Characterizing chiral, electronic and magnetic properties of molecular adsorbates by Scanning Tunneling Microscopy

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Scanning Tunneling Microscopy (STM) /Spectroscopy (STS) is a versatile tool to investigate the electronic structure of molecular adsorbates on (semi-)conducting substrates. Particularly its local probe approach allows correlation between molecular states and their spatial distributions and symmetries. At low energies, transport through molecules is often determined by many-body phenomena such as the Kondo effect, and inelastic channels where the electron charge appears coupled to the vibrational and magnetic degrees of freedom of the molecule.

We use STS to study the charge and spin configuration of copper and nickel phthalocyanines (Cu, NiPc) deposited on Ag(100). Based on spatial distributions and DFT calculations we are able to assign spectroscopic resonances to molecular orbitals (MO) of the organic ligand or the central ion of the molecules. We discuss possible origins for the differences observed between constant current dI/dV maps and calculated charge densities of MO. Further we characterize the changes induced in the molecular electronic structure by the interaction with the substrate. They manifest in (i) a chiral intensity distribution of only some of the frontier MO [1] and (ii) an additional spin originated from the charge transfer of one electron to the molecule, showing a Kondo interaction. From the spatial distribution of the Kondo resonance we can pinpoint the singly occupied MO where the induced spin is localized [2,3]. In the case of CuPc, the interaction between the molecular and metallic spins results in a Kondo effect that couples to vibrational and magnetic excitations inside the molecule with pronounced intramolecular variations of the conductance and spin dynamics [2,3]. Finally, we explore

different methods to manipulate the charge and spin states of the molecules, such as controlling intermolecular bonds in artificially fabricated molecular clusters (see Fig. 1).

References:

[1] A. Mugarza, C. Krull, et al., Phys. Rev. Lett. 105, 115702 (2010).
[2] A. Mugarza, R. Robles, C. Krull et al., Phys. Rev. B 85, 155437 (2012).
[3] A. Mugarza , C. Krull et al., Nat. Comm. 2:490 (2011).

Figures:

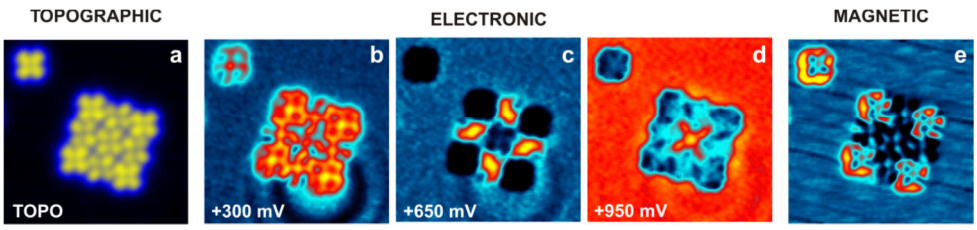

Figure 1: Tuning the charge and spin state with intermolecular interactions. (a) Topography of a 3x3 cluster of CuPc on the Ag(100) surface. (b-d) Spectroscopic (dI/dV) maps of the lowest unoccupied molecular orbital (LUMO). Its energy in each molecule depends on the number of intermolecular bonds (e) Spectroscopic map of the Kondo resonance, which reveals the spin that interacts with electrons from the metallic surface. The presence/absence of the resonance can be correlated with the behavior of the LUMO.