Differentiation of molecules in a mixed self-assembled monolayer of H- and Cl-terminated bicyclo[2.2.2]octane derivatives

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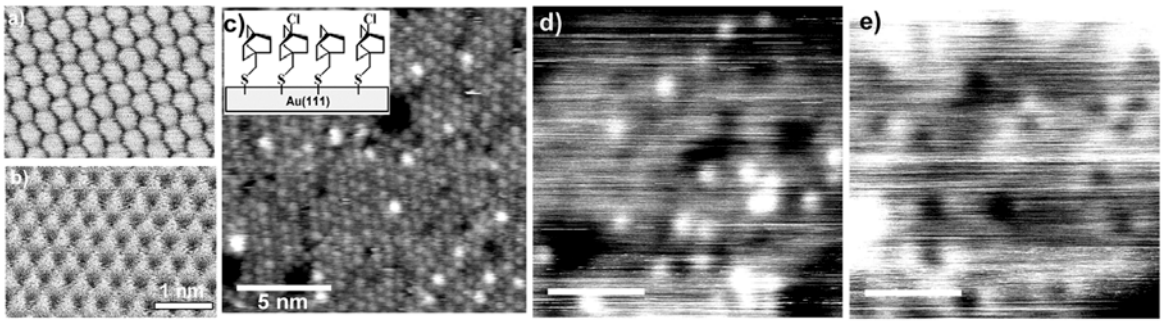
The atomic scale contrast in NC-AFM is generally interpreted as resulting from short-range interactions between an atom at a tip apex and an atom on the surface. Barth *et al.* has shown that two different contrast features on CaF_2(111) in NC-AFM images can be clearly explained in terms of the sign of the electrostatic potential at the tip apex due to a positive (Ca^{2+}) or a negative (F^-) terminal ion [1].
In the present study, first, the atomic details of CaF_2(111) were reinvestigated by NC-AFM in UHV. We reproduced atomically resolved FM-AFM images of CaF_2(111), in which a circular pattern (Fig. a)) and a triangular pattern (Fig. b)) were attributed to imaging with the negatively terminated and the positively terminated tip, respectively [1]. Secondly, we imaged a mixed monolayer (Fig. c)) of H- and Cl-terminated bicyclo[2.2.2]octane on Au(111) [2] with the tip terminated by Ca^{2+} or F^- ion. Prior to the molecular imaging, a Si tip was brought into contact with CaF_2(111) many times until atomically resolved images of CaF_2(111) were obtained. In order to increase the probability of covering the Si tip with a CaF_2 cluster, hard contact between the Si tip and the CaF_2(111) was repeatedly made. When atomically resolved images were obtained in a stable manner, we assumed that the tip had a CaF_2 cluster at its end. With such a Si tip with a CaF_2 cluster, we could distinguish very frequently the molecules on Au(111) with high resolution as shown in Figs. d-e. Depending upon the sign of the terminal ion, the negatively charged Cl- on the mixed monolayer (bright spots in the STM image (Fig. c)) was observed as protrusion (Fig. d)) or depression (Fig. e)). Here, it should be noted that probability of observing the Cl- as protrusion was much higher than that as depression. When the tip was again used for imaging on CaF_2(111) after high resolution imaging on the molecules, atomic scale images were still obtained. Even if the tip lost the ability to image the molecules with high resolution during the measurement by a sudden tip change, we recovered the ability by bring the tip into contact with CaF_2(111).



[1] C. Barth, A. S. Foster, M. Reichling, A. L. Shluger, J. Phys.: Condens. Matter **13**, 2061 (2001)
[2] S. Fujii, U. Akiba and M. Fujihira, Nanotechnology, 15 S19 (2004).