Single-electron Transport Spectroscopy Studies Of Magnetic Molecules And Nanoparticles

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SINGLE-ELECTRON TRANSPORT SPECTROSCOPY STUDIES
OF MAGNETIC MOLECULES AND NANOPARTICLES

by

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ABSTRACT

Magnetic nanoparticles and molecules, in particular ferromagnetic noble metal nanoparticles, molecular magnet and single-molecule magnets (SMM), are perfect examples to investigate the role of quantum mechanics at the nanoscale. For example, SMMs are known to reverse their magnetization by quantum tunneling in the absence of thermal excitation and show a number of fundamental quantum mechanical manifestations, such as quantum interference effects. On the other hand, noble metal nanoparticles are found to behave ferromagnetically for diameters below a few nanometers. Some of these manifestations are still intriguing, and novel research approaches are necessary to advance towards a more complete understanding of these exciting nanoscale systems. In particular, the ability to study an isolated individual nanoscale system (i.e. just one molecule or nanoparticle) is both challenging technologically and fundamentally essential. It is expected that accessing to the energy landscape of an isolated molecule/nanoparticle will allow unprecedented knowledge of the basic properties that are usually masked by collective phenomena when the systems are found in large ensembles or in their crystal form. Several approaches to this problem are currently under development by a number of research groups. For instance, some groups are developing deposition techniques to create patterned thin films of isolated magnetic nanoparticles and molecular magnets by means of optical lithography, low-energy laser ablation, or pulsed-laser evaporation or specific chemical functionalization of metallic surfaces with special molecular ligands. However, it is still a challenge to access the properties of an individual molecule or nanoparticle within a film or substrate.
I have studied molecular nanomagnets and ferromagnetic noble metal nanoparticles by means of a novel experimental approach that mixes the chemical functionalization of nano-systems with the use of single-electron transistors (SETs). I have observed the Coulomb-blockade single-electron transport response through magnetic gold nanoparticles and single-molecule magnet. In particular, Coulomb-blockade response of a Mn$_4$-based SET device recorded at 240 mK revealed the appearance of two diamonds (two charge states) with a clear switch between one and the other is indicative of a conformational switching of the molecule between two different states. The excitations inside the diamonds move with magnetic field. The curvature of the excitations and the fact of having them not going down to zero energy for zero magnetic field, indicated the presence of magnetic anisotropy (zero-field splitting) in the molecule. In addition, the high magnetic field slope of the excitations indicates that transitions between charge states differ by a net spin value equal to 9 ($|\Delta S| = 9$), as expected from the behavior of Mn$_4$ molecules in their crystalline form. Anticrossings between different excitations are indicative of quantum superpositions of the molecular states, which are observed for the first time in transport measurements through and individual SMM.
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CHAPTER 1
INTRODUCTION:

Nanoscale electric and magnetic systems are excellent candidates for understanding the relevant parameters governing the transition from the quantum to the classical regimes by changing the size of the system under study. At the nanoscale quantum properties play an important role in the electric and magnetic behavior of the system. Nanoscale magnetic and electric systems have great potential in emerging technologies, such as optoelectronics, molecular spintronics or quantum information and in the improvement of existing and well established technologies, such as solar energy or medical diagnosis. However, a better understanding of quantum properties of nanoscale systems is required to advance in the mentioned directions. The possibility of controlling and manipulating the spin, charge and optical degrees of freedom of a single nanoscale system is of particular importance in this regard.

1.1. Magnetic gold nanoparticles:

Noble metal nanoscale particles have shown great potential for future applications [1-4]. For example, gold nanoparticles deposited in surfaces are excellent catalytic agents for enhancing chemical reaction processes [5, 6], such as the elimination of toxic gases. Gold, as a noble metal, is diamagnetic. However, when gold particles of sizes below a few nanometers are functionalized with thiol groups they show ferromagnetic (FM) behavior [7-14]. The observance of hysteretic magnetic behavior is highly surprising attending to the electronic structure of gold, with completely filled 5d orbital. Two alternative explanations are still competing to account for the
FM behavior. On one hand, there are proposals by which FM is attributed to a size-dependent spin correlation of outer shell electrons, establishing an intrinsic origin of the observed FM behavior. On the other hand, it has been suggested that FM in thiol capped gold nanoparticles is due to a charge transfer between the 5d band of electrons at the gold surface and the sulfur-based ligands attached to the particle, setting FM as an extrinsic property of gold nanoparticles. Magnetic characteristics of nanoscale gold systems are different from transition metal ferromagnets. In particular, the magnetic moment of gold nanoparticles is temperature independent and decreases with increasing nanoparticle size. The latter is taken for some as proof of a surface originated FM response. This phenomenon has been observed in ensembles of particles, where the magnetization has been measured. My interest was directed to measure an individual particle by means of Single-Electron Transistor (SET) devices. The combination of FM in noble metal nanoparticles with established optical properties may have impact on current industries, such as data storage or biomedical imaging and diagnosis.

1.2. Molecular Magnets:

Molecular magnets are molecules with magnetic ions ordered by exchange interaction, showing a ground spin state at low temperature. Such a molecule is [PMo$_{12}$O$_{40}$(VO)$_2$]$^{2-}$, [15] (Figure 1.1) a polyoxometalate [16] which consists of a central mixed-valence core based on the [PMo$_{12}$O$_{40}$] Keggin [17] unit, able to act as an electron reservoir accommodating a variable number of delocalized electrons hopping over the Mo centers, capped by two vanadyl groups containing two localized
spins. The spins on these two $(\text{VO})^{2+}$ units in general are weakly magnetically coupled via the delocalized electrons of the central core.

![Ball-and-stick model of the polyoxometalate](image)

**Figure 1.1: Ball-and-stick model of the polyoxometalate: O (grey), Mo (blue), V (red), and P (yellow).**

For the description of the low-energy states of the polyoxometalate, two cases have to be distinguished: For an even number of electrons on the mixed-valence Keggin core, their spins pair antiferromagnetically to form a total spin 0 state. Then the system can be modeled by the two spins 1/2 on the vanadyl groups weakly coupled via an indirect exchange mechanism mediated by the core electrons. On the other hand, if the number of core electrons is odd, an unpaired spin 1/2 on the core remains and one obtains a set of three coupled spins 1/2 restricting us to two charge states differing by one electron. So changing the number of electrons in the core can change the state of
the molecule. Using this molecule an experimental setup has already been proposed to do quantum computation [18].

1.3. Single-Molecule Magnets:

Within the large molecular family single-molecule magnets (SMMs) present special significance. In particular, plonynuclear SMMs, are molecules, which consist of multiple transition-metal ions bridged by organic ligands. These ions are strongly coupled by an exchange interaction, usually in a ferro- or ferri-magnetic manner, resulting in large magnetic moments per molecule. The large spin, combined with a zero-field splitting, provides an anisotropy barrier to magnetization reversal at low temperatures. SMMs crystals offer several advantages relative to other magnetic structures. All molecules in the crystal have identical spin amplitude and orientation and the same magnetic anisotropy. Weak interactions between SMMs, as well as the dispersion of structural parameters such as molecular symmetry and anisotropy, complicate the study of the intrinsic quantum dynamics of the spin when the molecules are in the crystal. The ability to study an isolated individual SMM is both technologically and fundamentally interesting. The understanding of decoherence processes in nanoscale systems is necessary for the use of SMMs in quantum information processing devices. It is still a challenge to access the properties of an individual SMM within a film or substrate. My research was based on a novel experimental approach that mixes the chemical functionalization of SMMs with the use of SETs for the study of the high-spin states of an isolated SMM by means of transport measurements.
The general giant-spin Hamiltonian explaining a SMM is given by,

\[ H = D S_z^2 - g \mu_B S \cdot H + H_A + H_{\text{int}}, \]  

(1)

The first term represents the uniaxial anisotropy, which results from spin-orbit coupling and generates an easy magnetic axis for the magnetic moment of the molecule. This term causes an energy barrier separating opposite spin projections (Figure. 1.2A). The second term is the Zeeman energy arising from the interaction of the spin of the molecule with an externally applied magnetic field. The last terms correspond to transverse anisotropies (\(H_A\)) and inter- or intra-molecular interactions such as dipolar, exchange, or hyperfine interactions (\(H_{\text{int}}\)). A magnetic field applied along the easy axis of the molecule tilts the potential energy wells, favoring the spin projections in the direction of the field (the background of Figure 1.2B). At certain values of the field, known as resonances (\(H_k = kD/g\mu_B\), with \(k = 0, 1, 2...\)), opposite levels at both sides of the barrier coincide in energy (the background of Figure 1.2B shows the structure of spin levels for the resonance \(k = 6\)). At low temperatures, the hysteresis magnetization curve shows jumps of the magnetic relaxation that coincide with these resonant fields (blue line in Figure 1.2B). This phenomenon was first observed in 1996 by Friedman and coworkers [19] in a Mn_{12}-acetate SMM and interpreted in terms of resonant quantum tunneling of the magnetization (QTM) [19, 20].
Effectively utilizing SETs, fundamental quantum processes such as interference, coherent oscillations, and decoherence in SMMs can be identified at an individual SMM level. SMM-based SET devices would allow the implementation of quantum logic gates and procedures for writing and reading information in an individual molecular magnet [21]. It would also contribute in molecular spintronics applications, such as spin amplification [21, 22], current-induced magnetic switching [22, 23], and Berry-phase magnetic sensors [24, 25].

