Bottom-up Construction and Direct Characterization of Porphyrin- and Graphene-based Nanostructures

Dissertation

von

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Bottom-up Construction and Direct Characterization of Porphyrin- and Graphene-based Nanostructures

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Abstract

Bottom-up self-assembly utilizing different intermolecular interactions has shown promising potential for constructing atomically-precise nano-architectures. Nanostructures stabilized by metal-coordination bonds frequently exhibit increased flexibility in the formation process and structural versatility in the structures thanks to the introduction of metal adatoms. Beyond self-assembly, covalently bonded nanostructures can be constructed with rigid connections and present better stability and electronic conductivity. Well-defined interfaces are promising platforms for the formation and investigation of these nanostructures. Scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) are exploited for the characterization and unambiguous determination of their structures.

In this thesis, firstly 2D metal-organic networks formed by two porphyrin derivatives, one equipped with cyano and another with pyridyl terminated meso-substituents, with copper atoms are investigated. Networks with distinct structures are formed due to the different spatial constraints of cyano and pyridyl groups, as confirmed by Monte-Carlo simulation. Secondly, attempts of constructing covalently bonded nanostructures utilizing dehydrogenative coupling and radical coupling protocols demonstrate the strength of this approach and reveal that steric hindrance plays an important role. The same reaction protocols are adopted for the formation of covalently bonded heterostructures. Through dehydrogenative coupling, porphines are successfully fused to graphene edges with atomic precision. This heterostructure has great importance since it combines two highly active research fields, i.e., tetrapyrrrole and graphene-based nanoscience. Other small molecules also showed the capability of covalently fusing to graphene edges. Moreover, the coupling of porphines to graphene nanoribbons (GNRs) with well-defined edge terminations illustrates that certain selectivity can be achieved by tuning electronic properties of the GNRs, which are mainly determined by their shape and termination. This on-surface fusing of organic molecules to graphene-based nanostructures introduces a distinct, novel approach towards functionalization of nano-graphene and thus opens up a new pathway for applications in nanoelectronics and bioinspired technologies.
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1. Introduction

Top-down? Bottom-up! Nanotechnology, a concept proposed in 1974 by Norio Taniguchi\(^1\), initially described methods of processing and manipulating materials by one atom or by one molecule and was later extended to refer to techniques capable of producing features in the range below 100 nanometers. Such a vision had already been proposed in 1959 by Richard Feynman in his famous talk "There’s Plenty of Room at the Bottom"\(^2\). Nowadays, nanotechnology has become one of the foundations of modern civilization. Without it, the central processing units (CPUs), the heart of billions of computers, cellphones and other digital devices techniques would not exist. To produce CPUs, large silicon wafers are cut into smaller pieces and processed by sophisticated lithography techniques into designs, components of which can be mere nanometers in size. This lithography technique is called a top-down method. Moore’s Law recognized that the number of transistors on an integrated circuit will double every 24 months\(^3\), which is about to enter the atomistic domain and thus may reach fundamental limits. Opposite to the top-down method is the bottom-up approach. Instead of sculpting down from the raw materials, the bottom-up method utilizes the atoms and molecules as building blocks to construct desired structures from scratch\(^4\). These building blocks can either be put together to form the wanted structure by specialized instruments, step by step, or at a more advanced level, may combine themselves automatically. The latter process is called self-assembling, and widely exists in nature, e.g. in the formation of DNA and proteins. In the self-assembling process of molecules, one only needs to design functional groups of the building block and the rest of the work is done by nature. As easy as it sounds, using this method in the formation of predefined structures, requires a deeper understanding of the fundamental properties of materials down to the nanoscale, an understanding currently not available.

Well-defined interfaces, particularly different facets of single crystals and novel 2D materials, are excellent platforms for the bottom-up construction of nanostructures. These interfaces can not only serve as the support for these assemblies, but also provide the powerful techniques for the characterization of these systems, such as scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM).

Porphyrians. Two aspects are essential for a successful design of the molecular building block: the functional part responsible for the expression of the properties and the connection part controlling the intermolecular interactions and thus the structure of the self-assemblies. Frequently it is advantageous to decouple these parts as much as possible so that changing one will only have a minor influence on the properties of the other. A promising substance meeting these requirements is the family of porphyrins and their derivatives. The central part of a porphyrin is the tetrapyrole macrocycle, which can accommodate a metal center and serves as the functional part. Equipped with different metal atoms, it can exhibit distinct properties\(^5\). At various positions, especially at meso-positions, functional substituents can be added and serve as the
connection part\textsuperscript{6–9}. Porphyrins have been found to be of great importance in many biological processes, as prosthetic groups. In hemoglobin, they function as the carrier of respiratory gasses\textsuperscript{10,11}, such as oxygen and carbon dioxide and in chlorophyll as the charge transporter. In addition, artificial, custom-designed species can also be used in various applications, for example in solar cells\textsuperscript{12–14}, in gas sensors\textsuperscript{15,16} and as molecular switches\textsuperscript{17}.

**How to glue them together.** The connection part of the building blocks determines the interactions between molecules, and as a result, the structure of the supramolecular assemblies. Many intermolecular interactions can be exploited to combine the molecular building blocks, such as van der Waals forces, hydrogen bonds and metal-coordination bonds. The van der Waals forces generally exist between molecules and usually drive them to form dense-packed islands on metal surfaces\textsuperscript{17–19}. They present no directional properties and thus are not useful for the construction of site-sensitive nanostructures. Both hydrogen bond and metal-coordination bond are directional. Hydrogen bonds are formed between hydrogen atoms and atoms with high electronegativity, such as nitrogen and oxygen. Because of the many hydrogen atoms that exist at the periphery of molecules, it could be hard to tailor the hydrogen bond to a certain hydrogen atom. With pre-designed active ligands, metal-coordination bonds are formed exclusively between metal adatoms and the ligands\textsuperscript{20–25}. Introducing metal adatoms also provides an additional freedom for connecting molecular building blocks. An apparent drawback of these two bonds is their low bonding energy and, as a result, low stability against disturbance from the environment, such as temperature fluctuation and mechanical forces. For this reason, using covalent bonds to connect molecular building blocks has recently attracted considerable interest, especially in the construction of carbon-based nanostructures\textsuperscript{26–31}.

**Graphene.** Graphene is a single atomic layer of carbon in a sp\textsuperscript{2} honeycomb structure. Since its first production and characterization in the laboratory in 2004\textsuperscript{32}, it has been the star of many research areas, because of properties, including high electron mobility\textsuperscript{33,34}, high transparency\textsuperscript{35}, high thermal conductivity\textsuperscript{36} and high mechanical strength\textsuperscript{37,38}, and due to its potential in many applications, such as nano-electronics\textsuperscript{39}, transparent electrodes\textsuperscript{40}, and batteries\textsuperscript{41,42}. With these extraordinary properties, graphene is an ideal candidate as a supportive platform for combining other functional materials, such as molecules. Also, coupling or embedding distinct atoms into the graphene creates new heterostructures with different properties than graphene. Porphyrins, as introduced above, are a family of molecules with exceptional properties and are a perfect candidate to combine with graphene. This has already been achieved in solution using graphene oxide\textsuperscript{43–48}. However, controlled functionalization with atomic precision has still not been systematically explored. Surface-assisted covalent coupling of functional molecules to the graphene edges may achieve this goal.

Pristine graphene is a direct band semimetal and has a linear dispersion relation near the Dirac point\textsuperscript{34}. One challenging aspect of graphene is to open a band gap by modifying its structure. Graphene nanoribbons (GNRs) with specific crystallographic orientations are predicted to have energy gaps which increase with decreasing width. Through surface-assisted coupling reactions, atomically precise GNRs with well-defined edge terminations can be constructed bottom-up by delicately designed precursors\textsuperscript{26,27} and indeed show a variable band gap with respect to the length\textsuperscript{49}. These GNRs are
an ideal candidate for the formation of hetero-nanostructures with other functional molecules, which are of great importance for applications in nanoelectronics.

Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM). To investigate the nano-world, one needs to be able to 'see' the atoms and molecules. In 1982, such a tool was invented by Binnig et al.\textsuperscript{50}, the scanning tunneling microscope (STM). It can directly monitor the surface with atomic resolution and also can manipulate atoms and molecules. However, it also has the disadvantage that it can only be used with a conductive surface. The invention of atomic force microscopy (AFM) by Binnig et al.\textsuperscript{51} in 1986 solved this problem. AFM measures the forces between the tip and the sample surface and thus is not limited by the sample material. With help of small molecules, such as carbon monoxide (CO), functionalizing the tip, frequency-modulation AFM\textsuperscript{52,53} is capable of visualizing single C-C bonds\textsuperscript{54,55}.

Thesis Overview. This thesis comprises of four parts. In chapter two, the principles of STM, AFM and Monte-Carlo simulation are introduced. The instrumentation of the ultra-high vacuum system is also explained.

In chapter three, porphyrin-based metal-organic networks on Ag(111) are investigated by STM and Monte-Carlo simulation. Two slightly different porphyrin derivatives exhibit distinct behavior upon deposition of copper adatoms on Ag(111). This difference is attributed to the steric hindrance induced by the flat-lying phenyl ring and is confirmed by the Monte-Carlo simulation. Other experimentally unexplored porphyrin derivatives are further studied by Monte-Carlo simulations.

In chapter four, nanostructures are constructed through surface-assisted covalent coupling. Dehalogenated tetracene covalently couples to the head/tail of another tetracene, resulting in a T-, L- or tilted-shaped polymer. A parallel-coupled configuration through radical-radical coupling is not observed due to the steric hindrance of hydrogen atoms. By introducing of bromine atoms to the X-shaped porphine dimer, a directed growth of porphine into porphine tapes is expected. The solution chemistry of azomethine ylides (AMYs) is successfully adapted on the Ag(111) surface. Nitrogen-doped \textit{diaza}-HBC and 1D polymer chains are synthesized through the surface-assisted dimerization and 1,3-dipolar cycloaddition reaction, respectively.

In chapter five, edges of graphene islands and graphene nanoribbons are functionalized by molecules through thermally activated covalent coupling. With the help of nc-AFM using a functionalized CO tip, the structure at the interface is clearly resolved. For the porphine coupled to irregular graphene edges, distinct coupling motifs are observed. On Ag(111), no change in electronic properties of porphine and graphene are observed in STS. Molecules with radicals are also coupled to graphene edges through the radical, but the steric hindrance prevents a higher yield than for the case of porphine. To obtain a deeper understanding of the coupling behavior, porphine and pyrphyrin are covalently coupled to graphene nanoribbons with well-defined terminations. Although no preference of the coupling motifs is observed, only the end of the 7-AGNR is capable of coupling to these functional molecules.
2. Experimental and Theoretical Methods

In this chapter, the principles of the main experimental techniques used in this thesis, as well as the computer simulation methods, are introduced. The main experimental techniques include scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM), both operated at low temperature (LT). Their instrumental setup is introduced at the end of this chapter. The simulation method is mainly the Monte-Carlo method, coded by the author himself.

2.1. Scanning Tunneling Microscopy (STM)

Observing and manipulating single atoms has been the dream of scientists ever since Richard Feynman’s famous speech “There’s Plenty of Room at the Bottom”\(^2\). In his speech, he envisioned several interesting possibilities to investigate and arrange atoms the way we want, once the technical prerequisites would be accomplished. The invention of the scanning tunneling microscope (STM)\(^56\) and atomic force microscope (AFM) made this dream come true. The Nobel Prize in physics in 1986 was awarded to its inventors, Gerd Binnig and Heinrich Rohrer, and reflected the importance of this new tool. In the following the fundamentals of scanning tunneling microscopy are introduced, detailed explanation and other theoretical treatments of STM can be found elsewhere\(^57\).

2.1.1. Tunneling Effect

The tunneling effect plays the key role in STM. Understanding of its elementary principle helps us to understand both, the capability and functionality of STM. Consider a simple one-dimensional energy barrier as illustrated in figure 2.1, with an electron propagating from one side towards the barrier. In classical mechanics, it is easy to see that the electron can not overcome the barrier if its energy is smaller than the energy barrier.

On contrary, in quantum mechanics an electron is considered to be a wave \(\Psi(x)\) which in this situation satisfies the one-dimensional Schroedinger equation:

\[
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) + U(x) \Psi(x) = E \Psi(x)
\]

(2.1)

where \(\hbar\) is reduced the Planck’s constant, \(m\) is the electron mass, \(E\) is the total electron energy and \(U(x)\) is the potential. The solution for \(E > U(x)\) is

\[
\Psi(x) = \Psi_a e^{\pm i \frac{\sqrt{2m(E-U)}}{\hbar} x} = \Psi_a e^{\pm ik_a x}
\]

(2.2)

where \(\Psi_a\) is the amplitude in the region before encountering the barrier and \(\Psi_c\) is the amplitude after the barrier. This indicates a probability to observe the electron behind
2. Experimental and Theoretical Methods

Figure 2.1. A quantum wave propagating through a potential barrier. The blue line with sine shape on both sides represents a non-vanishing wave function which is the solution of the Schroedinger equation. Inside the barrier, the amplitude of this wave function decays exponentially. Image used with permission by Knud Seufert.\(^{19}\)

The probability density is given by

\[ \Gamma = ||\Psi_c(x)||^2 \]  

(2.3)

To determine this transmission probability the solution in the barrier region where \( E < U \) is wanted

\[ \Psi(x) = \Psi_b e^{-\sqrt{2m(U_0-E)/\hbar^2}x} = \Psi_b e^{-\kappa x} \]  

(2.4)

where \( U_0 \) is the potential of the barrier and \( \Psi_b \) is the amplitude in the barrier region. This also implies a possibility to observe the electron in the barrier. Meanwhile the relation between \( \Psi_a \) and \( \Psi_c \) and further the transmission probability \( T \) can be obtained by applying the continuity condition

\[ T = \frac{||\Psi_c||^2}{||\Psi_a||^2} = e^{-2d\sqrt{2m(U_0-E)/\hbar^2}} = e^{-2\kappa d} \]  

(2.5)

where \( d \) is the width of the barrier. This indicates a sensitive dependence of the transmission probability on the width of the barrier. With the same treatment, the scanning tunneling microscope can be simplified as a metal (tip)-insulator (vacuum)-metal (sample) junction, in which electrons from the sample tunnel through the vacuum barrier into the tip or vice versa. For simplicity, we consider only electrons tunneling from the tip into the sample. Thus \( \Psi_t \) represents the wave function of electrons in the tip, \( \Psi_s \) the wave function in the sample which is correlated to \( \Psi_t \) via the wave function in the vacuum and continuity condition. \( \Phi \) is the work function of the tip which in this case is the height of the potential barrier. When applying a bias voltage \( U_b \) to the tip the probability of an electron with the wave function \( \Psi_t \) and energy near Fermi level \( E_f \) to tunnel into the sample is

\[ \Gamma \propto ||\Psi_s||^2 = ||\Psi_t||^2 e^{-2d\sqrt{2m\Phi/\hbar^2}} \]  

(2.6)
2.1. Scanning Tunneling Microscopy (STM)

where \(d\) is the distance between tip and sample. By summing up all the states in the tip in the energy range between \(E_f\) and \(E_f - eV\) the tunneling current can be obtained

\[
I_t \propto \sum_{E_f - eV}^{E_f} \| \Psi_s \|^2 \propto U_b \cdot \rho_s(E_f) e^{-2d\sqrt{2m\Phi/\hbar^2}}
\] (2.7)

where \(\rho_t(E_f)\) and \(\rho_s(E_f)\) is the local density of states (LDOS) close to the Fermi level of tip and sample respectively and we assume that the LDOS near Fermi level is almost the same. As already mentioned before equation 2.7 indicates a strong sensitivity of the tunneling current on the distance between tip and sample.

The standard method nowadays for the theoretical treatment of a MIM junction is a time-dependent perturbation approach developed by Bardeen\(^57\). The main idea of Bardeen’s theory is to treat the MIM system as several independent subsystems, i.e. two metal electrodes. By solving the subsystem individually the stationary wave function in each subsystem, here \(\Psi_t\) and \(\Psi_s\), is obtained:

\[
\Psi_t = \psi_\mu e^{-iE_\mu t/\hbar}, \quad \Psi_s = \chi_\nu e^{-iE_\nu t/\hbar}.
\] (2.8)

Combining these two states the wave function of the whole system is assumed to be

\[
\Psi = \psi_\mu e^{-iE_\mu t/\hbar} + \sum_{\nu=1}^{\infty} c_\nu(t) \chi_\nu e^{-iE_\nu t/\hbar}
\] (2.9)

where \(c(0) = 0\) means the electron is moving from tip to the sample. Then the probability of tunneling from \(\mu\)-th state of tip into \(\nu\)-th state of sample is

\[
p_{\mu\nu} \equiv \| c_\nu(t) \|^2 = \| M_{\mu\nu} \|^2 \delta(E_\mu - E_\nu)
\] (2.10)

where delta function \(\delta(E_\mu - E_\nu)\) means the elastic tunneling can only happen between two states with the same energy value and \(M_{\mu\nu}\) is the tunneling matrix element and defined as follow which is just the surface integral of two wave functions over the separation surface. By applying a bias \(U_b\) to the tip the tunneling current can be obtained by summing up all the available states in the tip and sample in the energy range between \(E_f\) and \(E_f - eV\)

\[
I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} \left[ f(E - eV) - f(E) \right] (\rho_\mu(E)\rho_\nu(E - eV)) \| M_{\mu\nu} \|^2 dE
\] (2.11)

where \(\rho_\mu(E)\) and \(\rho_\nu(E)\) are the density of states in tip and sample respectively and \(f(E) = \left( 1 + \exp[(E - E_f)/k_B T] \right)^{-1}\) is the Fermi distribution function. If the operating temperature of STM is very low, i.e. \(k_B T\) very small, the Fermi distribution energy can be approximated by a step function and in this case the tunneling current is

\[
I = \frac{2\pi e}{\hbar} \int_{E_f - eV}^{E_f + eV} \rho_\mu(E)\rho_\nu(E - eV) \| M_{\mu\nu} \|^2 dE.
\] (2.12)

Here the tunneling current is the convolution of tip and sample density of states (DOS) mixed with topographic information. The expression in equation 2.12 is rather simple,
but the states of the tip and tunneling matrix element are difficult to know. Therefore Tersoff and Hamann introduced a particular model of the tip to simplify the situation\textsuperscript{58}. They proposed that the tip is represented by a geometrical point with an s-wave state

\[ \chi_s(r) = C_0 k_0(\kappa r) \sqrt{\frac{1}{4\pi}} \]  

(2.13)

where \( \kappa = (2m\phi)^{1/2} \hbar^{-1} \) is the decay constant in the vacuum. This leads then to the simplified tunneling matrix element

\[ M_s = \frac{2\pi C\hbar^2}{\kappa m} \psi(r_0) \]  

(2.14)

where \( r_0 \) is the center of apex atom of the tip. The tunneling current is then

\[ I \propto \int_{E_f}^{E_f+eV} \rho_s(E,r_0) dE. \]  

(2.15)

Consequently, the tunneling current is then only related to the sample surface and one can extract the intrinsic properties of the sample.

\[ \text{Figure 2.2. Simplified working diagram of STM. This graph is from Michael Schmid, TU Wien\textsuperscript{59}.} \]

Figure 2.2 shows a typical working principle of the STM. First, the tip is brought close to the sample. A bias voltage is applied between the tip and sample, resulting in a tunneling current. The piezo can drive the tip to move above the sample surface. In different operation modes, the height of the sample or the tunneling current is recorded and serve as the signal for imaging.
2.1. Scanning Tunneling Microscopy (STM)

2.1.2. Scanning Tunneling Spectroscopy (STS)

As mentioned before, the tunneling current depends only on the LDOS of the sample in the Tersoff-Hamann model. Differentiating equation 2.15 with respect to $V$, the dynamic tunneling conductance is found to be

$$\left(\frac{dI}{dV}\right) \propto \rho_s(E, r_0).$$

(2.16)

This equation is the extension of the Tersoff-Hamann model. Thus all the assumptions made before have also to be valid here. This relationship between LDOS and dynamical conductance is the basis of scanning tunneling spectroscopy. To obtain spectroscopic information of the sample, the tip is held at a constant height above the desired position while the sample bias is varied. By numerically differentiating the obtained I-V curve the LDOS of the sample can be obtained. In addition, with the help of lock-in technique the STS can also be measured directly. First, a high frequency modulation voltage is added to the sample bias. Then the feedback is disabled to keep the height constant while doing a bias sweep. Inserting the modulated bias into the equation 2.15 we obtain

$$I \propto \int_{0}^{eV_T+eV_m\sin(\omega_m t)} \rho_s(E)dE$$

(2.17)

where $V_T$ is the bias and $V_m\sin(\omega_m t)$ is the superimposed modulation. Expanding it in a Taylor series:

$$I \propto \int_{0}^{eV_T} \rho_s(E)dE + \rho_s(eV_T)eV_m\sin(\omega_m t) + \rho_s'(V_T)\frac{e^2V_m^2}{2}\sin^2(\omega_m t) + ...,$$

(2.18)

then after multiplying the current signal by a reference signal with exact the same frequency as the modulation signal but different phase, the first and third term in the right side of equation 2.18 vanish. Only the second term is kept which is directly proportional to the LDOS. This method is much more accurate and stable and thus is nowadays used mostly to get STS.

2.1.3. Operation Modes

As mentioned before, since its invention in 1986, STM has become a powerful tool, especially in surface science. It is not only able to image surfaces with atomic resolution, but it can also probe the local electronic states of the sample. Furthermore, with the ability to manipulate single atoms and molecules, it is possible to build structures on the atomic level. In the following, an overview of STM operation modes is given.

**Constant Height Mode.** As the name suggests, in the constant height mode the tip is kept at a constant height and scanned over the desired area (see figure 2.3(a)). The current at each point of a specified grid defined in this area is recorded, and these currents information are then combined and displayed by the software as a contrast image. Since the current is related to the distance between tip and sample and also to the local density of electronic states, the changes in the current represent the change in the distance or local electronic states. Thus the obtained image gives the information about both topography and also LDOS. However, this method is rarely used because
Figure 2.3. Different STM operation modes: (a) The constant height mode. (b) The constant current mode. (c) Lateral manipulation. (d) Vertical manipulation. (e) Scanning tunneling spectroscopy. (f) Typical graph obtained from STS. Image used with permission by Knud Seufert\textsuperscript{19}.

of the risk of the tip crashing into protrusions on the surface like clusters, step edges or similar. In addition, without a feedback system, the thermal drift of the piezo may significantly reduce the accuracy of the image.

**Constant Current Mode.** This mode is the most used STM mode today. In this mode, a feedback system is used to keep the current constant while scanning and thus reduces the influence of thermal drift in the vertical direction (z direction) and prevents the tip from crashing (see figure 2.3(b)). The height of the tip is then measured and used to generate a contrast image. Normally the feedback system is a Proportional-Integral-Controller (PI). Therefore one can change the frequency of the feedback system by adjusting the parameters of this PI-Controller to fit the scanning speed. In this mode, the height of the tip over the sample surface is recorded. As mentioned before the obtained signal and image also include the LDOS contribution.

$dI/dV$ Map Mode. As already explained before by doing STS over a point we can get
2.2. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) was invented in 1986 by Binnig, Quate and Gerber. It shares similar instrumental settings as the scanning tunneling microscopy (STM) they have invented before, both utilize a sharp tip to characterize the sample surface properties in a rasterized fashion. Unlike the STM, AFM senses the atomic forces between the tip and the sample surface. Therefore, no current flow is needed, and it can also be applied to non-conductive samples. In the following, the fundamental knowledge of the AFM are firstly introduced. Afterward, the working principles of the so-called qPlus sensor will be explained in detail.

2.2.1. Atomic Forces

There are always forces between atoms that are responsible for the formation of different materials and their individual properties. AFM utilizes these forces to extract information of the arrangement of atoms, i.e. the structure of sample surfaces. There are different types of forces between atoms, in AFM mainly three forces contributes to the tip-sample force.

Van der Waals force. The van der Waals interaction exists between all atoms or molecules. It originates from forces between fluctuating electric dipole moment of atoms, which stem from the quantum mechanical zero point energy. The van der Waals force is always attractive and is a long range force which means it does not change significantly on the atomic scale.

The potential of the van der Waals force between two atoms is given by (see Figure
2. Experimental and Theoretical Methods

2.4) \[ U_{vdW} \sim -\frac{1}{z^6}. \] (2.19)

Because van der Waals forces underly the superposition principle and by modeling the end of the tip as a paraboloid with radius R, it can be simplified to

\[ F_{vdW,ts} = -\frac{HR}{z^2} \] (2.20)

where \( H \) is the material-related Hamaker constant and \( z \) is the distance between the apex of the tip and a flat surface. If the AFM tip is sharp enough, this model is quite suitable.

Pauli Repulsion. Short-range repulsions originate from Pauli’s exclusion principle. When two atoms are very close to each other, and their electron clouds start to overlap, they will repel each other.

![Graph showing typical interaction between tip and sample. The total potential and force result from the competition of van der Waals force and the Pauli repulsive force. The frequency change is also shown. This graph is from ref. [60].](image)

Electrostatic force. Electrostatic forces exist between objects with different potentials. For example, in STM the tip and the sample are both conductive and the potential difference \( U \neq 0 \). In this case, the electrostatic interaction may be very prominent for the AFM measurement. The non-contact mode used in this thesis typically sets the potential difference \( U \) between the tip and sample to 0, by changing the applied bias voltage on the sample to compensate the potential difference. This method could not exclude the electrostatic force caused by the charged molecules on the sample surface.
2.2. Atomic Force Microscopy (AFM)

Fortunately, the contribution of charged molecules to the tip-sample force is usually relatively small compared to the chemical forces, thus it only results in some distortions of the obtained image data. Still, these distortions could cause some misinterpretation of the molecular structures or when the quantitative analysis of the bond lengths is desired. The electrostatic force for a spherical tip with radius $R$ is given by

$$F_{\text{electrostatic}}(z) = -\frac{\pi \epsilon_0 R U^2}{z}. \quad (2.21)$$

**Total Force.** In general, the whole interaction between two neutral atoms is thus the competition between attractive van der Waals force and the repulsive Pauli force. But unlike the van der Waals force which follows equation 2.19, there is no equation describing Pauli repulsion for all distances. Thus different empirical potentials have been proposed to model this interaction between two particles. The most widely used one is the Lennard-Jones (LJ) potential\textsuperscript{61} (see figure 2.4)

$$U_{\text{LJ}} = U_0 \left[ \left( \frac{z_0}{z} \right)^{12} - 2 \left( \frac{z_0}{z} \right)^6 \right], \quad (2.22)$$

where $U_0$ is the energy at the equilibrium distance $z_0$. This potential results in a force

$$F_{\text{LJ}} = \frac{12U_0}{z_0^2} \left[ \left( \frac{z_0}{z} \right)^{13} - \left( \frac{z_0}{z} \right)^7 \right]. \quad (2.23)$$

Figure 2.4 shows the total force between tip and sample. In the region where the distance between tip and sample is large, the force is attractive and subtle. When the tip approaches the sample, the attractive force increases and at one point the total force reaches zero where the van der Waals force equals the Pauli repulsion force. After this point the Pauli repulsive force begins to increase much faster than the van der Waals force, resulting in an upward bending of the total force towards the repulsive region. By further approaching, the total force becomes strongly repulsive.

2.2.2. *Operation Modes*

Depending on the type of forces that dominates the tip-sample interaction, there are different imaging modes in AFM.

**Contact Mode.** The first exploited mode is the contact mode which only uses the repulsive force. In this mode, the tip is brought into contact with the sample surface. While scanning, the tip is kept touching the surface and thus follows its topography (see Fig. 2.5(a)). The deflection of the cantilever is then used as the imaging signal (see Fig. 2.6(a)). The scan speed can be very high\textsuperscript{62} which is advantageous when many samples have to be measured within a short time and is employed especially for industrial applications, or when investigating dynamic phenomena. However, it also can be destructive due to the constant touching with the sample surface. Thus normally a relative soft cantilever is used to scan on a relatively hard surface.

**Intermittent Mode.** In this mode the cantilever oscillates in both, the repulsive and attractive regions, and has a very large oscillation amplitude (see Fig. 2.5(b)). As a result, the tip touches the sample surface regularly. Thus this mode is also called tapping mode. The motivation for this mode is to use a smaller interaction between tip and sample which leads to fewer destructions while still having the ability to measure
2. Experimental and Theoretical Methods

**Figure 2.5.** Different operating modes of AFM. The force-distance curve on the left of each panel is divided into four parts marked with distinct colors, which represents the working area of the cantilever in different modes. (a) Contact mode. The tip constantly touches the surface. (b) Intermittent mode. It is operated in the whole regime (dark green area), repulsive and attractive. It has the largest oscillating amplitude. (c) Non-contact mode one. It works in the attractive force regime (green area). Normally it has relatively large amplitude. (d) Non-contact mode two. It is also called non-contact mode, but it is different from (c) and operates in the repulsive region (orange area) with much smaller amplitude. (d) In modes (b)-(d), the tip is driven by external excitation and oscillates, and in mode (a) there are no external driving forces.

Mechanical properties of the surface. Comparing to the non-contact mode it is still very stable because the tip regularly touches the sample surface. As its name suggests, this mode is the combination of the contact and non-contact mode.

