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Derivatized cardo-polyetherketone anion exchange membranes for all-vanadium redox flow batteries

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Electronic Supplementary Information

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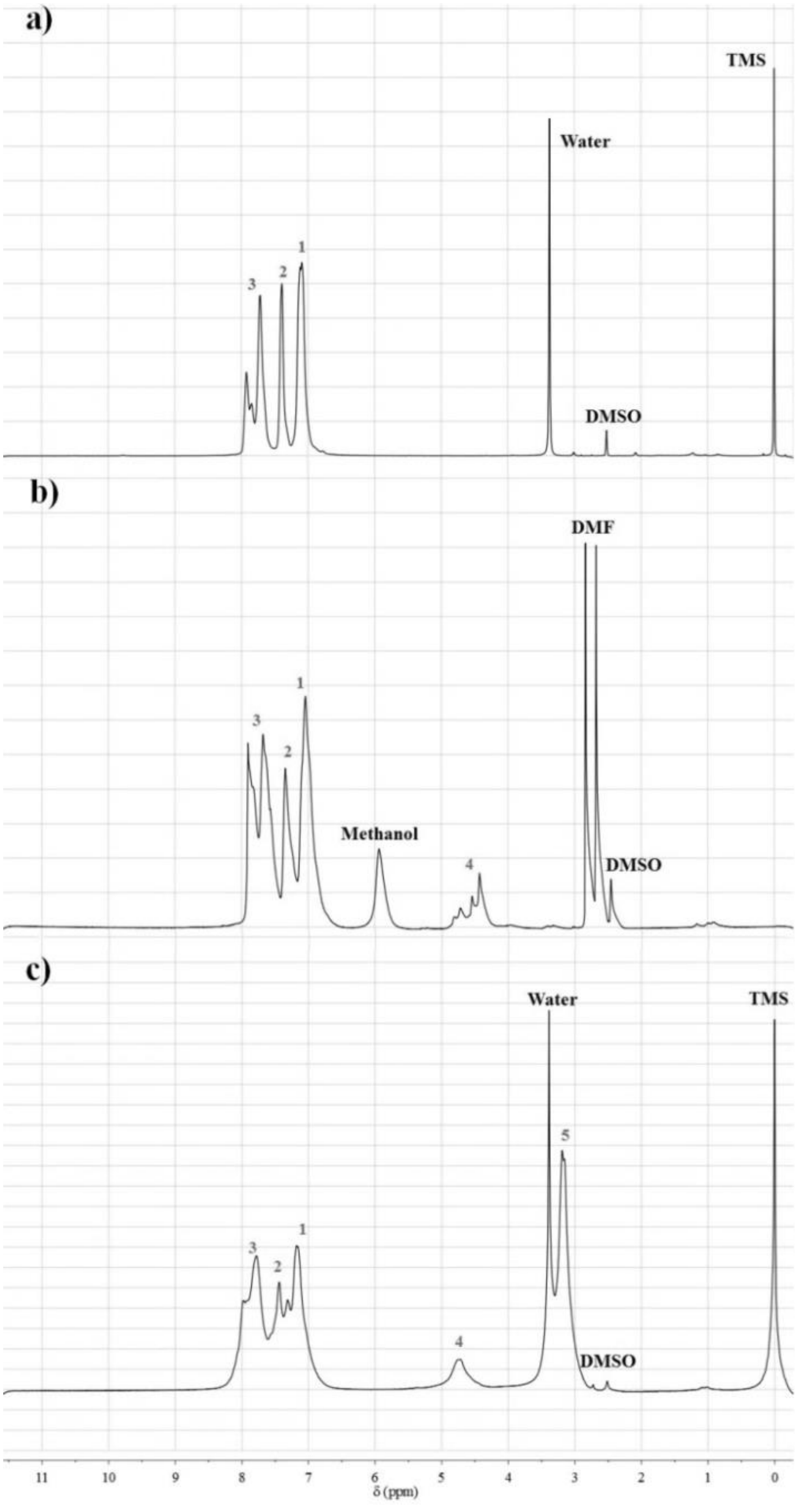

Figure S1. ^{1}H NMR spectra for a) PEK-C, b) CMPEK-C, and c) QPEK-C-TMA$^+$ SO$_4^{2-}$

FTIR spectra to confirm occurrence of chloromethylation and quaternization reactions

FTIR was performed on membrane films using a Bruker Tensor 27 instrument. The data were collected continuously in the 4000-400 cm^{-1} wavenumber range at a resolution of 4 cm^{-1}. All samples were dried completely in a vacuum oven prior to IR measurement to reduce the presence of water in the sample. Appropriate background corrections were performed.

