

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

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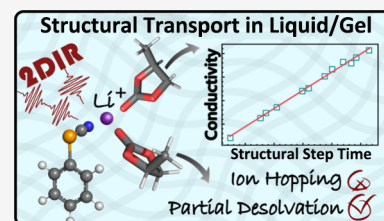


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ABSTRACT: A molecular-level understanding of ion transport is critical for optimizing lithium diffusion in gel polymer electrolytes (GPEs). Using polarization-selective pump-probe and two-dimensional infrared (2D IR) spectroscopy, we quantified lithium solvation structures and desolvation dynamics across the transition from propylene carbonate (PC)/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) liquid electrolytes to GPEs containing up to 60% poly(propylene carbonate) (PPC). Lithium ions remain preferentially coordinated by PC across all compositions, but the Li^+ -PC coordination number ($\text{CN}_{\text{Li-PC}}$) decreases from four to two with increasing polymer, exhibiting a sharp transition near 30% PPC. Li^+ -solvent residence times, extracted independently from 2D IR chemical exchange and spectral diffusion measurements, slow from ~ 500 ps in liquids to ~ 2 ns in 60% GPEs. Strikingly, we find that the residence time, a metric commonly used to quantify structural transport, fails to capture ionic conductivity trends when the coordination environment changes; instead, we introduce a new descriptor, the structural step times (τ_{ss}), which is defined as residence times normalized by $\text{CN}_{\text{Li-PC}}$, capturing the total rate of parallel dissociation pathways available to a lithium cluster. τ_{ss} quantitatively predicts ionic conductivity across both liquid and gel electrolytes, even when salt concentration and polymer fraction are varied independently. These findings show that lithium structural diffusion is initiated by partial desolvation events, not through concerted “hopping” between solvation sites, underscoring the need for caution when invoking ion hopping as the structural transport mechanism in common nonaqueous electrolytes.



1. INTRODUCTION

Lithium-ion batteries (LIBs) are ubiquitous in modern life, powering a wide range of devices, from wearable electronics to electric vehicles. However, conventional liquid electrolytes (LEs) used in LIBs present persistent challenges, including flammability,¹ leakage,² and limited electrochemical stability.³ Gel polymer electrolytes (GPEs), formed by incorporating LEs into polymer matrices, offer a promising route to address these limitations by combining enhanced safety with sufficient ionic conductivity and mechanical integrity. Decades of research have explored various polymer–solvent–salt combinations,⁴ polymer blends or copolymerization,⁵ and gel composite electrolytes,⁶ yet the ionic conductivity of current GPEs still lags behind that of state-of-the-art LEs, unable to meet the strict demands of modern applications.⁷ Therefore, a better understanding of the ion transport mechanism is needed to accelerate the rational design and commercialization of next-generation GPEs.⁸

The current experimental methods for studying structure and transport in GPEs, such as quasi-elastic neutron scattering (QENS),⁹ terahertz spectroscopy,¹⁰ and nuclear magnetic resonance (NMR) based techniques,¹¹ provide valuable evidence but remain limited in their temporal resolution and the ability to resolve ion–solvent interactions at the molecular level for processes like the desolvation dynamics. Ultrafast IR spectroscopy can resolve dynamics from femtoseconds to nanoseconds while offering molecular specificity.^{12,13} Recently,

we developed an ultrafast IR spectroscopy method that provides direct measurements of lithium cluster exchange kinetics and the average solvation structures by resolving distinct vibrational signatures of a long-vibrational-lifetime IR probe, phenyl selenocyanate (PSC).¹⁴ In propylene carbonate (PC) liquid electrolytes containing varying amounts of LiTFSI, our methods revealed that solvent dissociation from the lithium cluster takes several hundred picoseconds to a nanosecond, and lithium diffuses primarily through the structural mechanism.

Lithium transport can occur either through the vehicular mechanism (Figure 1A) or the structural mechanism (Figure 1B).^{15,16} For the vehicular mechanism, lithium ion is carried by the diffusion of the entire first solvation shell, which is influenced by both the bulk viscosity and the size of the solvation shell. The structural mechanism describes ion transport through the exchange of its first solvation shell. While many factors are known to influence structural transport, such as the Li^+ -solvent binding strength and temperature, the

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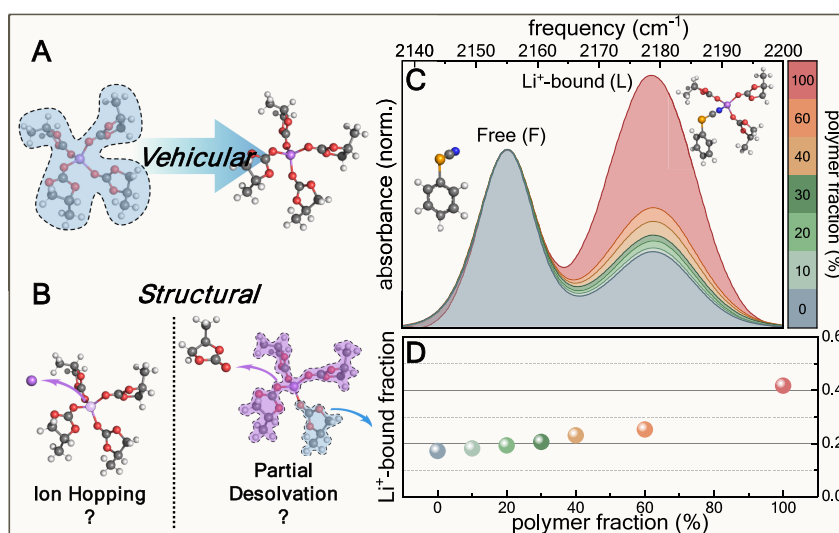


Figure 1. Overview of the lithium transport mechanism and FT-IR spectra. (A) Schematic depiction of vehicular mechanism. (B) Structural mechanism via ion hopping (left) or partial desolvation (right). (C) FT-IR spectra of PSC in PPC/PC/LiTFSI electrolyte containing various amounts of polymer. (D) Li⁺-bound PSC fraction extracted from the FT-IR.

exact molecular processes initiating the structural transport are still not clear.^{15–17} Literature often describes the structural mechanism as ion hopping (Figure 1B left), citing similarity to Grotthuss-type proton hopping in aqueous electrolytes. However, nonaqueous electrolytes do not have the same interconnected hydrogen bonding network as water. Instead, each lithium ion has a discrete solvation shell. Therefore, the occurrence of ion hopping would require the simultaneous dissociation of the entire solvation shell with an extraordinarily high energy barrier. Here, we propose that the structural diffusion occurs through the “partial desolvation” of the lithium cluster, i.e., a single solvent molecule leaves the solvation shell. The partial desolvation causes the remaining cluster to rearrange and find another free solvent, reconstructing the full solvation shell, which causes the lithium to move (Figure 1B right).

