

Chapter 8

Summary and Outlook

This work focuses on the investigation of single molecules for future applications in molecular electronic devices. Two different molecular families are investigated by means of LT-STM. On the one hand Lander molecules, specially designed to act as model systems for molecular wires on metal substrates and on the other hand derivatives of hexa-*peri*-hexabenzocoronene (HBC), which are chosen for their known promising tubular self-assembly. Moreover, various HBC derivatives have been proven interesting for applications in molecular electronic devices.

First, in Chapter 4, the adsorption properties of the molecules are studied. Due to the high spatial resolution of the LT-STM, the internal conformations of single molecules can be distinguished. In the case of Lander molecules, characteristic differences in STM images of single molecules are assigned to the molecular orientation and internal conformation, as shown in Fig. 4.3. By combining STM measurements with theoretical MM+ESQC calculations (done in the group of C. Joachim in Toulouse) the stable adsorption geometries of these molecules can be determined with high precision.

The build-up of test structures for single molecular devices is of great interest. In this work I show how Lander molecules can be aligned in molecular chains with the molecular boards parallel to the direction of the chain. Molecular chains are fabricated on Cu(211) by means of lateral STM manipulation, using the substrate

step edges as precise guidance to maintain molecular orientation and alignment during the manipulation process (see Fig. 4.11).

As a very important step on the route to hybrid molecular electronics (HME) and mono-molecular electronics (MME), the controlled contacting of a Lander molecule to an atomically defined contact pad is achieved, as demonstrated in Chapter 5 on Cu(111). To do so, I positioned the Lander molecule in different orientations at a mono-atomic step edge by STM manipulation and probed the interaction of the molecular wire with the upper terrace by observation of the scattered surface state wave patterns (see Fig. 5.10). The observations are in very good agreement with multiple scattering calculations, which reveal the naphthalene end group of the molecular wire as the cause of the characteristic scattering wave pattern (see Fig. 5.15). Beside the scattering of surface state electrons a protrusion caused by the electronic contact (“contact bump”) is observed and due to MM+ESQC and multiple scattering calculations both features can be related to the coupling between the molecular naphthalene end group and the metallic contact pad. This is the first controlled contacting of a molecular wire to a metal electrode at the atomic scale. Knowing and controlling the geometry of the molecule-metal contact is of fundamental importance, since the performance of molecular (HME or MME) devices strongly depend on the overlap of molecule and metal wave-functions. Building up on these experiments a further study of molecule-metal contacts, in knowledge of their exact geometry, is possible. In particular, conductance measurements depending on the molecule-metal geometry are of great importance.

Measuring the surface state wave patterns in the vicinity of Lander molecules on Cu(111) and calculating the patterns by means of multiple scattering, leads to the identification of the delocalized π -systems of the molecular board as the main scattering centres within the molecule, as described in section 5.3. This is the first time that surface state standing wave patterns are used to investigate the scattering properties of different parts inside a molecule. The findings point out that the molecular wire board of the Lander molecule is not completely decoupled from the metallic surface underneath.

To gather general knowledge about molecular self-organization, the monolayer formation and growth of four slightly different systems are investigated. The monolayer structures of HBC and three derivatives (all pure hydrocarbons) on Cu(111) are described and the different adsorption properties can be assigned to the presence of specific chemical groups, as presented in Chapter 6. It is found that the strongest molecular-substrate interactions of these molecules are mediated by the delocalized π -systems that are oriented parallel to the surface, while intermolecular forces are mediated by aromatic parts which are not parallel to the surface and by non-aromatic groups. This allows the identification of the chemical groups responsible for anchoring to the substrate, intermolecular bonding, and molecular orientation. Such general observations are of great interest for the design of molecules for applications in organic thin film technologies. Moreover, the findings are affirmed by lateral manipulation experiments, requiring different manipulation parameters and revealing characteristic manipulation signals for different molecules (section 7.1). To gather more information for the general expectations in the case of organic-on-metal epitaxy, the effect of the substitution of carbon atoms by nitrogen atoms is investigated in ongoing experiments.

For the future serial build-up of structured nano-molecular devices, self-assembly of molecules will presumably be the key technology. However, STM can be used to modify and therefore functionalize self-ordered monolayer structures as is demonstrated in Chapter 7. In this aspect I describe how molecules can be manipulated within molecular islands (Fig. 7.4), extracted from molecular monolayers (Fig. 7.5), and how molecular conformations of molecules inside the monolayer can be changed (Fig. 7.6). The most important result is that, in all these cases, the high precision of order - regarding position and orientation of molecules inside the monolayer structure - is maintained upon STM manipulation. Therefore the accuracy and reproducibility of man-made supramolecular structures by STM is greatly enhanced due to the molecular self-ordering processes. Furthermore, a switching between precisely defined molecular structures is possible by applying voltage pulses. It is also demonstrated that single molecules can be used to structure the metallic surface on the atomic scale. This is observed, on the one hand, for the thermally activated restructuring found for Lander

molecules on Cu(211), as displayed in Fig. 4.7. On the other hand it is shown how molecules can be used as nano-tools for the assembly of adatoms, in combination with STM manipulation (see Fig. 7.8).