1.4. Single-Electron transistors:

Electronic transport properties of individual molecules have received considerable attention over the last several years due to the introduction of SET devices [26-38]. A scheme of a three-terminal SET is represented in Figure 1.3A. The molecule is placed between three electrode leads (source, drain, and gate). The electrostatic coupling
between the molecule and the leads is of a capacitive nature, since the ligands surrounding the molecule act as insulating barriers. The capacitances depend primarily on the molecule/lead distances, but also on the molecule's ligand composition. While placed far from the gate, ligands attach the molecule to source and drain electrodes and provide tunneling barriers for the electron to move in and out of the molecule. Therefore, an electric current can flow between the source and drain electrodes through a sequential tunneling process.

**Figure 1.3:** (A) Schematic representation of a three terminal SET. (B) Energy representation of the electrostatic levels of the molecule with respect to the Fermi energies of the source and drain electrodes. $N$ represents the molecule on its neutral charge state, being $N+1$ and $N-1$ its first reduction and oxidation states, respectively. $E_c$ is the charging energy of the molecule. (C) The effect of a bias voltage on the energy configuration of the molecular SET. Note that the first exited state ($N+1$) of the molecule is now available for conduction, since it lies within the Fermi energies of the electrodes.

Figures 1.3B and 1.3C represent the energy landscape of an ideal molecular SET. The black regions on the sides represent the electron Fermi seas in the source and drain electrodes, with $\mu_S$ and $\mu_D$ being the Fermi levels of the leads. The grey blocks represent the tunnel barriers between the molecule and the source/drain leads (note that these barriers can be quite asymmetric since the disposition of the molecule with respect to the electrodes may vary). The horizontal lines in between the barriers represent the charge states of the molecule. The highest of all occupied states (solid
lines) represents the molecule with $N$ electrons and an electrochemical potential $\mu_N$. The first (empty) excited state is separated by an energy $E_c + \Delta E$, where $\Delta E$ is the molecular electronic level spacing and $E_c$ is the energy necessary to add one electron into the molecule (charging energy or redox potential). Conduction through a molecular SET only occurs when a molecular electronic level lies between the Fermi energies of the leads. A bias voltage $V$ applied between the source and the drain moves the Fermi level of one of the leads by $|eV|$. For small bias voltages, $|eV| < E_c + \Delta E$, no current flows though the device because the excited molecular levels are not available to accept conduction electrons (Figure 1.3B). This regime is known as Coulomb blockade. As the bias voltage is further increased, excited states open new conduction channels through the device. Abrupt and discrete changes in the current through the SET will be obtained every time a new molecular level becomes energetically accessible. The voltage values at which these current steps occur can be tuned by a potential applied to the gate electrode, $V_G$, which moves the molecular states with respect to the Fermi levels of the electrodes.

Coulomb blockade and the characteristic conduction behavior of an SET are illustrated in Figure 1.4, where numerical calculations of the current flowing through an ideal SET are presented. Figure 1.4A shows the typical $I-V$ curves observed in a SET at different gate voltages. Discrete steps are observed whenever a new excited state is accessible for conduction. Contour plots of the current (Figure 1.4B) and the current derivative (Figure 1.4C) as functions of the bias and gate voltages show the characteristic diamond structure representative of Coulomb blockade. Figure 1.4C
illustrates how two consecutive charge states of the molecule ($N$ and $N+1$) are separated by excitation lines. These lines intersect at the point where the gate voltage is equal to the charging energy of the molecule. The $dI/dV$ plot of an SET also reveals the level structure of the molecule and thus constitutes a powerful spectroscopy technique to study the energy landscape. Typically, the transition region between two charge states of the molecule contains multiple excitations that can be traced to the molecule’s energy levels. For example, Figure 1.4D shows the differential conductance of a molecule where the current flows through two levels of the first excited charge state. As in other spectroscopic techniques, the position, the shape, the magnitude, and the slope (among others) of the conduction excitations unveil characteristics that are both intrinsic (i.e., the electronic nature of the molecule) and extrinsic (i.e., the disposition of the molecule with respect to the electrodes) of the system under study.

Figure 1.4: A) Calculated current for an ideal single-state molecular SET (upper A-C scheme) as a function of the bias voltage, $V$, for different gate voltages, $V_g$. B) $I$ and C) $dI/dV$ contour-plots of a single-level molecular SET calculated assuming asymmetric barriers and tunnel rates. The dashed color lines in B correspond to the $I$-$V$ curves shown in A. D) $dI/dV$ contour plot of an ideal double-level molecule (lower D scheme).
CHAPTER 2
EXPERIMENTAL SETUP:

2.1. Atomic Force Microscopy:

Atomic Force Microscopy or Atomic Force Microscope (AFM) is often called the "Eye of Nanotechnology". AFM is also recognized as SPM or Scanning Probe Microscopy, is a high-resolution imaging technique and can resolve features as small as an atomic lattice in the real space. It permits researchers to study and control molecular and atomic level features.

Figure 2.1: Working principle of AFM in contact mode.

The working principle of AFM is illustrated in Figure 2.1. To image a surface AFM brings down a cantilever tip in contact with the surface. The cantilever bends upwards as a result of ionic repulsive force from the surface applied to the tip. A laser spot reflected off to a split photo detector measures the amount of bending and used in
calculating the force. The vertical movement of the tip follows the surface profile when scanning the tip across the surface with constant force and is recorded as the surface topography by the AFM.

The idea of AFM was originated from Scanning Tunneling Microscopy or the Scanning Tunneling Microscope (STM), which was invented in 1981 by G. Binnig and H. Rohrer who shared the 1986 Nobel Prize in Physics for their invention. Although an outstanding technique, STM is limited to imaging conducting surfaces.

As it can be used for imaging any conducting or non-conducting surface, AFM has much extensive potential and application. The number of applications for AFM has increased exponentially since it was invented in 1986 and now an essential tool for many fields of nanoscience and nanotechnology. It offers the ability to view and understand events as they happen at the molecular level which will broaden our understanding of how systems work and open the possibility of new discoveries in many fields. Life science, materials science, electrochemistry, polymer science, biophysics, nanotechnology, and biotechnology are some among them.

AFM has a number of advantages over other techniques that make it preferred among leading researchers. It made high-resolution and three-dimensional information in real space easily achievable with little sample preparation for low-cost. *In-situ* observations, imaging in fluids, temperature and environmental controls are all possible. The AFM technique has been greatly improved over the past decade. A number of imaging modes have been developed for various applications.

(Source: Agilent Technologies)
2.1.1. **Tapping mode:**

![Diagram of tapping mode AFM](image)

Figure 2.2: Working principle of tapping mode AFM where the cantilever and tip keep on vibrating at a certain frequency and map the surface from the variation of amplitude.

In tapping [acoustic AC] mode a transducer attached to cantilever housing is used to excite the cantilever into oscillation. The amplitude of oscillation when the tip is far from the surface reduces as the tip approaches the surface.

Contact mode AFM often has a disadvantage for samples that are either weakly bound or soft because the tip can simply move or damage the surface feature and the resulting images are generally not high resolution. The advent of AC mode AFM, which operates in the intermittent contact regime or in the non-contact regime, provides a solution to this problem.

In tapping mode, the cantilever nears its resonant frequency. Tapping or AC mode AFM can be classified into two categories, intermittent contact mode and non-contact mode, depending on the force regime and the tip-sample separation distance. The
interaction between the tip and the sample is predominately vertical, thus negligible lateral forces are encountered. Consequently, AC mode AFM does not suffer from the tip or sample degradation effects that are sometimes observed after many scans in contact mode AFM, and it is a technique for imaging soft samples. In AC mode, tip-sample force interactions cause changes in amplitude, phase and the resonance frequency of the oscillating cantilever. The spatial variation of the change can be presented in height (topography) or interaction (amplitude or phase) images that can be collected simultaneously. The system monitors the resonant frequency or amplitude of the cantilever and keeps it constant by a feedback circuit that moves the scanner up and down. The motion of the scanner at each probe location is used to generate a topographic data set. The amplitude change at each probe location forms the amplitude image. The phase data is the result of the phase lag between the AC drives input and the cantilever oscillation output at each probe location. Consequently, contrast in phase images, which are due to differences in material properties, can provide very useful information. In addition, fine morphological features are easily observed in amplitude and phase images.

2.1.2. Gold mica substrates:

Usually ligands attached to nanoscale system have affinity to gold, so in SETs the electrodes are made of gold. To successfully deposit molecules or nanoparticles on SET, extensive study of the process is necessary. I have used AFM imaging to examine deposition by self-assembly. Imaging nanoparticle or molecules, which are 1-5 nm in size requires very flat gold surfaces with roughness of one tenth of nm or
better. Prepare a flat gold is not a straightforward process as evaporated gold tend to become rough and grainy. First I tried evaporating gold on cleaved mica surface and then annealed the substrate in butane flame. Figure 2.3 is showing e-beam evaporated gold surface on mica with grain size of ~25 nm. So resolving anything smaller that 25 nm is not possible. So I choose to use commercially available flat gold surface.

