On-Surface Design of Lanthanide-Based Nanoarchitectures

Tesis doctoral presentada por

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Abstract

Lanthanide-directed nanoarchitectures on-surfaces are envisioned to have large impact in a wide variety of fields such as luminescence, magnetism, sensing or catalysis. In this thesis, the design of lanthanide nanomaterials on metallic supports exploiting distinct coordinative environments will be addressed. In particular, surface-confined supramolecular nanoarchitectures will be implemented in order to embrace the properties of lanthanides, taking the advantage of lateral and axial coordinative supramolecular approaches. These low-dimensional systems are mainly investigated using scanning tunneling microscopy (STM), known for its high spatial resolution in topography and characterization of electronic structure, while space-averaged techniques such as X-ray Photoelectron Spectroscopy (XPS) and density functional theory (DFT) calculations will complement the physico-chemical input.

First, a close-packed supramolecular assembly of novel species of single molecule magnets (SMM) featuring a double decker geometry (Ln(OETAP)$_2$ family) is described, whose magnetic anisotropy in bulk arises from the appropriate axial symmetry of the eight-fold coordinative environment of the lanthanide ion. Herein, the preservation of the chemical and electronic properties of these compounds upon adsorption on three coinage metals Au(111), Ag(111) and Cu(111) are demonstrated in a comprehensive STM, DFT and XPS study.

Second, the capability of lanthanides to direct surface-confined metal-organic networks via lateral coordination with ditopic carboxilate organic linkers (TDA) on Cu(111) is described. By selecting different lanthanide ions (Dy or Gd) and organic building blocks (TDA, PDA or TPA), both the node geometry or intermodal distance within the supramolecular lattices can be tuned.
Third, regarding macrocyclic coordination, the capability of two porphyrinoid species with distinct cavity size to host dysprosium ions is described. On one hand, intact expanded porphyrinoids (HTAP) show promising results for long-term information storage by single molecule tip-induced deprotonation, while demonstrating that their large macrocycle can complexate lanthanides in an off-centered fashion. On the other hand, the smaller tetraphenyl-porphyrin derivative (2H-4FTPP) evidences that tetrapyrroles on Au(111) cannot host dysprosium ions in the main macrocyclic plane, but beneath it. Importantly, when the Dy is physisorbed below the 2H-4FTPP macrocycle, a Kondo resonance of molecular origin is observed, affording a Kondo temperature of 120 K, which can be switched off by tip-induced pulses.

Finally, the catalytic activity of dysprosium on aryl bromides on Ag(111) upon annealing is comprehensively studied. In the absence of dysprosium, aryl bromides (DBTP) react following an Ullman-like coupling scheme forming poly(p-phenylene) wires, which after further annealing couple laterally giving rise to armchair Graphene Nanoribbons (aGNRs) and all-carbon heterojunctions built up by aGNR and poly(p-phenylene) wires. A local STS study of the inherent electronic structure, proves quantum confinement in the enclosed aGNR sections. In the presence of dysprosium, dehalogenation of aryl bromides occurs almost spontaneously at room temperature (RT), forming irregular organo-metallic Dy-directed nanoarchitectures, whose geometry inhibits the Ullmann coupling scheme upon further annealing, limiting the length of covalent reaction products.

Our results provide hitherto protocols to design new lanthanide-based nanoarchitectures on surfaces, opening a new arena to exploit their technologically relevant properties.
Resumen

Las nano-arquitecturas que incorporan lantánidos en superficies tienen un gran potencial para ser aplicadas en una amplia variedad de campos como luminiscencia, magnetismo, detección molecular o catálisis. En este trabajo se describen distintos enfoques para diseñar nano-materiales con lantánidos en soportes metálicos explotando diferentes ambientes de coordinación, como el lateral, axial, macrocíclico y organometálico; que permiten a las estructuras supramoleculares beneficiarse de las propiedades únicas de estos elementos. Para caracterizar estos sistemas principalmente se utilizará la técnica de microscopía de efecto túnel (STM) dada su alta resolución espacial y electrónica, siendo complementada con técnicas experimentales como la espectroscopía de fotoelectrones emitidos por rayos X (XPS) y de estudios teóricos enmarcados en la teoría de la densidad funcional (DFT).

Primero se ha estudiado una nueva familia de imanes moleculares (SMM) con estructura tipo sándwich \((\text{Ln(OETAP)}_2)\), cuya anisotropía magnética en volumen emerge de la adecuada coordinación axial del ión lantánido central. Después de describir su auto-ensamblado en las superficies metálicas de \(\text{Au(111)}, \text{Ag(111)}\) y \(\text{Cu(111)}\), la conservación de sus propiedades químicas y electrónicas al ser adsorbidas en superficies ha sido probada mediante un estudio combinado de STM, DFT y XPS.

En segundo lugar se ha investigado la capacidad de los lantánidos para dirigir redes metal-orgánicas confinadas en la superficie \(\text{Cu(111)}\) mediante la coordinación lateral con monómeros lineales ditópicos funcionalizados con grupos carboxilatos (TDA). Seleccionando distintos elementos (Dy o Gd) o monómeros orgánicos (TDA, PDA o TPA), se ha podido modificar la geometría nodal o la distancia entre vértices lantánidos de las redes supramoleculares resultantes.
En tercer lugar se han inspeccionado las capacidades de coordinación macrocíclica de dos especies de porfirinoides con cavidades de distintos tamaños. Por un lado los porfirinoides expandidos (HTAP), que presentan un macrociclo de mayor tamaño, pueden ser deprotonados individualmente mediante pulsos de voltaje efectuados localmente con la punta del STM, así como la capacidad para complejar lantánidos (Dy) de forma asimétrica. Por el otro, la tetrafenilporfirina (2H-4FTPP) ha demostrado que las cavidades tetrapirrólicas son demasiado pequeñas para albergar iones de dispropósito dentro del macrociclo, complejándolos fuera del mismo. Es importante remarcar que en las especies en las que el lantánido se encuentra físisorbitado debajo del macrociclo (Dy-2H-4FTPP) se ha encontrado una resonancia Kondo de origen molecular que muestra una $T_K$ de 120 K, cuya señal desaparece irreversiblemente mediante manipulación vertical con la punta del STM.

Por último se ha indagado en la actividad catalítica del dispropósito con arilos bromados (DBTP) en la superficie Ag(111). Por un lado, en la ausencia del metal lantánido los monómeros bromados han seguido una reacción tipo Ullmann, resultando en la formación de poli(p-fenilenos), que al calentar a mayor temperatura se enlanzan lateralmente formando tiras de grafeno (aGNR) y heterouniones. La estructura electrónica, analizada mediante espectroscopía de efecto túnel (STS), muestra confinamiento cuántico en las secciones de las tiras de grafeno conectadas en sus extremos por poli(p-fenilenos). Por otra parte, en presencia del lantánido se observa la dehalogenización terminal espontánea a temperatura ambiente y la formación de nano-arquitecturas organometálicas dirigidas por dispropósito, cuya geometría impide el desarrollo de la reacción de Ullmann al ser calentadas.

Estos resultados describen protocolos para diseñar nano-arquitecturas con lantánidos en superficie y abren un nuevo escenario para explotar sus interesantes propiedades físico-químicas.
## List of Acronyms

<table>
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<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>STS</td>
<td>Scanning Tunneling Spectroscopy</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XMCD</td>
<td>X-ray Magnetic Circular Dichroism</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>LT-STM</td>
<td>Low Temperature Scanning Tunneling Microscope</td>
</tr>
<tr>
<td>VT-STM</td>
<td>Variable Temperature Scanning Tunneling Microscope</td>
</tr>
<tr>
<td>CHM</td>
<td>Constant Height Mode</td>
</tr>
<tr>
<td>CCM</td>
<td>Constant Current Mode</td>
</tr>
<tr>
<td>LM</td>
<td>Lateral Manipulation</td>
</tr>
<tr>
<td>VM</td>
<td>Vertical Manipulation</td>
</tr>
<tr>
<td>LDOS</td>
<td>Local Density of States</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>CITS</td>
<td>Current-Imaging Tunneling-Spectroscopy</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>LN₂</td>
<td>Liquid Nitrogen</td>
</tr>
<tr>
<td>LHe</td>
<td>Liquid Helium</td>
</tr>
<tr>
<td>OMBE</td>
<td>Organic Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>OETAP</td>
<td>Octaethyltetraazaporphyrin</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>TDA</td>
<td>4,1',4',1&quot;-Terphenyl-1,4&quot;-Dicarboxylic Acid</td>
</tr>
<tr>
<td>TPA</td>
<td>Terephthalic Acid</td>
</tr>
<tr>
<td>PDA</td>
<td>Pyrene-2,7-Dicarboxylic Acid</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna Ab initio Simulation Package</td>
</tr>
<tr>
<td>HTAP</td>
<td>[30]trithia-2,3,5,10,12,13,15,20,22,23,25,30-dodecaazahexaphyrin</td>
</tr>
<tr>
<td>2H-4FTPP</td>
<td>5,10,15,20-tetrakis-(4-fluorophenyl)-21,23H-Porphyrin</td>
</tr>
<tr>
<td>DBTP</td>
<td>4,4&quot;-Dibromo-p-terphenyl</td>
</tr>
<tr>
<td>aGNR</td>
<td>Armchair Graphene Nanoribbon</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction Band Minimum</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence Band Maximum</td>
</tr>
<tr>
<td>GQB</td>
<td>Graphene Quantum Box</td>
</tr>
<tr>
<td>QWS</td>
<td>Quantum Well State</td>
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Introduction

The advent of nanotechnology was motivated in the last decades of the 20th century by new advances in experimental developments that made feasible the characterization and manipulation of matter at the nanoscale. During this period, nanotechnology has demonstrated its enormous potential and impact in a wide variety of fields such as material science, medicine, electronics, photonics, etc.; being considered the next technological revolution. This rapid progress responds to distinct industrial necessities to miniaturize components, such as drug delivery in pharmacy and nanomedicine or transistors and storage devices in microelectronics. Importantly, while diminishing the dimensionality of the systems, the role of surfaces and interfaces rises as a crucial phenomenon as their properties differ substantially from the ones exhibited in bulk. Thus, surface science is today a revitalized topic, steered by the growing interest in novel materials including two-dimensional materials such as graphene or topological insulators, while anticipating a new era in chemistry by on-surface synthesis protocols. In this sense, since the dawn of nanotechnology, a requisite for new nanofabrication protocols proved to be
compulsory, as the classic top-down approaches evidenced a lack of precision at the atomic scale. Therefore, the so-called bottom-up strategy, with a wide variety of possibilities regarding atomically precise design, is nowadays extensively investigated in surface science in order to tailor advanced materials with targeted functionalities.

Contemporary to the dawn of nanotechnology, lanthanide elements have attracted the attention of both the scientific and the industrial community, as their unique physico-chemical properties are being exploited in a large variety of applications, from mundane (glass polishing, mischmetals,...) to high tech (displays, strong magnets, lasers, magnetic storage...). Additionally, they are anticipated to play a crucial role in futuristic technologies such as spintronics, quantum information, high temperature superconductivity, magnetic cooling, etc. These elements feature a general electronic configuration [Xe]4f\(^{n}\)5d\(^{0}\)6s\(^{2}\) that comprises 15 elements, from \(n=0\) for lanthanum (Z=57) to \(n=14\) for lutetium (Z=71), having some exceptions such as lanthanum, cerium, gadolinium and lutetium, which present an unpaired 5d electron. Typically lanthanides present a +3 oxidation state, while cerium can also be oxidized to +4 and lanthanum, samarium, europium and ytterbium to +2; being suitable for redox chemistry. Importantly, all the lanthanide elements have the 4f valence band strongly protected by the outer 5s\(^{2}\)5p\(^{6}\) shells. This peculiar electronic structure, together with their large ionic radius, results in the high coordination numbers exhibited by lanthanide ions in bulk chemistry. Regarding their magnetic properties, lanthanides exhibit a strong spin-orbit coupling, with deep implications in their Hamiltonian electronic description whose states are characterized by the total angular momentum \(J\). Furthermore, lanthanides show the largest magnetic moments and single ion anisotropy of all the elements, establishing them in a privileged position to design magnets at the atomic scale. Concerning luminescence, lanthanides show both narrow light-emitting lines between "forbidden" f-f transitions, though accessible by ligand field coordination, which are almost unperturbed by the chemical environment, and broader f-d transitions that can be tuned by incorporating the ions in distinct environments. Hereby, the very narrow light emission from f-f
1.1 Outline of the Thesis

The thesis is organized as follows:

Chapter 2 briefly summarizes the theoretical background of the implemented techniques and describes the experimental set-ups employed during the thesis. After detailing the electron tunneling phenomenon between two electrodes and the photoelectric effect, the diverse operational modes of a STM are described. After that, the main experimental systems are introduced, together with the inherent instrumentation used to prepare samples and tips suitable for scanning tunneling microscopy at ultra high vacuum conditions.

Chapter 3 introduces a new species of double decker single molecule magnet (SMM) consisting in a lanthanide atom coordinated between two porphyrazine backbones functionalized with decoupling terminal ethyl groups. The chemical structure of these compounds, Tb- and Dy-substituted, shows no variation upon sublimation and adsorption on different coinage metals. Finally, the decoupling mechanism exerted by the functionalized ethyl moieties, suggested by density functional theory calculations (DFT), is investigated and corroborated by means of X-ray Photoelectron Spectroscopy (XPS).

Chapter 4 investigates the capability of lanthanide elements to direct transitions is highly appreciated in luminescent devices and bioprobes due to their high saturation color.

Despite the widespread usage of lanthanides and their great potential, the on-surface study of these elements is very incipient. To tackle this extraordinary scientific opportunity, the purpose of this work is to design functional nanostructures embedding lanthanide elements at surfaces. To this aim, the bottom-up strategy will be employed, exploiting the coordination capabilities of lanthanides in molecular architectures, together with the high versatility offered by the organic building blocks.
metallosupramolecular assemblies driven by Ln-carboxylate interactions on surfaces. First, linear ditopic linkers functionalized with carboxylic groups are deposited on Cu(111), whose reactivity ensures their terminal deprotonation. Upon gadolinium deposition, reticulated lattices are observed featuring thermal robustness up to 400 K. DFT calculations shed light on the prevalently ionic character of the Gd-O bond, further confirmed by minute shifts in XPS core level spectra. Second, the versatility of the networks is tested by depositing dysprosium, resulting in similar squared lattices stabilized by the same eightfold node. Importantly, annealing at 450 K results in the formation of hexagonal quasi-regular lattices featuring unprecedented diatomic dysprosium vertexes. Finally, the tunability of the internodal distance in the reticular networks is demonstrated by depositing organic linear linkers of distinct length.

Chapter 5 includes two systems involving porphyrinoid derivatives: (i) an expanded porphyrin featuring 27 atom in its cavity (HTAP) and (ii) a tetraphenyl-porphyrin functionalized with terminal fluorine atoms (2H-4FTPP). In the first part of the chapter, the adsorption and long-range orientational self-assembly of an expanded porphyrin is for the first time addressed on surfaces. A novel protocol to fully deprotonate HTAP species at the single molecular level on Au(111) is detailed, being able to transfer it to Ag(111). Finally, these large macrocycles show the ability to complexate dysprosium atoms in an off-centered fashion. In the second part of the chapter, dysprosium is deposited on top of submonolayer 2H-4FTPP samples on Au(111), affording the formation of three different Dy-related species: physisorbed Dy-2H-4FTPP, intermediate Dy-1H-4FTPP and the fully metalated Dy-0H-4FTPP species. The narrow low voltage bias resonance measured on the physisorbed Dy-2H-4FTPP is related to the Kondo effect, and can be irreversible switched off by vertical manipulation.

Chapter 6 addresses the potential of lanthanides to catalyze dehalogenation and their role in the Ullmann reaction. On one hand, in the absence of such dysprosium element, linear brominated linkers (aryl bromides) follow a reaction through annealing steps that comprises: organometallic, covalent
1.1 Outline of the Thesis

C-C coupling and lateral coupling via terminal dehydrogenation, resulting in the fabrication of armchair graphene nanoribbons (aGNRs). Their electronic structure is investigated by means of scanning tunneling spectroscopy (STS), revealing a quantum box electron confinement in the aGNR sections within the poly(p-phenylene)-aGNR-poly(p-phenylene) heterojunctions. On the other hand, in the presence of dysprosium, a spontaneous debromination at room temperature is observed with STM and corroborated by DFT calculations. Further increase of the annealing temperature reveals that the Ullmann reaction is strongly hindered, affording a precise control of the polymeric length, which indicates that the specific geometry of the organo-metallic phase is crucial for undergoing latter stages in the covalent reaction schemes.

Finally, Chapters 7 and 8 summarize the main results presented in this work, in English and Spanish respectively, followed by the bibliography, the list of publications and the acknowledgments.
Figure 1.1: *Graphical Table Of Contents of the Thesis.* This figure represents a graphical summary of chapters 3 (bottom right), 4 (upper left), 5 (upper right) and 6 (bottom left); highlighting with red the lanthanide elements investigated in this work.
This chapter will describe the basics of scanning tunneling microscopy (STM)\textsuperscript{1}. First, the quantum mechanical formalism necessary for understanding the electronic tunneling will be reviewed, followed by the approximation proposed by Tersoff-Hamann\textsuperscript{2}. Then, the modes of operation of the STM will be explained, focusing on manipulation techniques and Scanning Tunneling Spectroscopy (STS), followed by a short summary regarding the X-ray Photoelectron Spectroscopy (XPS). In the last section the main experimental set-ups used during the thesis will be detailed. Therein, the specific instruments used to scan and the procedures to prepare samples and tips suitable for STM measurements are described.
2.1 Tunnel Junction Theoretical Approach

Figure 2.1: Quantum Tunneling Through a Barrier. a) Scheme of a particle with defined energy \( E \) moving towards the right (+x) penetrating a wide energy barrier \( U_0 \) at \( x_0 \). The width of the barrier results in the vanishing at a certain point of the transmitted wavefunction \( \Psi_T(x) \). b) A wavefunction \( \Psi(x) \) trespassing a narrow energy barrier \( U_0 \) of width \( d \), resulting into the transmitted wavefunction \( \Psi_T(x) \).

In the classical approximation, a particle with mass \( m \), linear momentum \( p \) and energy \( E \), confined in a well-defined one-dimensional (1D) potential \( U(x) \), is described by the equation:

\[
\frac{p^2}{2m} + U(x) = E
\]  

(2.1)

In classic mechanics the term \( \frac{p^2}{2m} \) will be always \( \geq 0 \), implying that the particle has a strict zero probability to overcome an energy barrier \( U(x) \) when its total energy \( E \) satisfies \( E < U(x) \), i.e. it will be confined. This
means that the regions where the condition $E < U(x)$ is fulfilled, the probability to find the particle there will be strictly zero. In quantum mechanics the scenario is radically different, where the wavefunction $\Psi$ describes the behavior of a particle when it is a solution of the Schrödinger equation, whose most general expression is:

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi$$ (2.2)

where $\Psi$ is the wavefunction, $\hbar$ is the reduced Planck constant and $\hat{H}$ the Hamiltonian operator. In order to illustrate the quantum tunneling of an electron through an energy barrier some assumptions are taken for simplicity, describing the time-independent one-dimensional non-relativistic Schrödinger equation:

$$\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right) \Psi(x) = E\Psi(x)$$ (2.3)

There are two solutions to this equation, depending on the energy regime, for a particle moving towards positive values of $x$:

$$\Psi(x) = \begin{cases} \psi_0 e^{\sqrt{\frac{2m}{\hbar^2}}(E-U)\frac{x}{\hbar}} = \psi_0 e^{ikx} & \text{if } E > U \\ \psi_0 e^{-\sqrt{\frac{2m}{\hbar^2}}(U-E)\frac{x}{\hbar}} = \psi_0 e^{-kx} & \text{if } E < U \end{cases}$$ (2.4)

In analogy to the classical regime, the particle has a wave vector $k = \sqrt{\frac{2m}{\hbar^2}(E-U)}$ and a constant linear momentum $p = \hbar k$ for the $E > U$ case. On the contrary, when $E < U$ is satisfied, the particle has now a non-zero probability of being at $x_0$ for which $U(x_0) > E$, i.e. the region forbidden in classical mechanics. The probability density $\Gamma(x)$ can be expressed as:

$$\Gamma(x) = |\Psi(x)|^2$$ (2.5)

which in this case is $\Gamma(x) = |\psi_0^2|e^{-2kx}$. This describes how the probability density of a particle decreases exponentially with a decay constant $k = \frac{\sqrt{2m(U-E)}}{\hbar}$ in the regions where an energy barrier is present (see Figure
2.1 a). If now the barrier is finite and narrow, the particle, e.g. one electron, can pass through the energy barrier and its described by a different wavefunction $\Psi_T(x) = \psi_{0}^{ikx}$. This phenomenon is known as quantum tunneling, related to the fact that the particle can tunnel through an energy barrier, having no equivalent process in classical physics. In the described case (see Figure 2.1 b), a particle with a one-dimensional wavefunction $\Psi(x)$ tunnels through and energy barrier $U_0$ of width $d$ and, resulting in the transmitted wavefunction $\Psi_T(x)$.

The quantum tunneling process of electrons between a metal tip and a sample is precisely the basic principle of a STM, considering that the vacuum in between acts as an energy barrier. Nevertheless, this picture is just a simplified idealization of a much more complex description of the tunneling effect in the STM junction. Several attempts to theoretically describe the tunneling junction basic principle have been carried out to date. In general all the approximations have the same starting point, the work of Bardeen in 1961 entitled "Tunneling from a many-particle point of view". In this work, Bardeen described the tunneling of electrons through an insulator barrier between two electrodes $\mu$ and $\nu$. The derivation of Bardeen’s theory will not be detailed in this chapter, as it can be found elsewhere. This general approach requires to model separately the $\mu$- and the $\nu$-electrodes electronic structure, assuming that their electronic states are nearly orthogonal. This originates two different Hamiltonians for the two distinct regions, separated by a certain vacuum volume. They are modeled separately, since solving different equations for individual systems is much easier than trying to solve the combined set. In this regard, Bardeen realized that the amplitude of electronic transfer is proportional to the flux in an imaginary surface $\Sigma$ in the vacuum region, where both subsystem wavefunctions overlap. Following this approach, the specific form and position of the $\Sigma$ is arbitrary, since the results do no change appreciably. The expression for the tunneling current $I_t$ when an external bias voltage $V_b$ is applied to the electrode $\nu$ is:

$$I_t = \frac{2\pi e}{h} \sum_{\nu, \mu} f(E_{\nu})[1 - f(E_{\nu} + eV_b)]|M_{\mu,\nu}|^2 \delta(E_{\mu} - E_{\nu})$$  \hspace{1cm} (2.6)
Where $M_{\mu,\nu}$ is the tunneling matrix element, and $|M_{\mu,\nu}|^2$ is the electronic transfer amplitude at the separation surface $\Sigma$ between the states of $\mu$ and $\nu$ at the energy $E_{\mu,\nu}$. It is important to notice that this theory was derived 20 years before STM was first invented, therefore it represents a very general approach for the tip sample junction. The first work that adapted this formalism to the STM framework of the tip-sample junction was done by Tersoff-Hamann in 1985. They used Bardeen’s theory of the two electrodes separated by an energy barrier to model the tip-sample junction, in which a bias voltage $V_b$ is applied between them. The expression can be simplified by assuming small bias voltage $V_b$ and low temperature to:

$$I_t = \frac{2\pi e^2}{\hbar} V_b \sum_{t,s} |M_{t,s}|^2 \delta(E_t - E_F) \delta(E_s - E_F)$$

(2.7)

where $e$ is the charge of the electron and $E_F$ is the Fermi energy of the tip and the sample, assumed to be equal. From this expression one can directly see that the tunneling current $I_t$ is proportional to the bias voltage $V_b$. Furthermore, considering the ideal case of a point-probe tip, located at a distance $r_0$ of the sample, the matrix element $M_{t,s}$ is reduced to:

$$I_t \propto V_b \sum_s |\Psi_s(r_0)|^2 \delta(E_s - E_F) \equiv V_b \cdot \rho_s(r_0, E_F)$$

(2.8)

where $\rho_s(r_0, E_F)$ represents the local density of states (LDOS) of the surface at $r_0$ and at the Fermi energy $E_F$. This relation between the tunneling current $I_t$ and the LDOS has important implications and relies behind the principle of the scanning tunneling spectroscopy (STS). Taking into account that $\rho_s(r_0, E_F) = \rho_s(0, E_F)e^{-2kr_0}$ and substituting it into (2.8) the expression can be written as:

$$I_t \propto V_b \cdot \rho_s(0, E_F) \cdot e^{-2kr_0}$$

(2.9)

where $k = \sqrt{\frac{2m\phi}{\hbar}}$ and $\phi$ is the work function. Nevertheless, it is clear that in order to evaluate correctly the matrix elements, the geometry of the
tip has to be known with accuracy. In this regard, diverse authors attempted to theoretically model the tip-sample junction in the last years to evaluate the tunneling matrix elements in a more accurate way, such as pyramidal W tips or W surfaces with adatoms. For simplicity, in the original Tersoff-Hamann work the tip was modeled assuming that its terminal atom had an s-wave function, i.e. a locally spherically symmetric wavefunction with radius of curvature $R$. If the tip-sample distance is $d$, then $r_0 = R + d$ and $I_t$ can be written as the following expression:

$$I_t \propto V_b e^{-2kR} \rho_t(E_F) \rho_s(R + d, E_F)$$

(2.10)

where $\rho_s(R + d, E_F) = \rho_s(0, E_F) e^{-k(R+d)}$. This equation shows that the tunneling current exponentially depends on the tip-sample distance $d$, explaining the high vertical sensitivity exhibited by STM, as a change in $d$ of 1 Å results in change of an order of magnitude in $I_t$. Additionally, the relation between the LDOS of the sample and the tunneling current highlights the convolution of topographic and electronic information of STM imaging. Although this approximation assumes the condition of small $V_b$, which is not always true in practice, the Tersoff-Hamann approach provides the relevant dependences between the involved magnitudes.

Finally, a schematic representation of the tip-sample junction is displayed in Figure 2.2. Assuming that the tip and the sample have different workfunctions, $\phi_t$ and $\phi_s$ respectively, and no bias voltage is applied, their Fermi levels are aligned and there is no net electron current in either direction (see Figure 2.2 a). When a finite negative bias $V_b$ is applied to the sample, its Fermi level is shifted up and the electrons occupying the states of the sample in the energy region $E_f - eV_b$ can now tunnel through the vacuum into the tip unoccupied states (Figure 2.2 b). On the other hand, when positive bias voltages are applied to the sample its Fermi level shifts down allowing the occupied states of the tip in the energy window $E_f + eV_b$ to tunnel to the unoccupied states of the sample (see Figure 2.2 c).
2.2 Modes of Operation

In this section the main tools of the STM data acquisition modes will be described, demonstrating the enormous potential of this technique to characterize and manipulate matter at the atomic scale.

Real Space Imaging

From the expression of tunneling current $I_t$ (eq. 2.10) presented in the previous section, the control parameters for the STM real space imaging...
can be introduced. In addition to the dependence of the tip-sample distance $d$ and the bias voltage $V_b$, one has to add the position control parameters $x$ and $y$ to move along the plane (see Section 2.4 for more details). In this regard, two different topography imaging modes are available:

- **Constant Height Mode** Setting the bias voltage $V_b$ to a certain value and the initial tip-sample distance $d$, the tip moves across the $x−y$ plane maintaining constant its vertical position (see Figure 2.3 a). The tunneling current $I_t$ is acquired during the measuring process, recording $I_t(x)$ profiles every a certain defined $\Delta y$ (see Figure 2.3 b). In practice measurements can be carried out in any desired scanning direction. The number of lines per image and the number of points per line define the elemental area $\Delta x \cdot \Delta y$, which corresponds to the pixel size of the latter STM image. This mode is only used to scan areas with small profile differences, as no mechanism to prevent the tip from crashing into the sample is provided when surfaces exhibit high roughness.

![Figure 2.3: Constant Height STM Mode. a) The tip moves towards $+x$ direction keeping the initial tip-sample distance $d$ constant along the entire tip pathway. b) Schematic representation of the different $I_t(x)$ scan profiles acquired by a STM for different $y$ positions in order to create a topographic image of an adsorbed adatom.](image-url)
• **Constant Current Mode** This mode also sets two initial parameters: the tunneling current $I_t$ and the bias voltage $V_b$. The feedback loop is the most important mechanism included in this mode, which changes the tip-sample distance $d$ to maintain constant the value of $I_t$. This change is accomplished by applying a certain voltage to the central piezo (see section 2.4), which is the monitored magnitude. This parameter can be easily converted to $\Delta z$ and generate an image with a similar procedure as in the CHM. This imaging mode is the most common method due to the protection mechanism provided by the feedback, and all the images in this thesis are recorded with this mode unless specifically said otherwise. It is worth to notice that the feedback loop frequency is a crucial magnitude, as it has to be faster than the scanning speed in order to safely apply the voltage changes to the central piezo. Importantly, the concept of apparent height is introduced, as the changes in the tip-sample distance $d$ may not be caused by a real depression or protrusion. In fact, higher or lower LDOS will also affect how the feedback loop varies $d$, therefore highlighting the
convolution of electronic and topographic information present in STM imagery.

Atomic Manipulation

Scanning tunneling microscopy offers the possibility of in situ manipulating matter at the atomic level, giving raise to the possibility of not only tailoring architectures at the nanoscale, but also providing valuable information about the adsorbates. In this regard, one can distinguish between two main modes: the lateral (LM) and the vertical manipulation (VM).

Figure 2.5: Scheme of Lateral Manipulation with STM. (1) Initial scanning height with non-perturbative conditions. (2) Approach and switching to manipulation parameters. (3) Desired tip pathway maintaining the LM conditions in order to displace the adsorbate. (4) Tip retraction and changing back to the normal scanning settings.

- **Lateral Manipulation (LM)** By laterally manipulating a target atom or molecule, one can horizontally displace them on the surface. Even though there are different ways to perform LM, in figure 2.5 a general scheme is presented. First, the tip approaches to the targeted species, followed by the change of the scanning parameters to
2.2 Modes of Operation

perturbative conditions. Then, the tip follows the desired path indicated by the user, finally changing back to normal scanning settings and retracting the tip back to the initial height. If the conditions chosen for LM are the adequate ones, adsorbates will be displaced to the desired position through attractive (pull) or repulsive (push) forces depending on the nature of the interaction between them and the tip. This technique can be used to position adsorbate atoms to form specific nanoarchitectures, such as 2D quantum wells to study the scattering of surface electrons and the formation of interference patterns\textsuperscript{11,14}. Additionally, it can also be used to force intermolecular interactions, such as covalent\textsuperscript{15,16} and metal-organic bonds\textsuperscript{17}, or to qualitative evaluate the strength of intermolecular bonds\textsuperscript{18}.

![Figure 2.6: Scheme of Vertical Manipulation with STM. Protocol that leads to the breaking of a certain bond (1). Initial scanning height with non-perturbative conditions. (2) Applying vertical manipulation by changing the tunneling parameters on top of the targeted molecule. (3) Retracting tip back to normal settings, resulting in two separate surface adsorbates.](image)

- **Vertical Manipulation (VM)** Under the correct conditions, atoms and molecules can be picked up or/and dropped by varying the tip sample distance \(d\), the tunneling current \(I_t\), the bias voltage \(V_b\) or any combination between them. This can be implemented to functionalize tips by attaching certain atoms or molecules to the tip apex, making it feasible to obtain sub-molecular resolution\textsuperscript{19} or chemical
contrast. In addition to the modification of the tip properties, one can also use this approach to perform the so-called tip-induced chemistry. This can be applied in a controlled way in a local target using tunneling electrons to e.g. dissociate molecular compounds like \( O_2 \).

By using larger voltages, changes can be induced simultaneously to large areas with an electric field or led emitted electrons. Well-controlled nanochemistry can be also used to locally break existing covalent bonds, or to synthesize complexes by creating on-surface radicals. Additionally, the intrinsic properties of the adsorbates can be also modified, e.g. the controlled tautomerization of the H atoms of the macrocycles such as porphyrins, representing a powerful tool to characterize systems at the atomic scale.

