

Supplementary information

High conductive fluorine-based anion exchange membranes with robust alkaline durability

Xue Lang Gao, Li Xuan Sun, Hong Yue Wu, Zhao Yu Zhu, Nan Xiao, Jia Hui Chen, Qian Yang, Qiu

Gen Zhang, Ai Mei Zhu, Qing Lin Liu*

Department of Chemical & Biochemical Engineering, Fujian Provincial Key Laboratory of Theoretical
and Computational Chemistry, College of Chemistry and Chemical Engineering, Xiamen University,

Xiamen 361005, P. R. China

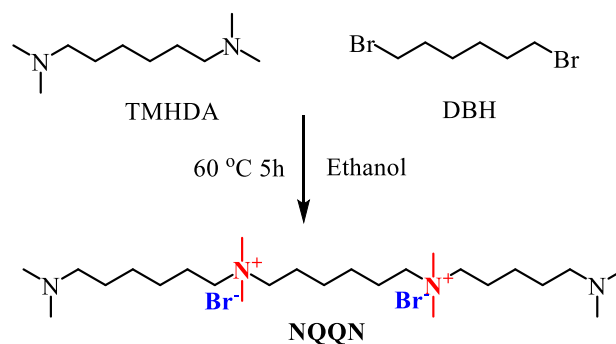
*Corresponding author:

Q.L. Liu, E-mail: qlliu@xmu.edu.cn, Tel: 86-592-2188072, Fax: 86-592-2184822

1. Synthesis of the ionic liquid 1,18-(N',N'-dimethylamino)-6,12-(N,N-dimethylammonium)octadecane bromide (NQQN)
2. [Scheme S1](#) Synthesis of NQQN
3. [Fig. S1](#) ¹H NMR of NQQN
4. [Fig. S2](#) ¹H NMR of PDBA-70%
5. [Table S1](#) Molecular weight, polydispersity index (Mw/Mn) of the PDBA-X polymers
6. [Fig. S3](#) ¹H NMR of Br-PDBA-70%
7. [Table S2](#) Solubility, gel fraction (GF) and degree of bromination (DB) data of the polymers and AEMs
8. [Fig. S4](#) FT-IR of the NQQN, PDBA-70%, Br- PDBA-70% and TQ- PDBA-70% AEM
9. [Fig.S5](#) DMA analysis of the TQ-PDBA-X AEMs as a function of temperature at 60% RH
10. [Fig.S6](#) DSC analysis of the TQ-PDBA-X AEMs as a function of temperature
11. [Scheme S2](#) Possible degradation mechanism of QA groups in the TQ-PDBA-70% AEM after alkaline treatment (a-b) nucleophilic substitution, and (c) Hofmann elimination
12. [Fig.S7](#) Durability test of the single cell assembled with TQ-PDBA-70% and commercial Tokuyama AHA AEM

1. Synthesis of the ionic liquid 1,18-(N', N'-dimethylamino)-6,12-(N, N-dimethylammonium) octadecane bromine (NQQN)

The synthesis of NQQN is shown in Scheme S1¹. Typically, 1.26 mL of 1,6-dibromohexane was dissolved in ethanol to form a 2% v/v solution. 15 mL of N, N, N, N-tetramethyl-1,6-hexanediamine (TMHDA) was added into a 150 mL three-necked round-bottomed flask with a magnetic stirrer. Then the 1,6-dibromohexane solution was added dropwise into the flask under stirring. The mixture was heated to 60 °C and stirred for 5 h. After that, the mixture was cooled to room temperature (RT) and transferred into 400 mL of anhydrous ether to precipitate a white powder solid. After being cooled at −18 °C for 12 h, a white precipitate was obtained via vacuum filtration. The crude product was purified with anhydrous ether for three times, followed by vacuum drying at RT for 24 h (yield 58.6%).



