

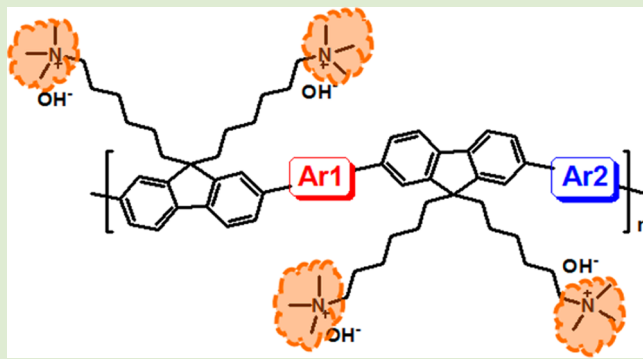
Fluorene-Based Hydroxide Ion Conducting Polymers for Chemically Stable Anion Exchange Membrane Fuel Cells

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S Supporting Information

ABSTRACT: Three novel fluorene-based polymers with pendant alkyltrimethylammonium groups were synthesized and characterized. The polymers were soluble in dimethylformamide, and dimethyl sulfoxide at room temperature and methanol at 40 °C while remaining insoluble in water. The polymeric membranes were transparent and flexible and exhibited hydroxide ion conductivities above 100 mS/cm at 80 °C. The results of ¹H NMR and titration measurements demonstrated an excellent chemical stability of the synthesized polyfluorene, even after treatment in 1 M NaOH solution at 80 °C for 30 days. The results of this study suggest a feasible approach to the synthesis and practical applications of a new class of alkaline anion exchange membranes.



Due to increasing demands for clean energy technology worldwide, fuel cells are attracting significant attention as environmentally friendly power generators that can replace fossil fuel-based generators.^{1–6} Among fuel cell types, proton exchange membrane fuel cells (PEMFCs), which use a solid polymer membrane as the electrolyte, have been the most extensively explored because they have high power density, high energy conversion efficiency, low start temperature, and no pollutant emission.⁷ However, the high costs of noble metal catalysts (e.g., platinum) and perfluorosulfonated polymer electrolytes have hindered the wide adoption of PEMFCs as a viable commercial technology.

Alkaline anion exchange membrane (AEM) fuel cells are an attractive alternative to PEMFCs because they can potentially use less expensive nonprecious metal electrocatalysts. One of the major challenges in AEM fuel cells is finding suitable hydroxide ion conducting polymeric membranes that maintain robust mechanical properties, chemical stability, and moderate water swelling while providing high hydroxide ion conductivity.^{8–10}

A variety of AEMs containing quaternary ammonium (QA) cationic groups based on polysulfones,^{11–13} polyphenylenes,^{14,15} polystyrenes,^{16–18} polyethylenes,^{7,19,20} and poly(phenylene oxide)s^{21–23} have been studied as AEM materials. These membranes are typically prepared via the chloromethylation of aromatic polymer backbones, followed by substitution of the chloromethyl group with trimethylamine to form QA groups. However, chloromethyl methyl ether, the reagent most commonly used to introduce a chloromethyl group to polymers, is carcinogenic, and precise control of the degree and location of functionalization is usually difficult. Therefore, the preparation of AEMs via alternative synthetic routes that avoid the use of the toxic reagents is desirable.

Despite the importance of AEMs in fuel cells, strategies to produce high-performance AEMs remain under-developed. Poor chemical stability of AEMs under high-pH conditions at elevated temperature is one of the most critical issues that limit the practical use in fuel cells. Particularly, robust stability above 80 °C is highly desired because the CO₂ solubility in water greatly diminishes above 80 °C, preventing carbonate/bicarbonate formation, and fuel cell operation at elevated temperature enhances the kinetics of electrochemical reactions. Unfortunately, AEMs that are stable under alkaline condition above 80 °C are rare until now. Owing to their strong nucleophilicity and basicity, OH⁻ ions attack counter cations as well as polymer backbones, leading to a number of known degradation pathways. Examples of known degradation pathways of tetraalkyl QA cation by OH⁻ ions include β -hydrogen (Hofmann or E2) elimination, direct nucleophilic substitution (S_N2), and ylide formations.^{20,24–29} Degradation of the polymer backbone can also occur in aryl ether-containing polymers (e.g., cleavage of C–O bonds in polysulfone-based AEMs under alkaline conditions, especially at high pH).^{30,31}

Currently, many research groups are actively developing AEMs with high anion conductivity and good alkaline stability. We believe the following criteria are critical in the design of advanced AEM materials: (1) New synthetic methods should allow convenient control of the degree and location of functionalization; (2) Polymer backbones should be made of alkaline-resistant, thermally stable building blocks; (3) Stable cation groups should be incorporated into the polymers.