**Non-contact Mode.** In the traditional non-contact mode, like the intermittent mode the cantilever oscillates, but only in the attractive region of the tip-sample interaction (see Fig. 2.5(c)). This mode is almost non-destructive. There is another non-contact mode, that operates mainly in the repulsive range (see Fig. 2.5(d)), where electron clouds of the front most atom of the tip and atoms of the surface already partially overlap. This mode is now widely used in surface science for high-resolution imaging. With tip functionalization and qPlus sensor (see later this section and section 2.4.5), it has the ability to resolve bonds between atoms.

Among the above-mentioned modes, the contact mode is also called static mode, and
the other two are called dynamic modes because their cantilevers are driven to oscillate close to their eigenfrequency during the measurement. In dynamic mode, the interaction is detected either with amplitude modulation (AM)\textsuperscript{64} or with frequency modulation (FM)\textsuperscript{65}. Intermittent mode normally uses a feedback system based on amplitude modulation. Our instrument is mainly operated in the frequency modulated non-contact mode (FM-AFM), thus in the next section, this mode will be explained exclusively.

Like STM, there are two main scanning modes for non-contact measurement, constant height mode and constant frequency shift mode (in the case of frequency modulation). In constant height mode, the tip moves across the sample surface at constant height, and the frequency shift signal is used as imaging signal (Fig. 2.6(b)). In constant frequency shift mode, an additional feedback loop is enabled to keep the frequency shift constant during the measurement by modulating the tip height. Then the height of the tip (sensor) is used as imaging signal (Fig. 2.6(c)).

Besides the above mentioned topographic modes, AFM can be operated to obtain other information of the sample surface, for example, mechanical properties.

**Force Spectroscopy.** This mode is similar to the scanning tunneling spectroscopy. While measuring, the x-y position of the tip is kept constant, and the tip ramps in the z-direction towards the sample surface. Therefore it measures the force-distance curve, as shown in Fig. 2.6(d). This mode is especially useful for detecting mechanical properties of molecules. For example, the three-dimensional structure of proteins or other large molecules can be probed with this mode\textsuperscript{66,67}.

**Static AFM vs. Dynamic AFM** In the static mode, the cantilever is left still, i.e. without external driving force, and kept in constant contact with the surface. The tip-sample force $F_{ts}$ is expressed as the deflection $q = F_{ts}/k_s$ of the cantilever which is then used as the imaging signal. In the scanning, two situations can cause a deflection of the cantilever, changes of the topography of the surface or deformations of the tip or sample. The latter one is unwanted and should be minimized. The solution is to use a cantilever with the spring constant $k_k$ significantly smaller than the bonds between atoms in the tip and sample (see Fig. 2.7). A typical interatomic force constant between atoms in solids is in the range between $10 \text{ N/m}$ and $100 \text{ N/m}$. A reasonable value of the spring constant $k$ is then below $5 \text{ N/m}$.

In the dynamic mode, here we only focus on the non-contact mode, the cantilever is deliberately vibrated and does not touch the sample surface when operating properly. To keep the stable vibrating of the cantilever, too small spring constant, as used in static mode AFM, can not be used, because it is too sensitive to small tip-sample force or other interference and it will often jump touching the surface. As a result, a cantilever with much larger spring constant $k_0$ is needed. To avoid the jumping of the tip to the sample surface, the spring constant $k_0$ of the cantilever should also be larger than the tip-sample force constant $k_{ts}$ (see Fig. 2.7). As the tip-sample force varies with materials of the tip and sample and also the distance between the tip and sample, different spring constant is needed. Another factor to be considered here is the vibrating amplitude of the cantilever since it also directly influences the distance between the tip and sample.
Figure 2.6. Different scanning modes of AFM. Yellow line is the moving path of the z position of the tip and red line is the signal used in the measurement. (a) Static mode. The tip constantly touches the surface during the scanning and follows the topography of the surface. (b) Dynamic constant height mode. The tip sweeps across the surface at constant height, and the frequency shift df is used as the imaging signal. (c) Dynamic constant frequency shift mode. Additional feedback loop is enabled to keep the frequency shift constant during the scanning. The moving of the piezo in the z-direction is then used as the imaging signal. (d) Force spectroscopy. The tip is swept toward the surface and then back. The frequency shift is recorded and plotted.

2.2.3. Frequency Modulation AFM (FM-AFM) with qPlus

In the dynamic non-contact modes, the cantilever is oscillating around its resonant frequency driven by an external excitation. To maintain the vibration of the cantilever, mainly two methods are used, amplitude modulation (AM) and frequency modulation (FM). AM-AFM\textsuperscript{51} was firstly introduced by Binnig and Quate. In this mode, the cantilever is driven by a fixed frequency $f_{\text{drive}}$ slightly off its resonant frequency $f_0$ and a fixed amplitude $A_{\text{drive}}$. Forces applied on the tip will cause a change in the amplitude of the cantilever. These changes are then either used as the feedback signal in topological mode (constant force mode) or as the mapping signal in constant height mode. An advantage of AM-AFM is its simple working mechanism that there is no feedback for the oscillation part and thus makes it very easy to implement in the early days. The drawback of AM-AFM is that the change of the amplitude has some delays to the change of the tip-sample force on a timescale of $\tau_{\text{AM}} \approx 2Q/f_0$, this makes it not suitable for the high Q-factor cantilever, which, on the other hand, can significantly reduce
2.2. Atomic Force Microscopy (AFM)

Figure 2.7. A schematic illustration showing a probe tip close to a sample. The cantilever is considered here as a rigid plate connected to a fixed base through a spring with spring constant $k$, only movable in vertical direction. The interaction between the tip and sample is characterized by the spring constant $k_{ts}$ and the bonds between atoms of the sample is characterized by $k_{ss}$.

noise. To overcome this problem, Albrecht et al. introduce frequency modulation (FM) mode. In FM-AFM, the delay of the change of frequency shift caused by the change of tip-sample force is on a timescale of $\tau_{FM} \approx 1/f_0$.

In FM-AFM, the cantilever is oscillating at a constant amplitude and always at its resonant frequency $f_0$. The tip-sample force is measured by the (resonant) frequency shift $\Delta f$ of the cantilever with respect to its unperturbed resonant frequency $f_0$. Consider the tip mounted on the cantilever as a mass $m$ connected to a spring with spring constant of $k_0$. Its eigenfrequency $f_0$ is given by

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k_0}{m}}. \tag{2.24}$$

Because the amplitude of the oscillation is very small, the tip can be considered to be perpendicular to the surface. Thus the vertical force between tip and sample is

$$F_{ts} = -\frac{\partial U_{ts}}{\partial z}, \tag{2.25}$$

where $U_{ts}$ is the potential energy between tip and surface. Changes in the tip-sample force $F_{ts}$ will cause a frequency shift $\Delta f$ of the cantilever. The tip-sample force $F_{ts}$ can be considered as another spring connected between mass $m$ and the surface with spring constant $k_{ts}$. If $k_{ts}$ is constant during the oscillation cycle, the new oscillation frequency of the cantilever is

$$f = \frac{1}{2\pi} \sqrt{\frac{k_0 + k_{ts}}{m}}, \tag{2.26}$$
2. Experimental and Theoretical Methods

where \( k_0 + k_{ts} \) is the effective spring constant. As already mentioned before, in an operation mode with small amplitude the spring constant \( k_0 \) is normally on the order of \( 1 \text{kN}^{-1} \) which is much larger than the force gradient \( k_{ts} \). Thus the square root can be expanded in Taylor series \( (\sqrt{1+x} = 1 + \frac{1}{2}x + \cdots) \)

\[
f = f_0 + f_0 \frac{k_{ts}}{2k_0} + \cdots .
\] (2.27)

If only the first order approximation is taken into account and considering the definition of the spring constant \( \delta F_{ts} = -k_{ts} \delta z \), the relation between the frequency shift and the differential of the tip-sample force is

\[
\Delta f = -f_0 \frac{\partial F_{ts}}{2k_0} \delta z.
\] (2.28)

It is obvious that the frequency shift is proportional to the force gradient of the tip-sample force. For the case where the force gradient \( k_{ts} \) can not be considered constant during the oscillation cycle, please refer to ref. [68].

**Experimental Setup.** To keep the cantilever oscillating at a constant amplitude and its resonant frequency, two feedback loops are needed, one for the constant amplitude and one for the frequency adjustment of the driving signal, as shown in 2.8. The cantilever is driven to oscillate at its resonant frequency \( f_0 \) by an actuator with driving frequency \( f_{\text{ref}} \). In the first feedback loop, the deflection of the cantilever is detected and filtered and then fed back to an automatic gain control module where it compares the input signal with the setpoint and adjusts the output accordingly for the actuator to maintain a constant oscillation amplitude of the cantilever. Besides the change in amplitude, the tip-sample force will also cause changes in the resonant frequency of the cantilever and as a result the relative phase with respect to the driving signal \( f_{\text{ref}} \). Therefore a second feedback loop is needed here. It compares the deflection signal with the driving signal and adjusts the driving signal so that it always matches the resonant frequency of the cantilever with a phase shift \( \varphi = \pi/2 \).

![Simplified working diagram of FM-AFM](image-url)

*Figure 2.8. Simplified working diagram of FM-AFM. This graph is from ref. [60].*
2.2. Atomic Force Microscopy (AFM)

The feedback loop for the amplitude adjustment is relatively easy to implement, since it is just a normal PI controller. The feedback loop for the frequency adjustment is more complicated. Modern designs\textsuperscript{69,70} utilized a phase-locked-loop (PLL) detector with a voltage-controlled oscillator (VCO). Basically, it is a frequency-to-voltage converter. It consists of a phase detector and a VCO. The phase detector compares the frequency $f_{\text{ref}}$ of the reference signal generated by the VCO and the frequency $f$ of the input signal and outputs a signal whose intensity is proportional to the frequency difference $\Delta f = f_{\text{ref}} - f$. This output is then the frequency shift signal recorded for the imaging. It is then fed to the VCO to control the frequency $f_{\text{ref}}$ of the reference signal, so that the reference signal will match the input signal in both the frequency and phase. This reference signal is sometimes also used as the driving signal for the actuator after shifting its phase of $\pi/2$ with respect to the deflection signal of the cantilever, because this signal is a very clean sinusoidal wave and always tracks the deflection signal of the cantilever.

**qPlus Sensor.** Firstly, microfabricated silicon were used as cantilever in AFM since 1990\textsuperscript{71–74}, because of its extraordinary properties, e.g. high Q-factor, and the easiness of fabrication by photolithography. Quartz, another interesting material, is also possible to be fabricated by photolithography with high Q-factor. Comparing to the silicon, quartz even has better thermal stability than silicon because it can be cut along certain crystal orientations in a way the thermal influence to the oscillation frequency could be internally compensated\textsuperscript{75}. This makes it a much better material for building cantilevers. To construct self-sensing force sensors two effects can be utilized, the piezoresistive effect and the piezoelectric effect. Cantilevers utilize piezoelectric effect is more favorable because its power dissipation is negligible. This makes it the ideal cantilever for low-temperature applications\textsuperscript{76,77}.

Quartz tuning forks are widely used in watch industry as frequency standards and are well-known for its very high precision and low cost. They are etched from a single quartz crystal along the $X + 5^\circ$ orientation\textsuperscript{78}, to ensure the least frequency variation at 300 K due to temperature changes. Several important properties of tuning forks are listed below:

1. Self-sensing. The piezoelectric effect of quartz and the gold electrodes around it enable tuning forks to measure forces without additional components. By cutting the electrodes at the end of the prongs, the eigenfrequency of the quartz tuning fork is adjusted to be exactly $2^{15}$ Hz ($32768$ Hz).

2. A high Q value. When the two prongs of the tuning fork with the same mass and stiffness oscillates opposite to each other, the energy loss will be extremely small and thus has a very high Q value.

3. Very Stiff. The stiffness of the prongs is on the order of 1 kN/m. By choosing different size of the prongs, one can have slightly different stiffness.

Because of these properties, quartz tuning forks have been used as force sensor already in 1989 by Guthner et al.\textsuperscript{79}, shortly after the invention of AFM. In the first few studies, the quartz tuning fork is normally mounted with its base part fixed. To cure the asymmetrical vibration of the tuning fork due to the introduction of the probe (tip) on
one prong, a counterweight has to be added to the other prong to maintain the high Q-factor oscillation mode\textsuperscript{80}. Otherwise, the Q factor will considerably drop. However, the symmetry still breaks when the tip is subject to tip-sample forces, which results again in a considerable dropping of the Q factor.

To overcome this drawback, one prong of the tuning fork is fixed on a heavy base plate. Thus only the free prong is able to oscillate. In this configuration, the addition of the tip and the tip-sample force will not cause a collapse of Q factor. Therefore this type of sensor has been called the 'qPlus sensor'\textsuperscript{69}.

2.3. Monte Carlo Simulation

Nowadays computer simulation methods are extensively applied in the research of surface science. It not only can help scientists to understand complex phenomena, but also is capable of predicting possible nano-structures formed on surfaces in many cases. The most used simulation methods include Molecular Dynamics (MD), Monte Carlo (MC), Density Functional Theory (DFT) and combinations of these methods.

Self-assembly of functional molecules on 2D surfaces are especially interesting, because with delicate design of molecular building blocks, 2D nano-structures with versatile properties could be formed automatically. Comparing to the traditional bottom-up fabrication methods where each building block has to be manually assembled\textsuperscript{81}, this method not only is more efficient, but also more straightforward and resembles the natural process, like the formation of DNAs.

Due to the enormous possibility of molecular building blocks, it is too time-consuming and inefficient to try out all of these possible building blocks experimentally. Therefore, computer simulation methods can be very helpful in this situation. However, because of the large amount of molecules existing in a self-assembled structure and the complexity of the self-assembly system, e.g. internal freedom of molecular building blocks, a variety of different intermolecular interactions, coupling between molecules and substrates etc., it is almost impossible to simulate this whole big system with DFT method, which has proved to be more accurate. Monte Carlo method, on the other hand, is more suitable for this task. It simplifies the system by focusing only on the interesting properties of the system and neglecting other less relevant parameters. However, sometimes this also causes problems. By simplifying the system, many strong assumptions of the system under investigation are made. Thus the results are strongly correlated to the correctness of these assumptions. If some or even only one of these simplifications are invalid, the results of the simulation may be far away from the actual situation. For example, in case of a strong structural deformation of the molecule, the assignment of a rigid structure to the molecule will make the simulation meaningless. Therefore, it is important to validate the results of Monte-Carlo simulation regularly by comparing to the experimental results.

2.3.1. Theory

Modern Monte Carlo methods can be traced back to 1940s\textsuperscript{82}. One of its typical use is the evaluation of the definite integrals, which can not be calculated analytically. For
2.3. Monte Carlo Simulation

example, if we wish to obtain the integral of a \( f(x) \) in the range of \([a, b]\), shown in Fig. 2.9a:

\[
I = \int_a^b f(x)dx. \quad (2.29)
\]

It will be exhausting trying to find the \( g(x) = f'(x) \), if \( f(x) \) has a very complicated form. On the other hand, Monte Carlo method can solve this problem very easily. Firstly, drawing a box from \([a, 0]\) to \([b, I_0]\), where \( I_0 > f(x) \) within the range \([a, b]\). Then put \( N \) points randomly with uniform distribution into this box, like throwing coins into a playground. Count the number, \( N_0 \), which represents how many points are below \( f(x) \). This is called ‘hit-or-miss’ (or acceptance-rejection) method. Now the integral of \( f(x) \) in range of \([a, b]\) can be estimated by

\[
I_{est} = \left( \frac{N_0}{N} \right) \times \left[ I_0 \times (b - a) \right]. \quad (2.30)
\]

As \( N \to \infty \), the estimation \( I_{est} \) becomes more and more precise and eventually converges to the exact integral \( I \). This method is called ‘random sampling’, as we sample the region of interest with a uniform distribution, and it is very efficient for the problems which are hard to solve analytically. However, in some cases, consider again the problem of the evaluation of the integral of \( h(x) \), as shown in 2.9b. \( h(x) \) is almost zero in most of the range and becomes very large close to \( b \). If we calculate the \( I_{est} \) using the Monte Carlo method introduced above, the error \( \Delta I = |I - I_{est}| \) will be pretty large when \( N \) is not big enough. Because most of the points will be in the upper right area of the box and thus \( N_0 \) can not reflect the true value of \( I \). In order to obtain a reliable estimation of the integral of \( h(x) \), a very large \( N \) is required, which makes this method inefficient.

![Schematic models showing the working principle of Monte-Carlo method in integration estimation.](image)

Monte Carlo importance sampling algorithm introduced by Metropolis et al. in 1953\(^{83}\) solved this problem of inefficiency. The problem of evaluating the integral of \( h(x) \) is that most of the points are in the upper-left area where \( h(x) \) is negligible. It will be more efficient if more points are in the bottom-right area where \( h(x) \) has large values. In other words, we want to sample the points nonuniformly. Denote this nonuniform nonnegative probability density as \( w(x) \). The integral \( I \) can be rewritten as

\[
I = \int_a^b f(x)w(x)dx. \quad (2.31)
\]

Monte Carlo importance sampling algorithm introduced by Metropolis et al. in 1953\(^{83}\) solved this problem of inefficiency. The problem of evaluating the integral of \( h(x) \) is that most of the points are in the upper-left area where \( h(x) \) is negligible. It will be more efficient if more points are in the bottom-right area where \( h(x) \) has large values. In other words, we want to sample the points nonuniformly. Denote this nonuniform nonnegative probability density as \( w(x) \). The integral \( I \) can be rewritten as

\[
I = \int_a^b f(x)w(x)dx. \quad (2.31)
\]
2. Experimental and Theoretical Methods

\[ I = \int_a^b dx w(x) \frac{h(x)}{w(x)}. \quad (2.31) \]

We further assume that \( w(x) \) is the derivative of another function \( u(x) \), with \( u(a) = 0 \) and \( u(b) = 1 \), which suggests that \( w(x) \) is normalized. The integral \( I \) can be further rewritten as

\[ I = \int_a^b du \frac{h[x(u)]}{w[x(u)]}. \quad (2.32) \]

Now instead of \( x \), \( u(x) \) is the variable to integrate and \( N \) random sample points are dropped uniformly in the interval \([a,b]\) to obtain the estimation of the \( I \)

\[ I_{est} = \frac{1}{N} \sum_{i=1}^{N} \frac{h[x(u_i)]}{w[x(u_i)]}. \quad (2.33) \]

It is straightforward to think if \( w[x(u_i)] \) is similar to \( h[x(u_i)]/w[x(u_i)] \) will be smooth like \( f(x) \). Thus the uniformly random sampling is also efficient to evaluate the integral \( I \) in this case. To be more rigorous, we can calculate the variance of \( I \)

\[ \sigma_i^2 = \frac{1}{N^2} \sum_{i=1}^{N} \left( \frac{h[x(u_i)]}{w[x(u_i)]} - \langle h/w \rangle \right)^2 \]

\[ = \frac{1}{N} \left( \langle (h/w)^2 \rangle - \langle h/w \rangle^2 \right), \quad (2.34) \]

where the angular brackets denote the true average. Here it clearly shows that if \( w(x) \) is properly chosen, such that \( h(x)/w(x) \) is smooth, the variance of \( I \) will be greatly reduced.

However, for some real physical problems the importance sampling method described above cannot be used, because we do not know how to construct the function \( w(x) \), so that the points randomly chosen in configuration space will follow the Boltzmann factor. One typical example is the calculation of the average of some observable \( A \). From classical statistical mechanics, the average of \( A \) can be calculated with the following equation

\[ \langle A \rangle = \frac{\int dr^N \exp[-\beta U(r^N)] A(r^N)}{\int dr^N \exp[-\beta U(r^N)]}. \quad (2.35) \]

The denominator is normally denoted as partition function by \( Z \):

\[ Z \equiv \int dr^N \exp[-\beta U(r^N)]. \quad (2.36) \]

With \( N \equiv \exp[-\beta U(r^N)]/Z \) as the probability density to find a state / configuration in \( r^N dr^N \). Equation 2.35 can be rewritten as

\[ \langle A \rangle = \int dr^N N(r^N) A(r^N). \quad (2.37) \]

Clearly, the \( \langle A \rangle \) has the same form as the Eq. 2.31. If we can construct a transformation which enables the sampling of configuration space with a probability density
proportional to Boltzmann factor \( \exp[-\beta U(r^N)] \), the average of \( A \) can be obtained by computing

\[
\langle A \rangle \approx \frac{1}{L} \sum_{i=1}^{L} n_i A(r_i^N), \tag{2.38}
\]

where \( L \) is the total space and \( n_i \) is the number of sampling points per unit around \( r_i^N \).

However, in this situation, we do not know the partition function \( Z \) analytically and thus such a transformation is not obtainable. Note that the \( \exp[-\beta U(r^N)] \) is already known, but partition function \( Z \) is unknown to us, which means the relative but not the absolute probability density in configuration space is known. Therefore if we can generate points in configuration space with probability density proportional to Boltzmann factor instead of being exactly equal to the \( \mathcal{N}(r^N) \), the importance sampling method is still effective.

Now the problem becomes how to make the points in configuration space follow a probability density proportional to the Boltzmann factor. The approach is to start with the system in a certain state \( r_{i0}^N \). By adding a small displacement \( \delta r^N \), we generate a trial state \( r_{i1}^N \). Their Boltzmann factors are \( \exp[-\beta U(r_{i0}^N)] \) and \( \exp[-\beta U(r_{i1}^N)] \), respectively. By choosing a proper rule of when to accept or reject the trial state, we can make the system satisfy the constraint that the probability to find the system in state \( r_i^N \) is proportional to \( \mathcal{N}(r_i^N) \). The most used rule is the proposed by Metropolis et al.\(^8^3\).

For a system in equilibrium, the probability of being in a state \( r_i^N \) should be dynamically stable, which means the probability the system transforms from state \( r_i^N \) to state \( r_j^N \) is equal to the probability the system transforms from the states \( r_j^N \) to state \( r_i^N \).

\[
\mathcal{N}(r_i^N)\pi(i \rightarrow j) = \mathcal{N}(r_j^N)\pi(j \rightarrow i), \tag{2.39}
\]

where \( \pi(i \rightarrow j) \) is the transition probability from state \( r_i^N \) to state \( r_j^N \). The transition probability can be viewed as two parts

\[
\pi(i \rightarrow j) = \alpha(i \rightarrow j) \times \text{acc}(i \rightarrow j), \tag{2.40}
\]

where \( \alpha(i \rightarrow j) \) is a coefficient of the transition probability and \( \text{acc}(i \rightarrow j) \) is the probability of accepting a trial move. Normally \( \alpha \) is chosen so that \( \alpha(i \rightarrow j) = \alpha(j \rightarrow i) \). Thus the \( \alpha \) coefficient on both side of Eq. 2.39 cancels

\[
\mathcal{N}(r_i^N)\text{acc}(i \rightarrow j) = \mathcal{N}(r_j^N)\text{acc}(j \rightarrow i). \tag{2.41}
\]

Note that the probability density \( \mathcal{N} \) follows the Boltzmann factor, Eq. 2.41 can be rewritten as

\[
\frac{\text{acc}(i \rightarrow j)}{\text{acc}(j \rightarrow i)} = \frac{\mathcal{N}(r_j^N)}{\mathcal{N}(r_i^N)} = \exp\{-\beta[U(r_j^N) - U(r_i^N)]\}. \tag{2.42}
\]

There are many choices for \( \text{acc}(i \rightarrow j) \) that satisfy this condition. The choice of Metropolis et al.\(^8^3\) is
2. Experimental and Theoretical Methods

\[
\text{acc}(i \rightarrow j) = N(r_j^N)/N(r_i^N) \quad \text{if} \quad N(r_j^N) < N(r_i^N) \\
= 1 \quad \text{if} \quad N(r_j^N) \geq N(r_i^N). \tag{2.43}
\]

For a trial move from state \( r_i^N \) to state \( r_j^N \), if \( U(r_i^N) > U(r_j^N) \), then the trial move is accepted. If \( U(r_i^N) < U(r_j^N) \), according to Eq. 2.43 the probability to accept the trial move is

\[
\text{acc}(i \rightarrow j) = \exp\{-\beta[U(r_j^N) - U(r_i^N)]\} < 1. \tag{2.44}
\]

In order to keep the transition probability satisfy in this condition, a random number \( R \) from a uniform distribution is generated in the interval \([0, 1]\). If \( \text{acc}(i \rightarrow j) \) is larger than \( R \), then the trial move is rejected, and if \( \text{acc}(i \rightarrow j) \) is smaller than \( R \), the trial move is accepted. Clearly, the probability of accepting the trial move is equal to \( \text{acc}(i \rightarrow j) \). With all the things mentioned above, now we are able to generate points in the configuration space with a relative probability density proportional to the Boltzmann factor. More details about the theory can be found in\(^84\).

2.3.2. Procedure

With the background knowledge introduced above, the procedure of performing Monte-Carlo method for modeling molecular structures on 2D surface is introduced here.

First of all, it should be noted that in order to utilize Monte-Carlo method to simulate molecular behaviors on surfaces, many simplifications are needed. These simplification should be simple enough so that the simulation would be computationally feasible. Meanwhile, they should catch the essential properties that we interested.

The first point to be considered is the choice of the substrate. If molecules can only occupy predefined points, it is called on-lattice Monte-Carlo method. If molecules can be anywhere, i.e. no restrictions on the coordinates, the method is called off-lattice Monte-Carlo method. In the on-lattice method, the information of molecule-substrate interactions and molecular symmetries are already buried into the choice of the lattice symmetry. Therefore, one has to choose it very carefully in order to fulfill (or reflect) the real properties of the system. On the other hand, for the off-lattice method the molecule-substrate interaction is provided by an additional potential energy. The off-lattice method is more accurate and closer to the real situation, but it is more challenging to design the algorithm and also computationally much more expensive. Therefore, the on-lattice method is more feasible. Moreover, the site-selective interaction under investigation in this thesis is negligible and thus on-lattice method is used in this thesis.

Because of the fourfold symmetry of the molecules, a square lattice is used to represent the substrate.

The next step is to determine how to describe the molecules on such a lattice substrate. In this thesis, there are mainly two types of objects, porphyrin derivatives and copper atoms. The latter one is easy, because a copper atom does not have an internal structure, thus we can easily assign it to occupy just one lattice site. For porphyrins, the flexibility of its internal structure is neglected, thus molecules will have a cross-like shape. Without losing the generality the length of the meso-substituents is set to occupy one site. Thus, a porphyrin is represented by five sites in a cross shape.
2.3. Monte Carlo Simulation

The last point to consider is intermolecular interactions. In this thesis, only van der Waals interaction, $E_v$, and metal-coordination bond, $E_c$, are considered and are expressed in $kT$ units. All of them are limited only to exist between neighbours next to each other.

With all these parameters defined, now the experiment can be started, an example of this process is shown in Fig. 2.10. First of all, elements are randomly put on the surface by giving them a random position. Afterwards, the trial moves begin. An element is selected either randomly or sequentially and then moved to another random position. The energy difference of the system $\delta E$ before and after the moving is computed. Since except for the selected / moved element, other elements are unaffected, therefore only energy changes of this molecule need to be considered. Thus the energy change of the system $\delta E$ can be easily obtained by computing the energy of this element before the trial move $E_{old}$ and after the trial move $E_{new}$. According to the Metropolis scheme introduced above, the acceptance probability of this trial move is

$$p = \min\{1, \exp[-(E_{new} - E_{old})/kT]\}.$$ \hspace{1cm} (2.45)

To determine whether this trial move is accepted or rejected, the acceptance proba-
2. Experimental and Theoretical Methods

Probability $p$ is compared with a randomly generated number $r$ in range $(0, 1)$. If $r < p$ the trial move is accepted and the selected element is moved to the new position. Otherwise, the trial move is rejected and the selected element stay in its previous position. When all the elements have been selected once, it is called one MC step is performed. To let the system reach equilibrium, normally $10^7$ to $10^{11}$ MC steps are needed, depending on the type of elements and the density.

2.4. Experimental Set-up

2.4.1. UHV System

In surface science a clean surface is always wanted, especially when STM or AFM is used, because contaminants, even a little amount of other atoms, could influence the reliability of the results obtained. Furthermore, some experimental procedures can not be carried out in air condition because of the active oxygen and water molecules in the gas phase which can react with the sample or the instrument. Therefore an ultrahigh vacuum (UHV) environment is obligatory for our experiments. It has several advantages for the investigation of surfaces. First of all, it provides a clean atmosphere with very few oxygen and water vapor, therefore preventing the oxidation or other reaction of the sample. Second, high vacuum extends the mean free path of molecules or atoms and thus makes sample surface preparation techniques like evaporation possible and more efficient. Third, ultrahigh vacuum is beneficial in terms of heat isolation which is critical for the cooling system and will be explained in the next section. Last, high vacuum is the necessary condition for the operation of many tools, like e.g. mass spectrometry.

In our experiment the instrument can reach a pressure lower than $2 \times 10^{-10}$ mbar by using a custom designed vacuum chamber with several pumps. The whole system consists of two parts, preparation chamber and SPM chamber (see figure 2.11). A gate valve can separate them to keep the SPM chamber clean while preparation procedures can be carried out in the preparation chamber.

