

Supplementary Information to Quantifying the Partitioning of Vehicular and Structural Lithium Transport in Binary Carbonate Electrolytes

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S1. Methods

S1.1. Sample Preparation

Dimethyl Carbonate, propylene carbonate (anhydrous), lithium bis(trifluoromethanesulfonyl)imide (anhydrous), and phenyl selenocyanate are purchased from Millipore Sigma. All chemicals were stored in an N₂ glovebox where water was kept below 1 ppm. Electrolyte solutions were prepared by mixing appropriate volumes of a prepared 1-7 salt-to-solvent ratio salt solutions of pure DMC and PC to achieve the desired final solvent and salt concentrations. The approach is appropriate because PC and DMC have essentially identical molar volumes. Then, phenyl selenocyanate was added to the mixture to reach a final concentration of 250 mM in PSC. For the ultrafast IR measurements and the FT-IR spectra of the CN stretch, the prepared electrolyte was sealed between two CaF₂ windows separated by a 150 μ m Teflon spacer and enclosed in a custom-made aluminum sample cell. All sample preparation procedures were performed in an N₂ glovebox to prevent moisture absorption. All ultrafast IR measurements are conducted in a temperature-controlled laser room at 22 °C.

S1.2. Ultrafast IR Spectroscopy

Detailed descriptions of the laser system used in this work have been published previously.^{1,2} Briefly, a regenerative amplifier is used to amplify the short femtosecond pulses from a Ti:Sapphire oscillator. The result is 3 kHz 800 nm pulses with average pulse energy of 2 mJ. The output of the regenerative amplifier is sent into a homebuilt optical parametric amplifier and a difference frequency generator where the light is converted to $\sim 4.6 \mu$ m, 30 μ J, at 3 kHz, with the frequency centered between the bound and unbound CN stretching modes of phenyl selenocyanate. The final pulse spectrum has a width of $\sim 90 \text{ cm}^{-1}$ and easily covers the entire relevant spectral range.

2D-IR experiments employ a sequence of four pulses. The first two pulses are pump pulses separated by a time delay, τ . This delay between the pulses is scanned, and the result is an interferogram for fixed waiting time, T_w . These interferograms are Fourier transformed, giving the ω_{pump} axis of the 2D-IR spectrum. At some fixed T_w later, a probe pulse interacts with the sample. This probe pulse stimulates emission of the vibrational echo that is heterodyne detected by combining it with the local oscillator, the probe pulse. The heterodyned signal is resolved using a spectrograph onto a 32-pixel MCT detector. These detected frequencies constitute the ω_{probe} axis of the 2D-IR spectrum. The spectra are collected at both parallel and perpendicular

polarizations to the pump pulses to generate the isotropic 2D-IR spectrum. The process is repeated as a function of T_w to generate time-dependent 2D spectra.

Polarizations selective pump probe (PSPP) spectroscopy is a two-pulse experiment in which a polarized pump pulse is followed by a probe pulse, which is used to measure the orientational relaxation of the vibrational probe molecule. The polarized pump pulse excites a cosine squared distribution of phenyl selenocyanate (PSC) molecules. After a set time, t , a probe pulse interacts with the sample and the resulting signal is resolved into parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) components. These components are combined as a function of time. The two signals decay as a function of the vibrational lifetime ($P(t)$) and the second Legendre polynomial orientational correlation function ($C_2(t)$) according to equations S1

$$\begin{aligned} I_{\parallel} &= P(t)(1 + 0.8C_2(t)) \\ I_{\perp} &= P(t)(1 - 0.4C_2(t)) \end{aligned} \quad (S1)$$

The parallel and perpendicular signals can be combined to extract the population decay, $P(t)$, and the so-called anisotropy, $r(t)$, which is proportional to $C_2(t)$ according to equations S2.

$$\begin{aligned} P(t) &= \frac{1}{3}(I_{\parallel}(t) + 2I_{\perp}(t)) \\ r(t) &= \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} = 0.4C_2(t) \end{aligned} \quad (S2)$$

Given the peak separations between the bound and free populations of PSC, separate anisotropies can be extracted for each population on a timescale slower than the exchange times. The anisotropies are fit to a wobbling-in-a-cone (WIAC) biexponential model,³ according to equation S4.

$$r(t) = 0.4S_0^2 \left(S_1^2 + (1 - S_1^2) \exp(-t / \tau_c) \right) \exp(-t / \tau_m) \quad (S4)$$

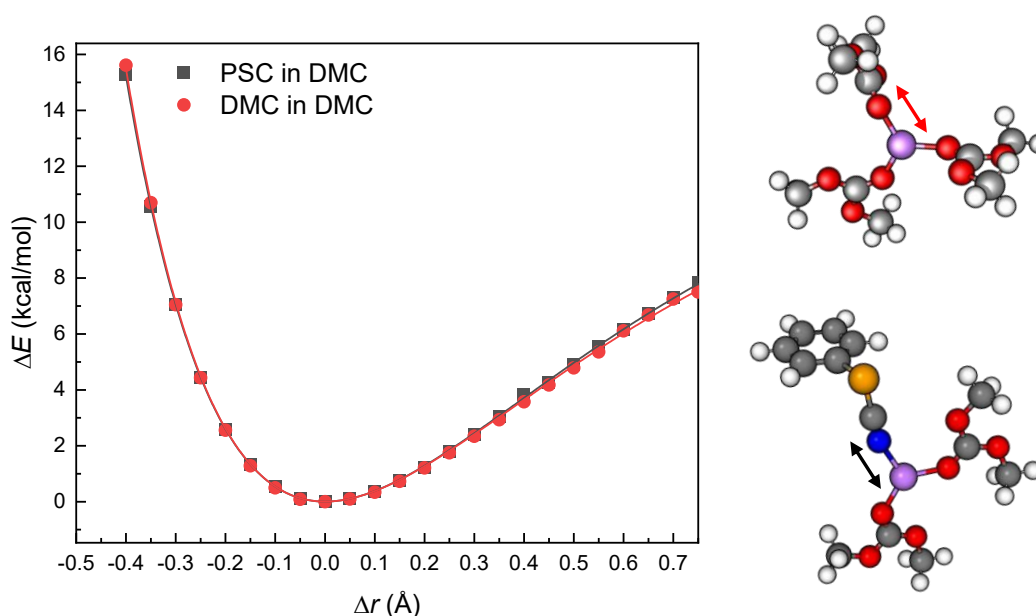
For all analyses performed in the present work, only the full reorientation time, τ_m , is considered. WIAC refers to rotational diffusion of molecules being limited by a solvent that defines a fix set of angles around the molecule being probed on a short time scale. This limits the range of angles accessible to the probe molecule by rotational diffusion until the neighboring solvent environment evolves allowing for the exploration of the entire range of angles on some longer time scale, τ_m .

S1.3. FTIR

FT-IR spectra were collected on a Thermo-Fisher iS50 infrared spectrometer with 0.24 cm^{-1} resolution. Absorption spectra of phenyl selenocyanate (PSC) were acquired by subtracting a PSC-free spectrum from a spectrum containing PSC for every DMC/PC concentration.

S1.4. Density Functional Theory Calculations

Geometry optimizations for every sample were performed in the Gaussian 16 quantum chemistry package using the B3LYP basis set at the 6-31+G(d,p) level of theory using an SMD implicit solvent model where for DMC the dielectric constant was 3.11 and the optical dielectric constant was 1.875 and for PC the dielectric constant was 64 and the optical dielectric constant was 2.03. All structures meant to represent intermediate concentration structures were used with SMD parameters set as the average of the dielectric and optical dielectric constant of DMC and PC to approximate the mixed solvent environment. It has been shown that the dielectric constant for any composition DMC-PC mixture, the dielectric constant is a simple linear combination of the component parts by concentration.⁴ Structures presented are one of many possible converged geometries. For better comparison of the pseudo-Morse potentials presented in this work, a converged probe-free cluster structure was taken and one solvent molecule was exchanged for a PSC and the resulting structure was reoptimized. Pseudo morse potentials were obtained by scanning the Li^+ -O coordinate for the $\text{Li}(\text{DMC})_3^+$ cluster and the Li^+ -N coordinate for the $\text{Li}(\text{DMC})_2\text{PSC}^+$ cluster. After each coordinate step, the cluster geometry was reoptimized. The resulting points were fit to Morse potentials. Figure S1 shows the pseudo Morse potential for a



cluster with three DMCs and one with two DMC and a PSC replacing one of the DMCs.

