

Supporting Information

Partial Desolvation Causes Lithium Structural Transport in Liquid and Gel Polymer Electrolytes.

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S1 Experimental Methods

S1.1 Materials and Sample Preparations

Propylene carbonate (anhydrous), Lithium bis(trifluoromethanesulfonyl)imide (anhydrous), poly(propylene carbonate) (average $M_n \sim 50,000$), and phenyl selenocyanate were purchased from Millipore Sigma. Phenyl selenocyanate and propylene carbonate were dried using 20 vol% 3 Å molecular sieves for a week before use. Poly(propylene carbonate) pellets were dried in a vacuum oven at 50°C for a week before use. All sample preparation steps are performed in a N₂-filled glovebox to prevent moisture absorption.

The electrolyte solutions were prepared by dissolving an appropriate amount of PPC pellets and LiTFSI salt in PC at an elevated temperature ($\sim 60^\circ\text{C}$). Then, phenyl selenocyanate was added to the mixture to reach a final concentration of 250 mM. The prepared electrolytes were then sealed between two CaF₂ windows, separated by a 250 μm Teflon spacer, and enclosed in a custom-made aluminum sample cell. They were subsequently transferred out of the glovebox for collecting the FT-IR spectra and the ultrafast IR data.

S1.2 Ultrafast Infrared Spectroscopy Instrumentation

A detailed description of the identical ultrafast laser system has been given previously.^{1,2} Briefly, a regenerative amplifier (Regen) was used to amplify the 800 nm femtosecond pulses generated by a Ti:Sapphire oscillator, which resulted in final output pulses at a 3 kHz repetition rate with 2 mJ energy per pulse. The Regen output was then converted by a homebuilt tunable optical parametric amplifier (OPA) to two near IR beam at 1.3-1.4 μm and 1.9-2.0 μm , which were then mixed using a AgGaS₂ crystal to produce a mid-IR output tuned to a frequency between the free phenyl selenocyanate peak and the Li⁺-bound peak ($\sim 4.6 \mu\text{m}$, 25 μJ , 3 kHz), so

that the two peaks are evenly pumped. The final mid-IR pulses have a bandwidth of $\sim 90 \text{ cm}^{-1}$ and are close to transform-limited ($\sim 190 \text{ fs}$). The data acquisition is performed using the pump probe geometry with an acousto-optic modulator (AOM), which acts as both a chopper and a pulse shaper.

S1.3 Polarization-selective Pump-probe (PSPP) Experiments

PSPP experiments use a two-pulse sequence to measure the orientational relaxation of the probes' transition dipole. A strong polarized pump pulse preferentially excites a cosine-squared distribution of the $\text{C}\equiv\text{N}$ vibrational mode along the pump polarization, labeling the initial orientations of the PSC molecules. After a variable time delay, t , a weaker probe pulse stimulates the emission of the signal, which is detected at polarization either parallel ($I_{\parallel}$) or perpendicular ($I_{\perp}$) to the pump pulse. The detected signal decays through a combination of the $\text{C}\equiv\text{N}$ excited state population lifetime, $P(t)$, and the second Legendre polynomial orientational correlation function, $C_2(t)$:³

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

Both the lifetime and the anisotropy, $r(t)$, can be separated from the para/perp signals:

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

The complete reorientation (randomization of the orientations) times (τ_m) can be extracted from the anisotropy using the bi- or tri-exponential wobbling-in-a-cone (WIAC) model ^{4, 5}:

$$\begin{aligned}
r(t) &= 0.4S_0^2 \left(S_1^2 + (1 - S_1^2) \exp(-t / \tau_c) \right) \exp(-t / \tau_m) \\
r(t) &= 0.4S_0^2 \left(S_1^2 + (1 - S_1^2) \exp(-t / \tau_{c1}) \right) \left(S_2^2 + (1 - S_2^2) \exp(-t / \tau_{c2}) \right) \exp(-t / \tau_m)
\end{aligned} \tag{3}$$

S_0 , S_1 , and S_2 are the generalized order parameters for the inertial cone and the diffusive cones; τ_{c1} and τ_{c2} are the correlation times associated with sampling the first and second diffusive cones. Here, we are only interested in the slowest component of the decay, τ_m , that describes the full molecular reorientation.

S1.4 Two-dimensional Infrared (2D IR) Experiments

2D IR experiments use three excitation pulses to extract time-dependent frequency evolution. The first two pump pulses are separated by a coherence time, τ . Scanning τ builds up an interference pattern that encodes the initial vibrational frequency (ω_{pump}). After a variable waiting time (T_w), the probe pulse interacts with the sample, inducing the emission of the vibrational echo. The echo/LO then passes through a computer-controlled rotating polarizer. It is frequency-dispersed by a monochromator before being captured by a 32-pixel array detector, producing an interferogram at each frequency channel. A Fourier transform of the interferograms along τ yields the ω_{pump} axis, while the monochromator array defines the probe frequency axis (ω_{probe}). By repeating the same processes for a variety of T_w , a time series of 2D-IR spectra is obtained. Additionally, spectra are collected in both parallel and perpendicular polarization configurations to produce isotropic spectra, thereby eliminating the effects of orientational relaxation of the vibrational probe molecules.

The center line slope method is used to extract the spectral diffusion dynamics from the 2D lineshape. It works by slicing the experimental 2D spectrum along ω_{probe} axis and fitting each slice to a Gaussian function to determine its peak position. The maxima of each slice is then

connected to form the center line. Plotting the slopes of these center lines (CLS) as a function of T_w yields the CLS decay (see Figures 4E and F). CLS decay can be viewed as the normalized frequency-frequency correlation function, which quantifies the rate of spectral diffusion.⁶

S1.5 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were collected using a Thermo-Fisher iS50 infrared spectrometer with a resolution of 0.24 cm^{-1} . The absorption spectra of phenyl selenocyanate (PSC) in different electrolytes were obtained by subtracting the spectra of the background samples prepared identically without the vibrational probes to remove background absorptions. The background-subtracted spectra are then normalized to the free PSC peak height at $\sim 2155 \text{ cm}^{-1}$.

S1.6 Density Functional Theory Calculation

Geometry optimizations of all structures were performed using the Gaussian 16 quantum chemistry package⁷ at PBE/6-31+G(d,p) level of theory with the SMD universal solvation model.⁸ The custom implicit solvent for GPE is defined using the weighted average of the dielectric constant of each component. For LE, GPE10-60, the dielectric constant is $\epsilon_{\text{PPC}}x + \epsilon_{\text{PC}}(1-x)$ (x = polymer fraction). For GPE40(SN), and GPE40(PCSN), the dielectric constants are 40.2 and 37.7, respectively. Additionally, frequency calculations are conducted at the same level of theory to ensure the absence of imaginary frequencies. For the cluster with coordination number 2, the optimization was first performed with Li^+ also bound to a PPC trimer, which was then removed for volume calculation, since the polymer segment does not undergo full reorientation.

