

Supporting Information

Controlling the Dynamics of Ionic Liquid Thin Films via Multilayer Surface Functionalization

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I. CLS Decays of Films on More Substrates

Figure S1 is an addition to Figure 4 in the main text. Time dependent CLS on 12 substrates are shown.

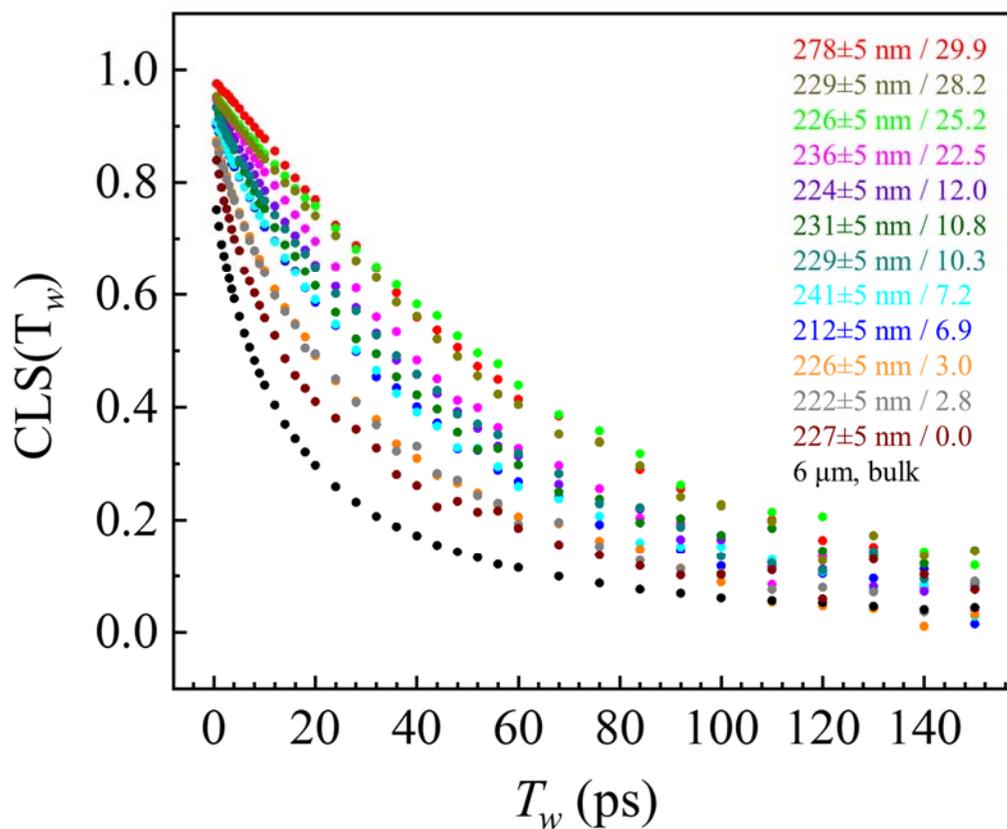


Figure S1. CLS(T_w) of ~220 nm IL films on different substrates. The inset shows the thicknesses of films, and the surface charge density on the substrate (in nm⁻²).

II. Dependence of Probe Concentration on Measured CLS

To verify that the measurements of CLS are not significantly affected by preferential absorption of SCN^- ions on the surfaces, we compared the $\text{CLS}(T_w)$ measured in IL thin films made using 1:10 and 1:20 mixtures of BmimSCN and BmimNTf₂. ~120 nm films made using both mixtures on a substrate with 25.2 nm^{-2} surface charge density, and ~230 nm films on a neutral substrate functionalized with triethoxy(ethyl)silane are compared in Figure S2. In both cases, the CLS decays of the 1:10 and 1:20 samples are identical within experimental error.

