SINGLE MOLECULE SWITCHES AND MOLECULAR SELF-ASSEMBLY: LOW
TEMPERATURE STM INVESTIGATIONS AND MANIPULATIONS

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Abstract

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SINGLE MOLECULE SWITCHES AND MOLECULAR SELF-ASSEMBLY: LOW
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This dissertation is devoted to single molecule investigations and manipulations of two porphyrin-based molecules, chlorophyll-a and Co-porphyrin. The molecules are adsorbed on metallic substrates and studied at low temperatures using a scanning tunneling microscope. The electronic, structural and mechanical properties of the molecules are investigated in detail with atomic level precision. Chlorophyll-a is the key ingredient in photosynthesis processes while Co-porphyrin is a magnetic molecule that represents the recent emerging field of molecular spintronics. Using the scanning tunneling microscope tip and the substrate as electrodes, and the molecules as active ingredients, single molecule switches made of these two molecules are demonstrated. The first switch, a multiple and reversible mechanical switch, is realized by using chlorophyll-a where the energy transfer of a single tunneling electron is used to rotate a C-C bond of the molecule's tail on a Au(111) surface. Here, the detailed underlying switching mechanisms are uncovered from the statistical analyses conducted over 1200 switching events together with the support of geometrically relaxed parametric calculations. The second switch, a spintronic switch, uses Co-porphyrin conformational changes to tune the spin-electron interaction between the Co atom and Cu(111) electrons. A change in the molecular conformation, from saddle to planar, leads to enhanced spin-electron coupling strength, and consequently, elevated Kondo temperatures. Self-assembly process is exploited for both the molecules and the analyses reveal important information regarding the layer growth and the electronic differences that appear due to the modified molecule-substrate environment.

Approved:

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to my family

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Chapter 1

Introduction

Since the famous Feynman's lecture from 1959 in which he states that "there's plenty of room at bottom" new experimental techniques have been developed to address the foreseen new avenue of the technology: the bottom-up approach. With the discovery of the scanning tunneling microscope (STM) in 1980's new opportunities to study small components of matter such as atoms and molecules arose. Now the scanning tunneling microscope is a versatile tool in determining the topographic and electronic structure of surfaces as well as in manipulating single atoms and/or molecules [EIG90, JOA00, MAN00]. Single atoms can now be extracted from the metal surface using the STM tip [HLA04], a procedure that explores new physics in the tip-sample mechanical contact or simply known as 'tip-crash'. Single atoms can not only be 'seen' or 'heard' [STR04] but also used to write or build small architectures. By combining STM manipulations with complementary spectroscopy techniques physical/chemical properties of single atom/molecules can be probed and single molecule chemical reactions can be induced [HLA00].

Since the hunt for smaller and more efficient electronic devices started, molecules have gained a special interest because of their attractive properties. Nowadays, their small sizes ranging between 1 and 100 nm make them a good choice for small and cheap devices. Their physical properties can be easily tailored thanks to the advances in chemical synthesis. Their potential to self-assemble on surfaces can be used in building extended 'farms' of molecules specialized in certain functions. In this way molecular

devices with specific functions, such as logic circuits [TOU03] or memory storage devices [LIU03] can be built. Electronic circuits made of molecules are useful in the scaling down process of devices to nanometer range.

In this research two porphyrin-based molecular systems were studied, chlorophyll-a and metallo-tetraphenylporphyrins, each representing one of the two emerging research areas: nanobiophysics and molecular spintronics. This study is motivated by the importance of these molecules in biological systems and their potential use in electronic devices. Porphyrin is a naturally occurring molecule that can be found in many biological systems such as hemoglobin (Fe-porphyrin), vitamin B (Co-porphyrin) or in photosynthesis complex (Mg-porphyrin). Its ring-shaped structure can easily lose or gain electrons and this makes it a good candidate for charge storage devices [ROT00, LIU03]. Easiness in changing the redox properties by chemical synthesis together with the high-temperature stability of porphyrin are two important advantages that porphyrin-based systems have over the silicon devices [LIU03]. Break junction experiments using porphyrin-based molecules have demonstrated their ability to function as single electron transistors [YAO06, PAR02, LIAN02]. Even though the above experiments have proven the applicability of molecules as either whole electronic devices or components of electronic devices such as switches or wires, many of these experiments are done in either bulk samples or without the possibility to check ‘visually’ the composition of the samples studied. Scanning tunneling microscope is an instrument that can break this obstacle being capable of studying molecules either individually or in self-assembled environments with a submolecular or even atomic resolution [NEW06, BRA06].

Motivated by the new advances in STM techniques and the importance of the molecules mentioned, our research goal is to fill the gaps that exist in the understanding of these molecules at molecular and submolecular levels. Here we present single molecule level investigations and manipulations of porphyrin-based molecular systems: chlorophyll-a and metallo-tetraphenylporphyrins. Our aim is to probe their electronic, structural and mechanical properties at single molecule level as well as in self-assembled structures and to initiate possible uses in molecular electronics and mechanical device fabrications. An outline of the dissertation follows.

Chapter two gives a detailed description of the apparatus, the spectroscopy and manipulation techniques used for the completion of the project. The apparatus used is a scanning tunneling microscope that was built in our lab during my first year of research. The STM is designed to operate at low temperatures and in ultrahigh vacuum environment and it is capable of single atom and molecule manipulations. Besides imaging and manipulation, the STM can also be used to perform spectroscopy. Density of states of a sample can be locally determined using the STM. Filled and empty electronic states can be resolved both spatially and in energy.

Chapter three introduces the substrates and the molecular systems used in this research. Working with STM requires usage of conductive substrates. Here we use noble metal substrates such as Cu and Au cleaved along (111) plane. The (111) face-centered-cubic surfaces present a nearly free two dimensional electron gas. Molecular systems studied are chlorophyll-a, Co- and Cu-TBrPP (5, 10, 15, 20-Tetrakis-(4-bromophenyl)-porphyrin-Co (II) and -Cu).

Chapter four presents a comprehensive study of Co-TBrPP molecules adsorbed on a Cu(111) substrate. Single molecules are found in two molecular conformations that have different electronic properties. Each conformation provides a different internal molecular environment for the Co atom that modifies the strength of the interaction between the magnetic atom and the free electrons from the substrate. This is reflected in the differential conductance measurements by a variation in the width of the resonance situated near the Fermi energy. A resonance at Fermi energy is a signature of the Kondo effect in the STM measurements. Our measurements have determined that the two molecular conformations have different Kondo temperatures which can be modified in a controlled manner by using tunneling electrons to change one conformation into another. Self-assembled structures are also investigated at low temperatures. Three possible arrangements of the molecules in a layer are found and their electronic properties were studied. The Kondo temperature is determined to be different for the molecules in the layers than for an isolated molecule. Different lattice arrangements with slight variation of the lattice constants (15 Å to 17 Å) were found not to change the Kondo temperature.

This result is important as it outlines nondestructive methods to change the electronic properties of molecules by changing their conformation or their environment.

Chapter five is devoted to another naturally occurring molecule of great importance, chlorophyll-a. The structural and electronic properties of chlorophyll-a are studied. In addition, the first multiple reversible single-molecule-switch is demonstrated. Tunneling electrons induced switches of the chlorophyll-a tail are achieved and quantitatively described. The underlying switching mechanism is explained from the statistical analyses and theoretical calculations, which reveal the switching as caused by rotation of parts of phytol tail induced by a single tunneling electron energy transfer to the molecule. Self-assembled layers are created and characterized with STM.

Finally, chapter six summarizes the research achievements of this thesis and discusses future research directions.

Chapter 2

Apparatus and experimental techniques

2.1 UHV-LT-STM system

A complete low temperature ultrahigh vacuum scanning tunneling microscope (LT-UHV-STM) system capable of atom and molecule manipulations (Fig. 2.2) was built in our laboratory during my first year of research.

STM employs the quantum mechanical principle of electron tunneling. Whenever a bias voltage is applied across an STM junction formed by a tip and a conductive sample separated by a few angstroms a tunneling current can be detected (Fig. 2.1). The tunneling current depends exponentially on the distance between the two electrodes, and is expressed by the following equation:

$$I \propto V \cdot \rho_s(0, E_F) \cdot e^{-1.025\sqrt{\Phi}W} \quad (2.1)$$

where V , ρ_s and Φ (eV) represent the bias voltage, the density of states of the sample and the work function, respectively [CHE93]. The distance between the tip and the sample is expressed by W (Å).

STM operation can be performed in two modes: constant height mode and constant current mode. In the constant height mode, the height between the tip and the sample is kept constant and the variation of the tunneling current due to surface structural changes is detected. In the constant current mode, the current is kept constant by means of a feedback loop and the height changes caused by the surface landscape are recorded.

Figure 2.1. Drawing that illustrates the STM junction; a tunneling voltage applied to a tip and a sample held in close proximity generates a tunneling current. Picture from [STM].

Working with individual atoms or molecules with an STM requires an atomically clean environment, therefore no contaminants should be present. Most experiments also require low temperature in order to freeze the diffusion of the studied particles.

2.1.1 UHV system

Our custom built ultrahigh vacuum system (UHV) consists of a main chamber and a load lock chamber. Both chambers are made of stainless steel. The main chamber is divided into two separate chambers by a built-in valve: the preparation chamber and the cryostat chamber. The preparation chamber is equipped with sample cleaning facilities, a sample storage-stage and a manipulator capable of cooling down the sample to liquid helium temperatures and heating up to $\sim 1200^{\circ}\text{C}$. The sample storage-stage can host up to 5 sample holders and one tip holder. Cleaning of the sample is performed by filling neon gas inside the chamber through a leak-valve and then a Ne ion beam generated by an ion bombardment gun is focused onto the sample. A liquid nitrogen trap is also located at the preparation chamber and it is used during the sample preparation procedure as a cryopump. The manipulator holds the sample during the preparation procedure and makes the transfer of the sample to the STM, which sits in the cryostat chamber. The cryostat chamber hosts the STM which is connected to the bottom of a liquid helium bath cryostat.

Figure 2.2. UHV-LT-STM system. Pictures of the main UHV chamber and the frame sitting on Newport vibration isolators taken during the construction are shown on the right. On the left there is a picture of the complete UHV-LT-STM system.

This UHV system uses five different types of pumps: rotary pump, turbomolecular pump, titanium sublimation pump, two ion pumps and a cold trap that acts as a cryopump. To pump from atmospheric to 10^{-3} torr pressure, the rotary pump is used for initial rough pumping of the system. The turbomolecular pump operation requires starting pressures of at least 10^{-2} torr. The rotary and turbomolecular pumps are located on the load lock chamber which when equipped with a transfer rod allows transferring the sample from UHV to atmosphere and vice-versa without breaking the UHV in the main chamber. Differential pumping is available for the manipulator also from the load-lock chamber. Both preparation and cryostat chambers are equipped with ion pumps that help getting a pressure lower than 2×10^{-10} torr provided that baking of the system took place. Baking of the system is required in order to get very low pressures. During the baking all the chambers are wrapped with electric heating tapes and temperature is set to 150°C for two days so that all the water present on the walls is removed. After the baking all the filaments are outgassed and pressure will drop below 10^{-10} torr as the system cools down.

The pressure monitoring is done using cold cathode gauges for high pressures and ion gauges for pressures below 10^{-5} torr.

Figure 2.3. Schematic illustration of the pressure ranges in which each type of pump can operate.

