Spectroscopic characterization of the interaction of lithium with thin films of the ionic liquid 1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide

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Figure S1: XPS Survey spectra of the copper surface before (top, red graph) and after lithium deposition (bottom, black graph). The Li 1s peak around 56 eV is displayed multiplied by 20.
Figure S 2: Area of the peak fits in the C1s and F1s waterfall plots versus measurement time. A linear background substraction was applied to the spectra and gauss-type profiles fit with CasaXPS. In the previously smoothed (see description of waterfall plots) spectra the C 1s cation components cannot be distinguished as done in the manuscript.

The peak area has been normalized by photoelectric cross-sections, asymmetry factors and the transmission function of the hemispherical analyzer.
Figure S 3: Waterfall plot of N 1s XPS spectra for [OMIm]Tf$_2$N deposited on lithium with rising measurement time (black plots) and line fits of Gaussian peaks (green plots). The peak at 399.3 eV is referred to [Tf$_2$N], the peak at 397.4 eV build in the interaction with lithium. Both peaks do not change during measurement.
**UPS spectra of [OMIm]Tf$_2$N on a lithium layer and on previously oxidized lithium**

Fig. S3 shows the UPS spectra recorded after deposition of [OMIm]Tf$_2$N on top of the lithium surface. The spectrum in the top was acquired immediately after deposition of [OMIm]Tf$_2$N, the last spectrum in the bottom 75 minutes later. Within this time the UPS spectra continuously changed.

As there are a plenty of possible transitions in UPS spectra of ionic liquids they are hard to analyze. DFT calculations and previous results show two prevalent features in the He I UPS spectra of [OMIm]Tf$_2$N: the first one at 7 eV BE is related to contributions from oxygen, fluorine, sulfur, carbon and nitrogen, thus is influenced by both anion and cation components, while the second one consists of contributions from fluorine, oxygen and sulfur, thus is anion dominated.

Due to charging of the sample those peaks were shifted by 2.5 eV to higher BE in our experiments and occur at 9.5 eV BE and 13.5 eV BE (Figure S 4, I and II). Beside those a small peak at 6.3 eV BE (Figure S 4, III) rises. In this region we would expect contributions of oxygen in Li$_2$O.

With increasing time after deposition of [OMIm]Tf$_2$N the two main peaks of the RT-IL decrease continuously, which could be caused by desorption of parts of the ionic liquid or by rearrangement of the components.

After 75 minutes the spectrum remains constant, but shows a new peak at 11.0 eV BE (Figure S 4, V) and a shoulder peak at 8.4 eV BE (Figure S 4, IV). While the peak at 11.0 eV BE can be assigned to fluorine in LiF, the shoulder at 8.4 eV BE might be related to carbon and nitrogen in [OMIm].

In contrast, Figure S 5 shows the spectra recorded in the first 20 minutes after the deposition of [OMIm]Tf$_2$N on top of the Li$_2$O layer. Compared to Figure S 4 the spectrum is less shifted, thus, the main peaks of [OMIm]Tf$_2$N were observed at 8.7 eV BE and 12.5 eV BE (Figure S 5, I and II). Besides those a small peak at approx. 5 eV BE (Figure S 5, III) may result from the O 2p transitions in Li$_2$O of the previously built layer.

Like shown in Figure S 4 the two main peaks of [OMIm]Tf$_2$N decrease continuously, which again could be caused by partial desorption of the ionic liquid. However after 20 minutes the UPS spectrum remains constant.
Figure S 4: He I (21.2 eV) UPS spectra of [OMIm]Tf$_2$N on lithium within the first 75 min after deposition. The main peaks referred to the RT-IL (I and II) continuously decrease revealing new features (III, IV, V). Peak III is referred to O 2p in Li$_2$O, while Peak V might be related to LiF.
Figure S 5: He I (21.2 eV) UPS spectra of [OMIm]Tf₂N within the first 20 min after deposition on Li₂O. The main peaks referred to the Rt-IL (I and II) continuously decrease. A small shoulder peak (III) at 5 eV might be related to O 2p in Li₂O.