FTIR spectra were used to identify the chemical structure of the polymer backbone and to confirm the chloromethlyation and quaternization reactions (Figure S1). The small peaks observed for all the membranes at 3065 cm^{-1} were attributed to the stretching of the [C-H] bond on the aromatic rings.[1] The absorption bands at 1594 and around 1500cm^{-1} bands were attributed to the [C=C] stretching vibration in the aromatic rings. After chloromethylation, the absorption band of PEK-C placed at 1500 cm^{-1} was shifted to 1495 cm^{-1}. The peaks between 1630 and 1670 cm^{-1} were associated with the ketone stretching vibration in the polymer backbone. It was suspected that the strong peaks around 1770 cm^{-1} resulted from the ketone group in the phenolphthalein pendant group attached to the aromatic rings. The ether linkages on the polymer backbone were identified from the [C-O] stretching band placed at 1244 cm^{-1}.[1] The absorption bands at 3290cm^{-1} of QPEK-C/TMA^{+} SO_4^{2-} indicated existence of quaternary ammonium groups.[2-5]

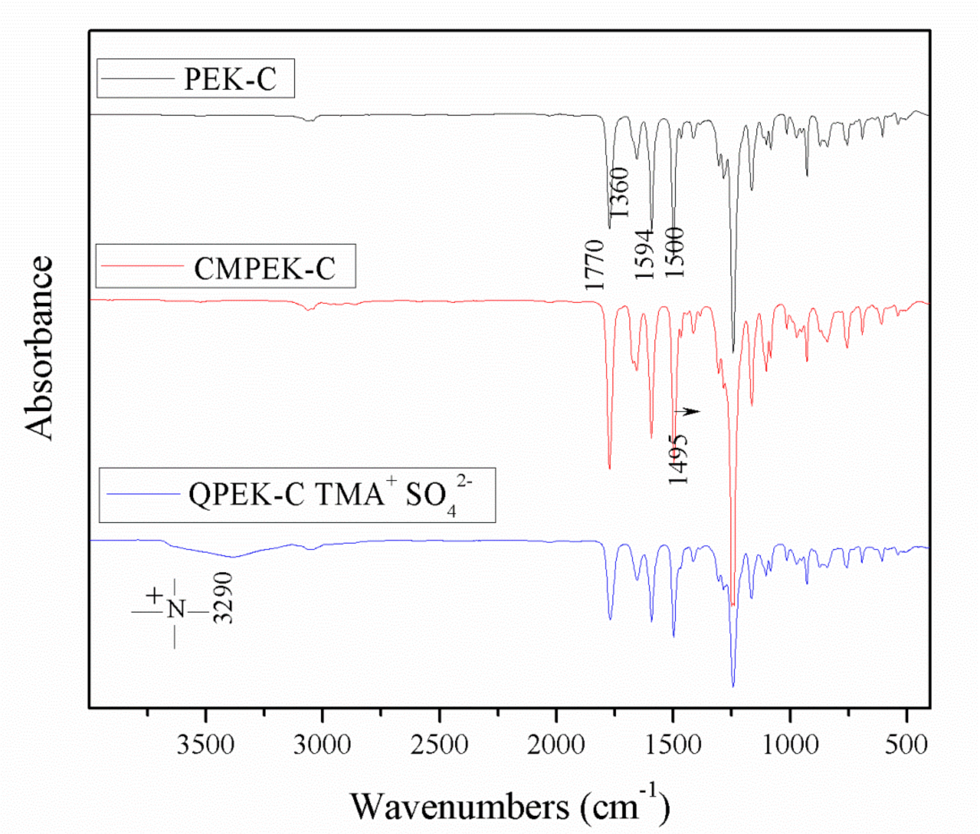

Figure S2. FTIR for PEK-C, CMPEK-C, and QPEK-C/TMA^{+} SO_4^{2-}

Vapor phase water adsorption (wt%) of PEK-C, CMPEK-C and QPEK-C-TMA$^+$ SO$_4^{2-}$

