Electronic Supplementary Information

Highly stable polyphenylene ionomer membrane from dichlorobiphenyls

Keisuke Shiino,[a] Junpei Miyake[b] and Kenji Miyatake*[bc]

[a]Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan

[b]Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan. Email: miyatake@yamanashi.ac.jp

[c]Fuel Cell Nanomaterials Center, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan

EXPERIMENTAL SECTION

Chemicals. Tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$], 1-chloro-3-iodobenzene, and 1-chloro-4-iodobenzene were purchased from TCI, Inc. and used as received. 2,5-Dichlorobenzenesulfonic acid dihydrate [SP monomer], 3-chlorophenylboronic acid, 4-chlorophenylboronic acid, bis(1,5-cyclooctadiene)nickel(0) [$Ni(cod)_2$], 2,2'-bipyridine, potassium carbonate [K_2CO_3], sodium carbonate [Na_2CO_3], magnesium sulfate [$MgSO_4$], dimethyl sulfoxide [DMSO], toluene dehydrate, methanol, 2-propanol, 0.01 M sodium hydroxide aqueous solution, hydrochloric acid, sodium chloride, hexane, chloroform-d_1 [$CDCl_3$], and dimethyl sulfoxide [DMSO-d_6] were purchased from Kanto Chemical Co. and used as received.

Synthesis of 4,4'-dichlorobiphenyl (BP$_{pp}$). The BP$_{pp}$ monomer was synthesized by Suzuki-Miyaura cross coupling reaction. A 300-mL three-neck round-bottomed flask equipped with a condenser, nitrogen inlet/outlet and magnetic stirring bar was charged with 4-chlorophenylboronic acid (7.82 g, 0.05 mol), 1-chloro-4-iodobenzene (11.9 g, 0.05 mol), 2 M aqueous Na_2CO_3 (75 mL), toluene (150 mL), and $Pd(PPh_3)_4$ (1.16 g, 0.001 mol). The mixture was stirred at 130 ºC for 21 h, cooled to room temperature, and then solution was recovered by filtration. After separation of two layers, the aqueous layer was extracted with toluene, and the combined organic layers were dehydrated using $MgSO_4$ and concentrated in vacuo. The crude product was purified by filtration with silica gel and recrystallization from 2-propanol. Pure BP$_{pp}$ monomer was obtained as a white solid (9.79 g, 89.2%).

Synthesis of 3,3'-dichlorobiphenyl (BP$_{mm}$). The BP$_{mm}$ monomer was synthesized under the similar reaction conditions with BP$_{pp}$. The BP$_{mm}$ monomer was obtained as a transparent and colorless liquid (6.08 g, 69.1%).

Synthesis of SPP-BP. A typical procedure is as follows (ion exchange capacity, IEC = 2.4 meq g^{-1}). A 100-mL three-neck flask equipped with a magnetic stirring bar and nitrogen inlet/outlet was charged with BP_{mm} monomer (4.48 mmol, 1.00 g), BP_{pp} monomer (1.12 mmol, 0.250 g), SP monomer (5.12 mmol, 1.16 g), 2,2'-bipyridine (33.8 mmol, 5.28 g), K_2CO_3 (5.63 mmol, 0.778 g), DMSO (62.5 mL), and toluene (10 mL). After the azeotropic removal of water at 170 ºC for 2 h with a dean-stark trap, the reaction mixture was cooled to 80 ºC followed by the addition of $Ni(cod)_2$ (32.2 mmol, 8.85 g). The polymerization reaction was carried out at 80 ºC for 3 h, and then the reaction mixture was poured into a large excess of methanol. The crude product was washed with 6 M hydrochloric acid and water repeatedly. After drying in a vacuum oven at 60 ºC, the desired polymer was obtained in 82.6% yield.

Membrane preparation. SPP-BP (0.49 g) was dissolved in 5 mL of DMSO and cast onto a flat glass plate. The solution was dried at 60 ºC to obtain a thin membrane. The membrane was further dried under reduced pressure at 80 ºC for at least 3 h. Then, the membrane was immersed in 1 M H_2SO_4 overnight, washed with water several times, and dried at room temperature.

