

Novel Highly Proton Conductive Sulfonated Poly(*p*-phenylene) from 2,5-dichloro-4-(phenoxypropyl)benzophenone as Proton Exchange Membranes for Fuel Cell Applications

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~Electronic Supplementary Information~

Materials and Measurements

1. Materials

All reagents and solvent were purchased from Aldrich and used without further purification. Triphenylphosphine was purified by recrystallization from *n*-hexane. *N*-methyl-2-pyrrolidinone (NMP, anhydrous grade from Aldrich) was also used as received. 2,5-dichlorobenzoyl chloride was prepared from 2,5-dichlorobenzoic acid and thionyl chloride.

2. Measurements

¹H- and ¹³C-NMR spectra were obtained on JEOL ECA-500 using CDCl₃ as the solvent with tetramethylsilane as the internal reference. Molecular weight and its distribution were estimated by gel permeation chromatography (GPC) equipped with two consecutive

columns(Asahipak: GF-7M HQ, GF-310 HQ) connected with Shimadzu SPD-20AU UV detector at 40°C (flow rate 0.05mL/min) using polystyrene standards and DMF containing 0.05 M LiBr as the eluent.

The thermogravimetric analysis (TGA) was performed with Shimadzu TGA-50 instrument. Polymer samples were dried at 100°C prior to the experiments and heat from room temperature to 800°C at a heating rate of 10°C/min under nitrogen atmosphere (flow rate 50 mL/min).

Ion exchange capacity of the copolymer membranes was determined through titration method. Polymer membranes in acid form were dried overnight at 100°C under vacuum, weighed and then immersed in saturated NaCl for 24 h. The amount of H⁺ ion released from the membrane samples was determined by titration with 0.01 M NaOH using phenolphthalein as an indicator.

$$\text{IEC} = (\text{C} \times \text{V})/\text{M}$$

where C and V are the concentration and volume of NaOH, respectively. M is the weight of membrane.

Water uptake and proton conductivity were measured using an isothermal absorption measurement system (MSB-AD-V-FC, BEL Japan Inc.) equipped with an impedance analyzer (Solartron SI 1260) with a temperature and humidity controllable chamber. This system enabled the simultaneous measurements of water uptake and proton conductivity in the same chamber. The impedance spectra were recorded with the help of ZPlot/Zview software under an AC perturbation signal of 10mV over the frequency range of 10 Hz to 100 kHz. Each membrane sample was dried at 80°C for 2 h under dry nitrogen flow, then

exposed to a humidified nitrogen environment at 40°C. After there was no further weight change of each sample, sample weight and proton conductivity were measured sequentially. Humidity conditions were changed stepwise from 10% RH to 95% RH. The proton conductivity (σ) was calculated from the impedance data according to following equation:

$$\sigma = d/A \cdot R$$

where A and d are the resistance value measured conducting area and the membrane thickness, respectively, and R is the resistance value measured.

Dimensional change was investigated by immersing the membrane samples into de-ionized water at room temperature and 80°C for a given time, the change of thickness and length was calculated from:

$$\Delta t = (t - t_s)/t_s$$

$$\Delta l = (l - l_s)/l_s$$

where t_s and l_s are the thickness and diameter of the dried state, respectively; t and l refer to those of the membrane in water for 5 h.

Gas permeability was measured by equal pressure method (ref JACS) equipped with a GTR-Tech 30XFST apparatus equipped with a Yanaco G2700T gas chromatograph by monitoring the amounts of H₂ that permeated across the membrane which is dehydrated and stored in dry N₂ at least 3 h before measurement from one side to the other (upstream). O₂ was also supplied from the other side (downstream). Temperature dependence of H₂ and O₂ permeability coefficient P was measured from 0 to 90%RH at 80°C using Ar and He as a carrier gases of permeated H₂ and O₂ to the gas chromatograph, respectively. A 40-60 μ m thick membrane was set in a cell with a gas inlet and outlet, where the temperature was

controlled. H₂ and O₂ was supplied at a flow rate of 30 mL/min. The gas permeability coefficient, P (cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹), were calculated according to the following:

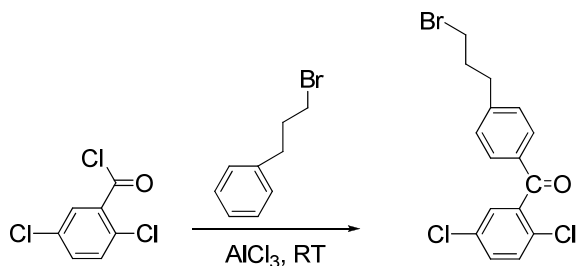
$$P = \frac{273}{T} \times \frac{1}{A} \times d \times \frac{1}{76 - P_{\text{H}_2\text{O}}} \times \frac{B}{60} \times \frac{C}{10^6}$$

where T (K) is the absolute temperature of the cell, A (cm²) is the permeation area, B (cm³) is the volume (flow rate) of test gas permeated through the membrane, C is the concentration of gases that permeated through the membrane evaluated by absolute calibration method, d (cm) is the thickness of the membrane, and $P_{\text{H}_2\text{O}}$ (cmHg) is the water vapor pressure.

3. Monomer, polymer synthesis and membrane preparation

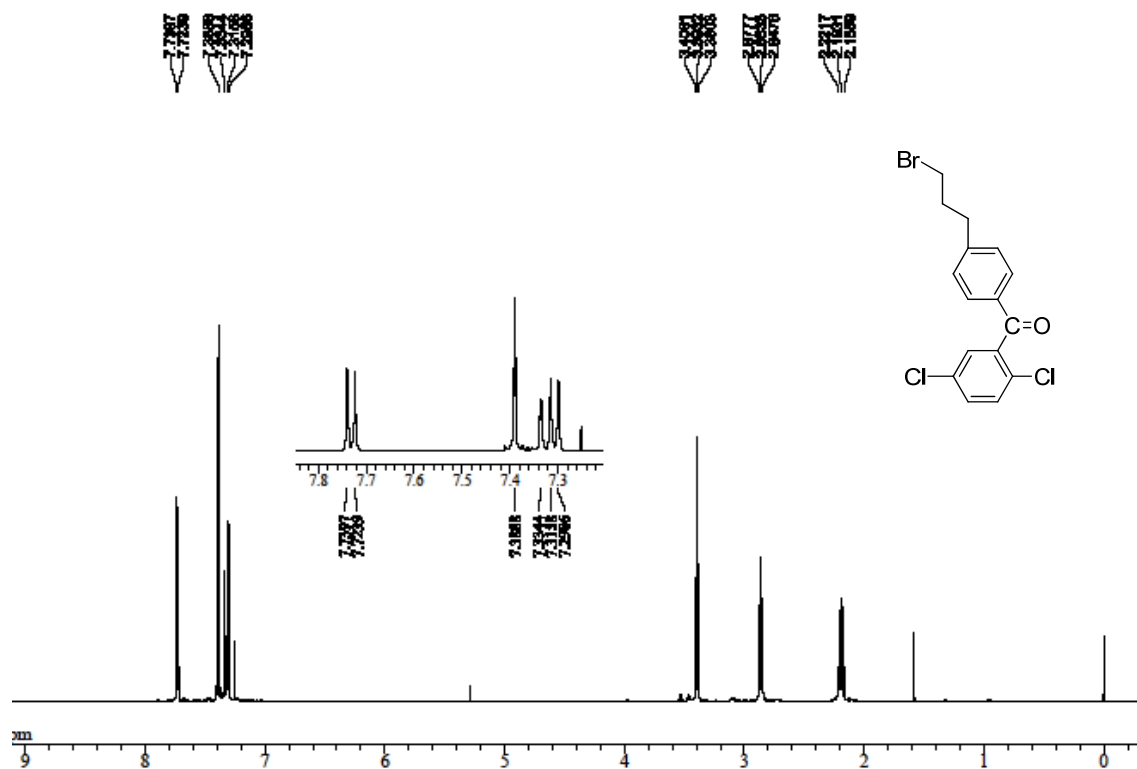
3.1 Monomer synthesis

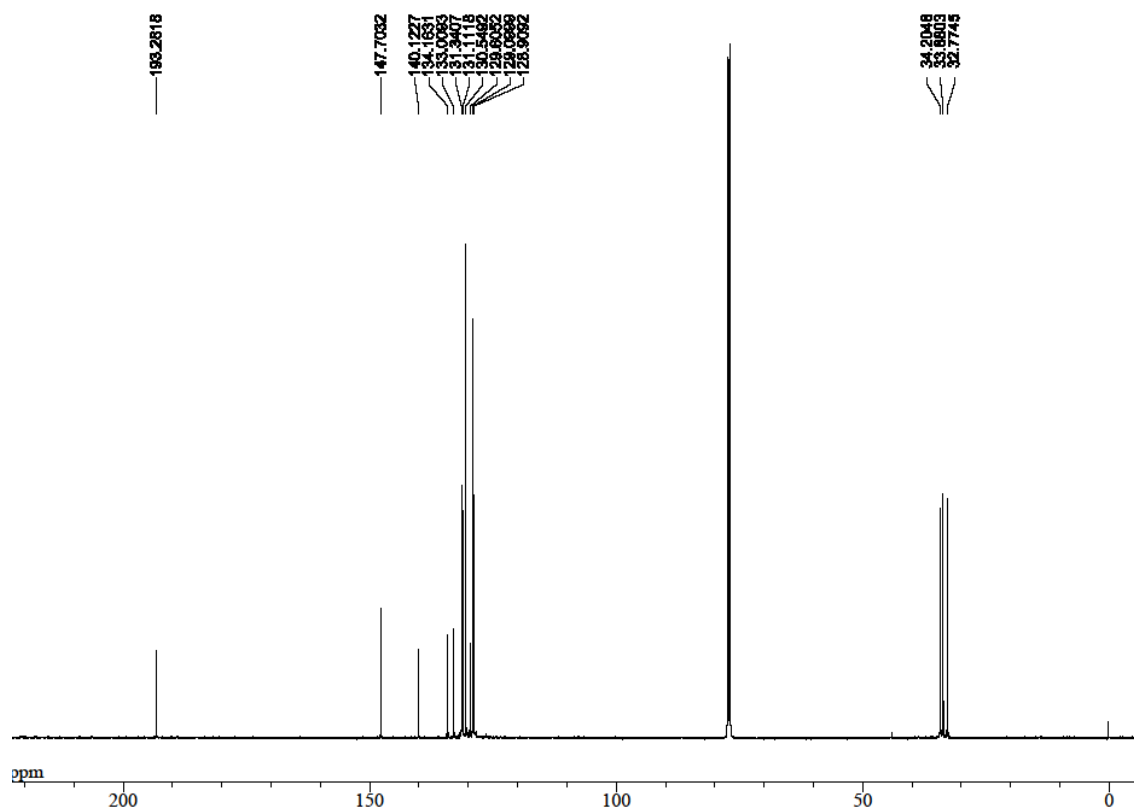
2,5- dichloro-4-bromopropylbenzophenone:



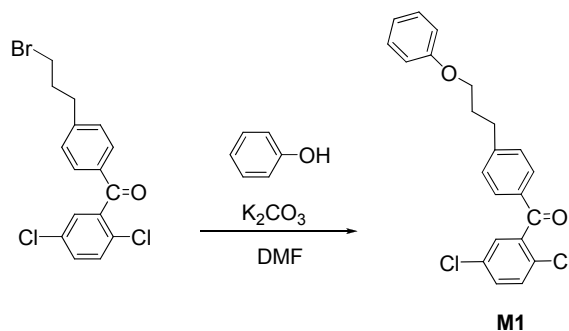
A solution of bromopropylbenzene (1 equiv) and 2,5-dichlorobenzoylchloride (1.1 equiv) in dichloromethane (5 equiv) was charged into three neck flask. The reaction mixture was cooled in an ice/water bath. Anhydrous AlCl₃ (1 equiv) was added gradually to the reaction mixture and the temperature was kept under 10°C. After the addition of all AlCl₃, the reaction solution was allowed to slowly warm to room temperature and kept stirred for

overnight. The reaction was stopped by pouring the solution into acidic ice water. The final product was purified by chromatography (CH₂Cl₂/hexane). Yield was 95%. ¹H NMR(500 MHz, CDCl₃): δ(ppm) 7.73 (d, 2H), 7.38 (s, 2H), 7.33 (s, 1H), 7.30 (dd, 2H), 3.39 (t, 2H), 2.86 (t, 2H), 2.19 (q, 2). ¹³C NMR (100MHz, CDCl₃) δ 193.2, 147.7, 134.1, 133.0, 131.3, 131.0, 130.5, 129.6, 129.0, 128.9, 34.2, 33.6, 32.7.