In this study, we reveal the molecular-scale picture of the lithium-ion structural mechanism by investigating the transition from LEs to GPEs. Poly(propylene carbonate) (PPC) was chosen as the polymer matrix,^{17–20} and PC/LiTFSI was used as the LE/plasticizer because the polymer and liquid are fully miscible across the entire concentration range. Previously, the dominant transport mechanism of PC/LiTFSI electrolytes was determined to be structural.¹⁴ With the effect of gelation, the viscosity dramatically increases, further decreasing the extent of vehicular transport. Therefore, the structural transport is expected to be the primary ion diffusion mechanism across the entire studied polymer fraction series, making it an ideal system to study the nature of this mechanism. By systematically tuning the molar ratio of PC to PPC monomer, we address the effect of the polymer fraction on the lithium solvation environments and dynamics. We find that increasing polymer content causes CN_{Li-PC} to decrease from ~ 4 in the LE to ~ 2 in the GPE with 60% polymer fraction, with a sharp transition at 30%. Furthermore, the solvent dissociation time, equivalent to the Li⁺-solvent residence time commonly used in molecular dynamics (MD) simulations, slowed down significantly from ~ 500 ps to > 2 ns for polymer fractions ranging from 0 to 60%. Compiling data from the current GPE series and the previously reported PC/

LiTFSI salt concentration series,¹⁴ we find that the commonly used Li⁺-solvent residence time^{15,16,21} is insufficient to predict ionic conductivity when the coordination number changes, revealing a critical gap in the prevailing “ion hopping” interpretation of structural transport. To address this limitation, we introduce the structural step time ($\tau_{ss} = \tau_d^{PC}/CN_{Li-PC}$), which accounts for the parallel desolvation pathway for a multicoordinated solvation cluster. τ_{ss} perfectly predicts the ionic conductivity when two different variables are independently tuned, demonstrating that the fundamental rate-limiting step is single-ligand dissociation rather than concerted hopping. On the basis of τ_{ss} descriptor, we propose a new molecular process, the partial desolvation mechanism, to describe structural diffusion.

Furthermore, we define the electrolyte regimes in which the partial desolvation mechanism applies and demonstrate that τ_{ss} can be used to rationalize the observed ionic conductivity enhancement for mixed PC/succinonitrile (SN) GPEs, relative to each solvent alone. Finally, employing this mechanistic insight, we outline several electrolyte-design principles.

Our findings elucidate the correct molecular origin of lithium structural diffusion and emphasize the critical role of the Li⁺ solvation structures in governing ion mobility. These results advance the fundamental understanding of ion motions in nonaqueous electrolytes and have significant implications in electrolyte design for solvent mixtures and gel polymer electrolytes.

2. RESULTS AND DISCUSSION

2.1. Probing Environment-Specific Dynamics

The choice of vibrational probe is critical for resolving the slow dissociation dynamics of native solvents in lithium electrolytes. The nitrile ($C\equiv N$) stretch of phenyl selenocyanate (PSC) is ideally suited for this purpose due to its long vibrational lifetime (~ 300 ps) and chemical similarity to PC,¹⁴ providing almost a nanosecond observation window.^{9,14} To isolate the effect of polymer content on the evolution of Li⁺ solvation environments and dissociation dynamics, we prepared a series of LiTFSI electrolytes with fixed salt-to-solvent molar ratio (1:6, where solvent = PC + PPC monomer units) and constant

PSC concentration of 250 mM, previously shown not to perturb the native dynamics.¹⁴ Samples are labeled as LE (0% PPC), GPE10–60 (10–60% PPC), and SPE (100% PPC).

In the lithium electrolytes, PSC serves as a site-specific reporter of its local environment. The nitrile stretching mode of free PSC (not a member of a Li⁺ solvation shell) exhibits an inhomogeneously broadened absorption band peaked at $\sim 2155\text{ cm}^{-1}$. Upon coordination with Li⁺, the peak blue-shifts to $\sim 2180\text{ cm}^{-1}$ (Figure 1C). The spectral separation enables us to resolve dynamic observables specific to PSC's environments and the interconversion rate (chemical exchange). The equilibrium populations of these two distinct species can be quantified from their peak areas after accounting for the transition dipole strength difference (Supplementary Note 1).²² Increasing the polymer content shifts the equilibrium toward the Li⁺-bound state, with its fraction increasing from ~ 0.2 in LE to just above 0.4 in SPE (Figure 1D).

To probe dynamics with solvation environment specificity, we employed two complementary ultrafast infrared techniques: PSPP and 2D IR spectroscopy. In PSPP experiments, a linearly polarized (+45°) pump pulse is used to preferentially excite the PSC molecules whose nitrile groups (transition dipoles) are aligned to the pump polarization (Figure 2A). After a variable

2D spectra. First, chemical exchange between free and Li⁺-bound PSC appears as off-diagonal peaks; the temporal evolution of the exchange peaks' volumes quantifies the chemical exchange rates. Chemical exchange between the free PSC and Li⁺-bound PSC directly measures the dissociation rate of the probe. Second, changes in the band shapes track spectral diffusion (frequency-frequency correlations), which reflect dynamics of the solvation environment. For the Li⁺-bound peak, we have previously shown that the slowest spectral diffusion component is directly related to the native solvent's dissociation time.¹⁴ The dissociation time is the central observable for the 2D IR experiments.