**Scanning Tunneling Spectroscopy**

One of the most powerful techniques offered by STM is to facilitate information about the electronic structure with high lateral resolution by means of Scanning Tunneling Spectroscopy (STS). As introduced in section 2.1 following the Tersoff-Hamman approximation for Bardeen's metal-vacuum-metal junction one can derive eq (2.10), where the dependence of \( I_t \) and the local density of states (LDOS) is highlighted. By assuming that the matrix elements \( M_{s,t} \) and LDOS of the tip \( \rho_t \) are independent of the applied bias voltage \( V_b \), the differential of the tunneling current can be written as:

\[
\frac{dI_t}{dV} \bigg|_{V=V_b} \propto \rho_s(eV_b)\rho_t(0)
\]

where the term \( \frac{dI_t}{dV} \bigg|_{V=V_b} \) represents the differential conductance and its directly proportional to the LDOS of the sample at \( V = V_b \). This relation can be used to extract the electronic fingerprints of metal substrates, such as confined surface electronic states. Additionally, it can be used to probe a large variety of adsorbate properties, such as molecular orbitals or single-atom magnetic fingerprints. In this regard it is important to introduce the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which are a typical object of interest.
2.2 Modes of Operation

for molecular systems. Experimentally, the tip is located on top of the desired (x,y) coordinate and the tunneling current is measured while changing the bias voltage in the targeted voltage range. Importantly, the feedback loop control (see section 2.4) is off during these measurements (feedback loop open) in order to record the $I$ vs. $V$ spectra at a constant height. At this point, there are two main approaches to obtain the $\frac{dI}{dV}(V_b)$ vs. $V_b$ spectra: (i) directly differentiating numerically the $I$ vs. $V$ curves or (ii) modulating $V_b$ with a reference AC signal with a small amplitude $V_m$ and a high frequency $\omega$ with a general form of $V_m \sin(\omega t)$. The modulation of the bias voltage results in a tunneling current with the general expression $I_t(V_b + V_m \sin(\omega t))$, which can be expanded in a Taylor series as:

$$I(V_b + V_m \sin(\omega t)) = I(V_b) + \frac{dI}{dV} V_m \sin(\omega t) + \frac{d^2I}{dV^2} V_m^2 \sin^2(\omega t) + \ldots \quad (2.12)$$

In practice, this is acquired with a lock-in amplifier, which compares two signals during a certain time and electronically gives an output of their correlation. In this case, the output of the lock-in is the correlation between the original sinusoidal reference signal and the modulated tunneling current. Therefore, the information about the differential conductance $dI/dV$ can be obtained from the first order term of the Taylor series. This technique is the most commonly used in the community and over all this thesis, as spectra can be acquired in significant shorter times and the signal to noise ratio is significantly increased. The second order term of the series is relevant to perform Inelastic electron tunneling spectroscopy (IETS)\textsuperscript{28}, but this technique is beyond the scope of this thesis, and will not be discussed.

In addition to simple STS spectra of single points, one can also perform a STS spectra for every single pixel in a topographic image, acquiring a so called current-imaging tunneling-spectroscopy (CITS) map. With this technique $I(V)$ spectra are recorded with their correspondent $dI/dV(V)$ curves in a spatial map, opening the feedback in each point, and obtaining real space images of the surface LDOS in the desired voltage range.

In order to visualize molecular orbitals such as the HOMO and LUMO in
real space, it is also common to use a technique that is less time-consuming. Throughout this thesis the so called lock-in dI/dV (x,y) or lock-in map have been used to this purpose. It consists in stabilizing at the bias voltage where the LDOS wants to be inspected, and recording the lock-in signal for each point with the feed-back on. In order to record lock-in maps with high signal to noise ratio, integration times of 10 ms per point are typically used.

2.3 X-ray Photoelectron Spectroscopy

![Schematic Representation of XPS Working Principle](image)

Figure 2.7: Schematic Representation of XPS Working Principle. After irradiating with a X-ray source the targeted sample with a workfunction $\phi$, electrons are ejected from the core levels to the vacuum with a certain $E_K$. Some of these free electrons arrive to the analyzer, which measures a targeted kinetic energy window in order to evaluate the surface composition.
In this section the basic principles that make X-ray Photoelectron Spectroscopy (XPS) a widely spread technique in the surface scientific community will be introduced. This method relies on the well-known photoelectric effect, first described by A. Einstein, in which an electron bounded in an atomic level will be emitted to a vacuum state if the energy of the adsorbed light is sufficient. If this condition is fulfilled, the electron will be ejected with a kinetic energy $E_K$ of:

$$E_K = h\nu - E_{\text{binding}} - \phi$$

(2.13)

where $h\nu$ is the energy of the incident photon, $E_{\text{binding}}$ is the binding energy of the electron with respect to the Fermi level and $\phi$ is the energy to promote an electron from the Fermi level to the vacuum state, i.e. the workfunction of the material. In practice, in order to excite deep core levels of different elements, whose $E_{\text{binding}}$ is in the hundred or thousand electron-volts regime, a X-ray source is required. Figure 2.7 shows a scheme of the working principle behind XPS technique. After the electrons arrive to the analyser with a certain $E_K$, data is converted to spectra taking into account that the detector also has a workfunction $\phi_d$ by just applying energy conservation arguments. In these spectra different phenomena such as Auger resonances can be observed, as a result of different relaxation processes, but through this work only photoemission peaks will be discussed.

In order to understand the surface sensitivity of this technique, the average distance traveled through a solid of an electron before inelastically scattering, i.e. the Inelastic Mean Free Path (IMFP) $\lambda$ is introduced. This magnitude depends on the initial kinetic energy of the emitted electrons and the nature of the solid, and determines the probability of an electron emitted at a depth $d$ to pass through a solid without undergoing scattering as $P(d) = e^{-d/\lambda}$. At a distance $3\lambda$ below the surface, ca. 95% of the electrons do not reach the surface before suffering inelastic scattering (>99% for $d = 5\lambda$). For the energy range used in this thesis (<1500 eV) and metallic substrates such as Au and Ag monocrystals, the IMFP $\lambda$ typically is between 1 and 3 nm. Hence, the main part of the unscattered electrons collected in the detector come from the upper layers of the sample, providing
this technique a high surface sensitivity.

The position of the binding energy is a unique fingerprint of the different core levels of distinct elements, therefore giving information about the surface composition, thus XPS is also called Electron Spectroscopy for Chemical Analysis (ESCA). At this point, it is important to notice that the binding energy of a core electron depends significantly on the environment, therefore shifts of core levels spectra towards higher or lower $E_{binding}$ give information about the chemical and electronic environment of a certain element. A large variety of phenomena such as charge transfer or different intermolecular bonds can be evaluated with XPS, being able to extract useful information about the atom or molecular environment and their interaction with the metallic surface. In conclusion, XPS combined with STM provide a very powerful set of techniques in order to investigate the processes occurring on a surface.

2.4 Experimental Set-Up

In this section the experimental details employed in order to prepare and characterize samples as well as the most important instrumentation are described. First of all, the importance of ultra high vacuum (UHV) will be presented, since all the experiments have been carried out under these conditions. During this thesis the experiments have been carried out mainly in two systems: a low-temperature STM (LT-STM) and a variable-temperature (VT-STM) combined with XPS. The main parts of the LT-STM system will be detailed, conformed by the analysis and the preparation chamber. The setup present to keep the system at cryogenic temperatures, in addition to the working mechanism of the scanner itself are explained. Regarding the preparation chamber, all instruments included in it to in situ prepare samples are illustrated, together with the electro-etching protocol to fabricate tips. Finally, since many parts are shared between both setups, the particularities of the VT-STM combined with XPS system will be shortly detailed.
2.4 Experimental Set-Up

UHV

In general, surface studies demand very low pressures in order to prevent the system from unwanted adsorbates or contaminants. At room temperature and atmospheric pressure, the formation of one monolayer of particles present in air takes just a few nanoseconds. Even at pressures around $10^{-6}$ mbar it only takes the order of seconds\[30\], therefore much cleaner environments are mandatory in order to perform these experiments without changing the physical or chemical properties of the adsorbates. It is commonly accepted that UHV is considered for pressures below $10^{-9}$ mbar\[31\], where a sample can remain unperturbed for a period of days. In order to achieve these conditions, a series of pumps are continuously working to drop the pressure to the desired order of magnitude. The ones used in our setup involve: (i) a membrane pump (ii) a turbo-molecular pump and (iii) a ion getter pump. Typical turbo-molecular pumps can drop the pressure to $10^{-10}$ mbar, but they require a fore-vacuum around $10^{-2}$ mbar which is supplied by installing in series a membrane pump. Additionally, every chamber has its own ion getter pump, which can drop the pressure to even lower magnitudes ($10^{-11}$ mbar). Its working principle consists in ionizing residual gases by applying strong electrical potentials, typically 7 kV, capturing the particles into an electrode. These kind of pumps require a base pressure of $10^{-8}$ mbar to operate, therefore a regular UHV chamber combines these there pumping systems to reach the lowest pressure possible. An other advantage of the ion pumps is that they do not have any moving mechanical part, making them appropriate to reduce unwanted vibrational noises when scanning. In general UHV chambers also include other mechanism to temporally reduce the pressure such as titanium sublimation pumps (TSP) and cold traps. TSP consists in evaporating Ti atoms by applying high currents (around 40 A) to a titanium rod installed inside the ion pump. The high reactive Ti atoms adsorb in the wall and eventually catch any contaminant residual gases. Regarding cold traps, they thermally trap ambient molecules, therefore lowering the pressure while they are at lower temperatures than the rest of the chamber. It is important to remark that when working at cryogenic temperatures, the cool parts of the system act as a
cold trap further lowering the pressure.

Low Temperature STM

Figure 2.8: Artificially Colored Photograph of the LT-STM Setup. Green: Liquid Nitrogen and Helium Cryostat. Red: Analysis chamber containing the STM head with the scanner. Blue: Preparation chamber. Yellow: Manipulator arm. Purple: Pumping system, including both ion pumps, the turbo-molecular pumps and an external pump station (in front) Cyan: Vibration isolation system.
A functional LT-STM requires a complex setup and maintenance to keep the system at UHV and liquid helium temperatures. The main parts of a generic LT-STM are colored in Figure 2.8. In the employed system, the analysis chamber contains a commercial Omicron LT-STM model, consisting in two cryostats and the STM scanner itself. Although working at cryogenic temperature is not mandatory, as it will be shown in the next section (VT-STM section 2.4), it offers a large variety of advantages. Under these conditions, the adsorbates diffusion is generally hindered, i.e. the thermal energy of the substrate-adsorbate system is strongly decreased. To achieve this temperature range close to 4 K, a liquid He tank is situated directly over the STM stage (1 in Figure 2.9). To prevent a quick evaporation of the helium, a second external tank is filled with liquid nitrogen. Between these two tanks, two radiation shield stages are installed to further minimize the LHe consumption, with optic windows and a main entrance hole to extract and insert samples (2 in Figure 2.9). All the parts assembled in the setup are made of stainless steel due to its low thermal conductivity. Since the inferior part of the inner cryostat is in direct contact with the scanner head, together with thick copper wires between the shields to favor thermalization, one can achieve working temperatures around 5 K. These conditions grant the system high stability to record high resolution images at the atomic scale together with spectroscopic data with high signal to noise ratio. However, as these measurements are highly sensitive to vibrational noises, different stages of vibration isolators are installed in the system. In order to decouple the system from the vibrations occasioned by other persons or machinery in the building, the lab floor is constructed on top of an isolated concrete base. Regarding the system itself, the primary isolation consists in decoupling the whole instrument by supporting the heavy parts on top of three damping legs (blue in figure 2.8), which are inflated with compressed air while scanning. At this position, the system is floating and the major low frequency vibrations are filtered. A second isolation stage is achieved by suspending the whole STM head with four springs (3 in Figure 2.9). The suspended position further filters low frequency noises and avoids vibrations from the boiling cryogenic liquids present in the cryostats. Finally, a common improvement for noise attenuation in this
kind of STMs is the magnetic eddy current damper (4). These flanges fit in their respective magnetized slots present in the inner shield, creating a magnetic field as a result of the eddy currents generated by a moving conductor. This opposing field blocks the radial movements of the STM scanner when suspended, hence acting as a damping mechanism.

Figure 2.9: Main Parts of the STM Chamber. 1 Inner cryostat usually filled with LHe. 2 Inner shield at the open position. 3 Suspension Springs. Their design offers 3 modes: scan position (fully suspended), stand-by (compressed), cool-down position (fully compressed). 4 Magnetic Eddy Current Dampers. 5 Scanner course movement control. 6 STM central piezo for fine movement with the tip holder containing a W tip. 7 Sample stage with a Au(111) sample.

**STM Head** The STM scanner consists mainly of three different parts: (i) the sample stage, (ii) a base plate mounted on a rail for z movement and (iii) a central piezoelectric ceramic. In order to introduce or extract samples
from the sample stage, both inner and outer shields have to be rotated to access the scanner. This is carried out with a UHV wooble-stick with pliers at its end, facilitating the shield manipulation and the sample grabbing. To manipulate samples safely, the whole stage is blocked by compressing the springs to the stand-by position. If no further manipulation is required, springs are stressed to the cool-down position, where the whole STM stage is firmly contacting the lower part of the LHe cryostat, thus favoring a faster thermalization. Regarding the movement control for the scanner itself, one can distinguish between the course and the fine movements. The whole base plate is situated on top of a $x-y$ table, allowing the course movement along these directions. This base plate is mounted on a rail, which is moved with a remote control to $+z$ when the user wants to approach the tip. This is called the course tip approach and its usually monitored with an external camera, leaving the tip at a safe distance of the sample. In order to enter tunneling conditions safely, i.e. without crashing the tip onto the sample, software controlled approaches or auto-approach are usually provided by the control programs. By fixing a value of the tunneling current, the tip starts to approach the sample by a tunable step $\Delta z$, usually in tenths of nanometers steps. After every step, the software compares the measured $I_t$ with the given value, and stops approaching when both match. To perform this auto-approach, as well as to move along the $x-y$ plane, the software applies a certain voltage to the central piezo. These components are used in a large variety of modern high-precision probing techniques, since they facilitate a high-controlled fine movement at nanometric scales. The working principle relies behind piezoelectricity: these materials expand or contract when an electric potential is applied to them. In this case, the central piezo is divided into four external electrodes, in a cross-like geometry, surrounding a fifth electrode located at the center. The latter one controls the fine movement in the $z$ direction, while the other four, depending on the applied voltage, are responsible for the fine $x-y$ control. These voltages are applied by the software, which also provides the possibility of selecting the size, resolution, scan direction and scan speed.
Preparation Chamber

In this section the main instruments present to prepare samples are described, followed by a brief description of the tip-etching process. In order to move samples along the positions of the chamber, and to export them from/to the STM chamber, a 60 cm long manipulator arm is located along the axis of the cylindrical chamber (yellow in figure 2.8). The head of this manipulator (see Figure 2.10 a) consists in a cavity that hosts the sample plate, beneath which an annealing filament is mounted. In this particular case, samples are annealed by resistive heating of a Pyrolitic Boron Nitride (PBN) heater, reaching temperatures up to 1000 K. To monitor the temperature, a type K NiCr/NiAl thermocouple is installed in contact with the sample holder. These kind of thermocouples are extensively used, as they are reliable in a wide temperature range. In this set-up, single crystals are welded with tantalum foil directly on top of molybdenum plates, whose high melting temperatures prevent from overheating such parts. Samples holders have two small flanges that impede them to slide through the manipulator head (as depicted in Figure 2.10 b), hence being able to move them along the distinct instrument positions safely. There are instruments that can be used to do quick analysis, such as the Quadrupole Mass Spectrometer (QMS). It can be used to evaluate the partial pressure of residual gases or contaminants, as well as to determine when molecular species start to sublime inside the chamber. Another common feature in UHV systems is the load-lock or quick-introduction chamber. It is a small chamber equipped with a transfer bar, pumped independently from the main chambers, used to introduce/extract samples or tip-holders without exposing them to ambient air. Next, the steps and instruments used in order to clean single crystals, deposit monomers or metal atoms are described:
Sample Cleaning. There are a large variety of cleaning procedures depending on the specific targeted substrate. This thesis mainly focused on investigating systems adsorbed on coinage metals, such as Au, Ag and Cu, which share a common protocol. The process to prepare one of these crystals involves several steps, firstly requiring a clean, flat, pristine surface. In order to achieve such sample, removing the top layers of impurities than can be adsorbed on a crystal is necessary. This is achieved by bombarding the surface with argon ions, most commonly known as ion sputtering. To this end, an ion gun connected to an Ar leak valve is used to accelerate $Ar^+$ in a cathode, and then aimed perpendicularly to the surface with usual values around 1.5 KeV. In order to have enough collisions to consider this process significant, the total pressure of the chamber is increased $\approx 2.5 \times 10^{-6}$ mbar by inletting Ar gas. When hitting the surface, high energy ions remove the upper layers together with the adsorbed contaminants. It is important to ground the sample, since floating targets would finally get ionized and the sputtering would be ineffective. The duration of this process is variable depending on the amount of contamination, requiring several cycles for new crystals. Sputtering the surface results in an irregular, cratered-like topography, not suitable for depositing molecules. To achieve a flat substrate an annealing cycle is applied to the sample, by letting a certain (depending on the crystal) current flow through the manipulator filament.
Over- and under-heating the sample will lead to impurity segregation and cratered terraces respectively. The temperature is generally chosen under a simple assumption: due to geometry arguments, an atom located in a flat terrace has around two thirds of the binding energy of a bulk atom. By annealing surfaces to around the sixty percent of the melting temperature, adatoms, together with kink atoms and step edges are though to desorb or reorganize. Although the resulting samples show some of these defects, repeatedly doing sputtering-annealing cycles minimizes their presence and large, virtually defect-free terraces are achieved.

Figure 2.11: Organic Molecular Beam Epitaxy Evaporator. a) Image of the 3-pocket KENTAX model used to evaporate molecules in powder with the travel setup necessary to introduce the evaporator in the chamber. b) Front view of the OMBE head without the shutter containing three crucible with different species. With this model, one can simultaneously evaporate monomers from pockets 1 and 2 or 3. c) One of the crucibles installed in the pockets after cleaning and filling it with halogenated species.

• OMBE Once the substrate is clean, molecules can be deposited on top of it by means of an Organic Molecular Beam Epitaxy (OMBE) source. In most of the experiments a commercial KENTAX model was used, presented in Figure 2.11 equipped with three different pockets. Even though pockets 2 and 3 are dependent, one of them can be simultaneously evaporated
2.4 Experimental Set-Up

with pocket 1. Quartz or crystal crucibles, depending on the sublimation temperature of species, are filled with molecules and inserted inside the pockets. These molecular species, usually in the form of powder, are resistively heated to the sublimation temperature, controlled by the evaporator electronics. The substrate temperature will depend on the targeted experiment. Exposure times vary depending on the desired amount and flux of molecules on the sample, being easy to control from minute amounts of units to few monolayers.

![Figure 2.12: Electron Beam Epitaxy Evaporator. a) Image of the EBE-1 SPECS model used to evaporate metal rods with the shutter open. b) Close view of a dysprosium Ø3 mm rod after being used to deposit controlled amounts on single crystals. The terminal rounded part is the typical geometry of rods once they are degassed and fully operational.](image)

- **Metal Evaporator.** Metal evaporation is used for *in situ* nanofabricating alloys, metal-organic networks or to metallate molecular macrocycles among other usages. In this thesis mainly lanthanide elements were evaporated, for which a commercial EBE-1 evaporator was used (see Figure 2.12). Although this model is compatible with crucible evaporation, lanthanide elements were deposited by installing outgassed rods with purities over 99.9%. The terminal part of the rod is placed nearby a filament, and a voltage difference is applied between them to sublimate metals by means of electron beam heating. The electronics permit to set the filament current and
voltage values, as well as to monitor the Flux (in nA) and the emission current (in mA). Applying 5.0 A to the filament and ca. 600 V between it and the rod, low fluxes of around 4 nA and emission currents of 6 mA are achieved. Under these conditions, evaporating over 50 s leads to a coverage of around 0.01 ML. In addition to the Ln evaporator, home made instruments based on the same e-beam design have been implemented to evaporate noble metals from a crucible filled with grains.

![Figure 2.13: Tip Electrochemical Etching. a) Scheme of the experimental setup to electrochemically etch tips outside UHV conditions in a KOH solution. b) Scanning Electron Microscopy (SEM) image of the tip apex. c) Zoomed-in image of the tip termination resulted from the electro-etching procedure.](image)

- **Tip preparation.** Different conductive materials are used to prepare STM tips, such as PtIr alloys and niobium, or softer metals as silver or gold. Nevertheless, in our experiments the more common tungsten tip was used, which offers high stiffness and low chemical reactivity. In order to fabricate the tip, a 2-3 cm long segment is cut from a Ø0.25 mm W wire. The desired length of the tip, around 3-5 mm for this particular set-up, is inserted in a KOH solution as schematically presented in Figure 2.13a). The W wire acts as an anode, and a ring-shaped metallic wire is sunken in the solution acting as the cathode, subsequently applying a voltage between them. The etching principle relies on the creation of a liquid meniscus around the wire, hence attacking W with different intensities along its height. In the set-up
15 V (AC) with an initial current of 150 mA were applied, until the wire is fractured and sinks into the solution usually taking around 3 minutes. Directly after, the tip is neutralized and cleaned by dipping it in distilled water and acetone, and dried with a flux of N\textsubscript{2} gas. The sharpness of the tip is first roughly confirmed by standard optical microscopy, selecting the ones whose that do no appear to be blunt or with an excessively long apex. Thanks to the installations present at the institute, one can further evaluate the tip at the micrometric scale by means of Scanning Electron Microscopy (SEM) (see Figures 2.13 b and c), finally selecting the appropriate ones. Selected tips are mounted in a tip-holder, whose bottom part is attached to the central piezo magnetically, and installed in a special sample holder designed to transport tips inside the chamber. In order to introduce them in the preparation chamber, tips are located in the load-lock transfer bar and pumped until UHV conditions are reached. Despite all the cleaning procedures, it is known that the outer layers of the tip apex contain tungsten trioxide\footnote{22} and some remnants of the solution. To \textit{in situ} remove these oxides and other possible contaminant, tips are sputtered with Ar\textsuperscript{+} ions in a similar process as the one used to clean single crystals. Additionally, as W wires are highly polycrystalline, and sputtering cycles leave high irregularities at the atomic scale, flash annealing rounds are performed. Inside the preparation chamber, a retractile tantalum foil of 4 cm long and 5 mm wide is located beneath the tip apex in contact with the W wire. The Ta foil and the whole chamber are grounded, and a DC current is sent through the manipulator head, in contact with the tip holder. Maintaining a base current of 4 A in order to degas the entire sample holder, subsequent current flashes to 5, 10, 12, 15 and 17 A are applied. This tip annealing reorganizes the atoms at its surface and further desorbs contaminants, resulting in a smoother tip geometry. After the procedure is finished, tip-holders are transferred into the STM chamber and stored in the parking. While scanning, usually tips get contaminated with adsorbates or its geometry changed by uncontrolled tip crashing. If the usual voltage pulses or tip-sample indentations do not improve scanning conditions, sputtering-annealing cycles can be repeated in the preparation chamber in order to regain a metallic atomically-sharp tip.
XPS and VT-STM Set-Up

Figure 2.14: **Set-Up of the XPS and VT-STM Laboratory.** Photography and scheme of the VT-STM setup present in the laboratory. The left chamber corresponds to the XPS chamber, with the SPECS X-ray monochromator Focus 500 and the hemispherical energy analyzer PHOIBOS 150. The central chamber contains the SPM 150 Aarhus model. The preparation chamber and its manipulator arm are colored green.
This section will shortly describe the characteristic elements of the VT-STM combined with XPS setup, as most of the features in the UHV system and in the preparation chamber are shared with the previously introduced LT-STM. The pumping system consists in three independent ion getter pumps for each chamber, together with two turbo molecular pumps installed in the preparation and in the XPS sections. Regarding the preparation chamber, it contains similar instruments as the ones described in section 2.4:

- Load-lock chamber
- Ion sputtering gun
- Manipulator arm with annealing stage
- OMBE evaporator
- EBE evaporator
- Quadrapole Mass-Spectrometer

**XPS chamber.** Samples are transferred from the STM chamber with a manipulator arm. In this specific setup, the manipulator head does not feature an annealing stage, since sample heating is carried out in the preparation chamber. Even so, it can be cooled down to cryogenic temperatures by inletting a LN$_2$ flow through an inner circuit that thermalizes the whole arm. Regarding the XPS instrument itself, it consists in three different parts: a X-ray source, a monochromator and an hemispherical electron energy analyzer. The X-ray source is a commercial XR 50 model from SPECS, with two Aluminum anodes that emit $K_\alpha$ radiation with a photon energy of 1486.6 eV. Electrons emitted by a filament are accelerated towards de Al anode with 15 kV voltage potential, therefore ionizing its inner core levels, resulting in the emission of X-ray radiation. This process involves continuous high-energy collisions, therefore a refrigerating circuit is installed in order to avoid the overheating of the anode. To achieve a higher monochromatic beam, the system also mounts a FOCUS 500 model from SPECS. Based on Bragg’s law, the monochromator can further reduce the average wavelength dispersion by reflecting the anode X-ray emitted photons in a quartz single crystal. Optimizing the whole setup gives us a full width at half maximum (FWHM) intensity of 0.8 eV for the $3d_{5/2}$ peak of a silver single crystal (Pass Energy 12 eV). Finally, the monochromatic beam hits
the targeted sample, located in the manipulator head, subsequently emitting electrons which are collected by the PHOIBOS 150 analyzer. Electrons that arrive to the the lens system of the analyzer are angularly selected and retarded to facilitate the energy analysis. Electrons then enter two concentric hemispherical electrodes, with a certain voltage difference, that will filter electrons with a specific energy from arriving to the detector. Therein, the detector consists in 5 channeltron electron multipliers.

**Figure 2.15: VT-STM Scanner.** Image of the STM stage together with a close view of the sample stage and a schematic representation of the scanner mechanism. ① Trapping mechanism to couple the STM stage while not scanning. In this setup it is also used to cool down the STM block by letting LN$_2$ flow through. ② Springs to suspend the STM stage while measuring to decouple the system from possible vibrational noises. ③ STM block where the scanner is installed, used to thermalize the sample in a temperature range between 90 and 400 K. **Inset.** Close view of the STM tip and the sample stage, with two copper clips that subject the sample. Additionally, the scheme of the scanning mechanism is presented, with the tip, the scanning piezo and the inchworm motor.

• **STM Chamber.** Samples are picked from the manipulators, or from the parking, with a perpendicular magnetic transfer bar, and can be directly
transferred face-down to the STM stage. Importantly, in this setup single crystals have a hut-like geometry (side view), in order to not protrude significantly through the upper part of the sample holder due to the reduced tip-sample distance. Therefore, its bottom part is welded with tantalum foil to the backside of the molybdenum plates. The STM stage is presented in Figure 2.15 (left), consisting in a blocking mechanism, a vibration isolation system and the block containing the scanner. When samples are not being scanned, the blocking mechanism pushes forward the STM block immobilizing it, hence preventing unwanted collisions. Inside this metallic cylinder, LN$_2$ can flow through a cooling circuit, hence reducing the block temperature to temperatures around 90 K once it is thermalized. In order to start measurements, it is retracted and the block is suspended with three springs, consequently reducing the noise by isolating the system from vibrations. Interestingly, the entire block can also be heated using Zener diodes up to 400 K, allowing the VT-STM to work in a wide range of temperatures. The STM scanner (figure 2.15 right) has two copper clips that hold the samples at the scanning position. The movement of the scanner, similar to the LT case, has two main modes: approach and scan. An inchworm motor located at the lower part of the scanner is responsible for the course approaching movement. It consists of a piezoelectric divided in three sections. The middle section is elongated upwards or downwards to approach/retract the tip, while the upper and lower sections clamp or unclamp a central ceramic rod, thus resembling a worm-like movement. By setting a control value of the tunneling current, the inchworm motor approaches safely the tip to the sample. For the scan mode, a four segment piezo with a central electrode, similar to the LT-STM case, controls the motion along the $x - y$ plane and the fine movement in $z$. The tungsten tip, prepared following the protocol presented previously, is welded to a plate and attached with epoxy to the upper part of the piezo. The main advantages of this STM model, apart from the obvious temperature dependence applications, are a fast approach and scanning, together with high mechanic stability due to the compact design.
In conclusion, the combination of XPS and VT-STM offers the possibility to extract complementary chemical and electronic information from a wide variety of samples. If combined with LT-STM, and specially with STS, a deep understanding of the investigated systems can be achieved. These variety of surface science studies, along with synchrotron-based techniques resulted from scientific collaborations, will be used to investigate different systems in the next chapters.
In recent decades scientists have dedicated enormous efforts investigating new approaches that can further minimize electronic devices. The hot topics of spintronics and information storage have driven the attention of the scientific community to the so called single atom magnets (SAM)\citep{33,35}. The idea of reducing a magnet dimension to the atomic scale without losing its main characteristics, such as high blocking temperatures and magnetic lifetimes, was first envisioned by pioneering studies with small transition metal clusters\citep{36,37}. Similar approaches, consisting in embedding single metal ions in molecular compounds proved to be a promising strategy, commonly known as Single Molecule Magnets (SMMs). Within this field, double decker sandwich-like geometries incorporating lanthanides emerged as prominent candidates\citep{38,39} due to the unrivaled single ion anisotropy of heavy lanthanide elements, affording magnetic hysteresis up to 60 K\citep{40}.
Importantly, the ligand field of SMMs has to preserve the specific distribution of the $4f$ electron shell$^{[60]}$ to maximize the single ion magnetic anisotropy$^{[60]}$. In this sense, recent studies have demonstrated the dramatic impact on these systems after adsorption on metallic substrates, reducing the hysteresis loop or even showing paramagnetic behavior$^{[61],[62]}$. Therefore, decoupling strategies are mandatory in order to protect the intrinsic magnetic properties of SMMs. Just recently, the deposition of TbPc$_2$ species on ultrathin film oxides and boron nitride preserved their magnetic properties to a certain extent$^{[63]}$. The underlying strategy is based on diminishing the interaction of the single ion and the hosting macrocyclic pockets with the metallic surface, preventing the modification of its electronic and magnetic properties. Following this strategy, an alternative approach is proposed in this chapter, based on incorporating decoupling termini on the single molecule magnet periphery to decouple it from the underneath metallic support$^{[64],[65]}$. This chapter addresses these concerns using a combined STM, DFT and XPS study of the adsorption, self-assembly and electronic properties of a novel double-decker compound equipped with terminal ethyl moieties, which help preserve the electronic properties of the single molecule magnet upon adsorption on metallic substrates, a prerequisite to conserve the inherent single ion magnet characteristics.

First, the structure of an *ex professo* synthesized double-decker species is described. Then, their adsorption and self-assembly on metallic surfaces is reported with the help of scanning tunneling microscopy. DFT calculations allow to assess the adsorption geometry and probe the decoupling effect provided by the ethyl moieties. Finally, comparative XPS of submonolayer and multilayer coverage regimes on different metallic supports corroborate the successful electronic decoupling of double-decker species from the metals underneath, thanks to the ethyl terminal functionalization. The results of this chapter have been published in *Physical Chemistry Chemical Physics.*$^{[66]}$
Ln-(OETAP)\textsubscript{2}

![Chemical Structure of Ln-(OETAP)\textsubscript{2}](image)

**Figure 3.1:** Chemical Structure of Ln-(OETAP)\textsubscript{2}. Side and top view of the chemical structure of Ln-(OETAP)\textsubscript{2}. Dysprosium and terbium substituted compounds were used in this chapter. In the right image OETAP monomers (upper and lower deckers) are rotated 45° for a clearer view.

The recently synthesized single molecule magnet\textsuperscript{67}, with chemical formula bis(2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraazaporphyrin)Ln, consists of two octaethyltetraazaporphyrins (OETAP) deckers coordinated by a lanthanide atom in the center, exhibiting a square antiprism geometry (see Figure 3.1). Each OETAP contains four pyrrole units, with ethyl terminal groups in the \(\beta\) positions, and -meso nitrogen atoms, thus differing from porphyrins and being commonly named as porphyrazine or tetraazaporphyrin. Importantly, these ligands preserve the oblate geometry of the orbital of the \(f\)-electron shell of heavy lanthanides such as Dy and Tb, concentrating the electron density plane above and below the metal center. The advantage of these neutral double decker compounds, in comparison with the related phthalocyanine species, is that their smaller skeleton makes them easily sublimable and soluble. This is enhanced by the ethyl functionalization, which also provides a decoupling effect with adjacent monomers and is envisioned to act as a spacer upon a flat-on adsorption geometry on surfaces.

