

Electronic Transport in Magnetic Materials at Different Dimensionalities



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Abstract

The miniaturisation of devices has become of paramount importance in modern technology in the last century. Since then, the lower bound of the *nanotech* world has been pushed down until the molecular and atomic scale. At these dimensions, classic and quantum processes coexist both for magnetic and electric phenomena. This is creating a physical limit for modern silicon-based technologies based on classic transport. Molecular spintronics is one of the most promising approaches to overcome these limits. This field relies on the exploitation of single-molecules magnets, the smallest possible molecular magnets that can be created. Not only it allows for the ultimate electrical miniaturisation to the molecular scale, but it also has the potential to unlock the power of quantum computation. However, the electric transport properties and the magnetic interaction with the environment at this scale require more investigation.

The present work focuses on the charge transport in molecular magnetic materials through different dimensionalities. We begin the journey by analysing microscopic crystals of nitronyl-nitroxide radicals, getting an insight on their conduction channels through space-charge-limited currents. We then scale down one dimension, and analyse thin-film devices based on rare-earth single-molecule magnets, to verify their behaviour when deposited on surfaces. Finally, we embed graphene nanoribbons and rare-earth single-molecule magnets in graphene break junctions, unravelling their magnetic properties as single-molecule transistor.

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Chapter 1

Motivation

There's Plenty of Room at the Bottom.

Feynman - 1959

In 1959 Feynman gave one of the most inspirational talks about nanotechnology [1], at a time when the term *nanotechnology* did not even exist. In his talk, he hypothesised about being able to write the whole Encyclopaedia Britannica on the tip of a needle, by manipulating single atoms and molecules. This is the very basic principle of *nanotechnologies*: the creation and exploitation of materials and devices with structural features in between those of atoms and bulk materials, with at least one dimension in the nanometer range (1 - 100 nm).

But why *nano*? The first important enhancement we obtain with miniaturisation is obviously the ability to build smaller machines and embed more functionalities in a single device while maintaining its overall dimensions. This is well known and perfectly represented by the evolution of mobile phones in the last four decades [2]. The second enhancement is the huge gain in the ratio between surface and volume obtained by scaling the size of the single elements that compose an agglomerate. Given a fixed amount of volume filled by discrete components, if we scale their linear dimensions by half we quadruplicate their total surface. Since applications involving

chemical catalysis or nucleation of physical processes scale with the active surface rather than the volume, miniaturising is of paramount importance. The third and most important reason for reaching nanometre scales is that materials gain properties far different from bulk systems. For instance, quantum effects become predominant over classical physics. By controlling and engineering materials at this level, new astonishing research branches came to life starting from the second part of the last century, with discoveries and technical developments that changed our era with unprecedented progress.

Modern electronics is probably the field where nanostructures played the most important role, providing a steady and rapid increase in the world's technological capacity to store data and computational power over the past few decades [3]. Since the realisation of the first transistor in 1926 [4], the development of electronics has been mainly granted by device scaling, obtaining impressive densities both for data memorisation and data processing. *Moore's Law*, one of the most famous empiric laws in electronics, describes this progression stating that the number of transistors in a dense integrated circuit doubles about every two years. Formulated in 1965 [5] and valid since then, it's now becoming widespread the realisation that this law is very close to reach its expiration date [6]. The continuous size scaling is reaching the fundamental limitations of semiconductors, where quantum effects hinder a deterministic control of the electrons, invalidating the basic need of a transistor to store a single, determined, binary value. Researching new materials and new technologies is now required.

A promising approach is provided by molecular spintronics [7, 8], which combines the ultimate miniaturisation at the molecular level with the capability of exploiting spins as information carriers, unlocking all the potential of quantum computation. This approach offers different advantages: the chemical tunability of the magnetic molecules allows precise manipulation of the properties of spintronic systems, the

conduction channels can be tuned by using rational chemical design, and the created molecules can be integrated into a huge variety of nanoelectronic devices, such as those based on graphene [9, 10] and carbon nanotubes [11, 12], or onto functional surfaces [13, 14, 15].

The aim of this work is to better understand the charge transport properties of magnetic materials, and how they change in different dimensionalities. From three-dimensional systems (3D, single crystals), to surface ones (2D, thin films), then one-dimensional (1D, nanoribbons) and finally to point-like objects (0D, single molecules). The latter two systems are usually referred to as 1D and 0D Quantum Dots (QD), stressing the fact that once a system has two (or three) dimensions in the nanometre range, quantum effects play a major role in their dynamics.

This thesis will begin with a description of the theoretical basis of charge transport in matter and its different regimes through dimensionalities. The spin information will then be added, explaining how devices can exploit the magnetic properties of materials to perform operations, especially in two dimensions. The introductory chapter finishes by discussing the basics of molecular magnetism first, and the properties of Single Electron Transistors (SETs) later, and how they combine in the novel field of Molecular Spintronics. Chapter 3 describes the typical scientific methods used to investigate electronic transport in materials at the different scales, and explains in detail the setups used for our measurements. The discussion on the experimental results of my studies will start in the forth chapter (Chapter 4), where the charge transport properties of single crystals (3D) of organic radicals belonging to the nitronyl nitroxide family are discussed. In Chapter 6 I will introduce a Single Molecule Magnet (SMM) based on a rare-earth core (a Dysprosium dimer). These molecules can be implemented both in 2D-devices, and I will show how they still keep their magnetic properties once deposited on a surface, as well as in 0D single-molecule transistor device, when the coupling of the molecule with a substrate unlocks the shaping of its

magnetic anisotropy. The last chapter, Chapter [5](#), is dedicated to 1D QDs, and in particular I will show for the first time how to embed molecular graphene nanoribbons (MGNRs) in graphene break junctions to create a single molecule transistor.

Chapter 2

Theoretical Background and State-of-the-art

Never memorise something that you can look up.

Albert Einstein

This chapter will introduce some basic concepts that the reader needs to understand in order to follow the results discussed in this thesis. The aim of every section is to provide a good, synthetic and pithy description of different aspects of charge transport in materials.

Section 2.1 will provide a broad look on charge transport mechanisms, focusing in particular in all those non-canonical transport regimes that differ from the basic known ohmic one. In Section 2.2, I will add a new degree of freedom to the picture: the magnetic environment; I will describe how the magnetic properties of the materials which compose a device allow one to modulate the current flowing through it. In the third section I will explain how the magnetic properties of materials change when scaling the size down to the smallest entity, a single molecule, with particular attention to how a molecule can keep its magnetic polarisation, and how to exploit it (Section 2.3). Section 2.4 will bring the focus back on transport, studying the quanti-

sation of charges flowing through nanoscopic localised regions delimited by potential barriers, the so-called Quantum Dots (QDs). The last section of this chapter will give an overview on all the different materials that have been studied during in this work, providing the reader with an insight to their fundamental properties (Section 2.5).

2.1 Macroscopic Transport Effects in Organic Semiconductors

Most organic semiconductors (OS) fall in the conduction regime in between conductors and insulators, but closer to the latter. Proper theoretical modelling of the dynamics involved in the transport of charge is requires to understand their electrical properties. In this work, organic radicals, i.e. systems that possess an unpaired electron, play an important role. However, the conventional band theories fail to describe the physics involved, and we need to appeal to models that take into accounts electron traps, hopping of charges or the injection at the electrodes of a surplus of free charge that subsequently drift under their self-generated electric field. A brief introduction to transport regimes will be given in Section 2.1.1

In particular, the study of the flowing of charge in a conductor upon a forced injection of a surplus of carriers, the so-called *Space-Charge Limited* (SCL) regime, can provide useful information on the number of carriers and their mobility. Section 2.1.2 will give a phenomenological description for a pure, trap-free, lattice, whilst Section 2.1.3 will explain the role of charge traps in the conduction and the additional information we can extract from the transport behaviour of a device.

2.1.1 Conduction Regimes

The conduction of charge in OS crystals does not obey the conventional band theories that describe very well the conduction behaviour in metals and inorganic semiconduc-

tors. This is due to the fact that the main binding forces in the cell of organic crystals are weak Van der Waals interactions, in contrast to the strong ionic or covalent bonds typical for the other materials. The bond is then too weak to let the molecular orbitals form bands that are de-localised over all the crystal. As a consequence, charges have to either hop from a molecule to the other(s), which in literature is known as *hopping conduction regime*, or find alternative ways to be promoted in the conduction band.

One of the key parameters to understand charge transport for both holes and electrons in matter is their *mobility* (μ). Most of the devices that rely on semiconductors require high mobilities for faster response and less heat generation, whilst others exploit switches and modulation of this parameter through external stimuli or material engineering in order to achieve advanced device operations.

The typical devices built with organic semiconductors can be grouped in three classes:

- Resistors
- Schottky barriers or metal-insulator-semiconductor (MIS) diodes
- Thin film transistors (TFTs)

The reason behind the fact that CMOS and FET devices are not developed using OS is because they require faster transitions responses, hence higher carrier mobilities, than the typical OS can provide.

