Supporting Information

Morphology and Cell Performance of Poly(fluorene)-based Anion

Exchange Membranes for Water Electrolysis: Effect of Backbone Core

Structure

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Experimental details

4-bromobenzaldehyde (99%), fluorene (98%), acetyl chloride (98%), Material: aluminium(III) chloride (AlCl₃, 98%), 1,6-dibromohexane (DHB, 96%), iodomethane (CH₃I, 99%), 2-aminobiphenyl (97%), potassium iodide (KI, 99%), magnesium (98%), sodium nitrite 99%), Tris(dibenzylideneacetone)dipalladium (NaNO₂, $(Pd_2(dba)_3,$ 97%), Tri(otolyl)phosphine (P(o-tol)₃, 97%), Potassium phosphate tribasic (K₃PO₄, 98%), 1,1'bis(diphenylphosphino)ferrocene] dichloropalladium(II) (Pd(dppf)Cl₂), potassium acetate (KOAc, 99%), tetrabutylammonium bromide (TBAB, 98%) were purchased from Sigma-Aldrich. Bis(pinacolato)diboron (B₂Pin₂), trifluoroacetic acid (TFA, 99%), triethylsilane (Et₃SiH, 98%), potassium tert-butoxide (KOtBu, 97%), 9-fluorenone (98%) were purchased from TCI. Potassium hydroxide (KOH, 95%), 1,4-dioxane (99.5%), acetic acid (AcOH, 99.5%), hydrogen chloride (HCl, 35-37%) were purchased from SAMCHUN chemicals. All other chemicals were obtained from other commercial sources.

Synthesis details



Scheme S1. Synthesis scheme for 2,7-bis(3-(4-bromophenyl)propyl)-9,9-dimethylfluorene (4) and 2,2-bis(3-(4-bromophenyl)propyl)-9,9-spirobifluorene (9).

Synthesis of 9,9-Dimethylfluorene (1).

To an iced-cooled solution of fluorene (12.47 g, 75.0 mmol) in dry THF (75 mL), under argon atmosphere, was added tBuOK (18.51 g, 165.0 mmol) and the solution was stirred at room temperature for 1.5 h. CH₃I (9.35 mL, 150.0 mmol) was added and a white precipitate of KI was formed. The reaction mixture was stirred for a further 2 h. The KI was then eliminated through filtration and the evaporation of THF and purified by column chromatography using hexane and DCM (20:1 v/v) as the eluent which afforded a white solid (12.97 g, 89% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.77-7.74 (m, 2H), 7.48-7.45 (m, 2H), 7.39-7.32 (m, 4H), 1.52 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 153.37,139.17, 127.19, 126.90, 122.56, 119.96, 46.80, 27.13.

Synthesis of 2,7-Diacetyl-9,9-dimethylfluorene (2).

A solution of AlCl₃ (21.60 g, 162.2 mmol) and acetyl chloride (12.72 g, 162.2 mmol) was added dropwise to an ice-cooled solution of 9,9-dimethylfluorene (6.23 g, 64.8 mmol) in dry

DCM (200 mL) under an N₂ atmosphere. The reaction mixture was stirred at 0°C for 1 h and further stirred at 40°C for 6 h under an N₂ atmosphere. The resulting mixture was poured into ice water (500 mL) and alkalized with an aqueous solution of K₂CO₃ until a neutral pH was achieved, and extracted with of DCM. The separated organic layer was dried over anhydrous MgSO₄ and purified by column chromatography using hexane and DCM (3:7 v/v) to DCM as the eluent to obtain a pure product as a white solid (7.84 g, 87% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.09-8.07 (d, *J* = 1.5 Hz, 2H), 8.02-7.98 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.86-7.83 (d, *J* = 7.9 Hz, 2H), 2.68 (s, 6H), 1.55 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 197.81, 154.98, 142.52, 137.02, 128.24, 122.51, 120.81, 47.22, 26.82, 26.75.

Synthesis of 2,7-Bis[3-(4-bromophenyl)acryloyl)-9,9-dimethylfluorene (3).