![AFM image of E-beam evaporated gold surface on mica.](image)

One such option is high purity atomically flat surface gold surface epitaxially grown onto green mica in a high vacuum. This surface is perfect for imaging nano materials. The resulting gold surface is 1500 angstroms thick and composed of flat Au (111) terraces up to 280,000 nm². These substrates were bought from Molecular Imaging and I used them as received. To improve the flatness I have tried annealing it in
furnace in inert atmosphere, but the improvement was little. Moreover it caused bubble formation on the surface may be because of overheated mica.

Figure 2.4: AFM image of (A) epitaxially grown gold on green mica, (B) Scope trace of the image showing height profile.

Epitaxially grown gold on green mica with approximately 500×500 nm² flat terrace is shown is Figure 2.4A. From the scope trace we can observe that the flat terrace has roughness of one tenth of a nanometer, which is ideal for imaging nanoscale system.
2.2. Fabrication of Single-Electron Transistors:

Measuring electrical conduction through an individual molecule is not a straightforward task. The main difficulty is the impossibility of obtaining electrodes separated by just a few nanometers (< 3 nm) using conventional lithographic techniques. There are several approaches that try to circumvent this problem. Scanning probe microscopy techniques, such as STM [39-42] or AFM [43] have been widely used to study the conduction through individual molecules deposited on a metallic surface. However, this approach requires sophisticated instrumentation, extensive expertise in low-temperature techniques, and cannot make use of a gate electrode to study the different charge states of the molecule. Alternative approaches involve the on-chip fabrication of nm-size gap electrodes. There are several such methods: The mechanical break junction technique [44] (where a suspended nanowire is broken by stress applied to the substrate), the electrodeposition technique [36] (where a large gap is reduced by electrodeposition), the electromigration technique [38] (where a metal nanowire is broken by a current), and others (Refs. [27-37]). Deposition of the nano scale system is an important step in the process. To get a single nanoparticle or molecule in the gap it is very important to have monolayer coverage on the nanowire, so the study of assembling them is necessary. It’s also very important in increasing the yield of the process, which is typically very low (~ 5%).
2.2.1. Lithography Process:

I have prepared the chip with the nanowires with the help of optical and e-beam lithography techniques on thermally oxidized doped silicon substrate. The insulating top silicon dioxide layer is ~ 1 µm thick. I used three layers of photolithography to pattern gold contact pads, nanowire connections and aluminum gate with smallest feature size of 6 µm. I carried out the whole process in clean room environment and used bilayer resist for better liftoff. The substrate was prepared for photolithography, following the steps below:

a) Spin on LOR 3A with a spin coater on a clean Si-SiO2 wafer at 3000 rpm for 30 seconds and bake it for 5 minutes at 170°C on a hotplate to evaporate the solvent of the resist.

b) Spin on Shipley S1813 at 5000 rpm for 30 seconds and bake on hotplate for 2 minutes at 115°C.

Then I UV-exposed the substrate on a mask aligner for 7 second and developed it by first immerse in CD-26 for 45 seconds, to remove the broken exposed polymer chains exposed to UV, followed by rinsing in deionized water to stop the process. Next I backed the substrate for 5 minutes at 125°C to make Shipley S1813 hard. Then I developed it for a second time in CD-26 for a minute. This time the developer worked only on LOR 3A to produce an under cut, which helps in metal liftoff.

After writing the first layer I evaporated 2 nm of chromium and 10 nm of gold by e-beam evaporation. I performed the liftoff process in warm PG Remover solution. I
kept this base layer underneath the contact pads to make the connection to the gates and nanowires smooth. A second layer of gold was aligned in the same way by evaporation of 3 nm of chromium and 220 nm of gold. This layer is made relatively thick to minimize the resistance of the circuit and facilitate micro wire bonding. The second layer overlapped with the first layer and leave only narrow steps where the gates and nanowires would later connect. In the next step I wrote the gate pattern on the substrate following the same optical lithography process and deposited 15 nm of aluminum by thermal evaporation at liquid nitrogen temperature. Our ultra high vacuum thermal evaporation setup has good control of the evaporation rate, which I kept it in between 0.2 - 0.3 Å/s to increase film uniformity. The low temperature evaporation was done to get a smoother aluminum film that would minimize gate leakage and improve its performance. The substrate was left in vacuum for at least 8 hours after the aluminum evaporation to let it warm to room temperature before taking it out from evaporation chamber to prevent moisture condensation. Afterwards the substrate was left in open air for 12 hours to let the aluminum to oxidize and form 1-2 nm Al₂O₃ layer. This oxide acts as insulator in between aluminum gates and gold nanowires. At this point the substrate was ready for the final step, which is to make nanowires. The smallest feature in the nanowire is 100 nm and is not attainable by optical lithography. Therefore, the nanowires are fabricated with the help of e-beam lithography. In this process high-energy electron is used instead of UV light as in case of optical lithography, thus has much better resolution because of the smaller beam size. A bilayer e-beam resist, consisting of MAA and PMMA was used in the process. To prepare the substrate for e-beam lithography I followed the steps bellow:
a) Spin on MMA resist at 4000 rpm for 60 seconds and bake on hotplate for 5 minutes at 175°C.

b) Spin on PMMA resist at 6000 rpm for 60 seconds and bake on hotplate for 5 minutes at 175°C.

Figure 2.5: (A) Design perspective and of our SET device. The substrate is pure silicon with a one-micrometer silicon oxide layer on top. (B) AFM image of a zoomed area in the chip where the wire nanoconstriction and the aluminum gate are shown. (C) SEM image of the gold nanowire.
After writing the nanowire pattern I developed the substrate by immersing in 1:3 solution of MIBK: IPA for a minute and rinse in IPA to stop the process. I thermally evaporated 17 nm gold and lifted off in warm PG Remover solution as the final step of single electron transistor preparation. AFM and SEM images of our nanowires are shown in Figures 2.5B and 2.5C. The 6 µm wide aluminum gate is shown in Figure 25B underneath the nanowire.

![Graph showing breaking current distribution of nanowires as a function of low temperature resistance.](image)

**Figure 2.6:** Breaking current distribution of nanowires as a function of low temperature resistance.

To get consistent result from the breaking of nanowires and gate performance, I needed to find optimum thickness for them. The breaking current density for a gold wire is approximately $10^{12}$ A/m$^2$ [45]. To break them within 10 mA, the cross section of the wire have to be less than $(100$ nm$)^2$. The thicker the nanowires are the higher
the current must be to break them, as their width is fixed (~ 100 mn) from the fabrication process. Figure 2.6 shows the breaking current distribution of nanowires as a function of the nanowire resistance. On the other hand if the thickness of the gold nanowire is less than 10 nm, it might become too grainy. As the nanowires are on top of aluminum gate, the gate thickness should also be less than that of the nanowires. I have performed AFM image thickness analysis on devices from six different batches of fabrication as shown in Figure 2.7 and 2.8. Each point in the graph represents average thickness of several devices from a particular batch. The desired ranges of values fall in the marked areas.

![Figure 2.7: Dependence of gate resistance on thickness from AFM analysis.](image-url)
Figure 2.8: Dependence of gold nanowire resistance on thickness from AFM analysis. The resistance of the SET device was measured in the cryostat, thus include its wire resistance (~ 140 Ω).

The desired thicknesses I found to be working are summarized below:

First layer: ~ 12 nm (orange in Figure 2.5A)
Second layer: ~ 220 nm (yellow in Figure 2.5A)
Gate layer: ~ 14-16 nm (gray in Figure 2.5A)
Nanowire: ~ 16-18 nm (pink in Figure 2.5A)

2.2.2. Nano-gap formation by Electromigration:

To create nano-gap size electrodes, I have employed the electromigration breaking technique [36]. Figure 2.9 shows the electromigration-induced breaking (T = 4 K) of a gold nanowire. The current across the nanowire increases linearly with the voltage, before starting to deviate at the beginning of the gap formation. Then a controlled feedback algorithm is used to complete the breaking of the wire in a controlled way.
This process is repeated until the breaking voltage reaches a much lower value compared to the initial. With the help of the feedback loop, I reduced the breaking voltage below 0.5 V and then ramp it up continuously.

![Graph](image_url)

**Figure 2.9:** The nanowires were broken by electromigration at low temperature to get nanogaps.
Figure 2.10: A histogram of low bias tunnel resistance of 220 nanowires broken by feedback-assisted electromigration process.

The histogram in Figure 2.10 shows the low bias tunnel resistance of 220 nanowires broken by feedback assisted electromigration. From measurements by A. Morpurgo et. al. [46] on the tunnel gap between two gold electrodes suggest that the resistance of ~1 nm gap is ~1 GΩ. Gap resistances of 100 nanowires were within 1 GΩ, indicating that the yield rate of 1 nm gap formation was 46%. Tunnel resistances of 192 wires were below 40 GΩ. So this process produces small gaps (< 3 nm) with high yields (~ 90%).
2.2.3. Multilayered Au/Pt/Au nanowires:

Single layer Au and Pt or multilayered Au/Pt/Au nanowires can be fabricated following this technique, depending on the specifics of the experiment. I used Au-nanowires for SMM-based SETs and Au/Pt/Au-nanowires for gold nanoparticle-based SETs.

