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Supplementary information

Partially fluorinated copolymers containing pendant piperidinium head groups as anion exchange membranes for alkaline fuel cells

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Materials. Perfluoro-1,6-diiodohexane (> 98%) was kindly supplied by Tosoh Finechem Co. 1-Chloro-3-iodobenzene (> 97%), copper powder (Cu, > 99.5%, particle size 75-150 µm), fluorene (> 95%), N-chlorocuccinimide (> 98%), 1,3-dibromopropane (> 98%), 1,6-dibromohexane (> 97%), 1,9-dibromononane (> 97%), tetrabutylammonium bromide (TBAB, 98%), 2,2'-bipyridyl (2,2'-bpy, > 99%) and piperidine (> 99%) were used as received from Tokyo Chemical Industry Co., Ltd. Hydrochloric acid (35.0-37.0%), potassium hydroxide (> 86%), sodium chloride (99%), diethyl ether (> 99.5%), sodium nitrate (> 99%), sodium hydrogen carbonate (> 99.5%), 0.01 M silver nitrate aqueous solution, nitric acid (60%), dimethyl sulfoxide (DMSO, > 99%), bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$, 95%), N,N-dimethylacetamide (DMAc, > 99%), hexane (> 96%), dichloromethane (> 99.5%), silica gel N60 (spherical, neutral, 100-210 µm), sodium sulfate (> 98.5%), tetrahydrofuran (THF, > 99.5%) and dimethyl sulfate were purchased from Kanto Chemical Co., Inc. and used as received. Dimethylsulfoxide-d_6 with 0.03% TMS (DMSO-d_6, Acros Organics) and chloroform-d_1 ($CDCl_3$, Acros Organics) were used as received.

Measurements. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$, $C_2D_2Cl_4$, or DMSO-d_6 containing tetramethylsilane as internal standard. The spectra were obtained at room temperature on a JEOL JNM-ECA500 spectrometer. High-resolution MS spectra were measured on a JEOL JMS-T100LP spectrometer and an AccuTOF LC-plus ESI-MS using positive or negative ion modes. Molecular weight (M_n and M_w) of the PAF copolymers was measured by gel permeation chromatography (GPC) using a Shodex KF-805L or SBSB-803 column with a Jasco 805 UV detector. The eluent was chloroform with 0.02 M triethylamine and calibration was done with standard polystyrene samples. Dynamic mechanical analyses (DMA) were carried out on an ITK DVA-225 dynamic viscoelastic analyzer. Storage modulus (E' (Pa)), loss modulus (E'' (Pa)) and tan δ (E''/E') were measured at 60% relative humidity (RH) as a function of temperature between room temperature and 95 °C at a heating rate of 1 °C min^{-1}. Ion exchange capacity (IEC) of the quaternized membranes was measured via Mohr titration method as reported in the literature.[S] Other properties measurements including water uptake, hydroxide ion conductivity, and chemical stability were carried as reported in the literature.[1] For transmission electron spectroscopic (TEM) images, 5 mm by 5 mm membrane samples were stained by tetrachloroplatinate ions via submerging them into 0.5 M potassium tetrachloroplatinate (II) aqueous solution at 40 °C for 24 h. Subsequently, the membranes were washed with deionized ultrapure water at 40 °C for 24 h and dried under vacuum overnight. The obtained membranes were embedded in an epoxy resin, cut to 50 nm thickness via a Leica microtome Ultracut UCT and finally placed on a copper grid. The images of the membranes were taken using a Hitachi H-9500 transmission electron microscope.

2,7-Dichloro-9,9-bis(3-bromopropyl)-9H-fluorene. 2,7-Dibromofluorene (3.0 g, 12.8 mmol) and tetrabutylammonium bromide (TBAB) (600 mg, 1.86 mmol) were dried under vacuum for 30 min. Degassed DMSO (15 mL), 50% aqueous NaOH (15 mL) and 1,3-dibromopropane (13 mL, 90 mmol) were added into the mixture and stirred under N_2 for 2 h at room temperature. Diethyl ether and deionized water were added into the mixture and stirred for 15 min. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography ($CHCl_3$/hexane = 2/8) to obtain pure 2,7-dichloro-9,9-bis(3-bromopropyl)-9H-fluorene as a white solid (3.2 g, 6.7 mmol, 53% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.58 (d, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 2.0 Hz, 2H), 7.33 (d, *J* = 1.5 Hz, 2H), 3.13 (t, *J* = 7.0Hz, 4H), 2.15 (t, *J* = 8.0 Hz, 4H) and 1.14 (p, *J* = 15.0 Hz, *J* = 7.0 Hz, 4H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ= 150.54, 138.53, 133.78, 128.12, 123.28, 121.08, 54.45, 38.56, 33.62 and 26.97 ppm.

