

Supplementary information

Anion exchange membranes containing no β -hydrogen atoms on ammonium groups: synthesis, properties, and alkaline stability

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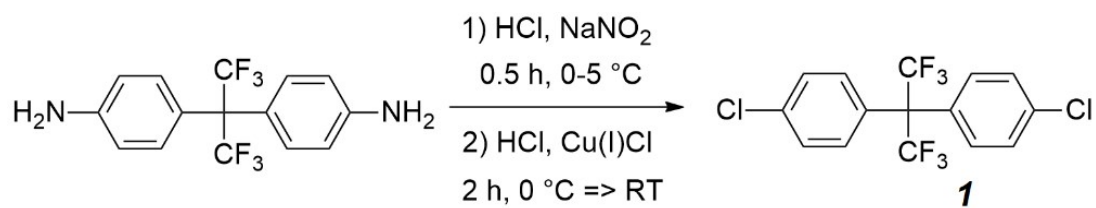
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Measurements. ^1H , ^{13}C , and ^{19}F NMR spectra were recorded in CDCl_3 , or $\text{DMSO-}d_6$ containing tetramethylsilane as internal standard. The spectra recorded on a JEOL JNMECA500 spectrometer at room temperature. Molecular weight (M_n and M_w) of the BAF-BS polymers were estimated by gel permeation chromatography (GPC) using a Shodex KF-805L or SBSB-803 column with a Jasco 805 UV detector. Chloroform with 0.02 M added triethylamine was used as eluent and calibration was done using polystyrene standards. Dynamic mechanical analyses (DMA) (Storage modulus (E' (Pa)), loss modulus (E'' (Pa)) and $\tan \delta$ (E''/E')) were measured on an ITK DVA-225 dynamic viscoelastic analyzer at either 60% relative humidity (RH) between room temperature and 95 °C at a heating rate of 1 °C min^{-1} , or as a function of RH at fixed 80 °C between 0% and 100% RH. Tensile strength of the membrane samples was determined at fixed 80 °C and 60% RH while stretching the membrane at a rate of 0.1 mm s^{-1} . Ion exchange capacity (IEC) of the quaternized membranes have been determined via Mohr titration method as reported in the literature.¹ Water uptake, ion conductivity, alkaline stability measurements were all carried out according to the literature.¹ For transmission electron microscopic (TEM) images, membrane samples (sized 5 mm by 5 mm) were ion exchanged to tetrachloroplatinate ions via submerging the samples into 0.5 M potassium tetrachloroplatinate (II) aqueous solution at 40 °C for 24 h. The ion exchange is followed by the washing of the membranes with deionized ultrapure (18 M Ω) water at 40 °C for 24 h and dried under high-vacuum overnight. The obtained dry membranes were embedded into an epoxy resin, cut to 50 nm thickness via a Leica microtome Ultracut UCT and placed onto a copper mesh. The images of the samples were taken using a Hitachi H-9500 transmission electron microscope.



Scheme S1 Synthesis of 2,2-bis(4-chlorophenyl)-hexafluoropropane (**1**).