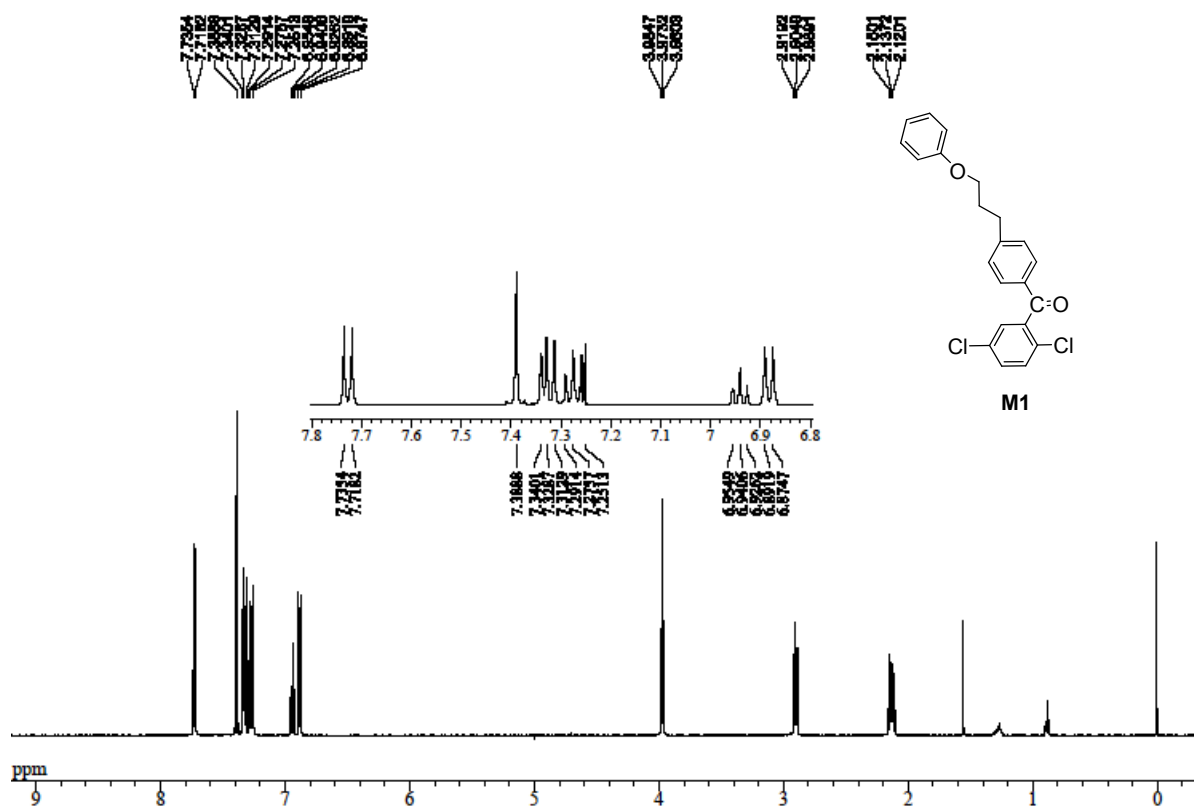


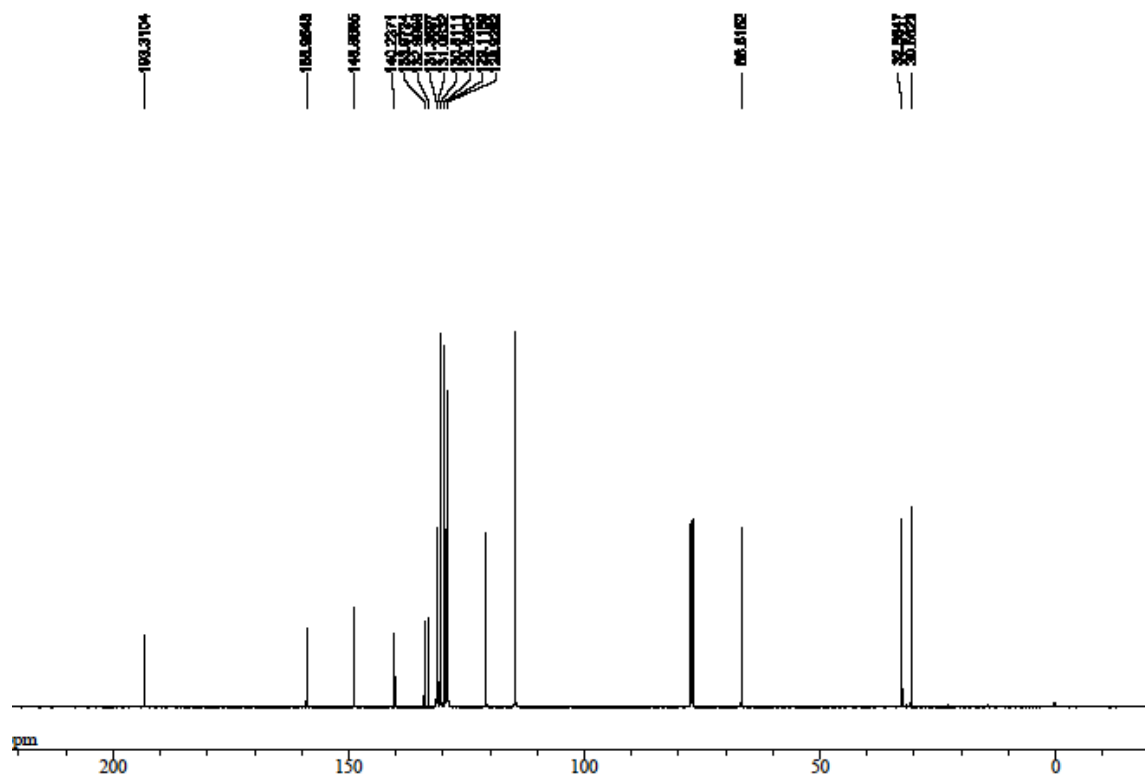


2,5-dichloro-4-(phenoxypropyl)benzophenone (M1):



2,5-dichloro-4-bromopropylbenzophenone (14.8 g, 0.039 mmol), phenol (9.4 g, 0.099 mmol), potassium carbonate (27.6, 0.2 mmol), and dimethyl formamide (200 mL) was added. Then, the reaction mixture was stirred at 130°C for 2 days under argon atmosphere. The mixture was cooled and water was added. Then, the mixture was extract with n-hexane several times. The combine organic layers were dried over anhydrous $MgSO_4$, filtered. The solvent was removed by evaporation under reduced pressure. The residue was purified by recrystallization with hexane or cyclohexane 2 times to give **M1** as a colorless crystal in 60% yield. Mp: 72-74°C. 1H NMR(500 MHz, $CDCl_3$): δ (ppm) 7.72 (d, 2H), 7.38 (s, 2H), 7.34 (s, 1H), 7.31 (d, 2H), 7.27 (dd, 2H), 6.94 (dd, 1H), 6.88 (d, 2H), 3.97 (t, 2H), 2.90 (t, 2H), 2.13 (q, 2H). ^{13}C NMR (100MHz, $CDCl_3$) δ 193.3, 158.9, 148.8, 140.2, 133.9, 132.9, 131.3, 131.0, 129.5, 129.1, 128.9, 66.6, 32.5, 30.5. FT-IR (KBr): 1673 cm^{-1} (C=O), 1605 and 1501 cm^{-1} (C=C, aromatic), 1250 cm^{-1} (C-O). MS(m/z): 385.06 [M+H] Anal. Calcd for $C_{22}H_{18}Cl_2O_2$: C, 68.58%; H, 4.71%. Found: C, 68.40%; H, 4.63%.





