# Exploring backbone-cation alkyl spacers for multi-cation side chain anion exchange membranes

Liang Zhu [a, **], Xuedi Yu [a], Michael A. Hickner [a, b, *]

[a] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[b] Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

## HIGHLIGHTS

- New AEM designs are needed to improve the performance of alkaline technology.
- Multi-cation PPO-based AEMs were synthesized with a variety of cation spacers.
- AEMs with 5-carbon or 6-carbon spacers had optimized conductivity and stability.

## GRAPHICAL ABSTRACT
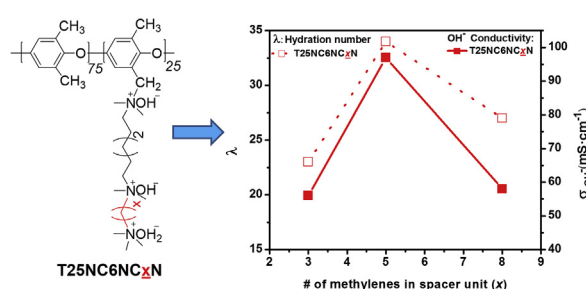
## ABSTRACT

In order to systematically study how the arrangement of cations on the side chain and length of alkyl spacers between cations impact the performance of multi-cation AEMs for alkaline fuel cells, a series of polyphenylene oxide (PPO)-based AEMs with different cationic side chains were synthesized. This work resulted in samples with two or three cations in a side chain pendant to the PPO backbone. More importantly, the length of the spacer between cations varied from 3 methylene (-$CH_2$-) (C3) groups to 8 methylene (C8) groups. The highest conductivity, up to 99 mS/cm in liquid water at room temperature, was observed for the triple-cation side chain AEM with pentyl (C5) or hexyl (C6) spacers. The multi-cation AEMs were found to have decreased water uptake and ionic conductivity when the spacer chains between cations were lengthened from pentyl (C5) or hexyl (C6) to octyl (C8) linking groups. The triple-cation membranes with pentyl (C5) or hexyl (C6) groups between cations showed greatest stability after immersion in 1 M NaOH at 80 °C for 500 h.

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## 1. Introduction

Over the last 10 years, the polymer, membrane, and electrochemical communities have pursued polymer structures directed towards fabricating high stability, high conductivity anion exchange membranes for a new generation of electrochemical devices. This large effort has been motivated by the pursuit of inexpensive fuel cells with low-cost, non-precious metal catalysts and also the development of advanced batteries based on membranes with superior selectivities. While there have been some interesting studies of outstanding fuel cell devices and application of high-performance, thin anion exchange membranes in other cells such as redox flow batteries and water and $CO_2$ electrolyzers,

there is no consensus in the community on the path forward towards a commercializable, stable, conductive, and thin anion exchange membrane that can be widely deployed.

Now that the community has surveyed a wide range of chemical structures in the development of high performance anion exchange membranes, systematic investigations into the detailed mechanisms of how to construct these materials are needed. Specifically, a number of backbones, cations, and tethers have been reported [1–15]. However, many of these structures have too low stability to be widely useful in electrochemical devices that require longevity on the order of years. Our recent work has shown that the addition of alkyl chains around the ammonium cation can have a significant effect on the overall membrane properties − including a simultaneous improvement in conductivity and stability [16–23]. The introduction of alkyl chains to AEMs influences the phase separation properties of the material [24,25]. Increased phase separation due to the hydrophobic alkyl chains appears to be one route to higher-performance AEMs than can be achieved with benzyl-trimethyl ammonium cations.

Recently, the multi-cation cation side chain strategy for new AEMs has been used as a method of simultaneously improving conductivity and stability due to reducing the degree of functionalization while increasing the charge number of the cationic groups [19]. Wang [11], et al. investigated poly (2,4-dimethyl-1,4-phenylene oxide) (PPO)-based AEMs with a well-defined number of quaternary ammonium groups on the side chains. When the number of cations was increased from 1 to 6, continuous improvement in conductivity was observed due to the improved hydrophilic−hydrophobic microphase separation. Although the multi-cation side chain AEMs prepared by Wang [11], et al. showed promising properties, the previous report did not detail studies to demonstrate the effect of length of the spacers on the performance of the AEMs. Dang [3], et al. revealed that the spacers between cations needs to at least 4 methylene (C4) groups in order to maximize the conductivity by avoiding counter-ion condensation. However, this report did not detail studies to demonstrate the effect of even longer spacers (like 8 methylene) groups on the performance of the AEMs. Thus, while side chain cations strategies are promising, more work is needed to explore the full range of possible structures and further demonstrate the ultimate utility of this approach.

Here, we report a detailed study on the tethering chemistry used to connect alkyl ammonium cations to the polymer backbone. Additionally, we investigated the details of the number of cations per side chain as well as the alkyl spacing between cations.