Figure S1: Pseudo Morse potentials for the Li-O bond coordinate scan for DMC (red points) and the Li-N bond coordinate scan (black points) for PSC both with SMD solvent parameters set for pure DMC. Solid lines are fits to morse potentials.

The curves are near their minima and only have very small differences at long distances. Therefore, PSC is a very good surrogate for the dissociation of a DMC.

S1.4. Molecular Dynamics Simulations

For MD simulations, the geometry of Li-salt (LiTFSI), solvent (PC and DMC) and probe (PSC) molecules were optimized at B3LYP 6-311++G(2d,p) using Gaussian 16 software,⁵ as

shown in Figure S1. The initial simulated boxes with 1:7 molar ratio of solvent to LiTFSI were built using Packmol software,⁶ as listed in Table S1, in which the ratios of DMC to PC are 1:0, 0.25:0.75, 0.5:0.5, 0.75:0.25, and 0:1. The all-atom optimized potentials for liquid simulations (OPLS-AA) force field were used to describe the complex interaction between the Li-salt, solvent and probe molecules, and the corresponding parameters of LiTFSI, PC, and DMC were taken from the previous work^{7, 8}. It should be noted the Coulomb parameters of LiTFSI are reduced to 0.92, and the Lennard-Jones and Coulomb parameters of PC and DMC were also slightly modified to obtain the more accurate diffusion coefficients of Li⁺ compared to the experimental values. In addition, the parameters of PSC were obtained based on the LigParGen website.⁹ All the charge of Li-salt solvent and probe molecules refitted using CHELPG method at the same basis set as the geometry optimization and the parameters of SeCN in PSC were taken from the previous work.^{10, 11}

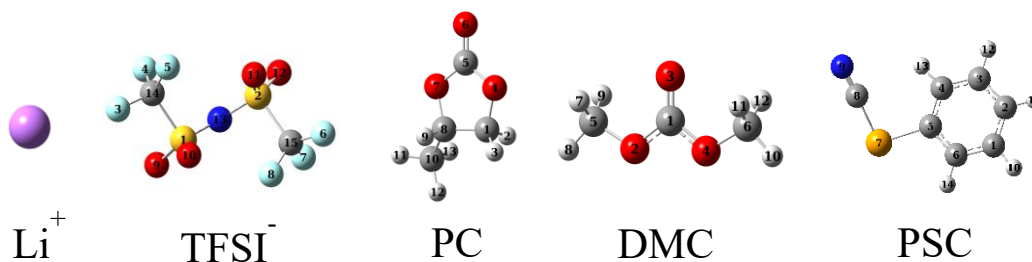


Figure S2. The structures of simulated molecules with atom labels. The structures used in the MD simulation for Li⁺, bis(trifluoromethanesulfonyl)imide anion, propylene carbonate, and phenyl selenocyanate. The carbonyl oxygen in the PC carbonyl group is O6 and the nitrogen in the PSC nitrile group is N9.

Table S1. The system compositions and simulation time.

systems	Number of each atom				Relaxation time /ns	Production time /ns
	LiTFSI	PC	DMC	PSC		
PC-100%	67	469	0	10	50	100
PC-75%	67	352	117	10	50	100
PC-50%	67	235	235	10	50	100
PC-25%	67	117	325	10	50	100
PC-0%	67	0	469	10	50	100

The MD simulations at different salt concentrations were conducted with Gromacs 5.0.7.¹² using the leap-frog algorithm with the time step of 1 fs. Initially, the energy minimization was performed for 5 ns and the annealing runs of 8 ns were conducted from 298.2 K to 500 K and then back to 298.2 K under the canonical ensemble (NVT) using a Nose-Hoover thermostat. Then, 50 ns of relaxation under the isothermal-isobaric ensemble (NPT) at 298.2 K and 0.1 MPa to generate full equilibration. Finally, 100 ns production simulations were continued under NPT conditions to obtain the properties of interest by saving the coordinates every 300 steps. The long-range electrostatic interactions were treated by Particle Mesh Ewald method. The cutoff for Lennard-Jones and Coulomb interactions was set at 1.2 nm using the Lorentz-Berthelot mixing rules. The initial atomic velocities were generated based on a Maxwellian distribution and the LINCS algorithm was used to constrain all covalent bonds with hydrogen atoms.

The Einstein equation was used to calculate the self-diffusion coefficient (D) by fitting the diffusive regime.⁷

$$D = \lim_{t \rightarrow \infty} \frac{\langle MSD(t) \rangle}{6t} \quad (S4)$$

The residence time function $H(t)$ can be established such that $H(t)$ is unity if the two species are within L_{cutoff} of each other and zero otherwise.¹³

$$H_{ij}(t) = \begin{cases} 1, & \text{if } x_i(t) - x_j(t) < L_{\text{cutoff}} \\ 0, & \text{otherwise} \end{cases} \quad (S5)$$

Then, the autocorrelation function of $H(t)$ can be calculated as:

$$\xi_{ij}(t) = \langle H_{ij}(t)H_{ij}(0) \rangle \quad (S6)$$

where L_{cutoff} represents the distance of the first solvation shell between N₉ of PSC, O₃ of DMC or O₆ of PC around Li⁺. The L_{cutoff} values are calculated as the minima after the first peak in the radial distribution function (RDF). The residence time (τ^{res}) was calculated as the integral from zero to infinity of the stretched exponential $\exp(-(t/\tau)^{\beta})$ fits to the $H(t)$. An additional consideration is that the extremely fast dissociation instances, where the $H(t)$ becomes 0 immediately after the first frame, are eliminated from consideration. This procedure eliminates the contributions from cases where the distances between PC(O₆)/DMC(O₃)/PSC(N₉) and Li⁺ satisfies the distance criteria but are not bound to each other. Following the procedure by Borodin et al. the contribution from molecules that left the cluster for a relatively long time and then returned is also eliminated.¹⁴

The L^S represents the solvation shell.¹³ $L^S = L_{\text{cutoff}} + 2R_g$, where R_g is the radius of gyration of solvent molecules. The R_g of PC and DMC are 1.717 and 1.689 Å, respectively.

S1.5. Pulsed Field Gradient NMR

All pfg-NMR measurements were conducted on a Bruker 400 MHz instrument using the step1s pulse sequence (monopolar gradients, stimulated echo, 1 spoiler pulse), with a smoothed rectangle gradient pulse shape. Maximum field gradients were calibrated by fitting the water H¹ decay as a function of gradient strength in a solution of 90:10 H₂O:D₂O. The maximum gradient strength in the measurements in this work was found to be 52.25 G/cm.

Samples were prepared in a Wilmad Coaxial NMR Tube with the sample in the external volume and deuterated dimethyl sulfoxide in the internal capillary for lock.

Signal decays were fit using the shape-adjusted Stejskal-Tanner Equation.¹⁵

$$-\frac{\ln(I)}{\ln(I_0)} = Dg^2\gamma_{\text{eff}}^2\delta^2 \frac{81}{100} \left[\Delta - \delta \frac{(1484\pi^2 - 207)}{4860\pi^2} \right] \quad (S7)$$

“Big Delta” Δ was chosen to be 0.1 and “Little Delta” δ was chosen to be 0.004 s for both ⁷Li NMR and ¹⁹F NMR. As both nuclei are very amenable to pfg-NMR, only 8 scans were required to have exceptional linearity in the decay signal. The reduced parameters to the right of “ D ” in the ST equation are fit vs the negative ln ratio of a given peak area vs the peak when no gradient is applied. The plots follow, noting that all have an r^2 of > 0.9999. Diffusion coefficients are in units of cm²/s.

S1.6. Viscosity

Viscosity measurements were conducted using a Rheosense model m-VROC-II with the B05 chip at room temperature (~20°C). Reported values are the average of 5 repeated measurements.