Scheme S1 Synthesis of the NQQN

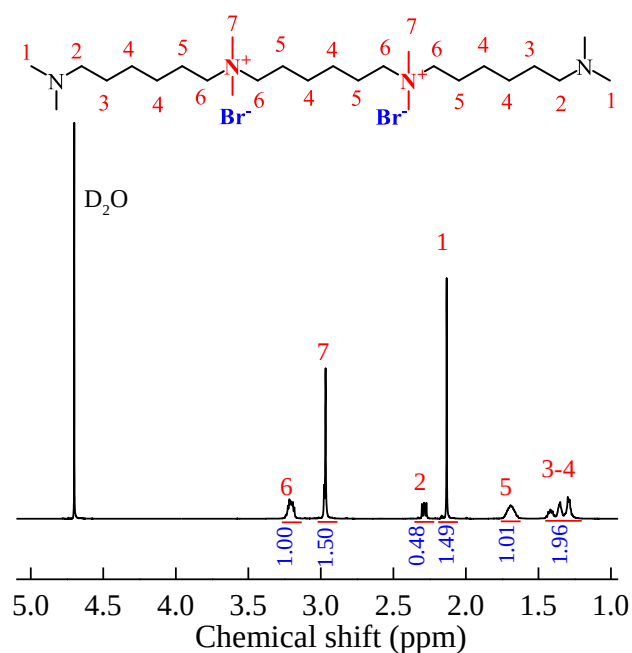


Fig. S1 ¹H NMR of the NQQN

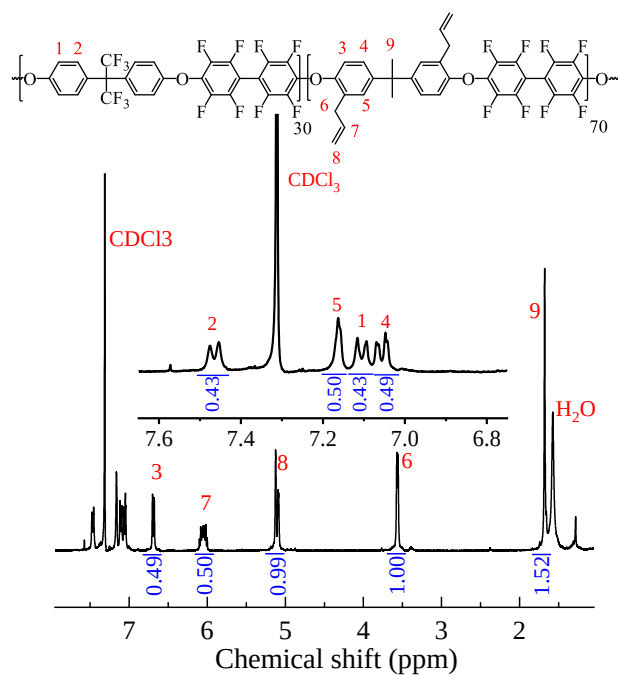


Fig. S2 ^1H NMR of PDBA-70%

Table S1 Molecular weight, polydispersity index (M_w/M_n) of the PDBA-X polymers

Polymers	$M_n(\text{kDa})$	$M_w(\text{kDa})$	M_w/M_n
PDBA-30%	75009	262147	3.49
PDBA-40%	74370	254746	3.43
PDBA-60%	63539	223180	3.51
PDBA-70%	48880	158152	3.24

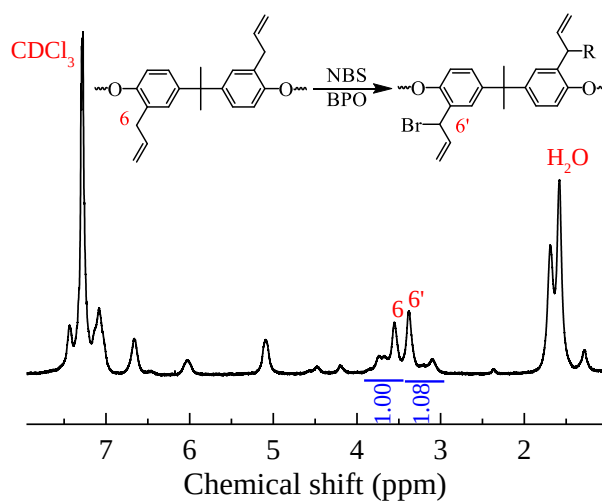


Fig. S3 ^1H NMR of Br-PDBA-70%

Table S2 Solubility, gel fraction (GF) and degree of bromination (DB) data of the polymers and AEMs

