

## Supplementary information

### **Poly(arylene piperidinium) terpolymer membranes with dual piperidinium cations and semi-fluoroalkyl pendants for anion exchange membrane water electrolyzers**

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## Materials

Triphenylphosphine (> 95%, TCI), 1H, 1H, 2H, 2H-nonafluorohexyl iodide (> 99%, TCI), 1H, 1H, 2H, 2H-heptadecafluorodecyl iodide (> 98%, TCI), 2,5-dichlorobenzaldehyde (>98%, TCI), 1H, 1H, 2H, 2H-tridecafluoro-n-octyl iodide (> 97%, TCI), K<sub>2</sub>CO<sub>3</sub> (> 99%, TCI), tetrabutylammonium bromide (TBAB) (> 99%, TCI), 1,4-dioxane (> 99%, TCI), Palladium/carbon (10% Pd) (TCI), 4,4'-(hexafluoroisopropylidene)dianiline (> 98%, TCI), N-chlorosuccinimide (NCS) (> 98%, TCI), 4-(*tert*-butoxy carbonyl) piperidine methanol (> 98%, TCI), Na<sub>2</sub>SO<sub>4</sub> (> 98.5%, Kanto chemical), acetonitrile (> 99%, Kanto chemical), diethyl ether (> 99%, Kanto chemical), tetrahydrofuran (THF) (> 99%, Kanto chemical), iodine (> 99%, Kanto chemical), bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)<sub>2</sub>) (> 95%, Kanto Chemical), N,N-dimethylacetamide (DMAc) (> 99%, Kanto Chemical), dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) with 0.03% tetramethylsilane (TMS) (100 atom% D, Kanto chemical), chloroform-d<sub>3</sub> (CDCl<sub>3</sub>) with 0.03% TMS (100 atom% D, Kanto chemical) were used as received. Other chemicals were of commercially available grade and used as received. N,N-dimethylacetamide was purified with a solvent refining apparatus before use for the polymerization.

## Synthesis of 1,4-dichloro(semi-fluoroalkyl)benzene monomers (3a-c)

### *Synthesis of (3,3,4,4,5,5,6,6,6-nonafluorohexyl) triphenyl phosphonium iodide (1a)*

A 100 mL round bottomed flask was charged with triphenylphosphine (3.86 g, 14.71 mmol) and acetonitrile (17 mL). To the solution, 1H,1H, 2H, 2H-nonafluorohexyl iodide (5.0 g, 13.37 mmol) in 10 mL acetonitrile was added slowly. The reaction mixture was refluxed for 48 h under N<sub>2</sub> atmosphere. Then, the mixture was concentrated under reduced pressure and diethyl ether was added to the viscous oil. The mixture was left overnight at

room temperature and subjected to sonication. The resulting milky white suspension was filtered and crude white product was washed with hexane (three-fold) followed by drying in vacuum at 50 °C to obtain 1a (5.60 g) in 55% yield.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.08 (q, 2H), 2.55 (m, 2H), 7.7-7.88 (15H).

$^{19}\text{F}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.9, -113.2, -123.6, -125.8.

$^{31}\text{P}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  26.1.

***Synthesis of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) triphenyl phosphonium iodide (1b) and (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl) triphenyl phosphonium iodide (1c)***

Precursor 1b and 1c were synthesized in a similar manner to 1a and obtained in 83% (5.52g) and 51% (3.62g) yields, respectively.

1b:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.13 (q, 2H), 2.57 (m, 2H), 7.7-7.91 (15H).

$^{19}\text{F}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.7, -112.9, -121.7, -122.6, -122.8, -126.1.

$^{31}\text{P}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  26.1.

1c:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.07 (q, 2H), 2.54 (m, 2H), 7.7-7.89 (15H).

$^{19}\text{F}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.7, -112.9, -21.5, -121.9, -122.6, -122.7, 126.1.

$^{31}\text{P}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  26.1.

***Synthesis of (E/Z)-1,4-dichloro-2-(4,4,5,5,6,6,7,7,7-nonafluorohept-1-en-1-yl) benzene (2a)***

To a 3 neck round bottomed flask, 2,5-dichlorobenzaldehyde (0.96 g, 5.50 mmol), (3,3,4,4,5,5,6,6,6-nonafluorohexyl) triphenyl phosphonium iodide (3.18 g, 5.00 mmol),  $\text{K}_2\text{CO}_3$  (1.04 g, 7.50 mmol) in 0.3 mL of degassed water, and 10 mL of 1,4-dioxane were

combined. Then, vacuo/nitrogen cycles were repeated three times and the flask was shifted to a pre-heated oil bath. The reaction was allowed for 4 h at 95 °C under N<sub>2</sub> atmosphere. The reaction was quenched with excess of water and product was extracted with ethyl acetate three times. Combined organic layer was washed with water (two-fold), and dehydrated over Na<sub>2</sub>SO<sub>4</sub> followed by evaporation under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane) to obtain 2a as colorless liquid (1.72 g) in 85% yield.

***Synthesis of (E/Z)-1,4-dichloro-2-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoronon-1-en-1-yl) benzene (2b) and (E/Z)-1,4-dichloro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundec-1-en-1-yl) benzene (2c)***

Precursors 2b and 2c were obtained as colorless liquid in 47% (1.19 g) and 79% (2.88 g) yields, respectively, following the procedure similar to 2a.

***Synthesis of 1,4-dichloro-2-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl) benzene (3a)***

To a 100mL single flask, (E/Z)-1,4-dichloro-2-(4,4,5,5,6,6,7,7,7-nonafluorohept-1-en-1-yl)benzene precursor (1.50 g, 3.70 mmol) and ethyl acetate (8.50 mL) were added. To the mixture was added Pd-C powder (0.37 g) followed by vacuo/nitrogen cycle. Hydrogenation reaction was performed for 48 h at 30 °C under H<sub>2</sub> gas atmosphere. Then, the catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane) to obtain 3a as colorless liquid (0.63 g) in 42% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.94 (q, 2H), 2.15 (spt, 2H), 2.79 (t, 2H), 7.16 (dd, 1H), 7.21 (d, 1H), 7.29 (d, 1H).

<sup>19</sup>F NMR (500 MHz, CDCl<sub>3</sub>) δ -81.02, -114.34, -124.34, -126.00.

***Synthesis of 1,4-dichloro-2-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl) benzene (3b) and 1,4-dichloro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl) benzene (3c)***

Hydrogenation reaction of 3b and 3c was performed following the procedure opted for 3a to give 3b as colorless liquid (2.97 g) in 94% and 3c as white crystalline solid (2.59 g) in 96% yields, respectively.

3b:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.94 (q, 2H), 2.14 (spt, 2H), 2.79 (t, 2H), 7.16 (dd, 1H), 7.21 (d, 1H), 7.29 (d, 1H).

$^{19}\text{F}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.76, -121.90, -122.85, -123.41, -126.10.

3c:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.94 (q, 2H), 2.14 (spt, 2H), 2.79 (t, 2H), 7.16 (dd, 1H), 7.21 (d, 1H), 7.29 (d, 1H).

$^{19}\text{F}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.70, -114.09, -121.66, -121.86, -122.65, -123.33, -126.05.

**Synthesis of di-*tert*-butyl 4,4'-((2,7-dichloro-9H-fluorene-9,9-diyl)bis(methylene)) bis(piperidine-1-carboxylate) (4b)**

***Synthesis of tert-butyl 4-(iodomethyl) piperidine-1-carboxylate (4a)***

A 250 mL round bottomed flask was charged with 4-(*tert*-butoxy carbonyl) piperidine methanol (10.00 g, 46.45 mmol), imidazole (2.85 g, 41.80 mmol), triphenylphosphine (14.62 g, 55.74 mmol), and tetrahydrofuran (65 mL). The flask was shifted to an ice bath upon getting transparent homogeneous solution. To the mixture was added iodine (14.16 g, 55.74 mmol) in THF (33 mL) dropwise at 0-5 °C under  $\text{N}_2$  environment. The reaction was allowed for 0.5 h at 0-5 °C and 4 h at RT. The reaction was quenched with  $\text{NaHSO}_3$  (5.83 g, 55.74 mmol) in 50 mL of water. The product was extracted with ethyl acetate,

combined organic layer was washed with brine (two-fold) and water (two-fold) followed by drying over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane: ethyl acetate = 9: 1 as eluent) to obtain 4a (10.65 g) as colorless liquid in 70% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.12 (m, 2H), 1.43 (s, 9H), 1.58 (m, 1H), 1.80 (d, 2H), 2.66 (m, 2H), 3.07 (d, 2H), 4.09 (d, 2H).

<sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 13.61, 28.51, 32.63, 38.67, 79.50, 154.68.

