Supplementary Information

In this section we give one possible structural solution for the ionic liquid against the mica surface obtained by fitting the NR data. As discussed in the main text, we do not believe this is a unique solution.

Here we have also endeavoured to constrain the model to be physically reasonable which also provides additional constraints. This includes constraining the model to have an excess of cations over anions such that the overall interface (with the mica negative charge) is neutral. The Si, SiO_2, Glue and mica structures used to fit the data with the ionic liquid are the same as used to fit the bare mica surface in the three toluene contrasts.

The overall structure of the ionic is schematically illustrated in the Figure S.1.

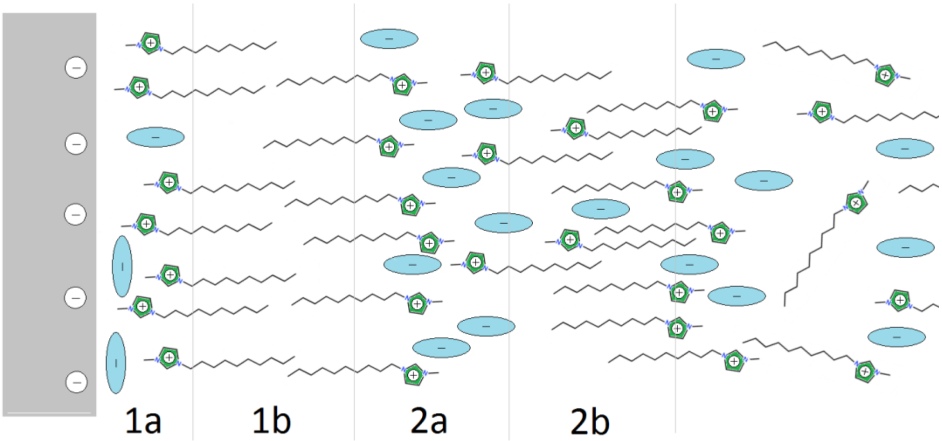

Figure S.1. Schematic illustration of the surface structure of the ionic liquid adjacent to the mica surface, consistent with the neutron reflection data. In the final fit there are seven layers included, although the outermost layer has essentially the same scattering length density as the bulk ionic liquid and will not contribute significantly to the reflectivity.

The layer adjacent to the mica, layer 1a, is a mixture of cations and anions (no alkyl tails).

The next layer, layer 1b, is entirely alkyl tails.

Subsequent layers alternate as predominantly ion rich then alkyl tail rich.

The outer layer is essentially the correct mix of ionic species and alkyl tails to be approximately the same composition as the bulk ionic liquid.

Tables

Species	Vol/Å^3	Σb_i/ fm	SLD (Å^{-2} x10^{-6})
MIM+	124	22.8	1.85
NTF2-	248	85.5	3.45
d-C10	282	206.6	7.32
Ionic Liquid bulk	657	314.9	4.82

Table S.1. Physical Characteristics of the ionic liquid chemical groups and their scattering length densities used in the structural analysis. Vol is the molecular fragment volume, b_i the scattering length of the atoms in the species and Σb_i is the sum of these for the fragment. SLD is the scattering length density. Fm is a femtometre, 10^{-15}m.

Substrate

	Silicon	SiO_2	Glue	Mica
d	N/A	17.0+/- 1.5 Å	7.5 +/- 1μm	30.5 +/- 1μm
SLD ($Å^{-2}x10^{-6}$)	2.1	3.5	1.0	3.8
Roughness	6.4 +/-4 Å	6.4 +/-1 Å	16.8 +/-1 Å	3.0 +/-3 Å

Table S.2. Structural characteristics of the substrate components (as given in main paper). d is the layer thickness and SLD the scattering length density of the layer calculated from the elemental composition.

Ionic Liquid

Layer	1a	1b	2a	2b	3a	3b	4a
Thickness/ Å	3 +/-3 Å	9 +/-0.5 Å	10 +/-1 Å	15.5 +/-1.5 Å	12.0 +/-2.5 Å	6.0 +/-4 Å	9.0 +/-9.0 Å
SLD / $Å^{-2}$ $x10^{-6}$	2.17 +/- 0.5	7.32*	2.81 +/- 0.15	5.54 +/- 0.3	4.40 +/- 0.4	5.40 +/- 0.2	4.80 +/- 0.2

Table S.3. Possible ionic liquid layer structure determined from the experimental neutron reflection data. All interfacial roughnesses are taken as 1.5 Å. *the calculated SLD of tails only.