2.1.2 LT-STM

The STM scanner is a modified Besocke-beetle type [Fig.2.4]. It uses piezoelectric tubes scanners. Each piezoelectric tube has its cylindrical surface divided in 4 sections along the tube axis which are isolated from each other. Four piezoelectric tubes are used for our STM scanner, one for the fine 'z' translation that holds the tip and three others for x-y movement. The tip piezoelectric tube is glued to a disc that has 3 ramps. The disc sits on the sapphire balls located on top of the x-y piezotubes. All the movements are a result of the inverse piezoelectric effect; an applied voltage creates an elongation or bending of the piezoelectric material. For the lateral movement (x, y) all the piezotubes are bent in the same direction. Vertical movement (z) is achieved when all three piezotubes are forced to move tangentially creating a rotation of the disc. A finer displacement in the z direction is achieved by applying voltage to the inside section of the piezotube that holds the tip. The scanner is also equipped with two silicon diodes, one at the base of the scanner and the other at the cryostat base, used for temperature measurements.

Figure 2.4. Pictures of the scanner. The scanner is hanging at the bottom of the inner cryostat.

Isolation from mechanical vibrations is very important for a scanning tunneling microscope as the tunneling current is exponentially dependent on the distance between the sample and the tip. To address this matter few vibration isolation systems are implemented. First the scanner is hanging from stainless-steel springs which are attached to the base part of the cryostat. Second, the base plate of the scanner holds three magnets for eddy current damping. Third, the whole UHV system sits on four Newport vibrations isolators filled with pressurized dry air. All these systems provide a vibration-free environment for the scanner allowing for performing state of the art measurements such as vibrational spectroscopy and atom/molecule manipulations.

Besides isolation from the mechanical vibration the scanner is also isolated from thermal radiation by being surrounded by two concentric radiation shields kept at LN_2 and LHe temperatures. The radiation shields are connected to the bottom of the cryostat. The cryostat consists of two concentric cylinders separated by the UHV. The outer cylinder is filled with LN_2 while the inner one is filled with LHe. The STM scanner is cooled by making direct mechanical contact with the base of the inner radiation shield. The lowest sample temperature achieved without pumping the cryostat is 4.6 K. The

thermal drift is small at this temperature and hence, it is possible to perform an STM experiment for a long time at the same surface site.

Figure 2.5. Picture of the sample mounted on the sample holder shown on the left. A drawing of the sample is illustrated on the right.

The metallic samples used are 8 mm in diameter at the base and are mounted on a button heater with a tantalum cap. The button heater sits on a sample holder made of oxygen free copper. The sample wiring is done using tungsten wires. During the cleaning procedure the sample is heated to 600-700 K.

One of the operation modes of the STM mentioned earlier, the constant current mode, requires maintaining the tunneling current constant during imaging. To fulfill this requirement an electronic feedback loop is introduced. The feedback loop checks the tunneling current with a reference value and the difference is converted to voltage which is used to drive the z piezo up or down.

2.1.3 Tip preparation

For the STM tips we use electrochemically etched polycrystalline tungsten wires. Most of our experiments require a very stable and sharp STM-tip. The tip modification can be realized in a couple of ways. Using vertical manipulation, single atom/molecule can be transferred from the surface to the tip-apex, which leads to a sharper tip [EIG91, HAH01]. Another way to modify the tip is by a controlled tip crash into the substrate.

Atoms from the surface can be transferred to the tip in this way and local heating produced by the tip-crash can lead to re-shaping of the tip apex [HLA04, IAN06F]. A different treatment of the tip is required whenever spectroscopy is performed with STM. The differential conductance is proportional with the sample local density of states only for a constant density of states of the tip. This is the case when we have a blunt tip and it is achieved by applying high currents to the STM tip in the range of the field emission, normally greater than 4V bias [CHE93]. Vazquez de Praga et al. have proved both by calculations and experiment [VAS98] that a tungsten tip with a (111) bcc structure of the tip apex gives better reproducible spectra than a (111) fcc one. This is due to the fact that the (111) bcc tip has a constant density of states while the (111) fcc tip DOS present two sharp resonances close to its Fermi energy. Therefore new states appear in the sample spectrum whenever a (111) fcc tip apex is present. To avoid such inconsistencies in our spectroscopy measurements taken on molecules we have always tested the tip by measuring test spectra on the substrates before and after the data acquisition. Only those tips that have shown proper spectra on the substrate were used for further measurements.

2.1.4 Molecular source

For molecular deposition a homebuilt Knudsen cell is used. The crucible is made out of tantalum in order to stand high temperatures. The crucible is heated by thermionic emission from a tungsten filament. The filament is connected to a DC voltage source of 6 A maximum. The temperature is monitored by a chromel-alumel type thermocouple wire mounted on the crucible for direct temperature measurement (see drawing in Fig. 2.6).

Figure 2.6. Schematic drawing of the molecular deposition source (left) and of the setup used for the deposition (right). Drawing is not to scale.

2.2 STM manipulation and spectroscopy techniques

Our STM system is capable of manipulation of adsorbates (atoms or molecules) on surfaces at cryogenic temperatures. Besides manipulation STM can also operate as a spectroscopic instrument being able to determine the local electronic density of states as well as the vibrational states of an atom/molecule.

STM manipulation schemes can be used to assemble man-designed structures on surfaces on an atom-by-atom basis. An STM manipulation technique to relocate the atoms/molecules on a surface is known as “lateral manipulation” (LM). This was first tested in the relocation of Xe atoms on Ni(110) to write IBM [EIG90]. LM employs the tip-atom/molecule interactions (Fig. 2.7A) to move the atom/molecule across the surface. By adjusting the tip-adsorbate distance one can switch from an imaging condition (weaker interactions) to a manipulating condition (stronger interactions). An attractive interaction between the tip and the adsorbate can result in a “*pulling*” mode manipulation while a repulsive interaction causes the “*pushing*” mode [BAR97]. The recorded current and/or tip-height signals during manipulation are useful to determine the detailed movements of atom/molecule with respect to the surface [HLA03] and to identify the nature of tip-atom/molecule interactions [STI97].

Figure 2.7. STM lateral manipulation (A) and vertical manipulation (B) of an adsorbate on a substrate. Pictures from [HLA03B].

Another STM manipulation scheme, known as vertical manipulation (VM) (Fig.2.7 B) involves transferring of an atom/molecule between the surface and the tip [EIG91, HLA00]. Provided that the tip is parked above the adsorbate, VM can be realized by applying voltage pulses, or by making tip-molecule contact, or by exciting the molecule with tunneling electrons. This method can be used to functionalize the tip [EIG91, HAH01] or carry atom/molecules over obstacles such as steps on surfaces.

The STM-tip can also be used as a source of tunneling electrons. In this regime one can perform electronic, vibronic and rotational excitations as well as dissociation of chemical bonds [STI97, HLA00] and change in the conformation of a molecule [QIU04, IAN06A]. By injecting tunneling electrons from the tip to the molecule, energy can be transferred to the molecule. If the transferred energy exceeds the energy barrier associated with a specific process such as conformational changes or dissociation, then the process can occur in a controlled manner (Fig.2.8). The reverse process of dissociation is the bond formation. The excitation and/or local heating with tunneling electrons to closely located molecular fragments can result in forming bonds between them [HLA00]. A bond formation was also tested using VM technique to pick-up one molecule and drop it on top of another molecule, together forming a new complex [LEE99].

Figure 2.8. Illustration of bond breaking by tunneling electrons. Picture from [HLA03B].

All the techniques mentioned above represent ways to manipulate the adsorbates either by means of forces applied or tunneling electrons injected. Imaging and spectroscopy performed with STM are nondestructive ways to read information from the samples studied. Tunneling current in STM is determined by the overlap of the tip density of states (DOS) and that of the surface when a bias voltage is applied [CHE93].

$$I \propto \int_0^{eV} \rho_S(E_F - eV + \varepsilon) \rho_T(E_F + \varepsilon) d\varepsilon \quad (2.2)$$

Assuming that the STM tip has a constant DOS, an STM image represents a summation over all the sample electronic states that have their energy in the $(0, eV)$ interval. If the tip DOS is constant, the differential conductance (dI/dV) is proportional to the surface DOS.

$$\frac{dI}{dV} \propto \rho_S(E_F - eV) \quad (2.3)$$

Therefore a measurement of the dI/dV will provide the local DOS of the sample at the energy corresponding to the applied bias. When the tip scans over the surface a map of dI/dV spectra can also be generated. The dI/dV map represents the density of electrons at a particular energy (bias voltage) as a function of position on the surface. Unlike other spectroscopic methods such as photoemission, the STM is capable of determining both the occupied as well as unoccupied electronic states of a sample or an adsorbate. Occupied electronic states are probed when a negative bias voltage is applied to the sample. A positive applied bias will probe the unoccupied electronic states of the sample (Fig. 2.9).

Figure 2.9. Picturing the flow of the electrons for positive and negative biases applied to the STM junction.

In scanning tunneling spectroscopy (STS), dI/dV spectra are measured by interrupting the tip's feedback loop and adding a small AC modulation (4 mV to 20 mV) to the DC bias. The resulting AC component of the tunneling current is then detected by using a lock-in amplifier and recorded as a function of the DC component of the bias.

$$V = V_b + A \sin(2\pi ft) \quad (2.4)$$

$$I(V) = I(V_b) + \frac{dI}{dV}(V - V_b) + \frac{1}{2} \frac{d^2I}{dV^2}(V - V_b)^2 + \dots \quad (2.5)$$

Detection of the first harmonic by the lock-in amplifier will provide a spectrum of dI/dV versus V where as detection of the second harmonic will provide a spectrum of d^2I/dV^2 versus V . A dI/dV vs. V spectrum reveals the surface DOS from the area located under the tip as a function of energy.

Depending on their incident energy, the tunneling electrons may experience elastic as well as inelastic scattering events in their journey through the tunneling junction. The tunneling electron may interact with the molecule adsorbed on a surface causing vibrational excitations of the molecule. This is associated with the electron energy loss. This metal (STM tip)-vacuum-molecule-metal (surface) junction is very similar to the metal-insulator-X-metal tunnel diode used to perform Inelastic Electron Tunneling

Spectroscopy (IETS) [HIP93]. A simple diagram of this junction is illustrated in Fig. 2.10 where the left and right gray boxes represent the filled states of tip and surface, respectively. The LUMO (lowest unoccupied molecular orbital) and HOMO (the highest occupied molecular orbital) as well as some vibrational levels of the adsorbed molecule are indicated. At a particular bias ($V = h\nu/e$), an inelastic channel will open leading to a sudden increase in tunneling current, which is associated with a step in the $(dI/dV-V)$ spectrum and a peak in the (d^2I/dV^2-V) plot. Since the vibrational energy is the fingerprint of a molecule, the STM-IETS is a powerful method to identify the type of molecules and/or individual bonds [STI98, WAL00].

Figure 2.10. Energy diagram for the tunneling junction (left) together with I-V, dI/dV -V and d^2I/dV^2 -V curves in case of a vibrational channel opening

Chapter 3

Materials used: substrates and molecules

3.1 Substrates: Cu(111) and Au(111)

For our STM experiments, noble metal surfaces with (111) orientations are preferred due to their nearly-free-electron states. These electron states appear in the projected gap of the bulk bands due to the termination of the infinite crystal by the surface. Figure 3.1 show the $n = 0$ Shockley surface state dispersion obtained from calculation as well as experimental data [SMI85].