***Synthesis of di-tert-butyl 4,4'-((2,7-dichloro-9H-fluorene-9,9-diyl)bis(methylene))bis(piperidine-1-carboxylate) (4b)***

A 100 mL 3 neck round bottom flask equipped with N<sub>2</sub> inlet/outlet was charged with 2,7-dichlorofluorene (2.89 g, 12.30 mmol), 4a (10.40 g, 31.98 mmol), TBAB (1.19 g, 3.69 mmol), and DMSO (44 mL). To the transparent homogeneous solution, three vacuo/nitrogen cycles were performed and 50% NaOH (1.18 g, 29.50 mmol) aq. was added dropwise followed by vacuo/nitrogen cycle. The reaction was allowed for 40 h at 30 °C. The reaction was quenched by adding 100 mL of water and the product was extracted with ethyl acetate three times. Combined organic layer was washed with brine (two-fold), water (two-fold), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The crude mass obtained was dissolved in hexane and ethyl acetate mixture (4:1) with vigorous stirring followed by sonication. The resulting dispersion was filtered through cotton plug and the filtrate was concentrated. The concentrated crude product was purified by silica gel column chromatography (hexane: ethyl acetate= 4:1) to obtain 4b (6.96 g) slightly reddish crystalline solid in 90% yield (quant.), which was further purified by recrystallization from dichloromethane.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.62 (m, 2H), 0.79 (8H), 1.36 (s, 18H), 1.94 (d, 4H), 2.20

(m, 4H), 3.70 (4H), 7.29 (s, 2H), 7.33 (d, 2H), 7.528 (d, 2H).

$^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  28.74, 32.23, 33.49, 48.05, 54.42, 79.21, 121.21, 123.82, 127.96, 133.44, 138.49, 151.84, 154.66.

## Measurements

### *Characterization of materials and membranes*

$^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ , and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JNM-ECA/ECX500 using deuterated chloroform ( $\text{CDCl}_3$ ), and/or deuterated dimethyl sulfoxide ( $\text{DMSO-d}_6$ ) as solvent. Tetramethyl silane (TMS) was used as an internal reference.

Viscosity of the quaternized terpolymers was measured in DMAc at 25 °C on Anton Paar MCR302. Reduced ( $\eta_{\text{red}}$ ) and inherent viscosity ( $\eta_{\text{inh}}$ ) ( $\text{dL g}^{-1}$ ) were calculated as follows:

$$\eta_{\text{red}} = \frac{(\text{Vis}_{\text{solution}} - \text{Vis}_{\text{solvent}}) - 1}{\text{concentration}} \quad (\text{S1})$$

$$\eta_{\text{inh}} = \frac{\ln\left(\frac{\text{Vis}_{\text{solution}}}{\text{Vis}_{\text{solvent}}}\right)}{\text{concentration}} \quad (\text{S2})$$

Intrinsic viscosity ( $\eta$ ) ( $\text{dL g}^{-1}$ ) was calculated by extrapolating  $\eta_{\text{red}}$  and  $\eta_{\text{inh}}$  to zero concentration and considering an intersection in y-axis of plot between concentration and  $\eta$ .

For transmission electron microscopy, membrane samples were stained with tetrachloroplatinate ions using 0.5 M  $\text{K}_2\text{PtCl}_4$  aqueous solution. Membrane samples were thoroughly rinsed with deionized water (DI) and vacuum dried at 60 °C for 24 h. The membrane samples were embedded in epoxy resin, sectioned to 50 nm thickness using Leica microtome Ultracut UCT and placed on a copper grid. Images were captured on Hitachi H-9500 transmission electron microscope with an accelerating voltage of 200 kV.

Small angle X-ray scattering (SAXS) profiles of the membranes were obtained for chloride counter anion form on Nano Viewer (Rigaku) with Cu(K $\alpha$ ) as an X-ray source. SAXS profiling was performed at 40 °C in humidified nitrogen and humidity range was from 30 to 90%. Before the measurement, membrane samples were equilibrated for 2 h at the set humidity. The wavelength of Cu(K $\alpha$ ) was 1.542 Å, and the scattering vector ( $q$ ) was calculated as:

$$q = \frac{4\pi \sin(\theta)}{\lambda} \quad (\text{S3})$$

The characteristic distance ( $d$ ) between the scattering center was calculated using Bragg's law:

$$d = \frac{2\pi}{q} \quad (\text{S4})$$

Dynamic mechanical analysis (DMA) for membrane samples of dimension 5 x 30 mm in chloride ion form was done under controlled temperature and humidity conditions on an ITK DVA-225 dynamic viscoelastic analyzer. Temperature dependent storage modulus ( $E'$  (Pa)), loss modulus ( $E''$  (Pa)), and  $\tan \delta$  ( $E''/E'$ ) were measured at 60% RH and 10 Hz from 30 °C to 90 °C at a heating rate of 1 °C min<sup>-1</sup>. Humidity dependence of  $E'$ ,  $E''$ , and  $\tan \delta$  was also analyzed at 80 °C and 10 Hz in humidity range of 0% to 90% RH at a humidifying rate of 1% RH min<sup>-1</sup>.

Tensile strength of dumbbell shaped membrane samples (12 x 2 mm) in chloride ion form was measured using Shimadzu universal testing instrument Autograph AGS-J500N equipped with a temperature and humidity controllable chamber. Measurements were performed at 80 °C and 60% RH at a stretching rate of 10 mm min<sup>-1</sup>. Prior to the test, samples were equilibrated under the test conditions for 3 h.

### **Hydroxide ion conductivity measurement and physicochemical characterization for**



## membranes

### *Hydroxide ion conductivity measurement ( $\sigma$ )*

The hydroxide ion conductivity of the membrane samples was measured in degassed, DI water (18 M $\Omega$ ) at 30, 40, 50, 60, 70, and 80 °C. AC impedance spectra were obtained using 4-probe conductivity cell connected to an AC impedance spectrometer (Solartron 1255B, Solartron Inc.) in the frequency range from 1 to 10<sup>5</sup> Hz. Membrane area resistance ( $R^m$  ( $\Omega$ )) was calculated from the real axis of the impedance plot. Hydroxide ion conductivity was calculated using the following equation:

$$\sigma = \frac{L^m}{R^m \times A} \quad (\text{S5})$$

where,  $L^m$ , and  $A$  are the cross-section area of the membrane (cm<sup>2</sup>) and distance between two reference electrodes (cm), respectively.

### *Water uptake (WU), and swelling ratios measurement*

For the measurements, membrane samples of 1 x 3 cm were vacuum dried at 60 °C for 24 h. Then, the dried membrane samples were immersed in DI water for 24 h at 30 °C. The water uptake, as well as the in-plane and through-plane swelling of the membranes in chloride ion form, were calculated using the following equations:

$$WU (\%) = \frac{W_w - W_d}{W_d} \times 100 \quad (\text{S6})$$

$$\text{Swelling ratio } (\%) = \frac{V_w - V_d}{V_d} \times 100 \quad (\text{S7})$$

where,  $W_w$  and  $W_d$  are weights of membrane sample in wet and dry states, respectively;  $V_w$  and  $V_d$  are the volume of the membrane under wet and dry conditions, respectively.

### *Ion exchange capacity (IEC)*

Classical Mohr's method was used to estimate IEC values. Vacuum dried membrane sample (ca. 20 mg) in chloride ion form was equilibrated in 0.2 M NaNO<sub>3</sub> (12.5 mL) at 30 °C for 24 h. The amount of chloride ions released in solution were titrated with 0.01 M AgNO<sub>3</sub> using K<sub>2</sub>CrO<sub>4</sub> as an indicator and NaHCO<sub>3</sub> as a pH adjuster. The IEC for membrane samples was calculated using the following equation:

$$IEC \text{ (meq. g}^{-1}\text{)} = \frac{V \times C}{W_d} \quad (\text{S8})$$

where,  $V$  is the volume of AgNO<sub>3</sub> consumed.

Hydration number ( $\lambda$ ) was calculated from the water uptake and ion exchange capacity of the membrane samples using the following equation:

$$\lambda = \frac{WU}{(18.01) \times (IEC)} \quad (\text{S9})$$

#### ***Volumetric IEC ( $IEC_{vol}$ )***

Volumetric IEC ( $IEC_{vol}$ ) expressed in moles of ammonium groups per unit volume of wet membrane (mmol cm<sup>-3</sup>) calculated using the following equation:

$$IEC_{vol} = \frac{\tau \times IEC \times \rho_m}{\Delta V} \quad (\text{S10})$$

where  $\tau$  is the fraction of free water volume in relation with per unit volume of wet membrane and measured using the following equation:

$$\tau = \frac{\Delta V}{1 + \Delta V} \quad (\text{S11})$$

where  $\Delta V$  is the volume fraction of water present in the membrane matrix and calculated using the following equation:

$$\Delta V = \frac{\Delta_w \rho_m}{\rho_w W_d} \quad (\text{S12})$$

where  $\Delta_w$  is the weight difference in membrane samples in wet and dry states, respectively;  $\rho_m$  and  $\rho_w$  are the density of membrane samples in dry and wet states, respectively.

The density of the membranes in dry state was calculated using the following equation:

$$\rho_m = \frac{W_d}{V_d} \quad (\text{S13})$$

where  $V_d$  is the volume of dry membrane sample.

