

Supplementary Information for
Extraordinary Slowing of Structural Dynamics in Thin Films of a Room Temperature Ionic Liquid

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A. Sample Preparation Procedure

Thin RTIL films could not be formed directly on either CaF₂ windows or on CaF₂ coated with SiO₂. Attempts to spin coat on these substrates resulted in isolated patches of the ionic liquid (Figure S1). To form uniform films, CaF₂ windows coated with 100 nm-thick SiO₂ were

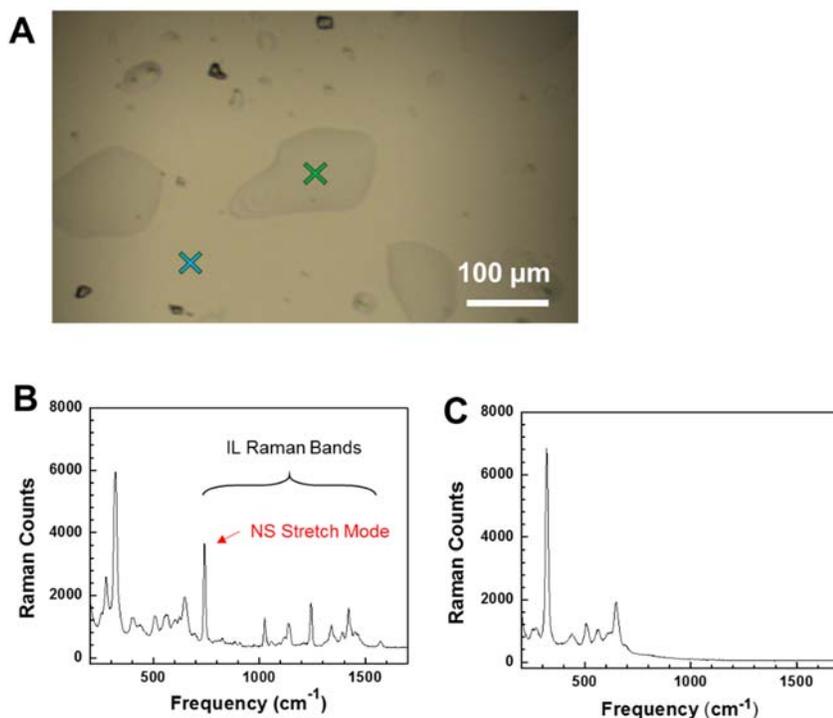


Figure S1. **A.** Optical microscope image of an SiO₂-coated CaF₂ substrate after an attempt to spin-coat BmimNTf₂ onto it. The ionic liquid forms isolated patches ~100 μm in diameter (e.g., the region with the green X); most of the substrate is uncoated (e.g., the region with the blue X). **B.** Raman spectrum at the location of the green X in the optical image, showing strong ionic liquid peaks. **C.** Raman spectrum at the location of the blue X in the optical image, showing no ionic liquid peaks.

first functionalized using a procedure adapted from Xin and Hao.¹ All the chemicals were purchased from Sigma-Aldrich and used without further purification. Each window was first cleaned by sonication in ethanol for ten minutes. Then, to functionalize the SiO₂ surface, the window was placed in a 0.8% (by mass) solution of triethoxy-3-(2-imidazolin-1-yl)propylsilane

in toluene and heated to 80 °C for 12 hours. The window was washed with toluene several times, sonicated in toluene for ten minutes, and blown dry with a stream of nitrogen.

To add a butyl group to the imidazoline ring and convert it to the cation, the window was placed in a 0.4% (by mass) solution of 1-iodobutane in toluene and heated to 80 °C for 12 hours (see Figure 1A). The window was then washed a few times with toluene, sonicated in toluene for ten minutes, washed with ethanol, sonicated in ethanol for ten minutes, and blown dry with a stream of nitrogen. The result of this procedure was a monolayer of butylimidazolidinium-like cations with iodide anions (see Figure 1A).

Then planar films on the functionalized SiO₂ surface were formed by spin coating. First, a 1:10 molar mixture of BmimSeCN:BmimNTf₂ was prepared to introduce the SeCN⁻ vibrational probe. Then, a portion of the 1:10 ionic liquid mixture was diluted with methanol to the extent that produced the desired thickness of the ionic liquid film. To make a 14 nm film, an ionic liquid concentration of 0.5% by mass was used; for a 39 nm film, a concentration of 1.6% by mass was used; for a 112 nm film, a concentration of 4.5% was used; and for a 278 nm film, a concentration of 11.3% was used. Before spin coating, the solution was stirred for ten minutes and then passed through a 0.2 μm filter. To prepare the film, 150 μL of the solution was deposited on a functionalized CaF₂ window, which was then spun for 30 seconds at 3000 rpm. The spin coating procedures were performed in a nitrogen-filled glove box to prevent water uptake by the RTIL and to avoid exposure of the SeCN⁻ anion to oxygen. Still in the glove box, the coated window was placed in a lens mount. An O-ring and a second CaF₂ window were stacked on top of the window containing the thin film. Finally, a threaded retention ring was screwed into place. The O-ring sealed the sample so no water could be taken up by the RTIL when the sample was removed from the glove box.

