thickness and length of the membranes measured at 30 °C/30% RH, respectively. t and l are the same parameters of the membranes under different RH conditions.

Ion Exchange Capacity (IEC). IEC was measured using the acid–base back-titration method. The acidified membranes were immersed in a 20 wt% sodium chloride solutions for ion exchange of H^+ at 50 °C for 3 days. Sodium hydroxide standard solutions were then used to neutralize the acid solutions by adding phenolphthalein as an indicator. The ion exchange capacity was calculated using Eq. (S-4).

$$\mathrm{IEC} = C_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}}/W_0 \tag{S-4}$$

where C_{NaOH} and V_{NaOH} refer to the concentration and consumed volume of NaOH solution, respectively.

Proton Conductivity (σ). The proton conductivity was estimated by means of an Hioki IM 3533-01 impedance analyzer at a frequency ranging from 1 to 10^6 Hz. The membranes were placed in a two-point probe conductivity cell equipped with two Pt plate electrodes. The cell was then kept in a thermo-controlled humidity equipment at different testing conditions for 1 h before each measurement. σ was calculated using Eq. (S-5).

$$\sigma = d/(t_s w_s R) \tag{S-5}$$

where d is the distance between the two Pt plates, t_s and w_s are the thickness and width of the membrane film, and R is the measured resistance.

Oxidative Stability. The oxidative stability was evaluated by the remaining weight in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C for 1 hour [1,2]. The oxidative stability of the membrane was calculated using Eq. (S-6)

$$\text{Residual Weight Percentage} = W_2/W_0 \times 100\% \tag{S-6}$$

where W_0 and W_2 refer to weights of the membrane samples before and after test.

Evaluation of Fuel Cell Performance. The membrane electrolyte assembly (MEA) was performed according to our previous method.[3,4] Briefly, commercial Pt/C (30.6 mg, 60 wt.%) (Hispec4000, Johnson and Matthey) was firstly soaked in 0.6 mL deionized water under sonication for 10 min. The suspension was then mixed with 257.3 mg Nafion isopropyl alcohol solution (5 wt%). Excess isopropyl alcohol was added to control the total solid content to 1 wt%. After 30 min of further sonication at 5 °C, the well-dispersed catalyst ink was sprayed on the membrane surface as conventional catalyst materials using an electrostatic spraying equipment with a platform heating temperature of 80 °C (SP 201, Kunshan Sunlaite New Energy Co. Ltd.). The active surface area of the MEA was measured as 9.0 cm^2 (3.0 cm × 3.0 cm) and the loading amounts of Pt on each side were 0.5 mg cm^{-2}.

The single-cell performance was investigated using an in-house fuel cell station (HTS-125, Shanghai Hephas Energy Co. Ltd.) under ambient pressure. At medium temperature testing, the cell temperature was set to 80 ^{o}C, and the gas humidifying temperatures were both controlled at 78.5, 71.5, and 52.5 ^{o}C for the anode and cathode, which corresponded 95%, 70% and 30% RH, respectively. During the tests, the H_2 gas and O_2 flow rates were fixed to 200 and 100 mL min^{-1}, respectively, with back pressure at 0.1 MPa.