To maintain the gap size constant after breaking, gold nanowires need to be broken and kept at low temperature as gold-gaps widen over time at room temperature (Figure 2.11A). I used Gold-based SETs to study SMMs, a monolayer of which was deposited before the electromigration breaking process at low temperature. Unfortunately, this is not possible when working with gold nanoparticles, since the local temperature raise during the electromigration breaking would melt the nanoparticles. So to study gold nanoparticles the nanowires need to be broken before deposition of the particles. Therefore, the gap needs to be generated before the deposition process, which, evidently, needs to be performed at room temperature. For this I used SET devices based on platinum (Pt) nanowires, on which nanoscale gaps are known to remain unchanged over a period of several days at room temperatures. Unfortunately, thiol-capped gold nanoparticles do not stick well to Pt surfaces. Figure 2.11B and 2.11C shows AFM images of Au and Pt surfaces after 3 hours deposition of ~ 2.6 nm diameter gold nanoparticles. It is clearly visible that the Au surface is homogeneously covered with particles, while the Pt surface barely contains a few. I used Pt nanowires (~20-25 nm thick) covered with a thin (~2-3 nm) gold layer to increase adhesion of the thiol-capped particles while maintaining nanometer-sized gaps constant for hours. Figure 2.11D shows how the gap resistance of a Pt/Au
nanowire remains constant for more than 15 hours (Gaps resistances are observed unchanged after several days)

Figure 2.11: (A) Room temperature resistance recorded on a Au-wire nanogap after formation, which increases steadily over time. (B) AFM of gold nanoparticles deposited for 3 hours in gold surface. (C) AFM of gold nanoparticles deposited on Platinum surfaces. (D) Resistance of a Pt/Au nanowire gap after formation, which remains constant for days at room temperature.
3.1. Magnetic gold nanoparticles:

Gold nanoparticles (NPs) stabilized by means of a surfactant, i.e., weak interaction between protective molecules and Gold surface atoms, are diamagnetic, as bulk Gold samples. It has been also shown that in Gold NPs capped with strong interacting thiols, the number of holes in the $5d$ band increases resulting in an induced ferromagnetic response. The apparent ferromagnetism is associated with $5d$ localized holes generated through Au-S bonds [47]. These holes give rise to localized magnetic moments that are frozen in due NPs the combination of the high spin-orbit coupling

Figure 3.1: The structure of a functionalized gold nanoparticle is represented by a stacking model of red balls. The capping molecules are also shown using a ‘ball–stick’ model: hydrogen (white), carbon (grey), nitrogen (blue), oxygen (green) and sulfur (yellow).
(1.5 eV) of gold and the symmetry reduction associated with two types of bonding: Au-Au and Au-S. In thiol-capped Au NPs the counterbalance between size effect and ligand effect tunes the structure and total number of $d$ holes. Since magnetic behavior is determined by the $d$ electrons, it is expected that the magnetic properties can be also tuned upon different capping and size. It should be remarked that nanosized particles holding a permanent magnetic moment play a key role for the basic understanding of magnetism as well as for miniaturized data-storage technology [48] and may reveal novel applications in energy related nanotechnology applications. My study was aimed at the understanding of the capping induced ferromagnetism at the individual nanoparticle level.

Crucial for the study of electrical transport through individual particles in a SET device is a controlled and homogeneous deposition of the particles in atomically flat surfaces, which sets the focus of the study I presented in this section of the thesis.

### 3.2. Deposition of gold nanoparticles:

To deposit the gold nanoparticles on the substrate, they need to be in a colloidal solution of suitable solvent and concentration. Gold nanoparticles were received from research group of Dr. Florencio Hernández (Department of Chemistry, University of Central Florida) in concentrated colloidal solution in toluene. Then I added more solvent to dilute the stock solution. For getting a monolayer of nanoparticles choosing the right concentration is very important. To find proper concentration I prepared several diluted solutions and deposited gold nanoparticles on gold-mica substrate for 5 minutes and imaged. Figure 3.2 shows images of nanoparticles deposited from 1:25
and 1:50 diluted solution. It is clearly visible that with these concentrations nanoparticles are not forming a uniform layer. So I further diluted the solution (1:100) to get slower and more uniform deposition. I dipped several pieces of gold-mica substrate onto the solution to self-assemble the nanoparticles and taken out at different time intervals to compare the effect of deposition time on self-assembly process. Right after taking out of the solution it was blow dried in nitrogen gas to minimize the surface tension effect. Once the samples were ready then I took AFM images. Each sample was imaged at several different areas to ensure uniformity.

Figure 3.2: AFM images of nanoparticles deposited from (a) 1:25 and (b) 1:50 diluted solution.
3.2.1. Deposition for 16 minutes:

Figure 3.3: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 16 minutes.

3.2.2. Deposition for 37 minutes:

Figure 3.4: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 37 minutes.
3.2.3. Deposition for 64 minutes:

Figure 3.5: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 64 minutes.

3.2.4: Deposition for 400 minutes:

Figure 3.6: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 400 minutes.
3.2.5: Deposition for 1100 minutes:

![AFM Image](image)

**Figure 3.7: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 1100 minutes**

3.2.6. **Discussion:**

From the AFM image analysis I observed that when assembled for 16 minutes individual molecules are distinguishable without significant layer formation. It was also confirmed by the scope trace height profile. From the height distribution of individual nanoparticles we can also find the average diameter of the molecules to be 2.6 nm, with a Gaussian distribution width of 1.46 nm (see Figure 3.8). This result agrees with the average diameter extracted from optical characterization (plasmonic resonance).

When I increased the deposition time to 37 minutes still there were mostly individual particles with higher surface density. The results of deposition for 64 minutes were similar to that of 37 minutes but the individual nanoparticles started to form clusters.
To get a uniform coverage of the surface I next tried 400 minutes. This time over 60% of the gold mica-surface was covered with gold nanoparticles with some larger clusters. It was evident from these studies that as the deposition time increases the assembly process becomes slower. So to get a monolayer I allowed 1100 minutes of deposition time and the result was a monolayer of molecules on the gold surface with some clusters of molecules on top of first layer. The cluster formation seemed to be unavoidable at this concentration. To be able to measure properties of an individual molecule it is very important to get a monolayer in the coverage. From my study of time dependant deposition and taking, concentration and deposition time in to account the best case scenario is to deposit from 1:100 diluted solution for 1000 minutes.
3.3. Gold nanoparticle-based SET results:

In the case of ferromagnetic nanoparticles (for example the study of Co-based SETs by Gueron et al. [49]), the magnetic field behavior of the transport excitations reveal the anisotropic nature of the ferromagnetic nanoparticle. The standard Hamiltonian used to explain the magnetic field dependence of FM-nanoparticle-based SETs is,

\[
H = -K_m \mu_n S_z^2 / \sqrt{S(S+1)} - \mu_n \vec{S} \cdot \vec{g}_{\text{eff}} \cdot \vec{H}.
\]  

The first term represents the uniaxial anisotropy of the nanoparticle and the second term is the Zeeman energy associated to the coupling between the spin and the external magnetic field. It is therefore expected that if gold nanoparticles behave ferromagnetically, this behavior will be observable through single-electron transport measurements.

I obtained preliminary results that demonstrate the characteristic coulomb diamond conduction at 4.2 K. I have employed Pt/Au-based SET devices (described in section 2.2.3) to investigate thiol-capped gold nanoparticles. Figure 3.9a shows several \( I-V \) curves obtained at different gate voltages. Steps corresponding to single-electron transport excitations that move with the gate voltage are clearly observed at this temperature. Figure 3.9b shows \( V_{\text{bias}}-V_{\text{gate}} \) contour-plot representative of the electrical conduction in a SET.
Figure 3.9: (a) $I-V$ curves recorded at 4.2 K on a thiol-capped gold nanoparticle SET. Steps in the current correspond to single-electron excitations of the transistor. The gate voltage moves the excitation steps as can be clearly seen in (b), where a $V_{bias}-V_{gate}$ contour-plot shows the characteristic Coulomb-blockade diamonds associated to different charge states of the nanoparticle.
Several Coulomb blockade diamonds are observed and associated to different charge states of the nanoparticle. From the geometry of the diamonds I extracted information about the capacitances associated to the connection between the particle and the three SET electrodes ($C_S = 0.65 \text{ aF}$, $C_D = 0.65 \text{ aF}$, $C_G = 0.3 \text{ aF}$) as well as the charging energy, $E_C \sim 50 \text{ meV}$, of the nanoparticle. These parameters are in good agreement with similar experiments reported in the literature. An approximated value of the energy spacing between excitation levels of this particle is $\delta E \sim 10 \text{ meV}$, in agreement with 2.6 nm gold nanoparticle (average size).