Nuclear magnetic resonance (NMR). ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on a JEOL JNM-ECA 500 spectrometer with $CDCl_3$ or DMSO-d_6 as a solvent and tetramethylsilane as an internal reference.

Gel permeation chromatography (GPC). Molecular weights of polymers were estimated from GPC equipped with a Jasco MD-4017 UV detector and a Shodex K-805L column at 50 ºC. DMF containing 0.01 M LiBr was used as an eluent. Molecular weight was calibrated with standard polystyrene samples.

Titration. IEC of the membranes was calculated from acid base titration. A piece of membrane (ca. 20 mg) was immersed in 2 M NaCl aqueous solution for 12 h at room temperature. HCl released by the ion exchange reaction was titrated with a standard 0.01 M NaOH aqueous solution using automatic potentiometric titrator (AT-510, Kyoto electronics manufacturing Co., Ltd.) at room temperature.

Transmission electron microscopy (TEM). For TEM observation, membrane sample was stained in 0.5 M lead(II) acetate aqueous solution, washed with ultrapure water, and dried. The stained membrane sample was embedded in resin, sectioned to 50 nm thickness with Leica microtome Ultracut UCT, and placed on copper grid. Image was taken on a Hitachi H-9500 TEM with an accelerating voltage of 200 kV.

Small-angle x-ray scattering (SAXS). The SAXS experiment was conducted with Rigaku NANO-Viewer diffractometer equipped with a temperature/humidity-controlled chamber. The membrane (ca. 150 μm) was equilibrated for at least 2 hours under the tested conditions.

Water uptake and proton conductivity. Water uptake and proton conductivity of the membranes were measured simultaneously at 80 ºC with a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Co.) equipped with a temperature/humidity-controlled chamber. Weight of the membranes was measured with a magnetic suspension balance at a given humidity, and the water uptake was calculated using the following equation: (weight of hydrated membrane – weight of dry membrane) / weight of dry membrane × 100. Drying for 3 h at 80 ºC under reduced pressure gave the weight of dry membrane, and exposure to a given humidity for at least 2 h gave the weight of hydrated membrane. Proton conductivity was measured with a four-probe conductivity cell equipped with a Solartron 1255B and SI 1287 impedance analyzers in the same chamber. Ion conducting resistances (R) were determined from the impedance plot obtained in the frequency range from 1 to 10^5 Hz. The proton conductivity (σ) was calculated from the equation: $\sigma = l / (A \times R)$, in which A and l are the conducting area and the electrode distance, respectively.

Tensile test. Stress-strain curve was obtained by a Shimadzu AGS-J 500N universal test machine attached with a Toshin Kogyo Bethel-3A temperature/humidity-controlled chamber. The membrane sample was cut into a dumbbell shape [DIN-53504-S3, 35 × 6 mm (total) and 12

× 2 mm (test area)]. The measurement was carried out at 80 ºC and 60% RH at a tensile rate of 10 mm min^{-1}.

Oxidative stability test (Fenton's test). Oxidative stability test was conducted by immersing a membrane (in H^+ form) in Fenton's reagent (i.e., 3% H_2O_2 aqueous solution containing 2 ppm Fe^{2+}) at 80 ºC for 1 h. As an Fe^{2+} source, iron(II) sulfate heptahydrate ($FeSO_4$ $7H_2O$) was used. Post-test membranes were subjected to gravimetry (weight), GPC (molecular weight), titration (IEC), ^{1}H NMR, water uptake, and proton conductivity.