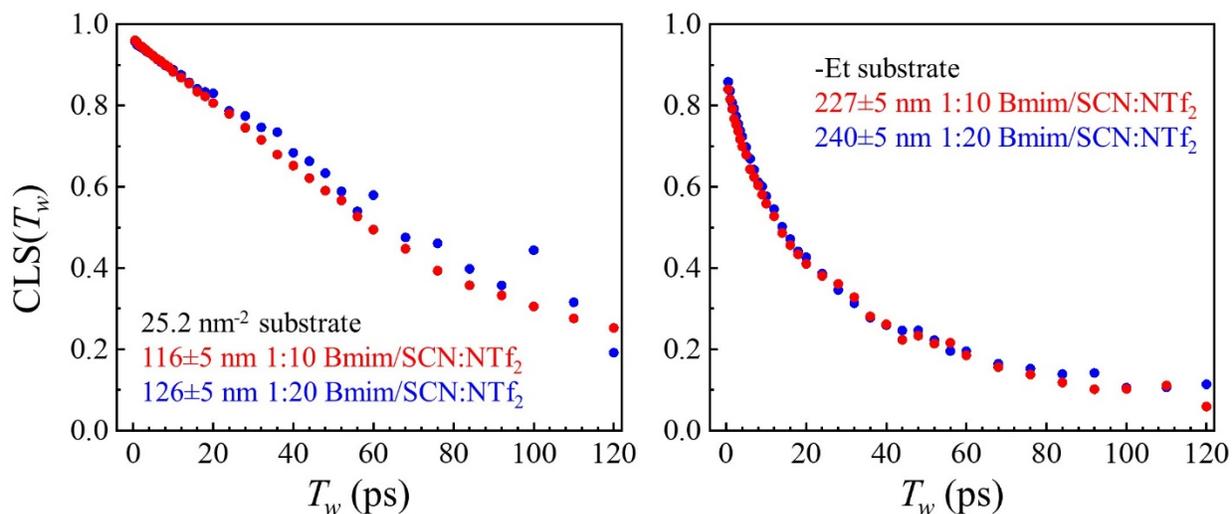


Figure S2: Comparison of CLS decays measured with 1:10 and 1:20 mixture of BmimSCN and BmimNTf₂ in ~120 nm films on a 25.2 nm^{-2} charge density substrate (left) and ~220 nm films on a -Et substrate (right).

III. Making IL Films on Neutral Substrates

The procedure for surface functionalization of neutral substrates is shown in Figure S3. SiO₂ coated CaF₂ windows are immersed in the toluene solution of triethoxysilyl-R reagents with different head groups R, and heated at 80 °C for 24 hours. The FT-IR spectra of functionalized substrates are shown in Figure S4.

