Supporting Information

Structural Dynamics in Ionic Liquid Thin Films: The Effect of Cation Size

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I. Influence of Thickness variation on the Observed CLS Dynamics of Thin Films

As discussed in the text, the variation in thickness of each film is measured with Raman microscopy. In the experiments, the IR spot size, 99% of the intensity, is ~200 μm. Over this distance, the thickness of the film varies in a manner that appears to be random from the Raman microscopy experiments. The variation can range from 5% to 25%. Therefore, the measurement for a given film thickness is actually an average over a range of thicknesses contained in the IR spot. The analysis presented in the main text treated each film as if it had a perfectly uniform thickness. He we show that taking a thickness distribution into account has a negligible impact on the results.

We take the thickness distribution to be described by a Gaussian distribution with an average thickness d_{avg} and a standard deviation σ. Then the probability density function for the thickness is

$$p(d) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\left(d - d_{\text{avg}}\right)^2}{2\sigma^2} \right) \tag{S1}$$

The CLS for a film with a thickness distribution is

$$\text{CLS}_{\text{film,distrib}}\left(d_{\text{avg}}, \sigma, T_{\text{w}}\right) = \int_0^\infty \text{CLS}_{\text{film}}\left(d, T_w\right) p(d) \left(\frac{d}{d_{\text{avg}}} \right) \text{d}d \tag{S2}$$

where $\text{CLS}_{\text{film}}(d, T_w)$ is given by Eq. 4 in the main text, and $p(d)$ is given by Eq. S1. The additional factor d/d_{avg} accounts for the fact that because the signal depends linearly on the thickness, thicker areas will contribute more to the CLS than thinner areas.

If we use Eq. 4 from the main text and Eq. S1 to substitute for $\text{CLS}_{\text{film}}(d,T_w)$ and $p(d)$, respectively, then, after simplifying Eq. S2, we obtain

$$\mathrm{CLS}_{\mathrm{film,distrib}}\left(d_{\mathrm{avg}},\sigma,T_w\right) = \frac{2}{\sqrt{2\pi}\sigma d_{avg}}\sum_{j=1}^{n}\int_{d=0}^{d=\infty}\exp\left(-\frac{\left(d-d_{\mathrm{avg}}\right)^2}{2\sigma^2}\right)\int_{r=0}^{r=d/2}\Delta_j^2(r)\exp\left(\frac{-T_w}{\tau_j(r)}\right)\mathrm{d}r\ \mathrm{d}d \tag{S3}$$

It is convenient to change the order of integration in Eq. S3, giving

$$\mathrm{CLS}_{\mathrm{film,distrib}}\left(d_{\mathrm{avg}},\sigma,T_{\mathrm{w}}\right) = \frac{2}{\sqrt{2\pi}\sigma d_{avg}}\sum_{j=1}^{n}\int_{r=0}^{r=\infty}\Delta_j^2(r)\exp\left(\frac{-T_{\mathrm{w}}}{\tau_j(r)}\right)\int_{d=2r}^{d=\infty}\exp\left(-\frac{\left(d-d_{\mathrm{avg}}\right)^2}{2\sigma^2}\right)\mathrm{d}d\,\mathrm{d}r \tag{S4}$$

Evaluating the integral with respect to d in Eq. S4 gives

$$\mathrm{CLS}_{\mathrm{film,distrib}}\left(d_{\mathrm{avg}},\sigma,T_{\mathrm{w}}\right) = \frac{1}{d_{\mathrm{avg}}}\sum_{j=1}^{n}\int_{r=0}^{r=\infty}\Delta_j^2(r)\exp\left(\frac{-T_{\mathrm{w}}}{\tau_j(r)}\right)\left(\mathrm{erf}\left(\frac{d_{\mathrm{avg}}-2r}{\sqrt{2}\sigma}\right)+1\right)\mathrm{d}r \tag{S5}$$

where erf is the error function.