S1.7. EIS Conductivity

Conductivity measurements were conducted in a custom small volume symmetric probe using potentiostatic electrochemical impedance spectroscopy on a CH Instruments 660D from 2 MHz to 10 kHz with a potential wave about OCP(what does this stand for) (0 V in the symmetric conductivity cell) which resulted in <5 mA of current. The cell constant was standardized with a two point calibration using Mettler Toledo 12.8 mS/cm and 1413 µS/cm conductivity standards. The high frequency intercept was taken as the bulk ionic resistance (the standard interpretation when both electrodes are blocking and the potential wave is sub-Faradaic) and inherent cell constant was determined as the excess impedance. Sample resistance was taken as a ratio of the standard resistances minus cell constant.

Sample Equations, where numeric subscript indicates conductivity standard identity and Ω indicates a measured high frequency intercept

$$\frac{\Omega_1^{meas} - Z_{cell}}{\Omega_2^{meas} - Z_{cell}} = \frac{\kappa_2}{\kappa_1} \quad (S8)$$

$$\frac{\Omega_{sample}^{meas} - Z_{cell}}{\Omega_{1,2}^{meas} - Z_{cell}} = \frac{\kappa_{1,2}}{\kappa_{sample}}$$

S2. Supplementary Text

S2.1. Two-Species Kinetic Model

To determine the dissociation and association times, the volumes from the 2D IR spectra are fit to a two species kinetic model, given in equation S9.

$$\begin{pmatrix} \dot{N}_F \\ \dot{N}_B \end{pmatrix} = \begin{pmatrix} -(k_F + k_{FB}) & k_{BF} \\ k_{FB} & -(k_B + k_{BF}) \end{pmatrix} \begin{pmatrix} N_F \\ N_B \end{pmatrix} \quad (S9)$$

The solution to the set of differential equations is (S10).

$$\begin{aligned}
V_F &= \frac{\mu_F^4 N_F(t=0)}{2\Delta} \left[(\Delta + m) \exp\left(-\frac{1}{2}(s + \Delta)t\right) + (\Delta - m) \exp\left(-\frac{1}{2}(s - \Delta)t\right) \right] \\
V_B &= \frac{\mu_B^4 N_B(t=0)}{2\Delta} \left[(\Delta + m) \exp\left(-\frac{1}{2}(s - \Delta)t\right) + (\Delta - m) \exp\left(-\frac{1}{2}(s + \Delta)t\right) \right] \\
V_{FB} &= \frac{\mu_F^2 \mu_B^2 N_F(t=0)}{\Delta} \left[k_{FB} \left(-\exp\left(-\frac{1}{2}(s + \Delta)t\right) + \exp\left(-\frac{1}{2}(s - \Delta)t\right) \right) \right] \quad (S10) \\
s &= k_F + k_B + k_{FB} + k_{BF} \\
\Delta &= \sqrt{s^2 - 4(k_F k_B + k_F k_{BF} + k_B k_{FB})} \\
m &= k_F + k_{FB} - k_{BF} - k_B
\end{aligned}$$

Given that the free-to-bound and bound-to-free exchange peaks are in equilibrium, they always have identical volumes and therefore only one volume is needed for a complete solution to the set of differential equations.

S2.2. Calculation of Transition Dipole Ratio

The transition dipole ratio of the bound and free peaks can be extracted because the 2D IR peak volume goes as the fourth power of the transition dipole whereas the FT-IR spectrum goes as the square of the transition dipole. Therefore, the ratio is obtained using Equations S11.

$$\begin{aligned}
V_i(t=0) &\propto N_i(t=0) \mu_i^4 \\
S_i(t=0) &\propto N_i(t=0) \mu_i^2 \\
\frac{\mu_F}{\mu_B} &= \sqrt{\frac{V_F/S_F}{V_B/S_B}} \quad (S11)
\end{aligned}$$

The transition dipole ratio increases with increasing propylene carbonate concentration, as shown in Figure S3.

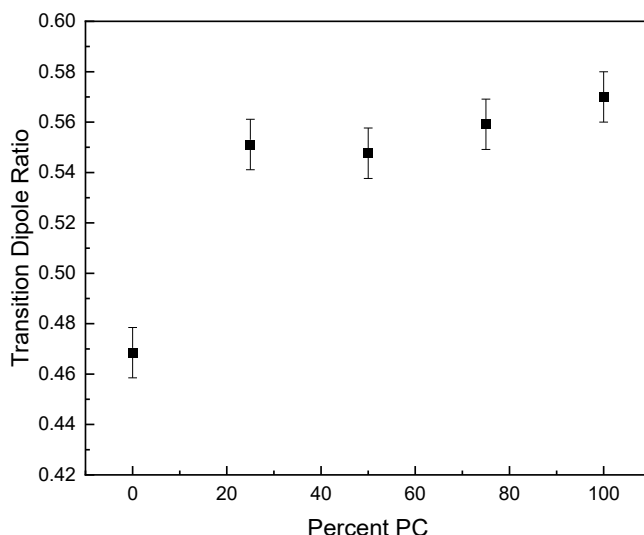


Figure S3: Transition dipole ratios for each solvent composition. They range from 0.47 ± 0.1 for pure DMC to 0.57 ± 0.1 for PC.

S2.3. Spectral Diffusion and confirmation of equivalence of the DMC and PC dissociation times

The center line slope (CLS) method is a technique for accurately determining the normalized frequency-frequency correlation function. Slices through the 2D spectrum are taken parallel to the ω_{probe} axis or a series of time-dependent 2D IR spectra. Each slice is a one-dimensional peak. The peak centers at each T_w are fit to a line, called the center line.¹⁶ The slopes of these lines are plotted vs T_w . This plot of the center line slopes is the normalized frequency-frequency correlation function. The decay of the CLS is the quantitative measure of the evolution in the environment surrounding the probe molecule as the environment contributes to the probe frequency because of intermolecular interactions.

Previous work in the Fayer lab has shown that the on-diagonal bound peak in the 2D-IR shows a triexponential decay compared to the biexponential decay of the free peak. This longer third component, τ_3 , was attributed to the dissolution of solvent molecules from the lithium-ion cluster. This attribution was confirmed because τ_D from the 2D IR chemical exchange analysis divided by the coordination number, N , minus one agrees well with the observed τ_3 from the CLS. N is determined by a combination of anisotropy measurements and DFT calculations and is discussed in the following section. The reason for the division by $N-1$ is that every solvent molecule coordinated to the Li^+ can dissociate. The probe PSC reports on the dynamics. Therefore, if it is dissociated, the CLS slow component cannot be measured. The other solvating molecules contribute to the CLS decay, therefore the rate is $(N-1)$ times faster than the dissociation rate.

This trend holds for the DMC-PC mixture system (Fig S3b). It can therefore be concluded that the dissociation times of PC, DMC, and PSC are all comparable.

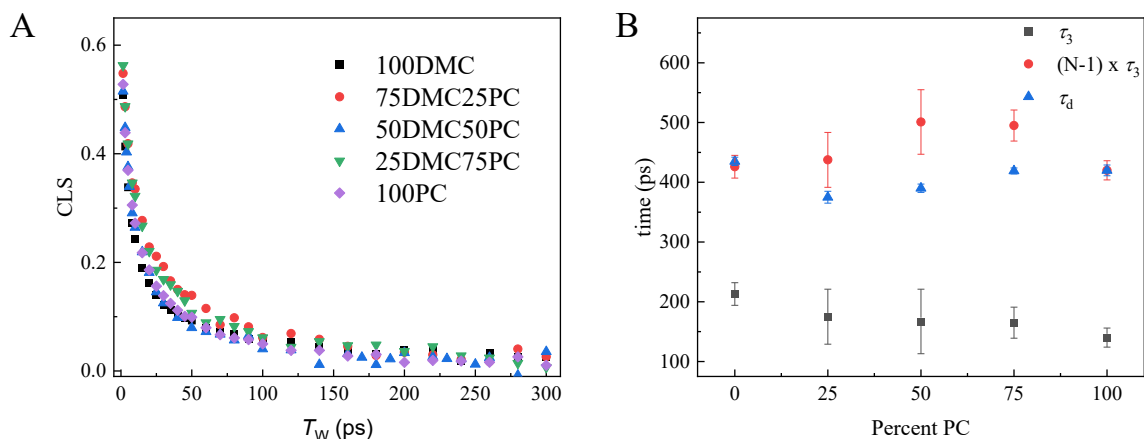


Figure S4: A. CLS decays of the bound 0-1 peak for all concentrations considered in the present study. Fits are not shown for clarity, but all decays were fit to tri-exponentials. B. Comparison of τ_d from 2D-IR measurements with τ_3 from the CLS decays as well as the CLS decays multiplied by the coordination number, N , minus 1.