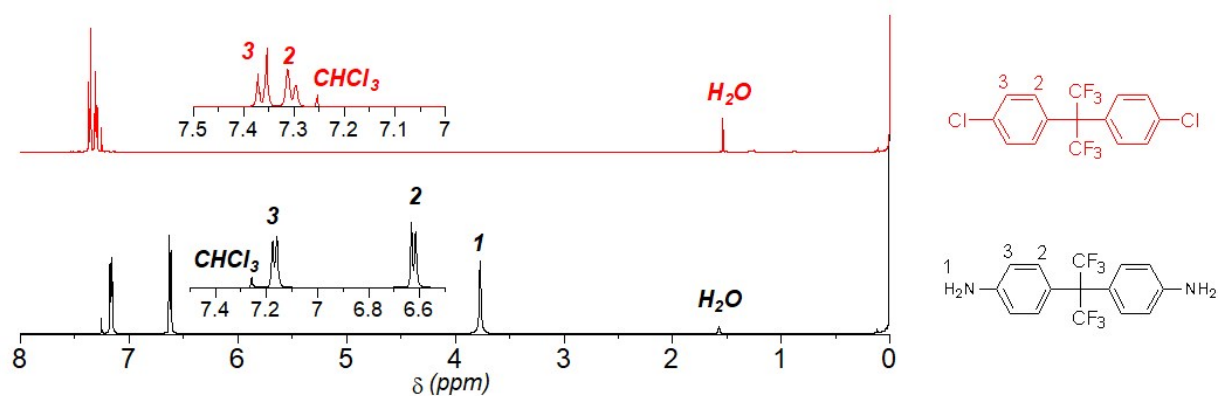


Fig. S1 ^1H NMR spectra of 2,2-bis(4-chlorophenyl)hexafluoropropane (**1**) (top) and 2,2-bis(4-aminophenyl)hexafluoropropane (bottom) in CDCl_3 .

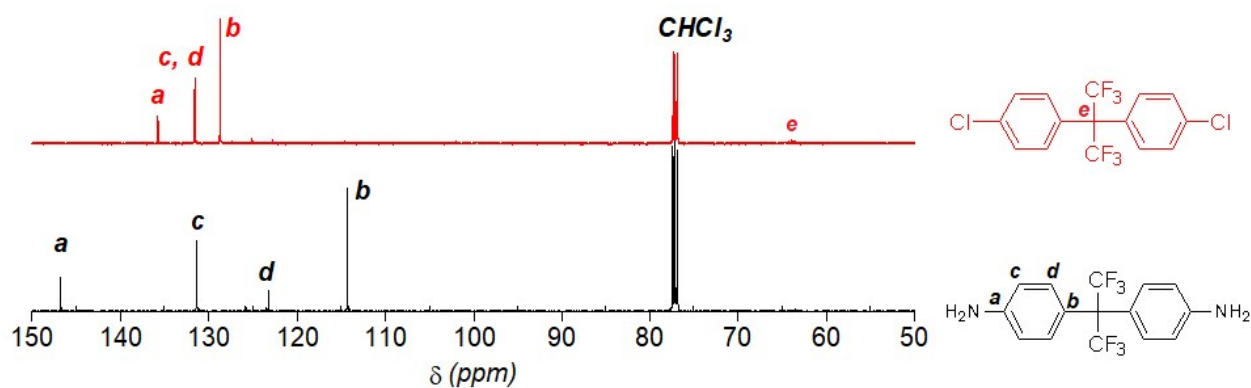


Fig. S2 ^{13}C NMR spectra of 2,2-bis(4-chlorophenyl)hexafluoropropane (**1**) (top) and 2,2-bis(4-aminophenyl)hexafluoropropane (bottom) in CDCl_3 .

