Supporting Information

Materials and Methods:

An ionic liquid (IL), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HMIm] FAP, purity > 99%, water content < 100 ppm, Merck) was investigated in this study. Highly ordered pyrolytic graphite (HOPG) surfaces (ZYB grade, NT-MDT) were freshly cleaved before experiments.

Both normal and lateral force measurements were performed using a Digital Instruments NanoScope IV Multimode AFM with an EV scanner in contact mode. Two sharp silicon tips (spring constant = 1.5 ± 0.2 N/m, tip radius 5 nm) from the same batch (model NSC36, Mikromasch, Tallinn, Estonia) were used over the course of the investigation. The IL was held in an AFM fluid cell, sealed with a silicone O-ring to prevent water ingression. The water content was lower than 300 ppm after the AFM measurement. The tip was cleaned immediately prior to use by careful rinsing in Milli-Q water, drying under nitrogen and irradiation with ultraviolet light for 40 min. The procedures used to setup the AFM electrochemical cell are exactly as described in Ref.¹. HOPG was used as both the working electrode and the solid substrate for force and friction measurements. A thin cylindrical strip of Cu metal and 0.25 mm Pt wire were used as the counter and "quasi" reference electrodes, respectively. Normal force curves were collected by moving the surface towards the tip and detecting the cantilever deflection as a function of separation. The ramp size was 30 nm and scan rate was 0.1 Hz. Standard methods were used to convert deflection vs separation data to normal force vs apparent separation curves.² Lateral force measurements were acquired by performing lateral AFM scans with a scan angle of 90° (with respect to the cantilever long axis) with the slow scan axis disabled.² The scan size was 100 nm, and scan rate was 30 Hz. The lateral deflection signal (i.e., cantilever twist)

was converted to lateral force using a customized function produced in Matlab 7.0 which takes into account the torsional spring constant and the geometrical dimensions of the cantilever.³ Repeat experiments revealed that the features of the normal and lateral forces were constant. The electrochemical windows (the difference between the cathodic and anodic limits) of the ILs were obtained from cyclic voltammetry measured in the AFM electrochemical cell.



Figure S1. Cyclic voltammogram of [HMIm] FAP at 100 mV.s⁻¹.

<u>Justification for 10 nN normal force for designating lubrication by a single ion layer, and</u> the origin of the sharp increase in lateral force at low normal loads.

Two regions are present in the lateral force data for all potentials except +1.5 V. The corresponding normal force vs distance data is shown in Figure S2. This normal force data consists of a series of steps for all potentials except 0 V. These steps are due to layers of IL ions near the HOPG surface.⁴ When the apparent separation is equal to 0 nm, the tip moves into contact with the interfacial layer. Thus, the rapid increase in lateral force at low normal forces for

-1.0 V, \pm 1.0 V and \pm 1.5 V corresponds to the tip sliding over multiple ion layers; the force at which the separation equals 0 nm in the normal force curve agrees well with normal force at which the rapid increase in friction ends in Figure 2. No increase in friction is noted for \pm 1.5 V; the lateral force at this potential is close to zero for all normal loads. At 0 V, the normal force curve is attractive, and the initial steep increase in normal force has a different origin.

At 0 V, the normal force curve is attractive, c.f. Figure S2 (supplementary information); near surface IL structure is weaker at 0V than at other potentials,⁵ and short range attractive forces cause the tip to jump into contact with the interfacial layer. This means that the initial steep rise in lateral force at 0V is not due to the tip sliding against multiple ion layers, as per -1.0 V, +1.0 V and + 1.5 V, so the change in slope at 10 nN must have a different cause. We contend that the change in slope is due to the composition of the interfacial layer changing as the normal load increases. ^{6, 7} The initial steep increase corresponds to the tip sliding over the mixed, relatively rough, interfacial layer. When the normal force is above ~ 10 nN, it becomes energetically more favourable for the composition and/or orientation of interfacial layer ions to change than for the tip to slide over this rough layer.



Figure S2. AFM force-distance profiles for a sharp AFM tip ($r \approx 5$ nm) approaching an HOPG electrode surface immersed in [HMIm] FAP at (a) 0V, (b) -1.0 V, (c) +1.0 V, (d) -1.5 V, and (e) +1.5 V. Scan size was 30 nm at 0.1 Hz.

References

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