Supporting Information

Solvation Structure around the Li⁺ Ion in Succinonitrile-Lithium Salt Plastic Crystalline Electrolytes

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1. FTIR spectra



Figure 1S. (A) FTIR spectra of succinonitrile (SN), 0.05, 0.1, 0.2, and 0.5 mol/kg $LiClO_4$ -SN at room temperature. (B) FTIR spectra of SN, 0.05, 0.1, 0.2, and 0.5 mol/kg $LiClO_4$ -SN at 80°C. (C) FTIR spectra of SN, 0.5 mol/kg $LiClO_4$ -SN, 0.5 mol/kg $NaClO_4$ -SN, 0.5 mol/kg $LiBF_4$ -SN at room temperature. The results suggest that the increasing of the peak at ~2276 cm⁻¹ in the Li^+ -SN is caused by the binding of Li^+ to SN.

2. Anisotropy decay of Li⁺-bound SN and unbound SN at 80°C



Figure 2S. Time dependent anisotropies of nitrile stretch of unbound succinonitrile (SN) and Li^+ -bound SN in (A) 0.5 mol/kg $LiCLO_4$ -SN and (B) 0.5 mol/kg $LiPF_6$ -SN at 80°C. Dots are experimental data, and lines are single exponential fit. The anisotropy

decay time constants are 2.4 \pm 0.2 ps for unbound SN, and 6.4 \pm 0.5 ps for Li⁺-bound SN in 0.5 mol/kg LiCLO₄-SN at 80°C. The anisotropy decay time constants are 2.6 \pm 0.2 ps for unbound SN, and 6.3 \pm 0.5 ps for Li⁺-bound SN in 0.5 mol/kg LiPF₆-SN at 80°C.



Figure 3S. Time dependent anisotropies of nitrile stretch of unbound SN in $0.05\sim0.5$ mol/kg LiClO₄-SN solutions (A) and $0.5\sim2$ mol/kg LiBF₄-SN solutions (B) at 80°C. The anisotropy decay time constants are 2.3 ± 0.2 ps, 2.4 ± 0.2 ps, 2.4 ± 0.2 ps for unbound SN in 0.05, 0.2, 0.5 mol/kg LiClO₄-SN solutions at 80°C, respectively. The anisotropy decay time constants are 2.7 ± 0.3 ps, 2.4 ± 0.2 ps, 2.8 ± 0.3 ps for unbound SN in 0.5, 1, 2 mol/kg LiBF₄-SN solutions at 80°C, respectively.

3. Li⁺-SN complex lasts much longer than its rotation decay time

There is an assumption that the Li^+ -SN complex rotate together for at least longer than ~7 ps in our above conclusion. This can be supported by the 2D IR measurements.



*Figure 4S. Waiting time dependent 2D IR spectra of 0.5mol/kg LiClO*₄*-SN solution.*

Fig.4S displays the waiting time dependent 2D IR spectra of the 0.5 mol/kg LiClO₄-SN solution (80°C). The peak generation mechanism has been described in the previous publications.¹⁻⁹ Here, only a brief explanation is provided. At time zero, only the diagonal peak pairs show up. The red peak 1 at (2276 cm⁻¹, 2276 cm⁻¹) is the vibrational transition 0-1 of the CN stretch of Li⁺-bound SN, and the blue peak 2 at (2276 cm⁻¹, 2256 cm⁻¹) is the vibrational transition 1-2 of the CN stretch of Li⁺bound SN. Similarly, the red peak 3 at (2253 cm⁻¹, 2253 cm⁻¹) is the 0-1 transition of the CN stretch of unbound SN, and the blue peak 4 at (2253 cm⁻¹, 2235 cm⁻¹) is the 1-2 transition of the CN stretch of unbound SN. If the Li⁺-bound SN can dissociate into unbound SN after a certain delay time, the dissociation must produce a blue cross peak at the position B at long waiting times, e.g. 10 ps. For the same reason, the binding between a free SN with a Li⁺ to form a Li⁺-bound SN must produce a red cross peak at the position A at long waiting times. However, as shown in fig.4, up to 10 ps, no blue cross peak at position B or red peak at position A grows up, indicating that the dissociation process of Li⁺-SN complex does not occur. The result implies that the lifetime of Li⁺-SN complex must be longer than 10 ps. It should be noted that the new peaks in the 5 ps and 10 ps spectra are the results of heat induced absorption