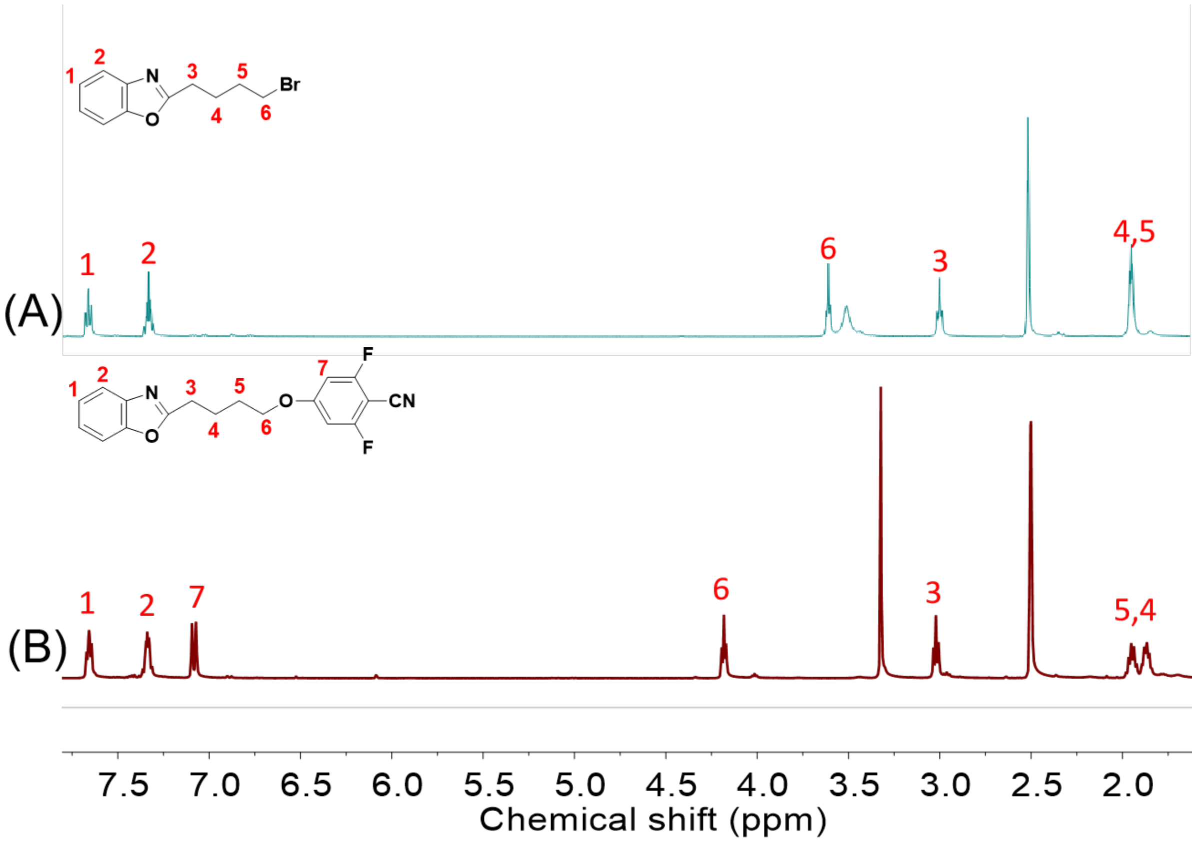

Figure S1. ^{1}H NMR spectra of (A) **BBBO** and (B) **BOBFBN** in DMSO-d_6.

