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Solvation structure around the Li⁺ ion in succinonitrile–lithium salt plastic crystalline electrolytes†

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Herein, we discuss the study of solvation dynamics of lithium–succinonitrile (SN) plastic crystalline electrolytes by ultrafast vibrational spectroscopy. The infrared absorption spectra indicated that the CN stretch of the Li⁺ bound and unbound succinonitrile molecules in a same solution have distinct vibrational frequencies (2276 cm⁻¹ vs. 2253 cm⁻¹). The frequency difference allowed us to measure the rotation decay times of solvent molecules bound and unbound to Li⁺ ion. The Li⁺ coordination number of the Li⁺–SN complex was found to be 2 in the plastic crystal phase (22 °C) and 2.5–3 in the liquid phase (80 °C), which is independent of the concentration (from 0.05 mol kg⁻¹ to 2 mol kg⁻¹). The solvation structures along with DFT calculations of the Li⁺–SN complex have been discussed. In addition, the dissociation percentage of lithium salt was also determined. In 0.5 mol kg⁻¹ LiBF₄–SN solutions at 80 °C, 60% ± 10% of the salt dissociates into Li⁺, which is bound by 2 or 3 solvent molecules. In the 0.5 mol kg⁻¹ LiClO₄–SN solutions at 80 °C, the salt dissociation ratio can be up to 90% ± 10%.

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1. Introduction

Batteries based on Li⁺ have been powering our daily digital life for many years.¹ The characteristics of combining high energy density with excellent charge retention have led to this success.² Despite the efficient lithium ion batteries currently available; there are still numerous shortcomings of liquid electrolytes (leakage, flammability, and toxicity).^{3,4} Consequently, considerable efforts have been focused on finding alternative electrolytes. An ideal electrolyte would be solid while maintaining the good transport properties of liquid electrolytes. However, most solid electrolyte systems do not perform as well as liquids at room temperature.⁵ Materials known as “plastic crystals” have interesting properties that may help achieve these contradictory requirements.⁵

Succinonitrile, N≡C–CH₂–CH₂–C≡N (SN), is one of the well-known organic plastic crystal materials, which can be used as an excellent solvent for dissolving a wide range of salts. It has been the subject of several studies due to its possible use as a matrix

for ionic conductors^{2,4,6} and forming a solid-state electrolyte for use in power sources similar to polymer-based electrolytes.⁷ Succinonitrile exhibits plastic crystal phase formation in a body centred cubic structure at temperatures between –30 and 60 °C.^{8–11} The crystal phase takes a monoclinic structure and shows the first-order transition to the plastic phase at –30 °C.¹¹ In the liquid and plastic crystal forms, succinonitrile exists in rotational isomers: *gauche* and *trans*.^{11–13} The proportion of the *trans* isomer in pure succinonitrile at room temperature is 23% and increases slightly as a function of temperature.⁸ Moreover, a higher salt content results in higher degree of disorder and faster conformational dynamics.¹⁴ However, at temperatures below –30 °C, only the *gauche* form exists.^{12,15} When doped with lithium salt, the plastic crystal range will be changed.²

SN is nonconducting at ambient temperatures.¹⁶ Because of its nonionicity and high polarity, SN forms a promising solvent for generation of solid ionic conductors with high ionic conductivity. The salt–SN electrolytic systems are conducting in the plastic solid of SN due to the presence of orientational disorder.^{14,16} In the molten phase, ion conduction mechanism is similar to that of a liquid solvent such as acetonitrile.¹⁷ In order to design this novel material to improve the conductivity of Li⁺, knowledge about how Li⁺ is solvated by succinonitrile molecules is indispensable. The X-ray diffraction experiments confirm that the parasitic phases in the LiPF₆ and LiClO₄ plastic crystal electrolytes were 1:2 salt: succinonitrile adduct.⁵ However, there is limited knowledge about the solvation of lithium with succinonitrile in the molten phase.

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Although the ion conduction mechanism of Li^+ -SN in the molten phase is similar to that in acetonitrile, the solvation dynamics are quite different. The existence of *trans* and *gauche* isomers in SN complicates the solvation structure of the lithium ion. In this study, we will focus on the solvation dynamics of Li^+ -SN in the plastic solid phase and molten phase.

In a previous study, we presented an approach for the direct determination of Li^+ coordination number in nonaqueous electrolyte solutions, which is under conditions that are close enough to the actual environments of applications.¹⁷ The method is based on the Stokes-Einstein equation in which the rotation diffusion time constant is proportional to the volume of the molecules. Thus, the volume ratio of free solvent and Li^+ -bound complex can be determined by measuring the rotational time constants of the same vibrational mode of free and Li^+ -bound solvent molecules in the same solutions. Therefore, the coordination number of Li^+ can be obtained straightforwardly from a comparison between the volume ratio of free solvent and Li^+ -bound complex. In this study, we applied the same method to determine the Li^+ coordination number of the lithium with succinonitrile crystalline electrolytes.