During this thesis the dysprosium substituted compound (Dy(OETAP)\textsubscript{2})
Ln-(OETAP)$_2$ on Coinage Metals

(1) was investigated, but complementary data of the Tb(OETAP)$_2$ (2) resulted from a collaboration with the E20 group of the Technische Universität München, is also presented. The implementation of these compounds was motivated by their high blocking temperatures $T_c$ observed in bulk, $T_c^{Dy} \approx 10K$ and $T_c^{Tb} \approx 50K$.

![STM Appearance of Isolated Ln-(OETAP)$_2$ Species](image)

Figure 3.2: STM Appearance of Isolated Ln-(OETAP)$_2$ Species. STM images showing isolated species on Cu(111) (left), Au(111) (Central Images) and Ag(111) (right). Characteristic eight-lobe and four-lobe appearance with a depression at its center for both negative and positive bias voltages respectively. No significant difference is appreciated between different Tb- (right image) and Dy-substituted (rest of the images) monomers on the different single crystals.

The deposition of minute amounts of Dy-(OETAP)$_2$ species on Cu(111) and Au(111) held at room temperature results in step-edge decoration and some isolated monomers on the terraces. This allows to image single units at different bias voltages distinguishing their submolecular features. By assuming a flat-on adsorption geometry on both surfaces, at negative bias eight lobular protrusions surrounding a central dim in a flower-like fashion are observed. As reported before, the eight lobes can be attributed to the eight ethyl moieties, and the dim to the center of the upper macrocycle. By imaging Dy-(OETAP)$_2$ at positive bias on Au(111), four elongated protrusions are imaged, assigning them to pairs of ethyl terminal groups from the four pyrroles present in the porphyrine macrocycle. Depositing Tb-(OETAP)$_2$ on Ag(111) leads to the same result, hence highlighting that
the STM appearance does not vary significantly by changing the substrate or the metallic center of the double-decker compounds, suggesting similar adsorption geometries.

**Self-Assembly of Ln-(OETAP)$_2$ on Metal Substrates**

Depositing higher amounts of (1) on Au(111) results in the formation of long-range ordered supramolecular islands (See Figure 3.3a). Islands are imaged as compact hexagonal lattices with distinguishable species appearing at negative bias as described before. The intermolecular interaction via van der Waals forces between ethyl terminal groups of adjacent molecules is responsible for the long-range assembly. Averaging various distances along the three main directions permits to extract the size and vectors of the unit cell, presented in Figure 3.3b. For the case of Dy-(OETAP)$_2$ on Au(111) the following experimental values are obtained:

\[ |\vec{a}_{Exp}| = (14.2 \pm 0.5) \text{ Å} \]
\[ |\vec{b}_{Exp}| = (14.6 \pm 0.5) \text{ Å} \]
\[ \alpha = (61 \pm 2)^\circ \]
Figure 3.3: Self-Assembly of Ln-(OETAP)\(_2\) Species on Au(111), Ag(111) and Cu(111). a) Long-range STM image of Dy-(OETAP)\(_2\) on Au(111) depicting the hexagonal unit cell (blue) and the high-symmetry directions (black star). \((I_t = 60 \, \text{pA} \, ; \, V_b = -2.3 \, \text{V} \, ; \, \text{Scale bar} = 3 \, \text{nm})\) b) Zoom-in image highlighting the unit unit vectors \(\vec{a}\) and \(\vec{b}\), enclosing angle \(\alpha\). \((I_t = 60 \, \text{pA} \, ; \, V_b = -2.3 \, \text{V} \, ; \, \text{Scalebar} = 1 \, \text{nm})\). Tentative model showing distinct molecular orientations as derived from tunneling images and basis vectors \(\vec{u}\) and \(\vec{v}\). c) Large scale STM image of Tb-(OETAP)\(_2\) on Ag(111). \((I_t = 100 \, \text{pA} \, ; \, V_b = 1.5 \, \text{V} \, ; \, \text{Scale bar} = 6 \, \text{nm})\). d) Unit vectors \(\vec{c}\) and \(\vec{d}\), enclosing angle \(\beta\) superimposed on a zoomed image. \((I_t = 100 \, \text{pA} \, ; \, V_b = 1.5 \, \text{V} \, ; \, \text{Scale bar} = 1 \, \text{nm})\). e) Model for Tb-(OETAP)\(_2\) on Ag(111). g) Long-range STM topograph of Dy-(OETAP)\(_2\) on Cu(111) \((I_t = 20 \, \text{pA} \, ; \, V_b = 1.4 \, \text{V} \, ; \, \text{Scale bar} = 4 \, \text{nm})\). h) Zoom in STM image. \((I_t = 35 \, \text{pA} \, ; \, V_b = -1.7 \, \text{V} \, ; \, \text{Scale bar} = 1 \, \text{nm})\). i) Atomistic model on Cu(111).
Importantly, there are two molecular orientations per domain, as illustrated in Figure 3.3c. Actually, the molecules alternate their orientation along the unit cell symmetry directions. Thus, in this case the unit cell is defined as the distance between the center of adjacent macrocycles. Each of these orientations present one of the monomers long axis aligned with one of the high symmetry directions of the crystals. For symmetry reasons three different molecular orientations are observed (just two presented and per supramolecular domain), related by 30° rotations. As only the upper decker of each molecule is accessible to STM, the registry of the lower one with respect to the substrate remains unknown. Even so, a tentative model with the underlying substrate is presented in Figure 3.3c. In order to build the model, $|\vec{a}| = |\vec{b}| = 14.4$ Å is assumed as well as $\alpha=60^\circ$. No apparent preferred registry with the substrate can be elucidated, evidencing a subtle balance between substrate-molecule and intermolecular interactions. Nevertheless, the obtained values for the model fit closely to the ones calculated for TbPc$_2$ on distinct metals, a consequence of the axial rotation capacity between both deckers and the flexibility of the ethyl groups. These freedom degrees offer the possibility to minimize steric repulsion, therefore obtaining close values to other sandwich like monomers.$^{69}$

Following the same procedure with Tb-(OETAP)$_2$ on Ag(111) the sample presented in Figure 3.3d is obtained. By imaging at positive bias (Figure 3.3e) the model of two monomers can be superimposed, further suggesting the existence of different rotational orientations. In this case, the experimental values are also similar to the results of Dy-(OETAP)$_2$ on Au(111):

\[
|\vec{c}_{Exp}| = (14.0 \pm 0.5) \text{ Å} \\
|\vec{d}_{Exp}| = (14.2 \pm 0.5) \text{ Å} \\
\beta = (66 \pm 2)^\circ
\]

which are compatible with the previous values deduced for the model. In this case though, it is straightforward to see that the central part of different macrocycles can be located in the same positions of the underlying
substrate in the model (See Figure 3.3f). In spite of the fact that no information about the inferior decker registry with the substrate can be discerned due to rotational orientations, one can write the unit cell in terms of the basis vectors of the crystal as $\vec{c} = 8\vec{v}$ and $\vec{d} = 8\vec{u}$ demonstrating some degree of commensurability with the surface. Finally, Figures 3.3 g-i show the data for the experiments on Cu(111), depositing Dy-(OETAP)$_2$ to obtain coverages close to the monolayer. The experimental values for the vectors of the unit cell are:

$$|\vec{f}_{Exp}| = (15.4 \pm 0.5) \, \text{Å}$$
$$|\vec{g}_{Exp}| = (13.6 \pm 0.5) \, \text{Å}$$
$$\gamma = (63 \pm 2)\degree$$

The obtained values are similar with the previously experiments on Au(111) and Ag(111), even though in Cu(111) the unit cell parameters are clearly incommensurate with the underlying basis vectors. It is important to remark that the set of experimental values for the different substrates or monomers is compatible, hence demonstrating that the self assembly is barely modified by changing substrate-molecule interactions or the metallic center.

**Integrity of Deposited Species**

As observed in Figure 3.3 brighter species are imaged in the islands on the distinct substrates. Even though they could be removed by scanning or by mild annealing, suggesting the presence of second layer adsorbed monomers, control experiments were carried out to discard molecular cracking upon adsorption. First, the comparison of the proton nuclear magnetic resonance (1H NMR) spectra of sublimated species and monomers in a CDCL3 solution is presented in Figure 3.4. This is a commonly spread technique among the community to evaluate if the evaporated species suffer molecular cracking upon sublimation. Molecules are deposited onto a cold cathode by heating a crucible up to 630 K, which is dyed with the characteristic blue of the Dy-(OETAP)$_2$ powder. The NMR spectra are then compared
to the ones acquired for intact species in a deuterated solution to not interfere with the H atoms of the molecules, in this case CDCl3. The recorded peaks are attributed to chemical shifts related to the different bondings of hydrogen with other elements, hence serving as a powerful tool for molecular structure characterization. Comparing both spectra, one can see that they exhibit the same features, highlighting that sublimated species and the ones in solution have the same structure.

![Cold cathode deposition](image)

**Figure 3.4: 1H NMR Comparative Spectra of Dy(OETAP)₂ Species Before and After Sublimation.** Spectra of Dy-(OETAP)₂ sublimated at 630 K on a cold cathode in a 10 mbar pressure atmosphere (up), with the characteristic blue dye left by these monomers. The same selected region of the 1H NMR spectra for the same compound in a CDCl₃ solution.

Second, in order to discard molecular cracking upon adsorption on the coinage metals two complementary studies were performed. The basic idea is to compare the different apparent height profiles of Dy-(OETAP)₂ in three scenarios: (i) intact species, (ii) altered monomers due to thermal cracking and (iii) *ex professo* synthesized single OETAP tectons (see Figure 3.5). For the first case, by imaging at \( V_b = -1.5 \) V an apparent height of \((4.4 \pm 0.4) \) Å is obtained between the average plane of the terrace and the border of suplamolecular nanosstructures. After annealing such samples at
400 K, the upper decker of the Dy-(OETAP)$_2$ is mainly desorbed. Even so, some intact species are observed in the remaining islands, permitting a direct comparison between the cracked species, assigned to single decker compounds, and Dy(OETAP)$_2$. Imaging at the same bias voltage (-1.5 V), results in a difference of around 3 Å in the height profile. Finally, OETAP (3) synthesized species (the single decker compounds) were independently evaporated on Au(111). Both the appearance and line profiles of OETAP monomers when imaged at -1.5 V match to those of the cracked species. The specific details for the self-assembly of the OETAP on Au(111) can be found in our study "Thermal selectivity of intermolecular versus intramolecular reactions on surfaces". In summary, the control experiments allow to state that the molecules are sublimated and deposited intact on the surface.

**Figure 3.5:** Height Profiles Analysis of OETAP vs Dy-(OETAP)$_2$ Species on Au(111). a) Supramolecular island of Dy-(OETAP)$_2$ adsorbed on Au(111) with a height line profile (green). The inset allows to measure an average apparent height of the assembly of (4.4 ± 0.4) Å ($I_t = 50$ pA ; $V_b = -1.5$ V ; Scale bar = 3 nm). b) Annealing samples at 400 K results in the desorption of the upper decker. However, some remnant intact species are observed in the islands, permitting the direct comparison in apparent height (inset) ($I_t = 50$ pA ; $V_b = -1.5$ V ; Scale bar = 8 nm). c) Detail of the border of a supramolecular assembly of directly deposited OETAP species, with an average apparent height of 1.4 ± 0.4 Å over plane of the surface ($I_t = 50$ pA ; $V_b = -1.5$ V ; Scale bar = 2 nm).
Absorption of Ln-(OETAP)$_2$: DFT Analysis

Figure 3.6: DFT Adsorption Analysis of Double-Decker Species on Au(111) and Cu(111). a-b) Side view of the chemical structure of the optimized model of Y(OETAP)$_2$ in the gas phase and on top of Au (yellow) and Cu(111) (orange), with H, C, N, Y, Au and Cu atoms colored in white, grey, blue, cyan, yellow and orange respectively. The angle $\beta$ is 110$^\circ$ in the gas phase, and $\beta'$ is 127$^\circ$ in Au(111) and 140$^\circ$ in Cu(111). c-d) Comparison of the height adsorption of both the lower molecular backbone and the metallic Y center between Y(OETAP)$_2$ and Y(TAP)$_2$ species (unfunctionalized), highlighting the decoupling effect in Au and Cu(111) respectively. e-f) Charge density isosurface (cut at 0.2 e$\cdot$Å$^{-3}$) for unfunctionalized and functionalized species in Au and Cu(111).

After identifying the deposited species and determining the parameters of the supra-molecular architectures in three distinct substrates, the adsorption geometry of the monomers is modeled by means of DFT analysis. This was carried out by Dr. J.M Gallego using the DMol3 package integrated in the Material Studio program of Accelrys Inc. The calculations were performed for Y(OETAP)$_2$ and Y(OTEAP)$_2$ species on top
of four unrelaxed layers of Au(111) and Cu(111). The objective of substituting the lanthanide cores by a transition metal such as yttrium, is to obtain a tractable computational description of the electronic valence band, which for the case of rare earth f-orbitals is still under debate. Prior studies of TbPc$_2$ already used yttrium for DFT calculations as it shares similar ionic radius in these compounds. Additionally, this double-decker geometry is isostructural with Dy and Tb derivatives, and shares the same oxidation state (+3), representing an ideal candidate in solid state chemistry to serve as a comparison for both electronic and structural properties.

First, the geometrical conformation of Y(OET AP)$_2$ in the gas phase is analyzed, finding that the two $\pi$ backbones of the monomer are slightly bent towards the metallic center. The ethyl moieties are pointing outwards due to the steric hindrance, forming an angle of 110° with the average plane of the macrocycle. To evaluate the changes suffered by these compounds when adsorbed on the surface, the optimized model of the monomers is presented in Figure 3.6 a and b for Au(111) and Cu(111) respectively. The angle formed by the ethyl groups with the average plane increases in both substrates, 127° in gold and 140° in copper. This is a result of the competition of molecule-substrate interactions via van der Waals between the $\pi$ backbones and the surface, and intramolecular interactions between the lower ethyl termini and the other parts of the unit. This effect bends significantly the lower macrocyclic planes towards the metal substrates. In the relaxed adsorption geometries, the lower molecular backbone lies 3.8 Å and 2.9 Å on top of the average plane of Au(111) and Cu(111) respectively. Still, in order to quantify the effect of the decoupling substituted terminal ethyl moieties the comparison with the unfunctionalized Y(TAP)$_2$ is presented in Figures 3.6 c and d. The average plane of the bottom macrocycle is at least 0.5 Å closer to the substrate in Y(TAP)$_2$ species (0.7 Å in the Cu(111) case). Similar behavior is found for the metallic yttrium center, standing 0.8 Å higher on Cu(111) for the Y(OETAP)$_2$ when compared with Y(TAP)$_2$, showing identical results on gold (0.5 Å). Finally, the charge density isosurface cut at 0.2 e·Å$^{-3}$ for the ethyl functionalized and not functionalized is presented in Figures 3.6 e and f for gold and copper respectively. Even for the Cu(111) case, much more reactive than other coinage metals, the
hybridization with substrate electronic states is significantly smaller for the Y(OETAP)$_2$ species. Hence, the effect of incorporating ethyl termini results in both the structural and electronic decoupling from the surface.

**Preservation of the Electronic Properties**

**Figure 3.7:** Comparative XPS of Dy(OETAP)$_2$ Species for Monolayer and Multilayer Regimes on Au(111) and Cu(111). Spectra of different elements contained in the Dy(OETAP)$_2$ species on Au(111) (red) and Cu(111) (blue). Cl$_1$s spectra are displayed in a, and N1$s$ and Dy3$d_{5/2}$ in b and c respectively. The upper set of curves corresponds to a coverage close to the monolayer, while the lower ones are acquired in multilayer samples.
In order to provide an experimental evidence of the results obtained by means of DFT, XPS studies were carried out to investigate the electronic and chemical properties of both Ln(OETAP)$_2$ compounds upon adsorption. It is important that note that there are only few XPS studies of double-decker compounds$^{72,74}$, despite being the most widespread technique to address spatially-averaged chemical and electronic properties of adsorbates. First, the spectra of C1s, N1s and Dy3d$_{5/2}$ core levels on Cu(111) (blue) and Au(111) (red) are presented for distinct coverages of Dy(OETAP)$_2$ in Figure 3.7. In the upper part of the panels the data for coverages close to the monolayer is provided. Importantly, the shape of the spectra and position of the maxima (chemical shifts $\leq 0.1$ eV) are almost identical when comparing the experiments on both substrates. For strong interacting systems one would expect large chemical shifts in the peak maximum as the reactivity of both substrates is significantly different. The apparent invariance between both experiments is an indication of the low interaction between the molecular backbone, and specially its rare earth center, and the chosen substrate.

To further investigate the molecule-substrate interactions upon adsorption, larger amounts of species were sublimated in order to achieve the multilayer regime. These samples are known to have decoupled species in the upper layers, thus providing information of molecules with minute interaction with the surfaces, as the lower layers act as an inter-spacer. The Dy3d$_{5/2}$ spectra exhibit negligible changes when comparing between both regimes in the two different substrates, thus suggesting that the +3 oxidation state of the initial SMM is preserved. On the contrary, the N1s and C1s curves show small energy shifts of 0.2 and 0.1 eV respectively. This phenomenon is attributed to the adsorption geometry derived from the DFT analysis. As demonstrated before, the flat-on adsorption indicates that the lower OETAP decker is in direct contact with the surface, bending both the ethyl groups and the average plane of the backbone. The small energy shifts are assigned to this effect and are responsible for the difference between the first layer and the more detached species in the upper layers, whose structure is closer to the gas phase.
Figure 3.8: XPS of Tb(OETAP)$_2$ Species on Au(111) for Monolayer and Multilayer Regimes. C1s (a), N1s (b) and Tb3d$^{3/2}$ (c) core levels acquired by XPS, comparing the monolayer and the multilayer regimes, colored orange and violet respectively.

The same set of experiments comparing both coverage regimes were performed in the Technische Universität München for the Tb(OETAP)$_2$ species on Ag(111). The results show a similar behavior when compared to the Dy related species. Minute differences of 0.1 eV are observed for the N1s and the C1s spectra between the monolayer and the multilayer regime, attributed to the weak interaction of the first layer with the substrate. For the case of the Tb3d$^{3/2}$ core level both curves appear to have the maximum at the exact same energy, 1275.0 eV, even though the signal is weak in the submonolayer case. Nevertheless, the same general conclusions can be derived as in the case of the Dy units, i.e. the effect of the substrate-molecule interaction on the electronic properties of the Ln-(OETAP)$_2$ can be neglected in the three coinage metals.
Conclusions

Within this chapter a combined STM, DFT and XPS study of the adsorption and electronic properties of *ex professo* synthesized double-decker single molecule magnet species on coinage metals has been presented. Importantly, these novel species were conveniently equipped with ethyl termini to facilitate both the sublimation and the decoupling of the inner structure from the metallic support. The self-assembly of such Tb(OETAP)$_2$ on Ag(111) and of Dy(OETAP)$_2$ species on Au(111) and Cu(111) affords the expression of a supramolecular close-packed architecture. DFT calculations revealed the capability of the ethyl moieties to decouple geometrically and electronically the inner structure from the metal, which is further corroborated by XPS experiments showing that the electronic properties of the Ln(OETAP)$_2$ species are barely changed when adsorbed on the metallic surfaces. Since the single ion magnetic properties of these compounds are totally dependent on the ligand field exerted to the lanthanide center, the observed preservation of the electronic properties is a good sign and mandatory to conserve the single molecular magnet behavior. However, minute variations of the ligand field could reduce or quench the magnetic anisotropy. Hence, to fully corroborate the preservation of single molecular magnet behavior of Ln(OETAP)$_2$ species on metals, we have been granted synchrotron beamtime at ALBA, experiments that will be performed after the submission of this thesis.
In this chapter the nanofabrication of surface-supported robust 2D lanthanide carboxylate coordination networks will be described. Metal-organic networks have been investigated widely in the last decade by means of STM and other surface techniques incorporating different organic linkers and metallic centers. The endless possibilities offered by designing the backbone and equipping well-known functional groups into the molecular building blocks, such as carboxylate, carbonitrile, pyridyl etc., combined with the election of the metallic center, has proven to be a very versatile tool offering tunability and functionality. Even so, regarding the metallic vertexes the scientific community mainly focused on alkali and d-block elements. Just recently, and during the development of this thesis, rare-earth metals have been implemented in supramolecular chemistry on surfaces, motivated by the high coordination number exhibited by lanthanides in bulk chemistry, affording unusual topologies.
Herein, the formation of lanthanide-directed carboxylate coordination networks is presented. Two different rare-earth elements will be deposited: gadolinium and dysprosium. Gadolinium, with a ground state electronic configuration \([\text{Xe]}^6\text{f}^7\text{d}^1\text{6s}^2\), is chosen since it is the ferromagnet with the highest Curie Temperature (292 K) in the lanthanide family, while dysprosium is commonly used in nanomagnetism due to its intrinsic bistable ground state in the +3 oxidation state \([\text{Xe]}^6\text{f}^9\text{6s}^0\) and in luminescence thanks to its yellow and narrow-line light emission.

In the first section, the formation of gadolinium-directed supramolecular square-like lattices on Cu(111) is reported. To this aim, linear molecular linkers equipped with carboxylic terminal moieties are deposited, which show deprotonation upon convenient annealing of the surface, and are able to coordinate with gadolinium. DFT calculations reveal an unprecedented eight fold Gd-O coordinative motif stabilizing the supramolecular architectures with a predominant ionic character. This ionic prevalence of the bond is further corroborated by XPS experiments, showing peak energy shifts in agreement with those of recently reported ionic metal-organic architectures. The +3 oxidation state of the Gd, as suggested by XPS spectra of the Gd 3d doublet, is validated by X-ray Adsorption Spectroscopy. The thermal robustness is evaluated by VT-STM, with supramolecular islands showing high stability up to 350 K, and dissociation at ca. 400 K.

In the second section, two distinct dysprosium-directed metal-organic architectures are reported, engineered by the coordination between deprotonated TDA species and Dy on Cu(111). By reproducing growth protocols employed with gadolinium, a similar reticular supramolecular architecture is achieved, thus revealing the possibility of inter-exchanging lanthanide node, while preserving topology. However, by annealing such architectures to 450 K, a unique quasi-regular hexagonal lattice is formed, being stabilized by dinuclear dysprosium vertexes, which are stable at room temperature, and therefore suitable for envisioned applications. Finally, Dy-carboxylate mononuclear lattice parameters are tuned by implementing linear linkers of different lengths. To this aim, novel synthesized PDA monomers are subli-
mated to reduce the internodal distances from 20.5 (TDA) to 15.4 Å, and terephthalic acid (TPA) is used to nanofabricate the smallest supramolecular architecture, with distances between dysprosium vertexes of (11.8 ± 0.5) Å.

The main results of this chapter have been recently published by us in Small and Chemical Communications\textsuperscript{109,110}. 
4.1 Gadolinium-Carboxylate Networks

The results presented in this section come from a collaboration with the E20 group led by Johannes V. Barth at the Technische Universität München and the theoretical group of Fernando Martín at the Universidad Autónoma de Madrid.

TDA on Cu(111)

The 4,1',4',1"-terphenyl-1,4"-dicarboxylic acid (TDA) is a linear conjugated building block that comprises a terphenyl moiety equipped with two functional COOH groups attached to its terminal positions (See Figure 4.1). The calculated distance between oxygen termini in the gas phase relaxed geometry is 15.5 Å. First, monomers are deposited onto pristine Cu(111) from a quartz crucible heated up to their sublimation temperature, around 540 K.
Figure 4.2: Room Temperature Deposition of TDA on Cu(111) and Deprotonation Upon Annealing. a) STM image of intact TDA species deposited at 300 K on Cu(111). The black star depicts the high-symmetry directions of the underlying substrate, and the green parallelogram highlights the unit cell of the tetragonal supramolecular self-assembly stabilized via directional H-bond interactions ($I_t = 150$ pA; $V_b = -1.0$ V; 11nm $\times$ 11nm). b) Tentative atomistic model built with the experimental values of the network (unit vectors $\vec{b} = (8.2 \pm 0.7)$ Å, $\vec{a} = (18.7 \pm 0.7)$ Å, angle $\alpha = (55 \pm 1)^\circ$), suggesting a H···O bond length of $(2.7 \pm 0.7)$ Å, depicted with red dashed lines. c) Annealing at 400 K or depositing monomers onto hot substrates, results in fully deprotonated isolated species ($I_t = 480$ pA; $V_b = -1.5$ V; 15nm $\times$ 15nm, recorded at RT).

By holding the substrate at room temperature, tectons are adsorbed intact on the surface. Molecules are imaged as bright rods and are self-assembled into close packed supramolecular islands. They feature an oblique unit cell, highlighted in green in Figure 4.2 with unit vectors $\vec{b} = (8.2 \pm 0.7)$ Å and $\vec{a} = (18.7 \pm 0.7)$ Å, enclosing an angle of $\alpha = (55 \pm 1)^\circ$. LT-STM imaging reveals that the supramolecular arrays are stabilized by directional H-bonding intermolecular interactions, with a projected H···O bond length of $(2.7 \pm 0.7)$ Å (See Figure 4.2b). When the substrate temperature is slightly higher than room temperature, ca. 310 K, the supramolecular nanoarchitectures are no longer observed. Instead, isolated species with a more oblate appearance are scattered through the surface (See Figure 4.2c). This change in appearance is associated with a chemical transformation.
mation that leads to fully deprotonated monomers\textsuperscript{111}, i.e. hydrogen atoms are detached from the carboxylic terminal groups, which is further corroborated by XPS measurements (See section 4.1 Gd-TDA XPS Analysis).\textsuperscript{112} This chemical transformation is required to form the latter metal-organic networks, as deprotonated carboxyl groups have a net negative charge, in contrast to the metal ions. Therefore Cu substrates are adequate to sustain the fabrication of these nano-architectures. Other tested substrates, such as Ag or Au, do not catalyze the deprotonation of the units, which are desorbed prior to any chemical change. Importantly, differing from other terminal carboxylate functionalized tectons, deprotonated TDA species remain isolated on the surface not forming any metal-organic array with the surface Cu adatoms.\textsuperscript{113}

**Gadolinium Metal-Organic Networks**

In order to form metal-organic lanthanide-carboxylate meshes, gadolinium atoms were evaporated from an out-gassed rod with purity over 99.9 \%\textsuperscript{114} using the EBE-1 evaporator on a TDA submonolayer sample on Cu(111). Depositing Gd onto a substrate held at 423 K leads to the sample presented in Figure 4.3. Keeping the substrate temperature at 423K for a short time after lanthanide deposition, ca 5-10 minutes, enhances the periodicity of the networks, as self-correcting processes are favored due to monomer diffusion. Large scale images depicted in Figures 4.3 a and b show the presence of reticulated porous networks with different orientational domains coexisting with minute amounts of isolated species. Even though islands exhibit border defects, long patches of well-ordered supramolecular porous lattices are found on the terraces. The inherent square unit cell, highlighted with two green vectors in Figure 4.3 c, gives an experimental internodal distance of $(19.5 \pm 0.7)$ Å, with an angle between unit vectors of $\beta = (91 \pm 1)^\circ$. High resolution imaging reveals that four linkers, each of them visualized as three lobed protrusions, are facing one single metal center, which can be observed as a void or as a protrusion depending on the tip geometry and tunneling conditions. Importantly, the metal-organic networks feature one single gadolinium atom per node, resulting in a unit cell with two TDA
monomers for each rare-earth vertex, i.e. a 1:2 metal to monomer ratio.

Figure 4.3: *Gd-TDA Metallosupramolecular Architecture on Cu(111).*

a) Large scale STM image showing lanthanide directed networks after depositing Gd onto a sample with previously deprotonated TDA species; the black star depicting the high-symmetry directions of the Cu(111) substrate (\(I_t = 300 \text{ pA} \ ; V_b = -1.00 \text{ V} \ ; 95\text{nm} \times 95\text{nm}\)). b) STM topograph highlighting the reticulated network and the island edges (\(I_t = 80 \text{ pA} \ ; V_b = 1.00 \text{ V} \ ; 24\text{nm} \times 24\text{nm}\)). c) High-resolution image with TDA monomers appearing as three-lobed protrusions and Gd atoms as bright spheres, with the unit cell defined by two identical vectors \(\vec{a} = (19.5 \pm 0.7) \text{ Å} \) and angle \(\beta = (91 \pm 1)°\). The superimposed model of four monomers highlights the 8-fold Gd-O coordination motif. The flexibility of the network when recorded at RT can be observed in the distinct nodes (\(I_t = 900 \text{ pA} \ ; V_b = -0.9 \text{ V} \ ; 7.2\text{nm} \times 7.2\text{nm}\)).

By superimposing a tentative model (see Figure 4.3 c), and from the experimental intermodal distance, the projected average Gd-O bond length is estimated to be of \((2.6 \pm 0.7) \text{ Å}\). In addition, each node has an unprecedented coordination number of eight, which hints for a different nature of the previously encountered lanthanide based metal-organic bonds in bulk chemistry\[^{31}\]. This result also differs from previously reported metal-carboxylate networks with diatomic Fe or Co clusters\[^{115,116}\]. In the so called Fe-TDA and Fe-TPA networks, four molecules faced two metallic centers, therefore forming a node featuring lower coordination number with a four-fold Fe···O bonding motif (1:1 monomer to metal ratio). It is important to notice that
in the present experiment some nodes do show binuclear gadolinium clusters. They are considered to be defects due to their low ratio recurrence and the impossibility to form extended networks for any of the tested Gd:linker stoichiometric or annealing conditions.

DFT Node Analysis

Figure 4.4: DFT Analysis of Gd-TDA Reticular Architecture on Cu(111). a-c) DFT optimized geometry of the metallosupramolecular networks corroborating the eight-fold Gd-O motif. Terminal carboxylate groups are rotated with respect to the main plane of the molecular backbone due to the intermolecular O···O steric hindrance. d) Charge-density displacement field of the node. Positive values, colored in yellow and red, represent charge accumulation. Negative values, in violet and black, indicate charge deficiency.

DFT simulations were performed in order to shed light on the nature and properties of the gadolinium-carboxylate coordination node\textsuperscript{[109]}. A transversal cut of the optimized geometry of the metallosupramolecular assemblies can be observed in Figure 4.4a. The adsorption height of the lanthanide
centers with respect to the average plane of the substrate is 3.1 Å. TDA linkers are adsorbed almost planar on top of the Cu(111) surface, with a dihedral angle of 10.9° between adjacent benzene rings, which are therefore tilted ± 5° with respect to the surface. This dihedral angle is similar to polyphenyl-dicarbonitrile species when inspected on metallosupramolecular arrays with gadolinium or cerium. The total binding energy per molecule on the gas phase is 3.27 eV, in comparison with the 4.99 eV in the presence of the underlying Cu(111) support. Figures 4.4 b and c highlight the eight-fold O-Gd node, displayed with a top view and in perspective respectively. As a consequence of the steric hindrance via intermolecular O···O interactions, carboxylate terminal groups are tilted 44.5° with respect to their sigma bonds, thus allowing the observed high coordination number. The Gd-O bond length derived from the calculations is between 2.4 and 2.7 Å, in excellent agreement with the experimental values previously presented and with bulky rare earth-oxygen donor complexes reported before. Once the geometry optimized model is compared to the experimental values, the electronic structure of the coupling motif is evaluated with two distinct theoretical approaches using first-principle calculations in the framework of the VASP package. First, the Bader analysis indicates that the gadolinium vertexes have a cationic character in the metal-organic networks. The model suggests a positive charge of +2.1 and negative of -1.1 electrons for each rare-earth node and molecular linker respectively, resulting in a -0.89e charge for the total metallosupramolecular network. Second, the analysis of the electron density displacement field of the node is presented in Figure 4.4 d. Charge density displacement field is a vector field with charge/area units that represents the electric field created by free charges. In this plot, yellow indicates charge accumulation (positive values) and violet-black color-code charge depletion (negative values). These calculations indicate that the carboxylate groups accumulate charge while the gadolinium center shows a strong charge depletion. This is an indication of the ionic character of the bond, typically encountered in coordination bonds stabilizing metal-organic frameworks in bulk chemistry, refuting the idea of covalent interaction between oxygen atoms and gadolinium. This evidence of the prevalently ionic interaction of the gadolinium-TDA₄ node
is in agreement with recently reported investigations for cesium-TCNQ$_4$\cite{121}.