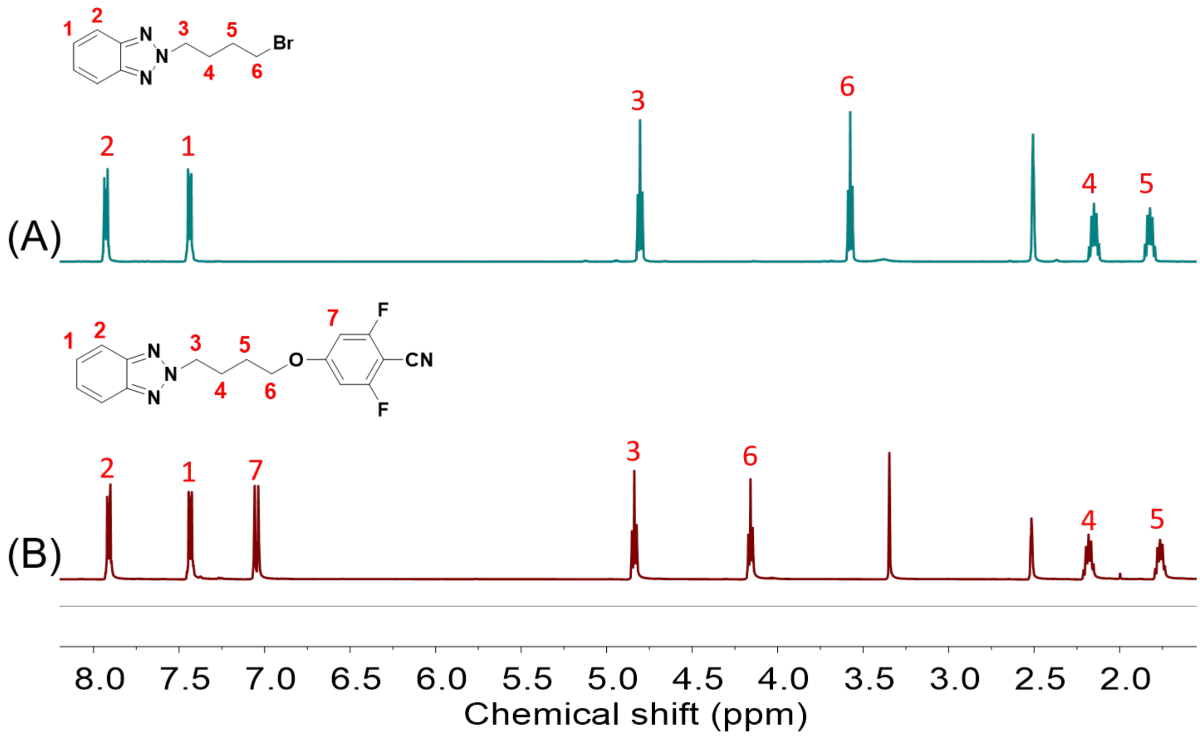

Figure S2. [1]H NMR spectra of (A) **BBBT** and (B) **BTBFBN** in DMSO-d_6.