S1.7 Electrochemical Impedance Spectroscopy

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 (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 μ S/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 the inherent cell constant was determined as the excess impedance. Sample resistance was taken as a ratio of the standard resistance minus the cell constant. Sample Equations, where the numeric subscript indicates conductivity standard identity and Ω indicates a measured high-frequency intercept:

$$\frac{\Omega_1^{\text{meas}} - Z_{\text{cell}}}{\Omega_2^{\text{meas}} - Z_{\text{cell}}} = \frac{\kappa_1}{\kappa_2} \quad (4)$$

$$\frac{\Omega_{\text{sample}}^{\text{meas}} - Z_{\text{cell}}}{\Omega_{1/2}^{\text{meas}} - Z_{\text{cell}}} = \frac{\kappa_{1/2}}{\kappa_{\text{sample}}} \quad (5)$$

S1.8 Raman Spectroscopy

Raman measurements are performed using the Horiba XploRA+ confocal Raman system, with a 532 nm green laser, x100 long working distance objective, and 2400 gr/mm grating. Data was collected in the same sample cell as ultrafast IR measurements (through the CaF₂ window).

S2 Supplementary Notes

S2.1 Supplementary Note 1: Transition Dipole Strength

The FT-IR peak area is proportional to the transition dipole strength squared, while the 2D peak volume is proportional to the transition dipole strength to the fourth power:⁹

$$\begin{aligned} V_i(t=0) &\propto N_i(t=0)\mu_i^4 \\ S_i(t=0) &\propto N_i(t=0)\mu_i^2 \end{aligned} \quad (6)$$

Therefore, if the transition dipole is different between two species, their relative population cannot be directly calculated from their peak area. Here, when PSC is bound to lithium, its transition dipole strength has been found to increase significantly, and the transition dipole ratio for the free PSC to Li-bound PSC has been previously determined to be 0.57 ± 0.01 in LiTFSI/PC electrolytes across different lithium concentrations:¹⁰

$$\frac{\mu_F}{\mu_L} = \sqrt{\frac{V_F/S_F}{V_L/S_L}} \quad (7)$$

In this study, we found that the addition of poly(propylene carbonate) did not perturb the transition dipole of the Li^+ -bound PSC even at 60% polymer, which is another indication that the solvation shell primarily consists of PC and does not bind strongly to the polymer groups.

When succinonitrile (SN) is introduced in GPE40(PCSN) and GPE40(SN), the transition dipole ratios are different from the PC samples. The transition dipole ratio for GPE40(PCSN) increased to 0.61, and the ratio for GPE40(SN) further increased to 0.77.

S2.2 Supplementary Note 2: Orientational Diffusion for high-polymer-fraction GPEs

For low polymer fractions (0-30%), each Li^+ ion is primarily coordinated by four or three PC molecules, which effectively shields the cation from direct interactions with the polymer backbone. At higher polymer fractions (40-60%), the PC coordination number decreases to two. This reduction reflects both the limited availability of free PC molecules and the increasing geometric constraints imposed by the polymer network. Under these conditions, Li^+ can

coordinate directly to functional groups on the polymer, such as the carbonyl oxygen of PPC. An example of such a configuration is shown in Fig. S3.7a, which presents a DFT-optimized structure where Li^+ binds to two PCs and the carbonyl of a PPC trimer.

When polymer coordination occurs, the orientational relaxation of the Li^+ solvation cluster can proceed either through wobbling motions about the $\text{Li}^+ \cdots \text{O}=\text{C}$ (polymer) axis or through transient breaking and reforming of this bond. Importantly, both processes produce indistinguishable depolarization effects for the vibrational probe. The functional form of $r^{\text{L}}(t)$ remains biexponential with a steep second decay throughout the entire GPE polymer fraction series, indicating no clear change in the molecular orientation randomization component. Moreover, the wobbling-in-a-cone (WIAC) model was originally formulated to describe restricted rotational motions, such as the liberation of polymer side-chains, which depend only on the polar angle θ .⁵ Thus, the WIAC formalism remains valid even when one rotational axis is constrained by Li^+ -polymer coordination.

The agreement between the PSC dissociation time ($\tau_{\text{d}}^{\text{PSC}}$) obtained from chemical exchange, and the PC dissociation time ($\tau_{\text{d}}^{\text{PC}}$) extracted from spectral diffusion (Figure 5B, main text) further validates our solvation-structure assignments derived from PSPP measurements. As discussed in the main text in conjunction with Figure 5A, the number of dissociation pathways measured by the τ_3^{L} is the total coordination number minus one, the PC dissociation time is calculated from the spectral diffusion decay time constant by: $\tau_{\text{d}}^{\text{PC}} = (CN_{\text{Li-PC}} - 1)\tau_3^{\text{L}}$. If our PSPP-determined coordination number were incorrect, this relationship would not produce the excellent agreement between $\tau_{\text{d}}^{\text{PSC}}$ and $\tau_{\text{d}}^{\text{PC}}$ shown in Figure 5B. The convergence of these independently measured quantities therefore provides strong internal consistency and supports the accuracy of the proposed solvation structures.

We also investigated the binding energy difference between the PC carbonyl and the PPC carbonyl through DFT calculations. Relaxed coordinate scans were performed for the distance between the carbonyl oxygen and Li^+ for both PC and PPC trimer. The obtained energies were fit to Morse potentials to extract the dissociation energy. The results clearly indicate that PC carbonyl binds to Li^+ (13.4 kcal/mol) more strongly than PPC (9.9 kcal/mol) (Figure S3.7b).

S2.3 Supplementary Note 3: Fitting 2D Spectra

To calculate the peak volumes for chemical exchange analysis and accurately determine the CLS for spectral diffusion analysis, we applied a robust fitting method to the 2D spectra.^{9, 10} Each peaks in the 2D IR spectra are modeled as a 2D Gaussian function, and the experimental spectra are fit to the sum of six 2D Gaussians. These peaks correspond to the two diagonal peaks for free (F) and Li^+ -bound (L) populations, the negative L peak for $|1\rangle \rightarrow |2\rangle$ vibrational transition, the $\text{F} \rightarrow \text{L}$ exchange peak on the top left, the $\text{L} \rightarrow \text{F}$ exchange peak on the bottom right, and the negative $\text{F} \rightarrow \text{L}$ exchange peak for $|1\rangle \rightarrow |2\rangle$ transition on the bottom left. Once a good fit is achieved, the peak of interest is isolated by subtracting the five unwanted peaks from the experimental spectra using the fits for each peak. As shown in Figure S3.4, both the free PSC peak and the Li^+ -bound peak can be isolated, leaving minimal residuals from the rest of the spectra. The CLS analysis is then performed on the isolated peaks to extract the CLS decay for free PSC and Li-bound PSCs separately.