For a full characterisation of charge mobility in an OS, the resistor configuration is the most convenient: either two planar metal contacts that sandwich a thin film of material, or two metal tips that pinpoint the surface. In the simplest description of the transport, the current density J can then be considered composed by two components: a *drift current* and a *diffusion current*. The first one is proportional to the local electric field $E = -\nabla V$, the number (density) of carriers n and their

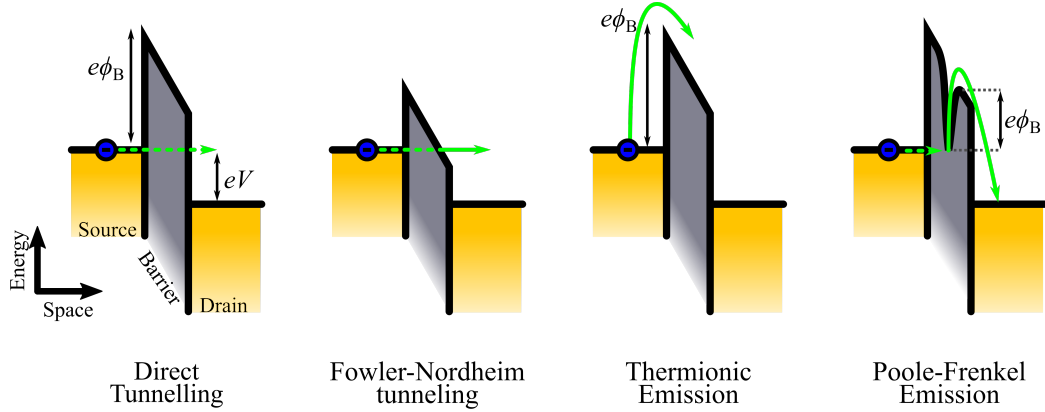


Figure 2.1: **Conduction Mechanisms, Band Structure.**

Conduction mechanisms that allow current to flow in presence of an energy barrier. The barrier may either be an insulating layer between two contacts (e.g. transistors) or a gap (e.g. break junctions). Energies involved are labelled as in Table 2.1

mobility μ_n . The latter is proportional to the gradient of the charge density ∇n :

$$J = -q\mu_n n \nabla V - qD_n \nabla n. \quad (2.1)$$

The parameter D_n is a constant of a material related to temperature and mobility following Einstein Relation $D_n = \mu_n k_B T / q$.

In the following I will discuss the different conduction regimes and how the mobility is affected in each case.

Ohmic Regime. If diffusion's contribute is negligible we are in the *Ohmic Regime*, and the current is mainly dependent on the geometry of the device:

$$A \cdot J = I = GV = \sigma \frac{A}{l} V = qn(T)\mu(T) \frac{V}{l}, \quad (2.2)$$

where A is the contact area, l is the length of the device and G is the *conductance*, which is measured in Siemens (S). In the last step of the equations above I used the relation between conductivity and mobility $\sigma = en\mu$, which is valid whenever hopping events are uncorrelated and the density of localised states is orders of magnitude lower

than the density number of carriers. In practice, the relation between current and voltage is rarely that simple, and has to take into account further parameters, like temperature, electric or magnetic fields, frequency of the probing bias, presence of traps, etc.

Pool-Frenkel. The *Pool-Frenkel* model takes into account the influence of traps with either a discrete or diffused energy distribution. Charge traps reduce the overall mobility of the OS localising otherwise free carriers. Thermal excitations may cause the bonded charge to break free again, and an external field will contribute lowering the trapping barrier. Both these effects can be formalised in the classic form of the Pool-Frenkel conduction, which is valid for systems with discrete, abundant traps:

$$J = J_0 V \exp \left(\frac{-E_a + \sqrt{qE/\pi\epsilon}}{kT} \right), \quad (2.3)$$

where E_a is the energy depth of the traps. Section 2.1.3 is dedicated to a deeper study of the effects of traps on the conduction behaviour.

Tunnelling. When the band gap is too large to be populated by external excitation we may still have conduction assisted by quantum effects (tunnelling). In this case the active region has to be sufficiently small (a thin film) to allow the evanescent component of the carriers wave function to actually have a non-negligible component on the other side of the barrier. When a bias is applied, the shape of the barrier between the two electrodes is distorted (Fig. 2.1) and the *Fowler-Nordheim (FN) tunnelling* takes place:

$$J_{FN} \propto \left(\frac{V}{d} \right)^2 \exp \left(-\alpha \frac{d}{V} \right). \quad (2.9)$$

Ohmic	
$J = qn(T)\mu(T)\frac{V}{d}$	$I \propto V \quad (2.4)$
Fowler-Nordheim Tunnelling (FN)	
$J = \frac{e^3 m}{8\pi \hbar m \phi_B} E^2 \exp\left(-\frac{8\pi\sqrt{2m}}{3he} \frac{\phi_B^{3/2}}{E}\right)$	$I \propto \left(\frac{V}{d}\right)^2 \exp\left(-\alpha \frac{d}{V}\right) \quad (2.5)$
Thermionic emission-diffusion (Schottky)	
$J = A^{**} T^2 \exp\left(-\frac{q\phi_{Bp}}{kT}\right) \left[\exp\left(\frac{qV}{k_B T}\right) - 1\right]$	$I \propto \exp\left(\frac{qV}{nk_B T}\right) - 1 \quad (2.6)$
Poole-Frenkel hopping	
$J = e\mu n \frac{V}{d} \exp\left(-\frac{e}{kT} \left(E_i^0 - \sqrt{\frac{eE}{\pi\epsilon}}\right)\right)$	$I \propto V \exp(V/V_0) \quad (2.7)$
Space-Charge-Limited	
$J = \frac{9\epsilon\mu V^2}{8d^3}$	$I \propto V^2 \quad (2.8)$

Table 2.1: **I-V relationships for different Electronic Transport Mechanisms.**

A^{**} = effective Richardson constant; ϕ_B = barrier height; E = Electric field in the material; ϵ = electric permittivity of the material; m^* = effective mass; d = device thickness; ΔE_{ac} = activation energy for electrons; ΔE_{ai} = activation energy for ions; $V \approx E \cdot d$, in the case of a constant field; $a \equiv \sqrt{q/4\pi\epsilon_i d}$, b , c , and d are constants. [16]

The factor α contains information on the quantum barrier carriers have to tunnel as well as their effective mass. The difference between the canonical quantum tunnelling and FN-tunnelling is that the blocked region is not treated as a complete forbidden zone for the carriers (like an insulator), but it is a triangular barrier with an accessible conduction band.

Simmons Model. A way to describe the tunnelling current through a barrier of arbitrary shape has been introduced in 1963 by J.G. Simmons [17, 18]. The model simplify the calculations considering an average barrier hight $\bar{\phi}$ modulated by a non-linearity factor α :

$$J_S = j_f + j_b = j_0 \bar{\phi} \exp\left(-\alpha \sqrt{\bar{\phi}}\right) - j_0 (\bar{\phi} + eV) \exp\left(-\alpha \sqrt{\bar{\phi} + eV}\right) \quad (2.10)$$

$$\text{where: } j_0 = \frac{e}{2\pi h d^2} \quad \text{and} \quad \alpha = \frac{4\pi d}{h} \sqrt{m}, \quad (2.11)$$

where we have considered the effects of both the forward and the backward current (j_f and j_b). The other parameters are the applied voltage V , the electrodes separation d and the constants e and h for the electron charge and Plank's constant. Fitting this relation to the I - V curves measured on break junctions, it is possible to have an estimation of the gap created in an electroburning process (see Section 3.3.1)

Space-Charge Limited Currents. Finally, we may have forced injection of an excess of free carriers in the proximity of the contact regions, which results in a drift of carriers through the device under their own electric field. This is the *Space-Charge Limited* (SCL) regime, and I will dedicate next section to describe it.

2.1.2 Space-Charge Limited Currents (SCLC)

An extensive study of SCL currents can be found in Mark and Lampert's book *Current injection in Solids* [19] and in their bibliography [20, 21, 22] from the 50s to 70s, and great part of this section takes inspiration from their work.

In the SCL regime, the density of injected charges is very high, so that we obtain a local charging of the material, generating an electric field that modifies its energy band structure. In a trap-free device, the current will have a quadratic dependence on the applied bias and we can obtain its formal equation with a little calculation, by deriving the field modulation from Poisson's Eq. (2.12). In the following I will make these basic assumptions:

- There is only one kind of carrier (usually holes for OS)
- There are no other charge carriers except the injected ones
- The material is homogeneous in both carrier mobility (μ_n) and dielectric permittivity (ϵ_s)
- The electric field at the injecting electrode is zero
- Diffusion currents are negligible, and carriers move only under effect of the self-generated electric field.

Once these are verified, starting with Poisson's equation:

$$\frac{dE(x)}{dx} = \frac{\rho(x)}{\epsilon_s} = \frac{qn(x)}{\epsilon_s}, \quad (2.12)$$

and combining it with Eq. (2.1), where the diffusion contribute to the current is considered negligible, we obtain:

$$J = q\mu_n n(x)E(x) = \mu_n \epsilon_s \frac{dE(x)}{dx} E(x) = \frac{1}{2} \mu_n \epsilon_s \frac{dE^2(x)}{dx}. \quad (2.13)$$

With two simple integrations, we obtain at first the electric field:

$$E^2(x) = \frac{2J}{\mu_n \epsilon_s} \Rightarrow E(x) = \sqrt{\frac{2J}{\mu_n \epsilon_s}}, \quad (2.14)$$

and with the second the potential:

$$V = - \int_0^d E(x') dx' = \frac{2}{3} \sqrt{\frac{2J}{\mu_n \epsilon_s}} d^{3/2}, \quad (2.15)$$

from which we get the current/voltage relation:

$$J = \frac{9}{8} \epsilon_s \mu_n \frac{V^2}{d^3}. \quad (2.16)$$

where d is the device length and V is the applied bias voltage. Equation 2.16 is the *SCL equation*, also commonly known as *Mott-Gurney Law*.

