

Supplementary Information

Optimization of pendant chain length in partially fluorinated aromatic anion exchange membranes for alkaline fuel cells

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Experimental

Materials

2,5-Dichlorobenzylbromide, dimethyl sulfate, 2,5-dichlorobenzaldehyde, potassium *tert*-butoxide (*t*-BuOK), (3-carboxypropyl)triphenylphosphonium bromide, (4-carboxybutyl)triphenylphosphonium bromide, 2,2'-bipyridine, 3-bromopropionic acid, *trans*-2,5-dichlorocinnamic acid, lithium aluminum hydride (LAH), dimethyl amine hydrochloride, and 2,5-dichlorobenzylbromide were purchased from TCI Inc. and used as received. Dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) with 0.03% tetramethylsilane (TMS) and chloroform-*d* (CDCl₃) with 0.03% TMS were purchased from Acros Organics and used as received. Bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)₂), hydrochloric acid, potassium carbonate, potassium hydroxide, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), anhydrous lithium bromide, triethylamine, triphenylphosphine, sulfuric acid, acetic acid, potassium cyanide, potassium carbonate, dichloromethane, acetonitrile, diethyl ether, N,N-dimethylacetamide (DMAc), and tetrahydrofuran (THF) were purchased from Kanto chemical Co. and used as received. Palladium-activated carbon (10% Pd) was purchased from Wako chemicals and used as received.

Synthesis of 2,5-dichlorophenyl monomers

Synthesis of (2,5-dichlorophenyl)acetonitrile (A1)

A 100 mL round bottomed flask was charged with 2,5-dichlorobenzylbromide (5.00 g, 20.80 mmol) and ethanol (15 mL). To the solution, 5 mL of aqueous potassium cyanide (1.51 g, 23.20 mmol) solution was slowly added. The mixture was refluxed for 24 h. A white solid of potassium chloride was formed within a few minutes. After the complete reaction (checked by TLC), the mixture was filtered quickly to remove the salts and then, the filtrate was allowed to cool and precipitate a white solid. The crude product was filtered and purified by sublimation in vacuum at 60 °C to obtain **A1** as a white crystal (2.46 g, 64% yield).

Synthesis of (2,5-dichlorophenyl)acetic acid (A2).

In a 100 mL round bottomed flask, **A1** (2.46 g, 13.30 mmol) was added to 15 mL of sulfuric acid, acetic acid, and water (1:1:1 by volume). The mixture was refluxed for overnight. The mixture was allowed to cool to room temperature to precipitate a white solid. The crude product was collected by filtration, washed with distilled water several times, and dried under vacuum to obtain **A2** as an off-white solid (2.37 g, 88% yield)

Synthesis of 2-(2,5-dichlorophenyl)-N,N-dimethylacetamide (A3)

A 100 mL round bottomed flask was charged with **A2** (2.37 g, 11.56 mmol) and 30 mL of dichloromethane. To the solution, oxalyl chloride (1.23 mL, 14.40 mmol) in 5 mL of dichloromethane was added dropwise. The mixture was stirred at room temperature for 24 h and cooled with an ice bath. To the mixture, dimethyl amine hydrochloride (2.34g, 28.80 mmol) and trimethylamine (6.00 ml, 43.20 mmol) were slowly and successively added. The mixture was allowed to warm at room temperature and stirred for 48 h. After the completion reaction, the mixture was washed with distilled water, 1 M HCl, saturated NaHCO₃, and distilled water several times. The combined organic layers were dried over MgSO₄ and evaporated under vacuum. The crude product was purified on silica gel column chromatography (hexane:ethyl acetate = 9:1 as eluent) to obtain **A3** as a yellow liquid (2.20 g, 82% yield).

Synthesis of 2-(2,5-dichlorophenyl)-N,N-dimethylethan-1-amine (A4)

A 100 mL round bottomed flask was charged with LAH (0.27 g, 7.38 mmol) and 10 mL of THF under nitrogen atmosphere. The mixture was cooled with an ice bath followed by slow addition of **A3** (2.20 g, 7.38 mmol) solution in 20 mL of THF. The mixture was heated at 90 °C. After the complete reaction, the mixture was allowed to cool to room

temperature and quenched carefully by dropwise addition of 0.27 mL of water and 0.27 mL of 15% NaOH aq. Then, 1.35 mL of water and 10 mL of THF were added to the mixture to precipitate a solid. The filtrate was evaporated under vacuum and the residue was purified by alumina column chromatography (hexane:ethyl acetate = 9:1 as eluent) to obtain **A4** as a colorless liquid (2.00 g, 93% yield).

Synthesis of 3-(2,5-dichlorophenyl)-N,N-dimethylprop-2-enamide (B1)

Using the same procedure for **A3**, trans-2,5-dichlorocinnamic acid. (15.00 g, 69.00 mmol) was amidated to obtain **B1** (14.70 g, 89% yield).

Synthesis of 3-(2,5-dichlorophenyl)-N,N-dimethylpropanamide (B2)

A 250 mL round bottomed flask equipped with hydrogen gas inlet/outlet was charged with **B1** (14.70 g, 60.50 mmol) and 200 mL of ethyl acetate. To the mixture was added Pd-C powder (2.36 g). Hydrogen gas was bubbled through the reaction mixture for 6 h. Then, the catalyst was removed by filtration and the filtrate was evaporated under vacuum. The crude product was purified by silica gel column chromatography (hexane: ethyl acetate = 9:1 as eluent) to obtain **B2** (12.90 g, 87% yield).

Synthesis of 3-(2,5-dichlorophenyl)-N,N-dimethylpropan-1-amine (B3)

Using the same procedure for **A4**, **B2** (12.90 g, 52.65 mmol) was reduced with LAH to obtain **B3** (11.30 g, 93% yield).

Synthesis of (2-carboxyethyl)triphenylphosphonium bromide (C1)

A 100 mL round bottomed flask was charged with 3-promopropionic acid (1.52 g, 10.00 mmole) and triphenylphosphine (2.62 g, 10.00 mmol). The mixture was heated under neat conditions at 140 °C. The mixture was cooled to room temperature. The resulting viscous product was washed with acetonitrile/diethyl ether several times to obtain **C1** as a white solid (3.00 g, 100% yield).

Synthesis of 4-(2,5-dichlorophenyl)but-3-enoic acid (C2a) and 4-(2,5-dichlorophenyl)but-2-enoic acid (C2b)

A 100 mL round bottomed flask was charged with **C1** (4.00 g, 9.50 mmol), 2,5-dichlorobenzaldehyde (1.40 g, 7.98 mmol), and 15 mL dichloromethane. The suspended mixture was cooled with an ice bath. To the mixture, *t*-BuOK (2.24 g, 19.90 mmol) was added slowly in several portions in 1 h. The mixture was stirred at room temperature for 24 h. After the complete reaction, the mixture was washed with 1 M HCl and 1 M

NaHCO₃, respectively, and extracted with ethyl acetate several times. The combined organic layers were dried over MgSO₄ and evaporated under vacuum. The crude product was purified by silica gel column chromatography (hexane: ethyl acetate = 9:1 as eluent) to obtain a mixture of **C2a** and **C2b** as a pale yellow liquid (0.65 g, 46% yield).

Synthesis of 4-(2,5-dichlorophenyl)-butanoic acid (C3)

Using the same procedure for **B2**, **C2a** and **b** (3.90 g, 19.00 mmol) were hydrogenated to obtain **C3** as a colorless liquid (3.00 g, 78% yield).

Synthesis of 4-(2,5-dichlorophenyl)-N,N-dimethylbutanamide (C4)

Using the same procedure for **A3**, **C3** (3.00 g, 12.93 mmol) was amidated to obtain **C4** (2.80 g, 82% yield).

Synthesis of 4-(2,5-dichlorophenyl)-N,N-dimethylbutan-1-amine (C5)

Using the same procedure for **A4**, **C4** (2.75g, 10.60 mmol) was reduced with LAH to obtain **C5** as a pale yellow liquid (1.60 g, 59% yield).

Synthesis of 5-(2,5-dichlorophenyl)pent-4-enoic acid (D1)

In a 1 L round bottomed flask, (3-carboxypropyl)triphenylphosphonium bromide (41.50 g, 97.29 mmol) was dissolved in 300 mL of THF. To the solution, 213 mL of 1 M *t*-BuOK solution in THF was added dropwise at 0 °C. The mixture was stirred at 0 °C for 2 h. TO the mixture, 2,5-dichlorobenzaldehyde (12.00 g, 68.40 mmol) solution in 100 mL of THF was added dropwise. Same work-up as that for **C2** afforded **D1** as a colorless liquid (14.90 g, 89% yield).

Synthesis of 5-(2,5-dichlorophenyl)pentanoic acid (D2)

Using the same procedure for **B2**, **D1** (12.17 g, 49.00 mmol) was hydrogenated to obtain **D2** (11.26 g, 92% yield).

Synthesis of 5-(2,5-dichlorophenyl)-N,N-dimethylpentanamide (D3)

Using the same procedure for **B1**, **D2** (11.26 g, 54.40 mmol) was amidated to obtain **D3** (7.99 g, 64% yield).

Synthesis of 5-(2,5-dichlorophenyl)-N,N-dimethylpentan-1-amine (D4)

Using the same procedure for **A4**, **D3** (7.99 g, 29.26 mmol) was reduced with LAH to

obtain **D4** (4.05 g, 55% yield).

Synthesis of 6-(2,5-dichlorophenyl)hex-5-enoic acid (E1)

Using the same procedure for **C2**, (4-carboxybutyl)triphenylphosphonium bromide (24.6 g, 60 mmol) was reacted with 2,5-dichlorobenzaldehyde (7.50 g, 42.50 mmol) to obtain **E1** (6.37 g, 85% yield).

Synthesis of 6-(2,5-dichlorophenyl)hexanoic acid (E2)

Using the same procedure of **B2**, **E1** (6.37 g, 24.59 mmol) was hydrogenated to obtain **E2** (6.30 g, 99% yield).

Synthesis of 6-(2,5-dichlorophenyl)-N,N-dimethylhexanamide (E3)

Using the same procedure for **B1**, **E2** (6.30 g, 24.13 mmol) was amidated to obtain **E3** (4.72 g, 75% yield).

Synthesis of 6-(2,5-dichlorophenyl)-N,N-dimethylhexan-1-amine (E4)

Using the same procedure for **A4**, **E3** (4.72 g, 16.38 mmol) was reduced with LAH to obtain **E4** (3.30 g, 70% yield).