**Gd-TDA XPS Analysis**

![Figure 4.5: Comparative XPS Data of the oxygen 1s and Gd 3d Core Levels of TDA Species and Gd on Cu(111). a) TDA multilayer, submonolayer and Gd-TDA supramolecular network samples in green, blue and red respectively of the Oxygen 1s core level. b) Gadolinium 3d $\frac{5}{2}$ and 3d $\frac{3}{2}$ doublet after subtracting the background signal of the Cu(111) substrate on a metallosupramolecular coordinated sample.](image)

In order to provide experimental evidences to validate the ionic character hypothesis, XPS experiments were performed. First the oxygen 1s core level is measured for three distinct samples. The green spectra is recorded for multilayer samples of TDA species deposited on Cu(111) holding the sample at 308 K (See Figure 4.5), whose features can be fitted by two Gaussian curves with peak maxima at 533.4 and 531.7 ± 0.1 eV respectively. According to prior studies the peak at higher binding energy corresponds to the C-OH oxygen present in the hydroxyl moiety, while the one at lower binding energy is attributed to the -C=O carbonyl group\cite{85,112}. By comparing these peak energies with the one obtained for samples at the submonolayer
regime deposited on Cu(111) held at 423 K (blue curve), it is directly evident that the peak at 531.4 ± 0.1 eV is related to the deprotonated TDA species with two identical carbonyl groups. The peak is shifted 0.3 eV to lower binding energies reflecting the negative charge acquired by oxygen due to the interaction with the substrate upon deprotonation. After depositing gadolinium on samples with fully deprotonated species kept at 423 K, the formation of metallosupramolecular reticular architectures results in an additional 0.1 eV shift of the oxygen 1s spectra to lower binding energies, indicating further charge gained by oxygen upon coordination with Gd. This small energy shift differs from previously reported coordinative networks with Fe-carboxylate bonds where charge transfer was demonstrated from the ligands to the metal centers. In the cited experiment, oxygen 1s core level shifted 0.6 eV to higher binding energies when coordination with iron atoms took place, totally differing from the Gd-O observed behavior. On the contrary, our results agree with recent experiments involving coordinative architectures on Cu(111), in which a predominant ionic character of the bond was claimed.

Simultaneously to the red curve recorded for O1s spectra in Gd-TDA mixtures, gadolinium 3d $^3/2$ and 3d $^5/2$ doublet spectra were also measured to gain insight of its chemical state. After subtracting the Cu(111) background signal for clarity, the spectrum (See Figure 4.5b) exhibits two broad main peaks with shake-up satellites typical of the lanthanide elements. The peak maxima are Gaussian fitted giving values for the 3d $^3/2$ and 3d $^5/2$ core levels of 1218.9 and 1187.4 respectively. The value for the 3d $^5/2$ maximum is in good agreement with previously reported experiments for Gd in a +3 oxidation state, differing from expected value of metallic Gd by ca. 1.4 eV (Metallic Gd 3d $^5/2$ is at 1186.0 eV).
To further confirm the oxidation state of the rare-earth centers, two complementary experiments were performed. First, figure 4.6 shows the comparison of gadolinium 3d spectra for Gd-TDA networks (violet) and a sample for in-situ grown gadolinium oxide (orange spectrum) by depositing large amounts from an outgassed Gd rod in UHV conditions. Vertical lines highlight that peaks are at the identical position for both oxide and metal-organic gadolinium samples. Additionally, X-ray Absorption Spectroscopy (XAS) experiments were performed on a sample with submonolayers of metallosupramolecular architectures, presented in Figure 4.7. The two lower curves are calculated using the CTM4XAS program that allows to plot the theoretical XAS spectra of gadolinium in +2 and +3 oxidation.
states\textsuperscript{126}, in blue and green respectively. The experimental curve (red) is obtained by averaging spectra taken with opposite circular polarities, and it is straightforward to relate its features to the $+3$ oxidation state, consequently determining the lanthanide chemical state.

**Figure 4.7:** Assignment of Gd Oxidation State on Cu(111). Experimental Gd XAS curve of a metal organic network grown on Cu(111) in red, compared to the theoretical curves of Gd $+3$ and $+2$ oxidation states in blue and green respectively.
 Thermal Robustness

**Figure 4.8:** *Temperature Dependent Scanning Tunneling Measurements of Gd-TDA Architectures on Cu(111).* a) STM topography recorded at 350 K, highlighting the robustness of the supramolecular assemblies. The noisy background is related to diffusing uncoordinated TDA species ($I_t = 370 \, \text{pA}$; $V_b = 1.1 \, \text{V}$; $50\,\text{nm} \times 50\,\text{nm}$). b) Zoomed-in STM image showing the flexibility of the network ($I_t = 400 \, \text{pA}$; $V_b = 1.6 \, \text{V}$; $10\,\text{nm} \times 10\,\text{nm}$). c-d) Consecutive STM images recorded on the same area at 400 K highlighting the initial steps of the dissolution of the networks (dyed in white) ($I_t = 270 \, \text{pA}$; $V_b = 1.4 \, \text{V}$; $50\,\text{nm} \times 50\,\text{nm}$).

Finally, motivated by the thermal robustness found in related surface confined metal-carboxylate networks with d-block and alkali metals, the stability of these assemblies featuring predominantly ionic bonds was tested by means of VT-STM. Controlled heating of the STM stage allows to measure the samples at different temperatures. Previous images recorded
at room temperature (see Figure 4.3) already showed a certain degree of flexibility, which is still evident when measuring samples up to 350 K, highlighted in Figure 4.8 a and b. Although the background is noisy due to uncoordinated monomer diffusion, nanoarchitectures in long- and short-range exhibit the same island edges and geometrical features as the ones recorded at helium temperature. When the STM block temperature reaches 400 K, metallosupramolecular islands start to evidence disintegration during continuously scanning the same area. This is highlighted with white-colored areas on top of the islands in Figures 4.8 c and d, where it is observed that the shape of the nanostructures varies within short time scales (ca. 30 seconds per image). Nevertheless, eight-fold lanthanide-carboxylate bonds exhibit more thermal robustness than previously reported for five-fold lanthanide-carbonitrile networks that dissolve at room temperature. This high thermal and chemical stability shown by the gadolinium-carboxylate metal-organic networks makes them suitable for future devices operating above 300 K.
In order to further exploit the versatility of lanthanide-carboxylate metal-organic networks based on predominant ionic interactions, different rare-earth metals were investigated. Dysprosium, thanks to the unique magnetic properties arisen from the nine 4f-shell electrons in the +3 oxidation state, is a promising candidate. This section will describe the metallo-supramolecular architectures achieved by coordination of TDA and dysprosium on Cu(111), i.e., monocarboxylate linker and a dicarboxylate quasiregular supramolecular architectures achieved by coordination of TDA and dysprosium on Cu(111), i.e., monocarboxylate linker and a dicarboxylate quasiregular lattices, respectively. These architectures are inspected with XPS to analyze the chemical and electronic state of both the linkers and the dysprosium vertices. After that, the tunability of the porous cavity is tested by depositing two linear linkers of different length: (i) a newly synthesized pyrene with carboxyl functional groups in the positions 2 and 7 (from now on PDPA), and (ii) the well-known terephthalic acid (TPA). By coordinating these linkers with dysprosium, the intermodal distance can be reduced to a mini-
4.2 Dysprosium-Carboxylate Networks

...mum of 11.8 Å, hence proving the versatility of the carboxylate-lanthanide metal-organic networks. Figure 4.9 shows a ball and stick model of the three monomers with the depicted distance measured between the terminal oxygen atoms, which will be employed to fabricate dysprosium directed nanomeshes with different lattice parameters.

Dy-TDA Metal-Organic Networks

Figure 4.10: **Dy-TDA Mononuclear Coordination Network on Cu(111).** a) Long-range STM image showing two metallosupramolecular reticulated networks recorded at room temperature ($I_t = 580 \ pA; V_b = -1.3 \ V; 50nm \times 50nm$). b) Zoom-in image depicting the square unit cell (green), described by the unit vectors enclosing the angle $\beta$, with TDA molecules as protrusions and Dy vertexes as depressions, recorded close to helium temperature. White stars shows the high symmetry directions of the Cu(111) ($I_t = 150 \ pA; V_b = -0.8 \ V; 14nm \times 14nm$). c) Model of the lattice as suggested by the experimental distances averaged over the images with Dy atoms coloured in blue.

Depositing dysprosium on samples with fully deprotonated TDA species on Cu(111) kept at 373 K leads to the formation of long-range well-defined reticular assemblies similar to the ones previously presented (see Figure 4.10 a), coexisting with isolated monomers on the Cu(111) surface. TDA building blocks are as well imaged as bright protrusions, while dysprosium vertexes appear as bright balls or dim voids depending on the tip state.
or scanning conditions. Figure 4.10 b highlights the square unit cell, colored in green, with two unit vectors with equivalent modulus. The white star shows the high-symmetry directions of the underlying Cu(111) surface, highlighting that one of the unit vectors of the reticulated networks is aligned with one of the basis vectors of the monocrystal. Averaging the internodal distances in various sets of images gives an experiential value for the unit vectors of \( (20.5 \pm 0.5) \) Å, enclosing an angle \( \beta = (88 \pm 1)° \), in good agreement with the ones previously observed in Gd-directed networks. Figure 4.10 c shows an atomistic model with the previous eight-fold geometry nodes, in which the projected distance of Dy···O is calculated to be \( (2.4 \pm 0.5) \) Å. In summary, the topology of the network is identical for the dysprosium and the gadolinium cases, thus suggesting the possibility of tuning physico-chemical properties by selecting appropriate lanthanide metals, while keeping the structure unmodified.

Figure 4.11: Dy-TDA Diatomic Coordination Networks on Cu(111). a) Supramolecular assemblies with hexagonal-like lattices resulting from annealing at 450 K, surrounded by scattered deprotonated species \( (I_t = 410 \ pA \ ; \ V_b = -1.0 \ V \ ; \ 30nm \times 30nm) \). b) High-resolution STM image exhibiting the quasi-hexagonal nanoarchitecture with two Dy atoms in each node \( (I_t = 320 \ pA \ ; \ V_b = -1.2 \ V \ ; \ 12nm \times 12nm) \). Both images recorded at RT. c) Model of the diatomic node with twelve oxygen atoms facing two Dy metallic centers.

The scenario is radically changed compared to previous gadolinium metal
organic networks when samples are annealed at 450K, as presented in Figure 4.11 a. In the case of dysprosium, annealing at higher temperatures leads to a phase transition in which monomers and Dy dinuclear clusters form quasi-regular hexagonal lattices. The rare-earth nodes are expressed with three different orientations with respect to the underlying Cu(111) crystal, with no apparent regular distribution. Monomers instead, are aligned with the close-packed directions of the crystal, as highlighted by the white star in Figure 4.11 b. No parameters describing the long-range geometrical distribution could be derived from these Dy-TDA arrays, probably due to the competition between substrate-molecule and molecule-molecule interaction. Still, a tentative model is presented in Figure 4.11 c by superimposing the chemical scheme of deprotonated monomers and Dy vertexes on high-resolution images. This model highlights that each dysprosium center is interacting mainly with six oxygen atoms, with a Dy···O distance range between 2.5-3.6 ± 0.5 Å, while the Dy···Dy distance in the node is (5.8 ± 0.5) Å. Regarding the TDA molecules, four of them are interacting mainly with one single Dysprosium atom, while two of them are positioned interacting with both metal centers in the dinuclear cluster. In contrast to the mononuclear eight-fold metal organic networks, with Gd/Dy:TDA ratio of 1:2, this unique binuclear six-fold Dy···O coordination bonds exhibit a Dy:TDA stoichiometry of 2:3. Importantly, upon annealing to 450 K no squared networks are observed, suggesting that the six-fold binuclear geometry is thermodynamic more favorable.
Dy-TDA XPS analysis

![Figure 4.12: XPS Spectra of the Oxygen 1s and Dy 3d $\frac{5}{2}$ evolution due to the Coordination of TDA and Dy on Cu(111).](image)

To obtain information about the chemical state of both the monomers and the dysprosium centers in the distinct phases, as well as the nature of the Dy···O metal-organic bond, XPS experiments were performed. First, the O 1s core level is evaluated for uncoordinated TDA species deposited at 373 K (deprotonated) on the Cu(111) surface, whose spectra is the black curve in Figure 4.12a. This peak can be fitted to a single Gaussian with the maximum at (531.5 ± 0.1) eV. This binding energy is associated with the two identical carboxyl groups present in the fully deprotonated species, a value that is within the error of the one obtained before (see Figure 4.5a). After the co-adsorption of Dy atoms on surfaces held at 373 K, the O 1s peak shifts 0.3 eV to a lower binding energy of (531.2 ± 0.1) eV, represented by the red spectra. This energy shift is larger than the one reported above
for gadolinium directed nanomeshes (0.1 eV), but it is still in agreement with cesium \(^{85}\) and sodium \(^{92}\) related metal-carboxylate networks, differing from the previously discussed iron-carboxylate architectures \(^{82,112}\). Finally, subsequently annealing to 450 K leads the formation of the quasi-regular hexagonal lattices, represented by the blue curve in Figure 4.12. The change in the node architecture from mononuclear to binuclear Dy clusters does not show a measurable energy shift in the O 1s core level, despite the significant structural phase transition.

In order to evaluate the oxidation state of dysprosium, its 3d \(^{5\over 2}\) core level (See Figure 4.12 b) was measured simultaneously in the same experiments addressed in Figure 4.12 a. These red and blue broad peaks, belong to mononuclear and binuclear samples respectively. Gaussian fitting gives two identical values for both curves, with maxima located at 1295.9 eV in each case. This value is in very good agreement with previous experiments reported in literature \(^{122}\) performed on samples with dysprosium in a +3 oxidation state. These results shed light on the chemical state of the dysprosium and TDA species, and by analogy to the Gd-TDA case, suggesting a predominant ionic character of both the eight- and six-fold coordination bond motifs.
Modulation of the Internodal Distance

Figure 4.13: Dy-PDA Coordination Networks on Cu(111). a) PDA deprotonated species after depositing the units onto a substrate held at 373 K \( (I_t = 80 \text{ pA} ; V_b = 1.0 \text{ V} ; 50\text{nm} \times 50\text{nm}). \) Inset: Zoomed-in image showing the isolated PDA species appearing as bright oblate lobes \( (I_t = 100 \text{ pA} ; V_b = -1.0 \text{ V} ; 9\text{nm} \times 9\text{nm}). \) b) Reticulated network resulted from depositing Dy onto a PDA/Cu(111) sample held at 373 K. The square unit cell and the high symmetry directions of the crystal are depicted in green and white respectively, together with the superimposed model of few monomers \( (I_t = 50 \text{ pA} ; V_b = 2.5 \text{ V} ; 6.5\text{nm} \times 6.5\text{nm}). \) Both images recorded close to LHe temperature. c) Model built averaging the distances with lattice vectors of 15.4 Å.

To further exploit the capabilities of the lanthanide-carboxylate directed metal-organic networks, the modulation of the inter-nodal distances is investigated by depositing linear linkers of different lengths. First, a novel synthesized pyrene dicarboxylic acid (PDA) is evaporated onto a Cu(111) substrate held at 373 K to achieve fully deprotonated monomers. Figure 4.13a (and the zoomed-in inset) shows the resulting sample, where isolated species are imaged as bright oblate protrusions scattered over the surface. Depositing dysprosium on top of a PDA submonolayer sample held at 373 K, results in the formation of metallosupramolecular reticulated architectures, as presented in Figure 4.13b. As shown above, monomers appear as rods and dysprosium vertexes as protrusions. A square unit cell is highlighted in
green, with an angle $\beta = (87\pm1)\degree$ and identical unit cell vectors (inter-nodal distance) of $(15.4 \pm 0.5)$ Å. The white star highlights the closed-packed symmetry directions, revealing that in accordance with Dy-TDA networks, one of the closed-packed directions of the underlying substrate is aligned with one of the unit vectors of the metal-organic network. Taking into account experimental lattice parameters, a tentative model is depicted in Figure 4.13c, revealing that the eightfold Dy⋯O coordination motif stabilizes the metallosupramolecular architecture. From this model, the projected Dy⋯O bond length is estimated to be $(2.4 \pm 0.5)$ Å, in agreement with previous experiments.

Figure 4.14: **Dy-TPA Coordination Networks on Cu(111).** a) STM image of deprotonated TPA species on Cu(111) recorded at room temperature ($I_t = 500$ pA ; $V_b = -2.0$ V ; $50$nm × $50$nm). Inset: Zoomed-in image showing Cu-metalorganic dimers and trimers ($I_t = 480$ pA ; $V_b = -1.9$ V ; $10$nm × $10$nm). b) After depositing Dysprosium, the smallest reticulated network is achieved with an internodal distance of $(11.8 \pm 0.7)$ Å, whose unit cell is depicted by a green square (Recorded at RT, $I_t = 150$ pA ; $V_b = 1.1$ V ; $6.5$nm × $6.5$nm). c) Tentative atomistic model of the Dy-TPA networks.

Finally, the smallest tecton, the well-known terptaltic acid (TPA)\textsuperscript{115}, is sublimated in order to ultimately diminish the Dy-Dy distance in the metal-organic networks. The monomer is first deposited on the Cu(111) substrate held at 373 K, resulting in the sample presented in Figure 4.14a.
Interestingly, in this case monomers do not appear isolated on the surface, but rather forming small aggregations scattered over the Cu(111) substrate. High-resolution imaging shows dimers and trimers with monomers appearing as bright lobes and a central node suggesting the formation of copper mediated metal-organic supramolecules. Nevertheless, no regular architectures are observed different than the described scenario by changing the molecular coverage or the substrate temperature. Therefore, when depositing dysprosium on the sample held at 373 K, the resulting square reticulated metal-organic networks presented in Figure 4.14b are exclusively attributed to lanthanide coordination rather than surface adatoms. In this figure, the square unit cell is depicted in green and defined by the two unit vectors, enclosing an angle $\beta = (93 \pm 1)^\circ$. Averaging the experimental inter-nodal distance gives a value of $(11.8 \pm 0.5)$ Å, with one of the unit vectors aligned with one of the high-symmetry directions of the underlying substrate, highlighted by the star. The experimental parameters allow to build a tentative model of the network, validating again the eightfold coordination motif observed in previous systems. The projected Dy···O bond length is $(2.4 \pm 0.5)$ Å, as only the linear backbone length is modified and thus the node geometry is not expected to change.

In summary, the capability of tuning the reticular nanomeshes parameters has been proven to be successful. It is important to remark that for both Dy-TPA and Dy-PDA directed architectures the phase transition detailed in the TDA case that lead to the sixfold Dy···O bond motif was not observed. Different monomer:rare-earth stoichiometry were tested at various annealing temperatures unsuccessfully. This suggests that the appearance of this phase is due to a subtle balance between linker and lanthanide diffusion, in addition to the steric hindrance arisen from the distinct backbone length, as the eightfold node geometry appears to be shared in the three systems.
4.3 Conclusions

This chapter revealed the capability of carboxylate moieties to form well-defined metal-organic networks by prevalent ionic coordination bonds with gadolinium or dysprosium centers, i.e. with lanthanide metals. Our study combined different surface-sensitive techniques and theoretical calculations that allowed to determine the geometrical, electronic and chemical properties of the gadolinium and dysprosium directed metal-organic networks.

On one hand, Gd-TDA thermally robust reticular coordinative mononuclear architectures were achieved on Cu(111). In addition, DFT calculations reveal the presence of unique eight-fold Gd···O bonding motifs based on prevalent ionic interactions, as further corroborated by XPS indicating chemical shifts in agreement with surface-confined ionic metallosupramolecular networks.

On the other hand, dysprosium-directed coordination chemistry was explored on Cu(111) to further investigate the feasibility of incorporating distinct rare-earth metals. This strategy proved to be successful, achieving a similar reticulated network as the one fabricated with gadolinium. However, upon thermal annealing, an unprecedented quasi-hexagonal dinuclear porous network is found. The bonding motif is tentatively assigned to diatomic dysprosium vertexes, surrounded by twelve oxygen atoms belonging to six adjacent monomers. XPS suggests a similar ionic character of the coordination bond to that found on Gd-directed assemblies.

Finally, in order to fully research the structural capabilities of lanthanide-carboxylate coordination networks, tunability of the internodal distance by selecting linear linkers of distinct lengths was presented. Thanks to this approach, the reticular topology is preserved, while the distance between mononuclear dysprosium vertexes can be tuned between 11.8 and 20.5 Å, demonstrating high versatility to modify the network parameters.

In summary, lanthanide-carboxylate networks are revealed as robust and highly tunable nanoarchitectures with envisioned potential in applications exploiting the properties of the rare-earth elements such as narrow-line
light emission or single atom magnetism. To further explore such possibilities, engineering of metallosupramolecular architectures directed by lanthanides are proposed on decoupling supports such as ultra-thin oxides or two-dimensional materials grown on metals.
Lanthanide Metallation of Porphyrinoids

Porphyrrins have attracted the attention of the scientific community due to their importance in biological process such as photosynthesis or oxygen transport in blood cells. This versatility allowed scientists to envision their potential for optoelectronic devices, bioprobes, sensors and catalysts. In particular, tetrapyrroles are of great interest in surface science as their magnetic, electronic and chemical properties can be tailored at will for different purposes such as catalysis, information storage, sensing or optoelectronics. The chemical versatility of porphyrins is enormous. On one hand, their terminal positions can be functionalized with different moieties to design diverse low dimensional nanoarchitectures with distinct intermolecular interactions: self-assembled arrays, metal-organic networks or covalent frameworks. On the other hand, the central cavity acts as a chemical pocket that can incorporate a large variety of metal ions, which can be used to the ligation of axial tectons. In the last
decade, many studies focused on the in situ metalation with transition metals\textsuperscript{151,155,158} but only recently lanthanides started to be investigated. This is particularly interesting as lanthanide-porphyrins can embrace the unique properties arising from the protected 4f electron shell for light emitting materials\textsuperscript{159,161} or sensitive devices\textsuperscript{162}. In addition to the porphyrin derivatives, different studies on surfaces focused on distinct porphyrinoids such as phthalocyanines\textsuperscript{163-165}, porphyrazines\textsuperscript{66,68}, porphycenes\textsuperscript{166-169} and corroles\textsuperscript{170,171}. Even so, these compounds share the basic geometry of four pyrrole (or isoindoline) units within their macrocycle. To tailor the optoelectronic properties, synthetic chemistry have dedicated recently substantial effort to provide different macrocycles including smaller or expanded porphyrinoids, i.e. having less or more than the traditional four pyrroles. In this sense, smaller subphthalocyanine units\textsuperscript{172} were successfully characterized on surfaces, even providing a rare 3D growth\textsuperscript{173}. A lot of effort was also invested on synthesizing expanded porphyrins, targeting to increase the number of conjugated $\pi$ electrons, though attempts on surfaces remained unsuccessful. J. Sessler\textsuperscript{174,175} defines expanded porphyrinoids as "macro cyclic compounds containing heterocyclic units (pyrrole, furan, or thiophene-like) linked together, either directly or through spacers, so that the internal ring pathway contains at least 17 atoms". The [30]trithia-2,3,5,10,12,13,15,20,22,23,25,30-dodecaazahexaphyrin was synthesized by our collaborators\textsuperscript{176}. This compound, to be termed HTAP, belong to the expanded porphyrinoid family\textsuperscript{177,178}.

In the first section of this chapter, a pioneer on-surface study of such HTAP compounds will be introduced. The deposition of HTAP species on Au(111) leads to a unique self-assembly characterized by a long-range orientational order templated by the substrate. Furthermore, these species can be vertically manipulated with STM pulses to induce selective deprotonation of the inner hydrogen atoms of the expanded cavity. This process is carried out by tunneling electrons, ensuring a reliable degree of molecular control without affecting adjacent HTAP species, and therefore of relevance for information storage. In addition, the complexation of the expanded macrocycle with in situ deposited dysprosium adatoms is achieved, reveal-
ing an unprecedented on-surface off-centered metatation. The synthesis of such species is first inspected with STM and STS experiments, and finally supported by DFT calculations, demonstrating the possibilities of expanded compounds to open new avenues in on-surface macrocyclic chemistry.

In the second section of this chapter, the adsorption, self-assembly and in situ metatation by dysprosium of 5,10,15,20-tetrakis (4-fluorophenyl)-21,23H-porphyrin (2H-4FTPP) on Au(111) is reported. First, room temperature deposition of 2H-4FTPP species results in a close-packed self-assembly, featuring tautomerization of the inner H atoms. Then, we explored the metatation of intact 2H-4FTPP species on Au(111) by dosing dysprosium. Due to the larger ionic radius of the Dy atoms in comparison with other transition metals, it is complexed out of the main plane of symmetry of the macrocycle, though due to role of the surface, the dysprosium is located between the macrocycle and the gold substrate. Importantly, three distinct states are observed and assigned to Dy-2H-4FTPP (where Dy is only physisorbed), Dy-1H-4FTPP (by removal of one H atom) and Dy-0H-4FTPP (by removal of two H atoms and representing the final fully metallated state). By STM pulses, a step-wise transformation from Dy-2H-4FTPP to Dy-1H-4FTPP and from Dy-1H-4FTPP to Dy-0H-4FTPP can be achieved. Remarkably, Dy-2H-4FTPP exhibits a strong Kondo signal, and the analysis of the broadening of this resonance versus temperature indicates a Kondo temperature $T_K = 120$ K. This Kondo signal can be switched off by STM pulses irreversibly changing the Dy-2H-4FTPP into the Dy-1H-4FTPP or into fully metallated Dy-0H-4FTPP species. Our results introduce a new porphyrin derivative on surfaces and demonstrate its potential for molecular self-assembly and for complexation with Dy adatoms, providing metallated species featuring a Kondo resonance and thus of relevance for transport in molecular electronics.

Partial results of this chapter have been published in the Journal of the American Chemical Society[179].
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Figure 5.1: *HTAP Chemical Structure.* Ball and Stick model of the HTAP monomer with carbon, nitrogen, sulfur and hydrogen atoms colored in cyan, blue, yellow and white respectively. The distance is calculated in the gas phase relaxed model between the terminal carbon atoms within the AM1 semiempirical method framework.\[180\]

HTAP is an expanded porphyrin displaying a 30-\(\pi\) electron heteromacrocycle with 27 atom in its internal cavity, build by alternating two distinct moieties: (i) 1,3-diiminoisoindoline in the corners and (ii) thiadiazole in the lateral positions of its triangular shape. The chemical structure of HTAP is presented in a ball and stick model in Figure 5.1 where its triangular
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geometry and its three inner hydrogen atoms can be appreciated. Both the augmented size of the macrocycle and the presence of inner hydrogen atoms will play an important role for \textit{in situ} metalation and single-molecule writing.

![Figure 5.2: STM Bias Dependence Appearance of HTAP on Au(111).](image)

STM images showing the appearance at positive (right) and negative (left) bias voltages, with the six building blocks clearly distinguished as bright protrusions. At negative bias conditions the diiminotsoindoline groups appear more blunt, while at positive voltages the corners look truncated (a: $I_t = 1.2 \text{ nA} ; V_b = -1.6 \text{ V} ; 5\text{nm} \times 5\text{nm}$) (b: $I_t = 1.2 \text{ nA} ; V_b = 1.5 \text{ V} ; 5\text{nm} \times 5\text{nm}$).

In order to sublime HTAP species, the crucible is heated at 573 K and subsequently monomers are deposited on a Au(111) substrate held at room temperature. For very low molecular coverages, individual species are observed on the steps and on the terraces. The HTAP appearance varies with bias voltage polarity (Figure 5.2 a and b), though at both scanning conditions the six building blocks (three isoindole and three thiadiazole moieties) are clearly distinguishable as bright protrusions and its central cavity as a dim depression. Importantly, the sides of each monomer are aligned with the high symmetry directions of the underlying Au(111) monocystal, highlighted by a white star in Figure 5.2.
Figure 5.3: Coverage Dependent Growth of HTAP on Au(111). a) At low coverage regime monomers are adsorbed only on the step edges on the fcc regions of the reconstruction ($I_t = 150 \, \text{pA} ; V_b = -1 \, \text{V} ; 37.5\,\text{nm} \times 37.5\,\text{nm}$). b) Tectons start to adsorb on the terraces on the elbows of the herringbone and the fcc regions ($I_t = 200 \, \text{pA} ; V_b = 1.5 \, \text{V} ; 50\,\text{nm} \times 50\,\text{nm}$). c) At certain fcc coverage, monomers start to adsorb on the hcp regions ($I_t = 200 \, \text{pA} ; V_b = 1.5 \, \text{V} ; 47\,\text{nm} \times 47\,\text{nm}$). d) Further increase of the coverage results in a close packed two-row self-assembly on the fcc regions ($I_t = 150 \, \text{pA} ; V_b = 1.5 \, \text{V} ; 50\,\text{nm} \times 50\,\text{nm}$). e) Fcc regions are fully decorated with the two-row self-assembly and the hcp regions show one-dimensional arrays of HTAP molecules ($I_t = 50 \, \text{pA} ; V_b = -0.5 \, \text{V} ; 50\,\text{nm} \times 50\,\text{nm}$). f) Depositing even more molecules once the hcp and fcc are fully occupied by one- and two-dimensional self assemblies respectively, results in the decoration of the frontiers between the two regions ($I_t = 50 \, \text{pA} ; V_b = 1 \, \text{V} ; 50\,\text{nm} \times 50\,\text{nm}$).
Next, the growth of HTAP on Au(111) is inspected as a function of the coverage. If minute amounts of these units are deposited on the substrate, monomers are only adsorbed on the step edges of the monocrystal as presented in Figure 5.3a, due to the larger adsorption energies. Importantly, there is a clear preference for steps edges at the fcc regions of the reconstructed Au(111). Increasing the coverage until all these step-edge sites are occupied results in the adsorption of monomers in the flat terraces of the surface (see Figure 5.3b). HTAP species adsorb first on the elbows of the herringbone reconstruction and subsequently on the fcc regions of the terraces, which are also known to have a higher reactivity than hcp regions. Increasing the coverage leads to a successive decoration of the fcc regions and the initial coverage of the hcp sites, mostly on the elbows of the reconstructed Au(111) (See Figure 5.3c). Importantly, at this coverage monomers start to form supramolecular assemblies, and only two different orientations are observed, highlighted with green and blue triangles, consistent with the alignment of the molecular symmetry group $D_3h$ with the basis vectors of the substrate. Remarkably, the distribution of both orientations does not appear to be random, as blue-colored molecules are observed mainly in the fcc regions, in contrast with the green-colored ones in the hcp sites. This is more evident by increasing the coverage, depicted in Figures 5.3d and e. HTAP species start to form two-molecule wide supramolecular rows on the fcc sites and one-molecule wide supramolecular rows on the hcp regions of the herringbone reconstruction, until the space is fulfilled following this decoration rule. Once this is accomplished, if coverage is further increased, monomers start to adsorb on the empty frontiers between hcp and fcc regions until the surface is completely covered with HTAP units (see Figure 5.3f).
Figure 5.4: Self-Assembly of HTAP on Au(111). a) STM image showing small close-packed islands at the elbows of the reconstructed Au(111) surface with the unit cell colored in green ($I_t = 200$ pA; $V_b = -0.5$ V; $29 \text{nm} \times 29 \text{nm}$). b) Model built from the experimental values $\vec{a} = (17.4 \pm 0.5) \text{Å}$, $\alpha = (61 \pm 1)^\circ$, and the long molecular axis tilted $(9 \pm 1)^\circ$ with respect to the unit vectors, highlighted with the red dashed line.