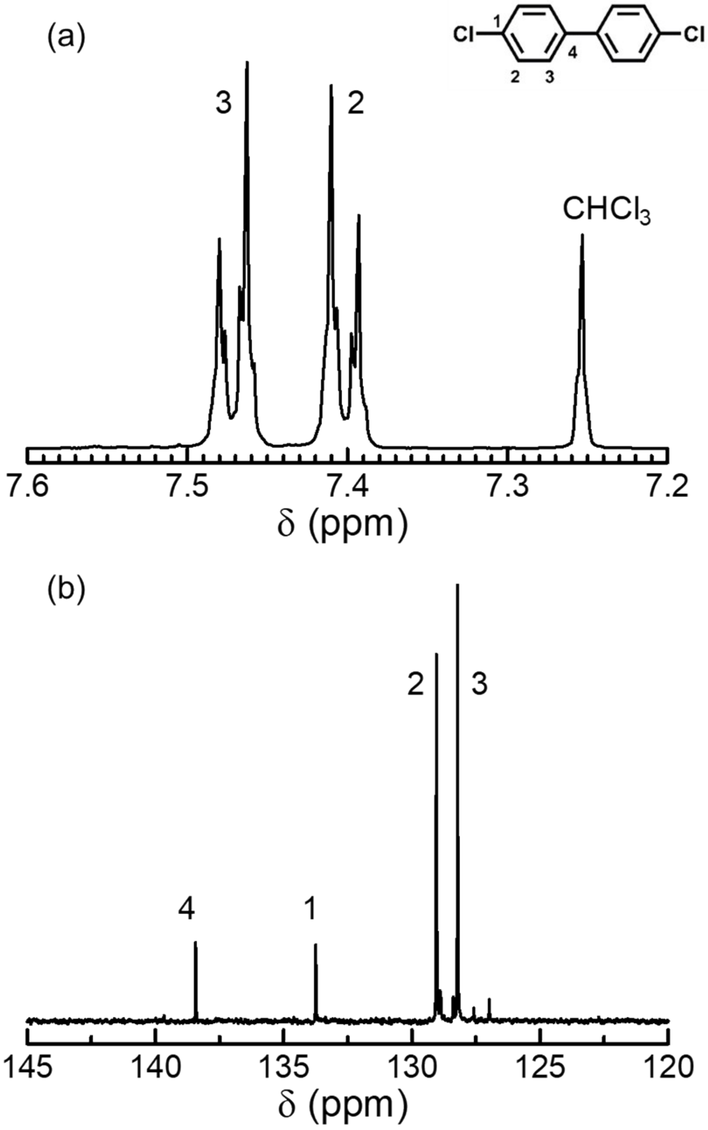

Fig. S1 (a) ^{1}H and (b) ^{13}C NMR spectra of the BP$_{pp}$.