Synthesis of PAF-Cx copolymers

A typical procedure for PAF-C3 (m:n = 1.00 : 0.96) is as follows. A 100 mL round bottomed flask equipped with a reflux condenser, a magnetic stirrer, and a nitrogen inlet-outlet was charged with perfluoromonomer¹ (1.04 g, 2.00 mmol), **B3** (0.44 g, 1.90 mmol), 2,2'-biyridine (2.14 g, 13.70 mmol), 5 mL of DMAc, and 4 mL of toluene. The mixture was refluxed at 150 °C for 2 h for azeotropic removal of water. The mixture was allowed to cool to 80 °C, to which Ni(cod)₂ (3.77 g, 13.70 mmol) was added. The mixture was stirred for 3 h at 80 °C, cooled to room temperature, and poured dropwise into a large excess of methanol to precipitate a black solid. The crude product was collected by filtration, washed with 6 M HCl, saturated potassium carbonate, and ultrapure water several times to obtain PAF-C3 as a yellowish brown solid (0.92 g, 90% yield).

Quaternization reaction

A typical procedure is as follows. In a 100 mL glass vial, 0.12 g of PAF-C3 copolymer was dissolved in 10 mL of DMAc. To the solution, dimethyl sulfate (5 equimolar to dimethyl amino groups) was added. The mixture was stirred for 48 h at room

temperature. The mixture was poured dropwise into a large excess of water to precipitate a white solid. The product was collected by filtration and dried under vacuum at 60 °C to obtain QPAF-C3 copolymer in methylsulfate ion form (0.15 g, 100% yield).

Membrane preparation

A typical procedure is as follows. QPAF-C3 (0.15 g) was dissolved in 4 mL of NMP and cast onto a flat glass plate at 60 °C to obtain flexible and transparent QPAF-C3 membrane (36 μm thick).

Ion exchange reaction

i) To chloride ion form

Membranes in methylsulfate ion forms were immersed in 1 M HCl for 24 h and washed with ultrapure water several times until the residual water became neutral. Membranes in chloride ion forms were used for titration and mechanical properties measurements.

ii) To hydroxide ion form

Membranes in methylsulfate ion forms were immersed in 1 M KOH at 60 °C for 24 h and washed several times with degassed ultrapure water until the residual water became neutral. Membrane in hydroxide ion forms were used for hydroxide ion conductivity and stability measurements.

Measurements

Dichloromonomers, PAF-Cx copolymers, and QPAF-Cx membranes were characterized by ¹H and ¹⁹F NMR spectra on a JEOL JNM-ECA/ECX500 using CDCl₃ or DMSO-*d*₆ as solvents and TMS as an internal reference. The molecular weight (M_w , M_n , M_w/M_n) was determined by gel permeation chromatography using a Shodex KF-805L column and a Jasco 805 UV detector (270 nm) with CHCl₃ containing 0.05 M triethylamine as eluent. Standard polystyrene samples were used for calibration. Ion exchange capacity (IEC) values of the membranes were determined by Mohr titration method. For water uptake measurement, membranes in hydroxide ion forms were dried in vacuum oven at 60 °C for overnight and weighed to obtain dry weights. The membranes were then immersed in deionized water for 24 h, wiped quickly with a paper to remove the surface water, and weighed immediately to obtain wet weights. *In-plane* hydroxide ion conductivity of the membranes was measured using an AC impedance system (Solartron 1255B, Solartron Inc.) in degassed and deionized water. Prior to the

measurement, the membranes were immersed in 1 M KOH for at least 48 h to ensure complete ion exchange reaction, rinsed thoroughly with degassed and deionized water. The resistances of the membranes were measured using a four-probe conductivity cell. Transmission electron microscopic (TEM) images and dynamic mechanical properties were measured according to our previous work.² SAXS profiles were obtained at 80 °C under a humidified N₂ atmosphere at 30-90% RH using a Nano-Viewer (Rigaku) and Cu(K α) as X-ray source.³ Tensile strengths was investigated by Shimadzu AGS-J 500N universal test machine equipped with a Toshin Kogyo Bethel-3A temperature and humidity controllable chamber. Detailed procedure for these measurements was reported previously.¹⁻⁴

Alkaline stability test

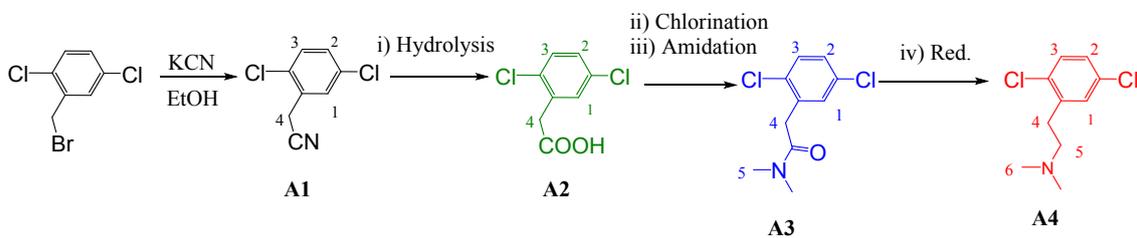
The membranes in hydroxide ion forms were placed in a conductivity measurement cell and the conductivity was measured as 0 h. The membranes fixed in the conductivity cell were immersed in 1 M, 4 M or 8 M KOH aqueous solution at 80 °C in a closed vial for 1000 h (1 M and 4 M) or 568 h (8 M). At the set time, the membranes were washed with and immersed in deionized water for 24 h prior to the conductivity measurement at 40 °C. After the stability test, the membranes were subjected to post-test NMR, TEM and DMA analyses.

Preparation of catalyst coated membrane (CCM) and fuel cell operation

A 50 wt% Pt-loaded catalyst (Pt/CB, TEC10E50E, Tanaka Kikinzoku Kogyo) was used for the cathode and anode sides. The catalyst paste was prepared from the Pt-loaded catalyst with QPAF-C3 ionomer (IEC = 0.98 meq. g⁻¹) as the binder as follows: In a glass vial, a mixture of Pt- catalyst: ethanol: water (1:7:7 by weight) was stirred at 270 rpm for 30 minutes at room temperature. A 5.0 wt% solution of QPAF-C3 (IEC = 0.98 meq. g⁻¹) in ethanol was added to the Pt-catalyst suspension and the mixture was stirred at 270 rpm for 30 min to obtain the catalyst paste. The mass ratio of the dry binder to carbon black (QPAF-C3 ionomer/carbon) was adjusted to 0.8. The CCM was prepared by spraying the catalyst paste onto both sides of QPAF-C3 (1.24 meq. g⁻¹, 36 μ m thick) membrane using a pulse-swirl-spray apparatus. The Pt loading was 0.2 ± 0.02 mg cm⁻² with active geometric area of 4.41 cm². The CCM was immersed in 1 M KOH for 48 h then in deionized water for 24 h for ion exchange reaction. The CCM was sandwiched between two gas diffusion layers for 3 min at 1 MPa and assembled into a single cell consisting of two carbon separator plates. The fuel cell was operated at 60 °C under an ambient pressure with fully humidified H₂ and O₂. The flow rate was 100 mL min⁻¹ for

both H₂ and O₂. The high-frequency resistance (HFR) of the cell was measured with a Kikusui FC impedance meter at 5.0 kHz.

Schemes and Figures



Scheme S1. Synthesis of 2-(2,5-dichlorophenyl)-N,N-dimethylethanamine.

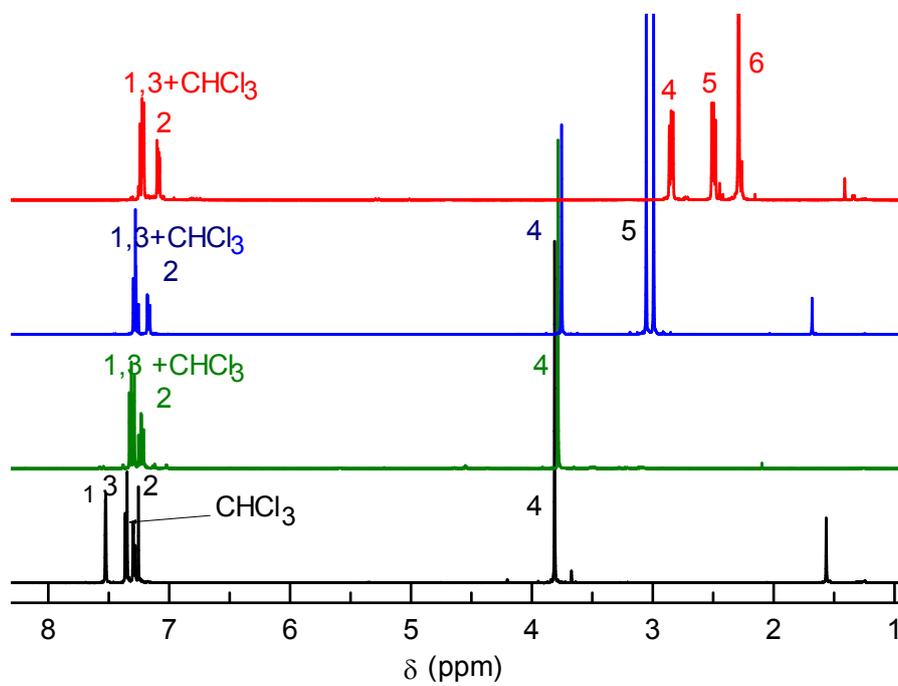
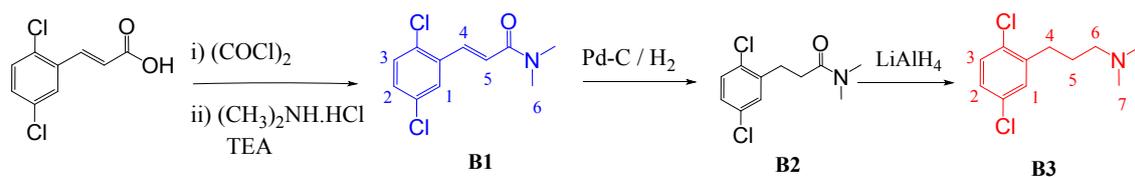


Figure S1. ^1H NMR spectra of A1, A2, A3, and A4.



Scheme S2. Synthesis of 3-(2,5-dichlorophenyl)-N,N-dimethylpropanamine.

