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Imaging an Ionic Liquid Adlayer by Scanning Tunneling Microscopy at the Solid | Vacuum Interface

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Ionic liquids (ILs), which are salts usually consisting of sterically hindered organic ions with melting points below 100 °C, are of high interest because of a number of distinct physical properties such as ionic conductivity, electrochemical stability in a wide potential window, a very low vapor pressure or low flammability.^[1–4] These properties make ILs interesting for various applications, for example, as electrolyte (additives) in lithium ion and lithium air batteries.^[5] The physical and chemical properties of ILs can be tuned in their synthesis and the variety of different substances is large.^[2] So far, however, there is little information on the structure and processes at the phase boundary between solid interfaces (electrodes) and ILs on a submolecular scale. It has been shown recently that solvation layers of ILs form on electrodes, and that these have an influence on electrochemical reactions.^[6] Such interfacial layering was observed by atomic force microscopy and high-energy X-ray reflectivity measurements.^[7–9] The surface structure of ILs on electrode surfaces has mainly been studied with vibrational spectroscopy (sum frequency generation; SFG) and electrochemical impedance spectroscopy (EIS).^[10] Pan and Freyland showed that PF₆[−] ions can be imaged by electrochemical (in situ) STM.^[11] Atkin et al. demonstrated by in situ STM that the interaction with the IL induces a restructuring of the Au(111) surface at potentials between −0.4 and −1.0 V.^[12]

In addition to these measurements in an electrochemical environment, the interaction of ILs with solid surfaces was also probed under high-vacuum conditions, allowing to apply typical surface science methods such as electron spectroscopy^[13,14] or temperature-programmed desorption (TPD).^[15,16] This offers new opportunities like measurements without a supernatant solvent and at low temperatures, which allows immobilization of the adsorbates. Monolayers of ILs on different substrates, adsorbed under UHV conditions, were investigated, for example, by electron spectroscopy, time-of-flight secondary ion mass spectrometry (TOF-SIMS) and infrared reflection absorption spectroscopy (IRAS).^[17–19] Recently, Cremer et al. studied the growth of 1,3-dimethyl-imidazolium bis(trifluoromethylsulfonyle)imide ([MMIm]Tf₂N) and 1-methyl-3-octylimidazolium bis-

(trifluoromethylsulfonyle)imide ([OMIm]Tf₂N) on Au(111) by angle-resolved X-ray photoelectron spectroscopy (ARXPS), and concluded that both anions and cations are in direct contact with the surface at a coverage of 0.5 monolayers, most likely in an alternating arrangement.^[20] Detailed structural information on IL adlayers under UHV conditions, however, is scarce. In analogy to the detailed knowledge on structure formation and self-assembly of large organic molecules,^[21–23] scanning tunneling microscopy (STM) measurements with molecular resolution would be highly interesting to learn more about various aspects of structure formation at the IL|solid interface. STM measurements at variable temperatures could provide detailed information on the ordering behavior of the adlayer, which in analogy to the bulk behavior can range from a two-dimensional (2D) solid to a 2D liquid. Despite the obvious potential of STM measurements on IL adlayers under UHV conditions, such measurements have not been reported so far. Herein, we report first results of a molecular-scale STM study on the adsorption of 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([Py_{1,4}]⁺[FAP][−],^[24] see Figure 1) monolayers on Au(111) under UHV conditions. It has been shown previously that [Py_{1,4}]⁺[FAP][−] can be evaporated without decomposition.^[16]

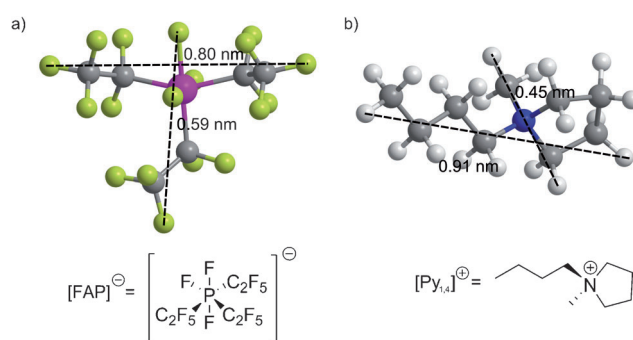


Figure 1. Energy-minimized structures of a) [FAP][−] and b) [Py_{1,4}]⁺. They have the maximum sizes that these ions can have (C: grey, H: white, F: yellow, N: blue, P: pink).

