Supporting Information

High-strength, ultra-thin anion exchange membranes with branched structure toward alkaline membrane fuel cells

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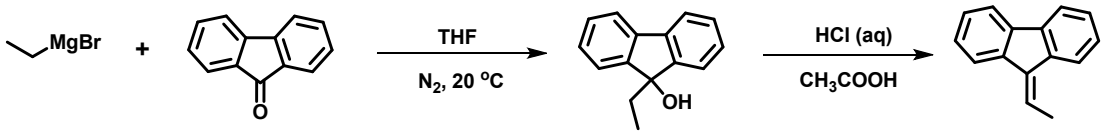
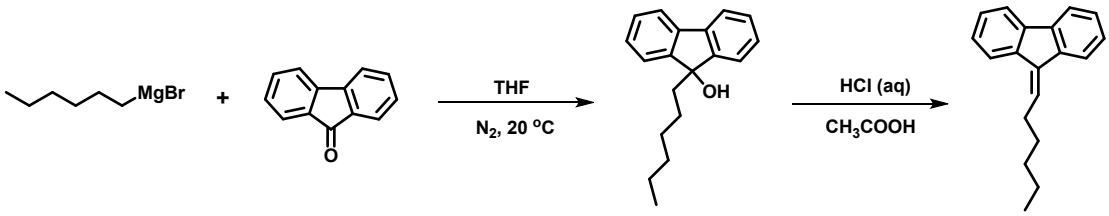
Synthesis of 9-ethylidene-9*H*-fluorene (EDF)



A B EDF

The synthetic procedures of model compounds EDF was referred to reported literature.[1] The obtained product was white power and final yield was 76.5%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.97 (d, 1H), 7.84-7.76 (dd, 2H), 7.72 (d, 1H), 7.46-7.33 (m, 4H), 6.92 (m, 1H), 2.46 (d, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 140.80, 139.41, 138.58, 137.78, 136.59, 134.84, 127.66, 127.38, 126.94, 125.11, 124.97, 119.86, 119.67, 119.54, 15.40. (Figure S1)

Synthesis of 9-hexylidene-9*H*-fluorene (HDF)



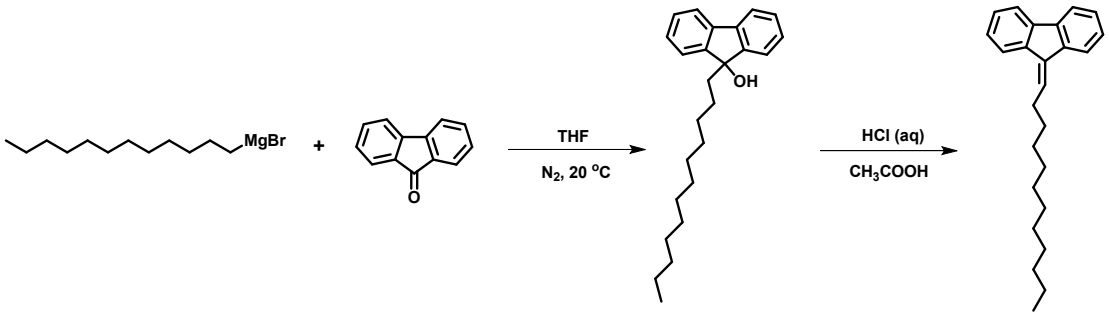
A B HDF

The hexylmagnesium bromide **A** was synthesized via Grignard reaction and prepared 1 M solution in dry tetrahydrofuran (THF). 9-Fluorenone (9.0 g, 0.05 mol) was completely dissolved in 150 mL dry THF with continuous ventilate of nitrogen. Then, monomer **A** (1M, 60 mL) was placed in dropping funnel and dripped into solution slowly. The temperature of reaction was controlled at 20 ℃. After dropping, the reacted solution was quenched by NH_4Cl saturated aqueous solution. The oil phase was dried with $MgSO_4$ and removed solvent in vacuum. Finally, the monomer **B** was purified via

column chromatography (hexanes: ethyl acetate =10 :1) to obtain white solid (10.2 g, 76.7% yield).

The monomer **B** (2.7 g, 0.01 mol) was dissolved in 100 mL dichloromethane (DCM) with 1.3 mL CH_3COOH. Then, excessive HCl aqueous solution (12 M, 10 mL) was dripped with continuous stir at room temperature. After dropping, the solution was heated to 60 ℃ overnight. The reacted solution was neutralized with $NaHCO_3$, and then oil phase was separated for further purification via column chromatography (hexanes: DCM =20 :1) to obtain white solid (2.1 g, 84.8% yield). ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.94 (d, 1H), 7.83 (d, 1H), 7.78-7.72 (m, 2H), 7.45-7.32 (m, 4H), 6.81 (t, 1H), 2.91 (m, 2H), 1.76 (m, 2H), 1.50 (m, 4H), 1.01 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 140.83, 139.48, 138.59, 137.64, 135.37, 131.39, 127.64, 127.35, 126.92, 129.87, 124.98, 119.83, 119.70, 119.51, 31.86, 29.80, 29.42, 22.79, 14.16. (Figure S2)

Synthesis of 9-dodecylidene-9*H*-fluorene (DDF)



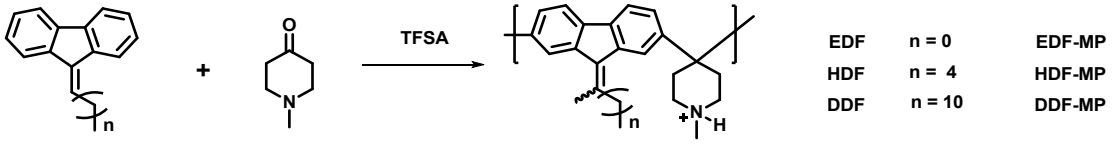
A B DDF

The dodecylmagnesium bromide **A** was synthesized via Grignard reaction which referred to literature[2] and prepared 1 M solution in dry THF. 9-Fluorenone (9.0 g, 0.05 mol) was completely dissolved in 150 mL dry THF with continuous ventilate of

nitrogen. Then, monomer **A** (1M, 60 mL) was placed in dropping funnel and dripped into solution slowly. The temperature of reaction was controlled at 20 ℃. After dropping, the reacted solution was quenched by NH_4Cl saturated aqueous solution. The oil phase was dried with $MgSO_4$ and removed solvent in vacuum. Finally, the monomer **B** was purified via column chromatography (hexanes: ethyl acetate =10 :1) to obtain yellow solid (14.6 g, 83.4% yield).

The monomer **B** (3.4 g, 0.01 mol) was dissolved in 100 mL DCM with 1.3 mL CH_3COOH. Then, excessive HCl aqueous solution (12 M, 10 mL) was dripped with continuous stir at room temperature. After dropping, the solution was heated to 60 ℃ overnight. The reacted solution was neutralized with $NaHCO_3$, and then oil phase was separated for further purification via column chromatography (hexanes: DCM =20 :1) to obtain white solid (2.7 g, 81.8% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.99-7.61 (m, 4H), 7.46-7.24 (m, 4H), 6.78 (t, 1H), 2.87 (m, 2H), 1.71 (m, 2H), 1.55-1.20 (m, 16H), 0.90 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 140.85, 139.50, 138.62, 137.66, 135.39, 131.40, 127.65, 127.36, 126.93, 126.88, 125.01, 119.85, 119.72, 119.53, 32.05, 29.80, 29.78, 29.73, 29.68, 29.50, 22.83, 14.26. (Figure S3)

Synthesis of model polymers (Route I: fluorene-type and *N*-methyl-4-piperidone)



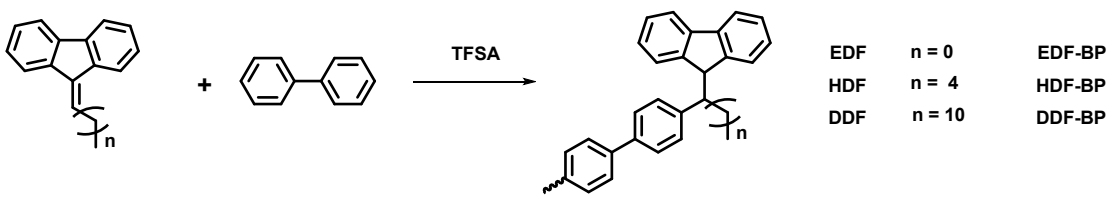
EDF-MP. The *N*-methyl-4-piperidone (0.17 g, 1.5 mmol) and EDF (0.20 g, 1.0

mmol) were added into a pressure bottle with 1 mL dry dichloromethane as solvent. Then, 0.2 mL TFA and 0.8 mL TFSA were added into system as catalysts when the temperature was reduced to 0 ℃. After 12 h of polymerization, the mixture was poured into water to precipitate the polymer. The solid was dried via lyophilization to obtain 0.30 g as yellow powder.