2. Experimental methods

The experimental setup has been described elsewhere.^{17–21} Briefly, the output of one oscillator is divided into two beams entering a picosecond amplifier and a femtosecond amplifier. The picosecond amplifier (~ 2.8 mJ per pulse) pumps an optical parametric amplifier (OPA) plus non-collinear difference frequency generator (NDFG) system to produce ~ 1.4 ps (vary from 1.0–1.5 ps in different frequencies) mid-IR pulses with a bandwidth ~ 15 cm^{-1} in a tunable frequency range from 500 to 4000 cm^{-1} with energy of 1–40 μJ per pulse at 1 kHz. The femtosecond amplifier (2.8 mJ per pulse) pumps another OPA and NDFG system to produce ~ 140 fs mid-IR pulses with a bandwidth ~ 200 cm^{-1} over a tunable frequency range from 500 to 4000 cm^{-1} with energy of 1–40 μJ per pulse at 1 kHz. In the pump-probe experiments, the ps IR pulse is the excitation beam and the excitation power is adjusted based on need. The fs IR pulse is the probe beam that is frequency resolved by a spectrograph yielding the ω_m axis

of a 2D spectrum. Scanning the pump frequency yields the ω_τ axis of the spectrum. Two polarizers are inserted into the probe beam pathway to selectively measure the parallel or perpendicular polarized signal relative to the pump beam. The entire system is computer controlled. The vibrational lifetimes are obtained from the rotation-free signal, $P_{\text{life}} = P_{\parallel} + 2 \times P_{\perp}$, where P_{\parallel} and P_{\perp} are the parallel and perpendicular data, respectively. The rotational relaxation times were acquired from $R = (P_{\parallel} - P_{\perp}) / (P_{\parallel} + 2 \times P_{\perp})$.

Succinonitrile and lithium perchlorate (LiClO_4) were purchased from ACROS ORGANICS. Lithium hexafluorophosphate (LiPF_6) and lithium tetrafluoroborate (LiBF_4) were purchased from Alfa Aesar. Lithium salts were dried in a vacuum oven with P_2O_5 and the solutions at 80 $^\circ\text{C}$ were prepared in a glove box. The samples were contained in a sample cell composed of two CaF_2 windows separated by a Teflon spacer. The thickness of the spacer was adjusted accordingly to the optical densities. All the experiments conducted at 80 $^\circ\text{C}$ were achieved by a temperature controller connected to separate heater and sample thermocouples.

The structures of the Li^+ bound SN complexes were determined by density functional theory (DFT) calculations.²² The DFT calculations were carried out as implemented in the Gaussian 09 program suite. The level and basis set used were Becke's 3-parameter hybrid functional combined with the Lee-Yang-Parr correction functional, abbreviated as B3LYP, and 6-311++G(d,p). B3LYP is appropriate here because it has successful applications in the geometry optimization of numerous structures that contain metallic element and organic molecules.²³ All results reported here do not include the surrounding solvent and therefore are for the isolated molecules.

3. Results and discussions

A. Fourier transform infrared (FTIR) studies

Fig. 1A and B show the FTIR spectra of succinonitrile (SN), 0.5 mol kg^{-1} LiBF_4 -SN, 1 mol kg^{-1} LiBF_4 -SN, and 2 mol kg^{-1} LiBF_4 -SN at room temperature and 80 $^\circ\text{C}$ in the CN stretch frequency region. There are two main peaks with the center at ~ 2253 cm^{-1} and ~ 2276 cm^{-1} . Based on DFT calculations, the