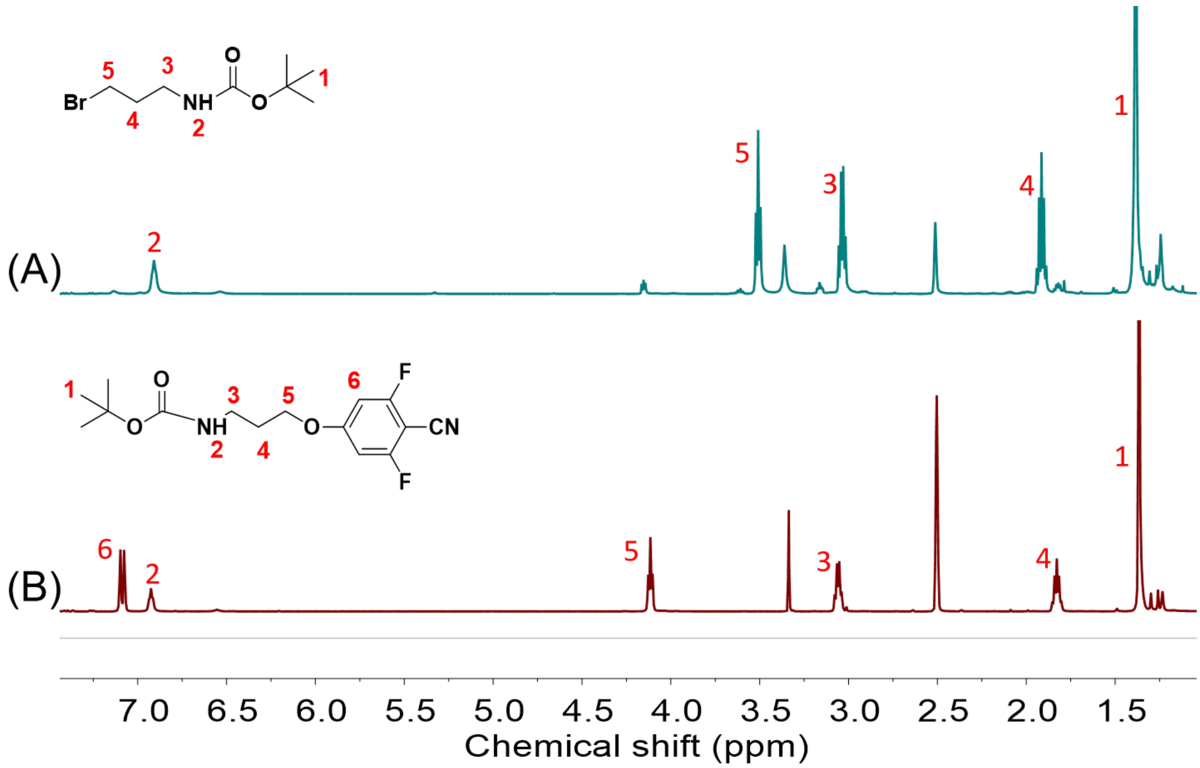

Figure S3. [1]H NMR spectra of (A) *t*-**BBPC** and (B) *t*-**BCFPPC** in DMSO-d_6.

