

Supplementary Information

Side-chain-type anion exchange membranes bearing pendant quaternary ammonium groups via flexible spacer for fuel cells

Chen Xiao Lin, Xiao Ling Huang, Dong Guo, Qiu Gen Zhang, Ai Mei Zhu, Mei Ling Ye, Qing Lin Liu*

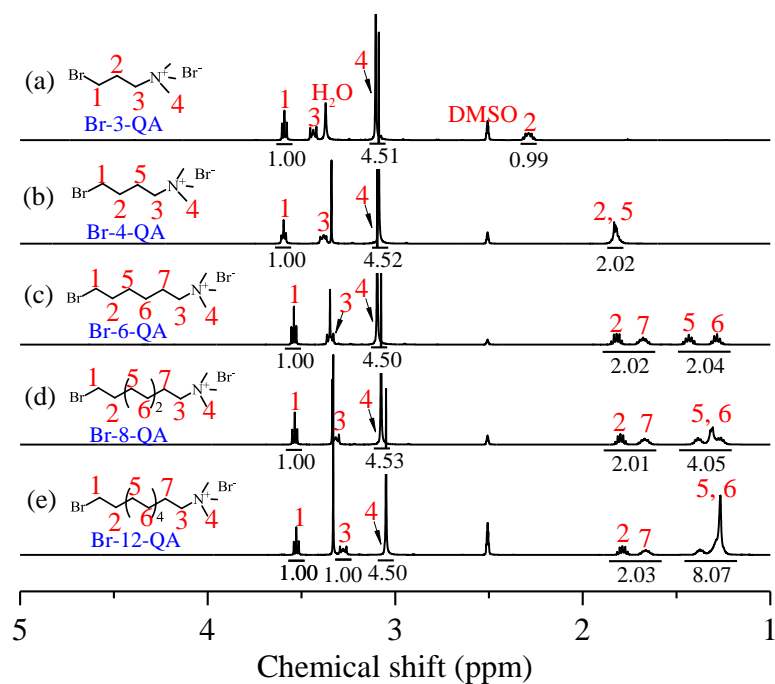
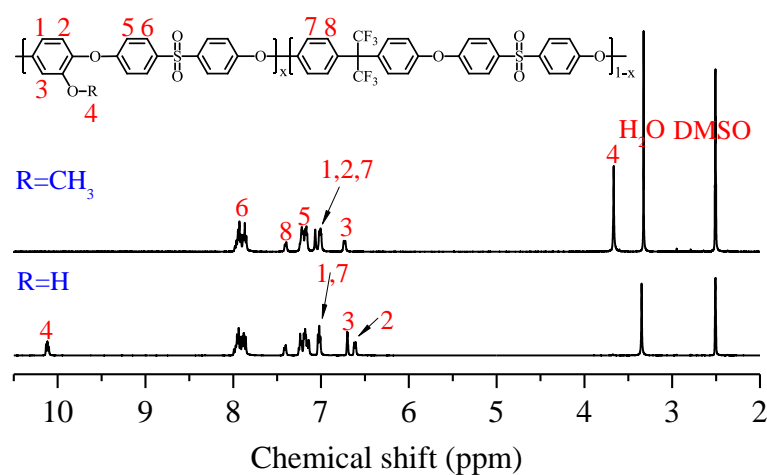
Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Department of Chemical & Biochemical Engineering, The College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China

*Corresponding author:

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

Table S1 Quaternization reaction of 1, ω -dibromoalkanes in THF.

| Chemical structure | Scale (mmol) | Bubbling time (h) | Reaction time (h) | Yield (%) |
|---|--------------|-------------------|-------------------|-----------|
| Br-(CH ₂) ₃ -Br | 100 | 4 | 24 | 68 |
| Br-(CH ₂) ₄ -Br | 100 | 4 | 24 | 60 |
| Br-(CH ₂) ₆ -Br | 100 | 4 | 24 | 56 |
| Br-(CH ₂) ₈ -Br | 50 | 2 | 24 | 65 |
| Br-(CH ₂) ₁₂ -Br | 50 | 2 | 24 | 61 |