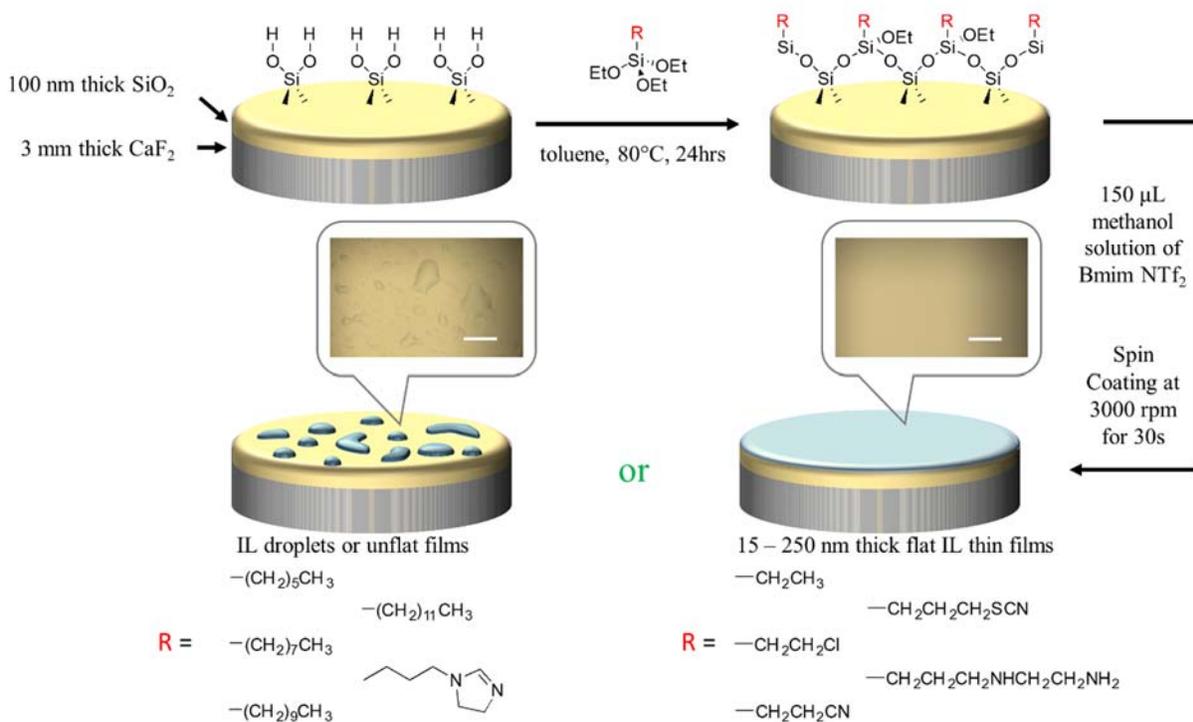


Figure S3: Surface functionalization and attempts to make ionic liquid thin films on neutral substrates.