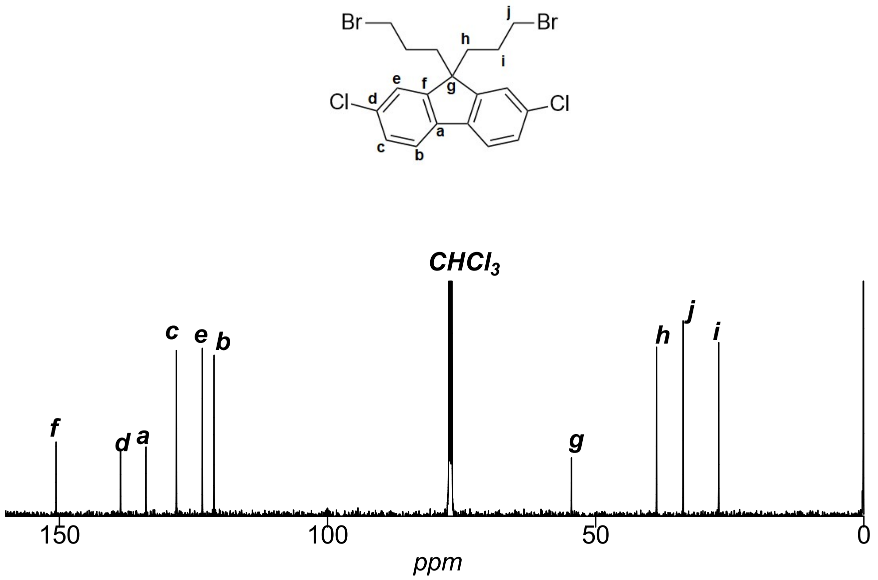

Fig. S1 ^{13}C NMR spectrum of 2,7-dichloro-9,9-bis(3-bromopropyl)-9H-fluorene.

2,7-dichloro-9,9-bis(9-bromononyl)-9H-fluorene. This compound was synthesized according to the literature.[2]

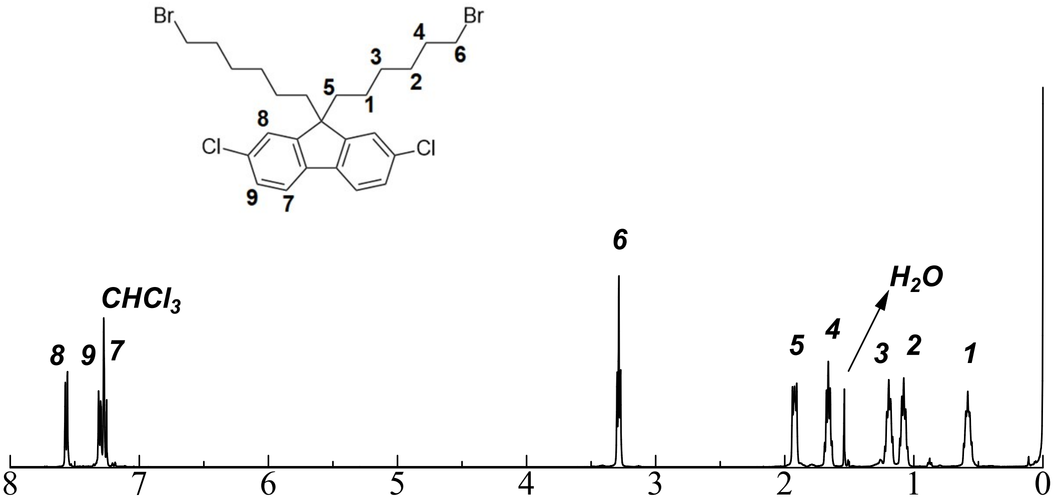

Fig. S2 ^{1}H NMR spectrum of 2,7-dichloro-9,9-bis(6-bromohexyl)-9H-fluorene.