S2.4 Supplementary Note 4: Detailed Explanation of CLS Decay Components.

As discussed in the main text, the center line slope (CLS) decay reflects the temporal evolution of local structural environments sampled by the vibrational probe. Both the free (CLS-

F) and Li⁺-bound (CLS-L) components of the PSC nitrile stretching mode can be well described by tri-exponential decay functions. However, the distinct time constants observed in each environment suggest different underlying molecular motions contributing to spectral diffusion. τ_1^F ranges from 3-8 ps, which could be caused by the fast translational fluctuation of free solvent molecules; For CLS-F, τ_2^F increased from 13 ps to 95 ps with increasing polymer fractions, associated with the orientational randomization of PC molecules; τ_3^F varies from 60 ps to 1086 ps, and is attributed to the ion cluster motions.¹⁰ For CLS-L, τ_1^L (3-6 ps) is likely caused by the fast fluctuation of the Li⁺-nitrile bond distance in the solvation shell;¹¹ τ_2^L (22-76 ps) is attributed to the angular fluctuation/wobbling motion of the other constituents of the solvation shell; τ_3^L (174-2073 ps) has been shown to be associated with the lithium desolvation dynamics.¹⁰

S2.5 Supplementary Note 5: Discussions of GPE40-PC/SN and GPE40-SN data

Figure S3.8A displays the linear absorption spectra of GPE40-PC/SN and GPE40-SN, compared to the GPE40 sample presented in the main text. With increasing SN content, the Li⁺-bound peaks grow in slightly, which is an indication of minutely weaker solvating strength of SN relative to PC. Additionally, there is a slight blue shift of the bound peak center frequency, but not for the free peak, which is an indication of the change in the average solvation structure.

The solvation structures of the SN-plasticized GPE sample are further investigated by PSPP experiments, where the anisotropies of the free and Li⁺-bound peaks are separately examined (Figure S3.8B). Similar to the other GPE samples, it is observed that the bound peak decays much more slowly due to the increased average volume of the rotating moieties. The complete molecular reorientation times are extracted from $r(t)$ by fitting to the biexponential or

triexponential forms of the WIAC model (Equation 3), which are shown in Figure S3.8C. Taking the τ_m ratio yielded 3.0 ± 0.1 for GPE40-PC/SN, and 3.1 ± 0.1 for GPE40-SN, corresponding to an average volume of $330 \pm 15 \text{ \AA}^3$ and $335 \pm 14 \text{ \AA}^3$ by multiplying the volume of free PSC ($109 \text{ \AA}^3$) (Figure S3.8D). GPE40-PC/SN's measured volume matches the cluster volume consists of a PSC, PC, and SN within error (Figure S3.8E); GPE40-SN's volume is slightly bigger than the cluster volume for lithium bound to a PSC and two SNs. This is likely due to some incorporation of TFSI anion into the solvation shell, as indicated by the small bump at the LiTFSI contact ion pair region in the Raman spectrum (Figure S3.9A), since TFSI's volume is bigger than SN. In comparison, the GPE40's solvation shell has an average volume of $252 \pm 13 \text{ \AA}^3$. The increase in average volume suggests that incorporating SN in the solvent increases the coordination number from two to three. The insertion of SN into the solvation shell of GPE40-PC/SN is further corroborated by the Raman spectrum at the nitrile stretching mode region, where the Li^+ -bound CN peak is observed for both GPE40-SN and GPE40-PC/SN.

The 2D IR spectra of the SN samples are presented in Figure S3.10A&B for two waiting times. The extracted 2D volumes for the free, Li^+ -bound, and exchange peaks are plotted in Figure S3.10C&D. These are fitted to the two species exchange equations to extract the PSC dissociation times. Additionally, the center line slope decay for the bound peak (CLS-L) is extracted from the change in lineshape (Figure S3.10E), and the slowest decay component (τ_3^L) is used to determine the solvent dissociation time (τ_d^{sol}) by multiplying by the $CN_{\text{Li-sol}}$. The comparison between the dissociation times of PSC and solvent is shown in Figure S3.10F, which are within error of each other for all samples. Since we expect PSC's binding strength to Li^+ to be similar to both PC and SN, the agreement between these two sets of time constants is another validation of the obtained coordination numbers and the time constants.

