STM characterization of molecular states on thin insulating films

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In 2005, J. Repp and al. [1] reported the use of a NaCl thin insulating layer to decouple molecular states from the substrate. In this case, the STM images greatly vary with the applied bias voltage and show great similarity with the calculations of the frontier orbitals of the free molecule. The capacity of a thin NaCl layer to decouple molecules from the substrate was confirmed in our laboratory for some terrylene derivatives, indigo and starphene molecules.

The indigo dye molecule presents two tautomeric forms which only differ in the position of one hydrogen atom. By using a thin insulating layer, it has been possible to evaluate the change in the electronic states associated with the propotropy process. When this molecule was deposited on a thin NaCl layer, we show that an electrostatic field is locally induced by the NaCl. This electrostatic field is able to shift the electronics states of the molecule and different states are observed for the same bias voltage. A monolayer of indigo was consequently used to obtain reproducible pictures before and after the prototropy process.

For starphene molecule, we could clearly associate electronics states with the calculated HOMO and LUMO of the free molecule [2]. In the case of the LUMO state, a functionalized tip allowed us to reveal nodal planes inaccessible to a clean metal tip.

In addition, localized applications of current pulses allowed us to identify inelastic processes associated with the energy of unoccupied states. This ability gives us a perfect, but limited, control on the molecular position and will be discussed.

References:

[1] J. Repp et al. Phys. Rev. Lett. 94, 026803 (2005)
[2] O. Guillermet et al. Chem. Phys. Lett. 511, 482 (2011)