Figure 3.1. Dispersion for the $n = 1$ image state and $n = 0$ Shockley surface state near $\bar{\Gamma}$ on Cu(111). The cross-hatched area is the projection of the bulk band structure. The

dashed curves are the prediction of the theoretical model; the solid (open) circles represent the photoemission (inverse-photoemission) data. The figure is from [SMI85].

Reinert et al. [REI01] performed photoelectron spectroscopy study on these face-centered cubic (fcc) samples and determined the surface states for Cu(111) and Au(111) to be located at 435 meV and 484 meV, respectively, below the Fermi energy [REI01]. Figures 3.2a and 3.3a show the scanning tunneling spectroscopy (STS) measurements that we performed on these two surfaces with the onset of the surface state starting at -437 meV for the Cu(111) and at -480 meV for the Au(111) surface. These measurements agree well with the photoemission study. In the STM measurements the Fermi level is situated at zero bias voltage. Spectroscopic measurements of the substrates serve as test measurements for determining the quality of the tip in terms of its constant DOS.

Figure 3.2. Cu(111) substrate characteristics. (a) STS spectrum shows the surface state onset at -0.437 V, (b) atomic resolution STM image with the nearest neighbor distance of 2.54 Å, and (c) STM image showing the standing waves. Imaging parameters are 100 nA and 50 mV for (b) and 1 nA and 50 mV for (c).

Atomic resolution images taken with STM on Cu(111) and Au(111) surfaces are shown in the Fig. 3.2b and Fig. 3.3b. Both surfaces present a hexagonal close packed

structure with the nearest neighbor distance of $2.54 \text{ \AA}$ for Cu(111), and $2.89 \text{ \AA}$ for Au(111). The two dimensional electron sea that resides on these surfaces gives rise to Friedel oscillations around point defects on the surface [FRI58, HAS93, PET98], also known as standing waves (Fig 3.2c). The wavelength associated with these electronic waves is half of the Fermi wavelength. For Cu(111) surface the standing wave wavelength amounts to $15.3 \text{ \AA}$.

Termination of the infinite crystal by a cut along the [111] direction leaves the Au(111) surface in a reconstruction state, known as the herringbone reconstruction (Fig. 3.3c). Domain walls with lower coordination separate the regions with surface atoms in fcc and hcp positions [BAR90].

Figure 3.3. Au(111) substrate characteristics. (a) Surface state onset is situated at -0.480 V , (b) STM image showing atomic resolution with $2.89 \text{ \AA}$ nearest neighbor distance, and (c) STM image showing the Au(111) reconstructed surface. Bright stripes are domain walls separating the fcc/hcp regions. The turning points are known as elbows. Imaging parameters are 100 nA and 50 mV for (b) and 1 nA and 50 mV for (c).

3.2 Molecular systems used

Recently, molecular systems have been intensely studied due to their potential applications in electronic industry. Electronic circuits made of molecules are useful in the

scaling down process of devices to nanometer range. By means of molecular self-assembly, the molecular devices with specific functions, such as logic circuits [TOU03] or memory storage devices [LIU03] can be built.

In this dissertation we performed low temperature (LT) STM investigations of two porphyrin based molecular systems: metallo-tetraphenylporphyrins and chlorophyll-a. Porphyrin molecules can be found in plants and blood cells. They are involved in biological processes such as sunlight capture, oxygen transport, and charge storage. Their potential applications include molecular storage devices [LIU03] and Schottky barrier diodes [HAR96]. Porphyrins can also be used as charge transfer models [SET94] to study artificial photosynthesis processes.

Figure 3.4. Molecular systems studied. Chemical structure for Co-TBrPP (A), Cu-TBrPP (B), and chlorophyll-a (C).

Metallo-tetraphenylporphyrin such as 5, 10, 15, 20-Tetrakis-(4-bromophenyl)-porphyrin-Co (II) and -Cu (Co- and Cu-TBrPP) are adsorbed on Cu(111) substrate and studied by LT-STM/STS. For the chlorophyll-a molecule we have chosen an inert substrate, such as Au(111) and studied with the same low temperature techniques.

Our single molecule investigations are performed by following a number of systematic steps. The first step is the molecular recognition. The STM images of single molecules adsorbed on Cu or Au surfaces are used to determine the integrity, orientation and location of the molecules. An atomically resolved STM image of the surface would reveal the adsorption sites of the molecules.

The mechanical stability of the molecule is examined by using LM. The manipulation signals (tip-height and current signals) can reveal detailed molecular conformational changes that occurred during the molecule movement. For instance, it has been observed by F. Moresco et al. that for a large organic molecule, like Cu-TBPP, the conformational changes are accompanied by changes in electronic properties of the molecule behaving like a molecular switch [MOR01, DON01].

Molecular electronic spectra are acquired by STS on different parts of a molecule. STS spectra can provide the location of HOMO and LUMO states with respect to the surface Fermi level. The molecule images acquired at different biases can help us understand if all the orbitals are involved in the tunneling process or not [SAU97]. A further insight into the tunneling process through the molecule can be given by the energy-resolved dI/dV maps taken for each orbital energy.

Self-assembled layers of each of the molecular systems mentioned above are also formed and studied by STM/STS techniques.

Chapter 4

Kondo physics with organic molecules

4.1 Introduction

An anomalous increase in the resistance at low temperatures for metals that contain a small fraction of magnetic impurities is referred to as the Kondo effect [KON64]. The critical temperature below which the resistance starts increasing is known as the Kondo temperature and it depends on the nature of the metal and magnetic impurity. Since its discovery in 1930 and theoretical explanation in 1960, the Kondo effect has become an interesting matter subjected to many experimental and theoretical studies. Nowadays, after the invention of the scanning tunneling microscope, the Kondo effect can also be addressed at a single atom/molecule level.

Presence of a magnetic impurity in a nonmagnetic metal leads to interactions between the spin of the magnetic impurity and the conduction electrons of the surrounding nonmagnetic metal. A many-body ground state is formed at a temperature below the Kondo temperature, in which the magnetic spin of the impurity is screened by the conduction electrons. The transport properties of such systems are altered by the formation of a resonance at the Fermi energy in the density of states (DOS) of the impurity, named the Kondo resonance. The Kondo temperature depends on the hybridization of the atomic orbitals of the impurity with the electronic states of the host metal, therefore

$$T_K \approx De^{-\frac{1}{2\rho_F J}} \quad (4.1)$$

where D is the width of the substrate band, ρ_F is the substrate density of states at the Fermi level and J is the antiferromagnetic coupling of the impurity to the electron spins. J is expressed by the Schrieffer-Wolff transformation as

$$\frac{1}{J} = \frac{\pi\rho_F}{\Delta U} |\varepsilon_d| \bullet |\varepsilon_d + U| \quad (4.2)$$

where ε_d and Δ are the energy of the impurity level and its width acquired through hybridization, and U is the on-site coulomb repulsion.

Figure 4.1. Cartoon demonstration of the Kondo effect. The spins of the surrounding electrons are scattered by the magnetic impurity and the spin flip gives rise to a Kondo cloud which is shown by the pink circle. Result of this scattering is the appearance of a resonance at the Fermi energy, shown on the right.

Scanning tunneling microscope (STM) is a unique instrument to investigate the surface Kondo effect. STM can be used to determine the change in the local density of states (LDOS) of the sample that appears due to the presence of the magnetic impurities at temperatures well below the Kondo temperature. In the STM experiments, magnetic atoms/molecules are adsorbed on metallic samples and studied by measuring the differential conductance for a small energy window around the Fermi energy. Several

research groups have demonstrated using the STM that for these Kondo systems a narrow resonance-like structure, having a Fano line-shape [FAN61], is detected in the LDOS of the sample near Fermi energy [MAD98, LI98, MAN00, KNO02]. The Fano line-shape detected in the STM measurements is determined by interference of the two tunneling paths: tunneling into the conduction LDOS as well as tunneling into the impurity level. Fit of a Fano function to the measured differential spectra determines the width, the energy and the line-shape parameter of the resonance. The width of the resonance is proportional to the Kondo temperature of the system. The Kondo temperature is a direct measure of the coupling of the magnetic-impurity-spin to the surrounding electrons. Level repulsion between the impurity d-level and the Kondo resonance creates an energy shift of the resonance from the Fermi level [UJS00]. The shape of the resonance gives an insight into the tunneling process through the impurity.

Some of the Kondo systems studied with an STM are Co/Au(111) [MAD98], Ce/Ag(111) [LI98], Co/Cu(111), and Co/Cu(100) [MAN00, KNO02] and for each system the Kondo temperature was determined and proved to be a lot smaller than for the bulk absorption, as the coupling of the impurity to the conduction electrons is stronger in the bulk. With the latest advances in nanotechnology Kondo effect was also observed in quantum dots [GOL98, CRO98] and carbon nanotubes [JAR05].

Of great interest recently are the molecules that contain magnetic atoms adsorbed on metallic substrates, as ligand attachments to the magnetic atom can change its electronic distribution and therefore novel interaction mechanisms can arise in such systems [WAH05, ZHA05]. Following this novel research route we have studied single Coporphyrin molecules as well as self-assembled layers adsorbed on a Cu(111) substrate. The self-assembly will serve as an opportunity to study Kondo effect in a 2D molecular arrangement, determining in this way the effects of the molecular environment on the Kondo resonance.

4.2 Single molecule investigation

The Co-TBrPP [5, 10, 15, 20-Tetrakis-(4-bromophenyl)-porphyrin-Co (II)] molecules were purchased from Porphyrin Systems and used as supplied. The molecules

were dosed in-situ on a cleaned Cu(111) surface through thermal evaporation using a homebuilt Knudsen cell. Before deposition the molecules were outgassed by repeated heating/cooling cycles. The molecules were found to sublime at temperatures around 600 K. For deposition the substrate temperature was lowered to 100 K in order to prevent the dissociation of the C-Br bond. For a comparative study, Cu-TBrPP molecules were separately deposited on a cleaned Cu(111) surface following the same procedure.

4.2.1 Molecular recognition

The Co-TBrPP molecules are composed of four Br-phenyl complexes attached to a porphyrin unit that hosts a Co atom at its center. Molecules position on the copper substrate with their Br atoms adsorbed in the three-fold hollow sites of the (111) oriented surface [JON97]. On this substrate both, the Co-TBrPP and Cu-TBrPP, molecules are found adsorbed in two molecular conformations: saddle and planar (Fig. 4.2, see appendix for Cu-TBrPP images). These conformations were also present for other similar metallo-tetraphenylporphyrins that were studied in gas or liquid phase [JEN97, UNG99]. On Cu(111) substrate 25% of the molecules are found adsorbed in the saddle conformation.

Figure 4.2. Two STM images showing the two conformations adopted by Co-TBrPP molecule on the substrate. (a) Planar conformation (3.5 nm x 3.5 nm), 1 V, 0.4 nA. (b) Saddle conformation (4 nm x 4 nm), 1 V, 0.4 nA.