S2.4. Stokes-Einstein-Debye (SED) Equation and Determination of Cluster Composition

The SED equation (equation S12) relates the full reorientation time of a rotator in a viscous medium to the viscosity of the medium (η), the volume of the rotator (V) and the energy ($k_B T$).

$$\tau_m = \frac{\eta V}{k_B T} \quad (\text{S12})$$

In the present study, there are two distinct accessible reorientation times. Namely, those of probe molecules free in solution and those bound to Li^+ (main text fig 3A) as part of the solvation cluster. The full reorientation time is found by fitting the anisotropy decay for both the bound and free probe to a biexponential WIAC model.

Given that the temperature and the bulk viscosity are kept constant, for two rotators in the same solution, the ratio of the full reorientation times is equal to the ratio of the volumes according to equation S13.

$$\frac{\tau_m^B}{\tau_m^F} = \frac{V_B}{V_F} \quad (\text{S13})$$

From the τ_m ratio (Fig 3B, main text) determined from equation S13, the effective volume for the Li-bound complex containing a single PSC can be found. The assumption is made for the pure DMC and pure PC samples that one PSC takes the place of a single DMC or PC, respectively. The volume of PSC, DMC, and PC are 109, 72, and 81 $\text{\AA}^3$ respectively. It has been found that DFT structures where a single PSC is swapped for either a DMC or a PC in a representative Li-containing cluster, the volume of the clusters differ by approximately the difference in the volume of DMC and PSC or the difference in the volume in PC and PSC, namely 37 and 28 $\text{\AA}^3$ respectively.

For the intermediate concentrations of PC-DMC mixtures where it is unclear if the PSC is in the place of a PC or a DMC, the structure of the PSC-free complex is taken to be 32.5 $\text{\AA}^3$

smaller than the volume predicted by the τ_m ratio. For pure PC and DMC, the difference in volume is taken to be exactly the difference in volume given by the difference in volume from the probe and the respective solvent molecule. Possible structures and their volumes were calculated. Structures are named with the following convention: D_nP_m , where D_n refers to the number, n , of DMCs in the structure, and P_m refers to the number, m , of PCs in the structure. Structures considered include D_3P_0 , D_2P_1 , D_2P_2 , D_1P_3 , and D_0P_4 . Additionally, $\text{Li}(\text{DMC})_2\text{TFSI}_1$ was considered. The geometry-optimized structures and their accompanying volumes are given in SI Fig S5.

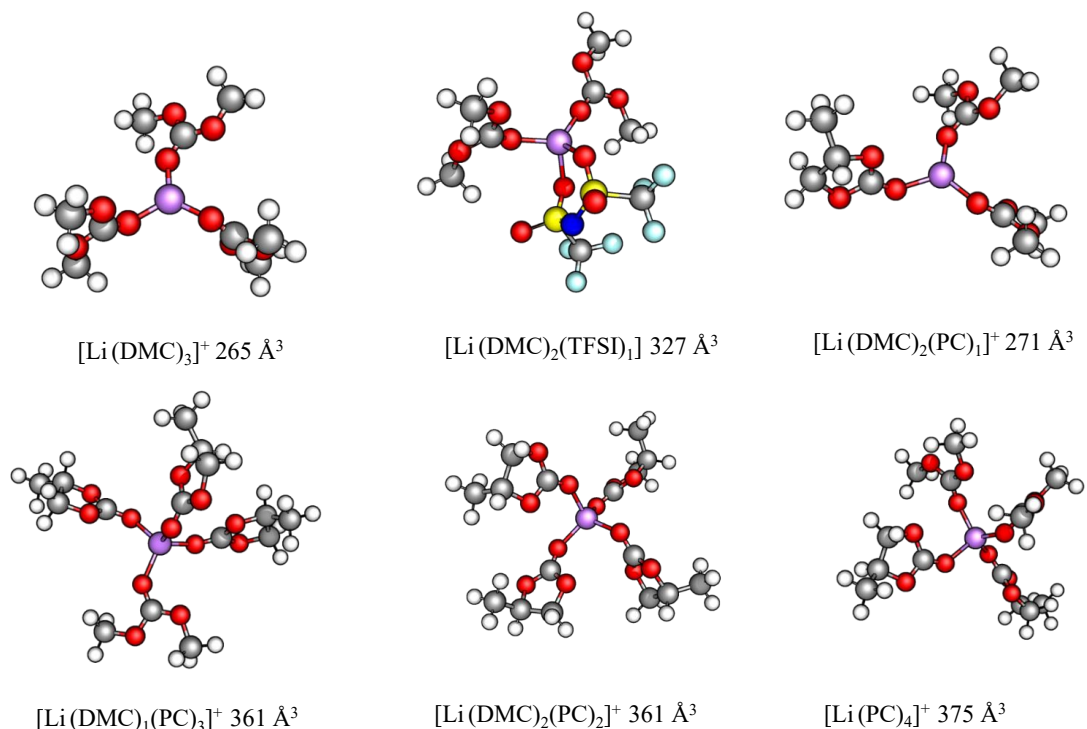


Figure S5: Potential structures considered for Li-ion clusters.

Table S2: Predicted volumes for lithium-containing clusters from PSPP measurements.

Composition	PSPP Volume (τ_m ratio*109 $\text{\AA}^3$)	Volume Predicted w/o probe
100DMC	327 $\text{\AA}^3$	290 $\text{\AA}^3$
75DMC25PC	349 $\text{\AA}^3$	317 $\text{\AA}^3$
50DMC50PC	392 $\text{\AA}^3$	360 $\text{\AA}^3$
25DMC75PC	421 $\text{\AA}^3$	393 $\text{\AA}^3$
100PC	414 $\text{\AA}^3$	386 $\text{\AA}^3$

Given the calculated volumes from PSPP and the volumes from predicted structures, coordination numbers can be estimated. For 100PC, the 4 coordinate D_0P_4 predicts the expected

volume of the probe-free structure most closely and is therefore assigned $N = 4$. For 25DMC75PC, the 4 coordinate structure most closely corresponds to the predicted volume, and it is also assigned $N = 4$. For 50DMC50PC, both D_2P_2 and D_1P_3 essentially agree with the predicted volumes and so it is also assigned $N = 4$. For 75DMC25PC, the predicted volume can be attained by evenly weighing D_3P_0 with either D_2P_2 or D_1P_3 ($(265 \text{ \AA}^3 + 360 \text{ \AA}^3)/2 = 313 \text{ \AA}^3$) very nearly agrees with the predicted volume. Thus, 75DMC25PC is assigned $N = 3.5$. The case of 100DMC is complicated by the fact that pure DMC has a relatively low dielectric constant and so non-negligible ion-pairing is expected. This results in the disagreement in the D_3P_0 volume ($265 \text{ \AA}^3$) disagreeing with the probe-free predicted volume ($290 \text{ \AA}^3$) due to contribution from the $\text{Li}(\text{DMC})_2\text{TFSI}_1$ structure. Still, the final coordination is assigned $N = 3$.

S2.5. Calculation of Stokes-Einstein Diffusion Coefficient from Predicted Radii

To calculate the expected diffusion coefficients for Li^+ clusters in each solvent composition studied, the radius was the radius predicted for a sphere with the volume predicted for each cluster with no probe (Table S2). This radius was then substituted for the radius, R in the Stokes-Einstein equation according to equation S14.