**Fig. S1** ¹H NMR spectra of Br-x-QA (x=3, 4, 6, 8 and 12).**Fig. S2** ¹H NMR spectra of PES-OCH₃ and PES-OH.

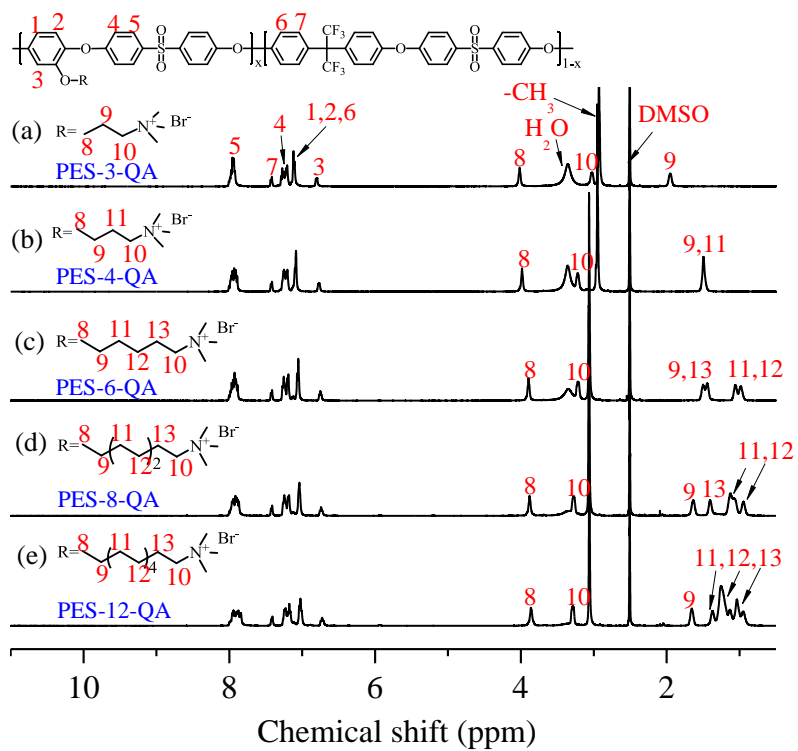


Fig. S3 ^1H NMR spectra of PES- n -QA ($n=3, 4, 6, 8$ and 12).

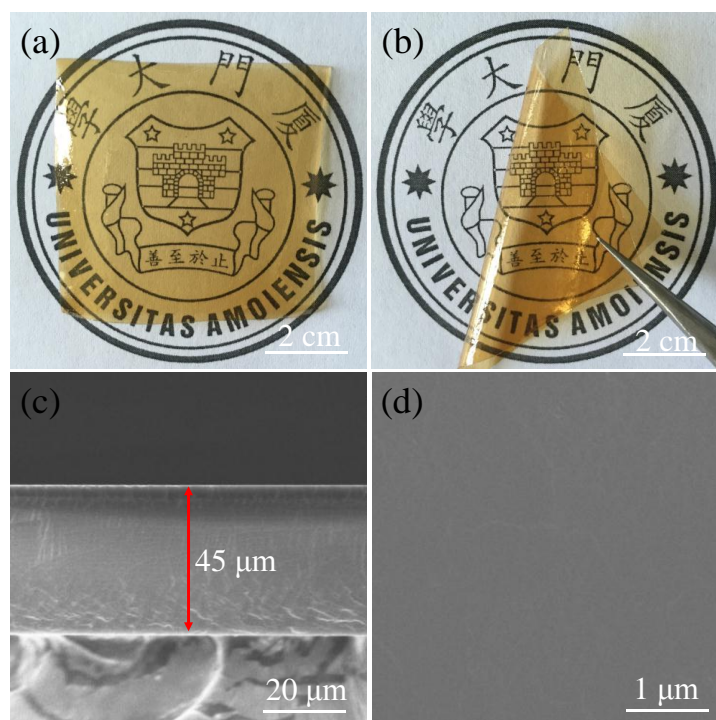


Fig. S4 The appearance (a, b), SEM images of (c) cross-section and (d) surface of PES-6-QA.