The vapor phase water uptake was estimated using a VTI-SA+ water sorption analyzer (TA instruments) at 25°C. Water desorption isotherms were measured by inducing step changes in the relative humidity: 98%, 90, 70, 50, 30, 10 and 0% relative humidity. The membrane was equilibrated at each humidity for 180 min.

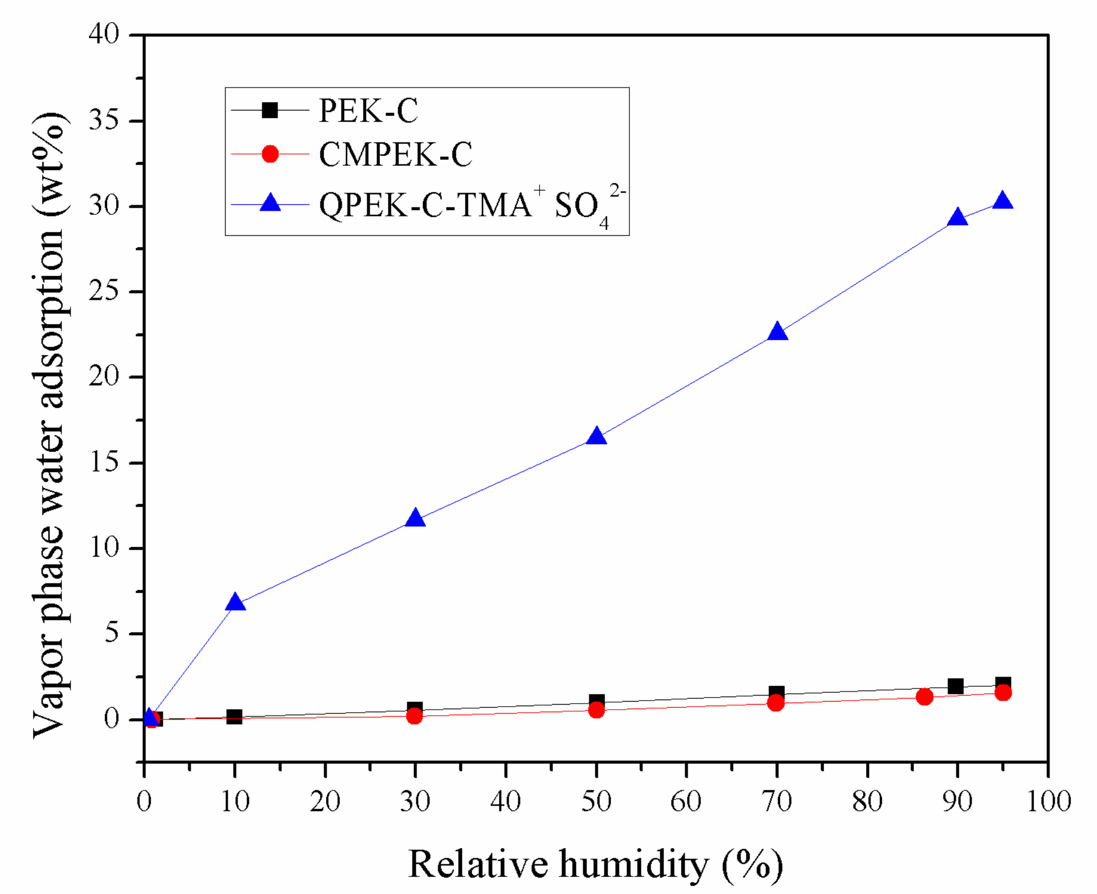

Figure S3. Vapor phase water adsorption (wt%) of PEK-C, CMPEK-C and QPEK-C-TMA$^+$ SO$_4^{2-}$

