Manipulation and Imaging of Single Molecules by Atomic Force Microscopy

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Non-contact atomic force microscopy (nc-AFM) has demonstrated true atomic resolution on metals, semiconductors and insulators. The application of nc-AFM to single molecules is a challenge because of relatively weak bonding to the substrate, which often leads to high diffusion rates of the molecules. Routes to stabilize molecular assemblies and single molecules involving various molecule-molecule and molecule-surface interactions have been developed. Porphyrin molecules which were designed to interact with specific sites on insulating surfaces forming molecular wires on ionic crystal surfaces [1,2]. Such molecular assemblies can even be localized between metallic nanoclusters and show a self healing mechanism after cutting them by the nc-AFM tip [3]. A complete immobilization at kink sites of KBr(001) is observed for single truxene molecules containing similar functional groups at room temperature [4]. Recently, intramolecular resolution is studied on a variety of molecules at low temperature by tuning fork based nc-AFM [5]. The mechanical properties of C_{60} molecules adsorbed on Cu(111) are measured by tuning-fork-based nc-AFM and spectroscopy at cryogenic conditions. Site-specific tip-sample force variations are detected above the buckyball structure. Moreover, high-resolution images obtained by nc-AFM show the chemical structure of this molecule and describes unambiguously its orientations on the surface (Fig. 1).

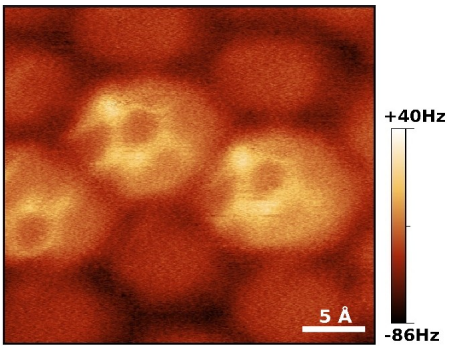

Fig. 1 Constant-current nc-AFM image revealing the upper atoms of three C_{60} adsorbed on top of a molecular island (I_t = 58 pA, V_t =+6 mV, A_{osc} = 60 pm) [5].

A further challenge is the manipulation of molecules on surfaces, including the controlled rotation, which means that the direction of rotation of the molecule can be chosen by the experimentalist [6]. The application of local mechanical forces was used to achieve directed rotations of single porphyrin molecules. Three-dimensional force spectroscopy with sub-Ångström precision was used on porphyrin derivatives with peripheral carbonitrile groups to determine extremely small areas on these molecules (≈ 100 x 100 pm^2) which have been used to control the rotations. In response to the local mechanical forces, the molecular structure elastically deforms and then changes its conformation, which leads to its rotation. Depending on the selection of one of four submolecular areas, the molecule is either rotated clockwise or counterclockwise (Fig. 2).

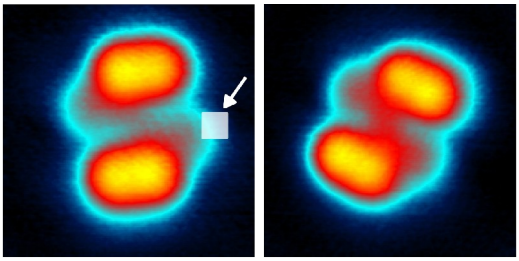

Fig. 2 Successive STM images showing a single rotation of a porphyrin molecule; the white area shows the position of the z-spectroscopic curve (I_t = 25 pA, V_t = 60 mV) [6].

Finally, the influence of physisorption and chemiesorption on the electronic properties of single molecules adsorbed on a surface was investigated using combined nc-AFM and scanning tunneling microscopy. Besides a comparison of the adsorption geometry and electronic structure of copper phtalocyanine (CuPc), the inner charge distribution on the pure Cu(111)- (strong chemiesorption) and on NaCl monolayers (weak physisorption) was studied based on the local contact potential difference determined by bias spectroscopy. This quantity is directly coupled to the induced dipole moment of the molecule-surface interaction.
With this we developed a comprehensive knowledge on single molecular adsorption properties and characterization techniques which allows us to focus on more sophisticated molecular systems in future [7].

[1] S. Maier et al., Small 4, 1115, (2008).
[2] T. Glatzel et al., APL 94, 063303, (2009).
[3] S. Kawai et al., APL 95, 103109, (2009).
[4] B. Such et al., ACS Nano 4, 3429, (2010).
[5] R. Pawlak et al., ACS Nano 5, 6349, (2011).
[6] R. Pawlak et al., ACS Nano 6, 6318, (2012).
[7] R. Pawlak et al., DOI: 10.1021/nl402243s.