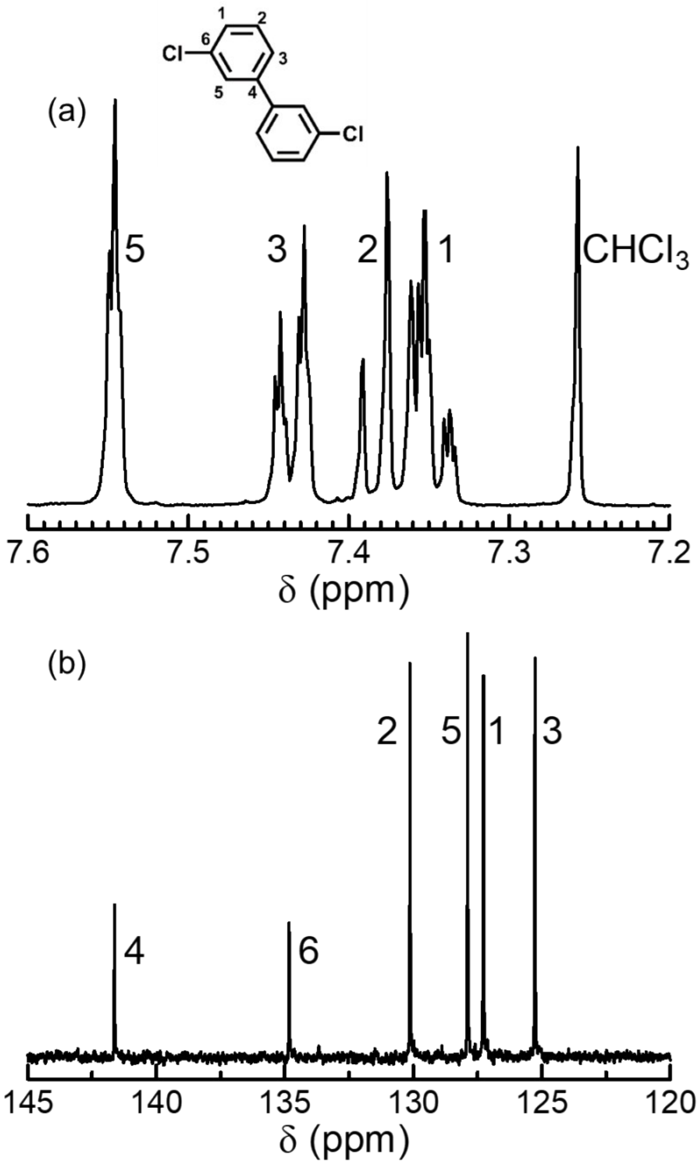

Fig. S2 (a) ^{1}H and (b) ^{13}C NMR spectra of the BP$_{mm}$.

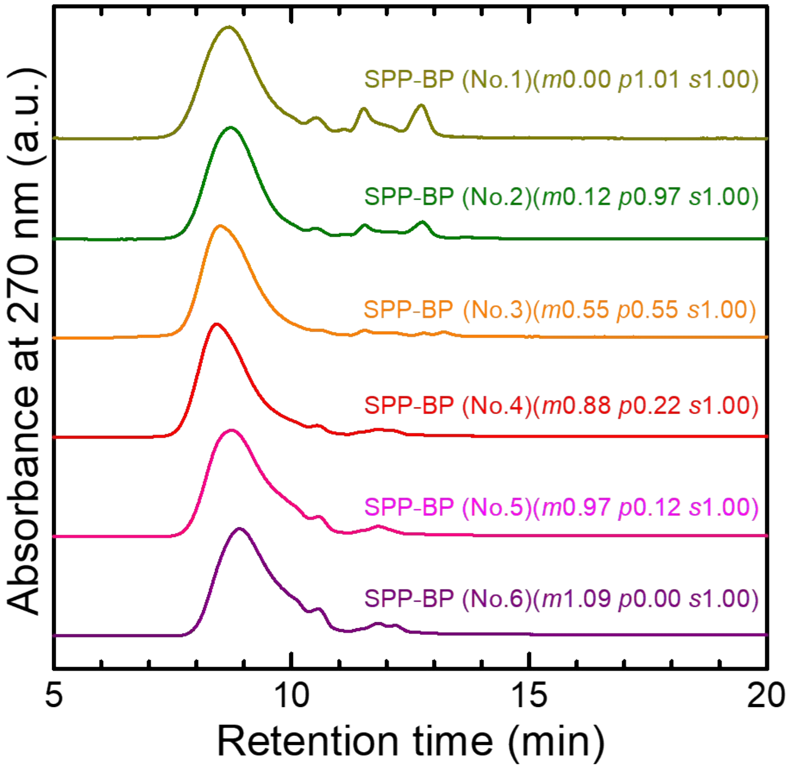

Fig. S3 GPC profiles of SPP-BP with various compositions.