2.2. Evolution of Solvation Structures with Polymer Fraction

In LIB electrolytes, the solvation structure of lithium ions is critical to their mobility and, ultimately, to the battery performance.⁹ However, due to overlapping bands and complicated line shapes (Figure S3.1), quantitative determination of the lithium ion solvation structure in GPEs and mixed solvent electrolytes is unattainable with FT-IR or Raman spectra alone.²³ Here, we combine ultrafast IR experimental measurement of Li⁺ clusters' volumes and DFT calculations to determine solvation structures. According to the Stokes–Einstein–Debye (SED) relation, molecular orientation randomization time (τ_m) is proportional to the volume of the rotating body (V) and viscosity (η):²⁴

$$\tau_m^i = V^i \eta / kT \quad (1)$$

where i indicates either the free probe (F) or the lithium cluster (L). Then, the τ_m ratio is the volume ratio:

$$\tau_m^L / \tau_m^F = V^L / V^F \quad (2)$$

The dominant cluster composition is determined by comparing the experimental τ_m ratios to the volume ratio of the Li⁺ cluster and PSC. The volumes are calculated by applying Connolly's solvent-excluded volume algorithm²⁵ to the DFT-optimized solvation structures (with one solvent molecule replaced by the PSC probe). For the cluster with two solvent/PSC coordination (species that can readily dissociate for Li⁺), the structure is optimized along with a PPC trimer, which is used as a model of the local polymer solvation (Figure 3E). The trimer is then removed for the volume calculation, because the polymer chain is too large to rotate and, therefore, is not part of the rotating moiety.

The anisotropy of the free probe, $r^F(t)$, reflects the solvent environments it experiences (Figure 3A). At low polymer fractions (0–20%), $r^F(t)$ is a biexponential decay: a fast (~ 10 –30 ps) component from the solvent caging effects,²⁶ followed by complete reorientation, which is described by the SED equation. As the polymer content increases to 30–60%, interactions with the polymer chains introduce an additional intermediate decay (~ 100 ps), attributed to confinement by the polymer chains.²⁷ At the solid polymer limit (100%), the probe's rotational freedom is severely restricted by the polymer chains, which causes $r(t)$ to decay to a constant offset.²⁷ Thus, the solvent motions are restricted beyond 30% polymer fraction. For the same GPE, Li⁺-bound peak's anisotropy, $r(t)^L$, always decays significantly slower than $r^F(t)$ due to the increased size of the Li⁺ solvation cluster (Figure 3B). $r^L(t)$ remains biexponential throughout, with a fast component (~ 10 –30 ps) reflecting angular fluctuations within the cluster

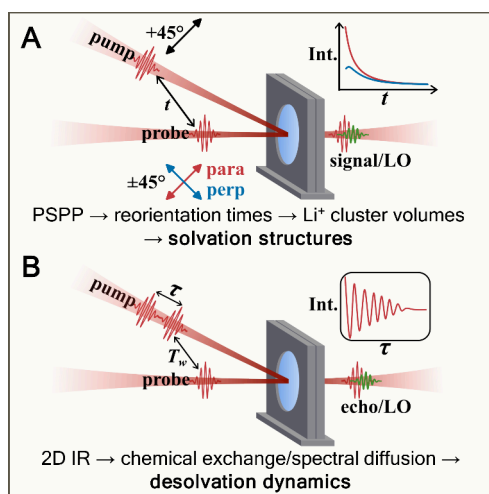


Figure 2. Ultrafast infrared spectroscopy experimental schematics. (A) Illustration of polarization-selective pump–probe spectroscopy and the steps to extract solvation structures. (B) Diagram of 2D IR experiment for measuring desolvation dynamics.

delay time t , a probe pulse measures the transient change in absorbance for both parallel (+45°) and perpendicular (−45°) polarizations. The time delay is systematically scanned to produce decay curves as functions of t . The signal decays are combined to obtain the anisotropy decay, $r(t)$, which reports on the orientational relaxation of PSC. We will use this technique to investigate the lithium cluster reorientation dynamics and compare it to that of the free probe to extract information on the lithium solvation structures.

In 2D IR spectroscopy, two pump pulses separated by a delay (τ) excite the PSC nitrile mode, generating an interferogram that encodes the initial vibrational frequency distribution (Figure 2B). After a variable waiting time (T_w), a probe pulse stimulates the emission of an echo pulse, which encodes the final distribution of frequencies, yielding 2D spectra that reflect the frequency evolution of probe molecules. Two types of dynamics are extracted from the time-dependent

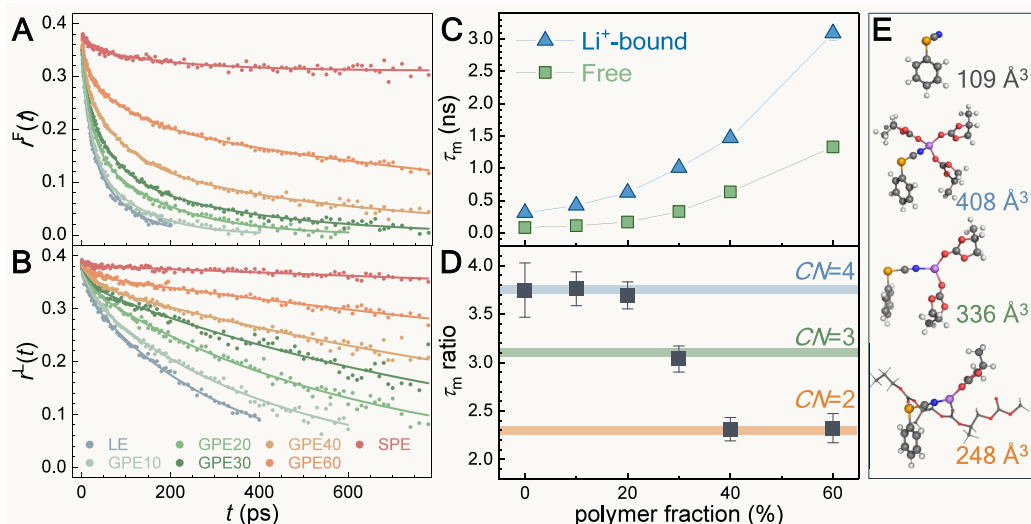


Figure 3. Solvation structures determined from PSPP spectroscopy. (A) Anisotropy decays of free probes and (B) anisotropy decays of Li⁺-bound probes in liquid electrolytes and GPEs with different polymer fractions. (C) Complete molecular reorientation times for free and Li⁺-bound probes in each sample. (D) τ_m ratio as a function of polymer fractions. The colored bars represent the cluster to free PSC volume ratio for different coordination numbers. (E) DFT-optimized cluster structures and their solvent-excluded volumes.