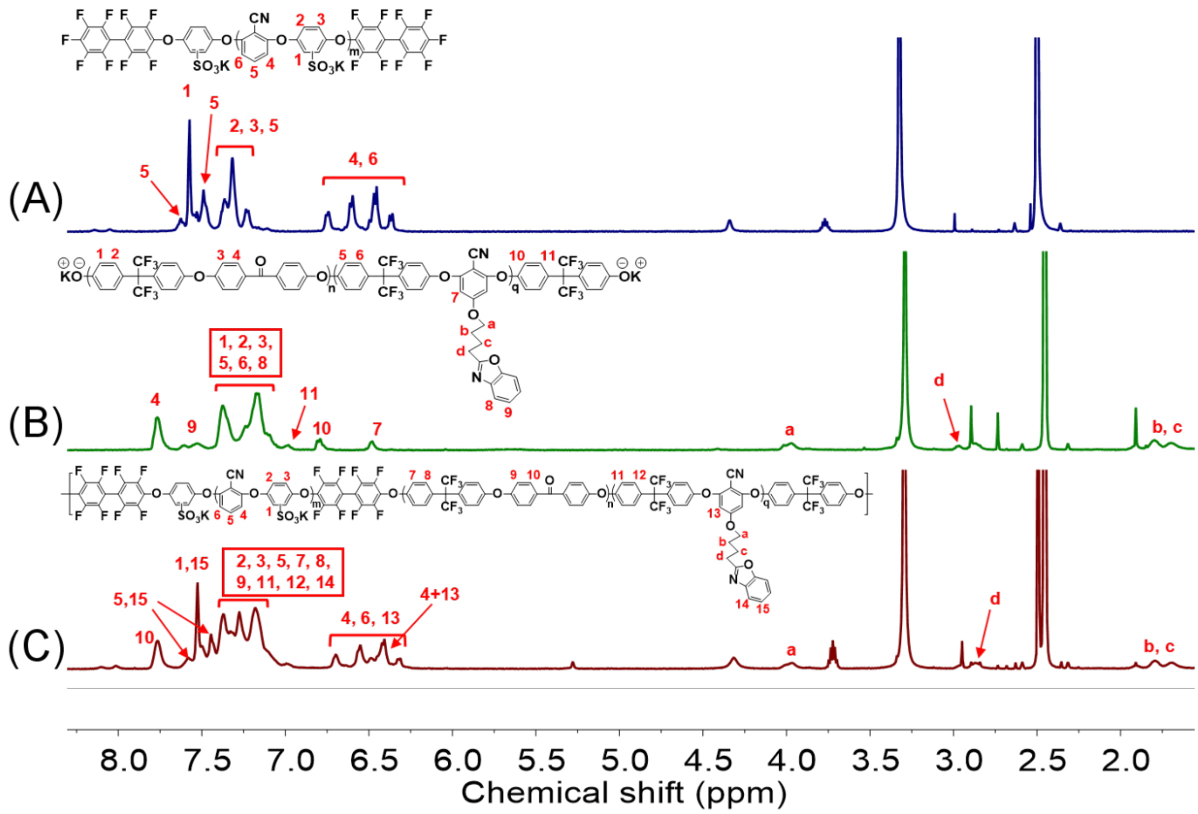

Figure S4. ^{1}H NMR spectra of (A) **O2**, (B) **O3-BOBFBN**, and (C) **P1-BOBFBN** in DMSO-d_6.

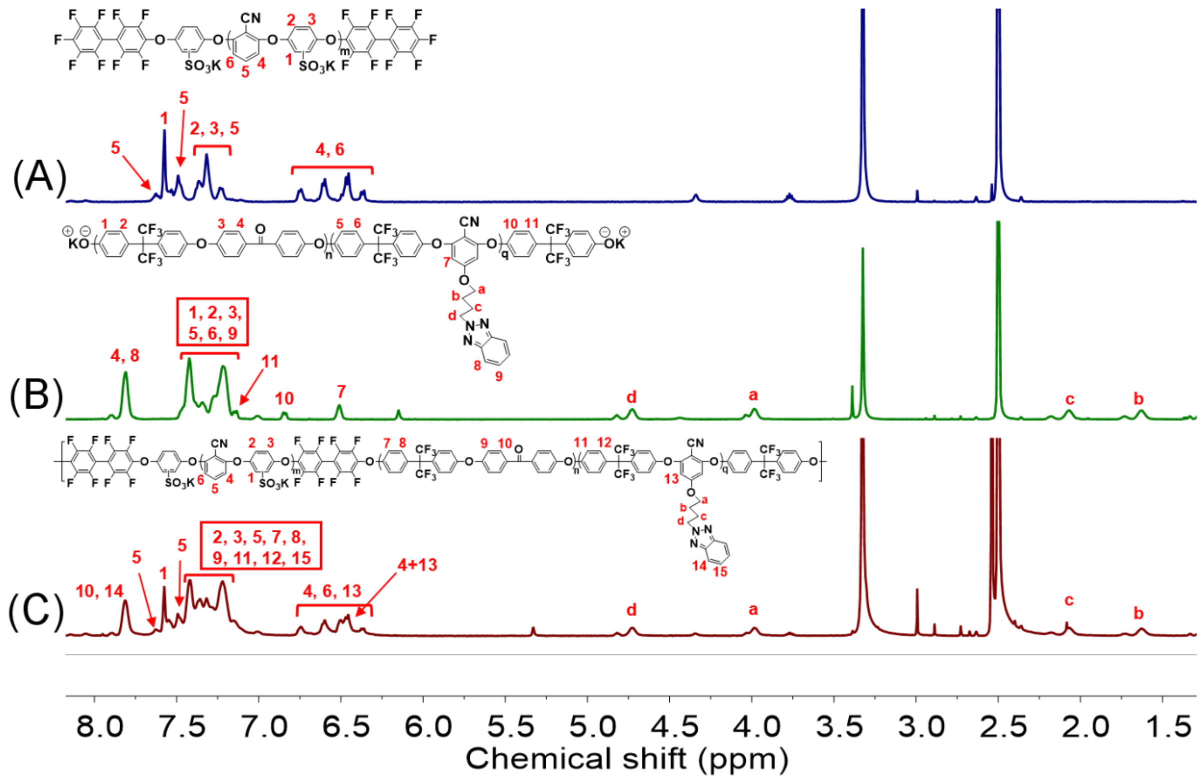

Figure S5. [1]H NMR spectra of (A) **O2**, (B) **O3-BTBFBN**, and (C) **P1-BTBFBN** in DMSO-d_6.