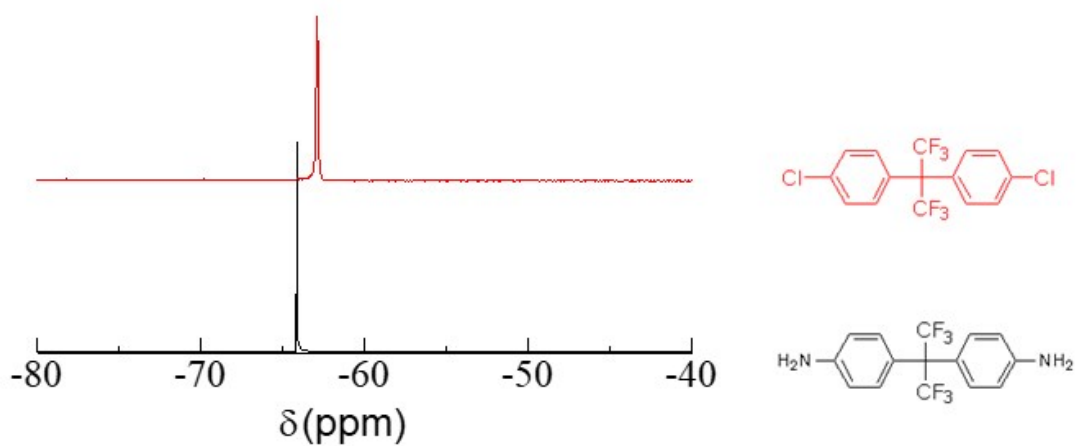


Fig. S3 ^{19}F NMR spectra of 2,2-bis(4-chlorophenyl)hexafluoropropane (**1**) (top) and 2,2-bis(4-aminophenyl)hexafluoropropane (bottom) in CDCl_3 .

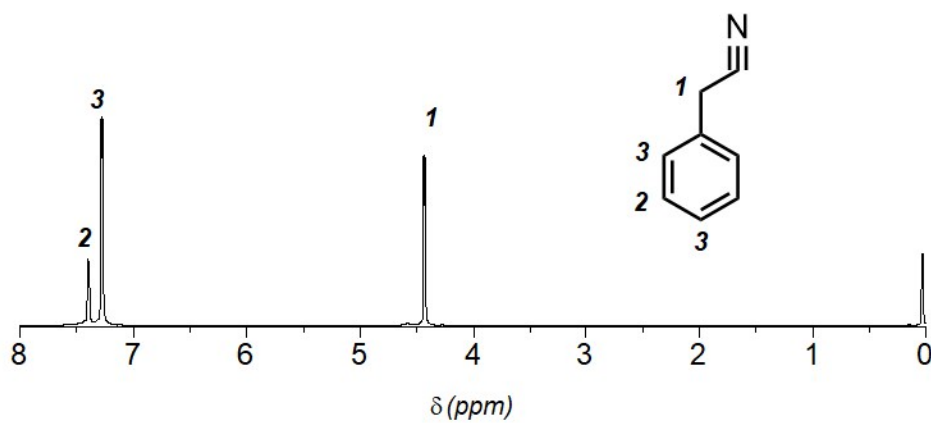


Fig. S4 ^1H NMR spectrum of phenylacetonitrile in CDCl_3 .

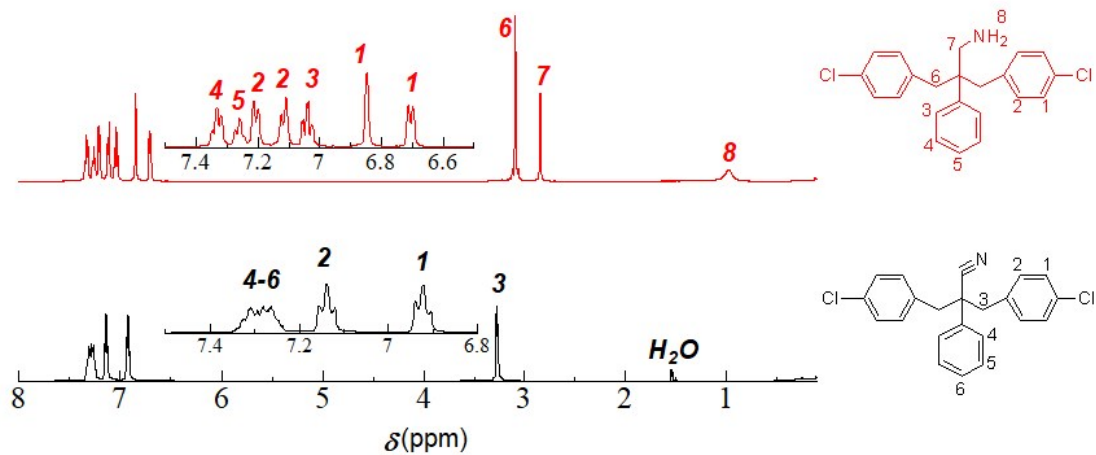


Fig. S5 ¹H NMR spectra of 2,2-bis(4-chlorobenzyl)-2-phenyl-ethylamine (**3**) (top) and 2,2-bis(4-chlorobenzyl)-2-phenylacetonitrile (**2**) (bottom) in CDCl₃.