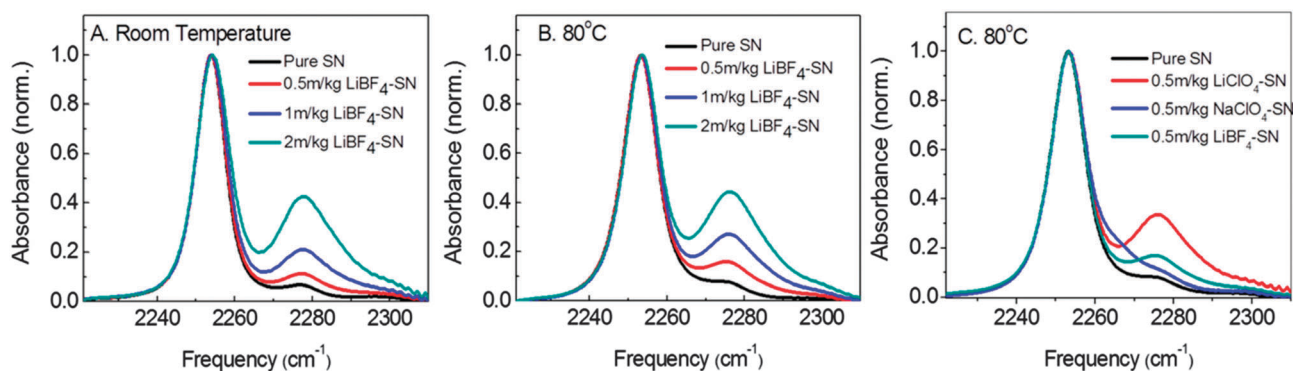


Fig. 1 (A) FTIR spectra of succinonitrile (SN), 0.5 mol kg^{-1} LiBF_4 -SN, 1 mol kg^{-1} LiBF_4 -SN, 2 mol kg^{-1} LiBF_4 -SN at room temperature. (B) FTIR spectra of SN, 0.5 mol kg^{-1} LiBF_4 -SN, 1 mol kg^{-1} LiBF_4 -SN, 2 mol kg^{-1} LiBF_4 -SN at 80 $^\circ\text{C}$. (C) FTIR spectra of SN, 0.5 mol kg^{-1} LiClO_4 -SN, 0.5 mol kg^{-1} NaClO_4 -SN, 0.5 mol kg^{-1} LiBF_4 -SN at 80 $^\circ\text{C}$.

peak at $\sim 2253\text{ cm}^{-1}$ is assigned to the CN stretch of SN; the small peak at $\sim 2276\text{ cm}^{-1}$ for pure SN is assigned to the combination band, which is the sum of the CN stretch and the low frequency mode of which the origin is unknown.²⁰ This small peak provides little signal in the pump-probe experiments, even in the 0.05 mol kg^{-1} $\text{LiClO}_4\text{-SN}$ solutions (see ESI†). With the addition of LiBF_4 , the intensity of the peak at $\sim 2276\text{ cm}^{-1}$ increases. This indicates that the increase in such peak is caused by the binding of either Li^+ or anion BF_4^- to SN. To further investigate which ion causes the frequency blue shift, the FTIR spectra of SN, 0.5 mol kg^{-1} $\text{LiClO}_4\text{-SN}$, 0.5 mol kg^{-1} $\text{NaClO}_4\text{-SN}$, 0.5 mol kg^{-1} $\text{LiBF}_4\text{-SN}$ at $80\text{ }^\circ\text{C}$ were obtained and displayed in Fig. 1C (the FTIR spectra of the same samples at room temperature can be found in ESI†). Changing the anions from ClO_4^- to BF_4^- does not change the frequencies of the peak at 2276 cm^{-1} . However, this peak disappears when Li^+ is replaced by Na^+ . The results suggest that the increase in the peak at $\sim 2276\text{ cm}^{-1}$ in the $\text{Li}^+\text{-SN}$ is caused by the binding of Li^+ to SN. The separate frequencies of the CN stretch of SN (2253 cm^{-1}) and $\text{Li}^+\text{-SN}$ (2276 cm^{-1}) allow us to measure the rotation decay dynamics.

B. Anisotropy decay studies

To monitor the fast rotational motions in real time, we can trace the anisotropy decay of the excitation signal of a certain vibrational mode of the molecule with ultrafast infrared laser pulses, in a way similar to that of the anisotropy measurement with time-resolved fluorescence.²⁴ It should be noted that there are some heat effects in the pump/probe signal due to the short CN stretch vibration lifetime, but not very serious. We need to subtract the heat effect in our data analysis (see ESI†). Fig. 2 shows the anisotropy decay of the CN stretch of pure SN at room temperature and $80\text{ }^\circ\text{C}$. The anisotropy decay time constant is determined to be $3.7 \pm 0.3\text{ ps}$ and $2.5 \pm 0.3\text{ ps}$, respectively. In these experiments, there are two major contributions to the signal anisotropy decay. One is the molecular rotation, and the other is the resonant energy transfer from one anion to another anion with the same frequency and random orientation. In pure liquids^{18,25} or concentrated ionic solutions,²⁶ resonant vibrational energy transfer can be comparable or faster than molecular rotations and make a significant contribution to the experimentally observed anisotropy decay. For these cases, one needs to independently measure the resonant