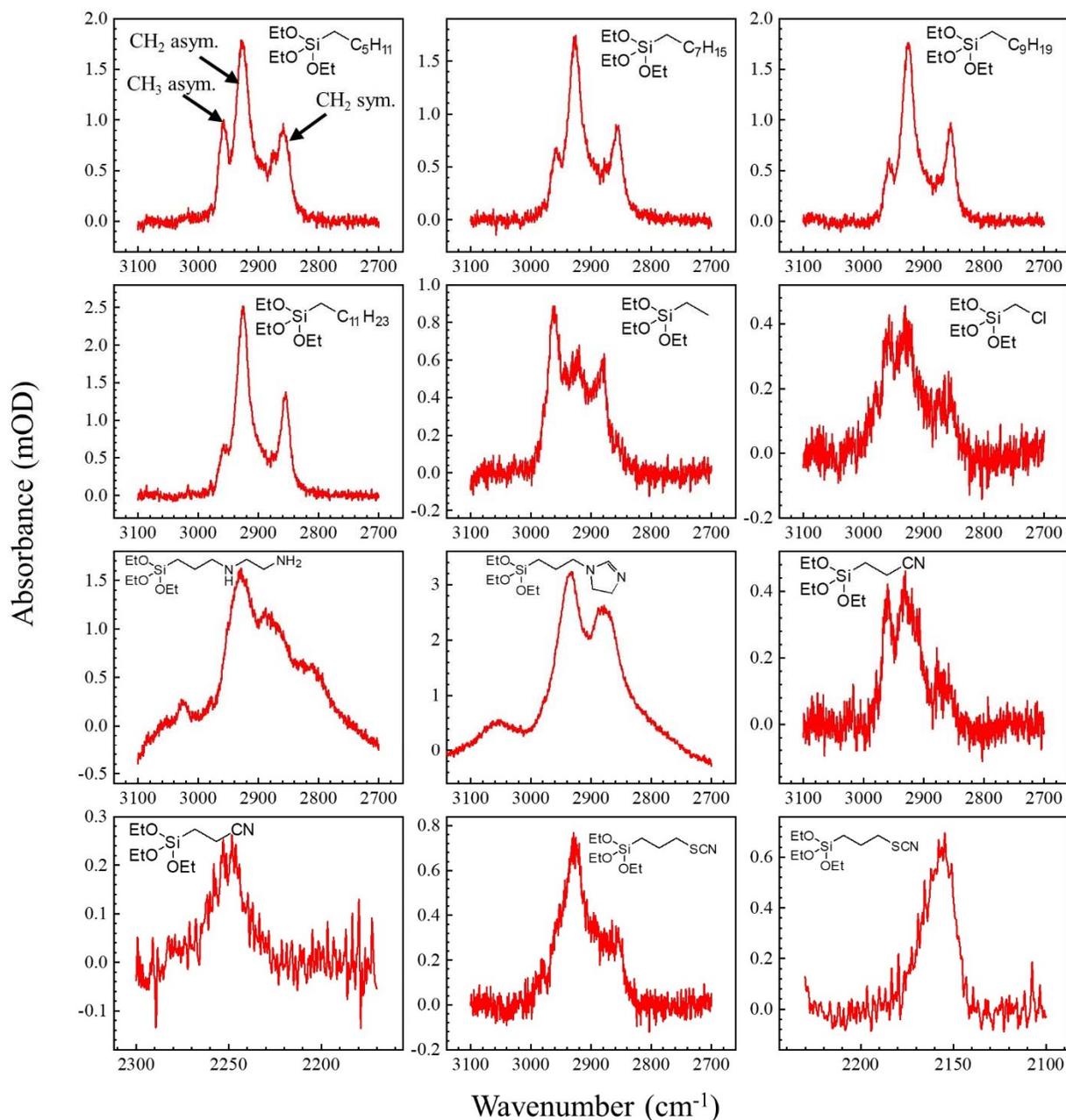


Figure S4. FT-IR spectra of functionalized neutral windows. The chemicals that were used for the functionalization reactions are shown in each graph.

Methanol solutions of BmimNTf₂ are spin coated on these substrates, and the thickness variations are also characterized using visible and confocal Raman microscopes. Figure S5(a1) shows the picture of a 121 nm BmimNTf₂ film on substrate functionalized by triethoxy(ethyl)silane, and S5(a2) shows the Raman spectrum taken at the center green dot. Raman spectra are taken at each green dot, and the N-S stretch peak from the NTf₂⁻ anions is

integrated for each spot. The results of the integration are plotted in S5(a3). The standard deviation of the signal is 8.5%, indicating the film is quite flat. Figure S5(c1) shows the result of spin coating on a substrate functionalized with triethoxy(hexyl)silane, where the IL beads up. Raman spectra taken at the green dot (on the IL droplet) show strong IL peaks, while spectra taken at the blue dot (on an empty spot) show only the Raman peaks from the substrate.

Attempts were made to make IL films on substrates functionalized by various triethoxysilyl-R chemicals. Their visible images are shown in Figure S6. The chemical used for surface functionalization is also shown on each plot. When the head group R is short or polar, like chloromethyl (-MeCl), cyanoethyl (-EtCN), ethyl (-Et), thiocyanate (-SCN) or 3-(2-aminoethylamino)propyl (-C₃NC₂N), very flat films with thickness variations around 5% can be formed. But when the head groups are long alkyl groups including hexyl, octyl, decyl and dodecyl, the ionic liquid beads up instead of making a flat film.

This difference can be explained by the incompatibility between long non-polar groups and ILs, which reduces the affinity between the surface and the ILs. Another possible explanation is that the mechanisms of forming surface layers are different for different head groups. When the head group is a long alkyl chain, the triethoxysilanes first form a precursor monolayer in toluene solution through physical absorption with the help of a thin water layer absorbed on the substrates. Then crosslinking occurs, which anchors the monolayer onto the surface.¹⁻² This mechanism leads to the formation of a well-established monolayer. When the chain is short or polar, multilayers can be formed,³ which might increase the polarity of the surface.