S3 Supplementary Figures

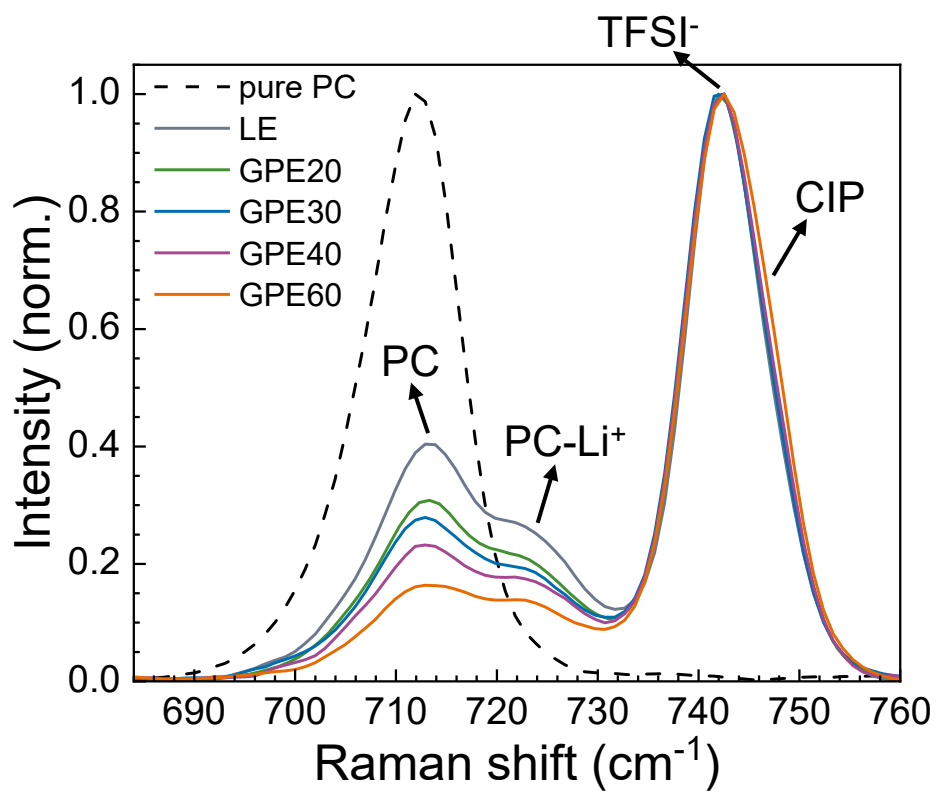


Figure S3.1: Raman Spectra of pure PC, liquid PC/LiTFSI electrolytes and, GPE20-60. The peak at $\sim 712\text{ cm}^{-1}$ is attributed to free PC's ring breathing mode, which shifts to $\sim 724\text{ cm}^{-1}$ when PC is complexed to Li^+ . The peak at $\sim 743\text{ cm}^{-1}$ is associated with TFSI's S-N-S mode, with the formation of contact ion pair (CIP) shifting this peak to the $\sim 747\text{ cm}^{-1}$.

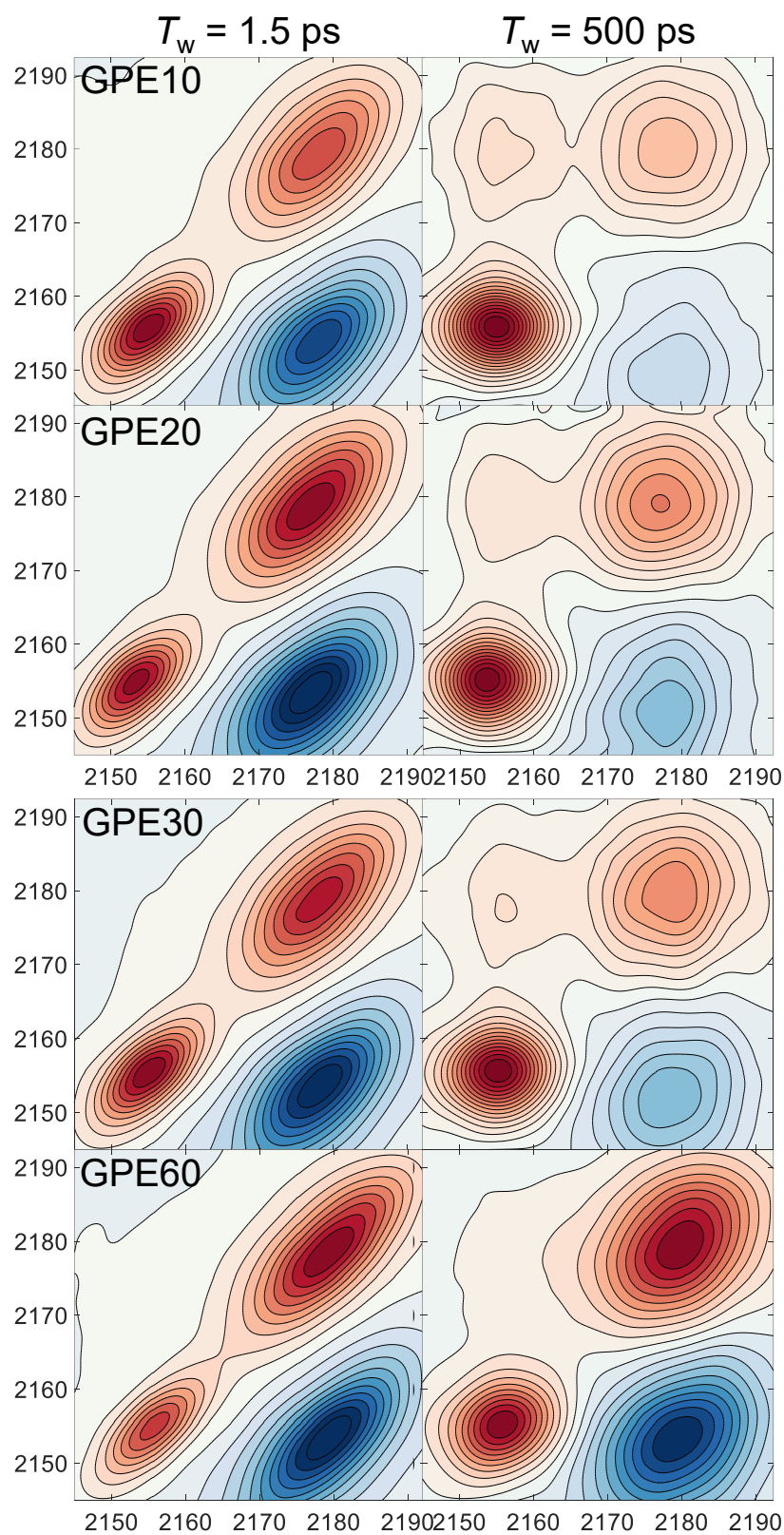


Figure S3.2: Experimental 2D IR spectra for GPE10, 20, 30, and 60 at waiting time (T_w) of 1.5 ps and 500 ps.