Given this equation, one may measure the mobility even for high resistive materials like OS, provided the knowledge of their dielectric constant, which happens in most cases to be $\epsilon_s = \epsilon_r \epsilon_0 \approx 3 \cdot 8.85 Fm^{-1}$.

2.1.3 Electronic Traps in Semiconductors

The calculations of the previous section are valid for a trap-free material. In most cases even a relatively pure one, but highly resistive and with a small density of carriers, may have enough impurities to drastically affect its conductivity. The effect of these traps is to localise otherwise free carriers, and locally modify the energy dispersion relation of the ones still available for conductance. Limiting our considerations on a two-bands medium, a conductance band and a trap-level with physically localised states, the Poole-Frenkel model introduced in Section 2.1.1 may be used to

describe the conduction. In this model, the mobility is expressed as:

$$\mu = \mu_0(T)e^{\alpha\sqrt{E}}, \quad (2.17)$$

and valuable information about the density of traps, their energy dependence and the mobility itself can be extracted using two terminal measurements [23]. The nature of the defects, in terms of their energy distribution, has also different effects on the conduction. For simplicity I will consider just the two opposite cases of traps with energy levels distributed in the band gap, or with discrete shallow states, as illustrated in Fig. 2.2. I will also assume to have just positive carriers (as acceptors are usually the most common dopants in OS), with a free hole density at room temperature of p and trapped density N_T^+ , giving a total charge density:

$$p + N_T^+ = \rho_0/q. \quad (2.18)$$

1. **Abundant, Discrete Traps.** In this regime we consider the trap levels more dense than the valence band states ($N_T \gg N_V$), the current loses its dependence on the field, but it is thermally activated and decreases exponentially with E_T :

$$J \propto \mu_0 \frac{N_V}{N_T} \exp\left(-\frac{E_T - E_V}{kT}\right) \quad (2.19)$$

2. **Exponentially-Distributed Traps.** Let's assume an exponential distribution of the traps in the energy diagram:

$$N_T(E) = N_{T0} \exp\left(\frac{E_V - E}{kT_2}\right), \quad (2.20)$$

where N_{T0} is the density at the top of the valence band and T_2 act as a parameter (in Kelvin units) that describes the slope of the exponential distribution in a

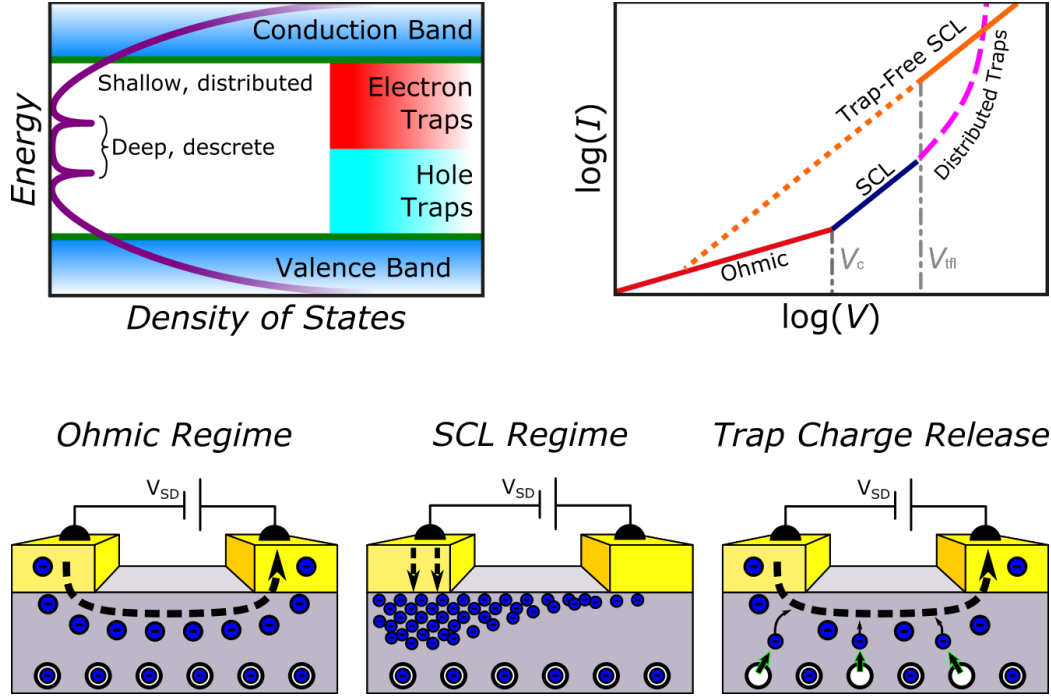


Figure 2.2: **Electronic Traps.**

(top left) Band diagram for a typical semiconductor, with density of states (DOS) of traps (violet line).

(top right) Log-log plot of current as a function of bias. At low biases the device is in the ohmic, linear, regime (red line). When increasing bias, the injected carriers overcome the density of dopants in the material, and space-charge limited (SCL) current takes over, with its typical quadratic dependence on bias (blue line). The number of free carriers is still influenced by the presence of traps, which start to free their charge at a certain voltage (V_{tfl}). Depending on their nature, we may see a sudden jump (orange line), or an higher than quadratic increase (purple line) in current.

(bottom) Schematic representations of the current regimes: Ohmic, Space-Charge Limited (SCL) and either two assisted by released charges from traps.

logarithmic plot. In this case to find the density of filled traps at the Fermi level and replace it in Eq. (2.18) an integration over the energy is necessary. The final density current has the following form:

$$J \propto \mu_0 N_V \left[\frac{\rho_0}{q} \frac{kT_2 - kT}{N_{T0} (kT_2)^2} \right]^{T_2/T}, \quad (2.21)$$

which has a fairly complicated temperature dependence, raised to the power T_2/T (where $T_2 \geq T$ is a condition to have the above mentioned integration converge).

3. Both Traps and Valence Band Exponentially Distributed. The last case is the one that considers also an energetic exponential distribution for the valence band:

$$N_V(E) = N_{V0} \exp \left(\frac{E_V - E}{kT_1} \right). \quad (2.22)$$

In this case also the density of free carriers p has to be integrated before replacing it in Eq. (2.18). The final relation for the current is:

$$J \propto \mu_0 N_{V0} \frac{(kT_1)^2}{kT_1 - kT} \left[\frac{\rho_0}{q} \frac{kT_2 - kT}{N_{T0} (kT_2)^2} \right]^{T_2/T_1}, \quad (2.23)$$

and in this case the dependence on temperature is raised to the power of T_2/T_1 , which could be any number.

2.2 Spintronics

Spintronics (from spin-electronics) aims to control the spin degree of freedom of electrons in solid-state systems. This control traduces in the manipulation of either the spin of a single electron, $\mathbf{s}$, as can be observed in its magnetic moment $-g\mu_B \mathbf{s}$ (g , elec-

tron g-factor, μ_B , Bohr magneton), or the relative population and phase of spins in an ensemble of electrons, as can be detected through the magnetisation of a material. Novel magnetic materials have shown interesting application in spintronics such as organic ferromagnets [24], as well as some materials that I will study in this work, like organic semiconductors [25], rare earth SMMs [26] and carbon based nano-materials [27]. The latter, in particular, are promising materials for use as nano-components such as leads, gates or wires in devices. Furthermore, the ability to be functionalised and hybridised with other magnetic centres offers an interesting play-ground for the study of quantum effects [28].

2.2.1 Giant Magnetoresistance and Spin Valves

The importance of spintronics has seen a huge boost since the appearance of the first magnetic memories for electronics [29], in particular after the commercial boom of personal computers. These memories rely on the giant magnetoresistive effect, discovered in 1988 [30] and observable in thin layers of different magnetic material subject to a current: if the magnetic moments of the layers are aligned then the resistance is lowest and the device is in an *ON* state (Fig. 2.3). This effect is called Giant MagnetoResistance (GMR), and the MR is defined as the maximum change in resistance over the magnetic field range of interest, divided by the high-field resistance:

$$\text{MR} = \frac{\Delta R}{R} = \frac{R_{AP} - R_P}{R_P} \quad (2.24)$$

This phenomenon has been largely exploited by industry since its discovery in a huge variety of devices dedicated to high-sensitivity magnetic field measurements. The most common application is as the storing element in magnetic Hard Disks Drives (HDDs). Even if the the advent of Solid Stated Drives (SSDs) is threatening their im-