Sample	DMSO	DMF	THF	NMP	DMAC	CHCl ₃	GF	DB
PDBA-X	+	+	+	+	+	+		
Br-PDBA-X	+	+	+	+	+	+		
TQ- PDBA -30%	-	-	-	-	-	-	85.9%	55.36%
TQ- PDBA -40%	-	-	-	-	-	-	89.3%	67.11%
TQ- PDBA -60%	-	-	-	-	-	-	93.2%	58.51%
TQ- PDBA -70%	-	-	-	-	-	-	96.8%	61.83%

+: soluble, -: insoluble

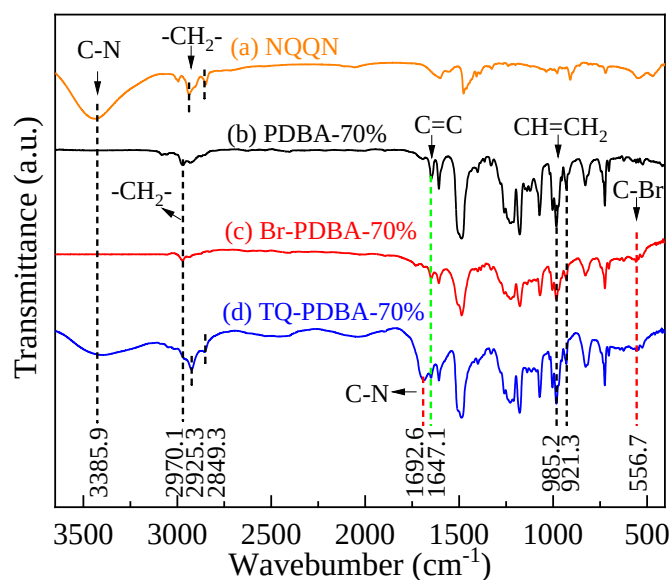


