Supplementary Information

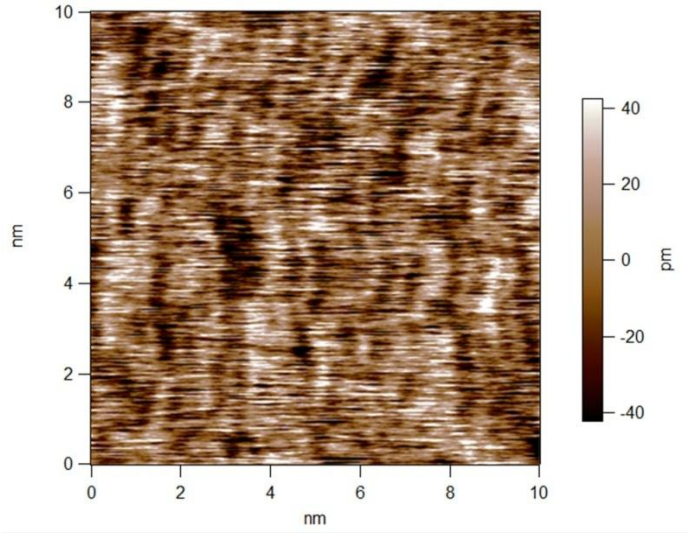

Figure A. Soft contact AFM height image of the EAN innermost layer adsorbed to mica.

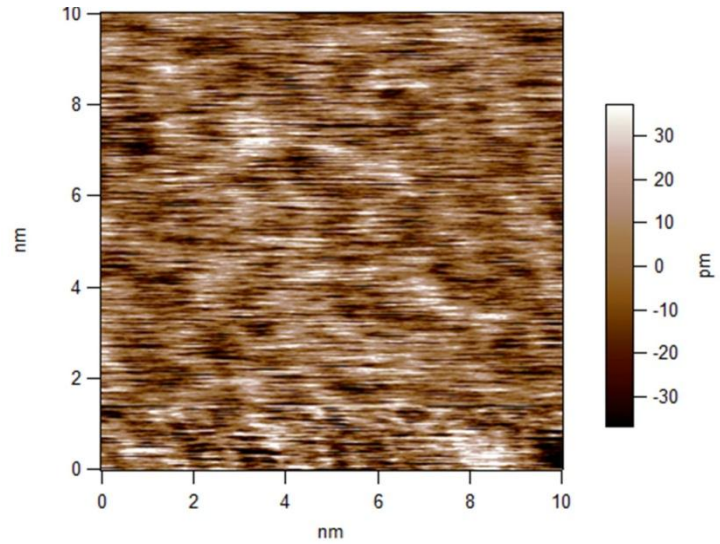

Figure B. Soft contact AFM height image of the EAN innermost and first transition zone layer adsorbed to mica.

Additional information for EMI TFSI experiments

Control of the tip-sample distance using the phase information.

Controlled removal of IL layers was achieved varying the amplitude setpoint while scanning. The phase signal is also shifted when passing through the IL layers, moving to lower values as the setpoint decreases (ie, as the tip scans closer to the mica surface). The amplitude vs distance force curves exhibits discrete maxima as the tip breaks through the IL layers. The phase signal, however, varies almost continuously as the scanning tip approaches the mica surface. In order to fully quantify the phase variation associated with a set decrease of the scanning setpoint when imaging, we repeatedly imaged a same area of the interface at constant scan speed while progressively decreasing the setpoint (movie S1). The average phase value for each image was extracted and plotted against the corresponding setpoint ratio in Fig. C for the stiffer lever (k_c = 6 N/m).