HDF-MP. The *N*-methyl-4-piperidone (0.17 g, 1.5 mmol) and HDF (0.25 g, 1.0 mmol) were added into a pressure bottle with 1 mL dry dichloromethane as solvent. Then, 0.2 mL TFA and 0.8 mL TFSA were added into system as catalysts when the temperature was reduced to 0 ℃. After 12 h of polymerization, the mixture was poured into water to precipitate the polymer. The solid was dried via lyophilization to obtain 0.33 g as yellow powder.

DDF-MP. The *N*-methyl-4-piperidone (0.17 g, 1.5 mmol) and DDF (0.33 g, 1.0 mmol) were added into a pressure bottle with 1 mL dry dichloromethane as solvent. Then, 0.2 mL TFA and 0.8 mL TFSA were added into system as catalysts when the temperature was reduced to 0 ℃. After 12 h of polymerization, the mixture was poured into water to precipitate the polymer. The solid was dried via lyophilization to obtain 0.41 g as yellow powder.

Synthesis of model polymers (Route II: fluorene-type and biphenyl)

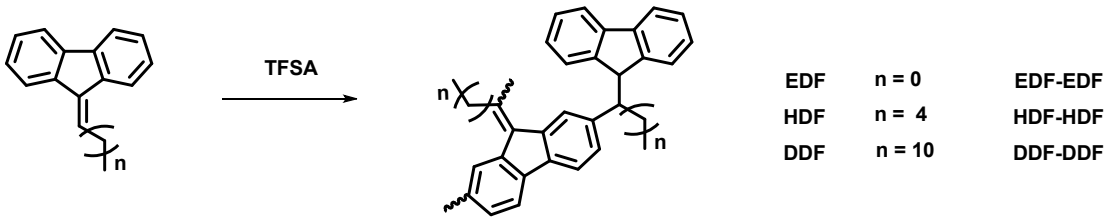


EDF-BP. The biphenyl (0.16 g, 1.0 mmol) and EDF (0.19 g, 1.0 mmol) were added into a pressure bottle with 1 mL dry dichloromethane as solvent. Then, 1 mL TFSA was added into system as catalysts when the temperature was reduced to 0 ℃. After 12 h of polymerization, the mixture was poured into water and neutralized with $NaHCO_3$. After removing extra solvent in vacuum, the final product 0.28 g was obtained as brown solid.

HDF-BP. The biphenyl (0.16 g, 1.0 mmol) and HDF (0.25 g, 1.0 mmol) were added into a pressure bottle with 1 mL dry dichloromethane as solvent. Then, 1 mL TFSA was added into system as catalysts when the temperature was reduced to 0 ℃. After 12 h of polymerization, the mixture was poured into water and neutralized with $NaHCO_3$. After removing extra solvent in vacuum, the final product 0.37 g was obtained as brown liquid.

DDF-BP. The biphenyl (0.16 g, 1.0 mmol) and DDF (0.33 g, 1.0 mmol) were added into a pressure bottle with 1 mL dry dichloromethane as solvent. Then, 1 mL TFSA was added into system as catalysts when the temperature was reduced to 0 ℃. After 12 h of polymerization, the mixture was poured into water and neutralized with $NaHCO_3$. After removing extra solvent in vacuum, the final product 0.44 g was obtained as brown liquid.

Synthesis of model polymers (Route III: fluorene-type and itself)



EDF-EDF. The EDF (0.38 g, 2.0 mmol) were added into a pressure bottle with 1 mL dry dichloromethane as solvent. Then, 1 mL TFSA was added into system as catalysts when the temperature was reduced to 0 ℃. After 12 h of polymerization, the mixture was poured into water and neutralized with $NaHCO_3$. After removing extra solvent in vacuum, the final product 0.33 g was obtained as brown solid.

HDF-HDF. The HDF (0.37 g, 1.5 mmol) were added into a pressure bottle with 1 mL dry dichloromethane as solvent. Then, 1 mL TFSA was added into system as catalysts when the temperature was reduced to 0 ℃. After 12 h of polymerization, the mixture was poured into water and neutralized with $NaHCO_3$. After removing extra solvent in vacuum, the final product 0.36 g was obtained as brown liquid.

DDF-DDF. The EDF (0.33 g, 1.0 mmol) were added into a pressure bottle with 1 mL dry dichloromethane as solvent. Then, 1 mL TFSA was added into system as catalysts when the temperature was reduced to 0 ℃. After 12 h of polymerization, the mixture was poured into water and neutralized with $NaHCO_3$. After removing extra solvent in vacuum, the final product 0.3 g was obtained as brown liquid.

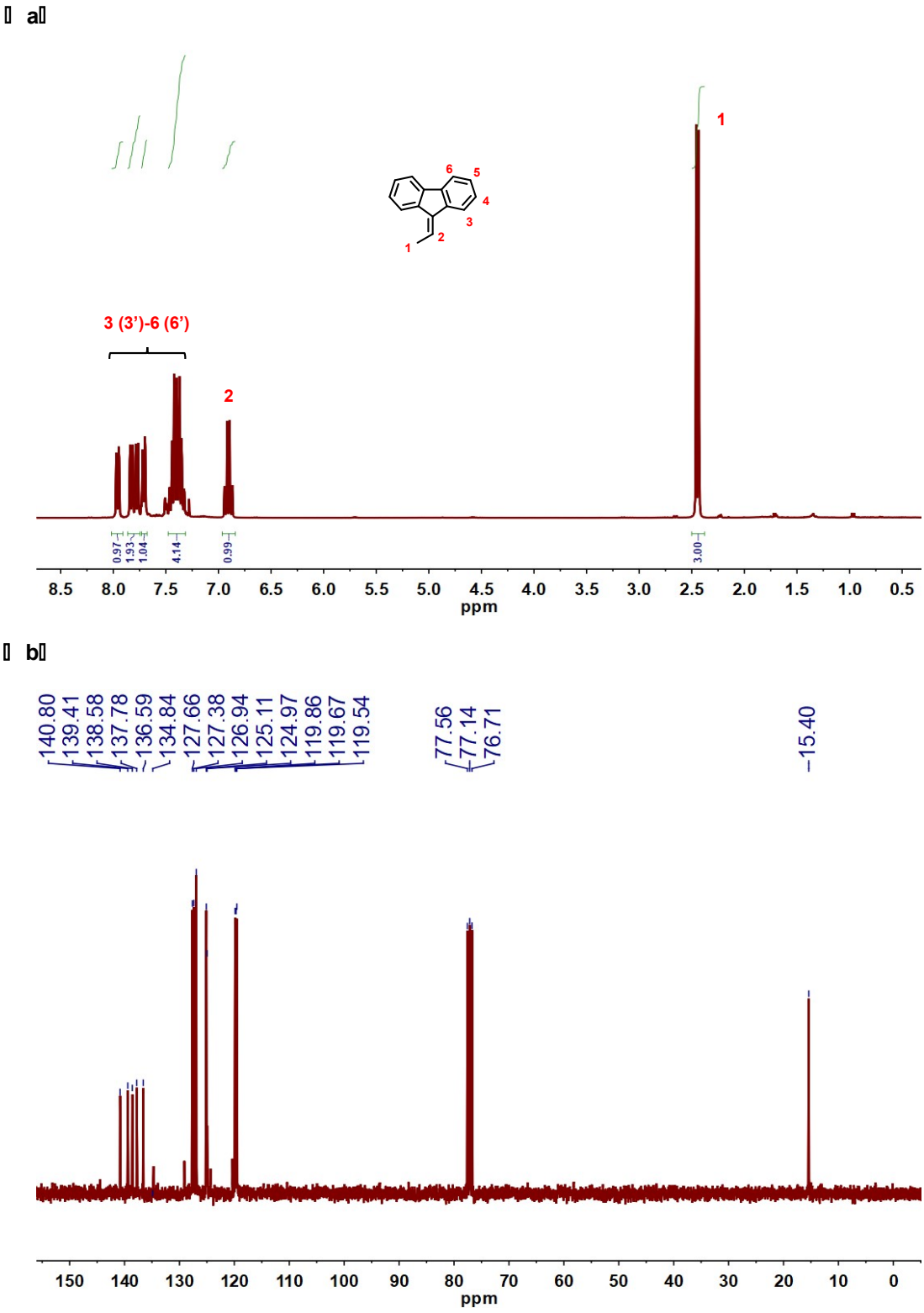


Figure S1 (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra of monomer 9-ethylidene-9*H*-fluorene in $CDCl_3$.

