

Supplemental Information for

**Difference between approximate and rigorously measured
transference numbers in fluorinated electrolytes**

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^1H NMR spectra

Figure S1a shows the ^1H NMR of the precursor C8-Diol dissolved in deuterated acetone. Figure S2a is the ^1H NMR of the product, C8-DMC, after synthesis and purification dissolved in deuterated acetone.

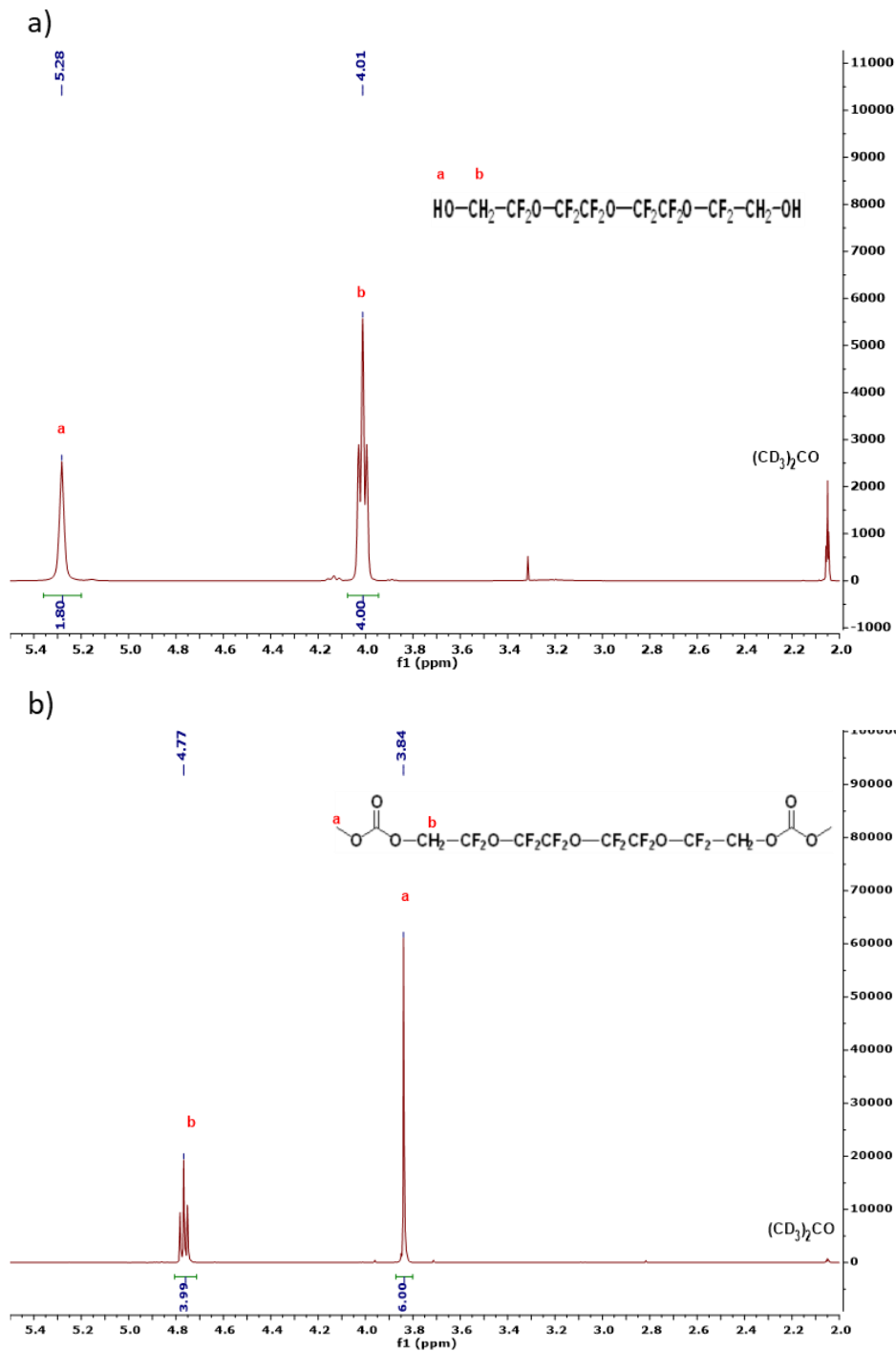
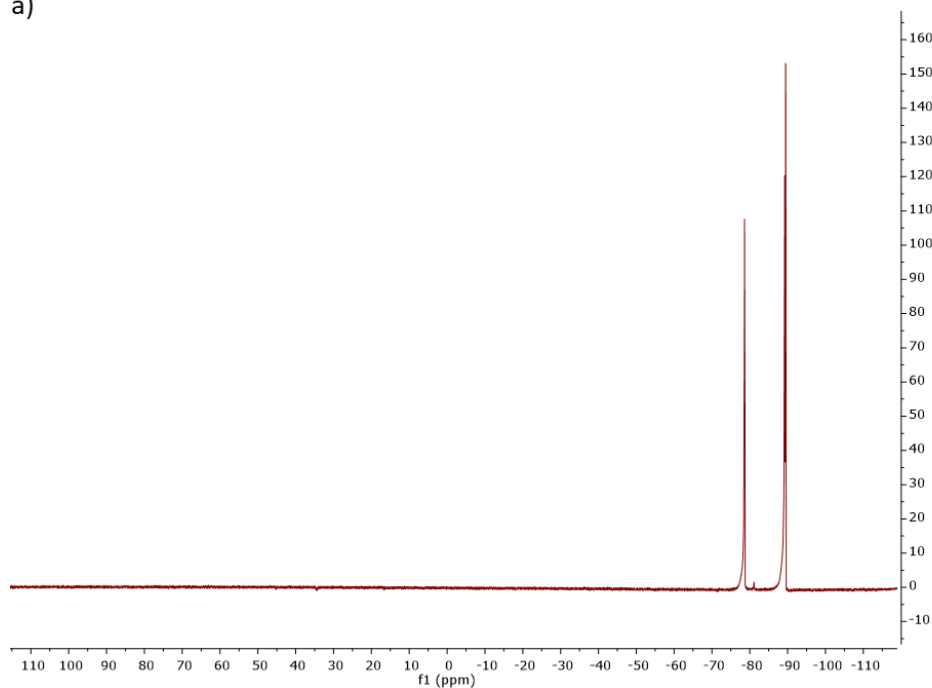