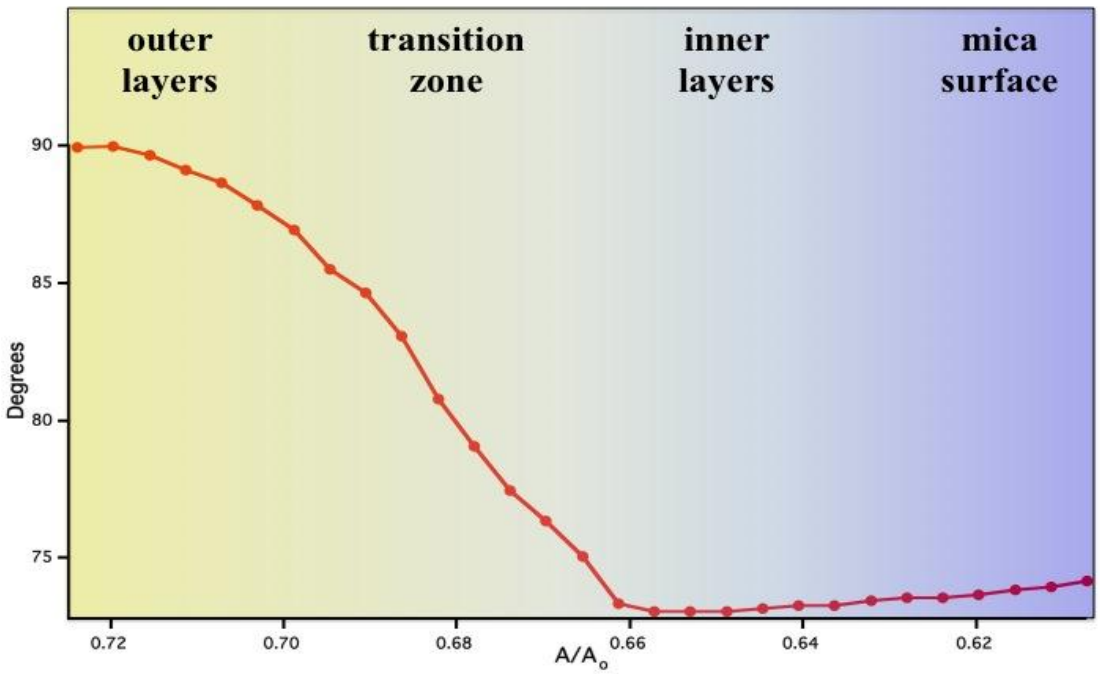

Figure C: Evolution of averaged phase signal for a series of 15x15 nm images scanned at 3.9 Hz as a function of the amplitude setpoint. Each point represents the averaged phase the image.

The phase shift associated with a given setpoint was fully reproducible between different sets of experiments. A similar behavior could be observed in experiments performed with the softer lever, but with a different magnitude in the maximum phase shift. Fig. C can be used as a calibration curve with the maximum shift reached when the tip scans directly onto the mica surface (Fig. 4c-d) and the phase used as a measure of the effective distance between the scanned layer and the mica surface underneath.

Observation of the discrete IL layers in the phase.

As shown in Fig. C, the phase exhibits a monotonic evolution with the decreasing scanning setpoint, making it impossible to identify discrete IL layers. This information could, however, be derived from the noise levels (root mean square roughness) of the different phase images obtained during these experiments. The measured RMS noise increases following discrete increments (and a subsequent decrease) as the tip approaches the surface. Figure D presents a plot of the phase RMS value (corresponding to data in the Fig. C) as a function of the amplitude setpoint.

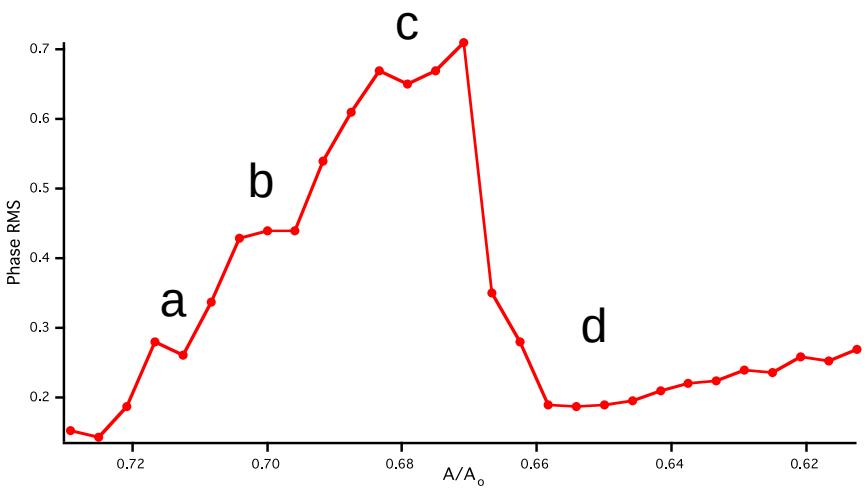

Figure D: Evolution of the phase RMS as a function of the scanning amplitude setpoint. Several plateaus are visible; they correspond to the different IL layers.

