

Dynamics in a Room Temperature Ionic Liquid from the Cation Perspective: 2D IR Vibrational Echo Spectroscopy.

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Supporting Information

I. Synthesis and Characterization of 2-selenocyanate-1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

The synthetic procedure for 2-selenocyanate-1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (2-SeCN-BmimNTf₂) is schematically represented in Figure S1.

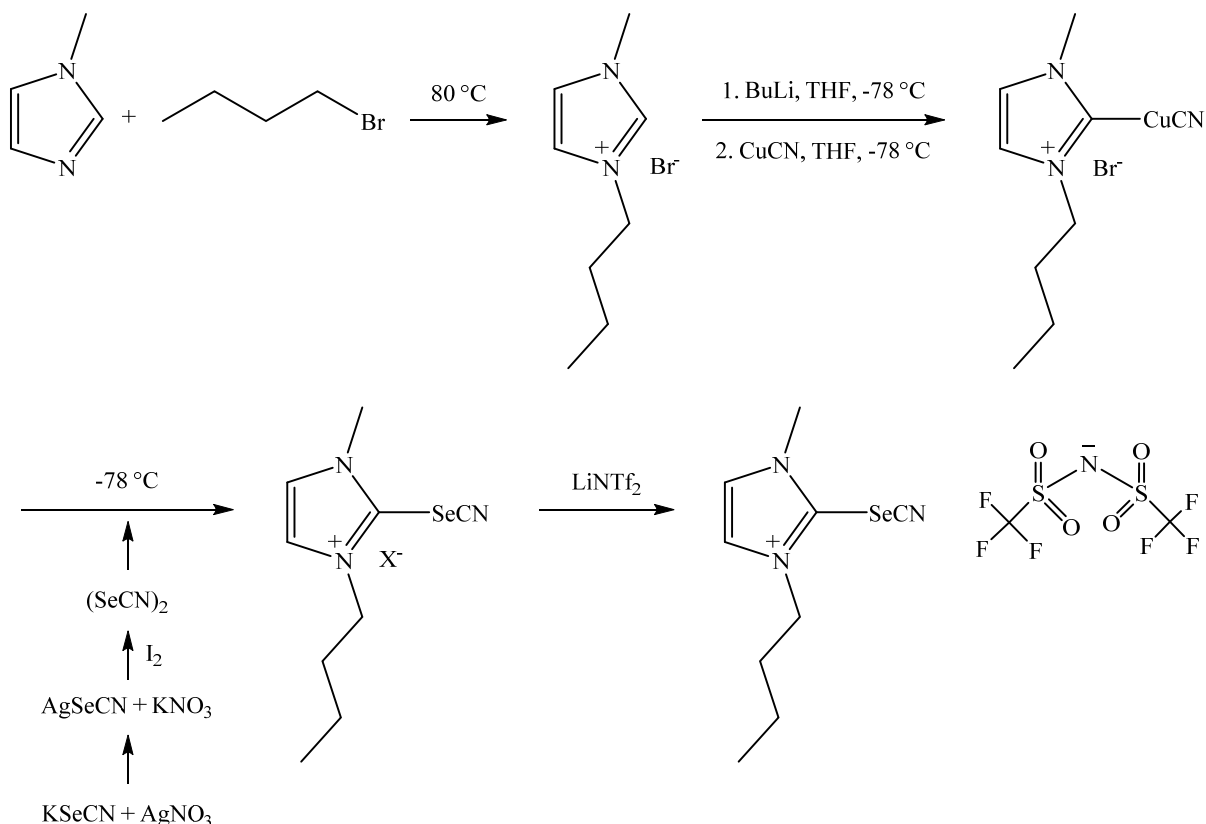


Figure S1. Schematic representation of the synthetic procedure for 2-selenocyanate-1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (2-SeCN-BmimNTf₂).