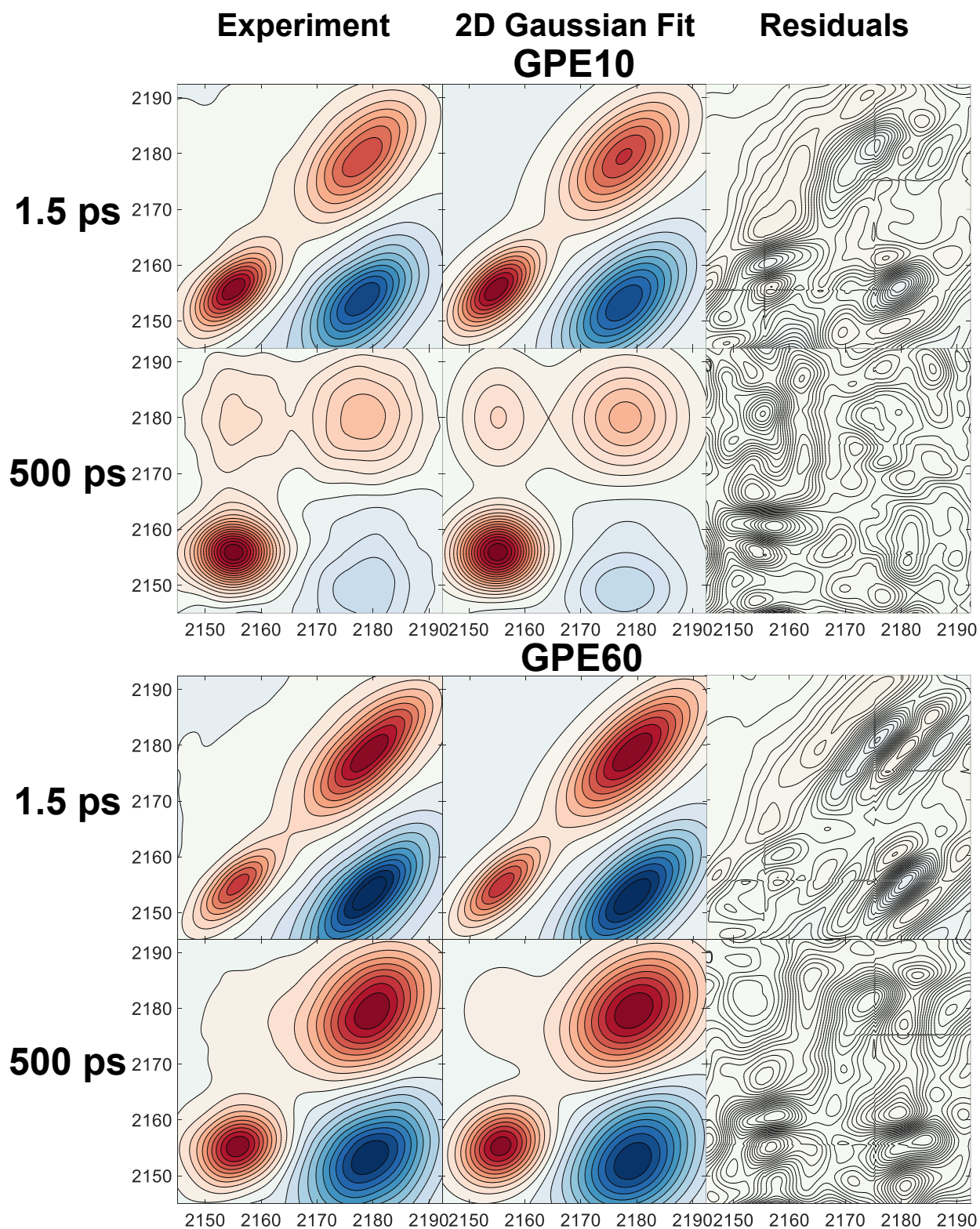


Figure S3.3: Experimental 2D IR spectra, 2D Gaussian fit, and its residuals for GPE10 and GPE60 at waiting times (T_w s) of 1.5 ps and 500ps.

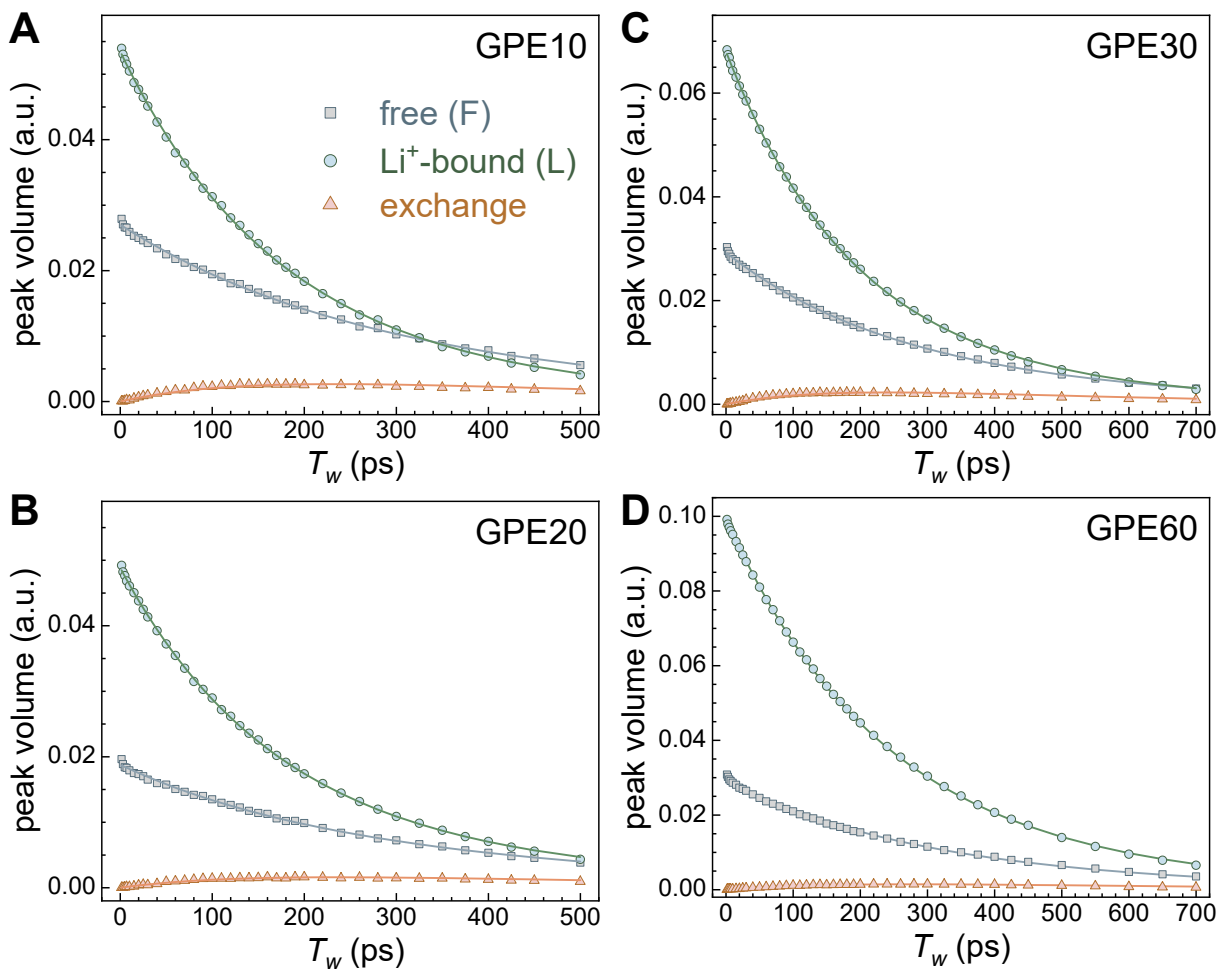


Figure S3.4: Time-dependent peak volumes from 2D Gaussian fits to the experimental spectra for (A) GPE10, (B) GPE20, (C) GPE30, and (D) GPE60. The lines are fit to the chemical exchange kinetic equations.