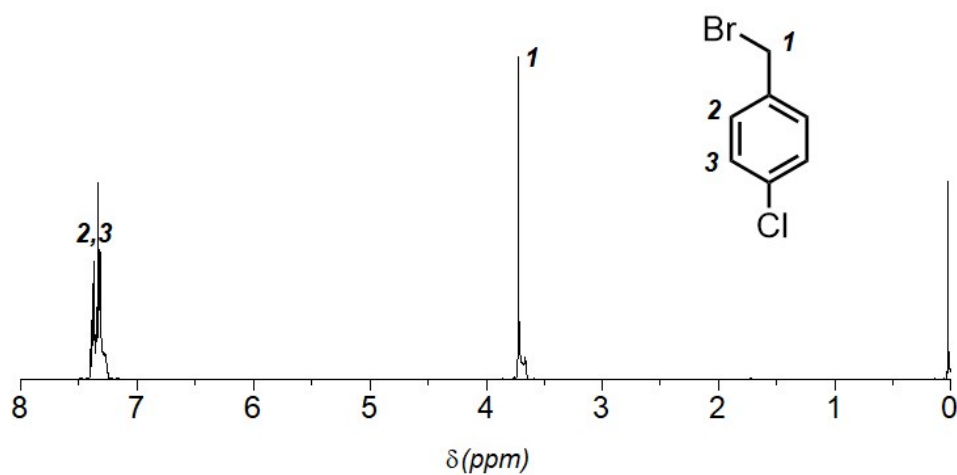


Fig. S6 ¹H NMR spectrum of 4-chlorobenzyl bromide in CDCl₃.

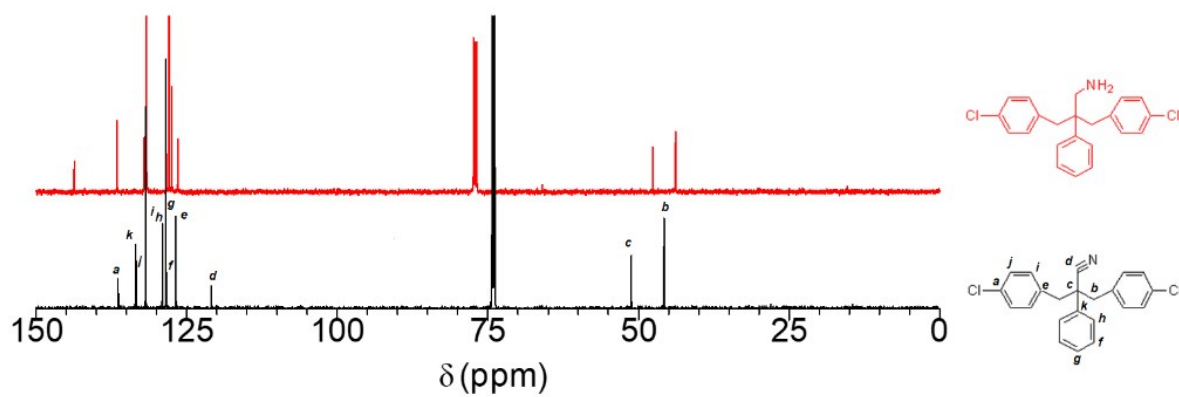


Fig. S7 ^{13}C NMR spectra of 2,2-bis(4-chlorobenzyl)-2-phenyl-ethylamine (**3**) (top) and 2,2-bis(4-chlorobenzyl)-2-phenylacetone nitrile (**2**) (bottom) in CDCl_3 .