Potassium selenocyanate (2.5 g, 17.5 mmol) and water (60 mL) were loaded into a 250 mL three necked flask under nitrogen protection. Silver nitrate (3 g, 17.5 mmol) was slowly added to the flask at room temperature in portions. After 30 min of stirring, the solution was filtered and the remaining solid was dried under vacuum. The white solid, silver selenocyanate (AgSeCN), was obtained in 93.6 % yield (3.5 g).

The anhydrous AgSeCN (3.40 g, 16 mmol) was dissolved in 20 mL of THF at 0 °C. Next, 2.02 g (8 mmol) of I₂ were directly added to the solution. The mixture was stirred under nitrogen atmosphere at 0 °C for 30 min until a clear, bright yellow selenocyanogen ([SeCN]₂) solution was obtained. The reaction was then cooled to -78 °C, filtered through a glass frit under vacuum, and collected in a flask maintained at -78 °C.

1-Methylimidazole (8 mL, 0.1 mol) and 1-bromobutane (10.7 mL, 0.1 mol) were dissolved in 40 mL of anhydrous toluene. The mixture was stirred at 60 °C for 12 h under the protection of nitrogen. The melt salt was separated from the solvent and was thoroughly washed with toluene (20 mL, 3 times). The white solid product was dried under vacuum to afford 1-butyl-3-methylimidazolium bromide (BmimBr) ionic liquid.

A volume of 1.55 mL of 2.5 M n-BuLi solution (3.90 mmol) was added dropwise to a solution containing 810 mg (3.70 mmol) of BmimBr in 15 mL of THF at -78 °C. After holding the temperature at -78 °C for 30 min, followed by 0 °C for 15 min, the reaction system was again cooled to -78 °C and transferred with a syringe to 10 mL of THF containing 358 mg (4.00 mmol) of anhydrous CuCN. The reaction mixture was warmed to 0 °C, solubilizing virtually all of the CuCN after 45 min. The resulting solution was added to the selenocyanogen solution at 0 °C with a syringe. The mixture was then held at -78 °C for 15 min. Finally, the solution was warmed to room temperature and stirred for 1 h.

Following stirring, the reaction was terminated, and the THF was evaporated under vacuum. The resulting solid was dissolved in 10 mL of ultrapure water (deoxygenated) and was thoroughly washed with diethyl ether (deoxygenated, 3×10 mL). Lithium bis(trifluoromethylsulfonyl)imide (1.4 g, 5 mmol) was dissolved in 10 mL of ultrapure water (deoxygenated). The above two solutions were thoroughly mixed and kept at room temperature for 1 h under nitrogen atmosphere. The mixture was filtered through a glass frit under vacuum and the remaining solid was washed with ultrapure water (deoxygenated, 3×100 mL). Finally, the solid was dried under vacuum, yielding the 2-SeCN-BmimNTf₂ product.

The compound was characterized with FT-IR (Figure S2), HPLC-MS (Figure S3), and ¹H NMR (Figure S4). In Figure S2, the strong absorption in the FT-IR at 2115.7 cm⁻¹ is consistent with the CN stretch of the -SeCN functional group, indicating the successful functionalization of the imidazolium ring with -SeCN. In the mass spectrum of Figure S3, the molecular ion peak at 244.07 m/z is in agreement with the calculated molecular weight of the 2-SeCN-Bmim⁺ cation ([C₉H₁₄N₃Se]⁺). The molecular ion peak at 279.82 m/z is in agreement with the calculated molecular weight of the ⁻NTf₂ anion ([C₂O₄NS₂F₆]⁻). The remaining peaks are the molecular weights of the residua in the HPLC column. The ¹H NMR spectrum in Figure S4 confirms the presence of all chemically distinct H atoms on the cation. The results confirm the successful synthesis of 2-selenocyanate-1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