### **Hydroxide ion diffusion coefficient ( $D_\sigma$ )**

Hydroxide ion diffusion coefficient was calculated from Nernst Einstein equation:

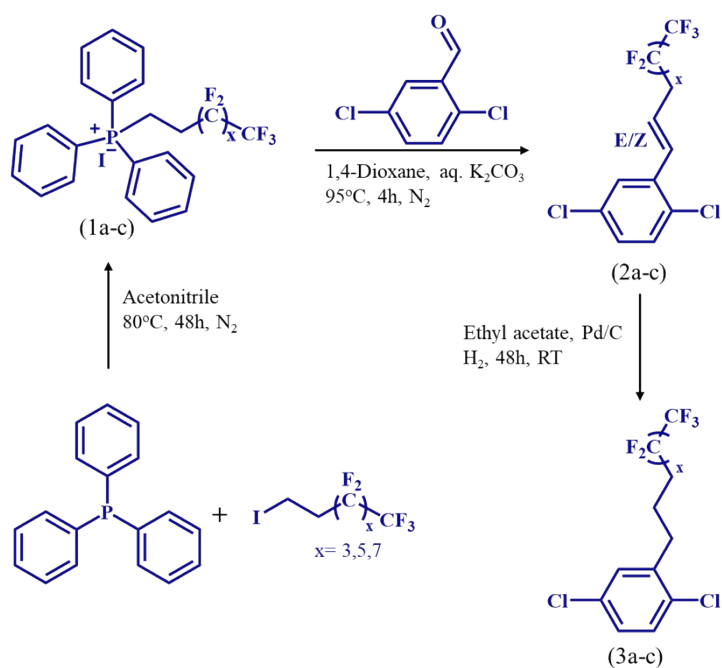
$$D_\sigma = \frac{\sigma \times R \times T}{IEC_{vol} \times F^2} \quad (\text{S14})$$

where  $\sigma$  is the measured hydroxide conductivity at 30 °C, R is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), T is the absolute temperature (303.15 K), and F is Faraday's constant (9.65 x 10<sup>4</sup> C mol<sup>-1</sup>).

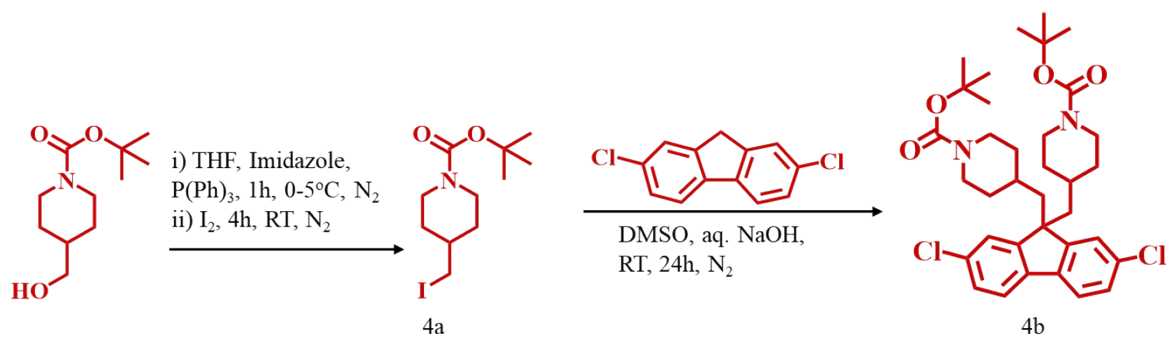
### **Alkaline stability test**

Alkaline stability of the membrane samples was assessed in 8 M KOH at 80 °C. The test solution was changed at a regular interval of 100 h in order to remove decomposed products. Hydroxide ion conductivity of the samples was monitored at a regular interval of 100 h in degassed, DI water in N<sub>2</sub> atmosphere at 30 °C and 80 °C. The IEC values for

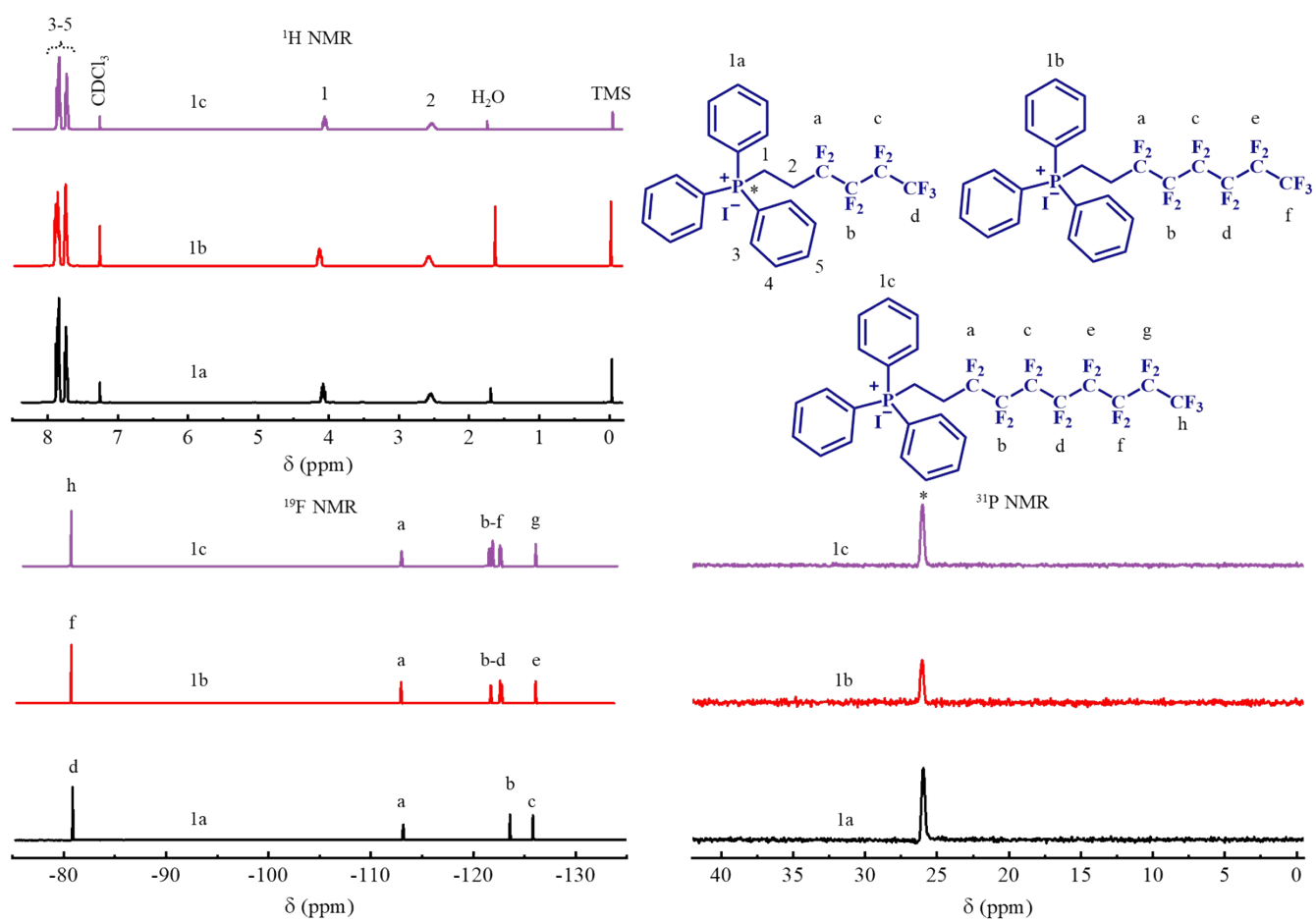
test samples in chloride ion form were also measured. Post-test analyses by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy and tensile strength test were also performed.