To investigate the effect of the thickness distribution on the CLS, Eq. S5 was used to calculate CLS curves for various values of d_{avg} and σ, while keeping all other parameters fixed to the values obtained from the fits to the experimental data using Eq. 4 in the main text. For each value of d_{avg}, changing σ has only a small effect on the CLS curve. For example, Fig. S1 shows the calculated CLS curves for two Bmim films, one of which has d_{avg} = 40 nm and σ = 0.01 nm, a negligible variation, and the other has d_{avg} = 40 nm and σ = 12 nm, a 30% variation. The two curves are very similar, differing by less than 0.013 across all values of T_w. For other values of d_{avg}, the difference between the low standard deviation and the high standard deviation curves is even smaller. Therefore, the effect of the thickness distribution is negligible, and it is sufficient to use Eq. 4 in the main text to fit the experimental data.

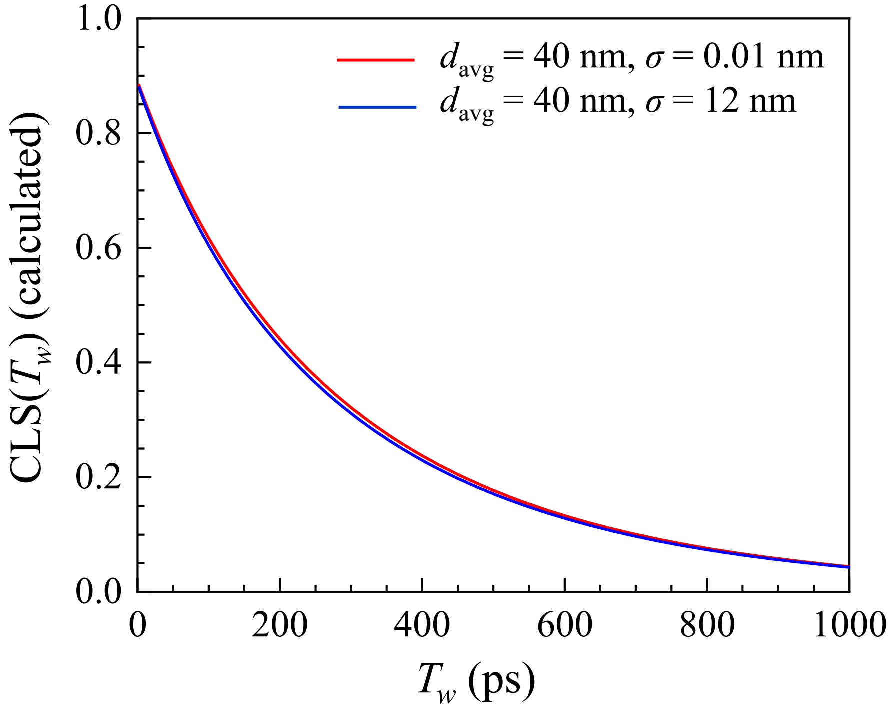

Figure S1. Calculated CLS curves for two Bmim films with the same average thickness but different standard deviations of the thickness. The two curves, one with negligible thickness variation and the other with 30% variation, are nearly identical, showing that the thickness distribution can be neglected without affecting the results.

II. FT-IR spectra of films

Fig. S2 shows the normalized FT-IR spectrum of the CN stretch of 1:10 HmimSeCN/$HmimNTf_2$ and DmimSeCN/$DmimNTf_2$ in films and in the bulk liquid. The CN stretch of $SeCN^-$ is used as the vibrational probe. Within experimental error, the spectra of the CN stretch in the films are the same as in the bulk ILs.