For 2D-IR experiments, SCN⁻ ions are added into the BmimNTf₂ ILs as vibrational probes in the form of BmimSCN. Films made with a 1:10 mixture of BmimSCN and BmimNTf₂ are of the same quality as films made using pure BmimNTf₂, as shown in Figure S5(b1/b2/b3). The 222 nm film made with 1:10 IL mixture is one of those used in the 2D-IR measurements.

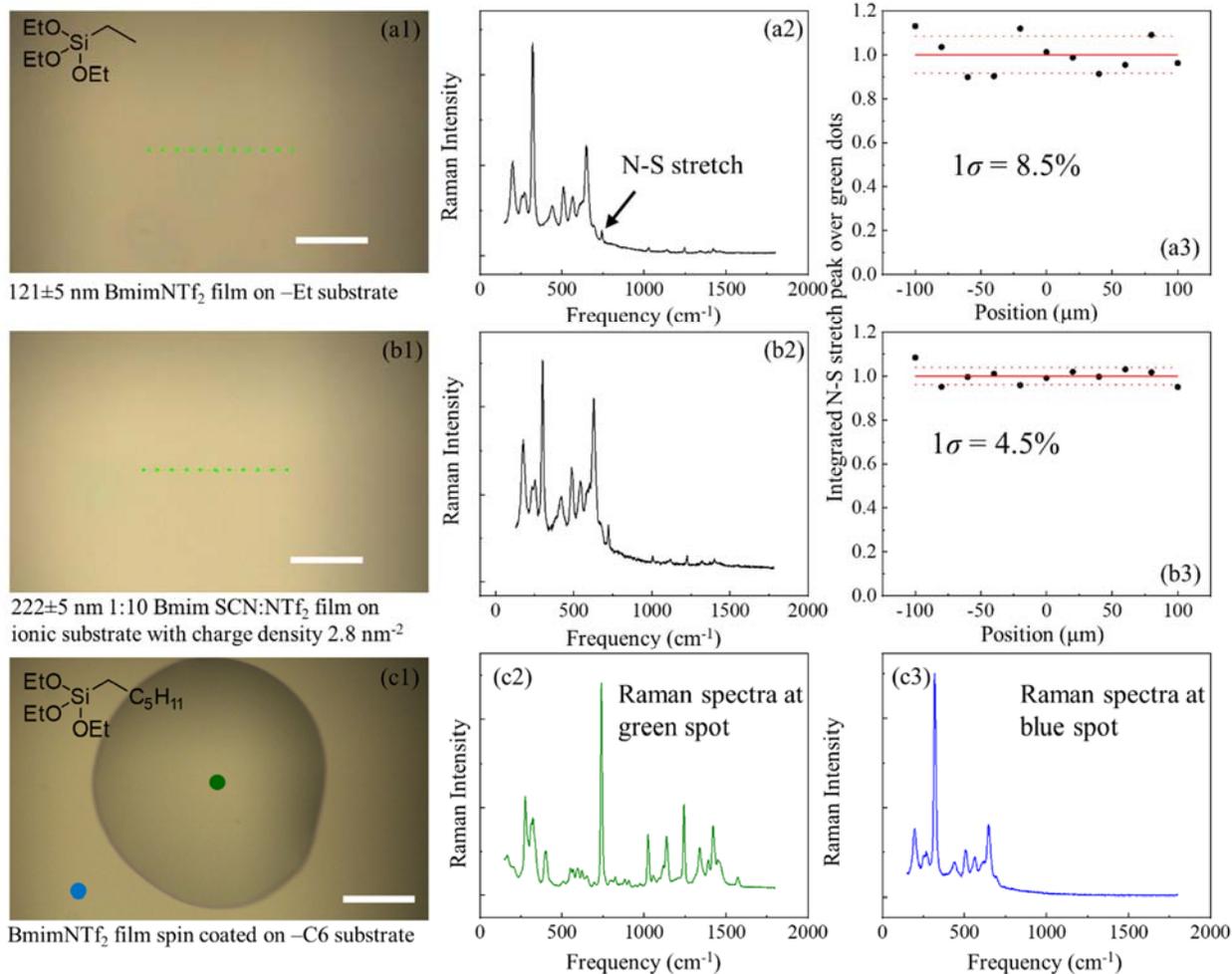


Figure S5: Top: Flatness characterization of a 121 nm film on neutral substrate functionalized with triethoxy(ethyl)silane. (a1): The visible image of the film. (a2): The Raman spectrum taken at the center green dot. (a3): Integrated N-S stretch intensity at each dot, and the standard deviation. Middle: Some graphs for a 222 nm film made with a 1:10 BmimSCN and BmimNTf₂ mixture on a charged group functionalize substrate. This is one of the films used in the 2D-IR experiments. Bottom: Spin coating BmimNTf₂ on a substrate functionalized by triethoxy(hexyl)silane. (c2) and (c3) are Raman spectra taken at the green and blue spots, respectively. The white bars shown in the graphs have a length of 100 μm in all images.