2,7-dichloro-9,9-bis(9-bromononyl)-9H-fluorene. To a mixture of 2,7-dichlorofluorene (1.0 g, 4.25 mmol), 1,9-dibromononane (8.7 mL, 42.8 mmol) and tetrabutylammonium bromide (270 mg, 0.84 mmol), a solution of potassium hydroxide (620 mg, 11.07 mmol) in water (1.0 mL) was added. The mixture was heated to 95 °C and stirred for 2 h. The mixture was then poured into large excess water and extracted with three portions of CH_2Cl_2 (30 mL). The combined organic layer was dried over Na_2SO_4, filtered and evaporated. The crude product was purified via flash silica gel chromatography (hexane, then hexane/CH_2Cl_2 = 7/1) to obtain a pale yellow oil (1.4 g, 2.17 mmol, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.57 (d, *J* = 8.0 Hz, 2H), 7.31 (s, 2H), 7.29 (d, *J* = 2.0 Hz, 4H), 3.37 (t, *J* = 6.5 Hz, 4H), 1.89 (t, *J* = 8.5 Hz, 4H), 1.78 (dt, *J* = 15.0 Hz, *J* = 7.0 Hz, 4H), 1.31 (p, *J* = 15.0 Hz, *J* = 7.5 Hz, 4H), 1.16 (p, *J* = 14.0 Hz, *J* = 7.5 Hz, 4H), 1.08 (s, 4H), 1.03 (s, 8H) and 0.58 (s, 4H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ= 155.55, 138.74, 133.12, 127.43, 123.41, 121.03, 55.67, 40.15, 34.89, 32.95, 29.97, 29.46, 29.22, 28.80, 28.27 and 23.75 ppm. HR-MS (ESI): *m/z*: calcd for $[C_{31}H_{62}{}^{79}Br_2{}^{35}Cl_2+Cl]^-$, 681.0659 $[M+Cl]^-$; found: 681.0651.

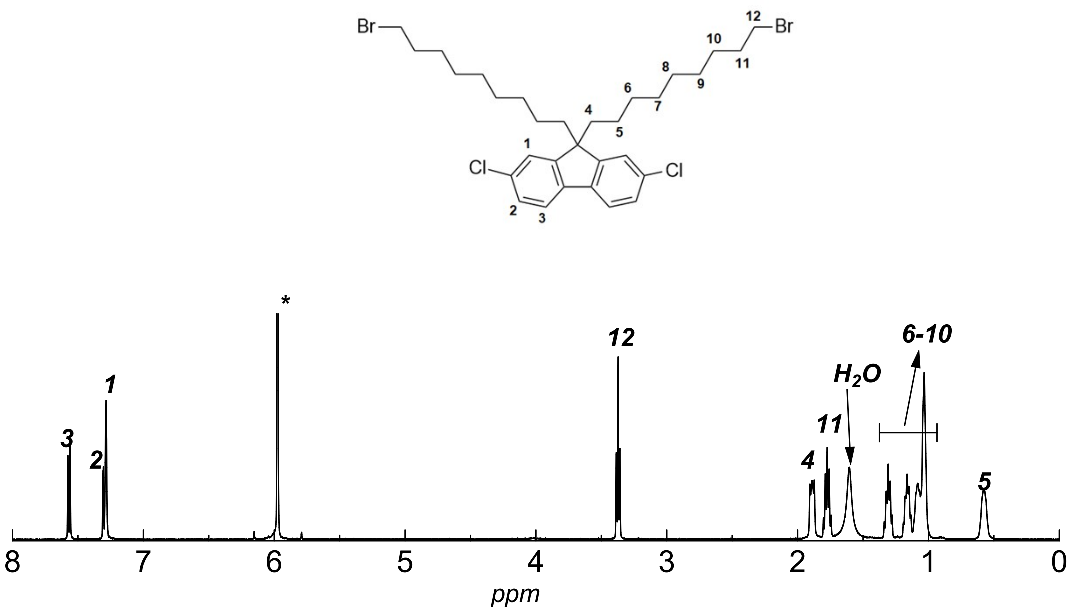

Fig. S3 ^{1}H NMR spectrum of 2,7-dichloro-9,9-bis(9-bromononyl)-9H-fluorene.