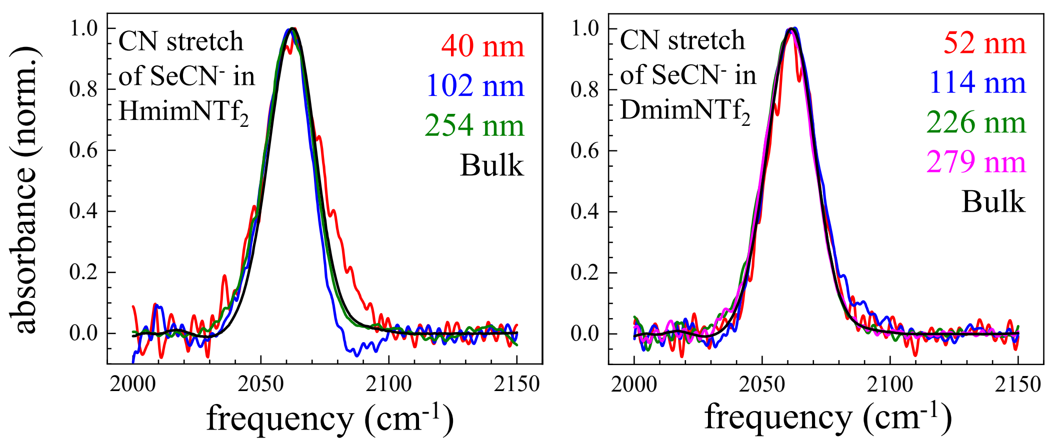

Figure S2: Normalized spectra of the CN stretch of $SeCN^-$ in thin films and the bulk ILs of $HmimNTf_2$ and $DmimNTf_2$. Within experimental error, the spectra in the films are the same as the spectra in the corresponding bulk ILs.

Figure S3 shows the aliphatic and aromatic CH stretches of the ILs $HmimNTf_2$ and $DmimNTf_2$ in films and in the bulk ILs. The areas of the curves have been normalized. The aromatic C-H stretches between 3070 – 3210 cm^{-1} are used to determine the thickness of the films by

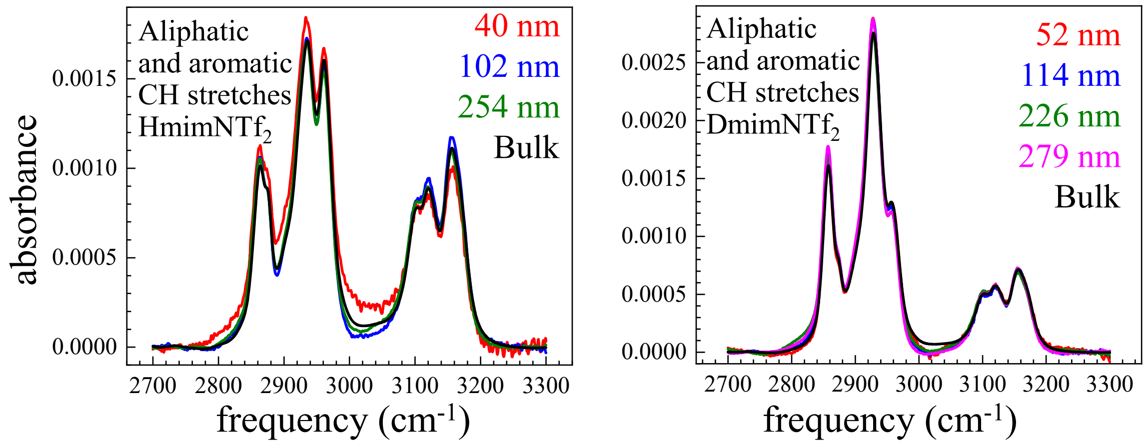

Figure S3: The aliphatic and aromatic CH stretches of $HmimNTf_2$ and $DmimNTf_2$. The aromatic stretch regions are used to determine the film thickness.

comparing their absorbances to those of the bulk IL of known sample thickness. Within experimental error the spectra are the same.