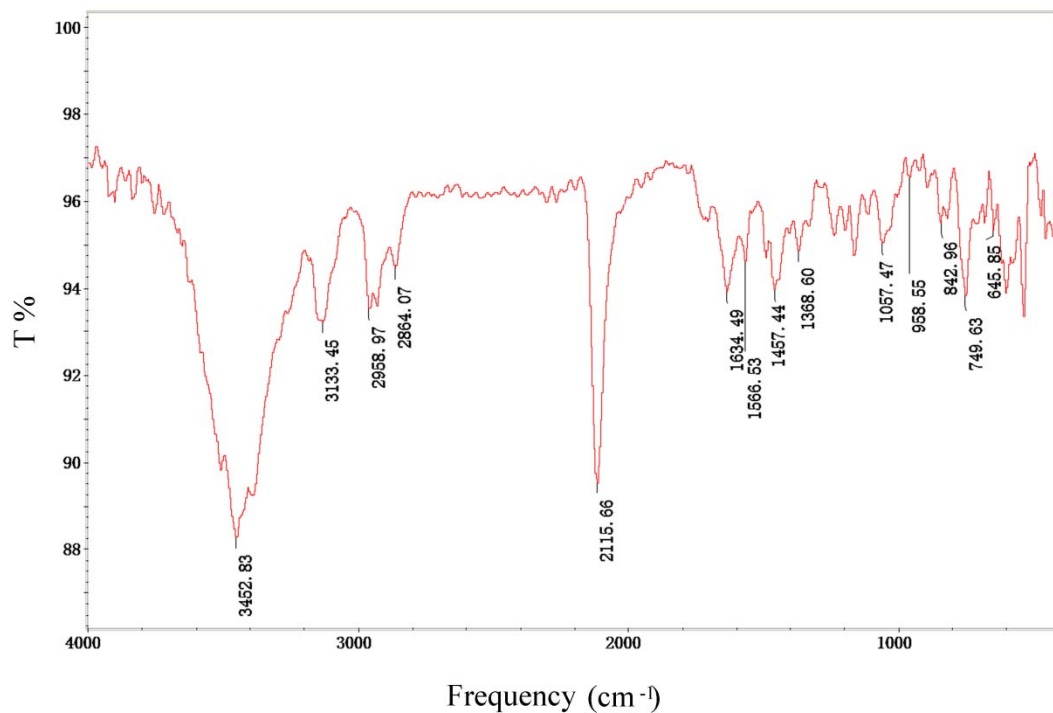


Figure S2. FT-IR spectrum of 2-selenocyanate-1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