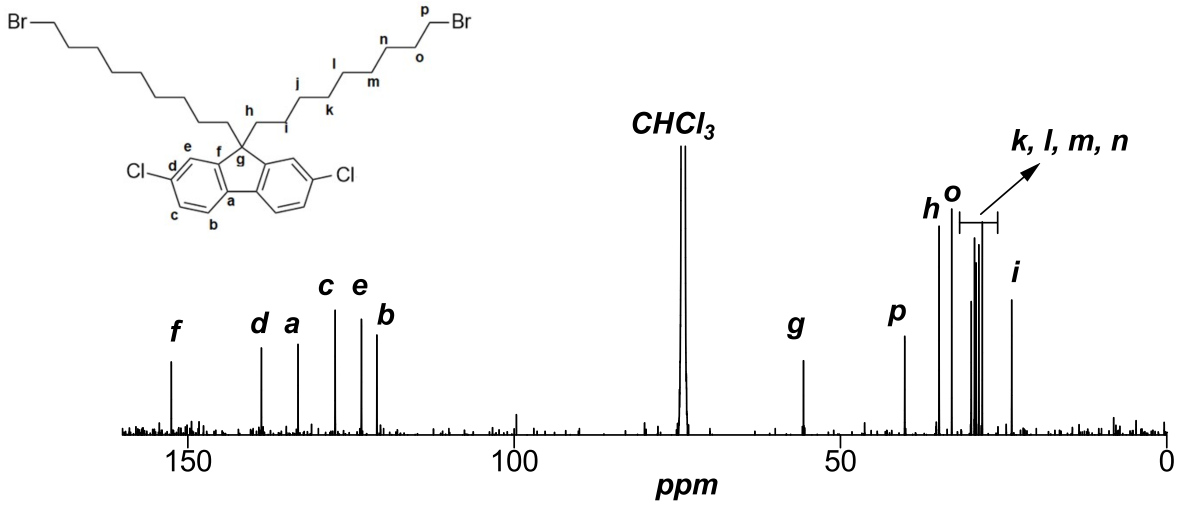

Fig. S4 ^{13}C NMR spectrum of 2,7-dichloro-9,9-bis(9-bromononyl)-9H-fluorene.

2,7-Dichloro-9,9-bis[3-(1-piperidinyl)propyl)-9H-fluorene (2). To a solution of piperidine (5.4 mL, 54.6 mmol) in 5 mL of THF, a solution of 2,7-dichloro-9,9-bis(3-bromopropyl)-9H-fluorene (1.3 g, 2.73 mmol) in 5.0 mL of THF was added dropwise, while the temperature was maintained around 0 °C with an ice-bath. After the addition, the mixture was stirred at 40 °C for 48 h. The mixture was evaporated to obtain oily product. To the crude product, 0.1 M aqueous KOH (50 mL) was added and extracted with three portions of

CH_2Cl_2 (20 mL). The combined organic layer was dried over Na_2SO_4, filtered, and evaporated. Precipitation from the mixture of THF and water (1/50 by volume) gave **2** as a white crystalline solid (1.22 g, 2.52 mmol, 92% yield). ^1H NMR (500 MHz, $CDCl_3$): δ= 7.45 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 2.0 Hz, 2H), 7.28 (d, J = 1.5 Hz, 2H), 2.11 (s, 8H), 2.03 (t, J = 8.0 Hz, 4H), 1.95 (t, J = 8.0 Hz, 4H), 1.46 (dt, J = 11.0 Hz, J = 5.0 Hz, 8H), 1.34 (s, 4H) and 0.72-0.82 (m, 4H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ= 151.78, 138.67, 133.31, 127.49, 123.29, 120.82, 59.33, 55.20, 54.16, 37.94, 25.88, 24.42 and 21.30 ppm. HR-MS (ESI): *m/z*: calcd for $C_{29}H_{38}Cl_2N_2$, 485.2490 $[C_{29}H_{38}{}^{35}Cl_2{}^{14}N+H]^+$; found: 485.2493.