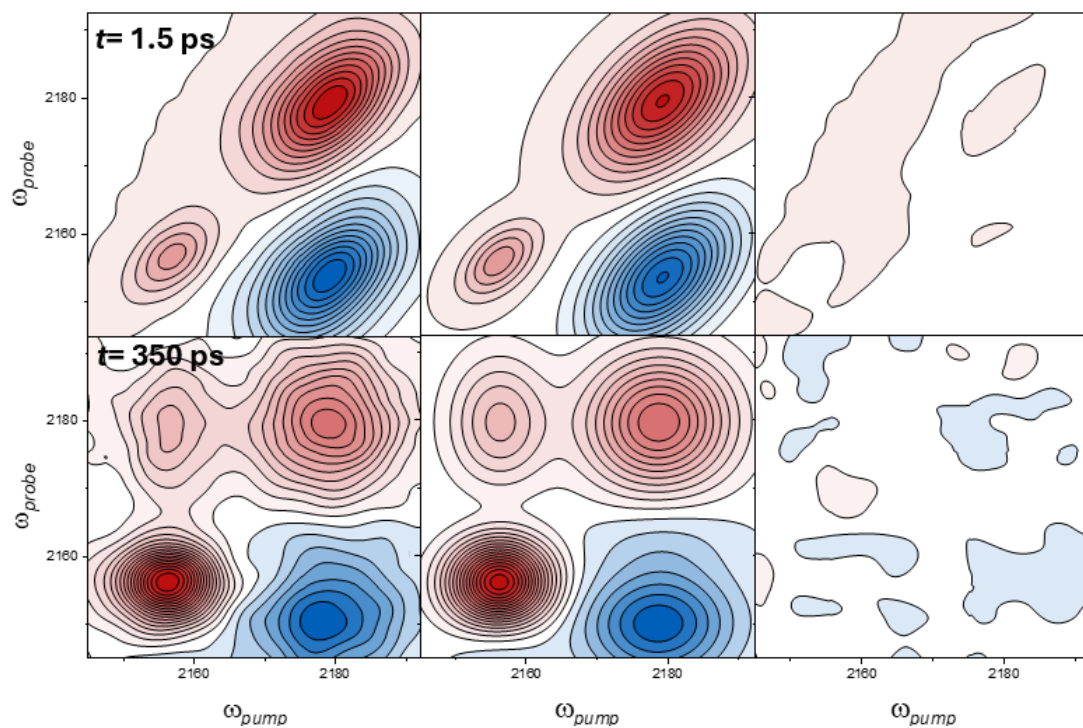
$$D_{SE} = \frac{k_B T}{6\pi\eta R} \quad (\text{S14})$$

These diffusion coefficients are plotted versus viscosity in Fig 4b (blue points) in the main text.

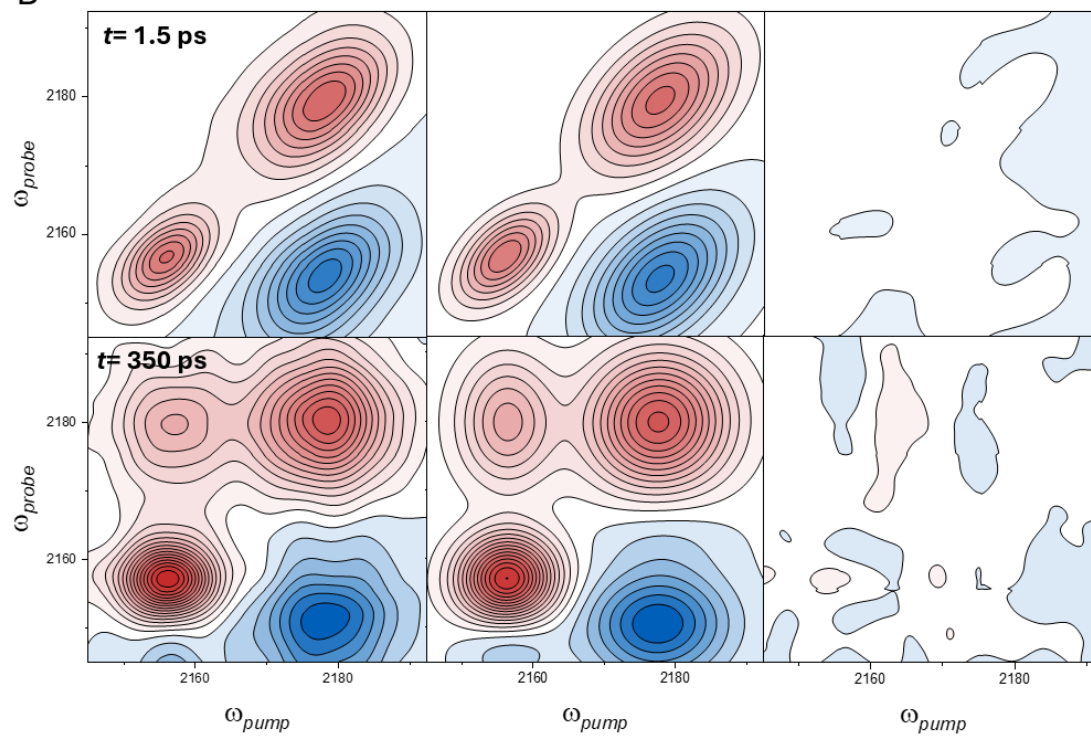
S3. Additional Figures

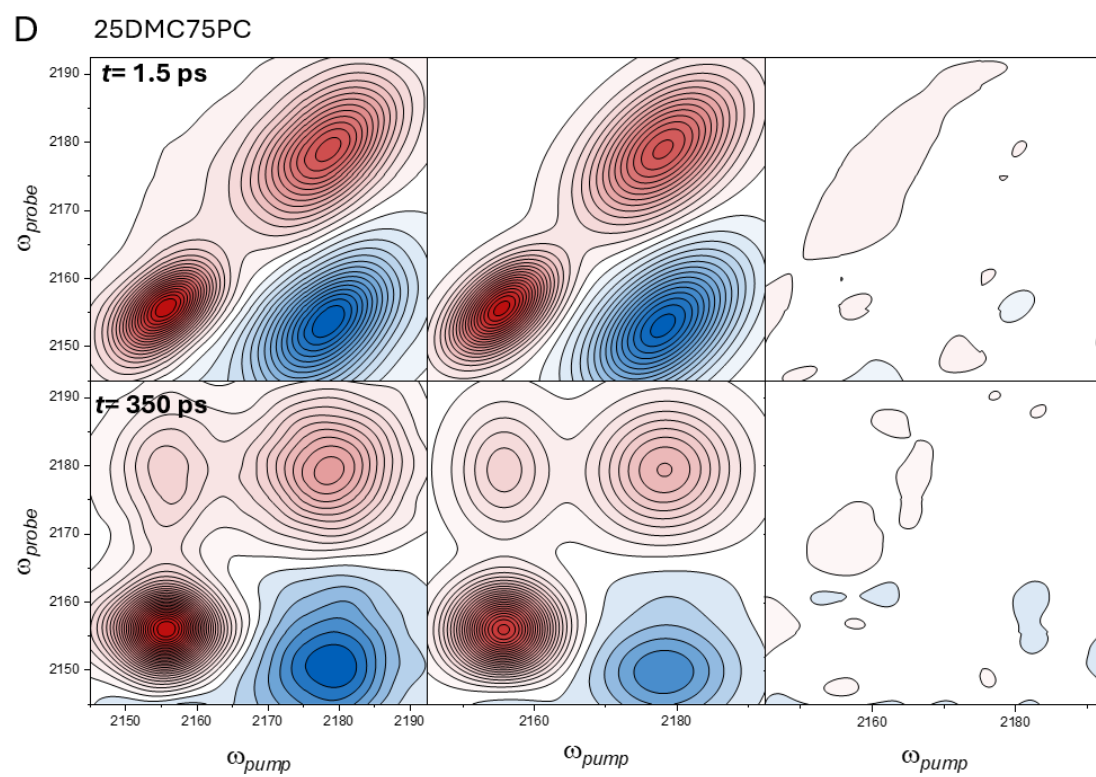
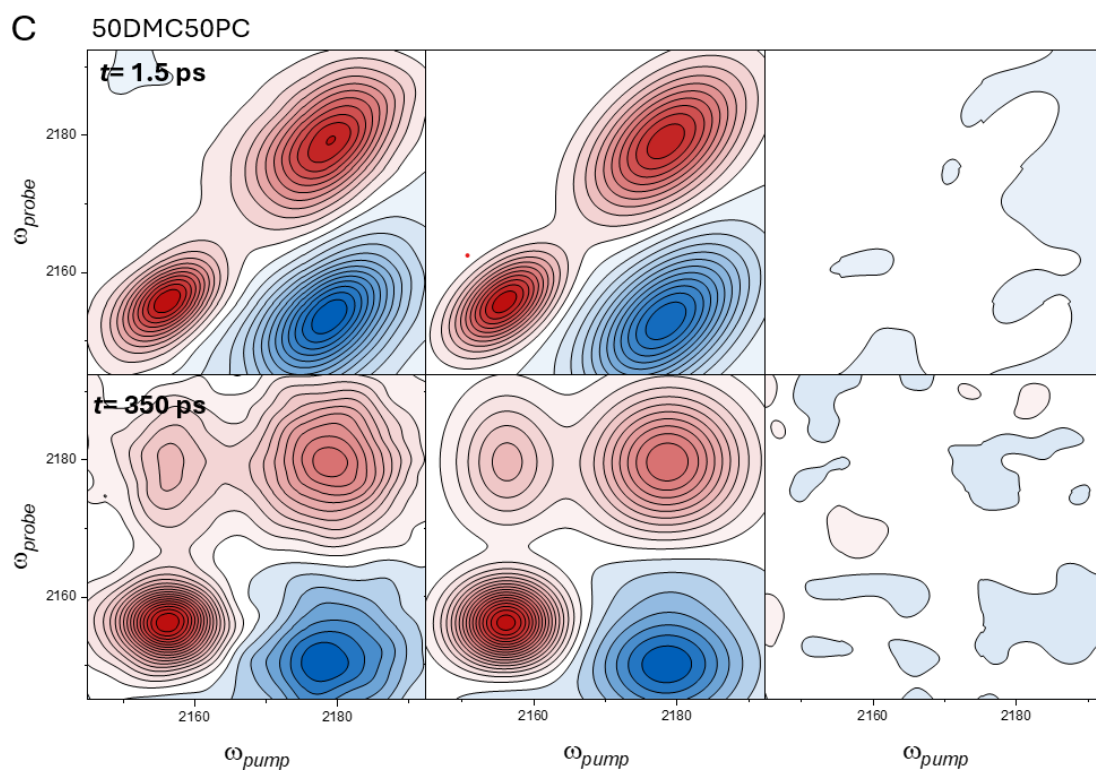
S3.1. 2D-IR Spectra, Residuals, and Kinetic Traces for Additional solvent compositions

