1 Introduction

The pursuit for the ever faster and more complex electronic devices inevitably leads to the miniaturization of the components involved. Nowadays, the production of such devices with dimensions on the order of 100 nm and below is a routine^[1]. An alternative promising route in the process of miniaturization is indicated by the fascinating idea of using organic molecules as components for these devices. This concept dates back to 1974, when Aviram and Ratner proposed a rectifier consisting of a single molecule^[2] and thereby set the cornerstone for molecular electronics. With its fundamental ideas already proposed by Feynman in 1960^[3], in molecular electronics individual molecules are employed to perform non-linear electronic functions as *e.g.* rectification, amplification or storage. Remarkably, the non-linearity required for most electronic devices accurately coincides with the non-linearity of quantum mechanical effects dominating in such systems. At these scales, however, unprecedented difficulties arise: the stability of the system is jeopardized, achieving reproducibility is extremely demanding *etc.* The reproducibility of such nanoscale systems is particularly of great importance since the non-linearity of quantum mechanical effects requires the energy levels involved in the functional mechanisms to be exactly defined.

The necessity for easily reproducible systems at the nanoscale makes molecular selfassembly, a fundamental aspect of the bottom-up approach, a suitable method to complement the top-down approach. Molecular self-assembly can be defined as the spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by non-covalent bonds^[4]. It can be exploited to generate structures with dimensions up to ~100 nm. The use of organic molecules as building blocks is a natural choice because large amounts of organic molecules having a precisely defined chemical structure can be repetitively synthesized. Additionally, the electronic properties of organic molecules can be fine-tuned by slight variations of their structure. However, in order to be of technological relevance, the self-assembly process of organic molecules must be controllable. Although an abundance of information about the self-assembly process in solution as well as in the bulk state is available, it turns out that it is often misleading to transfer these principles to 2D self-assembly. The differences arise from the two dimensionality, influence of the substrate *etc.* Therefore, deeper understanding of the self-assembly process of organic molecules on surfaces is of crucial importance.

Another aspect of the 2D self-assembly is that it allows investigations at the single molecule level. In combination with scanning probe microscopy methods, assembled structures form a "nanolaboratory" in which single molecules or molecular systems can be individually addressed and investigated. This opens new opportunities to study various processes occurring at the nanoscale. One of the most prominent of such processes is the electron-transfer.

The importance and complexity of electron-transfer reactions in nature has led many researchers to look for ways to duplicate the fundamental features of these reactions in simplified chemical systems. The design and development of molecular complexes which are capable of light-harvesting, photo conversion and catalytis and which self-assemble into integrated functional units could enable the realization of efficient artificial photosynthetic systems. While some progress has been made, researchers have not yet developed components that are both efficient and robust and they have not yet integrated the existing functional components into a working system^[5]. In order to achieve that, however, studies revealing the nature of the charge transfer process involved are essential.

In the framework of this thesis, the "nanolaboratory" setup was used to study an electron donor-acceptor complex consisting of a phthalocyanine derivative and C_{60} . In the last

few years, phthalocyanines are studied intensively as targets for optical switching and limiting devices, organic field effect transistors, sensors, light-emitting devices, low band gap molecular solar cells, optical information recording media and nonlinear optical materials^[6], among others. A phthalocyanine is a macrocyclic compound having an alternating nitrogen atom - carbon atom ring structure, closely related to that of the naturally occurring porphyrin systems. (Figure 1.1) Its first known reference dates back to 1907^[7]. The molecule is able to coordinate either hydrogen or metal cations in its center by coordinate bonds with the four isoindole nitrogen atoms. Most of the elements have been found to be able to coordinate to the phthalocyanine macrocycle.



Figure 1.1 Relationship between the phthalocyanine and the porphyrin macrocycle.

Also, various functional moieties can be attached in different positions to the phthalocyanine ring and thus, the properties of the phthalocyanine can be greatly altered. Therefore, a variety of phthalocyanine complexes exists. Essentially, the delocalized π -electron system of the planar phthalocyanine macrocycle makes phthalocyanines useful in different areas of materials science. In fact, the most efficient molecular photovoltaic device reported to date has been fabricated using a heterojunction based on copper phthalocyanine and $C_{60}^{[8]}$.

And last but not least, the investigation and visualization of the 2D self-assembly of organic molecules reveals not only its important morphologic and electronic properties, but also the aesthetic qualities of a plane symmetry group that governs the ordering of the building blocks. Here again, the nature proves itself to be an artist that combines functionality with beauty. The same beauty of ordered patterns that fascinated ancient decorators as well as modern artists.



Reptiles, M.C.Escher^[9]

This thesis discusses the self-assembly and hosting properties of phthalocyanine derivatives. In chapter 2, the instruments and experimental methods used to investigate the discussed systems are introduced. In chapter 3, the results of the experiments are presented. It consists of three main parts: The first part (3.2) discusses the self-assembly of a symmetrically substituted phthalocyanine derivative on noble metal surfaces. The second part (3.4) discusses the self-assembly of a related asymmetrically substituted phthalocyanine on noble metal surfaces. In the third part (3.6), the self-assembly of the symmetrically substituted phthalocyanine on conclusion is used as a "nanolaboratory" in order to investigate the interaction between C_{60} and a phthalocyanine. In chapter 4 the results are discussed and prospective experiments and research directions are outlined. In the last chapter, a brief summary of the thesis is given.