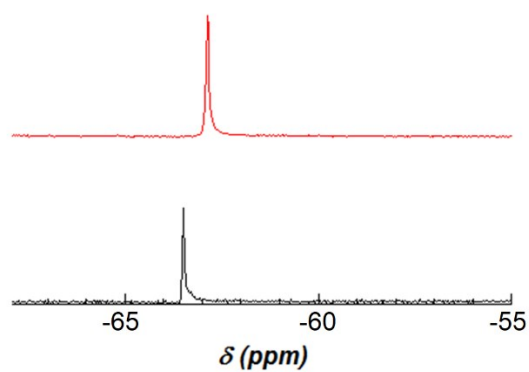


Fig. S8 ^{19}F NMR spectra of QBAF-BS in $\text{DMSO}-d_6$ (top) and BAF-BS in CDCl_3 (bottom).

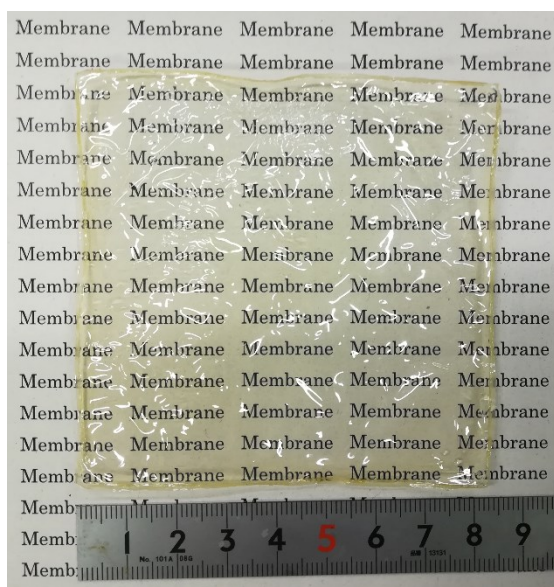


Fig. S9 QBAF-BS2.25 membrane (thickness = $40 \pm 7 \mu\text{m}$) obtained via casting from DMSO solution at 50°C overnight.

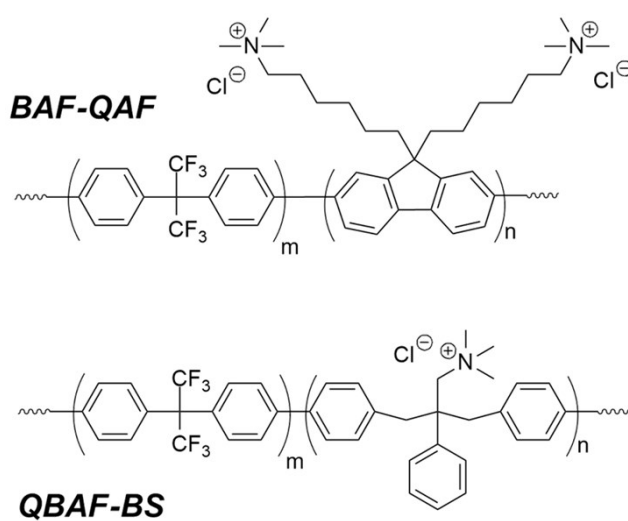


Fig. S10 Structure of BAF-QAF and QBAF-BS copolymers.

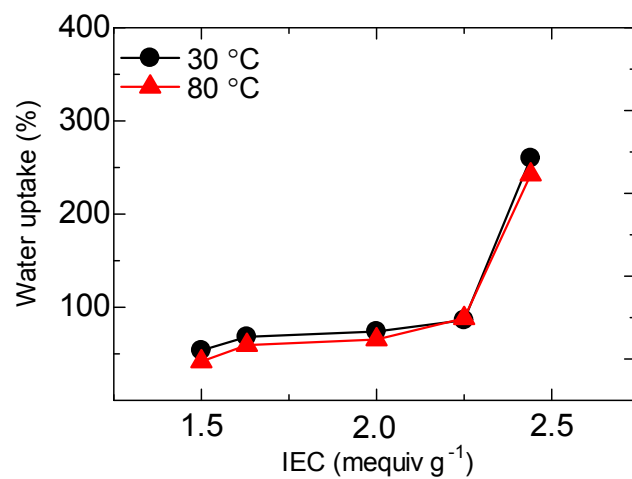


Fig. S11 Water uptake (at 30 and 80 °C) of QBAF-BS membranes as a function of ion exchange capacity.