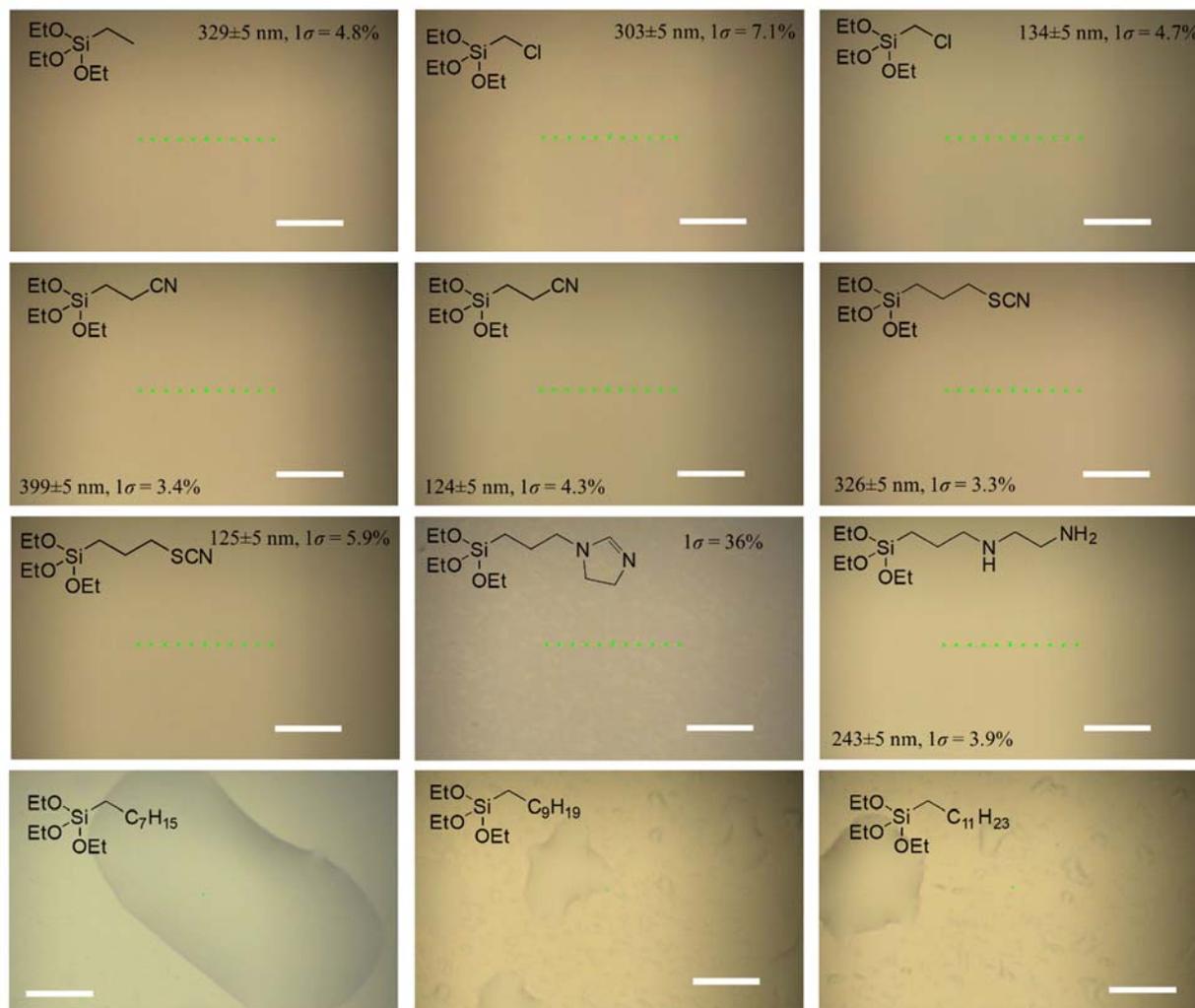


Figure S6: Results of spin coating BmimNTf₂ on substrates functionalized with triethoxysilanes with different head groups. The chemical used in functionalization is shown on each figure. After spin coating, if the IL forms a film, Raman spectra are measured at the green dots, and the variation of the N-S stretch in the NTf₂⁻ Raman signal is shown on the figure. White bars have lengths of 100 μm.

IV. Linear Spectra of IL Thin Films

Figure S7 shows the normalized FT-IR spectra of the imidazolium ring C-H stretching region of two films and the bulk liquid, both with the SeCN⁻ vibrational probe. Their spectra are almost