energy transfer rate or suppress the resonant energy transfer by diluting the liquid with isotope labeled species to obtain the molecular rotational time from the anisotropy decay measurement. Owing to the lack of isotope labeled SN species, e.g. $^{15}\text{N}^{13}\text{C-CH}_2\text{-CH}_2\text{-}^{13}\text{C}^{15}\text{N}$, it is difficult for us to exclude the resonant energy transfer process in this experiment immediately. However, in a previous study,¹⁷ we measured the resonant energy transfer of CN stretches among different CH_3CN molecules in CH_3CN liquids diluted with $\text{CH}_3^{13}\text{C}^{15}\text{N}$. The resonant energy transfer is significantly slower than molecular rotation. Because the transition dipole moment of the CN stretch of SN is similar to that in CH_3CN and the average molecular distances in SN and CH_3CN are similar. According to the dipole/dipole interaction, the resonant energy transfer of CN among the different SN molecules must be slow, which means the resonant energy transfer slightly contributes to the measured anisotropy decay. For this system, the SN molecules undergo *trans* \leftrightarrow *gauche* conformational exchange, which can also affect the measured anisotropy decay. We cannot measure the exchange time between the two conformations immediately. However, from previous reports,¹⁴ the activation energy, which corresponds to *trans-gauche* dynamics, was estimated to be 0.19 eV for the molten and 0.22 eV for the plastic crystal. From the Arrhenius equation,²⁷⁻²⁹ $k = A \exp(-\Delta E_a/RT)$, we can estimate the conformational exchange time as a few tens of ps for the molten and plastic crystals. This process is much slower than the anisotropy decay. We can ignore its effect. Therefore, the experimentally observed anisotropy decay in Fig. 2 is contributed mainly by the molecular rotation. It is interesting that the molecular rotation of SN is randomized completely in the plastic phase (the anisotropy decay curve can approach 0 at long waiting time at room temperature), which is consistent with previous predictions.^{14,16} This is an important property for ion conductivity in SN plastic phase (the ion conductivity mechanism in the plastic phase will be reported in the proceeding paper). It is noted that the anisotropy decay time constant is $2.5 \pm 0.3\text{ ps}$ at $80\text{ }^\circ\text{C}$, with the temperature effect the constant should be $\sim 3.0\text{ ps}$ at room temperature if no phase transition occurs. The rotation time constant of 3.7 ps at room temperature means that the phase transition does affect the molecular rotation.

Fig. 3A displays the time dependent anisotropies decay of the CN stretch of unbound SN ($\sim 2253\text{ cm}^{-1}$) and $\text{Li}^+\text{-SN}$

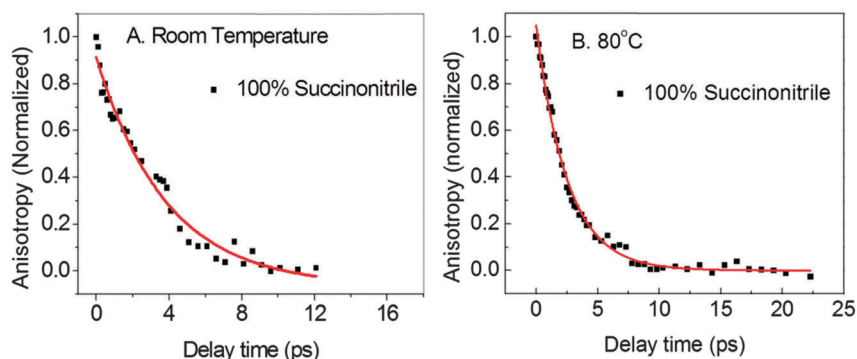


Fig. 2 Anisotropy decay curve of the CN stretch vibrational excitation signal of pure SN at room temperature and $80\text{ }^\circ\text{C}$. The dots are data, and the curves are the fits of a single exponential with time constants $\sim 3.7\text{ ps}$ (A) and $\sim 2.5\text{ ps}$ (B).

($\sim 2276\text{ cm}^{-1}$) in a 1 mol kg^{-1} LiBF_4 -SN solution at room temperature. The anisotropy decay of the Li^+ -SN is much slower than that of the unbound SN. The decay time constant of Li^+ -SN is $7.5 \pm 0.5\text{ ps}$, which is about 2.0 times of that of the unbound SN ($3.8 \pm 0.3\text{ ps}$). Fig. 3B displays the time dependent anisotropies of CN stretch of unbound SN and Li^+ -SN in a 0.5 mol kg^{-1} LiBF_4 -SN solution at 80°C . The decay time constant of Li^+ -SN is $6.8 \pm 0.5\text{ ps}$, which is about 2.5 times of that of unbound SN ($2.7 \pm 0.3\text{ ps}$) (note that this value is not necessarily the same with that for pure SN. The viscosity of pure SN and 0.5 mol kg^{-1} LiBF_4 -SN solutions are slightly different. Thus, the rotation decay times for SNs are slightly different). The anisotropy decays of LiClO_4/SN and LiPF_6/SN can be found in the ESI† and Table 1.

As discussed above, the anisotropy decay time ratio can be considered as the molecular rotation time ratio between the Li^+ -bound and unbound species. The reason for the much slower rotation of the Li^+ -bound species is that several SN molecules are bounded by one Li^+ so that the entire complex, of which the volume is larger than that of free SN, rotates together.

In the liquid solutions, lithium salts dissociate into Li^+ and anions. It is possible that the anions such as BF_4^- , PF_6^- and ClO_4^- could attach to Li^+ and rotate with the complex together. If so, the volume of the complex should increase and the rotation should decrease. This possibility can be tested by measuring the concentration dependent anisotropy decay. In a more concentrated solution, anions are more likely to attach to Li^+ and if so, the volume of the complex should increase and the rotation time should decrease.

