

Nanoscale Structure of Organic/Metal Interfaces

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Organic heterostructures based on blends of molecules with electron-accepting (large electron-affinity) and electron-donating (small ionization potential) character display interesting electrical and optical properties with promising technological applications. For example, they show electroluminescence for Organic Light Emission Diodes (OLEDs) [1], photovoltaic response for solar cell devices [2,3] and one-dimensional conduction for low molecular-weight metallic films [4]. These blends of molecules are deposited onto or contacted with metallic layers and their performance depends crucially on the alignment of energy levels, the molecular nanostructure and crystalline perfection. Interfaces between organic species with either donor or acceptor character and metal surfaces are, thus, of paramount importance for the performance of the devices described above.

In this contribution we will describe our recent efforts in order to understand, control and engineer molecular nanostructures on solid surfaces, especially those made out of organic donors and acceptors. In particular we will focus on three different topics:

- We will describe the subtle ways in which charge-transfer across organic-acceptors/metal interfaces can affect not only energy level alignment but also molecular self-assembly and atomic structure during thin film growth. Using a battery of experimental techniques (Scanning Tunnelling Microscopy, Low Energy Electron Diffraction and X-Ray Photoemission Spectroscopy, Near-Edge X-ray Absorption Fine Structure) and Density Functional Theory calculations, here we show that electron-transfer at the interfaces between a metal surface and the organic acceptor tetracyano-p-quinodimethane (TCNQ) leads to substantial structural rearrangements both on the organic and metallic sides of the interface.
- We will show how surface templates can help in organizing donor/acceptor blends at the nanoscale, opening new means of growing bulk-heterojunction devices for photovoltaic applications. In particular we demonstrated that Due to differences in bonding strength with the substrate and different interactions of the donating (a TTF derivative) and the accepting (a functionalized fullerene) species with the Au(111) herringbone surface reconstruction, mixed thin films spontaneously segregate into a lateral superlattice of interdigitated nanoscale stripes with a characteristic width of about 10-20 nm, a morphology that has been predicted to optimize the efficiency of organic solar cells [5,6].
- Organic nanoparticles show size-dependent absorption and fluorescence bands or single photon emission. Although these size effects in organic nanoparticles might have been expected on the basis of the optical properties of their inorganic counterparts, the detailed understanding of these effects is hindered by the difficulty in the synthesis of organic nanocrystals, i.e. organic nanoparticles with an ordered molecular arrangement,

as compared to the case of inorganic ones. A possibility that remains mostly unexplored is the synthesis of such nanocrystals on solid surfaces. In the same way in which crystalline inorganic nanodots can be epitaxially grown on suitable substrates under conditions in which 3D Volmer-Weber growth takes place, an organic system could in principle be devised such that the growth of crystalline 3D islands sets in before the completion of the first monolayer. In practice, however, for organic adsorbates deposited on inorganic substrates intermolecular interactions are usually much weaker than molecule-substrate interactions thus promoting a layer-by-layer growth mode, and preventing the fabrication of isolated 3D nanocrystals with regular shapes. Here we show that, upon deposition of cone-shaped subphthalocyanine molecules on Cu(111), isolated triangular nanocrystallites up to 3 ML high appear on the surface before the completion of the first monolayer. The different molecular layers show an alternating or antiferroelectric (AF) stacking of the molecular dipole moments.

References:

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Figures:

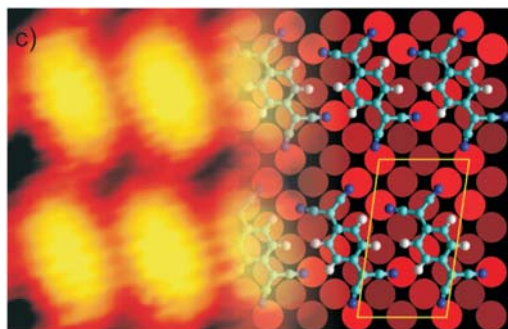


Figure 1: Charge transfer triggered, substrate mediated interactions between TCNQ molecules adsorbed on Cu(100)

Figure 2: Lateral superlattice at the nanoscale due to different interactions of the donating and accepting species with the surface reconstruction.

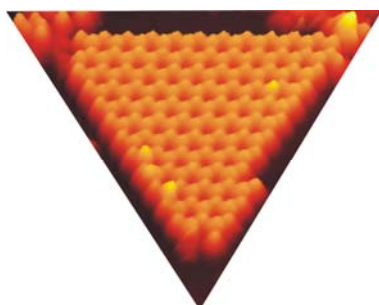


Figure 3: 2ML-thick molecular crystal of SubPc on Cu(111)