2,7-Diacetyl-9,9-dimethylfluorene (5.25 g, 18.89 mmol) and 4-bromobenzaldehyde (10.48 g, 56.7 mmol) were mixed in ethanol (750 mL), and the flask was heated until the mixture dissolved completely. A 10 wt% sodium hydroxide solution (45 mL) was added to the reaction system. The reaction mixture was stirred at 40°C for 2 day under an N₂ atmosphere. After cooling to room temperature, the reaction mixture was filtered, and the filter cake was washed with ethanol. The crude product was purified by column chromatography using DCM as the eluent to obtain a pure product as a pale yellowish solid (9.49 g, 82% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.15 (s, 2H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.80 (d, *J* = 15.4 Hz, 2H), 7.61 (d, *J* = 15.4 Hz, 2H), 7.60-7.52 (m, 8H). ¹³C NMR (125 MHz, CDCl₃) δ 189.70, 155.20, 143.40, 142.56, 138.00, 133.83, 132.23, 129.83, 128.29, 124.85, 122.99, 122.58, 120.93, 47.40, 26.87.

Synthesis of 2,7-Bis(3-(4-bromophenyl)propyl)-9,9-dimethylfluorene (4).

In a two-necked flask, 2,7-bis[3-(4-bromophenyl)acryloyl)-9,9-dimethylfluorene (5.36 g, 8.8 mmol) was dissolved in CHCl₃ (70 mL). Subsequently, trifluoroacetic acid (TFA) (8.05 mL, 105 mmol) and Et₃SiH (8.40 mL, 52.5 mmol) were added, and the reaction mixture was stirred at 70°C for 1 day under an N₂ atmosphere. After cooling to room temperature, the reaction mixture was poured into 1 M KOH solution until a neutral pH was achieved. The crude product was extracted by DCM and washed in deionized water 3 times. The separated organic layer was dried over anhydrous MgSO₄ and purified by column chromatography using hexane and DCM (9:1 v/v) as the eluent to obtain a pure product as a white solid (3.88 g, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.44-7.40 (m, 4H), 7.21 (d, *J* = 1.5 Hz,

2H), 7.14 (dd, J = 7.9, 1.5 Hz, 2H), 7.11-7.07 (m, 4H), 2.72 (t, J = 7.7 Hz, 4H), 2.65 (t, J = 7.7 Hz, 4H), 1.99 (tt, J = 7.7, 7.7 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 153.83, 141.24, 140.85, 137.03, 131.33, 130.23, 127.08, 122.56, 119.51, 119.44, 46.55, 35.56, 34.85, 33.00, 27.28. Elemental analysis: C = 67.28%, H = 5.28% (calcd: C = 67.36%, H = 5.48%).

Synthesis of 2-Iodobiphenyl (5).

To a suspension of 2-aminobiphenyl (6.77 g, 40.0 mmol) in concentrated hydrochloric acid (8.05 mL) and water (40 mL) cooled at 0°C was added carefully an aqueous solution of sodium nitrite (3.31 g, 48.0 mmol) in 10 min. The brown mixture was then stirred at 0°C for 1 h and added carefully to an aqueous solution of potassium iodide (13.28 g, 80.0 mmol) in 5 min. The final solution was stirred at room temperature for 12 h and then extracted four times with diethyl ether. The organic layers were then washed with a solution 3 N of hydrochloric acid, a saturated solution of sodium bicarbonate, sodium chloride, water and dried over anhydrous MgSO₄. The solvents were removed under vacuum and purified by column chromatography using petroleum ether as the eluent to obtain a pure product as a colorless liquid (10.31 g, 92% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.98 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.48-7.30 (m, 7H), 7.05 (td, *J* = 7.9, 1.2 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 146.57, 144.14, 139.44, 130.04, 129.22, 128.74, 128.07, 127.91, 127.60, 98.59.

Synthesis of 9,9-Spirobifluorene (6).

Under argon atmosphere 2-iodobiphenyl (10.0 g, 35.7 mmol) was added dropwise in 30 min to magnesium turning (3.48 g, 142.8 mmol) in anhydrous diethyl ether (50 mL). The mixture was heated to reflux for 1 h and then diluted with diethyl ether (50 mL). A solution of 9-fluorenone (7.08 g, 39.3 mmol) dissolved in diethyl ether (100 mL) was added dropwise. The mixture was heated to reflux for 12 h. After cooling to r.t, the precipitate was filtered and washed with diethyl ether. The solid material was added to an ice-cold aqueous NH₄Cl solution and stirred for 6 h. After stirring the precipitate was collected and dried in a vacuum and a white solid of carbinol was obtained. The carbinol was then dissolved in boiling acetic acid (100 mL), and several drops of concentrated hydrochloric acid were added. An intermediate reaction took place and the mixture solidified. The 9,9-spirobifluorene was filtered off and recrystallized from ethanol to give 14.2 g of white solid (9.15 g, 81% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 7.5 Hz, 4H), 7.38 (td, *J* = 7.5, 1.0 Hz, 4H), 7.12 (td, *J* = 7.5, 1.0 Hz, 4H), 6.75 (t, *J*

= 7.5 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 148.74, 141.74, 127.79, 127.67, 124.02, 119.95, 65.92.