Fig. 4A shows the anisotropy decay curves of the CN stretch of Li^+ -bound SN in 0.05 – 0.5 mol kg^{-1} LiClO_4 -SN solutions. The time constants of 0.05 , 0.2 , and 0.5 mol kg^{-1} are $7.2 \pm 0.5\text{ ps}$, $7.0 \pm 0.5\text{ ps}$ and $6.4 \pm 0.5\text{ ps}$, respectively (shown in Table 1). The decay time constants are similar within experimental uncertainty. The same results can be found in Fig. 4B. In the LiBF_4/SN solutions with concentrations of 0.5 , 1 and 2 mol kg^{-1} , the rotational time constants are 6.8 ± 0.5 , 6.8 ± 0.5 and $6.9 \pm 0.5\text{ ps}$, respectively. All the rotational time constants are similar within experimental uncertainty. This means the anion does not exist in the first solvation shell of the Li^+ ion or weakly binds to the Li^+ ion, which does not affect the complex rotation.

According to the Stokes–Einstein equation,^{17,30} the rotation decay time constant is proportional to the volume of molecules. Therefore, the coordinate number of Li^+ in succinonitrile could be determined by calculating the rotational time ratio between Li^+ -bound SN and the unbound SN in the same solution. As shown above, the rotational time ratio between the Li^+ -bound SN and unbound SN in 1 mol kg^{-1} LiBF_4/SN solution at room temperature is about 2 (Fig. 3A), which means that the coordinate number would be 2 at room temperature. This is consistent with the previous X-ray diffraction experimental results,⁵ in which in the LiPF_6 and LiClO_4 plastic crystal electrolytes forms a 1:2 salt:succinonitrile adduct. For the melt solutions (80°C), the ratios in the LiClO_4 and LiBF_4 solutions are listed in Table 1. Within the experimental uncertainty, the experiments suggest that in the Li^+ -SN solutions, one Li^+ binds to 2.5–3 SN molecules. Because the measured coordination number is the average result, the possible binding number of Li^+ -SN solutions at 80°C is 2 or 3. This result is not surprising because in the liquid phase, the solvation dynamics of Li^+ -SN are similar to that of Li^+ - CH_3CN . From our previous study,¹⁷ we found that one Li^+ ion binds to 4–6 CH_3CN molecules. The SN molecule has two CN moieties that can both bind to Li^+ or only one of these bind to Li^+ ; thus, the coordination number should be smaller than that of CH_3CN .

C. Solvation structure by DFT calculation studies

To seek the possible solvation structure of the Li^+ -SN complex, we performed DFT calculations. There are four possible conformations for one Li^+ directly binding to 2 SN molecules in the gas phase. The optimized structures are listed in Fig. 5 and its corresponding vibration frequencies of Li^+ -bound CN stretch (scaling factor 0.955) are listed in Table 2. It should be noted that the infrared intensities of free CN stretch in a complex are weak, and they will not contribute a signal at 2253 cm^{-1} in the FTIR spectra. In conformation A, the two SN molecules are solely in the *trans* conformation and its calculated vibrational frequency of Li^+ -bound CN stretch is 2263 (or 2261) cm^{-1} , which is 10 (or 8) cm^{-1} larger than that of the free CN (2253 cm^{-1}). It is difficult to say whether this conformation can exist. However, in a previous study, researchers reported that the proportion of the *trans* isomer is only 23%.⁸ Therefore, the possibility of one Li^+ binding directly to two *trans* isomers of SN would be small. In conformation B, the