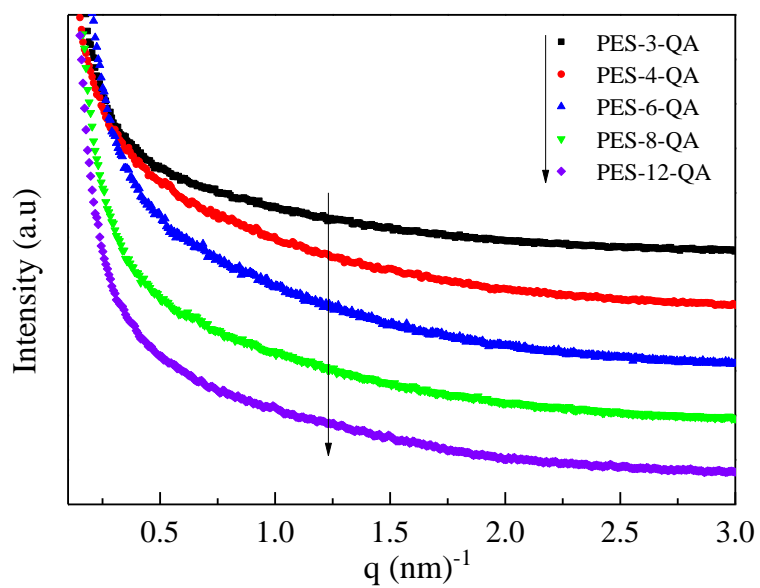


Fig. S5 Small angle X-ray scattering (SAXS) of the AEMs.

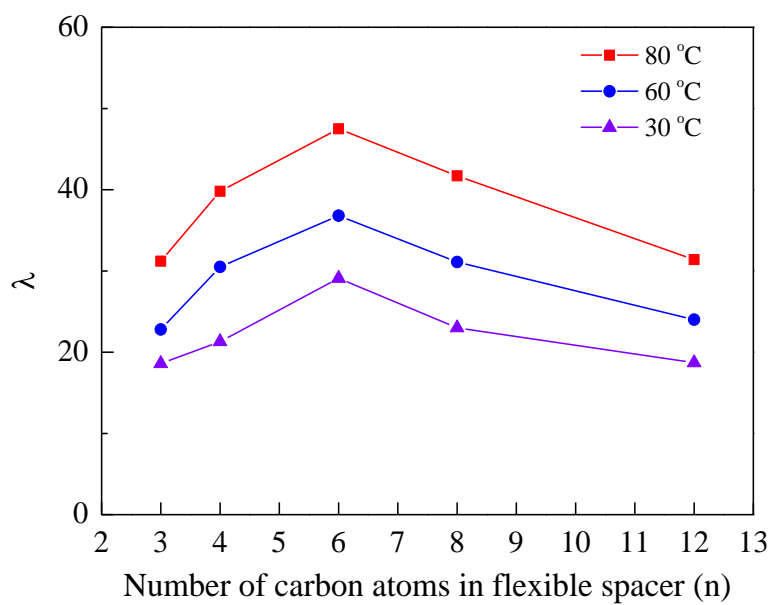


Fig. S6 The number of absorbed water molecules around each QA group (λ) as a function of flexible spacer length for the PES-n-QA membranes at 30, 60 and 80 °C.

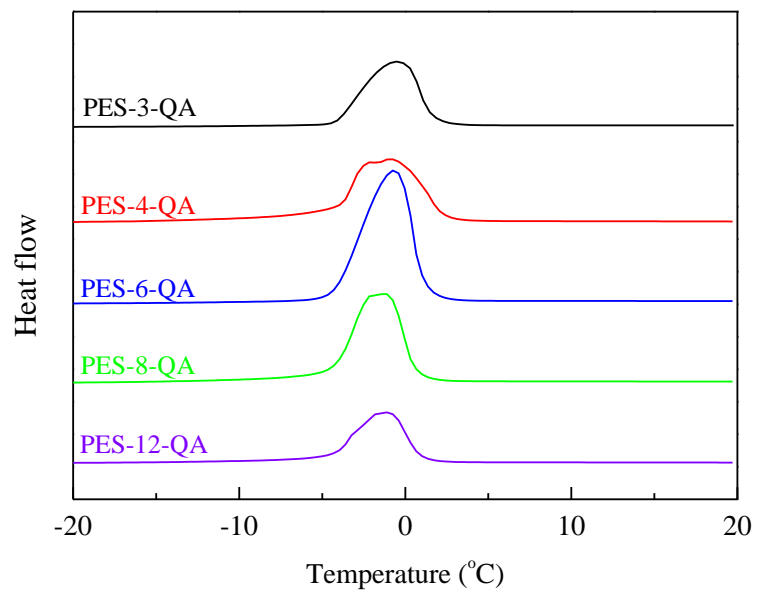


Fig. S7 Thermogram of water fusion enthalpy of the AEMs.