Synthesis of 2,2-Diacetyl-9,9-spirobifluorene (7).

Following the general procedure, the reaction was carried out with 2. The corresponding product 7 was isolated as a white solid (6.36 g, 91% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.03 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 2H) 7.42 (td, *J* = 7.6, 0.9 Hz, 2H), 7.31 (d, *J* = 0.9 Hz, 2H), 7.18 (td, *J* = 7.6, 0.9 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 2H), 2.47 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 197.47, 149.13, 148.30, 146.65, 140.43, 136.72, 129.26, 129.14, 128.25, 124.12, 123.78, 121.16, 120.05, 65.77, 26.67.

Synthesis of 2,2-Bis[3-(4-bromophenyl)acryloyl)-9,9-spirobilfluorene (8).

Following the general procedure, the reaction was carried out with 3. The corresponding product 8 was isolated as a white solid (9.79 g, 89% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.12 (dd, J = 8.1, 1.7 Hz, 2H), 8.00 (d, J = 8.1 Hz, 2H), 7.96 (dd, J = 7.3, 1.2 Hz, 2H), 7.63 (d, J = 15.4 Hz, 2H), 7.52-7.48 (m, 4H), 7.47-7.39 (m, 8H), 7.36 (d, J = 15.4 Hz, 2H), 7.20 (td, J = 7.6, 1.2 Hz, 2H), 6.76 (d, J = 7.6 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 189.30, 149.21, 148.39, 146.71, 143.23, 140.47, 137.59, 133.75, 132.11, 129.78, 129.35, 129.25, 128.31, 124.70, 124.25, 124.19, 122.51, 121.22, 120.23, 65.90

Synthesis of 2,7-bis(3-(4-bromophenyl)propyl)-9,9-spirobifluorene (9).

Following the general procedure, the reaction was carried out with 4. The corresponding product 9 was isolated as a white solid (7.57 g, 87% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.2, 4H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 8.2, 4H), 6.72 (d, *J* = 7.6 Hz, 2H), 6.53 (s, 2H), 2.45 (t, *J* = 7.7 Hz, 4H), 2.39 (t, *J* = 7.7 Hz, 4H), 1.76 (tt, *J* = 7.7, 7.7 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 149.24, 148.97, 141.87, 141.79, 140.93, 139.65, 131.26, 130.19, 127.90, 127.64, 127.43, 124.03, 119.87, 119.70, 119.38, 65.80, 34.96, 34.36, 32.44, 30.94.

Synthesis of poly[(9,9-bis(6-bromohexyl)fluorene)-co-(4,4-bis((3-phenyl)propyl)-9,9dimethylfluroene)] (PFPF-Br). The PFPF-Br polymer was synthesized from 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-9,9-(6-dibromohexyl)fluorene (compound A) and 2,7-Bis(3-(4-bromophenyl)propyl)-9,9dimethylfluorene (compound B) through a Pd-catalyzed Suzuki cross-coupling reaction. Under N₂ atmosphere in a 500 mL Schlenk flask under a nitrogen atmosphere, compound A (3.20 g, 4.30 mmol) and compound B (2.53 g, 4.30 mmol) were dissolved in toluene (120 mL), and 2 M K_3PO_4 solution (40 mL) were added to the flask. The mixture solution was degassed via freeze pump thaw for at least three cycles to remove oxygen; after that, Pd₂(dba)₃ (197 mg, 0.21 mmol) and P(o-tol)₃ (191 mg, 0.63 mmol) was added to the reaction mixture. The reaction mixture was stirred at 100°C for 5 days. After the reaction was complete, the mixture solution was precipitated by adding it to an HCl/EtOH solution under stirring conditions. The polymer was washed in cold EtOH, then dried in a vacuum oven overnight. The polymer was further purified by Soxhlet extraction with acetone and CH₂Cl₂ respectively. Finally, the polymer was dried in a vacuum oven, yielding a pale yellowish fibers (3.13 g, 83%). ¹H-NMR (500 MHz, CDCl₃) δ 7.83–7.71 (2H, broad signal, H₁₈), 7.69–7.53 (10H, broad signal, H₁₄₋₁₇), 7.38–7.28 (6H, broad signal, H_{12,13}), 7.22–7.13 (2H, broad signal, H₁₁), 3.33–3.19 (4H, broad signal, H₁₀), 2.85-2.66 (8H, broad signal, H_{8.9}), 2.16-1.95 (8H, broad signal, H_{6.7}), 1.71-1.59 (4H, broad signal, H₅), 1.57-1.42 (6H, broad signal, H₄), 1.33-1.01 (8H, broad signal, H_{2,3}), 0.85-0.62 (4H, broad signal, H_1). Elemental analysis: C = 78.10%, H = 6.81% (calcd: C = 75.81%, H = 6.80%).