identical. The minor mismatches are caused by errors in background subtraction of the functionalized substrate with no film. The same results are obtained for films with other surface charge densities. The peak positions of the IL films and the bulk IL are the same.

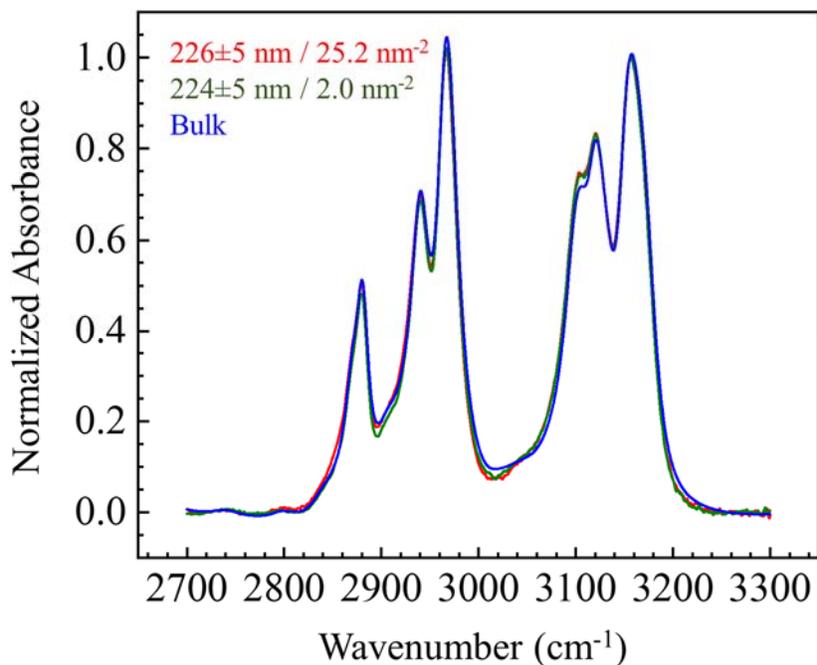


Figure S7: Normalized FT-IR spectra showing C-H stretching region of bulk IL and IL films. The film thickness and the surface charge density of the substrate are given in the figure. The spectra are the same within experimental error. Of particular importance is that the peak positions are identical.

References

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