

Chapter 1

Introduction

In terms of technological progress and also in the context of fundamental research, the application of single molecules as electrical and nano-mechanical devices seems very promising. Compared to standard semiconductor devices, the use of molecules allows a higher grade of miniaturization, and even more important, the physical properties of molecules can be exploited confining electrons to dimensions comparable to their wavelength. An ultimate goal of nanotechnology is to achieve functional molecular devices operating on a dimensional scale where quantum mechanics dominate.

The idea that a few molecules, or even a single molecule, could be embedded between electrodes in order to perform the basic functions of digital electronics, i.e. rectification, amplification, and storage, was suggested by Aviram and Ratner in 1974.¹ They proposed that a molecule with a donor-spacer-acceptor structure would behave as a diode when placed between two electrodes. Such devices, consisting of molecules embedded between several electrodes, are called hybrid molecular electronic (HME) devices. Recently, Joachim et al. proposed a different approach to molecular electronics, suggesting that all elementary functions and interconnections required for computation could be integrated into one single molecule;² such approach is called mono-molecular electronics (MME). It is important to note that both HME and MME devices, relying on the electronic properties of individual molecules, differ radically from bulk-material-based

molecular electronic devices such as dye lasers, light-emitting diodes, liquid crystal displays, and soft plastic transistors. Several fundamental problems need to be solved before the application of HME or MME devices can be realized. In this work I will address some of them, i.e. the electrical contacting of single molecular wires to metal electrodes, the directed build-up of molecular structures, and the control of electronic properties of molecule-metal structures.

The scanning tunnelling microscope (STM) enables, besides imaging surfaces with atomic resolution, controlled two-terminal conductance measurements. It therefore allows to experimentally probe electron transport through individual molecules, as shown for the first time by Gimzewski et al.³ Important works on the way to single molecular devices were the electrical single-atom switch realized by Eigler et al.⁴ using a single Xe atom and the first experimental determination of the electrical contact point of a C₆₀ molecule by Joachim et al.⁵ In the latter case a single molecular electromechanical amplifier was realized, using the tip of an STM to deform the C₆₀ molecule, thereby shifting the molecular orbitals.⁶ A single molecular switch was realized by Moresco et al.⁷ by changing the conformation of a porphyrin molecule in the tunnel junction. The conductance of single- and multi-wall carbon nanotubes could be measured electrically interconnected in a fully planar geometry^{8, 9} and, moreover, carbon nanotube transistors have been realized.^{10, 11} In recently reported break junction experiments, current-voltage characteristics of single (or few) molecules have been measured.¹²⁻¹⁵ However, the number of interconnected molecules, the molecular conformation, and the geometry of the molecule-metal junction is inaccessible in such experiments.¹³ This lack of information and control regarding the geometry is problematic since the contact quality crucially relies on the precise interaction of the molecule end groups and the surface of each electrode.¹⁵⁻¹⁸

The aim of this work is the investigation of single molecules deposited on metal surfaces and the fabrication of atomically precise molecular structures for HME and MME, i.e. molecule-metal contacts, intermolecular contacts, and molecular networks. The high spatial resolution and the ability to manipulate matter at the atomic level¹⁹⁻²¹ make LT-STM (Low Temperature-STM) the ideal tool for this

study. The goal is, besides the detailed description of the adsorption conformation of large organic molecules, to form atomically defined test-structures by STM induced manipulation of large organic molecules, as is needed for the investigation of metal-molecule and intermolecular contacting.

On the other hand, self-ordering of organic molecules is studied, as it presumably constitutes the route to economic fabrication of ensembles of molecular nano-structures in a parallel geometry²²⁻²⁴. The thin film growth of organic molecules has been subject of intense studies during the past decade finding that the self-ordering process sensitively relies on the interplay between molecule-substrate and intermolecular forces.²³⁻³² To achieve the directed synthesis of molecules for applications in organic film technology, knowledge on the correlation between the chemical molecular structure and the molecular epitaxial growth is desirable.

This thesis work is organized as follows: In Chapter 2, the central technique of this work, STM, is introduced, with emphasis on STM induced manipulation. Moreover, the elastic scattering quantum chemistry (ESQC) approach, which is used for the theoretical calculation of STM images is described. The experimental part, Chapter 3, describes the measuring chamber and the sample preparation. Furthermore, the investigated systems, i.e. the Cu surfaces and the different investigated molecules are introduced. Previous works on the molecules are reviewed.

In Chapter 4, the exact adsorption conformation of Lander molecule is studied and the formation of molecular chains by means of STM manipulation is demonstrated. In Chapter 5, the interaction of Lander molecules with surface state electrons on Cu(111) is investigated. The atomically defined contact of a Lander molecule to a step edge is established and analysed by ESQC and multiple scattering calculations.

A systematic study of monolayer structures of four slightly different HBC derivatives is presented in Chapter 6. By comparison of the molecular growth it is possible to assign the adsorption behaviour and self-ordering properties to specific chemical groups within the molecules.

In the last part of the work, Chapter 7, both addressed techniques for the fabrica-

tion of molecular nano-structures are combined, i.e. STM manipulation and molecular self-organization. The possibilities of STM induced manipulation to form artificial nano-structures in the case of molecular monolayers is investigated experimentally. One can expect that self-ordering properties of the molecules will influence or even determine the final conformation of molecules in STM manipulation experiments.