2.4.2. Cooling System

For surface analysis on an atomic scale, the stability of both sample and the instrument is required. A big problem is thermal drift of the instrument, i.e. the SPM scanner, and the thermal motion of molecules or metal atoms on the sample surface. The first problem will reduce the accuracy of the measurement and the second problem will lead to noise and mismatch of the obtained signal. As we know, the thermal energy is directly related to the temperature and thus can be greatly reduced at low temperature.

In our instrument a cryostat system (figure 2.11 red part) is used to keep the SPM scanner at about 5 K during the measurements. This is realized by a bath cryostat filled with liquid helium. To reduce the consumption of helium, a second cryostat filled with liquid nitrogen surrounds the first cryostat. These two dewars are separated by UHV to minimize the thermal transport by particles. To reduce the radiative transport two radiation shields, connected with the liquid helium stage and the liquid nitrogen stage respectively, are mounted under the cryostat to improve the temperature stability.
2.4. Experimental Set-up

Figure 2.11. Picture of experimental set-up built and used in this thesis. Red dyed is the cryostat filled with liquid helium and nitrogen. Yellow is the SPM chamber, hosting the scanner and an in situ evaporator. Blue is the preparation chamber with several evaporators, leak valves, a mass spectrometer and the possibility to sputter. Green is the manipulator used for the sample transfer between the two chambers. Light blue colored are the dampers and purple the whole pumping system.

2.4.3. Vibration Isolation

As mentioned in the last section, in order to have an accuracy on the atomic scale, mechanical and electrical stability is highly required. The tip is only several nanometers or even only a few angstroms from the sample surface, resulting in a tunneling current usually of several hundred pico or some nano Ampere. Thus a little vibration in $z$ direction (vertical direction) can strongly change the tunneling current or even destroy the tip.

By cooling down the sample to a low temperature of 5 K the inner stability is achieved, metal atoms from the surface and deposited molecules are frozen and anchored on the substrate. To reach outer stability the external mechanical and electronic noise has to be decoupled from the STM scanner. Here, three different methods are used.

First of all, four pneumatic dampers (figure 2.11 light blue part) are used to avoid low frequency vibrational noise. The whole instrument is placed on these dampers. It can greatly reduce the vibrations transferred from the ground, like door closing and opening and people walking, thus the whole instrument is decoupled from the outer
environment.

Secondly, the inner cryostat which is not rigidly mounted on the outer chamber is stabilized by eddy current damping with respect to the outer cryostat (see figure 2.12 and 2.13). It is realized by a magnetic plate mounted under the inner radiation shield above another metal plate that is rigidly mounted on the outer radiation shield. These two plates are aligned with respect to each other at the beginning. Once they are misaligned an eddy current is induced in the metallic plate and repels the motion. Because the outer cryostat is rigidly connected to the instrument, this stage can greatly reduce vibrations coming from the instrument itself.

At last the SPM head is resiliently suspended with three springs from the inner cryostat (see figure 2.13) which further reduces vibrations induced by the instrument or other additional modules that are mounted on the instrument, like hanging cables, different pumps and flowing cooling water. This stage is the finest stage and very sensitive to vibrations and thus can reduce the noise induced by vibrations to a very low level.
2.4. Experimental Set-up

Figure 2.13. The third damping stage. The SPM stage is resiliently suspended with three springs from the inner cryostat.

2.4.4. SPM Scanner

The SPM scanner is the core part of the whole instrument. A commercially available SPM scanner is used that was bought from Createc GmbH. It is a newly designed type of SPM scanner. Unlike the traditional Besocke-beetle type scanner that was developed by G. Meyer and Sven Zoephe at Freie Universitaet Berlin, which uses a base plate to enable coarse motion, it uses two slide piezo systems to perform the coarse motion. This provides much bigger motion range both in the horizontal plane and in the vertical direction.

Figure 2.14. SPM scanner. (a) Picture of SPM scanner. (b) Schematic drawing of SPM scanner. Adopted from ref. [89].
As mentioned before the SPM scanner is suspended with three springs from the bottom of the inner cryostat (see figure 2.13). It consists mainly of three parts: a base plate which holds the sample and also other parts, the XYZ slider for coarse motion of the tip and the main scanner for the fine motion of the tip, mounted in the middle of the XYZ slider.

The base plate (see figure 2.14) comprises two metal plates with a groove in the middle where the sample can be placed in. In the groove on the bottom plate is a plate with contacts for the sample. This plate has two states: up and down, and can be moved by pulling or releasing a T-shaped screw from underneath. If the T is pulled down, the plate is also pulled down to touch the bottom plate. In this position the sample can be transferred in or out. If the T is released, the plate is also released and pushes the sample to the top of the base plate. In this position the sample is clamped by the upper plate and this square plate and is in the measurement position. The T is connected via a wire system to a pulling system outside the cryostat.

![Figure 2.15](image)

**Figure 2.15.** Schematic drawing of the main piezo. By applying voltage in different direction on the piezo it can provide fine motion of the tip in x, y and z direction.

The XYZ slider’s three feet stand on three ceramic square plates on the upper surface of the base plate. Slide piezos are mounted under each foot and enable the XYZ slider to move in the horizontal plane. With this feature, the XYZ slider has a much bigger moving range (1 cm², the size of the ceramic plate) than the Besocke beetle type scanner. A head plate is rigidly mounted with the base plate and presses the XYZ slider downward to prevent unwanted movements and to provide enough friction force. In the middle of the XYZ slider there is a triangular prism with a ceramic plate on each side. It is clamped by three arms extended from the outer holder of the XYZ slider. On each arm there are two slide piezos mounted to enable the coarse motion of this prism in the vertical direction.

Inside this triangular prism is the tube shaped main piezo (see figure 2.15) which serves as the fine motion generator. By applying a high voltage in the different directions on this tube piezo, it can bend in different directions, which enables motion in the horizontal plane or elongate or shorten in the vertical direction, which enables motion in the vertical direction. Beneath it, a little magnetic plate, which can hold the tip, is mounted. There are three contacts at this magnetic plate. One contact is for the tunnling current and the other two contacts are for AFM signals.

The advantage of this configuration is the high mobility of the slide piezo. In the
horizontal plane a wider scanning range means the whole sample surface can be scanned. This increases the surface available for scanning and reduces the loss if some place of the sample is damaged. With the traditional Besocke-beetle type scanner one has limited motion in the z direction, it can only move 1-2 mm which makes the assembly of the sample very difficult. But using this slider scanner this is no more a problem.

**Slide Piezo.** The above mentioned advantages of the scanner originate from the usage of the slide piezos which are so called piezoelectric motors, because they function like a motor. The working principle is based on the change of the shape when applying an electric field. In our case, the deformation of the piezo in one plane is used to generate a series of moving steps along this plane, similar to the caterpillar.

![Figure 2.16](image)

**Figure 2.16.** Schematic drawing of the principle of the slide piezo. a) Working principle in the horizontal direction. (0) At the beginning of a step, no voltage is applied to the piezo. (1) While the voltage applied to the piezo slowly increases, the piezo begins to deform and due to the static friction force there is no displacement in the interface of piezo and table, resulting in a relative displacement between the object and the table. (2) The applied voltage steeply drops to zero and the piezo returns to its normal shape. b) Working principle in the vertical direction. The object is rigidly mounted on the piezo. (0) At the beginning of a step, no voltage is applied to the two piezos. (1) While the applied voltage to both piezos slowly increases, both piezos deform, resulting in a relative displacement between the object and the wall. (2) The voltage applied to one piezo ramps to zero, while the voltage applied to the other piezo stays. As result, the first piezo returns to its normal shape and the other piezo holds the object. (3) The voltage applied to the second piezo ramps to zero, then it returns to its normal shape. c-d) Signal (voltage) applied to the piezos in (a) and (b), respectively.

The principle of this motor is the difference between static friction force and kinetic friction force. Typically the kinetic friction coefficient is smaller than the static friction coefficient. Consider pushing an object on a table. If the pushing force is larger than the static friction force, the object is being moved and then the force needed to keep it moving, reduces to the kinetic friction force.

For the piezo motor, the principle is the same. Consider a system shown in figure 2.16a, an object mounted on a piezo which stand on a table. The piezo can deform along its longer side by applying an electric field, i.e. a voltage at its two ends. If the voltage applied increases or reduces slowly, which means the deformation of the piezo is also very slow, then the force between the piezo and the table is always smaller than
the static friction force, resulting in no motion of the bottom part of the piezo with respect to the table and a relative motion between the upper part of the piezo and the table, thus a relative motion of the object laid on the piezo with respect to the table. In contrast, if the voltage ramps fast up or down, the force between the piezo and the table is larger than the static friction force and there is a relative motion between the bottom surface of the piezo and the table. By using these two types of motion the object on the piezo can be moved relative to the table.

Figure 2.16c and d show the signal applied to the coarse piezos used in our instrument. For the vertical system, there are two signals for generator 1 and generator 2 respectively. Normally one signal is enough for driving piezos in the x and y direction. But in the z (vertical) direction, when voltage ramps, there is the risk that the object slips down because of gravity. Therefore two generators are used, one holds while the other one moves, just like a caterpillar.

### 2.4.5. Tip Preparation

A well defined tip is very important for scanning probe microscopy. A sharp apex is always wanted. Due to the different principles of STM and AFM their tips are also different. In this section both types of tips and their preparation procedure are introduced.

**STM Tip.** The tips used in the STM in our experiment are mainly etched tungsten tips. In the first test of the STM in air, a cut Pt-Ir tip is used due to its high stability and inertness in the air environment. However, in the UHV environment, a tungsten tip can offer us much better performance, thus here only tungsten tips will be introduced.

![Tip etching setup](image)

**Figure 2.17.** Tip etching setup. a) Schematic model and b) picture of the tip etching setup. Image used with permission by Knud Seufert.

To produce this tip, a tungsten wire with a diameter of 0.25 mm is used. As can be seen in figure 2.17, a tungsten wire is clutched by a metal clamp which acts as an electrode and penetrates a lamella of NaOH-solution (concentration of 1 mol/L). The lamella is held by a Au-formed noose which acts as counter electrode. By immersing
the noose into the solution of etching fluid the lamella can be easily formed. With an applied voltage of 3 V, an electrochemical reaction takes place in the lamella between the noose and the tungsten wire. The chemical reaction for the etching process is:

$$W(s) + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^-.$$  \hspace{1cm} (2.46)

After 15 to 20 minutes the tip is etched through and the bottom part falls down into a collection container with the sharp side pointing upwards. Usually both the falling part and the part that is still clutched by the clamp can be used as the tip, but because of the effect of the gravitation and continuous etching of the upper part after breaking the falling part is normally sharper and is used as the tip. Then the tip is cleaned sequentially by distilled water, acetone and isopropanol to remove the etching solution. Subsequently it is cut to the right length and mounted on the tip holder. Now it is ready to be transferred into UHV.

After it is transferred into the UHV environment, some other methods are available to further improve the sharpness and the conduction of the tip. First, it is sputtered with argon ions to remove the oxide layer that is easily formed in air. The sputtering process will be explained in detail in the following section. Another option to clean the tip apex is heating by an electron beam by applying a high voltage between a tungsten filament and the tip.

Afterwards the tip is transferred to the SPM chamber and attached to the central piezo by magnetic coupling. Because the sputtering process or the e-beam process needs the tip to be transferred back to the preparation chamber and the process itself also costs a lot of time, an additional in-situ preparation method while scanning is wanted. The most powerful method is the tip forming (TF). In the tip forming procedure the tip is brought in contact with, or even dip into, the clean metal surface of the sample, and then by a high current flow induced by applying a high voltage pulse between tip and sample, the metal is melted locally and coated on the tip. Afterwards the tip is withdrawn to its initial position. First of all, this procedure adds a metal layer to the tip and thus improves the conductivity of the tip. More important the coating procedure randomly changes the apex of the tip and may give the tip a sharp apex in microscopic view. This is also the origin of the name of this method.

Normally at the beginning of the scanning several strong TFs, means dipping deep into the metal and applying higher bias, have to performed to form a stable, well-defined tip. When the image quality becomes worse during the scanning, for example blurry and double image, where small modification of the tip is sufficient, some weak TF is suitable for improving the image quality. Due to the destructive feature of this method, the scanning site should be as far away as possible from the TF position. TF needs bare metal surface and thus can only work in submonolayer coverages. If the sample surface is fully covered by the molecules where clean metal surface is not available, one has to repeat the strong TF in the same place for several times until the bare metal is exposed.

If the quality of the image is very bad or one can even see nothing from the image, some radical tip preparation method may help. In this procedure the tip is dipped into the sample surface using the coarse piezo. If this still doesn’t work, one can further move the tip with coarse piezo in the XY plane. However, this method is very destructive both
2. Experimental and Theoretical Methods

to the sample and the tip, because the mechanical force on the tip is not controllable
the tip may even be destroyed. Therefore this radical method is only used when all
other methods failed.

In most situations, the tip only needs a little modification, for example when some
molecules are adsorbed to the tip or the tip has double or more apexes. Then voltage
pulses during the scanning is capable of removing these molecules or eliminating the
double apex. In addition, one can also ramp the bias from a high positive voltage to a
high negative voltage or inversely. These non contacting methods are more gentle and
are already able to improve the tip and image quality.

Figure 2.18. AFM sensor used in our AFM. (a) AFM sensor mounted on the "tip" holder.
(b) AFM sensor (qPlus). (c) Tuning fork mounted on the base plate.

**AFM Sensor.** The AFM sensor (figure 2.18) used in our experiment is a commercial
qPlus sensor bought from Createc GmbH\(^\text{87}\). It was invented by Giessible\(^{52}\). As can be
seen from the 2.18, the tuning folk is glued on one side of the ceramic base plate with its
one fork fixed. A tungsten tip is glued to the end of the other prong. The tip should be
cut as short as possible, ideally shorter than 1\(\text{mm}\), because the longer tip adds heavier
mass to the prong and as a result it will deteriorate the Q factor. Typical cutting method
include chemical etching and electron beam cutting. There are three electric contacts
on the backside of the base plate. Two of them are connected to the tuning fork and

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receive the vibrational signal of the tuning fork (tip). This signal is referred as AFM out and is the central signal in FM-AFM. The third contact is for the STM signal and connected to the tip via a ultra thin wire, so that its interference on the vibration of tuning fork is minimal. This contact is electronically isolated from the conductive parts of the tuning fork, so that there is no cross-talk between the AFM signal and STM signal. The tuning fork is excited by another piezo in the scanning stage.

2.4.6. Sample Preparation

Samples used in our experiment are mainly copper and silver, both are single crystals cut in the [111] orientation, thus has a (111) orientated surface. Both copper and silver are transition metals and have a face centered cubic (fcc) crystal structure, thus show a hexagonal ordering for both materials in the (111) orientation. Though Ag and Cu have the same crystal structure, they have a different lattice constant due to their different size of atoms, for Ag it is 4.09 Å and for Cu it is 3.61 Å. From these lattice constant the next neighbour distance in the (111) plane can also be calculated and it is 2.89 Å for Ag and 2.56 Å for Cu. Once the atomic resolution image of the bare metal is obtained, these well known distances can help us to calibrate the main scanning piezos. Another difference between Ag and Cu, besides the lattice constant, is the surface reactivity. Cu is more active and has also a higher adatom density at a given temperature. When a molecule is evaporated on the sample surface, Cu can provide more adatoms serving as the interaction media between molecules. On contrary, Ag surface is less reactive which means a weaker interaction between the Ag substrate and adsorbates.

Figure 2.19. Sample holder used in our SPM. It is based on a standard base plate from Createc. The sample is clamped on the oven and can be accessed via four contacts at the rear part. (a) Picture of the sample holder on the manipulator. (b) Schematic drawing of the sample holder. The drawing is adapted from ref. [90].

The samples are discoidal and have a diameter of about 6 mm and a height of about 1.8 mm (see figure 2.19). They are clamped on an oven with a molybdenum star set with six legs bending under the oven. Then it is mounted on a sample holder which is a standard part produced by Createc GmbH. As can be seen from figure 2.19, there are four electric contacts available. On the manipulator or on the storage place these contacts are used for heating and the inner two contacts are for the temperature measurement via a thermocouple mounted on the oven. In the measurement position all four contacts, all of them connected to the sample, can be used to apply a bias to
the sample. Because the transfer of the sample to the measurement position is done by
the manipulator, the contact of the sample to the bias pins can be different every time.
Thus after a transfer the contacts have to be checked.

The sample surface is contaminated under ambient conditions and can be contam-
ninated from the previous preparation, thus before the next preparation, it has to be
cleaned. This can be done by repeated cycles of sputtering and annealing processes.
Sputtering is the process that ionized argon atoms are accelerated onto the sample sur-
face and collide with the top layers of the sample. The particles, atoms or molecules of
the top layers will be then removed and the underlying bare metal layers are exposed.
By changing the acceleration voltage, i.e. the kinetic energy, and concentration of argon
ions, i.e. the partial pressure of the argon gas, the resulting flux of argon ions, which can
be measured as sputter current, can be set according to how many layers are wanted
to be sputtered away. In our experiment a kinetic energy of $1 \text{ keV}$ and a background
pressure of $2.5 \times 10^{-5} \text{ mbar}$ are used to produce a sputter current of typically $8 \mu\text{A}$.
The sputtering process can very efficiently remove contaminants, but it also creates
a rough, undefined surface and leaves argon atoms implanted in the sample which is
unwanted. In order to obtain a well defined surface and to remove argon atoms, an
annealing process has to be performed. In the annealing process, the sample is heated
up to a specific temperature for some time. As temperature increases, argon atoms can
gain enough energy to escape from the metal and metal atoms can get enough energy to
overcome an energy barrier and then move to its energetically more favorable position
which is the (111) surface. In our experiment the annealing temperature for both Ag
and Cu are $720 \text{ K} - 750 \text{ K}$. The duration of the process is normally 10 minutes. After the
annealing process is finished, the temperature has to be lowered slowly to give atoms
enough time to relax to their energetically favorable places. This is very important to
have an atomically clean and flat surface.
3. On-Surface Metal-Organic Structures

On the surface, metal-coordination chemistry is an active field of research because by introducing metal-organic bonds, distinct two-dimensional supramolecular structures with versatile functionalities can be formed compared to the self-assemblies solely stabilized by intermolecular interactions. In a 3D scenario, metal-organic compounds have been reported to be very promising candidates in information storage\textsuperscript{91} and processing\textsuperscript{92}, catalysis\textsuperscript{93}, energy storage\textsuperscript{94,95} and molecular electronics\textsuperscript{96}. Moreover, the properties of metal-coordination centers have been extensively studied in this scenario and are usually determined by the symmetry of their outermost electron distributions. On a surface, however, this symmetry is often broken due to the constraints enforced by the underlying substrate, and these principles from 3D scenarios are no more valid. Many efforts have been made to bridge this gap\textsuperscript{4,22}, but the underlying principles and the strategies to tailor the metal-coordination structures still need to be further developed.

Commonly, the 2D metal-organic coordination networks can be simply considered as meshes with metal atoms as nodes connecting molecular building blocks via the ligands. The pattern of the networks is mainly determined by the symmetry of the metal nodes\textsuperscript{97} and the molecular building blocks, while the size of unit cell is governed by the ligands\textsuperscript{98–102}. Many metal-organic architectures exploiting various metal nodes and molecular building blocks have been studied\textsuperscript{4,22,97–102}, although a comprehensive understanding of the underlying principles and deliberate engineering of the resulting structures still needs to be further developed and refined. One interesting metal-organic architecture features a grid-like structure with a square unit cell, which can extend over large areas due to the nature of the fourfold symmetry\textsuperscript{103–105}. This fourfold symmetry can be provided by either the metal nodes or the molecules. For a ditopic linear linker, a metal node capable of coordinating to four ligands is necessary to form a network with a square or rectangular unit cell. For a cross-shaped linker, a metal node preferring a two-fold linear coordination or a fourfold coordination can also lead to such a network. Porphyrins, as mentioned above, are promising candidates for self-assembled molecular structures\textsuperscript{5,106–111}. With its intrinsic fourfold nature, thus it is an ideal candidates for building an extended 2D network. Moreover, it can have different number and type of meso-substitutions\textsuperscript{5,103,106,107,112} and thus exhibits various symmetry when coordinating to a metal atom.

The coarse-grained lattice Monte-Carlo simulation technique\textsuperscript{84} is a powerful method for simulating large molecular systems at equilibrium. It has been applied to molecular self-assemblies on metal substrates stabilized by van der Waals interaction\textsuperscript{113}, hydrogen bonds\textsuperscript{114,115} and metal-coordination bonds\textsuperscript{116,117}. By simplifying the 2D self-assembled system, the computational cost is substantially reduced compared to the density functional theory (DFT), which currently is the method of choice in simulating molecular systems. In addition, it not only can replicate the 2D structure observed experimentally\textsuperscript{115}, but can also help to predict the possible pattern and the lowest en-
3. On-Surface Metal-Organic Structures

energy state\textsuperscript{116,118}. Furthermore, it can reproduce different phases and determine their stable conditions\textsuperscript{114}. For simplicity, the components and their interactions to be considered are usually limited\textsuperscript{114,116,119}. Especially for the porphyrin, due to its more complicated inner structure, the number of intermolecular interactions under consideration is strongly constrained\textsuperscript{117}.

This chapter is divided into two parts. In the first part, metal-organic coordination networks formed by two porphyrin species with different meso-substituents on Ag(111) are presented. Despite their similarity in shapes and ligands, they exhibit distinct behaviors of formation of metal-organic coordination networks. To elaborate this difference, Monte-Carlo simulations were performed. This part was published in the article ‘\textit{Tailoring Large Pores of Porphyrin Networks on Ag(111) by Metal-Organic Coordination}’ in Chemistry - A European Journal\textsuperscript{120}. In the second part, Monte-Carlo simulations are applied to other porphyrin derivatives and more complicated situations and some interesting network structures are obtained.

3.1. Large Pores Metal-Organic networks

Here, two porphyrin derivatives are used to construct metal organic networks On Ag(111). Namely, tetra[(4-cyanophenyl)phen-4-yl]porphyrin (2H-TPCN) with the endgroup biphenylene-cyano at all four meso positions and tetra[(4-pyridylphenyl)phen-4-yl]porphyrin (2H-TPyPP) with the endgroup phenylene-pyridyl at all four meso positions. Their structural models are shown in Fig. 3.1a and e.

3.1.1. Self-Assemblies of 2H-TPCN and 2H-TPyPP on Ag(111)

After depositing molecules onto the Ag(111) surface at room temperature, both type pf molecules self-assemble into highly-ordered dense-packed islands as shown in Fig. 3.1b and f. Both 2H-TPCN and 2H-TPyPP are characterized by a cross-shaped feature with a depression in the middle. High resolution images of 2H-TPCN and 2H-TPyPP are shown in Fig. 3.1c and g. The donut shape in the middle is assigned to the macrocycle and the legs around it are assigned to the meso-substituents, biphenylene-cyano for 2H-TPCN and phenylene-pyridyl for 2H-TPyPP. The meso-substituents of 2H-TPCN is longer than the one of 2H-TPyPP, resulting in a larger intermolecular distance. The macrocycle exhibits a twofold symmetry and depression in the center, as previously reported for 2H-TPP on the Ag(111) surface\textsuperscript{17}. The twofold symmetry is caused by the steric hindrance between the \( R_1 \) ring with the macrocycle, which results in a saddle-shape deformation of the macrocycle and the rotation of the \( R_1 \) ring out of the horizontal plane\textsuperscript{17,121}. The two upward bent pyrrole rings appear brighter than the downward bent pyrroles and define the main axis of the molecule, shown as green line in Fig. 3.1. The latter is also indicated by the asymmetric appearance of the \( R_1 \) ring in STM images. The \( R_2 \) ring, on the other hand, appears disk-like, indicating a planar adsorption, which is also favored for individual benzene and pyridyl rings on Ag(111)\textsuperscript{122}. This planar configuration of the \( R_2 \) ring is decisive for the distinct coordination behavior of 2H-TPyPP.

Both self-assembled islands of 2H-TPCN and 2H-TPyPP feature a square unit cell with side lengths \( a = (20.4 \pm 0.5) \text{Å} \) for 2H-TPCN and \( b = (18.2 \pm 0.5) \text{Å} \) for 2H-TPyPP.
3.1. Large Pores Metal-Organic networks

Figure 3.1. Self-assembled islands of 2H-TPCN and 2H-TPyPP on Ag(111). a, e) Structural models of the porphyrin derivatives. The higher parts of rotated molecular moieties are highlighted in orange. b, f) STM images of self-assembled, dense-packed islands of 2H-TPCN and 2H-TPyPP. The green lines highlight the molecular axis through the upward rotated pyrroles. A single molecule is outlined as a guide to the eye and the blue squares indicate the unit cells that include one molecule for both compounds. The substrate dense-packed directions are represented by yellow lines. c, g) High-resolution STM images of single 2H-TPCN and 2H-TPyPP molecules. d, h) Structural model of the dense-packed islands showing in b and f. Scan parameters: b) \( U = -1 \) V, \( I = 30 \) pA; c) \( U = -1 \) V, \( I = 70 \) pA; f, g) \( U = -1 \) V, \( I = 0.1 \) nA.

The main axis of both 2H-TPCN and 2H-TPyPP is aligned with the high symmetry directions of the Ag(111) surface. Despite the azimuthal preference induce by the Ag(111) surface, the arrangements of both 2H-TPCN and 2H-TPyPP are not commensurate with respect to the Ag(111) surface, indicating a weak interaction between the substrate and molecules.

3.1.2. Metal-Organic Networks

Copper atoms are deposited onto the Ag(111) surface to enable the formation of metal-organic networks. For 2H-TPCN, highly ordered networks are formed and can extend over hundreds of square nanometers (Fig. 3.2). The network has a rectangular unit cell of size \( c = (21.9 \pm 0.5) \) Å and \( d = (24.0 \pm 0.5) \) Å (blue rectangle). Fig. 3.2 shows a high resolution image of the network, where TPCN unit can be easily identified (red contour). The corresponding model of the network is shown in Fig. 3.2. The TPCN units lie on the corner of the rectangle with their legs pointing to the center. A copper atom is assigned to be located in the center and forms coordination bond with four carbonitrile termini around it. This results in a 1:1 stoichiometric ratio between TPCN and Cu. The projected Cu-N distance is \( 1.6 \pm 0.5 \) Å, in agreement with literature. As reported previously, the metal atom for coordination can not be resolved in STM images. However, there is an indirect fingerprint of the formation of the coordination bond. The coordinated endgroups of TPCN appear brighter than those that are not coordinated. With many preparations, the fully reticulated metal-organic network seems to be the
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Figure 3.2. Evolution of metal-organic networks of 2H-TPCN upon deposition of Cu atoms. a) After deposition of small amount of Cu atoms, dense-packed islands (left) and fully reticulated 2D metal-organic coordination network of 2H-TPCN coexist on Ag(111). b) The corresponding structural model is of a. c) Deposition of more Cu atoms converts the remaining dense-packed islands into 2D metal-organic coordination network. The inset shows a magnified image of the 2D coordination network. A single molecule is outlined as a guide to the eye and the unit cell is marked by a blue square. d) The corresponding structural model is of c. The yellow stars represent the substrate dense packed directions. Scan parameters: a) and c): $U = 0.7$ V, $I = 50$ pA.

only expression of TPCN engaging with copper atoms. Coexisting of copper clusters, dense-packed organic islands and fully reticulated metal-organic networks coexist on the surface confirms that no other architectures involving both TPCN and Cu will form\textsuperscript{126}.

After deposition of Cu adatoms onto the Ag(111) surface with a submonolayer of 2H-TPyPP, two metal-organic networks are observed depending on the local density of Cu adatoms. The first network evolves after deposition of small amounts of Cu adatoms onto the Ag(111) surface with a submonolayer of 2H-TPyPPi, as shown in Fig. 3.3. The network has a rhombohedral unit cell with size of $e = 28.0 \pm 0.5$ Å and $f = 18.2 \pm 0.5$ Å and an angle of $60 \pm 1^\circ$. Both sides of the rhombus are parallel to the high symmetry direction of the Ag(111) surface. TPyPP units can be identified easily and are marked with red lines (Fig. 3.3). The corresponding structural model can then be drawn and is shown in Fig. 3.3. Along the direction parallel to the short side of the rhombohedral unit cell, TPyPP tectons are dense-packed the same way as in the dense-packed island introduced in the last section. It should be noted that in the dense-packed island, both sides of the unit cell are not aligned with the high symmetry directions of the Ag(111) surface. Along the direction parallel to the long side of the unit cell, TPyPP tectons form a head-on configuration with two pyridyl endgroups in a linear fashion and is assigned to a pyridyl-Cu-pyridyl coordination bond. Similar twofold metal-coordination coupling motifs are often observed in surface-confined metal-coordination networks\textsuperscript{21,103,123,124,127}. Thus this network will be referred as 1D metal-organic network. The Cu adatoms are again not resolvable here. The only difference between this metal-organic network and the dense-packed islands is that the metal coordination bond is established and replaces the organic bond in one direction. From the azimuthal preference, the substrate clearly has some influence on the structure of the network. The dense-packed direction is different from the directions in the dense-packed
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Figure 3.3. Evolution of metal-organic networks of 2H-TPyPP upon deposition of Cu atoms. a) After deposition of small amount of Cu atoms, 1D metal-organic coordination network of 2H-TPyPP emerged. Along the direction f, 2H-TPyPP still packs densely and along the other direction e, 2H-TPyPP form twofold metal coordination bonds. b) As more Cu atoms were deposited, fully reticulated metal-organic metal coordination networks emerged within 1D networks. Along both directions, 2H-TPyPP are engaged forming a linear twofold metal coordination bond. c) After deposition of excessive Cu atoms, only 2D metal-organic networks are observed on Ag(111). d.f) Corresponding structural models of a,b and c. Single molecules are outlined in red and the unit cell is marked by a blue square. The yellow stars represent the substrate dense packed directions. Scan parameters: a, b): $U = -0.7$ V, $I = 100$ pA; f) $U = 0.9$ V, $I = 80$ pA

island, suggesting the formation of the coordination bond is energetically more favorable and forces molecules rotating from their original orientation in the dense-packed island. The network has a 1:1 stoichiometric ratio between Cu adatoms and TPyPP adatoms.