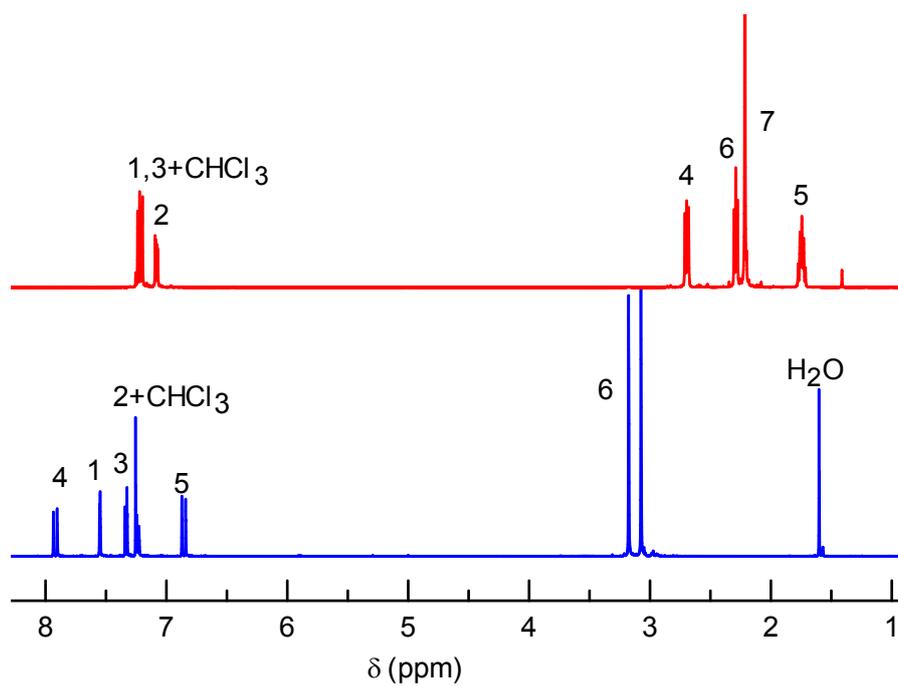
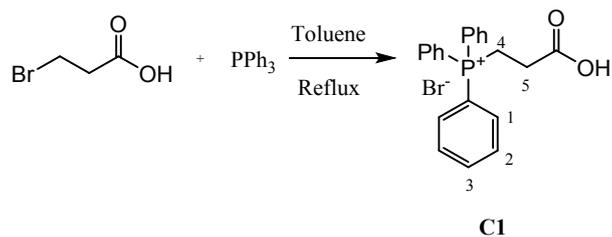


Figure S2. ^1H NMR spectra of **B1** and **B3**.



Scheme S3. Synthesis of (2-carboxyethyl)triphenylphosphonium bromide.

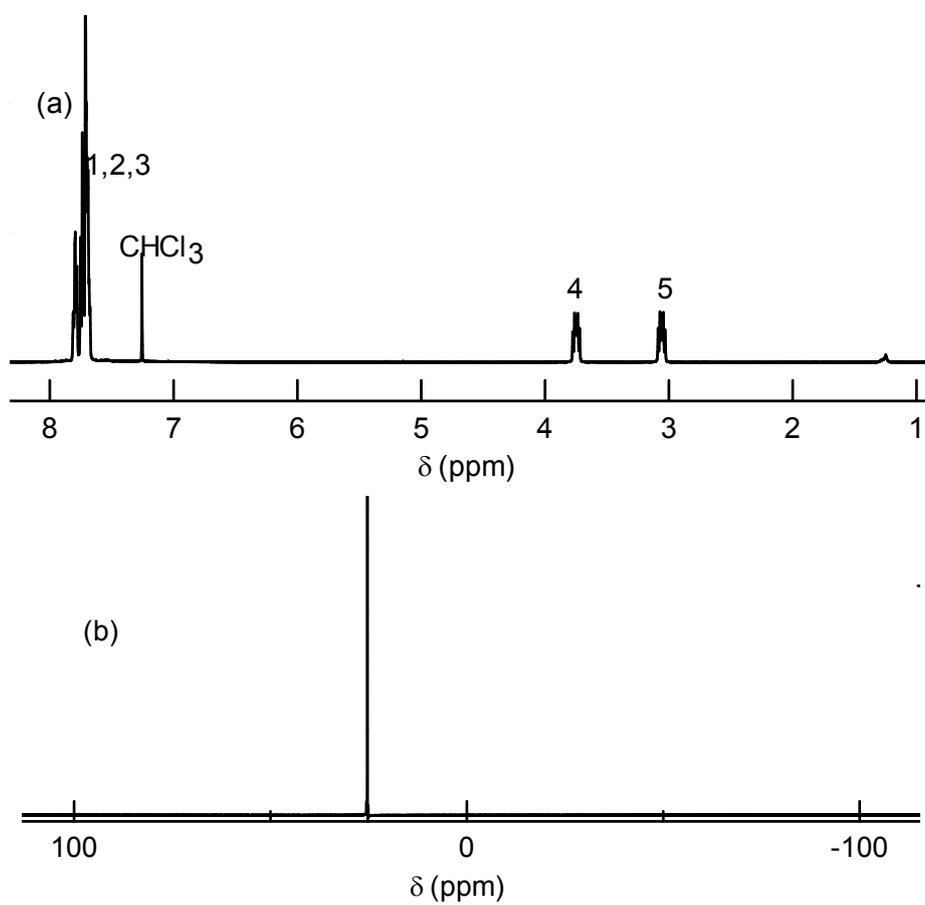
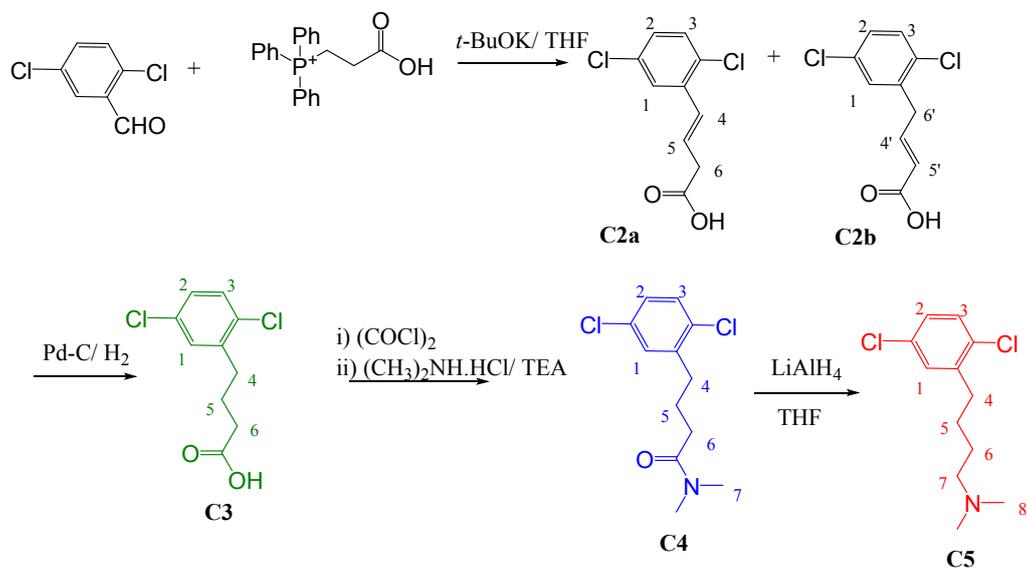


Figure S3. (a) ^1H and (b) ^{31}P NMR spectra of C1.



Scheme S4. Synthesis of 4-(2,5-dichlorophenyl)-N,N-dimethylbutanamine.

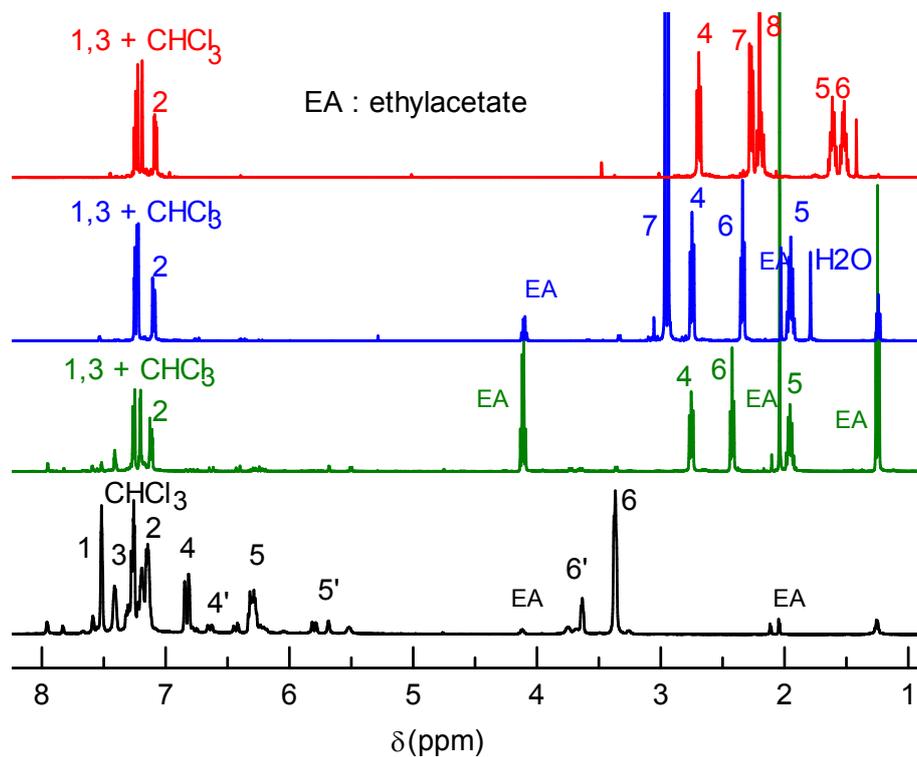
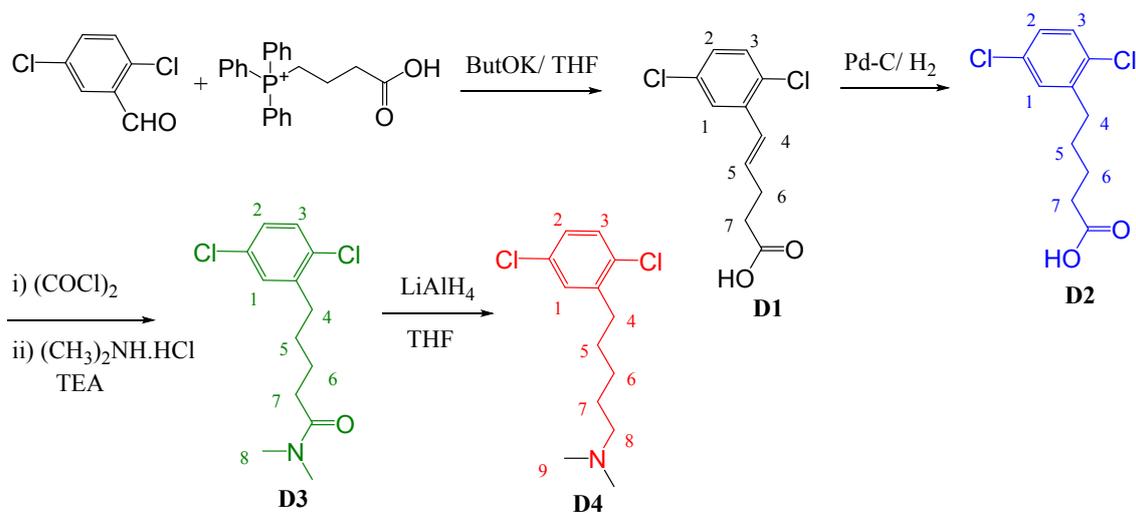


Figure S4. $^1\text{H NMR}$ spectra of C2, C3, C4, and C5.