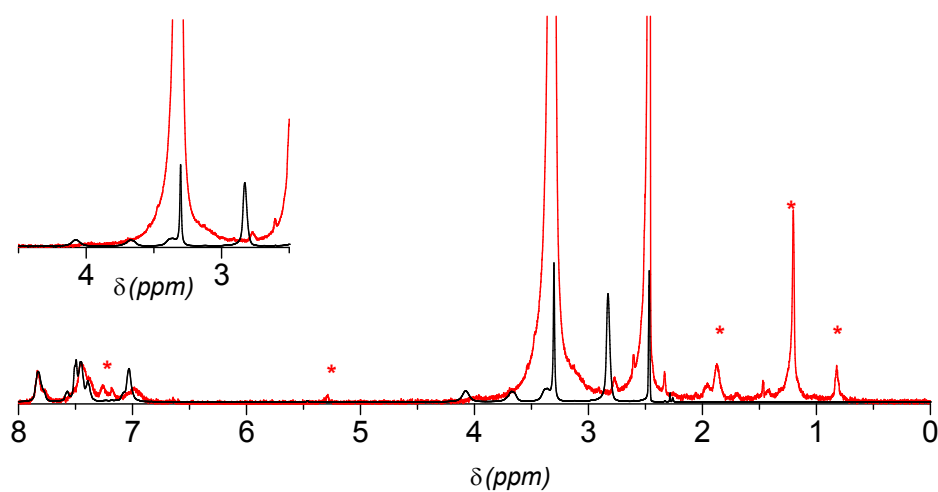


Fig. S12 ¹H NMR spectra of the pristine (black, 0 h) and post-test (red, 150 h) QBAF-BS2.00 membrane.

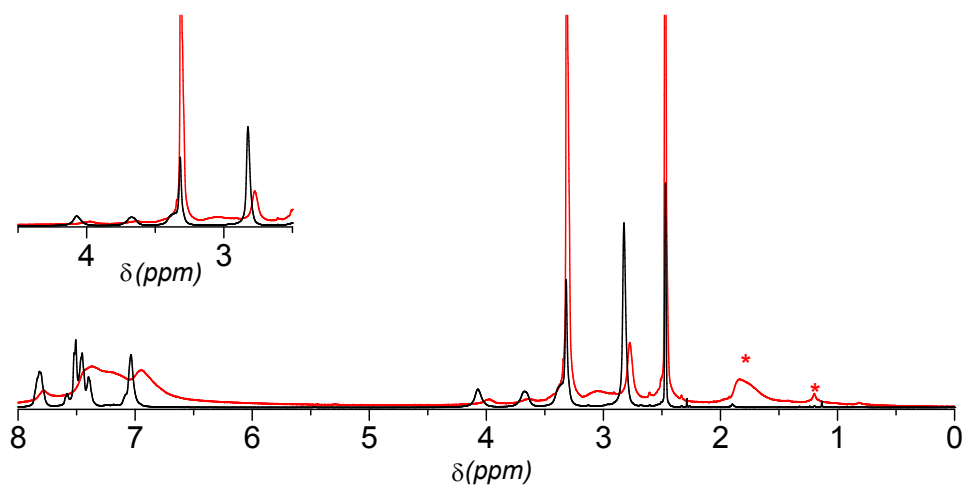


Fig. S13 ^1H NMR spectra of the pristine (black, 0 h) and post-test (red, 300 h) QBAF-BS2.25 membrane.