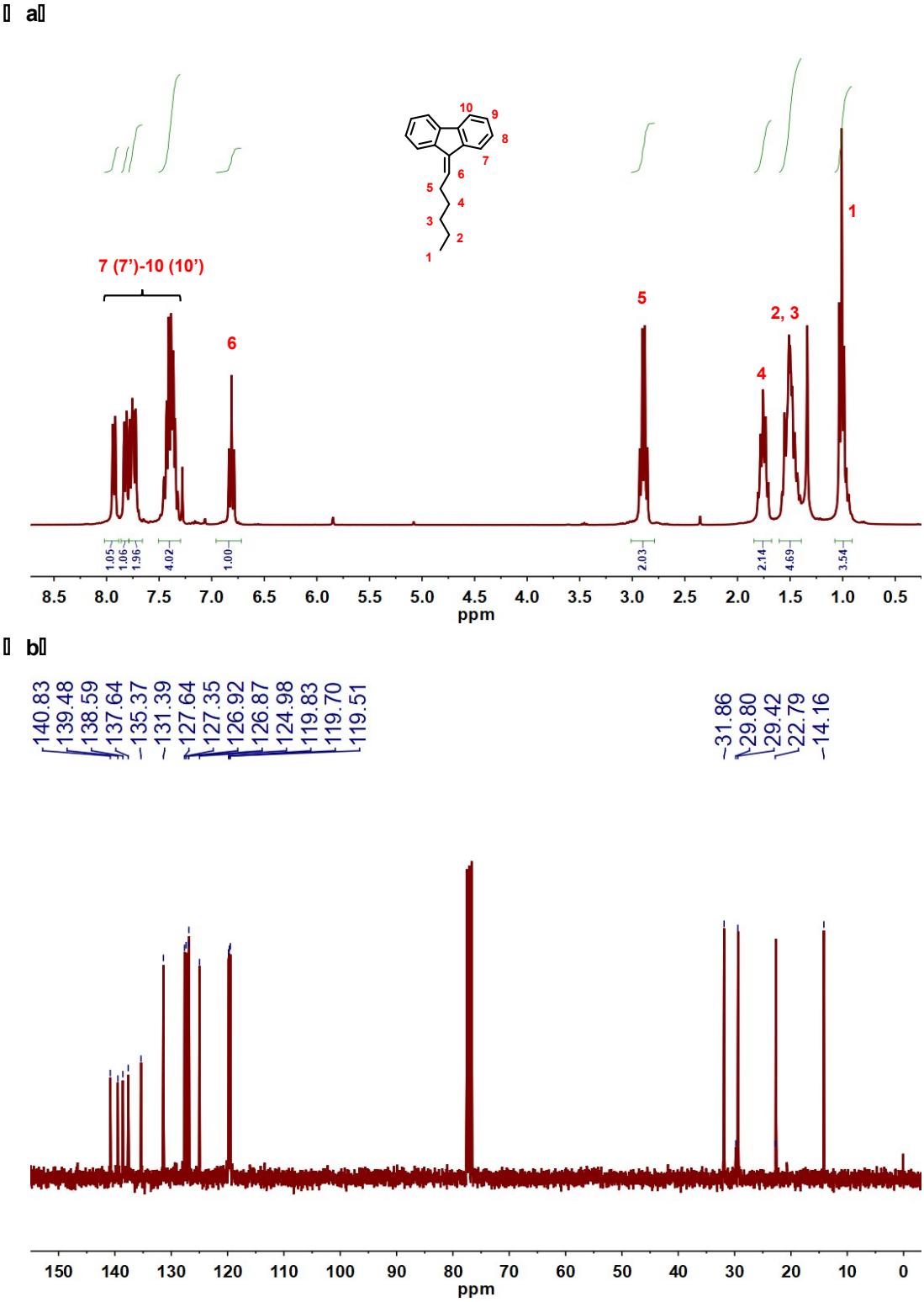


Figure S2 (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra of monomer 9-hexylidene-9*H*-fluorene in $CDCl_3$.

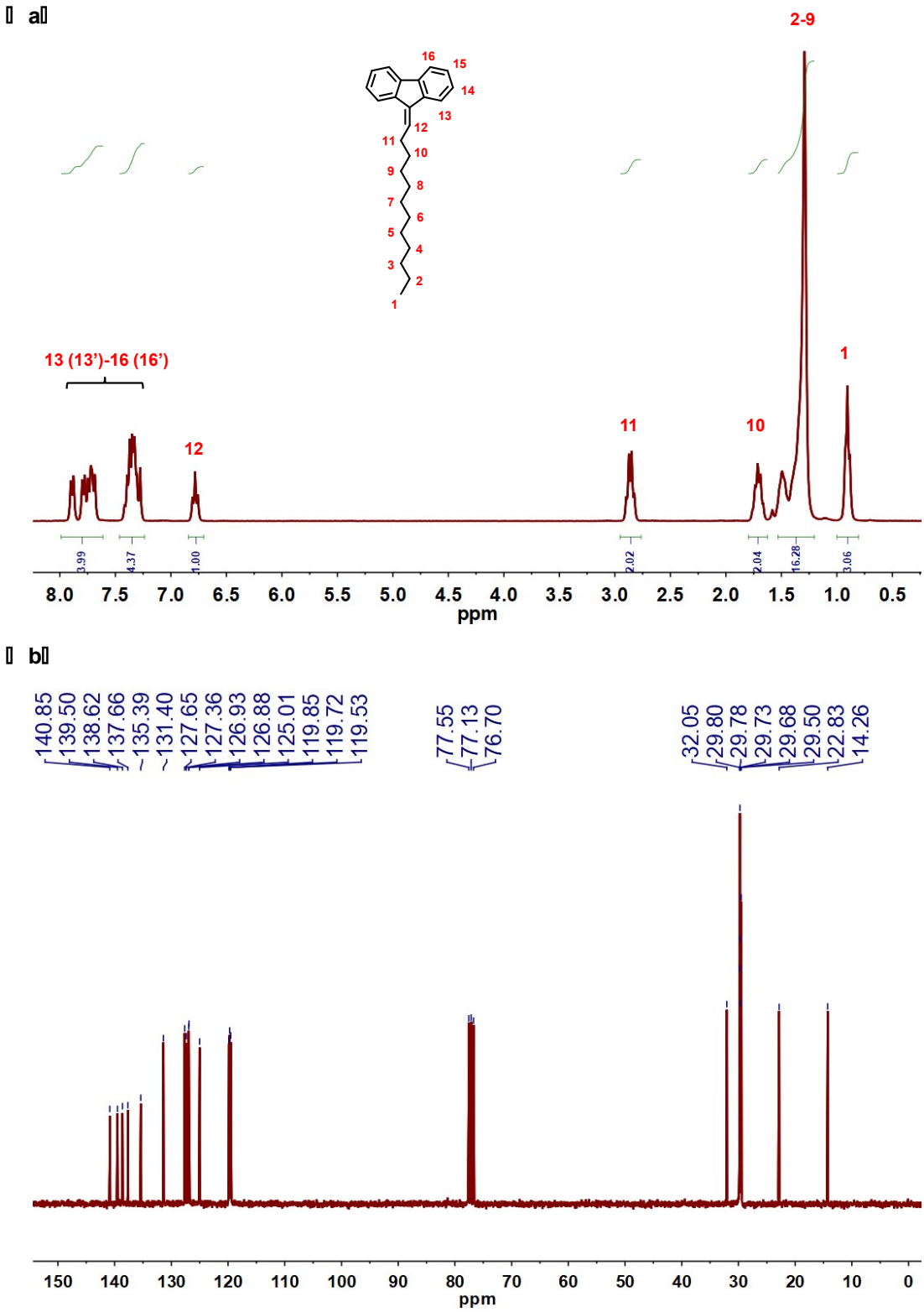


Figure S3 (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra of monomer 9-dodecylidene-9*H*-fluorene in $CDCl_3$.

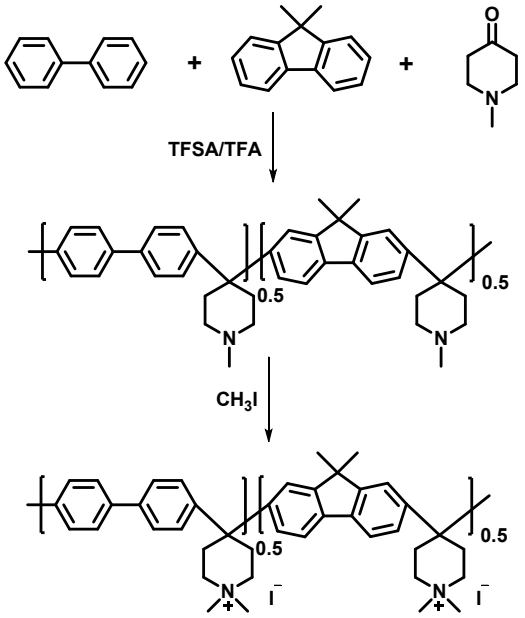


Figure S4 The synthetic procedure and chemical structure of poly(piperidinium-*co*-dimethylfluorene) which used as fuel cell binder.