The supramolecular assemblies observed in figures 5.3 d and e can form extended hexagonal close-packed assemblies on the elbows of the reconstructed fcc regions of the Au(111) substrate, illustrated in Figure 5.4 a, with the unit cell highlighted in green. The intermolecular distances are experimentally measured to obtain the lattice parameters and to build the model presented in Figure 5.4 b. The unit vectors have the same modulus $|\vec{a}| = (17.4 \pm 0.5) \text{Å}$, that enclose the angle $\alpha = (61 \pm 1)^\circ$. Importantly, the molecular long axis, depicted with a red dashed line, is tilted $(9 \pm 1)^\circ$ with respect to the unit cell vector to enhance the S···H intermolecular interactions, with an experimental projected distance of $(2.5 \pm 0.5) \text{Å}$. In the case of the hcp regions, once the molecular pressure results in one-dimensional arrays, the intermolecular distances and tilting of the molecular long axis are experimentally compatible with the value in the fcc regions.
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Figure 5.5: Orientational Selectivity of HTAP on Au(111). a-b) Most stable adsorption orientations on Au(111). The small energy difference (20 meV) arises from the interaction of the inner protons with the second layer of surface atoms, positioned on top of hcp (a) or fcc hollow sites (b). c-e) Different coverage regimes showing the orientational preference in hcp and fcc regions, resulting in long-range ordered geometries. (c: \( I_t = 125 \) pA ; \( V_b = 1.5 \) V ; 30nm \( \times \) 30nm, d: \( I_t = 200 \) pA ; \( V_b = -0.5 \) V ; 21.5nm \( \times \) 21.5nm, f: \( I_t = 50 \) pA ; \( V_b = -0.5 \) V ; 13.7nm \( \times \) 13.7nm)
To gain a better understanding of the adsorption geometry exhibited by HTAP units on Au(111), and to focus on the understanding of the site-selective molecular orientation on the regions of the herringbone reconstruction, DFT calculations were performed\textsuperscript{179}. Figures 5.5 a and b show the most stable adsorption configurations, demonstrating that the molecular sides are aligned with the high symmetry directions of the underlying Au(111) substrate. Even though both orientations appear to be equivalent, a small 20 meV difference in their adsorption energy arises from the interaction with the second layer of surface atoms, resulting in the orientational selectivity observed. In Figure 5.5 a the inner hydrogen atoms of the heteromacrocycle are positioned on top of hcp hollow sites, while in Figure 5.5 b they are positioned on fcc hollow sites, which results in the small energy difference of 20 meV. Thus, when imaged at 4 K, one orientation is observed mainly in the hcp regions and the other one on the fcc ones of the herringbone reconstruction, as highlighted in Figures 5.5 c-e. At different coverage regimes the orientational preference is maintained along large distances, and over 99% of the molecules at the fcc regions are oriented opposite with respect to the ones on hcp reconstructed areas.

In order to inspect the electronic structure of HTAP monomers upon adsorption on Au(111), STS was performed to identify the HOMO and LUMO orbitals. As shown in Figure 5.6 a, two features are observed at -1.6 and 1.5 V when compared to the spectra taken on the pristine Au(111) (the peaks at -1.15 and -0.85 V are related to tip states, and do not represent relevant information regarding HTAP electronic structure). In order to visualize the orbitals in the real space, lock-in maps were recorded at the approximate resonance energies, as shown in figures 5.6 b and c. At -1.6 V, three small bright protrusions can be observed at the approximate position of the inner protons, while at 1.5 V the central cavity and the diiminoisindoline groups are imaged as a depression and the thiadiazole moieties appear as bright protrusions. As a result, the tentative experimental gap for HTAP on Au(111) is approximately 3.0 eV.
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Figure 5.6: **Electronic Structure of HTAP on Au(111).** a) STS spectra showing the HOMO-LUMO resonances of HTAP molecules, with a gap of ca. 3 V, and the spectra recorded on the pristine Au(111) surface, with tip states between -1.3 and -0.75 V (STS Parameters: Modulation: 10 mV, Frequency: 773 Hz, Integration time/point: 33 ms, Sampling Energy = 4 meV/point). b-c) High-resolution STM topographs (left) with three monomers recorded simultaneously with a lock-in map (right) at the approximate voltages of the HOMO-LUMO resonances (a: $I_t = 200$ pA; $V_b = -1.6$ V; $6.6\text{nm} \times 6.6\text{nm}$, b: $I_t = 200$ pA; $V_b = 1.5$ V; $6.6\text{nm} \times 6.6\text{nm}$, Lock-in Maps Parameters: Modulation= 10 mV, Frequency=773 Hz, Integration time/point= 11 ms).

While recording long-range lock-in maps, a minority species was discovered, which shows a darker appearance at the LUMO resonance when compared to the majority of HTAP species. This is highlighted in Figure 5.7a with green circles. Although the topographic image does not show a significant difference between both species, lock-in maps recorded at 1.5 V permit unambiguously to distinguish between them. A closer zoomed-in image is depicted in Figure 5.7b, where the minority species, representing
around a 4% at this molecular coverage, appear clearly darker than the majority (96%) species described before. Surprisingly, the electronic structure is analogous to majority HTAP, but solidly shifted 0.5 V towards lower energy values, with the HOMO and LUMO at -2.1 and 1.0 V respectively. In order to inspect the minority species, lateral manipulation experiments where performed, as depicted in Figure 5.7 c, whose inset displays the topographs corresponding to the lock-in maps represented in the main figure. In the left part of the panel, the lock-in map reveals two minor species, which can be turned into the majority ones by laterally displacing the upper monomer, as showed in the right panel. It is important to remark that the density of minor species per area is independent of the molecular coverage, therefore indicating that the presence of minority HTAP is related with the adsorption on the surface and not with the intrinsic nature of the molecule. Hence, it is not attributed with different conformations or removal of inner hydrogen atoms, as derived in previous studies regarding porphyrin derivatives. For the same reason the charge transfer, which would explain the rigid shift of the molecular orbitals, is also discarded. Recent studies have shown that this behavior is explained by supposing the adsorption of this species on top of surface adatoms or more generally substrate defects, which can be laterally manipulated to switch from one to the other.
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Figure 5.7: Minority Species: Manipulation. a) Long-range STM image at a medium coverage regime, acquired simultaneously with a lock-in map at 1.5 V. Whereas in topography green-circled monomers show a similar appearance, in the lock-in map the brightness is clearly different ($I_t = 150 \, \text{pA}$ ; $V_b = 1.5 \, \text{V}$ ; $50 \, \text{nm} \times 50 \, \text{nm}$). b) Zoomed-in STM image highlighting the difference between the minor species (4%, left) with the major one (96%, right) ($I_t = 200 \, \text{pA}$ ; $V_b = 2 \, \text{V}$ ; $6.6 \, \text{nm} \times 6.6 \, \text{nm}$). (a-b Lock-in Maps Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 10 ms). c) Lateral manipulation sequence showing that minor species can be turned into major ones by laterally displacing them (the inset depicts the topographs corresponding to the lock-in maps of the figure) ($I_t = 200 \, \text{pA}$ ; $V_b = 1.5 \, \text{V}$ ; Height: 19.5 nm) (c Lock-in Maps Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 1 ms. Manipulation Parameters: $I_{\text{Man}} = 20 \, \text{nA}$ ; $V_{\text{Man}} = -0.1 \, \text{V}$)
Spatially-Controlled Deprotonation

Figure 5.8: **Electronic Structure of HTAP(-3H).** a-b) STM images showing two HTAP monomers, which after applying a 2.7 V pulse on the right one is irreversibly transformed into HTAP(-3H), with the correspondent change in appearance (a-b: $I_t = 200 \ pA \ ; \ V_b = -1.9 \ V \ ; \ 6.6nm \times 6.6nm$). c) STS spectra recorded in the center of a deprotonated HTAP(-3H) species, showing two strong resonances at -1.9 and 2.0 V, identified as the HOMO and LUMO orbitals respectively ($I_t = 200 \ pA \ ; \ V_b = 2 \ V \ ; \ 6.6nm \times 6.6nm$, STS Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 36 ms, Sampling Energy= 4 meV/point). d-e) Lock-in maps recorded at the energy positions of the molecular resonances showing the orbitals in the real space (Lock-in Maps Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point: 10 ms).

Once the self-assembly and the electronic structure of HTAP species was reported, we focused our attention to the capabilities of the macrocycle of HTAP for information storage by pulse-induced deprotonation. Before attempting deprotonation experiments through vertical manipulation, several tests were performed to monitor the tautomerization of the inner protons. Contrary to other porphyrinoid derivatives, no telegraphic signal of $I_t$ vs. time was measured while positioning the tip on different positions of HTAP species at various current and voltage set points, which suggests that tau-
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tomerization does not occur on Au(111) or it cannot be monitored with this method. One argument supporting the absence of this tautomerism phenomenon is the lack of free pyrrole units, as in the case of porphyrins and phthalocyanines, or a significantly larger distance between pyrrole moieties once a temporal vacancy is promoted (see Figure 5.9).

However, the single-molecule selective deprotonation of HTAP species can be carried out through vertical manipulation by positioning the tip on top of the central cavity and applying voltage pulses above a threshold of 2.7 V. This can be performed both by applying a certain voltage over time or by ramping between two bias voltage values that surpass the mentioned threshold. The resulting HTAP(-3H) species after a 2.7 V pulse, can be observed in Figure 5.8b, where the three inner protons have been irreversibly removed. In order to inspect the electronic structure of the \textit{in situ} synthesized species, STS spectra are acquired on its central cavity. Two strong molecular resonances can be observed at -1.9 and 2.0 V, attributed to the HOMO and LUMO orbitals respectively. In comparison with intact HTAP species, the HOMO-LUMO gap is rigidly opened with respect to the Fermi level, with a value of ca. 3.9 eV. In order to visualize both orbitals in the real space, lock-in maps were recorded at the molecular resonance energies, as showed in figures 5.8d and e. The HOMO shows a bright central cavity, while the LUMO shows three inner bright lobes dramatically different than the intact HTAP species. Regarding the mechanism of the deprotonation, it turned out to be a highly localized process, as one could vertically manipulate target molecules without affecting adjacent ones. Therefore, a primary role of the electric field created by applying a voltage difference between the tip and the sample was discarded, and a much more localized mechanism through tunneling electrons is suggested\textsuperscript{24,194}. 

Figure 5.9: Step-by-step Deprotonation of HTAP on Au(111). a) STM images recorded at -0.5 V of the process that transforms an intact HTAP species into HTAP(-1H), HTAP(-2H) and HTAP(-3H) (from left to right) in a step-by-step fashion. b) Models of the corresponding species, where the inner hydrogen atoms are subsequently removed. c) Constant current STM simulated images at -0.5 V (25nm×25nm). d) Tunneling current versus Voltage while ramping between 2.65 and 2.78 V, where the three abrupt decreases correspond to the three protons detached from their respective pyrrole at different moments.
Although most of the manipulation experiments resulted in the full deprotonation of the inner cavity of HTAP species, some experiments ended in intermediate deprotonation states. As showed in Figure 5.9a, it could be observed intermediate monomers assigned to HTAP(-1H), HTAP(-2H) or the already described HTAP(-3H), highlighted with a ball and stick model in Figure 5.9b. The STM appearance shows darker pyrrole units once they loose the corresponding proton. This is further confirmed by DFT simulation of the STM images, represented in Figure 5.9c. It is important to mention that tautomerization is not observed in any of the species, as the inner protons can only be removed and not displaced in the inner cavity. The stepwise deprotonation process is better illustrated in Figure 5.9d, where the tunneling current is recorded while ramping the voltage from 2.65 to 2.78 V at the center of the heteromacrocyclc. Each of the abrupt changes represents the desorption of an inner hydrogen atom attached to a pyrrole moiety, resulting in a fully deprotonated HTAP(-3H) species. Despite the observation of the stepwise deprotonation is not a marginal event, the selective removal of a target hydrogen atom inside the macrocycle was not a controlled mechanism with the tested manipulation parameters, thus preventing the system under study to create octal memory devices.

Motivated by the highly-localized full inner deprotonation of HTAP species, a "writing" protocol was tested on a two-row supramolecular island on the fcc region of the herringbone reconstruction, as showed in Figure 5.10a. The panels illustrated in Figure 5.10b show the transformation of twelve HTAP species into HTAP(-3H) entities by selectively applying 2.8 V pulses in their central cavity. Importantly, only the targeted species were deprotonated in each step without a single error, demonstrating the degree of local control of the writing protocol. This sequential deprotonation procedure could be continued up to 43 HTAP species along the same fcc region, illustrated by figures 5.10c-e. Thus, the potential of this system for information storage is demonstrated, as the process can be performed selectively without perturbing adjacent molecules, which was not observed for smaller porphyrinoid derivatives.
Figure 5.10: Spatially-Controlled Sequential Deprotonation of HTAP on Au(111). a) STM image of the selected area where the sequential deprotonation starts ($I_t = 200$ pA; $V_b = -0.5$ V; 45nm x 45nm). b) Zoomed-in STM images set of the region where a total of twelve monomers are sequentially deprotonated with 2.8 V pulses without affecting other units than the targeted one. (all images: $I_t = 50$ pA; $V_b = -0.5$ V; 12.3nm x 12.3nm) c-e) Long-range images showing the complete sequence of 43 HTAP monomers deprotonated successfully without defects ($I_t = 200$ pA; $V_b = -0.5$ V; 45nm x 45nm).
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HTAP on Ag(111)

Figure 5.11: Self-Assembly and Bias Dependence Appearance of HTAP on Ag(111). a) Long-range STM image showing the close packed self-assembly of HTAP monomers on Ag(111) \((I_t = 50 \text{ pA} ; V_b = -0.5 \text{ V} ; 50 \text{nm} \times 50 \text{nm})\). b) Topography showing the hexagonal lattice with the unit cell described by the unit vectors \(\vec{b}\), enclosing the angle \(\beta\), and two molecular models superimposed \((I_t = 15 \text{ pA} ; V_b = -0.5 \text{ V} ; 9\text{nm} \times 9\text{nm})\). c-d) High-resolution zoomed-in images showing the appearance of an isolated HTAP monomer at negative and positive bias \((c: I_t = 25 \text{ pA} ; V_b = -0.2 \text{ V} ; 3.4\text{nm} \times 3.4\text{nm}, d: I_t = 25 \text{ pA} ; V_b = 0.5 \text{ V} ; 3.4\text{nm} \times 3.4\text{nm})\).
Inspired by the "writing" protocol described in the previous section, HTAP species were deposited on a substrate where the surface reconstruction does not prevent the formation of long-range architectures. For that purpose HTAP monomers were sublimated on the Ag(111) surface, as depicted in Figure 5.11a, giving rise to well-ordered close-packed hexagonal lattices on the flat terraces of the silver substrate. The supramolecular self-assembly is described by the unit vectors \( \vec{b} \), with the same modulus \( |\vec{b}| = (17.2 \pm 0.5) \text{ Å} \), enclosing the angle \( \beta = (58 \pm 1)^\circ \). Again, the long molecular axis is tilted \( (8 \pm 1)^\circ \) with respect to the unit vector \( \vec{b} \), concluding that all parameters are compatible with the ones in Au(111). In addition, the white star highlights the alignment of the molecule sides with the underlying high-symmetry directions of the Ag(111) monocrystal. Figures 5.11 c and d depict the bias voltage appearance dependence of isolated HTAP monomers, which show similar features when compared with Figure 5.2, i.e. blunt vertexes at negative and truncated at positive bias voltages.

**Figure 5.12:** Transformation into HTAP(-3H) on Ag(111). a-c) Sequence of the in situ deprotonation of HTAP species on Ag(111). In a, a prior deprotonated monomer is showed in the bottom right corner, together with other three intact species. While scanning in b, the central tecton is transformed into HTAP(-3H) by applying a 2.3 V pulse. Scanning again the same area confirms the transformation (a-c: \( I_t = 50 \text{ pA} \); \( V_b = -1.5 \text{ V} \); 10nm \( \times \) 10nm).

In order to attempt deprotonation on Ag(111), the same ramping voltage
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protocol was tested on isolated HTAP species. In this case, the voltage threshold appears shifted towards lower energies, as 2.3 V pulses already trigger the transformation into HTAP(-3H). The sequence of deprotonation of a single monomer is depicted in Figure 5.12. First, three intact species are showed together with a previously manipulated species in order to compare the latter transformation. During the scan presented in Figure 5.12b, once the tip is located above the central monomer, a 2.3 V voltage pulse is performed and the image changes abruptly. Scanning again the same area confirms that the targeted molecule has been transformed into a HTAP(-3H).
Figure 5.13: **Step-by-step Deprotonation on Ag(111).** Sequential deprotonation of an isolated HTAP species into HTAP(-1H), HTAP(-2H) and HTAP(-3H) by successively applying 2.0 voltage pulses on the targeted diiminoisoindoline moiety (a-d: $I_t = 75 \text{ pA}; V_b = -1.5 \text{ V}; 8 nm \times 8 nm$).

In analogy with the previously described step-by-step deprotonation on Au(111) (See Figure 5.9), the experiment reported in Figure 5.13 shows the sequential deprotonation of the hydrogen atoms inside the cavity on Ag(111). Figure 5.13a shows for comparison a previously deprotonated species and an intact HTAP on the upper left and bottom right corners respectively. Applying a 2.0 V pulse in the left vertex of the intact HTAP leads to the desorption of the corresponding proton, resulting in HTAP(-1H). This can be successively performed in the remaining central protons, achieving HTAP(-2H) and finally HTAP(-3H) species. Again, no tautomer-
ization evidence is observed in form of telegraphic current vs. time signal or change in contrast in the STM images.

Figure 5.14: Spatially Controlled Deprotonation on Ag(111): Molecular Writing. a) IMDEA Institute logo achieved after deprotonating 68 monomers with just one defect ($I_t = 100\,\text{pA} ; V_b = -0.5\,\text{V} ; 70\,\text{nm} \times 32\,\text{nm}$).

Finally, once the ideal vertical manipulation parameters for the full deprotonation of HTAP species on Ag(111) were determined, the "writing" protocol was tested on close-packed supramolecular assemblies. Figure 5.14 shows the attempt to write the name of our institute, i.e. "IMDEA NANO", on a large island by applying 2.3 V pulses on the central cavity of each monomer to use them as single pixels. Even though a defect can be appreciated in the "N", 68 targeted HTAP species were successfully deprotonated to form the logo of our institution in less than 1200 nm$^2$, hence demonstrating that the localized deprotonation protocol for single molecule writing can be transferred to other substrates.
Off-Centered Dysprosium Metalation

Figure 5.15:  **Off-centered Dysprosium Metalation of HTAP species on Au(111).**  

a) After depositing dysprosium atoms a new asymmetric species is observed in both fcc and hcp regions. High-resolution STM image shows the different appearance between Dy-HTAP (blue) and intact HTAP species (white). (\(I_t = 150 \, pA\); \(V_b = 2 \, V\); 11.8nm × 11.8nm).  
b) Zoomed-in STM image of an isolated Dy-HTAP species emphasizing its asymmetry (\(I_t = 150 \, pA\); \(V_b = 2 \, V\); 3nm × 3nm).  
c) Ball and stick model of the dysprosium-HTAP species, with the off-centered rare earth metal bonded to the lower corner.  
d-e) Molecular tip allows to resolve the off-centered metalation of a Dy atom inside the heteromacocycle (d: \(I_t = 100 \, pA\); \(V_b = -0.55 \, V\); 10nm × 10nm, e: \(I_t = 50 \, pA\); \(V_b = 0.5 \, V\); 3.7nm × 3.7nm).

Motivated by the capability of a previously synthesized HTAP derivative to host three d-block metals in its central cavity\(^{173}\), dysprosium atoms were
evaporated on submonolayer HTAP samples to investigate the potential of the expanded porphyrinoids to allocate large metallic ions. To this end, after dysprosium deposition, samples were annealed at 373 K to enhance the metalation of the macrocycle. Following this protocol, a new asymmetric species is observed and identified as Dy-HTAP (Figure 5.15 a, highlighted with a blue circle), which clearly differs from the intact monomers described in previous sections, encircled in white. A high-resolution zoomed-in image of an isolated Dy-HTAP species is presented in Figure 5.15 b, in which the central cavity does not appear as a depression anymore, and features a protrusion in the bottom corner. A model of the off-centered metallated porphyrinoid (Figure 5.15 c) highlights that the rare-earth ion is interacting with two thiadiazole moieties and the corresponding diiminoisindoline group. Additionally, by scanning these metallated entities with a molecular tip, the inner dysprosium atom is resolved as a bright sphere, clearly displaced from the center of the cavity (Figures 5.15 d and e). At these scanning conditions it is clearly visible that the two thiadiazole moieties that interact closely with the lanthanide metal have a higher apparent height in comparison with the remaining one, demonstrating the new off-centered coordination motif. As expected from suffering such a significant chemical transformation, metallated monomers do not conserve the orientational preference in the hcp and fcc regions of the herringbone reconstruction, even though the molecular sides remain aligned with the high-symmetry directions of the underlying Au(111) surface.

The electronic structure of the in situ synthesized Dy-HTAP species is inspected by means of STS, as shown in Figure 5.16. The three displayed spectra are measured at the center of the cavity (in red), at one of the thiadiazole moieties interacting closely to the Dy ion (in blue), and at the pyrrole bonded to the metal (in black). The red curve shows no clear peaks, but a shoulder at 1.1 V and a sharp increase in intensity beyond 1.5 V. On the other hand, the blue and black spectra show a peak at around 1.0 V, and a steady increase above 1.5 V. The region of negative bias showed no significant feature in both STS spectra or lock-in maps.
Figure 5.16: Electronic Structure of Dy-HTAP Species on Au(111).

a) STS spectra measured at the distinct positions indicated by the colored crosses ($I_t = 150 \text{ pA} ; V_b = 2 \text{ V} ; 3 \text{nm} \times 3 \text{nm}$, STS Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 36 ms, Sampling Energy= 2.75 meV/point). b-d) Lock-in Maps at different voltages exhibiting different orbital features, clearly revealing an asymmetric molecular orbital distinct from the intact monomers ($I_t = 150 \text{ pA} ; \text{Voltage indicated in the Figures}; 3 \text{nm} \times 3 \text{nm}$). c) Long-range topography highlighting the efficiency of the lanthanide metalation upon annealing at 373 K ($I_t = 200 \text{ pA} ; V_b = 1.5 \text{ V} ; 19.5 \text{nm} \times 19.5 \text{nm}$). d) Lock-in map of the same area recorded at 1.5 V ($I_t = 200 \text{ pA} ; V_b = 1.5 \text{ V} ; 19.5 \text{nm} \times 19.5 \text{nm}$). e) At 2.0 V, lock-in maps of the new species show a strong LDOS in the cavity of the monomers ($I_t = 200 \text{ pA} ; V_b = 2 \text{ V} ; 19.5 \text{nm} \times 19.5 \text{nm}$, Lock-in Maps Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 13 ms).
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To inspect the different orbital distribution in the real space, lock-in maps were acquired at three targeted voltages where STS spectra showed significant features. Figure 5.16 b displays the LDOS at 1.0 V, where as expected by the information extracted from the blue spectra, the brightest features are the thiadiazole moieties closely interacting with the dysprosium atom, in clear contrast with the opposite one. At 1.5 V (see Figure 5.16 c), a bright protrusion can be observed in the cavity of the heteromacrocycle, while the pyrrole moiety bonded to the rare-earth metal is clearly different than the other two pyrroles, which look dimer. At 2.0 V, the main observed feature corresponds to the lanthanide ion, as its intensity (red spectra) surpasses any other fingerprint (see Figure 5.16 d). As mentioned before, the HOMO could not be accessed with STS or lock-in maps. Tentatively, these molecular orbitals are assigned to LUMO, LUMO+1 and LUMO+2 respectively. Finally, a medium-range STM image is presented to demonstrate the predominance of the metallaion in Figure 5.16 e. Herein, only two species remain intact after annealing the sample at 373 K, which can be better discerned in the lock-in maps recorded at the voltages of the LUMO+1 and LUMO+2 (see Figures 5.16 g and h).

Figure 5.17: Simulated Off-Centered Metallation of HTAP by Dysprosium on Au(111). STM simulated image of a Dy-HTAP representing a constant current scan at the LUMO bias voltage of the molecule. In the left monomer a model of a Dy off-centered metallated HTAP is superimposed.
Finally, in order to investigate the final configuration of the Dy-HTAP species as well as the steps that lead to the metalation reaction, DFT calculations were performed. The first hypothesis is that dysprosium is interacting with one single pyrrole unit, thus leaving intact the other two pyrrole moieties with their respective inner protons. Figure 5.17 shows the DFT simulation of a STM image recorded at constant current for such configuration, i.e. Dy-HTAP(-1H), at the voltage correspondent to the LUMO orbital. The simulation agrees well with the experimental data, highlighting that the closely interacting thiadiazole groups have a higher apparent height.

Figure 5.18: DFT-Calculated Off-Centered Asymmetric Metalation Reaction of HTAP by Dysprosium on Au(111). DFT calculation of the reaction that leads to the asymmetric metalation of HTAP by dysprosium atoms presented with the top (upper panels) and side (lower panels) view. The initial S0 state represents the arrival of a Dy atom to the center of the cavity. The transition state TS1 leads to the desorption of one inner proton and the formation of the off-centered Dy-HTAP(-1H) species. Transition state 2 (TS2) results in the formation of Dy-HTAP(-2H) monomer, and subsequent TS3 leads to the formation of the Dy-HTAP(-3H), where all the inner hydrogen of the heteromacrocycle are desorbed. The energy profile depicted below indicates in eV the energy cost/gain for each step.
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In order to validate the hypothesis that this represents fairly the final state, the energy profile of the metalation reaction is presented in Figure 5.18. At the initial S0 state, the dysprosium atom arrives to the center of the cavity, subsequently removing one of the inner protons with an activation energy of 0.76 eV (transition state TS1). This process leads to S1, which is found to be exothermic by -0.27 eV, where the dysprosium ion is off-centered and only one hydrogen is removed. At this state, any further deprotonation process (S2 and S3) is found to be highly endothermic, with activation energies of 1.95 and 1.72 eV to desorb the second and third proton respectively. Therefore, any state beyond S1 is found to be highly improbable, corroborating the off-centered metalation with dysprosium proposed from the experimental evidences, where the other two diiminoisoindoline groups remain intact.
5.2 Fluorinated Porphyrin

![Chemical Structure of 2H-4FTPP species. Ball and Stick model of the 2H-4FTPP monomer with carbon, nitrogen, fluorine and hydrogen atoms colored in gray, blue, red and white respectively. The distance is calculated in the gas phase relaxed model between the terminal fluorine atoms within the AM1 semiempirical method framework.](image)

In order to further inspect the on-surface lanthanide metalation of monomers with a different macrocyclic size, the 5,10,15,20-Tetrakis(fluorophenyl)-porphyrin (from now on 2H-4FTPP) was selected, depicted in Figure 5.19. This halogenated tetrapyrrole derivative is equipped with four phenyl units at the positions 5,10,15 and 20, each one functionalized with a fluorine atom at its terminal position. The distance between the terminal fluorine atoms is 13.3 Å, calculated from the relaxed model using the AM1 semi-empirical method. The election of halogenated termini intends both to supply lateral coordination properties to form metal-organic coordination motifs and to provide mechanisms to couple upon thermal annealing in a Ullmann-like reaction scheme. Additionally, the fluorination of macrocycles or aromatic monomers ensures a preservation of their chemical structure while strongly changing its electronic properties. 
4FTPP on Au(111): Self-Assembly, Electronic Structure and Macrocycle Properties

Figure 5.20: Low and High Coverage Regimes of 2H-4FTPP on Au(111). a) Long-range STM image showing the preferential adsorption sites at low coverage regime ($I_t = 50 \text{ pA} ; V_b = +0.7 \text{ V} ; 100\text{nm} \times 100\text{nm}$). b) Together with the step-edges, the elbows of the herringbone reconstruction are preferentially decorated ($I_t = 50 \text{ pA} ; V_b = +0.7 \text{ V} ; 30\text{nm} \times 30\text{nm}$). c) Zoomed-in image showing the main features of the 2H-4FTPP: the central macrocycle and four lobes in the corners ($I_t = 1000 \text{ pA} ; V_b = +0.7 \text{ V} ; 10\text{nm} \times 10\text{nm}$). d) Large scale topography showing an extended close-packed island of 2H-4FTPP monomers ($I_t = 100 \text{ pA} ; V_b = +0.7 \text{ V} ; 100\text{nm} \times 100\text{nm}$). e) STM image showing the herringbone reconstruction through the supramolecular self-assembly ($I_t = 50 \text{ pA} ; V_b = +0.7 \text{ V} ; 30\text{nm} \times 30\text{nm}$). f) High-resolution topography with the model of a 2H-4FTPP tecton superimposed, highlighting the square unit cell described by vectors $\vec{a}$ and $\vec{b}$, enclosing the angle $\beta$ ($I_t = 500 \text{ pA} ; V_b = +0.7 \text{ V} ; 5\text{nm} \times 5\text{nm}$). All images recorded close to LHe temperature.
First, minute amounts of 2H-4FTPP were evaporated on the Au(111) monocrystal held at RT by heating the quartz crucible of the OMBE at its sublimation temperature (ca. 573 K), as depicted in Figures 5.20 a. For coverages lower than 0.1 monolayers, species adsorb mainly on the most reactive parts of the reconstructed surface, i.e. the step edges and the elbows of the herringbone. This surface template effect is highlighted in Figure 5.20 b, where all the elbow sites are decorated with 2H-4FTPP species as observed with other monomers. A closer zoomed-in image reveals the appearance of the species at +0.7 eV, indicating an approximate planar adsorption geometry, with the characteristic macrocycle imaged as a ring, surrounded by four bright lobes at the positions of the fluorinated benzenes, featuring an apparent height of 1.5 Å (at +0.7 V). This appearance does not differ significantly from tetraphenylporphyrin (2H-TPP) species, probably due to the fact that fluorine is the smallest non-hydrogen substituent, featuring an ionic radius of 1.47 Å. Increasing the coverage results in the formation of extended well-ordered close-packed assemblies on the flat terraces of the substrate, as shown in the long-range topography in Figure 5.20 d. This finding can be better observed in Figure 5.20 e, where the reconstructed surface geometry is perfectly visible suggesting that the monomers are physisorbed. The supramolecular self-assembly can be described by a rectangular unit cell with vectors $\vec{a}$ and $\vec{b}$, with experimental values of $|\vec{a}| = (14.4 \pm 0.5)$ Å and $|\vec{b}| = (14.0 \pm 0.5)$ Å, enclosing an angle $\beta = (92 \pm 1)^\circ$. One of the unit vectors of the lattice is aligned with one of the basis vectors of the underlying single crystal, as highlighted by the white star.
Figure 5.21: *Electronic Structure of 2H-4FTPP Species on Au(111).*

a) STM topography and STS spectra recorded on the pristine Au(111) surface (black) and on a 2H-4FTPP (red) monomer, showing two strong resonances at -0.9 and 1.6 V, identified as the HOMO and LUMO orbitals of the molecule respectively ($I_t = 250$ pA; $V_b = -0.88$ V; $5.4$nm × $8.8$nm, STS Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 36 ms, Sampling Energy= 3 meV/point). b) Topography imaged at the approximate HOMO voltage ($I_t = 100$ pA; $V_b = -0.8$ V; $12$nm × $12$nm). c) Lock-in map recorded simultaneously exhibiting the HOMO orbital with a "bowtie" shape. d) STM image at the LUMO bias voltage ($I_t = 250$ pA; $V_b = 1.6$ V; $12$nm × $12$nm). e) Lock-in map of the LUMO orbital showing a four-lobed geometry (Lock-in Maps Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 11 ms). All images and spectra recorded close to LHe temperature.
After that, the electronic structure of the adsorbed 2H-4FTPP monomers is studied by means of STS. Figure 5.21 shows the edge of a supramolecular island recorded at negative bias voltage, with the corresponding spectra acquired on the pristine Au(111) surface and on top of a molecule, depicted with black and red crosses respectively. The spectra observed in the left panel show the surface state of the gold single crystal at -0.5 V, and the 2H-4FTPP exhibiting two clear resonances at 1.6 and -0.9 V. These peaks, in analogy with other tetrapyrrole derivatives, are associated unambiguously to the HOMO and LUMO orbitals of the species, resulting in a gap of ca. 2.5 V, in agreement with non fluorinated species on Au(111). The gap of 2H-TPP in decoupled surfaces such as graphene/Si(0001) or calculated by photoemission experiments in multilayer samples is estimated to be 2.9 eV. In order to visualize the LDOS of these orbitals in the real space, constant current lock-in maps were acquired simultaneously with topographic images at the targeted bias voltages. This is displayed in Figures 5.21b to e. At the HOMO voltage (-0.9 V), the spatial distribution of the orbital has a "bowtie" shape, while at the LUMO energy position (1.6 V), the orbital features a four-lobed flower geometry. It is important to remark that, as observed in Figures 5.21c and e, the intensity of the different self-assembled monomers varies significantly, attributed to their distinct adsorption sites on the herringbone reconstruction and conformations derived from the rotational degree of freedom of the fluorobenzenes and the position of the inner protons of the macrocycle (tautomerism).

