Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Base stable poly(diallylpiperidinium hydroxide) multiblock copolymers for anion exchange membranes

Derek J. Strasser, Brendan J. Graziano and Daniel M. Knauss

Department of Chemistry

Colorado School of Mines

Golden, Colorado 80401

dknauss@mines.edu

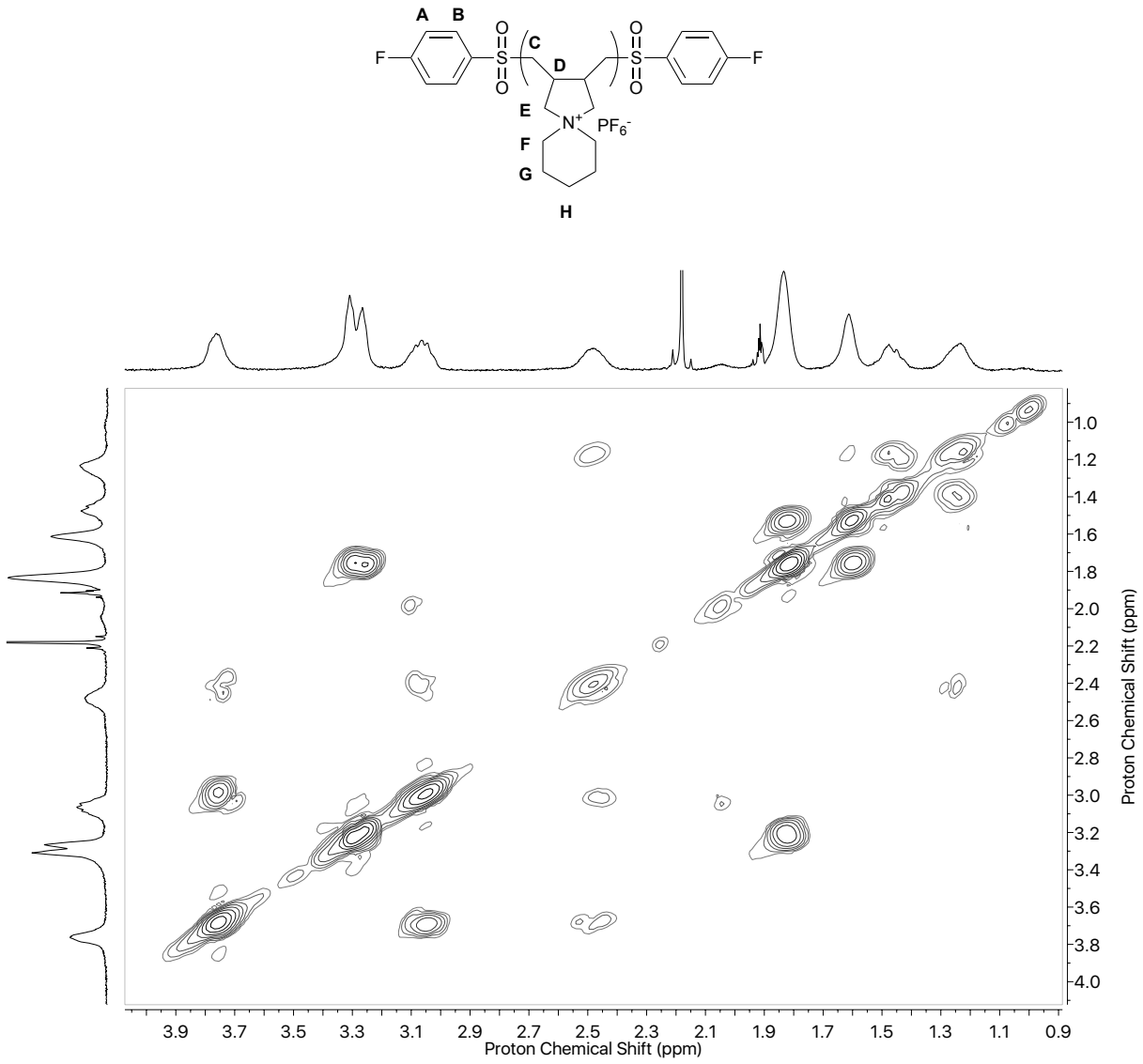

Figure S1. DQF-COSY NMR spectrum of PDApipPF$_6$ in acetonitrile—d_3.

Proton NMR signals were assigned from the DQF-COSY NMR Spectrum. Proton assignments for the PDApipPF$_6$ repeat unit are as follows: C protons δ = 1.24 & 1.48 ppm, D protons δ = 2.47 & 2.05 ppm, E protons δ = 3.76 & 3.07 ppm, F protons δ = 3.31 & 3.27 ppm, G protons δ = 1.83 ppm, H protons δ = 1.61 ppm. Correlations of the D protons with both the E and C protons and correlations of G protons with both F and H protons supports the assignment.