Fig.S4 FT-IR of the NQQN, PDBA-70%, Br-PDBA-70% polymers and TQ-PDBA-70% AEM

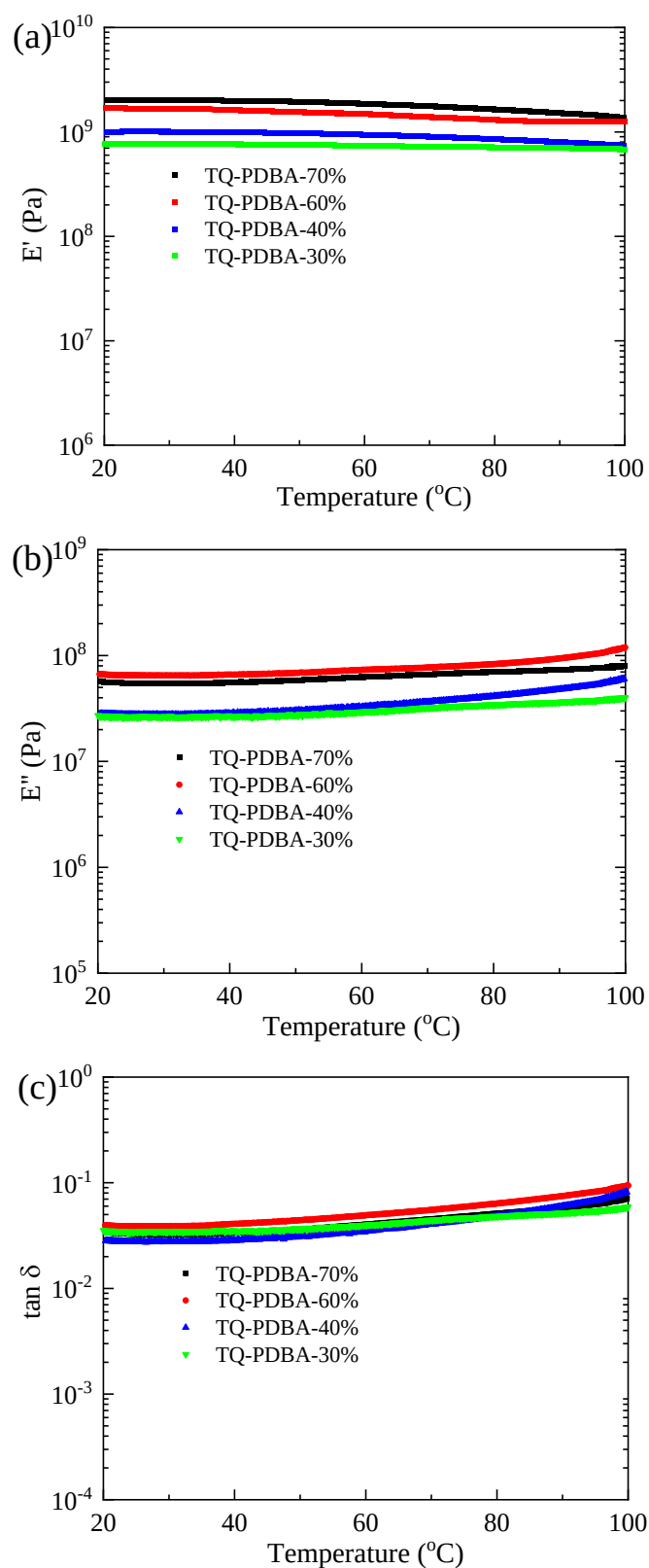


Fig.S5 DMA curves of the TQ-PDBA-X AEMs as a function of temperature at 60% RH

((a) storage modulus (E'), (b) loss modulus (E'') and (c) $\tan \delta$ ($\delta = E'/E''$))

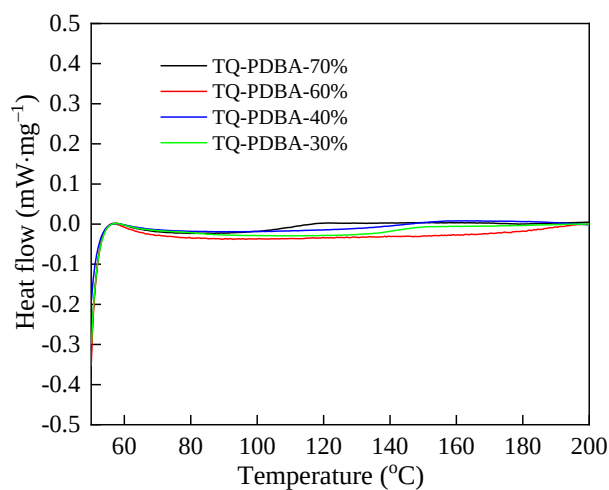
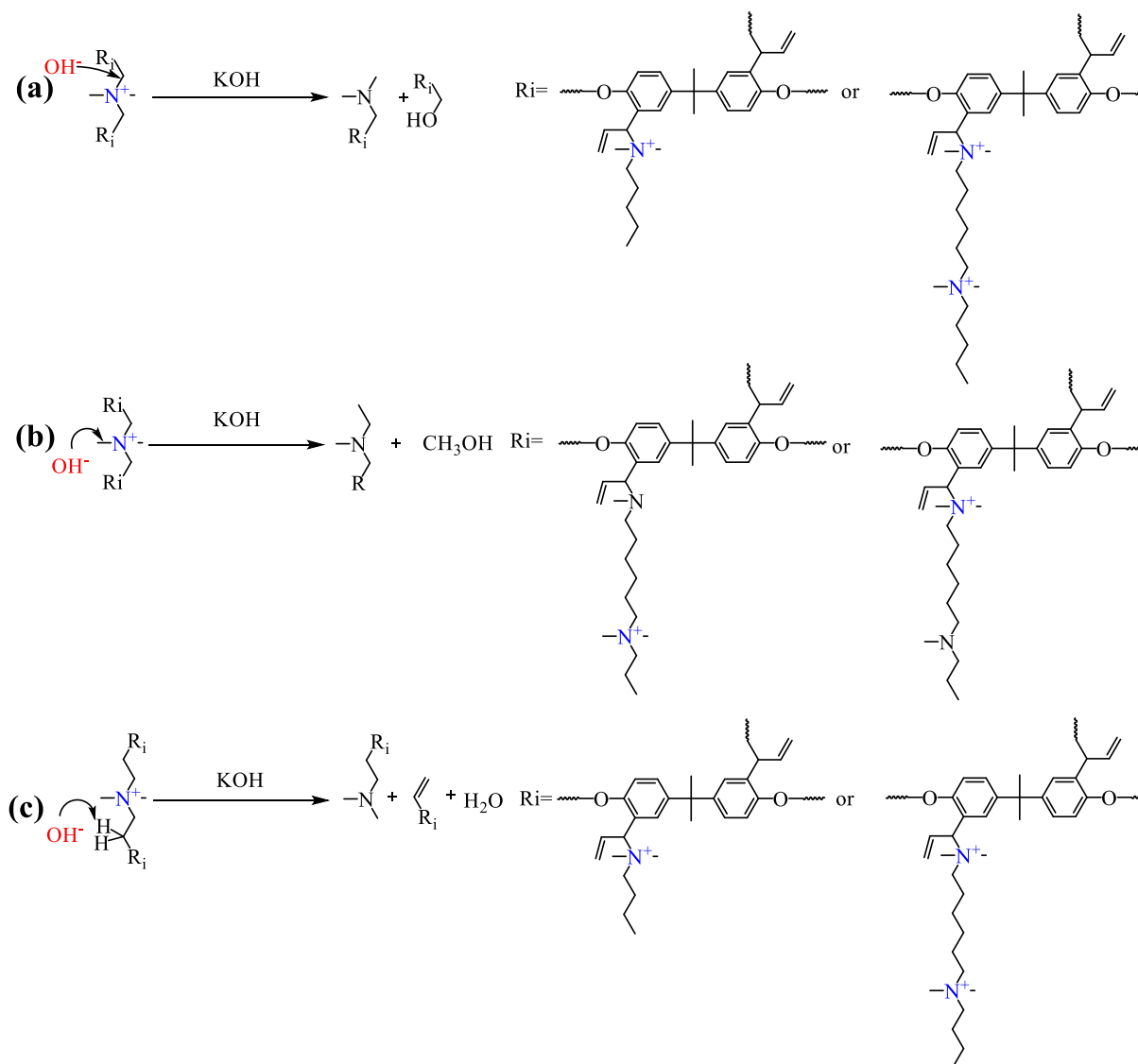