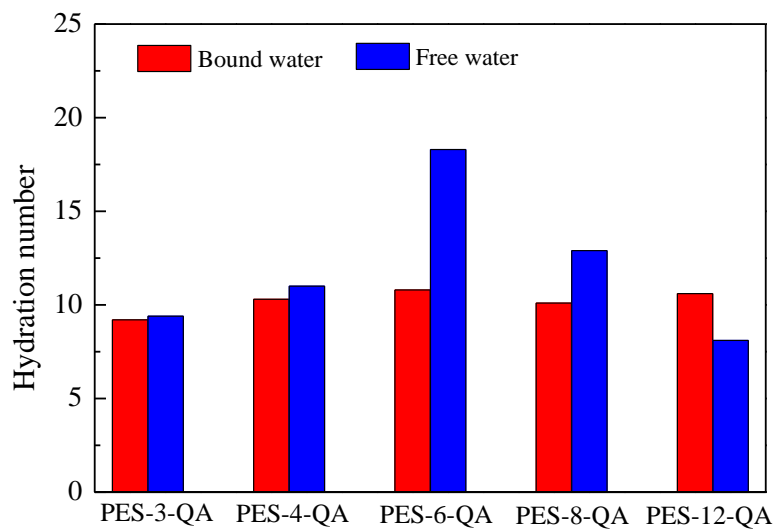
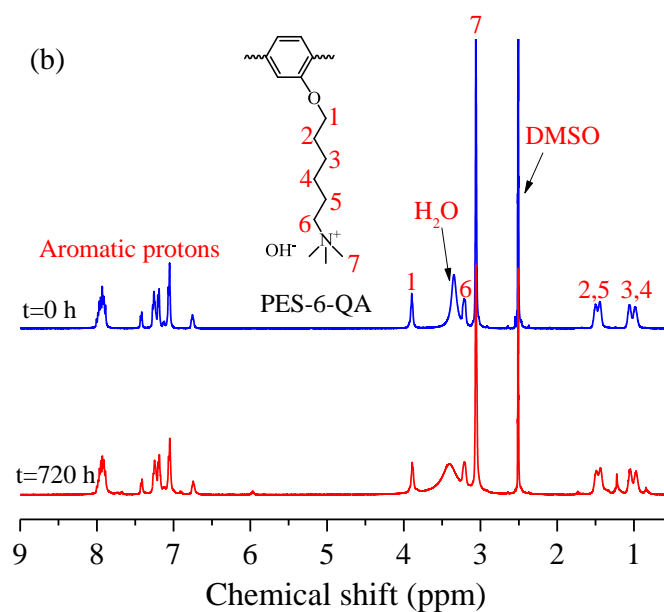
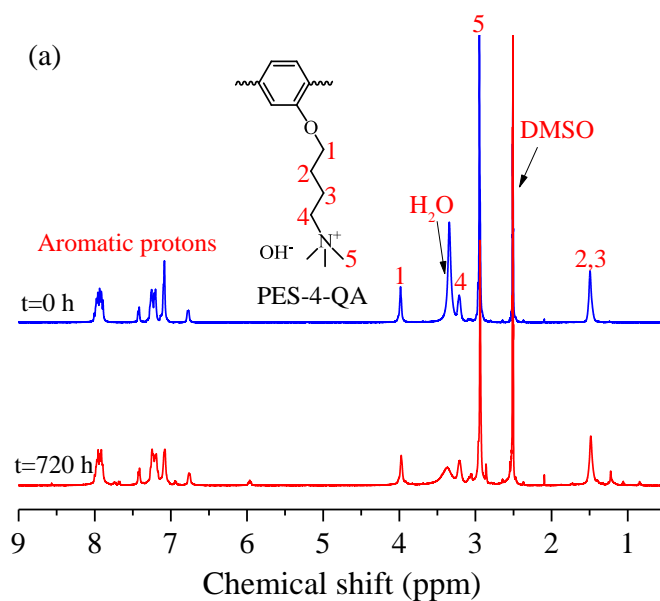


Fig. S8 Water state and hydration number of the AEMs.