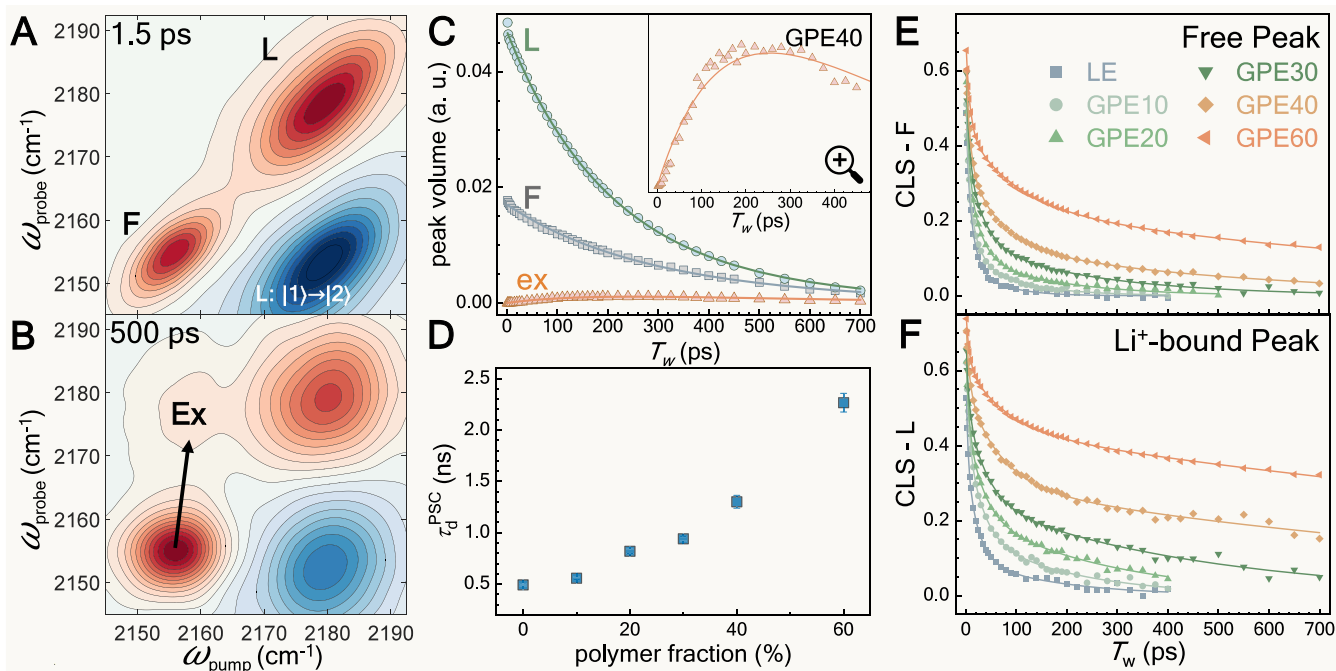


Figure 4. Characterizing desolvation times from 2D IR experiments. (A) 2D IR spectra of GPE40 at 1.5 ps. (B) 2D IR spectra of GPE40 at 500 ps. (C) Time-dependent 2D volumes as a function of T_w for the free peak, Li⁺-bound peak, and exchange peak. The inset shows the zoomed-in exchange peak trace. (D) PSC dissociation times determined from the 2D volumes. (E) CLS decays for the free peak in each sample. (F) CLS decay for the Li⁺-bound peak in each sample. The slowest decay component is caused by solvent dissociation events.

and a slower component corresponding to complete reorientation of the entire Li⁺-solvent complex.

To determine τ_m , $r(t)$ are analyzed using the well-established wobbling-in-a-cone model with bi- or triexponential forms.^{28,29} The slowest component (τ_m) of both peaks slows by almost an order of magnitude when transitioning from LE to GPE60 (Figure 3C), which reflects the increase in viscosity caused by gelation. The τ_m ratio (Li⁺-bound/free) displays a sharp transition between 20 and 40% polymer (Figure 3D), which coincides with the emergence of polymer confinement effects

in $r^F(t)$, suggesting the change in coordination number could be caused by the polymer confinement.

The τ_m ratios are then translated to lithium solvation structures by comparing to volume ratios between lithium solvation clusters and PSC. In dilute PC electrolytes, Li⁺ is typically coordinated to four PC molecules,^{14,30} forming a cluster with a volume of 408 Å³, versus 109 Å³ for PSC (Figure 3E). Taking the volume ratio yielded 3.74, consistent with the τ_m ratio for LE, GPE10, and GPE20. Similarly, the τ_m ratio of GPE30 matches the volume ratio of the triple-coordinated