In the saddle conformation the center of the molecule, the porphyrin macrocycle, is distorted. Two pyrrole units of the porphyrin macrocycle are lifted leaving the molecules in a reduced symmetry state. In the STM images this conformation shows two central protrusions with a rectangular shape. On the other hand, in the planar conformation, the porphyrin center remains flat and parallel to the substrate. In this conformation the four Br-phenyl groups can interact strongly with the surface via π -interactions. The STM images of planar Co-TBrPP reveal a set of four lobes. In the STM images the molecule dimensions are $11 \text{ \AA} \times 18 \text{ \AA}$ for the saddle and $15.5 \text{ \AA} \times 15 \text{ \AA}$ for the planar conformations. The diagonal of the molecule is $\sim 22 \text{ \AA}$ for both conformations.

Figure 4.3. Drawings of the two molecular conformations together with the underlying surface. Blue and pink color balls represent the Br and C atoms, respectively. H atoms are not shown. The encircled regions of the molecules indicate areas that provide more tunneling current in the STM images. The length of the molecule along the diagonal is the same for both conformations.

4.2.2 Molecular switch

The distortion (saddling) of the molecule can be removed by applying a voltage pulse from the STM-tip. This voltage pulse supplies the necessary energy to switch the molecule from the saddle to the planar conformation. To switch the molecule, the STM-tip is positioned at a fixed height above the center of a saddled molecule and a fixed voltage pulse of +2.2 V is applied for a few seconds. The switching event is directly observed by monitoring the tunneling current; an abrupt change in the tunneling current corresponds to a change in the conformation of the molecules. The subsequent STM image confirms that the molecule switches into a planar conformation. The tunneling current signals recorded during the switching events mostly include two discrete steps, indicating that a two-step switching mechanism has been involved. By varying the duration of the applied voltage pulses these two steps can be individually observed. Injection of a short voltage pulse changes only half of the molecule while the other half remains in the saddle conformation. The molecule can then be conformed into the planar conformation by providing another voltage pulse. Figure 4.4 captures the switching steps.

Figure 4.4. Single molecule switch. (a) A three dimensional rendering of an STM image shows a Co-TBrPP molecule in a saddle conformation. (b)-(d) A sequence of STM images showing the two-step switching mechanism obtained by injection of voltage

pulses. The corresponding models for each step of the process are shown on the right side. Tunneling current versus time recorded during a switching event is shown on the left.

The molecules remain intact after switching. This is verified by laterally moving the molecule with the STM tip across the surface and/or by dissociating the bromine atoms from the four bromo-phenyl groups using higher voltages [HLA00]. A reverse switching [QIU04] from planar to saddle conformation requires voltage pulses higher than 3 V at this low temperature. Thus, it is difficult to achieve this in the current experimental framework as higher energy transfer can lead to the fragmentation of the molecules.

4.2.3 Mechanical stability

STM tip can be used in many ways to characterize a molecular system adsorbed on a substrate. Along with molecular recognition and conformational changes the tip can also be used to test the mechanical stability of a molecule by dragging it along the surface at different applied interactions. If the interaction between the tip and molecule is strong enough the molecule will follow the tip provided that it does not collapse under the applied force. A fine control of the interaction is given by the tunneling resistance of the STM junction. We have employed different tunneling resistances to test the mechanical stability of the molecule under the influence of the tip. As was reported earlier [NAZ03] a higher probability of successful manipulation is achieved when a functionalized tip is used. The presence of a molecule at the tip apex reduces the probability of adsorbing another molecule during manipulation. For manipulation of Co-TBrPP on Cu(111) surface a tunneling resistance of $\sim 2 \text{ M}\Omega$ and bias voltage of 50mV were used. All the molecules remain intact after the manipulation (Fig.4.6). Usage of smaller tunneling resistances, in particular $0.1 \text{ M}\Omega$, reduces the surviving probability to 20% during the lateral manipulation.

Figure 4.5. STM images before and after the molecules were manipulated on the surface along the red lines. Imaging parameters are 0.46 nA and 1 V, imaged area is 8 nm x 19 nm. Lateral excursion of the molecules is 6.5 nm and 2.5 nm, respectively. Manipulating parameters are 50 mV and 2 M Ω .

4.2.4 Electronic properties

Electronic properties in terms of occupied and unoccupied orbitals of the molecules can be determined by scanning tunneling spectroscopy, often referred to as orbital mediated tunneling spectroscopy (OMTS) [SCU01]. The first occupied orbital of Co-TBrPP in the planar conformations lies in OMT spectrum at 0.7 V below the Fermi level (Fig.4.6). This orbital corresponds to the ionization of the d_z^2 orbital of the Co atom [SCU01]. In case of the OMTS determined on Cu-TBrPP no orbital is present at 0.7 V below the Fermi level. This further verifies that the observed orbital in Co-TBrPP OMTS is due to the presence of Co atom. The two molecules studied differ only in the type of the center atom caged by the porphyrin ring. The absence of this orbital from the spectra corresponding to the saddle conformation of Co-TBrPP indicate less interaction between the d_z^2 orbital of the Co atom and the substrate electrons in this particular conformation. This can be explained by an increase in the distance that separates the Co atom and the substrate which effectively reduces the coupling of the Co d_z^2 orbital to the surface.

Figure 4.6. OMT spectra for Cu- and Co-TBrPP molecules. (a) and (c) are the spectra for the saddle conformations, (b) and (d) spectra correspond to the planar conformations.

The first unoccupied molecular orbital of the planar conformation of both Cu-TBrPP and Co-TBrPP molecules lies at ~ 0.75 V. Imaging of the molecules using 0.75 V bias voltage as well as dI/dV mapping suggests that this orbital is a contribution from the tetraphenyl-porphyrin cage of the molecule having little to do with the central atom. In the saddle conformation the distortion of the porphyrin macrocycle provides a different interaction of molecule with the substrate leading to the absence of these orbitals from the OMT spectra (fig. 4.6).

Figure 4.7 shows the spectra taken with the tip kept at a fixed height above the center of the molecule (blue line) and above one of the four lobes seen (red line) in the planar conformation. An increase in the dI/dV intensity of the LUMO over the lobe of the molecules is another indication of the origin of this orbital.

Figure 4.7. OMT spectra measured at the center and on top of a lobe of a molecule in the planar conformation. Both spectra are normalized to their minimum values. The spectrum taken on the lobe is vertically shifted by 0.4 for clarity of the picture.

The HOMO-LUMO gap for the planar Co-TBrPP molecules adsorbed on a Cu(111) substrate amounts to ~ 1.45 eV. The calculated energy gap for a free standing molecule that has hydrogen atom substituted for bromine is ~ 2.5 eV [LIA02]. Once the molecule is adsorbed on a metallic substrate charge transfer can occur between the substrate and the molecule and this can influence the location in energy of the HOMO or LUMO as was already proven for other molecules [LUX04]. This can stand as an explanation for the differences observed in the measured and calculated gap energies.

4.2.5 Kondo physics with single molecule

A sharp resonance or anti-resonance appearing near the Fermi level of the sample is the signature of the Kondo effect in the STM measurements taken on top of the magnetic atoms/molecules adsorbed on metallic substrates. Our molecule of interest, Co-TBrPP has a magnetic atom, Co, at its center. Differential conductance spectra were measured for both conformations by placing the tip at a fixed height above the center of the molecule and ramping the voltage between ± 60 meV. Test measurements were taken on

the substrate to check the condition of the tip, and also on the Cu-TBrPP molecule to verify that the signal detected is a contribution of the Co atom and not of the surrounding molecule.

Representative measured signals for both conformations are illustrated in figure 4.8. A ‘dip’ is present in both conformation of the Co-TBrPP molecule and absent in the Cu-TBrPP molecule. The experimental data is fitted using the following formula derived by Ujsaghy et al. [UJS00] that defines the correction of the LDOS due to the appearance of the Kondo resonance.

$$\delta_{\rho_R}(\omega) = \frac{[\text{Im} G_{R,\sigma}^{(0)}(\omega - i\delta)]^2}{\pi\rho_0} \times \left\{ \frac{2q_R\varepsilon + q_R^2 - 1}{\varepsilon^2 + 1} + C_R \right\}; \varepsilon = (\omega - \varepsilon_K)/T_K \quad (4.3)$$

where q_R , T_K , and ε_K represent the line-shape parameter, the Kondo temperature, and the energy shift of the Kondo resonance, respectively. The first part describes the scattering due to the Kondo resonance and gives a Fano line-shape in the tunneling density of states. The fit provided different Kondo temperatures for the two conformations, as the Kondo temperature is directly proportional to the width of the resonance.

Differential conductance measurements were repeated for a large number of molecules in both conformations and the resultant Kondo temperatures are 130 ± 15 K for the saddle and 170 ± 10 K for the planar conformation. The errors stated here represent the statistical deviation of the measured data (Fig.4.8).

Figure 4.8. Kondo signatures. (a) A differential conductance spectrum of the saddle Co-TBrPP molecules showing a dip (Kondo resonance) around the surface Fermi level (0V). The solid line represents the Fano line-shape fit to the data. The fit parameters are $q =$

0.29 ± 0.01 , $\varepsilon_K = 4.52 \pm 0.29$ mV. (b) The dI/dV spectrum taken on a planar molecule. The solid line represents the Fano line-shape fit to the data. The fit parameters are $q = 0.01 \pm 0.03$, $\varepsilon_K = 3.70 \pm 0.97$ mV. The dI/dV spectra of the saddle and planar Cu-TBrPP molecules do not reveal any features around the surface Fermi level, i.e. 0 V. The spectra for Co-TBrPP saddle, Co-TBrPP planar have been shifted vertically by 0.07 and 0.04, respectively.

In case of single Co atoms adsorbed on Cu(111) surface, the Kondo temperature is measured as ~ 53 K [MAN00, KNO02]. The observed high Kondo temperature in Co-TBrPP molecules is caused by an enhanced coupling of the magnetic impurity, caged by the porphyrin molecule, to the conduction electrons of the surface through the molecular bonding [WAH05, ZHA05]. The difference in the Kondo temperatures of the two conformations can be explained based on their electronic differences discussed before. In the saddle conformation there is less overlap between the Co d_z^2 orbital and the substrate electronic states, therefore a reduced coupling of the magnetic impurity to the substrate electrons. Both molecule conformations bind to the substrate via bromine atoms and hence, spin-electron coupling through molecular bonding is still permitted in the saddle conformation, which provides the observed Kondo temperature of 130 K.

4.3 Self-assembled structures of Co-TBrPP

For the experiment, a sub-monolayer coverage of molecules are deposited on a atomically clean Cu(111) surface held at ~ 120 K and ~ 90 K using a homebuilt Knudsen cell. At sub-monolayer coverage, areas of bare Cu surface exist and are used as a reference for the spectroscopic measurements. For a comparative study non-magnetic Cu-TBrPP molecules are separately deposited on Cu(111). Co-TBrPP molecules are self-assembled in three different arrangements on the Cu(111) substrate. Images of the Cu-TBrPP molecular assembly are shown in the appendix.

4.3.1 Layer arrangements

A. Ribbon like structures

Both molecules, Co- and Cu-TBrPP, self-assemble to form ribbon-like monolayer islands on Cu(111) with a preferential growth direction along a 7° deviation from the surface close-packed row, i.e. $[110]$ surface directions (Fig. 4.9). The length of these ribbons can reach 10 nm to over 100 nm long and their aspect ratio (length/width) is from 2 to 10. Inside the ribbon, the molecules have a planar conformation [IAN06A] with the porphyrin plane positioning parallel to the surface.