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Fluorene-containing molecules are important class of aromatic compounds and have received considerable attention for their unique photophysical properties and diversity of possible chemical modifications. Dibromination at the 2- and 7-positions of fluorene and subsequent palladium-catalyzed Suzuki coupling reaction with a diborylated arene generates polyfluorene (PF). Alkylation (or dialkylation) at the 9-position of the fluorine ring is commonly employed before the polymerization to enhance the solubility and molecular weights of the polymer. Accordingly, a variety of functionalized PFs with extended conjugation systems have been developed. Fluorene-based conjugated polymers also have good film-forming properties and exceptional chemical stability.^{32–37} In this study we chose PF as the polymer backbone since it can provide high chemical stability in alkaline media owing to its absence of aryl ether bonds.

The chemical stability of an AEM is supposed to depend strongly on the structure of pendant cation groups. To examine the stability of cation groups, we recently undertook a stability study of various QA cation structures in pure OH[−] (or OD[−]) form by using a straightforward Ag₂O-mediated ion-exchange reaction and NMR spectroscopy.³⁸ One of the key findings was that long alkyl-substituted cation moieties are more thermally stable than benzyl-substituted cation moieties under alkaline conditions. Particularly, QA hydroxide with a trimethylhexylammonium group showed no signs of degradation in boiling water for a month, making it the best QA candidate for long-term stability in AEM fuel cells.

In this study, we present a facile synthetic strategy for solvent-processable AEMs based on QA-functionalized PFs. We synthesized a series of novel fluorene-based ionic polymers, poly[9,9-bis(6'-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene)-*alt*-(1,4-benzene)] (PFB⁺), poly[9,9-bis(6'-(*N,N,N*-trimethylammonium)hexyl)-fluorene)-*alt*-(9,9-dihexylfluorene)] (PFF⁺), and poly[[9,9-bis(6'-(*N,N,N*-trimethylammonium)-hexyl)-9*H*-fluorene)-*alt*-1,4-benzene]-*ran*-[9,9-bis(6'-(*N,N,N*-trimethylammonium)-hexyl)fluorene)-*alt*-(9,9-dihexylfluorene)] (PFBFF⁺), all with long alkyl-tethered QAs on the side chains of their PF backbones (Figure 1). These soluble QA-PF

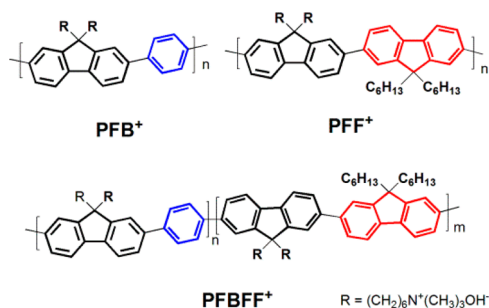


Figure 1. Polymer structures of PFB⁺, PFF⁺, and PFBFF⁺.

ionomers afforded well-controlled ion exchange capacities (IECs), high hydroxide conductivity, and excellent chemical stability, which are highly desirable in AEM applications. The effects of the fluorene group of the polymer backbone on fuel cell membrane properties, including water uptake, ionic conductivity, and thermal and alkaline stability, were fully evaluated.

The synthetic routes to the polymers used in the present study are shown in Scheme S1. Compounds **2**, **3**, and **5** were prepared according to previously published methods.^{39,40} The

precursor polymers PFB, PFF, and PFBFF (containing tethered *n*-hexyl bromide form) were synthesized from **3**, **4**, and **5** by Pd(PPh₃)₄-catalyzed Suzuki couplings. The precursor polymers were soluble in organic solvents such as chloroform and tetrahydrofuran (THF). The weight-average molecular weights (*M_w*) of PFB, PFF, and PFBFF, determined with gel permeation chromatography (GPC) using THF eluent were found to be 30.3, 77.7, and 50.9 kg/mol, respectively (Tables 1 and S1).

Table 1. Molecular Weight Properties of Precursor Polymers

polymer	<i>M_w</i> ^a	PDI ^b	viscosity ^c (dL/g)
PFB	30.3	2.1	0.85
PFF	77.7	3.3	1.76
PFBFF	50.9	2.5	1.23

^a*M_w*, weight-average molecular weight in kg/mol. ^bPDI, polydispersity index. ^c0.5 g/dL in NMP at 30 °C.