The RMS shows a step-like evolution with clear plateaus (labeled a, b, c and d) that coincide with the most stable imaging conditions (as visible in Fig. E) and correspond to the different layers identified. The topography and phase images corresponding to the different plateaus are shown in

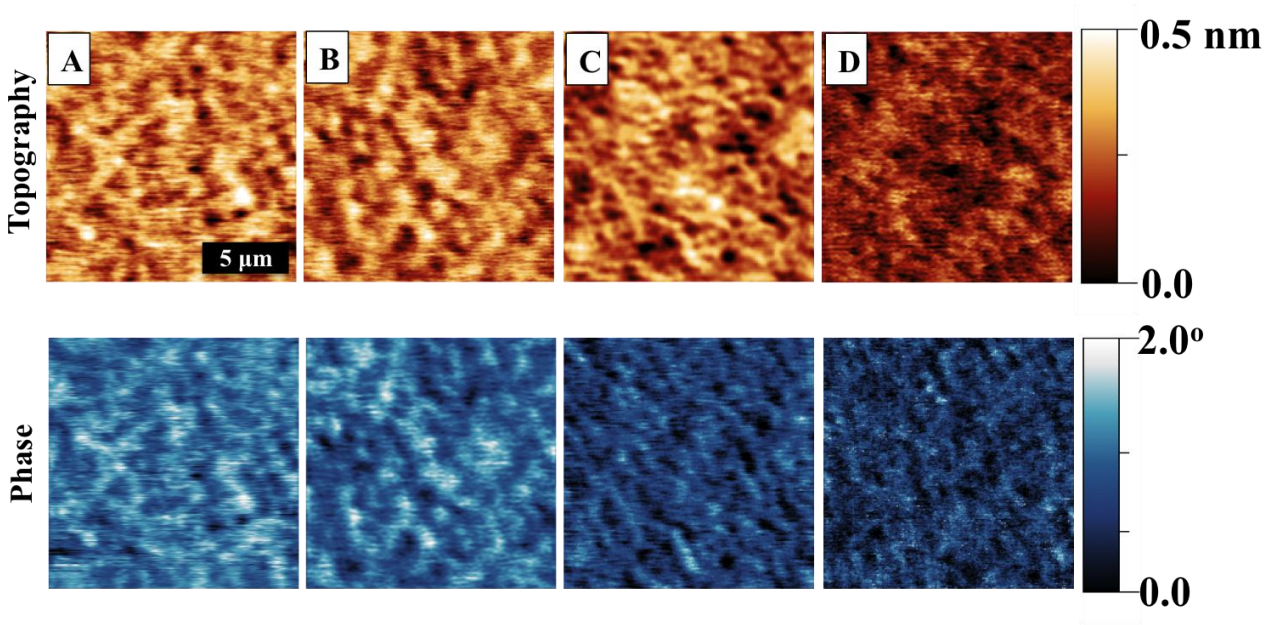

Figure E: Topography (up) and phase images (down) corresponding to the different plateaus in Fig. C (corresponding labeling letters).

Movie 1:

The movie show a set area of the interface repeatedly scanned as while progressively decreasing the imaging setpoint. The sequence of images in the move was used for the analysis presented in Figs. C-E. The movie shows the evolution of the lateral organization of the ions in the different EMI TFSI layers as the tip progressively approaches the mica surface. The controlled decrease of the imaging setpoint slightly modifies the position of the cantilever, which in turn induces an apparent lateral drift of the surface features throughout the movie. This drift is not related to the mobility of the IL molecules. Many ions can be seen retaining their relative position in the layer over several consecutive frames, emphasizing the stability and cohesion of the ionic layers. The setpoint

decrease eventually induces the removal of ions and the formation of new features. When the tip finally reaches the innermost layer (constant phase), the mica lattice becomes visible...