After depositing more Cu adatoms, the local ratio between Cu adatoms and TPyPP exceeds 2:1. The 1D metal-organic network evolves into a metal-organic network with a square unit cell with a side length of $e = 28.2 \pm 0.5$ Å, as shown in Fig. 3.3. Along both directions of the unit cell of this network, TPyPP units form a head-to-head configuration, resulting in a network with pore size much larger than of 1D metal-organic network. Comparing to the 1D metal-organic network, remaining organic bonds are transformed into pyridyl-Cu-pyridyl coordination bonds. Thus all four pyridyl termini of TPyPP are connected with the adjacent molecules by pyridyl-Cu-pyridyl coordination motifs. This metal-organic network is fully reticulated and is referred as 2D
metal-organic network. The projected N-Cu distance amounts to 1.9 ± 0.5 Å, in agreement with the previous reports\textsuperscript{21,124}. One side of the unit cell remains unchanged and parallel to the high symmetry direction of the Ag(111) surface while the newly evolved one is perpendicular to it. Similar to the 1D metal-organic network, TPyPP tectons are rotated by 45° compared to the dense-packed arrays, indicating a weak molecule-substrate interaction. The network can extends over hundreds of square nanometers and exhibit long-range periodicity, however, the high-resolution STM image (Fig. 3.3) shows that TPyPP units deviate from a perfect cross and thus resulting in a variation of the pore size. This local irregularity is mainly attributed to the flexibility of the pyridyl-Cu-pyridyl coordination bond\textsuperscript{21,123}. This network with a variety of pore shapes deviating from a perfect square is classified as a 2D short-range disordered crystalline network\textsuperscript{128,129}. To our knowledge, the network with such a large pore with an average size of 340 Å\textsuperscript{2} is unprecedented for homomolecular surface-supported porphyrin-based architectures.

On the same sample, the intermediate network transitioning from 1D metal-organic network into 2D metal-organic network can be observed. Fig. 3.3 shows within the 1D metal-organic network, 2D metal-organic networks are evolved. Here, the local density ratio between Cu/TPyPP is above 1:1 but still below 2:1. The extra Cu adatoms begin to form metal-coordination bond with unreacted pyridyl termini from 1D metal-organic network, transforming remaining organic bonds into pyridyl-Cu-pyridyl coordination motif row by row.

The TPyPP coordination follows a hierarchic pathway upon increasing the density of Cu adatoms, from 1D metal-organic network to 2D metal-organic network. On contrary, TPCN directly forms 2D reticulated metal-organic network, which is also the only existing motif. Another major difference of the coordination behaviour between TPyPP and TPCN is that in fully reticulated metal-organic network a Cu adatom can engage with four cyano termini of TPCN and forms a fourfold metal-coordination bond while it only engages with two pyridyl termini of TPyPP and forms a twofold metal-coordination bond in a linear fashion. This difference mainly originates from the spatial constraint induced by the flattened pyridyl endgroup of TPyPP, whose steric hindrance forbids the coordination of Cu adatom with more than three pyridyl endgroup. For TPCN, although the outermost phenyl ring is also flat, the extended cyano group is slender enough to have four of them fitting into a fourfold coordination motif with one Cu adatom. For TPyP, which does not have the phenyl ring between the macrocycle and the pyridyl ring, fourfold coordination with Cu adatoms is also observed. This is because the pyridyl ring is directly linked to the macrocycle and due to the saddle-shaped conformation it is rotated out of the horizontal plane, thus becoming slender. In this sense, the pyridyl–phenylene substitution of the de novo-synthesized 2H–TPyPP providing rotational flexibility to the termini is crucial for the formation of linear pyridyl–Cu–pyridyl binding motifs and for the construction of large-pore Cu-mediated coordination networks. Spatial constraints at the coordination center, which can be tuned by the geometric footprint of the terminal moieties, can be deliberately exploited to control the coordination number and thus the topology of the network architectures. Additionally, the Monte Carlo simulations show that the spatial constraints of the pyridyl groups not only influence the final architectures, but also induce an energetic preference for
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the formation of 1D coordination chains and therefore are the origin of the hierarchic assembly protocol in the case of TPyPP.

As for the metal center, from the experimental results Cu adatoms can form coordination bonds to two\textsuperscript{21,123,124,130}, three\textsuperscript{131}, or four nitrogen atoms and without steric hindrance it favors a fourfold coordination to the nitrogen termini of porphyrins on Ag(111). This is very different from other 3d metals such as Co, which exhibits a random expression of both three- and fourfold symmetries with TPCN molecules on Ag(111)\textsuperscript{132}. This implicates that the symmetry of the resulting metal-organic architecture is not only determined by the molecular symmetry, but also by the preferred coordination geometries of the metal nodes.

3.1.3. Monte Carlo Simulation

Figure 3.4. a,b) Chemical models of TPCN and TPyPP overlaid with models for Monte-Carlo simulation. c,d) Schematic models showing the intermolecular interactions included in the simulation.

The experimental results reveal striking differences in the formation of metal–organic coordination networks and the corresponding coordination motifs, despite the similarities of the systems, that is, mononuclear Cu nodes coordinated to nitrogen of quasi-fourfold symmetric porphyrins on Ag(111). To rationalize the experimental findings, Monte Carlo modeling was performed, as structure formation is known to be correctly reproduced in such simple simulations for a variety of functional tectons, including porphyrins\textsuperscript{23,112,117} and phthalocyanines\textsuperscript{133}. For these simulations, both TPyPP and TPCN are represented by a fourfold symmetric cross and metal adatoms are depicted as circles (Fig. 3.4), following a representation previously introduced for similar systems\textsuperscript{134}. Within the description of this simplified model, the two porphyrin species are identical. To distinguish the two modules, TPyPP is restricted to form onefold coordination and twofold coordination in linear fashion, as observed in the experiment, and TPCN is allowed to engage in one-, two-, three-, or fourfold coordination. Two interactions are considered here, namely van der Waals interaction and metal coordination bond, as shown in Fig. 3.4.
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Snapshots of the Monte Carlo simulations are depicted in Figure 3.5. Naturally, the metal-free dense-packed islands are identical for the two species (Figure 3.5). After including a small amount of adatoms, TPyPP forms metal-organic chains (Figure) that evolve into an open-porous 2D coordination network (Figure 3.5) when more metal is added. In contrast, for TPCN the addition of small amounts of adatoms already leads to the formation of a 2D coordination network (Figure 3.5). Importantly, the simulations reflect all assemblies observed experimentally and correctly reproduce a key difference...
between TPyPP and TPCN, namely the fact that 1D metal-organic chains emerge exclusively from TPyPP, even though they would be allowed for TPCN.

![Figure 3.6](image)

**Figure 3.6.** a, b) Phase diagrams of the MC simulations for fixed interaction ratio $E_o / E_c$ and variable temperature and variable unit ratio (metal to molecule ratio). c, d) Phase diagrams for a fixed number of units with varying temperature and varying interaction strengths.

To further characterize the system, additional Monte Carlo simulations were carried out for different interaction energy ratios $E_o / E_c$ (van der Waals interaction vs. metal-coordination). The results are summarized in phase transition diagrams for TPyPP and TPCN, shown in Fig. 3.6 k and l, respectively. To generate these plots, the resulting structures are color-coded: blue for the dense-packed organic network, red for the 1D coordination chains, and green for the 2D metal-organic network. Note that the 2D fully reticulated coordination networks are different for the two species (TPyPP in a twofold fashion and TPCN in a fourfold fashion), despite being both represented in green (see insets in Figure and 3.5, respectively). The most prominent difference between the two diagrams is the lack of 1D coordination for TPCN — although it is allowed — regardless of the ratio of $E_o / E_c$ evidenced by the lack of red in Fig. 3.5. Apparently, a separation of organic islands and fully reticulated fourfold coordinated arrays is energetically favored over mixed organic / twofold coordination assemblies. Furthermore, the simulations yield no 1D metal-organic chains for TPCN at any probed temperature (see 3.6), thus ruling out any influences of the experimental preparation conditions. The TPyPP structure formation proceeds via 1D chains (red, Figure 3.5) for all calculated $E_o / E_c$ ratios, despite the possibility to directly form 2D coordination networks. Therefore, in
the case of terminal groups expressing only in a twofold coordination motif, the ob-
served chaining seems energetically clearly favored even for large relative values of $E_c$. 
In the modeling, the only difference between the two species is the permitted coordina-
tion geometry at the node; no effects of the electronic structure are considered. As the 
simulations qualitatively reproduce the experimentally observed networks, it suggests 
that the different formation pathways and the resulting network topologies are mainly 
determined by distinct spatial constraints at the coordination center.

3.2. Additional Monte-Carlo Simulations

As showed in the previous section, Monte-Carlo simulations can be very helpful in 
the investigation of molecular self-assemblies on well-defined surfaces. Furthermore, 
with some experiences from the comparison of previous simulations with experimental 
results, more realistic models can be proposed and predictions of the structure of new 
molecular systems can be made. In this section, Monte-Carlo simulation is further 
extended to different, but similar, porphyrin derivatives. More variable parameters are 
introduced into the system, leading to more sophisticated models and some interesting 
results.

3.2.1. Molecular Models

More Types of Meso-Substituents. In the last section, Monte-Carlo simulations 
of two porphyrin derivatives, TPyPP and TPCN, were presented. Both molecules are 
represented by a cross with a leg length equal to one lattice site. For TPyPP, its pyr-
ridyl endgroup is only allowed to form a twofold metal-coordination bond with another 
pyridyl endgroup in a linear fashion. For TPCN on the other hand, its cyano endgroup 
can form cross-shaped fourfold metal-coordination bond with other three cyano-ended 
TPCN molecules. To differentiate these two endgroups, they are assigned with different 
numbers in the simulation, as well as different colors (see Fig. 3.7).

In addition to these two meso-substituents, more meso-substituents with different 
properties can be proposed, as shown in Fig. 3.7. Typically, the properties of these meso-
substituents are determined by two factors, the ability to form the metal-coordination 
 bond and the strength of vdW interactions. For the metal-coordination bond there 
are three situations: (i) able to form metal coordination bond; (ii) not able to form 
metal coordination bond and (iii) not allowed to stay next to a metal atom. For vdW 
interactions, there are only two possibilities for simplicity: i) strong enough to attract 
two molecules; ii) very weak to be negligible. A detailed description of these meso-
substituents is listed in Fig. 3.7. For some of them, examples of their corresponding 
molecular representation are showed in the last column.

meso-substituents 2 and 3 are already introduced as the representations of the end-
group of TPyPP and TPCN respectively. Meso-substituents 4 and 5 can not form the 
metal-coordination bond with a metal atom and could be phenyl terminated and tert-
butylphenyl group, respectively. Meso-substituents 6 and 7 not only are inactive to 
the metal atom, but even forbidden to be next to a metal atom. An example is the 
endgroup terminated with a large bulk structure, such as a propyl group. The vdW
interaction exists when the T-type configuration is present. Meso-substituent 8 is similar to 2 but with a different bonding energy $E_{c2}$. This could either be because of the different length of the metal-coordination bond or a different coordination geometry. For meso-substituent 9, multiple coordination to the same metal atom is forbidden due to the steric hindrance. However, it can coordinate to the metal atom which is bonded to a slender ligand, such as a cyano group. Although these meso-substituents have different length, for the simplicity, they are all considered to have a length equal to one lattice site. Two colors are assigned to the macrocycles (11 and 12), in order to get a clearer view of the result, when two types of molecules are present. Combining these endgroups, different molecular models representing distinct molecules can be made.

**Breaking the Symmetry.** Until now, all models have a fourfold symmetry, which means they always have the same substituents at their four meso-positions. The reason behind this is that this assumption makes the coding much easier. In actual situations, this assumption is too strong and greatly limits the molecular system that can be investigated. If only meso-substituents at opposite meso-positions are the same, the symmetry of the molecule is then reduced from fourfold to twofold, an example would be the porphyrin derivative used in $^{21}$ (also see Fig. 3.8). Another example with reduced symmetry is the one with same endgroups at two adjacent meso-positions, an example can be found in ref. [20].

**More than one Molecule.** In the previous simulations, only one type of molecule is included. As shown in $^{20}$, combining a line-shaped porphyrin derivative with a cross-
shaped porphyrin derivative can achieve larger cycle on Ag(111) surface by having the line-shaped derivative extending the side length. Following the same idea, combining molecules with different functional meso-substituents may lead to distinct metal-organic architectures.

Figure 3.8. Monte-Carlo representations and corresponding possible molecular structures.

**Summing up.** With all the above-mentioned ammunitions ready, new molecular systems for Monte-Carlo simulation can be proposed, as shown in Fig. 3.8. The colors of the meso-substituents have already been specified in Fig. 3.7. In the remainder of this section, Monte-Carlo simulation results for these molecules are presented and discussed.

### 3.2.2. Applying to Known Systems

**Figure 3.9.** Self-assemblies of porphyrin derivatives obtained from STM measurements and Monte-Carlo simulations. a-d) STM images from experiments. a,c,d from ref.20 and b from ref.21. e-h) Snapshots from Monte-Carlo simulations.
3.2. Additional Monte-Carlo Simulations

Firstly, the molecular system that have already been studied experimentally\textsuperscript{20,21} are investigated with Monte-Carlo simulations, i.e. porphyrin modules 3, 5 and 7 (see Fig. 3.8). The results are shown in Fig. 3.9. For porphyrin module 3, only one meso-substituent terminated with pyridyl ring is active. In both experimental (Fig. 3.9a) and simulation (Fig. 3.9) results, a metal coordination bond is formed between two porphyrin 3, resulting in dimers with two pyridyl terminated endgroups pointing at each other. For porphyrin module 5, two meso-substituents at the opposite positions are terminated with pyridyl rings. In the experiment, one-dimensional chains are formed as shown in Fig. 3.9b and f. For the porphyrin module 7, pyridyl rings are at the end of two adjacent meso-substituents. Supramolecules consisting of a different number of 7s were observed due to the flexibility of the meso-substituents. In Monte-Carlo simulation, only the square supramolecule consisting of four porphyrin 7s is formed. This is because in the Monte-Carlo simulation the molecular model is set to be a rigid cross. Indeed, because of this assumption not all supramolecules are replicated, but the essence of the metal-coordination behavior of porphyrin 7 is captured by the simulation and is sufficient for our purpose. When both porphyrin 5 and 7 are deposited on the surface, supramolecules with larger cavities were observed in experiments (Fig. 3.9d). In Fig. 3.9h, Monte-Carlo simulation of mixed 5 and 7 also produces similar large supramolecules. To summarize, the Monte-Carlo simulation are in good agreement with the experimental results for porphyrin modules 3, 5, 7 and mixed 5 and 7. This confirms the validity of the proposed molecular models and the properties assigned to the endgroups.

3.2.3. Predicting Unknown Systems

Predicting the self-assembled structures from the precursor has always been pursued by scientists. On the one hand, it can save a lot of experimental time of trying all the precursors, and on the other hand, successful prediction can provide a deeper understanding of the properties regarding the intermolecular interactions and molecule-substrate interactions. Monte-Carlo simulation has been proven to be a promising candidate for this task for large molecular systems due to its low needs of computational powers. Here, the Monte-Carlo simulations are performed in an attempt to predict the self-assembled structures of molecules that have not been studied experimentally.

Firstly, porphyrin modules 4, 6 and 8, whose active meso-substituents are terminated with cyano groups, are simulated as the comparison experiments for porphyrin modules 3, 5 and 7. The results are shown in the first row of Fig. 3.10. For porphyrin module 4, it forms a tetramer with one metal atom by forming four metal-coordination bonds, which resembles the dimer formed by the porphyrin module 3. Porphyrin module 6 forms 2D metal-organic coordination networks, similar to the networks formed by the TPCN with copper adatoms on Ag(111). The only difference is that no metal atoms sit in the center pointed by four tert-butylphenyl groups. For porphyrin 8, 1D coordination polymer is formed, which consists of two rows of 8 at the sides and one row of the copper adatom in the middle. Each adatom is fourfold coordinated to the neighboring porphyrins. This structure may be a promising candidate for nanowires. When both 6 and 8 are present on the surface, the 2D coordination networks formed by 6 and 1D coordination lines formed by 8 coexist. No new regular structures are observed. This is probably because
3. On-Surface Metal-Organic Structures

Figure 3.10. Self-assemblies of porphyrin derivatives obtained from STM measurements and Monte-Carlo simulations. a-d) STM images from experiments. a,c,d from ref.\textsuperscript{20} and b from ref.\textsuperscript{21}. e-h) Snapshots from Monte-Carlo simulations.

Both structures have similar energy and none of them is energetically more favorable. The self-assembled structures of porphyrin modules, 4, 6 and 8, are very distinct from the porphyrin modules 3, 5 and 7. The structural differences solely originate from the distinct coordination behaviors of the cyano group and the phenyl group and it has already been discussed in the section 3.1.

Moreover, instead of using the inert tert-butylphenyl group (5), biphenylene group (4) can be equipped and supposed to make vdW forces more prominent. The results for porphyrin modules 9, 11 and 13 are shown in Fig. 3.10e-h. Comparing to the porphyrin modules 3, 5 and 7, the previous 1D self-assemblies now can extend in the other direction via vdW interactions. Moreover, for porphyrin module 13, a different network stabilized by both metal-coordination bond and vdW forces is observed (red square in Fig. 3.10g). Each cavity is surrounded by six molecules, that form four metal-coordination bonds, and two vdW bonds. Mixing modules 11 and 13 results in coexistence of 1D metal-organic metal-coordination networks, as well as rectangular supramolecules (see Fig. 3.10h). Results of porphyrin modules 10, 12 and 14 are shown in the third row of Fig. 3.10. The vdW interactions compete with the metal-coordination bonds, resulting in a variety of locally ordered structures. For porphyrin 10, similar structures as for porphyrin 9 are formed, as well as the fourfold coordinated tetramer as for porphyrin 4. For porphyrin 12, fourfold metal-coordination networks are formed, similar to
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Figure 3.11. Self-assemblies of two porphyrin derivatives from Monte-Carlo simulations. a) TPyPP (1) mixed with TPCN (2). b) TPyP mixed with porphyrin module 6. c-d) Possible structural models for the assemblies shown in (a) and (b). Certain bending of the meso-substituents or rotation of porphyrin 1 are needed to realize these predicted structures.

It has been shown in the previous section that TPyPP forms 2D metal-organic coordination networks with large pore size, which is a promising candidate as host for the accommodation of guest molecules. Here, porphyrin module 1 (TPyPP) is mixed with porphyrin module 2 (TPCN) and 6, respectively. Fig. 3.11a shows the self-assembled structure from the Monte-Carlo simulation. Porphyrin module 1 forms the same 2D
Figure 3.12. Monte-Carlo simulation for large porous network. a) Monte-Carlo simulation of porphyrin 1 mixed with 5. b) Monte-Carlo simulation of porphyrin 1 mixed with 15. The bond strength of phenylpyridyl group to the copper atom is set to 20. For both cases, no networks with extended pores are formed.

metal-organic coordination network as shown in the section 3.1.3. Most of the pores are occupied by the porphyrin 2, and some empty cavities are also present. Porphyrin 1 coordinates to the copper adatom in a twofold linear fashion, while porphyrin 2 sit in the pore coordinates to the four neighboring copper adatoms. The slender cyano group makes this fourfold coordination configuration possible. Similar structures are obtained when mixing porphyrin 1 and 6. The porphyrin 1 forms the 2D coordination network again, acting as the support. The porphyrin 6 are accommodated in the pores. Since 6 has only twofold symmetry comparing to 1, there are two possible orientations of it inside the pores. In the Monte-Carlo simulation, the molecular models are simplified, and the difference of the length of the meso-substituents are not taken into account. If the real size of the porphyrin modules 1, 2 and 6 are considered, the cyano terminated meso-substituents of porphyrins 2 and 6 are longer than the pyridyl terminated meso-substituents of the porphyrin 1. As a result, porphyrin modules 2 and 6 can not fit into the square pores of the networks formed by porphyrin 1. However, in real situation molecules are not strict cross like as assumed in the simulation, but have a certain degree of flexibility. For example, the meso-substituents can slightly bend from the perpendicular position, thus forming an angle of 120° or 60° with neighboring substituents, as reported in ref. [20]. This has also been observed by TPCN in the fully reticulated 2D metal-organic coordination networks and TPyPP in the quasi-crystal like the structure of the fully reticulated 2D coordination networks (section 3.1). Taking this flexibility of porphyrin 1 into account, a possible self-assembling structure can be proposed and is shown in Fig. 3.11c. The meso-substituents of porphyrin 1 are laterally bend, results in an opening angle of adjacent meso-substituents of, for example, either 120° or 60°. Thus, in this 2D network pores surrounded by the porphyrin 1 with the large opening angle are larger. As a result, their neighboring pores have a smaller size. The porphyrin 2 can
3.2. Additional Monte-Carlo Simulations

thus be accommodated in the large pores. For porphyrin 6, a packing order similar to the mixed 1 and 6 is also possible. Moreover, noticing that the tert-butylphenyl group occupies less space, thus another packing scheme can exist, which does not need any conformation of porphyrin 1, but only a slight rotation of it, as shown in Fig. 3.11d. The porphyrin 6 can fit into the pores with its long axis parallel to the long side of the rectangular cavity. It also should be noted here that metal atom is coordinated to two phenyl rings and one pyridyl ring. The angle between the phenyl ring and the pyridyl ring is less than $90^\circ$. Whether the steric hindrance will forbid this configuration or not, needs to be examined experimentally.

![Monte-Carlo simulation for large porous network](image)

**Figure 3.13.** Monte-Carlo simulation for large porous network. a) Figure from ref. [135] showing the metal coordination network with extended pores. 2) Proposed schematic model of the network formed by porphyrin 1 and 16 c) Monte-Carlo Simulation of porphyrin 1 and 16. d) Monte-Carlo Simulation of porphyrin 1 and 16. The bond strength of phenylpyridyl group to the copper atom is set to 30.

An interesting property of the 2D metal-organic coordination network formed by TPyPP is the large pores, which can serve as templates anchoring other molecules. The larger the pore size, the larger are the molecules that can be trapped. For monomolecular systems, construction of such a network requires molecules with long legs, meaning a larger molecular mass. Deposition of such a molecule needs a high temperature, which often results in the dissociation of the molecule. Therefore, a straightforward way to enlarge the pore size is to introduce another linear molecule to extend the
side of the pore, for example by introducing the porphyrin module 5, the size of the supramolecules formed by porphyrin 7 can be enlarged\textsuperscript{20}. Thus, an extended network may be formed by mixing porphyrin 5 and 1 following the same protocol. However, Monte-Carlo simulation (Fig. 3.12a) shows this is not the case. Instead of the network with large pores, irregular networks with pores of various sizes emerge, as well as 1D lines and 2D porous networks. No extended regular networks with larger pore size are formed. The origin of this irregular shape may be the variable number of porphyrin 5 that are able to be incorporated between two porphyrin 1, as observed by mixed porphyrins 1 and 5 (Fig. 3.10d and ref. [20]). To overcome this problem, the number of the incorporated porphyrin module, here porphyrin module 5, should be fixed. One way that may tailor this problem is to use porphyrin 15 instead of 1. The active nitrogen terminated endgroups of porphyrin 15 are assumed to have different strength of the metal-coordination bond to copper atoms than the phenylpyridyl group, which will influence the preference of the coordination behavior. An example is shown in Fig. 3.12b. Here the metal-coordination bond strength $E_{c1}$ for porphyrin 15 is set to 20 and the bond strength $E_{c2}$ for porphyrin 5 is 40. Clearly, the formation of 1D chains constructed by porphyrin 5 is more favored. By varying $E_{c1}$, however, no networks with extended pores are formed. Another possible way is to introduce spatial constraints. In ref. ??, such a network is constructed with the help of an on-surface synthesized ligand, as shown in Fig. 3.13a. A "dogbone" like molecule, both sides equipped with a terpyridyl group, is co-deposited with TPyP on Ag(111) surface. After supplying iron atoms on the surface, metal-organic coordination networks with large pores are formed, where TPyP acts as fourfold nodes and the "dogbone" molecules connecting these nodes. Due to the large size of the terpyridyl group, an adatom already coordinated to a terpyridyl group can no more coordinate to another terpyridyl group, but it is still possible to coordinate to a pyridyl or cyano group. Therefore, the 'dogbone' molecule will not form 1D coordination chain by itself, as a result between two TPyP nodes only one "dogbone" molecule is possible to fit in. The same protocol can be adopted here, and the 'dogbone' molecule is replaced by porphyrin module 16 equipped with two terpyridyl groups. Fig. 3.13b shows the structural model of the expected network. From the simulation, combining porphyrin 16 with 1 indeed results in this structure as shown in Fig. 3.13c. However, it can be noted that although the number of the porphyrin 16 between the nodes can not exceed one, but it can be zero. Thus prolonged rectangles as well as purely porphyrin 1 formed 2D network also emerged. Noticing that three N-Cu metal-coordination bonds are formed between the terpyridyl group and the copper atom, thus this total bond strength may be much stronger than the single pyridyl-Cu coordination bond. As shown in Fig. 3.13d, by reducing the bond strength between the phenylpyridyl group and the copper atom to 30, indeed the network with extended pores is formed. This means distinct bond strength and the spatial constraint are both necessary for the construction of such a network.

In this section, Monte-Carlo simulations are applied to various porphyrin derivatives. With the abstraction of several meso-substituents, many unexplored porphyrin systems can be investigated. By equipping individual porphyrin with more than one type of meso-substituents, networks with distinct symmetries can be simulated. By including more than one type of molecules in the simulation, more delicate networks can be investigated. Such a systematic investigation of porphyrin-based metal-organic architectures
has not been done so far. Although many interesting results are obtained from the simulation, they may be meaningless if any of the assumptions is invalid. Here, the simulation are tightly related to the experiments, by regularly comparing the simulation results with experimental results. This also thanks to the many experimental works that have already been done for porphyrins. This close relation to the experiment is also an specialty of this work. Still, the abstractions and assumptions proposed in this thesis always need more inputs and comparisons from/with experiments.

3.3. Summary

In this chapter, coordination behaviors of porphyrin derivatives to copper atoms on Ag(111) were investigated experimentally by STM and theoretically by Monte-Carlo simulation. With the slight difference in the meso-substituents, TPCN and TPyPP exhibit distinct coordination behavior with copper atoms. TPCN directly forms 2D fully reticulated metal-organic coordination networks with each copper adatom coordinated to four adjacent TPCN units. For TPyPP, as the density of copper atoms on the surface increases, TPyPP evolves from 1D to 2D metal-organic coordination network. The distinct behavior is attributed to the steric hindrance of the flat phenyl ring, which makes TPyPP only engage with copper adatoms in a linear twofold configuration, and Monte-Carlo simulation confirms this suggestion. Afterwards, Monte-Carlo simulations were applied to more porphyrin derivatives. Firstly, Monte-Carlo simulations are performed for porphyrins that have already been studied experimentally and thus validate the proposed molecular models. Afterwards, unexplored molecular systems were simulated. It showed that mixing TPyPP and TPCN results in a 2D TPyPP constructed coordination network with TPCN sitting in the pores. It also demonstrated that large porous networks can only be formed when utilizing meso-substituents that present both the spatial constraint and different bond strength. The systematic investigation of porphyrin-based metal-organic architectures using Monte-Carlo simulation provides us much information regarding the coordination behavior of porphyrins on the weakly interacting substrate and can help us gain understanding of the coordination mechanism and the design of more elegant precursors.
4. On-Surface Reactions

Recently, on-surface synthesis has been shown as a promising way to fabricate atomically-precise covalently bonded nano-architectures. These well-defined structures are essential for the construction of novel molecular materials with specific functionalities\textsuperscript{26,136}, molecular electronics\textsuperscript{4,157,138} and molecular machines\textsuperscript{139}. Many efforts have been made to fabricate well-defined nanostructures\textsuperscript{140–147}. Special efforts were dedicated to the construction of graphene nanoribbons with various edge topologies, such as armchair\textsuperscript{26,28,29}, zigzag\textsuperscript{27}, chevron-type\textsuperscript{26,142,148} and modified zigzag edges\textsuperscript{27,30,31}. Ullmann coupling\textsuperscript{149,150} is up to now the most successful method for building such nanostructures. With pre-defined connection points, molecules can be linked in a controlled scheme, for example, the well-known 7-armchair graphene nanoribbon (7-AGNR) is synthesized by coupling 10,10'-dibromo-9,9'-bianthryl (DBBA)\textsuperscript{26}.