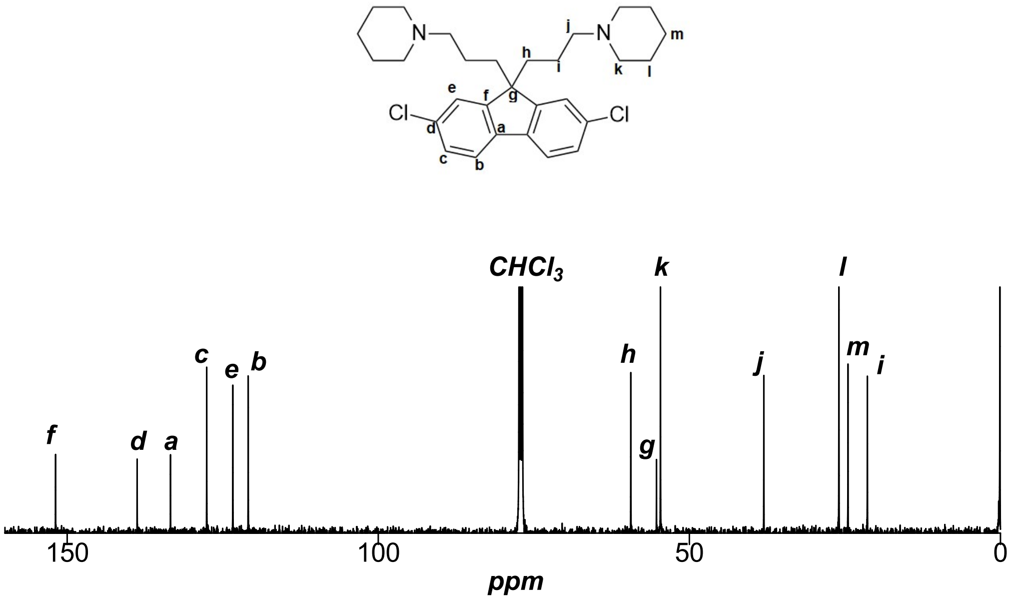

Fig. S5 ^{13}C NMR spectrum of **2**.

2,7-Dichloro-9,9-bis[6-(1-piperidinyl)hexyl)-9H-fluorene (3). Similar to **2** as mentioned above, **3** was prepared from piperidine and 2,7-dichloro-9,9-bis(6-bromohexyl)-9H-fluorene. Yield 89%. ^1H NMR (500 MHz, $CDCl_3$): δ= 7.56 (d, J = 8.0 Hz, 2H), 7.30 (dd, J = 2.0 Hz, 4H), 2.28 (s, 2H), 2.13 (t, J = 7.5 Hz, 8H), 1.91 (t, J = 8.0 Hz, 4H), 1.54 (dt, J = 11.0 Hz, J = 8.0 Hz, 8H), 1.39 (s, 4H), 1.29 (p, J = 15.0 Hz, J = 8.0 Hz, 4H), 1.06 (s, 8H) and 0.51-0.62 (m, 4H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ= 152.26, 138.62, 133.18, 127.34, 123.21, 120.74, 59.55, 55.56, 54.65, 40.20, 29.78, 27.35, 26.77, 26.01, 24.51 and 23.58 ppm. HR-MS (ESI): *m/z*: calcd for $[C_{35}H_{50}{}^{35}Cl^{14}N+H]^+$, 569.3429 $[M+H]^+$; found: 569.3413.

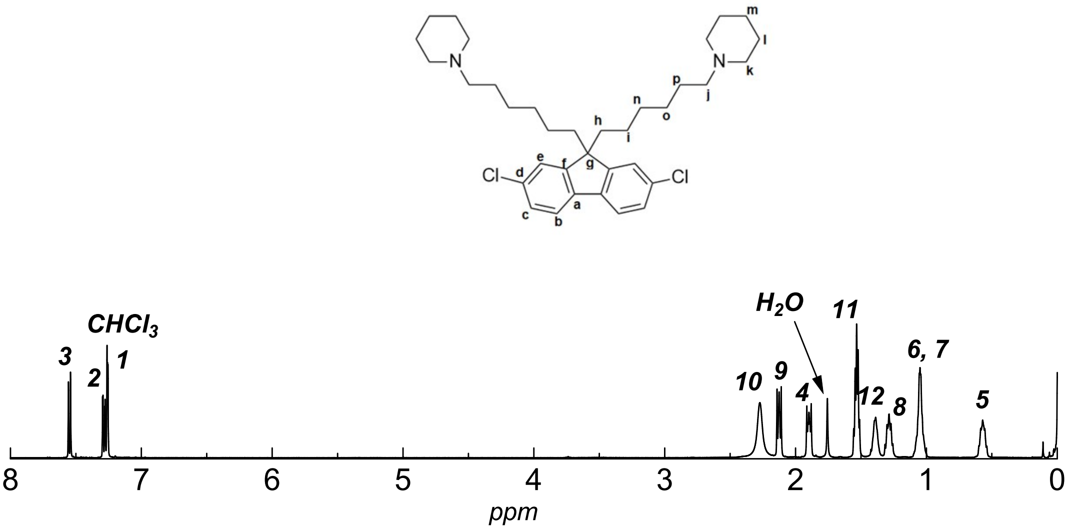

Fig. S6 ^{1}H NMR spectrum of **3**.