Fig.S6 DSC curves of the TQ-PDBA-X AEMs as a function of temperature



Scheme S2 Possible degradation mechanism of QA groups in the TQ-PDBA-70% AEM after alkaline treatment (a-b) nucleophilic substitution, and (c) Hofmann elimination

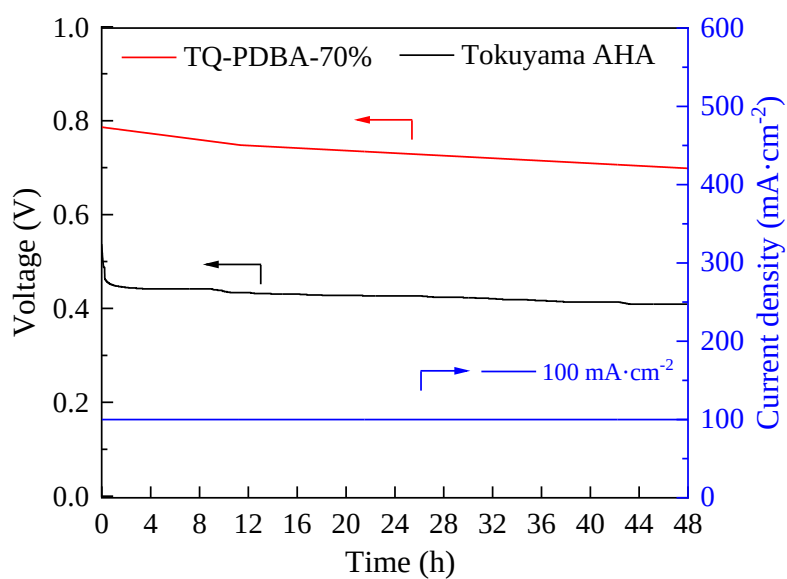


Fig.S7 Durability test of the single cell assembled with the TQ-PDBA-70% and commercial Tokuyama AHA AEM

Reference

1. Han, J., et al., Elastic long-chain multication crosslinked anion exchange membranes. *Macromolecules*, 2017, **50**(8):3323-3332.