Figure S1: (a) ^1H NMR of the precursor, C8-Diol and (b) ^1H NMR of the product, C8-DMC in deuterated acetone

^{19}F NMR spectra

Figure S2 shows ^{19}F NMR spectra of C8-DMC with and without LiFSI. Figure S2a is that of neat C8-DMC and Figure S2b is of an electrolyte of composition $m = 0.60$ mol/kg. The fluorine peak from LiFSI appears at a shift of 51.7 ppm. This peak shift was used during ^{19}F PFG-NMR in order to determine the FSI tracer-diffusion coefficient.

a)



b)

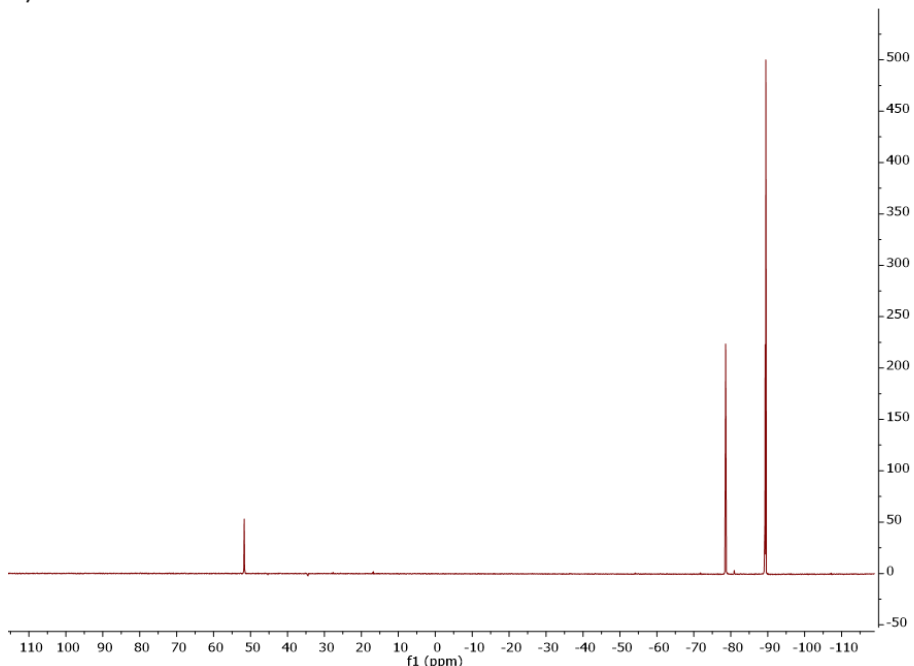


Figure S2: ^{19}F NMR spectra of C8-DMC (a) neat C8-DMC (no salt) and (b) a C8-DMC based electrolyte with $m = 0.60$ mol/kg

PFG-NMR data

Figure S3 displays the natural log of the PFG-NMR attenuation signal vs the constants within the exponential of equation 11 in the main manuscript. The red circles are the experimental data and the black line is a linear fit to the data. The magnitude of the slope of the line-of-best-fit is the self-diffusion coefficient of D_{Li} , which is $3.23 \times 10^{-7} \text{ cm}^2/\text{s}$ in this case.

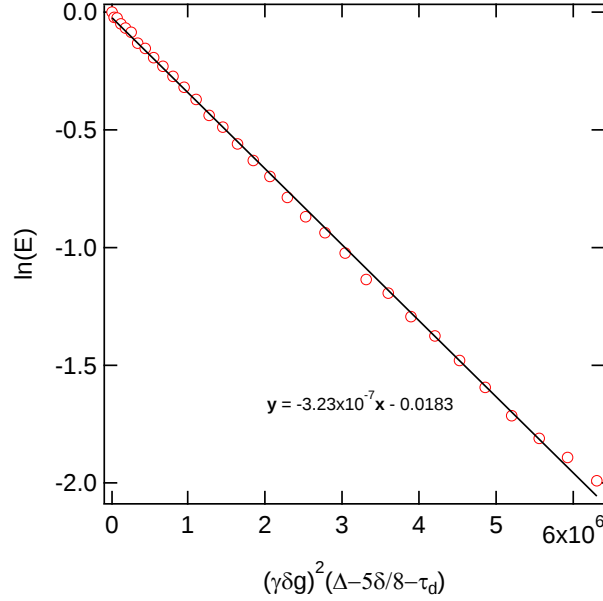


Figure S3: ^7Li PFG-NMR diffusion data for a C8-DMC electrolyte with $m = 0.05$. The red circles are experimental data and the black line is the line of best fit. The slope is the self-diffusion of lithium.

Error Propagation

Rigorously defined transference number, t_+^0 :

$$\delta t_+^0 = |t_+^0| \sqrt{\left(\frac{\delta \kappa}{\kappa}\right)^2 + \left(\frac{\delta D_s}{D_s}\right)^2 + \left(\frac{\delta t_{+,id}}{t_{+,id}}\right)^2 + \left(\frac{\delta \phi_c}{\phi_c}\right)^2}$$

Thermodynamic factor, $1 + \frac{d \ln \gamma_{\pm}}{d \ln m}$:

$$\delta \left(1 + \frac{d \ln \gamma_{\pm}}{d \ln m}\right) = \left|1 + \frac{d \ln \gamma_{\pm}}{d \ln m}\right| \sqrt{\left(\frac{\delta \kappa}{\kappa}\right)^2 + \left(\frac{\delta D_s}{D_s}\right)^2 + \left(\frac{\delta t_{+,id}}{t_{+,id}}\right)^2 + \left(\frac{\delta \phi_c}{\phi_c}\right)^2}$$

Overall tracer-diffusion coefficient, D_{NMR} :

$$\delta D_{NMR} = \sqrt{\left(\frac{2D_{FSI}}{(D_{Li} + D_{FSI})^2} \delta D_{Li}\right)^2 + \left(\frac{2D_{Li}}{(D_{Li} + D_{FSI})^2} \delta D_{FSI}\right)^2}$$