Together with the advent of graphene science, an important chapter in organic chemistry has opened exploring the precise synthesis of extended polycyclic aromatic hydrocarbons (PAHs). Large PAHs, as represented by hexa peri-hexabenzocoronene (HBC) with \(\pi\)-conjugated structures extending over 1 nm, can be regarded as structurally defined, nanoscale cutouts of graphene, namely nanographene molecules\textsuperscript{26,151,152}. Such systems can serve as platforms for investigating the physical and chemical properties of graphene upon heteroatom doping or other structural modifications.

Compared to metal-organic coordination networks, covalently coupled nanostructures may exhibit higher stability against temperature variations and mechanical disturbances and provide new prospects to be exploited in applications. Also, in a 2D scenario, imaging the structure of an individual molecular unit is possible in an ultra-high vacuum environment with STM and nc-AFM, which is impossible for a solution environment\textsuperscript{54,146}. Furthermore, thanks to the constraints enforced by the substrate, molecules that are hard to synthesize in a traditional solution environment can be constructed on the surface with bottom-up methods\textsuperscript{152}. However, covalently coupled nanostructures also suffers some obvious drawbacks. The covalent coupling is typically not reversible, so once the bonds are formed, whether wanted or not, they can not be broken easily. Thus, large-scale defect-free covalently bonded structures are difficult to achieve. This nature also makes the formation of ordered structures extending in two directions very hard to synthesize. Thus a significant challenge of utilizing surface-assisted reactions is to gain a better understanding of the reaction mechanism on surfaces and design of better reaction routes.

In this chapter, reactions of three molecules, i.e. bromo-tetracene (BT), dibromo-tetrakis[3,5-di(tert-butyl)phenyl]-biporphyrin (DBTBP) and dibenzo-9a-azaphenalene (DBAP) salts with two different substitutes, on Ag(111) are investigated by STM and nc-AFM. Firstly, the covalent coupling of Bromo-tetracene (BT) through the radical is introduced. Afterward, the attempt of forming porphyrin tapes using DBTBP molecules via Ullmann coupling is presented. In the next part, the solution chemistry of azome-
4. On-Surface Reactions

thine ylides (AMYs) is tested on Ag(111) with Dibenzo-9a-azaphenalene (DBAP) salts.

4.1. Bromo-tetracene (BT)

Functional molecular units equipped with carbon-halogen bonds can form covalently coupled nanostructures in a controlled way via Ullmann-coupling\textsuperscript{26,145,149,153–155}. By changing the position and number of the halogen atoms, various nano-architectures can be constructed, such as linear chains and 2D arrays\textsuperscript{26,154,156,157}. Conjugated organic layers consisting of aromatic molecules are of special importance in electric conduction\textsuperscript{158}, light-sensing\textsuperscript{107,159} and energy conversion\textsuperscript{160,161}. Reactions of 5,11-dibromo-tetracene have been studied on Ag(110)\textsuperscript{162} and Cu(110)\textsuperscript{163} and no covalently bonded networks were formed. In addition, on Cu(110) structures that are not covalently coupled at halogenated positions were observed and were attributed to radical migration. To simplify the situation and clarify the reaction behavior of halogenated tetracene systems, tetracene halogenated only at one position, 5-bromo-tetracene, is employed and the resulting products are characterized by both STM and nc-AFM.

5-bromo-tetracene (BT) molecules were deposited by molecular beam evaporation at 350 K on Ag(111) kept at 290 K. Loosely packed islands, as well as individual molecular units, were observed on the surface (Fig. 4.1). Three different species can be identified and are outlined with green, cyan and red color, respectively. In Fig. 4.1b, the contrast is adjusted, such that bright dots between molecules (pointed by black arrows) can be resolved and are assigned to bromine atoms. No bright dots were observed on terraces. High-resolution STM images of the three species are shown in Fig. 4.1c-e. The single rod-like species is assigned to the tetracene moiety. The other two species (Fig. 4.1d and e) feature two bright rods at the side connected by a central protrusion, but with different geometries. The bright protrusion is assigned to a silver atom and forms a C-Ag-C bond with neighboring two BT units. Similar structures have been observed for 5,11-dibromo-tetracene on Cu(110)\textsuperscript{163} and Ag(110)\textsuperscript{162}. The difference between these species originates from the asymmetric position of the bromine atom at the tetracene.

For species in Fig. 4.1d, the longer part of both BT point to the opposite direction and resembles the letter N, while for species in Fig. 4.1e they are in the same direction and resembles the letter H. The N-like species tends to form islands and sometimes with BT monomers in between. On the contrary, the H-like species prefer to arrange along a direction one by one, resulting in a straight line.

When the surface is heated up to 570 K, the C-Ag-C bond stabilized dimers disappeared, and small islands consisting of oligomers with different shapes emerged (Fig. 4.2a). Bright dots were observed around and also within the islands (pointed by the yellow arrows in Fig. 4.2a) and are assigned to bromine atoms. It is likely that these bromine atoms help to stabilize the islands. In the STM image, BT molecules can be identified from some oligomers, and the structure of the corresponding oligomers can be suggested. However, for some oligomers, electronic interference is observed and hinders a clear determination of the molecular structure\textsuperscript{164}. Thus nc-AFM measurements were performed. The AFM data in the frequency channel are shown in Fig. 4.2 b, d and j. The corresponding STM images are marked with the rectangle in Fig. 4.2 with the same color as their borders. To enhance the contrast of the AFM data, a Laplace filter
4.1. Bromo-tetracene (BT)

Figure 4.1. Self-assemblies of BT on Ag(111). a) Overview STM image shows self-assembled islands of BT. Three different species were observed and are outlines with red, cyan and green, respectively. \((U = 50 \text{ mV}, I = 50 \text{ pA})\). b) STM image with adjusted contrast, so that small round protrusions inbetween molecules can be resolved. These protrusions are assigned to bromine atoms. \((U = 50 \text{ mV}, I = 50 \text{ pA})\). c-e) High-resolution STM images of the three species. Their corresponding structural models are shown beneath the STM images.

is applied, and the results are shown in Fig. 4.2c, e and k. Structural models can be drawn and are shown in 4.2f-h. Three major covalently coupled motifs between two BT units are observed. For the coupling motif shown in Fig. 4.2 b and j, two BT units are covalently coupled perpendicularly, resemble a letter T and letter L, respectively. The dehalogenated carbon atom and the carbon atom from the adjacent benzene ring, either in the center (symmetric) or at the head/tail (asymmetric), form two C-C bonds with two carbon atoms at the head/tail of another BT. For the motif shown in Fig. 4.2d, two BT molecules are covalently coupled in a tilted fashion. Here, an asymmetric motif is shown. It is reasonable to assume that a symmetric motif should also exist on the surface, but due to the limited measurements, it is not observed in our data. Fig. 4.2l and f show the AFM image and Laplace-filtered image of an individual BT molecule.
4. On-Surface Reactions

**Figure 4.2.** a) STM image of BT islands after heating up to 570 K \((U = -15 \text{ mV}, \, I = 7 \text{ pA})\). Bright dots pointed by the black arrows are probably bromine atoms. The colorful rectangles mark the area measured with nc-AFM. The obtained AFM data are bordered with same color. b,d,j,e) AFM data in frequency shift channel. c,e,k,m) Laplace filtered AFM data. f-i) Corresponding structural models drawn from Laplace filtered data.

Furthermore, some larger oligomers observed do not only contain intact BT units (Fig. 4.2j and k), indicating that at this annealing temperature BT molecules may already dissociate into small molecular fragments.

In Fig. 4.2, all the coupling motifs involve one and only one radical generated by the dehalogenation. Actually, from the limited STM and AFM data of this sample, no polymers were observed, that do not involve any radical at the debrominated carbon position. Thus radical migration\^{162,163} and dehydrogenative coupling\^{165} at this temperature may be excluded, which will lead to the formation of polymers with a variety of configurations. This leaves only the reaction path that involves firstly the side-to-head / tail radical coupling and subsequent cyclization, as shown in Fig. 4.3. In the first row, four engaging configurations of two BT molecules are shown. Similar to the dibromo-tetracene on Cu(110)\^{163}, no oligomers with adjacent rows covalently coupled were observed on the surface, due to the steric hindrance between the hydrogen atoms.
4.1. Bromo-tetracene (BT)

**Figure 4.3.** Coupling mechanism for tetracene radicals. a-d) Four possible coupling configurations. a) and d) are head-to-side configurations and can lead to T-shaped, L-shaped and tilted dimers. b) and c) depict radical-to-radical configuration and is forbidden due to the steric hindrance.

On the sides of the BT molecules (Fig. 4.3b and c). For reaction path a and d, the head/tail of a BT molecule points to the radical of another BT molecule to minimize the steric hindrance. In these configurations, a single C-C bonded dimer of tetracene can be formed, as shown in the second row in Fig. 4.3a and d. The BT molecule on top can then pivot either to the left or the right and cyclizes with the bottom BT molecule forming fused dimer (third row in Fig. 4.3a and d). A similar process has been reported for 10,10'-dichloro-9,9'-bianthryl (DCBA)\(^{166}\). In that case, cyclodehydrogenation happens before dehalogenation, which results in flat lying bisantrene. Thus ill-defined polybisantrene chains are formed instead of well-defined graphene nanoribbons. The authors of ref. [166] also have demonstrated that without the radical, no coupling products could be observed.

From the previous discussion, it is clear that at the moderate annealing temperature the radical is more reactive and dominates the reaction path. As a result, it can also help to tailor the coupling position and thus partly determines the structure of the final product, since the subsequent cyclization cannot be pre-defined. Another important factor that influences the coupling configuration is the steric hindrance. The configuration with least steric hindrance has the highest chance to be formed. However, for flat molecules, as in this case and the cases in the refs. [162, 163, 166], the steric hindrance generally interferes at the periphery of the molecule and is difficult to minimize. A solution is to change the molecules from 2D to 3D by lifting it from the surface, as in the case of 10,10'-dibromo-9,9'-bianthryl (DBBA)\(^{26}\).
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4.2. Dibromo-tetrakis[3,5-di(tert-butyl)phenyl]-biporphyrin (DBTBP)

Free-base porphine (2H-P), consisting of four interconnected pyrrole rings, is the simplest unit of porphyrins, with every side featuring a zigzag-like termination. Similar to the structure of graphene nanoribbons, if porphines can be linked aligned by forming three C-C bonds with their sides parallel, a conjugated one-dimensional porphine array can be formed. It has been shown that this porphine tape exhibits the capability for light harvesting and tunability of the band gap by changing the length\textsuperscript{167,168}. Such porphine tapes have already been synthesized and characterized in solution\textsuperscript{168–170}. Recently, it has been reported that porphines can be covalently linked to form dimers or oligomers through dehydrogenative homocoupling on Ag(111)\textsuperscript{165}. However, porphines can couple at different positions, resulting in a variety of products. This is mainly attributed to the reaction mechanism of dehydrogenative homocoupling. Thus it is necessary to steer the reaction pathway, for example using Ullmann coupling by introducing reactive sites into the porphine. However, simply using the trans-dibromo-porphine did not result in porphine tapes, but individual unreacted porphines\textsuperscript{171}. This is probably due to the steric hindrance that prohibited the closing of two porphine units. A similar situation is encountered with the 9,10-dibromo-anthracene (DBA) in an attempt to form graphene nanoribbons\textsuperscript{172}. In the end, graphene nanoribbons (GNR) were synthesized using DBBA as precursor\textsuperscript{26}. The success of this precursor is attributed to the tilting of the two parts which avoids the steric hindrance. Following this idea, the precursor 15,15'-dibromo-10,10',20,20'-tetrakis[3,5-di(tert-butyl)phenyl]-5,5'-biporphyrin (DBTBP), as shown in Fig. 4.4a, is used in an attempt to form graphene nanoribbons\textsuperscript{172}. In the end, graphene nanoribbons (GNR) were synthesized using DBBA as precursor\textsuperscript{26}. The success of this precursor is attributed to the tilting of the two parts which avoids the steric hindrance. Following this idea, the precursor 15,15'-dibromo-10,10',20,20'-tetrakis[3,5-di(tert-butyl)phenyl]-5,5'-biporphyrin (DBTBP), as shown in Fig. 4.4a, is used in an attempt to form the porphine tapes. The two macrocycles are expected to be rotated out of plane similar to the DBBA in the gas phase (Fig. 4.4a). The tert-butylphenyl group should also be rotated with respect to the plane of the connected macrocycle. Different colors are used to highlight the 3D features. Green marked parts indicate downward rotated, and red marked parts upward rotated groups, respectively.

DBTBP molecules were deposited on Ag(111) at room temperature by vapor deposition at 740 K. Irregular aggregates, as well as ordered islands are observed at the step edges of Ag(111) (see Fig. 4.4b). From the STM image, it is hard to deduce the exact arrangement of the DBTBP molecules in the ordered island because of their non-planar adsorption geometry. A tentative arrangement is given as overlaying models in Fig. 4.4b. No symmetric lobes representing a DBTBP molecule could be resolved as observed later after annealing (see Fig. 4.4d), suggesting that two macrocycles of the DBTBP molecules may not be flattened at this stage. It has been reported that a similar porphine dimer, dibromo-tetraphenyl-bisporphyrin (DBDP), is already flattened after landing on the surface at room temperature\textsuperscript{172}. Also, without using XPS it is not straightforward to determine if the molecules are already debrominated or not with STM. Annealing to 570 K, DBTBP molecules can be clearly resolved as four bright lobes and are aligned mostly along the step edges. The four bright lobes are assigned to the four tert-butylphenyl groups and exhibit similar brightness, which suggests a similar apparent height. From the high-resolution STM image (inset of Fig. 4.4d), more details can be resolved for the bright lobes. A less bright lobe (yellow arrows) is observed next to the bright lobe (red arrows). They are assigned to the butyl group bent downward
4.2. Dibromo-tetrakis[3,5-di(tert-butyl)phenyl]-biporphyrin (DBTBP)

Figure 4.4. DBTBP deposited on Ag(111) and then heated up to 570 K. a) Structural model of the gas-phase DBTBP molecule. b) STM image of self-assembled islands of DBTBP molecules on Ag(111) ($U = -0.1$ V, $I = 100$ pA). c) Structural model of macrocycle-flattened DBTBP molecule. d) STM image of the DBTBP molecules aligned parallel along the step edges of Ag(111) ($U = 0.1$ V, $I = 100$ pA). In the inset shows a high-resolution STM image. The two rings in the center of the DBTBP molecule are highlighted with green dashed circles. Red and yellow arrows point to the bright and less bright spots at the side of the DBTBP molecule. Green and red lines are drawn in the chemical model of the DBTBP molecules in (a) and (c) to highlight the rotating direction. Green lines indicates downward bended and red lines upward bended.

and upward, respectively. Moreover, two faint rings can be resolved between these four bright lobes and may represent the macrocycles. From this information, the most likely
4. On-Surface Reactions

structure corresponding to these STM features is shown in Fig. 4.4c. Two macrocycles are flattened, probably during the annealing, and the two tert-butylphenyl groups on the same side are rotated in the same direction, possibly with the same angle. The intermolecular distance amounts to 2.5 nm, indicating no covalent bonds are formed between them because for a coupled DBTBP dimer, the intermolecular distance of two DBTBP monomers should be around 1.7 − 1.8 nm.

![Figure 4.5. Annealing DBTBP on Ag(111) to higher temperatures. a) Annealing to 570 K, DBTBP appears flatter and the macrocycles can be clearly resolved (U = 0.1 V, I = 100 pA). b) Schematic reaction path. Red lines highlights the bonds formed by cyclization and red circles indicate the parts that are higher. c) High-resolution STM image of the area marked with green square in (a). d-g) STM, AFM, simulated AFM and structural model of two DBTBP molecules next to each other (U = 0.1 V, I = 100 pA). h-k) STM, AFM, Laplace filtered AFM and structural model of a flattened DBTBP molecule (U = 0.1 V, I = 30 pA).](image)

After annealing to 620 K, DBTBP decorate at step edges, but its appearance is significantly changed (Fig. 4.5a and c). The two macrocycle rings are clearly resolved with two central depressions. Instead of four bright lobes, the tert-butylphenyl groups exhibit weaker contrast than before annealing, indicating a structural change induced by the annealing. Most of the DBTBP molecules are aligned along the step edges, and some of them appeared to be closer to each other. Nc-AFM measurements are performed in an attempt to identify the exact structures. However, for non-planar molecules, it is known that the large height difference hampers a clear determination of the molecular structure, not mentioning the molecule lies at the step edge. In the AFM image (Fig. 4.5e),
only bright spots are observed, which are assigned to the tert-butyl groups. Macrocycles can not be resolved, suggesting the tert-butyl groups are protruding out of the macrocycle plane. For the upper molecule in the Fig. 4.5d and e, each tert-butylphenyl group is featured with two bright spots with slightly different contrasts. They are not parallel to the long axis of the porphine dimer, but are symmetric with respect to the short symmetric axis of the DBTBP molecule. This strongly indicates a rotation of the phenyl ring about the z-axis. Most likely, the phenyl ring pivot towards the outer side of the molecule, because the other direction is less favorable due to the steric hindrance, followed by a subsequent cyclization to the macrocycle (Fig. 4.5b right). The AFM simulation of this structure (Fig 4.5f) exhibits four white lobes that matches very well the measured AFM image (Fig. 4.5e), except for the brightness. In the AFM simulation, the tert-butyl groups in the DBTBP model are of similar height (Fig. 4.5g), which leads to almost the same brightness. On the contrary, in the measured AFM image the lobes at the side are clearly brighter than the lobes in the middle, suggesting the two tert-butyl groups on the outer side are stronger upward bent, probably due to the steric hindrance with the macrocycle. For the molecule at the bottom (Fig. 4.5g), only three bright lobes in the AFM image are observed, suggesting one of the tert-butyl group is cleaved off. Indeed, the simulated AFM image of such a molecular model replicates this feature (Fig. 4.5f). In the STM image (Fig. 4.5d), this tert-butylphenyl group also appears smaller than the other three. Moreover, some DBTBP are covalently coupled through the tert-butylphenyl group, as shown in Fig. 4.5h. In this case, the tert-butyl groups are cleaved off, and the cyclization of the phenyl ring to the macrocycle is clearly observed (Fig. 4.5i-k). After annealing to 670 K, large irregular polymers were observed. Most of the molecules appeared flat, meaning their tert-butyl groups are cleaved off. Within the polymers, DBTBP molecules couple mostly through the tert butyl-group. This is probably because of the radical created by removing the tert-butyl group.

In summary, upon annealing to 570 K, DBTBP are aligned parallel at the step edges with the macrocycle flattened. Further annealing to 620 K, the phenyl ring of the tert-butylphenyl group cyclizes to the macrocycle, and some of the tert-butyl groups are cleaved off, leaving a radical that can covalently couple to other molecules. In the last step, annealing to 670 K leads to the formation of large irregular polymers mostly by linking via these radicals. During the whole annealing procedure, no porphine chains were observed that covalently coupled at the debromination position. This behaviour is ascribed to the steric hindrance induced by the tert-butylphenyl group or the early flattening of the macrocycles.

4.3. Dibenzo-9a-azaphenalene (DBAP)

Nitrogen-doped nanographenes have attracted considerable attention due to promising electronic and magnetic properties\textsuperscript{173} offering potential applications in metal-free catalysis\textsuperscript{174,175} and sensing\textsuperscript{176,177}. However, the existing synthetic protocols do not allow the precise control of the doping level and heteroatom positioning. The chemical nature of nitrogen dopants (i.e. pyridinic, pyrrolic, and "graphitic" N-atoms) remains largely undefined\textsuperscript{178}, restricting the fine-tuning of the resulting properties as well as reliable structure-property relationship elucidation. In this regard, structurally well-
defined N-doped nanographene molecules offer an opportunity to accurately investigate N-doping effects. Notwithstanding, N-doping of defined nanographenes has been predominantly limited to pyridinic\cite{142,179,180} and pyrrolic nitrogen atoms, which only resulted in replacing benzene rings with other N-containing 6\(\pi\) aromatic rings, such as pyrimidines and pyrroles. To develop nanographenes with strong antiaromatic ring dopants, we considered the possibility of incorporating a pyrazine structure inside the aromatic core, which employs two 'graphitic' N atoms in the framework, thus providing two more \(\pi\)-electrons when compared to a benzene ring. 1,4-Disubstituted pyrazine entails highly intriguing chemistry, showing 8\(\pi\) antiaromatic (neutral), 7\(\pi\) non-aromatic (cationic), or 6\(\pi\) aromatic (dicationic) properties, depending on its oxidation state. Thus, a pyrazine ring embedded in the graphene's hexagonal structure can potentially serve as a localized antiaromatic-ring dopant, giving rise to a new type of graphene materials with unconventional electronic and magnetic properties. Cyano-substituted Dibenzo-9a-azaphenalene (DBAP) are used in an attempt to construct such a graphene nanoflake.

DBAP molecules were deposited by molecular beam evaporation at 590 K on Ag(111) kept at room temperature. Elliptical DBAP units with a protrusion on the longer side are observed spreading across the Ag(111) surface (Fig. 4.6a). Some of them form the dimer-like structure with the protrusion pointing to each other, stabilized by van der Waals interaction. By zooming in, the STM image with higher resolution (Fig. 4.6b) shows that DBAP monomers are not of the same shape, but slightly different. The side of the DBAP with a prominent protrusion is referred as the head and the other side the tail (see inset of Fig. 4.6b). Mainly two types of heads and three types of tails were observed. Based on the length of the head and the shape of the tail, DBAP monomers can be categorized and some of them are investigated with nc-AFM as shown in Fig. 4.6c-h. The corresponding nc-AFM measurements and Laplace-filtered AFM data are shown in the second and third column respectively. In the STM image, the head of species A, B and C appear shorter than species D and E. The longer head is identified in AFM data as the cyano group. Clearly, the cyano group of species A, B and C are cleaved off, either during the heating inside the crucible or the landing on the surface. For the case of tails, the situation is more complicated. Species A and D exhibit a small protrusion on the tail side in STM, while in AFM the tail is resolved as a ring merged to the DBAP backbone. The polycyclic aromatic azomethine ylide salt, 2-(tert-butyl)-8H-isoquinolino[4,3,2-de]phenanthridin-9-ium tetrafluoroborate has previously been shown to undergo 1,3-dipolar addition with hexacyclic ethylenes and further oxidize under mild conditions to the target nitrogen-containing polycyclic aromatic compound\cite{181}. One should notice that some of the DBAP have lost their cyano groups. Thus it is reasonable to assign this tail to a five-membered ring formed between a broken cyano group and the DBAP backbone. This suggestion is supported by the results shown later in this section for another precursor. It also should be noted that the central two benzene rings of species A and D are hardly resolved even at close tip-molecule distance. One possibility would be that the central part of the DBAP molecule is downward bent, and another possible situation could be that the nitrogen atom of the DBAP is charged and the electrostatic force contributes to the tip-sample force. The tail of species B and E is characterized by a dent in the DBAP backbone. In the AFM image, on the contrary to species A and D the four benzene rings are better resolved. The part where
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Figure 4.6. Cyano-DBAP salts on Ag(111). a,b) Overview STM images of the surface (V = 0.1 V, I = 50 pA). The inset in b shows the chemical structure of the cyano-DBAP unit. The cyano part is marked with a red circle and referred as the head and the salt part is marked with a green circle and referred as the tail. c-h) Different species observed on the surface. In the first column are STM images. AFM data, Laplace-filtered AFM data, proposed structural modes are shown in the second, third and fourth columns respectively.

The nitrogen atom sits presents darker contrast, indicating a significant contribution of the electrostatic force. The bright spot next to species B is assigned to a CO. For species C, the tail looks very flat in STM. Indeed, in AFM the tail part appears almost like a straight line. The central segment exhibits a brighter contrast than other parts, and the inner structure of the DBAP backbone cannot be resolved, similar to species A and D. From these AFM data, chemical structures can be proposed and are shown in
the fourth column of Fig. 4.6. Simulated AFM images using the proposed models are shown in the fifth column for comparison with experimental data. The backbone of all molecules is set flat for simplicity. For species B and E, a radical is present at the carbon site next to the nitrogen atom. Thus a flat geometry of hydrogen atoms is expected, as confirmed by the AFM simulation. For species C, the two carbon adjacent to the nitrogen atom are fully hydrogenated, which means two hydrogen atoms protrude out of the plane, leading to a stronger contrast in the AFM image, as evidenced by the AFM simulation. In all the AFM simulated images, the central part of the molecule shows a weaker contrast comparing to the side, resembling the measured AFM images, and is most likely attributed to the charged central nitrogen atom.

Figure 4.7. Cyano-DBAP salts on Ag(111) heating to 543 K. a) Overview STM image. (U = 0.1 V, I = 50 pA). Different species are highlight. b-e) High resolution STM images of the species marked in a.

The sample was annealed to 540 K to activate the reaction. 1D molecular chains, and hexagonal nanoflakes were observed on the surface (4.7a). Nc-AFM measurements revealed that the hexagonal flake consists of two DBAP units coupled at tails and is called diaza-HBC. Four C-C bonds are formed between the two DBAP units. The cyano groups of both DBAP are cleaved off. Observation of the $D_{2h}$ symmetry points
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toward the nitrogen atoms sitting at the positions indicated by white arrows (see Fig. 4.8b). Strong distortions are observed for the rings on the outer parts of the diaza-HBC. This is because of the bending of the flexible CO functionalized tip at the edge of the molecule. Interestingly, comparing to the HBC molecule\textsuperscript{182}, which purely consists of the carbon atoms, the central pyrazine ring of diaza-HBC appears strongly distorted under nc-AFM, and as a result, the rings around it also deviate from a perfect hexagon. This may be caused by the different lengths of the C-C bond and the N-C bond. Indeed, the predicted DFT C-C bond length of the central pyrazine ring is 1.40 Å vs. 1.42 Å for the N-C bond which can be reflected in the AFM data\textsuperscript{54,182,183}. However, electrostatic interaction with the CO-tip considerably contributes to data distortion in nc-AFM\textsuperscript{184–186}. For example, a tentatively negative CO tip will bend away from negatively charged N-C regions towards C-C bonds, making N-C bonds appear longer. To gain an idea of the charge distribution within the molecules, AFM simulations are performed for the flat diaza-HBC with different charge assignments to the atoms of the central pyrazine ring and the results are shown in Fig. 4.8e-h. Fig. 4.8e shows the simulated AFM without charges. Rings in the central part look symmetric, resembling the HBC molecule\textsuperscript{182}. The structural optimization predicted a charge of $-0.3 \, \text{e}$ at the nitrogen position and almost no charge at other carbon positions. The simulated AFM image using this charge distribution is shown in Fig. 4.8f, the central pyrazine ring appears slender along the axis of the two nitrogen atoms, which contradicts the experimental results (Fig. 4.8b). Fig. 4.8g shows the simulated AFM with nitrogen atoms charged with $-0.1 \, \text{e}$. The pyrazine ring is enlarged in both horizontal and vertical directions. This matches only in the horizontal direction to the experimental results (Fig. 4.8b). To compensate the charge assigned to the nitrogen atoms, the four carbons are also charged with $-0.1 \, \text{e}$. The simulated AFM image in Fig. 4.8h perfectly matches the experimental results (Fig. 4.8b), indicating that in addition to the nitrogen atoms, the central pyrazine ring is also negatively charged. It should be noted that many factors are not considered here, like the influence of the surface and the structural relaxation on the surface. Thus this simulation is not a strict way to determine the charge distribution within the molecule. Still it can serve as a quick check of the properties of the molecule and give us a rough idea of the influence of introducing the nitrogen atoms. The more strict way of investigating it requires geometry optimization and relaxation of the molecule on the surface and the determination of the electrostatic potential using the density functional theory (DFT), which then should be used in such an AFM simulation. The results using such a method can be found recently submitted manuscript with the title "Nitrogen-doped antiaromatic nanographenes via azomethine ylide homocoupling"\textsuperscript{187}.

To investigate the electronic properties of the diaza-HBC, dI/dV maps are recorded as shown in Fig. 4.8i-j. At a bias between 1.1 V - 1.7 V, six bright lobes were observed at the corners of the hexagonal molecule. At these biases, the $D_{2h}$ symmetry can also be clearly resolved. At 1.7 V, the two lobes on the N-resided axis are brighter than the other four, and the contrast is inverted at reduced bias. At negative biases, the dI/dV maps features a $D_{4}$ symmetry instead of $D_{3}$. No prominent symmetry preference was observed for the nitrogen-resided axis.