A 100DMC



B 75DMC25PC





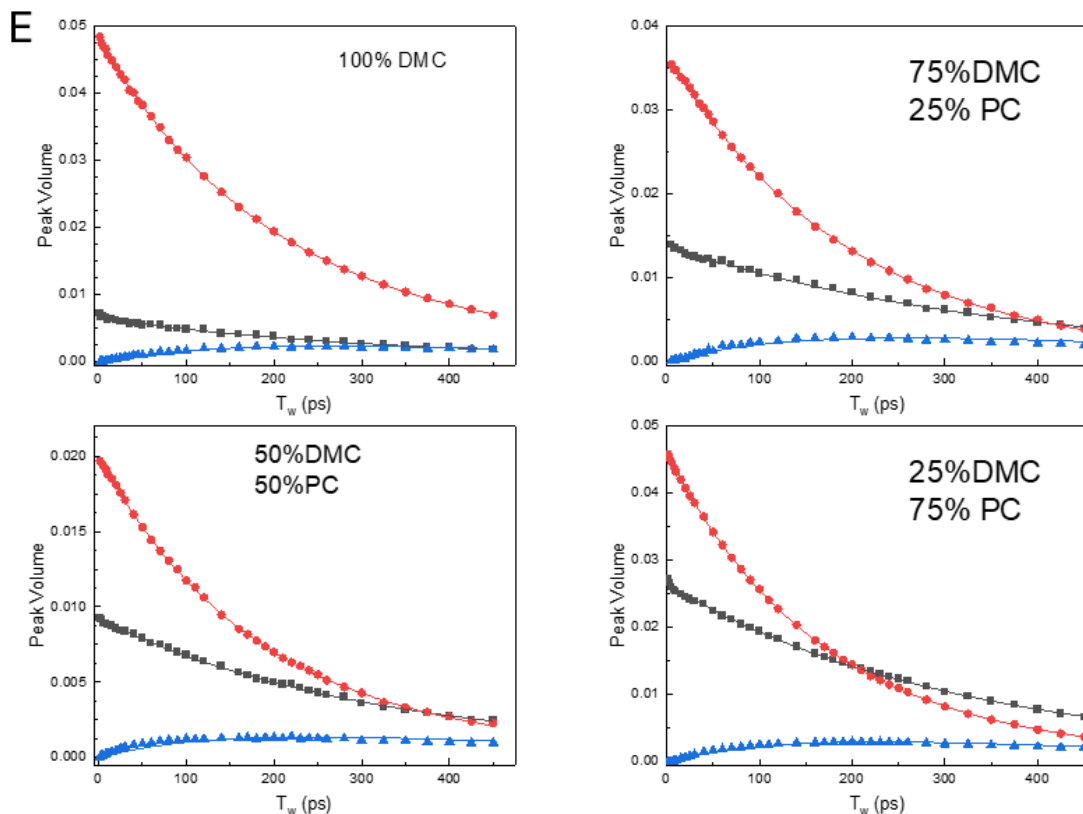


Figure S6: A,B,C,D For each of these figures, the first row is the experimental 2DIR at 1.5 ps, a fit to six 2D gaussians to the experimental data, and the residuals for that fit, respectively. The second row for each of these figures is the experimental data at 350 ps, a fit to six 2D gaussians to the experimental data, and the residuals for that fit, respectively. The four figures are in order of increasing [PC], with pure PC not shown, but can be found in reference 15.¹⁷ E. Fits to two species kinetic model for the various solvent compositions considered in this study. For each, the red points are the volume of the on-diagonal bound PSC peak, the black points are the volume of the on-diagonal free PSC peak, and the blue points are the volume of the exchange peak. Solid curves are the fits to experimental data.

S3.2. Anisotropy Decays

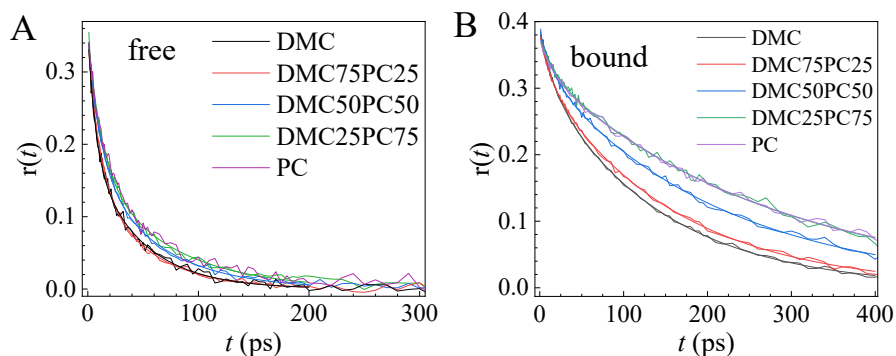


Figure S7: A. Anisotropy decays of the free peak for every solvent composition considered, with biexponential WIAC fits overlayed. B. Anisotropy decays of the bound peak for every solvent composition considered, with biexponential WIAC fits overlayed.