(blue) or bleaching (red), as observed in other systems.^{2, 8, 10} The heat induced peaks have different frequencies from the normal 0–1 and 1–2 transition frequencies, as shown in fig.4.

In our previous work⁸, we have estimated the lifetime of Li⁺-bound CH₃CN complex by calculating the formation enthalpy. The formation enthalpy of Li-CN in Li⁺-CH₃CN complex is about 47 kcal/mol and the estimated lifetime is longer than 19 ps, while that of Li-CN in Li⁺-SN is about 69 kcal/mol, which suggests that the lifetime of complex Li⁺-bound SN should be longer than Li⁺-CH₃CN. This is consistent with our 2D IR experimental observation.

4. Combination band at 2276 cm⁻¹ has little contribution in pump/probe signals

The weak shoulder at 2276 cm⁻¹ in pure SN is a combination band which should be a sum of two fundamental vibrations, one is the CN stretch of unbound SN (~2253 cm⁻¹), the other is the low frequency mode of which the origin is generally unknown⁹. Combination bands have weak infrared absorption intensity due to small transition dipole^{9, 11}. Because the FTIR signal I_{FTIR} is proportional to μ^2 (μ is the transition dipole moment), and the pump/probe signal I_{pp} is proportional to μ^4 , this means the PP signal from combination band should be much smaller.

We certainly measure the pump-probe signal of the combination band in pure SN. Please see the below figure.



Figure 5S. The transient spectrum of pure SN at 80 °C when pumping at 2276 cm⁻¹. The PP signal is only 0.008, which is five times smaller than that of Li⁺-SN at 80 °C when pumping at 2276 cm⁻¹ at 0.05mol/kg LiClO4 sample.

We measure the anisotropy of the combination band in pure SN, and its decay time is also about 2.3 ps, which is the same as that of the unbound SN band. This means the anisotropy decay of Li⁺-SN we measured has little contribution from the combination band.

5. Subtracting the heat effect in PP signals

There are some heat effect in pump/probe signal, but not too serious. We have already subtracted the heat effect in our data analysis. See one of data below.



Figure 6S. Time dependent pump/probe signal of nitrile stretch of (A) unbound SN (pump: 2253cm⁻¹, probe: 2233 cm⁻¹, which means 1-2 transition) and (B) Li⁺-bound

SN (pump: 2276 cm⁻¹, probe: 2276 cm⁻¹, which means 0-1 transition), where p means parallel polarization and s means perpendicular polarization. The signals at long waiting time can't decay to zero due to heat effect. (C) Subtracting the heat effect. The black, red, and blue lines represent the fit to the relaxation model, the heating contribution, and the modified pump-probe signals, respectively. All the data are for the 0.5 mol/kg LiClO4-SN solution at 80 °C.

To subtract the heat effect, we used the method which has been determined efficiently by *Zhenget al.*² and Bakkeret al. ¹², and also described in our previous paper (CJCP, 2016, ASAP). Briefly speaking, the contributions from heat effect can be simulated by generating the exponential curve in which the decay time is same with the vibrational lifetime. The real pp signals can be obtained by subtracting the exponential curve from the experimentally measured decay curve.

Actually, the vibrational relaxation time of the CN stretch of SN in solid is about 2.9 ps (for both bound and unbound SN), in melt is about 2.5 ps (for both bound and unbound SN). Previous studies show that very good results can be obtained even when the vibrational lifetimes are three times shorter than that of dynamical times^{7, 13}, therefore we are able to obtain anisotropy decay time constants in this work.

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