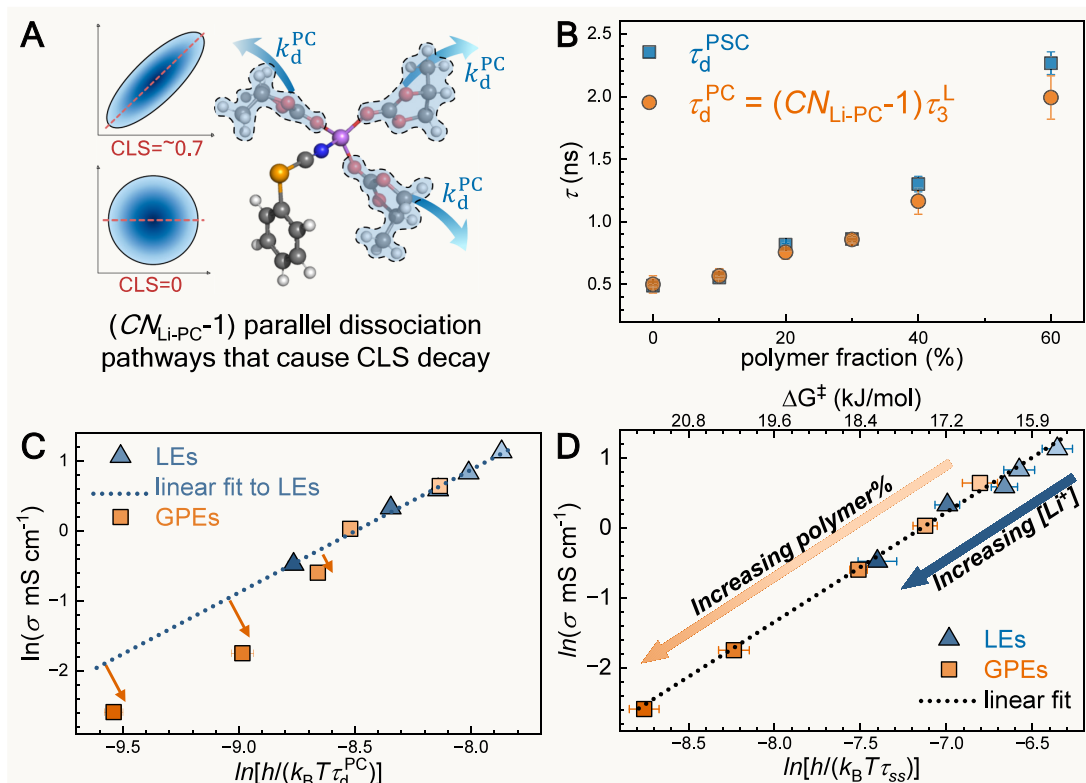


Figure 5. Relationship between ionic conductivity and desolvation times. (A) Schematic illustration of the parallel dissociation pathways that could cause CLS decays. (B) PSC dissociation time measured from chemical exchange is the same as the PC dissociation time from spectral diffusion analysis. (C) Relation between ionic conductivity and PC dissociation time on a natural log scale. Deviation from the LE trend happens when the CN_{Li-PC} changes. (D) Relation between ionic conductivity and structural step time. The top axis displays the corresponding energy at 295 K. A consistent trend is observed across the GPE polymer fraction series and the LE salt concentration series.

lithium cluster to free PSC. For GPE40 and GPE60, CN_{Li-PC} decreased further to 2.

The presence of contact ion pairs (CIP) can modestly increase cluster volume because TFSI⁻ is larger than PC. However, Raman spectra (Figure S3.1) show only a minor CIP contribution, indicating solvent coordination dominates the cluster structure. For high polymer-fraction GPEs (GPE40 and 60), coordination to the polymer chain can occur and affect how the lithium clusters undergo orientational relaxation. In this case, the lithium clusters can rotate around the Li⁺...O=C (polymer) axis. As discussed in more detail in Supplementary Note 2, the coordination to the polymer chain does not affect our solvation shell structure assignment, which involves species that can readily dissociate.

2.3. Structural Transport Is Caused by Partial Desolvation

To investigate solvent dissociation dynamics (Li⁺ desolvation), we performed 2D IR experiments to examine the chemical exchange kinetics between free and Li⁺-bound PSC, as well as their spectral diffusion dynamics. At an early waiting time (1.5 ps) (Figure 4A), the 2D IR spectrum exhibits two positive diagonal peaks corresponding to free PSC (F) and Li⁺-bound PSC (L) populations, as also seen in the FT-IR (Figure 1C). Only the GPE40 spectra are shown here as an example; the rest are given in Figure S3.2. The negative off-diagonal peak originated from the |1⟩→|2⟩ vibrational transition of the L population. By 500 ps (Figure 4B), a new off-diagonal “exchange” peak appears on the upper left, caused by F→L species conversion.¹⁴

We modeled each peak as a 2D Gaussian,³¹ and six peaks were required to reproduce the experimental spectrum, allowing us to determine the time-dependent peak volumes and shapes (see Supplementary Notes 3). As demonstrated by the low amplitude residuals (Figure S3.3), the fitted spectrum reproduces the experimental one extremely well. Then, the three sets of time-resolved volumes were fit to the exchange kinetic equations^{14,31} to obtain the time constants (Figures 4C and S3.4). The L→F exchange time is the PSC dissociation time (τ_d^{PSC}), which has been shown to be almost identical to PC dissociation time by DFT calculations and MD simulations.¹⁴ This will be further corroborated by the spectral diffusion data presented below. Upon adding polymers, τ_d^{PSC} slows down significantly from ~500 ps to ~2 ns (Figure 4D). Even at 2 ns, this time scale is still orders of magnitude faster than the segmental relaxation time of the polymer chains (μs-ms),³² demonstrating that lithium transport is caused by solvent dissociation, decoupled from the ultraslow polymer dynamics.

A distinct 2D IR observable from chemical exchange, spectral diffusion tracks the time evolution of vibrational frequency correlation that occurs between pump (ω_{pump}) and probe (ω_{probe}) pulse times. It is quantified by the frequency-frequency correlation function (FFCF),³³ which we extracted from the time dependence of the 2D lineshapes using the center line slope (CLS) method.³⁴ The influence of the overlapping bands is eliminated using a method described previously (isolated peaks shown in Figure S3.5).^{14,31} Because PSC exists in two environments, we separately analyze CLS decays for the free (CLS-F, Figure 4E), and the Li⁺-bound

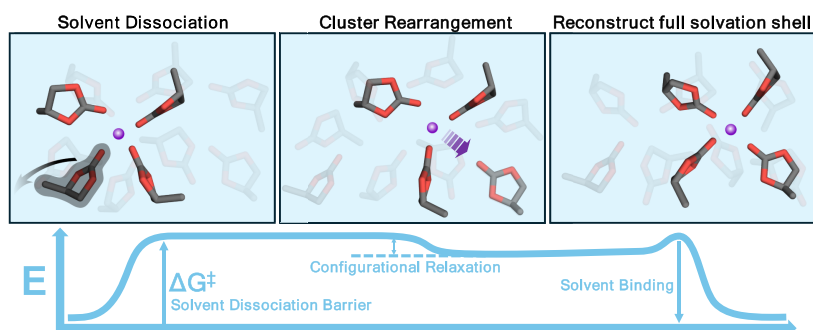


Figure 6. Illustration of ion diffusion through the partial desolvation mechanism and the associated diagram for each step. The energy scale is arbitrary and is shown for concept demonstration only.