2 Experimental methods

2.1 STM

2.1.1 Introduction

In 1714 the Longitude prize was offered for a simple and practical method for the precise determination of a ship's longitude. Many great minds devoted their work to assembling and analyzing astronomic data in order to solve the problem. John Harrison, on the other hand, had little interest in astronomy. His hobby was building and repairing clocks. Eventually, he was awarded the major amount of the Longitude prize for constructing the first sufficiently reliable marine chronometer. Moreover, he proved that the most obvious path doesn't necessarily lead to the simplest solution, yet again.

In the beginning of the 20th century, the concept that the matter consists of atoms was a well established theory, supported by a range of experiments. But the limitations imposed by the de Broglie wavelength of light made seeing the atoms virtually impossible (and seeing is believing), since the wavelength of light is *cca*. 1000 times larger than the distances between atoms. The obvious way to circumvent this limitation is to reduce the wavelength. The use of an electron beam proved to be a secure, nonetheless slow and complicated solution^[10]. Gerd Binnig and Heinrich Rohrer, on the other hand, took a different approach. In 1981 they invented the STM (scanning tunneling microscope/microscopy)^[11, 12], a powerful and reasonably simple tool that allows "seeing" atoms routinely. Eventually, in 1986 they were awarded the Nobel Prize for their invention.

STM is a local (non-averaging) probing technique, providing real space images. Hence, the interpretation of the data can be often much faster compared to the methods dealing with reciprocal space. It allows for investigating the morphologic and/or electronic properties of samples as well as the manipulation of individual atoms or molecules.

The astonishing resolution capabilities, the flexibility and fast operation of STM made this technique particularly suitable for the systems investigated in this thesis.

2.1.2 Basic principle

The STM consists essentially of a sharp metallic tip (mostly made of W or PtIr) positioned in close proximity to a (semi-) conductive surface, typically in the range of a few Å. The quantum mechanical tunneling effect, occurring at these small distances, allows the electrons to tunnel from the tip to the sample and vice versa. By applying a small bias voltage between tip and sample (usually in the range of 0.01 to 3 V), a directed tunneling current occurs depending strongly on the separation distance.



Figure 2.1 Simple schematic of the working principle of STM (not sized to scale). The motion of the tip operated in constant current mode over a surface step is indicated.

Therefore, while the tip scans over the surface in a lateral raster motion by means of high precision piezoelectric drivers (x- and y-piezos), even minor corrugations of the surface lead to changes in the measured tunneling current. By another piezoelectric element (the zpiezo) the vertical position of the tip above the surface is controlled. Several different scanning modes are possible to obtain a 2D map of the scanned surface. In the constant height mode, the tip scans over the surface at a constant vertical position, while the current is measured. Alternatively, in the constant current mode a computer-operated feedback system is used to keep the tunneling current constant. This is achieved by adjusting the tip-sample separation by means of the z-piezo. The changes in the voltage applied to the z-piezo are measured. The latter mode prevents the tip from crashing into large protrusions or a tilted surface, but the scanning speed is reduced due to the required feedback process, in comparison to the constant height mode. This mode was used for all STM measurements in this thesis. To visualize the STM image, the recorded z-piezo signal is depicted at every point of the two dimensional raster by a predefined color code. Notably, these maps are derived from the tunneling current and therefore correspond to the electronic rather than morphologic features of the surface. This is due to the intrinsic properties of the technique, described in the following.

2.1.3 Theoretical description of the tunneling process

Obtaining an exact theoretical description of the tunneling process in STM is practically impossible due to the lack of a complete description of the quantum mechanical states of the tip and the scanned sample. In particular, the states of the tip are problematic, since its geometry and chemical composition cannot be entirely identified. Moreover, the structure of the tip can change even during an experiment. Still, models assuming various approximations have been developed in the past^[13-15].



Figure 2.2 One-dimensional schematic diagram of a tip-sample junction. A positive bias U has been applied to the sample, therefore electrons can tunnel from occupied tip states into unoccupied sample states. The size of the horizontal arrows indicates the different transmission coefficients (tunneling probabilities) for electrons of different energies.

Despite the complexity of the system, most of the aspects of scanning tunneling microscopy can be explained considering the simple theory developed by Bardeen^[16]. In this theory the specific geometry of the tip-sample junction is neglected and the tunneling junction is modeled as a one-dimensional system. (Figure 2.2) Elementary quantum mechanics imply that the probability Q for an electron with energy E to tunnel through a potential barrier of energy E_{bar} (with $E_{bar} > E$) is

$$Q \propto \exp\left[-\frac{2d\sqrt{2m(E_{bar}-E)}}{\hbar}\right]$$
 2.1

where m and d are the electron mass and the barrier width, respectively. In the approximation proposed by Bardeen the net tunneling current between tip and sample measured while applying a bias U will simply be

$$I = \frac{4\pi e}{\hbar} \int_{0}^{eU} \rho_s(E) \rho_t(e \cdot U - E) T(E, e \cdot U, d) dE$$
 2.2

where ρ_s and ρ_t are the density of states of the sample and of the tip, respectively, while $T(E, e \cdot U, d)$ is the transmission coefficient for electrons with energy *E* tunneling from the tip into the sample.