The molecular weights of PFB were smaller than those of the other two polymers, probably because rigid benzene moieties of the polymer gave lower solubility. By contrast, PFF and PFBFF, which contain dialkyl fluorene moieties in comonomer, achieved higher molecular weights. The higher molecular weights of PFF and PFBFF were also reflected in the viscosity results.

Quaternization of the fluorene precursor polymers with trimethylamine provided PFB⁺, PFF⁺, and PFBFF⁺ in bromide ion form (Scheme S1). These ionic polymers were not soluble in water, THF, CHCl₃, or dichloromethane, but were completely soluble in DMF and DMSO at room temperature and methanol at 40 °C (Table S2). The chemical structures of the ionic PFs were analyzed with ¹H NMR spectroscopy (Figure 2). Comparison of the integral ratio of the QA methyl

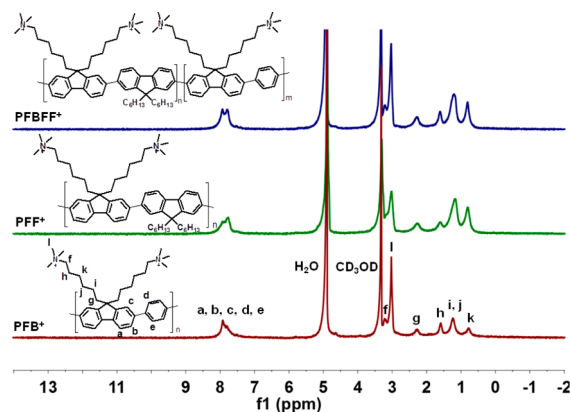


Figure 2. ¹H NMR spectra of PFB⁺, PFF⁺, and PFBFF⁺ in bromine form in CD₃OD.

protons at 3.02 ppm (see Figure 2, peak I) with reference to the aromatic proton peaks at 7.5–8.2 ppm indicated that the quaternization reaction was quantitative.

The IECs of the PFB⁺, PFF⁺, and PFBFF⁺ were calculated to be 3.61, 2.34, and 2.89 mequiv/g, respectively, from the ¹H NMR spectra, and these values were in good agreement with the titrated IEC values (3.59, 2.45, and 2.93 mequiv/g, respectively; Table 2). As expected, IEC decreased monotonically as the amount of 9,9-dihexylfluorene monomer in the polymers increased.

Table 2. Ion Exchange Capacity (IEC), Water Uptake, and Swelling Degree (Δl) of Quaternary Ammonium Polyfluorenes

	IEC (mequiv/g)			water uptake (%)	swelling degree (%)
	theo. ^a	¹ H NMR	titration		
PFB ⁺	3.56	3.61	3.59	71 ^b /76 ^c	10 ^b /10 ^c
PFF ⁺	2.44	2.34	2.45	25 ^b /26 ^c	5 ^b /5 ^c
PFBFF ⁺	2.90	2.89	2.93	40 ^b /43 ^c	7 ^b /7 ^c

^aTheoretical values calculated from the monomer ratio. ^bAfter immersion in water at room temperature for 24 h; an average of two measurements. ^cAfter immersion in water at 80 °C for 24 h; an average of two measurements.

The membranes were prepared by dissolving the ionic polyfluorenes in DMF and casting the solution on a flat Teflon sheet. The transparent and flexible membranes could be easily cut into any desired size and shape (Figure S1). The solvent processability of ionic polyfluorenes may enable their use not only as alkaline AEMs but also as ionomer electrode materials.

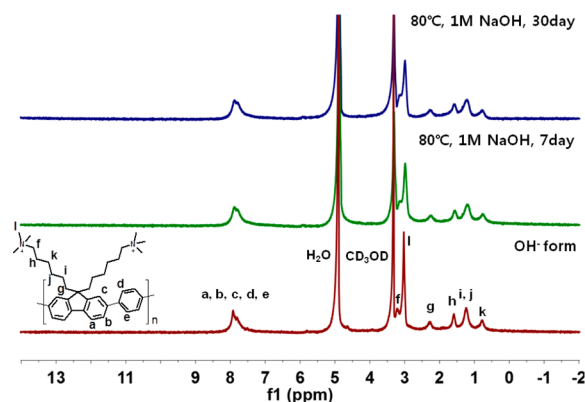
Thermal analysis of the polymers was conducted with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC; Figure S2). All three membranes showed a slight weight loss between 50 and 120 °C, which corresponds to the evaporation of absorbed water. A second weight loss between 230 and 300 °C was attributed to the loss of the QA groups in polymer. A third weight loss at temperatures above 390 °C was due to the degradation of the polymer backbones. The thermal stability of our long alkyl-tethered QA polyfluorenes in this study was better than those of reported benzyl-substituted cationic poly(arylene ether sulfone)s containing hydroxide groups (e.g., benzyltrimethylammonium^{11a} and benzyl guanidinium⁹). DSC analysis showed no obvious thermal transition between 90 and 200 °C, which may be attributed to the high chain rigidity of the polymer backbone structure and hindered movement of molecular segments, as observed in other aromatic polymers.^{39–41} These results confirmed that the fluorine-based alkaline QA-polymer membranes have excellent thermal stability.

The presence of water is critical for ion conductivity in AEMs; however, excessive water uptake may lead to dimensional instability. Generally, water uptake and swelling degree increase with IEC. Water uptake of the membranes (room temperature and 80 °C) increased with increasing IEC, ranging from 25 to 76 wt %, as shown in Table 2. Due to the rigid polyfluorene backbone, the water uptakes and swelling ratios measured at 80 °C were not significantly different from those of room temperature (Table 2). Considering high IECs of these ionic polymers, the swelling and water uptake, particularly after treatment at 80 °C, are remarkably low. All three membranes had a significantly lower water uptakes and degrees of swelling than those of other reported aromatic AEMs [e.g., quaternized poly(arylene ether ketone)s⁴² and poly(arylene ether sulfone)s⁴⁴] with similar IEC values, probably due to the presence of the rigid aromatic backbone without flexible moieties (e.g., ether or thioether bonds).

Achieving robust thermochemical stability in AEMs remains a major challenge for the practical application of alkaline fuel cells owing to the high-pH environment of such cells. Polymer backbone degradation via aryl ether cleavage of quaternized poly(arylene ether)s is known to occur even under relatively mild conditions due to the strong electron-withdrawing effect

of the tethered benzyltrimethylammonium groups and the facile access of hydroxide ions to the cation-tethered polymer backbone.^{30,43}

To examine the alkaline stability of PFB⁺, PFF⁺, and PFBFF⁺, they were tested in a 1 M NaOH solution at 80 °C for 7 and 30 days. The change in the chemical structure of the polymers due to the possible backbone degradation was

**Figure 3.** ¹H NMR spectra of PFB⁺ before and after stability tests.

analyzed by ¹H NMR spectroscopy (Figures 3 and S3). The ¹H NMR spectra of PFB⁺ in OH⁻ form before and after 1 M NaOH treatment at 80 °C for 7 and 30 days are shown in Figure 3. No change in chemical shift was observed even after 30 days in 1 M NaOH at 80 °C, which clearly indicates that the fluorene-based membranes have excellent thermochemical stability in high-pH solution. The alkaline stability of the polyfluorene ionomer membranes was quantitatively evaluated by measuring changes in IEC with ¹H NMR and titration after specific test periods. The ¹H NMR data suggest that all three membranes maintained their initial IECs even after immersion in 1 M NaOH solution at 80 °C for 30 days; the NMR-based IEC values for PFB⁺, PFF⁺, and PFBFF⁺ were 3.73, 2.44, and 2.62 mequiv/g, respectively, which are close to the initial values (3.61, 2.34, and 2.89 mequiv/g, respectively; see Table S3). The NMR-based IECs of the PFB⁺, PFF⁺, and PFBFF⁺ were also in good agreement with the titrated IECs values (3.40, 2.42, and 2.91 mequiv/g, respectively; see Table S3). The ionic polyfluorene membranes can achieve better alkaline stability than those of other reported aromatic AEMs (e.g., quaternized polysulfone-based polymers^{30,31,42}) because of (1) the lack of aryl C–O bonds in its backbone structure and (2) the separation of cation group from polymer backbone by a long alkylene spacer.

In spite of this long-term chemical stability, the membrane of PFB⁺ became fragile after 7 days of the stability test at 80 °C. To determine whether chain scission occurred in the polymer backbone, we measured viscosity before and after the stability test and compared the data (Table S4). Almost identical viscosity values were obtained (2.63 vs 2.70 dL/g for before and after the test), which indicates no degradation has occurred in the PFB⁺ main chain. This phenomenon may be attributed to the high IEC of PFB⁺ (3.61 mequiv/g) and strong ionic aggregations among the QAs in the polymer that may increase membrane fragility. Comparatively, PFF⁺ and PFBFF⁺ membranes, which have lower IECs than PFB⁺, maintained flexibility of the films throughout the stability test period. All

these results indicate the excellent long-term alkaline stability of these AEMs in high-pH environments.