Figure 2a shows an STM image of [Py_{1,4}]⁺[FAP][−] on Au(111) recorded at 298 K. The herringbone reconstruction^[25] is visible through the monolayer. This observation resembles findings in previous in situ STM measurements of [Py_{1,4}]⁺[FAP][−] on Au(111) at negative electrode potentials.^[24] We did not find any indication of a vertical restructuring of the Au(111) surface in the nm regime, as it was reported for the interaction of bulk 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyle)imide [Py_{1,4}]Tf₂N with Au(111) at low negative potentials,^[12] in our

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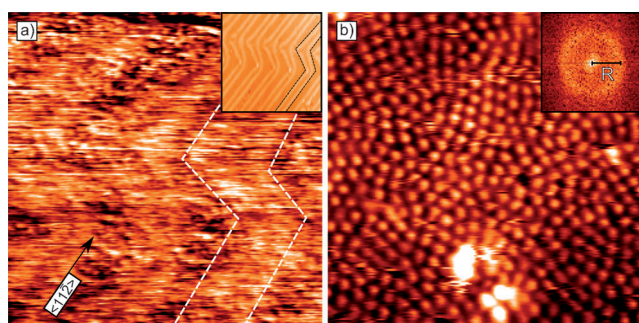


Figure 2. a) STM images of $[\text{Py}_{1,4}]^+[\text{FAP}]^-$ on Au(111) at room temperature ($20 \text{ nm} \times 20 \text{ nm}$, $I_t = 50 \text{ pA}$, $U_t = -2.087 \text{ V}$, $T = 298 \text{ K}$). The $\langle 11\bar{2} \rangle$ direction is marked by the arrow, and the reconstruction lines are marked by the dashed lines to guide the eye. The inset shows the clean substrate ($35 \text{ nm} \times 35 \text{ nm}$, $I_t = 70 \text{ pA}$, $U_t = -1.9 \text{ V}$). b) STM image recorded at low temperature ($10 \text{ nm} \times 10 \text{ nm}$, $I_t = 30 \text{ pA}$, $U_t = -2.28 \text{ V}$, $T = 210 \text{ K}$). The FFT in the inset shows no preferred directions.

measurements, where only monolayers of the liquid were deposited. The adlayer itself exhibits streaks along the fast scan directions, due to diffusion or rotation processes of the adsorbates that are faster than the STM temporal resolution at 298 K. Hence, the interactions between the adsorbed ions are comparatively weak, most likely due to the shielding of the partial ion charges by their organic side groups, and adsorbed $[\text{Py}_{1,4}]^+[\text{FAP}]^-$ behaves like a 2D liquid at 298 K, in analogy to its 3D bulk phase at room temperature. In the following discussion, we neglect the partial discharging of the ions upon adsorption and continue to use the term “adsorbed ions”.

If the sample is cooled down to 210 K, the IL adsorbates are “frozen” and immobilized, and round objects can be identified in low-temperature STM images (Figure 2b). The fast Fourier transformation (FFT) in the inset of Figure 2b shows a diffuse ring, indicating that there is a clear tendency for short-range order, but no long-range ordering. The mean diameter of this ring is $R = 2.24 \pm 0.09 \text{ nm}^{-1}$, reflecting a mean distance of the adsorbates of $0.45 \pm 0.02 \text{ nm}$ at the considered coverage of $4.5 \pm 0.1 \text{ objects nm}^{-2}$. There is no indication that the lateral adsorbate distribution at 210 K is affected by the herringbone reconstruction. A high-resolution image, which was used to evaluate the apparent heights of the objects, is shown in Figure 3a. The mean height is $0.08 \pm 0.01 \text{ nm}$, which is determined from evaluating the apparent heights of 110 molecules from STM images taken from different sample preparations