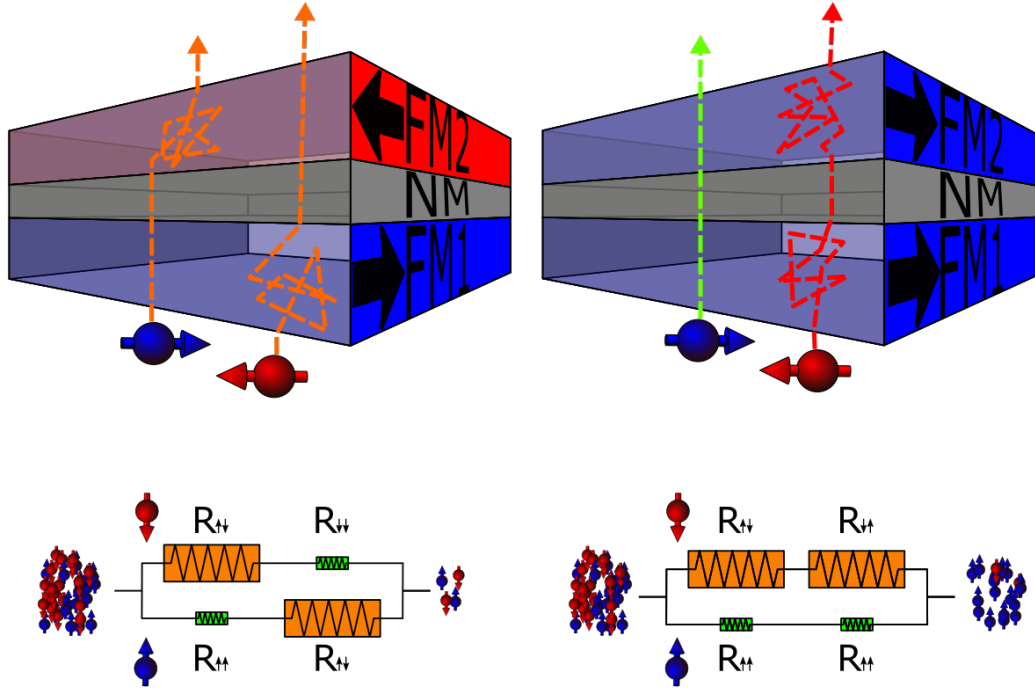


Figure 2.3: **Spin Valve Effect.**

(top) Schematic representation of a *current-perpendicular-to-plane* spin-valve (CPP-SV), comprising a trilayer film with two identical ferromagnetic layers FM1 and FM2 sandwiching a non-magnetic layer NM. On the left there is the antiparallel (AP), highly resistive, configuration and on the right the parallel (P), low resistive and spin filtered one.

(bottom) An electrical schematic is also provided below each model: the SV can be represented as two parallel path for the two different spin orientation of the electron, each one having two resistances in series. The value of the resistances is higher when the electron spin points in the opposite direction respect the magnetic orientation of the layer crossed.

portance, magnetic memories are still unrivalled for longevity and cost-effectiveness.

The simplest device configuration based on GMR is a spin valve (SV) in current-perpendicular-to-plane geometry (CPP-SV). With reference to Fig. 2.3, two ferromagnetic layers (FM1-2), usually metallic alloys containing cobalt, iron or nickel, are separated by a non-magnetic (NM) conductive layer, like copper. The thickness L of NM is chosen to be smaller than the electron mean free path λ_e^{NM} of the metal, which is typically $\sim 8\text{-}30$ Å, so that no scattering is expected in NM. As a consequence, the device resistance R arises only from scattering of carriers in the two ferromagnetic

films. The magnetic orientation of one of the two FM layer is "pinned" in a fixed direction, while the other one can be flipped applying an external field [31]. The resistance R of such a device shows a large change, depending on whether the magnetic moments of the two FM layers are aligned or not, and it is a direct evidence of *spin-dependent scattering* in the active layers [32, 33].

2.2.2 Tunnelling Magnetoresistance (TMR)

Magnetic tunnel junctions (MTJ) [34] are devices with a structure very similar to that of SVs. In such devices, the FM layers are divided by a very thin layer (~ 1 nm) of insulating material, generally an oxide. The transport through this region happens by quantum tunnelling and the resistance ratio is much higher compared to a GMR device, reaching values as high as 400% at room temperature with the implementation of MgO as insulating layer over the classical Al_2O_3 . At low temperatures, below 10 K, ratios up to 3000% have been reported in superlattices of Co-Fe nanoparticles [35, 36]. This large TMR arises from the spin-dependent tunnelling mechanism. Like in canonical tunnelling the electrons wave-function is exponentially decaying in the insulating medium, with a *decay length* λ_α that depends on the wave function symmetry Δ_α [37, 38]. This decay length is different for the two spins alignment and, with a proper choice of insulator thickness L , only the electrons with $\lambda_\alpha > L$ will make it through the barrier while the other species is filtered out.

The interface plays a fundamental role in tuning the conduction channel, and the ability of engineering its properties at the nanoscale level represents a potential way for controlling spintronic phenomena, such as the interaction between magnetic elements (indirect exchange [39]) and the polarisation of spin-currents (spin-filtering [40]).

Further discussion about spintronics in bulk systems goes beyond the scope of this work, since I will mainly focus on the basic concept of SV to apply it at the

molecular scale. For interested readers, Žutić in Das Sarma's group produced a rather exhaustive review on the fundamental theory and applications back in 2004 [41].

2.2.3 Organic Spintronics

Although spintronics was born exclusively using and developing inorganic materials, towards the end of last century Organic Semiconductors-based devices became popular and widely studied. Up to now, OS have been successfully used as tunnel barriers in magnetoresistive tunnelling devices and as spin-polarisers in transport devices. Furthermore, several families of devices based on OS are available to the consumer market, like Organic Light Emitting Diodes (OLEDs) for TV and portable devices, or Photovoltaic cells, popular for being cheap and easy to replace. What makes OS popular both for research and for applications in spintronics devices is, from one side, the capability of engineering the molecules by chemical means and from the other side the creation of materials lightweight, usually low-cost and with a relative easy application on large surfaces.

Considering the spin properties of OS, one of the things that makes them interesting is the weak spin-relaxation mechanism [42]. This is due to the small spin-orbit coupling that characterises low-Z atoms, like carbon, since the magnitude of the force scales with the fourth power of the atomic number. On the other hand, the hyperfine interaction is generally weak, since C nuclei have no magnetic moment [43]. The combination of the two things implies that the carriers retain their spin information for longer time before their state faces decoherence, allowing more time for interaction or manipulation of the spin states.

However, OS are still lacking a proper theory of electrical spin transport able to explain and predict the injection of carriers, especially at the interfaces with inorganic layers [44]. This is of paramount importance, since an interface with metal electrodes and/or layers is common to any devices based on OS. Even more so for vertical

geometries, like the devices I will show in Chapter 6, that have an electrode deposited on top of a layer of molecules, giving an interface difficult to model [45].

2.3 Molecular Electronics

We have seen in the previous section how magnetism in bulk materials play a fundamental role in many devices, most importantly for magnetic memories. There is, however, a scaling limit for a classical magnet to keep its macroscopic magnetic behaviour. At smaller scales one has to start considering the single molecules instead of collective magnetic domains. In this section I will introduce the class of materials called Single Molecule Magnets (SMMs), which are able to retain magnetisation at the molecular level at sufficient low temperatures. In particular, I will discuss their classical and quantum behaviour in order to understand their importance for molecular spintronics devices.

2.3.1 Single Molecule Magnets

SMMs are a special class of magnetic materials based on a single molecule. Due to this ultimate miniaturisation, they are always in the superparamagnetic regime, i.e. their magnetisation may flip randomly by thermal excitation. However, at sufficient low temperatures SMMs are able to retain their magnetisation state without any external field for long time, up to more than a year below 2K [46], turning them in perfect magnets at the nano scale. Their first appearance is dated in early '90s [47] with the discovery of the unique magnetic properties of the iconic manganese acetate (Mn_{12}ac) [48]. Since then, a fervent community of both physicists and chemists built up analogue systems based on manganese [49], iron [50], cobalt [51], nickel [52] and recently rare earth compounds [53].

The electronic channels can be tuned by using rational chemical design, and the

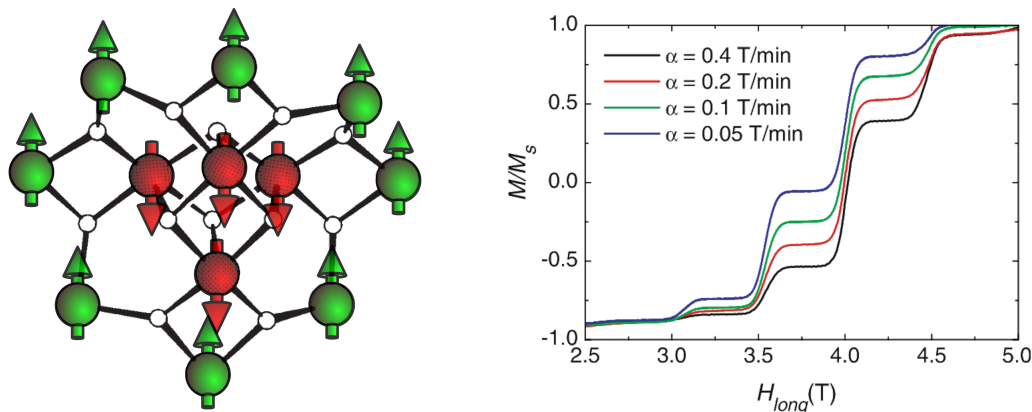


Figure 2.4: **Mn₁₂ac**.

(*left*) Molecular structure of Mn₁₂ac. Its magnetic bistability was first reported by Sessoli in 1993 [48]. (*right*) Mn₁₂ac magnetisation plotted against field for several sweep-rates ($\alpha = dH/dt$), in pure quantum regime ($T = 0.6\text{K}$): the steps in the plot are associated with magnetic quantum tunnelling without thermal excitations. Figures adapted from [48] and [54].

created molecules can be integrated into nanoelectronic devices, such as those formed by graphene [55] and carbon nanotubes [56], or onto functional surfaces [57]. This may happen either by changing the magnetic core of the SMM, which usually consists of one or more transition metals or rare earth ions, or by engineering the ligands to optimise the bonding properties to specific materials, or by studying the best combination of both ligand and core to achieve a multi-QD configuration within the same molecule. In addition to that, scalability is possible by bottom-up chemical synthesis, which allows one to produce a large amount of identical molecules. All these properties make SMMs an extremely promising material for spintronic applications.