Future study of single-electron transport measurements are pending on the availability of research funds.
CHAPTER 4
TRANSPORT STUDY THROUGH A MALECULAR
NANOMAGNET:

4.1. Introduction:
At the nanoscale, quantum properties play an important role in the electric and magnetic behavior of the system. The control and manipulation of spin and charge degrees of freedom of molecular nanomagnets has developed into a major challenge during the last years, motivated by potential applications in emerging technologies, such as optoelectronics, molecular spintronics or quantum information and computation. There is also a significant effort within the molecular nanomagnetism community aimed in this direction. However, a better understanding of the quantum properties of molecular systems at the individual molecule level is required to advance in the mentioned directions.
4.2. Mn$_{12}$-acetate Single-Molecule Magnet:

Mn$_{12}$-acetate [Mn$_{12}$O$_{12}$(O$_2$CR)$_{16}$(H$_2$O)$_4$] was synthesized and reported in 1980 by Lis (1980). In our case R = Me$_3$CH$_2$, which is a derivative of Mn$_{12}$ molecule known as Bu$^{t}$-acetate. This particular derivative has weaker coupling to the Au electrode. Figure 4.1 shows a ball and stick model of the molecular structure including only some organic ligands. No water of crystallization and acetic acid molecules are included, although they may play an important role, in particular for the process of tunneling of the magnetization. The inner four Mn atoms which are in the charge state Mn$^{4+}$ (s = 3/2) form, together with four O atoms, a (slightly distorted) cube. The eight outer Mn

Figure 4.1: The ball and stick model of Mn$_{12}$-acetate. (a) The entire molecule, with methyl groups replaced for clarity by hydrogen atoms (golden). Here, H (golden), O (red) and Mn (blue). (b) A different perspective of the magnetic core of Mn$_{12}$O$_{12}$ with inner four Mn$^{4+}$ ions (golden) and surrounded by a ring of eight Mn$^{3+}$ ions (blue).
atoms are in the $\text{Mn}^{3+}$ ($s = 2$) charge state. The inner Mn ions are coupled antiferromagnetically to the outer ones, yielding a ferrimagnetic ground state with a total spin $S = 8 \times 2 - 4/3 \times 2 = 10$. An evidence of the $S = 10$ ground state has been obtained from high field magnetization studies. There are lots of interests and efforts to study $\text{Mn}_{12}$ out of its natural crystalline environment by for example depositing the molecule in different surfaces. However, the $\text{Mn}_{12}$ molecules tend to degrade and lose particular properties when taken out of their natural environment, that they poses when in crystal form.

4.2.1. Deposition on gold surface:

To deposit the molecules on the substrate they need to be in a solution of suitable solvent and concentration. $\text{Mn}_{12}$-acetate molecules were received in crystalline form. I added 2 mg of microcrystalline molecule to 10 ml of dichloromethane ($\text{CH}_2\text{Cl}_2$) and stirred gently. The resulting solution was of concentration $\sim 2$ mMol. I then dipped several pieces of gold-mica substrates onto the solution to self-assemble the molecules and took them out at different time intervals to compare the effect of deposition time on self-assembly process. Right after taking out from the solution the substrate was blow dried in nitrogen gas to minimize the surface tension effect. Once the samples were ready, I took AFM images. I imaged each sample at several different areas to ensure uniformity.
Deposited for 6 minutes:

Figure 4.2: (a) AFM Image of Mn$_{12}$-acetate magnetic molecules on gold-mica surface deposited for 6 minutes. (b) Scope trace of the image showing height of the molecules.
Deposited for 10 minutes:

Figure 4.3: (a) AFM Image of Mn_{12}-acetate magnetic molecules on gold-mica surface deposited for 10 minutes. (b) Scope trace of the image showing height of the molecules.
Deposited for 20 minutes:

(a) AFM Image of Mn$_{12}$-acetate magnetic molecules on gold-mica surface deposited for 20 minutes. (b) Scope trace of the image showing height of the molecules.

Figure 4.4: (a) AFM Image of Mn$_{12}$-acetate magnetic molecules on gold-mica surface deposited for 20 minutes. (b) Scope trace of the image showing height of the molecules.
Deposited for 32 minutes:

(a) AFM Image of Mn$_{12}$-acetate magnetic molecules on gold-mica surface deposited for 32 minutes. (b) Scope trace of the image showing height of the molecules.

Figure 4.5: (a) AFM Image of Mn$_{12}$-acetate magnetic molecules on gold-mica surface deposited for 32 minutes. (b) Scope trace of the image showing height of the molecules.
Deposited for 47 minutes:

Figure 4.6: (a) AFM Image of Mn$_{12}$-acetate magnetic molecules on gold-mica surface deposited for 47 minutes. (b) Scope trace of the image showing height of the molecules.
Discussion:

From the AFM image analysis I observed that when assembled for 6 minutes individual molecules are distinguishable without significant layer formation (Figure 4.2). It was also confirmed by the scope trace height profile. From the height profile of individual molecules I found the average diameter of the molecules to be ~ 1.5 nm. And it agrees very well with the chemical structure of Mn$_{12}$-acetate. When I increased the deposition time to 10 minutes, still there were mostly individual molecules with higher surface density (Figure 4.3). When deposited time was 20 minutes 30% of the gold surface was covered by mono-layer of molecules (Figure 4.4). At this point I could conclude that as I increased the deposition time the coverage of the gold surface by molecules also increased and with 32 minutes 85% gold surface was covered with monolayer (Figure 4.5). So to get a monolayer I allowed 47 minutes of deposition time and the result was a monolayer of molecules on the gold surface with some molecules on top of the first layer and very small amount of uncovered surface (Figure 4.6). To be able to measure properties of an individual molecule it is very important to get a monolayer of molecules on the substrate. From my time dependent study I concluded that by depositing from solution of 2 mMol concentration for 40-43 minutes, I could get a monolayer of Mn$_{12}$ molecules suitable for SET experiments.
4.2.2. $\text{Mn}_{12} \text{-acetate nanorings}$:

While depositing $\text{Mn}_{12} \text{-acetate}$ on the gold-mica substrate from dichloromethane solution, I observed a very strange behavior of the molecules. Most of the time the molecules arranged themselves on the gold surface and if deposited for enough time they form a monolayer and then bilayer and so on. But for this derivative of $\text{Mn}_{12}$-acetate for some depositions in some area of the gold substrate the molecules arranged themselves in ring shape structures of different heights and diameters. The diameter of the rings mostly varies from 100 nm to 600 nm, though some of them are as large as 1.4 µm. I first noticed these rings while depositing the molecules for 30 minutes from three days old solution for initial study. Some area of the substrate was covered with molecules not forming any regular structures. But in some other area of the substrate they form rings. The same type of ring formation was also found in another gold substrate where I deposited the molecules for 6 minutes from fresh solution.
Three days old solution (30 minutes deposition):

(a) 

(b)
Figure 4.7: AFM image of molecules on gold-mica substrate deposited from three day old solution in different areas (a, b, c) showing ring formation.

Figure 4.8: Diameter distribution of the Mn_{12}-acetate rings deposited from three day old solution.
Discussion:

Figure 4.9: Height distribution of the Mn$_{12}$-acetate rings deposited from three day old solution.

From AFM images I observed uniform distribution of Mn$_{12}$ nano rings through the substrate. The diameter distribution shows that most of the rings are of diameter close to around 150 nm and only very few are 600 nm. The exact reason of this behavior is not yet known. To confirm that the nanorings are indeed formed by Mn$_{12}$-acetate I analyzed the height data of the shorter (smaller height) nanorings. Figure 4.9 shows the height distribution of the nanorings. Closely observing the histogram I noticed that the distribution is not continuous and seems to follow a periodic nature, with a 1.6 nm period is a good indication that Mn$_{12}$ molecules are the unit building blocks of the rings. Further detail study is required to reach any concrete conclusion.
Fresh solution (6 minutes deposition):

(a) [Image of AFM scan]

(b) [Image of AFM scan]

Digital Instruments NanoScope
Scan size: 10.00 μm
Scan rate: 1.001 Hz
Number of samples: 512
Image Data: Height
Data scale: 70.00 nm

Digital Instruments NanoScope
Scan size: 10.00 μm
Scan rate: 1.001 Hz
Number of samples: 512
Image Data: Height
Data scale: 60.00 nm
Figure 4.10: AFM image of molecules on gold-mica substrate deposited from fresh solution in different areas (a, b, c) showing ring formation.

Figure 4.11: Height distribution of the Mn$_{12}$-acetate rings deposited from fresh solution.
Discussion:

After noticing rings in three days old sample I thought that the rings may form as the solution ages. But as shown in Figure 4.10, rings are also observed from fresh made solution deposited for 6 minutes. The rings density in this substrate is lower than in the 30 minutes deposition one, which is reasonable. Figures 4.12 and 4.13 show three dimensional presentation of the AFM images of deposited from three day old solution and deposited from fresh solution respectively. I noticed that the structures are cylinder rather than rings. So the molecules keep piling on top of the other rather than
lying directly on the gold surface. I would be very interesting to further investigate the molecular ring formation since it might allow the fabrication of single molecule magnet based devices.

Figure 4.13: 3D presentation of the AFM image of molecules on gold-mica substrate deposited from fresh solution (FIG. 4.10c).
4.2.3. SET results:

I have measured the Mn_{12}-acetate molecules in the transistor geometry. First the molecules from dichloromethane solution were deposited on the chip with nanowires by self-assembly. To carry this process the chip was dipped in the solution of molecules and kept there for 42 minutes to get a monolayer on the gold nanowires. The chip was placed in a He\textsuperscript{3} cryostat and cool down to 4 K. The wires were broken at low temperature to get smaller gap. To measure a single molecule I needed a gap of the order of the diameter of the molecule. Approximately 90 nanowires were broken at 4 K, typical pre-breaking resistance was 250 ohms at low temperature, with an average break voltage of 1.1 volts and an average breaking current of 4.1 milliamps.