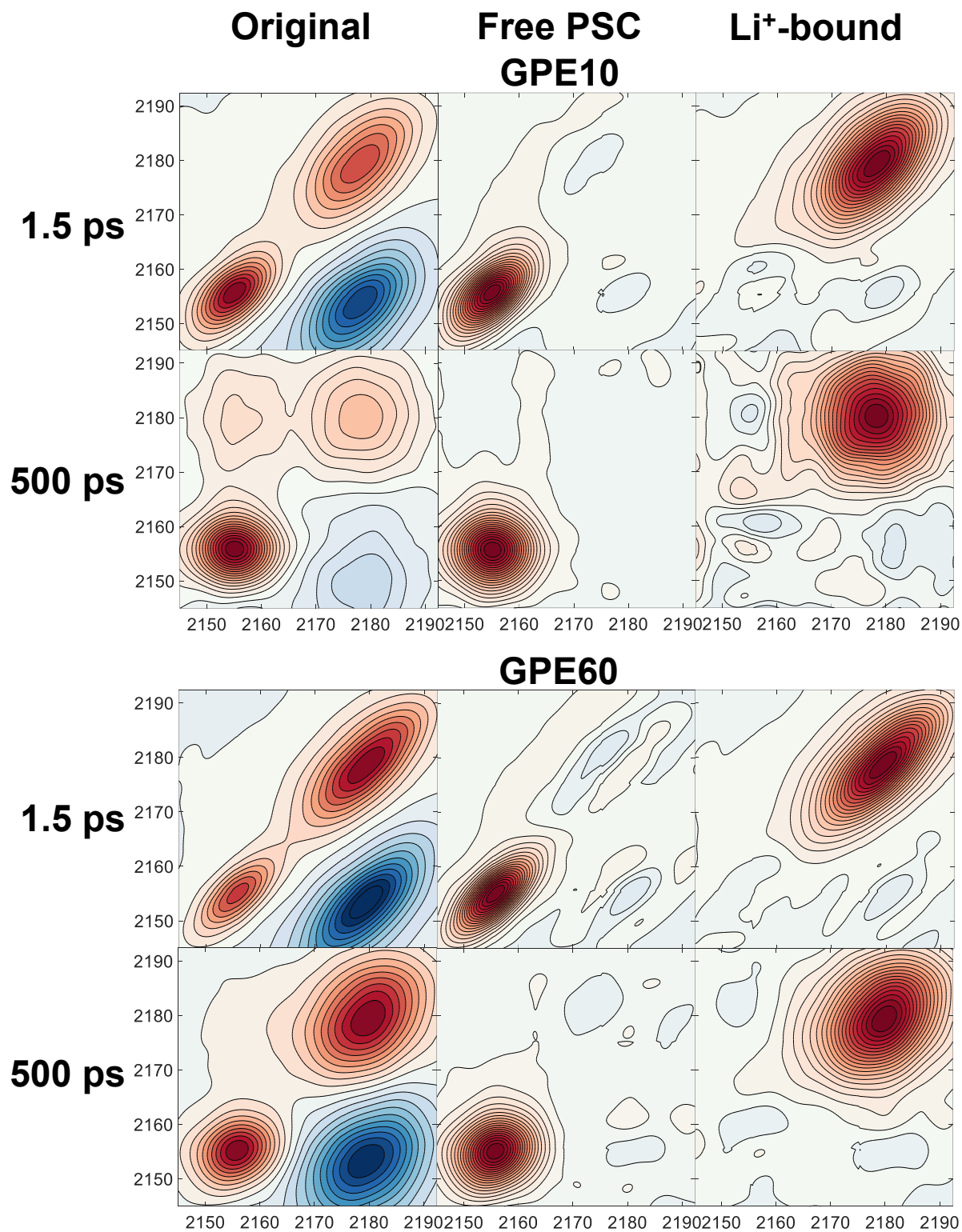


Figure S3.5: Peak Subtraction to isolate free PSC and Li⁺-bound peaks for accurate CLS analysis (GPE10 & GPE60) for waiting times of 1.5 ps and 500 ps.

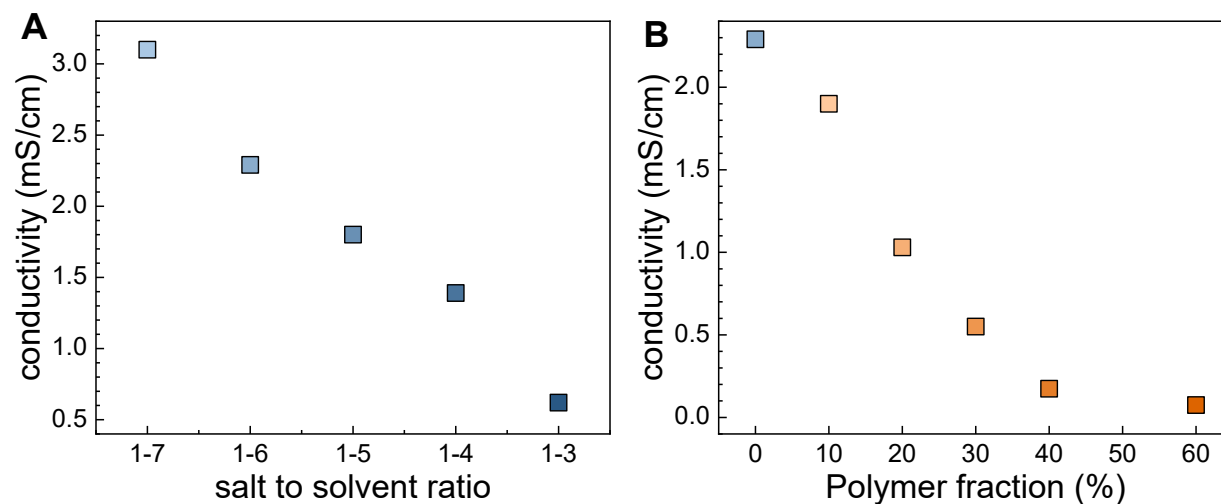


Figure S3.6: Ionic conductivity of liquid and gel polymer electrolytes. **A.** The ionic conductivity of liquid electrolytes as a function of salt to solvent ratio (1-7 being the least concentrated, while 1-3 is the most concentrated). **B.** Ionic conductivity of GPEs as a function of polymer fractions.