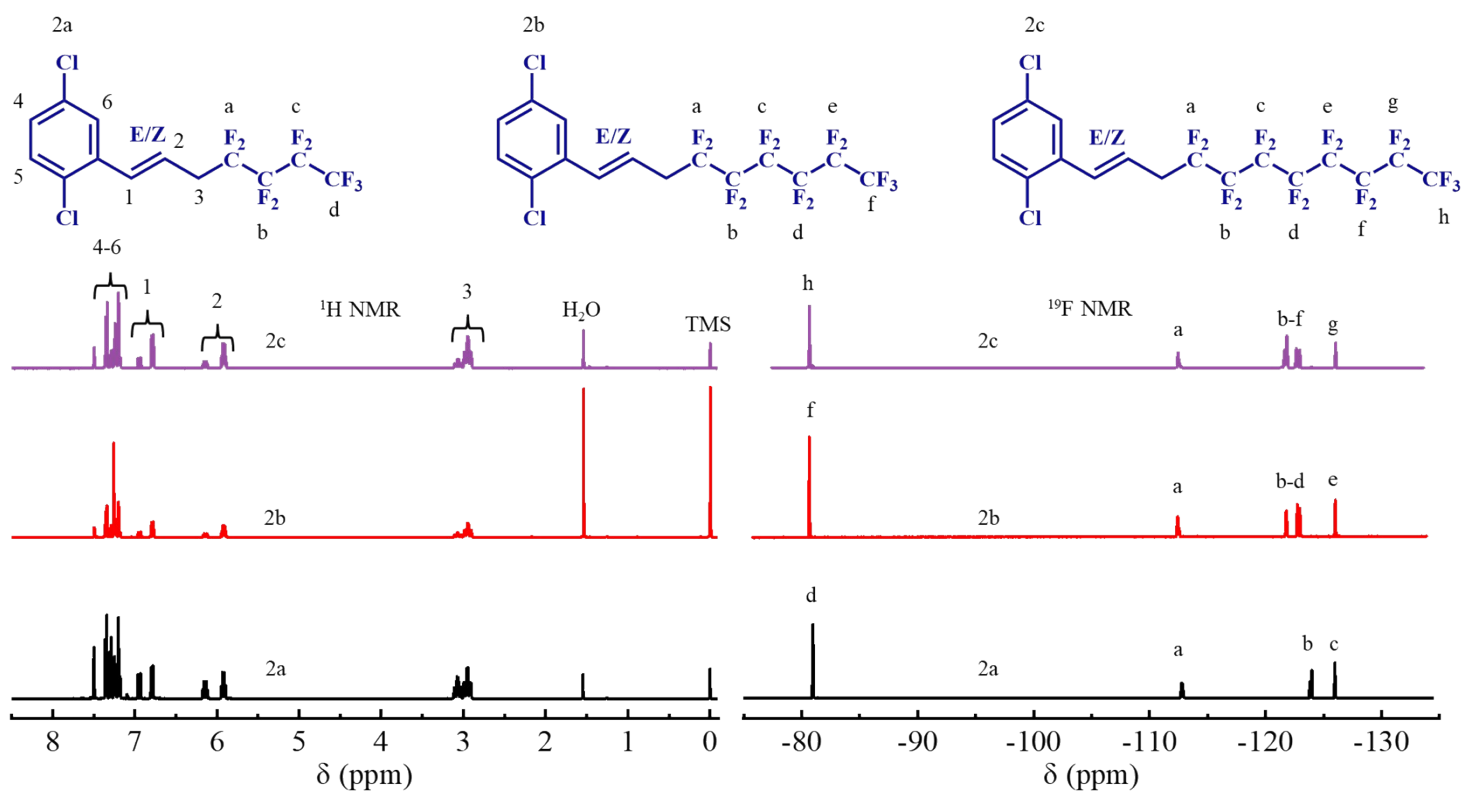
**Scheme S1.** Synthesis of 1,4-dichloro(semi-fluoroalkyl) benzene monomers (3a-c).



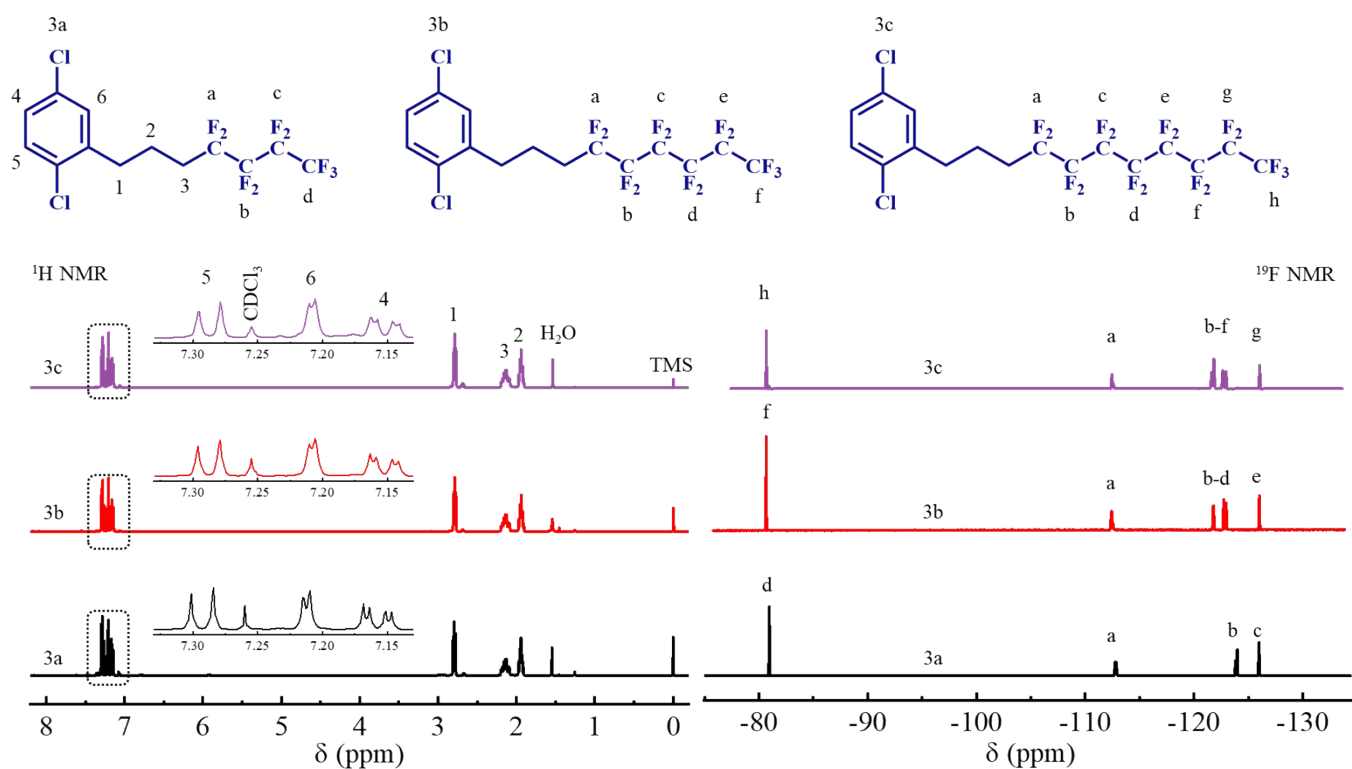
**Scheme S2.** Synthesis of di-tert-butyl 4,4'-((2,7-dichloro-9H-fluorene-9,9-diyl)bis(methylene)) bis(piperidine-1-carboxylate) (4b) monomer.



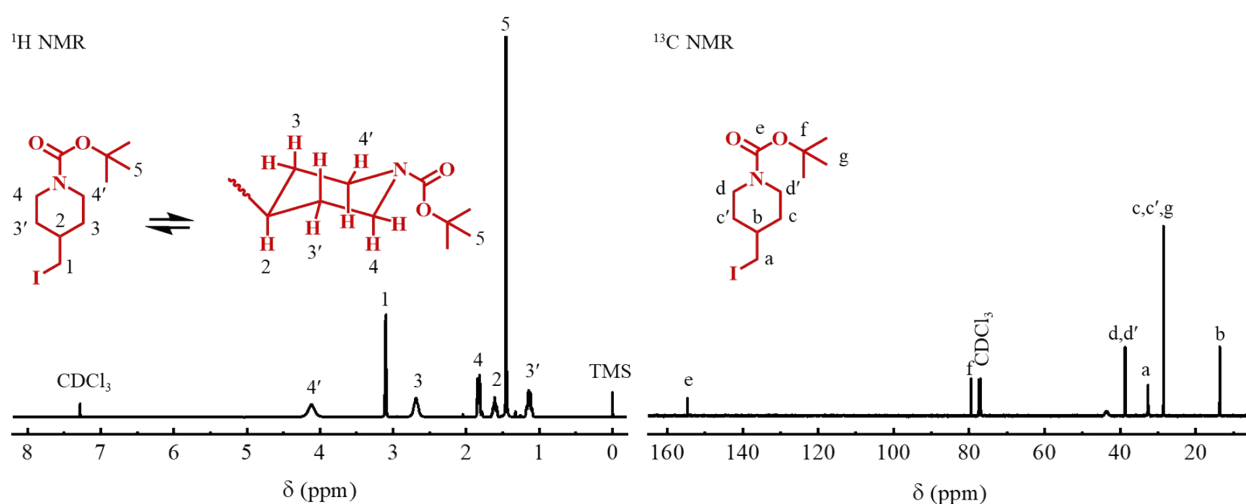
**Figure S1.**  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR spectra of 1a, 1b, and 1c recorded in  $\text{CDCl}_3$ .



**Figure S2.**  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of 2a, 2b, and 2c monomers recorded in  $\text{CDCl}_3$ .