Synthesis of poly[9,9-bis(6-(N,N,N-trimethylammonium)hexyl)fluorene]-co-[4,4-bis((3-phenyl)propyl)-9,9-dimethylfluroene)] (PFPF-QA)

PFPF-QA was quaternized via the Menshutkin reaction with trimethylamine (TMA). PFPF-Br (3.0 g, 6.54 mmol) was dissolved in DMF (24 mL). Subsequently, a TMA (28 wt%) (13.80 g, 65.4 mmol) solution was added to the mixture to form a homogeneous solution. The reaction was performed in DMF at 40°C for 24 h. After the reaction, the crude mixture was poured into ethyl acetate (500 mL), and the precipitated fibers were filtered, washed with ethyl acetate several times, and dried at 40°C under vacuum to give the PFPF-QA as pale yellowish fibers (3.26 g, 93%). ¹H-NMR (500 MHz, DMSO-d₆) δ 8.03–7.49 (12H, broad signal, H₁₆₋₁₉), 7.47–7.02 (10H, broad signal, H₁₂₋₁₅), 3.20–3.03 (4H, broad signal, H₁₁), 3.03–2.83 (18H, broad signal, H₁₀), 2.83–2.56 (8H, broad signal, H_{8,9}), 2.23–1.83 (8H, broad signal, H_{6,7}), 1.53–1.28 (10H, broad signal, H_{4,5}), 1.22–0.92 (8H, broad signal, H_{2,3}), 0.74–0.45 (4H, broad signal, H₁).

Synthesis of poly[(9,9-bis(6-bromohexyl)fluorene)-co-(2,2-bis((3-phenyl)propyl)-9,9spirobifluorene)] (PFPS-Br).

The PFPF-Br polymer was synthesized from 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-(6-dibromohexyl)fluorene (compound A) and 2,2-bis(3-(4-bromophenyl)propyl)-9,9-spirobifluorene (compound C) through a Pd-catalyzed Suzuki cross-coupling reaction. Under N₂ atmosphere in a 500 mL Schlenk flask under a nitrogen atmosphere, compound A (3.20 g, 4.30 mmol) and compound C (3.05 g, 4.30 mmol) were dissolved in toluene (120 mL), and 2 M K₃PO₄ solution (40 mL) were added to the flask. The mixture solution was degassed via freeze pump thaw for at least three cycles to remove oxygen; after that, Pd₂(dba)₃ (197 mg, 0.21 mmol) and P(o-tol)₃ (191 mg, 0.63 mmol) was added to the reaction mixture. The reaction mixture was stirred at 100°C for 5 days. After the reaction was complete, the mixture solution was precipitated by adding it to an HCl/EtOH solution under stirring conditions. The polymer was washed in cold EtOH, then dried in a vacuum oven overnight. The polymer was further purified by Soxhlet extraction with acetone and CH₂Cl₂ respectively. Finally, the polymer was dried in a vacuum oven, yielding a pale yellowish fibers (3.80 g, 87% yield). ¹H-NMR (500 MHz, CDCl₃) § 7.90–7.66 (2H, broad signal, H₁₉₋₂₁), 7.61–7.43 (2H, broad signal, H_{17,18}), 7.43– 7.30 (12H, broad signal, H₁₆), 7.30–7.20 (8H, broad signal, H₁₅), 7.20–6.98 (8H, broad signal, H₁₂₋₁₄), 6.83–6.67 (8H, broad signal, H₁₁), 6.66–6.50 (8H, broad signal, H₁₀), 3.33–3.12 (4H, broad signal, H₉), 2.68–2.36 (8H, broad signal, H_{7.8}), 2.19–1.96 (4H, broad signal, H₆), 1.96– 1.73 (4H, broad signal, H₅), 1.74–1.58 (4H, broad signal, H₄), 1.35–0.96 (8H, broad signal, $H_{2,3}$), 0.89–0.55 (4H, broad signal, H_1). Elemental analysis: C = 79.10%, H = 6.17% (calcd: C = 78.45%, H = 6.20%).