In analogy to other porphyrinoid derivatives, tautomerization was investigated in this system. Porphyrin tautomerism is a well-known and extensively studied phenomena, consisting in the migration of the hydrogen atoms of its macrocycle to the free positions of the unhydrogenated pyroles. On surfaces, in the tetrapyrrrole moieties only two states are permitted, associated with a corresponding change in the saddle-shape conformation (see chemical sketches in Figure 5.22).
Figure 5.22: Spatially Controlled and Uncontrolled Tautomerization of 2H-4FTPP Species on Au(111). a) STM image showing minority tautomer (1) surrounded by major tautomers (2) ($I_t = 35$ pA ; $V_b = +0.4$ V ; 4.6nm × 4.6nm). b) $I_t$ vs $t$ spectra showing the telegraphic signal corresponding to the switch between the two tautomeric states when the tip is located on the center of the encircled monomer in a. c) Topographic image demonstrating that the targeted species has changed to tautomer (2) ($I_t = 35$ pA ; $V_b = +0.4$ V ; 4.6nm × 4.6nm). d) Zoomed-in image with tautomers at different states, better observed with high contrast ($I_t = 35$ pA ; $V_b = +0.4$ V ; 4.6nm × 4.6nm). e) Scanning at perturbative conditions shows spikes in the STM images as monomers are changing while the image is being recorded ($I_t = 35$ pA ; $V_b = +1.8$ V ; 4.6nm × 4.6nm). f) Scanning the same area after the perturbation reveals that some tectons changed from (1) to (2) or vice versa ($I_t = 35$ pA ; $V_b = +0.4$ V ; 4.6nm × 4.6nm). All images recorded close to LHe temperature.
The tautomerization experiment can be performed with two different approaches: (i) with a controlled protocol applied locally to targeted species or (ii) scanning at perturbative conditions a certain area affecting indistinctly all the monomers in the region and surroundings. The first approach is depicted in Figures 5.22 a-c. A selected area is scanned at a bias voltage that permits the identification of both tautomers, tagged as (1) and (2). Figure 5.22 a shows a tautomer (1) surrounded by tautomers in the other state. Positioning the tip on top of the center of the molecule, encircled in black, and monitoring the tunneling current versus time results in the spectra presented in Figure 5.22 b, where two conduction channels can be observed corresponding to the two tautomers. At \( t = 0 \), the tautomer (1) shows a conductivity of ca. 2.9 nA. The spectra exhibits a telegraphic noise during the 52 seconds that the signal is monitored, where the tunneling current switches between two values (2.9 and 2.67 nA) back and forth. When \( t = 52 \) s the monomer shows a tunneling current ca. 2.67 nA, which corresponds to state (2). Scanning with unperturbative conditions the same area after performing the vertical manipulation confirms that the target monomer has changed to tautomer (2).

The tautomerization can be observed also with a non-controlled approach, displayed in Figures 5.22 d-f. Once a selected area has been scanned with unperturbative conditions and the different tautomers identified, the scanning parameters are changed to perturbative conditions (\( V = 1.8 \) V). Figure 5.22 e clearly shows lines around the center of the macrocycles, signaling that tautomerism is occurring while scanning. This effect is more evident when the bias voltage is increased. Scanning again the same area with normal conditions reveals that two monomers are in a different tautomeric state, highlighted with black circles. Thus, 2H-4F TPP shows identical macrocyclic properties as other porphyrin derivatives, as expected as the molecular backbone remains unmodified. Despite this phenomena has been previously reported in a large variety of tetrapyrrole moieties, it is of high relevance for the subsequent discussion, as it will be used as a fingerprint to identify intact 2H-4F TPP species.
5.2 Fluorinated Porphyrin

Figure 5.23: Deprotonation of 2H-4FTPP on Au(111). a-b) STM images showing the target monomer, pointed with a white arrow, where a 2.1 V voltage pulse is applied to transform a 2H-4FTPP species into a 1H-4FTPP monomer ($I_\text{t} = 100$ pA; $V_\text{b} = 0.4$ V; 7nm × 7nm). c) Same area imaged at negative bias, where a subsequent 2.4 V pulse is applied in the same tecton. d) The applied pulse resulted in the full deprotonation (0H-4FTPP) of the original monomer and the collateral transformation into a 1H-4FTPP of the adjacent species. e) $I_\text{t}$ vs $t$ spectra applied over 40 s displaying a telegraphic signal corresponding to different positions of the inner proton. f) Scanning the area again demonstrates that the inner hydrogen has been displaced to the opposite pyrrole moiety (c-f: $I_\text{t} = 100$ pA; $V_\text{b} = -0.75$ V; 7nm × 7nm).

Deprotonation experiments were also investigated by means of vertical manipulation on supramolecular islands. Applying on top of a monomer voltage pulses of 2.1 V, or ramping the voltage above this threshold, results in the transformation of the molecular species as a result of the loss of a
proton of its macrocycle, affording the formation of 1H-4FTPP (see Figure 5.23 a and b). To remove the remaining hydrogen the voltage threshold increases to 2.4 V (see Figure 5.23 c), resulting in the irreversible transformation to 0H-4FTPP displayed in Figure 5.23 d. As the tip was positioned at the flank of the monomer, a collateral transformation of the adjacent monomer into 1H-4FTPP species could not be avoided. In fact, one can perform tautomerism experiments on the 1H-4FTPP species, with an identical procedure as the one described for 2H-4FTPP species (Figure 5.22). Setting a -2.0 V bias voltage and monitoring the tunneling current vs. time results in a telegraphic-like signal between two states, as displayed in Figure 5.23 e. At \( t = 0 \) the signal starts steady at ca. 4.85 nA, and through the 40 seconds clearly changes between two defined states. At the end of the spectra \( (t = 40 \text{ s}) \) the tunneling current is ca. 3.69 nA, which corresponds to the state where the inner proton is bonded to the opposite pyrrole unit. This is corroborated by scanning the same area under normal conditions, where the charge accumulation can be observed in the opposite position. It is important to notice that the four-level conductance switch observed previously on free-base tetraphenyl-porphyrins is not observed in our experiment\(^\text{24}\). We attribute the observation of a two-level conductance switch in this case to the fact that one of the tautomers is clearly favored due to the adsorption and conformational geometry upon the formation of supramolecular arrays, strongly hindering the probability of finding the inner hydrogen at the other positions. Even so, the deprotonation and switching of the macrocyclic protons serves as a further fingerprint to identify these species, important to discern further changes induced upon metalation with lanthanide elements.
5.2 Fluorinated Porphyrin

Metalation by Dysprosium

Figure 5.24: On-Surface Synthesis of Dy-2H-4FTPP Species on Au(111). 

a) Long-range STM topograph showing the transformation of the supramolecular self-assembly of 2H-4FTPP Species on Au(111) upon deposition of minute amounts of dysprosium ($I_t = 250$ pA; $V_b = -0.75$ V; $130\text{nm} \times 130\text{nm}$). 
b) As observed in a, at negative bias a new species clearly appears brighter, corresponding to the Dy-2H-4FTPP ($I_t = 250$ pA; $V_b = -0.75$ V; $25\text{nm} \times 25\text{nm}$). 
c) Zoomed-in region showing nineteen in situ synthesized Dy-2H-4FTPP species ($I_t = 100$ pA; $V_b = -0.7$ V; $10\text{nm} \times 10\text{nm}$). 
d) Atomistic model of the Dy-2H-4FTPP species with the dysprosium atom colored in blue.
In order to metalate the tetapyrrole derivatives with rare-earth ions, minute amounts of dysprosium were evaporated on top of a submonolayer 2H-4FTPP sample on Au(111) held at room temperature (Figure 5.24a). Large scale STM topography indicates that a rearrangement of the islands, now appearing smaller and with better defined edges, has taken place upon dysprosium exposure. This experimental finding suggests that some molecular desorption and a hindering of the diffusion of the species has been produced during the sublimation of dysprosium. A closer image, displayed in Figure 5.24b, reveals that a new species appears when scanning at negative bias voltage, imaged as two parallel lobes, with a clear brighter contrast when compared to the rest of the supramolecular island. This molecular species is identified as an intact 2H-4FTPP monomer weakly bonded to a dysprosium atom, from now on Dy-2H-4FTPP. As lanthanide ions do not fit completely inside the macrocycle of tetapyrrole derivatives due to their large ionic radius, it is important to discuss the exact geometry of this configuration. The fact that the metallic center is not observed at any bias voltage, and that the whole monomer exhibits a higher apparent height compared to intact 2H-4FTPP species (Imaged at -0.75 V: 2.4 vs. 1.5 Å) supporting the idea that the rare-earth ion lies underneath the monomer. Our hypothesis are corroborated by similar studies suggesting adsorption of 2H-TPP species on top of gold or cerium adatom. Furthermore, as we will report in the next sub-section, a Kondo resonance is observed for Dy-2H-4FTPP and the electronic density of states of such resonance is distributed through the molecule, being absent on the lanthanide center, which refutes the the hypothesis of the metal ion adsorbed on top on the organic entity. This \textit{in situ} synthesized Dy-2H-4FTPP monomer can be better observed in the zoomed-in STM image depicted in Figure 5.24c, whose atomistic model is displayed in Figure 5.24d.
5.2 Fluorinated Porphyrin

Figure 5.25: In Situ Metalation of 2H-4FTPP Species on Au(111), Affording Three Different Porphyrinato Complexes. a) Zoomed-in topograph showing the Dy-2H-4FTPP (black), Dy-1H-4FTPP (red) and Dy-0H-4FTPP (blue) new species at negative bias ($I_t = 100 \, pA$ ; $V_b = -0.7 \, V$ ; 10nm $\times$ 10nm). b) Same area imaged at positive bias displaying the appearance of the new species ($I_t = 100 \, pA$ ; $V_b = 1 \, V$ ; 10nm $\times$ 10nm). c) Atomistic model of the different Dy-complexed monomers.

While inspecting the sample at different bias voltages, two additional species could be distinguished: the intermediate Dy-1H-4FTPP (encircled in red) and the fully metallated Dy-4FTPP (encircled in blue). Although at this bias (-0.7 V) the differentiation is complicated (see Figure 5.25 a), Dy-1H-4FTPP shows a brighter macrocycle without a clear depression in its center, and the fully metallated species Dy-0H-4FTPP are almost identical to intact molecules, with a slightly brighter appearance. Of course, these monomers coexist with the previously observed 2H-4FTPP. Imaging at positive bias voltages ($V > 0.5 \, V$) allows a clearer identification of the distinct species (see Figure 5.25 b). At this voltage, Dy-2H-4FTPP shows a "donut"-like shape and Dy-1H-4FTPP appear as a "C" or a "O" depending on which macrocyclic hydrogen is desorbed.

Regarding fully metallated species, it is important to remark that their appearance is similar to intact 2H-4FTPP molecules. In order to distin-
guish them two approaches are used: (i) spectroscopy and lock-in maps (see Figure 5.29 below) and (ii) vertical manipulation, in which the absence of telegraphic tunneling current versus time signal, i.e. tautomerism, and of deprotonation reveals that Dy-0H-4FTPP can not be transformed into any other species. The three dysprosium-derived species are depicted in Figure 5.25c with the respective atomistic models.

Figure 5.26: Dy-1H-4FTPP Species on Au(111). a) STM image showing the asymmetric appearance of twelve monomers in the intermediate state Dy-1H-4FTPP due to the different location of the inner H atom ($I_t = 100 \, pA ; V_b = +0.25 \, V ; 6.6 \, nm \times 6.6 \, nm$). b) Atomistic models of the two tautomers highlighting the presence of an inner hydrogen (orange circle) in the left or in the right pyrrole of the macrocycle, with green arrows pointing both examples. c) At higher positive voltages is more evident the mirrored shapes of both tautomers ($I_t = 100 \, pA ; V_b = 0.7 \, V ; 6.6 \, nm \times 6.6 \, nm$).

Figure 5.26a highlights the asymmetry observed in the intermediate Dy-1H-4FTPP species, showing the appearance of these tautomers at +0.25 V for a better differentiation. In this configuration, one of the inner protons of the macrocycle has been desorbed and the associated pyrrole is coordinated to the dysprosium atom. Depending on which pyrrole is involved in the coordination (see models in Figure 5.26b), Dy-1H-4FTPP species are imaged as a "C" or a "Ω" at +0.7 V (see Figure 5.26c).
5.2 Fluorinated Porphyrin

Figure 5.27: Tip-induced Irreversible Transformation of Dysprosium Porphyrinato Complexes. a-b) Sequence showing that the dysprosium related species can be irreversibly transformed from Dy-2H-4FTPP into Dy-1H-4FTPP and subsequently into the final Dy-0H-4FTPP configuration, as a result of the desorption of one inner proton (or two) and the subsequent bonding to the lanthanide ion underneath (All Images: $I_t = 150$ pA; $V_b = +1$ V; 3.9nm × 3.9nm).

Importantly, all the described species coexist if dysprosium is deposited on a substrate held at room temperature. Upon annealing at 423 K, only intermediate Dy-1H-4FTPP and fully metallated Dy-0H-4FTPP are observed, while after annealing to 500 K only Dy-0H-4FTPP species are observed. Hence, the states where one or both pyrrole moieties are not coordinated with the lanthanide atom are identified as metastable state, i.e. less energetically favorable configurations. This is also evidenced by means of vertical manipulation, as highlighted in Figure 5.27. Dy-2H-4FTPP species can be irreversible transformed into Dy-1H-4FTPP monomers by applying a 1.4 V pulse or ramping the voltage beyond this threshold. Depending on the targeted flank of the manipulation, one can control if the resulting Dy-1H-4FTPP species display a so-called "C" or "Ω" shape. Again, Dy-1H-4FTPP species can be transformed to fully metallated Dy-0H-4FTPP monomers by positioning the tip on top of the remaining macrocyclic hydrogen and applying a 1.6 V pulse. The final result is a porphyrin derivative without central protons, with the correspondent pyrrole units coordinatively bonded to the lanthanide core underneath.
Figure 5.28: **Electronic Structure of Dysprosium-Derived 4FTPP Species on Au(111).**

a) High-resolution STM images of the three dysprosium species (All Images: $I_t = 50\; pA$ ; $V_b = 1\; V$ ; $2\; \text{nm} \times 2\; \text{nm}$).

b) Ball and stick model of the three units, obtained by removing one macrocyclic hydrogen each time.

c) STS spectra of Dy-0H-4FTPP (blue), Dy-1H-4FTPP (red) and Dy-2H-4FTPP (black) (STS Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point = 36 ms, Sampling Energy = 3.5 meV/point).
STS spectra were recorded on the dysprosium derivatives in order to determine their electronic structure, (see Figure 5.28). The original Dy-2H-4FTPP species show some features between -0.5 and 0.1 V, radically differing from the other tectons, which could implicate a charge transfer from the Dy atom to the monomer. Still, once the voltage reaches $V_b = 1.4$ V, the spectra abruptly decreases indicating the transformation to the intermediate Dy-1H-4FTPP monomer. Such species features a resonance around 0.8 V, with the characteristic shoulder of the tetrapyrrole entities at 1.2 V, and an abrupt increase once the 1.6 V threshold is trespassed signaling the final transformation to the fully metallated Dy-0H-4FTPP monomer. This latter species has two strong resonances at -1.0 and 1.6 V, assigned tentatively to the HOMO and LUMO orbitals of the molecule respectively, resulting in an electronic gap of 2.6 V, slightly larger than before. Even though Dy-0H-4FTPP can be identified by its lack of tautomerism and the impossibility to be deprotonated, it is clear that both the shape and the energies of the orbitals are similar to the ones displayed for intact 2H-4FTPP species, which is surprising taking into account the chemical change experienced by these monomers upon chemical bonding with a lanthanide ion.

In order to unambiguously differentiate between both monomers (2H-4FTPP vs Dy-0H-4FTPP species), which can be complicated on supramolecular assemblies, two species (one metallated and one intact) were laterally displaced from the supramolecular island edge to study their electronic structure and bias dependence in an isolated environment. Figure 5.29a shows at 0.4 V the two monomers, a 2H-4FTPP (top) and a Dy-0H-4FTPP (bottom) species, revealing a slightly brighter contrast for the metallated monomer. The comparison of the spectra depicted in Figure 5.29 evidences that the HOMO-LUMO gap is slightly larger for the metallated tetrapyrrole. Additionally, lock-in maps and topographs acquired at the HOMO and LUMO energy positions also show appreciable differences, more evident at the unoccupied region. Here, at 1.5 V, both the STM image and the lock-in map exhibit spikes only on the intact species as a result of the inherent tautomerism taking place while scanning, a phenomenon that is
not observed in the metallated monomer due to the lack of inner protons.

Figure 5.29: Topographic and Electronic Comparison Between 2H-4FTPP and Dy-0H-4FTPP Species on Au(111). a) STM image of two laterally displaced monomers by lateral manipulation to study their properties isolated ($I_t = 180 \text{ pA} ; V_b = 0.4 \text{ V} ; 4.6\text{nm} \times 7\text{nm}$). b) STS spectra of Dy-0H-4FTPP (blue) and 2H-4FTPP (black), highlighting a larger HOMO-LUMO gap for the metallated species (STS Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 36 ms, Sampling Energy= 3.5 meV/point). c-d) Lock-in maps and topographies recorded at the approximate energy positions of the molecular orbitals (c: $I_t = 180 \text{ pA} ; V_b = -0.8 \text{ V} ; 4.6\text{nm} \times 7\text{nm}$, d: $I_t = 180 \text{ pA} ; V_b = 1.5 \text{ V} ; 4.6\text{nm} \times 7\text{nm}$).
Kondo Signal in Dy-2H-4FTPP Species

The presence of a magnetic impurity in a sea of conduction electrons results in the formation at low temperatures of a many-body ground state in which the electrons from the substrate screen the magnetic impurity\textsuperscript{204}. Experimentally, the scattering from a single magnetic impurity by spin flip results in the appearance of a sharp resonance, that can be detected by STS close to the Fermi level. Despite the Kondo effect had been known for almost a century, it was first experimentally observed in single atoms using STS in 1998 simultaneously by Crommie \textit{et al.}\textsuperscript{205} and Schneider \textit{et al.}\textsuperscript{206}. Since then, many STM studies have been focused on investigating this effect in a large variety of systems, from single atoms to metal-organic mixtures\textsuperscript{207-211}. Within the Anderson impurity model, in the low temperature Fermi liquid regime\textsuperscript{212}, the Kondo resonance has a Half Width at Half Maximum (HWHM, commonly denoted by $\Gamma$) with a temperature dependence given by:

$$\Gamma(T) = \frac{1}{2} \cdot \sqrt{(\alpha \cdot k_B \cdot T)^2 + (2 \cdot k_B \cdot T_K)^2}$$  \hspace{1cm} (5.1)

where $\alpha = 2\pi$, $k_B$ the Boltzmann constant and $T_K$ the Kondo temperature.

The spectral shape of the tunneling conductance $\frac{dI}{dV}$ is well described by the function: $fano(\epsilon) = \frac{(q+\epsilon)^2}{1+(\epsilon)^2}$, with $\epsilon = \frac{eV-w_0}{\Gamma}$ being the reduced energy, where $eV$ is the applied voltage and $w_0$ is the energy shift of the resonance from the Fermi level. This is known as the Fano function\textsuperscript{213}, which describes the interference between a discrete state (a resonance state) and a continuum state (background state). In the STM scenario, where the tip is located on top of an adsorbate, the electrons can tunnel through two different channels: (\textit{i}) from the tip to the adsorbate followed by charge transfer to the substrate or (\textit{ii}) directly from the tip to the substrate\textsuperscript{214}. If the adsorbate has a spin, the indirect tunneling channel causes the Kondo
resonance, while the two paths cause the Fano resonance\textsuperscript{215}. In the expression, \( q \) corresponds to the form factor, which gives the ratio between the indirect (through the magnetic impurity) and direct tunneling processes at the resonance. In this simplified model in which \( q \propto \frac{t_{\text{indir}}}{t_{\text{dir}}} \), \( q \) values close to zero describe strong coupled systems, as tunneling electrons easily find a direct channel to tunnel directly to the sample. On the other hand, large \( q \) values reflect that the indirect channel dominates, meaning that electrons mainly tunnel from the tip to the impurity and then to the sample, implying weak interactions between the magnetic impurity and the substrate. Regarding the line-shape of the Kondo resonance, when the direct tunnel channel dominates the \( \frac{dI}{dV} \) spectrum features a dip-like shape, while in weak coupled systems peak-like spectra are observed.

The experimentally recorded spectra are broadened by two additional factors: the modulated voltage and the temperature of the system. Therefore, in order to fit the experimental spectra the Fano function has to be convoluted first with the derivative of the Fermi function\textsuperscript{216}, responsible for the intrinsic temperature broadening, and the resulting expression convoluted with the function \( y(x) = \frac{8}{\pi(V_{\text{pp}})^2} \cdot \sqrt{(\frac{V_{\text{pp}}}{2})^2 - x^2} \), which describes the intrinsic broadening by the voltage modulation provided by the lock-in amplifier\textsuperscript{217}.\)
With the aim to investigate the magnetic fingerprints of the distinct species, scanning tunneling spectroscopy was performed at low bias voltage. In the case of Dy-2H-4FTPP species, a strong and narrow resonance was observed around the Fermi level, as showed in Figure 5.30. The experimental spectrum (black curve) is fitted with the function described above (red dots), giving a value for the parameters of: $\Gamma = 10.3$ meV, $g=30$, and $w_0=0$ meV (see Figure 5.30 a). The large value of $q$ indicates a weak coupling with the substrate, as observed for other adsorbed monomers with magnetic moments\[207\]. Importantly, this feature was not detected for any of the other species, e.g. the blue curve acquired on top of an intermediate Dy-1H-4FTPP species (blue cross) shows no features around the Fermi level.
level. This is better illustrated in Figures 5.30 b-d, which correspond to simultaneously acquired STM images (left panels) and lock-in maps (right panels), highlighting that the only species featuring a Kondo signal are the Dy-2H-4FTPP derivatives, showing a molecular Kondo distribution due to the underneath dysprosium atom.

**Figure 5.31:** Spatial Distribution of the Kondo Resonance in the Dy-2H-4FTPP Species on Au(111). A 3D representation of a STM topograph (bottom) superimposed by slices of constant energy LDOS maps. Cold and warm colors represent low and high $\text{dI/dV}$ intensity respectively ($I_t = 300 \text{ pA} ; 1.9 \text{nm} \times 1.9 \text{nm}$, CITS Parameters: Modulation $= 2 \text{ mV}$, Frequency $= 773 \text{ Hz}$, Integration time/point $= 100 \text{ ms}$, Sampling Energy $= 0.5 \text{ meV/point}$, 17x17 pixels).

To better display the distribution of the Kondo resonance within the molecular orbital, CITS experiments were performed on single Dy-2H-4FTPP
species, as displayed in Figure 5.31. The lower image corresponds to a three-dimensional STM topograph (in perspective) of a single Dy-2H-4FTPP monomer. The successively stacked slices of constant energy LDOS maps are extracted from a CITS map at selected energies. The color code in the $\mathrm{dI/dV}$ spectra at the target energy for each pixel displays cold and warm colors for low and high intensity respectively. From the -10 mV LDOS slice, one can observe that the intensity of the Kondo resonance is spatially distributed over the four lobes of the molecule. This effect becomes clearer for the -3 and 9 mV LDOS slices. At 19 mV the Kondo resonance starts to fade out. Importantly, the Kondo signal can be turned off by means of vertical manipulation transforming Dy-2H-4FTPP species into Dy-1H-4FTPP or Dy-0H-4FTPP, demonstrating the existence of a magnetic Kondo switch in the system of relevance for future transport devices based on molecular electronics.

Finally, to corroborate the Kondo nature of the observed resonance close to the Fermi level, and to extract a value for the Kondo temperature $T_K$ of the Dy-2H-4FTPP species, the width $\Gamma$ of the resonance was tracked as a function of the temperature. This experiment was carried out by heating an internal diode located in the STM head, which allowed to vary the temperature between 4 and 100 K. Above this point, drift was too critical to perform spectroscopic experiments within a reasonable timescale. Figure 5.32 a displays six spectra acquired at distinct temperatures evidencing a clear broadening as the measurement temperature increases. The dependence of the width $\Gamma$ of the Kondo resonances with the temperature $T$ is described by the equation 5.1. In order to estimate a value for the Kondo temperature $T_K$, a series of consecutive measurements were acquired by increasing the scanning head temperature over 13 points (see Figure 5.32 b). Hereby, the width of the spectra are calculated by fitting the curves with the same function described above, and the set of $\Gamma$ vs. $T$ data is subsequently fitted with the function 5.1 giving a value $T_K = 120$ K. Importantly, $\alpha$, responsible for the slope in the linear regime, was left as a free parameter as derived from similar studies and the fitted value $\alpha = 5.4$ is very close to the value $2\pi$ in the Fermi liquid model. Since $T_K$ is relatively
large, one can actually give a good approximation of this magnitude when evaluating the Kondo resonance at 4.4 K by using the $T << T_K$ regime (two order of magnitude) relation at which

$$T_K \simeq \frac{\Gamma}{k_B} \simeq 119 \text{ K},$$

in perfect agreement with the value extracted from the temperature set.

![Figure 5.32: Kondo HWHM Temperature Dependence of Dy-2H-4FTPP on Au(111).](image)

a) Six normalized Kondo spectra recorded at different temperatures (4.4, 10, 20, 30.6, 49.9, and 88.6 K) vertically offset to highlight the thermal broadening of the Kondo resonance (STS Parameters: Modulation= 2 mV, Frequency= 773 Hz, Sampling Energy= 0.5 meV/point). b) Using equation 5.1 to fit the experimental points shows a $T_K = 120 \text{ K}$, leaving $\alpha$ as a fitting parameter with $\alpha = 5.4$.

To unambiguously attribute this behavior to the Kondo effect, experiments with large magnetic fields should be performed to see that the resonance vanishes at a certain point. However, these results show a strong indication that the resonance around the Fermi level can be described as a Kondo phenomenon, as thermal broadening alone cannot describe the evolution of the spectra with temperature.
5.3 Conclusions

In summary, two molecular systems involving macrocyclic species of distinct macrocycle size have been studied on coinage metals.

First, a seminal work about expanded porphyrinoids on surfaces has been reported, by studying an archetype of such species (HTAP) on Au(111) and Ag(111). The focus was set on three main aspects: 

(i) the long-range orientational self-assembly on Au(111) operative at different coverages; 
(ii) the development of a protocol to in situ remove the inner protons of the expanded macrocycle in a well-controlled local manner, suitable for single-molecule writing; and 
(iii) the capability of these large cavities to host off-centered lanthanide metals, in this case dysprosium ions. The introduction of a new class of porphyrinoid derivative with a large cavity able to complexate large cations or more than one metal, offers a new tool for on-surface molecular chemistry and electronics involving macrocycles. Additionally, the locally controlled deprotonation driven by tunneling electrons opens up new protocols for long term information storage. Finally the off-centered complexation of the macrocycle with rare-earths could be of great potential for sensing and catalysis, as well as to tune the luminescent properties of lanthanide elements when grown on insulating layers such as MgO or NaCl.

Second, the metalation capabilities by dysprosium of the well-known tetraphenyl porphyrin family was inspected on Au(111). Evaporation of 2H-4FTPP, a fluorinated tetraphenyl porphyrin, resulted in the formation of close-packed assemblies of intact monomers, whereby tautomerism and tip-induced deprotonation was observed. The exposure of submonolayer 2H-4FTPP sample to dysprosium afforded the formation of three novel species: Dy-2H-4FTPP species, the intermediate Dy-1H-4FTPP monomer, and the fully metalated Dy-0H-4FTPP species. By tip-induced voltage pulses, the species could be irreversible transformed from Dy-2H-4FTPP to Dy-1H-4FTPP and from Dy-1H-4FTPP to Dy-0H-4FTPP. Remarkably, a strong Kondo resonance was found for the Dy-2H-4FTPP metastable species. In order to accurately attribute this phenomenon to the Kondo effect, a thor-
ough thermal dependence of the width of the peak was carried out from 4.5 to 100 K, revealing an approximate Kondo temperature $T_K$ of 120 K. Such Kondo resonance was suppressed for the Dy-1H-4FTPP or the Dy-0H-4FTPP species, thus revealing a novel approach to nanofabricate tunable Kondo supramolecular systems, which could be of great relevance for future molecular electronics, whereby molecules exhibiting Kondo would exhibit an increased molecular conductivity.
On-Surface Chemical Transformations of Aryl Halides: from Dy-directed Organometallic Complexes to Graphene Nanoribbons

This chapter describes the on-surface transformations of aryl halides on surfaces in the absence and in the presence of dysprosium adatoms.

Upon sequential surface annealing, dibromo-terphenyl species (an archetype of aryl bromides) on Ag(111) are able to undergo debromination, formation of organo-metallic supramolecular chains, creation of covalent wires via Ullmann coupling reaction, and finally promotion of 3p armchair Graphene Nanoribbons (aGNR) through dehydrogenation and C-C lateral
coupling between chains. Taking into account the relevance of GNR for molecular electronics, a detour spectroscopic analysis of such structures is presented, revealing their behavior as perfect and tunable quantum boxes.

This scenario is dramatically changed in the presence of dysprosium adatoms, whose catalytic role gives rise to the formation of C-Dy-C organometallic supramolecular complexes and after gentle annealing inhibits the Ullmann coupling reaction, limiting the reaction products to covalent dimers and trimers. This part will be firstly presented, and in the last section the electronic structure of 3p-aGNR will be discussed.

6.1 Dy Catalyzed Debromination Of Aryl Halides on Ag(111)

The Ullman reaction has been extensively studied on surfaces by means of scanning tunneling microscopy. In order to engineer well-defined covalent networks, the election of halogenated termini, mainly bromine and iodine or a combination of both, demonstrated to be a versatile and promising route. The so called Ullmann coupling has been tested on different metallic substrates and with a large variety of monomers, achieving nanoarchitectures with different dimensionality by ab-initio designing the targeted precursors. On certain metallic surfaces the Ullmann coupling proceeds through stable organometallic intermediates, which require the presence of metal adatoms on the surface to subsequently establish the C-C coupling. To date, only transition metals, either provided by the surface or evaporated in-situ, have been investigated to this end. In this chapter, the role of lanthanide atoms in the process of dehalogenation, formation of lanthanide-directed organo-metallic complexes, and evolution to oligomeric covalent compounds is presented. First, the different reaction steps of the Ullman coupling of the linear 4,4'-dibromo-p-terphenyl monomer (see Figure 6.1), termed DBTP, are studied on the flat Ag(111). Then, the deposition of dysprosium atoms on samples containing intact DBTP species is studied, revealing that debromination is spontaneous in
the presence of lanthanide ions resulting in Dy-directed organo-metallic oligomers. The evolution with temperature of this system exhibits the inhibition of the classical Ullman coupling-like reaction scheme. Nevertheless, short covalent polyphenyl units, such as dimers and trimers, are formed at a significantly lower temperature. Complementary DFT calculations indicate a more exothermic process in the case of the debromination triggered by lanthanide atoms, compared with the pristine silver surface. This result highlights the efficiency of dysprosium to dehalogenate and to inhibit uncontrolled C-C couplings, hence serving as a new tool to design polymers with atomically controlled length, while simultaneously reveals the capability of dysprosium to direct organo-metallic intermediates on surfaces.

Ullman Coupling of Dibromoterphenyl Species on Ag(111)

![Chemical Structure of DBTP Species](image)

**Figure 6.1:** Chemical Structure of DBTP Species. Ball and stick model of the relaxed geometry of the dibromoterphenyl (DBTP) monomer, with carbon, hydrogen and bromine colored in gray, white and red respectively, featuring an intramolecular distance in the gas phase between terminal bromine atoms of 15.1 Å.