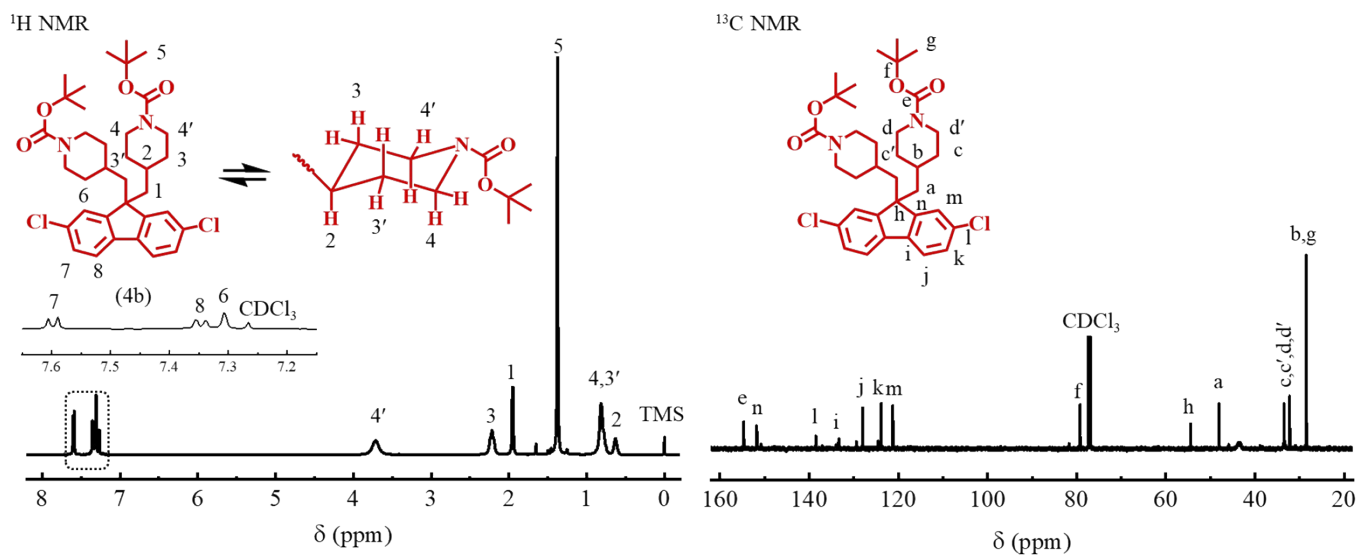


**Figure S3.**  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of 3a, 3b, and 3c monomers recorded in  $\text{CDCl}_3$ .

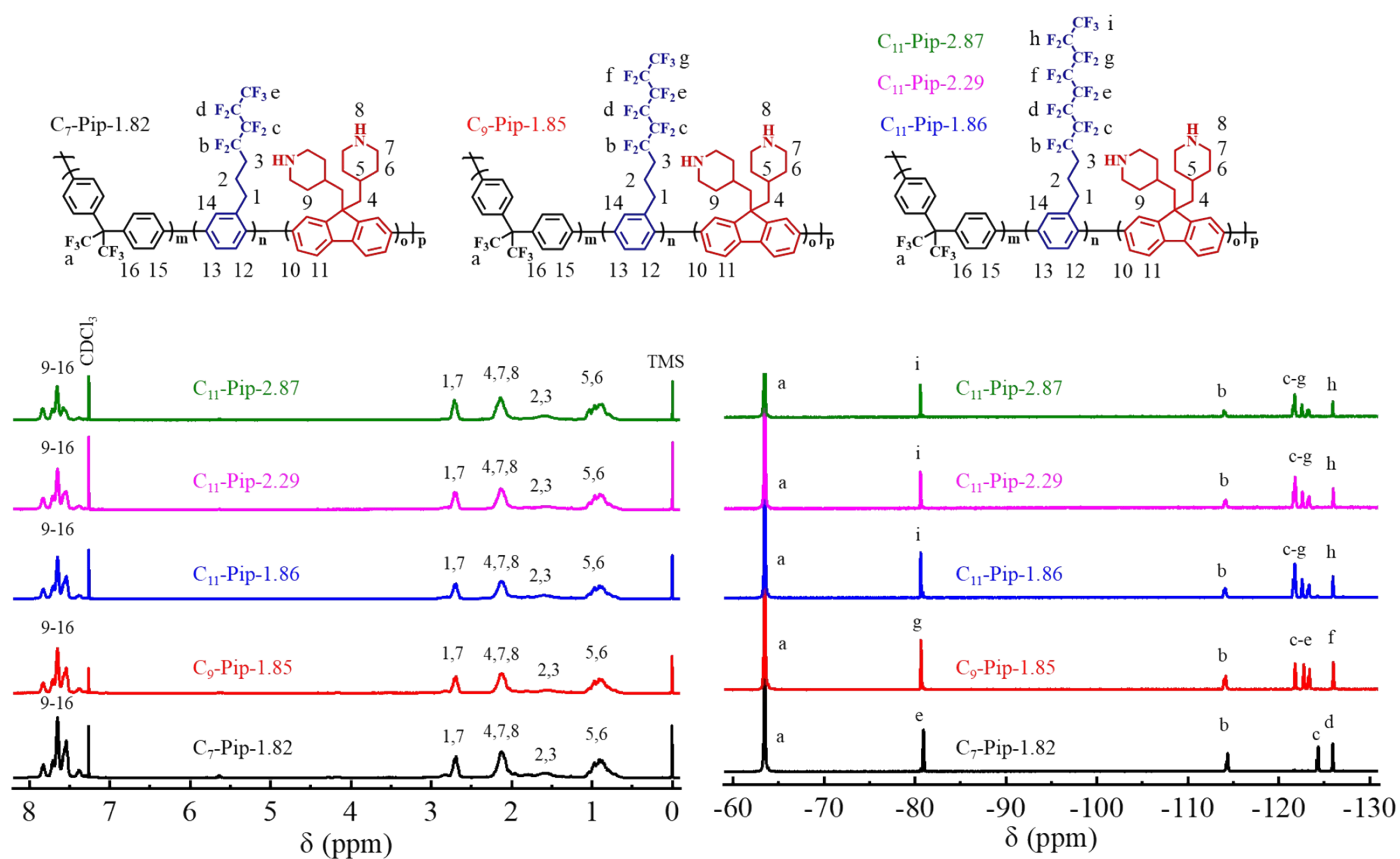


**Figure S4.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of *tert*-butyl 4-(iodomethyl) piperidine-1-carboxylate recorded in  $\text{CDCl}_3$ .