III. Relation between Precursor Solution and Film Thickness

Figure S4 shows the relation between the concentration spin coating precursor methanol solution and the film thickness. A linear relation is observed for all three ionic liquids with a negligible intercept. Higher concentrations are needed to for Bmim films to obtain the same thickness as

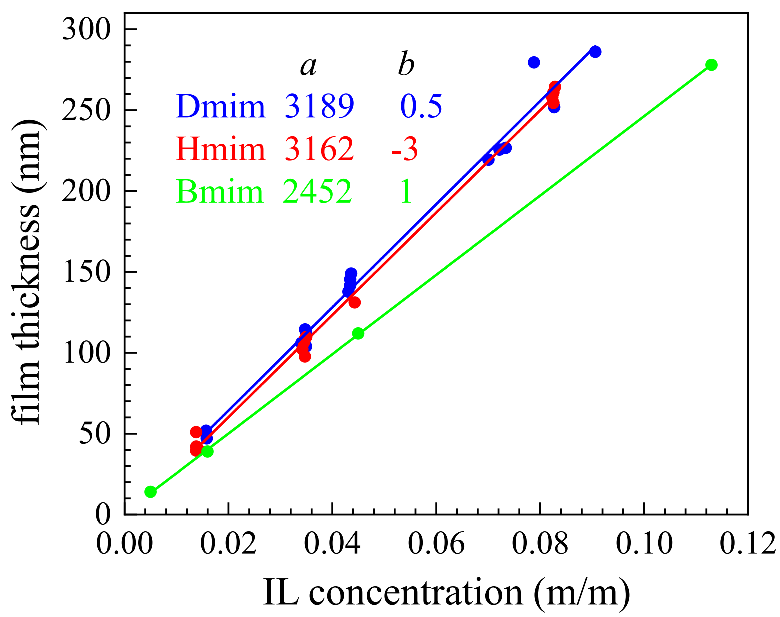

Figure S4. The relationships between the concentrations of the ILs in the methanol spin coating solution and the film thickness. The points were fit (lines) to liner equations, thickness = a×[concentration] + b.

Hmim or Dmim films. All of the Dmim and Hmim films we studied in this work are plotted in Fig. S4. For Bmim films, we used averaged numbers from a previous publication.[1]

IV. Reproducibility of Dynamics for Nominally the Same Thickness Film

As mentioned in the main text, films prepared on different substrates that are approximately the same thickness yield somewhat different dynamics. Typical data sets are shown in Fig. S5 for the three ILs with approximately the same thicknesses.

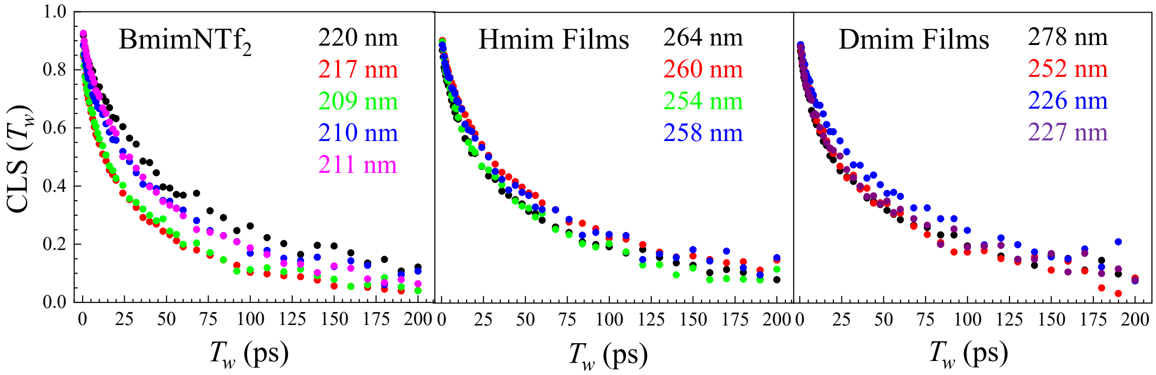

Figure S5: 2D IR data taken on films of the three ILs, $BmimNTf_2$, $HmimNTf_2$ and $DmimNTf_2$. Each set of data points was taken of a different substrate. The data show a spread in the measured dynamics that is greatest for $BmimNTf_2$.