The BmimSeCN:BmimNTf₂ ratio of 1:10, rather than a lower ratio, was used to ensure acceptable signal-to-noise in the 2D IR experiments on the thin films. To verify that this relatively high concentration of SeCN⁻ was not perturbing the dynamics of the BmimNTf₂, 2D

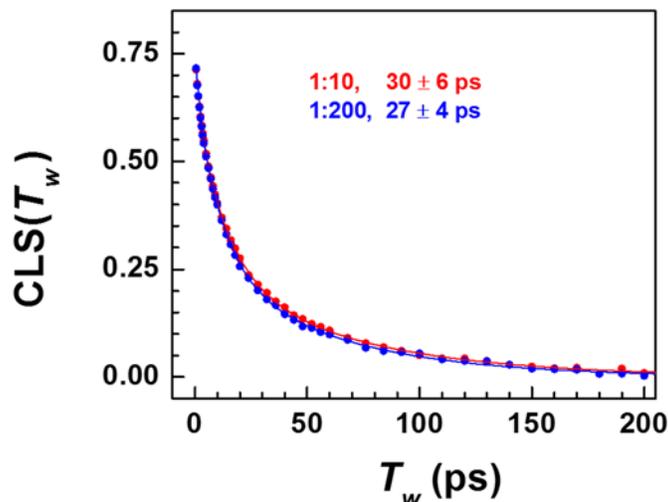


Figure S2. CLS(T_w) decay curves and correlation times for bulk samples of BmimSeCN in BmimNTf₂, using the SeCN⁻ as the vibrational probe. Red = sample with 1:10 ratio of BmimSeCN:BmimNTf₂; blue = sample with 1:200 ratio. The points are experimental data; the curves are tri-exponential fits. The numbers in the legend are correlation times of the decays calculated based on the fits. The dynamics of the two samples are essentially identical.

IR experiments were performed on bulk samples of BmimSeCN:BmimNTf₂ with ratios of 1:10 and 1:200. The CLS decay curves of these two samples are nearly identical, and the correlation times are equal within error (Figure S2). Therefore, even in a 1:10 ratio, the BmimSeCN does not significantly affect the dynamics of the BmimNTf₂.

B. Thickness Characterization by FTIR Absorption Spectra

The average thickness of each ionic liquid film was determined from its FT-IR spectrum, using the three aromatic C-H stretching modes of the Bmim cation, located in the 3050-3200 cm⁻¹ region (Figure S3A). For each film, the three overlapping peaks were fit simultaneously with three Gaussian peaks (Figure S3B). The resulting height of the strongest peak (3159 cm⁻¹)

was used to calculate the thickness of the film, by comparing it to the corresponding peak height in a 25 μm -thick bulk sample of the 1:10 molar mixture of BmimSeCN:BmimNTf₂. The

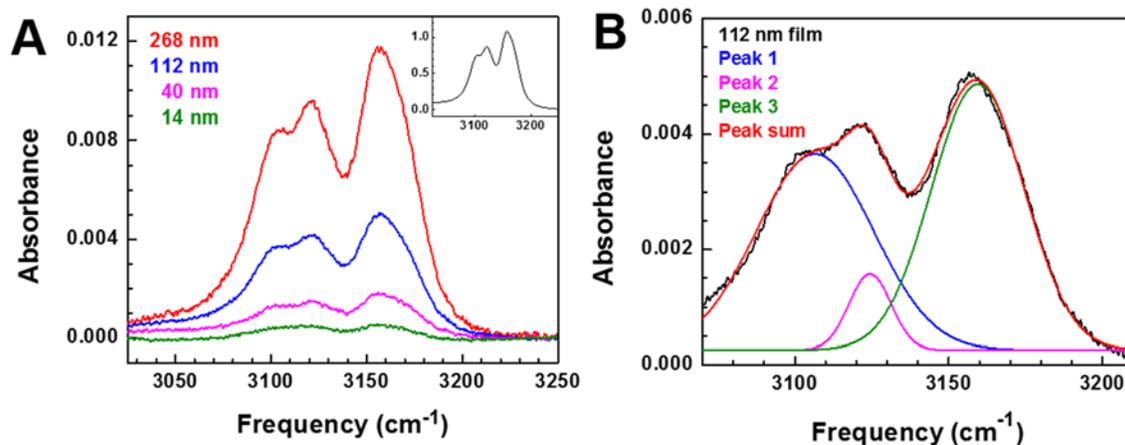


Figure S3. FTIR spectra in the aromatic C-H region for 1:10 BmimSeCN:BmimNTf₂ samples. **A.** Spectra of thin films of various thicknesses, showing three peaks in this region. Inset: Spectrum of a 25 μm -bulk sample. **B.** Spectrum of a 112 nm-thick film, plotted along with the results of a simultaneous three-peak Gaussian fit. The height of the peak at 3159 cm^{-1} was used to quantify the thicknesses of the samples.

extinction coefficients in the films were assumed to be equal to those in the bulk sample. The spectrum of the substrate functionalized with the ionic monolayer was subtracted from each film spectrum before the fitting procedure.