Scheme S5. Synthesis of 5-(2,5-dichlorophenyl)-N,N-dimethylpentanamine.

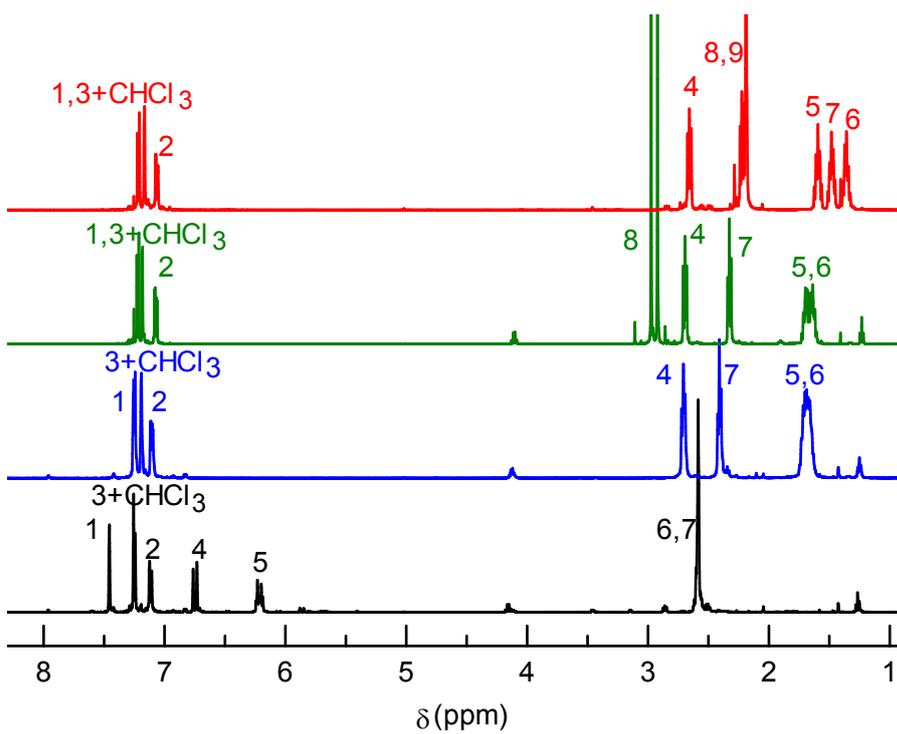
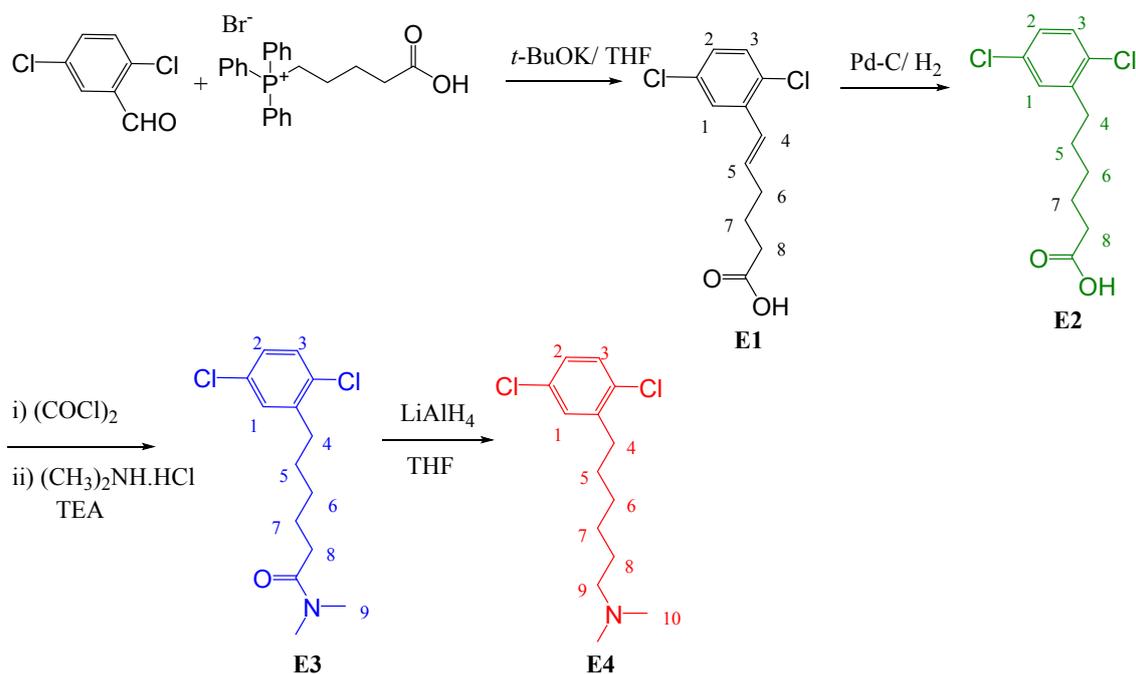


Figure S5. ^1H NMR spectra of D1, D2, D3, and D4.



Scheme S6. Synthesis of 6-(2,5-dichlorophenyl)-N,N-dimethylhexanamine.

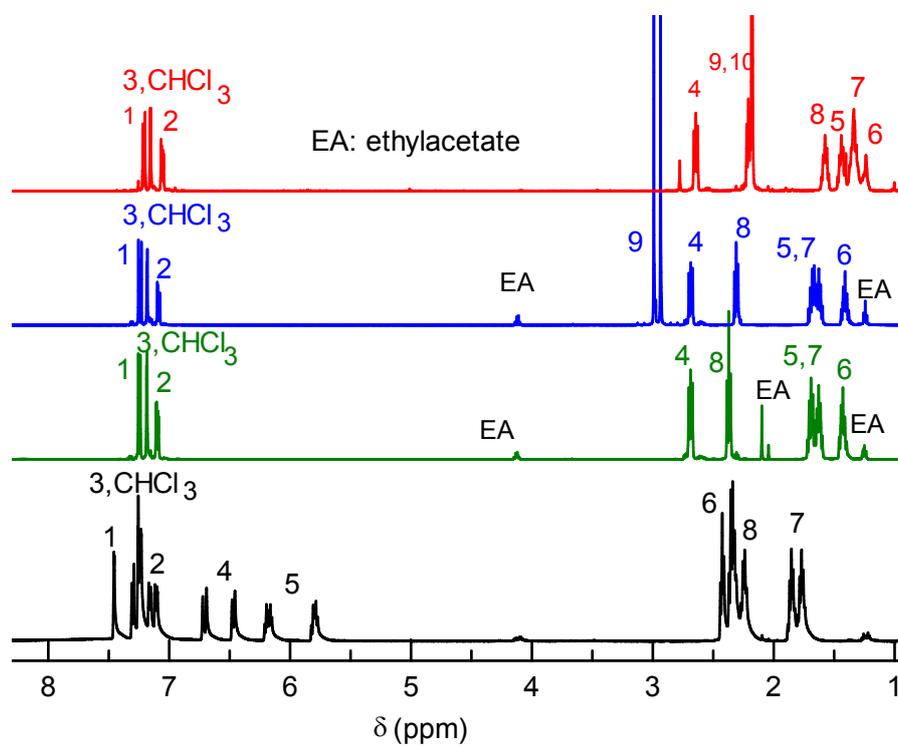


Figure S6. ^1H NMR spectra of **E1**, **E2**, **E3**, and **E4**.