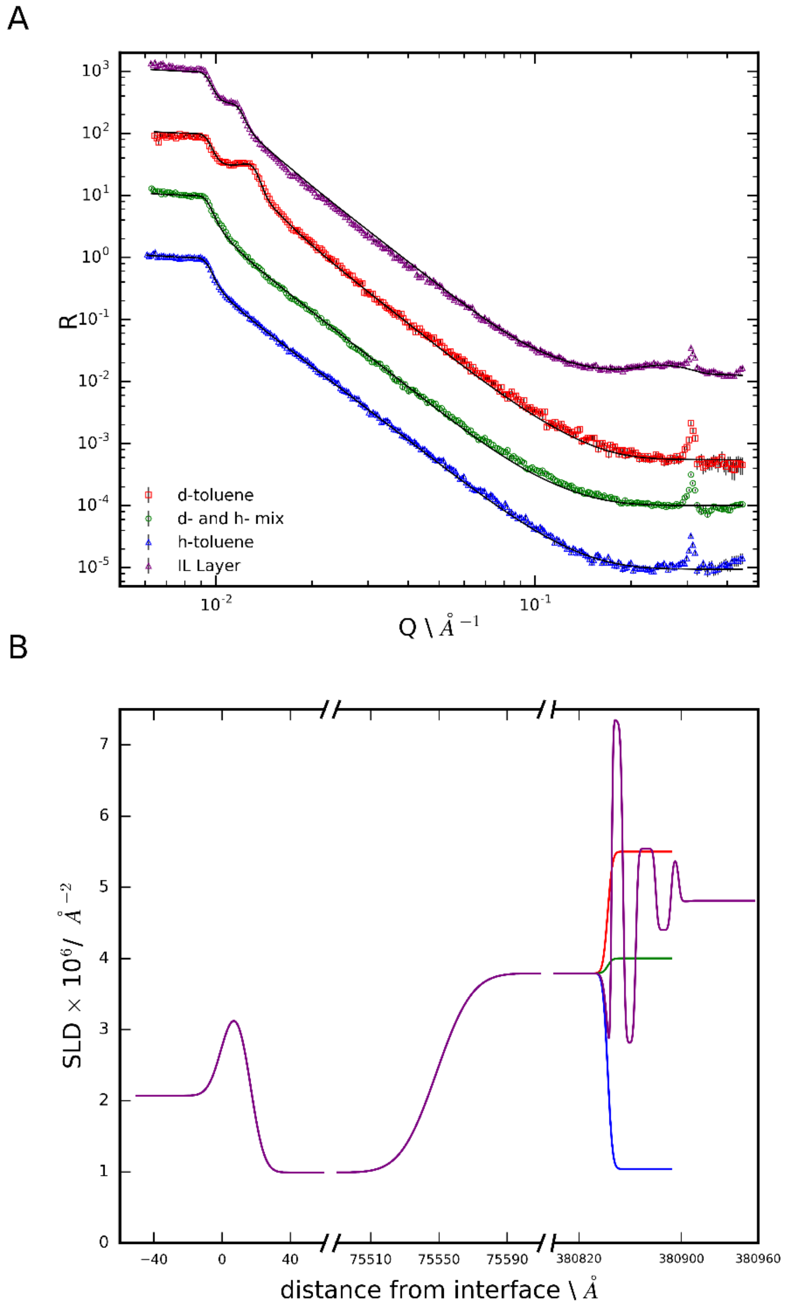

Figure S.2. Neutron reflectivity data and calculated reflectivity using the structural parameters in the tables above with the SLD profile used to calculate the reflectivity. (top three data sets: bare mica in different toluene contrasts. Bottom data set: C10-deuterated ionic liquid on the mica)

Overall the agreement with experiment and model is reasonably good, particularly given the difficulty of this experiment. The principle feature of the ionic liquid at Q= 0.29 $Å^{-1}$, is well captured. The layer structure is complex so one cannot readily identify a periodicity and the reflection is not particularly sensitive to the outer two layers 9which have a low contrast to the bulk liquid). The inner layers (representing approximately two ionic liquid bilayers) is approximately 43.5 Å, corresponding to approx. 22 Å per bilayer.

The biggest discrepancy between experiment and calculation is over the low/intermediate Q region, just below and above the critical angles, where the calculated scattering is slightly higher than experimentally determined. This is attributed to a possible slight difference in alignment. However, this region of the data does not depend on the adsorbed ionic liquid structure and essentially arises only from the mica/glue/silica/silicon interfaces and should not affect the fitting of the ionic liquid structure..

The structural model at high Q, where the ionic liquid feature is present is sensitive to the structural model of the ionic layering. However, there are several reasonable structures that are similarly consistent with this data, as expected (only one presented here). The physical constraints discussed above significantly limit the possible solutions. However, there are still a number of possible alternative structures such as the location of the excess of the cations over the anions, which can be located entirely in the first ionic layer or spread over several layers (as in the case presented here).

It is important to note that there is a possibility that the high Q feature arising from the ionic liquid may arise from some off-specular scattering of the bulk ionic liquid, as in Grazing Incidence Small Angle Neutron Scattering (GISANS). However, no evidence of such excess scattering was observed on opening the detector slits. Hence we can conclude that this feature can be attributed to the ionic liquid layering.