Figure 4.9. Co-TBrPP molecules adsorbed on Cu(111). STM image picturing a self-assembled ribbon together with clusters of molecules in planar and saddle conformations is shown on the left. A zoom of the yellow rectangle is shown on the right; drawing of the molecule is placed on top of the STM image for a better eye guidance. Image parameters $I = 0.4$ nA, $V = 1$ V. Inset showing how the molecules assembled on Cu(111) substrate.

B. Parallel and triangular arrangement

When the Co-TBrPP are deposited onto the Cu(111) at ~ 90 K, two novel self-assemblies can be formed in addition to the ribbon-like structure. In one structure, Co-TBrPP assemble in a parallel arrangement with the unit cell distances of 1.7 and 1.5 nm. The second structure is only partially ordered and the basic molecular unit is formed by a triangular arrangement of three molecules with 120° rotated to each other. The distance

between the molecules here is 1.7 nm. Based on the differences in lattice arrangements, these molecular clusters are useful as viable experimental platforms to test the spin networking effect on the Kondo resonance.

Figure 4.10. STM images illustrating two additional arrangements of Co-TBrPP molecules on the Cu(111) substrate. (a) Parallel arrangement with unit cell constants: $a = 1.7$ nm and $b = 1.5$ nm. (b) Triangular arrangement with a lattice constant of $a = 1.7$ nm. STM imaging parameters: 1 V, 0.4 nA, STM image sizes: 15 nm x 9 nm (a) and 17 nm x 10 nm (b). Drawings of the structures with respect to the underlying substrate orientation are shown on the right side of the figure.

4.3.2 Electronic properties

To check the electronic structure of the molecules inside the self-assembled layer, scanning tunneling spectra are taken at the center of a molecule inside the ribbon. The

spectrum of Co-TBrPP shows the HOMO-LUMO gap of 1.5 eV, and the first occupied orbital is located at 0.7 V below the Fermi level. Similar to the case of the isolated molecule, the origin of this orbital is assigned to the ionization of d_z^2 orbital of the Co atom, which is absent in case of Cu-TBrPP. The first unoccupied orbital lies at ~ 0.8 V above the Fermi level for the Co-TBrPP ribbons (Fig. 4.11). This orbital, similar to the single molecule case, is associated with the unoccupied orbital of the tetraphenylporphyrin cage.

Figure 4.11. OMT spectra of Co-TBrPP and Cu-TBrPP molecules assembled in the ribbons showing the occupied and unoccupied orbitals. The HOMO located at 0.7 V for Co-TBrPP is originated from the Co d_z^2 orbital. This orbital is absent in the spectra of Cu-TBrPP ribbon. Co-TBrPP spectrum is vertically displaced for clarity.

These orbital energies are close to the ones observed on isolated Co-TBrPP molecules. A small increase of 50 meV of the HOMO-LUMO gap for the molecules assembled in the layer is determined. In this case the LUMO is shifted away from the Fermi level by 50 mV, i.e the energy required to add one electron is higher, therefore a higher electron-electron Coulomb repulsion exist for the molecules in the layer as

compared to the isolated molecule case. Differential conductance spectra for the layer and the single molecule are illustrated in Fig. 4.12.

Figure 4.12. Electronic properties of the isolated Co-TBrPP molecules and the ones in the layer. A 50 mV shift of the LUMO is determined for the ones in the layer. Spectra are normalized to their minimal value and vertically shifted for clarity.

A further insight into the tunneling process through the molecules can be given by the energy-resolved dI/dV maps taken for each orbital energy. These maps reveal the spatial dependence of the differential conductance for a particular bias voltage. Figure 4.13 illustrates two of these maps taken at 0.75 V (b) and -0.75 V (d), visualizing the electronic density distribution of HOMO and LUMO, respectively [IAN06D]. The HOMO orbital is a contribution from the center part of the molecule, where the Co atom binds to the ligand. The LUMO is localized on the surrounding molecule i.e. the tetraphenyl-porphyrin cage. This is consistent with the conclusion that the first occupied orbital is due to the presence of the Co atom. The constant height images recorded at the same time with the maps are shown in figure 4.13 (a) and (c).

Figure 4.13. Energy resolved dI/dV maps of the Co-TBrPP ribbon. (a) Current image and (b) dI/dV map taken simultaneously at 0.75 V, 0.3 nA with an open feedback loop. Red circles are drawn on top of the image to highlight the maxima. (c) Current image and (d) dI/dV map taken simultaneously at - 0.75 V, 0.3 nA with an open feedback loop. Pink ellipse indicates the location of the maxima. All images are 3.75 nm x 3.75 nm. Drawings of the molecules expressing the location of the maxima seen in the maps are presented on the left side of the figure.

4.3.3 Kondo physics in a 2D arrangement

The differential conductance (dI/dV) tunneling spectra are acquired on both Co-TBrPP and Cu-TBrPP ribbons at 4.6 K by positioning the STM tip above the center of a molecule inside the ribbon. Like in the case of isolated molecules, the resultant dI/dV spectra of Co-TBrPP consistently reveal a resonance located around the substrate Fermi level, while that of Cu-TBrPP show no apparent features (Fig. 4.14). Since the Co-TBrPP includes a spin-active cobalt atom, we attribute the observed resonance as caused by the Kondo effect. The dI/dV measurements were repeated with different tips on a large number of molecules inside the layer for consistency. The Kondo temperature was

determined to be 105 ± 10 K for the molecules in the ribbon [IAN06B]. The error stated here represents the statistical deviation of the measured data.

Figure 4.14. A differential conductance spectrum of a Co-TBrPP molecule inside the ribbon shows a dip (Kondo resonance) while that of Cu-TBrPP does not show any resonance around surface Fermi level (0V). The red solid line represents the Fano line-shape fit to the data. The fit parameters are $q = 0.38 \pm 0.01$ and $\varepsilon_K = 7.11 \pm 0.12$ mV

In case of isolated planar Co-TBrPP on Cu(111), the Kondo temperature is measured as 170 ± 10 K [IAN06A]. This value is $\sim 38\%$ higher than the value obtained for the layer. To understand the cause of the lower Kondo temperature in the two-dimensional molecular layer, we first investigate the influence of spin network on the Kondo effect. The Kondo signatures of the parallel and triangular structures are determined by using the same procedure as above by positioning the STM-tip at the center of a molecule inside the clusters. The observed Kondo temperatures, 111 ± 21 K for the triangular arrangement and 108 ± 12 K for the parallel arrangement, respectively, are close to that of the ribbon within the error bar (Fig.4.15). This indicates that the effects of spin network and hybridization inside the molecular layer to the Kondo effect are negligible in these molecular assemblies.

Figure 4.15. Kondo signatures obtained from the two other layer arrangements. The solid red lines represent the Fano line-shape fit to the experimental data. The fitting parameters are: $q = 0.06 \pm 0.01$ and $\varepsilon_K = 5.8 \pm 0.4$ mV for (a), the triangular arrangement, and $q = -0.16 \pm 0.01$ and $\varepsilon_K = -0.4 \pm 0.2$ mV for (b), the parallel arrangement.

To better characterize the change in the Kondo temperature from the isolated molecule to the layer we have measured the differential conductance for a molecule having different number of nearest-neighbors (nn). By using STM lateral manipulation technique a small cluster of molecules, 7 molecules arranged in a hexagon, was separated from the ribbon (Fig.4.16b). The dI/dV spectra are measured at the center of the middle molecule. The molecules from the cluster were removed one by one after new spectra were recorded (Fig.4.17). The recorded spectra for different number of nearest neighbors are illustrated in figure 4.18.

Figure 4.16. The molecules from the ribbon (a) are removed by using STM LM to create a hexagonal cell (circled) (b). Imaging parameters: 28 nm x 50 nm, 1 V, 0.2 nA.

Figure 4.17. A sequence of STM images with different number of nearest neighbors created by removing one-molecule-at-a-time with the STM-tip. The pink dots indicate the tip position during the recording of the dI/dV spectra.

Figure 4.18. Kondo resonances for different number of nearest neighbors. All the spectra are taken at the center of the molecule, positions indicated by the pink dots in Fig.4.17. The filled circles represent the experimental data and the red solid lines represent the Fano line-shape fits to the data.

The smaller Kondo temperature obtained for the layer is supported by the decreasing trend that appears when measuring the Kondo temperature for a molecule having 0nn (isolated molecule), 1nn, and so on till 6nn (Fig. 4.19). The Kondo temperatures together

with the line-shape parameter and the energy shift of the Kondo resonance for the different ‘nn’ are given in table 1.

From the STS spectra no additional hybridization was observed for the molecules in the layer. The remaining parameters that may vary in the two cases discussed, the isolated molecules and the layers, are the electronic density of the substrate under the layer and a small shift in the LUMO away from the Fermi level.

Figure 4.19. The plot of Kondo temperatures vs. the number of nearest neighbors

Table 1. Fitting parameters obtained for different nearest-neighbor Kondo resonances.

Number of nearest-neighbors	T_K (K)	q	ϵ_K (mV)
6	105 ± 10	0.38	7.17
5	116 ± 11	0.01	4.52
4	130 ± 13	0.01	6.38
3	132 ± 26	0.04	0.84
2	157 ± 15	0.15	14.85
1	159 ± 19	0.12	6.82
0	170 ± 10	0.01	3.70

Many studies were carried out, both experimental and theoretical, to determine the contribution of the surface versus bulk states in the Kondo effect [LIM04, LIN05, BARR04]. It was determined that the bulk states have a bigger contribution than the surface states, for example Co atom d_z^2 orbital hybridize more with the bulk states than the surface states [BARR04]. Cu(111) surface has a surface state that lies at 0.45eV below the Fermi level therefore the Kondo resonance on Cu(111) is assumed to be originated from the spin-electron interactions involving both surface and bulk electronic states [MER04, LIN05]. In their calculated result, Barral et al. [BARR04] have predicted that the Shockley surface state in Cu(111) is quenched if a two dimensional network of adatoms are formed. If this were true, quenching of surface state would decrease the spin-electron coupling strength, and consequently, it would reduce the associated Kondo temperature. This is in agreement with our experimental observations of a reduced Kondo temperature for the self-assembled ribbons.

Distance dependent spectra

STM/STS has the advantage that it can probe spatially the electronic distribution of the molecules. This can be done by recording either differential spectra at different locations or energy-resolved spatial density maps. For the single magnetic impurity on a metallic substrate the Kondo resonance could be observed up to 10 Å away from the magnetic atom. [LI98, MAN00]. This defined the Kondo cloud to be ~ 10 Å in radius for a single magnetic impurity. To determine the spatial distribution of the Kondo resonance in the layer we have measured differential tunneling spectra for different distances away from the center of one molecule. Figure 4.20 illustrates the STM images together with corresponding dI/dV spectra taken at the locations indicated by the colored dots. The corresponding fitting parameters are given in the table 2 and 3. The spectra taken at locations away from the center of the molecule reflect a more complicated picture as they can be contributed by both the substrate and the molecule. A thorough investigation of this matter is going to be addressed in the near future.

Energy-resolved spatial density maps were proven to be a novel method to visualize the location of the spin centers in a Kondo complex [WAH05]. Addressing the same

matter we have recorded Kondo spatial maps for the Co-TBrPP ribbons at 5 mV. This voltage is very close to the Fermi energy level, which is situated at 0V in the STM experiments and it also lies within the Kondo resonance width. Figure 4.21 illustrates the topographies taken at 1 V and the dI/dV maps at 5 mV. The spatial maps reflect the parts of the molecule that provide most of the signal at 5 mV. Along with the center of the molecule, where the Co atom is located, the rest of the molecule also provides some signal. This agrees with the previous conclusions that the interaction between the magnetic spin and the substrate electrons occurs through two paths: a direct one between the Co d_z^2 orbital and the substrate electrons, and an indirect one that occurs through the molecular bonding to the substrate.