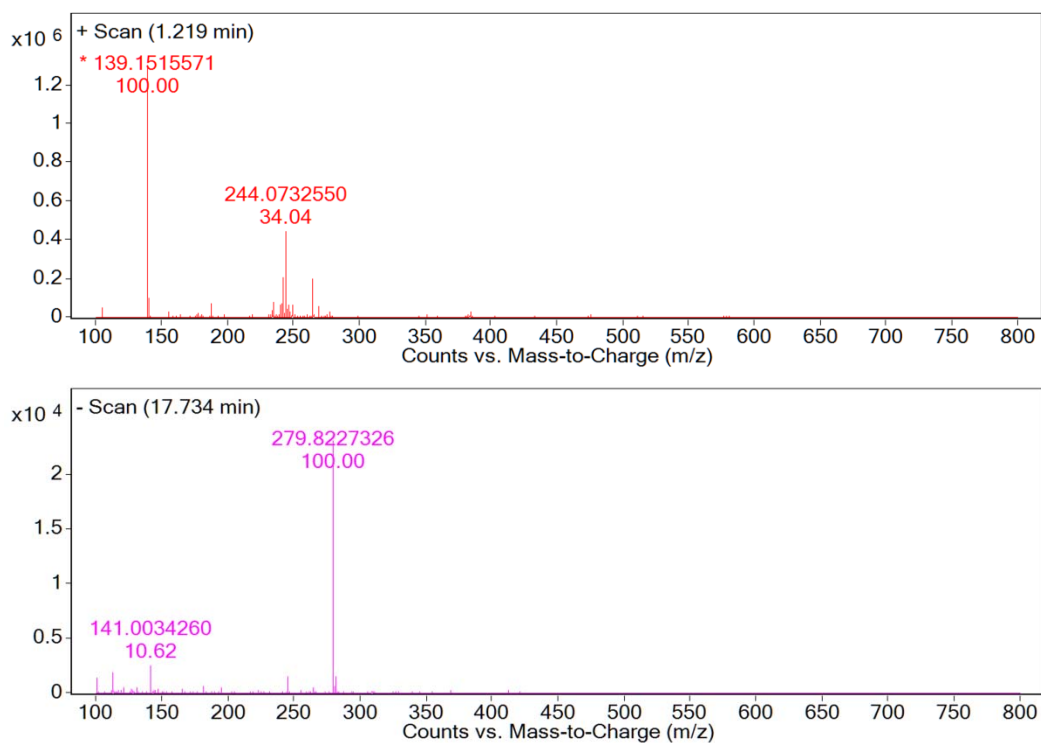


Figure S3. Mass spectrum of 2-selenocyanate-1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide obtained with HPLC-MS.

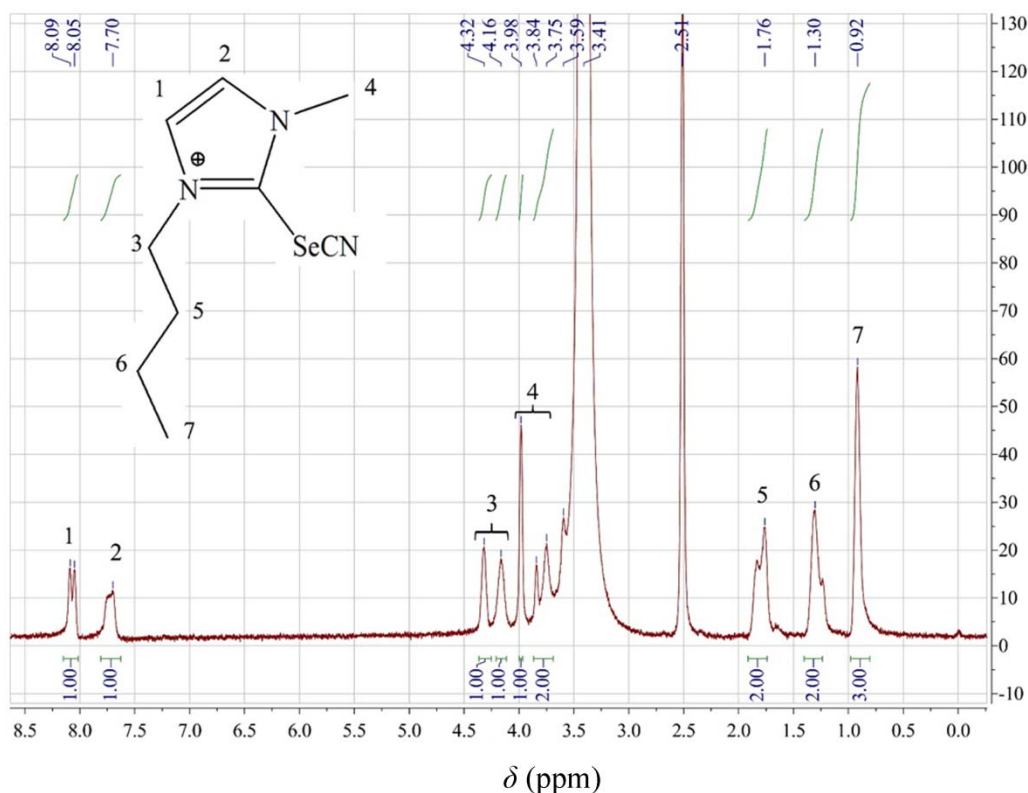


Figure S4. ^1H -NMR spectrum of 2-selenocyanate-1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in DMSO-d_6 . Chemical shifts (δ) are in ppm. 1: 8.09, 8.05 (1H, d) 2: 7.70 (1H, d) 3: 4.32, 4.16 (2H, d) 4: 3.98, 3.84, 3.75 (3H, t) 5: 1.76 (2H, d) 6: 1.30 (2H, d) 7: 0.92 (3H, s).