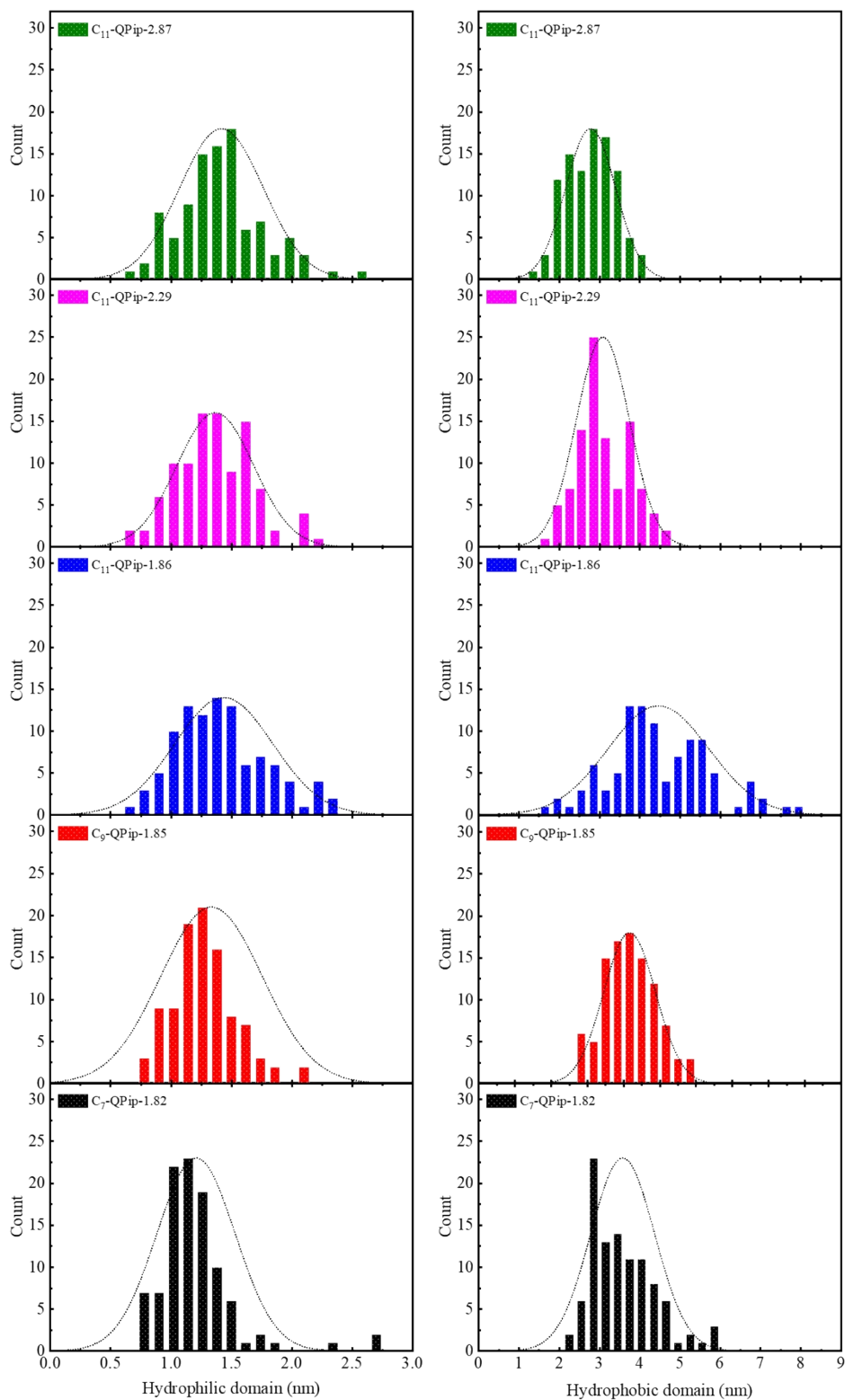




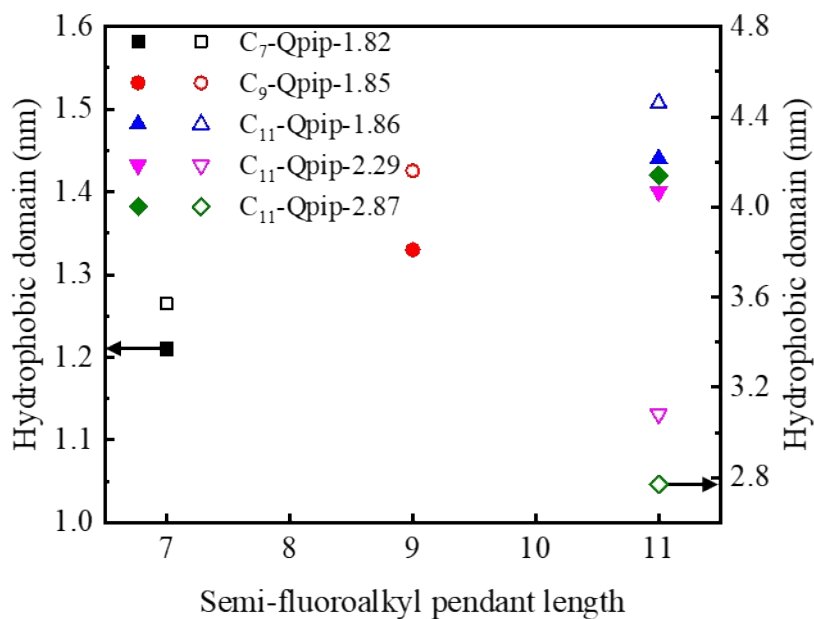
**Figure S5.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of di-*tert*-butyl 4,4'-((2,7-dichloro-9H-fluorene-9,9-diyl)bis(methylene)) bis(piperidine-1-carboxylate) recorded in CDCl<sub>3</sub>.



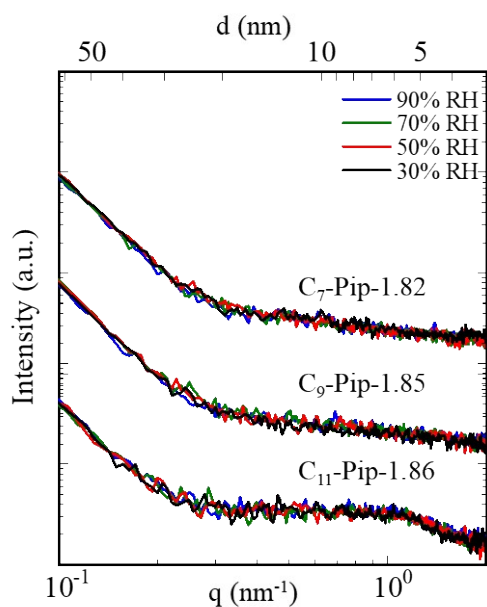
**Figure S6.**  $^1\text{H}$  (left) and  $^{19}\text{F}$  (right) NMR spectra for precursor terpolymers tethered with different semi-fluoroalkyl chains recorded in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .



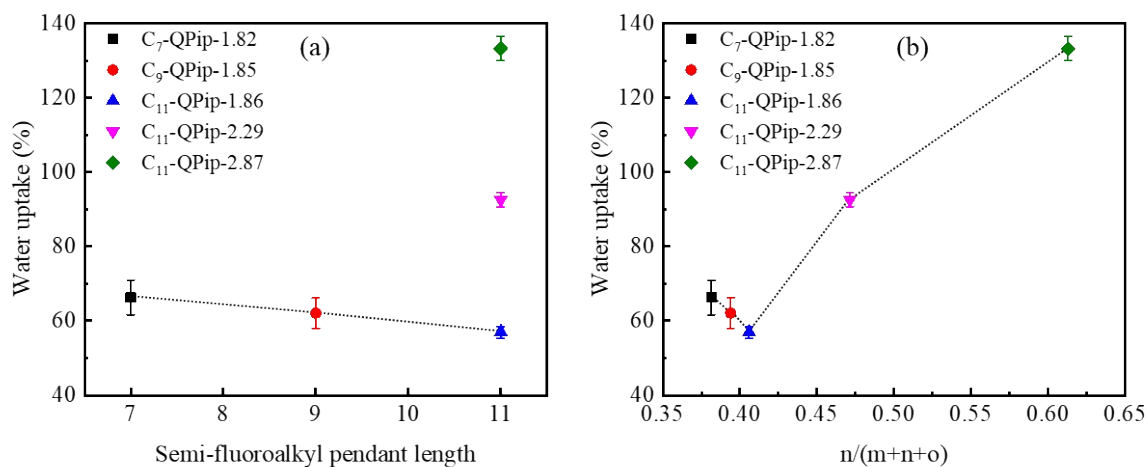
**Figure S7.** Histogram fitted with normal distribution on the hydrophilic domains (left) and hydrophobic domains (right) (nm) of  $C_x$ -QPip- $n$  membranes.



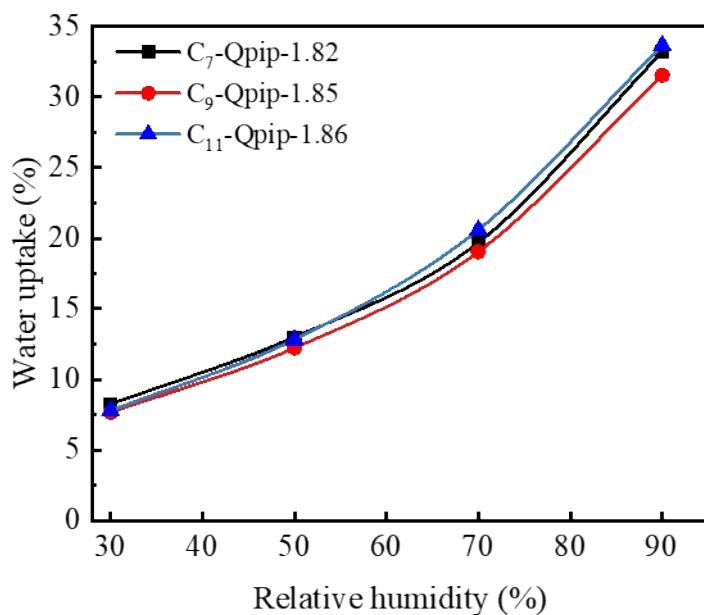
**Figure S8.** Effect of number of carbon atoms in semi-fluoroalkyl pendant on hydrophilic and hydrophobic domain size.



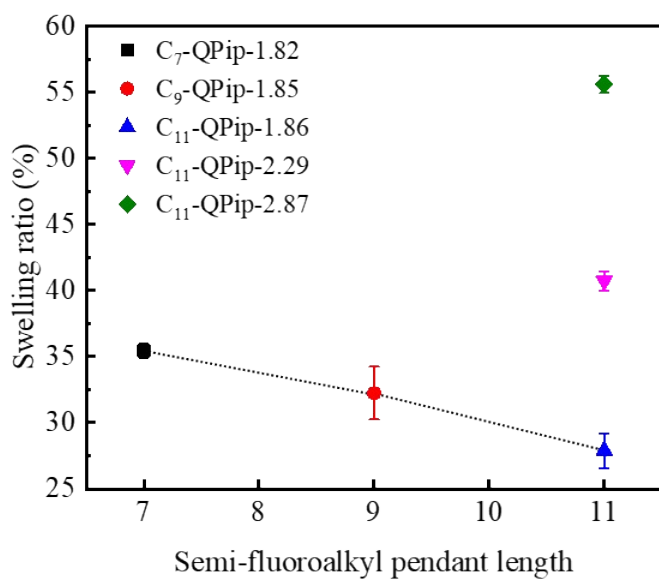
**Figure S9.** Relative humidity dependent SAXS patterns of  $C_x$ -QPip- $n$  membranes at 40 °C.