S3.3. Molecular Dynamics Results

S3.3.1 Validation of MD using Diffusion constants and PSC residence Time

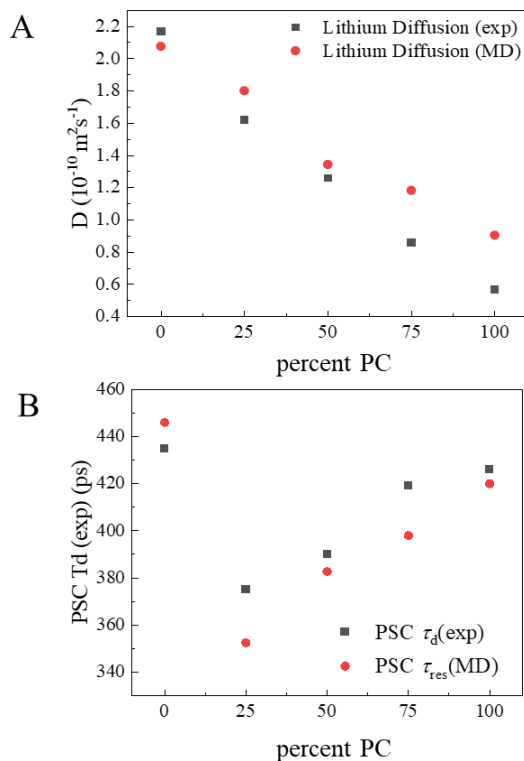
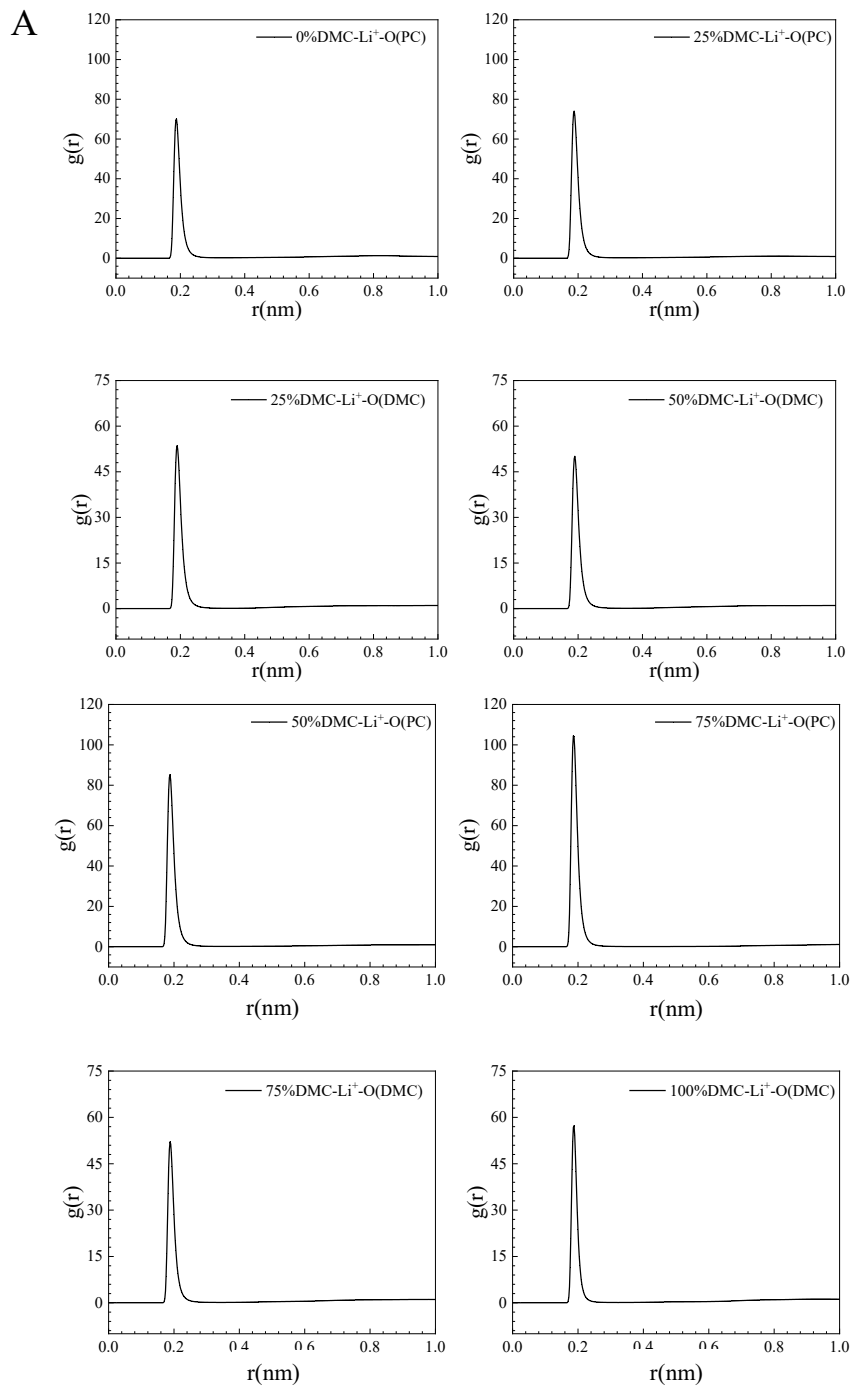


Figure S8: A. Comparison of diffusion coefficients extracted from pfg-NMR (red points labeled exp) and those extracted from MD simulations (black points labeled MD).

S3.3.2 Radius Probability Distributions and L^c/L^s analysis for each solvent composition



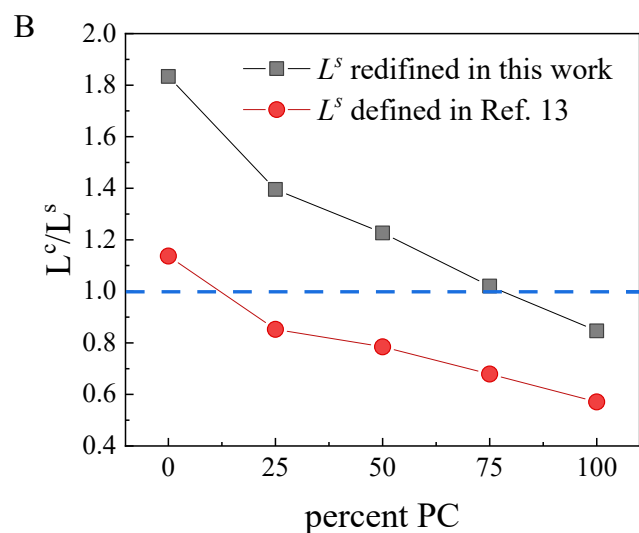


Figure S9: A. Radial distribution functions for Li-O(=C) for Li-PC and Li-DMC distance for every composition considered in the present study. B. Comparison of L^c/L^s using either L^s defined in this work as the radius of a representative solvent cluster (black) versus the definition in reference 13.¹³

Table S3: L^{cutoff} (defined as first minima from RPD) and L^s value (defined as $L^{cutoff} + 2 R_g$, where $R_g(\text{DMC}) = 1.689 \text{ \AA}$ and $R_g(\text{PC}) = 1.717 \text{ \AA}$) for each solvent composition.

	L^{cutoff} (Å)		L^s (Å)	
Percent DMC	Li ⁺ -O(PC)	Li ⁺ -O(DMC)	Li ⁺ -O(PC)	Li ⁺ -O(DMC)
0	3.26	/	6.69	/
25	3.38	3.5	6.79	6.91
50	3.54	3.48	6.95	6.89
75	3.62	3.44	7.03	6.85
100	/	3.24	/	6.62

S3.4. Structural Step Length

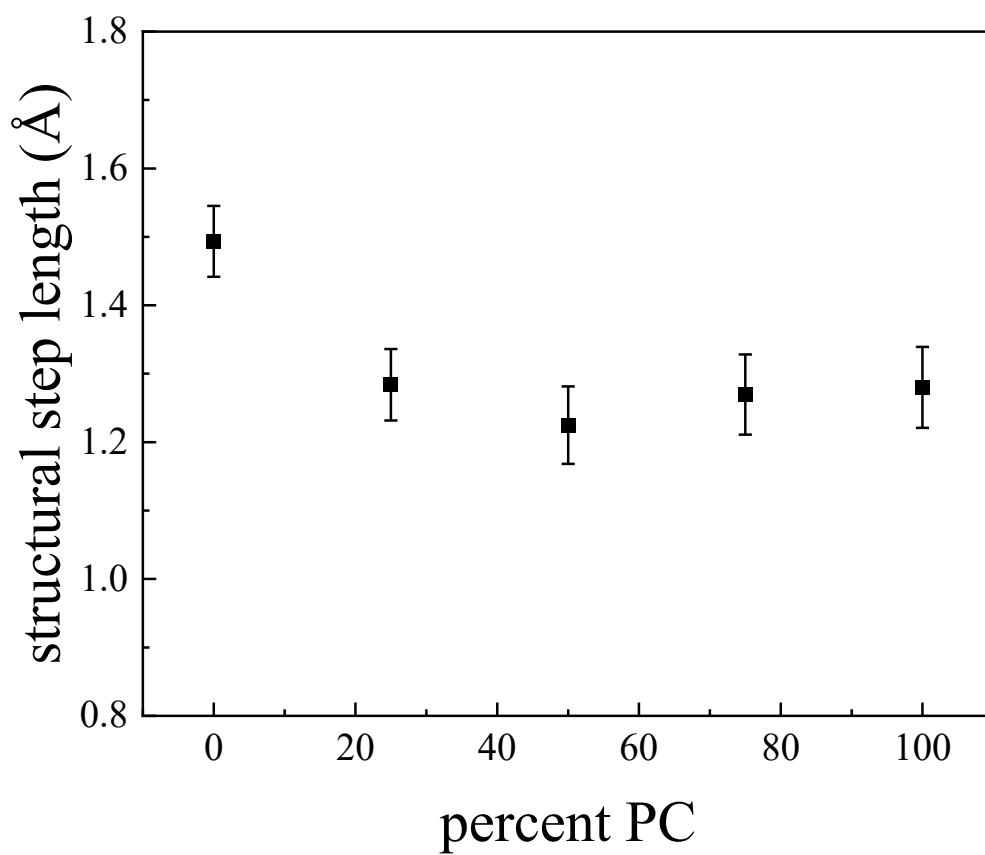


Figure S10: Structural step length as calculated from equation 3 in the main text for every solvent composition considered.