II. Characterization of 1-butyl-3-methylimidazolium selenocyanate.

BmimSeCN was synthesized according to a previously published synthetic procedure.¹ The clear yellow liquid product was dried under vacuum (~ 100 mTorr) at a temperature of 40°C overnight. The product was characterized with FT-IR, NMR, and ICP-MS for K^+ and Cl^- ion content. A strong peak at 2063 cm^{-1} originating from the CN stretch of SeCN^- was observed in the FT-IR spectrum of BmimSeCN dissolved in BmimNTf₂ at 1:100 ion pairs to BmimNTf₂ ion pairs (see inset to Figure 2). ^1H NMR (300 MHz, DMSO-d_6 , δ ppm): 0.91 (CH_3 , t), 1.27 (CH_2 , m), 1.77 (CH_2 , m), 3.86 (CH_3 , s), 4.18 (CH_2 , t), 7.75 ($\text{H}_2\text{C}=\text{CH}_2$, d), 9.13 (CH, s). The concentration of residual K^+ in the BmimSeCN product was found to be ~ 13 ppm with ICP-MS. The Cl^- content was below the detection limit.

III. Wobbling-in-a-cone Model of Orientational Relaxation.

When orientational relaxation of a single population proceeds in a multi-exponential fashion, it is an indication that the motion is restricted relative to the case of simple free diffusion.^{2,3} The wobbling-in-a-cone model⁴⁻⁶ provides a framework in which the spatial

restrictions and associated correlation times that limit orientational sampling can be quantified. In this model, the transition dipole moment undergoes orientational diffusion within the angular space bounded by a cone of half angle θ_c . Then, instead of decaying to zero, the orientational correlation function,

$$C_2(t) = Q^2 + (1 - Q^2) \exp[-t / \tau_c], \quad (\text{S.1})$$

where τ_c is the correlation time for restricted angular diffusion, decays to a plateau whose value is determined by the square of a generalized order parameter

$$Q^2 = \left[\frac{1}{2} \cos \theta_c (1 + \cos \theta_c) \right]^2. \quad (\text{S.2})$$

Because the 2-SeCN-Bmim⁺ anisotropy in Figure 4 will decay to zero in the long time limit, the final decay involves the complete, unrestricted reorientation of the transition dipole, which occurs by free diffusion. This means that an inertial cone, describing the ultrafast inertial motion, and two diffusive cones, accounting for the short and intermediate exponential decays that precede the complete reorientation, must be included to fit the full extent of the anisotropy. The resulting orientational correlation function is³

$$C_2(t) = T^2 (S^2 + (1 - S^2) \exp[-t / \tau_{c1}]) \times (R^2 + (1 - R^2) \exp[-t / \tau_{c2}]) \exp[-t / \tau_m], \quad (\text{S.3})$$

where T , S and τ_{c1} , and R and τ_{c2} are the generalized order parameters and correlation times for the inertial cone, first diffusive cone, and second diffusive cone, respectively. The remaining correlation time, τ_m , is the free diffusion time that leads to complete orientational randomization. Comparing the last exponential in Equation (S.3) to that in Equation (6) gives

$$D_m = \frac{1}{6\tau_m}, \quad (\text{S.4})$$

the orientational (free) diffusion constant. Since the inertial motion is so rapid that it is not observed (i.e. $\tau_{in} \sim 0$), only the order parameter for the inertial cone, T , appears in Equation (S.3).