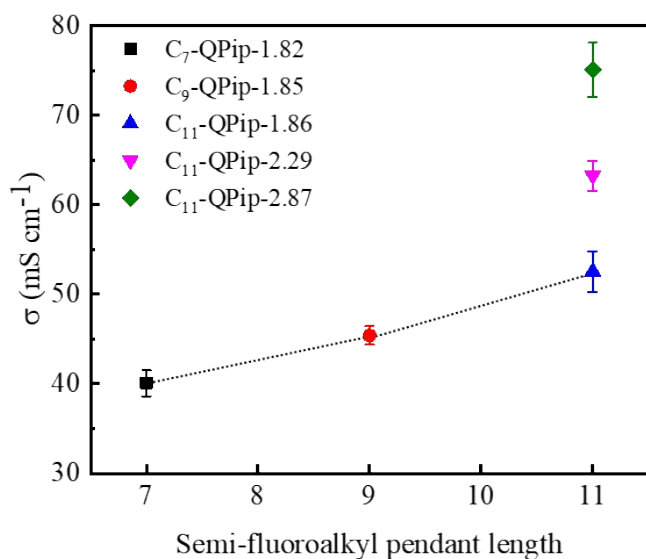
**Figure S10.** Water uptake as a function of number of carbon atoms in the semi-fluoroalkyl pendant (a) and hydrophilic monomer composition in the terpolymers (b).



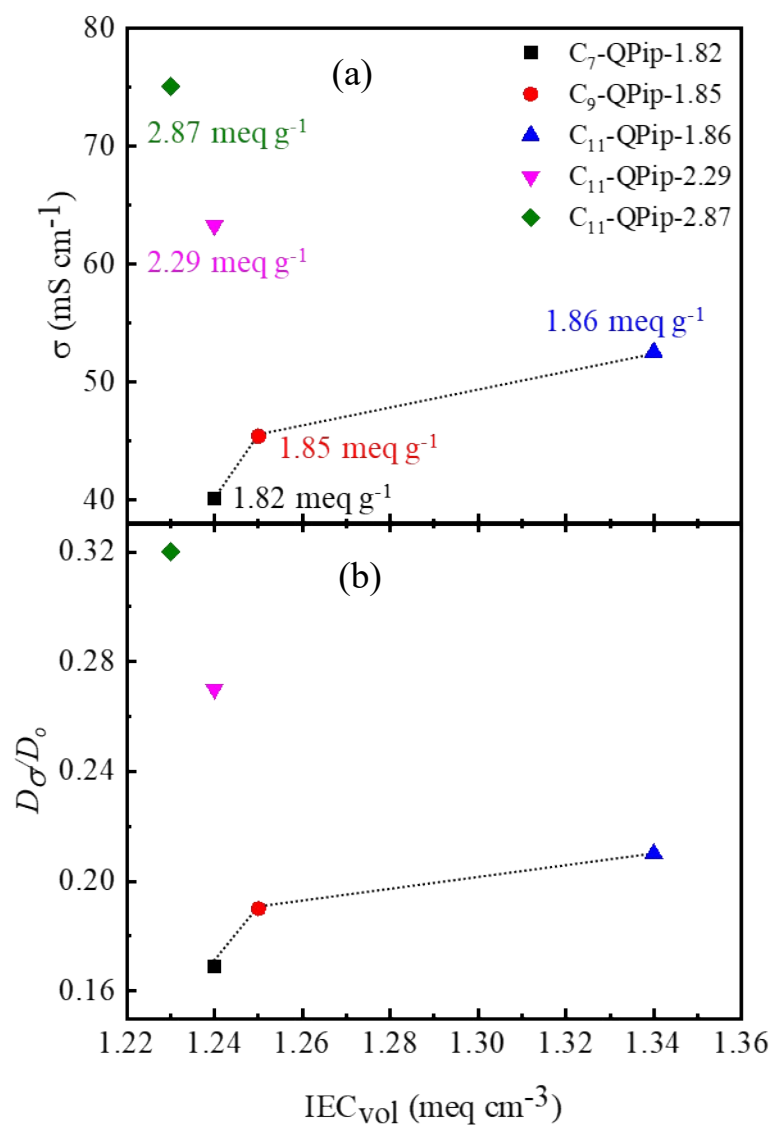
**Figure S11.** Water uptake as a function of relative humidity at 80 °C for C<sub>x</sub>-QPip-n membranes.



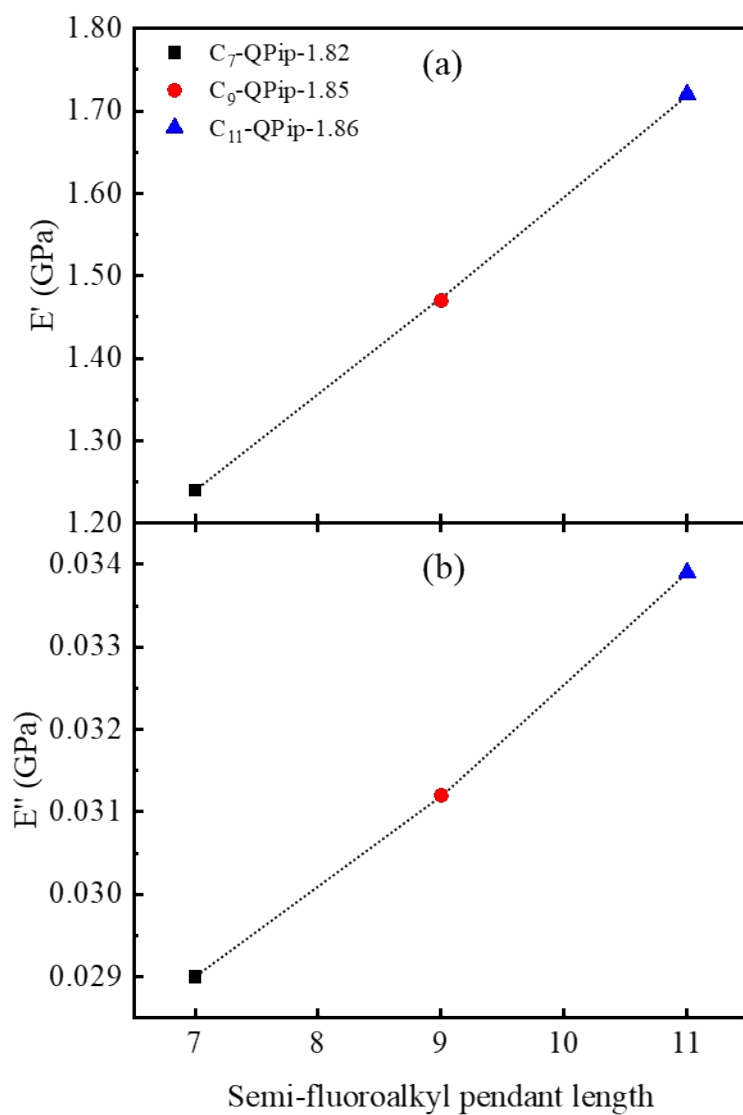
**Figure S12.** Effect of semi-fluoroalkyl pendent length on swelling ratio of C<sub>x</sub>-QPip-n membranes.



**Figure S13.** Effect of semi-fluoroalkyl pendant length on the hydroxide ion conductivity for C<sub>x</sub>-QPip-n membranes.

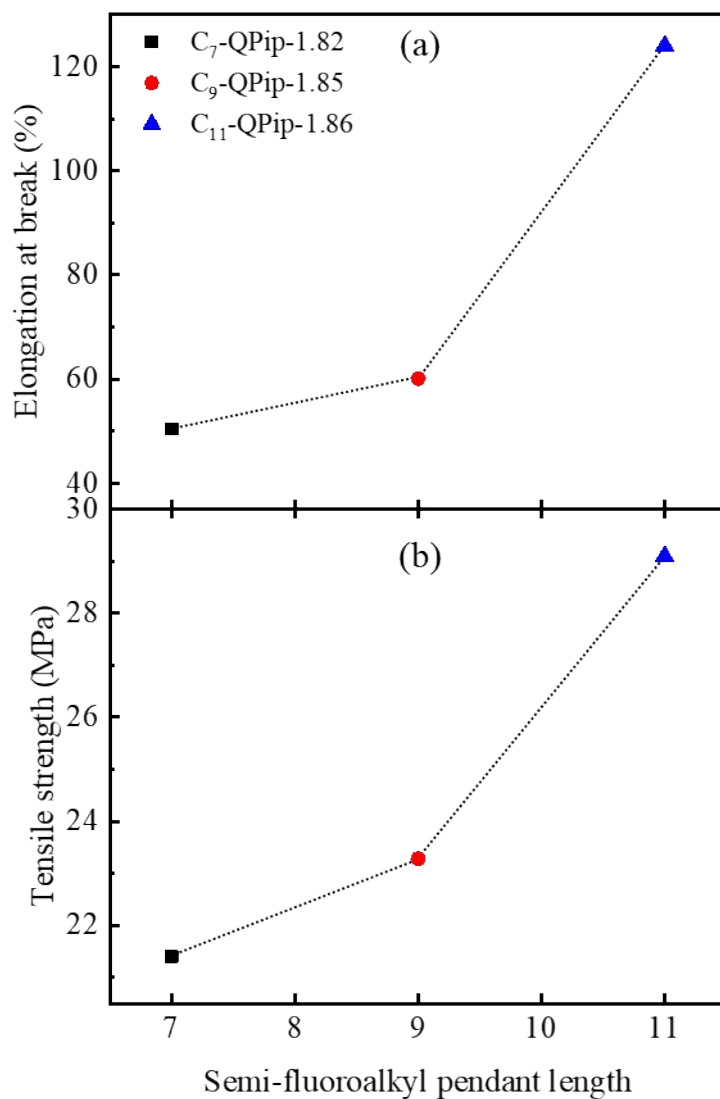


**Figure S14.** Hydroxide ion conductivity at 30 °C (a) and normalized diffusion coefficient ( $D_\sigma/D_0$ ) (b) as a function of their IEC<sub>vol</sub> for C<sub>x</sub>-QPip-n membranes.