Synthesis of poly[9,9-bis(6-(N,N,N-trimethylammonium)hexyl)fluorene]-co-(2,2-bis((3-phenyl)propyl)-9,9-spirobifluorene)] (PFPS-QA).

PFPS-QA was quaternized via the Menshutkin reaction with trimethylamine (TMA). PFPS-Br (3.0 g, 5.93 mmol) was dissolved in DMF (24 mL). Subsequently, a TMA (28 wt%) (12.51 g, 59.3 mmol) solution was added to the mixture to form a homogeneous solution. The reaction was performed in DMF at 40°C for 24 h. After the reaction, the crude mixture was poured into ethyl acetate (500 mL), and the precipitated fibers were filtered, washed with ethyl acetate several times, and dried at 40°C under vacuum to give the PFPF-QA as pale yellowish fibers (3.22 g, 94% yield). ¹H-NMR (500 MHz, DMSO-d₆) δ 8.06–7.74 (6H, broad signal, H₂₀₋₂₂),

7.74–7.46 (6H, broad signal, H_{18,19}), 7.46–7.20 (4H, broad signal, H_{16,17}), 7.20–6.95 (8H, broad signal, H₁₃₋₁₅), 6.68–6.49 (2H, broad signal, H₁₂), 6.49–6.31 (2H, broad signal, H₁₁), 3.24–3.01 (4H, broad signal, H₁₀), 3.01–2.78 (16H, broad signal, H₉), 2.62–2.25 (8H, broad signal, H_{7,8}), 2.25–1.91 (4H, broad signal, H₆), 1.86–1.53 (4H, broad signal, H₅), 1.53–1.26 (4H, broad signal, H₄), 1.23–0.79 (8H, broad signal, H_{2,3}), 0.74–0.39 (4H, broad signal, H₁)

Structure characterization

The chemical structure of the synthesized monomers and polymers were identified via ¹H and ¹³C NMR spectroscopy. ¹H, ¹³C NMR spectra using a 500 MHz NMR instrument (Bruker 500-MR) using an internal deuterium lock or CDCl₃ and DMSO- d_6 as a reference.

Membrane fabrication

The PFPB-QA, PFPF-QA, and PFPS-QA membrane was prepared in an DMSO solution using thesolution-casting method, and the film thickness was 45 μ m. In its Br⁻ form, anion exchange polymer (0.45 g) was dissolved in DMSO to a concentration of 5 wt%. The solution was then filtered through a cotton plug and poured onto a clean glass plate with a diameter of 11 cm, and the film was cast and dried in a vacuum oven at 60°C for 24 h, followed by 80°C for 4 h. Each membrane was removed after immersion in deionized water, and the resultant membrane was then immersed in 1 M KOH at room temperature for 24 h in a closed container to obtain the membrane in its OH⁻ form. Finally, each membrane in its OH⁻ form was washed with and immersed in deionized water for 24 h prior to further measurements.

Ion exchange capacity (IEC)

Using the back titration method, the ion exchange capacity (IEC) value of each membrane was calculated. To neutralize the OH⁻ ions, the OH⁻ form membranes were kept for 24 h in a 0.01 M HCl standard solution. Residual HCl was back titrated with a 0.01 M NaOH standard solution using a phenolphthalein indicator. The membranes were then dried to determine their weight (W_{dry} , g). The following equation was used to calculate the experimental IEC (in meq g⁻¹) as the moles of exchangeable hydroxide per gram:

$$IEC (meq g^{-1}) = \frac{(V_{0NaOH}C_{NaOH} - V_{xNaOH}C_{NaOH})}{W_{dry'}}$$

Water uptake (WU) and swelling ratio (SR)

