## Highly conductive mechanically robust high $M_w$ polyfluorene anion exchange membrane for alkaline fuel cell and water electrolysis application

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## Synthesis

2-bromo-9,9-bis(6-chlorohexyl)fluorene (4)



Similar synthetic procedure of 2,7-dibromo-9,9-bis(6-chlorohexyl)fluorene (**2**) was applied. 2bromo-9,9-bis(6-chlorohexyl)fluorene (**4**) (5.4 g) was obtained from 2-bromofluorene (4.9 g, 20 mmol) and 1,6-dichlorohexane (31g, 200 mmol) in a 56% yield.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz): δ 7.67 (1H, t), δ 7.56 (1H, d), δ 7.46 (2H, m), δ 7.34 (3H, m), δ 3.41 (4H, t), δ 1.95 (4H, m), δ 1.58 (4H, m), δ 1.20 (4H, m), δ 1.08 (4H, m), δ 0.61 (4H, m)

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Similar synthetic procedure of polymerization was applied. After the reaction, the residue was quenched with 1M HCl aq. and extracted with chloroform. The organic layer was washed with water twice and then solvent was removed by rotary evaporator. Column chromatography of the residue (elusion: hexane) afforded **5**.

The compound (**5**) (1.49 g) was obtained from 2-bromo-9,9-bis(6-chlorohexyl)fluorene (2.41 g, 5 mmol) and tetrafluorophenylene (300 mg, 2 mmol) in a 78% yield.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz): δ 7.84 (2H, d), δ 7.77 (2H, m), δ 7.51 (4H, m), δ 7.37 (6H, m), δ 3.41 (8H, t), δ 2.02 (8H, m), δ 1.58 (8H, m), δ 1.22 (8H, m), δ 1.09 (8H, m), δ 0.70 (8H, m) <sup>19</sup>F-NMR (DMSO, 400MHz): δ -144.3

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In a closed vial, **5** (953 mg) was dissolved in 1,4-dioxane and trimethyl amine methanol solution was added. The reaction mixture was stirred for 12 h at 100 °C. After the reaction, solvent of the mixture was removed by rotary evaporator. The residue was dried in vacuum to afford **6** (1.09 g) in a 92% yield.

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400MHz): δ 8.01 (2H, d), δ 7.90 (2H, t), δ 7.64 (2H, s), δ 7.54 (2H, d), δ 7.50 (2H, t), δ 7.40 (4H, t), δ 3.12 (8H, t), δ 2.95 (36H, s), δ 2.03 (8H, t), δ 1.46 (8H, m), δ 1.05 (16H, m), δ 0.57 (8H, m)

<sup>19</sup>F-NMR (DMSO, 400MHz): δ -144.2

Figure S1. <sup>1</sup>H-NMR spectra of the monomers







Figure S2 <sup>1</sup>H-NMR and <sup>19</sup>F-NMR spectra of the polymers



















Scheme S1<sup>*a*</sup>. Synthesis of the model compound

- <sup>a</sup> Reagent and condition
- (i) 1,6-dichlorohexane, *n*-Bu<sub>4</sub>NCl, NaOH aq. 90 °C
- (ii)Pd<sub>2</sub>(dba)<sub>3</sub>-CHCl<sub>3</sub>, P(o-C<sub>6</sub>H<sub>4</sub>-OMe)<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, pivalic acid, THF, 90 °C
- (iii) Trimethlamine aq. 1,4-dioxane, 100 °C



Figure S3. <sup>1</sup>H-NMR and <sup>19</sup>F-NMR spectra of synthetic intermediate of the model compound





AEM	CHCl <sub>3</sub>	THF	MeOH	EtOH	n-PrOH	DMF	DMSO	H <sub>2</sub> O
								(80 °C)
PFOTFPh-C <sub>6</sub> -TMA (Cl <sup>-</sup> )			++	+	+	-	++	
PFOTFPh-C <sub>8</sub> -TMA (C <sup>1-</sup> )			++	+	+	-	++	
PFOTFPh-C <sub>10</sub> -TMA (Cl <sup>-</sup> )			++	+	+		++	

Table S1. Solubility of the synthesized polymers in various solvents<sup>*a*</sup>

<sup>*a*</sup> ++: highly soluble (>50mg/mL), +: soluble (>10mg/mL), -: partially soluble and --: insoluble <sup>*b*</sup> measured in air

AEM	MeOH-H <sub>2</sub> O	EtOH-H <sub>2</sub> O	<i>n</i> -PrOH-H <sub>2</sub> O	2-PrOH-H <sub>2</sub> O	
	(1:1 vol)	(1:1 vol)	(1:1 vol)	(1:1 vol)	
PFOTFPh-C <sub>6</sub> -TMA (Cl <sup>-</sup> )	+	+	++	+	
PFOTFPh-C <sub>8</sub> -TMA (Cl <sup>-</sup> )	-	+	+	+	
PFOTFPh-C <sub>10</sub> -TMA (Cl <sup>-</sup> )	-	++	+	+	

Table S2. Solubility of the synthesized polymer in alcoholic aqueous solvents<sup>*a*</sup>

<sup>*a*</sup> ++: highly soluble (>50mg/mL), +: soluble (>10mg/mL), -: partially soluble and --: insoluble <sup>*b*</sup> measured in air

AEM	Н	С	Ν	F	Cl
PFOTFPh-C <sub>10</sub> -TMA (Cl <sup>-</sup> )	8.27	69.3	3.59	9.74	9.09
(Theory)					
PFOTFPh-C <sub>10</sub> -TMA (Cl <sup>-</sup> )	8.72	67.4	3.24	9.48	8.89
(Experimental)					
PFOTFPh-C <sub>10</sub> -TMA (OH <sup>-</sup> air)	8.00	67.9	3.37	9.14	0
(Theory) <sup>a</sup>					
PFOTFPh-C <sub>10</sub> -TMA (OH <sup>-</sup> air)	9.27	69.4	3.42	8.95	0
(Experimental)					

Table S3. Elemental analysis of PFOTFPh-C<sub>10</sub>-TMA (Cl<sup>-</sup>) membrane (20  $\mu$ m) before and after ion exchange in 1M NaOH 24 h at 25 °C

<sup>*a*</sup> It is assumed all hydroxide ions are converted to bicarbonate ions in air.

Figure S4 Nyquist plot of (a) PFOTFPh-C<sub>6</sub>-TMA(Cl<sup>-</sup>), (b) PFOTFPh-C<sub>8</sub>-TMA(Cl<sup>-</sup>) and (c) PFOTFPh-C<sub>10</sub>-TMA(Cl<sup>-</sup>) membrane conductivities in RH 95% as a function of temperature (40, 50, 60, 70 and 80 °C).







Figure S6 <sup>1</sup>H-NMR and <sup>19</sup>F-NMR spectra of the model compound before degradatdion and after soaked in8M NaOH aq. at 80 °C for 3 h and 200 h



Figure S7 ESI-TOF-MS of the degradation product of **M1** 

(a) ESI-TOF-MS spectra of the degradation compound in model alkaline stability test





(b) Magnified image of the spectra around M/Z=261.6913 (upper) with theoretical spectra (middle and bottom)



(c) Magnified image of the spectra around M/Z=360.5801 with theoretical spectra (middle and bottom)

![](_page_28_Figure_0.jpeg)

(d) Magnified image of the spectra around M/Z=558.3538 with theoretical spectra (middle and bottom)

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![](_page_29_Figure_1.jpeg)