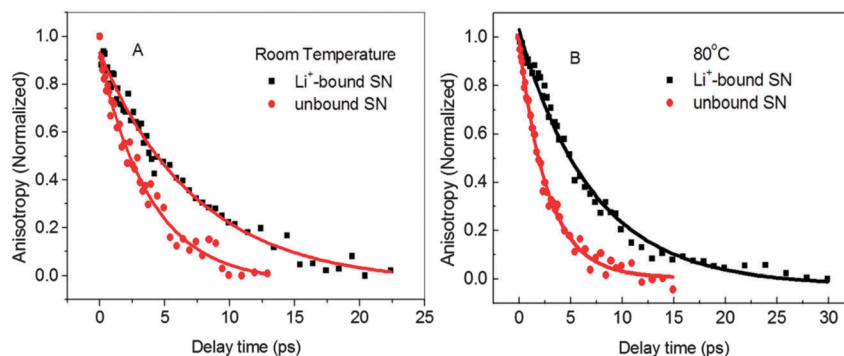
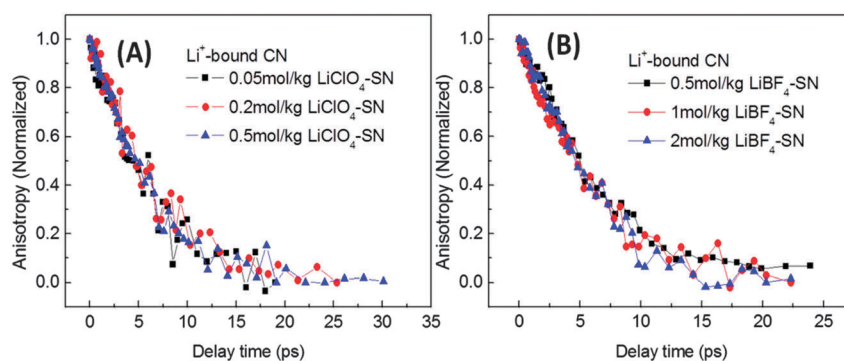
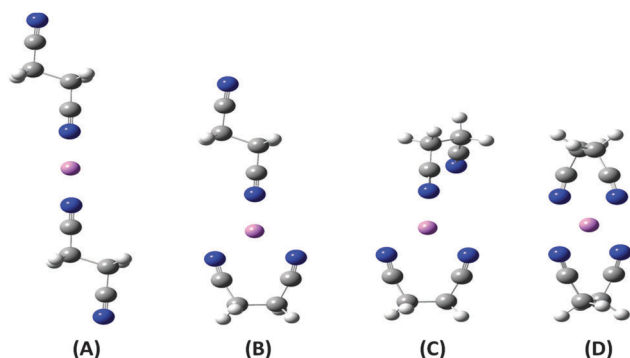


Fig. 3 Time dependent anisotropies of nitrile stretch of unbound succinonitrile (SN) and Li^+ -bound SN in (A) 1 mol kg^{-1} LiBF_4 -SN at room temperature and (B) 0.5 mol kg^{-1} LiBF_4 -SN at 80°C . The dots are experimental data, and the lines are single exponential fit.

Table 1 Anisotropy decay time constants of nitrile stretch of the unbound SN and Li⁺-bound SN in LiClO₄-SN and LiBF₄-SN solutions at 80 °C, respectively

LiClO ₄ -SN	0.05 mol kg ⁻¹		0.2 mol kg ⁻¹		0.5 mol kg ⁻¹	
	Free CN	Li ⁺ -bound CN	Free CN	Li ⁺ -bound CN	Free CN	Li ⁺ -bound CN
Anisotropy (ps)	2.3 ± 0.2	7.2 ± 0.5	2.4 ± 0.2	7.0 ± 0.5	2.4 ± 0.2	6.4 ± 0.5
Ratio	3.13		2.92		2.66	
LiBF ₄ -SN	0.5 mol kg ⁻¹		1 mol kg ⁻¹		2 mol kg ⁻¹	
	Free CN	Li ⁺ -bound CN	Free CN	Li ⁺ -bound CN	Free CN	Li ⁺ -bound CN
Anisotropy (ps)	2.7 ± 0.3	6.8 ± 0.5	2.4 ± 0.2	6.8 ± 0.5	2.8 ± 0.3	6.9 ± 0.5
Ratio	2.52		2.83		2.46	

**Fig. 4** Time dependent anisotropies of the nitrile stretch of Li⁺-bound SN complex in 0.05–0.5 mol kg⁻¹ LiClO₄-SN solutions (A) and 0.5–2 mol kg⁻¹ LiBF₄-SN solutions (B) at 80 °C.**Fig. 5** Simulation images of Li⁺ interacting with two succinonitrile molecules. (A) Two SN molecules are solely in the *trans* conformation. The lithium ion is centered between each of the nitrogens in the SN. (B) One molecule is in the *trans* conformation and the other is in the *gauche* conformation. The lithium ion is positioned at the center of the triangle defined by the three nitrogen atoms of the SNs. (C) Two molecules are solely in the *gauche* conformation and the lithium ion binds to three nitrogen atoms of the SNs. (D) Two molecules are solely in the *gauche* conformation. The lithium ion is positioned at the center of the equilateral tetrahedron defined by the four nitrogen atoms of the SNs. The binding energy of conformations A–D are –69.3, –73.9, –76.7, –76.5 kcal mol⁻¹, respectively. All the Li⁺-bound complexes were calculated with DFT at the B3LYP/6-311++G(d,p) level.

vibrational frequencies of CN stretch of Li⁺-bound *gauche*-SN red shift and that of Li⁺-bound *trans*-SN blue shift to about 2276 cm⁻¹. In conformation C, the two molecules are solely in

the *gauche* conformation. One molecule only has one CN binding to Li⁺ and its calculated vibrational frequency is 2274 cm⁻¹, the other has two CNs binding to Li⁺ and its calculated vibrational frequencies red shift. In conformation D, the two molecules are also solely in the *gauche* conformation, which both have two CNs binding to Li⁺. The vibrational frequencies are red shifted. Because this structure does not produce a peak at 2276 cm⁻¹, this conformation can be ruled out. Thus, for the coordination number 2 of Li⁺-SN complex, the solvation structure of B and C would be possible. According to the binding energy, the most stable component would be conformation C. As discussed above, such conformation can exist in the plastic crystal phase and in the molten phase. It is noted that conformation B and C can convert to each other by the rotation of the CN moieties about the central C–C bond of the SN molecule. From previous results,^{14,16} such orientational disorder is possibly the ion conduction mechanism in the plastic crystal phase (room temperature).