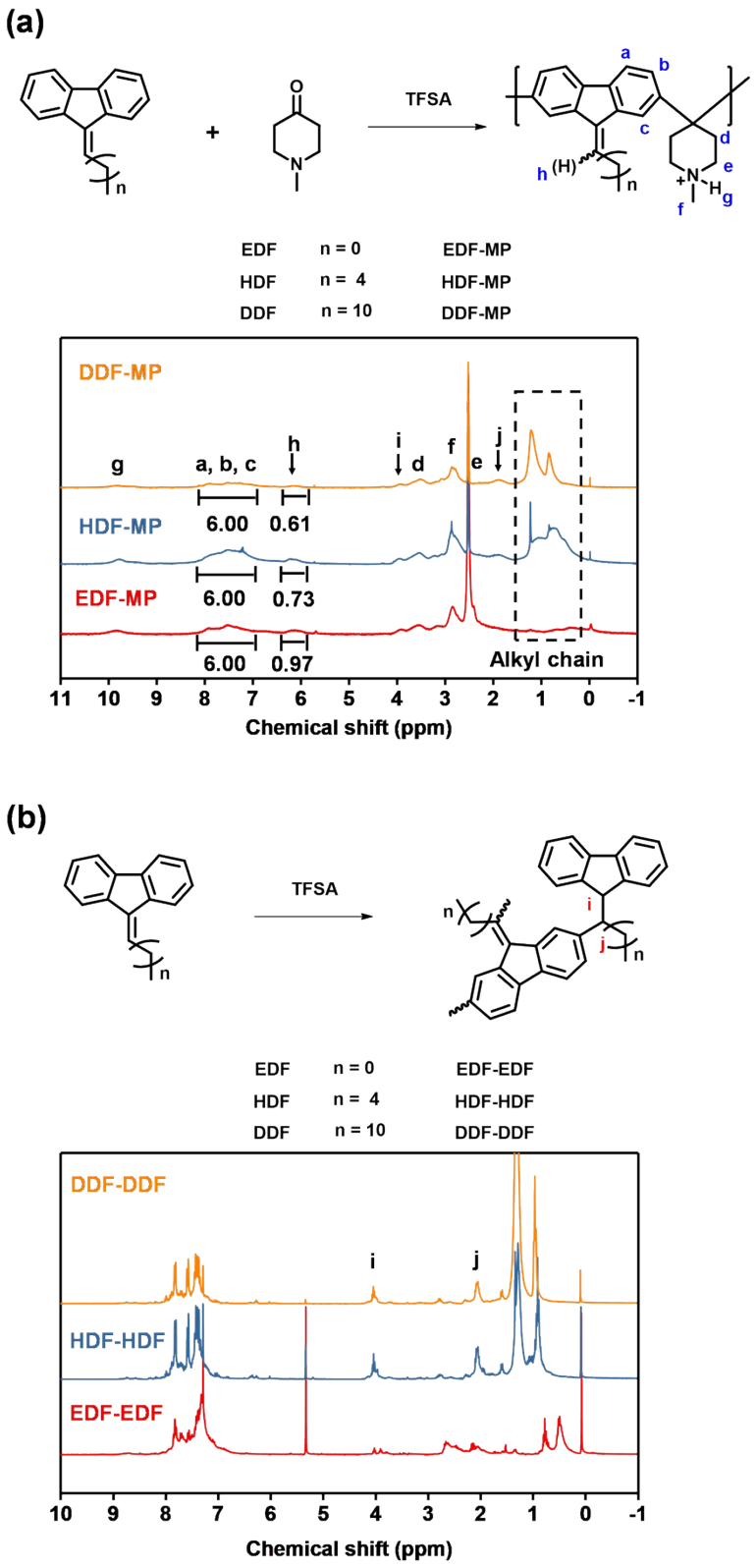


Figure S5 (a) ^{1}H NMR spectroscopy of model polymers EDF-MP, HDF-MP and DDF-MP in d_6-DMSO. The 5 wt% TFA to move water peak from 3.3 ppm to 11−14 ppm. (b) ^{1}H NMR spectroscopy of EDF-EDF, HDF-HDF and DDF-DDF in $CDCl_3$.

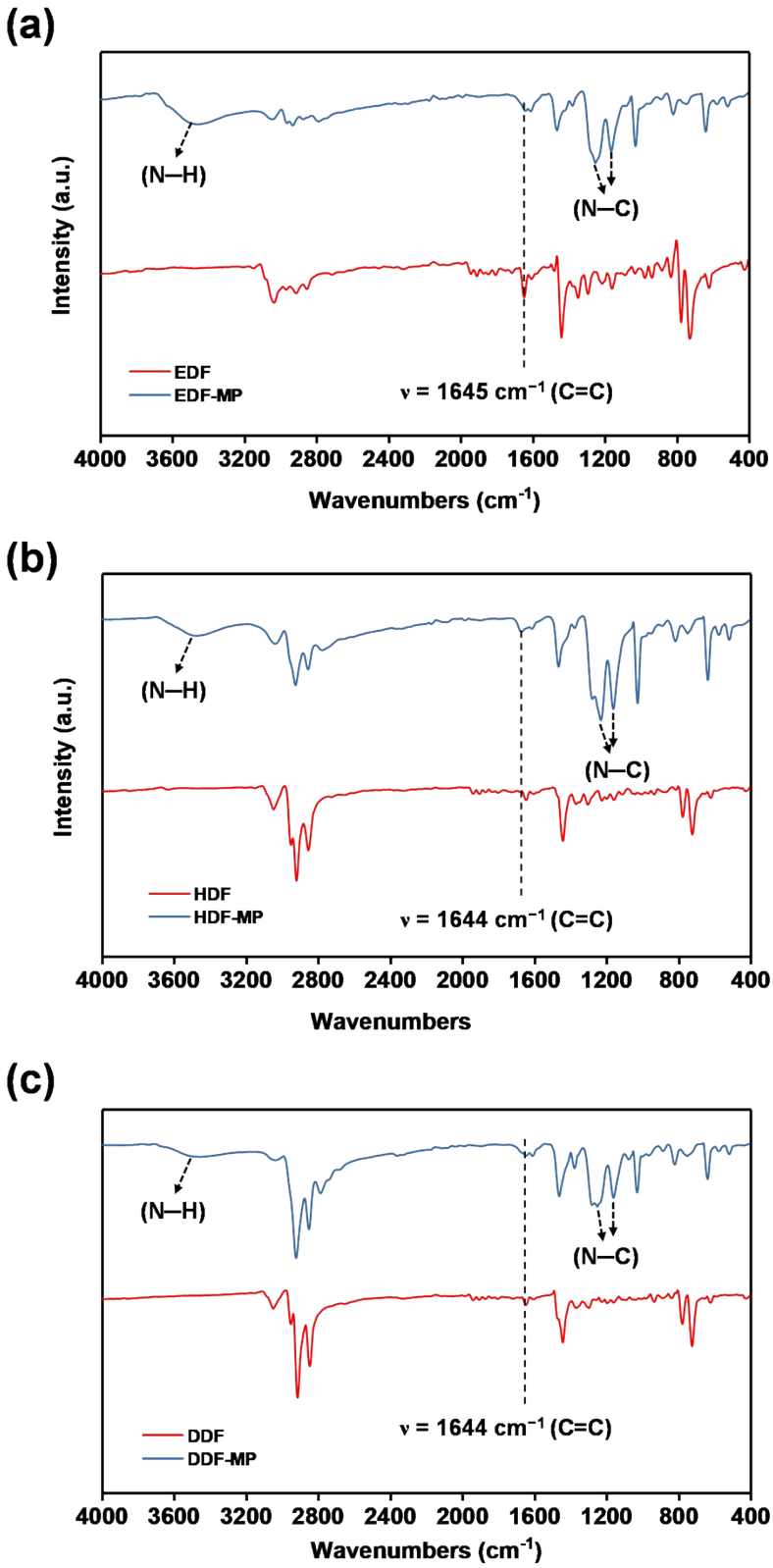
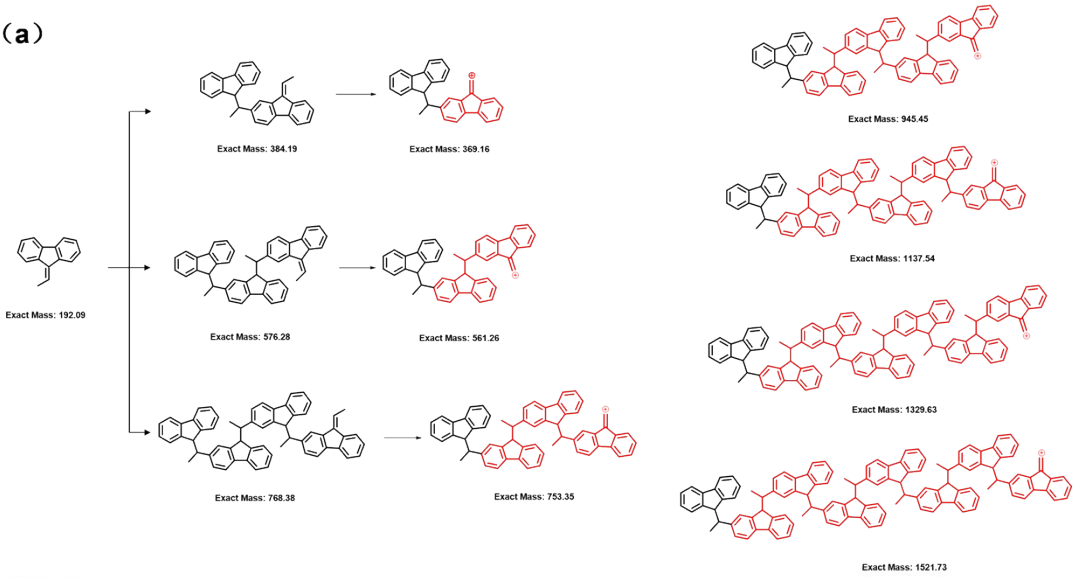


