High-Resolution Molecular Imaging with STM and AFM using Functionalized Tips

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The contrast mechanisms of noncontact atomic force microscopy (NC-AFM) and scanning tunnelling microscopy (STM) using functionalized tips are discussed for the case of single organic molecules, such as pentacene, naphthalocyanine (see Fig. 1), and PTCDA.

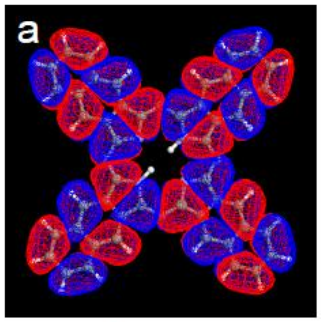
Using atomic manipulation, the tip of an AFM or STM can be functionalized in a controlled manner. As a result the contrast can be increased, and even more important the interpretation of images benefits from the knowledge of the chemical composition of the tip apex [1].

Using NC-AFM with CO terminated tips, atomic resolution on molecules has been demonstrated and the contrast mechanism was assigned to the Pauli repulsion [2] (see Fig.1c) . On the other hand, by using STM and by decoupling the molecules from the metallic substrate by an ultrathin insulating film, the molecular frontier orbitals, i.e. the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO), were mapped [3] (see Fig1b). Moreover, using a CO terminated tip for orbital imaging with the STM, the images correspond to the gradient of the molecular orbitals due to the p-wave character of the tip states [4] (see Fig. 1d).

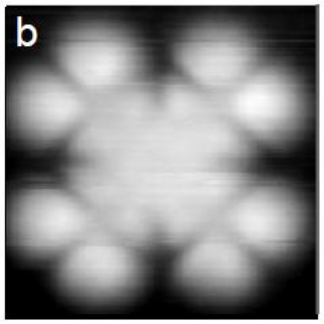
Thus, combining AFM and STM with different tip functionalization, complementary information is obtained. We made use of this combination of methods for the investigation of a molecular switch based on the reversible bond formation in an atom-molecule complex [5].

References:

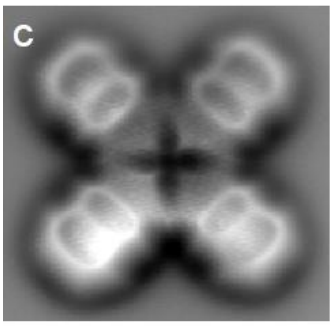
[1] L. Gross, Nature Chem. **3**, 273 (2011)
[2] L. Gross et al. Science **325**, 1110 (2009)
[3] J. Repp et al. Phys. Rev. Lett. **94**, 026803 (2005)
[4] L. Gross et al. Phys. Rev. Lett. **107**, 086101 (2011)
[5] F. Mohn et al. Phys. Rev. Lett. **105**, 266102 (2010)



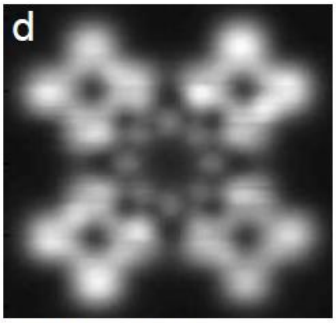
Model of naphthalocyanine structure and HOMO



STM, Cu tip (s-wave): Orbital density (wave function squared)



AFM, CO tip: Atomic structure



STM, CO tip (p-wave): Wavefunction gradient squared