The DFT results show that there are four possible conformations for one Li⁺ directly binding to 3 SN molecules at the gas phase. The optimized structures are listed in Fig. 6 and its corresponding vibration frequencies of Li⁺-bound CN stretch are also listed in Table 2. In conformation A, three SN molecules are solely in the *trans* conformation. Owing to the minor *trans* isomers of SN, the possibility of one Li⁺ directly binding to three *trans*-SN would be small. In conformation B, three molecules are solely in the *gauche* conformation. All the SN molecules only have one CN binding to Li⁺ and their calculated vibrational

Table 2 Vibrational frequencies of Li⁺-bound CN stretch (scaling factor 0.955)

Li ⁺ interacting with two SNs	A		B		C		D		
	Li ⁺ -bound CN of <i>gauche</i>	Li ⁺ -bound CN of <i>trans</i>	Li ⁺ -bound CN of <i>gauche</i>	Li ⁺ -bound CN of <i>trans</i>	Li ⁺ -bound CN of <i>gauche</i>	Li ⁺ -bound CN of <i>trans</i>	Li ⁺ -bound CN of <i>gauche</i>	Li ⁺ -bound CN of <i>trans</i>	
Freq. (cm ⁻¹)	1	—	2261	2245	2269	2245	—	2247	—
	2	—	2263	2249	—	2249	—	2251	—
	3	—	—	—	—	2274 ^a	—	—	—

Li ⁺ interacting with three SNs	A		B		C		D		
	Li ⁺ -bound CN of <i>gauche</i>	Li ⁺ -bound CN of <i>trans</i>	Li ⁺ -bound CN of <i>gauche</i>	Li ⁺ -bound CN of <i>trans</i>	Li ⁺ -bound CN of <i>gauche</i>	Li ⁺ -bound CN of <i>trans</i>	Li ⁺ -bound CN of <i>gauche</i>	Li ⁺ -bound CN of <i>trans</i>	
Freq. (cm ⁻¹)	1	—	2267	2273	—	2248	2270	2247	2271
	2	—	—	2275	—	2251	—	2251	2272
	3	—	—	—	—	2276 ^a	—	—	—

^a The succinonitrile molecule is in the *gauche* conformation and only one of its CN groups binds to Li⁺.

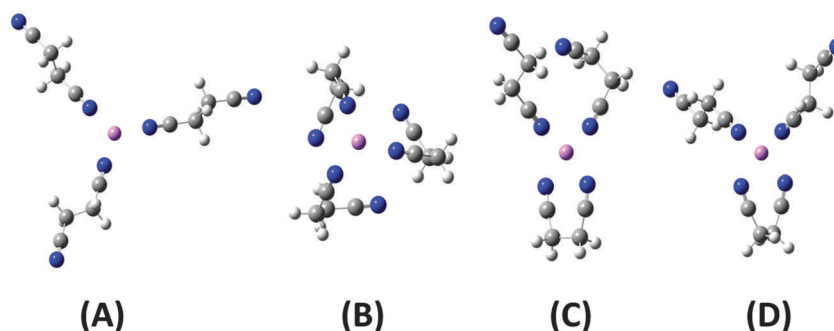


Fig. 6 Simulation images of Li⁺ interacting with three succinonitrile molecules. (A) Three molecules are solely in the *trans* conformation. The lithium ion is positioned at the center of the equilateral triangle defined by the three nitrogen atoms of the SNs. (B) Three molecules are solely in the *gauche* conformation and the lithium ion binds to three nitrogen atoms of the SNs. (C) One molecule is in the *trans* conformation and the others are in the *gauche* conformation. The lithium ion is positioned at the center of the tetrahedron defined by the four nitrogen atoms of the SNs. (D) One molecule is in the *gauche* conformation and the others are in the *trans* conformation. The lithium ion is positioned at the center of the tetrahedron defined by the four nitrogen atoms of the SNs. The binding energy of the conformations A–D are -88.9 , -105.0 , -95.5 , and -90.0 kcal mol⁻¹, respectively. All the Li⁺-bound complex were calculated with DFT at the B3LYP/6-311++G(d,p) level.

frequency is 2273 cm⁻¹ or 2274 cm⁻¹, which is very close to 2276 cm⁻¹. Therefore, it is possible for one Li⁺ binding directly to three *gauche*-SNs. In conformation C, one molecule is in the *trans* conformation and the others are in the *gauche* conformation. One *gauche* isomer SN only has one CN binding to Li⁺ and its calculated vibrational frequency is the same as 2276 cm⁻¹. The other has two CNs binding to Li⁺ and its calculated vibrational frequencies red shift. The calculated vibrational frequency of *trans*-SN is 2270 cm⁻¹, which is close to 2276 cm⁻¹. In conformation D, one molecule is in the *gauche* conformation and the others are in the *trans* conformation. Owing to the same reason with conformation A, the possibility of this conformation is small. Therefore, for the coordination number of 3, the solvation structure of B and C would be possible. According to the binding energy, the most stable component is conformation B. Such conformation can exist in the molten phase.