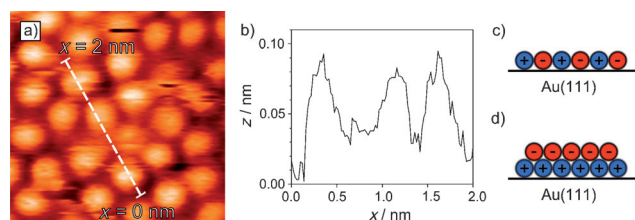


Figure 3. a) High-resolution image of $[\text{Py}_{1,4}]^+[\text{FAP}]^-$ on Au(111) ($2.5 \text{ nm} \times 2.5 \text{ nm}$, $I_t = 20 \text{ pA}$, $U_t = -2.28 \text{ V}$, $T = 210 \text{ K}$). b) Line plot of the apparent height along the dashed line in (a). Tentative models of c) ions with alternating charges in one monolayer and d) one ion species in the first and the other in the second layer.

(see also the sample height profile in Figure 3b). The mean lateral extensions of the closed-packed objects are $\sim 0.5 \text{ nm}$, identical to their mean distances as shown above. To compare the sizes of the observed objects to those of the ions in the IL, we performed force-field calculations of the free $[\text{FAP}]^-$ and $[\text{Py}_{1,4}]^+$ ions in the gas phase. The minimum-energy structures shown in Figure 1 allow us to estimate the upper limits of the ion dimensions of $0.8 \text{ nm} \times 0.6 \text{ nm}$ for $[\text{FAP}]^-$ and of $0.9 \text{ nm} \times 0.5 \text{ nm}$ for $[\text{Py}_{1,4}]^+$. The values for the shorter distance are in good agreement with values calculated by Atkin et al.^[24] However, due to the flexibility of the fluorinated and unfluorinated alkyl chains of the ions it can be expected that the ions behave like disordered coils, allowing for a variety of possible conformations. This would also explain the round appearance in the STM images. The different conformations of $[\text{Py}_{1,4}]^+$ and $[\text{FAP}]^-$ lead also to a thermodynamic stabilization of the adlayer by configurational entropy.

Since the measured apparent heights could be influenced by electronic effects, we compare the calculated ion sizes with the approximate lateral extensions of the objects and their distances in the STM images, which are both in the range of $\sim 0.5 \text{ nm}$ (see above). This comparison suggests two possible arrangements: In the first one, each protrusion in the STM images represents either an anion or a cation. In the second one, each object represents an ion pair. In the first case, the charges of neighboring adsorbed ions are supposed to have opposite signs, like for crystalline ionic adlayers. Since ILs are present as ion pairs in the gas phase,^[15] and therefore also when leaving the evaporator, they land on the surface in this arrangement, and anions and cations are likely to adsorb next to each other, with both species in direct contact with the substrate (Figure 3c). Such a structure was proposed for the adsorption of $[\text{MMIm}]\text{Tf}_2\text{N}$ and $[\text{OMIm}]\text{Tf}_2\text{N}$ on Au(111) by Cremer et al.^[20] Based on ARXPS measurements, they concluded that for both liquids cations and anions are in direct contact with the gold surface. In their picture, the imidazolium cations adsorb flat on the surface and the SO_2 groups from the $[\text{Tf}_2\text{N}]^-$ anion are oriented toward the gold surface, whereas the CF_3 groups are directed towards the vacuum. In contrast, alkyl chains as present in the $[\text{FAP}]^-$ anion tend to form disordered coils, leading to a large number of conformations. The calculated sizes of the ions in the gas phase would fit to such kind of arrangement, where anions and cations are both located in the surface layer. In that case, the observed protrusions represent $[\text{FAP}]^-$ and $[\text{Py}_{1,4}]^+$ ions, which are of comparable size, in an alternating arrangement. It is unlikely that the protrusions represent $[\text{FAP}]^-$ ions, and the $[\text{Py}_{1,4}]^+$ ions are (coplanar) adsorbed in between the imaged objects (in the dark regions), or other way around, since they are too large for such kind of structure and the observed packing density.