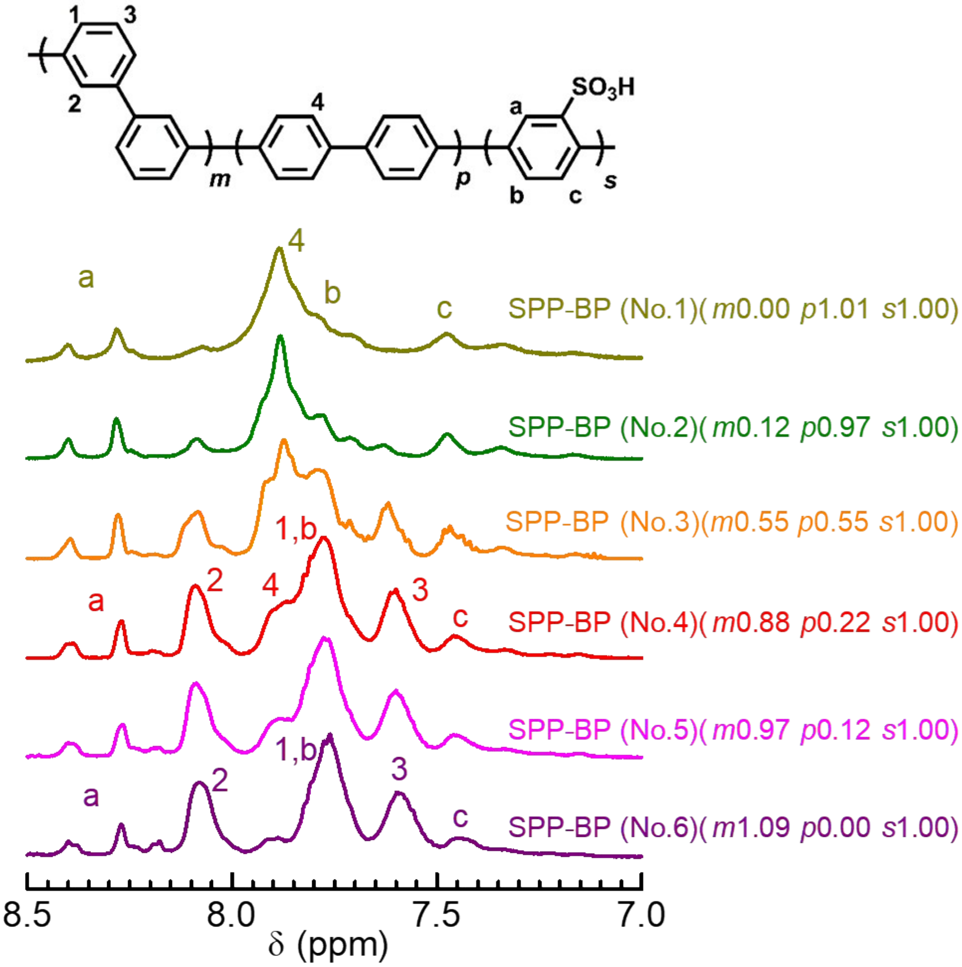

Fig. S4 ^{1}H NMR spectra of SPP-BP with various compositions.