peak (CLS-L, Figure 4F). In every sample, CLS-L decays more slowly than CLS-F, indicating the Li^+ -bound probe's spectral diffusion dynamics are highly shielded from the influence of the free solvent environment. Furthermore, the $\text{C}\equiv\text{N}$ group points toward the lithium and is physically isolated from the outside by the phenyl-Se group (Figure 5A). The CLS-L decays are triexponential functions, and the slowest decay component (τ_3^{L}) is caused by the solvent dissociation processes¹⁴ (detailed discussions of other decay components and CLS-F are provided in Supplementary Note 4). A careful examination of the exact observed process provides critical information. In Figure 5A scheme, for a four-coordinated Li^+ cluster, each of the three PC could independently dissociate at a rate (k_{d}^{PC}), leading to loss of frequency correlation (CLS decay). Additionally, PSC must remain attached to the cluster for the process to be observed, resulting in three leaving pathways that affect the data. Therefore, τ_3^{L} measures the total solvent dissociation rate for the coordination number minus one ($\text{CN}_{\text{Li-PC}} - 1$) number of pathways. The PC desolvation time can be calculated as follows: $\tau_{\text{d}}^{\text{PC}} = (\text{CN}_{\text{Li-PC}} - 1)\tau_3^{\text{L}}$. Using this analysis, $\tau_{\text{d}}^{\text{PC}}$ from spectral diffusion dynamics matches $\tau_{\text{d}}^{\text{PSC}}$ from chemical exchange almost perfectly (Figure 5B), further validating the accuracy and interpretation of the measurements.

To establish the relation between desolvation times and ionic conductivity, each dissociation event can be modeled as an activated process. The corresponding time can be expressed by the Eyring equation:³²

$$\frac{1}{\tau} = \frac{k_{\text{B}}T}{h} \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) \quad (3)$$

where τ is the time constant for the desolvation process, and $\Delta G^{\ddagger}$ is the energy barrier. Independently, the ionic conductivity (σ) for the structural mechanism has been described by the empirical Arrhenius equation:³⁵

$$\sigma = \sigma_0 \exp\left(\frac{-E_{\text{a}}}{RT}\right) \quad (4)$$

where σ_0 is the pre-exponential factor, and E_{a} is the activation energy for lithium diffusion. If we assume the $\Delta G^{\ddagger}$ for the desolvation is the activation energy (E_{a}) required for ion transport, we can take the natural log of both equations, and establish a relation between the time constant and ionic conductivity:

$$\ln \sigma = \ln \sigma_0 + \ln\left(\frac{h}{k_{\text{B}}T\tau}\right) \quad (5)$$

where $\ln(h/k_{\text{B}}T\tau) = -\Delta G^{\ddagger}/RT$ is unitless and quantifies the activation energy for ion diffusion. If our prior assumption holds, a linear relation between $\ln \sigma$ and $\ln(h/k_{\text{B}}T\tau)$ should be observed. The important question here is which time constant should be substituted into eq 5. One choice is the dissociation time, $\tau_{\text{d}}^{\text{PC}}$; however, this implicitly assumes that the lithium simultaneously dissociates from the entire solvation cluster and hops into another site, since $\tau_{\text{d}}^{\text{PC}}$ is observed from the perspective of a particular solvating molecule, without consideration of the total Li^+ coordination structure. Another option is to consider the time constant from Li^+ 's perspective. For an n -coordinated cluster, any of the n solvating species can dissociate, resulting in n pathways for dissociation from the Li^+ . Since each pathway contributes to structural diffusion independently, the corresponding time constant will be n times faster than $\tau_{\text{d}}^{\text{PC}}$. Here, we define the characteristic time for any of the solvation shell species to dissociate as the structural step time $\tau_{\text{ss}} = \tau_{\text{d}}^{\text{PC}}/\text{CN}_{\text{Li-PC}}$. Compiling the 5 GPEs investigated in this work (orange) along with the 5 PC/LiTFSI liquid electrolytes with different salt concentrations, where structural mechanism also dominates¹⁴ (blue), we plotted the relation using both $\tau_{\text{d}}^{\text{PC}}$ (Figure 5C) and τ_{ss} (Figure 5D). The conductivities on the normal scale are given in Figure S3.6.

In Figure 5C, all five LEs follow a linear trend, with GPE10 and GPE20 overlapping this line. Deviation from the LE line happens at GPE30, with GPE40 and GPE60 deviating further from the line while retaining a similar slope. In PC/LiTFSI liquid with different salt concentrations, the Li^+ is coordinated by four species.¹⁴ From our analysis of the solvation structures (Figure 3D), GPE10 and 20 retain the coordination of four; GPE30 has a coordination of three; and GPE40 and 60 have a coordination number of two. These changes in $\text{CN}_{\text{Li-PC}}$ perfectly coincide with the deviation from the line. Despite two completely different variables (LiTFSI concentration and polymer fraction) being altered, because $\text{CN}_{\text{Li-PC}}$ is accounted for in τ_{ss} , all of the data fall on a single line in Figure 5D, confirming the assumption made above in eq 5. This evidence strongly demonstrates that Li^+ transport in both LEs and GPEs is initiated by partial cluster desolvation, not concerted hopping to a neighboring solvation site. In the following sections, we examine the molecular processes underlying the partial desolvation mechanism, its range of applicability, and its broader implications. We also show that this mechanism extends to GPEs plasticized with a different solvent, succinonitrile (SN), and that it explains why plasticization with a PC/SN mixture yields higher conductivity than either PC or SN alone.

2.4. Proposed Molecular Process and Applicability of Partial Desolvation Mechanism

Partial desolvation describes a structural transport mechanism in which Li^+ diffusion is driven by a sequence of individual solvent dissociation and rebinding events rather than by concerted ion hopping. As illustrated in Figure 6, the process begins with the rate-limiting step where one solvent molecule in the first solvation shell overcomes its binding free-energy barrier ($\Delta G^\ddagger$) and dissociates from the cluster. Following dissociation, the partially desolvated cluster undergoes structural relaxation to form a lower-energy intermediate configuration (middle panel). The structural rearrangement causes the Li^+ to move to a new position. The change in position is one step in the random walk that is responsible for structural diffusion. A free solvent molecule then overcomes a small rearrangement barrier and binds to the cluster, restoring the full solvation shell (right panel).