Each data set is for a separately functionalized SiO_2 coated CaF_2 substrate. The results for $BmimNTf_2$ have a wider spread in the dynamics than the films composed of cations with longer alkyl chains. This may be due to the fact that $BmimNTf_2$ films deviate more from bulk dynamics than films made from $HmimNTf_2$ and $DmimNTf_2$ (see Figs. 4 and 5). We found if a single substrate is used for several films of the same thickness the results are virtually the same. This is done by functionalizing a substrate, spin coating a film, taking data, and then cleaning off the IL film, spin coating another film of the same thickness, and taking data. The current hypothesis is that functionalization step is not completely reproducible, resulting in a different density of surface bound cations from one substate to another. The results suggest that the density of surface bound cations influences the film dynamics.

IV. Effect of Probe Concentration

In the experiments, the IR probe $SeCN^-$ ions are added to the Bmim/Hmim/Dmim NTf_2 ILs in the form of Bmim/Hmim/Dmim SeCN. Therefore only the anion is different. To verify that the probe does not influence the IL dynamics in the films, we did the following experiments. Previsously[1] the CLS decays of IL samples with 1:200 and 1:10 Bmim SeCN/NTf_2 mixtures were found to be identical. In this work, we also measured a 1:5 BmimSeCN/NTf_2 mixture.

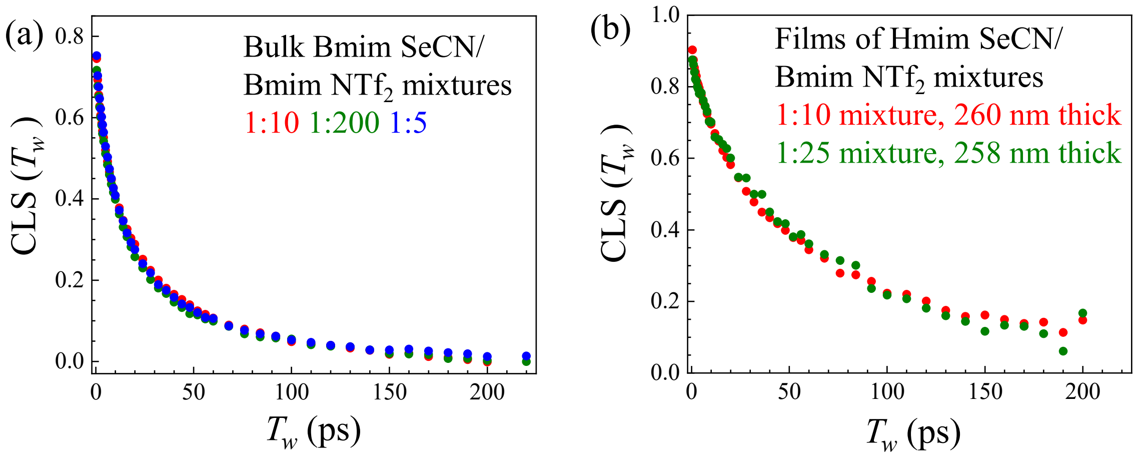

Figure S6: 2D IR data (a) in the bulk liquid at three probe concentrations; (b) in films at two probe concentrations. The results show that the 1:10 concentration use in the experiments does not affect the results.

The CLS decays are plotted in Fig. S6. Adding the probes has no effect on the measured dynamics of the bulk ionic liquids. In Fig. S6 (b), two films are made on the some substrate, one using 1:10 (10%) Bmim SeCN/NTf_2 mixture and the other using 1:25 (4%) Bmim SeCN/NTf_2 mixture. The CLS decays are identical within the noise. The experiments demonstrate that the addition of the probe does not influence the film dynamics by changing the IL dynamic properties or through preferential interactions with the interface.

References:

1. Nishida, J.; Breen, J. P.; Wu, B.; Fayer, M. D., Extraordinary Slowing of Structural Dynamics in Thin Films of a Room Temperature Ionic Liquid. *ACS Central Science* **2018,** *4* (8), 1065-1073.