Species dominating on the Ag(111) surface are chains with various lengths. The shortest one consists of two DBAP units, and the longer one consists of more than ten DBAP units. Nc-AFM reveals that in this chain-like structure DBAP units engage in a head-
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**Figure 4.8.** Characterization of diaza-HBC. a) STM image, b) AFM image, c) Laplace filtered AFM image and d) structural model of the diaza-HBC. The green line indicates the nitrogen-containing symmetry axis. White arrows point the position of nitrogen atoms. e-h) Simulated AFM images with different charge assignments to the atoms of the central pyrazine ring. The values of charges assigned are shown above the corresponding atoms. e) and f) are series of dI/dV maps at positive biases and negative biases, respectively.

to-tail configuration (Fig. 4.9). Fig. 4.9e shows an AFM image of a chain consisting of only two DBAP units. Both DBAP units have a bulky tail, which corresponds to species A and D. As already mentioned for the DBAP monomer, the "big" tail is a five-membered ring formed by the DBAP backbone with a cyano group cleaved from another DBAP unit. Here, two DBAP units undergo 1,3-dipolar polymerization in a head-to-tail fashion, affording conjugated polymers. The cyano group of the molecule on the left side is cleaved off. Thus this chain can not extend with another DBAP unit. From both STM and AFM, the backbones of two molecules are not parallel but rotated with their left side closer to each other. The phenyl ring on the left side of the left molecule exhibits a stronger contrast in the AFM image, indicating it is upward bent due to the steric hindrance. Owing to the off-axis reaction and in-plane confinement, two possible orientations of the monomer in the chains are possible, which are denoted as left and right with respect to the molecule in the back. Thus, the type of chain in Fig. 4.9b can be referred as left. Chains consisting of three and four DBAP
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Figure 4.9. Internally N-doped conjugated polymers via 1,3-dipolar additions on Ag(111). a) Cyano-substituted DBAP salt forms conjugated polymers via consecutive homomolecular 1,3-dipolar cycloadditions and dehydrogenations. b-d) STM data of a chain dimer, trimer and tetramer respectively. e-f) The corresponding AFM data and h-j) the Laplace filtered AFM data. k-m) Structural models drawn from the AFM data. Red circle highlights a phenyl ring bending upwards from the molecular plane. n) STM image showing longer chains. In the blue line marked chain, all DBAP salts rotated in one direction. In the green marked chain, DBAP units rotating in opposite direction alternatively.

molecules are shown in Fig. 4.9c and d respectively. For the chain in Fig. 4.9c, the front DBAP units are rotated to the left and it is a left-left type. The chain in Fig. 4.9d is a right-left-left type. Longer chains can be formed when thermally annealing monolayer of cyano-DBAP units at 520 K (Fig. 4.9n). The chain marked with the blue line has all DBAP units rotating in the same direction (right), resulting in a curly configuration of the chain with a small curvature. For the one marked with the green line, neighboring DBAP units rotate in opposite directions alternatively, resulting in an almost straight chain. For other chains, due to the randomness of the rotating direction, various shapes are observed.

Statistical investigation of the chain length is performed by counting several tens of STM images, and the results are shown in Fig. 4.10. For chains, the count decreases with increasing length and can be fitted with an exponential curve (red line in Fig. 4.10). This observation excludes a favored length of the chains, for example, due to stabilizing effects invoked by the commensurability with the surface atomic lattice. In the inset of Fig. 4.10 the percentage of each motif is given. Almost half of the formed structures on the surface are dimer chains. Totally, 86.6% of the cyano-DBAP salts form
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Figure 4.10. Bar chart shows the counts of different motifs. The occurrence of chains decreases exponentially with increasing length, highlighting the statistical assembly process and excluding effects stabilizing a preferred chain length. The inset shows a pie chart listing the percentage of each motif.

chains and only 13.4% of them form diaza-HBC, which indicates a clear preference of the 1,3-dipolar addition reaction. This trend is more prominent if starting with higher coverage of cyano-DBAP salts. On that sample, only a few of diaza-HBC were observed, and long chains consisting of more than ten monomers dominate (see Fig. 4.9n).

To this point, it is always assumed that the bulky tail of the DBAP is a result of the 1,3-dipolar addition of a DBAP unit with a cyano group. The high yield of chains hinders the efficient production of diaza-HBC. To further confirm this proposition and increase the yield of diaza-HBC, propyl substituted DBAP dimer is used (inset of Fig. 4.11). The propyl group is expected to be less reactive than the cyano group, and by suppressing the formation of chains, more diaza-HBC are supposed to form. After deposition on Ag(111) kept at room temperature, "dogbone"-like structures were observed spreading on the surface (marked with yellow contour in 4.11a). High-resolution STM images shows the "dogbone" consists of two T-shaped molecules with their heads parallel pointing to each other (Fig. 4.11c). The T-shaped molecule is assigned to the propyl-substituted DBAP monomer. No flattened DBAP dimers are observed on the surface. The head of the propyl-DBAP is clearly longer than the cyano-DBAP. In AFM, the propyl chain is clearly resolved as three segments (green lines in Fig. 4.11e). The two segments at the far end appear brighter, which indicates that they are upward bent. In the AFM image,
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**Figure 4.11.** Propyl-DBAP salts on Ag(111) and after annealing to 570 K. a) Overview STM image of propyl-DBAP salts on Ag(111) ($U = 0.1$ V, $I = 50$ pA). c-i) STM, AFM, Laplace filtered AFM image and structural model of a "dog-bone" dimer. d-j) STM, AFM, Laplace filtered AFM image and structural model of a propyl DBAP unit with a big tail. b) STM image after annealing to 570 K ($U = 0.1$ V, $I = 50$ pA). k-n) STM, AFM, Laplace filtered AFM image and structural model of a tail-to-tail dimer connected by a long chain.

The DBAP backbone appears similar to the species C of cyano-DBAP, indicating full hydrogenation. This "dogbone" dimer is stabilized by the van der Waals interaction between the two parallel lying propyl chains. In addition to the T-shaped monomer, elliptic shaped propyl-DBAP monomers without a long head were also observed. Similar to the cyano-DBAP, the propyl chains are cleaved off from these monomers (Fig. 4.11f). As expected, monomers with a big tail are much less observed comparing to the cyano-DBAP salt. Fig. 4.11d shows a STM image of a propyl-DBAP monomer with a big tail. In AFM data (4.11f), the tail looks the same as for the cyano-DBAP, except an additional part protruding outside the molecule (pointed by a yellow arrow). This additional part, together with the short line segment forming the big tail with DBAP backbone, are assigned to a propyl chain. In the STM image, the tail is also asymmetric and points towards the direction of the protrusion shown in the AFM image. In Figs. 4.11g and h, the Laplace-filtered AFM data are shown, and the structures can be better resolved. The structural model can be drawn from the AFM data and are shown in Fig. 4.11i-j.

After annealing the sample to 570 K, the "dogbone" species were not observed. More propyl-DBAP monomers with big tails were observed (blue square in Fig. 4.11b), indicating more propyl groups are cleaved off during the annealing (red square in Fig.
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4.11b. Head-to-tail chains formed through 1,3-dipolar polymerization are also observed, but the length is normally limited to two (yellow square in Fig. 4.11b). Tail-to-tail coupled dimers were observed as shown in Fig. 4.11b marked with a green square. STM contrast can be resolved between the two DBAP units, and the distance between them clearly exceeds the reasonable length of a C-C bond, indicating additional structures are formed between the tails of two DBAP units. A similar dimer with a longer distance between two DBAP units is shown in Fig. 4.11k-n. In the STM image, two DBAP units appear to be connected by a line at the tails. In the AFM image (Fig. 4.11l), the line contrast indeed is resolved as a single-atom-wide carbon chain. Such chains have been previously reported at graphene edges. Both DBAP units have a big tail with the propyl group stretching out as pointed by the yellow arrow. Carbons forming them are probably from the cleaved propyl groups. Having identified the structure of this tail-to-tail dimer, the one in Fig. 4.11b marked with a green square can be considered of having the same structure but with a shorter line between two DBAP units. No diaza-HBC was observed on the surface. The increasing number of DBAP units with a big tail observed on the surface after annealing clearly indicates a higher reactivity of propyl groups, which is against our initial expectation. The short chain length suggests that the propyl group is more unstable when mounted to an aryl group than the cyano group and is very easily to break upon annealing. Although no diaza-HBC was formed with propyl-DBAP dimer salts, it proves that the big tail is indeed formed by the 1,3-dipolar polymerization with cyano groups for cyano-DBAP molecules and propyl groups for propyl-DBAP molecules.

In summary, two reaction paths are observed for DBAP molecules on Ag(111) upon annealing. Through the first reaction, fully cyclized diaza-HBC is formed. The central pyrazine ring is a promising candidate of holding antiaromaticity. Via 1,3-dipolar reaction, internally N-doped conjugated wires between a molecule bearing azomethine-ylide and aryl-cyanide functional groups are formed with very high yield.

4.4. Summary

In this chapter, three different molecules are used in an attempt to construct ordered covalently coupled nanostructures. After annealing on Ag(111), the radical generated by the debromination of a BT unit couples to the head/tail of an another BT unit. The subsequent cyclization results in a T-shaped, L-shaped or tilted dimer. No side-by-side coupled polymers are formed due to the steric hindrance of hydrogen atoms. Despite the radical coupling partly anchors the connecting position, the radical For the DBTBP, the two macrocycles and the tert-butylphenyl groups flattens sequentially upon annealing on Ag(111). Polymers connected at the phenyl ring instead of at debrominated radical positions are formed. This may be because of the cyclodehydrogenation, i.e. flattening of the macrocycles, happens before the debromination, or the large tert-butylphenyl groups prevent the approaching of the radicals. The cyano-substituted DBAP salts form nitrogen doped diaza-HBC through surface-assisted dimerization followed by the cyclodehydrogenation. The pyrazine rings are potential candidates to be included in graphene and similar two-dimensional materials to spawn novel functional properties induced by breaking of the conjugated lattice via antiaromatic-ring dopants. Molecular
chains through 1,3-dipolar polymerization with cyano groups are also formed with a very high yield. These chains may be fully cyclized to graphene nanoflakes by annealing to higher temperature.
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Controlled covalent coupling of functional molecular units at interfaces enables new routes for creating hybrid systems where individual components perform specific functions. Tetrapyrroles are particularly interesting molecular building blocks because of the important role they play in many biological or artificial systems due to their versatility and robustness. For instance, porphyrins and related species are at the center of crucial processes in nature such as light harvesting in photosynthesis or oxygen and chemical-energy transport. Recently, porphyrins and other tetrapyrroles incorporating different metal centers have been systematically explored at interfaces and reveal promise for various technological applications such as molecular electronics, gas sensing or catalysis, and light harvesting. It is particularly important to combine the functionalities of (metal-)organic molecules with charge transport materials.

The exceptional properties of graphene make it a promising component in such hybrid structures. Indeed, covalent linking of molecules – including porphyrins – to graphene has already been achieved in wet chemical routes using graphene oxide to enable solution processing. However, this methodology lacks specificity and thus complex multicomponent architectures may not be realized on its basis. To achieve atomically precise hybrid nanostructures, detailed insight into the anchoring of complementary functional units is mandatory. This may be achieved by surface-assisted covalent coupling of molecular species under well-defined ultra-high vacuum (UHV) conditions, which have already been extensively applied for synthesizing novel low-dimensional materials with atomic precision. Moreover, well-defined and modified graphene edges can play an important role for catalytic conversions and are particularly desired for such an ordered covalent coupling. Such edges can be obtained from graphene nanoribbons synthesized by deliberately designed precursors.

Recently, the homocoupling of porphines, the simplest porphyrin consisting only of a tetrapyrrole macrocycle, on Ag(111) substrates by a surface-assisted dehydrogenation reaction yielding fused derivatives by covalent C-C bond formations were demonstrated. The same reaction protocol may be adopted for the linkage of porphines to graphene edges. Moreover, other reaction protocols presented in the last chapter may be exploited to fuse functional molecules to graphene edges as well. The Ag(111) surface is also a promising substrate for graphene-edge functionalization because unlike on many other transition-metal supports, the carbon sheets only interact weakly with the noble metal substrate. Reduced graphene-edge/substrate interactions will likely reduce barriers for lateral decoration and thus can enable on-surface covalent reactions.

In this chapter, firstly growth of graphene on copper foils, Cu(111) and Ag(111) is introduced. Afterward, the thermally activated dehydrogenative coupling of porphines
5. On-Surface Graphene Edge and Nanoribbon Functionalization

...to graphene edges on Ag(111) is presented. Results of this part were published in the article "Fusing tetrapyrroles to graphene edges by surface-assisted covalent coupling" in Nature Chemistry. In the next section, two types of molecules are shown also to be able to couple to graphene edges covalently via radicals. Afterwards, instead of coupling to irregular edges of graphene islands, porphines and pyrphyrins are linked to graphene nanoribbons with well-defined edges, in order to get a deeper understanding of the coupling behavior between functional molecules and graphene edges.

5.1. Graphene Growth on Metal

It has been shown that graphene can grow on many metal substrates. On Copper, Nickel, Iridium, monolayer graphene can be obtained by chemical vapor deposition (CVD) with proper gas precursors. These metals have relatively low carbon solubility and act as catalysts for dissociation of hydrocarbon precursors. Silver and gold, on the other hand, have relatively low catalytic activity and thus can hardly dehydrogenate the precursors. To grow graphene on these metals, instead of hydrocarbon precursors, carbon atoms are directly deposited via physical vapor deposition.

5.1.1. Graphene Growth using Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is a method often used to produce high-quality solid materials. Using this method, monolayer graphene can be grown on copper under ambient pressure or low pressure, buffered with argon and hydrogen gases. During the growth procedure, the metal needs to be heated above a certain temperature to enable the decomposition of gaseous precursors.

On copper foil. Copper foil is a promising substrate for synthesizing graphene using CVD method due to its low-cost and the simple procedure. The graphene grown on it presents relatively high qualities and can have a size on the order of meters. By dissolving the copper support in an acid etchant, isolated graphene can be obtained and then transferred to other substrates. These two advantages make graphene growth on copper foils a promising candidate for graphene-based applications.

Copper foils are normally put inside a quartz tube heated by a furnace. After heating to the reaction temperature $T_r = 1300 \text{ K}$ in mixed gases of hydrogen and argon, hydrocarbon precursors, e.g. methane or ethylene, are introduced for graphene formation. Several minutes of post-annealing at the reaction temperature afterward helps to improve the quality of the graphene. The procedure is shown in Fig. 5.1a. Details about the transfer and patterning process of graphene onto other substrates can be found in Appendix A.

Fig. 5.1b shows a Scanning Electron Microscopy (SEM) image of graphene grown on the copper foil. Copper steps bunch as bright clearly visible as bright lines. This is also an indication of the formation for graphene layers on it. Without its protection the copper steps can not stand in the ambient environment and will be oxidized and become flat. The dark lines crossing the copper steps are wrinkles of graphene layer (red arrows). They are a typical feature of CVD synthesized graphene. The dark flakes, pointed by the green arrow, are where second layer of graphene has formed. The steps of on copper surface, as well as the wrinkles of the graphene layer, are also visible in...
5.1. Graphene Growth on Metal

Figure 5.1. Graphene growth on copper foils with CVD method. a) Growth procedure. b) SEM image of graphene grown on the copper foil. c) AFM image of graphene grown on the copper foil.

the ambient AFM image (5.1c). In contrast to the SEM image, wrinkles of graphene appear as white protrusions in the AFM image.

On Cu(111). Single crystal of metals are preferably handled in the ultra high vacuum (UHV) environment with a base pressure around $10^{-10}$ mbar to protect its well-defined surface structure. As a result, the partial pressure of gases can only be on the order of $10^{-4}$ mbar. Under this pressure, compared to the case of copper foils there may not be enough gas molecules to break at the copper surface and thus not enough carbon atoms to form graphene. Another effect caused by the low pressure is the lowering of the evaporation temperature of the metal. This will limit the highest possible reaction temperature. Unlike the copper foil, the single crystal cannot be melted. Otherwise, its well-defined surface arrangement will be destroyed. This further limits the reaction temperature, it not only cannot be higher than the evaporation temperature of the metal, as in the case with copper foil but need to keep well below it to avoid local melting. Both these factors deteriorate the performance of the CVD method in the UHV condition.

The procedure adapted for growing graphene on Cu(111) is shown in Fig. 5.2a. Ethylene was filled into the chamber until reaching a partial pressure of $1.5 \times 10^{-4}$ mbar while the sample is kept at room temperature. Then it is annealed to 1070 K for 5 min and slowly cooled down to room temperature. In order to increase the graphene coverage, this process is repeated for several cycles (3 – 6 times). In the last cycle, ethylene was switched off after reaching 1070 K. After cooling down again to room temperature, the sample is post-annealed at 1070 K for 5 – 10 minutes to improve the graphene quality.

Figure 5.2c shows a STM image of graphene grown on Cu(111). The coverage of graphene can vary from very low to about 40%, depending on the pressure of hydrocarbons and the number of cycles. The copper surface acts as catalysts for the dissociation
5. **On-Surface Graphene Edge and Nanoribbon Functionalization**

![Figure 5.2](image)

**Figure 5.2.** Graphene growth on Cu(111) and Ag(111) with CVD method. a) Growth procedure of graphene growth on Cu(111). b) Growth procedure of graphene growth on Ag(111). c) STM image of graphene grown on Cu(111) ($U = 4$ V, $I = 200$ pA). d) STM image of graphene grown on Ag(111) ($U = 1$ V, $I = 200$ pA, inset: $U = 0.017$ V, $I = 725$ pA).

of hydrocarbons, thus the graphene growth process is self-terminated once the surface is covered with graphene. Domains with distinct Moire patterns can be observed at the high bias voltage (for example, $U = 4$ V). Bright dots on the Cu(111) surface are impurities segregated from the bulk during the high-temperature annealing.

**On Ag(111).** It is more difficult to grow graphene using CVD method on silver than on copper. First of all, the reactivity of silver is even lower than copper. Thus even fewer carbon atoms are present on the surface for graphene formation. Second, silver has lower evaporation temperature of around 920 K at a pressure of $10^{-10}$ mbar. At this temperature, there is not enough thermal energy to dissociate the gaseous precursor. To overcome this problem, a sputter gun is used to help breaking the gaseous precursor. After filling in ethylene with a partial pressure of $10^{-8}$ mbar, Ag(111) was heated to 900 K with sputter gun running with a voltage of 300 V and an emission current of 4 µA for 15 minute. Then the ethylene was switched off, and the sample was further annealed to 910 K for another 5 minutes. This procedure is shown in Fig. 5.2b.

Fig. 5.2d shows an STM image of 'graphene' grown on Ag(111) following the similar procedure as on Cu(111). The island is rough and fractured with many defects, indicating an incomplete growth process. The high-resolution STM image (inset of Fig. 5.2d) clearly shows a high density of defects within the island.
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5.1.2. Graphene Growth using Solid Carbon Source

To overcome the limitations of CVD method on metals with low evaporation temperature and low activity, solid carbon source is exploited to directly supply carbon atoms on the surface\textsuperscript{199}. We used a carbon rod mounted inside a homemade e-beam evaporator to generate a relatively high flux of carbon atoms. This ensures sufficient carbon atoms on the surface for graphene formation. As a result, the required growth temperature can be significantly reduced.

**On Cu(111).** The Cu(111) is kept at 1020 K while depositing atomic carbon onto it. Afterward, it is annealed at the same temperature for 10 minutes to improve the graphene quality. The growth procedure is shown in Fig. 5.3a. Large graphene islands are observed, as shown in Fig. 5.3c. The coverage can be much higher than using CVD method. However, comparing to the graphene grown using CVD many holes (dark contrast) and bubbles (white contrast) are preset within the graphene layer, which may be caused by inhomogeneous stretching during the cooling down. On the bare metal surface, a high density of dirt is observed, which are likely impurities, segregated from the copper bulk at the high annealing temperature.

**On Ag(111).** The Ag(111) is kept at 900 K while depositing atomic carbon onto it, following the protocol introduced by Kiraly et al.\textsuperscript{199}, as shown in Fig. 5.3b. Graphene

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**Figure 5.3.** Graphene growth on Cu(111) and Ag(111) with atomic carbon source. a) Growth procedure of graphene growth on Cu(111). b) Growth procedure of graphene growth on Ag(111). c) STM image of graphene grown on Cu(111) ($U = 1$ V, $I = 5$ nA). d) STM image of graphene grown on Ag(111) ($U = -0.5$ V, $I = 500$ pA).
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islands are formed on Ag(111) as shown in Fig. 5.3d. The graphene islands are very flat and feature a dendritic shape with a high density of kinks and edge defects. This is quite different from graphene grown on other transition metals using CVD method and is mainly due to the moderate growth temperature limited by the low melting point of silver.

The edges of graphene islands are very irregular and exhibit many white protrusions (Fig. 5.3). Some of these bright spots are investigated with nc-AFM, as shown in Fig. 5.4. Many short segments of zigzag and armchair edges can be observed, forming plenty of transitions between these two types of edge terminations. The white protrusions at the graphene edges often appear at these transition positions where the regular edge is disturbed (highlighted with the green square), for example by the incorporation of a pentagon ring.

![Figure 5.4. STM and AFM images of graphene edges on Ag(111). a, d) STM images \( (U = -200 \text{ mV}, I = 50 \text{ pA}) \). b, e) Corresponding AFM images. c, f) Laplace-filtered AFM image overlaid with STM images. Bright protrusions reflecting defects at the edge transitions are marked with green squares.](image)

5.2. Graphene Functionalization with Porphine

5.2.1. Coupling Porphines to Graphene Edges on Ag(111)

Fig. 5.5 shows the procedure of coupling porphines to graphene edges. Firstly, graphene is grown on Ag(111) using atomic carbon as described in section 5.1 (Fig. 5.5a). On the partially graphene covered surface, free-base porphines (2H-P) were vapor deposited at
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room temperature. After subsequent cooling to 5.5 K, the STM measurements reveal that the porphines exclusively adsorb as individual units on the bare Ag(111) surface with three different orientations\(^{210}\), decorating also the graphene edges (Fig. 5.5c). In order to induce the coupling reaction, the sample is annealed to 620 K. Here, we usually employ an initial porphine coverage in the multilayer regime, to enhance the coupling efficiency, compensating for molecular desorption (vide infra). Indeed, some porphines appear now directly attached to graphene edges (Fig. 5.5e), suggesting a covalent coupling (see the dashed green squares in Fig. 5.5e highlighting several locations). The covalent interaction between the molecules and the graphene can override site-specific molecule-substrate interactions, partially even inducing deviations from the preferred adsorption orientations of individual porphines on Ag(111). Furthermore, the annealing of porphines on Ag(111) triggers dehydrogenative homocoupling, self-metallation and the desorption of porphine monomers resulting in a reduction of the porphine density on the surface, as previously reported\(^{165}\).

Several distinct hetero-coupling configurations are observed that are influenced by the local structure of the graphene edge and the ability of porphines to engage in lateral bonding schemes involving different numbers of \(\beta\)- and meso-carbons\(^{165}\) (cf. Fig 5.6). From the orientation and distance of the molecules with respect to the graphene edge four main configurations can be identified. The first row of Fig. 5.6 shows the corresponding STM images revealing the orientation of the porphines that expose either a single pyrrole ring (Fig. 5.6a and b) or two pyrrole rings (Fig. 5.6c and d) towards the graphene edge. In the case of epitaxial graphene, electronic interference effects at the edges complicate the precise determination of the edge position and structure by STM\(^{211–213}\). Thus, a conclusive determination of the bonding configuration based solely on STM images is not feasible. To nevertheless corroborate our claim of covalent coupling of porphines to graphene and to determine the detailed bond configuration we performed nc-AFM with CO-functionalized W-tips. Previous achievements with such functionalized tips directly revealed the C-C bonds in various systems, including (nanostructured) graphene and tetrpyrroles\(^{54,164,214–216}\).

In the second and third row of Fig. 5.6, nc-AFM data are depicted corresponding to the configurations measured by STM (first row). The second row displays the AFM data in the frequency shift channel (\(\Delta f\)). To enhance the contrast and to better visualize the bond characteristics, Laplace-filtering is applied to the AFM images and the results are shown in the third row. In these nc-AFM images the interfacial bond structure between graphene edges and porphines is clearly resolved. Based on the data, we classify the four configurations by the number of C-C bonds formed between the porphine and the graphene. Thus, porphines might form one C-C bond at a \(\beta\)-position (configuration A), two C-C bonds at \(\beta\)-positions (configuration B), three C-C bonds at \(\beta\)-, meso-, \(\beta\)-positions (configuration C) or even four C-C bonds (\(\beta\)-, meso-, \(\beta\)-, \(\beta\)-positions, configuration D). AFM images of individual unreacted porphines in close proximity to graphene edges do not show any interfacial bonds whereas the C-C bonds in graphene and the adjacent porphine are clearly resolved. This corroborates our assignment of the AFM contrast in configuration A-D to covalent bonds, where distinct coupling motifs are observed. For configuration A, Fig 5.6e shows that one \(\beta\)-carbon from the pyrrole ring is coupled to the graphene edge with a protrusion as link. Even though a precise bond-length determination is hampered by the flexibility of the CO terminating the
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Figure 5.5. STM images and corresponding models showing the experimental procedure. a STM image ($U = -0.5$ V, $I = 0.5$ nA) of graphene islands grown on Ag(111) using atomic carbon deposition. c After deposition at room temperature, individual 2H-P molecules decorate the bare Ag(111) terraces and the graphene edges ($U = -0.1$ V, $I = 50$ pA). e STM image recorded after inducing dehydrogenative coupling reactions by annealing the 2H-P on graphene/Ag(111) at 620 K ($U = 0.2$ V, $I = 90$ pA). Porphines coupled to graphene are marked with green squares. b, d, f Schemes of the experimental situations in (a, c, e). The $\beta$- and meso-carbon positions are labeled in the structural model of 2H-P in (d).

AFM tip$^{217,218}$, the separation between the graphene edge and porphine’s $\beta$-carbon clearly exceeds a reasonable C-C distance. Therefore we tentatively assign the protrusion in the junction to a carbon atom protruding from the graphene edge, acting as a connecting bridge. Similar constrictions and carbon atom chains at graphene edges have been previously reported$^{188,189}$. For configuration B, two bonds between the $\beta$-carbons of porphine and the graphene edge are clearly resolved in Fig. 5.6f and j. Fig.
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Figure 5.6. STM and AFM data of distinct covalent coupling configurations at the graphene edge. a-d) STM images of configuration A (one C-C bond at a β-position), B (two C-C bonds at β-positions), C (three C-C bonds at β-, meso-, β-positions) and D (four C-C bonds at β-, meso-, β-positions) (I = 50 pA, (a-c): U = 200 mV, (d): U = −200 mV). e-h) AFM images representing the frequency shift Δf (Δh = 0.6 to 0.7 Å with respect to the STM setpoint on Ag(111)). i-l) Corresponding AFM images after Laplace-filtering. The covalent bonds of the graphene lattice, the porphine and their interface are clearly resolved. The bright protrusion in (f) and (j) corresponds to a co-adsorbed CO molecule. m-p) Schematic models illustrating the coupling configurations. The red lines represent the C-C bonds formed by the dehydrogenative coupling reaction. The characters A-D on top of the figure specify distinct coupling groups based on the number of formed C-C bonds.

5.6g and k show an AFM image of configuration C. Here, the graphene is terminated by a regular, defect-free zigzag edge. The porphines on this edge are triply-fused to the graphene edge with one of its side parallel to the edge, i.e., via β-, meso-, β-carbons of the porphine macrocycle. Furthermore, even the formation of four C-C bonds, involving a carbon atom protruding from the graphene edge occurs (configuration D, Fig. 5.6h and l). From the filtered images, schematic models are drawn and presented in the fourth row of Fig. 5.6. Based on AFM image simulations, the apparent distortions of

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carbon hexagons at the graphene / porphine interface and at edges (e.g., Fig. 5.6e-l) are assigned to imaging artifacts induced by the flexibility of the CO terminated tip (vide infra).

Figure 5.7. Metallation and ligation of graphene-anchored tetrapyrrole macrocycles. a) Scheme illustrating the metallation of fused 2H-P with Ag adatoms to form Ag-P and the reversible binding of a CO molecule to Ag-P. b) STM image revealing the different types of porphine coupled to graphene edges \((U = 200 \text{ mV}, I = 70 \text{ pA})\). Porphines marked with green squares represent Ag-P (faint central protrusion). Porphines marked with blue squares are assigned to CO / Ag-P complexes, featuring a pronounced central protrusion. The porphine marked by a red square lost a CO during scanning. c-e) STM \((U = 200 \text{ mV}, I = 70 \text{ pA})\), AFM \((\Delta h = 0.6 \text{ Å})\) and Laplace-filtered AFM images of an Ag-P fused to the graphene edge. f-h) STM \((U = 200 \text{ mV}, I = 50 \text{ pA})\), AFM and Laplace-filtered AFM image of a CO / Ag-P complex. At close tip-sample distances the graphene lattice is resolved (h).