I found two wires which, after breaking showed conduction with gate dependent steps.

Figure 4.14: I-V curves of single or multiple molecules for different gate voltages (device-I)
Figure 4.15: \( \frac{dI}{dV} \) as function of bias and gate voltage in a contour plot (Device-I).

Figure 4.14 shows coulomb blockade and the characteristic conduction for different gate voltages in device-I. The differential conductance \( \frac{dI}{dV} \) is presented as a function of bias and gate voltages for device-I in Figure 4.15. I observed discrete steps whenever a new excited state is accessible for conduction. It follows the characteristic diamond structure representative of Coulomb blockade. The \( \frac{dI}{dV} \) plot also reveals the level structure of the molecule and thus constitutes a powerful spectroscopy technique to study the energy landscape.
Figure 4.16: (a) $I$-$V$ curves observed at different gate voltages (b) contour plot of the current, $I$ and (c) $dI/dV$ as a function of bias and gate voltage. (Device-II)

Figure 4.16 presents the data for the second device.
4.2.4. Conclusion:

Heersche and coworkers [62] first reported Coulomb blockade and conduction excitations characteristic of a molecular SET in an individual Mn$_{12}$ SMM functionalized with thiol groups. Negative differential conductance and current suppression effects were explained in terms of relaxation between excited spin levels of the charged and uncharged states of the Mn$_{12}$. Also Jo and coworkers [63] reported transport through an individual Mn$_{12}$ SMM without any functionalization of the molecules. They found evidence of magnetic anisotropy in some of the studied molecules. Although all these results are very encouraging, they have failed to provide unambiguous evidence that transport occurred through individual SMMs preserving the key quantum properties found in their solid-state form (i.e. QTM, quantum Berry-phase interference, etc.). On the contrary, the data seems to indicate that Mn$_{12}$ molecules tend to change and lose these properties when deposited on surfaces. Not surprisingly, the current effort is focused on the study of more robust SMMs as well as to obtain novel means of preserving the molecules when placed/deposited on surfaces or nanoscale devices (i.e. SETs).

Within this context, I choose to study single-electron transport measurements on mono nuclear magnet i.e. polyoxometalate and Mn$_4$ SMM containing pyridyl-alkoxide chelating groups to electrically protect the magnetic core and to increase the stability of the molecule when deposited on a SET device.
4.3. Polyoxometalate Molecular Magnet:

I have performed a preliminary study of the transport properties of [PMo$_{12}$O$_{40}$(VO)$_2$]$^{q-}$ [15] (Figure 4.17) a polyoxometalate [16] which consists of a central mixed-valence core based on the [PMo$_{12}$O$_{40}$] Keggin [17] unit, able to act as an electron reservoir accommodating a variable number of delocalized electrons hopping over the Mo centers, capped by two vanadyl groups containing two localized spins. The spins on these two (VO)$_2^+$ units are weakly magnetically coupled via the delocalized electrons of the central core. The size (diameter) of the molecule is around 1 nm.

Figure 4.17: Ball-and-stick model of the polyoxometalate: O (grey), Mo (blue), V (red), and P (yellow).
4.3.1. Deposition on gold surface:

To deposit the molecules on the substrate they need to be in a solution of suitable solvent and concentration. Polyoxometalate molecules were received in crystalline form. These magnetic molecules oxidize very quickly in air, so to prevent the molecules from degradation I stored them in nitrogen gas. All process of solution preparation and deposition of the molecules by self assembly were carried in nitrogen environment in a homemade glove box. Deionized water was chosen as solvent as the molecules dissolved in warm water. I flew nitrogen gas through deionized water for 30 minutes to get rid of dissolved oxygen gas. I added 0.2 mg of microcrystalline powder to 20 ml of freshly prepared deoxygenated water and warmed to 50\(^\circ\) C. The resulting solution was of concentration \(\sim 0.1\) mMol. I then dipped several pieces of gold-mica substrate onto the solution to self-assemble the molecules and took them out at different time interval to compare the effect of deposition time on self-assembly process. Right after taking out from the solution the substrate was blow dried in nitrogen gas to minimize the surface tension effect. Once the samples were ready, I took AFM images. Each sample was imaged at several different areas to ensure uniformity.
Figure 4.18: (a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 5 minutes. (b) Scope trace of the image showing height of the molecules.
Deposited for 11 minutes:

Figure 4.19: (a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 11 minutes. (b) Scope trace of the image showing height of the molecules.
Deposited for 38 minutes:

(a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 38 minutes. (b) Scope trace of the image showing height of the molecules.

Figure 4.20: (a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 38 minutes. (b) Scope trace of the image showing height of the molecules.
Deposited for 60 minutes:

![AFM Image](image)

**Figure 4.21:** AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 60 minutes.

### 4.3.2. Discussion:

From the AFM image analysis I observed that when assembled for 5 minutes individual molecules are distinguishable without significant layer formation (Figure 4.18). It was also confirmed by the scope trace height profile. From the height profile of individual molecules I also found the average diameter of the molecules to be ~0.9 nm. And it agrees very well with the chemical structure of polyoxometalate. When I increased the deposition time to 11 minutes still there were mostly individual molecules with higher surface density (Figure 4.19). When deposition time was 38
minutes, most of the gold surface was covered by a mono-layer of molecules (Figure 4.20). At this point I concluded that as the deposition time was increased the coverage of the gold surface by molecules also increased and with 38 minutes nearly reached monolayer coverage. So, to get a monolayer I allowed 60 minutes of deposition time and the result was monolayer of molecules on the gold surface with some molecules on the first layer and very small amount of uncovered surface (Figure 4.21). From my study of time dependant deposition we concluded that by depositing from a solution of 0.1 mMol concentration for 55-60 minutes I could get a monolayer of molecules suitable for SET experiments.

4.3.3. Preliminary SET studies:

I have measured the polyoxometalate molecules in the transistor geometry. First the molecules from the deoxygenated and deionizer water were deposited on the chip with gold nanowires by self-assembly. To carry this process I dipped the chip in the solution with the molecules and kept there for 60 mins to get a monolayer of molecules on the gold nanowires. I placed the chip in a He$^3$ cryostat and cool down to 4 K. The wires were broken at low temperature to get small gaps. I broke approximately 150 nanowires at 4 K with average resistance of 300 ohms at low temperature, with an average break voltage of 0.97 volts and an average breaking current of 2.72 milliamps.
Figure 4.22: (a) Breaking voltage and (b) current of nanowires as a function of low temperature resistance.

Figure 4.23: Typical breaking curve for a 10 nm tall 100 nm wide gold nanowire.
The statistics of electromigration-breaking shows that, the majority of wires (nearly half) were completely broken during the process. Figure 4.24 contains typical post-electromigration states of the nanoscale gaps.

![Graphs](a) CB, Coulomb Blockade, the current goes to zero near zero S-D bias. (b) STP where we see steps in the conduction near zero bias indicating we may be near a changing charge state of the molecule. (c) SMT where we see an asymmetric curve about zero bias. (d) ZBE, non-ohmic behavior near zero bias but at higher S-D bias appears to be ohmic.

NC stands for non-conducting, ZBE stands for zero bias enhancement (non-ohmic), CB stands for coulomb blockade, STP stands for a measurement where we see
conductance steps, and SMT stands for some asymmetric tunneling curve that doesn’t pass through zero current.

A summary of the post-electromigration conduction through the nano-gap after self-assembling of polyoxometalate molecules can be observed in Figure 4.25 in wires broken at 4 K. Note that I did not use the feedback algorithm in breaking these nanowires, explaining the low (~ 50%) yield of conducting steps.

Figure 4.25: Breakdown of post-electromigration statistics based on 155 wires being broken.

I found a few broken wires showing discrete steps in the conductance response. However no gate dependence was observed, with the exception of one molecule,
which was lost after a few measurements. The conclusion is that the molecule should be functionalized with ligands (such as carboxilate groups) to increase the size of the molecule and, thus, increase the chances to bridge the gap in the SET device. Further study of this molecule is waiting research funding.

4.4. Mn₄ Single-Molecule Magnet:

![Figure 4.26: Ball-and-stick model of the [Mn₄(hmp)₆(CH₃CN)₂](ClO₄)₄: Color code: Mn³⁺ green; Mn²⁺ yellow; O red; N blue; C gray; Br brown.](image)

After my inconclusive studies of high nuclearity SMMs (e.g. Mn₁₂) I focused my research efforts on the transport properties of low-nuclearity SMMs. In particular, [Mn₄(hmp)₆(CH₃CN)₂](ClO₄)₄ (where hmp stands for 2-hydroxymethylpyridine), which contains a diamond-shaped magnetic core of four Mn ions ferromagnetically coupled to give a grand spin state, \( S = 9 \). Mn ions are arranged in a double-cuboidal fashion where Mn²⁺ are hepta-coordinated and Mn³⁺ centers hexa-coordinated. Mn³⁺
ions are in a distorted octahedral geometry revealing an expected Jahn–Teller elongation along the axial positions [50]. The Mn₄ SMMs do not contain high oxidation state (Mn⁴⁺), only low Mn oxidation states (Mn²⁺, Mn³⁺) and are less fragile. Mn₄ molecules are structurally robust and resistant to degradation because of containing pyridyl-alkoxide organic groups that both chelate (attach to Mn atoms at multiple positions) and bridge multiple Mn atoms with one or more alkoxide O atoms. One more advantage is that the organic groups can be easily varied, and additional derivatives can be synthesized, providing a family of related Mn₄ SMMs.