Thermogravimetric analysis (TGA) and derivative curve of thermogravimetric profile (DrTGA) for PEK-C, CMPEK-C, and QPEK-C-TMA$^+$ SO$_4^{2-}$ membranes

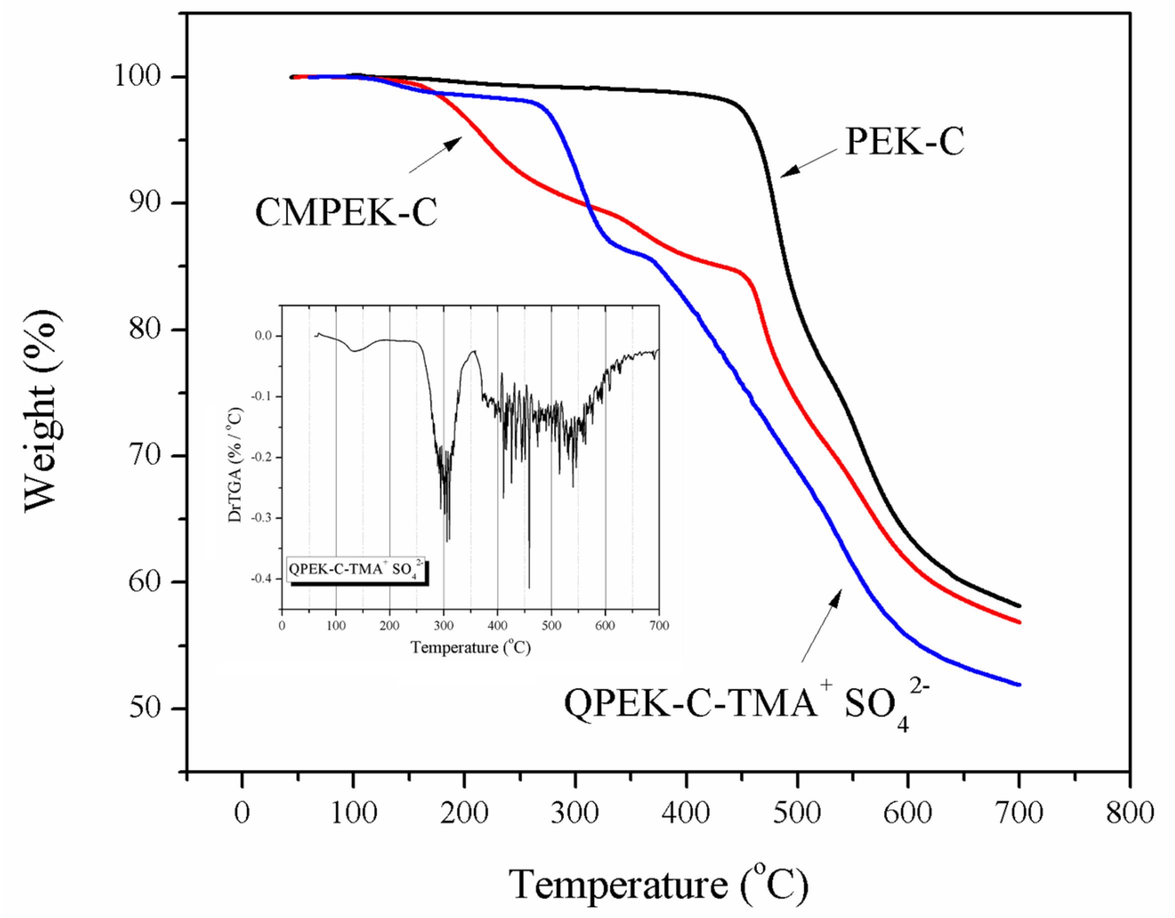

Figure S4. Thermogravimetric analysis of PEK-C, CMPEK-C, and QPEK-C-TMA$^+$ SO$_4^{2-}$ membranes and derivative curve of thermogravimetric profile (DrTGA) for QPEK-C-TMA$^+$ SO$_4^{2-}$