Figure 4.20. Distance dependent spectra taken for the layer. The spectra on the left are taken at the dots specified in the STM images on the right. Imaging parameters 0.4 nA, 1 V, image size: 4 nm x 3 nm. The spectra are taken with open feedback loop and by applying a 4 mV and 700 Hz modulation to the bias.

Table 2. Fitting parameters determined for the distance dependent spectra shown in Fig.4.21a.

Spectra #	$T_K(K)$	q	$\varepsilon_K(mV)$
1	110 ± 3	0.3 ± 0.01	2.66 ± 0.21
2	131 ± 4	0.25 ± 0.01	2.85 ± 0.20
3	200 ± 12	0.26 ± 0.02	5.62 ± 0.52
4	131 ± 4	0.38 ± 0.01	6.07 ± 0.20
5	158 ± 8	0.57 ± 0.02	7.91 ± 0.34
6	128 ± 8	0.65 ± 0.04	6.7 ± 0.47
7	113 ± 5	0.35 ± 0.01	5.29 ± 0.26
8	110 ± 5	0.37 ± 0.01	2.5 ± 0.29

Table 3. Fitting parameters determined for the distance dependent spectra shown in Fig.4.21c.

Spectra #	$T_K(K)$	q	$\varepsilon_K(mV)$
1	100 ± 2	0.32 ± 0.01	3.75 ± 0.25
2	97 ± 2	0.23 ± 0.01	2.66 ± 0.14
3	137 ± 3	0.37 ± 0.01	2.28 ± 0.17
4	107 ± 2	0.40 ± 0.02	2.68 ± 0.29
5	105 ± 4	0.41 ± 0.01	6.06 ± 0.23
6	100 ± 2	0.37 ± 0.01	5.90 ± 0.16
7	109 ± 3	0.42 ± 0.01	6.35 ± 0.21
8	92 ± 5	0.31 ± 0.01	4.14 ± 0.22

Figure 4.21. Energy resolved maps together with topographs of the layer. (a) and (c) are STM topographs taken at 0.4 nA and 1 V , (b) and (d) are energy-resolved maps of the area shown in the topographs. The maps are taken at 5 mV, close to Fermi energy (0 V), with an open feedback loop. The scanned areas are 4.8 nm x 7.5 nm for (a) and (b) and 2.8 nm x 2.8 nm for (c) and (d).

4.4 Discussions

Co-TBrPP molecules were adsorbed on Cu(111) and studied at low temperature in two configurations, isolated molecules and self-assembled structures. Isolated molecules having two conformations were tested for their electronic properties and using tunneling electrons the conformation of the molecule was changed. Not only the electronic states were different for the two conformations but also the Kondo temperature was proven to vary with the change in conformation.

Self-assembled structures were created and depending on the substrate temperature three different arrangements were found. These molecular domains are useful as experimental platforms to test the spin networking effect on the Kondo resonance. No effect of the lattice arrangement on the Kondo resonance was found in this case. The proximity of other molecules was determined to be important as the Kondo temperature was determined to be smaller for the molecules inside the self-assembled structures.

In conclusion the Kondo resonance of the Co-TBrPP/Cu(111) system can be manipulated by two means: by using tunneling electrons, changes in the molecular conformation of the molecule can be induced that were proven to have different electronic properties, and therefore different Kondo temperatures. Another way of manipulating the Kondo temperature is by changing the environment of each molecule by adding more neighbors, in this way a smaller Kondo temperature was obtained. Fine tuning of the Kondo temperature may be useful in designing novel electronic device functions.

Chapter 5

Chlorophyll-a switch and its self-assembled layers

5.1 Introduction

Photosynthesis is one of the most important processes that fuels life on earth. Without photosynthesis the oxygen in the atmosphere will be depleted within several thousand years. A mystery for many years, photosynthesis was deciphered in 1770's and all its magic stands in the function of photosynthetic organisms such as plants, algae and photosynthetic bacteria that use sunlight energy, water and CO₂ to produce oxygen and sugar.

The capture of sunlight energy and conversion to chemical energy is associated with the action of the green pigment chlorophyll. The function of the chlorophyll was identified not earlier than 1913 by Dr. Richard Willstatter [WIL28]. Among all chlorophylls, chlorophyll-a is the most abundant in the photosynthesis complexes. Chlorophyll-a is found in both the antenna complexes, the ones that harvest the sunlight, as well as in the reaction centers, where the primary electron transfer takes place. Chlorophyll-a absorbs all the wavelengths of the visible light except the ones associated with the green light. Additional pigments found in the photosynthetic complexes, such as chlorophyll-b and betacarotene, absorb the energy that is not absorbed by chlorophyll-a. When light is absorbed by a pigment, the captured energy can be dissipated as heat,

emitted by means of fluorescence or can be converted into chemical energy as in the case of photosynthesis. In the reaction centers a pair of chlorophyll molecules is believed to exist, which upon absorption of a photon generates an electron. Here the first electron transfer takes place. This pair is called P680 because of the wavelength that it can absorb.

Figure 5.1. Illustration of the antenna complex along with the reaction center found in the photosynthesis complex. Picture from [PHO].

Chlorophyll-a consists of a porphyrin ring and a phytol chain. The porphyrin is a stable ring-shaped molecule around which the electrons move freely. This highly delocalized system allows easy capture and release of electrons, therefore has a great potential to provide energized electrons to other molecules. The phytol chain, a hydrophobic complex, facilitates the binding of the chlorophyll to the lipid membrane.

Because of their multiple implications in the photosynthesis process as well as their non-toxic nature and abundance, chlorophyll-a molecules have been intensely investigated lately for their electronic and transport properties. Recently, a bio-solar cell exceeding 12% efficiency has been developed using photosynthetic reaction centers with chlorophyll-a as a part of the ingredients [DAS04]. Molecular layers of

ferredoxin/chlorophyll-a heterostructures proved to have rectifying properties and photoinduced current flow was detected for this heterostructure under illumination [NAM04]. These achievements open up further exciting opportunities to generate “green” energy using naturally occurring plant molecules. Even though there have been many studies carried out on chlorophyll-a, a study at the single molecular level is yet missing. It is therefore desirable to investigate single molecules of chlorophyll-a for both fundamental understanding of biological processes and technological applications.

5.2 Single molecule switch

The chlorophyll-a molecules ($C_{55}H_{72}MgN_4O_5$) were purchased from Sigma Aldrich and used as supplied. The molecules were dosed in-situ on a UHV cleaned Au(111) surface through thermal evaporation using a homebuilt Knudsen cell. Au(111) was chosen as the substrate due to its relative inertness as compared to other fcc surfaces such as Ag(111) and Cu(111). Before deposition the molecules were outgassed by repeated heating/cooling cycles. The molecules were found to sublime at temperatures around 420K. A sub-monolayer coverage of chlorophyll-a/Au(111) was obtained presenting both regions of single molecules as well as self-assembled islands. At sub-monolayer coverage, areas of bare Au surface exist and are used as a reference for the spectroscopic measurements. The measurements were taken at 4.6 K. For comparison molecules were also dosed on a Cu(111) substrate following the same procedure.

5.2.1 Molecular recognition

Chlorophyll-a consists of two main components: a porphyrin unit as the head and a long carbon chain as the tail. Figure 5.2 shows an STM image of a chlorophyll-a molecule adsorbed on the Au(111) surface together with the chemical structure of the molecule. In the STM image the molecules resemble the chemical structure showing a head and a tail formed of 3 lobes. The measured 2.7 ± 0.2 nm length of molecule is in agreement with the calculated value of 3 nm [ARG4.1].

Figure 5.2. STM topography of a single chlorophyll-a molecule adsorbed on Au(111) substrate and the chemical structure shown on the right. Imaging parameters are 0.1 nA and 1 V. Imaging size is 3.5 nm x 3.5 nm.

5.2.2 Mechanical stability

A. Chlorophyll-a on Au(111)

Mechanical stability of chlorophyll-a is tested by using lateral manipulation technique. Using the STM tip, molecules are displaced on the surface and information about the interaction between the molecules and the substrate can be extracted. For chlorophyll-a this is done by placing the tip at a fixed distance above the molecule tail (head), lowering the tunneling resistance from the imaging value of $\sim 2\text{ G}\Omega$ to $33\text{ M}\Omega$ ($14\text{ M}\Omega$) and moving the tip along a predefined path. The molecules then follow the tip in discrete steps (Fig. 5.3a, b).

When separated from the islands, most of the molecules move in pairs suggesting a stronger interaction between each other than with the substrate (Fig 5.3c, d). This conclusion also implies that self-assembled layers can be easily created on Au(111). The individual chlorophyll-a from the pair can be separated if it is manipulated along the direction perpendicular to the long molecular-axis. This is suggestive of the absence of a chemical bond between them. After manipulation all the molecules are intact on the surface, however whenever smaller tunneling resistance (stronger force) was used the molecules jumped on the tip.

Figure 5.3. Lateral manipulation of chlorophyll-a. (a) and (b) STM images before and after a single molecule was displaced on the surface. The white fragment encircled here serves as a landmark. Yellow lines represent the tip path during the manipulation. (c) and (d) are STM images showing the separation of a chlorophyll-a pair from a cluster using lateral manipulation. Imaging parameters are 0.14 nA and 0.3 V. Manipulation parameters are 33 M Ω , 100 mV.

During the lateral manipulation scheme the tip height versus the lateral distance is recorded. This information is useful in characterizing the tip-molecule interaction, the diffusion barriers and the dynamic of the molecule trapped under the tip during the lateral movement. When laterally manipulated the molecules move in discrete jumps providing signals similar with the atom responses in the pulling regime [HLA03]. The multiple degrees of freedom of chlorophyll generate a more complicated pattern as can be seen in the figure 5.4. Large molecules can spend the gained energy also in internal processes before overcoming the diffusion barrier, therefore they can change conformation or reorient with respect to the substrate [GIM99, BAR04]. This will lead to new features in the tip height signal, besides the nicely described “sawtooths” pattern well known as translation fingerprints [BAR97, HLA03].

Figure 5.4. Tip-height versus the lateral distance recorded during the lateral manipulation of the molecules from figure 5.3 a.

B. Chlorophyll-a on Cu(111)

Lateral manipulation of chlorophyll-a was also performed on Cu(111) substrate. In the STM images the molecules look similar to the ones adsorbed on Au(111), however they are more bound to Cu(111) (Fig.5.5). This is proven by lateral manipulation as well as imaging. In order to displace them on the substrate the tunneling resistance was set to 50 k Ω and the bias voltage to 50 mV. The tunneling resistance used is here is $\sim 10^3$ smaller than in the case of manipulating chlorophyll on gold. This suggests that a stronger force between the tip and the substrate had to be applied in order to move them on the surface. Even though a stronger force was used the molecules remain intact after manipulation.

Figure 5.5. STM lateral manipulation of chlorophyll on Cu(111) substrate. (a) STM image of two molecules together with some CO contaminants. (b) STM image of the two molecules from (a) after one of them was laterally displaced along the yellow arrow from

(a). Imaging parameters are 50 nA and 0.7 V. Imaged area is 16 nm x 10 nm. Manipulation parameters are 50 k Ω , 50 mV.