4.4.1. Deposition on gold surface:
To deposit the molecules on the substrate they need to be in a solution of suitable solvent and concentration. [Mn₄(hmp)₆(CH₃CN)₂](ClO₄)₄ molecules were received in crystalline form. I added 1.4 mg of microcrystalline molecule to 10 ml of acetonitrile (CH₃CN) and stirred gently. The resulting solution was of ~0.1 mMol concentration. I then dipped several pieces of gold-mica substrates onto the solution to self-assemble the molecules and took out at different time intervals to compare the effect of deposition time on self-assembly process. Right after taking out from the solution I blew dried the substrate in N₂ to minimize the surface tension effect. Once the samples were ready, I took AFM images of them. I imaged each sample at several different areas to ensure uniformity of self-assembly.
Deposited for 30 minutes:

Figure 4.27: AFM Image of magnetic Mn₄ molecules on gold-mica surface deposited for 30 minutes.

Deposited for 75 minutes:

Figure 4.28: AFM Image of magnetic Mn₄ molecules on gold-mica surface deposited for 75 minutes.
Deposited for 225 minutes:

Figure 4.29: AFM Image of magnetic Mn₄ molecules on gold-mica surface deposited for 225 minutes.

Figure 4.30: Height distribution of the Mn₄ molecules deposited from 0.1 mMol solution.
Discussion:

From the AFM image analysis, I observed that when assembled for 30 minutes, a monolayer of Mn₄ molecules cover 85% of the gold surface (Figure 4.27). When I increased the deposition time to 75 minutes most of surface was covered with monolayer and very few molecules may be sitting on top of others (Figure 4.28). When deposition time was 225 minutes, in addition to monolayer coverage, 5-10% was covered by bilayer (Figure 4.29). From my study of time dependant deposition I concluded by that depositing from solution of 0.1 mMol concentration for 70-80 minutes I was able to get a monolayer of molecules suitable for SET experiments. From the height profile of individual molecules I extracted the average diameter of the molecules to be ~1 nm as shown in Figure 4.30, in good agreement with the chemical structure of [Mn₄(hmp)₆(CH₃CN)₂](ClO₄)₄.
4.4.2. Single-electron transport studies:

The quantum properties of SMMs have been typically studied in experiments with macroscopic single crystals containing a large number of nearly identical and decoupled SMMs. Thus the magnetic response of the crystal tends to reflect the quantum properties associated to each individual SMM within the sample. Perhaps the most striking property of SMMs is the presence of steps in the magnetic hysteresis loops that are attributed to resonant quantum tunneling of the magnetization (QTM) [56]. This unique feature of SMMs is a consequence of the quantum superposition of high-spin states of the molecule and has led to the observation of a variety of fundamental phenomena, such as quantum (Berry-phase) interference (BPI) between equivalent QTM trajectories [57,58]. Indeed, BPI in SMMs permits fast tuning of the energy associated with a quantum superposition between spin states. This effect has been proposed for the implementation of two-qubit quantum logic gates in dimeric SMMs where the exchange interaction between opposite sides of the dimer could be tuned [59]. In addition, quantum interference in SMMs would lead to extremely sensitive magnetic sensors at the molecular level [51-55], which could be integrated in nanoscale spintronic devices. Novel features of QTM are expected to manifest themselves in other observables as well. In particular, the effects of QTM on electronic transport remain to be explored in depth both theoretically and experimentally.
The study of an isolated individual SMM is both of fundamental and technological interest, since the ability to control decoherence processes in nanoscale systems is a prerequisite for using SMMs in quantum information processing devices. Several approaches along this direction are currently under development by a number of research groups – for instance, the creation of thin films of isolated SMMs by means of optical lithography, low-energy laser ablation, or pulsed-laser evaporation techniques, and the chemical functionalization of SMMs with special molecular ligands that attach themselves to Au surfaces. Notable advances have occurred in the last few years after several groups obtained strong evidence of the preservation of functionalized SMMs deposited on surfaces [60, 61]. Despite the fact that these are interesting attempts to obtain isolated molecules, it is still a challenge to access the properties of an individual SMM within a film or substrate.

As already discussed in this thesis, an alternative approach to address the magnetic properties of individual SMMs is based on the use of single-electron transistors (SETs) to measure the electronic transport through individual molecules placed between nano-gapped electrodes. Along these lines, several groups have reported observations of electrical transport through a SMM-based SET [62-65]. This is the technique I have implemented to study the magnetic field dependent transport through a Mn₄ based SMM.

I have performed single-electron transport measurements at temperatures down to 240mK in the SMM \([\text{Mn}_4(\text{hmp})_6(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_4\). This molecule forms part of a family of Mn₄ SMMs identified as particularly attractive for the proposed studies
for several reasons: (i) they contain low Mn oxidation states ($2\text{Mn}^{2+}, 2\text{Mn}^{3+}$) and thus no high oxidation state Mn$^{4+}$ that may be the main reason for the fragility (due to redox reactions) of the Mn$_{12}$ SMMs initially employed by many groups for SET and other studies on surfaces; (ii) they contain pyridyl-alkoxide organic groups that both chelate (attach to Mn atoms at multiple positions) and bridge multiple Mn atoms with one or more alkoxide O atoms, thus making these Mn$_4$ molecules more structurally robust and resistant to degradation than Mn$_{12}$; and (iii) the organic groups can be easily varied, and additional derivatives can be targeted, providing a family of related Mn$_4$ SMMs for comparative subsequent studies. In particular, some of the possible chelates to be employed (hmpH, pdmH$_2$) are aromatic, some (mdaH$_2$, teaH$_3$) are not, and this will allow comparative studies with different Mn$_4$ SMMs to address the involvement of ligand aromatic groups in the transport of an electron onto and off the molecule.

I used three-terminal SET devices to measure the electrical transport through individual Mn$_4$ SMMs at low temperatures ($T = 235$ mK). Figure 4.31a shows the dependence of the electrical current ($I$) through a single molecule as a function of the bias voltage ($V_{\text{bias}}$) for different gate voltages ($V_{\text{gate}}$). Steps in the $I$-$V$ curves correspond to transitions between the transistor electrodes through an accessible charge state of the molecule. At $V_{\text{gate}} = 0$ (black line), a large bias voltage ($V_{\text{bias}} \sim 80$ meV) needs to be applied in order to allow current to flow through the molecule. This corresponds to the charging energy (i.e. redox potential) necessary to add/subtract one electron into/from the molecule. Below this energy, the current is
suppressed (CB regime). Figure 4.31b shows the Coulomb-blockade response of a Mn₄-based SET device recorded at 235 mK. The appearance of two diamonds (two charge states), with a clear switch between one and the other is indicative of a conformational switching of the molecule between two different states separated by energy of 49 meV. Figure 4.32 shows differential conductance of the Mn₄-SET device as a function of the bias and gate voltages at different magnetic fields. In all the graphs regardless of magnetic field the switch of states is present. Given the fact that the excitations of the two charge states do not cross and are independent of the experimental condition i.e. magnetic fields, I think that these two states may be associated to different ground state configurations of the molecule, which affect the coupling to the electrodes, making the diamonds centers to be shifted in gate voltages.
Figure 4.31: (a) Electrical current through a Mn$_4$ SMM as a function of the bias voltage, measured at different gate voltages at a temperature of 235 mK. (b) Contour plot of current through the Mn$_4$-SET device as a function of the bias and gate voltages.
Figure 4.32: Differential conductance of the Mn₄-SET device as a function of the bias and gate voltages at different magnetic fields. The two observed charge states separated by 49 meV correspond to a conformational electrostatic change of the molecule relative to the gate.

As the gate voltage is increased, the current step moves to lower bias values. This can be clearly observed in Figure 4.33, where the differential conductance ($dI/dV$) of the device is given as a function of $V_{\text{bias}}$ and $V_{\text{gate}}$, showing the characteristic electrical excitation crossings separating CB areas (dark) with $N$ and $N+1$ electrons in the molecule. The sudden vertical transition ($V_{\text{gate}} = -0.82$ V) is indicative of a
conformational switching of the molecule between two different states. All the excitations have the same slope (same coupling between molecule and electrode leads), which is indicative of transport through the same single molecule, exclusively. In other words, the two zero-bias crossings belong to the same transition between the same two charge states ($N$ and $N+1$) occurring at different gate voltages because the molecule “moves”.

**Figure 4.33**: Differential conductance (logarithmic scale) of the Mn$_4$-SET device as a function of the bias and gate voltages. Transport excitations (white arrows) associated to excited spin states are observed outside the Coulomb-blockade areas (dark).
Figure 4.34: Behavior of the excited transport excitations ($V_{\text{gate}} = -0.4$ V) as a function of external magnetic fields applied at orthogonal directions, $x$- and $z$-axes (arbitrarily chosen). The continuous lines highlight the motion of the excitations with the field. The thin dashed lines represent slopes that would be generated by transitions involving a net change of spin equal to 9.