The second case corresponds to a bilayer structure, where one type of ions is in direct contact with the substrate and the other type resides on top of that layer (Figure 3d), most likely on the hollow sites of that layer, which results in a dipole moment vertical to the surface. Such a structure was derived from in situ atomic force microscopy measurements in an electrochemical environment for $[\text{Py}_{1,4}]^+[\text{FAP}]^-$ on a negatively

charged Au(111) surface.^[24] From the present measurements we cannot distinguish between this structure (Figure 3d) and a monolayer structure with both species in contact with the substrate and resolved as spherical protrusions (Figure 3c).

In analogy to previous experiments with uncharged adsorbates, it is possible to image adsorbed ionic liquids on the molecular scale by STM under UHV conditions. Further experiments are under way to gain in depth information on the structure of the electrode|ionic liquid interface.

Investigating the structure of a monolayer of $[\text{Py}_{1,4}]^+[\text{FAP}]^-$ on Au(111), we could obtain first molecularly resolved STM images of an ionic liquid adlayer on a single crystalline surface under UHV conditions. At 298 K, the adlayer was found to be mobile to an extent that individual adsorbates could not be resolved. This shows that the interactions between the IL adsorbates are relatively weak, like in the 3D bulk phase. The mobility in the adlayer is frozen at a temperature of 210 K, and close-packed, short-range ordered objects with apparent heights of 0.08 ± 0.01 nm, mean distances of 0.45 ± 0.02 nm and similar lateral extensions can be resolved. Comparison of the size of the adsorbed species with minimum-energy structures of the ions in the gas phase, which are obtained from MM2 force-field calculations, shows that the observed objects could be either ion pairs in a double layer arrangement or individual ions, with both ions in contact to the surface.

Experimental Section

The STM experiments were carried out in a standard UHV chamber with a base pressure $< 4 \times 10^{-10}$ mbar. The Au(111)-surface (MaTeck GmbH) was cleaned by repeated cycles of Ar^+ sputtering (0.5 keV, 4 μA , 30 min) and subsequent annealing at 770 K (5 min). The cleanness of the surface was checked by STM imaging, showing atomically clean, well ordered terraces of > 200 nm width, separated by monatomic steps. Prior to evaporation, $[\text{Py}_{1,4}]^+[\text{FAP}]^-$ was degassed in UHV several times in an evaporator made for the evaporation of organic solid matter (Ventiotec OVD-3) in a temperature range between 165 and 190 °C. Evaporation was performed by heating the IL to 450 K (the desorption temperature from IL bulk is known from previous TPD experiments^[16]) and placing the clean Au(111) surface held at room temperature (298 K) in front of the evaporator for 10 s. Using these conditions, the pressure in the UHV chamber was $\sim 10^{-9}$ mbar for the degassed IL, while it was $\sim 10^{-7}$ mbar at the same temperature of the IL before the degassing procedure. The surface was scanned with electrochemically etched tungsten tips in an Aarhus-type variable temperature STM (SPECS) at 298 and 210 K. Cooling of the STM was achieved by liquid nitrogen. All images were acquired in constant current mode with tunneling currents in the pA range and negative tunneling voltages. The lateral length scales in the STM images were calibrated by atomically resolved images of the clean Au(111) surface, the apparent height z was calibrated by the known step height of Au(111). For the calculations of the minimum-energy structures of the isolated ions in the gas phase, we used the MM2^[26] force field implemented in ChemDraw, see Figure 1.

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