5.2.3 Molecular switch

On the Au(111) substrate many different conformations of the isolated chlorophyll-a were observed. We branch them in two main categories: conformations that involved changing of the orientation of the tail with respect to the head of chlorophyll, named here type I, type II, and type III, and conformations that involve only changes in the conformation of the tail. The latter are four for each type of the conformation and here they are referred to as 1, 2, 3, 4. Thus, in all we discuss 12 conformations. Among all the molecules, 64% of them were found in the conformation 1, 24% in the conformation 2, 10% in conformation 3 and the rest, $\sim 2\%$, were found in conformation 4.

Figure 5.6. STM images of different conformations of chlorophyll-a adsorbed on Au(111) substrate. Images are taken with 0.1 nA and 0.3 V, imaged areas are all 4.5 nm x 3 nm.

Voltage pulses injected from the tip into the molecule can switch the molecule into any of these conformations. Figure 5.7 illustrates the switching between type III and type I as well as type II to type III. In all cases the head of the molecule remains in the same place while the tail orients at different angles.

Figure 5.7. Conformational changes. (a) and (b) 2.5 nm x 5.6 nm, (c) and (d) 3.5 nm x 5.5 nm, (e) and (f) 3 nm x 4.5 nm.

In this research, we are interested in switching the conformation of the tail which can be implemented as a molecular switch in nanoscale devices. We have achieved controlled switching of all these conformations using inelastic electron tunneling (IET) scheme [GAD95, STI97] with the STM-tip [IAN06C]. To induce the conformational changes, the STM-tip is parked at fixed height above the tail's end and tunneling electrons are injected into the molecule. For all switching trials a fixed voltage pulse of 1.5 V is used, i.e. injected electrons have a kinetic energy of 1.5 eV. During each switching event the tunneling current is recorded as a function of time. The abrupt changes in the tunneling current correspond to changes in the conformation of the molecules, and determine the switching time. I-V spectroscopy taken on the molecule determines the energy barrier for this process, which amounts to 0.8 V in this case (Fig.5.8a). If the duration of the process is increased the molecule can repeatedly switch between two states creating a toggle-like

switch. In this case, the current oscillates between two discrete values corresponding to the two states (Fig.5.8c).

Figure 5.8. Tunneling current characteristics determined during the switching process. (a) I/V spectroscopy measured on top of the molecule showing the threshold voltage needed to trigger the conformation change. (b) The current trace obtained during a 1.5 V pulse showing the moment when the conformation of the tail changed. (c) The current trace determined for longer voltage pulse duration.

During an IET process, the tunneling electrons transfer energy to the atom or molecule via a resonant state [HLA05, QIU04, GAD95, REP04]. By varying the tunneling current, the number of tunneling electrons passing through the molecule varies. The probability of energy transfer also changes accordingly [GAD95]. The IET induced switching have been repeated by varying the tunneling current between 0.2 nA and 2 nA at a fixed 1.5 V pulse. For each current, over 100 switchings have been performed to get enough statistical data for analysis. The switching frequency can be adjusted by varying the tunneling current. An increase or decrease in current causes faster or slower switching rate, respectively. A binned distribution of the switching times for a particular current determines the time constant. The switching rates are determined from the inverse of the time constants. The switching rate “R” and tunneling current “I” are related by

$$R \propto I^N$$

where “N” is the number of inelastic tunneling electrons involved in the energy transfer process [HLA05, STI97, PAS03]. A logarithmic plot of the rate versus the current determines the number of electrons involved in the process.

Besides being a source of tunneling electrons, the tip can also have some other influence on the process. Electric field effect is considered very small or inexistent because of the low currents used, which means the tip-molecule vertical distance is relatively large. For the highest current used, 2 nA at 0.3 V bias, a tunneling resistance of 150 M Ω corresponds to ~ 3.5 Å distance between the tip and the molecule [HLA03]. This sets the highest electric field to be 0.4 V/Å. Furthermore, the switching can be done at both positive and negative polarities. This verifies that the process is relatively independent of the electric field. It is also known that the presence of the tip can modify the surface potential creating a lower potential region underneath [STR91, KUR99, DES] (Fig.5.9b). This effect can be considered for some conformations in which the tip position is closer to a specific conformation rather than other. The type II and III conformation provides this situation for the particular switching between the conformation 2 to 1 and 2 to 3. For the type II conformation 2 the tip is closer to conformation 1 than 3 where as for the type III conformation 2 the tip is closer to 3 than to 1 (Fig.5.9a).

Figure 5.9. (a) STM images of the conformation 2 of type I, type II, and type III molecules. The yellow (pink) drawings on top of the STM images express the conformation 1 (3). The dots show the position of the tip during the injection of the electrons. In type II (III) molecule the tip is situated closer to conformation 1 (3). (b) Schematic drawing showing how the presence of the tip influences the surface potential.

(c) Current signal obtained for type II molecule, conformation 2, when the tip oscillates between the conformation 1 and conformation 3.

The small influence of the tip can be reflected in the determined yields, defined as Re/I (events/electron), for the switching described above. The yields amount to 6.5×10^{-10} for $2 \rightarrow 1$ switching of type II, and 3×10^{-10} for $2 \rightarrow 1$ switching of type III, with higher yields for the case in which the tip is closer to the final position of the tail. For the type III, transformation $2 \rightarrow 3$ has a yield of 5.5×10^{-10} as compared to 3×10^{-10} for $2 \rightarrow 1$ switching.

Tip influence is minimum in the case of type I molecules when the tip position is symmetric between both 2 and 3 positions. From now on, our focus will be this type I molecule and in particular the quantitative description of the switching mechanism used to change the conformation of the tail (Fig.5.10).

Figure 5.10. Chlorophyll-a type I conformations. Imaging parameters are 0.1 nA and 1 V. Imaged area is 2.5 nm x 3 nm.

The binned distribution of the switching times for a fixed current of 0.6 nA is illustrated in Fig.5.11a. The time constant of this exponential decay has been determined as 0.87 ± 0.06 s. For each current the rate is determined as the inverse of the time constant. Figure 5.11b illustrates the switching rate dependence on the tunneling current. Here, each data point is determined by plotting a curve like Fig. 5.11a. From the slope of this curve, N is determined as ≈ 1 for current smaller than 1 nA. Therefore, the energy transfer of a single tunneling electron to the molecule causes such conformation change. At currents higher than 1 nA the rate for the switching process is reduced suggesting the participation of the tunnelling electrons in other processes also. Similar IET procedure

can also be used to induce the switching between the tail conformations 2 and 3, and 3 and 4. A voltage pulse of 1.5 V is used for all data sets. To ensure enough statistical data, we have performed over 1200 IET induced switching processes at different currents for the four structures described in Fig.5.10. From the switching rate and current relationship, the number of tunneling electrons involved in other tail conformational changes is determined. A single tunneling electron energy transfer causes the observed conformational changes in all these events.

Figure 5.11. (a) Binned distribution of the switching times for 0.6 nA current. (b) Switching rate versus the tunneling current.

Whenever the tip is positioned on top of a conformation 2 molecule, the injecting electron can lead to either conformation 1 or 3. These concurrent transformations were in particular investigated for their rates and yields. Figure 5.12 provides the rate and yield plots for 2-1 and 2-3 switching events. Both transformations are triggered by the same number of inelastic electrons however the yields are slightly different. Here, the yield “y” is related to the switching rate “R” and current “I” as, “ $y = Re/I$ ”, where “e” is the electronic charge. The determined yields are 3.2×10^{-10} and 1.5×10^{-10} for switching from 2 to 3, and 2 to 1, respectively. Almost zero slopes of the yield plots verify again the single electron energy transfer process; here the yield follows $Y \propto I^{N-1}$ [PAS03]. The measured yields for 3→2 and 3→4 switching events are 3.8×10^{-10} and 3.3×10^{-10} , respectively.

Figure 5.12. Switching rates and yields versus the tunneling current for type I molecule. The transformations considered are the 2 to 1 and 2 to 3. Unitary slopes (a) are determined for both processes suggesting only one electron involved in the process, however the yields are different making the 2 to 3 switching favourable.

To understand the structural changes during switching, we have performed geometrically relaxed calculations of chlorophyll-a using quantum chemical PM3 method [ARG4.1]. The calculations were carried out for a free-standing molecule and a rich variety of conformations of the chlorophyll-a tail were proven to be possible. Experimental results showed that the adsorption on the surface limit these conformations to four. Therefore only the four conformations that resembled the ones in the STM images are discussed next. The calculations reveal that the three bent molecular conformations are caused by rotations of parts of the phytol chain. Figure 5.13 illustrates all four calculated structures of phytol chain corresponding to the four conformations obtained by switching. The 1-2 switching involves bending of phytol chain at C12 joint. This is caused by rotation of $\sigma_{C11-C12}$ bond, which effectively rotates the last part of the phytol chain, from C12 to C15, into a counter clockwise direction. This results in 60° bending of the phytol. Switching from conformation 2 to 3 is due to bending of the phytol at C8 joint. This could be achieved by rotating σ_{C7-C8} bond, which rotates a part of the phytol chain from C8 to C15 into a counter clockwise direction. A clockwise rotation of the end part of phytol at C13 in conformation 3 changes to the conformation 4. Since the phytol chain is lifted up from the surface by the support of CH_3 groups, such chain

rotations can easily take place. These calculations have determined the rotation sites to be different for each transformation suggesting that a controlled switching can be achieved by addressing the particular bond involved in each transformation.

Figure 5.13. Calculated structures of chlorophyll corresponding to the conformations 1, 2, 3, and 4 seen in figure 5.10. Arrows show the rotation site as well as the direction of the rotation.

5.3 Self-assembled molecular structures

Self-assembled layers of chlorophyll were intensively studied through different methods due to their potential role in explaining the packing of the chlorophylls in the photosynthetic membrane [BEN03, ROS03, BAH04]. Boussaad et al. [BOU97] have studied Langmuir-Blodgett films created at air/water interface and placed on a graphite substrate and reported the formation of the chlorophyll-a dimer through the Mg-O bonding of two closely located chlorophylls. This was proposed as a suitable model for the chlorophyll dimer P680 of the reaction center, the primary electron donor.

We have formed self-assembled layers of chlorophyll deposited from vapor on Au(111) and studied them at low temperature (4.6K) and in ultrahigh vacuum environment, methods not yet employed for the study of the chlorophyll-a self-assembly [IAN06E].

5.3.1 Structural characterization

On Au(111) substrate the molecules nucleate at the low coordination sites, i.e. the elbows and domain walls of the reconstructed surface. At submonolayer coverage on the surface they can be found as isolated molecules as well as ordered domains reaching sizes of hundreds of nanometers (Fig. 5.14).

Figure 5.14. STM images of chlorophyll-a adsorbed on Au(111). Single molecules as well as self-assembled domains are present. Domains with different orientation as well as defects in the layer are created due to the reconstruction of the surface. Imaging parameters are 0.4 nA and 1 V.

Self-assembled chlorophyll-a domains grow epitaxially on Au(111) substrate forming a close packed structure with a unit cell of 16 Å. In the domains, the molecules arrange with their tails positioned along the [211] direction of Au(111) substrate. The unit cell makes an angle of 10° with the close packed direction of Au(111), i.e. direction [110]. Domain boundaries or small defects are formed in the layers whenever the molecules follow the substrate reconstruction. The herringbone reconstruction can be seen through the molecular layer and it is not influenced by it.