In order to investigate the role of lanthanide elements in the chemical transformations of aryl halides on surfaces, i.e. dehalogenation and Ullmann coupling, DBTP species were sublimated by heating the crucible of the OMBE at 380 K and deposited on Ag(111). This monomer, depicted in Figure 6.1, contains three benzene rings and two bromine atoms in a linear fashion, with a calculated distance in the gas phase between the halogen termini of 15.1 Å.
Figure 6.2: Deposition of DBTP on Ag(111) at Room Temperature. a) STM topography highlighting the supramolecular phase $\alpha$ of intact self-assembled species ($I_t = 10\; pA$; $V_b = -1.0\; V$; $19\; nm \times 19\; nm$). b) Atomistic model depicting the lattice with alternating three- and four-fold node motifs, stabilized by C-Br····Br interactions. c) Minority phase $\beta$ showing organometallic C-Ag-C linear chains with fully and partially debrominated species in between the chain and the termini respectively ($I_t = 50\; pA$; $V_b = 1.0\; V$; $7.9\; nm \times 7.9\; nm$). d) Atomistic model of a one-dimensional organometallic chain with four monomers.
After depositing a submonolayer coverage of these precursors on a clean Ag(111) substrate held at RT, two distinct phases were observed by STM, as highlighted in Figure 6.2. On one hand, the predominant phase is a supramolecular lattice built up by intact brominated species, featuring three- and fourfold bond motifs, previously observed on Au(111). The chiral node geometry is driven by Br···Br and Br···H interactions, with a projected distance of (2.8 ± 0.5) Å and (1.8 ± 0.5) Å respectively. As depicted by the black star, monomers are aligned with the high-symmetry directions of the underlying Ag(111) surface. Figure 6.2b highlights the two different nodes exhibited by intact DBTP supramolecular assemblies with a ball and stick model, with the main intermolecular interactions highlighted in blue and red dashed lines. On the other hand, the minority phase is based on linear organometallic supramolecules displayed in Figure 6.2c. A tentative model (Figure 6.2d) shows that the chains consist of partially dehalogenated species at the terminal positions of the chain, while the two central monomers have already lost both bromine atoms, forming C-Ag-C bonds. The projected distance of this bond, calculated from the ball and stick model, is (2.0 ± 0.5) Å, signaling that the energy barrier to undergo dehalogenation of this system is approximately room temperature. Step-wise controlled annealing of such samples results in the formation of different nanostructures (see Figure 6.3), which signal the formation of C-C couplings through an adatom-based Ullmann coupling reaction. Such process consists of three steps: (i) an initial state of intact monomers, (ii) an intermediate state based on organometallic architectures and (iii) a final state where the covalent C-C coupling occurred. The temperatures necessary to undergo each stage and their stability depend strongly on the specific substrate-monomer system. In this case, annealing at 340 K already dehalogenates all the monomers and extended one-dimensional organometallic chains are observed on the terraces, as depicted in Figure 6.3b. High-resolution STM imaging allows to discern terphenyl units as three-lobed protrusions, intercalated by Ag adatoms appearing as spherical lobes. In between the organometallic chains, pairs of dim protrusions are identified as bromine atoms, adsorbed parallel to the position of the debrominated molecules, thus indicating a preference for Br···H interaction rather than with Ag adatoms. The ge-
omentry of this intermediate state is highlighted in the inset of the image, where the model of dehalogenated monomers, Ag adatoms and Br atoms is superimposed.

![Diagram](image)

**Figure 6.3: Formation of Poly(p-phenylene) Wires by Stepwise Annealing of DBTP on Ag(111).** a) Reaction scheme showing the Ullman-like coupling of DBTP on Ag(111). After the debroration of intact species, an organometallic C-Ag-C intermediate state takes place. Subsequent annealing at 540 K leads to the formation of poly(p-phenylene) one-dimensional covalent architectures. b) Annealing at 340 K leads to fully debrorinated species forming organometallic intermediates \( (I_t = 100 \, pA \, ; \, V_b = 1.0 \, \text{V} \, ; \, 9.3nm \times 9.3nm; \, \text{inset:} \, 2nm \times 2nm) \). c) Increasing temperature at 440 K triggers the formation of dimeric, trimeric and larger linear covalent species (left: \( I_t = 950 \, pA \, ; \, V_b = -2.0 \, \text{V} \, ; \, 21.2nm \times 21.2nm/ \, \text{right:} \, I_t = 200 \, pA \, ; \, V_b = -0.5 \, \text{V} \, ; \, 12.5nm \times 12.5nm \) ). d) Final annealing step at 540 K leads to extended poly(p-phenylene) covalent wires. Bromine atoms are present within the different nanostructures through the distinct annealing stages \( (I_t = 200 \, pA \, ; \, V_b = -1.0 \, \text{V} \, ; \, 25nm \times 25nm; \, \text{inset:} \, 1.8nm \times 1.8nm) \).

In order to track the temperature-dependent Ullman coupling reaction, further annealing step at 440 K is applied to the samples, depicted in Figure 6.3 c. Similar one-dimensional structures are observed on the flat terraces, even though the silver adatoms are not equally spaced. This is a consequence of the covalent coupling of monomers forming dimers, trimers, etc. This indicates that at this temperature the system already had energy to undergo some C-C couplings, but a higher annealing step is required in order to trig-
ger a complete covalent reaction. A zoomed-in image (right) highlights this fact by superimposing the models of a monomer, covalent dimer and trimer. Similarly to the previous pure organometallic phase, bromine atoms avoid the interaction with silver adatoms. Finally, annealing the sample at 540 K leads to the formation of elongated one dimensional poly(p-phenylene) wires assembled in a parallel fashion, with bromine atoms in between them, as displayed in Figure 6.3 d. High-resolution imaging allows to distinguish protrusions within the wires that are associated with the phenyl rings, where the dim spheres in between are attributed to bromine atoms (see the inset).
Dysprosium Catalyzed Debromination of Aryl Halides

**Figure 6.4:** *Spontaneous Debromination of DBTP Species on Ag(111) after Deposition of Varying Amounts of Dy at RT.*  

a) Long-range topography after depositing insufficient amounts of dysprosium, where irregular organometallic structures of both partially and completely debrominated species are formed, coexisting with intact self-assembled islands (upper part) \((I_t = 100 \, \text{pA} ; V_b = -1.25 \, \text{V} ; 55\,\text{nm} \times 55\,\text{nm})\).  
b) Zoomed-in STM image showing intact supramolecules (right) and hybrid structures (left) \((I_t = 20 \, \text{pA} ; V_b = -1.0 \, \text{V} ; 11\,\text{nm} \times 6.8\,\text{nm})\).  
c) Ball and stick model of b with the dysprosium atom depicted as a blue sphere.  
d) STM topograph exhibiting a trimeric organometallic supramolecule based on radial C-Dy interactions \((I_t = 100 \, \text{pA} ; V_b = -1.25 \, \text{V} ; 5.2\,\text{nm} \times 5.2\,\text{nm})\).  
e) Model of d.  
f) Increasing the lanthanide:monomer ratio leads to the complete debromination of the organic species \((I_t = 15 \, \text{pA} ; V_b = -1.0 \, \text{V} ; 100\,\text{nm} \times 100\,\text{nm})\).  
g) High-resolution STM image showing a pentameric organometallic supramolecule with completely debrominated monomers, stabilized by directional C-Dy interactions \((I_t = 10 \, \text{pA} ; V_b = -1.0 \, \text{V} ; 4.4\,\text{nm} \times 4.4\,\text{nm})\).  
h) Ball and stick model of g.
To inspect the catalytic properties of dysprosium upon dehalogenation, minute amounts of Dy were evaporated on top of a submonolayer of DBTP species held at room temperature. The result can be observed in Figure 6.4a. In this long-range topograph two distinct phases are observed: 

(i) previously described phase α and (ii) irregular supramolecular assemblies surrounding small clusters, imaged as bright protrusions. These structures are identified as dysprosium clusters, to which debrominated species are attached. This is more evident when isolated supramolecules are imaged (Figures 6.4b and d), where a new type of bond motif is observed. In addition to the previously described chiral three- and four-fold non-covalent bonds formed by intact species, a new three-fold directional motif is identified as an organo-metallic node with dysprosium as the coordinative center. Importantly, as highlighted by the atomistic models in Figures 6.4c and e, monomers involved in this node are debrominated, stabilized by C···Dy interactions with a projected distance of (2.4 ± 0.5) Å. Additionally, hybrid supramolecules made up of intact species, debrominated and lanthanide-directed ones are are formed. Hence, dysprosium catalyzes the debromination of aryl halides at room temperature, and tend to form small clusters surrounded by terphenyl debrominated units. Therefore, the dysprosium to monomer stoichiometric ratio is crucial to achieve samples with completely debrominated species. This is further confirmed by increasing the Dy dosage, as depicted in Figure 6.4f. Depositing enough lanthanide ions results in a sample where no intact species are present, i.e. no α phase is observed, appearing all dehalogenated aryl moieties forming organometallic bonds with the dysprosium clusters. Imaging isolated supramolecules with a molecular tip allows to easily differentiate the radial threefold node and distinguish both the monomers and the rare-earth centers, as highlighted in Figure 6.4g and h.
Dysprosium as Ullman Reaction Inhibitor

Figure 6.5: Self-Assembly of Debrominated DBTP Monomers on Ag(111): Phase $\zeta$. a) Long-range STM topography showing the major $\zeta$ phase after gentle annealing at 330 K samples with sufficient dysprosium dosage. Well-defined regular lattices coexist with irregular clusters (upper left) ($I_t = 25$ pA; $V_b = -1.0$ V; $60\text{nm} \times 60\text{nm}$). b) Medium-range image highlighting the assembly of debrominated DBTP species where a missing monomer and few bromine defects can be observed. The black star shows the high symmetry directions of the Ag(111) monocrystal ($I_t = 200$ pA; $V_b = -0.5$ V; $24.6\text{nm} \times 24.6\text{nm}$). c) Zoom-in highlighting the unit cell (green) and a superimposed model of a dehalogenated terphenyl unit with four bromine atoms ($I_t = 200$ pA; $V_b = -0.5$ V; $5\text{nm} \times 5\text{nm}$). d) Ball and stick model of the supramolecular self-assembly of organic monomers and halogen atoms, whose parameters are described by $\vec{a}$, $\vec{b}$ and $\alpha$. 

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In order to inspect if the Ullman coupling can be achieved using lanthanide elements, the temperature is ramped in analogy with the previous section. The resulting sample after annealing at 330 K is displayed in Figure 6.5 where the major phase $\zeta$ can be observed. The scenario is radically different from the sample without dysprosium and from the previous sample prepared at room temperature. On one hand, dysprosium atoms diffused to form three dimensional clusters. On the other hand, fully debrominated species self-assemble into extended well-ordered supramolecular islands stabilized by C-H···Br interactions. Regarding phase $\zeta$, it consists entirely of terphenyl units and bromine atoms and its unit cell can be described by vectors $\vec{a}$ and $\vec{b}$, whose experimental values are $(15.3 \pm 0.5) \text{ Å}$ and $(9.9 \pm 0.5) \text{ Å}$ respectively, enclosing an angle $\alpha = (50 \pm 1)^\circ$. Remarkably, as depicted by the black stars (also in the distinct phases described below) the long molecular axis of the different species is aligned with one of the high symmetry directions of the underlying Ag(111) surface. Although the major reaction products are terphenyl (monomer) units, which represent over 99% of the species, some dimeric and trimeric units are also observed (less than 1%), as depicted in Figure 6.6. This variety of reaction products gives rise to different ordered supramolecular self-assemblies: pure monomeric supramolecules (Figure 6.6 a), heterogeneous supramolecules (Figure 6.6 b), well-defined dimeric islands (Figure 6.6 c) and extended heterogeneous monomeric/dimeric nanoarchitectures. Additionally, as displayed in Figures 6.6 e-h, different disordered heterogeneous phases can be observed containing monomers, dimers and trimers, all of the mentioned ones stabilized by the same C-H···Br interactions. Importantly, larger poly(p-phenylenes) are not observed, neither architectures similar to the organometallic phase. Therefore, even though dysprosium appears to be highly efficient regarding debromination, the decisive organometallic stage mandatory for the latter Ullman reaction is hindered. Thus, dysprosium mainly preserves the length of the initial aryl halide precursors, in contrast with the role of the d-block elements observed to date.
Figure 6.6: Ordered and Disordered Supramolecular Assemblies of Debrominated Species of Distinct Length on Ag(111). a) Homogeneous monomeric star-like supramolecules (Top Panel: $I_t = 50 \text{ pA }$; $V_b = -1.5 \text{ V }$; $7.3\text{nm} \times 4.1\text{nm}$; bottom panel: $I_t = 50 \text{ pA }$; $V_b = -0.75 \text{ V }$; $11\text{nm} \times 6\text{nm}$). b) Heterogeneous monomeric and dimeric triangular-like supramolecules (Top Panel: $I_t = 10 \text{ pA }$; $V_b = -1.0 \text{ V }$; $10.4\text{nm} \times 6\text{nm}$; bottom panel: $I_t = 10 \text{ pA }$; $V_b = -1.0 \text{ V }$; $24.8\text{nm} \times 11.7\text{nm}$). c) Well-defined extended supramolecular self-assembly of covalent dimers stabilized by hydrogen bonds and C-H···Br interactions ($I_t = 20 \text{ pA }$; $V_b = -0.5 \text{ V }$; $8\text{nm} \times 8\text{nm}$). d) Close-pack ordered heterogeneous nanoarchitecture ($I_t = 100 \text{ pA }$; $V_b = -0.75 \text{ V }$; $10\text{nm} \times 10\text{nm}$). e-f) Four STM topographic images showing distinct disordered heterogeneous self-assembled superstructures consisting in monomers, dimers and trimers. Parameters: e) ($I_t = 10 \text{ pA }$; $V_b = -1 \text{ V }$; $22.7\text{nm} \times 22.7\text{nm}$). f) ($I_t = 10 \text{ pA }$; $V_b = -1 \text{ V }$; $22\text{nm} \times 22\text{nm}$). g) ($I_t = 50 \text{ pA }$; $V_b = -0.5 \text{ V }$; $16.4\text{nm} \times 16.4\text{nm}$). h) ($I_t = 25 \text{ pA }$; $V_b = -1 \text{ V }$; $7\text{nm} \times 7\text{nm}$).

The hypothesis exposed above are further investigated performing different control experiments. First, subsequent annealing steps show that the formation of organometallic bonds, either C-Ag-C or C-Dy-C, is not
favorable at 420 K, where monomers still express the phase $\zeta$. Increasing the substrate temperature at 460 K results in the desorption of the organic species, and only metallic clusters can be observed in the terraces and the step-edges of the silver substrate. Thus, dysprosium debrominated monomers are completely hindered upon further C-C coupling reactions. It is important to remark that this phenomena is only observed when sufficient amounts of Dy are sublimated. For insufficient dosages of dysprosium the formation of few C-Ag-C organometallic chains can be observed upon annealing. Second, the order of deposition is inverted and dysprosium is sublimated in the first place, as shown in Figure 6.7a. Depositing similar amounts of lanthanide ions as the experiments described in section 6.1 on Ag(111) held at room temperature results in the decoration of the step-edges by irregular metallic clusters. Next, a submonolayer of DBTP species is deposited, as observed in Figure 6.7b. In the flat terraces, self-assembled intact species form the previously observed phase $\alpha$, and in the step-edges monomers are attached to the dysprosium clusters. This evidences that Dy atoms do not diffuse at room temperature once adsorbed in the step-edges. Finally, as depicted in Figure 6.7c, sample is annealed at 330 K, giving rise to small patches of organometallic nanoarchitectures mediated by C-Ag-C interactions in the flat terraces, but contrary to the phenomena observed without dysprosium, extended organometallic structures are not observed. Additionally, no threefold C-Dy-C nodes are imaged. This behavior shows that even though some substrate adatoms were available, the main source of Ag adatoms to facilitate the organometallic stage of the Ullman coupling, i.e. the step-edges, has been strongly hindered by the presence of Dy. The conclusion derived from these experiments is that, once the C-Dy-C bonds are formed, debrominated monomers are impeded to form the subsequent C-Ag-C nor C-C couplings by thermal annealing.
A possible explanation for the inhibition of the Ullman coupling by dysprosium can be found in the geometry of the respective organometallic intermediates. When DBTP species are deposited on a pristine Ag(111) surface and slightly annealed, extended C-Ag-C organometallic chains are formed, appearing in long-range assemblies which confine the units within them. By increasing the substrate temperature, having the debrominated terminal positions of the monomers facing each other and very close, the vibration of the C-Ag-C bond enhances the formation of C-C couplings. The fact that when poly(p-phenylene) architectures are formed they have the same linear geometry and approximate size as the previous organometallic state, can be seen as a proof of the confinement exerted by the superstructures. In the case of Dy organometallic architectures, debrominated species are linked randomly in an open architecture, i.e. there is no evident confinement. When the C-Dy bond is broken by slightly annealing the sample, monomers diffuse and form different self-assembled architectures stabilized by residual bromine atoms via Br···H interactions. Additionally, the source
of Ag adatoms is strongly hindered due to the dysprosium decoration of the step-edges. This is further confirmed by DFT calculations\cite{237}, indicating that Ag adatom clustering around Dy is 80 mV more favorable per silver adatom when compared in the absence of the lanthanide, highlighting the nucleation effect of dysprosium. This results in the inhibition of the Ullman coupling (less than 1%), as extended intermediate organometallic nanoarchitectures with a particular linear geometry are of great relevance for this reaction scheme.
DFT Insights

Figure 6.8: *Debromination Reaction of Bromobenzene in the Absence and Presence of Dysprosium on Ag(111)*. a) Energy barrier for the debromination of bromobenzene assisted by silver adatoms, to form the final organometallic Ag-benzene species. b) Same reaction catalyzed by a dysprosium adatom, highlighting that the process of debromination is almost spontaneous.
6.1 Dy Catalyzed Debromination Of Aryl Halides on Ag(111)

In order to evaluate the energetic landscape of the different reactions involving d-block and rare-earth metals, DFT calculations were performed by Dr. Jonas Björk from the University of Linköping. First, the role of Ag adatoms to aid debromination is evaluated\cite{footnote237}, as shown in Figure 6.8a. To facilitate calculations, the test monomer is considered to be a bromobenzene, i.e. a single benzene ring with a bromine atom. After the initial approach of this monomer to a surface adatom, an intermediate state (\textit{IntS}_\textit{Ag}) is formed in which the bromine is directly interacting with the metal. The subsequent debromination step in the reaction (\textit{TS2}_\textit{Ag}) has an energy barrier of 0.85 eV, which is slightly smaller if compared with a debromination process that is only mediated by the flat Ag(111) surface (ca. 1.0 eV depending on the density functional applied\cite{footnote238}). Hence, the experimentally observed organometallic state mediated by adatoms is more favorable than a substrate mediated debromination. Finally, the energy cost to break the bond of the bromine atom with the Ag adatom is 0.35 eV. On the other hand, the scenario is evaluated in the presence of Dy, as depicted in Figure 6.8b. By comparing the same intermediate state (\textit{IntS}_\textit{Dy}) with the one shown in a, it is directly evident that there is a strong interaction between dysprosium and the bromobenzene, which has more energy than the entities separately (-0.98 eV). In fact, this intermediate state can not be considered as a local minimum, as there is no energy barrier with the final state (\textit{FS}_\textit{Dy}) in which the debromination occurred and both the phenyl and the Br atom are bonded to the Dy. In practice one can consider this process to be spontaneous and more exothermic compared to Ag mediated debromination, considering that the net energy of the reaction is -2.70 eV. In this case also the Br atom is more strongly bonded to the Dy, costing 1.10 eV to break the bond between them, leaving the dysprosium-benzene complex isolated. Finally, calculations also show that final state (\textit{FS'}) in which the Br atom is stably adsorbed on the surface is 1.05 eV larger in the case of Dy.

Conclusions

This section showed the distinct catalytic capabilities of d-block and f-block elements towards dehalogenation and Ullmann coupling reactions of aryl
halides on surfaces. First, a successful example of Ullman coupling is detailed with DBTP units on Ag(111), where the different stages of intact species, organometallic and covalent wire formation are observed for each annealing step. Second, the addition of dysprosium to a submonolayer DBTP sample results in spontaneous dehalogenation at room temperature and the formation of C-Dy organometallic supramolecules. Theoretical DFT calculations quantitatively corroborate these experimental results, showing a more exothermic process in the case of rare-earth mediated debromination, suggesting an almost zero energy barrier for this process. Further annealing dissolves these Dy-directed organometallic structures and leads to different supramolecular assemblies stabilized by Br⋯H interactions, even though no signal of C-Ag-C nor C-C coupling is observed. The inhibition of the Ullman coupling is maintained despite of the annealing temperature, until all organic species are desorbed from the substrate. Additionally, by reverting the order of deposition, the role of Dy to diminish the source of silver adatoms due to decoration of the step-edges has been demonstrated. Importantly, we tentatively suggest that the specific geometry of the organometallic stage, confined for the C-Ag-C supramolecular chains and open for the C-Dy-C complexes, is crucial for latter stages in the Ullman-like coupling reaction. Therefore, these results represent a new route to atomically control the length of target brominated monomers, as dysprosium inhibits uncontrolled C-C coupling reactions. We envision our results will provide new ways to tailor on-surface nanoarchitectures, while expand new horizons to create Dy-directed surface-supported organo-metallic nanostructures of great relevance for catalysis.
6.2 A Detour to Graphene Nanoribbons

After the discovery of graphene and its unique properties, in recent years Graphene Nanoribbons (GNRs) have raised the interest of the scientific community as they are envisioned to play an important role in futuristic semiconducting all-carbon electronics. The electronic structure of these nanoarchitectures strongly depends on the edge termination, mainly distinguishing between zig-zag and armchair GNRs. In the latter case, lateral quantum confinement has been shown to create a band gap, which can be tuned, since the gap is inversely proportional to the width of the GNR. In order to be used in real devices operated at room temperature, large electronic band gaps are required, i.e. widths of the order of few nanometers, something not achievable with top-down approaches such as e-beam lithography. Additionally, such techniques lack atomic precision at the edges of the GNRs, destroying the coherent electron propagation and the carrier mobility. For that reason, in the last years the bottom-up approach, consisting in synthesizing GNRs by covalently tailoring organic precursors, has demonstrated to be a powerful strategy to control the chirality, width and edge functionalization of these nanostructures, i.e. their electronic structure. As an example, the electronic structure of armchair GNRs (aGNRs) strongly depends on their lateral symmetry, being able to distinguish between three families: 3p-, 3p+1- and 3p+2-aGNR, being p the number of carbon atoms across the width of the GNR. While 3p- and 3p+1-aGNR have a strict semiconducting behavior, 3p+2-aGNR species can be considered as zero band gap semiconductors. In addition, different efforts have been dedicated to fabricate and describe in-situ grown Graphene Quantum Dots (GQDs), such as inserting boron atoms inside aGNRs, resulting in a discretized Valence Band (VB) with confined modes between the borilated sections, which act as scatterers. Contemporary to this thesis, the energy separation dependence with the size of these GQDs has been suggested by a combined STM+DFT approach.

Herein, the bottom-up fabrication via terminal dehydrogenation and
the subsequent lateral C-C coupling of linear halogenated precursors is presented. Graphene Quantum Boxes (GQBs) with well-defined discrete states coming from the tunable quantization of the aGNR Conduction Band (CB) are achieved with this approach. The energy separation of the discrete energy states is investigated as a function of the aGNR length, and can be described in terms of the relativistic massive dispersion relation. The confined states are separated in energy of the order of $10^{-1}$ eV, which could be of potential interest for applications in optically active, near infrared, THz communication systems.

**Synthesis of 3p-aGNR**

![Figure 6.9: Chemical Reactions of DBTP Species on Ag(111) by Increasing Substrate Temperature to Afford the Formation of 3p-aGNR.](image)

*a) Reaction scheme that leads to the formation of 3p armchair graphene nanoribbons via Ullman coupling and the subsequent terminal dehydrogenation to laterally couple poly(p-phenylene) wires. b) STM topographs of the different stages, to finally achieve 3p-aGNR. In the image (right), p=1, 2 and 3 species are shown (Parameters from left to right: $I_t = 50\ pA$ ; $V_b = -1.0\ V$ ; $10nm \times 10nm$ / $I_t = 505\ pA$ ; $V_b = -1.0\ V$ ; $16.7nm \times 16.7nm$ / $I_t = 200\ pA$ ; $V_b = -1.0\ V$ ; $15nm \times 15nm$ / $I_t = 100\ pA$ ; $V_b = -1.0\ V$ ; $2.7nm \times 2.7nm$).
6.2 A Detour to Graphene Nanoribbons

In order to nanofabricate GNRs, the previously shown Ullman coupling scheme is carried out by annealing samples containing the DBTP precursor at 540 K. Once the poly(p-phenylene) structures are formed, a final annealing step at 650 K ensures the lateral C-C coupling with neighboring units via terminal dehydrogenation, as schematically depicted in Figure 6.9a. It is important to carry out the annealing in a stepwise fashion, as direct deposition onto hot substrates leads to irregular polymers due to the lack of previous organometallic stages with the adequate geometry. Due to the structure of the initial precursors, and considering that only an integer number of wires can be laterally coupled, i.e. polymer cracking is discarded, atomically precise 3p armchair GNR are achieved. Figure 6.9b (right panel) shows an extended 6-aGNR and a 9-aGNR, which results from the coupling of a nanowire and a p=2 aGNR.

Figure 6.10: Coverage Dependence of Reaction Products Width after Annealing DBTP Species at 650 K on Ag(111). a) For initial coverages of the DBTP precursor below 0.5 ML the reaction yield for 3p-aGNRs with \( p \geq 2 \) is strongly hindered, and mainly poly(p-phenylene) wires are produced. White star highlights the high-symmetry directions of the underlying Ag(111) substrate \((I_t = 100 \text{ pA} ; V_b = -1.0 \text{ V} ; 100 \text{nm} \times 100 \text{nm})\). Inset shows polyphenyl wires which form threefold nodes but no lateral coupling is observed \((I_t = 50 \text{ pA} ; V_b = -1.0 \text{ V} ; 9 \text{nm} \times 9 \text{nm})\). b) Increasing precursor coverage close to the monolayer \((\geq 0.9 \text{ ML})\) results in the fabrication of aGNRs whose width is up to \( p=5 \) \((I_t = 505 \text{ pA} ; V_b = -1.0 \text{ V} ; 100 \text{nm} \times 100 \text{nm} / I_t = 200 \text{ pA})\). Inset shows different heterojunctions forming aGNRs \((I_t = 50 \text{ pA} ; V_b = -1.0 \text{ V} ; 15 \text{nm} \times 15 \text{nm})\).
Additionally, the coverage of the initial precursors plays an important role in the width of the latter nanoribbons. As displayed in Figure 6.10, for initial coverages before the reaction below 0.5 ML (0.45 ML in Figure a), the resulting sample mainly consists in one-dimensional polyphenylene units and wider structures are hardly observed. On the contrary, increasing the precursor coverage close to the ML (0.9 ML in Figure 6.10 b) results in the fabrication of aGNRs with widths up to \( p = 5 \), i.e. 15-aGNR.

Electronic Structure of 3p-aGNR Heterojunctions

![Figure 6.11: Onset of the Conduction Band vs. Width Dependence of Poly(p-phenylene) Wires and 3p-aGNR.](image)
a) Zoomed-in STM image of \( p = 1 \) (right), 2 (left) and 3 (center) aGNRs with the atomistic model superimposed and the position where STS of b are acquired indicated by colored crosses (\( \text{I}_b = 10 \text{ pA} \); \( \text{V}_b = 0.5 \text{ V} \); 7.8\( \text{nm} \times 7.8\text{nm} \)). b) Stacked STS spectra acquired at different positions indicated by the same color. The nanowire (black) shows a maximum at around 1.5 V, and a flat profile below the Fermi level. The onset of the conduction band (CB) of \( p = 2 \) (green) and 3 (blue) aGNRs is located at 0.45 and 0.25 V respectively (STS Parameters: Modulation = 10 mV, Frequency = 773 Hz, Integration time/point = 30 ms, Sampling Energy = 4.25 meV/point).
The electronic structure of the different 3p-aGNRs is evaluated by means of local scanning tunneling spectroscopy (STS), as the differential conductance is directly proportional to the LDOS. Figure 6.11 a shows an area of the sample where isolated long sections of p=1, 2 and 3 aGNRs can be observed. First, to confirm the metallic nature of the tip a control spectrum is acquired on top of the pristine Ag(111), showing the well-known Shockley surface state of the substrate with the onset at around -70 mV \(^{259,260}\), displayed in orange in Figure 6.11 b. As expected from theory \(^{244}\), the 3p-aGNR family will behave as a semiconductor with the onset of the Conduction Band Minimum (CBM) inversely proportional to the width of the ribbon. This is validated by comparing the respective CBM for each species, identified as the maxima of each spectra (highlighted with colored arrows). In the case of the polyphenylene, i.e. p=1, the most prominent feature is located at ca. 1.5 V, while the edge of the CBM is observed at around 1.2 V. Regarding p=2 and p=3, i.e. 6- and 9-aGNRs, the onsets of the CBM are located at around 0.45 and 0.25 V respectively, and the maxima at 0.8 and 0.7 V for each case. It is worth mentioning that the region below the Fermi level appears featureless, indicating that the Valence Band Maximum (VBM) is not detected. Prior studies \(^{252}\) revealed that due to the symmetry of the frontier orbitals in the 3p-aGNR species, the signal of the Valence Band (VB) is almost suppressed, being only accessible when the set point currents are in the order of tenths of nA, implying very small tip-sample distances. As a consequence of the opening of an energy gap in the 3p-aGNR family, the charge carriers do not behave as massless fermions, but they are treated as particles with an effective mass \(m^*\). Even though no direct measurement of the band gap is provided, the inverse proportionality between the onset of the CBM and the width derived from theory is demonstrated.
Figure 6.12: **Junction of Two Poly(p-phenylene) Wires.** a) STM image showing the junction of two poly(p-phenylene) wires featuring two kinks with the atomistic model superimposed ($I_t = 100 \text{ pA} \ ; \ V_b = -1.0 \text{ V} \ ; \ 5\text{nm} \times 12\text{nm}$). b) STS spectra recorded at the junction, and symmetrically separated from it in both wires, together with the surface state spectrum acquired on the pristine Ag(111) substrate (STS Parameters: Modulation$= 10 \text{ mV}, \text{Frequency}= 773 \text{ Hz}, \text{Integration time/point}= 36 \text{ ms}, \text{Sampling Energy}= 2.5 \text{ meV/point}$). c) Lock-in maps at constant bias voltage: 1.5 V (up) and 1.8 V (down) (Lock-in Parameters: $I_t = 100 \text{ pA} \ ; \ 5\text{nm} \times 10.6\text{nm}, \text{Modulation}= 10 \text{ mV}, \text{Frequency}= 773 \text{ Hz}, \text{Integration time/point}= 10 \text{ ms}$).

In order to serve as a comparison for latter studied heterojunctions, first the homojunction of two polyphenylene species is investigated. Figure 6.12a shows a STM topography of two nanowires connected in a zig-zag fashion, resulting in two kinks along the long polymer axis, highlighted by the superimposed model. The STS spectra displayed in 6.12b are recorded at the center of the junction, and at symmetrically separated positions from it. Additionally, the spectrum acquired on the pristine Ag(111) surface verifies the good condition of the tip, featuring a step-like shape at ca. -70 mV. For STS recorded $\sim 6\text{nm}$ from the junction (green and black curves), a maximum at around 1.4 eV with a shoulder at higher energy can be
observed. This feature shifts to 1.2 eV as the spectra are acquired closer to
the junction (pink and red curves). The blue curve, recorded at the center
of the junction, shows a steady increase and no peak is observed below 2 V.
The electronic structure can also be visualized in the real space by recording
lock-in maps at targeted energies, as depicted in 6.12 c. At 1.5 V (upper
panel), a LDOS accumulation is observed near the junction, while at the
center of it one observes a depression. For energies above 1.8 V, the intensity
around the kinks is the main feature, as they act as scattering centers.