The hydroxide ion conductivity of membranes plays a significant role in fuel cell performance. The conductivity of AEMs is significantly influenced by IEC because IEC is linked to the density of the ionizable functional group in the membranes. As IEC increases, membranes become more hydrophilic and absorb more water, which facilitates ion transport.

The anion conductivity of the synthesized AEMs was measured with a four-point probe method. The hydroxide ion conductivity, measured at 30, 60, and 80 °C, is shown in Figure 4 and Table S5. As expected, the conductivity of all AEMs

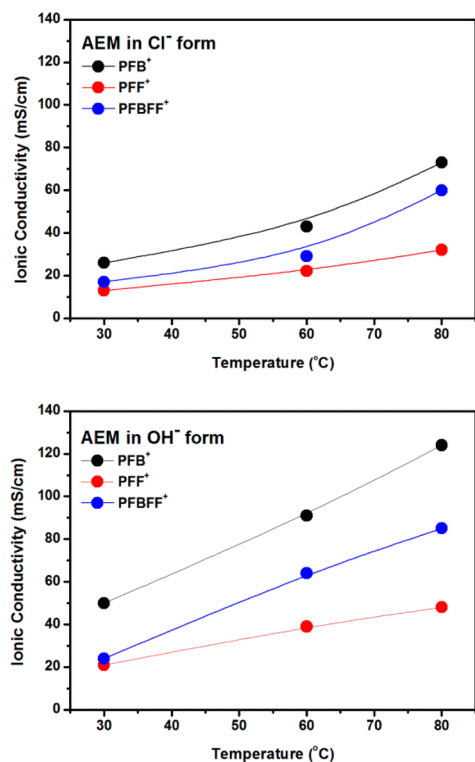


Figure 4. Anion conductivity of PFB⁺, PFF⁺, and PFBFF⁺.

increased as IEC and temperature increased. For example, the highest IEC membrane PFB⁺ showed OH⁻ conductivity of 50 mS/cm at 30 °C, which was almost 2× higher than that of the PFF⁺ and PFBFF⁺ membranes (21 and 24 mS/cm, respectively). Cl⁻ conductivity is generally lower than OH⁻ conductivity because of the lower dilute solution mobility of Cl⁻ and lower water uptake in halide forms. As shown in Figure 4, conductivity in all of the AEMs was lower in their chloride forms than in their hydroxide forms.

Increasing the temperature increased the OH⁻ and Cl⁻ conductivity of the polymer samples. For example, PFF⁺ and PFBFF⁺ had similar conductivity values of 21 and 24 mS/cm at 30 °C, respectively. At 80 °C, the conductivity was increased to 85 mS/cm for PFBFF⁺ but reached only 48 mS/cm for PFF⁺. The greater conductivity of PFBFF⁺ at higher temperature can be ascribed to the higher IEC and water uptake, which is further increased at the higher temperature. PFB⁺ exhibited the highest OH⁻ conductivity (124 mS/cm) at 80 °C.

Polyfluorene derivatives are also known as hole conductive materials.^{32–37} In order to prove that the reported conductivity

values are solely from the ion conductivity of quaternary ammonium functionalized polymers but not from the hole/electron conductivity of fluorene polymer backbone, the precursor polymers (PFB, PFF, PFBFF) that do not have an ionic group were subjected for conductivity measurement (Table S5). All precursor polymers showed a negligible ion conductivity value (0.74–1.06 mS/cm), which is identical to that of DI water without a membrane sample (0.8–1.08 mS/cm). This result clearly indicates that the conductivity values of Figure 4 are not from the fluorene-based polymer backbone, but from the ionic side groups.

In summary, alkyl QA-functionalized polyfluorene AEMs were synthesized and analyzed for alkaline fuel cell applications. The AEMs were prepared via Suzuki coupling, cast from DMF solvent, and anion-exchanged with OH⁻ anions. These AEMs were flexible and tough enough for potential use as fuel cell membrane materials. The hydroxide conductivity of PFF⁺ AEMs reached 124 mS/cm at 80 °C. Compared with the synthesis of other alkyl QA-functionalized polymer AEMs, the synthetic strategy reported herein affords the major advantage of a simple procedure that avoids complicated postpolymerization modifications. In addition, the synthesized QA-functionalized polyfluorene membranes showed excellent long-term alkaline stability at 80 °C, which fulfills a critical requirement for application in alkaline fuel cells. The solvent processability of these ionomers makes them useful as both AEMs and ionomer electrode materials. The results of this study provide a new design strategy for the preparation of high-performance AEMs.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details of synthetic procedures, and characterization and properties of polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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