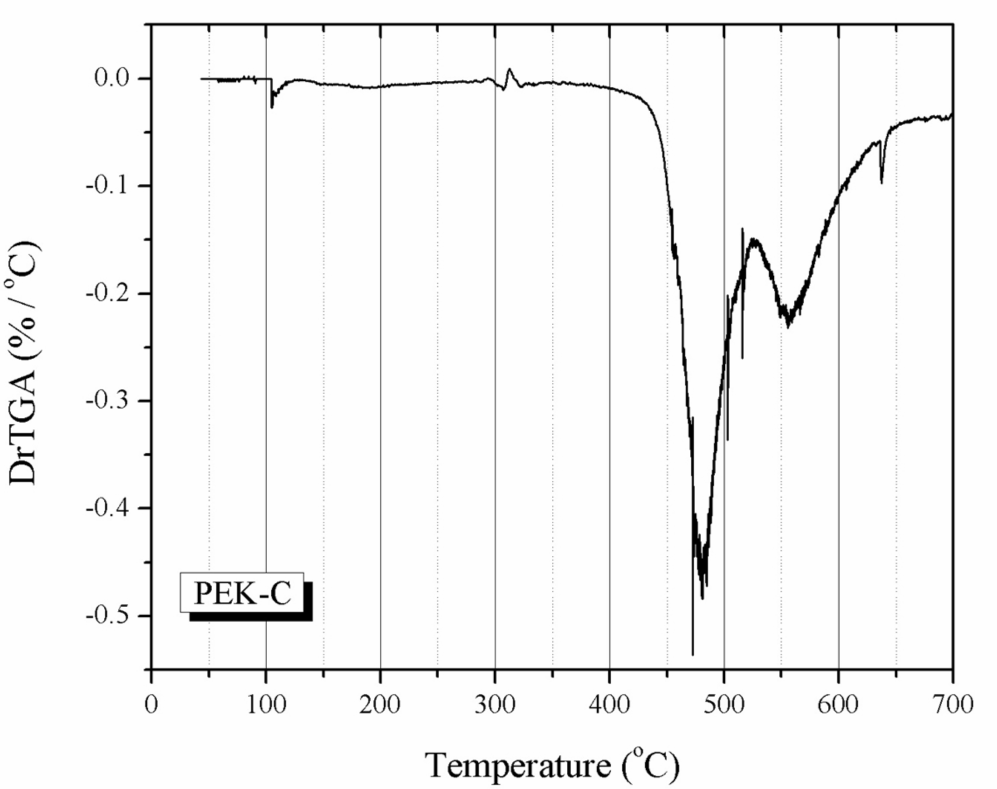

Figure S5. DrTGA spectra of PEK-C

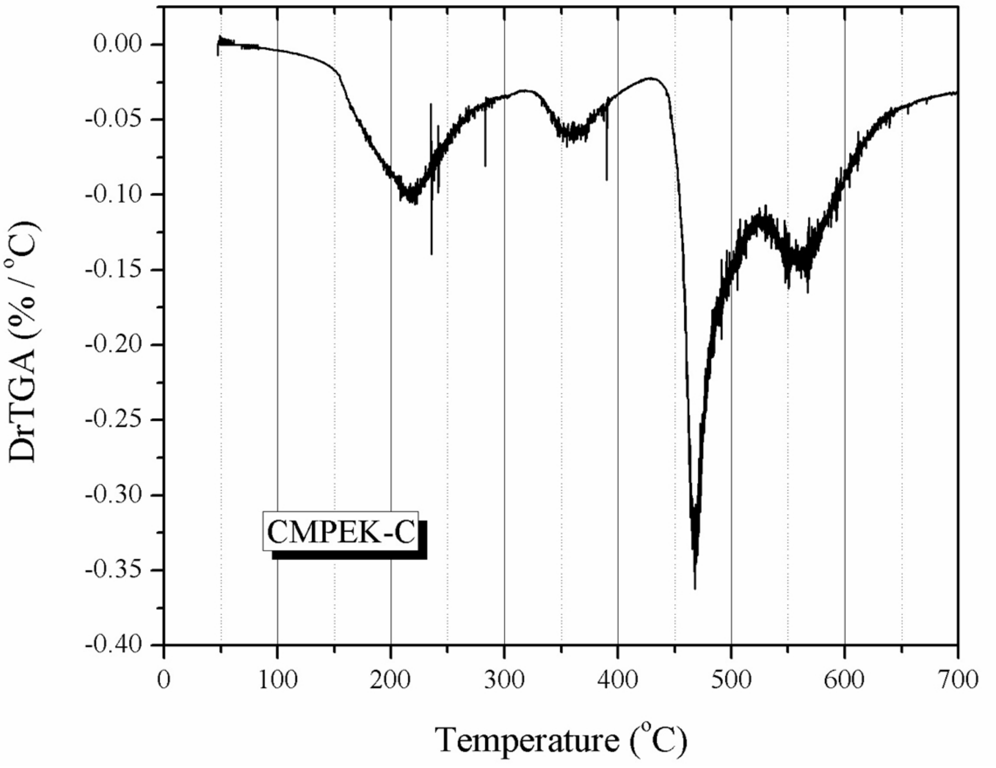

Figure S6. DrTGA spectra of CMPEK-C

Scanning electron microscope (SEM) images before and after the VRFB cycling test

A Hitachi S-3000N SEM with a variable pressure chamber was used to image the AEM samples before and after the charge/discharge cycling tests. The