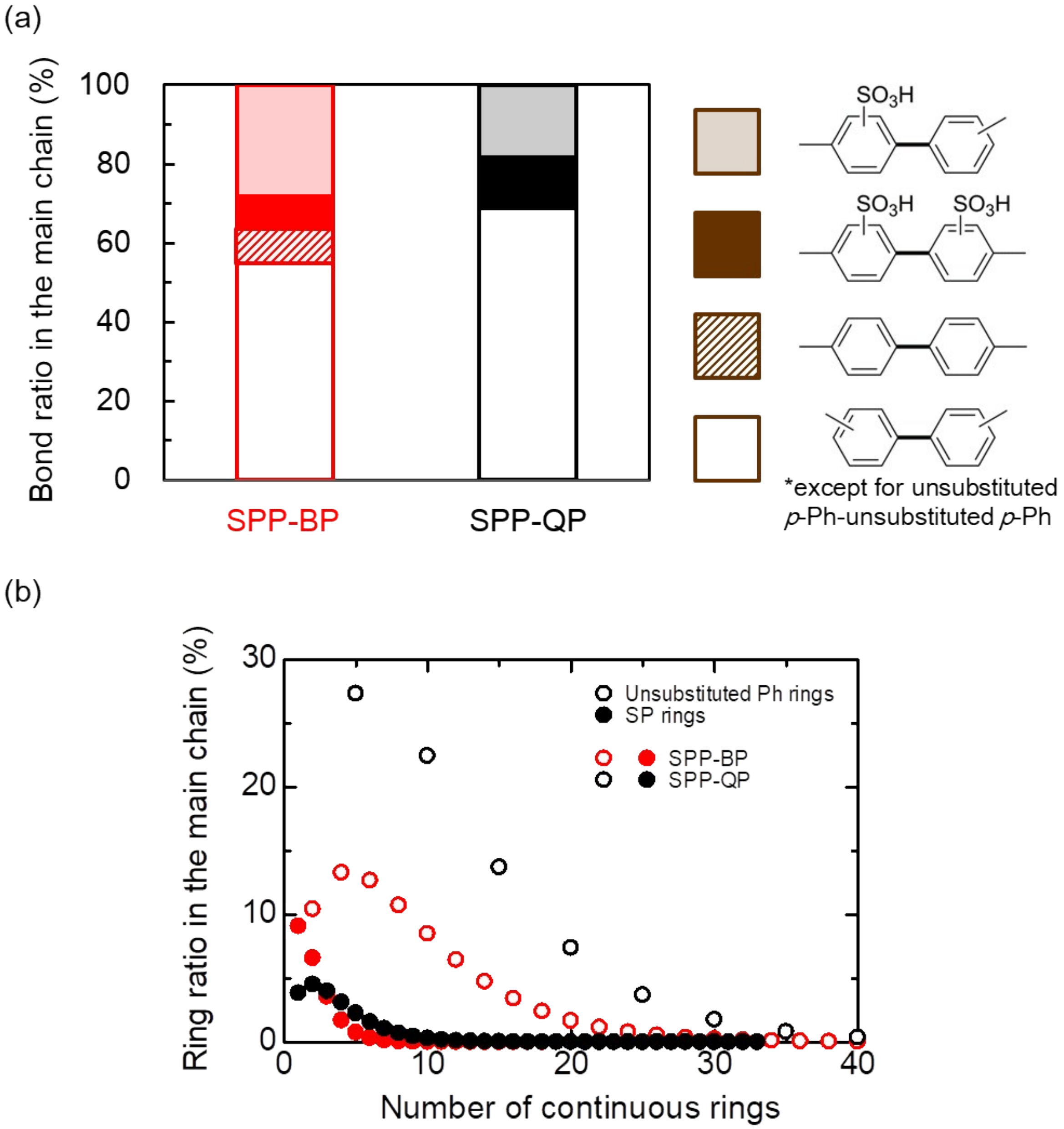

Fig. S5 The ratios of (a) each bond and (b) each phenylene ring were estimated by numerically averaging 1,000,000 polymer chains randomly generated. Each polymer chain was set to have IEC (2.37 meq g^{-1}) and molecular weight (ca. 42 kDa, number of unsubstituted *m*-, *p*-Ph, and SP rings were 280, 70, and 100, respectively), which simulated the SPP-BP (No.4) and SPP-QP. The calculation was performed with Mathematica.