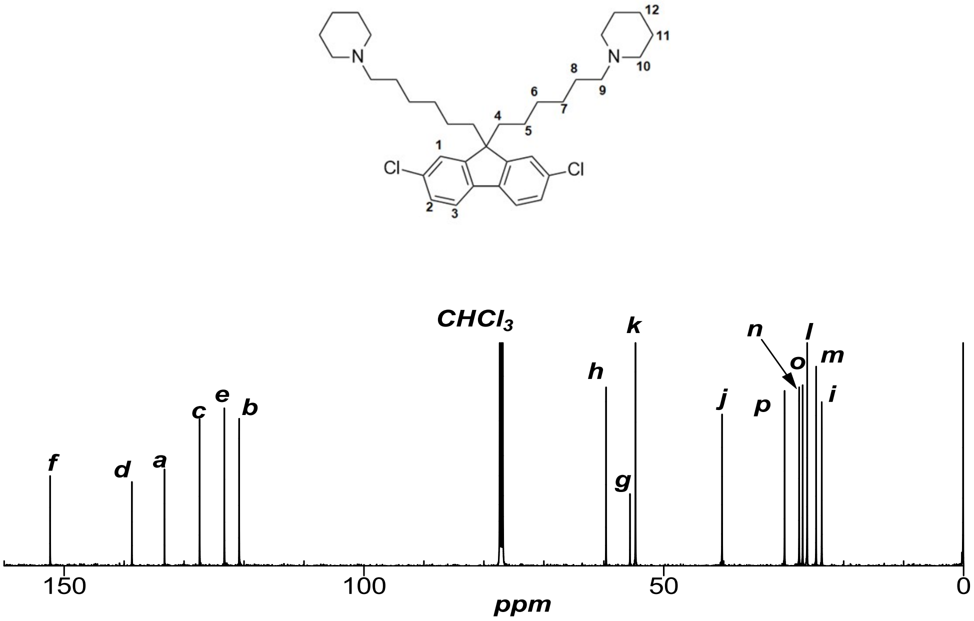

Fig. S7 ^{13}C NMR spectrum of **3**.

2,7-dichloro-9,9-bis[9-(1-piperidinyl)nonyl)-9H-fluorene (4). Similar to **2** as mentioned above, **4** was prepared from piperidine and 2,7-dichloro-9,9-bis(6-bromononyl)-9H-fluorene. Yield 95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.57 (d, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 8.0 Hz, 4H), 7.28 (d, *J* = 1.5 Hz, 2H) 2.34 (s, 8H), 2.31 (t, *J* = 7.5 Hz, 4H), 1.91 (t, *J* = 7.0 Hz, 4H), 1.58 (t, *J* = 5.0 Hz, 8H), 1.43 (s, 8H), 1.17 (s, 8H), 1.09 (s, 4H), 1.04 (m, 8H) and 0.51-0.61 (m, 4H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ= 155.55, 138.74, 133.12, 127.43, 123.41, 121.03, 55.67, 40.15, 34.89, 32.95, 29.97, 29.46, 29.22, 28.80, 28.27 and 23.75 ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ= 152.34. 138.61, 133.14, 127.27, 123.23, 120.71, 59.66, 55.57, 54.63, 40.19, 29.86, 29.46, 29.45, 29.16, 27.68, 25.95, 24.49 and 23.62 ppm. HR-MS (ESI): *m/z*: calcd for $[C_{41}H_{62}{}^{35}Cl^{14}N+H]^+$, 653.4368 $[M+H]^+$; found: 653.4362.