## 2. Experimental section

### 2.1. Materials

Poly (2,6-dimethyl-1,4-phenylene oxide) with a number average molecular weight of 20,000 g/mol (~PDI = 1.50) was purchased from Sigma-Aldrich and dried under vacuum at room temperature overnight. N,N,N′,N′-tetramethyl-1,6-hexanediamine, N,N,N′,N′-tetramethyl-1,3-propanediamine, 1,8-dibromooctane, 1-bromohexane, (5-bromopentyl)trimethylammonium bromide, (3-bromopropyl)trimethylammonium bromide, N-bromosuccinimide, and 2,2′-azobis (2-methylpropionitrile) were obtained from Sigma-Aldrich and used as received. The solvents and other chemicals used in this work were obtained from VWR International and used as received. The brominated PPO polymers with different degrees of functionalization (DF) ranging from 15 to 40 mol % of the repeat units on the backbone with benzyl bromide groups were synthesized according to the reported literature procedure [26].

### 2.1.1. Synthesis of 1-(N′, N′-dimethylamino)-3-(N,N,N-trimethylammonium) nonane bromine (**1a**)

To 600 mL of chloroform, 300 mmol of N, N, N′, N′-tetramethyl-1,3-proanediamine and 30 mmol of 1-bromohexane were dissolved and heated at 60 °C for 12 h [27,28]. After evaporation of the chloroform, the residual liquid reagent was removed under vacuum. The crude product was further purified through recrystallization in methanol. The recrystallized product was dried in a vacuum oven at room temperature with a yield of 85%. The chemical structure and purity of the product was characterized by $^1$H NMR in CDCl$_3$.

### 2.1.2. Synthesis of 1-(N′,N′-dimethylamino)-6-(N,N,N-trimethylammonium) dodecane bromine (**1b**)

The synthesis of 1-(N′,N′-dimethylamino)-6-(N,N,N-trimethylammonium) dodecane bromide was similar to the procedure described above. To 600 mL chloroform, 300 mmol of N,N,N′,N′-tetramethyl-1,6- hexanediamine and 30 mmol of 1-bromohexane were dissolved, and heated at 60 °C for 12 h. The crude product was purified using the same method described above. The final product was dried in a vacuum oven at room temperature with a yield of 83%. The chemical structure and purity of the product was characterized by $^1$H NMR in CDCl$_3$.

### 2.1.3. Synthesis of 1-(N′,N′-dimethylamino)-6,9-(N,N,N-trimethylammonium) nonane bromide (**2a**)

To 400 mL of chloroform, 200 mmol of N,N,N′,N′-tetramethyl-1,6-hexanediamine and 20 mmol of (3-bromopropyl)trimethylammonium were dissolved, and heated at 60 °C for 12 h. After evaporation of the chloroform, the residual liquid reagent was removed under vacuum at 80 °C. The crude product was further purified through recrystallization in methanol. The recrystallized product was dried *in vacuo* at room temperature to afford a yield of 91%. The chemical structure and purity of the product was characterized by $^1$H NMR in DMSO-$d_6$. The synthesis of 1-(N′,N′-dimethylamino)-6,11-(N,N,N-trimethylammonium) undecane bromide (**2b**) was similar to the procedure described above. The chemical structure and purity of the product was characterized by $^1$H NMR in DMSO-$d_6$.

### 2.1.4. Synthesis of 1-(N′,N′-dimethylamino)-6,14-(N,N,N-trimethylammonium) tetradecane bromide (**2c**)

(8-Bromooctyl)trimethylammonium bromide was synthesized according to the reported literature [29]. 1, 8-dibromooctane (11.0 g, 40.4 mmol) was mixed with tetrahydrofuran (10 mL) on ice. To the mixture, H$_2$O (11 mL) was added with vigorous stirring. Trimethylamine solution in ethanol (4.2 M, 11.2 g, 20 mmol) was added and the mixture was reacted at 0 °C for 3 h. Before ether and water were added, the mixture was further reacted for 20 h at room temperature. The aqueous phase was washed with diethyl ether three times and the combined solvent was removed under vacuum. The resulting solids were refluxed in isopropanol for 3 h. After the mixture was cooled to room temperature, the crystals (mostly the bismethonium species) were removed by filtration. After evaporation of the isopropanol, the crude product was further purified through recrystallization in isopropanol/diethyl ether. The recrystallized product was dried in a vacuum oven at 80 °C. To 200 mL of chloroform, 100 mmol of N,N,N′,N′-tetramethyl-1,6-hexanediamine and 10 mmol of (8-bromooctyl)trimethylammonium were dissolved and then heated at 60 °C for 12 h. After evaporation of the chloroform, the residual liquid reagent was removed under vacuum at 80 °C. The crude product was further purified through recrystallization in methanol. The recrystallized product was dried in a vacuum oven at room temperature with a yield of 87%. The chemical structure and purity of the product was characterized by