C. Optical Images and Raman Microscopy

The homogeneity of the films was evaluated with a Horiba XploRA Confocal Raman microscope, using a 10X objective for optical images and a 100X objective for Micro-Raman spectra acquisition, a 532 nm laser, an 1800 g/mm grating, a 300 μm detector slit, and a 500 μm confocal pinhole. The spatial resolution is better than 1 μm . Using the N-S vibrational mode of the ionic liquid at $\sim 740 \text{ cm}^{-1}$,² one-dimensional Raman intensity profiles were acquired using a 20 μm step size, with five accumulations of 10 seconds at each spot. The 2.5 cm diameter sample was scanned over a number of 300 μm regions. For $\sim 278 \text{ nm}$ -thick films, it was found that in most regions, the one sigma variation in thickness was approximately $\sim 10\%$, i.e. $\sim 30 \text{ nm}$ in thickness, with the variation increasing as the films become thinner ($\sim 30\%$ or $\sim 30 \text{ nm}$ variation for $\sim 112 \text{ nm}$ -thick films, and $\sim 45\%$ or $\sim 20 \text{ nm}$ variation for $\sim 39 \text{ nm}$ films). The thickness variation of the $\sim 14 \text{ nm}$ -thick films could not be evaluated using this method, due to the small Raman signal from such thin samples. For the discussion given in section II-F in the main text, we assumed that the variation for the thinnest ($\sim 14 \text{ nm}$) film is on the same order as

the second thinnest (~ 39 nm) film. For some film samples in a small number of the measured regions there were large deviations from the average that appeared to be bumps on the film surface.

In the 2D IR experiment, the laser spot sizes cause the signal to arise from a sample area that is ~ 180 μm in diameter. Therefore, the 2D IR signal averages over the point to point variations. For each sample, the thicknesses listed shown in Figures 4 and 5 are the average thicknesses, and the signal is from the average about the nominal thickness, that is, short distance variations in thickness are averaged by the size of the IR spot. As discussed in the main text, the thickness variations do not significantly affect the results of the 2D IR experiments.

D. Ultrafast Infrared Laser System

The laser system and the implementation of near-Brewster's angle reflection pump-probe geometry were described in detail in a previous publication.³ A Ti:Sapphire oscillator/regenerative amplifier (Mai Tai SP, Spectra Physics / Spitfire Ace, Spectra Physics) is used to pump a home-built multi-stage optical parametric amplifier to generate infrared pulses at 3 kHz repetition rate. The IR pulses were ~ 25 μJ in energy with a pulse duration of ~ 160 fs full width half maximum (FWHM) with a bandwidth of ~ 95 cm^{-1} FWHM, centered at 2065 cm^{-1} . The IR pulse was split into a pump pulse (92%) and a probe pulse (8%). The pump pulse was sent to a germanium acousto-optic modulator (Ge-AOM, Isomet) pulse shaping system to generate two pulses, pulses 1 and 2 in the 2D IR three pulse sequence, and to control the pulses' timing and phase. A four-shot phase cycle sequence was used to suppress the effects of scattered light that otherwise interfere with the measurements; additional scatter suppression was achieved by setting the pump polarization perpendicular to the probe polarization, and then resolving the signal with polarization perpendicular to the pump (i.e., parallel to the probe). The pump pulses were focused into the sample with a $f=15$ cm lens to produce a spot size of ~ 110 μm ($1w$), and the probe pulse was focused with a $f=10$ cm lens to ~ 80 μm ($1w$). The probe pulse arrived after the pump pulses with a controlled delay time determined by a mechanical delay line.

Using a pulse shaping system results in the 2D IR vibrational echo signal being collinear with pulse 3 (the probe pulse). Pulse 3 acts as the local oscillator (LO) for heterodyne detection. Because pulse 3 generates the echo and heterodynes it, the LO has a well-defined phase relationship to the echo signal, which eliminates post data collection processing to correct for

phase errors between the LO and the signal. There are many other advantages of using pulse shaping, e.g., phase cycling and electronically scanning the time between pulses 1 and 2 shot-to-shot. However, it is not possible in the normal transmission geometry (see Figure 3A) to change the signal-to-LO amplitude ratio. The signal is detected as the percent modulation of the LO. When the signal is very small compared to the LO, as it is from a thin film or monolayer in transmission, the modulation is very small, resulting in poor signal-to-noise ratio.

The near-Brewster's angle reflection geometry overcomes this problem.³ For a thin film, the polarization induced in the sample by the three incident pulses produces the signal electric fields that propagate in both the transmission direction and in the reflection direction (see Figure 3B). Pulse 3, the LO, also reflects in the same direction but the reflection is much weaker than the transmitted LO. By using *p*-polarization for pulse 3 and using an incident angle close to the Brewster's angle, the LO can be reduced such that the percent modulation is greatly increased. The enhancement can be up to a factor of 50.³ By detecting the signal/LO in reflection, high quality data was obtained from the thin films. The incident angle to the sample surface was set to 53°.

References

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