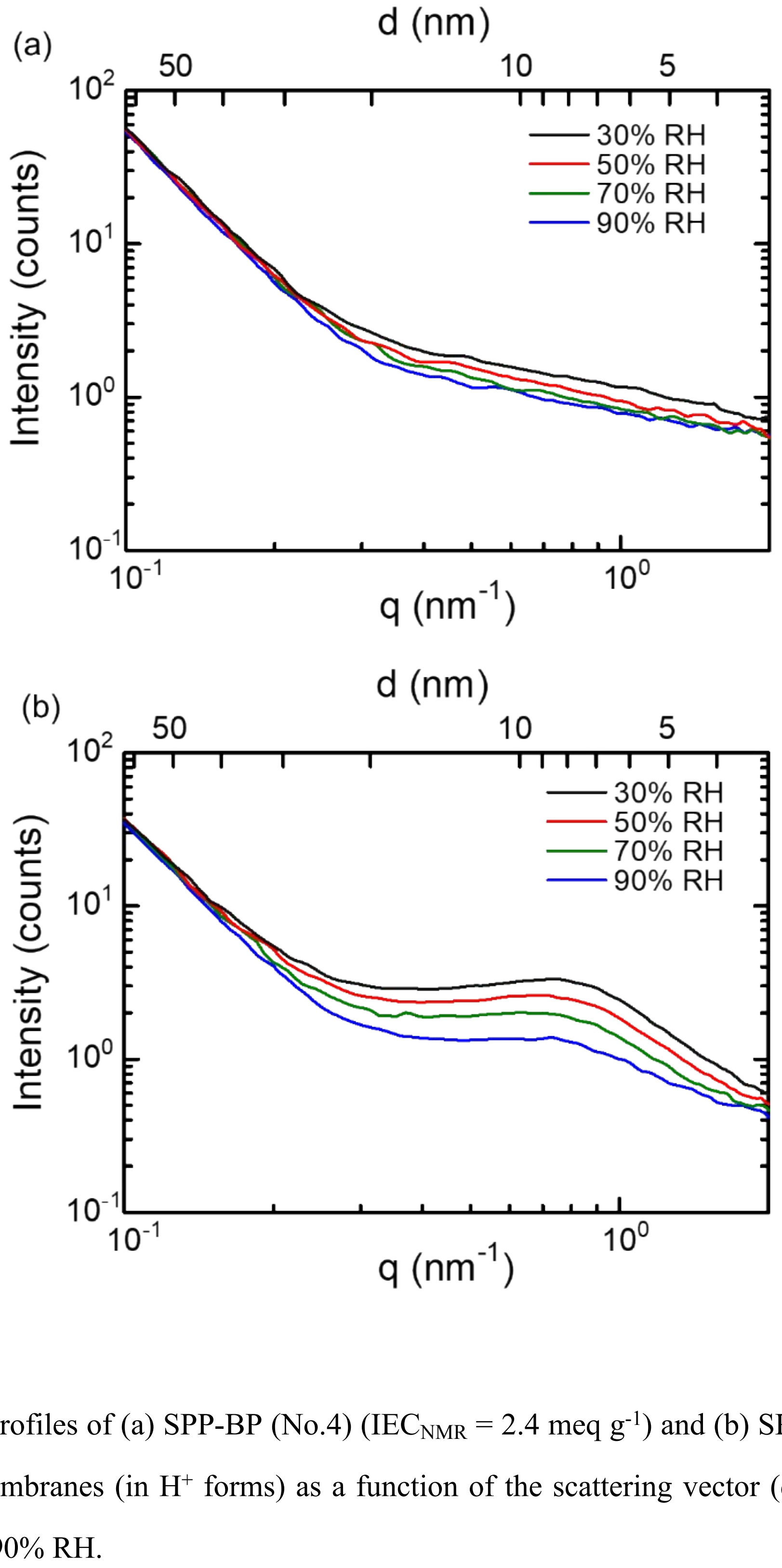

Fig. S6 SAXS profiles of (a) SPP-BP (No.4) (IEC_{NMR} = 2.4 meq g^{-1}) and (b) SPP-QP (IEC_{NMR} = 2.2 meq g^{-1}) membranes (in H^+ forms) as a function of the scattering vector (q) value at 80 °C and 30, 50, 70, 90% RH.