3.2 Polymer synthesis

A typical example of polymerization is as follows: Into a 100 mL three-neck round bottom flask, NMP, Ni(PPh₃)₂Cl₂ (0.03 equiv), Zn (2 equiv), PPh₃ (0.4 equiv), and NaI (0.13 equiv) under argon atmosphere were charged to a flask under argon atmosphere. Solvent was added via a syringe, and the mixture was stirred at 50 °C for 10-20 min. A red brown color was observed. The monomer (1 equiv) was added and allowed to react for 3-5 h or until the reaction mixture became too viscous to stir. The polymer was then precipitated in 10% hydrochloric and acetone, filtered, washed with acetone, then dried and then dried at 80 °C for 24 h under reduced pressure to give product with 90-95% yield. **PP**: GPC measurement showed $M_n = 37,900$ Da, $M_w = 136,440$. ¹H NMR(500 MHz, CDCl₃): δ(ppm) 7.59-7.40 (br, 3H), 7.22 (s, 3H), 7.05 (br, 3H), 6.90-6.84 (br, 3H), 3.89 (s, 2H), 2.75

(s, 2H), 2.01 (s, 2H). FT-IR(KBr): 1662 cm^{-1} (C=O), 1600 and 1496 cm^{-1} (C=C, aromatic), 1244 cm^{-1} (C-O). Anal. Calcd for $(\text{C}_{22}\text{H}_{18}\text{O}_2)_n$: C, 84.05%; H, 5.77%; O, 10.18%. Found: C, 83.37%; H, 5.65%; O, 10.90%.

3.3. Sulfonation

The post sulfonation of **PP** was carried out using concentrated sulfuric acid as a sulfonating agent at room temperature for several days.

In a typical reaction: 1.0 g of synthesized polymer **PP** was dissolved in 30 mL of concentrated sulfuric acid. The solution was maintained at room temperature for the desired time before precipitating into a large amount of water. The sulfonated polymers was filtered and washed through with deionized water, and then dried at 80°C for 24 h under vacuum.

SPP:FT-IR(KBr): 1662 cm^{-1} (C=O), 1600 and 1467 cm^{-1} (C=C, aromatic), 1160 and 1024 cm^{-1} (asymmetric and symmetric stretching of $-\text{SO}_3\text{H}$).

3.4. Membrane preparation

Polymer membranes were prepared by solution casting from DMF. The dried sulfonated polymer **SPP** was dissolved in DMF to form 5% solution, then centrifuged to remove insoluble material. The filtrate was cast onto glass plate and dried on a hot plate at 60°C for 2 h and then at 80°C for 24 h under vacuum. Free standing membranes were removed from glass plate by immersing in deionized water. The membranes were treated with in 1 M HCl overnight, then rinsed and soaked for 3-4 h at room temperature in deionized water and dried in vacuum at 100°C overnight. The thickness of all membrane samples was in the range of 40-70 μm .

