Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2018

Electronic Supplementary Information (ESI)

## Poly(arylene alkylene)s with pendant *N*-spirocyclic quaternary ammonium cations for anion exchange membranes

Thanh Huong Pham<sup>*a*</sup>, Joel S. Olsson<sup>*a*</sup>, Patric Jannasch<sup>*a,b*\*</sup>

 <sup>a</sup> Polymer & Materials Chemistry, Department of Chemistry, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden
<sup>b</sup> University of Tartu, Institute of Technology, Nooruse 1, EE-50411 Tartu, Estonia



**Figure S1.** <sup>1</sup>H NMR spectra of a) PBP55Ph, b) P5Ph-1.8 and c) P6Ph-1.8. TFA was added in order to shift the water signal (originally at 3.34 ppm) to above 10 ppm, revealing signals between 3.0-3.5 ppm. The signals between 7.0-8.0 ppm were assigned to aromatic protons.



**Figure S2.** SAXS profiles of P6Ph-1.8, P6Ph-2.2 and P6Me-2.0 AEMs in the bromide form after equilibration at 75% RH. No ionomer peaks were observed.

Sample	In-plane swelling (%)				Through-plane swelling (%)			
	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C
P5Ph-1.8	9	10	14	20	13	17	25	25
P5Ph-2.3	21	24	25	39	18	18	26	31
P6Ph-2.2	21	27	29	49	15	15	15	22
P5Me-2.2	11	13	18	25	19	22	33	40
P5Me-2.0	11	11	14	21	29	34	34	46

Table S1. Swelling of the AEMs in hydroxide form at different temperature



**Figure S3.** <sup>1</sup>H NMR spectra of a) P5Ph-2.3 and b) P6Ph-2.0 in DMSO- $d_6$ /TFA before and after immersion in 2 M aq. NaOH at 90 °C during different periods of time. TFA was added to shift the water signals (originally at ~3.3 ppm) to above 10 ppm, revealing the sample signals between 3.0-3.5 ppm. The red arrows mark new signals originating from degradation products.



**Figure S4.** <sup>1</sup>H NMR spectra of a) P5Me-2.2 and b) P6Me-2.0 in DMSO- $d_6$ /TFA before and after immersion in 2 M aq. NaOH at 90 °C for different periods of time. TFA was added to shift the water signals (originally at ~3.3 ppm) to above 10 ppm, revealing the sample signals between 3.0-3.5 ppm. The red arrows mark new signals originating from degradation products.



**Figure S5.** <sup>1</sup>H NMR spectra of a) P6Ph-2.2 and b) P6Me-2.0 in DMSO- $d_6$ /TFA before and after immersion in 2 M aq. NaOH at 120 °C for 360 h. TFA was added to shift the water signals (originally at ~3.3 ppm) to above 10 ppm, revealing the sample signals between 3.0-3.5 ppm. The red arrows mark new signals originating from degradation products.



Scheme S1. Possible degradation pathways of the *N*-spirocyclic QA cations through (1) ring-opening Hofmann  $\beta$ -elimination in Pi1, (2) ring-opening Hofmann  $\beta$ -elimination in pendant rings Py2 and Pi2, (3) ring-opening nucleophilic substitution in ring Pi1, and (4) ring-opening nucleophilic substitution in pendant rings Py2 and Pi2 (see Scheme 1 for ring designations).