The spin of an SMM ranges from a few to many times that of an electron. Even when organised in crystals, SMMs are relatively far apart and magnetic interactions between them are usually negligible. Under these circumstances, a sample can be considered an ensemble of identical, non-interacting, nanoscale magnets.

Although some properties may vary substantially from one type of SMM to another, the most important features are in common and can be understood by analysing the archetype Mn₁₂ac (Fig. 2.4). The magnetic core of Mn₁₂ac counts four Mn⁴⁺ ions

each coupled ferromagnetically giving a total spin $S = 4 \cdot 3/2 = 6$; the outer shell counts eight Mn^{3+} ions that account for $S = 8 \cdot 2 = 16$. Since the inner core couples with the outer ions via superexchange through oxygen bridges, the result is a total net spin of $S = 10$. This spin is rigid at low temperatures and shows a large magnetocrystalline anisotropy with a barrier $U \sim 70$ K with a relaxation time that follows Arrhenius law [58]. Magnetic hysteresis loops are present below the blocking temperature ($T_B = 3$ K) [48]. Fig. 2.5 shows the model for slow relaxation of magnetisation. Since the anisotropy barrier scales with S^2 , the spin states are represented by a double-well potential: each well represents one of the two possible directions for the spin, with a two doubly degenerate ground state in zero field. The separation between the wells is due to the magnetic anisotropy. The energy level for the different spin states are quantised and represent the projection (m) of the total spin S along the axis of the molecule.

2.3.2 Quantum tunneling of magnetisation

The possibility of quantum tunnelling of the magnetisation has been conceived just after a few years from the first discovery of the magnetic properties of Mn_{12}ac . Several early experiments reported peculiar features at very specific field values like modulation in the magnetic relaxation time $\tau(H)$ with minima at zero field [60] and 0.3 T [61], and sudden complete magnetisation reversal (spin avalanche) at 1 T [62]. These clues have finally lead to the confirmation of macroscopic quantum tunnelling of the magnetisation of Mn_{12}ac in 1996 [63, 62, 64].

Below the blocking temperature the hysteresis loops of SMMs sport peculiar steps [65], like depicted in Fig. 2.4, which are related to magnetic relaxation. At certain field values, levels with opposite spins will align triggering a resonant tunnelling spin flip. This is the source of the steps observed in the hysteresis loops of Mn_{12}ac and in general in all SMMs. Recently this behaviour has been also found in some high-spin

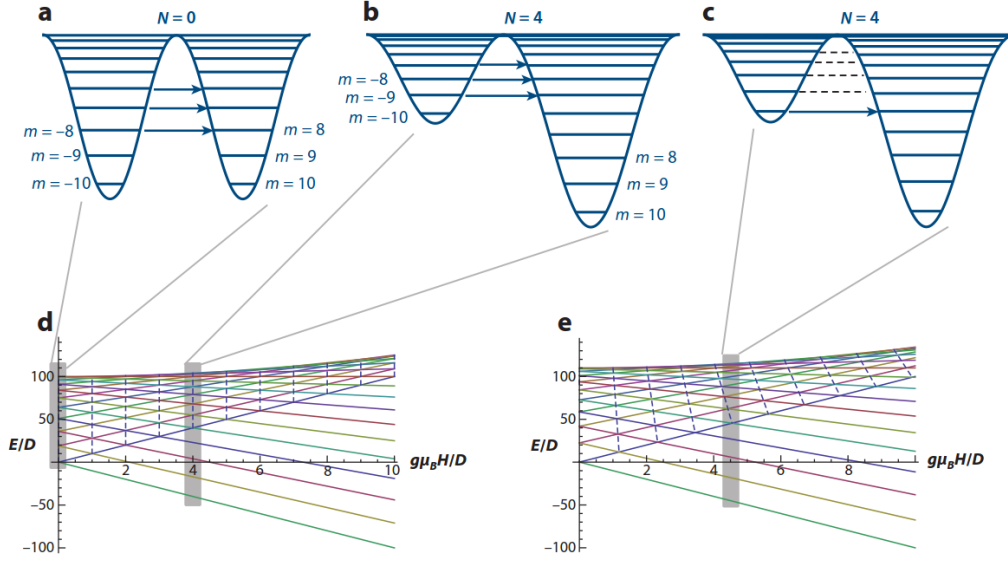


Figure 2.5: **SMMs double-well scheme.**

Sketch view of a double-well potential for an SMM with spin $S = 10$ and the relative energy splitting when an external magnetic field lifts the degeneracy between spin-up and spin-down states. Arrows denote quantum tunnelling. (a) Double-well potential in the absence of an external magnetic field.

(b) Applying a resonant magnetic field quantum tunnelling from low spin-down states to higher spin-up ones is activated.

(c) A small fourth-order term in the Hamiltonian $\propto S_z^4$ induces an energy shift that depends on the spin, and levels are no more evenly spaced. This means that spin pairs align at different magnetic fields.

(d) Energy of spin projection states $|m\rangle$ versus applied magnetic field derived from the first two terms of the Hamiltonian (Eq. (2.25)). Vertical dashed lines show level crossing at the same field value.

(e) Same as (d), but with a fourth-order term included in the Hamiltonian that depends on the spin absolute value. Now different level pairs are resonant at different field values. Figures adapted from [59].

rare-earth ions. [66, 67].

The Hamiltonian that describe a SMM take the form:

$$\mathcal{H} \approx DS_z^2 - g_z\mu_B S_z H_Z - AS_z^4 + \mathcal{H}', \quad (2.25)$$

where the first term describe the anisotropy barrier, responsible for the creation of the two wells in Fig. 2.5; the second is the Zeeman splitting that takes into account the different energies for spin-up and spin-down states in a magnetic field, lifting the degeneracy of the states; the third is the next-highest-order crystal-field term; and the last term, $\mathcal{H}'$, contains all symmetry-breaking operators that do not commute with S_z and then break its conservation, allowing tunnelling.

The main features described in the double-well model arise from the first two terms of Eq. (2.25) and are sufficient to characterise an SMM behaviour when it is highly symmetric. Higher-order parameters have to be taken into account for low-symmetry SMMs. The steps in the hysteresis loop relate to resonant fields with Zeeman splitting equal to the anisotropy term ($H_N = ND/g_z\mu_b$).

At sufficiently low temperatures, tunnelling arises mainly from the ground state and the hysteresis loop is wider. With increasing temperature, the hysteresis loops become narrower: spins are thermally activated to higher levels, from which they can more easily tunnel across the barrier. Once the blocking temperature T_B is reached, the hysteresis loop is completely closed and the thermal energy is sufficient for the magnetisation to fast achieve equilibrium.

2.3.3 Single Molecule Spintronics

As we have already seen in Section 2.2.3, the use of OS has been widely used in spintronics to replicate common devices previously based on inorganic materials. However, with the possibility of tailoring the properties of the molecules based on the

researchers need, molecular electronic with organic materials open the road towards single molecule spintronics (SMS) [68, 69]. In particular, the most appealing feature of this field would be the ultimate control of single spin centres for new generation of nano-spin valves as well as spin transistors [70, 71].

However, one of the major concerns that afflicts the field of SMS is the stability of the molecules, both under a physical point of view (are they mechanically stable in the device?) and under a chemical point of view (what is the nature of the bond with the contacts?). The field is relatively new, and still requires further study. The last project of this thesis is dedicated to the study of the hybridization of a SMM with hybridised states with graphene contacts (Chapter 6).

The following section is dedicated to the study of the general behaviour of such ultimate electronic components, with a section dedicated to molecular transistors.

2.4 Single Electron Tunnelling

This section will treat the transport properties of small islands of metal or semiconductor with a spatial extension small enough to induce quantisation of charge at equilibrium. Such a device is known as *single-electron transistor*, and has been suggested first in 1951 by Gorter [72] to explain the raise in resistance of thin granular metallic films when the thermal energy kT is comparable with the energy necessary to separate charges on different grains. To see it experimentally proven we actually had to wait more than 30 years, when Fulton and Dolan [73] observed the quantisation of charges in the Bell Laboratories.

These electric quantum dots behave as small capacitors with self capacitance C_Σ , weakly coupled with the leads through tunnelling capacitances $C_{s,d}$. If the thermal energy of the device is inferior to the Coulomb energy necessary to add an electron to the dot ($k_B T \ll e^2/C_\Sigma$), the electric transport is blocked. This is the so-called

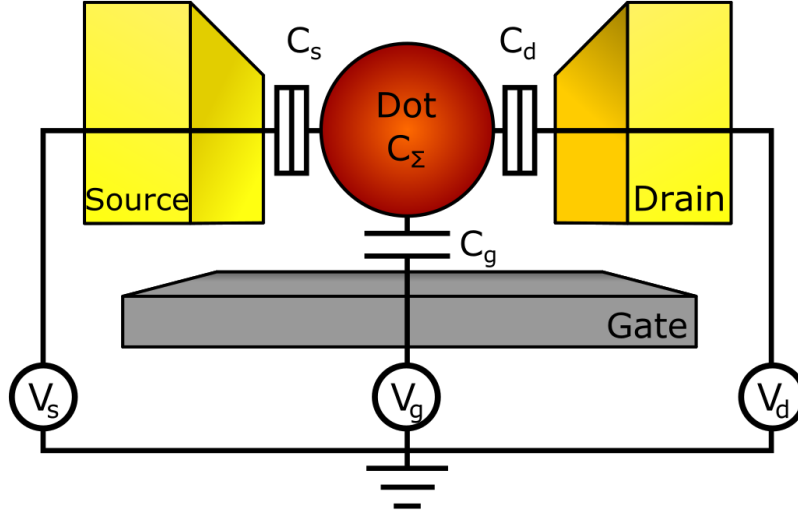


Figure 2.6: **Quantum Dot - Electrical Scheme.**

Schematic representation of the electrical circuit that constitute a Quantum Dot Transistor. The dot is coupled with a tunnelling capacitance C_s to the source and C_d to the drain lead, and with a standard capacitance C_g to a gate electrode. C_Σ is the self-capacitance of the dot.