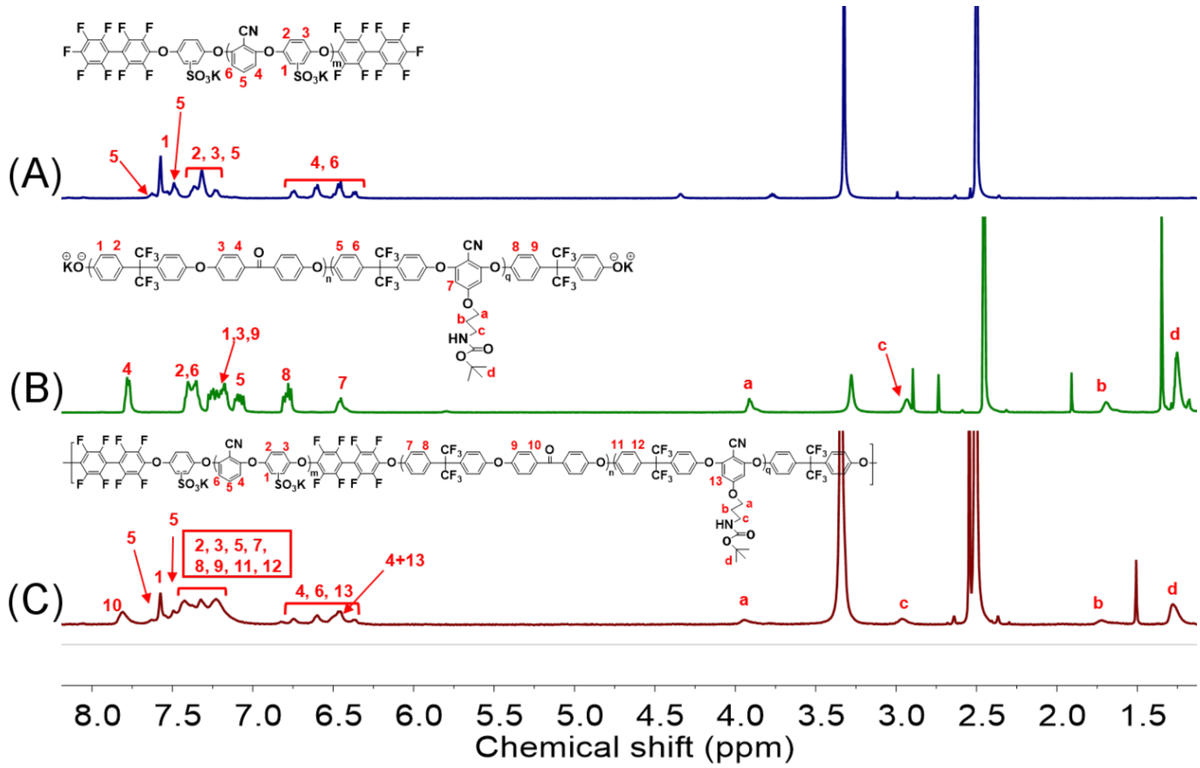

Figure S6. [1]H NMR spectra of (A) **O2**, (B) **O3-*t*-BCFPPC**, and (C) **P1-*t*-BCFPPC** in DMSO-d_6.