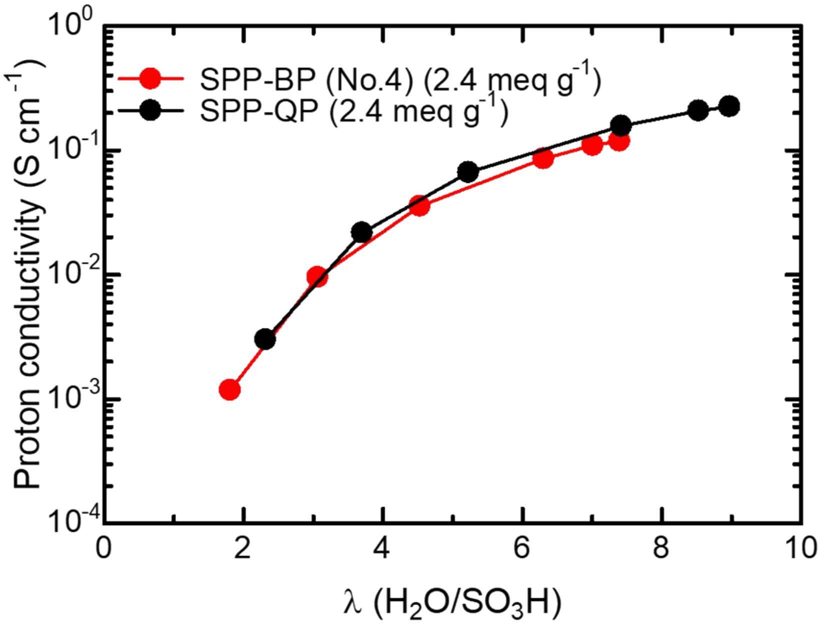

Fig. S7 Proton conductivity of SPP-BP and SPP-QP membranes at 80 °C as a function of number of absorbed water molecules per sulfonic acid group (λ). The data for the SPP-QP membrane was obtained from our previous literature (*Sci. Adv.*, 2017, **3**, eaao0476).

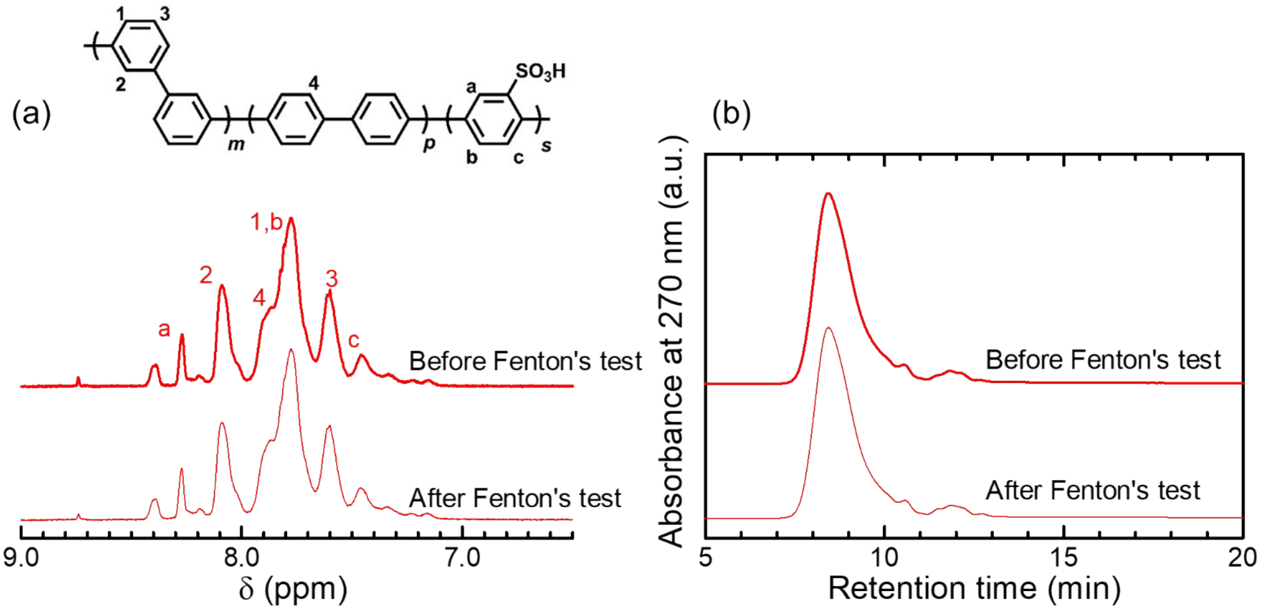

Fig. S8 (a) ^{1}H NMR spectra and (b) GPC profiles of SPP-BP (No.4) before and after Fenton's test.