For this simplified one-dimensional model (Equation 2.1) the transmission coefficient is

$$T(e, e \cdot U, d) = \exp\left[-\frac{2d}{\hbar}\sqrt{2m(\frac{\phi_s + \phi_t - e \cdot U}{2} - E)}\right]$$
 2.3

where Φ_s and Φ_t are the work function of the sample and of the tip, respectively. It is important to note that expression 2.2 is just the integral of the transmission coefficient over the density of states of the tip and of the sample (indicated by the arrows in Figure 2.2) within the energy interval allowed for tunneling. This interval corresponds to the energy range where the occupied states of the tip and the unoccupied states of the sample overlap. In this simplified model, tip and sample have a perfectly symmetric role. Thus, the same applies for negative sample bias (i.e. for electrons tunneling from occupied states of the sample to unoccupied states of the tip).

In reality, the geometries of tip and sample are different and the asymmetry affects the system. As stated before, this complicates the situation significantly and makes it almost impossible to develop a first principles model. Nevertheless many attempts have been made to treat the problem with approximations closer to the real situation. Among those, the so called s-wave-tip model developed by J. Tersoff and D. R. Hamann^[17, 18] is certainly one of the most important ones. It models the tip apex as a little metal sphere, implying that only the s-states of the tip take part in the tunneling process. For low biases (much smaller than the tip work function Φ_i) the current turns out to be proportional to the local density of states (LDOS) at the center of the sphere with radius r_0

$$I \propto e \cdot U \rho_s(E_{F,s}) \rho_t(E_{F,t}, r_0) \exp\left[-\frac{2d}{\hbar} \sqrt{m \frac{\phi_s + \phi_t}{2}}\right]$$
 2.4

The current decays exponentially with increasing tip-sample distance, and this dependence is responsible for the extraordinary sensitivity of STM. Interestingly, in this approximation the dependence of the current on the DOS of the tip is expressed only by the factor ρ_t ($E_{F,t}$, r_0) which, remarkably, is just a constant. Therefore, in the frame of the Tersoff and Hamann theory, the variations of the tunneling current while scanning the tip over the sample surface turn out to depend only upon the local properties of the sample and not on the tip. In the case of metal surfaces, these properties reflect the surface topography^[16], nevertheless, this doesn't necessarily apply for the case of adsorbates as described in section 2.1.4.

However, this simple model failed to explain the observed atomic resolution on closepacked metal surfaces. Eventually, this was achieved by C. J. Chen in 1990 by considering the d_{z^2} states of the tip^[19, 20].

2.1.4 Imaging adsorbates

As stated above, interpreting constant current STM images of single atoms or molecules adsorbed on a conductive surface in the same way as the images of uniform metal substrates is often misleading. A typical example is the case of O on $Pt(111)^{[21, 22]}$, which appears counterintuitively as a depression. Another example is the imaging of CO on $Cu(211)^{[23, 24]}$ where CO can appear as both a depression or a protrusion, depending on the proximity of neighboring molecules and the modification of the tip by adsorbed CO. A theoretical study clarifying the interpretation of the contrast mechanism of simple atomic adsorbates was performed by $Lang^{[25, 26]}$, who proved that these adsorbates are imaged as protrusions or depressions, depending on whether they increase or decrease the electron

density at the Fermi level. Therefore even insulating atoms can be seen in STM as discussed by Eigler et al. for the case of Xe physisorbed on $Ni(110)^{[27]}$.

In the case of organic molecules, before the first successful STM measurements were published^[28-31], it was unclear whether molecular imaging would be possible at all. The doubts stemmed from the fact that most organic molecules have a rather large energy gap between their highest occupied molecular orbital (HOMO) and their lowest unoccupied molecular orbital (LUMO). This energy gap was supposed to hinder the imaging of molecules. But since the molecular orbitals (MO) interact with the band structure of the metal surface, these MOs are altered^[32] in a way that the imaging is possible. However, it also means that HOMO and LUMO of adsorbed molecules can differ from those of molecules in the gas phase.^[33, 34]

Also in the case of large organic molecules with an extended π -electron system, the height interpretation is not necessarily straightforward. The appearance in STM images can depend on the applied voltage (Figure 2.3)^[35], the adsorption site^[36], but also on the surface geometry^[37]. However, by combining the data obtained by different imaging modes of the same system, additional information can be gained. (Figure 3 in publication A)



Figure 2.3 Different appearance of the imaged molecules induced by a change of the bias voltage. H2Pc-DTPO (publication A) on Ag(111) (20x20 nm2, 10 pA).

As opposed to the Tersoff and Hamann model, the tunneling current - and thus also the STM image - also depends on the properties of the tip. Any change of the tip which can spontaneously occur during an STM experiment can affect the tunneling current and consequently the recorded STM image. (Figure 2.4)