Figure S6 The IR spectra of (a) monomer DDF and polymer DDF-MP, (b) monomer EDF and polymer EDF-MP and (c) monomer HDF and polymer HDF-MP.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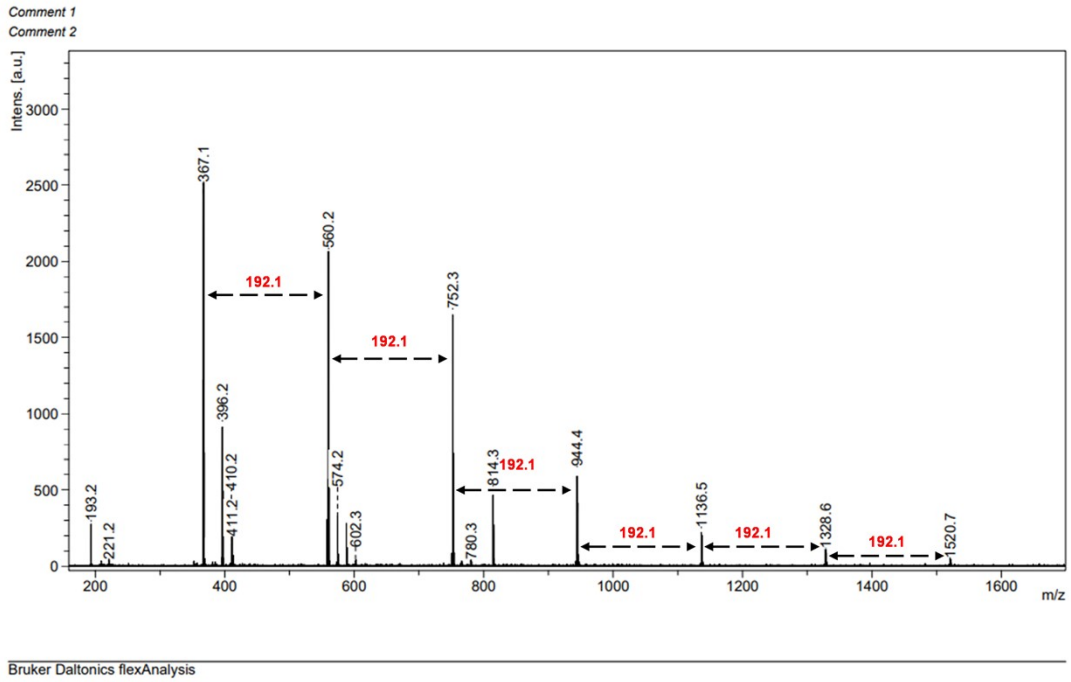
Exact Mass: 1137.54
Exact Mass: 1329.63
Exact Mass: 1521.73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Comment 2
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1328.6
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814.3
193.2
221.2
410.2
602.3
780.3
Bruker Daltonics flexAnalysis

1

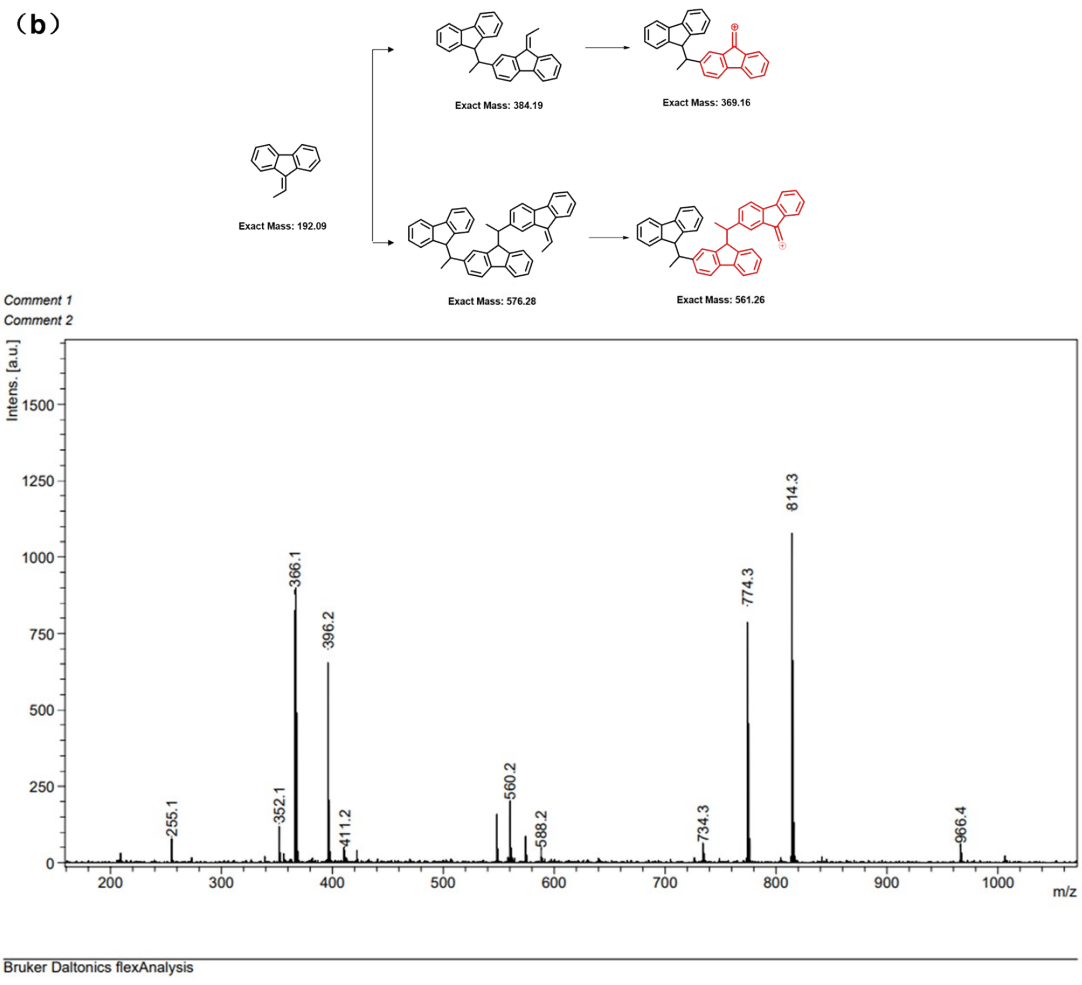
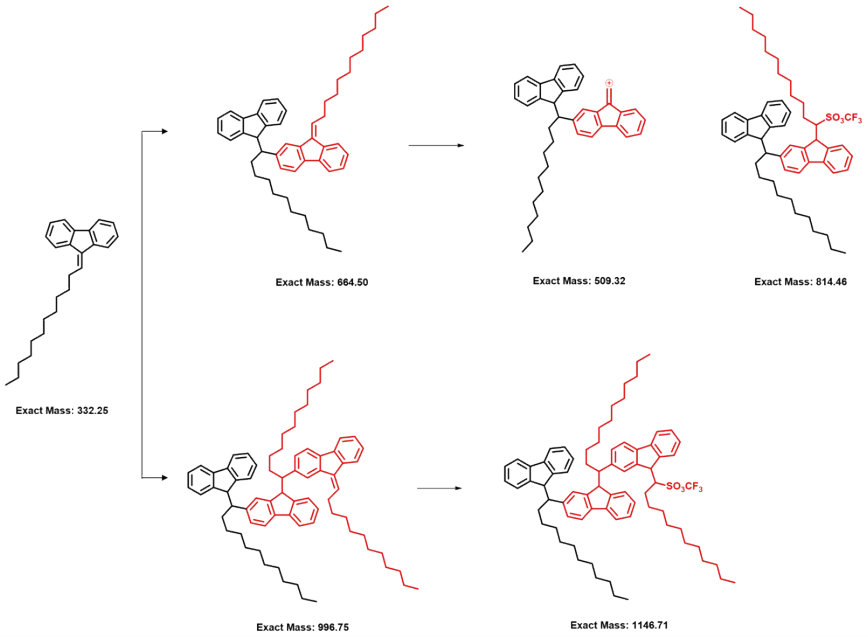


Figure S7 The MS analysis of (a) EDF-EDF self-polymerization and (b) reaction of EDF and biphenyl.