Table S2 The mechanical properties of the membranes before and after the alkaline stability test.

| Membranes | Tensile strength | | Young's modulus | | Elongation at break | |
|-----------|------------------|-------|-----------------|-------|---------------------|-------|
| | (MPa) | | (MPa) | | (%) | |
| | Before | After | Before | After | Before | After |
| PES-3-QA | 13.6 | 8.5 | 285 | 196 | 28.0 | 14.2 |
| PES-4-QA | 11.5 | 9.6 | 219 | 189 | 42.1 | 38.5 |
| PES-6-QA | 9.2 | 8.5 | 158 | 131 | 57.6 | 55.4 |
| PES-8-QA | 11.2 | 10.5 | 199 | 166 | 38.6 | 35.3 |
| PES-12-QA | 13.1 | 11.9 | 270 | 249 | 23.8 | 22.4 |



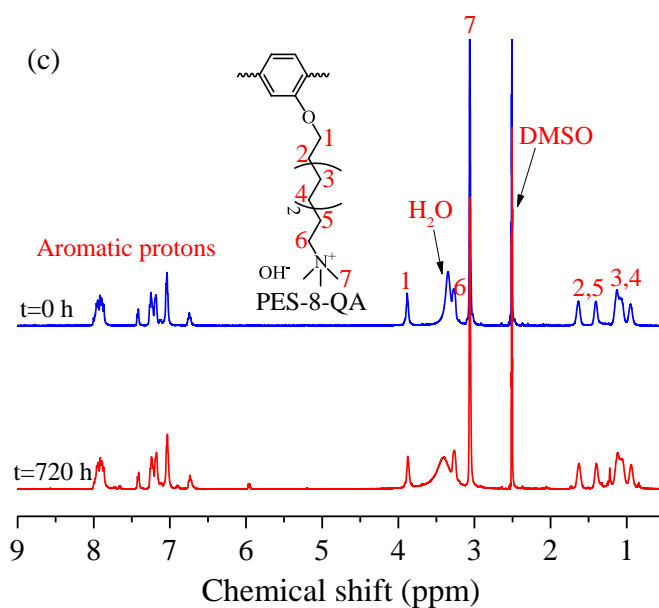
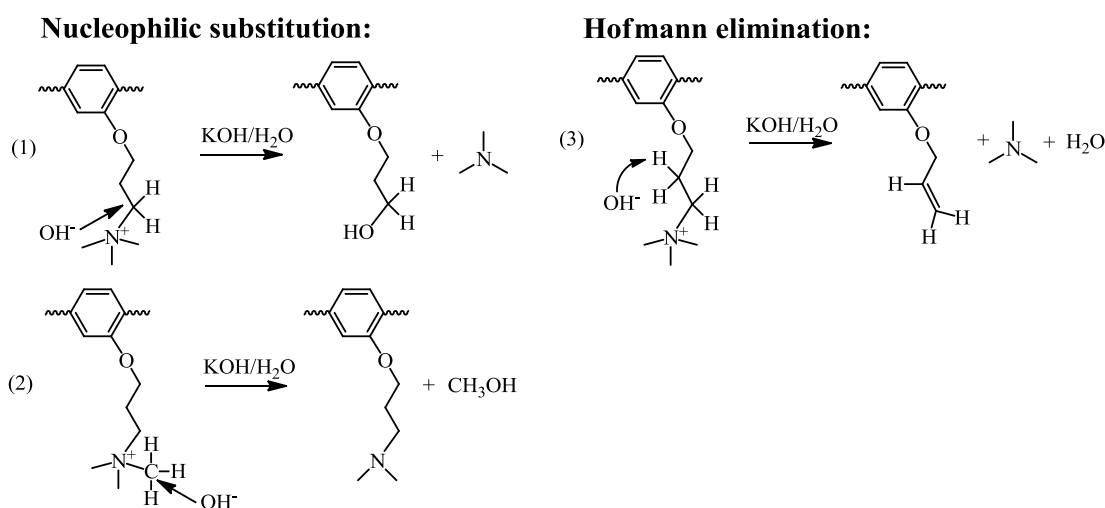


Fig. S9 ¹H NMR spectra of (a) PES-4-QA, (b) PES-6-QA and (c) PES-8-QA stored in a 1 M aqueous KOH solution at 60 °C for 0 and 720 h, respectively.



Scheme S1 The proposed degradation pathways of QA groups in PES-3-QA in alkaline media.¹

References

- 1 K. M. Meek, Y. A. Elabd. *Macromolecules*, 2015, **48**, 7071-7084.