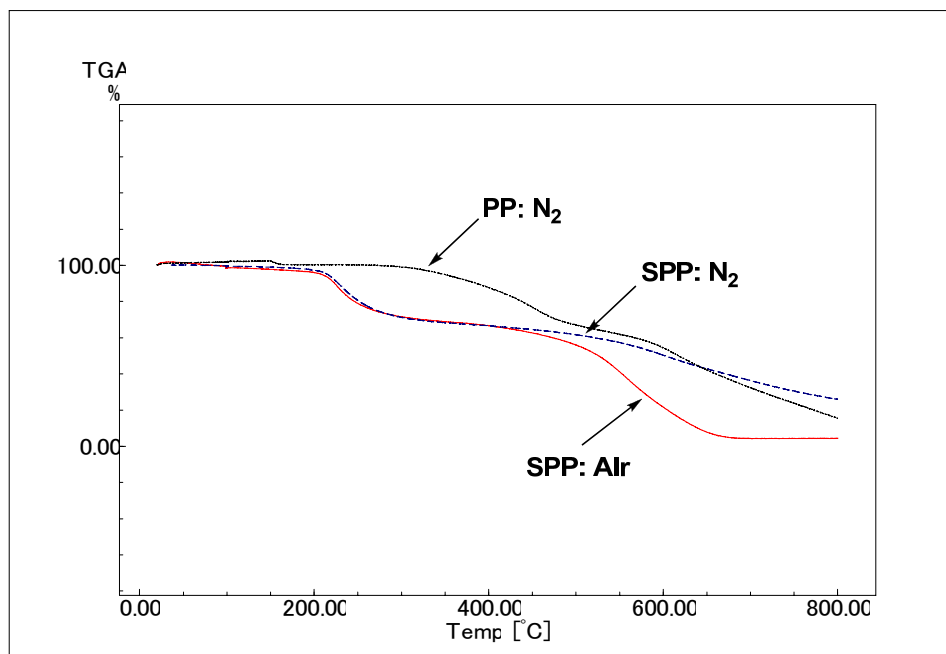


Figure S11. TGA thermograms of **PP** under N₂ and **SPP** under air and N₂ atmosphere.

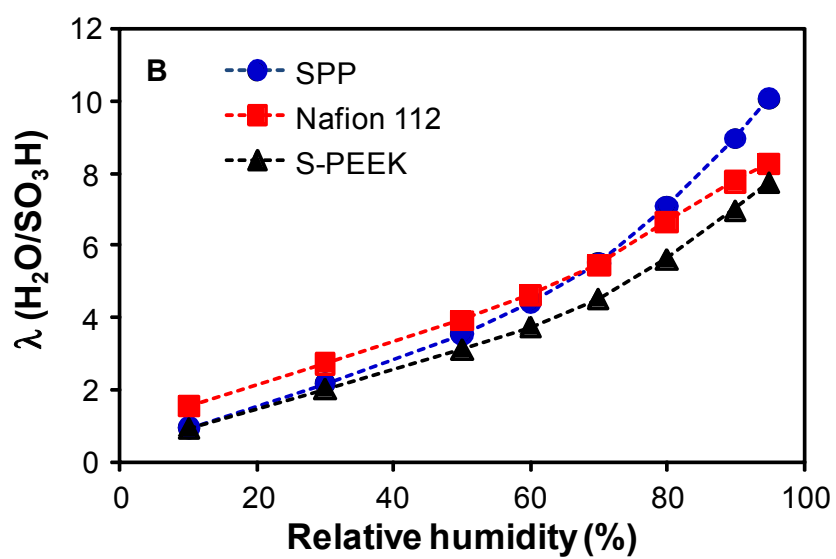


Figure SI2. Relative humidity dependence of water content of **SPP** membrane compared with Nafion 112 and **S-PEEK**.

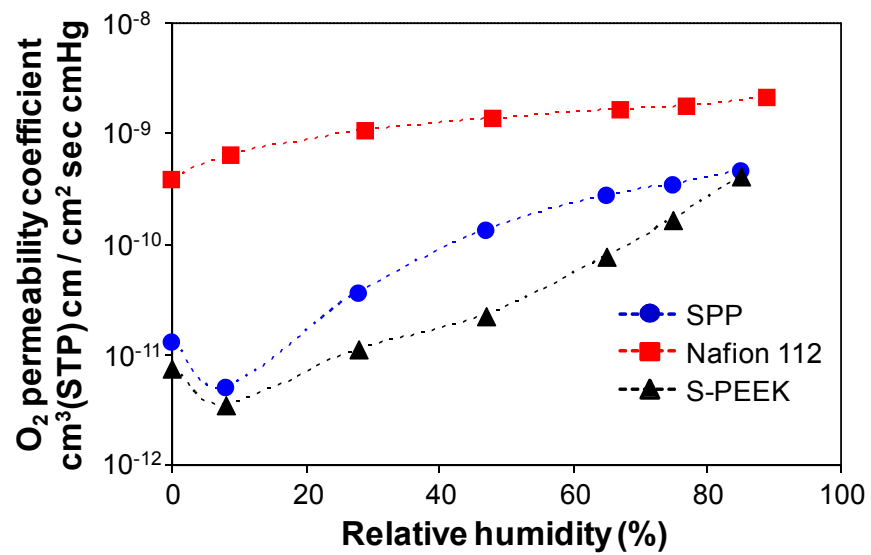


Figure SI3. Relative humidity dependence of oxygen permeability of **SPP** membrane compared with Nafion 112 and **S-PEEK**.