

Chapter 1

Introduction

Already at the early time of 1960, Richard Feynman suggested in his visionary talk "There is plenty of room at the bottom" [1] the idea of "manipulating and controlling things in a smaller scale". Such miniaturization could be achieved by atom rearrangement or chemical synthesis and with the development of tools that allow the required manipulation. He was talking not only about decreasing the size of components, but also about making them functional.

What at that time was almost pure science-fiction has become nowadays standard in science. Since Aviram and Ratner proposed in 1974 the fabrication of an electric rectifier based on a single molecule with donor and acceptor groups [2], a lot of effort has been directed to the use of organic molecules as electronic devices. In this field it is important to remark the research focused in the growth of organic thin films. The interest on this type of materials stems from the ability to deposit the organic compound on low-cost substrates like glass, plastic or metals, and the relative ease of processing and tailoring properties of the organic compounds synthesized. The enormous advances achieved in the last two decades regarding the understanding of the electronic properties of organic films and their mechanisms of growth [3] have boosted their use as electronic "sandwich" between metal electrodes. Actual examples of the utilities of these materials are, for example, organic-light emitting diodes (OLEDs) [4, 5], photovoltaic cells for solar energy generation [6, 7, 8], and thin-film transistors [9].

Detailed knowledge about both the connections among the molecules forming part of the organic film and the interaction with the supporting substrate is required to tailor the properties of the molecular device. Solids based on organic compounds are typically bonded by weak non-covalent interactions with energies in the range of 100 meV. The large variety of interactions (van der Waals forces, dipolar interactions, donor-acceptor recognition, π -stacking, and hydrogen bonds) increases the difficulty on the design of the devices but also opens many possibilities for their construction, with an eventual custom made functionality based on different molecular configurations.

Within this scenario, the growth of mixed heteromolecular systems is also in the focus of nanotechnology research. Co-deposition of molecules with complementary structure or electronic properties increases the versatility of the supramolecular materials. The molecular growth is also dominated by non-covalent recognition processes that lead to the formation of self-assembled systems. The tunability and reversibility

of the interactions make of these supramolecular structures a dynamic system. Small changes such as exchange or incorporation of constituents allow a continuous development in the constitution and electronic properties of the self-assembled system. From this variability point of view, a good characterization of molecular systems, both from the structural and electronic properties perspective, is a challenge.

This thesis is focused on the study of two mixed heteromolecular systems: i) Triptycene (TPC) and C_{60} , and ii) tetrathiafulvalene (TTF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), investigated by means of Low Temperature Scanning Tunnelling Microscopy and Spectroscopy (LT-STM and STS). The research is done in the regime of ultra-thin film deposited on a Au(111) surface, i.e. for molecular coverages in the order of one monolayer (ML). Both molecular systems have very interesting structural and electronic properties in bulk. Our approach includes the presence of a surface that acts as a planar support and constrains the molecular motion to a plane. Inter-molecular interactions are thus partially hindered and, in most of the cases, chemical connections can arise between the surface and the molecular species grown on top, modifying their electronic properties.

The mixing of C_{60} and TPC is an ideal example of a molecular key-lock scenario. The complementary shapes of these molecules together with their weak respective acceptor and donor characters, drive the formation of molecular inclusion complexes similar to those reported in bulk [10, 11]. We have found that different two-dimensional phases can be controlled by simply tuning external parameters such as molecular ratio and temperature of the surface during deposition. We explore the electronic properties of a single molecule embedded in the different C_{60} -TPC self-assembled systems, focusing specially on their variations for distinct polarizable surroundings.

Discovered more than 30 years ago, TTF-TCNQ is a model low-dimensional organic metal. Built upon donor-acceptor interactions, it presents in bulk quasi one-dimensional conduction along homomolecular π -stacked chains. Due to the reduced dimensionality it also exhibits interesting phenomena at low temperatures like Peierls instabilities leading to Mott metal-insulator transitions, accompanied by the development of charge density waves (CDW).

Despite these fascinating bulk properties no investigations have been carried out so far in the ultra-thin film limit. Such a research is of great interest for understanding and tracking the development of the bulk properties with the addition of layers. The presence of the metallic surface may modify the electronic properties of the molecular layer at the organic-metal interface. The mixing of the high charge mobility characteristic of the metal substrate with the orbitals of the organic layer may give rise to new interesting interface phenomena characterized by a mixture of properties of both surface and molecular layer. The charge transfer between TTF and TCNQ may also get modified by the interaction with the underlying surface creating new charge redistribution, intermediate between the free molecule and the bulk behaviors.

LT-STM serves as a very powerful tool for this research. Its atomic-scale resolution allows both the imaging of nanostructures and the performance of local spectroscopy with intramolecular resolution. The working conditions of the STM at a temperature of 4.8 K ($k_B T \sim 0.4$ meV) reduce the thermal motion of atoms/molecules and increase the energy resolution of spectroscopy measurements. Local STS performed at the atomic scale is the first tool able to resolve with sub-molecular precision the electronic

structure and vibrational excitations of adsorbates and to correlate them with the neighborhood. We can say that local physical/chemical phenomena that are averaged in another macroscopic techniques becomes now available with STS [12].

This thesis is organized as follows:

Chapter 2 introduces LT-STM and STS and briefly describes the basics of Density Functional Theory (DFT), since some experimental results are corroborated by theoretical simulations.

Part I focuses on the local spectroscopy performed in the mixed system C_{60} and TPC. It is divided in two chapters. The first describes the growth properties of TPC. The second chapter addresses the adsorption and electronic properties of different C_{60} and TPC mixed structures. The screening from molecular neighborhood and surface is determined by checking the electronic properties of a single molecule embedded in the variety of C_{60} -TPC self-assembled systems.

Part II is devoted to the study of an ultra-thin layer of TTF-TCNQ adsorbed on Au(111). It is divided in three parts. The first chapter describes the properties of the individual components, TTF and TCNQ, on the surface. The second chapter focuses on the mixed TTF-TCNQ films, where an interesting interface structure has been found. Finally, we report on the magnetic state of TCNQ molecules due to the transfer of one single electron from TTF. A brief outlook describing further investigations on TTF-TCNQ is given at the end of this part.

Chapter 9 summarizes the results presented in this thesis.