For high PPC fractions GPEs (40–60%), coordination to polymer carbonyl is expected, but several lines of evidence indicate that such coordination neither changes the transport mechanism nor participates in the structural transport. First, DFT calculations show that Li^+ binds significantly more strongly to PC than to PPC (Figure S3.7b), meaning that dissociation of a PC imposes the highest energetic barrier within the solvation shell. Second, the polymer segmental relaxation time lies in the microsecond-millisecond range,³² orders of magnitude slower than the ~ 1 ns solvent dissociation steps we measured. Thus, polymer motion cannot initiate Li^+ transport on the relevant time scale. Third, despite the increased probability of polymer coordination at high PPC content, GPE40 and GPE60 fall precisely on the same τ_{ss} -conductivity trend as the liquid electrolytes (Figure 5D). This indicates that the rate-limiting step remains solvent dissociation, and that any Li^+ -polymer coordination is efficiently broken during these events.

Partial desolvation is the correct description of structural diffusion in liquid electrolytes and GPEs, and is distinct from the ion hopping model. Ion hopping is the appropriate description in solid electrolytes, e.g., ceramics and polymer glasses, in which there is no significant fast structural relaxation. Partial-desolvation-driven diffusion differs from the ion hopping in liquids descriptions in several critical aspects. First, the energy barrier for partial desolvation corresponds to breaking a single Li^+ -solvent coordination bond, whereas ion hopping would require the concerted rupture of the entire solvation shell, which has a prohibitively high energetic cost. Second, in the partial-desolvation picture, each coordinating species provides a parallel dissociation pathway, so the overall rate reflects the sum of these routes. Third, partial desolvation naturally allows each coordinating molecule to exhibit a distinct dissociation time, as the strength of any individual Li^+ -solvent interaction depends on the overall electron-withdrawing environment created by the remaining ligands. In contrast, a true hopping mechanism would require all solvating molecules to dissociate simultaneously and therefore share the same dissociation time. The third point has important consequences for rationalizing the observed changes in conductivity in mixed solvent electrolytes.

The partial desolvation mechanism would apply when the cations in the electrolytes form distinct solvation shells. Many commonly used electrolytes with organic solvents, such as nitriles, carbonates, and short-chain ethers, fall into this category.^{36–38} For GPEs, the partial desolvation mechanism

will apply if the added LE/plasticizer molecules bind more strongly to the Li^+ than the polymer functional groups, forming solvent/anion-dominated solvation shells. These electrolytes are in contrast to systems like crystalline inorganic ion conductors that have well-defined defect vacancies for ion hopping to occur.³⁹ Lithium hopping is often compared to proton hopping in aqueous acid solutions (Grotthuss mechanism).⁴⁰ In the Grotthuss mechanism, a proton moves from a hydronium cation to water. The water then becomes a hydronium, and any of the three hydrogens on this new hydronium cation can take the next hop. So, even the identity of the hopping cation is not preserved. Therefore, the hopping mechanism of ions like Li^+ or Na^+ should not be associated with proton hopping in acid solutions.

To demonstrate that the partial-desolvation framework is not limited to carbonate electrolytes and to further test whether τ_{ss} reliably predicts structural diffusion, we replaced PC in GPE40 with either succinonitrile (GPE40-SN) or a 1:1 PC/SN solvent mixture (GPE40-PC/SN). The solvent dissociation times ($\tau_{\text{d}}^{\text{sol}}$) were obtained from their spectral diffusion dynamics using the CLS analysis (τ_3^{sol}).

As shown in Figure 7A, the solvent dissociation time ($\tau_{\text{d}}^{\text{sol}}$) slows down with increasing SN content. The orientation

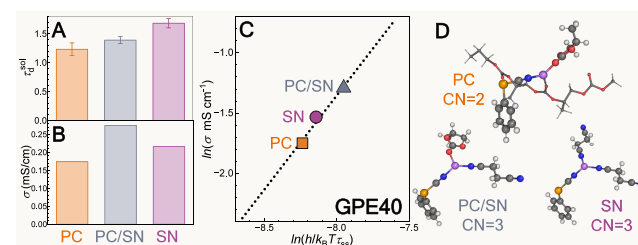


Figure 7. GPE40 plasticized with PC, an even mixture of PC/SN, and SN. (A) Comparison of solvent dissociation time (Li-solvent residence time). (B) Ionic conductivities do not track the prediction from the solvent dissociation time. (C) Both GPE40-PC/SN and GPE40-SN fall on the same linear trend from Figure 5D. (D) DFT-optimized solvation structures for GPE40, GPE40-PC/SN, and GPE40-SN.

relaxation times also follow the same trend (Figure S3.8B), consistent with the higher local viscosity of SN-rich environments. However, the measured ionic conductivities follow a different order: GPE40-PC/SN > GPE40-SN > GPE40 (Figure 7B). This trend agrees with earlier reports in similar GPE systems, where plasticization by mixed PC/SN solvents yields higher conductivity than either solvent alone.⁴¹ Yet the conventional metric, such as $\tau_{\text{d}}^{\text{sol}}$ and viscosity, predicts that GPE40 should exhibit the highest conductivity and GPE40-SN the lowest, which is incorrect. The resolution lies in the solvation structure. Both GPE40-SN and GPE40-PC/SN maintain a solvent coordination number of three (Figure 7D, detailed discussion given in Supplementary Note 5), whereas GPE40 retains only two. When τ_{ss} is computed by normalizing $\tau_{\text{d}}^{\text{sol}}$ by the coordination number, a consistent picture emerges: the mixed-solvent system has slower single-pathway dissociation but more total dissociation pathways, explaining its enhanced structural transport and conductivity. As shown in Figure 7C, using τ_{ss} produces the correct ordering of the conductivities. Furthermore, both SN-containing samples fall on the same trend line established in Figure 5D.

2.5. Implications for Electrolyte Design

The identification of partial desolvation as the mechanism for lithium ion structural diffusion shows that ion hopping in most instances is not the correct mechanism in liquid electrolytes and GPEs, although it is frequently invoked in the literature. This realization leads to several possible electrolyte design considerations for improving Li^+ conductivity in liquid and gel polymer electrolytes. First, maintaining a high coordination number to maximize desolvation pathways. For the partial desolvation mechanism, each coordinating molecule provides a parallel route for a structural step, so the overall exchange rate increases with the number of dissociable ligands. Electrolytes that preserve a high coordination number provide more dissociation routes and result in faster Li^+ diffusion. This principle highlights the importance of selecting solvents and polymer combinations that sustain a solvent-rich solvation shell, even at high polymer fractions. Strategies include using compact solvents with high dielectric constant to stabilize multisolvant coordination, employing cosolvent mixtures to increase entropic stabilization of the solvation shell, selecting polymers that weakly interact with Li^+ , and engineering high-free-volume polymers to facilitate forming solvent-rich domains.