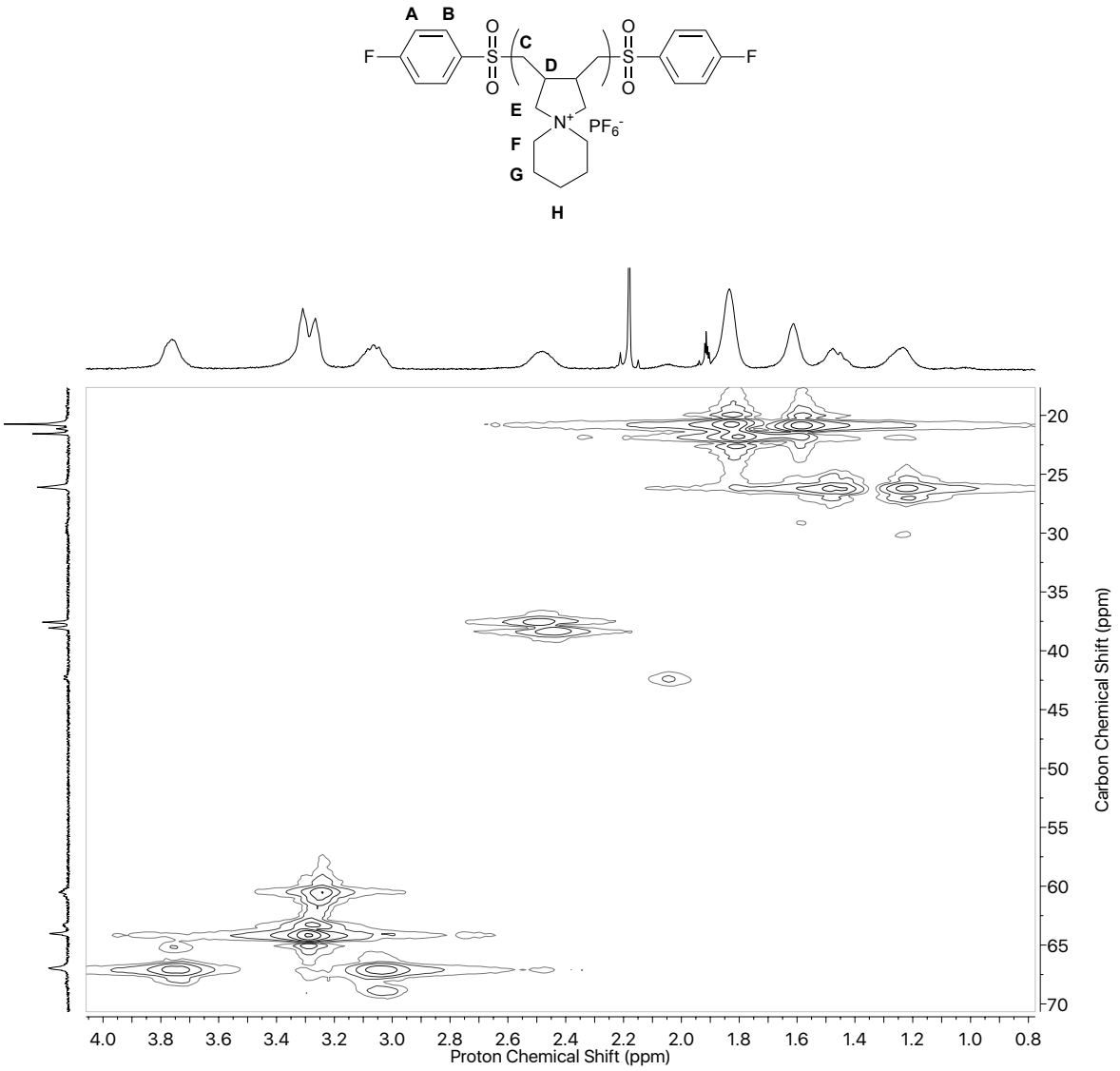

Figure S2. HMQC NMR spectrum of PDApipPF$_6$ in acetonitrile-d$_3$.

Proton and carbon assignments were made from the HMQC NMR spectrum. C protons were assigned to carbon signals at δ = 26.2 & 29.5 ppm for *cis* and *trans*. The *trans* carbon signal and correlation at 29.5 ppm was very weak. D protons were assigned to carbon signals at δ = 37.8 & 42.3 ppm for *cis* and *trans*. E protons were assigned to carbon signals at δ = 67.0 and 68.3 ppm. The *trans* carbon signal and proton correlation at 68.3 ppm was very weak. The assignment for protons and carbons C, D & E support the formation of the 5-member ring.

Synthesis of 4-fluorothioanisole

Synthesis of 4-fluorothioanisole was completed using an established procedure.[1] λmax(MeOH)/nm 251 (ε/dm^3 mol^{-1} cm^{-1} 7500) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (2H, m), 6.99 (2H, m), 2.46(3H, s).