（a）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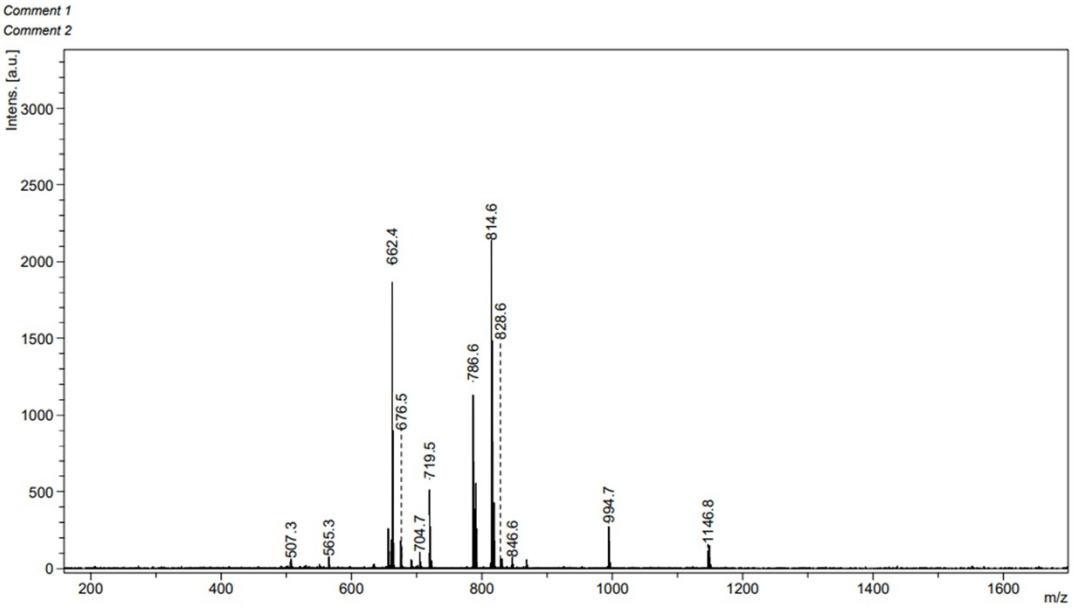
SO3CF3
SO3CF3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Comment 2
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719.5
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1400
1600
m/z
Bruker Daltonics flexAnalysis

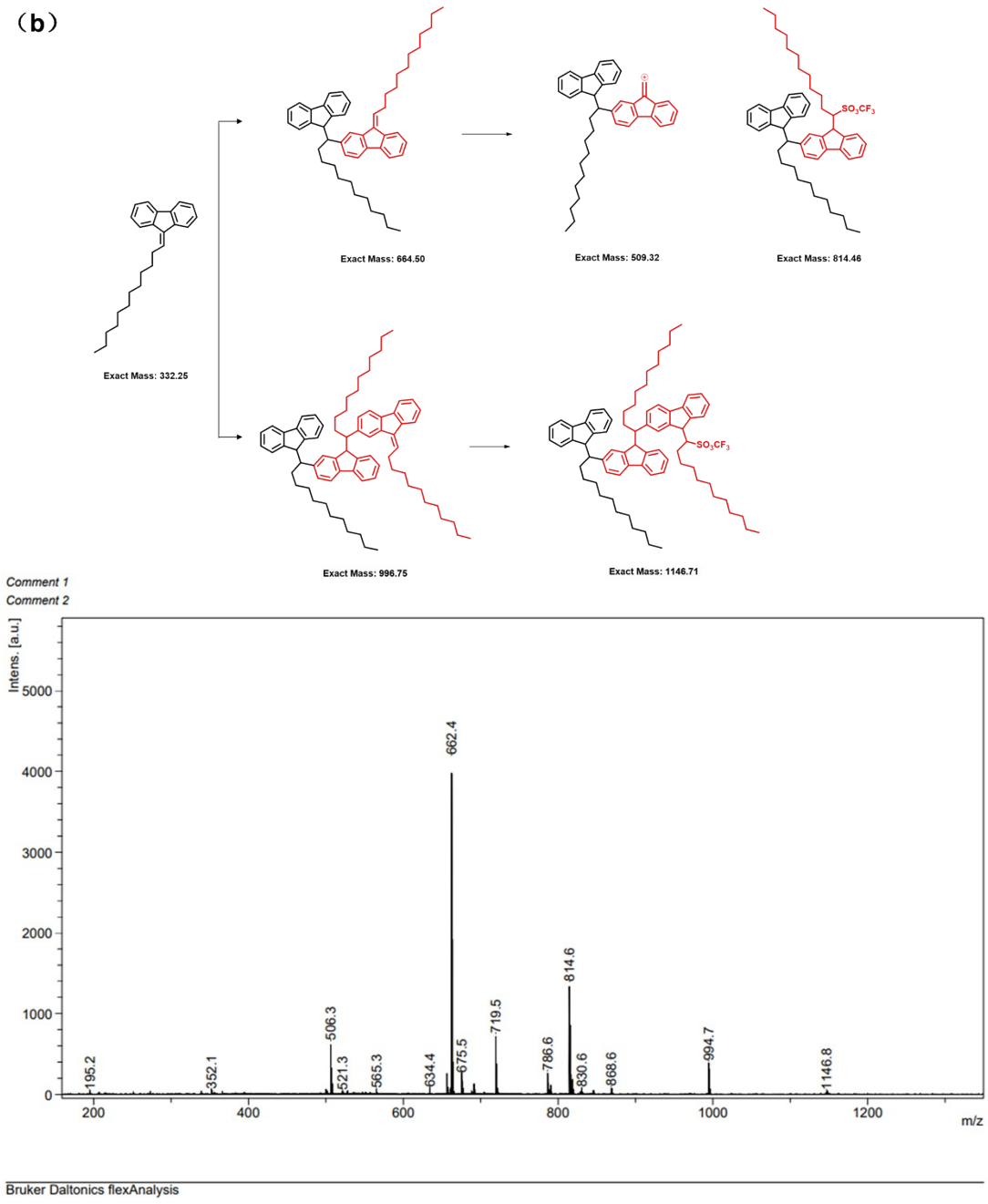
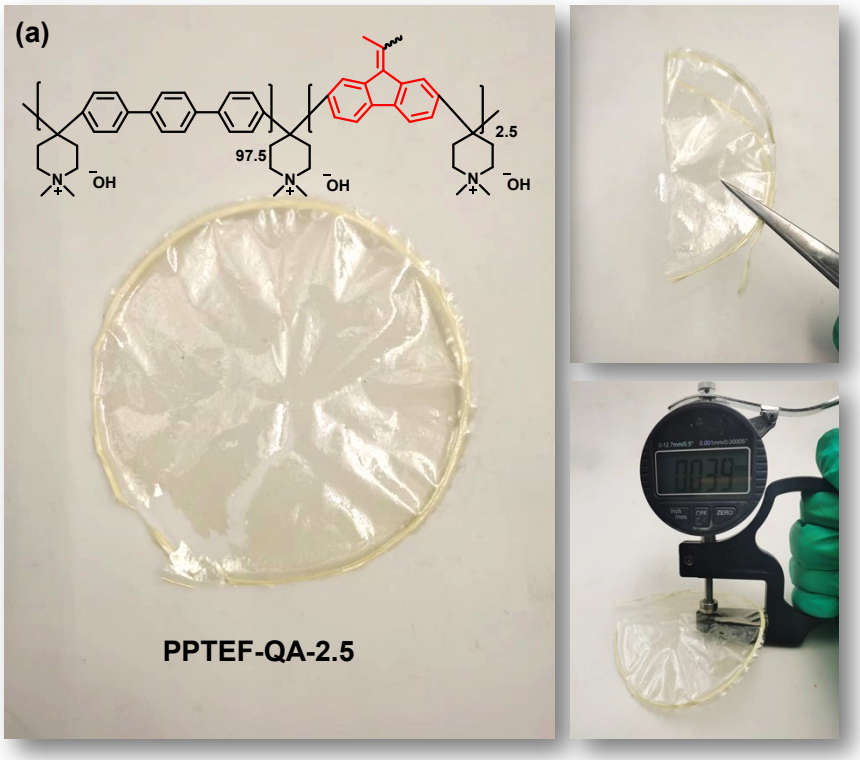
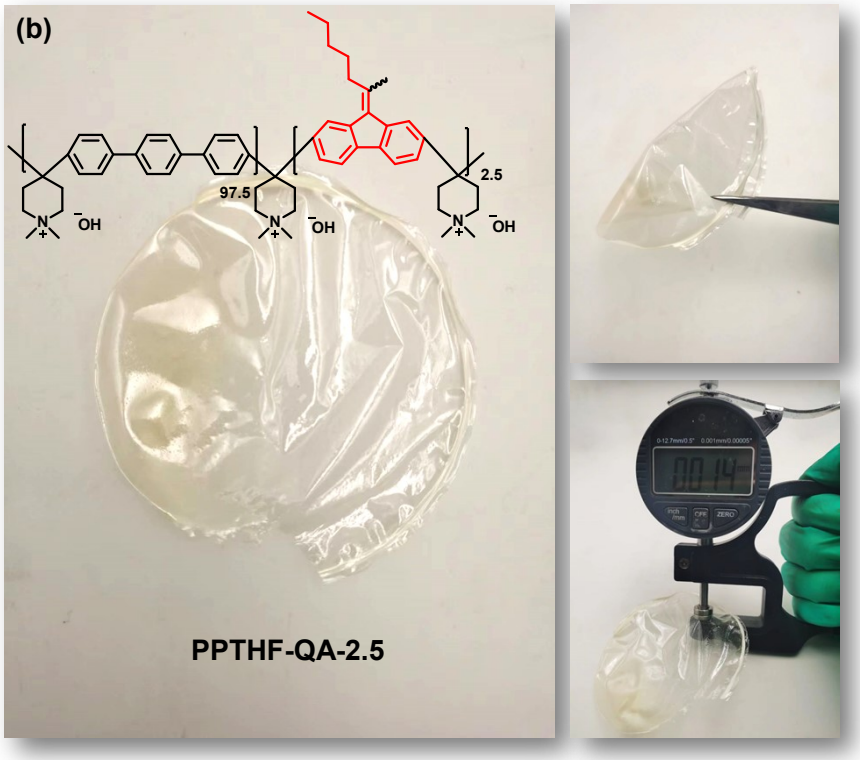