The generalized order parameters (including the total order parameter $Q_{tot} = TSR$) and correlation times are obtained from the data by inserting Equation (S.3) into Equation (5) and fitting the data with the resulting expression. The orientational diffusion constant for wobbling-in-a-cone of half angle θ_c , order parameter Q , and correlation time τ_c is then given by⁵

$$D_c = \frac{x_c^2(1+x_c)^2 \{ \ln[(1+x_c)/2] + (1-x_c)/2 \}}{\tau_c(1-Q^2)[2(x_c-1)]} + \frac{(1-x_c)(6+8x_c-x_c^2-12x_c^3-7x_c^4)}{24\tau_c(1-Q^2)}, \quad (\text{S.5})$$

where $x_c = \cos \theta_c$.

IV. Hydrodynamic Calculation of 2-SeCN-Bmim⁺ Diffusive Orientational Relaxation Time.

In this section, we describe the hydrodynamic calculation of the diffusive orientational relaxation time of 2-SeCN-Bmim⁺ in BmimNTf₂ under slip boundary conditions. The viscosity of BmimNTf₂ at the experimental temperature, $T = 294.8$ K, was determined to be 59.9 cP from a linear interpolation ($\ln \eta = 3651.4(1/T) - 8.2941$) of a series of viscosity measurements taken in the temperature range 292 – 339 K.⁷ The volume was taken to be the molecular van der Waals volume⁸ of 2-SeCN-Bmim⁺, $V_{eff} = 181 \text{ \AA}^3$, determined using the Connolly volume computation method⁹ with a probe radius of zero. To determine the ratio of the semi-axes, the molecule was modeled as an oblate spheroid. The short semi-axis was estimated as the distance between the far edges of the H atom van der Waals spheres of the methyl substituent, given an ideal tetrahedral H-C-H bond angle $\gamma = 109^\circ$, C-H bond length $r_c = 1.09 \text{ \AA}$, and H atom van der Waals radius $r_w(H) = 1.2 \text{ \AA}$. The short semi-axis value obtained, $c = 2.1 \text{ \AA}$, gave a long semi-axis value $a = 4.5 \text{ \AA}$ via the formula for the volume of a spheroid, $V_{eff} = (4\pi/3)a^2c$, resulting in $\rho = 0.47$. The dimensionless friction coefficients have been previously tabulated as function of ρ .¹⁰ Two values of $\lambda(\rho)$ were used in the calculation, the nearest tabulated value, 1.77, and the value obtained by cubic spline interpolation of the tabulated values, 2.15. Using Equation (S.4) and Equation (7), we calculated the complete orientational relaxation time to be 790 ps and 960 ps using the tabulated and interpolated values of the friction coefficient, respectively.