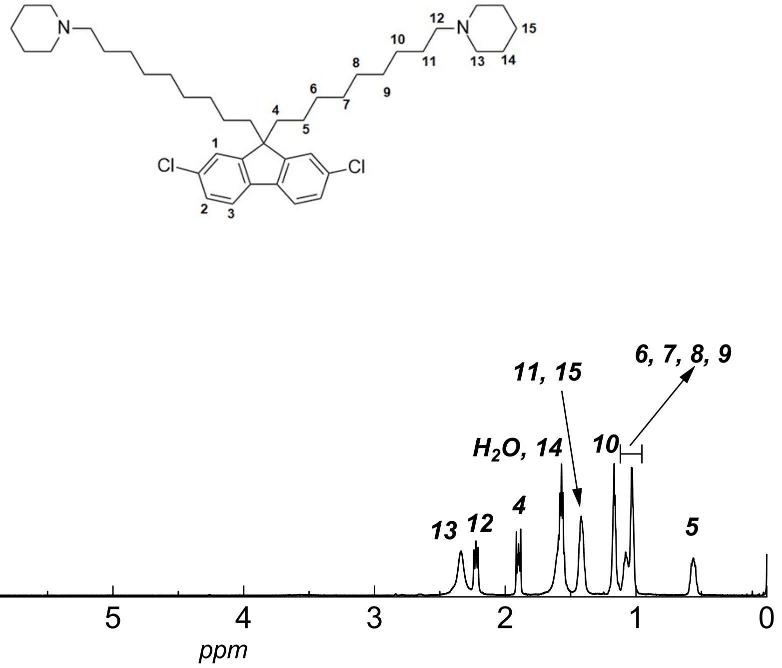

Fig. S8 ^{1}H NMR spectrum of **4**.

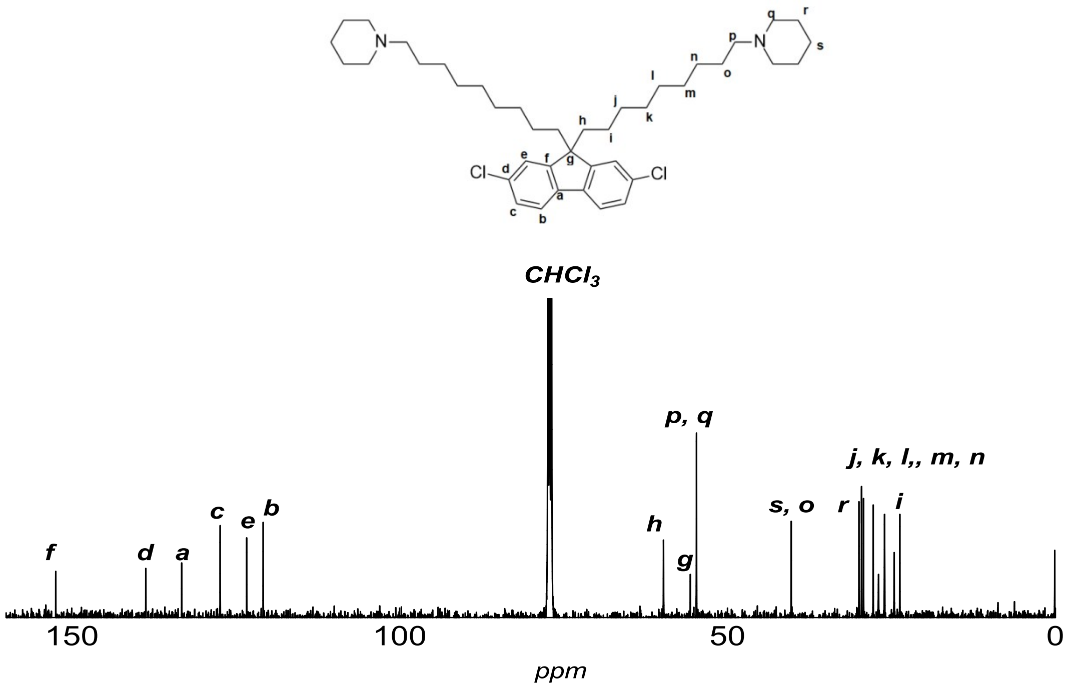

Fig. S9: ^{13}C NMR spectrum of **4**.