After that, the quantum box formed by a 6-aGNR segment connected
by two poly(p-phenylene) wires is studied. Figure 6.13 a displays the neigh-
boring area of the quantum box, showing that the heterojunction is isolated.
The quantum box consists in a 5.0 nm long 6-aGNR with a width between
terminal hydrogen atoms of 0.8 nm, as calculated in the superimposed model
highlighted in Figure 6.13 b. The quantum confinement is originated by the
large mismatch between the energy band gaps of the 3- and 6-aGNR, where
a low transmission is expected, only limited by inelastic processes at the
junctions. To evaluate this phenomena, STS spectra are recorded at differ-
et position of the box, as well as in the nanowires, as displayed in Figure
6.13 c. The spectra recorded at two different positions outside the box
(black and green), show shapes quite similar to the 1D nanowire (Figure
6.11) with the onset of the CB at ca. 1.2 and 1.4 eV. Inside the box one
can observe that, while the onset of the surface state remains unaltered in
the different spectra, the shape of the curves in the conduction band of the
6-aGNR is strongly affected. In fact, the red, blue and violet curves feature
a series of peaks that correspond to the Quantum Well States (QWS) origi-
nated from the quantization of the conduction band of the finite 6-aGNR.
Up to five peaks are clearly distinguished, identified as the n=1,...,5 quan-
tum states as highlighted by horizontal dashed lines. In order to visualize
this discretization in the real space, lock-in maps are acquired at the ap-
proximate energies of the peaks maxima and displayed in Figure 6.13 d.
These differential conductance maps reveal the standing wave pattern of
each QWS, with its corresponding number of maxima (indicated by n).
Figure 6.13: Wire/6-aGNR/Wire Junction: Quantum Box. a) STM topography showing the region neighboring the studied quantum box ($I_t = 50 \text{ pA} ; V_b = -0.5 \text{ V} ; 45 \text{nm} \times 75 \text{nm}$). b) Zoomed-in image of the targeted area showing a 5.0 nm long 6-aGNR box connected by two nanowires, with the atomistic model superimposed ($I_t = 50 \text{ pA} ; V_b = -0.5 \text{ V} ; 4.3 \text{nm} \times 9.7 \text{nm}$). c) STS spectra acquired at the positions indicated by the color code position in b (STS Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 36 ms, Sampling Energy= 2.5 meV/point). d) Lock-in maps at constant bias voltage which correspond to the approximate energies of the peaks observed in the STS spectra (Lock-in Maps Parameters: $I_t = 100 \text{ pA} ; 5 \text{nm} \times 10.6 \text{nm}$, Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 10 ms).
If the energy separation between levels is analyzed from the experimental spectra, $E_2 - E_1 = (245 \pm 10)$ meV, while the subsequent separations are found to be constant and equal to $E_{n+1} - E_n = (330 \pm 10)$ meV for $n > 1$. The simplest 1D particle-in-a-box model for graphene describes the energy separation between the QWS with the linear dispersion $\Delta E = \pi \hbar v_F / L_\parallel$, where $v_F$ is the Fermi velocity and $L_\parallel$ the length of the quantum well. If the values from graphene are introduced, i.e. $v_F = 10^6 m/s$, together with the experimental length of 5.0 nm, the separation between levels should be constant and equal to 0.41 eV. This value is clearly larger than the one observed experimentally, and as the length $L_\parallel$ is a direct measurable parameter, a slightly smaller Fermi velocity than the one from graphene could be deduced, of the order of $v_F \approx 8 - 9 \cdot 10^5 m/s$.

**Figure 6.14:** Distribution of the Energy Levels of the GNR in the Real and Momentum Space. a) Stack of STS spectra recorded along the black line of the lower STM image (STS Parameters: Modulation= 10 mV, Frequency= 773 Hz, Integration time/point= 36 ms, Sampling Energy= 2.5 meV/point). b) Line-by-line Fast Fourier Transform (FFT) showing the dispersion relation of $E$ vs. $k$, with a hyperbola fitting the points giving an effective mass of 0.09 $m_e$ and the bottom of the band at $+0.42$ eV.
In order to evaluate better the dispersion relation, first a spatial map of the energy distribution of the QWS is acquired (see Figure 6.14a). This is carried out by recording STS spectra along the length of the 6-aGNR, adjusting the tunneling current to the set-point between consecutive spectra, and stacking the resulting curves. One can clearly distinguish the first four states in the spatial map of the energy distribution. Next, the band dispersion of the discrete states is obtained by performing a line-by-line Fast Fourier Transform of the spectra in Figure 6.14a, as displayed in Figure 6.14b. To fit the dispersion in the reciprocal space, one has to take into account that the energy separation between QWS is approximately constant for large quantum numbers, while between the first two states ($\Delta E_{1-2}$) is significantly closer. Thus, a linear dispersion relation is deduced for large $k$ values, deviating from linearity only for small $k$ values. From this facts, a linear or parabolic fitting is discarded, corresponding the blue curve in Figure 6.14b to the hyperbolic dispersion relation for relativistic massive particles:

$$ E = \sqrt{p^2 \cdot v_{F,GNR}^2 + \left( m^* \cdot v_{F,GNR}^2 \right)^2} = \hbar v_{F,GNR} \cdot \sqrt{k^2 + \left( \frac{m^* v_{F,GNR}^2}{\hbar} \right)^2} $$ (6.1)

The fitting to the experimental data gives an effective mass of 0.09 $m_e$, a Fermi velocity in the nanoribbon of $v_F = 9 \cdot 10^5 m/s$ and the bottom of the band $E(k = 0)$ at 0.42 eV. The effective mass is similar to the results obtained for 9-aGNR on Au(111)\textsuperscript{252}, where a weak interaction with the underlying metallic surface was deduced.
6.2 A Detour to Graphene Nanoribbons

Theoretical Model

![Graphene Nanoribbon Diagram](image)

**Figure 6.15:** Theoretical Model and Comparison of a 6-aGNR of width $L_{\perp}$ and length $L_{||}$. a) Real and reciprocal space model of a $L_{||}$ long and $L_{\perp}$ wide 6-aGNR. b) 2D dispersion relation of graphene and the discrete sub-bands obtained for the confinement in the perpendicular direction $L_{\perp}$. c) Left panel: Zoom of the conduction sub-bands for 6-aGNR in the experimentally accessible range of energies. The discrete values of the parallel momentum and the corresponding discrete energy levels are highlighted with square symbols. The correspondence between these calculated energy levels and the peaks of the experimental $dI/dV$ curves (right panel) is shown by horizontal arrows.
In order to understand the experimental results and the corresponding hyperbolic fitting, first the theoretical electronic structure of a free-standing nanoribbon is investigated. A ribbon with finite length $L_\parallel$ and width $L_\perp$ (see Figure 6.15a left panel) will indeed have a discretized conduction band as a result of the quantized values of the momentum perpendicular to the long axis of the 6-aGNR, i.e. $q_\perp$, taking the Dirac points as the zero coordinates (see Figure 6.15a right panel). This quantization is the result of the elastic scattering at the edges of the ribbon between the electrons traveling downwards from the upper K point with the electrons traveling upwards from the lower K’ point. Only certain values of the perpendicular momentum $q_\perp$ will produce constructive interference, given by the general expression:

$$q_{\perp,m} = K_\perp - k_{\perp,m} = \frac{m\pi}{L_\perp} \quad (6.2)$$

where $K_\perp$ is the distance in the reciprocal space from the center of the Brillouin zone ($\Gamma$ point) to the upper vertex (K point), and $k_{\perp,m}$ the vector from the $\Gamma$ point to the m-state, with m being an integer number. As a result of the discretized perpendicular momentum $q_{\perp,m}$, the energy levels are also discretized in $m$-sub-bands. In this case the dispersion relation is considered to be close to the analytic solution of the tight-binding calculation of graphene to first nearest-neighbors:

$$E_{k_\parallel,k_\perp} = \sqrt{1 + 4\cos^2\left(\frac{\sqrt{3}k_\perp a}{2}\right) + 4\cos\left(\frac{\sqrt{3}k_\perp a}{2}\right)\cos\left(\frac{3k_\parallel a}{2}\right)} \quad (6.3)$$

where $\gamma = 2.8$ eV is the hopping element between nearest-neighbors and $a$ the carbon-carbon distance in the graphene lattice (1.42 Å). Substituting 6.2 into this equation results in the sub-bands displayed in Figure 6.15b as dashed horizontal lines. It is important to notice that the energy band gap is determined by the bottom of the $m=2$ band, and not by $m=1$, as it cuts the Brillouin zone very close to the Dirac point K’, with the minimum
6.2 A Detour to Graphene Nanoribbons

energy at 0.43 eV in agreement with both the hyperbolic fitting and the experimental data.

Once the sub-bands are introduced by confinement along the width of the ribbons, the confinement along long axis of the ribbon gives the discretization of these bands in quantized energy levels. Again, the quantized values of the parallel momentum that ensure constructive interference are described by the expression:

\[ q_{||,n} = K_{||} - k_{||,n} = \frac{n\pi}{L_{||}} \]  \hspace{1cm} (6.4)

where \( K_{||} \) is the distance in the reciprocal space from the center (\( \Gamma \) point) to the lateral of the Brillouin zone, and \( k_{||,n} \) the vector from the \( \Gamma \) point to the \( n \)-state (see Figure 6.15 right panel). If the resulting discretized energy levels are plotted, as displayed in Figure 6.15 c (left panel), and compared with the experimental curves (right panel), the agreement is obvious, as highlighted with the horizontal arrows. Differences smaller than 20 meV are found between the experimental data and the model, which does not require fitting parameters. Additionally, it can explain the experimental broadening of the \( n=5 \) state, whose width differs from the lower states, as the \( m=2 \) sub-band overlaps in that region with the \( m=3 \) sub-band. As this model is derived from free-standing graphene, and the agreement between the model and the experimental data is accurate, the effect of Ag(111) is deduced to be very small, suggesting that the electronic structure of the investigated system would barely change in the absence of the substrate.

The accuracy of this simple model is tested in Graphene Quantum Boxes of different lengths. Figure 6.16 a shows the STM topography of a 7.5 nm long 6-aGNR connected by one-dimensional polyphenylene wires. As expected from the introduced model, a longer graphene nanoribbon will lead to discretized energy levels closer to each other. This can be observed in the STS spectra displayed in Figure 6.16 b, where energy levels are unambiguously closer when compared to Figure 6.13. Moreover, depending on the specific points where the STS are acquired along the 6-aGNR, only odd
(orange squares) or even (violet circles) energy levels from \( n=1, \ldots, 8 \) are observed. At the extreme position of the nanoribbon one expects to observe all the different QWS, as highlighted in the blue spectra. By calculating the position and separation of the discretized energy levels for a 7.5 nm long 6-aGNR, depicted as vertical dashed lines labeled with \( n=1, \ldots, 8 \), one can directly see that the model indeed predicts accurately the energy positions. The correspondence between the model and the experimental data is better illustrated by Figure 6.17. Again, the energy spacing between the first and the second \((n=1 \text{ and } 2)\) QWS is smaller (0.13 eV) than the separation exhibited between \( n \) and \( n+1 \) for large \( n \) (ca. 0.2 eV). Additionally, for large QWS number the plateau is caused by the overlap of QWS from the \( m = 2 \) and \( m = 3 \) sub-bands, resulting in a perfect agreement between the model and the experiment. Therefore, the validity of the model is further demonstrated. Finally, the discrete energy levels are imaged in the real space by means of the lock-in map technique, recording images at the approximate voltage where the energy levels appear in the STS spectra, as shown in Figure 6.16 c. The difference in the position in the lock-in maps is due to the drift while acquiring the images, as the whole series takes approximately 3 hours to be recorded.
Figure 6.16: Electronic Structure of a Confined 6-αGNR Section. a) STM topography showing a 7.5 nm long 6-αGNR quantum box, with the atomistic model superimposed and the position of the STS spectra highlighted with colored crosses ($I_t = 100 \text{ pA}; V_b = -1.0 \text{ V}; 6\text{nm} \times 10\text{nm}$). b) Stacking of STS spectra showing odd and even discrete energy levels $n=1,...,8$ in orange squares and violet circles respectively (STS Parameters: Modulation = 10 mV, Frequency = 773 Hz, Integration time/point = 36 ms, Sampling Energy = 2.5 meV/point). c) Lock-in maps at constant bias voltage recorded at the approximate energies where discrete states $n=1,...,7$ can be observed in the STS spectra (Lock-in Maps Parameters: $I_t = 100 \text{ pA}; 5\text{nm} \times 10.6\text{nm}, \text{Modulation} = 10 \text{ mV, Frequency} = 773 \text{ Hz, Integration time/point} = 36 \text{ ms}$).
Figure 6.17: **Experiment vs. Model Agreement for Longer Graphene Quantum Boxes.** Left panel: Zoom of the conduction sub-bands for 6-αGNR with $L_\parallel = 7.5$ nm. The discrete values of the parallel momentum and the corresponding discrete energy levels are highlighted with square symbols. The correspondence between these calculated energy levels and the peaks of the experimental $dl/dV$ curves (right panel) is shown by horizontal arrows.

The correspondence between the introduced model and the hyperbolic dispersion relation for massive fermions used for the fitting is evaluated. In order to do so, $\zeta_m = \cos \left( \frac{\sqrt{3}k_\perp a}{2} \right)$ is defined and considered to be constant for a given sub-band $m$ in equation 6.3. Then, the dispersion of the $m^{th}$ sub-band can be written as:

$$E_m(k_\parallel) = \gamma \sqrt{1 + 4\zeta_m^2 + 4\zeta_m \cos \left( \frac{3k_\parallel a}{2} \right)}$$

(6.5)
This expression close to the Brillouin zone boundary ($k_{∥,n} \approx K_{∥}$) can be further simplified by Taylor expansion to second order considering $k_{∥,n} = K_{∥} - q_{∥}$, with $K_{∥} = \frac{2\pi}{3a}$. Then the equation can be written as:

$$E_m(q_{∥}) \approx \frac{3a\gamma}{2} \sqrt{2\zeta_m} \sqrt{q_{∥}^2 + \frac{2(1 - 2\zeta_m)^2}{\zeta_m(3a)^2}}$$

(6.6)

Which can be directly compared with the relativistic dispersion relation for massive fermions by defining:

$$\hbar v_{F,GNR} = \frac{3\gamma a}{2} \sqrt{2\zeta_m} \hbar v_{F,\text{graphene}} \sqrt{2\zeta_m}$$

(6.7)

$$\left(\frac{m^*v_{F,GNR}}{h}\right)^2 = \frac{2(1 - 2\zeta_m)^2}{\zeta_m(3a)^2}$$

(6.8)

At this point the values for $m^*$ and $v_F$ can be calculated from the model for the 6-aGNR nanoribbon, considering that $a$ and $\gamma$ are well known parameters, 1.4 Å and 2.8 eV respectively, and the width $L_{∥}$ is extracted from the atomistic model, being 8 Å. The resulting values obtained from the model, $m^* = 0.11m_e$ and $v_F = 9.1 \cdot 10^5 m/s$ are in excellent agreement with the experimental values deduced from the hyperbolic fitting. Within this interpretation, it is implicit that both the Fermi velocity and the effective mass will be modified as a result of the confinement originate by the finite length and width.

Importantly, this model also predicts other properties attributed to aGNRs. First, for very wide aGNRs, the separation between discretized values of $k_{⊥}$ will be very small and thus at least one sub-band will be close to the Dirac point (in analogy with graphene). Second, the condition for metallic aGNRs (the 3p+2-aGNR family) is also fulfilled, as for those specific widths $\zeta_m \approx 1/2$, and a sub-band crosses the Dirac point, conferring an approximate zero effective mass and the Fermi velocity of graphene to the carriers (see equations 6.7 and 6.8).
Conclusions

In summary, during this section the formation of nanoribbons belonging to the 3p-aGNR family has been described. The synthesis is carried out by a step-by-step reaction with the final stage consisting in the lateral coupling of polyphenylene wires by terminal dehydrogenation, hence facilitating the fabrication of ribbons with different widths. By investigating the electronic structure of these nanoarchitectures, it is demonstrated that indeed the CBM decreases as the width increases, as expected from theoretical studies. Moreover, the mismatch of band gaps between structures with different widths results in the formation of 6-aGNR quantum boxes connected by polyphenylene wires at the terminal positions. The energy level separation increases as the length of these 6-aGNR sections decreases, demonstrated by means of STS. Additionally, the position of the discrete energy levels can be accurately described by a model without fitting parameters, highlighting that the graphene structures are weakly interacting with the underlying Ag(111) substrate. The energy level spacing, in the order of tenths of eV, corresponding to the infrared regime, could be of great interest for modern telecommunications in case that light emission can be obtained from the GNRs grown on suitable substrates and properly excited.
General Conclusions

This thesis reports the on-surface design of lanthanide nanomaterials. To this aim different coordination supramolecular approaches have been implemented, including: \textit{in situ} metalation of distinct macrocycles, self-assembly of \textit{ex professo} synthesized single molecule magnets, engineering of lanthanide directed and laterally coordinated metallosupramolecular networks, and reactivity of lanthanide elements towards the dehalogenation of aryl bromides to afford organo-metallic complexes.

First, sandwich-like double decker compounds with dysprosium and terbium centers (Dy(OETAP)$_2$ and Tb(OETAP)$_2$, respectively), were investigated on three coinage metallic surfaces: Ag(111), Au(111) and Cu(111). After confirming that the chemical integrity of these species was not affected upon sublimation and adsorption on the distinct surfaces, the effective electronic decoupling mechanism provided by the ethyl moieties was investigated. DFT simulations showed for Ln(OETAP)$_2$ a larger absorption height and diminished interaction with the surface when compared with
double-deckers without decoupling terminal groups. Furthermore, comparative XPS corroborated the electronic decoupling hypothesis, thus revealing \( \text{Ln(OETAP)}_2 \) species as a promising candidate for single molecular magnetism on metallic supports. In this sense, demonstrating the preservation of the single ion anisotropy of SMMs on metals at relative high temperatures using synchrotron-based techniques, would be of particular interest in the fields of spintronics, information storage and quantum information.

Second, the capability of lanthanide ions to serve as vertexes and direct metallosupramolecular networks on surfaces was described, motivated by their high coordination number exhibited in three-dimensional chemistry. Initially, a ditopic terphenyl backbone equipped with terminal carboxylic ligands (TDA) was evaporated onto Cu(111) to ensure dehydrogenation upon mild annealing temperatures and thus transformation into coordinative carboxylate moieties. After depositing gadolinium on a TDA submonolayer sample, reticulated supramolecular networks with squared unit cells were observed. The unprecedented eight-fold coordination node, previously not reported for d-block elements such as Fe, was investigated by DFT and XPS, determining its predominant ionic character. The robustness of the Gd-O coordination node up to 400 K was demonstrated by VT-STM. Moreover, the versatility and tunability of lanthanide-carboxylate directed networks were tested by employing dysprosium as lanthanide vertex. Coordination of deprotonated TDA and Dy afforded similar reticulated networks as the Gd case, while gentle annealing at 450 K triggered the formation of a novel quasiregular hexagonal supramolecular assembly exhibiting unique binuclear dysprosium centers, engaged with adjacent carboxylates in predominantly ionic bonds. Additionally, by using linear ditopic linkers of different lengths (TPA and PDA), topologically equivalent reticulated networks were achieved, but exhibiting a tunable lanthanide-lanthanide intermodal distance. The thermal robustness and the chemical versatility of the networks, together with the intrinsic properties of the lanthanide elements, allows to envision their future application in sensing and catalysis through apical coordination, as well as in nanomagnetism and optoelectronics upon
decoupling of the metallic supports.

Third, the self-assembly and \textit{in situ} metalation by dysprosium of porphyrinoids featuring distinct sizes of the macrocycle were investigated on Au(111). On one hand, an expanded macrocycle, the HTAP monomer, was adsorbed intact and observed on the pristine Au(111) and Ag(111) single crystals, opening the field of expanded porphyrins on surfaces. A careful study of the molecular growth versus coverage revealed a long-range orientational self-assembly. Next, a novel local single-molecule protocol to fully deprotonate the inner cavity of targeted porphyrinoid monomers via tunneling electrons was developed, envisioning its application for long-term information storage at the molecular level. The capability of such larger macrocycles to host metallic ions was tested by depositing dysprosium, showing a unique off-centered metalation of the macrocycle. This observation opens a new route for tuning the luminescent properties of lanthanides by complexing the cavity with a second metal ion, as well as for potential applications in sensing and catalysis due to the asymmetric coordination motif.

On the other hand, a novel 2H-4FTPP tetrapyrrole species was studied on the Au(111) surface. Importantly, after depositing dysprosium on a submonolayer 2H-4FTPP sample, three new lanthanide related species were identified and assigned to: (i) Dy-2H-4FTPP (Dy is physisorbed below the macrocycle backbone), (ii) Dy-1H-4FTPP (Dy bonded to one pyrrole), and (iii) the fully metallated Dy-0H-4FTPP species (Dy bonded to both pyrroles). Remarkably, the strong low voltage bias resonance at Dy-2H-4FTPP species could be unambiguously attributed to a Kondo resonance by ramping the substrate temperature from 4.5 to 100 K, being the first observed Kondo phenomena on \textit{in situ} synthesized lanthanide porphyrinoids. Thanks to tip-induced voltage pulses, metallated species could be transformed from Dy-2H-4FTPP to Dy-1H-4FTPP and finally to Dy-0H-4FTPP, whereby only physisorbed species revealed a Kondo resonance, thus anticipating novel avenues for tunability of Kondo systems by coordination chemistry, of relevance for transport in molecular electronics.

Finally, the chemical activity of dysprosium towards aryl bromides on
Ag(111) was addressed. On one hand, in the absence of dysprosium, the chemical transformations of aryl bromides on Ag(111) upon substrate annealing via Ullmann-like coupling reactions afforded the on-surface synthesis of poly(p-phenylene) wires. Further annealing resulted in the fabrication of 3p-aGNR via terminal dehydrogenation and lateral coupling of the poly(p-phenylene) wires. The relation between the conduction band onset and the width of the 3p-aGNR was demonstrated to be inversely proportional. Additionally, investigating the heterojunctions built up by graphene nanoribbons and poly(p-phenylene) wires, a quantum box behavior was found in the 6-aGNR sections. Hereby, the comparison of experimental results with theoretical modeling revealed that the intrinsic properties of the graphene nanoribbon section are unperturbed upon connection to poly(p-phenylene) wires, also indicating minute interaction with the surface.

On the other hand, in the presence of dysprosium, debromination of aryl halides was clearly promoted demonstrating the efficient catalyst behavior of lanthanides on surfaces towards dehalogenation. Importantly, the formation of three-fold Dy-directed organo-metallic coordination complexes was observed. Due to the irregular geometry of the clusters and the sequestering of Ag adatoms by dysprosium, further annealing of the sample resulted in the formation of supramolecular islands of debrominated aryl monomers or dimers, drastically inhibiting the Ullmann reaction beyond trimers and thus not forming polymeric wires. Our results highlight the importance both of the nature and the geometry of the coordination bond to direct covalent reactions on surfaces, and open new catalytic protocols for the on-surface synthesis from molecular precursors with atomic control of the polymeric length.

In summary our results highlight the great potential of organic, supramolecular and surface chemistry to tailor lanthanide nanoarchitectures on surfaces, where lanthanides are hosted on distinct coordination environments, ranging from lateral- to macrocycle-coordination. Future studies are necessary to elucidate the magnetic, optical, sensing and catalytic properties of the distinct nanoarchitectures. In this regard we anticipate the use of
single atom paramagnetic resonance or X-ray Magnetic Circular Dichroism to corroborate the magnetic properties envisioned in this thesis. In order to decouple lanthanides from the perturbing influence of a metal, strategies to grow metal-organic architectures on ultra-thin film insulators (such as h-BN, graphene, MgO or NaCl) are mandatory. Provided sufficient decoupling, tip-induced electroluminescent experiments would be highly interesting, since lanthanide elements have unique narrow-line emitting properties, with emission both in the visible and the infra-red. Finally, the response of the metal-organic frameworks or metallated porphyrinoids towards molecular gases would be of high relevance both for the fields of sensing and catalysis.

Thus, the field of on-surface synthesis of lanthanide nanomaterials is just emerging and offers fascinating opportunities and challenges for the science and technology of the 21st century.
Conclusiones

Esta tesis describe el diseño en superficies de nanomateriales que incorporan lantánidos. Con este propósito, se han seguido diversas estrategias de coordinación supramolecular: la metalación in situ de distintos macrociclos, el auto-ensamblado de imanes moleculares sintetizados ex profeso, la fabricación de redes metal-orgánicas dirigidas por lantánidos y la reactividad de los elementos lantánidos en el proceso de dehalogenización y formación de complejos organometálicos. La principal técnica para este fin ha sido la microscopía de efecto túnel (STM) por su privilegiada resolución espacial y capacidad para manipular la materia a escala atómica. Como complemento de susodicha técnica, se han utilizado técnicas de promediación espacial como la espectroscopía de fotoelectrones emitidos por rayos X (XPS), y marcos teóricos como la teoría del funcional de la densidad (DFT).

Primero, dos imanes moleculares con geometría de doble tapa (double decker), Dy(OETAP)₂ y Tb(OETAP)₂, han sido investigados sobre los mono-cristales de metales nobles Au(111), Ag(111) y Cu(111). Después
de confirmar que la integridad química de estos compuestos no se había visto modificada al ser sublimados y adsorbidos en las diferentes superficies, se investigó si el desacoplamiento electrónico provisto por los grupos etilos seguía siendo operativo. Las simulaciones DFT demostraron una altura mayor de adsorción y una menor interacción con el substrato en las especies \( \text{Ln(OETAP)}_2 \) en comparación con las especies que no habían sido funcionalizadas. La hipótesis de desacople fue corroborada mediante estudios comparativos llevados a cabo mediante XPS, haciendo de las moléculas \( \text{Ln(OETAP)}_2 \) un candidato prometedor como imanes moleculares en substratos metálicos. Demostrar mediante técnicas de sincrotrón que la anisotropía magnetocrystalina sigue preservándose encima de metales a temperaturas relativamente altas, sería de gran interés para los campos de espintrónica, almacenamiento de información e información cuántica.

Segundo, motivado por el alto número de coordinación exhibido por los lantánidos en química en volumen, se ha evaluado su capacidad para dirigir redes metallosupramoleculares en superficies. Inicialmente se han depositado sobre Cu(111) ligandos ditópicos lineares (TDA), funcionalizados con grupos carboxílicos terminales, para asegurar su transformación en grupos carboxilatos al perder los hidrógenos mediante la acción catalítica de la superficie. A continuación, se ha depositado gadolinio, observando la formación de redes supramoleculares reticuladas con celda unidad cuadrada. El óctuple nodo de coordinación resultante ha sido investigado mediante XPS y DFT, revelando su carácter predominantemente iónico. La robustez térmica de las redes ha sido constatada al realizar medidas a alta temperatura mediante un microscopio VT-STM, dando los primeros signos de disociación alrededor de los 400 K. Después, la versatilidad de estas redes se ha puesto a prueba al usar disprosio como vértice coordinativo en las redes lantánido-carboxilato. Aunque se han conseguido las mismas redes cuadradas al coordinar este lantánido con TDA, al calentar los substratos a 450 K ha surgido en una nueva red hexagonal quasi-regular con vértices séxtuples binucleares exhibiendo el mismo carácter iónico. Finalmente, la modulación de la distancia internodal entre centros de disprosio en las redes con nodos óctuples (redes cuadradas) ha sido demostrada con la sustitución...
de los ligandos lineares. Variando la longitud de los mismos se ha observado la consiguiente variación de distancia entre los vértices de lantánidos sin modificar la teselación cuadrada. La robustez térmica y la versatilidad exhibida por estas redes hacen de ellas prometedoras candidatas para sensores y catalizadores por medio de la coordinación apical. Desarrollar métodos de desacople de las superficies metálicas en las que se soportan sería también relevante para aplicaciones en nano-magnetismo y optoelectrónica.

Tercero, el auto-ensamblado y la metalación in situ con disfropio de porfirinoides con distinto tamaño macrocíclico han sido explorados en Au(111). Por una parte, se ha abierto el campo de porfirinas expandandadas en superficie al observar especies intactas de moléculas HTAP en los mono-cristales de Au(111) y Ag(111). El estudio relativo a su crecimiento en función del recubrimiento ha revelado un auto-ensamblado orientacional de largo alcance. Asimismo, se ha desarrollado un protocolo local de deprotonación de moléculas individuales, mediado por electrones-túnel. También se ha depositado disfropio para inspeccionar la capacidad de los porfirinoides para complejar metales, mostrando una metalación asimétrica del macrocículo, pudiendo servir para aplicaciones de luminiscencia y de reconocimiento molecular.

Por otra parte ha sido estudiada una nueva especie de tetrapirrol con flúor en las posiciones terminales, la 2H-4FTPP. Se han encontrado tres nuevas especies después de dosificar disfropio: (i) Dy-2H-4FTPP, (ii) Dy-1H-4FTPP y (iii) la Dy-0H-4FTPP. Además, se observó una resonancia a bajo voltaje túnel en la especie Dy-2H-4FTPP, que pudo ser atribuida inequívocamente a una resonancia Kondo mediante un estudio de su anchura en función de la temperatura, siendo éste el primer fenómeno Kondo observado en porfirinas lantánidas sintetizadas in situ. Mediante manipulación vertical esta especie puede ser transformada irreversiblemente en Dy-1H-4FTPP o Dy-0H-4FTPP, desapareciendo la resonancia Kondo en el proceso, y anticipando el protocolos para el control de sistemas Kondo en porfirinas.
Por último, la reactividad química del disprosio frente a los arilos bromados ha sido examinada en Ag(111). Por un lado, al ser calentados en ausencia del lantánido los organobromos han seguido una reacción tipo Ullmann resultando en productos poli(p-fenilenos). Incrementando la temperatura se han conseguido fabricar nano-hilos de grafeno (3p-aGNR) mediante dehidrogenización terminal y enlace lateral de los productos. Se ha podido demostrar que la relación entre el inicio de la banda de conducción y la anchura de los nano-hilos es inversamente proporcional. Así mismo, las heteroeuniones entre poli(p-fenilenos) y 6-aGNR han demostrado comportarse como una caja cuántica en las secciones de los nano-hilos. Mediante la comparación con un modelo teórico de los datos experimentales se ha demostrado que las propiedades de los nano-hilos no se ven significativamente alteradas al ser conectadas a los poli(p-fenilenos), así como se ha inferido una interacción débil con el substrato.

Por otro lado, en presencia del lantánido, se ha demostrado la eficiencia catalizadora para llevar a cabo la debrominación de los arilos. Igualmente, se ha podido observar la formación de estructuras organometálicas dirigidas por Dy. Dada la geometría irregular de estos complejos y el hecho que el Dy disminuya la presencia de adátomos de plata, un incremento de temperatura ha resultado en la formación de islas supramoleculares de arilos debrominados, inhibiendo casi por completo la reacción de Ullmann más allá de dímeros o trímeros y por tanto frenando la formación de poli(p-fenilenos). Estos resultados resaltan la importancia de la naturaleza y la geometría del enlace coordinativo para garantizar el posterior enlace covalente, abriendo un nuevo protocolo catalítico en superficies para controlar atómicamente la longitud de los productos de la reacción.

En resumen, los resultados obtenidos en la tesis remarcan el potencial de la química orgánica, supramolecular y de superficies para diseñar nanoarquitecturas con lantánidos en distintos ambientes coordinativos, aunque futuros estudios son necesarios para elucidar las propiedades catalíticas, de reconocimiento molecular, ópticas y magnéticas de estas nano-estructuras. Además, para poder extraer su máximo potencial muchos de los sistemas
abordados exigen su desacople de las perturbaciones ejercidas por la superficies metálicas, por ello son necesarias estrategias para crecer estas muestras en láminas aislantes ultra delgadas como h-BN, grafeno, MgO o NaCl. Con seguir este objetivo sería sumamente interesante para hacer experimentos de luminiscencia inducida por la punta del STM, y que los lantánidos poseen propiedades de emisión de luz altamente monocromática. Por último, la respuesta de las redes metal-orgánicas y las porfirinas metaladas a gases sería de gran relevancia para los campos de detección molecular y catálisis.

Con todo ello, el emergente campo de los nano-materiales con lantánidos sintetizados en superficies ofrece fascinantes oportunidades y retos para la ciencia y la tecnología del siglo 21.
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1. 2D Self-Assembly and Catalytic Homo-coupling of the Terminal Alkyne 1, 4-Bis (3, 5-diethynyl-phenyl) butadiyne-1, 3 on Ag (111). Borja Cirera, Yi-Qi Zhang, Svetlana Klyatskaya, Mario Ruben, Florian Klappenberger, Johannes V Barth. ChemCatChem. 11, 5, 3281-3288 (2013).


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