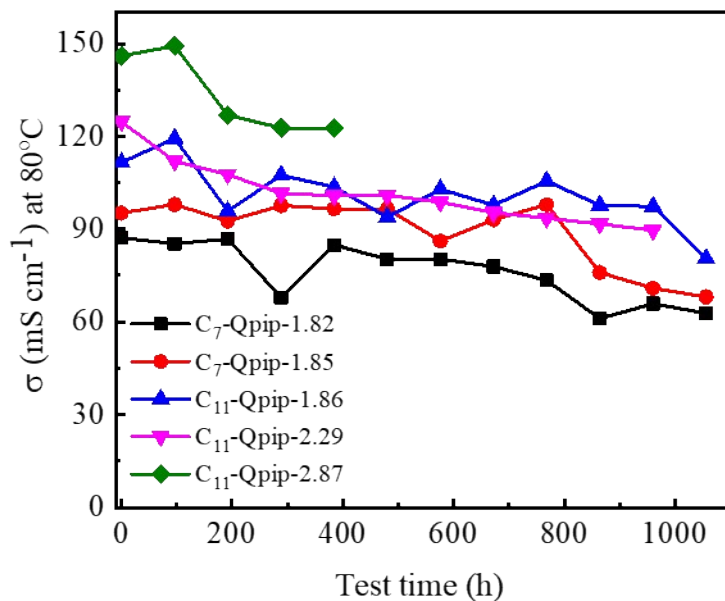


**Figure S15.** Dependence of  $E'$  (a) and  $E''$  (b) on semi-fluoroalkyl pendant length in  $C_x$ -QPip- $n$  membranes with comparable IECs (*ca.* 1.85 meq  $g^{-1}$ ) at *ca.* 80 °C and 0% RH.

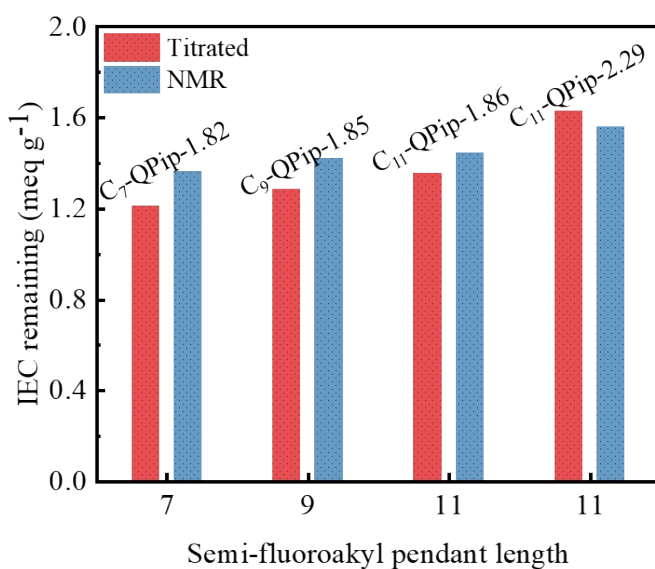




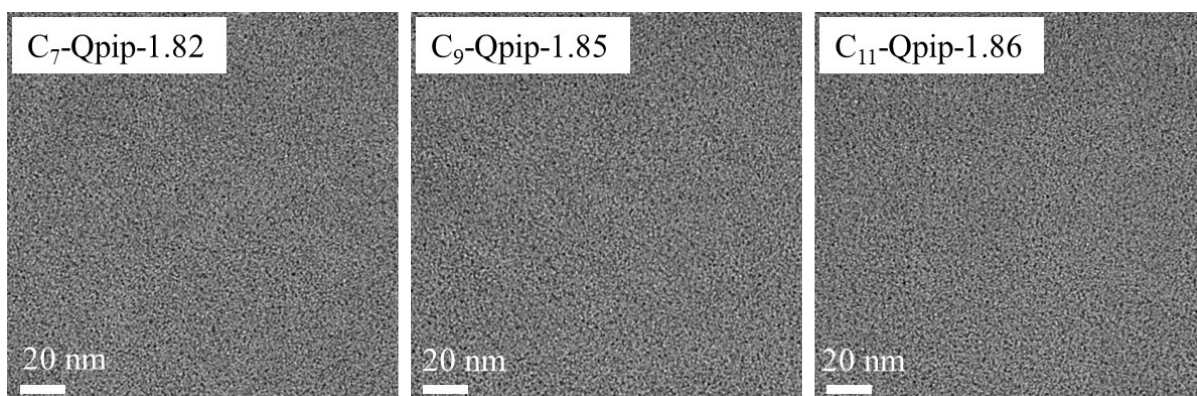
**Figure S16.** Elongation at break(a) and tensile strength (b) at 60% RH and 80 °C for C<sub>x</sub>-QPip-n membranes with comparable IEC as a function semi-fluoroalkyl pendant length.



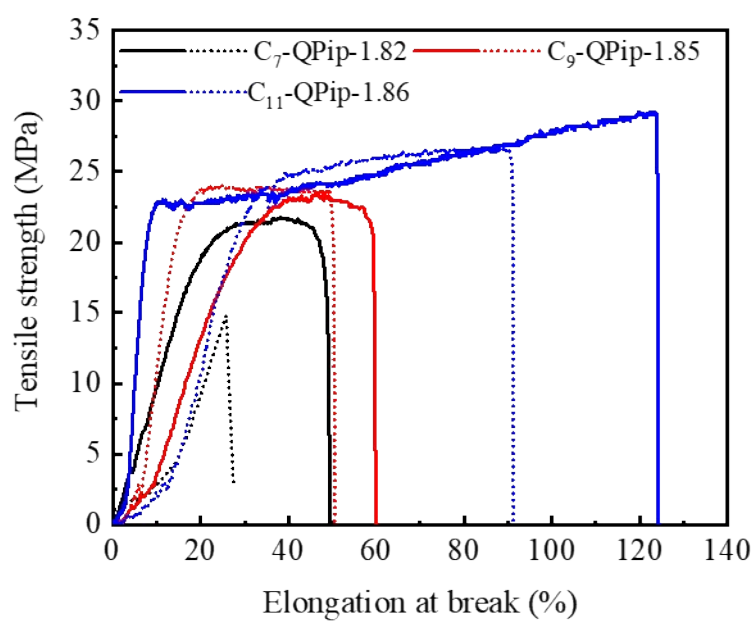
**Figure S17.** Change in hydroxide ion conductivity at 80 °C for C<sub>x</sub>-QPip-n membranes during the alkaline stability test in 8 M KOH at 80 °C.



**Figure S18.** Ion exchange capacity for C<sub>x</sub>-QPip-n membranes before and after alkaline stability test as a function of pendant length.



**Figure S19.** TEM images for post alkaline stability test  $C_x$ -QPip-n membrane samples stained with tetrachloroplatinate ions.



**Figure S20.** Tensile properties for  $C_x$ -QPip-n membranes in chloride counter anion form at 80 °C and 60% RH before and after alkaline stability test in 8 M KOH at 80 °C for 1056 h.

**Table S1.** Alkaline water electrolysis cell performance comparison of C<sub>11</sub>-QPip-1.86 membrane with recent reports at 1.0 A cm<sup>-2</sup> with 1 M KOH fed at 80 °C and Pt/C cathode catalyst.

Membranes	Membrane thickness (μm)	Anode catalyst	Cell voltage (V)	Reference
QPAF-4	25	Ni <sub>0.8</sub> Co <sub>0.12</sub> Mo <sub>0.08</sub> O	1.63	1
PE(VBTAC)	25	Ni <sub>2</sub> P-Fe/NF	1.73	2
PTP-C1	NR	IrO <sub>2</sub>	1.66	3
FAA-3-50	45-55	H-Co <sub>0.9</sub> Fe <sub>0.1</sub> -CNF	1.73	4
PBPA	50	IrO <sub>2</sub>	1.69	5
X37-50	50	Ir-Ni/Mo <sub>5</sub> N <sub>6</sub>	1.78	6
C <sub>11</sub> -QPip-1.86	50	Ni <sub>0.8</sub> Co <sub>0.2</sub> O	1.64	This work

NR – Not reported

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