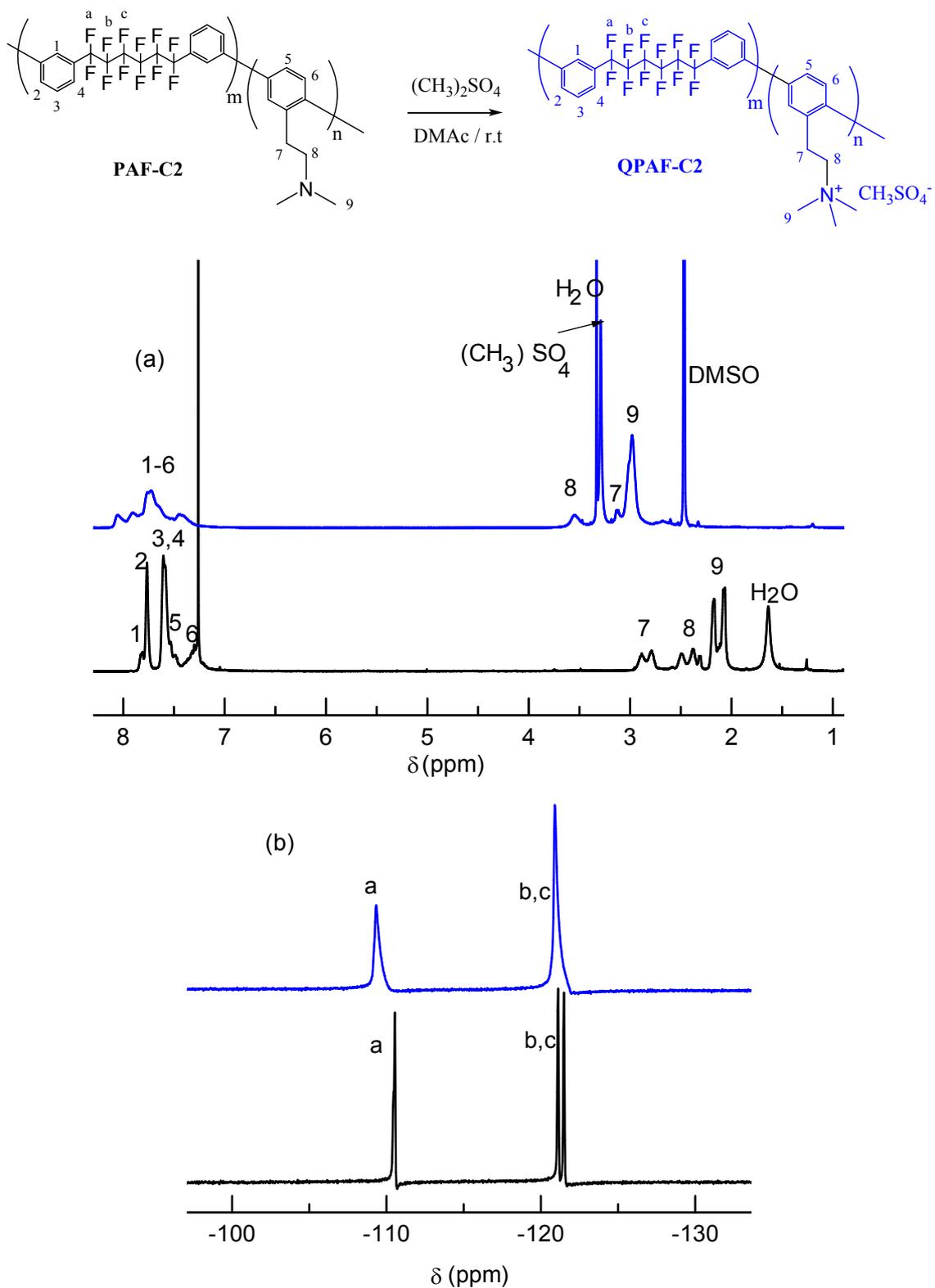


Figure S7. (a) ^1H and (b) ^{19}F NMR spectra of PAF-C2 in CDCl_3 and QPAF-C2 in $\text{DMSO}-d_6$.

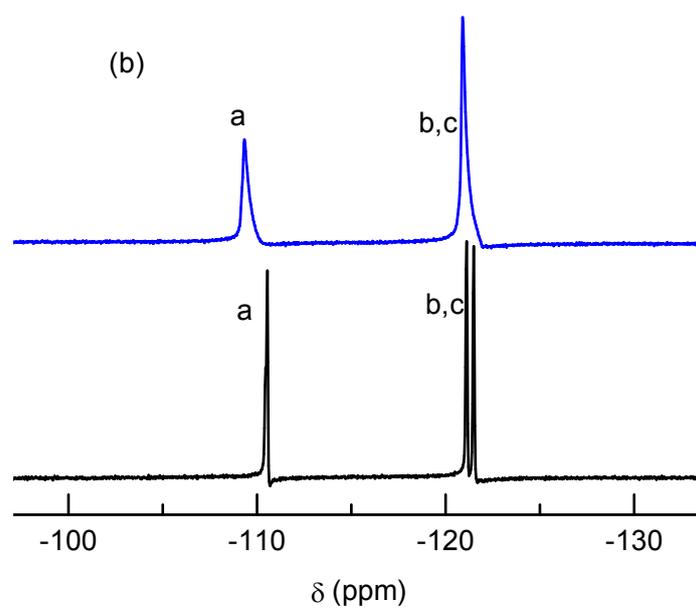
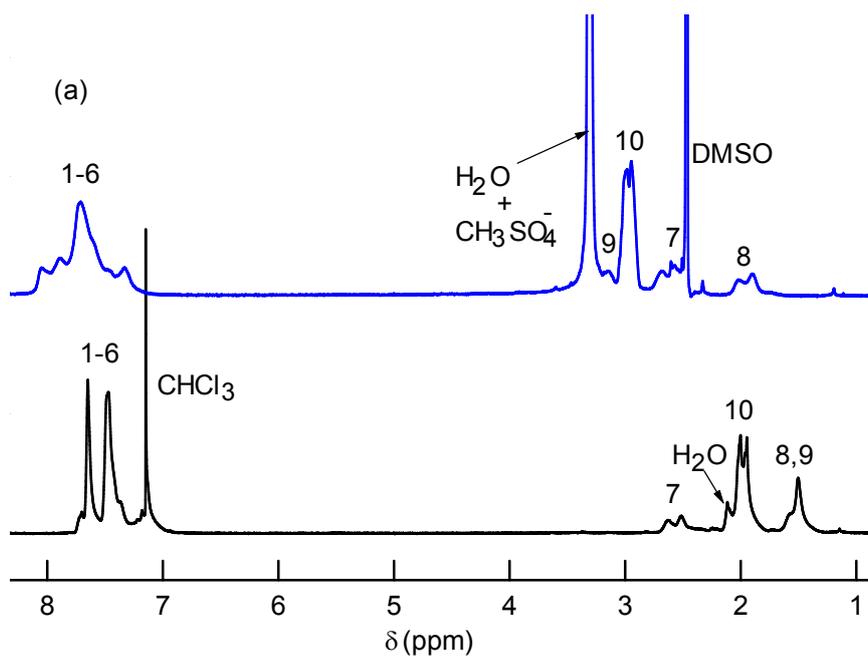
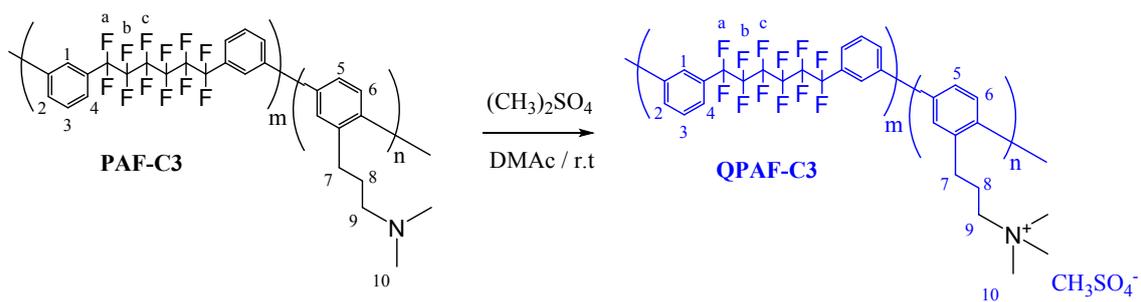


Figure S8. (a) ^1H and (b) ^{19}F NMR spectra of PAF-C3 in CDCl_3 and QPAF-C3 in $\text{DMSO-}d_6$.

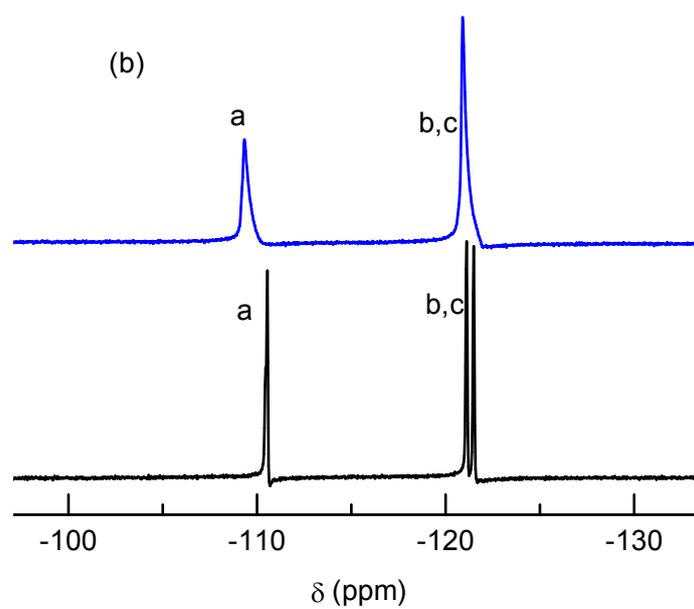
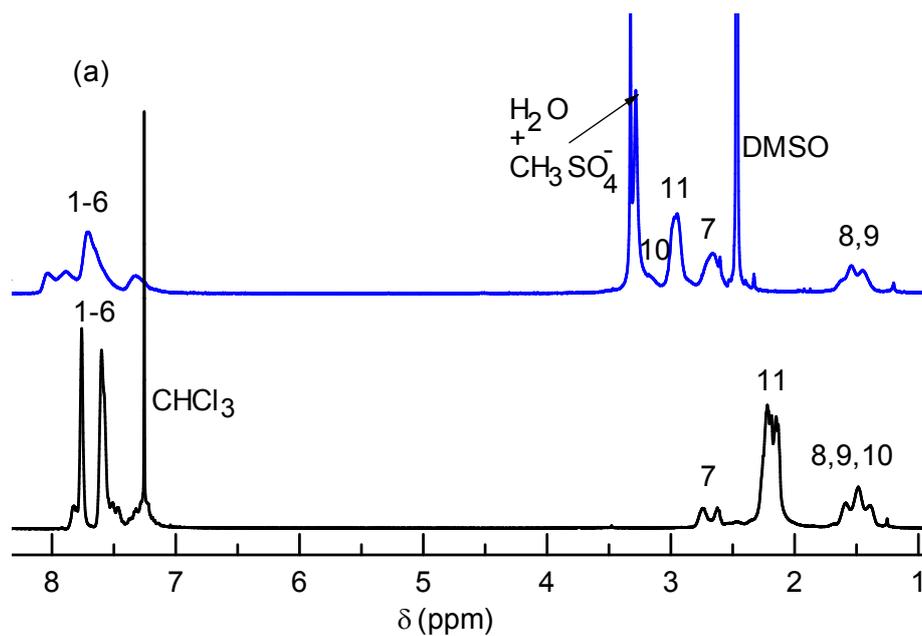
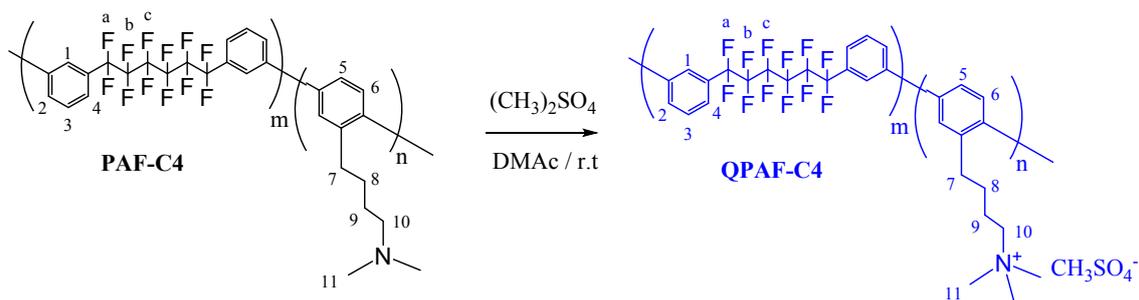


Figure S9. (a) ^1H and (b) ^{19}F NMR spectra of PAF-C4 in CDCl_3 and QPAF-C4 in $\text{DMSO}-d_6$.

