

On-surface synthesis of unsubstituted Tetraazapentacene network by controlled electric field effect

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Since the pioneering work during the nineties on the dissociation of molecules induced by the tip of an STM (Scanning Tunneling Microscope) [1] [2], many advances have been made in the control of on-surface reactions triggered by the tunneling current. In particular, this research has demonstrated the possibility of breaking intramolecular covalent bonds, either on individual molecules or in self-assembled layers [3]. In all of these cases, the tunneling electrons are used to excite molecular vibrations, which induce the chemical changes. The measure of this tunneling current implies the presence of an electric field between the STM tip and the substrate, a major issue in such studies is the effect of this electric field on the chemical reaction and the difficulty of separating processes resulting from the presence of the electric field from those resulting from the inelastic tunneling current. In this presentation, we will show how dihydrotetraazapentacene (DHTAP **1** in figure 1) molecules self-assembled in the second layer on Au (111) can undergo a controlled modification of their molecular topology by the application of voltage pulses between the STM tip and the surface. Based on a series of pulses carried out at a relatively important distance from the surface and using current-voltage spectroscopy recorded at different tip-surface distances as well as current-distance spectroscopy, we will show that the physical quantity responsible for this modification is the electric field, and not the inelastic tunneling current. By combining STM images, DFT calculations and tunneling spectroscopies, we have characterized the products of the pulse-induced reaction. We will show that we can induce a single or a double dehydrogenation of DHTAP at the N-H sites which finally leads to the synthesis of a tetraazapentacene molecule (TAP **3**), a compound which cannot be obtained by conventional organic chemistry.

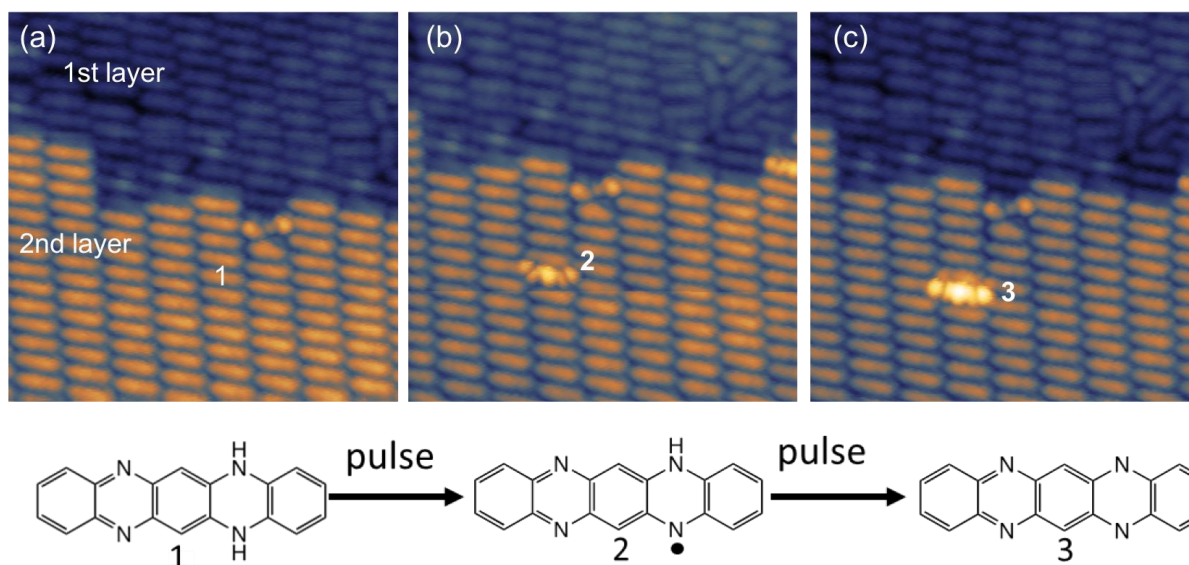


Figure 1: Image STM showing the successive switching of a molecule of DHTAP (a) to a MHTAP 2 (b) then to a TAP 3 (c). Each switching is induced by the same one second voltage pulse performed at 4.1V and zoffset = 900pm above the molecule in the white circle. The same imaging conditions for (a) (b),(c) : $I_t = 20\text{pA}$, $V_{\text{bias}} = 1.3\text{V}$. $14\text{nm} \times 14\text{nm}$.

References:

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- [3] Kim, Y.; Motobayashi, K.; Frederiksen, T.; Ueba, H.; Kawai, M. Prog. Surf. Sci. **90** 85 (2015).