## **Supplementary Information**

## Layering of Ionic liquids on Rough Surfaces

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The Supplementary information contains the optimized geometries and sizes for [HMIM] Ntf2, SEM images of the smooth and rough colloids, the frequency of layering in the resolved force-distance curves for all investigated systems with [HMIM] Ntf2, layer size and layering force measured with a sharp tip on mica for the same IL, and results of the kinetics experiments.



HMIM, size ~ 11.5 Å x 4.2 Å x 2.6 Å

Ntf2, size ~ 7.5 Å x 3.45 Å x 3.0 Å

Figure SM1: Optimized geometries and sizes of HMIM+, and Ntf2– calculated by molecular mechanics with the software Avogadro (force field = MMFF94s, version 1.0.3).



**Figure SM2**: SEM images of typical  $SiO_2$  spheres (rough and smooth batches). Images: **a**) shows the typical surface morphology of a rough sphere; **b**) is a profile image focusing on the roughness found at the approximate contact area of a rough sphere; **c**) shows the typical surface morphology of a smooth sphere; and **d**) is a profile image focusing on the roughness found at the approximate contact area of a smooth sphere.



Figure SM3: Percentage of curves with a specific number of resolved IL layers in an individual forcedistance curve for substrates with NP surface densities of 0, 170 and 1100  $\mu$ m-2. The measurements were performed with a sharp tip (a), smooth sphere (b) and rough sphere (c).



Figure SM4: a) Characteristic force-distance isotherms measured with a sharp tip on mica in [HMIM] Ntf2, b) layer size vs. layering force, and c) histograms for the measured layer thicknesses (bin size =1 angstroms).

a)		Average	
- /		Force (nN)	Step Size (Å)
	0 min	0.08	5.3
	2 min	0.08	6.3
	5 min	0.07	5.7
	7 min	0.08	6.1



Figure SM5: a) Average force and layer thickness for transition 1, and (b) percentage of resolved layers on force isotherms with a delay time of 0, 2, 5, and 7 minutes between consecutive force measurements on 0  $\mu$ m<sup>-2</sup> substrate using a smooth silica sphere (diameter 10 $\mu$ m) glued to a tipless cantilever (CSC37/tipless/Al Bs, 0.03-0.09 N/m, Mikromasch). Approach speed = 30 nm/s. Force distance separation = 160 nm, maximum applied load = 8 nN. The results summarize two experiments (on different days), and at least 10 forces curves for each delay time.