

Chapter 9

Summary

This thesis presents the investigation of electronic properties emerging at the molecular/Au(111) interface by combined STM-STS measurements and DFT calculations. Two bi-molecular ultra-thin films were studied. The organized nanostructures form a perfect scenario where both intermolecular and molecule-surface electronic properties can be investigated with sub-molecular resolution. On the one hand, charge screening on single molecules has been studied as a function of the molecular and metal neighborhood. On the other hand, intra-layer and interface charge transfer have been characterized in a donor-acceptor complex, which develops fascinating properties. Upon charge transfer, one of the molecular components becomes magnetic, thus offering the possibility to study the coupling of spin with molecular vibrations. Moreover, the selective interaction of the molecular components with the underlying metallic surface gives rise to one-dimensional metal-like dispersive bands at the interface.

As a first step to analyze intermolecular interactions we have chosen TPC. Its three-dimensional shape let us to predict the dominance of intra-layer over molecule-surface interactions. TPC presents a self-assembled structure whose organization is based on hierarchical π interactions activated with the temperature. At sufficiently low temperatures, TPC molecules mainly remain as individual adsorbates. For a threshold between 80 K and 100 K, TPC molecules diffuse and self-assemble in very stable multimolecular clusters that act as the basic building units of highly organized molecular islands, whose structure has been determined by STM and DFT calculations.

The adsorption mediated by π interactions makes of TPC an ideal partner for the creation of different mixed structures with a probe molecule: C₆₀. Variables such as molecular ratio and surface temperature can be tuned during molecular co-deposition resulting in a variety of self-organized systems: mixed ordered islands with different C₆₀-TPC ratios and individual C₆₀-TPC clusters.

By means of STS, the local electronic properties of C₆₀ are investigated and compared for the different molecular neighborhoods. As spectroscopy fingerprint we have used the HOMO-LUMO gap of C₆₀. In tunneling spectra, this gap is the result of a neutral molecule gap plus a Coulomb term due to the repulsion imposed on tunneling electrons by charges in the fullerene cage. This Coulomb term is inversely proportional to the screening produced by the polarizability of the molecular surrounding. A comparison between individual and self-assembled fullerenes results in a polarizability of 90 Å³ for the molecular cage that decreases the C₆₀ HOMO-LUMO gap for the self-

assembled case. Substitution of C₆₀ molecules by TPC reveals the lower polarizability of the latter. Such polarizability has been proven to depend on the relative molecular orientation of C₆₀ and TPC, and also on the adsorption orientation of C₆₀. In particular cases, the fullerene molecule is lifted and partially decoupled from the surface.

In the second part of the thesis we have investigated the adsorption of TTF and TCNQ on Au(111), both individually and upon co-adsorption. These molecules are powerful electron acceptor (TCNQ) and donor (TTF) but the different interaction with the surface leads to distinct structures at the interface.

The covalent S–Au bonding between TTF and Au and the donor character of this molecule, results in the formation of a TTF lattice based on long-range repulsive forces. DFT calculations unravel the nature of the repulsive interaction as of electrostatic origin. Upon adsorption on the surface, TTF donates 0.3 e⁻ of charge towards the substrate, becoming thus positively charged. The characteristic pattern of the Au(111) herringbone reconstruction imposes a one-dimensional character to the repulsive lattice. The system can be considered as a molecular Wigner crystal, where each molecule defines a spatial location at the interface with charge accumulation. However, the increase of TTF density leads to dense self-assembled phases. The long-range repulsive potential has to compete with a short-range attractive interaction of hydrogen bond origin, which leads to the formation of complex molecular structures at dense coverages.

The adsorption of TCNQ is not mediated by strong interactions at the molecular/metal interface. This molecule exhibits a planar adsorption on the Au(111). The molecules self-assemble in a saturated hydrogen bond network. Interestingly, TCNQ does not involve charge transfer with the underlying surface, remaining fairly unperturbed upon adsorption.

The co-adsorption of both TTF and TCNQ on Au(111) in the ultra-thin film regime constitutes an example of the combination and selective mixing of both molecular and metal properties at the interface. TTF and TCNQ form, in the monolayer regime, two different phases with distinct stoichiometry, i.e., 2(TTF):1(TCNQ) and 1:1. The latter structure exhibits a high anisotropy due to molecular distribution in rows, resembling the bulk organization. STS measurements reveal the existence of two interface peaks on the TTF and TCNQ rows. In particular, a one-dimensional metal-like dispersive behavior is resolved for TCNQ rows by means of conductance maps. DFT calculations enlighten the origin of this dispersive band. The PDOS resolved in k-space together with three dimensional charge density plots, allow to understand the nature of the states located at the molecule/metal interface. The different adsorption of TTF (chemisorption) and TCNQ (physisorption) creates a periodic potential on the molecular/metal interface across the molecular chains. It results in the formation of two interface hybrid bands, which are split at the \bar{X} point and spatially separated below the TCNQ (lower band) and the TTF (higher band) rows. These two bands exhibit different dimensionality: the lower band is one-dimensional like, it only disperses in the direction parallel to the rows, and the higher is two-dimensional like. These bands have both molecular and metal character but the weight of each component depends on the k point of the surface brillouin zone. In particular, at \bar{X} the lower band, detected in the conductance map measurements, has pure surface state character. The higher band has both surface state and TTF molecular components.

These results suggest that by tuning two factors, i.e., the strength of the mixed

molecule-metal interaction, and the spacing between the TTF rows, it would be possible to engineer the organic/inorganic interface. By combining the properties of the organic "tunable" film and the high carrier mobility of the metal reservoir it is possible to create new electronic structures at the metal/organic interface with large carrier mobility and reduced dimensionality.

Another spectroscopic fingerprint obtained in this system is related to the single molecule π - magnetism developed in TCNQ. The lateral donor-acceptor interaction between TTF and TCNQ results in the donation of one electron to the TCNQ. This unpaired electron leads to Kondo screening, whose spectroscopic fingerprint is identified by STS as a quasi-lorentzian resonance at the Fermi level. Its dependence with the temperature is studied, confirming the spin 1/2 nature of the Kondo effect and a Kondo temperature of ~ 26 K. Furthermore, this Kondo peak is accompanied by fingerprints related to vibration phenomena within the TCNQ molecule: vibronic side bands and inelastic steps are resolved in the conductance curves taken at the center of the molecule.

Hence, organic donor-acceptor interactions are a promising avenue towards the spontaneous self-assembled organization of metal-free molecular magnets. The π orbital character of the unpaired electron provides new phenomenology (vibrations) in comparison with the heavy atom-based magnetism.

The study of the electronic and magnetic properties in nanostructures at the single molecule scale provides a good insight into the variables affecting the transport inside molecular complexes. This knowledge, together with chemical custom-made synthesis, may allow in the future an effective functionalization of molecular-based devices.