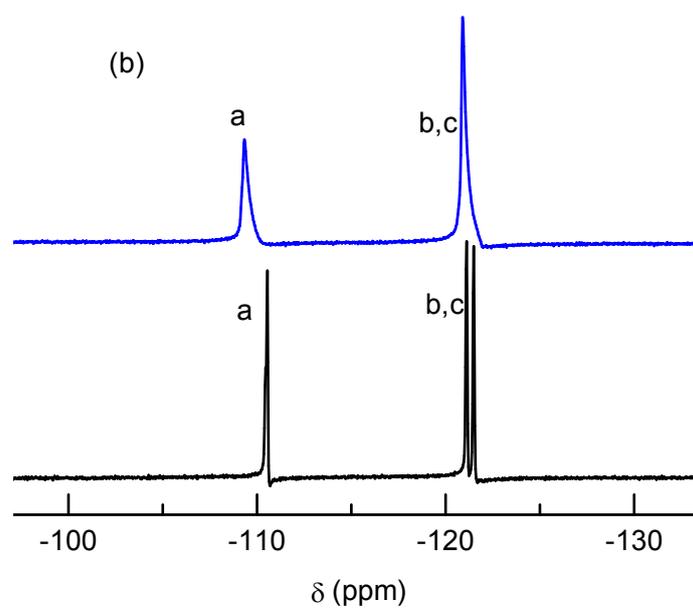
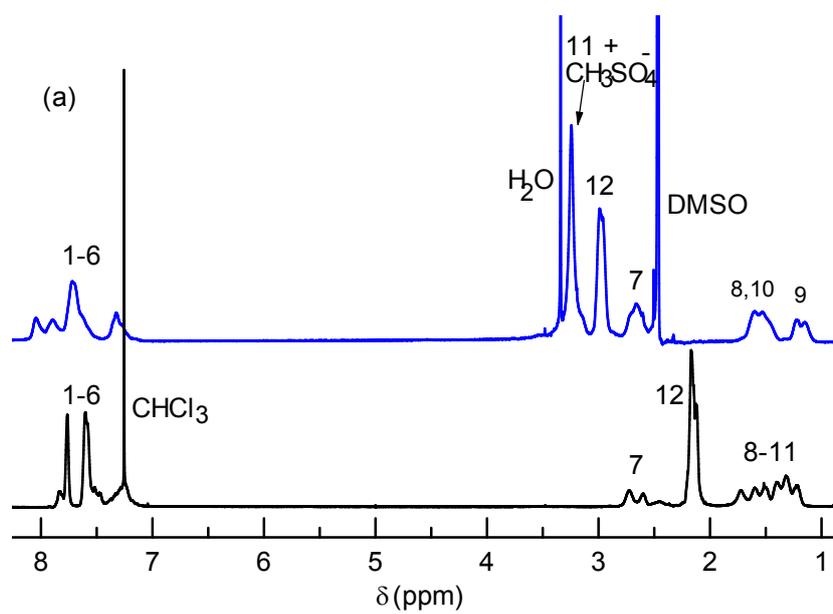
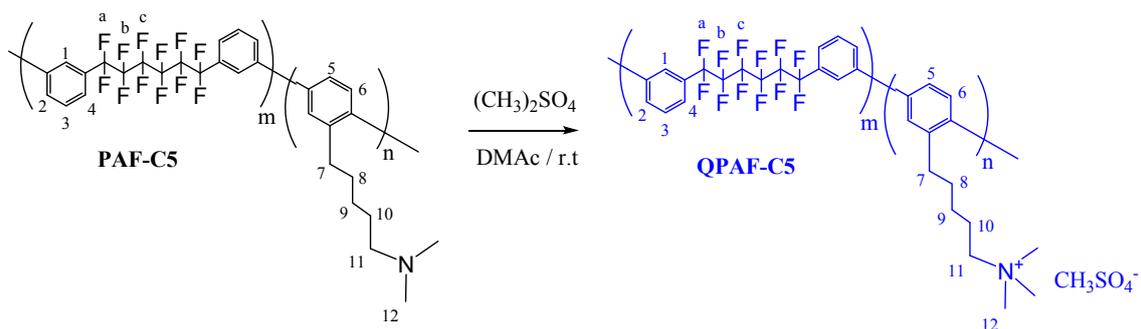


Figure S10. (a) ^1H and (b) ^{19}F NMR spectra of PAF-C5 in CDCl_3 and QPAF-C5 in $\text{DMSO-}d_6$.

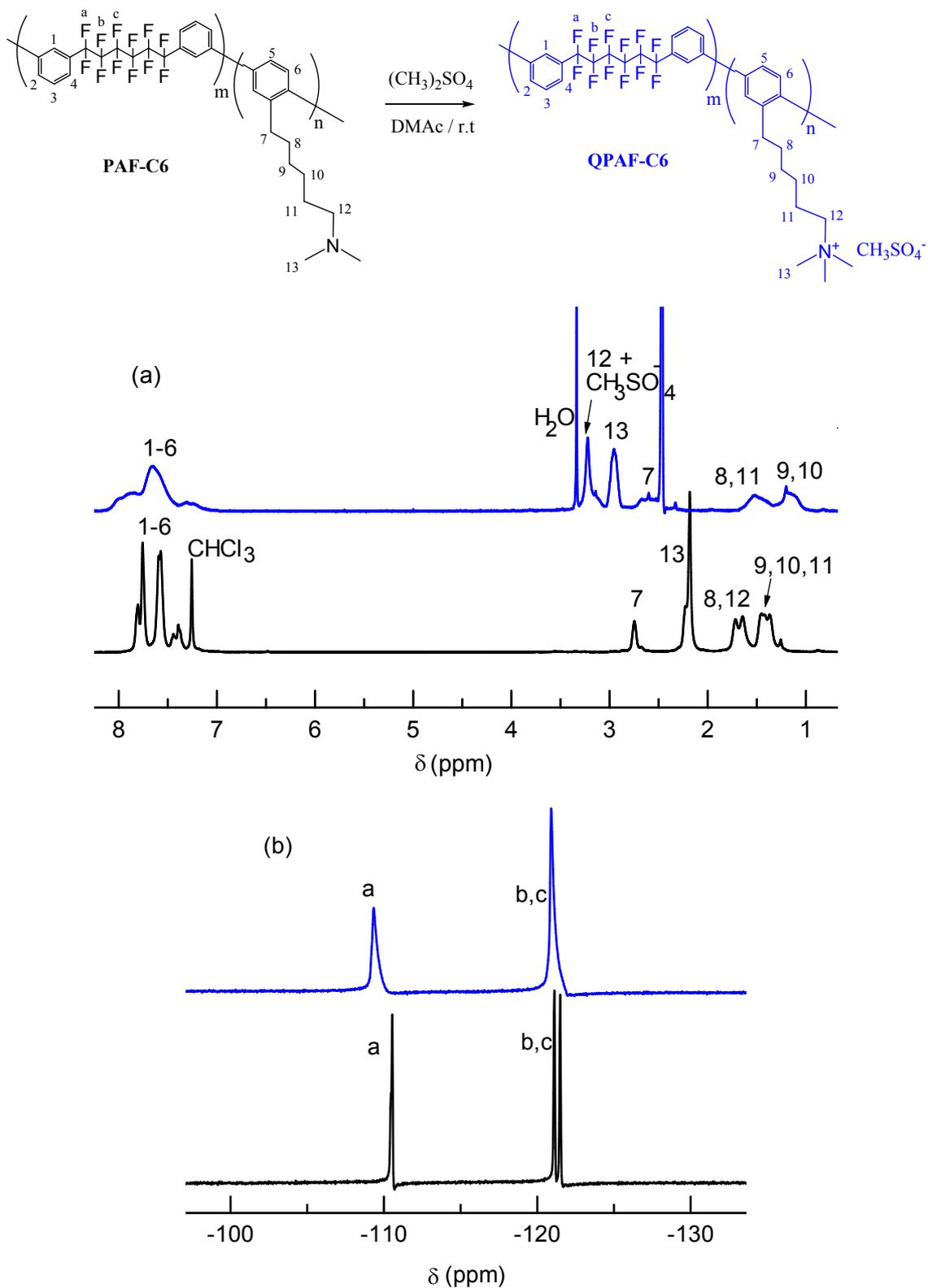
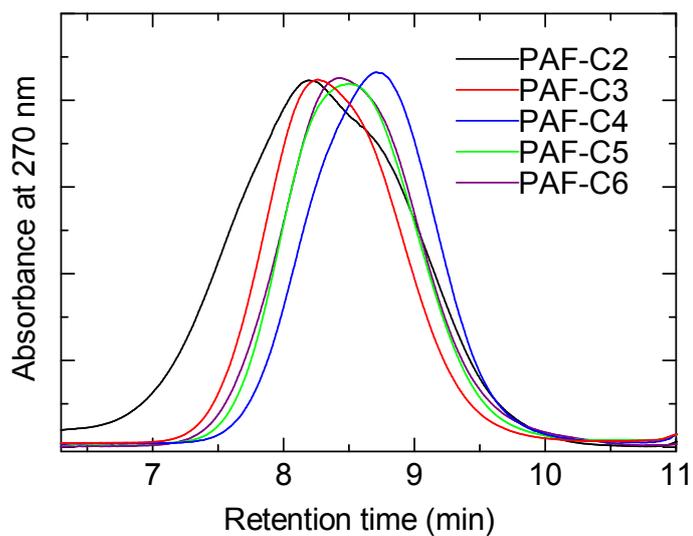


Figure S11. (a) ^1H and (b) ^{19}F NMR spectra of PAF-C6 in CDCl_3 and QPAF-C6 in $\text{DMSO}-d_6$.

Figure S12.
of PAF-Cx
(the peaks were
for clarification).