Figure S8 The MS analysis of (a) DDF-DDF self-polymerization and (b) reaction of DDF and biphenyl.



1



2

3 **Figure S9** (a) The picture of model polymer PPTEF-QA-2.5 membrane and (b) The

4 picture of model polymer PPTEF-QA-2.5 membrane in OH^- form.

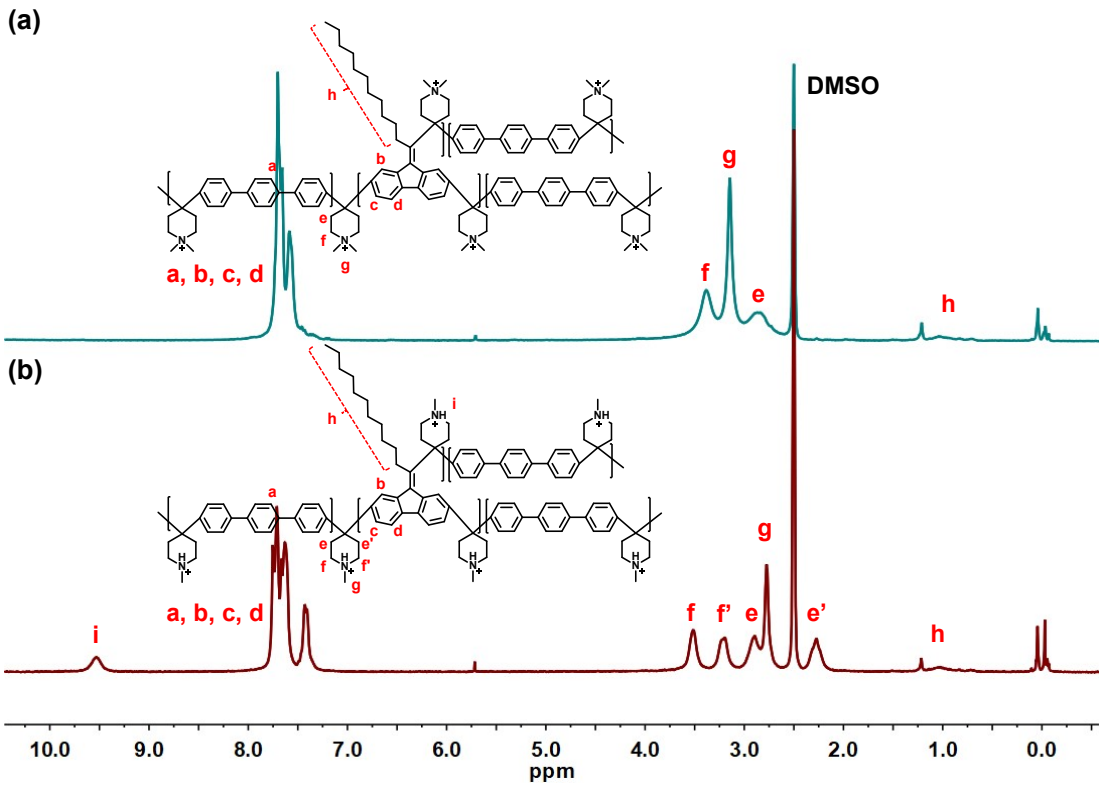


Figure S10 ^{1}H NMR spectroscopy of (a) PPTDF-QA-2.5 and (b) PPTDF-2.5 in d_6-DMSO with 5 wt% TFA to move water peak from 3.3 ppm to 11-14 ppm.

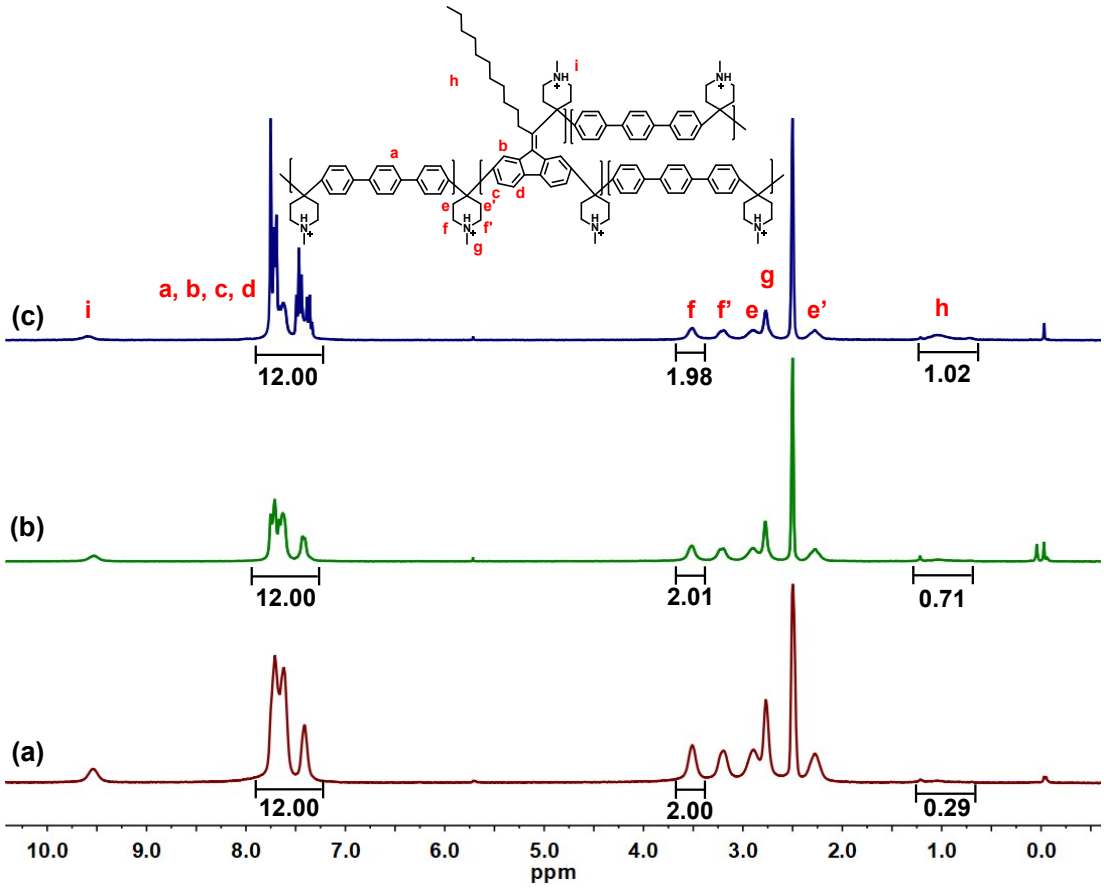


Figure S11 The ^{1}H NMR spectra of (a) PPTDF-1, (b) PPTDF-2.5 and (c) PPTDF-5 membrane in d_6-DMSO. 5 wt% TFA was added to move water peak from 3.3 ppm to 11-14 ppm.