The water uptake (%) of each membrane was measured. The OH^- form membranes were immersed in deionized water for at least 24 h, the surface of the membrane was dried by wiping, and the sample was weighed as soon as possible (W_{wet}). The membrane was dried under vacuum for 24 h, and the dry membrane's weight was taken (W_{dry}). Water uptake measurements in 95% RH at 60°C were executed in a humidity temperature oven. The membrane was kept to RH of 95% for 24 h before each measurement The following equation was used to determine water uptake (%):

$$IEC (meq g^{-1}) = \frac{(V_{0NaOH}C_{NaOH} - V_{xNaOH}C_{NaOH})}{W_{dry'}}$$

The swelling ratio (%) was calculated by soaking round membranes in water at temperatures of 20°C, 40°C, 60°C, and 80°C. Subsequent changes in size due to expansion were measured both in-plane and through-plane. These changes were applied to the following equation:

$$\Delta l = \frac{l_{wet} - l_{dry}}{l_{dry}} \times 100$$

, where twet is the thickness after soaking at 20°C, 40°C, 60°C, and 80°C, and t_{dry} is the thickness of the membranes after drying under vacuum at 40°C for 4–5 h before measuring length and thickness.

Mechanical properties and thermal stability

Benchtop tensile tester (Mech Tester Instron 5567) was used to measure the mechanical properties of membranes at a crosshead speed of 1 mm min⁻¹ at 25°C under 50% relative humidity. The cross-sectional area of the sample's initial state was used to determine the engineering stress. The initial slope of the stress-strain curve was used to calculate Young's modulus (E). For this test, samples of the membrane were prepared in dumbbell shapes of 40 mm x 10 mm total area and 20 mm x 10 mm test area. The cast membranes' thermal stability was investigated by thermogravimetric analysis (TGA) using a Scinco TGA N-1000 instrument. The TGA was operated at a heating rate of 10°C min⁻¹ from 30 - 500°C under the N₂ atmosphere.

A PerkinElmer DSC 4000 was used to measure the glass-transition temperature (T_g). Samples were prepared in aluminum pans and measured from 30 to 200°C for 2 cycles at heating and cooling rates of 10°C per minute. The second heating plot was used to determine the T_g .

Morphology characterization

Topography of the membranes was investigated via Atomic Force Microscope (AFM: Dimension 3100 + Nanoscope V 7.0, VEECO) in tapping mode using Si tips and FE-Transmission Electron Microscope (TEM : JEM-2100F, Jeol). For the grazing-incidence wide-angle X-ray scattering (GIWAXS) analysis, thin films were prepared by spin-coating from a 5 mg mL⁻¹ solution in DMSO on 1 by 1 cm² silicon wafer. The GIWAXS analysis was conducted at the Pohang Accelerator Laboratory (beamline 9A, Republic of Korea) with incidence angles at 0.12°. For SAXS measurement X-Ray diffraction analysis of membranes performed Rigaku D/Max-2200/PC with measurement range of 0° to 4° and 0.1° min⁻¹ of scan speed.

Hydroxide ion conductivity

The hydroxide conductivity (σ) of each membrane was measured using a four-probe impedance spectroscopy method using an AC impedance analyzer (SP-200, Bio-Logic SAS, Claix, France). The electrode systems were connected at frequencies from 100 mHz to 2 MHz. Rectangular samples were prepared with the dimensions 1 × 4 cm. The hydroxide ion conductivity was measured using the resistance (R) in deionized water from 20°C to 80°C. The hydroxide ion conductivity was calculated using the following equation:

$$\sigma = \frac{L}{R \times A}$$

where L is the distance between the reference electrodes and A is the cross-sectional area of the membrane.

Alkaline stability

The OH⁻ form membranes were soaked in 1 M KOH solution at 80°C for at most 1000 h in order to evaluate the membranes' chemical stability. The changes in IEC, ionic conductivity, and mechanical properties were examined. Before the measurements, each membrane was washed several times with DI H₂O, and the free KOH inside the membrane was removed by soaking in DI H₂O for at least 24 h at room temperature. Each membrane's ionic conductivity was measured in DI H₂O at 20°C

Fabrication of Membrane Electrode Assemblies (MEAs) and single cell measurements

The AEMWE cell, assembled for the application of developed AEMs, consists of a Membrane Electrode Assembly (MEA), a Porous Transport Layer (PTL) and stainless steels current collectors. The MEA comprises the anode with Co_3O_4 (electrode size of 7.065 cm²), the cathode with Pt/C (electrode size of 4.9 cm²), and the developed AEMs (PFPB-QA, PFPF-QA, and PFPS-QA) positioned between the anode and cathode. Both the anode and cathode were fabricated using the catalyst coated substrate (CCS) method.

