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Electronic Supplementary Information

Direct observation of layered structures at ionic liquid/solid interfaces by using frequency-modulation atomic force microscopy

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Dotted lines in Fig. S1 show frequency spectra of a Pt-coated cantilever measured in various media (the same curves as those shown in Fig. 2). The noise in the deflection signal includes noise arising from the deflection sensor and the thermal Brownian vibration of the cantilever [1, 2]. The noise density of the thermal Brownian motion (n_{zB}) at temperature T is given by

$$n_{zB} = \sqrt{\frac{2k_B T}{\pi f_0 k Q} \frac{1}{[1-(f/f_0)^2]^2 + [f/(f_0 Q)]^2}}, \quad \text{(S1)}$$

where f, f_0, and k are the vibration frequency, the resonance frequency, and the spring constant of the cantilever, respectively and k_B is Boltzmann constant. Assuming the deflection sensor noise (n_{zs}) as a white noise, the overall deflection power spectral density (n_z) can be written by

$$n_z(f) = \sqrt{n_{zB}(f)^2 + n_{zs}^2}\ . \quad \text{(S2)}$$

By fitting the thermal spectrum with these equations, f_0 and Q and for each media are obtained as depicted in Fig. 2 in the main text and Fig. S1. Note that when fitting the spectrum in air, the Q value was fixed due to the limited number of data point around the sharp peak.

Obtained f_0 and Q values for each media were compared with theoretically estimated values. Following the method proposed by Basak et al. [3], f_0 and Q values were calculated as depicted in Fig. 2 in the main text, and compared with those obtained by the above fitting. The density and viscosity of the media, and the density and geometry of the cantilever are required for the calculation. The f_0 value in vacuum was assumed to be 289 kHz.

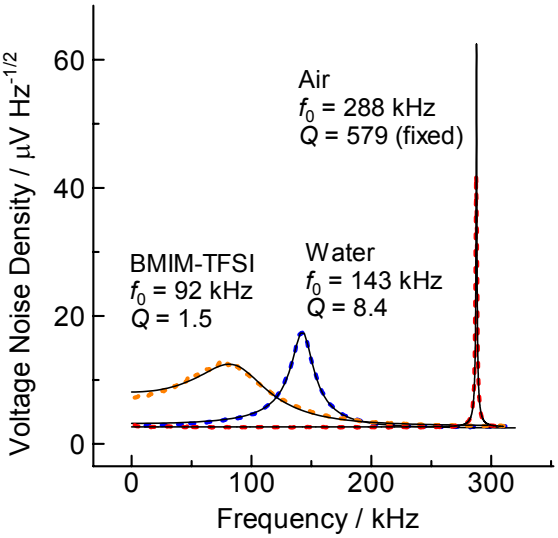

Fig. S1 Frequency spectra for Brownian motion of a Pt-coated cantilever measured in BMIM-TFSI, in water, and in air, respectively. The dotted lines show experimentally measured values while the solid lines show theoretically calculated values with Eqs. S1 and S2.

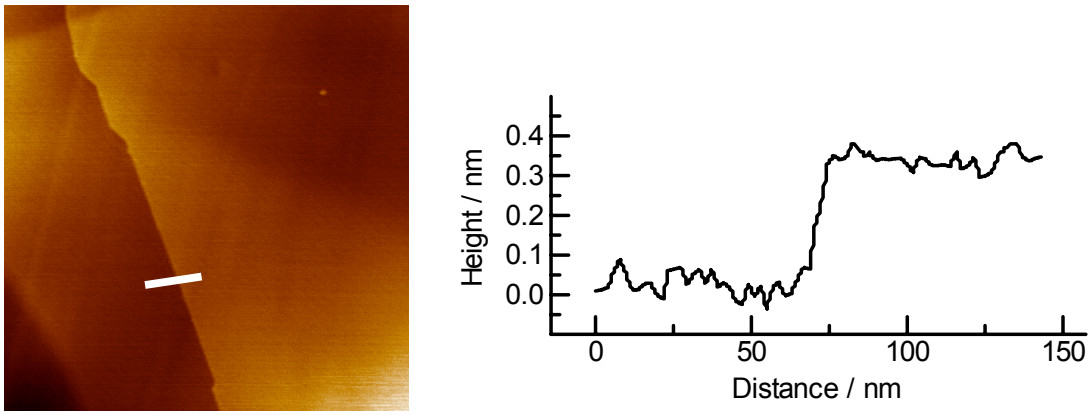

Fig. S2 (left) FM-AFM image of a cleaved HOPG substrate in BMIM-BF_4. The imaging conditions: 1×1 μm^2, Δf = +55 Hz, $A_{p\text{-}p}$ = 0.72 nm. (right) Line profile along the solid line in the left panel. The step height corresponds to that of the HOPG substrate (a peak at the shorter height in Fig. 3(f)).

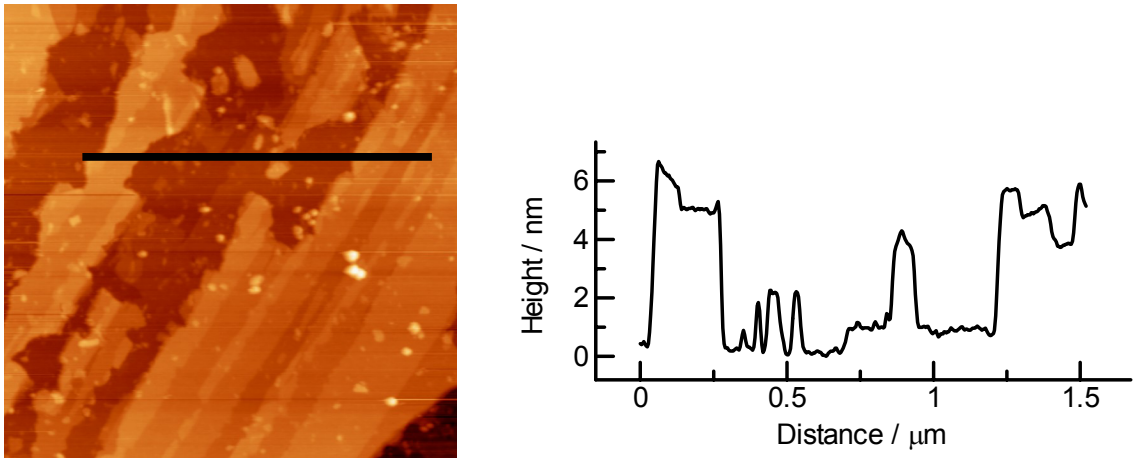

Fig. S3 (left) FM-AFM image of a cleaved mica substrate in BMIM-TFSI. Layered structure with multi-layer-steps was observed. The imaging conditions: 2×2 μm^2, $\Delta f = +200$ Hz, $A_{p\text{-}p} = 0.39$ nm. Note that this image was taken by using the second harmonics ($\sim 2 f_0$) of cantilever's resonance. (right) Line profile along the solid line in the left panel.

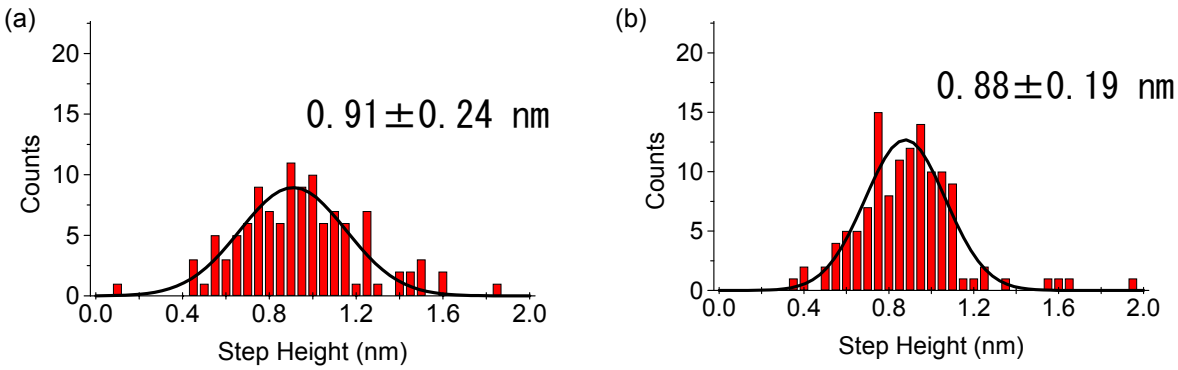

Fig. S4 Histograms of step heights in FM-AFM images of (a) BMIM-TFSI/mica and (b) BMIM-BF_4/mica.

References

[1] T. Fukuma and S. P. Jarvis, *Rev. Sci. Instrum.*, 2006, **77**, 043701.
[2] T. Fukuma, *Rev. Sci. Instrum.*, 2009, **80**, 023707.
[3] S. Basak, A. Raman and S. V. Garimella, *J. Appl. Phys.*, 2006, **99**, 114906.