pressure of the chamber was 100 Pa and the accelerating voltage was 20.0 kV. All samples were rinsed with deionized water and dried in a vacuum oven at 25°C for 6 hours prior to making measurements.

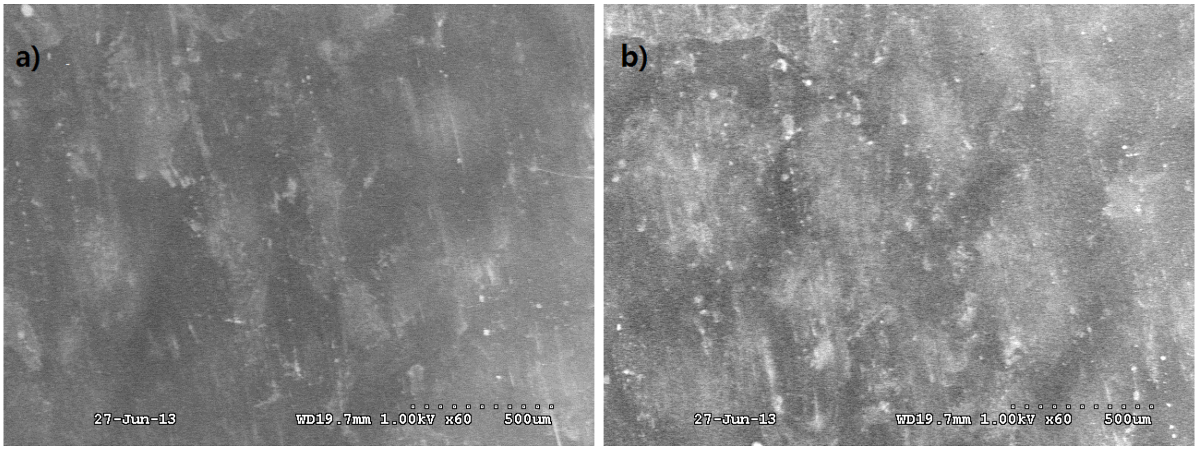

Figure S7. SEM images of QPEK-C-TMA$^+$ a) before and b) after exposure to VRFB operating conditions over 20 charge/discharge cycles and 100 hours