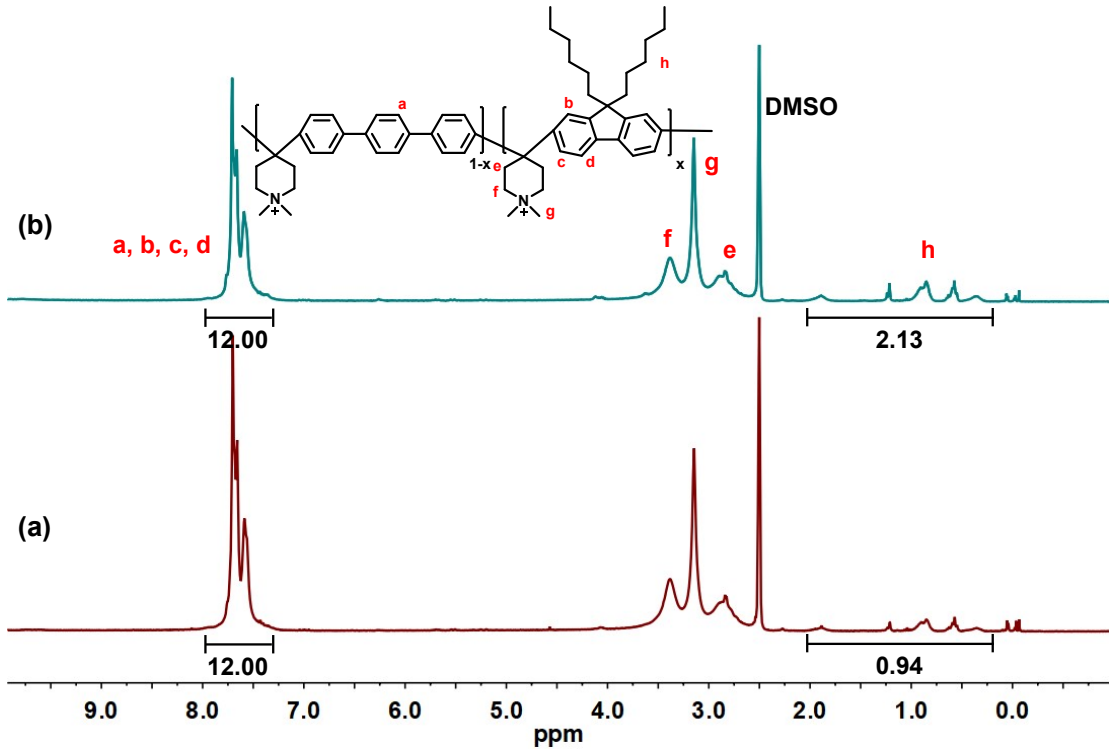


Figure S12 The ^{1}H NMR spectra of (a) PPTF-QA-5 and (b) PPTF-QA-10 membrane in d_6-DMSO. 5 wt% TFA was added to move water peak from 3.3 ppm to 11-14 ppm.

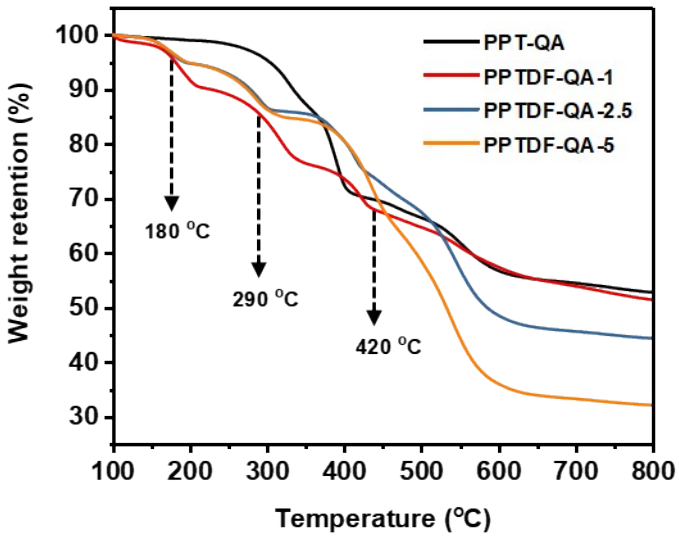


Figure S13 The TGA curves of PPTDF-QA-x membranes.

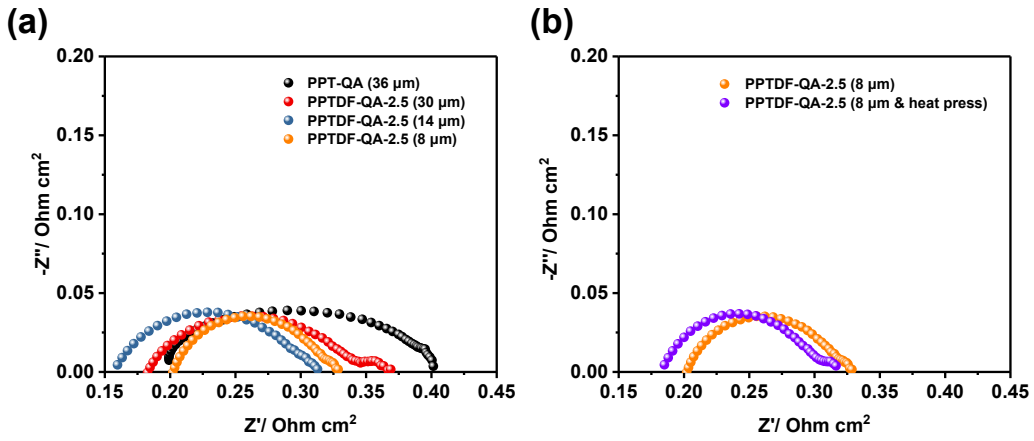


Figure S14 (a) and (b) In situ impedance curves of the MEAs with different PPT-QAs at 200 mA cm^{-2}.

Table S1. Polymerization of poly(arylene piperidinium)-based copolymers.

Samples [a]	TFSA: DCM	Piperidone: TP: (EDF/HDF/DDF)	Polymerization time [b] (h)	[η] [c] (dL g^{-1})	Yield (%)
PPT-QA	1:1	100:100:0	12	2.13	90.5
PPTDF-QA-1	1:1	100:99:1	6	5.71	91.2
PPTDF-QA-2.5	1:1	101:98:2.5	3	6.46	87.9
PPTDF-QA-2.5	1:1	101:98:2.5	6	—	93.3
PPTDF-QA-5	1:1	100:95:5	1	—	89.5
PPTDF-QA-5	1:2	100:95:5	3	—	92.4
PPTEF-QA-2.5	1:1	101:98:2.5	3	2.66	91.5
PPTHF-QA-2.5	1:1	101:98:2.5	3	5.05	89.1
PPTF-QA-5	1:1	100:95:5	12	—	91
PPTF-QA-10	1:1	100:90:10	12	—	95.1

[a] The PPTDF represents the components of piperidone, TP and DDF; PPTEF represents the components of piperidone, TP and EDF; PPTHF represents the components of piperidone, TP and HDF. [b] The solid content is 25%. [c] Measured at a concentration of 0.5 g dL^{-1} in DMSO at 30 °C.

Table S2. The mechanical properties of branched PPT-QAs with different chain length

Membranes	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
PPTDF-QA-2.5	70.0	35	1670
PPTHF-QA-2.5	29.0	5.7	655
PPTEF-QA-2.5	15.8	3.4	613

Table S3. Properties of PPTDF-QA-2.5 and other poly(arylene piperidinium)-based AEMs.

Samples	IEC_{theor} (mmol g^{-1})	SR [a] (%)	σ_{OH^-} [a] (mS cm^{-1})	Tensile strength (MPa)	Thickness in FC [b] (μm)	Ref.
PPTDF-QA-2.5	2.77	24	162	70	8	This work
PPTDF-QA-5	2.76	25	168	54.3	25	This work
PFTP-13	2.81	20	176	85	20 ± 3	3
PQP-100	2.30	22	119	84	4	4
PAP-TP-85	2.37	10	170	67	25	5
b-PTP-2.5	2.81	26	147	62	20	6

PD_6TP-15	2.35	42	155	48	22 ± 3	7
PTP-90	2.52	15	129	29	—	8
PDTP-25	2.54	30	121	61	25 ± 3	9
PFTP@W-PE	2.35	7	72	121	10	10

[a] Measured at 80 °C. [b] The minimum thickness tested in fuel cell.

Reference

1 K. S. Reddy, L. Solà, A. Moyano, M. A. Pericàs and A. Riera, *Synthesis,* 2000, **1**, 165-176.

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