LOCK-AND-KEY EFFECT IN THE SURFACE DIFFUSION OF LARGE ORGANIC MOLECULES PROBED BY STM

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The adsorption and assembly of large organic molecules on solid surfaces has attracted considerable attention in recent years [1], partly due to the interest from a basic science point of view, partly because of the potential applications in emerging nanotechnological fields, such as molecular electronics [2], optoelectronics [3], or nanomechanical sensors [4]. In general, the molecular assembly will be controlled both by thermodynamic factors – the molecules tend to assemble on surfaces into the energetically most stable structures – and by kinetic factors – the molecules diffuse and interact at surfaces, thereby creating metastable molecular nanostructures that may hinder the molecules at a given temperature to attain the minimum-energy arrangement.

A nano-scale understanding of the complex dynamics of large molecules at surfaces is essential for the bottom-up design of molecular nanostructures. Although a large number of previous studies has discussed the formation of molecular assemblies in terms of the molecule-molecule and molecule-substrate interactions [5,6], thus addressing the thermodynamic aspects of molecular assemblies, very few studies have addressed the dynamical processes that a large organic molecule can undergo when anchored on a solid surface.

Here we address how the orientation and shape of large and complex organic molecules influence their dynamics (diffusivity). To this end, we have exploited the capability of the scanning tunneling microscope (STM) (i) to resolve the conformation and orientation of single individual molecules on the atomic scale, (ii) to manipulate the orientation of individual molecules by using the STM tip as a nano-scale tool to gently push molecules adsorbed on surfaces, and finally with the fast-scanning Aarhus STM, see Figure 1, and (iii) to track the surface diffusivity of the different molecular configurations by acquiring dynamic STM movies at low temperatures.

In this way, we will show that the diffusion coefficient of the complex organic molecule named the Violet Lander (VL, $C_{108}H_{104}$) on a Cu(110) surface can be changed by two orders of magnitude by purposefully manipulating the VL molecules, thereby modifying the molecular orientation with respect to the substrate. From an interplay with Molecular Dynamics simulations, we interpret the results within a lock-and-key model similar to the one driving the recognition between biomolecules: the molecule (key) is immobilized only when its orientation is such that the molecular shape fits the atomic lattice of the surface (lock); otherwise the molecule is highly mobile, see Figure 2.

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Figures:

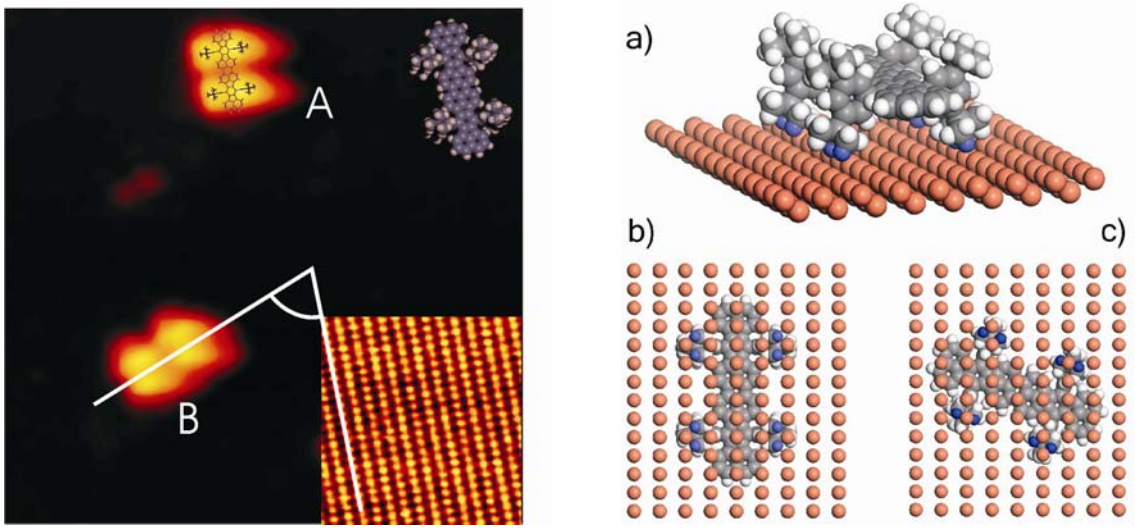

Figure 1
STM image (14×14 nm^2) showing a VL oriented along $[1\bar{1}0]$ (molecule A) and a molecule rotated with the STM tip (molecule B). The orientation can be determined by comparing with atomically resolved images of the Cu(110) surface (see inset). A space-fill model of the VL is shown in the upper right corner. Superimposing a stick model of the VL molecule on top of molecule A shows the correspondence between the molecular geometry and the STM image.

Figure 2
Ball-models for VL molecules adsorbed on a Cu(110) surface. (a) Model for a VL molecule adsorbed on a Cu(110) substrate. The contact H atoms are depicted in bright blue. (b) and (c) Bottom views of the adsorbed VL molecule and first Cu layer, showing the different registries between the contact H-atoms and the 4-fold hollow sites for the non-rotated (b) and rotated (c) molecules.