Coulomb Blockade (CB) regime.

2.4.1 Electronic Properties of Quantum Dots

The simplest electrical representation of a Quantum Dot (QD) can be seen in Fig. 2.6, where the capacitive coupling of the dot respectively with source (C_s), drain (C_d), and gate (C_g) as well as the self capacitance C_Σ are depicted. Whenever a potential is applied to one of the device contacts, an induced charge appears on the other ones that is described as follows:

$$Q_i = \sum_{j=0}^n C_{ij} V_j. \quad (2.26)$$

The indexes i and j cycle through the values 0 for the dot, 1 and 2 for source and drain, and 3 (and above) for the gate(s). C_{ij} is the capacitance matrix that describes the coupling of each element to the others, and in order to maintain the overall charge neutrality has to obey the relation $\sum_{i=0}^n C_{ij} = 0$ which gives, for the self capacitance

$$C_\Sigma \equiv C_{00} = -\sum_{j=1}^n C_{0j}.$$

From Eq. (2.26) we can calculate the electrostatic potential when a charge $Q_0 = -eN$ populates the dot:

$$V_0(Q_0) = \frac{1}{C_\Sigma} \left(Q_0 - \sum_{j=1}^n C_{0j} V_j \right) \quad (2.27)$$

where I made the assumption that there is no charge on the dot in absence of an applied potential to the leads. To calculate the total energy $U(N)$ of a QD charged with N charges, one needs to integrate the relation above over the charge:

$$U(N) = \int_0^{-eN} V_0(Q_0) dQ_0 = \frac{e^2 N^2}{2C_\Sigma} + eN \left(\sum_{j=1}^n \frac{C_{0j}}{C_\Sigma} V_j \right), \quad (2.28)$$

where we can see how the energy of the system is composed by a Coulomb repulsion of the N charges and a term that represents the tuning via external gating. The *addition energy* is the energy required to add a single electron to an island, and to add the N th to a system that already has $N - 1$ charges, it takes this form:

$$\mu_N = U(N) - U(N - 1) = \frac{e^2}{C_\Sigma} \left(N - \frac{1}{2} \right) + e \left(\sum_{j=1}^n \frac{C_{0j}}{C_\Sigma} V_j \right). \quad (2.29)$$

From Eq. (2.29) we may see how, by tuning the gate(s), it is possible to modulate the energy levels of the dot so that they fall between the electrochemical potentials of source and drain, allowing for electrons to tunnel through the island. This opens a conduction channel that lifts the CB and allows a current to flow through the device, with the total number of electrons on the island that continuously fluctuates between $N + 1$ and N .

During an experiment, the typical electrical characterisation of a QD can be displayed as a map of the current I_{sd} as a function of the applied gate V_g and bias V_{sd} (Fig. 2.7). This plot is named *Stability Diagram* (SD), and the typical diamond-

shaped zones with higher conductance are called *Coulomb Diamonds*. An alternative way of displaying the results is plotting the differential conductance dI_{sd}/dV_{sd} , which clearly shows smaller features that modulate the current as sharp lines, like I will show in Chapters 5 and 6.

Coulomb blockade in semiconductors. In all the above discussion I used only classical arguments which are enough when the island has a continuous distributions of electronic states (metallic). When the QD is composed by a semiconductor also size quantisation effects have to be taken into account. The *constant-interaction model* is the simplest way to integrate the size quantisation with Coulomb blockade theory. It is based on the assumption that the total energy of the dot is given by the sum of the single-particle energies and the electrostatic one:

$$E(N) = \sum_{i=1}^N \epsilon_i + U(N), \quad (2.30)$$

where $U(N)$ has the form calculated in Eq. (2.28). Also in this case, the addition energy necessary to add just the N th electron to a dot can be calculated with:

$$\mu(N) = E(N) - E(N-1) = \epsilon_N + \frac{e^2}{C_\Sigma} \left(N - \frac{1}{2} \right) + e \left(\sum_{j=1}^n \frac{C_{0j}}{C_\Sigma} V_j \right). \quad (2.31)$$

It is often useful to define a quantity that represents the quality of the coupling of a gate to the dot, the so-called *lever arm* α :

$$\alpha_i \equiv -\frac{C_{0i}}{C_\Sigma}. \quad (2.32)$$

While this quantity may be constant and well defined for metallic gates, this is not the case for semiconducting gates, which show a slow change as a function of the applied voltage, making Eq. (2.31) not linear. On top of the quantisation effects,

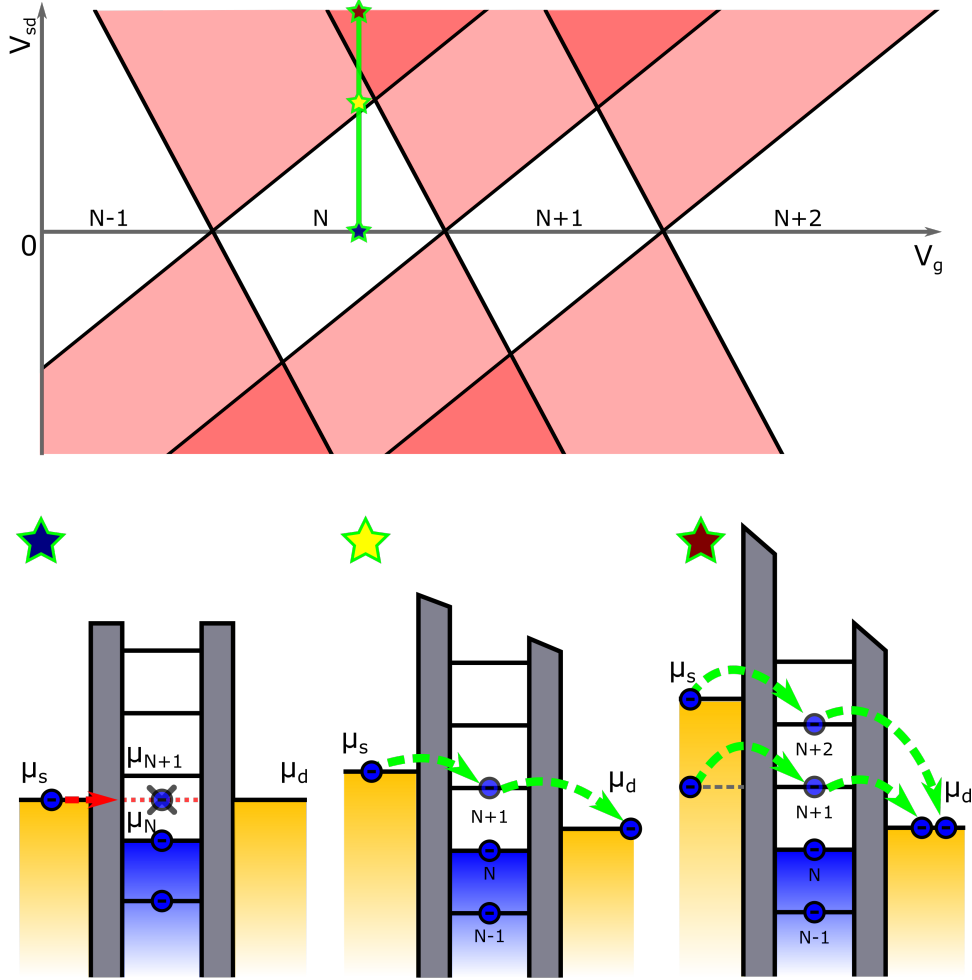


Figure 2.7: **QD Stability Diagram and Energy Levels.**

Example of a stability diagram for a SET with the relative energy diagrams. (*top*) SD displaying the absolute value of the current that tunnels through a dot, I_{sd} , as a function of the applied V_g and V_{sd} . The intensity of the current has discrete sharp jumps as more states are available in the bias window. In the white region there is no current, since all the states of the QD below the Fermi level (μ_F) are occupied by electrons that have not enough energy to tunnel out.

(*bottom*) Energy levels of the leads and the QD, related to the starred points in the SD above.

the ϵ_N term may also account for other external parameters that may influence the energy levels; for instance it can experience a shift due to an external magnetic field (induced) or electric field (induced or from charge traps): $\epsilon_N = \epsilon_N(B, E, \dots)$.

Coulomb blockade in single molecule transistors. Considering an island composed by a single molecule, the energy term in Eq. (2.30) will not only account for the classical charging energy, but also for the energy of the molecular orbitals filled. Furthermore, any excited state of the molecule may be accessed by tunnelling electrons, showing as additional lines in the conducting regions of a SD.