As mentioned above, one of the most appealing features of porphyrins is their robustness with functionalities bestowed by metal centers hosted in the macrocycle. In a surface science scenario, in-situ metallation was introduced as powerful method to incorporate specific metal centers into tetrapyrroles\(^{219,220}\). Thus, their electronic and magnetic properties as well as their reactivity can be tailored, as exemplified by the reversible ligation of gaseous species\(^{16,221–223}\). If intrinsic properties of porphyrin macrocycles, i.e. incorporation of metal centers capable for axial ligation of adducts, were preserved upon the coupling to graphene, further options for the functionalization of graphene nanostructures emerge. Figure 5.7a sketches the metallation and ligation processes that are manifested in the experimental STM data shown in Fig. 5.7b. The annealing step and the exposure of the sample to minute amounts of CO at low temperature induces novel characteristics at the graphene edge, highlighted with green and blue squares, respectively. In contrast to the fused free-base porphines, featuring a central depression in the STM topography, these new species are characterized by a pro-
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The entities exhibiting a faint protrusion in the center are assigned to macrocycles self-metallated by silver substrate atoms, similar to Ag-P formations in earlier reports\textsuperscript{165,224} (green square, Fig. 5.7c and Fig. 5.6d). The species marked by blue squares are characterized by a brighter protrusion (Fig. 5.7f), which dominates the AFM contrast at large tip-sample distances (Fig. 5.7g). Only at smaller distances, the graphene lattice is resolved (Fig. 5.7h). Furthermore, this species can be converted to Ag-P upon scanning (see Fig. 5.7b, porphine marked with red square, where a transition takes place during the data recording). Reversible attachment of CO and other diatomic molecules to surface-anchored metalloporphyrins in STM experiments has been previously reported\textsuperscript{16,225}. Thus, our observations strongly point to a CO molecule adsorbed on Ag-P as origin of the pronounced central protrusion. Consequently, we provided a proof-of-principle that the intrinsic properties of porphine as metallation and ligation can be exploited following the covalent coupling to graphene edges.

5.2.2. Structural Analysis

These AFM images clearly demonstrate that we can functionalize graphene edges with porphines through on-surface dehydrogenative coupling. Among the four main coupling configurations, the configuration \textbf{B} and \textbf{C} are especially interesting, because...
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the graphene edges are well defined in these two configurations, i.e. armchair terminated in B and zigzag terminated in C. These ordered coupling motifs are very promising towards atomically precise functionalization of graphene and construction of graphene-based nanostructures, such as nanographenes or graphene nanoribbons\textsuperscript{26,142,144,164}. One critical factor for successful formation of a covalently coupled heterostructure is the good structural match at the coupling junction. Here, defect-free graphene edges, either with armchair terminations or zigzag terminations, feature a system with six-membered rings, while porphines, on the other hand, consists of four five-membered rings interconnected with each other. The subtle difference between the six-membered ring and five-membered ring may have caused the formation of the four main coupling configurations. Fig. 5.8 shows a geometrical investigation of some possible coupling motifs between porphines and graphene edges with armchair (a) and zigzag terminations (b and c). The coupling motifs shown in Fig. 5.8a and b corresponds to the configuration B and C, respectively. In both these cases, porphines and graphene edges form six-membered rings at the junction. In Fig. 5.8c, two \(\beta\)-carbons from one pyrrole ring of the porphine forms a five-membered ring with the zigzag terminated graphene edge. The C-C distances marked with lines in color green (within graphene) and in color red (porphine) are listed in the top right table, in the first column obtained from the literature\textsuperscript{226}, in the second column measured from the AFM images and in the third column calculated by density functional theory (DFT). The lengths from the literature are used to compare the mismatch between the graphene edge and the porphine. Results in the bottom right table show a minor mismatch, 4.2\% for coupling motif (a) and (c) and 2.4\% for the coupling motif (b), which indicates a very good structural match. One thing to notice is that the coupling motif (c) has not been observed in our experimental data, although it also presents a good structural match. In section 5.4, this coupling motif is indeed observed between graphene nanoribbons and porphines. Thus, it is very likely that the coupling motif (c) also exists on the surface, but from STM images it is very hard to differentiate it from the configuration B without performing AFM measurements and resolving the termination of the graphene edge. Due to the time consuming nature of the AFM measurements, only around 20 coupling junctions are measured with AFM. Therefore it is very possible, the coupling motif (c) has been missed.

The nc-AFM measurements of both, bare graphene and graphene/porphine interfaces reveal three distinct distortions. (i) In constant height \(\Delta f\) images, some graphene edges are imaged with less repulsive contrast than the inner part of the graphene islands that appears brighter (e.g., Figs. 5.4 and 5.6). (ii) The hexagons at the edge of the carbon honeycomb structure appear elongated, with a larger extension perpendicular to the edge (e.g., Fig. 5.6e-l) and (iii) hexagons at the graphene/porphine interface seem distorted (e.g., Fig. 5.6e-l). Such distortions can either reflect a real geometric structure or represent imaging artifacts caused by the flexibility of the CO at the tip apex\textsuperscript{182,186,217,227–231}. In order to clarify the influence of the CO tip, we performed AFM simulations using the mechanical model and codes proposed and developed by Hapala \textit{et al.}\textsuperscript{218,232}. Fig. 5.9a shows a structural model of a regular, planar porphine-graphene junction. The corresponding simulated \(\Delta f\) images representing two different tip-sample separations are presented in Fig. 5.9b. Clearly, an elongation of the outermost hexagons at the graphene edge as well as a distortion of the hexagon at the graphene / porphine
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Figure 5.9. Simulated AFM images of a porphine/graphene junction. a) Planar, regular structural model used as input for the $\Delta f$ image simulations reproduced in b) for different tip-sample separations $z$. c) Structural model featuring downwards bent carbon hexagons at the edge of the graphene. d) Corresponding $\Delta f$ image simulations for two tip-sample separations $z$.

interface is observed. Thus, effects (ii) and (iii) are dominated by the flexibility of the CO tip. However, the dimmer appearance of the graphene edges (i) is not reproduced by the planar model and thus not a simple artifact induced by the CO. To further address this issue, we used a structural model where the terminal carbon rings at the graphene edge are bent downwards (Fig. 5.9c). Indeed, the corresponding simulated $\Delta f$ images now clearly show a less repulsive, dimmer contrast at the edge of the graphene. Thus, effect (i) is tentatively assigned to a real geometric origin, i.e., a downward bending of some graphene edge segments towards the Ag(111) substrate.

5.2.3. Electronic Properties

To investigate the influence of the porphine decoration on the electronic structure of graphene, we recorded the tunneling current simultaneously with the $\Delta f$ signal in a constant height scan at very low bias voltages. The resulting current images approximate the local density of states near the Fermi level. Applied to graphene nanostructures, this approach proved to yield fingerprints for specific defects\textsuperscript{164,233,234}. Fig. 5.10 shows current images of an Ag-P fused to a zig-zag edge of graphene recorded at $\pm 1$ and $\pm 5$ mV, respectively. This regular configuration D (cf. AFM image and structural model in Fig. 5.6) was chosen to exclude effects intrinsically related to defects and irregularities of the graphene edge itself. Interestingly, no pronounced modification of the current signal at or near the porphine/graphene interface can be observed. This indicates that the porphine attachment hardly affects the electronic structure of graphene at the Fermi level, in marked contrast to sizeable modifications in graphene nano-ribbon junctions reported recently\textsuperscript{164}. 

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Figure 5.10. Low-energy electronic structure of the porphine / graphene interface. a-d) Current images recorded at $-1 \text{ mV}$ (a) and $1 \text{ mV}$ (b) bias voltage in constant height mode ($\Delta h = 0.6 \text{ Å}$), respectively. e-h) Current images recorded at $-5 \text{ mV}$ (e), $-1 \text{ mV}$ (f), $1 \text{ mV}$ (g) and $5 \text{ mV}$ (h) bias voltage. The graphene electronic structure near the Fermi energy at the interface is hardly affected.

Figure 5.11. STM images and line sets of spectra in different locations: (a) across a graphene edge ($U = -1.5 \text{ V}$, $I = 50 \text{ pA}$), (b) crossing a 2H-P and a Ag-P ($U = -1 \text{ V}$, $I = 50 \text{ pA}$), (c) from silver to graphene via a fused 2H-P ($U = -1 \text{ V}$, $I = 50 \text{ pA}$) and (d) from silver to graphene via a fused Ag-P ($U = -1.5 \text{ V}$, $I = 50 \text{ pA}$).

To further explore the electronic properties of the porphine/graphene system, scanning tunneling spectroscopy (STS) was conducted. Fig. 5.11a addresses the case of the graphene edges. The bare silver spectra show the classic step-like feature around $-60 \text{ mV}$ related to the presence of the two-dimensional surface state of silver. The same feature, but shifted to higher energies appears in the spectrum acquired on the graphene layer. This shift has been observed before and arises from the presence of a weakly interacting graphene layer.$^{235}$ At the edge, instead of a smooth shift of the surface state going from the bare Ag(111) to the graphene, the transition is abrupt and the surface...
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state even disappears. The same behavior has been observed for different edge shapes. Figure 5.11b shows a set of dI/dV spectra acquired across a 2H-P and a Ag-P monomer. For the porphines on silver, as has been previously reported, the spectra are featureless and no clear electronic molecular resonances can be resolved. Finally, Fig. 5.11c and Fig. 5.11d show the dI/dV spectra along a line from the bare silver to the graphene where a 2H-P and a Ag-P is attached, respectively. There are no specific electronic features due to the presence of the fused porphines, confirming the statement that the porphine attachment hardly affects the electronic structure of graphene or introduce defect states.

5.2.4. Thermal Stability and Statistics

Thermal stability of the different porphine/graphene configurations were also explored by gradually annealing the sample to 900 K. STM images for increasing annealing temperatures are shown in the Fig. 5.12a-c. For the attached molecules, we have performed a detailed analysis of hundreds of STM images considering the orientations and distances of the molecules with respect to the graphene edges. Following this approach based on the limited STM resolution, we can separate the configurations in three groups: group 1 (corresponding to configuration A and the no bond configuration), group 2 (corresponding to configuration B where the molecule is closer to the graphene edge than the ones in group 1 and 45° rotated with respect to the graphene border) and group 3 (corresponding to configuration C and D where the molecule is parallel to the graphene edge). The result is shown in Fig. 5.12d.e. Concerning the graphene edges, the dendritic shape of the graphene islands gives rise to a wide range of edge structures oriented in different directions along the silver surface. Nevertheless, from the analysis of all available nc-AFM images, for configurations C and D, we can conclude that zigzag graphene edges are the most favourable ones for the coupling. On the other hand, transitions between armchair and zigzag or other more complex edge configurations promote the coupling motifs A and B. Compared to 620 K (cf. Fig. 5.5a), increasing the temperature to 670 K yields more porphines fused to graphene edges and longer oligomers. As reported earlier, annealing to higher temperatures results in a further reduction of the density of porphine monomers on the Ag(111) surface, triggered by concomitant desorption (≈ 0.03 ML/min) and formation of extended, irregular covalently-coupled porphine oligomers. Indeed, such oligomers are frequently coupled to the graphene edges (Fig. 5.12b,c). In particular, we observed a 17% increase of the number of molecules attached to graphene after annealing the sample to 770 K (Fig. 5.12d). Importantly, even after annealing to 900 K — the temperature used to grow graphene on Ag(111) — we still observe single porphines coupled to the graphene edges. The prevailing motif (97% of the molecules fused to graphene) corresponds to configurations C and D, with a parallel alignment to the graphene zig-zag edge. The thermal stability of edge-bonded porphines up to the growth temperature of graphene may enable the embedding of such units in the graphene matrix during graphene growth and thus to create not just edge-modified graphene but also intra-sheet functionalization. Interestingly, similar hybrid structures have been predicted to be potential catalysts for CO₂ and CO reduction.
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Figure 5.12. Annealing procedure and thermal stability of porphines/graphene on Ag(111). a) STM image after annealing the sample to 670 K (\(U = 200\) mV, \(I = 50\) pA), b) to 770 K (\(U = 200\) mV, \(I = 50\) pA) and c) to 900 K (\(U = 200\) mV, \(I = 50\) pA). Green circles highlight individual porphines fused to graphene. d) Bar chart showing the percentage of different porphine species after annealing to different temperatures. e) Bar chart showing the percentage of porphines attached to graphene in different configurations.

5.3. Graphene Functionalization Through Radical Coupling

In the last section (section 5.2), it has been presented that graphene edges can be functionalized with porphines through surface assisted dehydrogenative coupling, but the yield is relatively low. On one hand, this is due to the reaction mechanism and on the other hand due to the irregularity of graphene edges. More importantly, the dehydrogenative covalent coupling on metal surfaces lacks certain controllability and strongly depends on the energy barrier of the formed product. Although this can be partially solved by doing the deposition and annealing procedure repeatedly, a more
efficient reaction mechanism is highly desired. Coupling through radicals generated by dehalogenation has been shown to be a more effective way than dehydrogenative coupling, for example, via Ullmann-coupling \cite{149,150}. Here, two other molecules that are already introduced in the last chapter (chapter 4), bromo-tetracene (BT) and cyano-substituted DBAP are used in an attempt to decorate graphene edges more efficiently and regularly via radical coupling.

### 5.3.1. Coupling with BT

The reason of using BT molecules is that if BT molecules can decorate graphene edges in a side-by-side fashion, i.e., the long axis of the BT molecule parallel to the local graphene edge, then the other zigzag side of the BT molecule will replace the irregular graphene edge. BT molecules were deposited on Ag(111) kept at 470 K with graphene partially covered. As already shown in section 4.1, tank-like dimers are formed on the surface and aggregate into islands or chains. At this temperature, the radicals of the BT molecules form C-Ag-C bonds and no coupling to the graphene edge occurs.

To activate the radicals, the sample was annealed to 550 K. Similar to the previous preparations, tank-like dimers disappeared, and islands consisting of covalently coupled

![Figure 5.13. BT covalently coupled to graphene edges.](image)

a) Depositing of BT on Ag(111) with graphene partially covered. No coupling observed \((U = 1.118 \text{ V}, I = 20 \text{ pA})\). b) After annealing the sample, BT embedded into graphene were observed, as marked with red eclipse \((U = -0.015 \text{ V}, I = 8 \text{ pA})\). c-f) STM, AFM, Laplace filtered AFM images and structural model of a BT fused to the graphene edge in a side-by-side fashion \((U = 0.015 \text{ V}, I = 8 \text{ pA})\).
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BTs emerged at the graphene edges. Some BT units appeared directly attached to graphene edges (Fig. 5.13b marked with red eclipses). First of all, this coupling has a very low yield comparing to the coupling between BT molecules. Second, in most of the coupling motifs the backbone of BT molecules is perpendicular to the local graphene edge (cf. Fig. 5.13b), which contradicts the initial expectation. As already discussed in the section 4.1, the reason for this may be that steric hindrance between BT molecules and graphene edges hinders their approaching in a side-by-side fashion. Only if the BT unit meets a hump of the local graphene edge, which will reduce the steric hindrance, the BT molecule then can have a chance to covalently couple to the graphene edge. An example is shown in Fig. 5.13c-e. The backbone of the BT molecule is aligned parallel to the graphene edge. In the STM image, both the local graphene edge and the BT molecule are not well resolved due to electronic interferences, but it can still be noticed that the local edge is not well-defined. Although relatively strong distortions are revealed in the AFM image (Fig. 5.13d) near the BT molecule, it can be deduced from the Laplace-filtered image (Fig. 5.13e) that two bonds are formed between the graphene edge and BT molecule. A schematic model for this junction is shown in Fig. 5.13f. In this case, indeed the irregular graphene edge is replaced by the regular zigzag side of the BT molecule.

Despite low yield and unexpected coupling behavior, the connecting position at the BT molecule is the same radical position. This means with the help of the radical, the relative coupling configurations between BT molecules and graphene edges can be fixed. Comparing to the dehydrogenative coupling reaction, it exerts some control over the formed structure. To overcome the steric hindrance and increase the yield, tetracenes equipped with one or two bromo-aryl groups instead of a bromine atom may decorate graphene edges more efficiently. Nevertheless, locally ordered edges may be achieved following this idea.

5.3.2. Coupling with DBAP

It has been shown in section 4.3 that DBAP molecules can covalently couple either in a tail-to-tail fashion forming a nitrogen doped nanoflake or in a tail-to-head fashion forming nitrogen doped nanochains. In the tail-to-tail coupling scheme, it can be considered that the DBAP unit is coupled to a zigzag termination. This indicates it may also be able to couple to other zigzag-like edges, like graphene edges. One advantage of DBAP molecules is that it can introduce nitrogen atoms to other molecules or materials in a controlled way. Thus by coupling it to graphene edges, nitrogen-doping of graphene can be achieved.

Cyano-substituted DBAP molecules were deposit on Ag(111) with graphene islands partially covered. After annealing to 573 K, diaza-HBC dimer and chains are observed on the surface as introduced before in section 5.14. In addition, some DBAP molecules appeared directly attached to graphene edges (Fig. 5.14 marked with blue and green rectangles and red circles), suggesting a covalent coupling between DBAP and graphene edges. To resolve the exact interfacial bonding structure, nc-AFM measurements are performed, and the results are shown in the second and third columns of Fig. 5.14. Fig. 5.14b shows a DBAP monomer fused to the graphene edge. In the AFM image (Fig. 5.14c), four C-C bonds are formed between the graphene zigzag edge and the backbone
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Figure 5.14. Cyano-DBAP covalently coupled to graphene edges. a) After annealing cyano-DBAP salts on Ag(111) with partially covered graphene, covalent coupling between DBAPs and graphene edges were observed, as highlighted by the green and blue squares and red dashed circles ($U = 0.1 \text{ V}, I = 50 \text{ pA}$). b-d) STM ($U = 0.1 \text{ V}, I = 50 \text{ pA}$), AFM and Laplace filtered AFM images of a DBAP monomer fused to the graphene edge. e-g) STM ($U = 0.1 \text{ V}, I = 50 \text{ pA}$), AFM and Laplace filtered AFM images of a DBAP dimer chain fused to the graphene edge.

of the DBAP molecule. The cyano group is cleaved off, as already mentioned in section 4.3. One ring at the graphene edge shows stronger contrast (marked by the red arrow in Fig. 5.14c), similar to the 1-D chain formed by the cyano-substituted DBAP molecules,
is thus attributed to the slightly upward bending due to the steric hindrance with the graphene edge. This also suggests that the edges of the graphene islands are probably passivated by hydrogens. Fig. 5.14e-g shows a chain dimer covalently coupled to the graphene edge. In the AFM image (Fig. 5.14f), three C-C bonds between the DBAP unit and the graphene edge are resolved. The strong contrast in the AFM image, marked by the red arrow, indicates an elevation of this part. Considering the high intensity of the contrast, it is very likely the phenyl ring is bent out of the plane and the fourth C-C bond is not formed.

The AFM data clearly demonstrate that the DBAP molecules can covalently couple to graphene edges with their tails. The fused DBAP monomer can further couple to other DBAP molecules via an intact cyano group, forming a nanochain starting from the graphene island. Moreover, the cyano group anchored at the graphene edges may further be combined with metal-coordination systems. This may open a new way to combine the excellent properties of graphene with on-surface metal-coordination chemistry.

5.4. Fusing Porphine to Graphene Nanoribbons

It has been shown in the section 5.2 that porphines can covalently couple to graphene edges through the dehydrogenative coupling. Due to the irregularity of the edge termination of graphene islands grown on Ag(111) using atomic carbon source, different coupling configurations were observed without significant preferences at room temperature. Furthermore, the irregularity of graphene edges also makes a quantitative investigation of the electronic properties at the junction very difficult164,211-213,233,234. Graphene nanoribbons (GNRs) can be considered as one-dimensional structures cut from the two-dimensional graphene islands. Instead of being a zero-gap semiconductor, GNRs can have a tunable band gap by changing their widths34,237, which is essential for graphene-based electronic applications237. Because of these exceptional properties of GNRs, great efforts have been dedicated to the formation of GNRs with atomically precise edge terminations26,27. GNR, such as 7-armchair GNR (7-AGNR) with armchair terminations at the long sides and zigzag terminations at the short ends26, is an ideal candidate to investigate the coupling behavior of porphines to graphene edges, as well as the electronic properties of the coupling junction.

5.4.1. Synthesis of Nanoribbons

The precursor used to form 7-AGNR is the well-known 10,10'-dibromo-9,9'-bianthryl (DBBA). It has been shown to form armchair nanoribbon of width N=7 on the Au(111) surface through Ullmann-coupling. Following a similar procedure described in ref. [26], GNRs can be synthesized on Ag(111). Firstly, DBBA precursors were deposited on Ag(111) kept at room temperature instead of on the hot sample as in the case of Au(111). This is because on Ag(111) DBBA has a similar temperature for dehalogenation and cyclodehydrogenation. Then the sample was annealed at 520, 570 and 620 K, each for 10 minutes, to activate the dehalogenation and the cyclodehydrogenation sequentially. Comparing to GNRs grown on Au(111), GNRs on Ag(111) were much shorter (Fig. 5.15). Nevertheless, long GNRs are not crucial for the purpose here, because what is needed here are well-defined terminations of graphene edges. Fig. 5.15a
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shows some GNRs aligned parallel to the high symmetry directions of Ag(111), as evidenced by the step edges. Some of the GNRs appear as fuzzy long stripes, indicating they move along their long axis when scanning. In Fig. 5.15b, porphines were deposited on Ag(111) with GNRs kept at room temperature. With a higher local density of GNRs, it is more clear that the long axis of GNRs is aligned with the high symmetry direction of Ag(111).

![Figure 5.15](image)

**Figure 5.15.** STM images showing each step of the coupling procedure. a) GNRs synthesized on Ag(111) \((U = 1.511 \text{ V}, I = 110 \text{ pA})\). GNR appears as fuzzy strip, indicating it moves along a direction during the scanning. The step edges of Ag(111) indicate GNRs are aligned along the high symmetry direction of Ag(111). b) Porphines are deposited on Ag(111) with GNRs kept at room temperature. c) STM image recorded after inducing dehydrogenative coupling reactions by annealing the sample at \(620 \text{ K}\). Green dashed circles highlight some coupling interfaces of porphine and GNR. In the inset are the chemical structures of a porphine and a GNR monomer. Labels for carbon positions are marked. Yellow stars indicate the high symmetry directions of Ag(111) surface.

Covalent coupling of porphines to GNRs can be achieved by further annealing this sample. However, to maximize the coupling efficiency, the porphines were deposited on a hot metal surface with GNRs on it. At the elevated temperature, the coupling efficiency of porphines to GNRs can be maximized. Similar results have been reported for the homocoupling of porphines\(^{165}\). Then the sample was post-annealed at 620K for another 10 minutes, to further activate unreacted individual porphines and also reduce the density of 2H-P on the surface. Fig. 5.15c shows an overview STM image of the Ag(111) surface after activating the covalent coupling. As already reported, the annealing triggered dehydrogenative homocoupling of porphines\(^{165}\) and of GNRs\(^{26}\) and also self-metallation of porphines\(^{165}\). Moreover, some porphines appeared directly attached to the GNR (highlighted by the green dashed circles), which suggests a covalent coupling.
5. On-Surface Graphene Edge and Nanoribbon Functionalization

Figure 5.16. STM and PSM data of distinct covalent coupling configurations between porphines and GNRs. a-f) STM images of different configurations. g-l) Proposed schematic models illustrating the coupling configurations. m-q) PSM images representing the phase shift $\Delta\Phi$. r-v) Corresponding PSM images after Laplace-filtering. The covalent bonds between the porphine and GNR are clearly resolved. The characters A-F on the left side of the figure specify distinct coupling groups.

Similar to the case of porphines fused to graphene edges, several distinct heterocoupling motifs between porphines and GNRs were observed. From the orientation of porphines with respect to the GNR, six main coupling configurations can be identified.
5.4. Fusing Porphine to Graphene Nanoribbons

The first column of Fig. 5.16 shows the corresponding STM images. For configuration A, B, C and D, porphines are covalently coupled to the short zigzag edge of the GNR. For configuration E and F, porphines are coupled to the long armchair edge of the GNR. Comparing to the graphene islands grown on Ag(111) using solid carbon source, the structure and the edge termination of GNRs are well-defined. Without the interference of defects, tentative structural models can be drawn from STM images with high confidence, and they are shown in the second column of Fig. 5.16. For configuration A, the porphine is triply fused to the short zigzag edge of the GNR with one of its side parallel to this edge, that is, via $\beta$-, meso-, $\beta$-carbons of the porphine and C$_2$-, C$_1$-, C$_2$-carbons of the GNR. For configuration B, one side of the porphine is still parallel to the zigzag edge of the GNR, but comparing to configuration A, only two C-C bonds are formed between the $\beta$-, meso-carbons of the porphine and C$_2$-, C$_1$-carbons of the GNR. For configuration C, two C-C bonds are formed between two $\beta$-carbons of the porphine and C$_2$-, C$_1$-carbons of the GNR. Configuration D is similar to configuration B, but the porphine is shifted with respect to the GNR, and forms two C-C bonds with C$_2$-, C$_3$-carbons of the GNR. In configuration E and F, porphines are covalently coupled to the armchair edge of the GNR. For configuration E, two $\beta$-carbons of the porphine form two C-C bonds with C$_4$- and C$_5$-carbons of the GNR. For configuration F, one side of the porphine is parallel to the armchair edge, and two C-C bonds are formed between $\beta$-, meso-carbons of the porphine and C$_3$-, C$_4$-carbons of the GNR. To confirm the proposed structure, a high-resolution STM imaging technique is exploited to resolve the structure of the junction between the porphine and the GNR and the results are shown in the third column of Fig. 5.16. To enhance the contrast, the data are Laplace-filtered (fourth column). This technique was introduced by Michael Crommie et al. Similar to the dI/dV mapping, during the scanning a small modulation is applied on the bias. With CO-functionalized tip, it scans slowly over the molecule, and the phase channel generates a similar imaging quality/resolution as to the nc-AFM. Since this technique is not published yet, it will be referred here as Phase Sensitive Microscopy (PSM). The working principle will be discussed elsewhere. In the PSM images, the internal structure of the GNRs can be resolved. It can be seen that strong distortions are present in PSM images, especially the edge of GNRs and the porphine, which appear very different from its chemical structure. Nevertheless, the structure at the coupling interfaces can be resolved for most cases, and confirms the previously proposed models (second column).

5.4.2. Statistics of the Coupling Motifs

To investigate the coupling preference of the porphine with respect to the edges of the GNR, statistical analyses of hundreds of STM images regarding the occurrence of each configuration are performed (Fig. 5.17). From the statistics 5.17a, the most favorable configuration is C of 38%. Configuration D with 19% is the second favorable. Configurations A, B and E have similar occurrences of 12%, 15% and 11%, respectively. No single motif prevails when considering them individually. To gain a deeper understanding of the coupling mechanism, these motifs are categorized with different criteria. First, we can classify them according to the edge of the GNR that porphines are attached to (Fig. 5.17b). Configurations A, B and C belong to the same group, in which porphines
are covalently coupled to the zigzag edge of the GNR. Configurations E and F are in the "armchair edge" group. For configuration D, one carbon from the zigzag edge (C_2) and one carbon from the armchair edge (C_3) of the GNR formed two C-C bonds with porphine. Thus it is considered to contribute to the "zigzag edge" group and the "armchair edge" group equally. The zigzag edge of the GNR (75\%) is clearly favored for coupling of porphines than the armchair edge (25\%). Moreover, for the armchair edge, only the first dent from the zigzag edge appears to be involved in the coupling with porphines. Other parts of the armchair are porphine-free. Second, we consider that
5.4. Fusing Porphine to Graphene Nanoribbons

Individual porphine and GNR have preferred orientations on Ag(111). The main axis of porphines is aligned with the high symmetry direction of Ag(111) surface\textsuperscript{210}. For GNRs on Ag(111), the long axis is aligned with the high symmetry directions of the Ag(111) surface (cf. Fig. 5.15a and b). Therefore, configurations can also be classified into three groups according to the relative orientation of the porphine with respect to the GNR. The first group includes configuration A, B and F, where one side of the porphine is parallel to the zigzag edge of the GNR. The second group includes configuration C and E, where the sides of porphine form a 45° angle with the zigzag edge of the GNR. Configuration D belongs to the third group, where one side of the porphine forms a 30° angle with the zigzag edge of the GNR. Before the annealing, both the main axis of the porphine and the long axis of the GNR are aligned to the high symmetry directions of Ag(111) surface, which is supposed to lead to configurations in the second group. However, as can be observed from the STM image 5.16c, the shorter diagonal, which marks the main axis, is parallel to the zigzag edge, i.e. perpendicular to the long axis of the GNR. This indicates that one of them deviates from its preferred orientation or even both of them. To figure this out, the orientations of GNRs and coupled GNRs after covalent coupling are analyzed. It should be noted that many GNRs are coupled to more than one porphine and often also coupled to other GNRs, which may introduce other factors. Therefore, only heterostructures consisting of solely one GNR and one porphine are taken into account. Although this limits the amount of available data, it can still give us some hint about the distribution. The results are shown in Fig. 5.17d and e. Purple star points the high symmetry direction of Ag(111) surface and the red star is rotated about 60° with respect to it. Red and purple lines mark the angles corresponding to the red and purple stars. Fig. 5.17d shows the angle distribution of free GNRs after annealing and Fig. 5.17e shows the angles of GNRs with single porphine attached. Clearly, not only the free GNRs, but also the coupled GNRs are deviated away from the high symmetry direction of Ag(111). Both of them are rotated about 60° with respect to the high symmetry direction of Ag(111) (purple lines). Comparison to Fig. 5.15 before annealing indicates that the adsorption preference of GNRs on Ag(111) is changed during the annealing. One possible explanation for this could be that the hydrogenative status of GNRs is changed during the annealing. As for the porphines, the main axis in some configurations are hardly discernible, which makes the statistics regarding the porphines very unreliable.

