Supplementary information for

Robust anion conductive polymers containing perfluoroalkylene and pendant ammonium groups for high performance fuel cells

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Materials. N,N-dimethylacetamide (DMAc) (> 99.0%, Kanto Chemical) was purified with a solvent refining apparatus before use. Fluorene (> 95.0%, TCI), N-chlorosuccinimide (NCS) (> 98.0%, TCI), acetonitrile (> 99.5%, Kanto Chemical), hydrochloric acid (35-37%, Kanto Chemical), 1,6-dibromohexane (> 97.0%, TCI), tetrabutylammonium bromide (TBAB) (> 98.0%, TCI), potassium hydroxide (> 86.0%, Kanto Chemical), dimethylamine aqueous solution (40%, Kanto Chemical), tetrahydrofuran (> 99.5%, Kanto Chemical), 2,2'-bipyridine (> 99.0%, TCI), bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)₂) (> 95.0%, Kanto Chemical), and iodomethane (> 99.5%, Kanto Chemical) were used as received.

2,7-Dichloro-9,9-bis[6'-(N,N-dimethylamino)hexyl[fluorene (monomer 2)



Scheme S1 Synthesis of monomer 2.

2a.¹ A 500 mL round bottomed flask was charged with fluorene (83.1 g, 0.50 mol), NCS (166.9 g, 1.25 mol), and acetonitrile (166 mL). To the mixture, concentrated hydrochloric acid (16.6 mL) was added dropwise carefully to keep the temperature below the boiling point of acetonitrile. After the completion of the addition, the product was slowly precipitated from the homogeneous mixture while cooling the temperature down to r.t. The suspension was stirred for 24 h and the solid was collected by filtration. The crude product was washed with methanol (100 mL) three times and water (200 mL) twice, respectively. The product was dried under vacuum oven at 60 °C to obtain 18.4 g of **2a** as white solid in 65% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.85 (s, 2H), 7.35 (dd, J = 0.7, 4.4 Hz, 2H), 7.50 (d, J = 0.6 Hz, 2H), 7.63 (d, J = 4.3 Hz, 2H).

2b.^{2,3} A 300 mL round bottomed flask was charged with **1** (8.23 g, 35.0 mmol), 1,6dibromohexane (53 mL). To the mixture, a solution of potassium hydroxide (35.0 g) and TBAB (2.26 g, 7.00mmol) in water (35 mL) was added. The mixture was heated at 80 °C and the reaction was continued for 1 h. The reaction was quenched by adding water (100 mL). The organic layer was washed with water (100 mL) and brine (100 mL), dried over magnesium sulfate, and concentrated on a hot plate heated at 120 °C to evaporate excess 1,6dibromohexane. The resulting oily crude product was purified by silica gel column chromatography (eluent: dichloromethane/hexane = 1/4) to obtain 13.8 g of **2b** as pale yellow solid in 70% yield. ¹H NMR (500 MHz, TCE-d₂): δ 0.59 (m, 4H), 1.08 (m, 4H), 1.20 (m, 4H), 1.67 (m, 4H), 1.93 (m, 4H), 3.29 (t, *J* = , 6.9 Hz, 2H), 7.28 (s, 2H), 7.31 (d, *J* = , 4.3 Hz, 2H), 7.57 (d, *J* = 4.0 Hz, 2H).

Monomer $2.^2$ A 300 mL round bottomed flask was charged with 2b (13.16 g, 23.4 mmol), THF (117 mL) and 40% dimethylamine aqueous solution (58.6 mL). The mixture was stirred for 24 h and quenched by adding saturated sodium bicarbonate aqueous solution (200 mL). The mixture was extracted with hexane (100 mL) three times and then the combined organic layer was washed with brine (100 mL) twice. The organic solution was dried over magnesium sulfate and concentrated under reduced pressure. The residue was cooled with an ice bath to obtain 8.64 g of monomer **2** as light yellow crystalline solid in 75% yield.

Measurements. ¹H and ¹³C NMR spectra were obtained on a JEOL JNM-ECA/ECX500 using deuterated chloroform (CDCl₃), 1,1,2,2-tetrachloroethane (TCE-d₂), or dimethylsulfoxide (DMSO-d₆). Tetramethylsilane (TMS) or the solvent was used as an internal reference. Molecular weight was measured with gel permeation chromatography (GPC) equipped with a Shodex K-805 L column and a Jasco UV 2077 detector (270 nm) with CHCl₃ containing 0.05 M triethylamine as eluent. Molecular weight was calibrated with standard polystyrene samples (ranged from $M_n = 1.26$ to 423 kDa, 10 samples). Solubility of

QPAF-4 was tested by dissolving 10 mg of a membrane sample in chloride ion from in an organic solvent (1 mL) at 80 °C or boiling temperature. Ion exchange capacity (IEC) was determined by titration. A membrane sample (ca. 20 mg) in chloride ion form was immersed in 0.2 M NaNO₃ (12.5 mL) at 40 °C for 24 h. The amount of chloride ions released from the membrane was titrated with 0.01 M AgNO₃ using K₂CrO₄ as an indicator and NaHCO₃ as a pH adjuster.

