

Supporting Information

Aromatic polyelectrolytes via polyacylation of pre-quarternized monomers for alkaline fuel cells

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1. Experimental section

Before testing of the ionic conductivities, the membranes were transformed into the desired counter-anions type as follows: Firstly, a 1 × 3 cm sized piece of membrane (Cl⁻ type) was immersed in a 30 cm³ vial full of 1 mol dm⁻³ aqueous solution containing the target anion (NaOH or Na₂CO₃) at 25°C for 24 h during which the ion-exchange solution was refreshed every 8 h. Subsequently, the membrane sample was immersed in a 30 cm³ vial full of de-ionized water at 25°C for at least 24 h during which the water was refreshed 4 times every 2 h followed by 2 times every 8 h to drain inorganic electrolytes out as possible. These experiments were repeated with different samples of each membrane as required. An important point to note is that the 1 h washing procedure (with three changes of water in this 1 h period) commonly encountered in the previous literature^[1] was found to be not enough to remove all the excessive metal alkali species trapped in the alkaline membranes, which led to over-estimated conductivities. The procedure adopted above was used to mitigate against this; however, this procedure risks underestimating the OH⁻ conductivities due to the inevitable exposure of the OH⁻ type membranes to atmospheric CO₂ (conversion of OH⁻ anions to less conductive HCO₃⁻ / CO₃²⁻ anions).

2. Spectrometry characterization

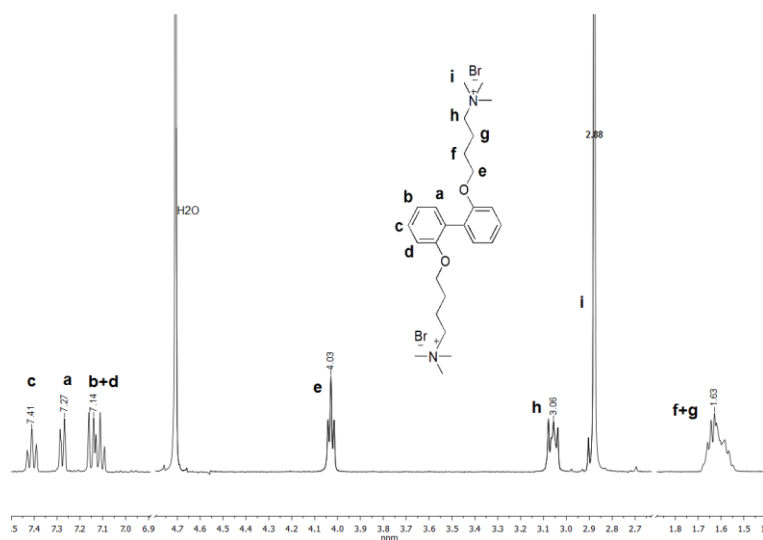


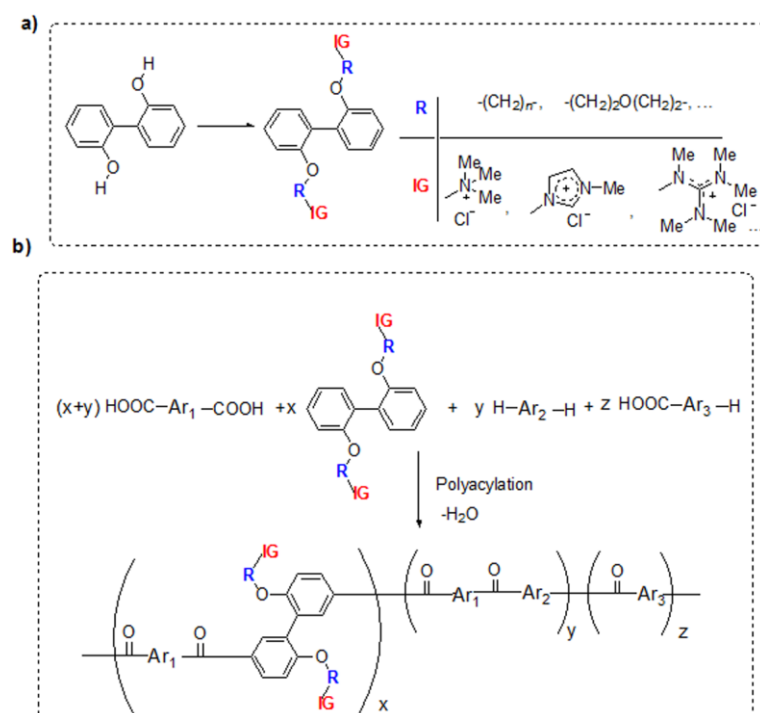
Figure S1. ^1H NMR spectrum of pre-ionized monomer QBP.



Figure S2. Digital photograph of membrane OBUtMA-AAEPs-1.0 (A4 paper as background).