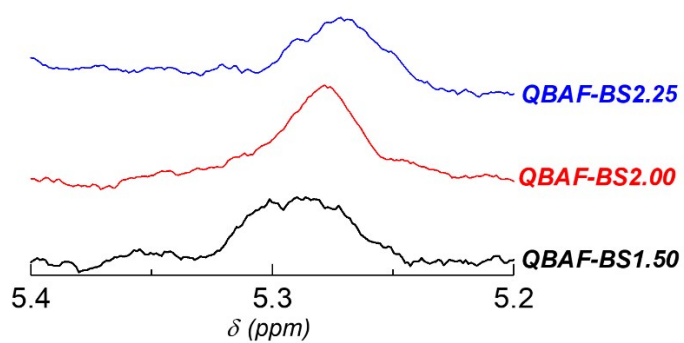


Fig. S14 ^1H NMR spectra of QBAF-BS copolymers after the alkaline stability test.

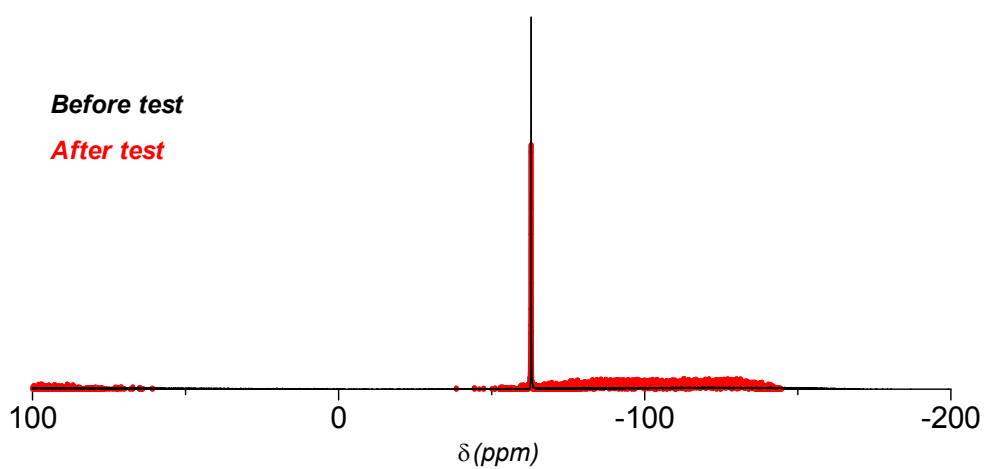


Fig. S15 ^{19}F NMR spectra of QBAF-BS1.50 before (black, 0 h) and after (red, 300 h) the alkaline stability test.

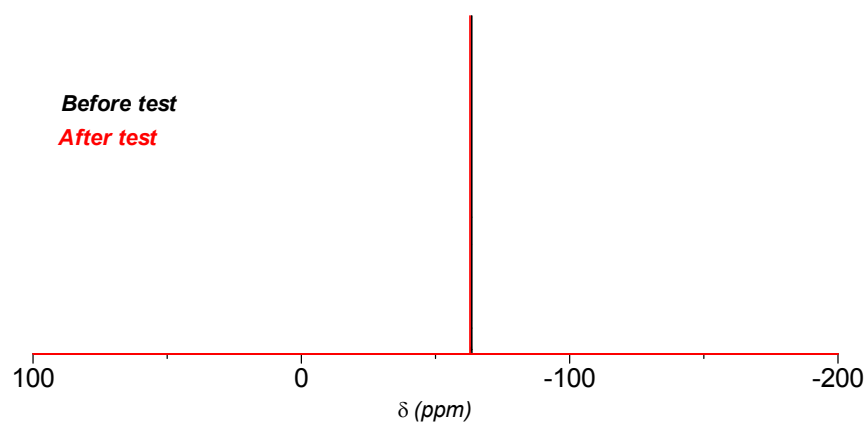


Fig. S16 ^{19}F NMR spectra of QBAF-BS2.00 before (black, 0 h) and after (red, 150 h) the alkaline stability test.