S3.5. pfg-NMR Diffusion Coefficient

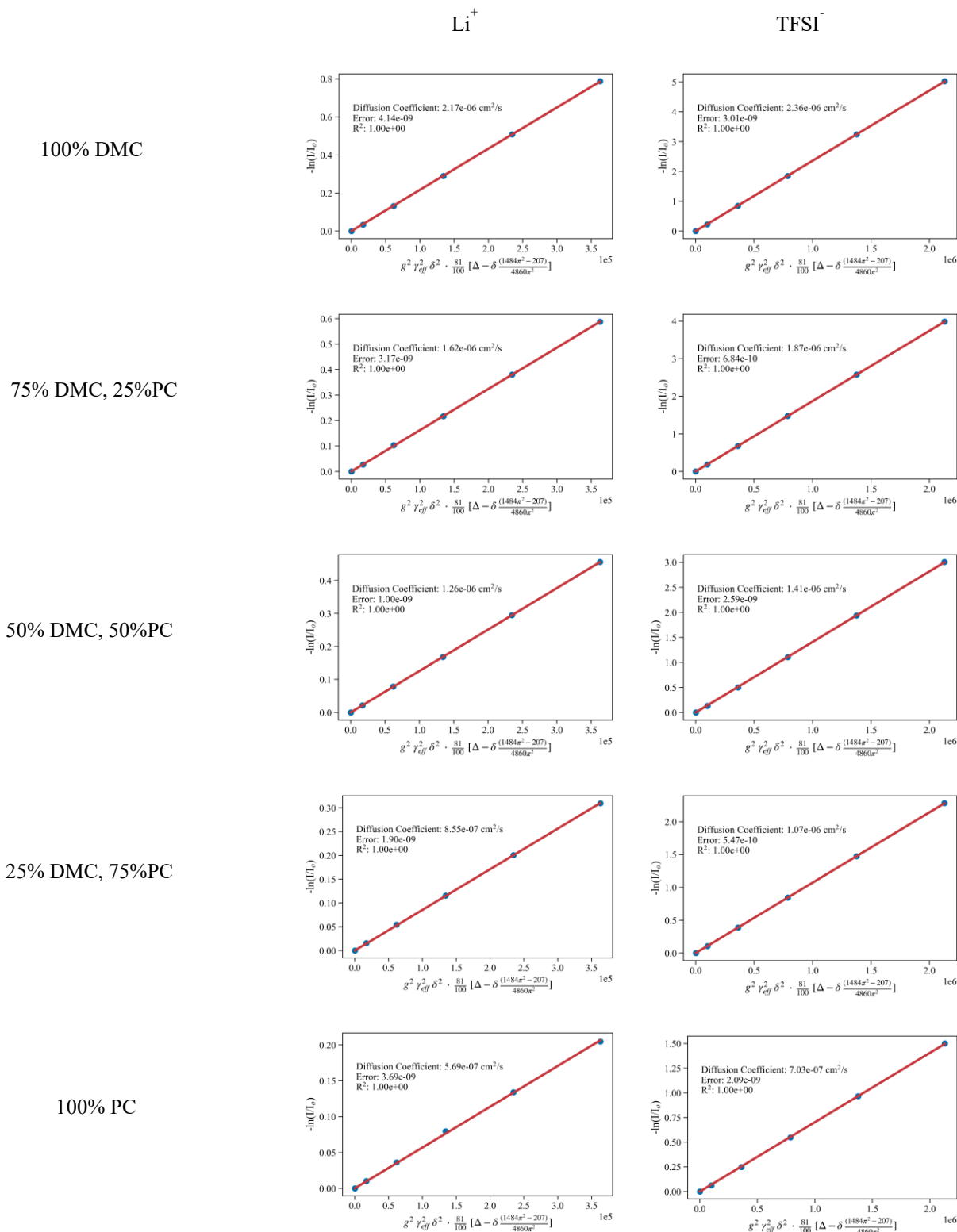


Figure S11: Fits to the shape-adjusted Stejskal-Tanner equation for both Li^+ (^7Li) and TFSI^- (^{19}F) to extract diffusion coefficients for each ion in each solvent composition considered.

S3.6. Ionicity and Discussion of Correlated Ion Motions

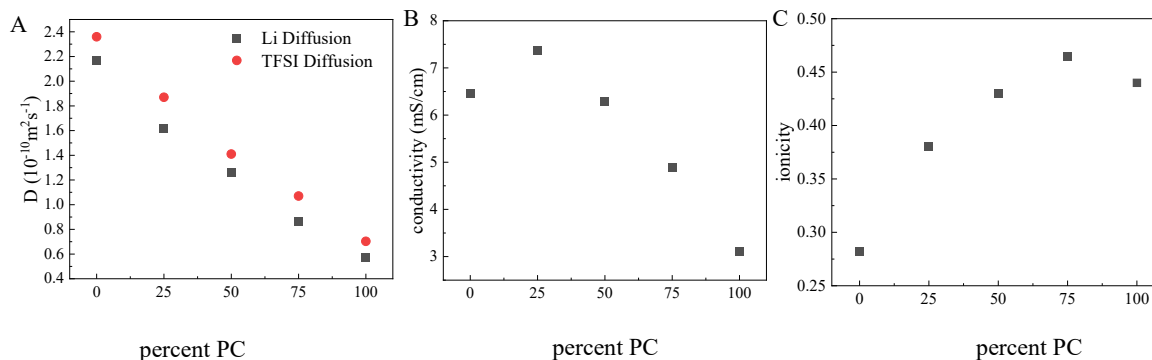


Figure S12: A. Diffusion coefficient for Li^+ (black points) and TFSI^- (red points) versus solvent composition. B. Conductivity for each solvent composition from EIS. C. Ionicity for each solvent composition defined as measured conductivity divided by the Nernst-Einstein Predicted conductivity.

The ionicity can be used as a measurement of the correlated ion motions. In terms of the Onsager conductivity coefficients (σ_{++} , σ_{--} , and σ_{+-}) ionicity can be expressed alternatively as

$$\text{Ionicity} = \frac{\sigma_{\text{tot}}}{\sigma_{\text{NE}}} = \frac{\sigma_{++} + \sigma_{--} - 2\sigma_{+-}}{\sigma_{++} + \sigma_{--}} \quad (\text{S14})$$

We have calculated the Onsager conductivity coefficients and have provided them in Table S4. It is important to note that this analysis assumes there are no like-charged ion correlations (cation-cation or anion-anion).

Table S4: Onsager conductivity coefficients as a function of solvent composition from pfg-NMR and EIS

% PC	σ_{--} (S)	σ_{++} (S)	σ_{+-} (S)
0	0.011	0.012	0.020
25	0.0084	0.0096	0.015
50	0.0065	0.0073	0.011
75	0.0044	0.0055	0.0076
100	0.0029	0.0036	0.0051

The ion-solvent correlations do not directly influence the solution's conductivity because solvent molecules are neutral, but they could, in principle, provide some insight into the mechanism of transport.

It is reasonable to assume that the diffusion of solvent molecules not associated with a lithium is independent of the lithium diffusion. Then, in the limit of infinite dissociation time, the cross term for ion-solvent transport would be nL_- where L_- is the Onsager transport coefficient in appropriate units and n is the solvation number. However, the dissociation time is not infinite, but the time

between dissociation and association is very short. Therefore, the coefficient of L_- will be slightly smaller than n .

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