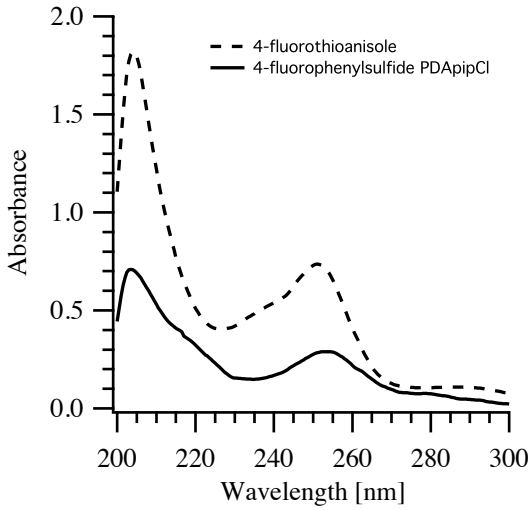

Figure S3. UV/vis absorbance spectrum of 4-fluorophenylsulfide terminated PDApipCl

The concentration of 4-fluorophenyl sulfide end groups was determined from a Beer's Law calibration curve of 4-fluorothioanisole as a model for the end groups. The UV-Vis absorbance spectrum of 4-fluorothioanisole indicated two strong absorbance maxima at 204 nm and 251 nm, S3. The calibration curve was built from the absorbance at 251 nm. The 4-fluorophenylsulfide terminated PDApipCl oligomers presented similar absorbance spectra.

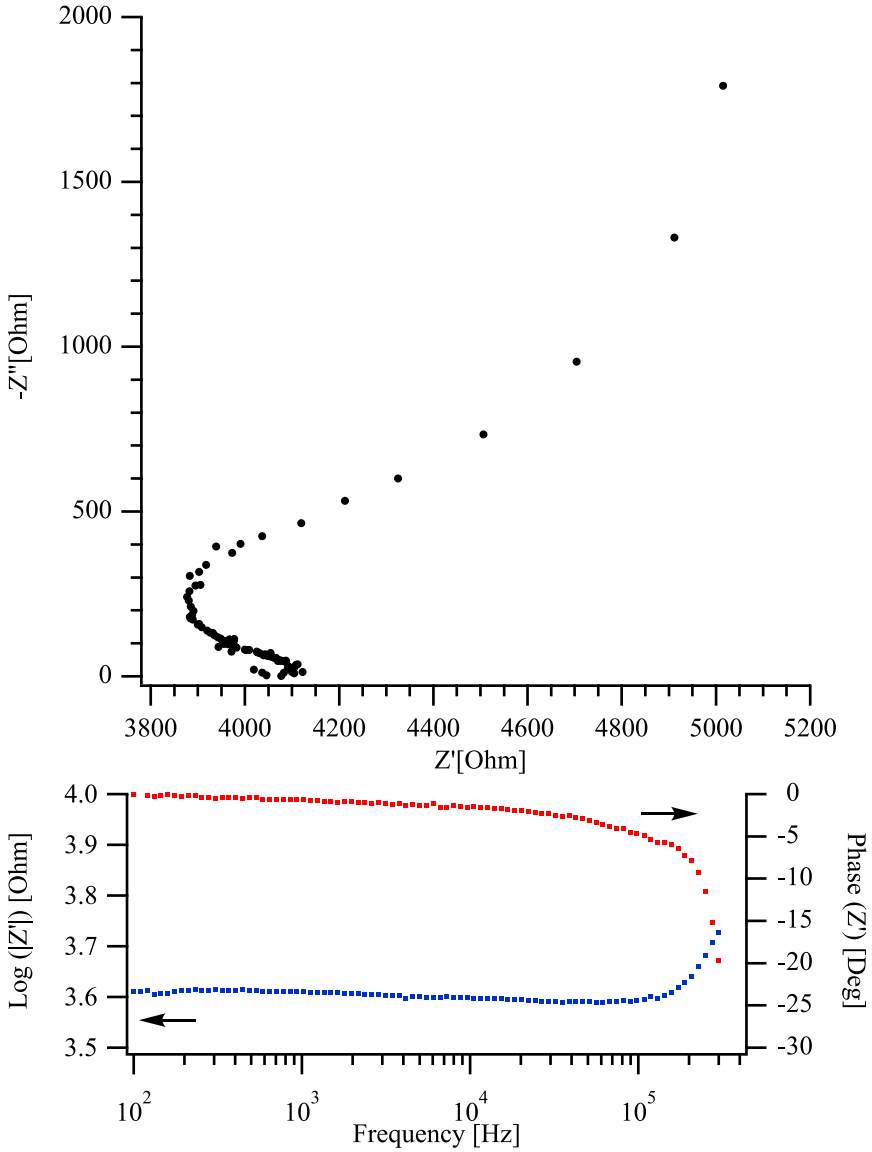

Figure S4. Sample Nyquist (Top) and Bode (Bottom) plots

Hydroxide conductivity for all membranes was measured in the frequency range of 100 Hz to 300 kHz. A Bode plot was used to validate the frequency range with constant impedance. The intercept on the real resistance axis in the Nyquist plot was taken as the membrane resistance R.

Notes and references

1. K. F. Morgan, I. A. Hollingsworth and J. A. Bull, *Org. Biomol. Chem.*, 2015, **13**, 5265-5272.