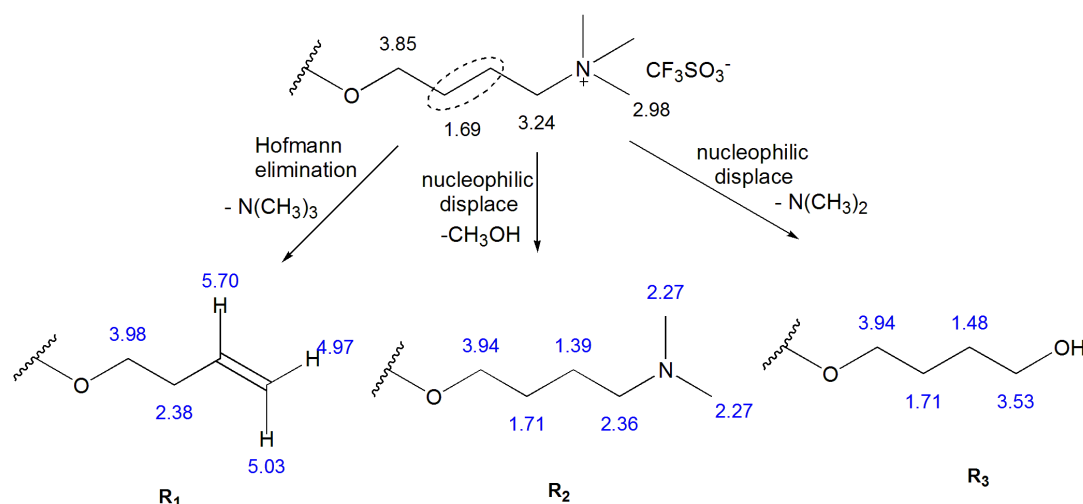
3. Results and discussion

Scheme S1 illustrates the concept of direct polyacylation of pre-quarternized monomers to obtain side-chain-type quarternized aromatic polyelectrolytes, which shows great flexibility to tailor the length of the side chain spacer, the species of the cationic group and moieties of the main-chain.



Scheme S1. Illustration of the concept of a) pre-quarternized monomers and b) their polyacylation to obtain side-chain-type AAEPs.

Scheme S2 illustrates the 1H chemical shifts of pristine pendent $-O-(CH_2)_4-N^+(CH_3)_3CF_3SO_3^-$ group (determined by 1H NMR in DMSO- d_6) and possible degradation residues after accelerated long-term alkaline stability test: **R₁** from Hofmann elimination by taking off trimethylamine while **R₂** and **R₃** from nucleophilic displace by taking off methanol and trimethylamine, respectively (predicted by Chemdraw soft). Firstly, although there is β -H on $-O-(CH_2)_4-N^+(CH_3)_3CF_3SO_3^-$ group to allow Hofmann elimination, no such substituents like phenyl, vinyl, $-CO-$, $-SO_2-$, $-O-$, $-N-$, etc. to afford π - π or p - π conjugation effect to stabilize alkene residue **R₁**, thus minimizing Hofmann elimination; Secondly, the α -H on $-O-(CH_2)_4-N^+(CH_3)_3CF_3SO_3^-$ group are less acidic than those on conventional benzyl-type quarternary ammonium groups, which should make $-O-(CH_2)_4-N^+(CH_3)_3CF_3SO_3^-$ group less reactive to nucleophilic displace by OH^- via the ylide mechanism^[2].



Scheme S2. ^1H chemical shifts of pristine pendant quaternary ammonium group (determined by ^1H NMR in DMSO-d_6) and possible degradation residues (predicted by Chemdraw software).

Moreover, the degradation mechanism of $-\text{O}-(\text{CH}_2)_4-\text{N}^+(\text{CH}_3)_3$ group could be roughly analyzed according to **Fig. 4c** and **Scheme S2**. Firstly, no ^1H chemical shift of possible degradation residues would appear at around 2.98 ppm (peak **e** assigned to CH_3-N^+ , **Fig. 4**), therefore the total loss of quaternary ammonium groups can be calculated by the change of integration area of peak **e** as $1-(3.90/4.46)=12.6\%$, that is, the total loss of quaternary ammonium groups was 12.6%; Secondly, among the three possible degradation residues, only the proton chemical shift of $-\text{C}-\underline{\text{CH}_2}-\underline{\text{CH}_2}-\text{C}$ in residue **R₁** would move greatly downfield (2.38 and 5.70 ppm by prediction) and would not appear at around 1.69 ppm (peak **b+c**, assigned to $-\text{C}-\underline{\text{CH}_2}-\underline{\text{CH}_2}-\text{C}$, **Fig. 4**), therefore the loss of $-\text{C}-\underline{\text{CH}_2}-\underline{\text{CH}_2}-\text{C}$ along with the loss of quaternary ammonium groups can be calculated by the integration change of peak **b+c** as $1-(1.82/2.00)=9.0\%$, that is, 9.0% of quaternary ammonium groups was lost via the pathway of Hofmann elimination; Thirdly, given that the total loss of quaternary ammonium groups is composed of the loss caused by Hofmann elimination and nucleophilic displace, the loss of quaternary ammonium groups via nucleophilic displace can be calculated as $12.6\%-9.0\%=3.6\%$. In summary, after being treated with 1 mol dm^{-3} NaOH at 85°C for 40 d, the total loss of quaternary ammonium groups was 12.6%, where 9.0% was lost via the pathway of Hofmann elimination and 3.6% via nucleophilic displace, indicating that Hofmann elimination was the main cause for degradation of $-\text{O}-(\text{CH}_2)_4-\text{N}^+(\text{CH}_3)_3$ ammonium groups (about 71% of the total lost quaternary ammonium) under this test condition.

References:

- [1] Robertson, N. J.; Kostalik, H. A.; Clark, T. J.; Mutolo, P. F.; Abruña, H. c. D.; Coates, G. W. *J. Am. Chem. Soc.* **2010**, *132*, 3400-3404.
- [2] Chempath, S.; Einsla, B. R.; Pratt, L. R.; Macomber, C. S.; Boncella, J. M.; Rau, J. A.; Pivovar, B. S. *J. Phys. Chem. C* **2008**, *112*, 3179-3182.