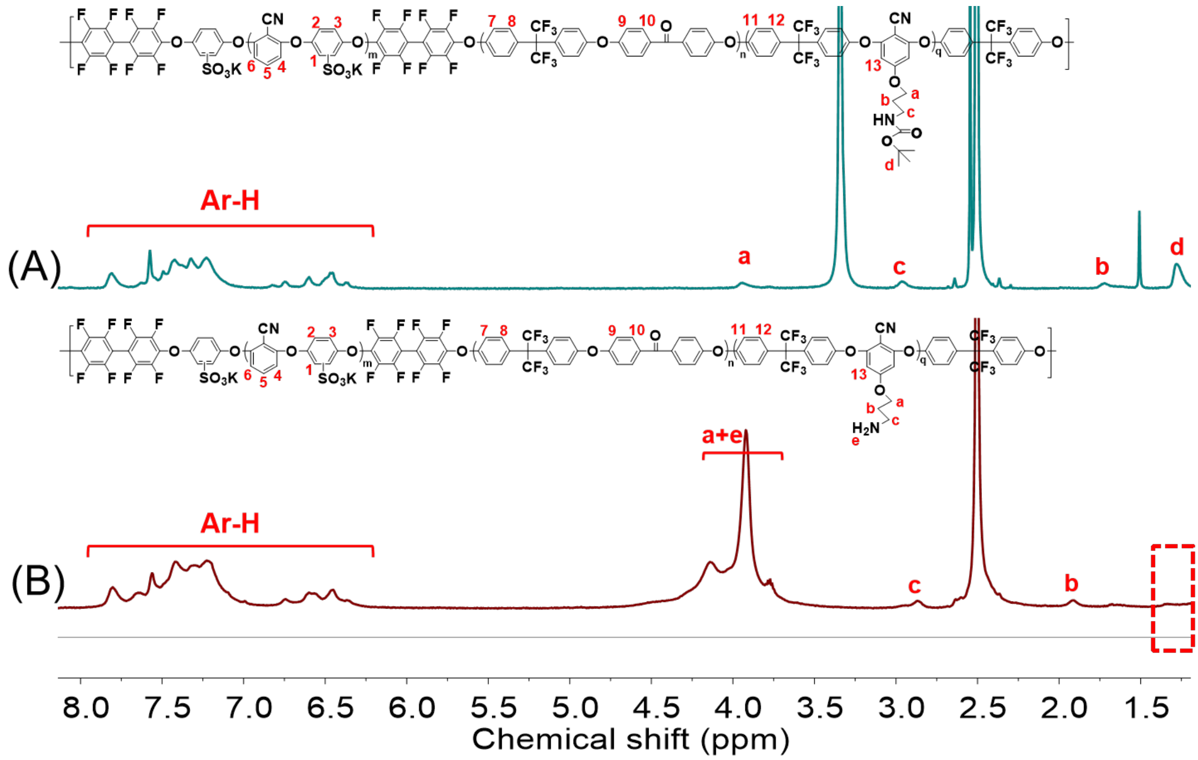

Figure S7. [1]H NMR spectra of **P1**-*t*-**BCFPPC** before (A) and after (B) deprotection of propylamino groups in DMSO-d_6.

Reference

[1] T. Yoo, A. Aziz, K. Oh and S. Shanmugam, Modified sulfonated Poly(arylene ether) multiblock copolymers containing highly sulfonated blocks for polymer electrolyte membrane fuel cells, Journal of Membrane Science, 2017, 542, 102-109.

[2] X. Zhang, L. Sheng, T. Higashihara, M. Ueda, Polymer electrolyte membranes based on poly(m-phenylene)s with sulfonic acid via long alkyl side chains, Polymer Chemistry, 2013, 4, 1235-1242.

[3] Huayuan Hu, Yuqian Sui, MitsuruUeda, JieshuQian, LianjunWang, XuanZhang, Multi-block sulfonated poly(arylene ether nitrile) polymers bearing oligomeric benzotriazole pendants with exceptionally high H_2/O_2 fuel cell performance, J. Membr. Sci., 2018, 564, 342-351.

[4] Huayuan Hu, Tiandu Dong, Yuqian Sui, Nanwen Li, Mitsuru Ueda, Lianjun Wang and Xuan Zhang, A thermally crosslinked multiblock sulfonated poly(arylene ether ketone nitrile) copolymer with a 1,2,3-triazole pendant for proton conducting membranes, J. Mater. Chem. A, 2018, 6, 3560-3570