The anode was fabricated using a slurry coating process. To prepare the Co_3O_4 slurry solution, $Co(OH)_2$ powder was synthesized via the precipitation method in a solution of cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, $\geq 97.0\%$, Samchun) adjusted to pH 9.5. The synthesized $Co(OH)_2$ powder was then mixed with a solvent and a 10 wt% Polytetrafluoroethylene (PTFE, Sigma Aldrich) binder to create a high-viscosity slurry. Subsequently, the anode was fabricated

by coating the slurry onto a Nickel Foam (NF, Alantum, pore size: 450 μ m) substrate with a hot press.

The cathode was prepared by the spray coating method. The ink solution was prepared by mixing 500 mg of Pt/C, deionized (D.I.) water (3 g), isopropyl alcohol (10 g), and a 5 wt% Nafion solution (2.5 g) and sonicating for 10 minutes. The dispersed catalyst ink solution was spread onto the carbon cloth using an ultrasonic spray coating, with a loading amount of Pt was approximately 1.0 mg cm⁻².

The AEMWE single cell was assembled using the aforementioned components. All membranes were activated by soaking them in 1 M KOH for 24 hours, and washed with fresh 1 M KOH. A 1 M KOH solution was also used as the electrolyte. The single cell had an active area of 4.9 cm² and operated within a temperature range of 45 to 70°C.

All electrochemical analyses of single cells were performed using a potentiostat (VSP, BioLogic) in a single cell with a high-current booster (20 A, BioLogic). The AEMWE cell performance was measured by linear sweep voltammetry (LSV) in the range of 1.3 to 2.0 V_{cell} at a scan rate of 1 mV s⁻¹. After the cell stabilized, durability testing was performed using a chronopotentiometer at a fixed cell temperature of 70 °C.

The cell efficiency is calculated as follows.

Cell efficiency (%) = $\frac{E_{Output}}{E_{Input}} = \frac{V_{H_2} \cdot H_0}{W_h} \times 100$

- V_{H2} : The volume of H₂ per hour (m³/h)
- H_0 : The calorific value of hydrogen (10.8 × 106 J m⁻³, lower heating value)
- Wh: The electric power to produce hydrogen for an hour

The energy consumption is converted as follows.

Energy consumption (*Wh* kg⁻¹) = $\frac{V \cdot I \cdot 22.414}{V_{H2} \cdot 2.016}$

V : The voltage of the cell

I : The current of the cell

 V_{H2} : The volume of H₂ per hour (m³/h)

Volume of 1 mole of gas under STP = 22.414

The weight of 1 mole of $H_2 = 2.016$



Figure S1. (a) ¹H and (b) ¹³C-NMR spectrum of 9,9-dimethylfluorene.



Figure S2. (a) ¹H and (b) ¹³C-NMR spectrum of 2,7-diacetyl-9,9-dimethylfluorene.



Figure S3. (a) ¹H and (b) ¹³C-NMR spectrum of 2,7-bis[3-(4-bromophenyl)acryloyl)-9,9-dimethyllfluorene.



Figure S4. (a) 1 H and (b) 13 C-NMR spectrum of 2,7-bis(3-(4-bromophenyl)propyl)-9,9-dimethylfluorene.



Figure S5. (a) ¹H and (b) ¹³C-NMR spectrum of 2-iodobiphenyl.



Figure S6. (a) ¹H and (b) ¹³C-NMR spectrum of 9,9-Spirobifluorene.



Figure S7. (a) ¹H and (b) ¹³C-NMR spectrum of 2,2-Diacetyl-9,9-Spirobifluorene.



Figure S8. (a) ¹H and (b) ¹³C-NMR spectrum of 2,2-bis[3-(4-bromophenyl)acryloyl)-9,9-spirobilfluorene.



Figure S9. (a) ¹H and (b) ¹³C-NMR spectrum of 2,7-bis(3-(4-bromophenyl)propyl)-9,9-spirobifluorene.