Another effect that worth noticing is that the molecular orbitals may hybridise with the contact leads, depending on the nature of the adsorption of the molecule in the gap (either physisorbed or chemisorbed). As a consequence, a broadening of the molecular levels and a modulation of the electron transfer rate appears. I will discuss these effects in the following section.

2.4.2 Coupling Regimes

Depending on the hybridisation between the molecule's orbitals and the leads, we may have different coupling regimes with the leads. In the following I will analyse the two extreme: the weak coupling, when the molecule's orbitals are spatially well-confined in the barrier potential, and the strong coupling, when some orbitals overlap with the leads leading to an hybridization.

Weak coupling. In the weak coupling regime the quantum dot is connected to the leads via weak electrostatic forces with no overlap of molecular orbitals, and hence $\hbar\Gamma \ll k_B T \ll \Delta, E_C$. This regime is also called *quantum-Coulomb blockade*. In this case the energy levels of the molecule are well separated, and close to Dirac delta functions. This permits the passage of just one single electron at any time with a

conductance G given by:

$$G = \frac{e^2}{4k_B T} \left(\frac{1}{\Gamma_s} + \frac{1}{\Gamma_d} \right)^{-1} \cosh^{-2} \left(\frac{\alpha (V_{G0} - V_G)}{2k_B T} \right) \quad (2.33)$$

where V_{G0} is the position of a specific coulomb peak in the gate voltage axis. We can see from this relation that the amplitude of the peak scales inversely with the temperature T and it is affected by the coupling with the leads ($\Gamma_{s,d}$). Moreover, the shape of the peak is exclusively temperature broadened, as the coefficient of the hyperbolic cosine in the formula shows. This allows for an estimation of the electron temperature of the quantum system:

$$T \leq \frac{e\alpha\Delta V_G}{4 \operatorname{acosh}(\sqrt{2})k_B} \approx 3.29 \alpha\Delta V_G \text{ K/meV} \quad (2.34)$$

where $\alpha\Delta V_G$ is the full width half maximum of the peak in units of energy (meV).

Strong Coupling. Whenever the thermal broadening of the energy levels induced by thermal excitation is smaller than the coupling to the leads ($k_B T \lesssim \hbar\Gamma$), the line shape of the coulomb peak is well represented by a Lorentzian, and the conductance is given by the Breit-Wigner formula [74]:

$$G = \frac{2e^2}{h} \left(\frac{1}{\Gamma_s} + \frac{1}{\Gamma_d} \right)^{-1} \frac{\hbar^2 \Gamma}{\alpha^2 (V_G^{max} - V_G)^2 + (\hbar\Gamma/2)^2}. \quad (2.35)$$

This equation is valid in considering the case of non-interacting electrons (charging energy $e^2/C_\Sigma \ll k_B T, \hbar\Gamma, \Delta$). Furthermore, the passage of charge in the dot does not need to be sequential and for any energy level, two opposite spin electrons can tunnel at the same time. When the hybridisation between lead states and dot states is large, higher order processes in the transport may occur, involving more than a particle at a time. The most common phenomena are cotunnelling (elastic or inelastic) of multiple

electrons and the Kondo effect, as we may see in the following sections.

2.4.3 Higher order Processes

Higher-order processes involve more than a particle at a time, and for this reason the magnitude of the related current scales with the power of the order of the process itself ($I \propto \Gamma^i$). For this reason the only detectable effects are the second order ones, when two electrons tunnel through the dot fast enough to access virtual states. In particular, the time τ that the system is in a forbidden state must satisfy the uncertainty principle of Heisenberg ($\tau < \hbar/E$).

Cotunnelling. An electron that populates a state with energy μ_N below the lead energy μ_d can tunnel into the drain leaving the dot in a virtual state with a free level. If a second electron tunnels from the source into the dot in a time that respects the Heisenberg principle, the net outcome is the net transport of a single charge through the QD and the energy conserved. This effect, that involves the simultaneous tunnelling of two electrons in the device, is called *cotunnelling* [75]. The net effect is a non-zero current in the blockade region, which is always present and depends on the magnitude of the coupling constants $\Gamma_{s,d}$. If the virtual state is unique, and there is no loss of energy in the barrier, the cotunnelling is *elastic*. Otherwise, when excited or vibrational states are accessible, electrons may tunnel from the source to one of these, while another electron from the fundamental level tunnel to the drain. The net energy of the electron is not conserved during this process, since the molecule is left in an excited state after the transport of charge. In this case the cotunnelling is called *inelastic*. In contrast to elastic cotunnelling, this effect may happen only when a sufficiently large bias voltage is applied ($V_s d > \Delta E/e$, with ΔE the energy of the excited state), and it is detectable in a stability diagram as an horizontal line in the blockade region intersecting the corresponding excitation line in the SET region.

Kondo Effect Back in the 60s, Juan Kondo formalised the theoretical explanation for a phenomenon observed in metals with magnetic impurities: below a certain temperature (the Kondo temperature T_K) their resistance unexpectedly increases instead of keeping reducing as expected from band theories. This can be explained in first approximation with the creation of an hybrid collective state of charge carrier with spin states that screen the spins of the magnetic impurities. In metals this collective states represent impurities with a high cross-section for the charges flowing in the material, resulting in an increase of resistance. On the other hand, in a molecule coupled with metallic leads the net result is the opposite: an increase of conductance. An explanation for this case is that the screening electrons in the leads create a higher localised density of states that hybridise with the molecule, causing a rise in the conductance. In a stability diagram, the presence of Kondo effect can be detected as a conductive line at zero bias in Coulomb diamonds with an odd number of electrons in the QD, since that is the condition for having a collective state with spin $S = 1/2$ that hybridise with the leads.

2.5 Materials

We saw in the first sections of this work how integrating magnetic materials and impurities into nanoelectronic devices unlocks a new channel of information, the electronic spin, which may be exploited in parallel with the canonical charge/potential information. Both spintronics and molecular electronics deeply depend on the development, study and integration of diverse magnetic materials, tailored and engineered down to atomic-level scale.

In particular, the last decades we have seen an increasing research activity in the field of organic compounds and advances in production techniques for carbon-based nanomaterials, which from one side enables a huge experimental ground with

many possible synthetic possibilities, and from the other side a fast and reproducible bottom-up creation of nano-components.

In this work I studied and exploited the electronic and magnetic properties of different materials (organic radicals, rare earth SMMs, carbon nano-structures) at different dimensionalities (from microscopic crystals to single molecules). Hereafter, I will present a resume of the materials that are matter of further studies in the following chapters of this thesis.

2.5.1 Organic Radicals

Free radicals are single atoms, ions or molecules with an unpaired valence electron, and they may be either organic or inorganic. The presence of a half-filled orbital makes these compounds chemically very reactive, hence fundamental in intermediate stages of chemical reactions, as well as processes like polymerisation [76], combustion [77] and a fair number of biological mechanisms, like cellular metabolism and immuno-response [78]. The first family of magnetic materials I study in this work are molecular organic radicals of the nitronyl-nitroxide (NIT) family [79, 80]. The unpaired electron is located in a nitrogen atom with a missing bond to complete its outer shell. Furthermore, different oxidation states are possible (Fig. 2.8), making them interesting materials for memory electronic components [81]. These compounds have already been studied and are well characterised in literature, and they have always been categorised as *Mott insulators* [82], i.e. materials that should be conductors according to the classic band theories (thanks to their unpaired electron), but that actually prove to be insulators. The reason for this is ascribed to electron-electron interactions which play a fundamental role hindering electronic transport through unit cells in the crystal; effects that are not considered in the band theories at all. During my studies I actually found out that this is not completely true: intermolecular stacking between the NIT motif and its decorations may create useful electron

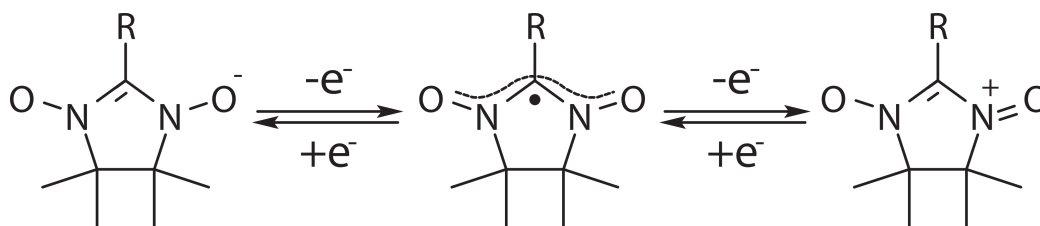


Figure 2.8: NITs, Oxidations States.

Schematic representation of the general structure of the nitronyl-nitroxide (NIT-R) radicals, showing the different oxidation states that are available at room temperature and the reduction or oxidation processes from the pristine neutral form.

transport channels, as we shall see in Chapter 4, re-opening the discussion on the subject.

One of the most appealing properties of NITs, and the main reason I chose this family for my studies, is their capability to be decorated with (or to decorate) a wide variety of other compounds [83, 84, 85], in particular carbon-based organic complexes [28, 86]. This opens ways to design new magnetic materials with a whole set of different, customisable, features, like the crystal structure and bulkiness, the distance between spin centres and the possibility to dope with either donor or acceptor species [87, 88].