For transmission electron microscopic (TEM) observation, membrane samples were stained with tetrachloroplatinate ions by ion exchange of the ammonium groups in 0.5 M K_2PtCl_4 aqueous solution, rinsed with deionized water, and dried in a vacuum oven overnight. The stained membrane was embedded in an epoxy resin, sectioned to 50 nm thickness with a Leica microtome Ultracut UCT, and placed on a copper grid. Images were taken on a Hitachi H-9500 transmission electron microscope with an accelerating voltage of 200 kV. SAXS profiles were collected using a Nano-Viewer (Rigaku) with Cu(K α) as an X-ray source. The SAXS measurement was performed at 40 °C under nitrogen atmosphere humidified at 30 - 90% RH. The membrane sample in chloride ion form was placed in an SAXS cell and equilibrated in the humidified nitrogen for 2 h before the measurement.

Hydroxide ion conductivity of the membranes was measured in degassed, deionized water (18 MΩ) at 30, 40, 60, and 80 °C using a 4-probe conductivity cell attached with an AC impedance spectroscopy (Solartron 1255B, Solartron Inc.). Ion conducting resistance (R (Ω)) was determined from the impedance plot obtained in the frequency range from 1 to 10⁵ Hz. The hydroxide ion conductivity (σ) was calculated from the equation, $\sigma = l/AR$, where A (cm²) and l (cm) are the cross-section area of the membrane and the distance between two reference electrodes, respectively. The water uptake was calculated using the following equation: Water uptake (%) = ($W_w - W_d$) / $W_d \times 100$, where W_w is the wet weight and W_d the dry weight (dried in a vacuum oven at 80 °C overnight) of the membrane.

Gas permeability of the membranes was measured using a GTR-Tech 20XFYC gas permeation measurement apparatus containing a Yanaco G2700T gas chromatography with a Porapak-Q column and a TCD detector. Argon and helium were used as a carrier gas for the measurement of hydrogen and oxygen, respectively. A membrane sample in chloride ion form (40 mm in diameter and 50 µm thick) was set in a cell that had a gas inlet and an outlet on both sides of the membrane. On one side of the membrane, hydrogen or oxygen test gas was supplied at a flow rate of 30 mL min⁻¹, while on the other side of the membrane, the same gas as the carrier used in the gas chromatograph (flow gas) was supplied at a flow rate of 20 mL min⁻¹. Both gases were dried or humidified under the same conditions to ensure homogeneous wetting of the membrane samples. Then, 7.4 mL of the flow gas was sampled and subjected to the gas chromatography to quantify the test gas permeated through the membrane. The measurement was repeated until stable permeation data were obtained at least for 5 h. Gas permeation coefficient, Q (cm³ (STD) cm cm⁻² s⁻¹ cmHg⁻¹) was calculated by the following equation: $Q = 273/T \times 1/A \times B \times 1/t \times 1/(76-P_{H2O})$, where T (K) is the absolute temperature, A (cm²) is the permeation area, B (cm³) is the amount of permeated test gas, t (s) is the sampling time, l (cm) is the thickness of the membrane, and $P_{\rm H2O}$ (cmHg) is the water vapor pressure.

Dynamic mechanical analysis (DMA) was carried out with an ITK DVA-225 dynamic viscoelastic analyzer. Temperature dependence of storage modulus (E' (Pa)), loss modulus (E' (Pa)), and tan δ (= E''/E') at 60% RH and 10 Hz was measured for the membranes in chloride ion forms (5 × 30 mm) between r.t. and 95 °C at a heating rate of 1 °C min⁻¹. Humidity dependence of E', E'', and tan δ at 80 °C and 10 Hz was also measured between 0% and 90% RH at a humidifying rate of 1%RH min⁻¹. Tensile strength testing was carried out with a Shimadzu universal testing instrument Autograph AGS-J500N equipped with a temperature and humidity controllable chamber. A membrane sample in chloride ion form

was cut into a dumbbell shape ($35 \times 6 \text{ mm}$ (total) and $12 \times 2 \text{ mm}$ (test area)). Stress strain curves were obtained at 80 °C and 60% RH at a stretching rate of 10 mm min⁻¹ after equilibrating the membrane at least for 3 h. Alkaline stability test of the membranes was performed in 1 M KOH aqueous solution at 80 °C. The hydroxide ion conductivity was recorded in degassed water at 40 °C as a function of testing time. The post-test membranes were subjected to tensile strength test and ¹H NMR spectra. Oxidative stability test of the membrane was performed in Fenton's solution (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C for 8 h.

References

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Fig. S2 Photograph of QPAF-4 (IEC = 1.47 meq g^{-1}) membrane.

| ane | membrane | membrane m |
|-----|----------|------------|
| ne | membrane | membrane 1 |
| ne | membrane | membrane |
| 1e | membrane | mhrane |
| е | membrane | membrane |

Fig. S3 Photograph of QPAF-4 membrane with IEC = 1.47 meq g^{-1} after the alkaline stability test in 1 M KOH at 80 °C for 1000 h.



Fig. S4 (a) Photograph and (b) ¹H NMR spectra (in DMSO-*d*₆.) of QPAF-4 membrane with IEC = 1.47 meq g^{-1} after the oxidative stability test in Fenton's solution at 80 °C for 8 h.