GPC profiles
copolymers
normalized

Figure S13 Background-subtracted SAXS profiles for QPAF-Cx (IEC = 1.19 meq. g⁻¹) and QPAF-C1 (IEC = 1.26 meq. g⁻¹) as a function of scattering vector (q) from 30% to 90% RH at 40 °C.

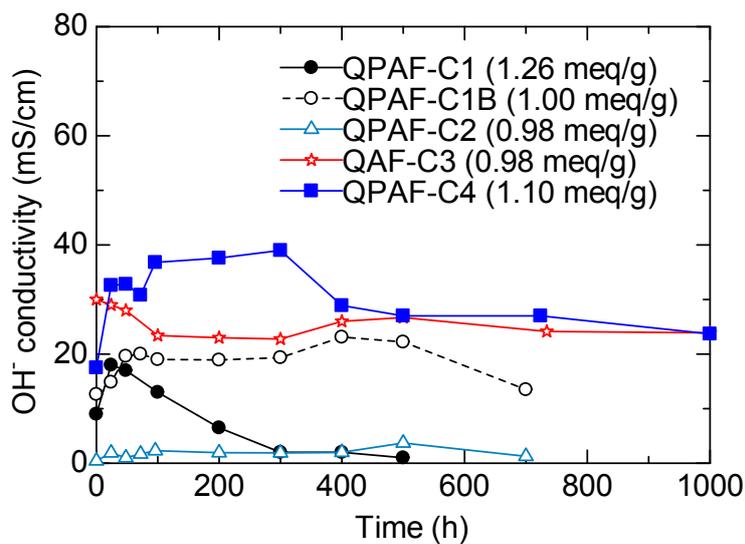
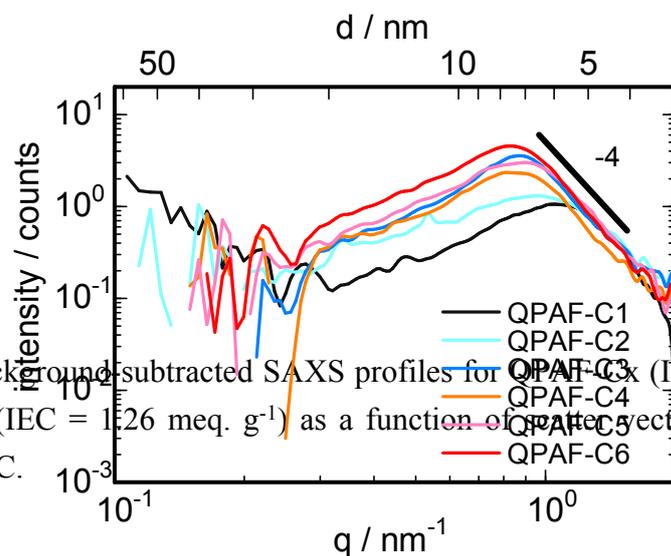


Figure S14 Alkaline stability of QPAF membranes in 1 M KOH at 80 °C. The conductivity was measured at 40 °C.

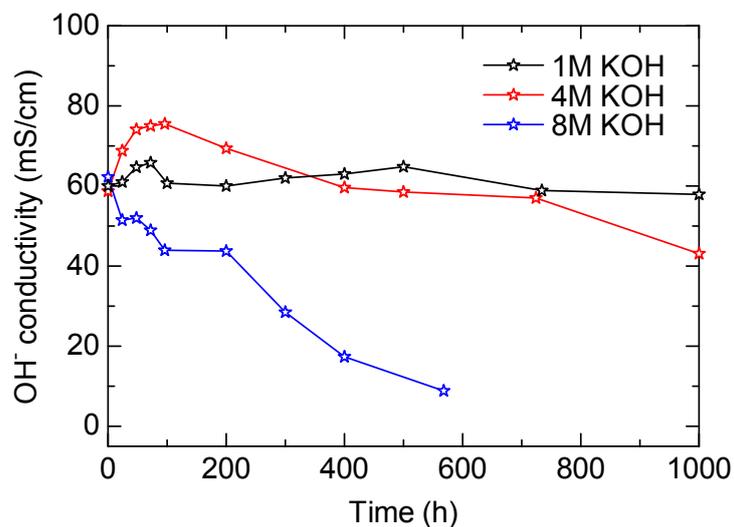


Figure S15 Alkaline stability of QPAF-C3 (IEC = 1.24 meq. g⁻¹) in 1 M, 4 M, and 8 M KOH at 80 °C. The conductivity was measured at 40 °C.

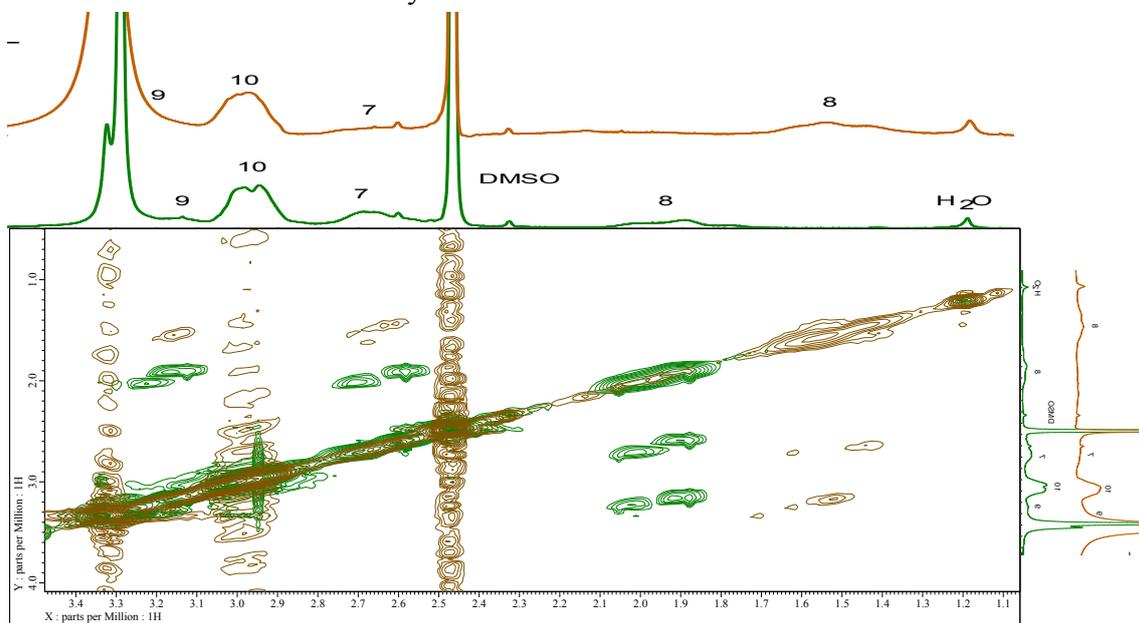


Figure S16 Zoomed-in 2D COSEY NMR spectra of the pristine QPAF-C3 (IEC = 1.24 meq. g⁻¹) (green line) and post-test QPAF-C3 (brown line) membranes after 1000 h in 4

M KOH at 80 °C in DMSO- d_6 .

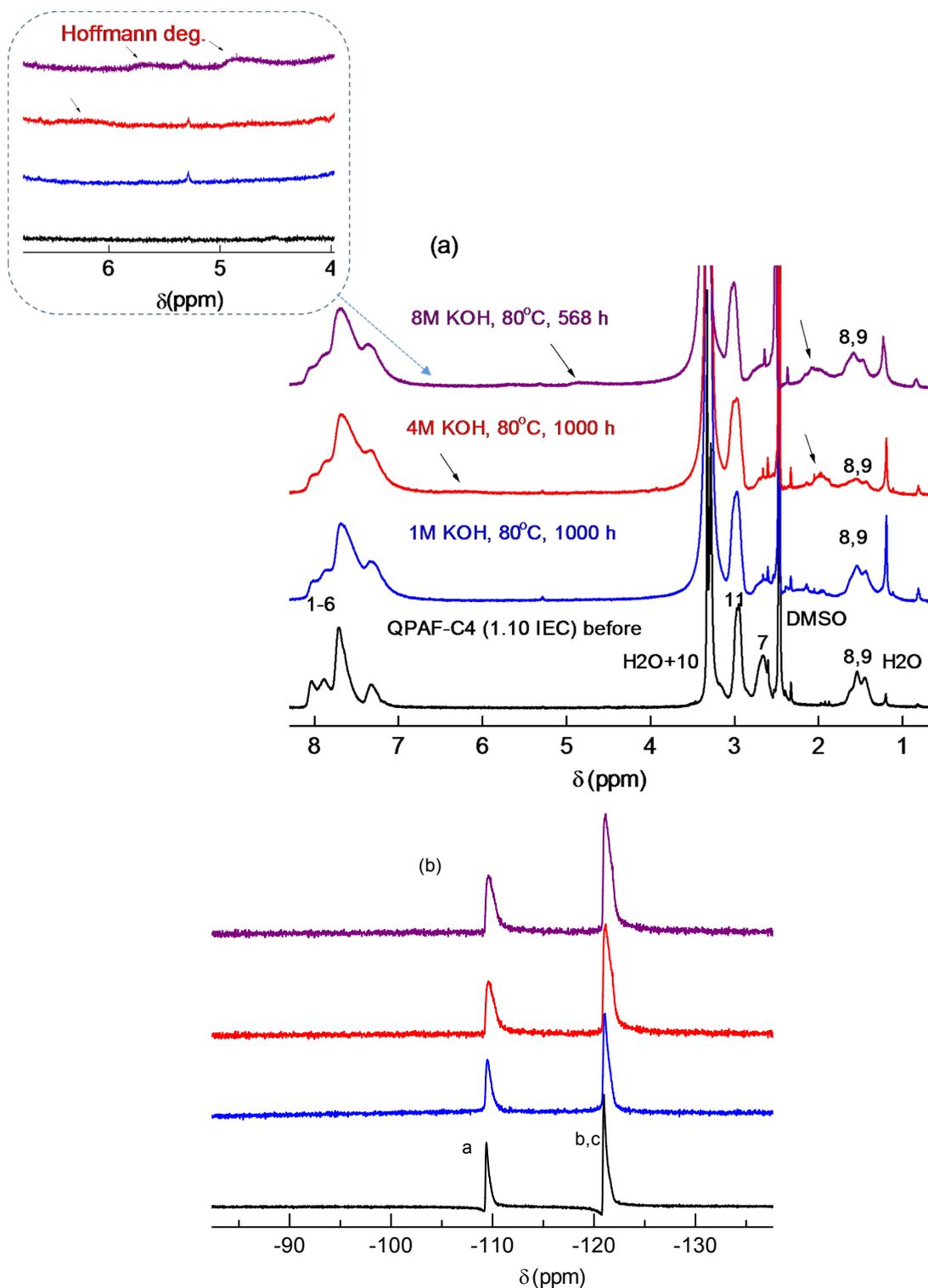


Figure S17 (a) ^1H and (b) ^{19}F NMR spectra of QPAF-C4 membrane (IEC = 1.10 meq. g^{-1}) before and after the alkaline stability test in DMSO- d_6 .