Another statistics is made with respect to the carbons involved in these coupling motifs, and the result is shown in Fig. 5.17f. In the inset, circles are drawn in the structural model over the carbon atom with the diameter proportional to the counts of the corresponding carbon atom. The most involved carbon atom is C\textsubscript{2} and the second is C\textsubscript{1}. Other carbons are clearly less active comparing to these two, which can be clearly observed from the size of the circles. This is also evidenced in Fig. 5.17b. A possible explanation would be the radical generated by dehalogenation. It has been mentioned before that radicals can transfer within the molecule at high temperature (section 4.1). However, according to ref. \textsuperscript{239} the radicals should be all passivated after the formation of the GNRs, thus ruling out his possibility. An edge state\textsuperscript{239} (‘Tamm state’\textsuperscript{240}) is expected to exist at the end of the zigzag edge of the 7-AGNR. The DFT calculation shows that C\textsubscript{1}, C\textsubscript{2} and C\textsubscript{4} are the carbons with highest weight of the Tamm state, which suggests that an unpaired electron locates most probably at these carbon sites.
This is in agreement with the coupling probability shown in the inset of Fig. 5.17f and thus suggests it may be responsible for the coupling with porphines. This also explained why only the first dent of the armchair edge is preferably involved in porphine fusing. Moreover, side-by-side coupled GNRs are rarely observed on the surface and most covalent coupled GNRs either features a head-to-head or a head-to-side configuration. This further suggests the edge state at the zigzag edge of the GNR is crucial for the successful covalent coupling with other molecules. This behavior indeed exhibits a certain selectivity of the coupling motifs and suggests the coupling behavior between porphines and GNRs could be partially tuned by the edge state of the GNRs. It should also be noted that other factors may contribute to this coupling preference.

5.5. Coupling Pyrphyrin to Graphene Nanoribbon

Pyrphyrin, a molecule similar to the well-known porphyrin, is an interesting but widely unexplored molecule. It consists of four pyridyl subunits instead of pyrroles (Fig. 5.18). Recently, metallated pyrphyrins have shown to be promising catalysts for water reduction\textsuperscript{241}. The behavior of pyrphyrins on surfaces is of great importance to understand their roles in the water reduction process. Pyrphyrins have already been studied experimentally on Cu(111)\textsuperscript{242} and Au(111)\textsuperscript{243} and theoretically on Ru(110)\textsuperscript{244}, but on Ag(111) no studies exist. Furthermore, its behavior upon annealing is also of great interests. As already mentioned before, porphines form dimers and oligomers through dehydrogenative homocoupling\textsuperscript{165}. For pyrphyrin, two cyano groups at opposite sides block the coupling possibilities with these two sides, the remaining free sides are the only places coupling reactions could happen at moderate temperature. Such a spatial constraint may lead to the formation of long chains. This property is especially desired since the previous results showed that porphine could covalently couple to GNRs with various configuration. With pyrphyrins, there may be a dominating coupling motif. In addition, comparing to the porphine, the free sides of pyrphyrins exhibit an armchair termination instead of a zigzag. This will also influence the structure of the resulting products.

5.5.1. Pyrphyrin on Ag(111)

Pyrphyrin molecules were deposited on Ag(111) surface kept at room temperature by molecular beam evaporation at 570 K. Large dense-packed ordered islands are formed on the surface (Fig. 5.18a). There are also some small molecular clusters on the surface, consisting of intact pyrphyrin and fragments with irregular shapes. This suggests that at this evaporation temperature, some pyrphyrin molecules are already dissociated. The ordered island has a square unit cell of size $a = 1.4\pm0.2$ nm. Within the island, pyrphyrin unit is featured with a square with a central depression, similar to the porphine on Ag(111). The high-resolution STM image of the island (inset of Fig. 5.18a) shows that the pyrphyrin unit actually is rectangular with longer sides brighter than the shorter. Considering the structure of the pyrphyrin, the longer side is assigned to the part where two pyridine rings are connected through a carbon atom. Faint protrusions are resolved next to the longer sides and is assigned to the cyano group. Looking at the STM image carefully, it can be noted that neighboring pyrphyrins are perpendicular to
5.5. Coupling Pyrphyrin to Graphene Nanoribbon

Each other, indicating they arrange in a T-type order, as reported for PTCDA\textsuperscript{245}. To clearly confirm this, Fourier Transformation (FT) of the STM image is performed, as shown in Fig. 5.18d. To justify our suggestion, model images are made to elaborate the FT results. In Fig. 5.18b, pyrphyrin units are represented by grey squares with black stripes at the sides, to highlight the asymmetry of the pyrphyrin unit. For comparison, the pyrphyrin unit in Fig. 5.18c is represented by a pure black square. Their FT are shown in Fig. 5.18e and f. Comparing these three FTs, the FT in Fig. 5.18e perfectly reproduces the points observed in the FT of the STM image (Fig. 5.18d). The points marked with green circles in Fig. 5.18 are observed in both Fig. 5.18d and e and are absent in Fig. 5.18f. Also, the FT resembles the LEED pattern of PTCDA islands with a similar arrangement\textsuperscript{245}. This confirms our suggestion that the pyrphyrins change their orientations alternatingly, as shown in Fig. 5.18g. This arrangement not only spares space, making pyrphyrin stacking more compact, but also may lead to the formation of hydrogen bonds between cyano groups and neighboring pyrphyrins. To further confirm the structural assignment, nc-AFM measurements are performed, and the results are shown in Fig. 5.18i. The internal structure of the pyrphyrin, four six-membered rings, are clearly resolved. In addition, the two cyano groups are also resolved as lines.

5.5.2. Coupling Pyrphyrin to Nanoribbon on Ag(111)

To investigate the possible coupling behavior between pyrphyrins and graphene nanoribbons, pyrphyrins are deposited on Ag(111) with a submonolayer of nanoribbons on it. The sample is then annealed to 570 K to activate the covalent coupling. Indeed, some covalently coupled structures are observed Fig. 5.19a. However, most of them are covalently coupled GNRs, as reported previously\textsuperscript{164}, and only a few of them look like pyrphyrin coupled to GNR or homocoupled pyrphyrins. Furthermore, some undefinable structures in STM are observed. As mentioned previously, fragments of pyrphyrins are present when depositing on Ag(111) at room temperature. Therefore, these irregular structures are probably due to the covalent coupling of these fragments with other units. Fig. 5.19c shows a pyrphyrin coupled to the zigzag edge of a GNR by forming two C-C bonds. One pyridine ring shows a stronger contrast in AFM, indicating it is upward bent and higher than other parts. This is due to the steric hindrance induced between this ring and the GNR. Actually, this is the only coupling motif between the pyrphyrin and GNR observed on the surface. Similar to porphyrins, pyrphyrins with different central features are observed on the surface. Most of the pyrphyrins feature a central depression, and some of them exhibit a central protrusion. The latter is assigned to pyrphyrins metallated with a silver atom. Moreover, there is a pyrphyrin presenting brighter protrusion in the center. Height profiles of two pyrphyrins with bright centers along the lines in Fig. 5.19a are shown in Fig. 5.19b. The red line crossed pyrphyrin shows a higher apparent height than the yellow line crossed one, indicating it is a metallated pyrphyrin with a CO molecule or other adducts ligated by the metal center.

Besides the dense-packed islands with a square unit cell shown in Fig. 5.20a, a new motif of pyrphyrin with triangular unit cell emerged after annealing (marked with yellow triangles in Fig. 5.20a). Three pyrphyrin units occupy the three corners of a triangle. By repeating this unit cell with the neighboring triangles turned upside-down, a ring is formed as shown in Fig. 5.20a. Two possible structures are shown in Fig. 5.20b. From
Figure 5.18. Pyrphyrin deposited on Ag(111). a) STM image of dense-packed highly ordered pyrphyrin islands (U = 0.1 V, I = 50 pA). Inset: high-resolution STM image of the island (U = 0.1 V, I = 50 pA). b-c) Model images with pyrphyrins represented by squares. d-f) Fourier Transforms of (a-c). g) Schematic model of the pyrphyrin island. h-k) STM (U = 0.1 V, I = 50 pA), AFM, Laplace-filtered AFM and chemical model of a pyrphyrin.

the STM image, the cycle arrangement shown as the upper one is the most likely one. AFM measurements are performed to clarify the exact packing order. In Fig. 5.20d, three pyrphyrin units are rotated 120° with each other. All of them have lost one cyano group that points outward the triangle. The remaining cyano groups point towards the dent of the armchair side of the neighboring pyrphyrin. In this configuration, hydrogen bonds can be formed between the nitrogen atom and the hydrogen atom. White lines are observed between them and may be a sign for the formation of the hydrogen bond. The N-C distance is about 0.3 nanometers in good agreement with the
5.6. Summary

In this chapter, functionalization of graphene edges with tetrapyrrolic species by a dehydrogenative coupling reaction directly on a metal surface used for graphene synthesis is demonstrated. The high thermal and structural stability of this bonding motif up to 900 K open pathways to incorporate porphines and related species in extended graphene sheets, to apply solution processing or to transfer such hybrid structures to other substrates. Two other molecules are also successfully linked to graphene edges covalently through the radicals of the molecules. Despite the strong steric hindrance, the radicals do help to tailoring the coupling configurations to some extent. To investigate the coupling behavior quantitatively, 7-AGNR with well-defined edge terminations are used to replace the irregular edges of graphene islands grown on Ag(111). Distinct coupling motifs are observed for porphines and GNRs. Due to the preferred orientation of the GNR and porphine, as well as the edge state at the zigzag edge of the 7-AGNR, the coupling only occurs at the zigzag edge and the first dent of the armchair edge of the

5.6. Summary

Figure 5.19. Pyrphyrin annealed on Ag(111) with GNRs. a) STM image recorded after annealing ($U = 0.2 \text{ V}, I = 70 \text{ pA}$). b) Height profiles along the red and yellow lines shown in a. c-f) STM ($U = 0.2 \text{ V}, I = 70 \text{ pA}$), AFM, Laplace-filtered AFM and chemical model of a pyrphyrin covalently coupled to a GNR.

literature, and thus supports our assignments. Fig. 5.20g-j, show two pyrphyrins in an arrangement identical as in the dense-packed islands in Fig. 5.18. The remaining cyano group of the pyrphyrin in the upper left resemble a letter T and points towards the dent of the armchair edge of another pyrphyrin. Hydrogen bonds are supposed to be formed and stabilize this arrangement and thus the dense-packed islands.
5. On-Surface Graphene Edge and Nanoribbon Functionalization

**Figure 5.20.** New self-assembling motifs of pyrphyrin after annealing. a) STM image of the self-assembly with the unit cell highlighted by the red and yellow triangles ($U = 0.1$ V, $I = 50$ pA). b) Possible schematic models of the triangular packing motif in (a). c-f) STM ($U = 0.2$ V, $I = 70$ pA), AFM, Laplace-filtered AFM and chemical model of three pyrphyrins forming a triangular unit cell. g-j) STM ($U = 0.2$ V, $I = 70$ pA), AFM, Laplace-filtered AFM and chemical model depicts hydrogen bonds formed between two pyrphyrins.

GNR, respectively. When using pyrphyrin, whose free sides resemble an armchair edge, coupling at the zigzag edge of the GNR is observed, but with much lower yield and only one coupling motif is observed.
In this thesis, atomically precise nanostructures are synthesized at surfaces and studied with experimental techniques, notably STM and AFM, and theoretical methods, such as Monte-Carlo simulations. The structure of metal-coordination bond stabilized metal-organic networks can be deliberately tuned by sophisticated design of substituents at the meso-positions of porphyrin and the selection of metal adatoms. Moreover, covalently coupled nanostructures with atomic precision and high thermal stability can be constructed through surface-assisted reactions. Importantly, these on-surface reaction techniques can be further extended to construct covalently coupled heterostructures. Graphene and porphyrin, two stars in their fields, are fused via thermally activated coupling reactions. This hybrid nanostructure opens up a new way for functionalization of graphene and for anchoring functional molecules to its edges.

The structure of metal-organic coordination networks can be tuned by both the employed metal center and the properties of the ligands. The slender cyano group can form fourfold metal-coordination bonds with a copper adatom on Ag(111), which leads to fully reticulated metal-organic coordination network of TPCN with fourfold coordination nodes. This is also the only expression of the coordination network of TPCN on Ag(111). On the contrary, the flat-lying phenyl group terminated meso-substituents of TPyPP can not engage with copper adatoms in the same way, because of steric hindrance. As a result, twofold linear metal-coordination bonds are energetically more favorable. By gradually increasing the local density of copper adatoms on the surface, the 1D coordination network transforms to a 2D fully reticulated coordination network. On-lattice Monte-Carlo simulation confirms this difference originates from the difference of spatial constraint between the phenyl group and the cyano group. Moreover, Monte-Carlo simulations are applied to other molecules, reproducing the experimental results of already studied porphyrin derivatives and predicting the structure of self-assemblies of unexplored molecules, e.g. combining TPCN and TPyPP will result in 2D metal-organic network of TPyPP with TPCN sitting in the pores. Also, we demonstrated that the 2D network with extraordinary large pores formed by introducing a ditopic linear molecule to extend the side of the pore can not easily achieved, but requires a special meso-substituents, such as the terpyridyl group. The investigation of other porphyrin-based metal-organic networks using Monte-Carlo simulation is proved to be very helpful in the prediction of unknown metal-organic nanosystems.

Towards more applicable nanomaterials, higher stability against temperature and external forces is required, meaning a stronger bonding between building blocks is necessary. Covalently coupled nanostructures synthesized through bottom-up surface-assisted reactions fulfill these requirements. Three molecular building blocks were exploited to construct atomic precise covalently bonded nanostructures in order to gain a deeper understanding of the coupling mechanism. After dehalogenation, 5-Bromo-tetracene (BT) molecules, form a C-C bond with the head/tail of another BT molecule at the radical
position. Followed by a subsequent cyclization reaction, T-, L- or tilted-shaped polymer are formed. A side-by-side coupling motif was not observed due to steric hindrance of the hydrogen atoms. Almost no monomer was observed after annealing, indicating a higher coupling efficiency of the radical coupling than the dehydrogenative coupling. 2D flat molecules normally suffer from the spurious steric hindrance and thus makes the prediction of coupling structures very hard. One solution would be to proceed from 2D to 3D, i.e. letting the molecules stand up, like the DBBA forms well-defined graphene nanoribbons. Following this idea, a single C-C bond linked porphine dimer is exploited trying to synthesize porphine chains. Tert-butylphenyl groups are added to the meso-positions at the side to enhance the lifting effect. Upon annealing, the macrocycles firstly undergo cyclodehydrogenation, i.e. flattening. Then the phenyl rings cyclize to the macrocycle with some of the tert-butyl groups cleaved off. No porphine chains are observed, which may be because of the steric hindrance between the tert-butylphenyl groups, or the cyclodehydrogenation preceding the debromination and thus preventing the approaching of two radicals. In addition to the aryl bromide Ullmann coupling, the solution chemistry of azomethine ylides (AMy) is adapted to on-surface synthesis. The fully cyclized diaza-HBC has been successfully fabricated on Au(111) surface by cyano-substituted DBAP salts and unambiguously identified by STM and nc-AFM.

We suggest that pyrazine rings are potential candidates to be included in graphene and similar two-dimensional materials to spawn novel functional properties induced by breaking of the conjugated lattice via antiaromatic-ring dopants. Importantly, the on-surface dimerization of DBAP molecules may already grant an exploratory protocol for the selective addition of AMy to graphene or two-dimensional materials and the pertinent fabrication of antiaromatic ring-doped nanomaterials. Via the 1,3-dipolar reaction between an azomethine ylide and aryl cyanide functional groups, internally N-doped conjugated wires with lengths of tenths of nanometers are constructed with very high yield. By annealing to a higher temperature, it may further dehydrogenate and form internally N-doped graphene nanoribbons.

Towards hetero-nanostructures, a proof of principle for the functionalization of graphene edges with tetrapyrrolic species by a dehydrogenative coupling reaction directly on a metal surface used for graphene synthesis is provided. Due to the irregular graphene edges and the different bonding mechanism, distinct bonding motifs are observed. Their high thermal and structural stability up to 900 K open pathways to incorporate porphines and related species in extended graphene sheets, to apply solution processing or to transfer such hybrid structures to other substrates. Graphene grown on copper foils is etched by H\textsubscript{2} and then successfully transferred on targeted substrate with exposed edges preserved for the functionalization with molecules. However, due to the low density of the incorporated nitrogen atoms it is not straightforward for a macroscopic technique, such as XPS, to detect the nitrogen signal, and also hard for STM to find such a place with coupled molecules. Moreover, two further molecules, bt and DBAP, are shown to be able to decorate graphene edges via their radicals. A significant advantage of using these molecules is that they will couple to the graphene edge in a more controlled way. However, they also suffer from the steric hindrance and the yield is relatively low.

It is expected that a further enhancement of the control on the coupling is necessary to fully exploit the introduced methodology. This may be achieved by specifically designed
precursor molecules and/or improved synthesis protocols yielding well-defined graphene edges. 7-AGNR with well-defined armchair edges at the long side and zigzag edges at the short side couples to porphines in various configurations. However, it showed that only the zigzag edge and the first dent of the armchair edge are capable of coupling to porphines, which is attributed to the preferred orientation of both the GNR and porphine on Ag(111) and the edge state at the zigzag edge of the GNR. This property may be exploited to connect two molecules, such as porphines, with a clean nanowire. To further investigate the coupling mechanism, pyrphyrins, with two free sides resembling the armchair edge, couple solely to the zigzag edge of the GNR. The on-surface dehydrogenative coupling protocol introduced here will enable the direct functionalization of graphene nanostructures whose synthesis has already been demonstrated on Ag(111) and similar substrates. Specifically, the findings provide a new tool for the controlled modification of surface-anchored nano-graphenes and graphene nanoribbons. Such structures are anticipated to play a significant role in diverse application fields such as molecular electronics, sensing or optoelectronics and catalysis.

These results demonstrated that bottom-up self-assembly of nanostructures is a promising method towards next generation nanoelectronics. Nanostructures with pre-defined patterns and atomic precision can be constructed by delicately designed precursors. At present, deeper understanding and better control of the coupling is required. Future experiments could aim at the exploration of:

- Metal-organic networks involving two or more porphyrin derivatives that have already been simulated by the Monte-Carlo simulations. On one hand, to examine the coordination behavior of such molecular systems experimentally. On the other hand, to compare with Monte-Carlo simulations and further improve it.

- Use another precursor of porphine dimer to form extended porphine chains, for example, the dibromo-bisporphine, without any additional meso-substituents. With this simple system, we may find out whether the macrocycles are already flattened after landing on the surface.

- Coupling of porphine to well-defined edges of graphene islands. Such a graphene edge can be obtained by etching graphene grown on Ir(111) with molecular oxygen. In this case, the factors influencing the coupling motifs can be better understood.

- Picking up GNRs coupled with porphines onto NaCl islands\textsuperscript{49} to investigate the electronic properties of the covalently coupled heterostructure.

- Optimizing the $H_2$ etching process of graphene grown on copper foils, to expose more graphene edges. Then functionalizing the patterned graphene either on copper foil or on targeted substrates after transferring.

- Patterning graphene grown on the copper foil with more controlled technique, such as lithography.
List of Publications


A. Graphene Patterning

It has been presented in the previous parts of this thesis, that graphene edges can be functionalized with molecules, such as porphine, via on-surface coupling. In this sense, for a full graphene sheet, only its edges can be functionalized and the density of coupled molecules is limited by the length of exposed graphene edges. One way to obtain more graphene edges is to create vacancies inside the graphene sheet, which leads to more edges. It would be ideal, if the location, size and density of the created vacancies can be controlled. Many methods have been reported being capable of etching graphene sheets, such as using molecular hydrogen\(^\text{253–261}\), hydrogen plasma\(^\text{262,263}\), molecular oxygen\(^\text{264–266}\), atomic oxygen\(^\text{267,268}\), oxygen plasma\(^\text{269–271}\), lithography\(^\text{262,272}\) and nanoparticles\(^\text{273–276}\).

In this chapter, the graphene grown on copper foils using CVD growth in a reaction tube furnace is etched by molecular hydrogen at high temperature. The etched graphene is then transferred onto MoS\(_2\) and Au(111) and studied with AFM and STM.

A.1. Hydrogen Etching of Graphene Monolayer on Copper Foils

Here, molecular hydrogen etching, as described in ref. [254], is employed to produce pores within the graphene layer. Hydrogen etching was chose because of its anisotropic etching behavior and also it does not require other equipment. Graphene was grown on copper foil using the procedure described in section 5.1.1. After having checked the graphene quality with SEM, the graphene covered copper foil was put back into the tube furnace again. To produce holes in the graphene layer, the partial pressure of hydrogen gas is adjusted higher (5.0\(^{-1}\) Torr) than in the growth process (2.5\(^{-1}\) Torr), to reverse the decomposition process of CH\(_4\). The annealing temperature is set lower than the temperature used in the growth process, to constrain the activity and the reaction rate of the CH\(_4\) formation. Several different etching temperatures were tested and the results are shown in Fig. A.1. In addition to the copper step edges and the black graphene wrinkles, white stripes in Fig. A.1a-e were observed, which are assigned to copper oxide, indicating a successful etching of graphene, because copper oxide only forms in the area where graphene is etched away and the bare copper is exposed without protection. The shape of etched parts resembles the fractured surface and most of them are perpendicular to the copper step edges, especially clear in Fig. A.1c, like the wrinkles. This suggests that these etched areas are where wrinkles used to be. This has been reported previously\(^\text{261}\) and is attributed to the high reactivity of the carbon atoms at the curling positions. A quantitative analysis of the size of the etched area at different etching temperature is shown in Fig A.1 (red line). Remembering the initial idea of having this etched areas to produce more graphene edges. Thus the length
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Figure A.1. Graphene etched by molecular hydrogen at high temperature. a-f) SEM images of graphene on the copper foil etched at different temperature. g) Analysis of the size of the etched area and the length of the exposed graphene edges at different etching temperatures.

of the exposed graphene edges is also calculated and is shown as the dashed blue line in Fig. A.1. As the temperature increases, the size of the etched areas increases from 6% at 1020 K to 80% at 1170 K. After heating to 1170 K, almost no graphene was left on the copper foil, while heating to 1020 K, the graphene layer was almost intact with only a few white areas. Regarding the length of the exposed graphene edges, it spikes at the 1080 K with a length of 7.3 millimeters per 0.02 mm², this corresponds to a density of the nitrogen atom below 0.1% assuming half of the edges is decorated with porphines. This low density of nitrogen atoms is far below the threshold detectable by XPS.

Fig. A.2a shows a SEM image of the etched graphene on the copper foil. The copper step edges are all in one direction in the scanned area, and their direction is pointed out
A.1. Hydrogen Etching of Graphene Monolayer on Copper Foils

Figure A.2. Hydrogen etched graphene at 1070 K studied by SEM and AFM. a) SEM image shows a large copper grain, where all step edges are in one direction. b-c) Flat areas were observed in AFM images, as highlighted with green and marked with green dashed hexagons.

by the red arrow. The white stripes are also only in one direction and are perpendicular to the step edges. In addition to the stripe-shaped white areas, small white dots can also be resolved, and a better characterization of these small dots is beyond the ability of this SEM. Thus AFM measurements were performed. In Fig. A.2b, some areas (masked with green) appear flatter than the other area and no step edges were observed. The edges of these were straight. These flat areas are assigned to the white stripes observed in the SEM. The green dashed hexagon marked areas in Fig. A.2b and c also appeared
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flattened and corresponded to the small white dots observed in the SEM. A bright spot was observed in the center of all these hexagons and is probably a dirt. It has been reported such dirt often acts as reaction center and thus it is likely the starting point of the etching reaction. Because of these small etched holes, which can not be resolved in SEM, the calculation of the size of the etched area, as well as the length of the graphene edges, can only be considered as a rough estimation.

A.2. Transfer of Patterned Graphene onto MoS₂ and Au(111)

Transfer of large-area graphene obtained by CVD on copper foils onto targeted substrate is required for graphene-based applications. With the help of the PMMA, the graphene layer can be successfully extracted from the copper foil and then placed on the destination substrate. Here, a similar process as described in ref. [277] is used to transfer the patterned graphene onto an exfoliated MoS₂ sample as shown in Fig. A.3. One major obstacle is the completeness of the graphene layer after the transfer. After etching the graphene layer may no longer be a whole piece, but several separated small graphene flakes, for example, the one shown in Fig. A.1e. To reduce the risk of making the graphene falling apart during the transfer, less intensely etched graphene, here the one heated to 1070 K, was used in the transfer.

Figure A.3. The transfer process of graphene grown on copper foils onto MoS₂, adapted from ref. [277]

Firstly, PMMA was spin-coated on one side of the copper foil with graphene on it.
A.2. Transfer of Patterned Graphene onto MoS$_2$ and Au(111)

After the PMMA had been dried in air, the graphene on the other side of the copper foil was removed using the oxygen plasma etching. Without this step, the graphene grown on the other side will protect the copper foil from etching. Afterwards, the PMMA/graphene/copper foil sample was put into the aqueous ammonium persulfate for 12 hours to remove the copper substrate. After the copper foil is removed, transparent PMMA/graphene membrane can be observed floating on the surface of the solution. It is then scooped out from the solution using a glass slide and then places on the surface of another solution. The same scooping out and placing back procedure was repeated for deionized water and isopropyl alcohol, each for several times, to remove the aqueous ammonium persulfate. Now the PMMA/graphene can be transferred onto target substrate, i.e. MoS$_2$ or Au(111). After drying in the air for half an hour, the sample was annealed in the tube furnace at 450 K for 1 hour to remove the water. Then it was put in an acetone solution to remove the PMMA coating. Finally, the sample was annealed in the tube furnace in air at 570 K for 5 hours.

A.2.1. Patterned Graphene on MoS$_2$

Fig. A.4a shows an AFM image of the etched graphene transferred on MoS$_2$. In addition to the white areas and stripes, which have already been identified as water or PMMA residuals and wrinkles respectively, two different contrasts were clearly resolved, indicating there are two layers. The area with brighter contrast is assigned to single layer graphene, and the areas with darker contrast are MoS$_2$ where graphene is etched away. Both closed hexagonal holes and unclosed large etching area with irregular shapes were observed. Most of their edges are straight, which are attributed to the anisotropic etching by molecular hydrogen. The large irregular dark areas correspond to the white stripes observed in the SEM and AFM and the small etched holes may be the hexagons observed in the AFM prior to the transfer.

![Figure A.4](image)

**Figure A.4.** Etched graphene transferred onto MoS$_2$. a) Etched area appears darker in the AFM image. b) STM image shows a graphene/MoS$_2$ interface ($U = 0.1$ V, $I = 5$ nA).

The same sample was then put into a room-temperature UHV-STM. Before checking it with STM, it was annealed at 570 K in UHV for 3 hours to remove the water trapped
A. Graphene Patterning

beneath the graphene. Fig. A.4 shows a STM image of the graphene/MoS$_2$ surface. Two layers were present and the edges are very straight and form 120° angles at the turning position. The bottom left lower layer is assigned to MoS$_2$, because dark holes (yellow arrows) were observed, which are the signature feature of MoS$_2$ after annealing. The higher part on the top right is thus assigned to graphene. STM image with atomic resolution of the graphene part was also obtained. These AFM and STM images clearly demonstrate that graphene and MoS$_2$ surfaces are both observed on the sample and confirm a successful transfer of the etched graphene from the copper foil onto MoS$_2$.

A.2.2. Patterned Graphene on Au(111)

Figure A.5. Etched graphene transferred onto Au(111). a,b) AFM images and c,d) STM images of the etched graphene on Au(111). Scan parameters: c) $U = 0.5$ V, $I = 400$ pA; d) $U = 0.5$ V, $I = 500$ pA.

Comparing the exfoliated MoS$_2$, Au(111) surface is very rough, although it is a single crystal. On such a "rough" surface, graphene sheets tend to fold and produce a lot of wrinkles, which makes the surface even rougher. Nevertheless, the etched graphene layer was transferred onto the Au(111) single crystal. From the AFM images shown in Fig. A.5a, it can be seen the surface is much rougher than the MoS$_2$ with transferred graphene layer. More bright stripes were observed, corresponding to the wrinkles, as mentioned before. Multiple heights were observed, probably due to the folding of the graphene sheet or step edges of Au(111). Featureless areas with straight edges were present, indicating these areas are exposed Au(111) surface. The sample was also measured with STM, after annealing to 600 K to remove the trapped water or PMMA. The rough surface appears rougher under STM and makes a clear imaging very hard. From a few good images, step edges of Au(111) surface can be resolved, but there were no signs of the graphene layer. Porphines form very large polymers on Ag(111) when annealing to very high temperature (870 K). Similar behavior is expected for porphines on Au(111), due to the similar reactivity of Au(111) and Ag(111). Since porphines only stay on Ag(111) (Au(111)), not on graphene. These polymers are expected to only ex-
A.3. Summary

In this chapter, it is demonstrated that graphene grown on copper foils using CVD method can be etched in a controlled way by adjusting the annealing temperature and the partial pressure of the hydrogen. The etched graphene was successfully transferred onto other substrates, such as MoS$_2$ and Au(111), and was evidenced by the AFM and STM measurements. The exposed edges of graphene can be further functionalized on the target surface by functional molecules. A quick calculation showed that produced etched edges are still too few for coupling with a significant amount of porphines. Thus further optimization of the hydrogen etching process or even another more efficient patterning method is required.
References


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