Summarizing all the experimental and calculated results presented above, the coordination number of the lithium with SN in the plastic crystal phase is 2 and in liquid phase is 2 or 3. Larger complex could be formed by increasing the temperature.

D. The dissociation rate of Li salts

It is important to explore how many of the LiBF₄ molecules can dissociate (LiBF₄ → Li⁺ + BF₄⁻) in the SN solutions at 80 °C. Because only the dissociated lithium salts can move under an applied electrical potential and contribute to the ion conductivity of the solutions. Based on the fact that the FTIR signal I^{DIR} is proportional to $k_1 C \mu^2$ and the pump/probe signal I^{2DIR} is proportional to $P k_2 C \mu^4$ (k_1 , k_2 are constants, C is the concentration, and P is the pump power, which can be measured in the experiments, and μ is the transition dipole moment), we are able to calculate the percentage of the dissociated LiBF₄ in the 0.5 mol kg⁻¹ LiBF₄-SN solutions at 80 °C. In the 0.5 mol kg⁻¹ LiBF₄-SN solutions, the molar ratio of SN/LiBF₄ is 25. The CN stretch transition dipole moment square ratio of free SN/Li⁺-SN can be determined experimentally as follows:

$$\begin{aligned} \mu_{2254}^2 : \mu_{2277}^2 &= \frac{I_{2254}^{\text{2DIR}} / P_{2254}}{I_{2254}^{\text{DIR}}} : \frac{I_{2277}^{\text{2DIR}} / P_{2277}}{I_{2277}^{\text{DIR}}} \\ &= \frac{0.093888 / 5.73}{1} : \frac{0.01291757 / 5.52}{0.08160541} = 0.571. \end{aligned}$$

The FTIR peak area ratio of the free/Li⁺-bound SN ($A_{2253\text{cm}^{-1}}/A_{2276\text{cm}^{-1}}$) is determined by the equation, $\frac{A_{2254}}{A_{2277}} = \frac{N_{2254}\mu_{2254}^2}{N_{2277}\mu_{2277}^2}$, where N is the number of free SN or Li⁺-SN. Therefore, we can obtain the free SN/ Li⁺-SN number ratio: $N_{2254} : N_{2277} = \frac{\mu_{2277}^2}{\mu_{2254}^2} \cdot \frac{A_{2254}}{A_{2277}} = \frac{1}{0.571} \cdot \frac{16.89263}{1.88667} = 15.68$. Based on the determined binding number (2.52) of Li⁺ in the LiBF₄/SN solutions (note that the number of CN moieties contributing to frequency peak 2276 cm⁻¹ is similar to the number of SN molecules binding to Li⁺ ion, as can be found in DFT the calculations), the dissociation percentage of LiBF₄ is calculated to be $25 \times \frac{1}{16.68} \times \frac{1}{2.52} = 59.5\%$, where 1/16.68 means $N_{2277} : (N_{2254} + N_{2277})$. This process can be found in our previous studies.¹⁷ Considering the experimental uncertainty, the dissociation percentage of LiBF₄ is taken to be 60% ± 10%. In other words, 60% ± 10% of LiBF₄ dissociated into Li⁺, which is fully solvated by succinonitrile in the 0.5 mol kg⁻¹ LiBF₄-SN solutions at 80 °C. Following the same procedure, the dissociation percentage of LiClO₄ in 0.5 mol kg⁻¹ LiClO₄-SN solutions at 80 °C is determined to be 90% ± 10%.

4. Conclusions

In this study, we demonstrated the solvation dynamics of Li⁺ salts in succinonitrile plastic crystal phase (22 °C) and liquid phase (80 °C) using ultrafast vibrational spectroscopy and DFT calculations. The Li⁺ coordination number is 2 in plastic crystal phase and 2.5–3 in the liquid phase. DFT calculations have shown the possible solvation structures of solvation number 2 or 3. In addition, the dissociation rate of Li⁺ salts in the SN liquid phase has been determined. In 0.5 mol kg⁻¹ LiBF₄-SN solutions at 80 °C, 60% ± 10% of the salt dissociates into Li⁺, which is bound by 2 or 3 solvent molecules. In 0.5 mol kg⁻¹ LiClO₄-SN solutions at 80 °C, 90% ± 10% of the salt dissociates into Li⁺. Such information would help better understand the ion conductivity and design new electrolytes with optimal properties for battery applications.

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