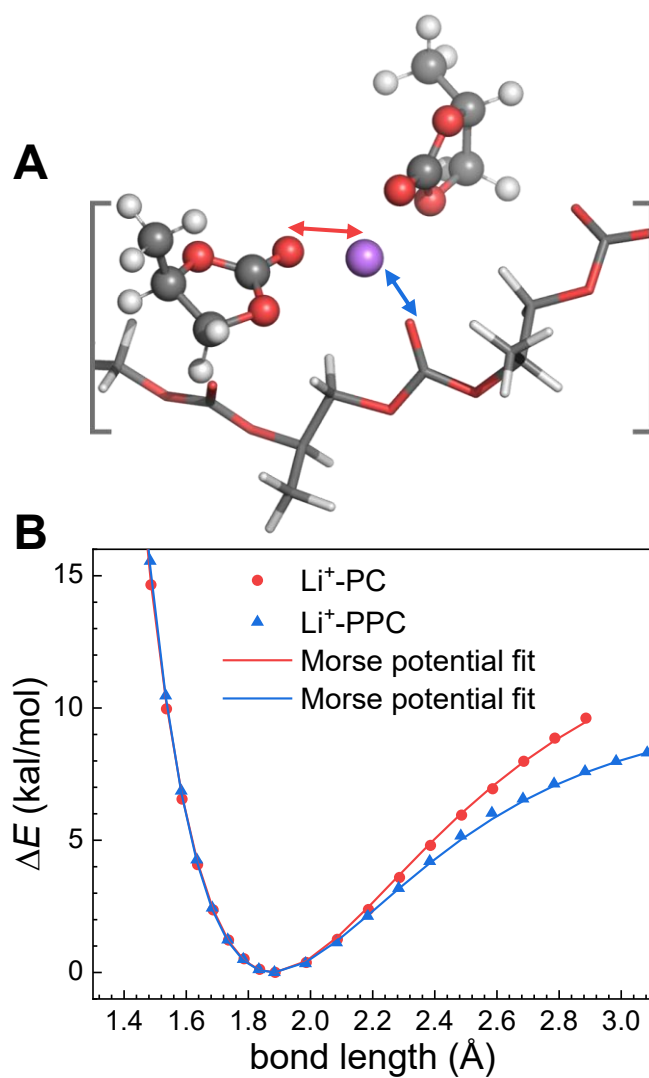


Figure S3.7: **A.** DFT-optimized structure of lithium solvation structure with 2 PCs and a PPC trimer representing the polymer. **B.** Potential energy surface scan along the Li⁺...C=O bond for PC and PPC, which are fit to Morse potentials. The fit reveals PC's binding energy to lithium ion is 13.4 kcal/mol, while PPC to Li⁺'s binding energy is 9.9 kcal/mol.

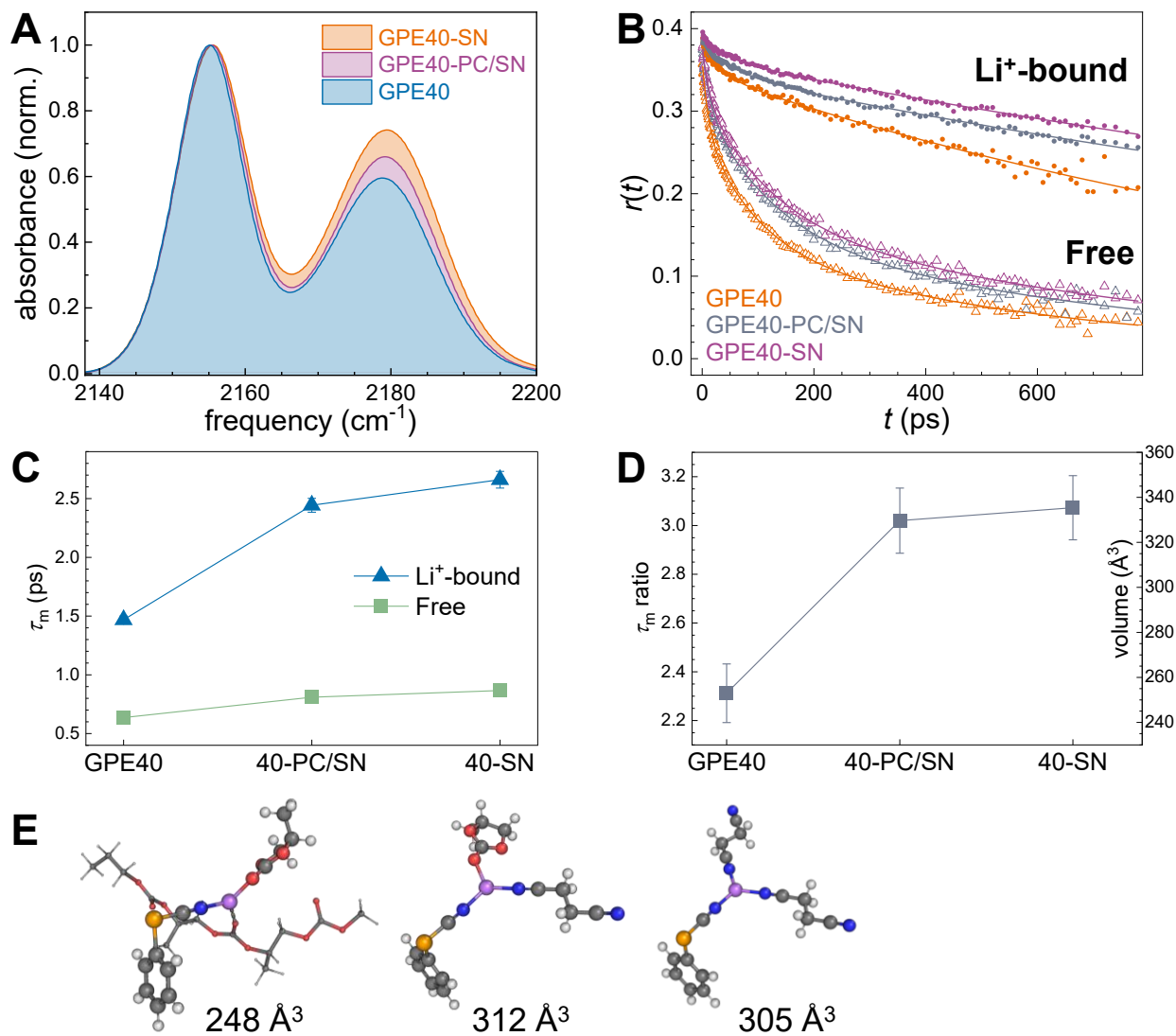


Figure S3.8: **A.** Linear absorption spectra for GPE40, GPE40-PC/SN, and GPE40-SN. **B.** Anisotropy decays for the free PSC peak and the Li^+ -bound peak. **C.** Complete molecular reorientation times determined from $r(t)$. **D.** τ_m ratios comparisons for the three samples. **E.** Solvation structures from DFT calculation and their solvent-excluded volumes.