Figure S10. ¹H-NMR of (a) poly[9,9-bis(6-bromohexyl)fluorene]-co-[4,4-bis((3-phenyl)propyl)-9,9-dimethylfluroene] (PFPF-Br) and (b) poly[9,9-bis(6-bromohexyl)fluorene]-co-[2,2-bis((3-phenyl)propyl)-9,9-spirobifluorene] (PFPS-Br).



Figure S11. GPC data of PFPB-Br, PFPF-Br, and PFPS-Br.



Figure S12. TEM and fast Fourier transform (FFT) images of PFPB-QA in Br⁻ form.



Figure S13. Out-of-plane line-cut profiles of PFPB-QA, PFPF-QA, and PFPS-QA



Figure S14. ¹H NMR spectra of the PFPB-QA, PFPF-QA, and PFPS-QA membranes before and after alkaline stability test (1 M KOH solution at 80°C for 1000 h).



Figure S15. The I-V performance of PFPB-QA AEM using Pt/C for the cathode and IrO₂ for the anode in a previous work and Pt/C for the cathode and Co₃O₄ for the anode in this work.



Fig

ure S16. Cell efficiency and power consumption at 500 mA cm⁻² for 500 h in AEMWE.

Membrane code	$M_n(g/mol)$	M _w (g/mol)	PDI
PFPB-Br	21.0k	53.3k	2.53
PFPF-Br	22.6k	58.6k	2.51
PFPS-Br	17.1k	45.2k	2.64

 Table S1. Molecular weights of PFPB-Br, PFPF-Br, and PFPS-Br.

Table S2. IEC, water uptake, swelling ratio, hydroxide conductivity, and mechanical properties of PFPB-QA, PFPF-QA, PFPS-QA, and X37-50T.

Membrane code	IEC (meq g ⁻¹)		Water uptake (%)		Swelling ratio (%)		OH ⁻ conductivity (mS cm ⁻¹)		TS (MPa)	EB (%)
	Theo	Exp	20°C	80°C	20°C	80°C	20°C	80°C		
PFPB-QA	2.28	2.02	32.5	88.2	10.1	16.9	40.6	125.0	27.9	33.8
PFPF-QA	2.18	1.94	25.6	76.3	9.0	14.5	25.8	90.5	29.7	31.7
PFPS-QA	1.97	1.82	13.5	38.2	7.4	11.4	15.0	65.6	26.2	15.3
X37-50T	-	1.23	28.2	74.1	7.8	15.1	24.5	79.9	8.4	5.1

OER	HER	AEM	Electrolyte	Current density (A cm ⁻²)	Temp (°C)	Degradation rate (µV h ⁻¹)	Time (h)	ref
C0 ₃ O ₄	Pt/C	PFPB-QA	1 M KOH (Anode)	2.68 (2.0V)	70	36 (at 70°C)	500 (0.5 A cm ⁻²)	This work
IrO ₂	Pt/C	QBNTP- MP11	1 M NaOH (Both)	2.7 (at 2.0V)	80	2000 (at 80°C)	100 (1 A cm ⁻²)	1
Fe _x Ni _y OO H-20F	Pt/C	PAP-TP-85	1 M KOH (Anode)	1.02 (at 1.8V)	80	1810 (at 80°C)	70 (0.5 A cm ⁻²)	2
NiFe	NiMo	PVBC-Mpy	1 M KOH (Both)	0.6 (at 1.9V)	80	661 (at 80°C)	168 (0.5 A cm ⁻²)	3
IrO ₂	Pt/C	PFTP-13	1 M KOH (Anode)	7.68 (at 2.0V)	80	< 200 (at 60°C)	1100 (0.5 A cm ⁻²)	4
IrO ₂	Pt/C	PTP-85	1 M NaOH (Anode)	< 0.91 (at 2.0V)	55	1610 (at 60°C)	120 (0.4 A cm ⁻²)	5
CuCo ₂ O ₄	Pt/C	X-37-50T	1 M KOH (Anode)	1.39 (at 1.8 V)	45	1250 (at 45°C)	64 (0.5 A cm ⁻²)	6
CuCoO	Pt/C	X-37-50T	1 M KOH (Anode)	1.54 (at 1.8 V)	50	>1100 (at 50°C)	100 (0.5 A cm ⁻²)	7
Etched CuCoO	Pt/C	QPC-TMA	1 M KOH (Anode)	4.2 (at 1.9 V)	70	12 (at 45°C)	500 (0.5 A cm ⁻²)	8

Table S3.	Comparisons	of durability	of current	AEMWEs.

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