Note that fainted excitations, parallel to the main ones, are also observed (white arrows). Their faintness is indicative of short-lived states that the conduction electrons visit when transiting through the molecule. These weak excitations outside the CB areas move with an applied magnetic field, as can be seen in Figure 4.34, in
where it is shown the magnetic field behavior of the data taken at a fixed gate voltage, 
\( V_{\text{gate}} = -0.4 \) V, for two arbitrary but orthogonal orientations of the field (i.e. along \( z \)- and \( x \)- axes). In this measurement it is clear how some of these excitations bend with the magnetic field. Solid lines highlight the electrical excitations to help identify their behavior with the applied magnetic field. The curvature of the excitations, and their distinct behavior for different orientations of the magnetic field, plus the fact of having them not going down to zero energy for zero magnetic field (\( E_0 > 0 \), measured from the main excitation), indicates the presence of magnetic anisotropy (zero-field splitting) in the molecule. In addition, the high magnetic field slope of the excitations (dashed lines) points towards transitions between states with very different spin values (\(|\Delta S| \sim 9\)). Also, anticrossings between different excitations may be indicative of quantum superpositions of the molecular spin states, which are observed for the first time in transport measurements through and individual SMM.

One possibility is that the conduction electron jumps into one of the manganese ions, most likely a Mn\(^{3+}\) (converting it into a Mn\(^{2+}\)), when entering the molecule, thus directly changing the molecular spin value. For the purpose of our discussion we can assume that the neutral state of the molecule (with \( N \) electrons) possesses spin \( S = 9 \) (as when the Mn\(_4\) molecule is in the crystal), and the charged state corresponds to \( S = 19/2 \) \((9 + 1/2)\), as depicted in Figure 4.35a. Note that for this the ferromagnetic coupling between the manganese ions must remain unchanged upon addition of an electron, which may not always be the case. Assuming this, we can get a simple picture using a giant-spin description and the parameters given in Lecren \textit{et al.} [66],
where the magnetization behavior of Mn$_4$ in solid state form was first reported. The results according to this interpretation are pictured in Figure 4.35. Here, 3 meV (the energy of the lowest transport excitation in Figure 4.34) is similar to the separation between the ground projection state $m = 19/2$ and the highest projection state $m = 1/2$ of the spin multiplet $S=19/2$ (orange arrow in Figure 5a), as obtained from diagonalization of the spin Hamiltonian with the parameters given in Ref. [66]. Note that the uncertainty on the anisotropy parameters describing this molecule when out of the crystalline environment, the anisotropy barrier and the energy separation between the spin states of the molecule can substantially differ from the ones shown in Figure 4.35b. Therefore, a possibility is that the main observed excitation corresponds to a transition from $m = 9$ (state $N$, with $S_N = 9$) to $m = 19/2$ (state $N+1$, with spin $S_{N+1} = 19/2$) [blue arrow # 1 in Figure 4.35a], and then the first excited excitation (the one at 3 meV) would correspond to transitions from $m = 9$ (state $N$, with $S_N = 9$) to $m = 1/2$ (state $N+1$, with spin $S_{N+1} = 19/2$) [blue arrow # 2 in Figure 4.35a]. This would explain the observed separation and the slope with the magnetic field. However, things are more complicated in this molecule, which makes the data difficult to be explained quantitatively. Actually, according to Lecren et al. [66] the weak exchange coupling constant between the Mn ions makes the excited state $S_N=8$ to be only 5.2 K (0.44 meV) away from $S_N=9$. This means that the ground projection state $m = 8$ (of $S_N = 8$) is about the same distance from the ground projection state $m = 9$ (of $S_N = 9$) than the first excited state $m = 8$ (of $S_N = 9$), as pictured in Figure 4.35a. In addition, reduction of Mn$^{3+}$ into Mn$^{2+}$ may have important consequences for the molecular zero-field splitting (Mn$^{2+}$ is known to be
very isotropic), altering significantly the anisotropy barrier and consequently the separations between spin projections of the charged state \((N+1)\) with respect those of the uncharged molecule \((N)\).

Figure 4.35: a) Representation of the possible two lowest lying spin states corresponding to the neutral \((N)\) and charged \((N+1)\) configurations of the Mn₄ SMM when placed in the SET device. b) Energy of the spin \(S = 9\) ground state multiplet as a function of the longitudinal (black) and transverse (orange) magnetic fields.
I also need to consider the direction of application of the magnetic field with respect to the anisotropy axis of the SMM. Figure 4.35b shows the energy of the spin $S = 9$ ground state multiplet as a function of magnetic field applied along the easy ($H_{\text{long}}$) and hard ($H_{\text{trans}}$) anisotropy axes, respectively. In addition to these levels, one needs to consider the excited spin states (not shown in the Figure for clarity). Note that there are other observed excitations at zero field ($\sim 7.5$ meV, $\sim 12$ meV, and an extra one at $\sim 6$ meV when a 0.6 T field is applied along the $x$-axis). They also move with magnetic field and show anticrossings, and will likely correspond to crossings between spin levels of the molecule expected to occur within this field range. However, it is difficult to tell which ones would correspond to each transition, due to the uncertainty in the molecular orientation.

An alternative possibility that one needs to consider is that the electron does not change directly the spin of the molecule but is accepted by a non-magnetic center (i.e. one of the aromatic rings). Actually, this may be the most likely possibility in this compound since Mn$_4$ SMMs have not been established as capable of easily changing their Mn oxidation state, unlike other SMMs (i.e. Mn$_{12}$). It is then likely that the transport of the electron onto and off the molecule may involve a combination of Mn and the pi-orbitals of the aromatic ligands, since aromatic organics are known to be “good” conductors. Given this situation, the spin of the conduction electron is expected to couple antiferromagnetically to the molecular spin ($S = 9$). However, the coupling will be much weaker in this case (almost negligible splitting of each molecular spin projection level), leaving the molecular spin almost unaffected and
making the conduction electron to act basically as a proximity probe of the molecule’s magnetic behavior. This would naturally explain the high magnetic field slopes \((S \sim 9)\) of the electrical excitations. In addition, the magnetic core will remain unaltered (no reduction of any manganese), maintaining the anisotropic characteristics of the uncharged molecule. However, the uncertainty in the molecular orientation and the presence of excited spin states in \(\text{Mn}_4\) prevents a quantitative explanation of the observed phenomena also in this case.

4.4.3. Discussion:
The present results [67] constitute a first step towards the understanding of the transport properties of more robust and larger SMMs. Future effort will be focused on studies of other Mn-based SMMs with better isolated ground spin states, and functionalized with larger ligands to increase the overall size of the molecule and enhance the yield of the measurements as well as protect the magnetic core from degradation/oxidation.
CHAPTER 5
CONCLUSION:

I studied molecular nanomagnets and ferromagnetic noble metal nanoparticles by means on a novel experimental approach that mixes the chemical functionalization of nano-systems with the use of SETs. The goal of my research project was to study the transport properties of individual nano-scale system by means of single-electron transport experiments. To fulfill my research objectives I have: (i) optimized fabrication process of SETs; (ii) developed a controlled way of depositing a uniform monolayer of molecules/nanoparticles on atomically-flat gold surface; (iii) employed feedback assisted electromigration process to produce small gaps (< 3 nm) with high yields (~ 90%).

I fabricated single layer Au, Pt or multilayered Au/Pt/Au nanowires depending on the specifics of the experiment. I used Au-nanowires for SMM-based SETs and Au/Pt/Au-nanowires for gold nanoparticle-based SETs. At room temperature Au-nanowire nanogap increases steadily over time. I found that Pt/Au nanowire nanogaps remain fixed as the gap resistance of them remains constant for days.

I extensively examined the deposited layer of nano-material on gold substrate using AFM image analysis to find the optimum monolayer formation time. I have studied three different magnetic nano-materials (a) a molecular magnet; (b) Mn\textsubscript{12} and Mn\textsubscript{4} based single-molecule magnets; (c) a functionalized magnetic gold nanoparticle.
I have also observed interesting behavior of Mn$_{12}$-acetate molecules as they form nano-rings. These nano-rings have periodic height of 1.6 nm, which nearly equal to the diameter of the Mn$_{12}$ molecules, a good indication that Mn$_{12}$ is the unit building block of the nano-rings.

My studies revealed Coulomb-blockade response of a Mn$_4$-based SET device recorded at 240 mK. The appearance of two diamonds (two charge states) with a clear switch between one and the other is indicative of a conformational switching of the molecule between two different states. The excitations inside the diamonds move with magnetic field. The curvature of the excitations and the fact of having them not going down to zero energy for zero magnetic field, indicated the presence of magnetic anisotropy (zero-field splitting) in the molecule. In addition, the high magnetic field slope of the excitations indicates that transitions between charge states differ by a net spin value equal to 9 ($|\Delta S| = 9$), as expected from the behavior of Mn$_4$ molecules in their crystalline form. Anticrossings between different excitations are indicative of quantum superposition of the molecular states, which are observed for the first time in transport measurements through and individual SMM.
LIST OF REFERENCES:


