Supporting Information

Nanostructure of the H-terminated p-Si(111) / Ionic Liquid Interface and the effect of added Lithium Salt

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Figure S1. FTIR spectra of a thin layer of (a) [EMIm]TFSA on H-Si(111) (green line) and (b) $[Py_{1,4}]$ TFSA on H-Si(111) (blue line) between 400 and 1500 cm⁻¹ and between 2800 and 3200 cm⁻¹ wavenumbers.

Methods

 $[Py_{1,4}]$ TFSA and [EMIm]TFSA were purchased in the highest available quality (99.9 %) from IoLiTec and were used after drying under vacuum at 100 °C to achieve a water content of below 10 ppm. The water content was measured using Karl-Fischer titration.

p-Si(111) was bought from CrysTec GmbH, Germany. For making the H-terminated silicon, a three-step procedure was applied. First the Si(111) was sonicated in ultrapure acetone (99.9%, Sigma Aldrich). Then the substrate was dipped into a hot solution (100 °C) of $1:4 \text{ H}_2\text{O}_2/\text{H}_2\text{SO}_4$ for 10 minutes followed by washing in distilled (0.055 μ S cm⁻²) water and drying in nitrogen. The substrate was then introduced into a 1% HF solution for 30 seconds at 22 °C followed by washing in distilled water and drying in nitrogen. Finally, for hydrogen termination, the Si(111) substrate is introduced into a 40% NH₄F solution 22 °C for 15 minutes. The Si(111) is then washed again in distilled water and dried in nitrogen. All the above mentioned acid solutions are extremely hazardous and utmost care must be taken in handling them.

AFM experiments were perfomed with a Cypher S (Asylum Research) AFM inside of a glove box under argon atmosphere. A silicon SPM-sensor from Asylum research was employed for all experiments presented in this study from the same batch. The spring constant was 0.065±0.005 N/m. Force curves were collected using a Molecular Imaging Pico Plus AFM in contact mode with the same batch of cantilevers used in Cypher. All force curves were acquired at room temperature in an argon-filled glove box. The temperature of the experiment was 23 °C.

Fourier transform infrared spectroscopy (VERTEX 70 V, Bruker Optics GmbH) with an attached attenuated total reflectance (ATR) module was used to characterise the interface.