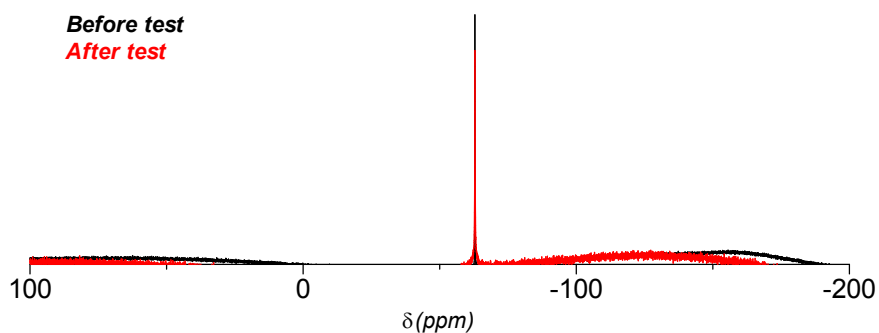


Fig. S17 ^{19}F NMR spectra of QBAF-BS2.25 before (black, 0 h) and after (red, 300 h) the alkaline stability test.

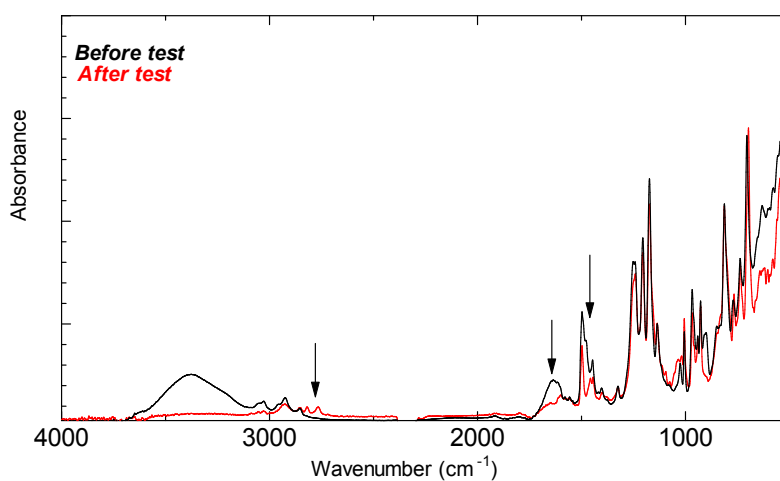


Fig. S18 FTIR spectra of the pristine (black, 0 h) and post-test (red, 150 h) QBAF-BS2.00 membrane.

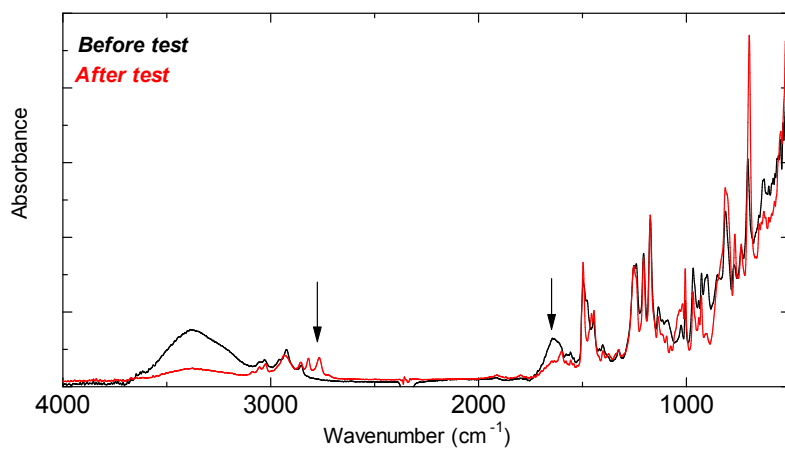


Fig. S19 FTIR spectra of the pristine (black, 0 h) and post-test (red, 300 h) QBAF-BS2.25 membrane.

Reference

1 D. Koronka, A. M. A. Mahmoud and K. Miyatake, *J. Polym. Sci., A: Polym. Chem.*, 2019, **57**, 1059-1069.