Second, strong-binding additives can be used to asymmetrically tune the dissociation energy barrier. The barrier for partial desolvation reflects the strength of a single Li^+ -ligand interaction rather than the total solvation-shell binding energy. A strongly binding additive can localize the charge to one coordination site, selectively weakening the Li^+ interactions with the remaining ligands. This effect lowers the activation barrier for individual dissociation steps and can accelerate structural transport even if the additive itself binds strongly, provided the increased rate of single desolvation is sufficiently large to offset the loss of one pathway.

Third, selecting solvents and anion combinations with the appropriate donor number (DN). Long-lived ion pairs have been shown to increase cooperative motion between cation and anion, thereby decreasing the ionic conductivity.⁴² DN represents a molecule's ability to donate electrons and is generally associated with the strength of the interaction with the cations. By selecting solvents to match or slightly exceed the anion's donor number, the ion pair lifetime could be systematically tuned. However, the solvent should not vastly exceed anion's solvating strength as to totally exclude it from the solvation clusters, since anion-rich solvation shell structure has been linked to the formation of a better solid electrolyte interphase (SEI).⁴³ This is supported by the superior performance of matching high DN anions like LiNO_3 and lithium triflate with moderate DN solvent.^{44,45}

As discussed above, partial desolvation initiates the structural transport in systems that form segregated solvation shells because the departure of a single dissociable moiety has a lower energy barrier than simultaneously breaking several coordination bonds. Ion hopping can occur when full solvation shells do not form. In this situation, the key is the availability of nearby solvation sites. When the local landscape provides a dense manifold of accessible solvation sites, the effective barrier for hopping is reduced. Li^+ can begin to coordinate to the next site before fully dissociating from the previous one.³⁹ Therefore, multidentate solvents⁴⁶ or anions that can form an extended ion network with a high concentration of solvation sites are likely to promote ion hopping. As suggested by the SI Figure S3.7, complete bond breaking happens at $\sim 3\text{--}4$ Å

separation in the absence of other interactions, implying any new coordination site must remain within this distance to facilitate concerted hopping.

These principles establish a foundation for rational electrolyte design. By explicitly engineering the coordination environment of the solvation shell, electrolyte optimization can progress beyond empirical trial-and-error toward a predictive framework grounded in the first-principle understanding of molecular transport.

3. CONCLUDING REMARKS

In conclusion, we investigated the PC/PPC/LiTFSI GPEs with polymer fractions from 10 to 60% to reveal how the solvation cluster composition is modified, as well as how the desolvation time evolves with increasing polymer fractions. The total lithium solvent coordination number was reduced from four to two, while the solvent dissociation time (Li^+ -solvent residence time) increased from ~ 500 ps to ~ 2 ns. The change in coordination number occurs at 30% polymer fraction, coinciding with the appearance of the polymer confinement effect experienced by the probe. Furthermore, it was found that the Li^+ -solvent residence time alone does not predict the ionic conductivity; instead, we define a new quantity called the structural step time, τ_{ss} , which is the residence time divided by the lithium coordination number. τ_{ss} is the characteristic time for any of the dissociable moieties to break from a Li^+ solvation shell, initiating a step in the structural diffusion.

τ_{ss} accurately predicts the ionic conductivity across the PC/LiTFSI LEs and PC/PPC/LiTFSI GPEs, even though both lithium salt concentration and polymer fraction are altered independently. The fact that this trend only holds if the lithium coordination number is accounted for demonstrates that lithium structural diffusion occurs through partial desolvation events rather than the traditional picture of "hopping" between solvation sites. Therefore, each solvating molecule can independently drive lithium diffusion, highlighting the Li^+ coordination number as a variable that should be considered when designing LIB electrolytes. We further demonstrate that τ_{ss} correctly explains why the ionic conductivity in PPC-based GPEs is higher when plasticized by a mixture of SN and PC compared to plasticization by either solvent alone. Despite their surface-level similarity, the two structural transport mechanisms arise from fundamentally different molecular processes and therefore have distinct rate-limiting steps. Ion hopping relies on the availability of nearby solvation sites and the overall binding strength of the entire lithium solvation shell.⁴⁷ In contrast, partial-desolvation-driven structural diffusion has contributions from multiple independent pathways with lower activation energy. Our results show that hopping is less prevalent in typical nonaqueous electrolytes than previously assumed and that partial desolvation provides a more accurate and generalizable description of structural ion transport in liquid and gel electrolytes. By pinpointing the molecular motions that govern macroscopic conductivity, our findings can guide predictive design and optimization for next-generation lithium-ion batteries.

■ ASSOCIATED CONTENT

Data Availability Statement

All data supporting the analysis and conclusions of this work are presented within the main article and its Supporting

Information files. Further data is available upon request from the corresponding author.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.5c18290>.

Experimental methods; supplementary notes 1–5: transition dipole strength, orientational diffusion for high-polymer-fraction GPEs, fitting 2D spectra, detailed explanation of CLS decay components, discussions of GPE40-PC/SN and GPE40-SN data; Raman spectra for GPE10-60; complete 2D IR spectra; fitted 2D spectra and residuals; complete T_w -dependent peak volumes from 2D fits; peak subtraction for isolating free and Li^+ -bound peaks; ionic conductivity of liquid and gel polymer electrolytes; DFT-optimized solvation structure with 2 PC and PPC trimer; FT-IR and PSPP data for SN-plasticized GPEs; Raman spectra for SN-plasticized GPEs; and 2D IR data for SN-plasticized GPEs (PDF)

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Notes

The authors declare no competing financial interest.

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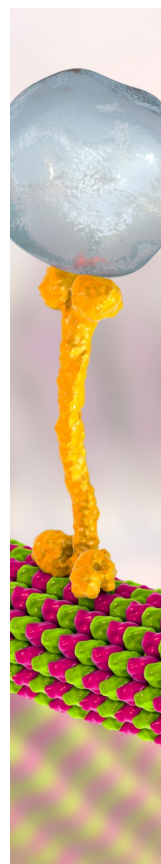
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