2-D HMQC NMR and ^{1}H NMR spectra after the VRFB charge/discharge cycling test

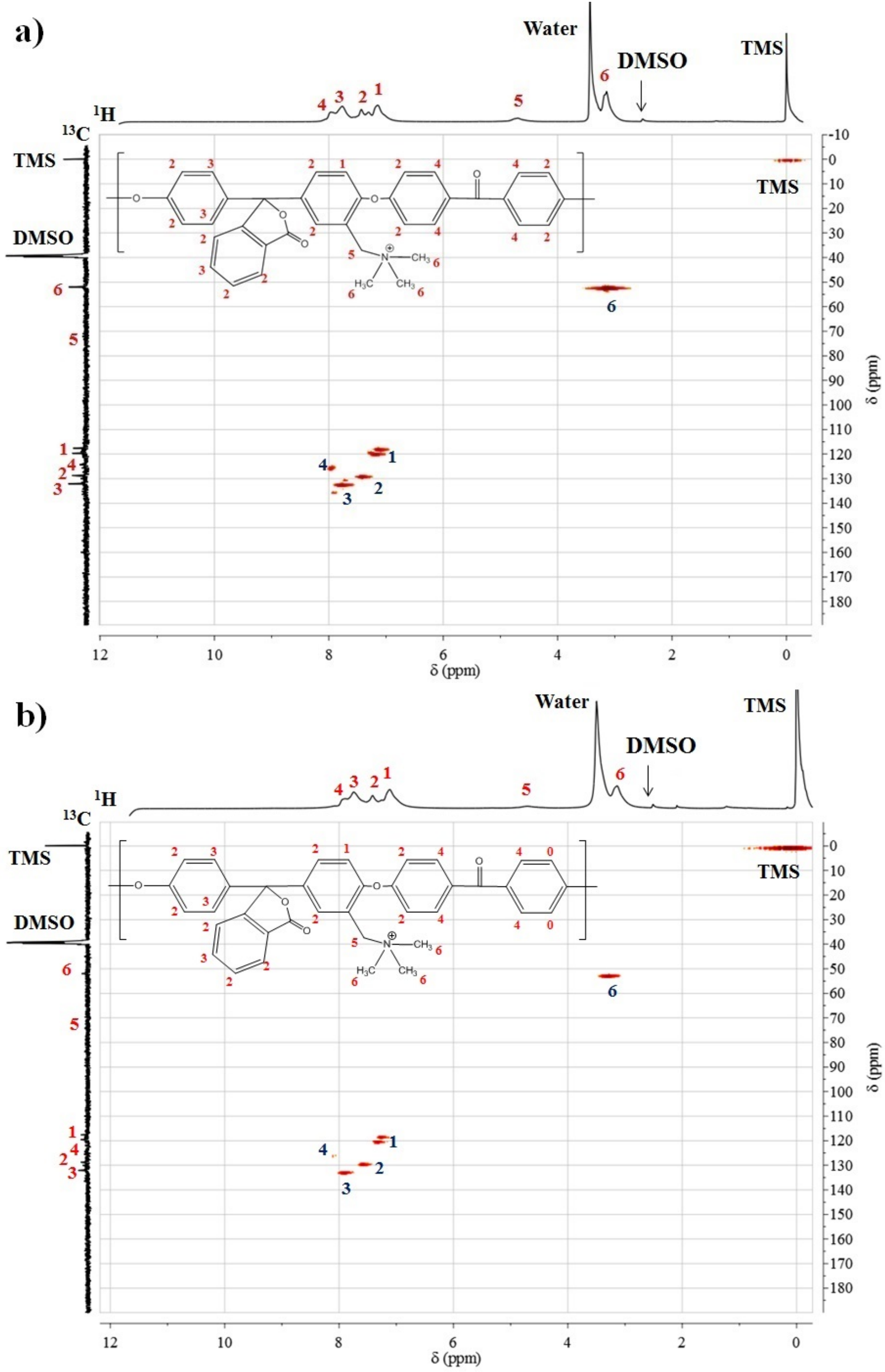

Figure S8. HMQC (^{1}H-^{13}C) NMR spectra of QPEK-C-TMA$^+$ a) before and b) after 20 charge/discharge cycles (30mA cm^{-2}) in a VRFB using 1.5 M vanadium solution in 3 M H_2SO_4 solution

Figure S9. ^{1}H NMR spectra of QPEK-C-TMA$^+$ a) before and b) after 20 charge/discharge cycles (30mA cm^{-2}) in a VRFB using 1.5 M vanadium solution in 3 M H_2SO_4 solution

References

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