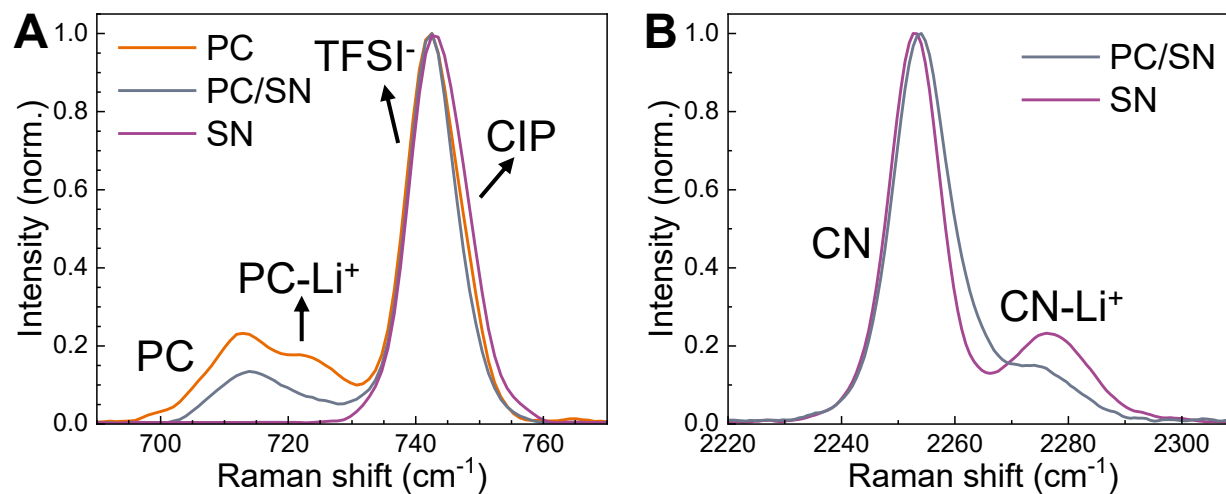


Figure S3.9: **A.** Raman spectra for GPE40, GPE40-PC/SN, and GPE40-SN at the PC and TFSI⁻ peak region. **B.** Raman spectra for GPE40-PC/SN and GPE40-SN at the nitrile mode region.

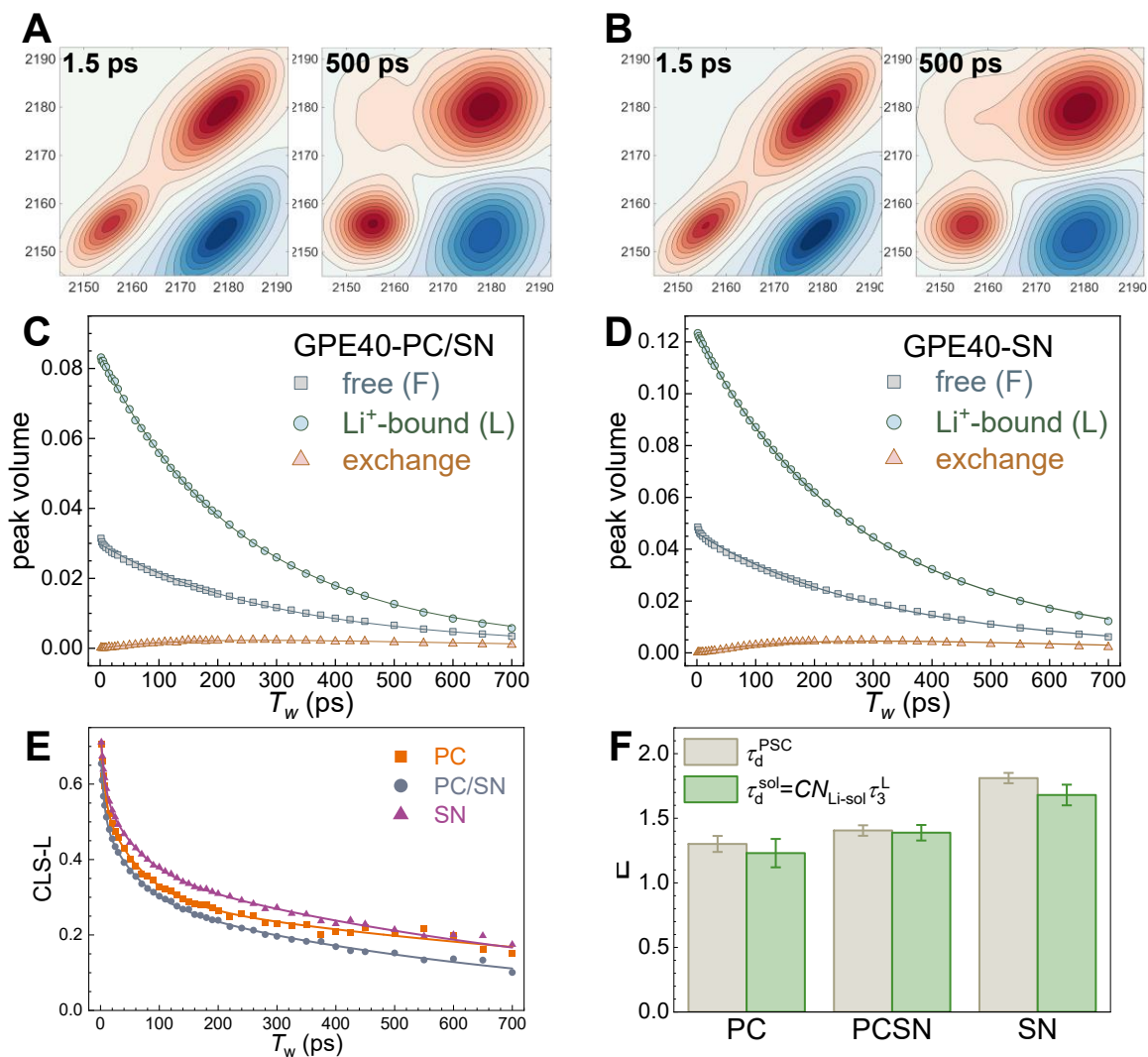


Figure S3.10: **A.** 2D IR spectra for GPE40-PC/SN. **B.** 2D IR spectra for GPE40-SN. **C.** Time-dependent peak volumes from 2D Gaussian fits to the experimental spectra for GPE40-PC/SN. **D.** Time-dependent peak volumes from 2D Gaussian fits to the experimental spectra for GPE40-SN. **E.** Center line slope decay of GPE40, GPE40-PC/SN, and GPE40-SN for the Li⁺-bound peaks (CLS-L). **F.** Comparison between the probe dissociation times extracted via chemical exchange and the solvent dissociation time measured from CLS-L.

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