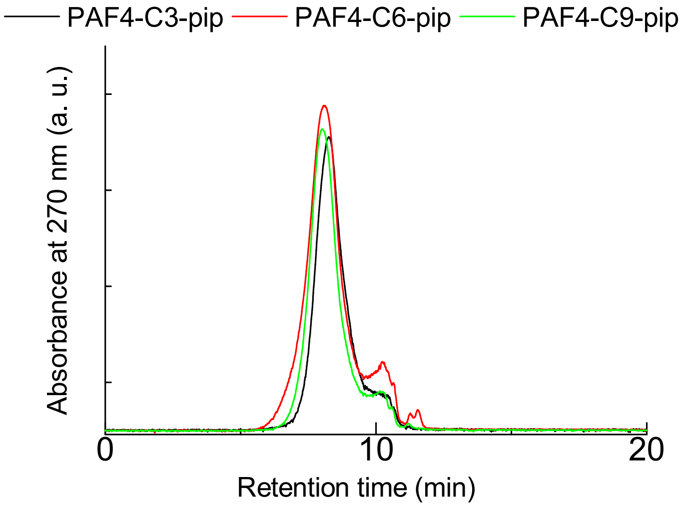

Fig. S10 GPC curves of the PAF4-C(3, 6 and 9)-pip polymers.

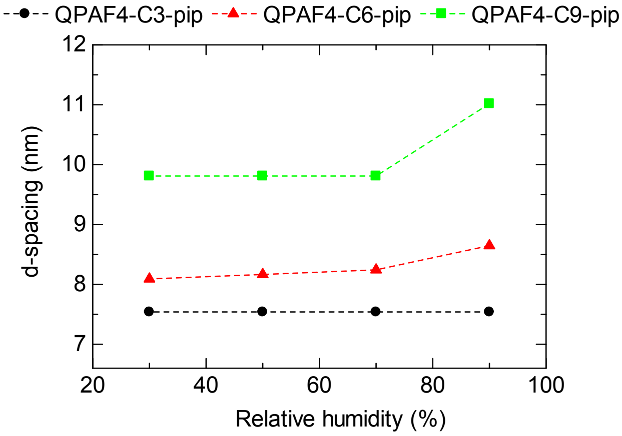

Fig. S11 *d*-spacing of SAXS patterns of QPAF4-C(3, 6 and 9)-pip membranes in Cl^- ion forms as a function of the relative humidity.

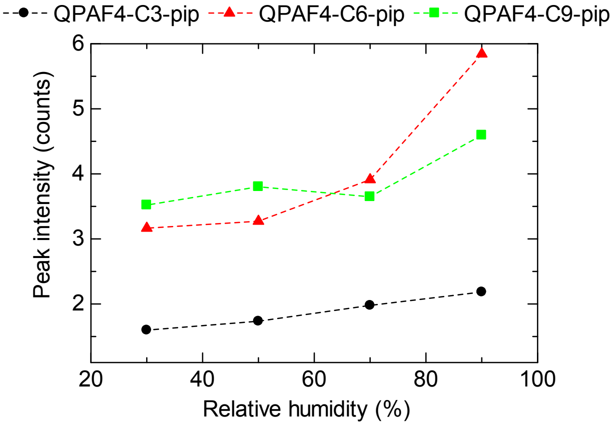

Fig. S12 Peak intensity of SAXS patterns of QPAF4-C(3, 6 and 9)-pip membranes in Cl^- ion forms as a function of the relative humidity.

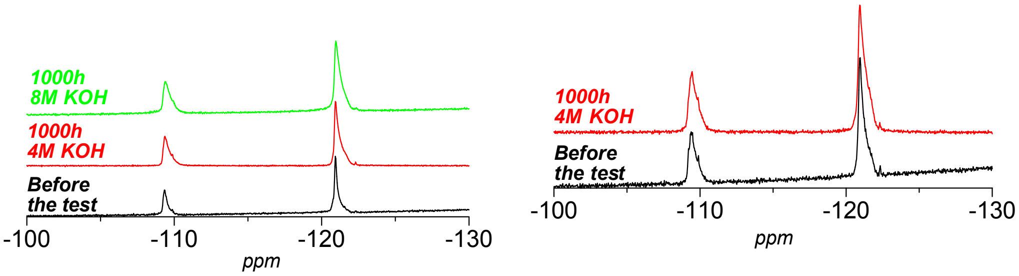

Fig. S13 ^{19}F NMR spectra of QPAF4-C3-pip (left) and QPAF4-C6-pip (right) after the alkaline stability tests in different concentration of KOH aqueous solution at 80 °C.

References

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2. H. Ono, T. Kimura, A. Takano, K. Asazawa, J. Miyake, J. Inukai and K. Miyatake, *J. Mater. Chem. A,* 2017*,* **47***,* 24804-24812.