Figure 5.15. Drawing shows how the molecules sit with respect to the underlying substrate. The molecules form a rhombic unit cell oriented at 10° with respect to the close-packed directions of Cu(111) substrate.

In the domains, the molecules arrange parallel to each other. They form lines in which they sit in an alternating head-tail-tail-head arrangement. High resolution STM images of the self-assembled layer show the detailed structure of the tail.

Structural calculations were done using the quantum chemical PM3 method [ARG4.1] and by comparing the calculated structure of the molecule with the high resolution images, the carbon atom positions inside the tail unit are determined (Fig.5.16). The calculated structure of free standing chlorophyll-a shows that the phytol chain is folded on the porphyrin unit [ARG4.1, LIN00]. Chlorophyll-a adsorbs on Au(111) by maintaining a similar structure: The porphyrin unit lies flat on the surface while the phytol chain is elevated from the surface by the support of four CH₃ groups. The STM

images show the phytol as a chain of three bright triangular units, which are assigned to the elevated C-H groups corresponding to the following carbon atoms (C4, C5, C6), (C8, C9, C10), and (C12, C13, C14), respectively (Fig.5.16). The carbon atoms C3, C7, C11, and C15 are attached to CH₃ groups, and are located slightly lower than their neighbors in this conformation. The calculated charged density contour plots of the chlorophyll tail revealed a similar profile for the molecule with the one determined from the STM images (yellow line).

Figure 5.16. Structural characterization of the molecules in the layer. (a) Free standing molecule calculation, (b) Charge density contours of a chlorophyll-a tail (side view). (c) STM image showing a part of a self-assembled domain. (d) High resolution STM image of the layer showing the detailed structure of the tail. Drawings of the molecule are placed on top for eye guidance. The numbers represent the carbon atoms shown in (e), the top view of the phytol chain. The yellow line from (b) represents the line profile measured along the tail of the molecule. Red arrows point to the features seen in the line profile also.

5.3.2 Electronic properties

Electronic properties were determined by scanning tunneling spectroscopy performed on the molecules assembled in the cluster. The spectrum illustrated in figure 5.17 shows the position of the lowest unoccupied molecular orbital to be at 2.8 V above the Fermi level. The highest occupied molecular orbital is present at ~ 0.5 V below the Fermi level. A shoulder is present at ~ 1.6 V below the Fermi level illustrating another filled molecular orbital. The HOMO-LUMO gap amounts to 3.3 eV. The large number of atoms that form chlorophyll-a, 137, limits the computational power and most of the calculations present in the literature either consider simplifying approximations or do not consider the phytol chain. Calculations of the molecular orbital energy spectrum for a porphyrin skeleton of chlorophyll-a determine the inter-frontier molecular energy gap to be 5.84 eV from PM3 semiempirical calculation or 7.26 eV from ab-initio calculation [ERK02]. ZINDO calculations determined the same energy gap to be ~ 4.5 eV for Mg-pheoporphyrine-a [NON97]. Whenever molecules are adsorbed on a metallic substrate charge transfer can occur between the substrate and molecule leading to the differences in the energy location of the occupied and unoccupied orbitals.

Figure 5.17. Orbital mediated tunneling spectrum of chlorophyll-a adsorbed on Au(111) substrate showing the position of HOMO and LUMO and HOMO-1.

5.4 Discussions

Chlorophyll-a molecules were investigated at both single molecule level as well as in self-assembled domains. For a better characterization of the influence of the substrate we have deposited chlorophyll-a on both Au(111) and Cu(111). The higher reactivity of copper resulted in a stronger interaction between the molecules and the substrate. On the other hand gold is more inert and molecules were easily displaced on the substrate. Self-assembled layer formation was also favorable on Au(111) substrate. Our formation of close-packed chlorophyll-a domains shows that high quality chlorophyll-a films can be formed, which is a good development for bio-solar-cell and electronic applications. Furthermore, our low temperature STM study in combination with structural calculations reveals the molecular arrangement inside the clusters and the atomistic details of the carbon chain from the chlorophyll-a tail for the first time.

Single molecule conformational changes were achieved using injection of electrons from the STM tip. Four conformations of the molecule's tail were reversibly switched in a controlled manner and characterized by means of tunneling electrons. The switching process was described quantitatively and a single inelastic tunneling electron was determined to be involved in the transformation. Structural calculations have determined the rotation sites to be different for each transformation suggesting that a controlled switching can be achieved by addressing the particular bond involved in each transformation. These results open up new possible uses of this molecule as switches in nanoscale devices.

Chapter 6

Summary

Low temperature STM studies were carried out on porphyrin-based molecules that play an important role in biological systems and are of great interest in nanoscale devices. Two different molecular switches are discussed as important results of this dissertation. Both switches can be operated by injection of tunneling electrons, therefore using the same input mechanism, but with different outputs. For the first one, a spintronic switch, changes in the conformation of the molecules lead to changes in the spin-electron coupling. This was proven to be the case for the Co-TBrPP molecules. The Kondo temperature, a measure of the spin-electron coupling, was determined to be different for the two conformations of the molecule: saddle and planar. The STM tip is used to transform one conformation into another. The second switch, a mechanical one, deals with changing the conformation of a chlorophyll-a tail upon injection of tunneling electrons. Single tunneling electron energy was proven to be the necessary energy that can trigger this process. Connections between different paths of an electronic circuit using chlorophyll-a may be one practical application of this switch.

Self-assembled layers of Co-TBrPP were formed on Cu(111) and their analysis provided new ways to manipulate the electronic properties of the molecules. Kondo temperature was proven to vary for molecules that have different number of nearest neighbors as the electronic distribution of the underlying substrate was altered by the two dimensional arrangement. Chlorophyll-a assembled on Au(111) substrate forming well

organized defect free structures that extend for hundreds of nanometers providing new information about the growth process and the intermolecular interactions.

Porphyrin-based molecules are known as very stable molecules given the very different biological environments in which they function under extreme temperature and pressure conditions. Chlorophyll-a and Co-TBrPP molecules were tested for their mechanical stability and their adsorption on different metallic substrates was found not to alter their mechanical stability. A lateral manipulation technique was employed to displace them on surfaces and a corresponding threshold on the tunneling resistance was determined.

As a future research direction new experiments are initiated to address the problem of Kondo physics in a two dimensional assembly. By exploiting existing STM techniques new architectures of molecules can be created and studied. The future results together with the present data can shed more light on the different electron-spin interaction paths that can occur for a magnetic molecule/metallic substrate system.

The multiple roles of chlorophyll-a in the photosynthetic complexes supplemented by the advances in scanning tunneling microscopy represent an inexhaustible source of future experiments. Continuation of this work to study charge transfer between two chlorophyll-a molecules may lead to a better understanding of the photosynthesis process especially regarding the function of chlorophyll-a pairs that are found in the reaction centers.

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Appendix

Cu-TBrPP LT-STM study

The Cu-TBrPP (5, 10, 15, 20- Tetrakis-(4-bromophenyl)-porphyrin-Cu(II)) molecules were purchased from Porphyrin Systems and used as supplied. The molecules were dosed in-situ on a cleaned Cu(111) substrate through thermal evaporation ($\sim 600\text{K}$). After deposition the sample was transferred to the cold STM for further cooling and STM imaging. In this experiment we have studied individual Cu-TBrPP molecules as well as molecular ribbons formed by Cu-TBrPP molecules. The molecules were studied by STM imaging and STS.

Single Cu-TBrPP molecules adsorbed on the metallic substrate showed the same conformations as the Co-TBrPP molecules mentioned before: planar and saddle. The two molecular conformations have different apparent heights in the STM images, the planar configuration providing more tunneling current than the other.

Figure A 1. STM images of Cu-TBrPP molecules adsorbed on Cu(111) substrate showing the two molecular conformations: saddle and planar. Imaging parameters are 0.4 nA, 1 V.

At a higher coverage, Cu-TBrPP form self-assembled molecular ribbons. In the SAM ribbons, the Cu-porphyrin molecules assembled in a hexagonal lattice, with a lattice constant of $17 \text{ \AA}$.

Figure A 2. STM image shows molecular ribbons as well as single molecules. Imaging parameters are 0.25 nA and 1 V.

STS was performed on both single molecules and self-assembled domain in order to determine the molecular orbital spectrum and also to investigate the LDOS for a small energy window around the Fermi energy for comparison with previous results obtained on a similar molecule, Co-TBrPP. The electronic spectra, i.e. the variation of LDOS with the applied sample voltage, were acquired using the lock-in technique by applying a small AC modulation to the DC component of the applied bias (400-600 Hz, 2-30 mV_{rms}). The spectra were recorded with the STM-tip placed above the center of the porphyrin.

For the single molecules in the planar conformation 4 electronic states were measured: -1.75 V, -1.40 V, 0.68 V, 2.46 V. The assignment of each electronic state is shown in the diagram of Fig. A3. The HOMO-LUMO gap is 2.08 eV (or 597 nm, yellow-orange range). Electronic spectra were measured for different tip-molecule distance as some of the orbitals have proven to be more localized to the molecules and less extended into the vacuum junction. These localized orbitals were able to be resolved at tunneling resistances smaller than 4 GΩ. Calculated energy gap for similar molecules such as Cu-tetraphenylporphyrin, Br atom are replaced with H, amounts to 1.71 eV [LIA02]. These calculations are done on free standing molecules with no substrate considered. The small difference between the calculated and measured value for the HOMO-LUMO gap, ~0.3 eV, can be due to either the adsorption on the surface or to the Br atom which are present

in the Cu-TBrPP molecule. It was determined for other molecules that upon adsorption the HOMO and LUMO levels position can be altered by substrate induced charge transfer [LUX04].

Figure A 3. Scanning tunneling spectra shown are for an isolated molecule in the planar conformation. A schematic drawing of the energy spectrum is shown on the left.

In the saddle conformation the STS spectrum shows a larger gap as the distorted porphyrin ring provides a different interaction of the molecule with the substrate leading to the absence or shifting of some orbitals (Fig.A4). The first occupied levels can be seen at -1.7 V and the onset of the next one (HOMO-1) starting beyond 2 V. For the unoccupied level only an onset can be seen starting at ~ 2.5 V.

Figure A 4. Spectrum taken for an isolated molecule found in a saddle conformation.

In order to observe the behavior of the LDOS near the Fermi energy we measured the $(dI/dV, V)$ spectra for smaller bias ranges. These are test measurements for the previous STS measurements taken on a Co-TBrPP that showed a depression of the local density of states at the Fermi energy and was interpreted as Kondo resonance. This phenomenon is not observed here.

Electronic spectra were recorded for the molecules that formed a self-assembled molecular domain. Here three electronic states were determined for a 6 eV energy window centered on the Fermi energy (Fig. A5). The determined energy gap is 2.18 eV (568 nm, yellow). This energy gap is very close to the single molecule case, the only difference in the spectra is a small shift of the electronic levels towards the Fermi energy. STS measurements were repeated for smaller bias ranges to observe the behavior of the LDOS around the Fermi energy. In contrast to the Co-TBrPP self-assembled layer no depression in the LDOS was observed here.

Figure A 5. Scanning tunneling spectra taken on top of the molecules self-assembled in the layer with different tip heights. Shown on the right is a schematic of the energy spectrum.