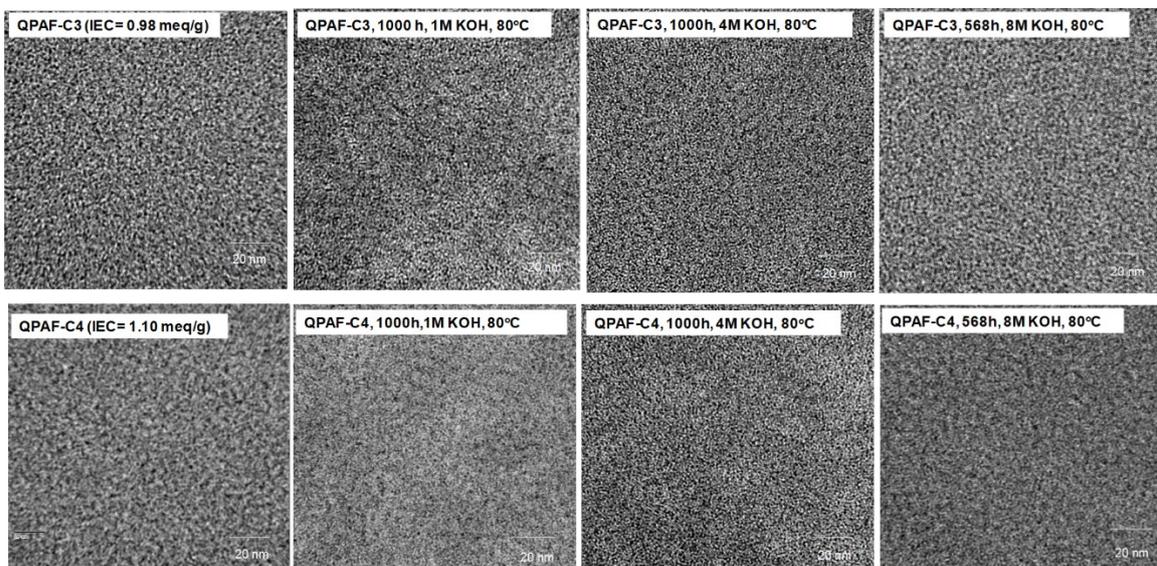


Figure S18 TEM images of the QPAF-C3 (IEC = 0.98 meq. g⁻¹) and QPAF-C4 (IEC = 1.10 meq. g⁻¹) membranes before and after the alkaline stability tests.

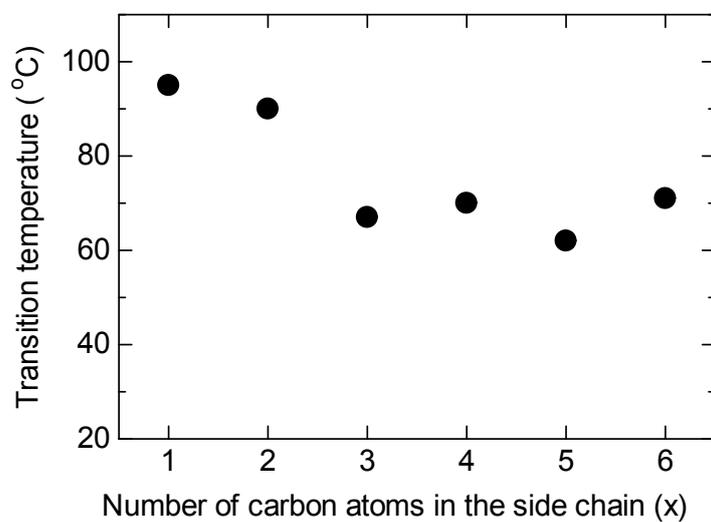


Figure S19 Transition temperature in tan δ curves (Figure 10) of QPAF-C_x as a function of number of carbon atoms in the side chain (x).

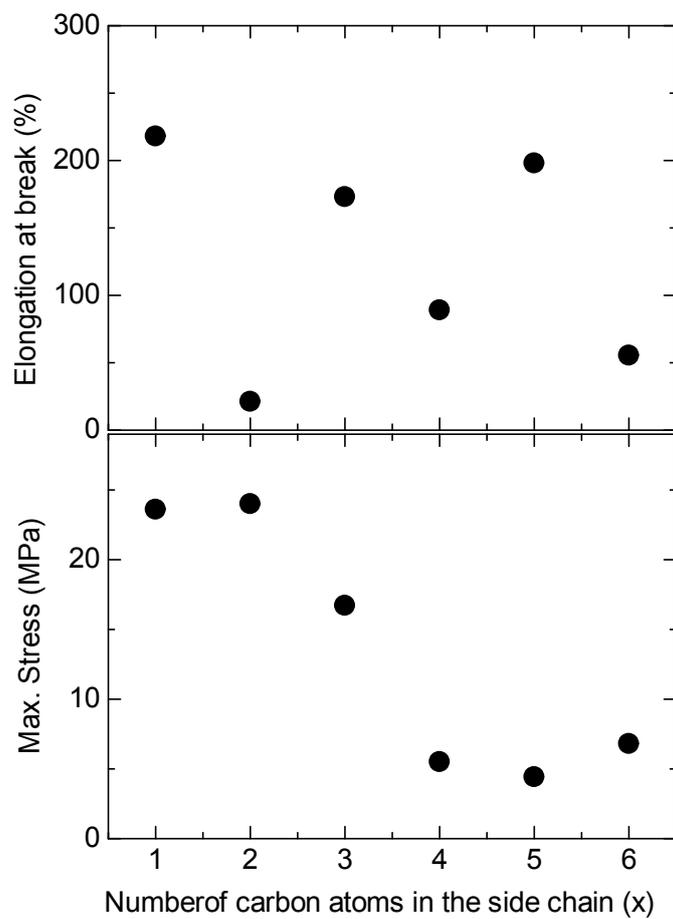


Figure S20 Maximum stress and elongation at break of QPAF-C_x membranes as a function of number of carbon atoms in the side chain (x).

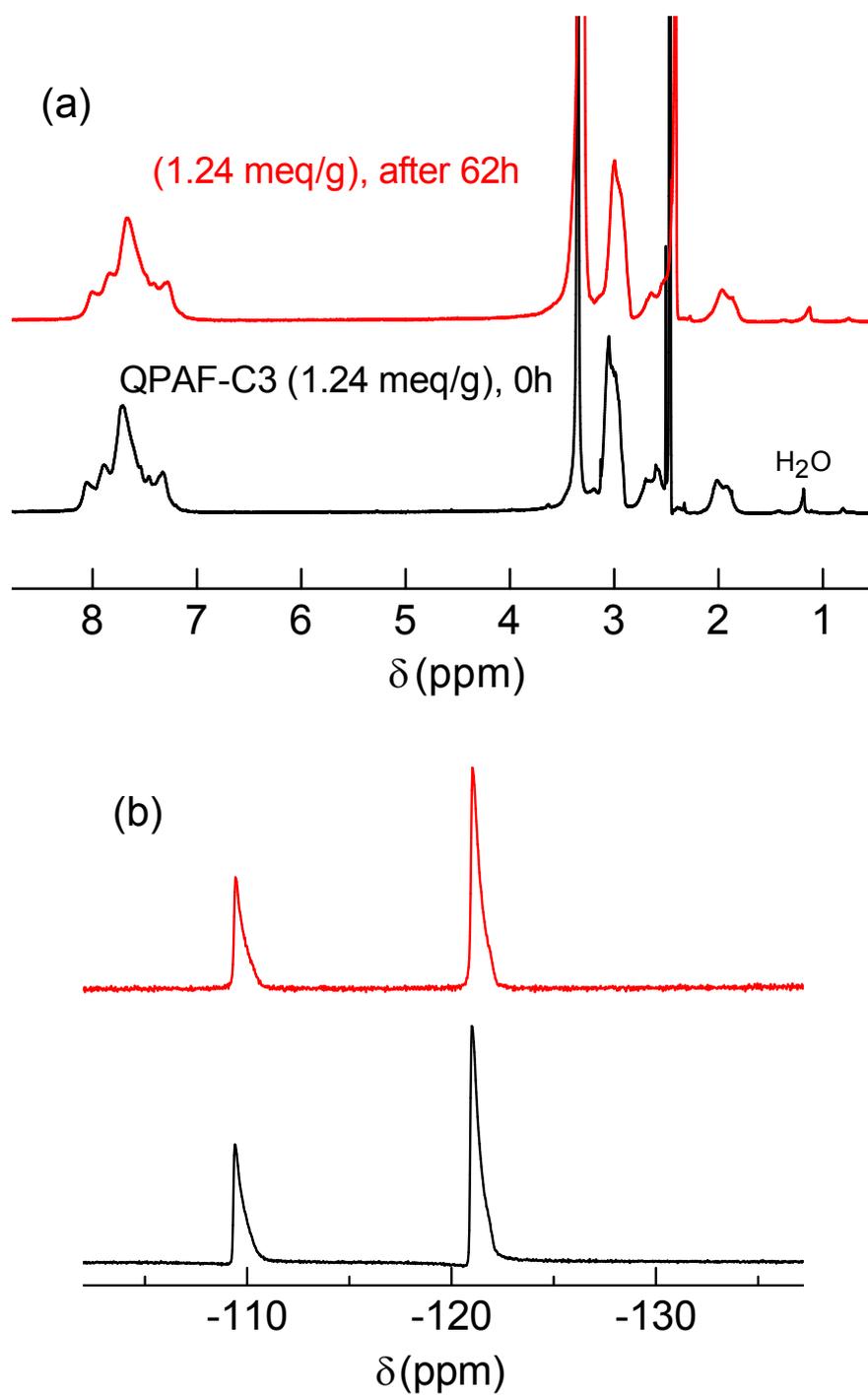


Figure S21 (a) ^1H and (b) ^{19}F NMR spectra of QPAF-C3 membranes before and after the fuel cell durability test at constant current density (0.05 A cm^{-2}).

References

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