V. Data Figures and Tables.

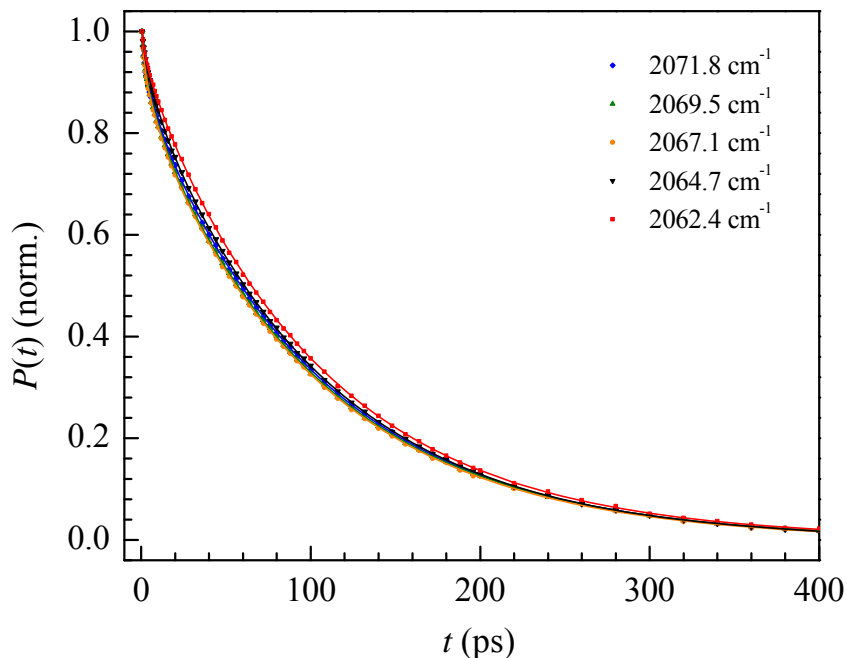


Figure S5. Isotropic pump-probe decays for SeCN⁻ (BmimSeCN) in BmimNTf₂.

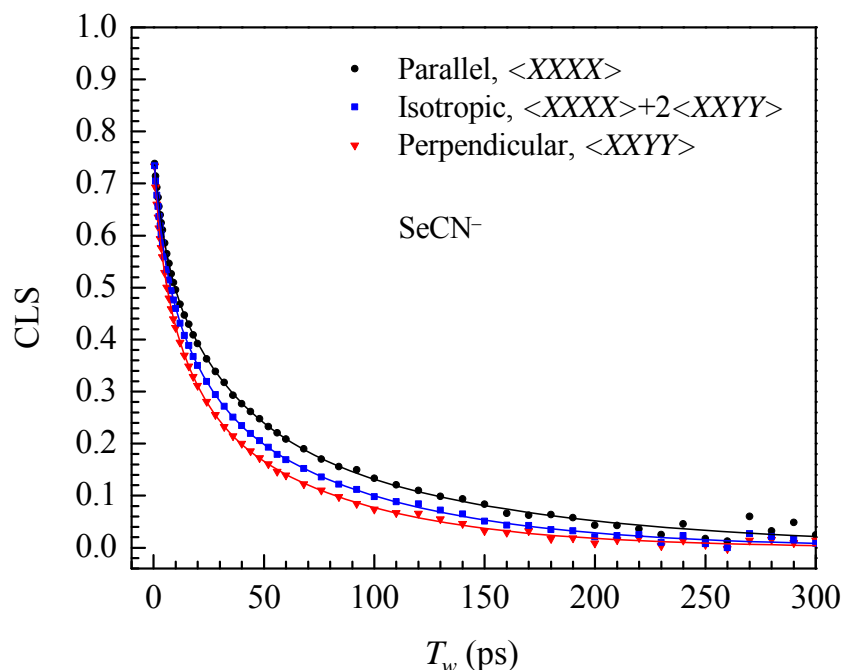


Figure S6. Triexponential CLS decays for SeCN^- (BmimSeCN) in BmimNTf₂.

Table S1. Frequency-dependent population lifetimes obtained from the isotropic pump-probe decays of 2-SeCN-Bmim⁺ (2-SeCN-BmimNTf₂) in BmimNTf₂.

Freq. (cm ⁻¹)	τ_3 (ps)
2117.6	325 ± 2
2116.3	325 ± 2
2115.0	322 ± 2
2113.7	321 ± 2
2112.4	317 ± 2
2111.2	315 ± 2
2109.9	310 ± 2
2108.6	305 ± 2
2107.4	300 ± 2
2106.1	294 ± 1
2104.9	287 ± 1

Table S2. Triexponential decay amplitudes and time constants from fits to the orientational anisotropy of vibrational probes dissolved in BmimNTf₂.

Probe	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)
2-SeCN-Bmim ⁺ *	0.054 ± 0.003	6.9 ± 0.9	0.063 ± 0.003	65 ± 7	0.263 ± 0.003	900 ± 20
SeCN ^{-†}	0.060 ± 0.004	2.4 ± 0.3	0.101 ± 0.003	21 ± 2	0.198 ± 0.004	159 ± 3

*Data averaged across frequency range 2104.9-2117.6 cm⁻¹. †Data averaged across frequency range 2061.3-2071.8 cm⁻¹.

References

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