2.5.2 Rare Earth SMMs

Coordination complexes are chemical compounds consisting of a metallic core atom or ion (the *coordination centre*), surrounded by a structured array of molecules or ions (*complexing agents* or *ligands*) [89]. When the coordination centre is a single rare-earth, slow relaxation of the magnetisation can happen [90]. Furthermore, the energy necessary to flip the magnetization of a molecule with slow relaxation, and hence revert it back to a normal paramagnet, has been demonstrated to be higher in systems with a high ion-core anisotropy [91]. This makes lanthanide and actinides the best candidates amongst all the elements of the periodic table to build SMMs. More important, a large family of compounds based on rare earth, especially lanthanides,

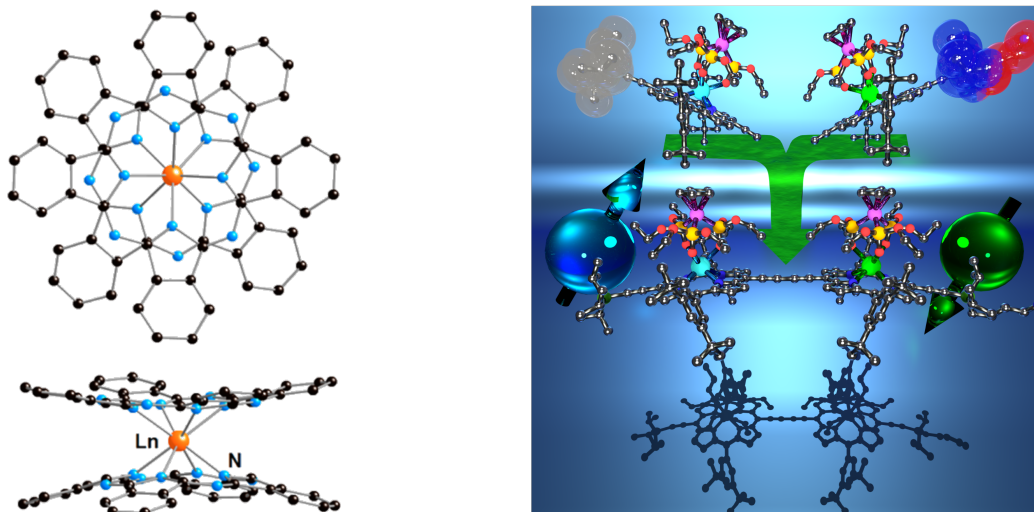


Figure 2.9: **Lanthanide SMMs.**

(left) Typical molecular structure of a double-decker SMM based on a lanthanide ion core (Pc_2Ln). The top and bottom ligands are phthalocyanines groups (Pc, $(C_8H_4N_2)_4H_2$). Figure adapted from [53].

(right) Artistic view of the LEGO-like approach to build single molecule electronic components based on two Ln-ion cores: two SMMs with a different metal core combine in a lanthanide-porphyrin dimer. This brings the two nuclei spins in close contact, with the capability of interacting via the coupling induced by the ligand. The representation is based on actual crystallographic data [94].

proved to have great potential in device applications, especially when deposited on surfaces or embedded in nano-devices [92, 93].

In this work I focus on a dimer based on two molecules with a dysprosium core, bond together with an hexafluoroacetylacetonate (hfac) ligand: the $Dy_2(hfac)_6(bpym)(EtOAc)_2$ complex, or Dy_2bpym . In Chapter 6 I will describe its properties when evaporated on different substrates forming thin films, while in Chapter 6 I will embed single molecules in nanodevices with the aim of studying the magnetic anisotropy of a single molecule.

2.5.3 Graphene

A single sheet of carbon atoms disposed in a honeycomb geometry: this is *graphene*, the thinnest material man is able to produce. Even though the theory behind such

a peculiar material has been largely developed in the last century, graphene is one of the last carbon based nanomaterial that has been experimentally isolated, back in 2004 [95]. Since then, theoretical and experimental research thrived around this topic, given the unprecedented electronic, optoelectronic, thermal and mechanical properties that graphene sports. All this makes it an ideal candidate for various applications in next generation electronics, as possible substitute to silicon, high-density energy storage, sensors and as ideal nano-membrane for filtering or DNA-sequencing.

2.5.3.1 Electronic Structure

A carbon (C) atom counts six electrons and they are in a $(1s)^2(2s)^2(2p)^2$ configuration. The orbitals in the outer electronic shell ($n = 2$) can hybridise allowing it to form up to 4 bonds with other atoms when combined in a molecule or in a crystal. In diamonds, all four orbitals of the carbon atoms that compose the crystal are hybridised (sp^4) and bonds to each other with strong σ covalent bonds. In the more common form of graphite, which is basically a stacking of graphene sheets, one on top of the others, one p -orbital does not participate in the hybridisation, while the other, together with the two $2s$ ones, form three sp^3 orbitals. These three hybridised orbitals are the ones that constitute the backbone of the hexagonal lattice and allow for each carbon atom to form strong covalent σ bonds with other three carbons in the lattice. Their energy is high above the Fermi level and their main contribution is structural, explaining the great mechanical properties of the material [96]. The remaining p_z -orbital contributes an electron that is actually shared via a weakly localised π -bond with all the carbons in the same ring, creating a π -band with energies around the Fermi level (Fig. 2.10), which grants graphene its peculiar transport and thermodynamic characteristics.

The unit cell of the crystal structure is actually composed by two neighbouring atoms distant $1.42 \text{ \AA}$ and has a triangular shape, with crystallographic axes $a_{1,2} = 2.46 \text{ \AA}$ long and separated by an angle of 60° . This could also be seen as the

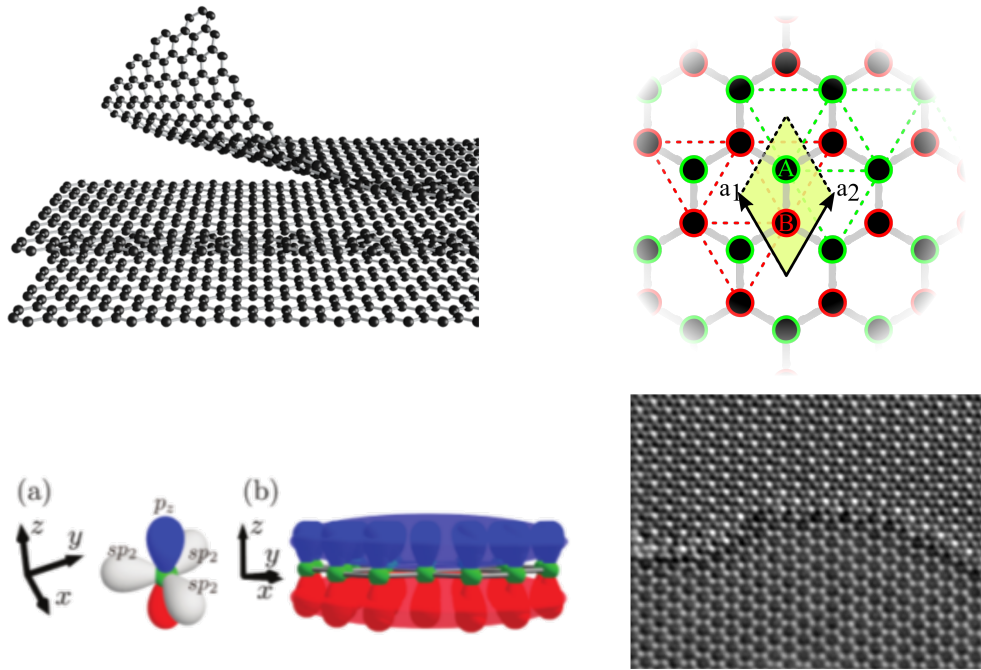


Figure 2.10: **Graphene, Structure.**

(top left) Artistic view of a single sheet of graphene peeled from graphite.

(top right) The base cell of graphene is composed by two carbon atoms (A and B), repeated along its crystallographic axes ($a_{1,2}$).

(bottom left) Electronic orbitals in a graphene ring, and their hybridisation that generates the π and π^* bands

(bottom right) High-Resolution Transmission Electron Microscopy (HRTEM) image of mono- and bi-layer graphene (from [97]).

presence of two equivalent triangular sub-lattices superimposed. Using a simple nearest neighbour tight-binding approach [98] it is possible to describe the band structure of the graphene, with a dispersion relation given by:

$$E = \pm \gamma_0 \sqrt{1 + 4 \cos \left(\frac{\sqrt{3}}{2} k_x a \right) \cos k_y a + 4 \cos^2 k_y a} \quad (2.36)$$

where $\gamma = 3.033$ eV is the hopping parameter obtained from the nearest neighbour overlap integral. The resulting band structure is displayed in Fig. 2.10, where we can see that the conduction and valence band meet in six points, called *Dirac* or *charge neutrality points*, of which only two are non-equivalent in the phase-space: K and K' . Considering that every carbon contributes exactly with one electron to the band structure, the valence band in an undoped material is full, the conduction band is empty, and the Fermi level cross the band structure exactly at the Dirac points. In proximity of each charge neutrality point we can expand Eq. (2.36), obtaining the linear dispersion peculiar to graphene:

$$E^\pm(\vec{k}) = \hbar v_F |\vec{k} - \vec{K}|, \quad (2.37)$$

where $v_F = \sqrt{3}\gamma a/2\hbar \cong 10^6$ m/s is the *Fermi velocity* and it is constant.

2.5.3.2 Fabrication

The simplest way to produce graphene, which is also the way it was first discovered in a stable form, is the so-called *scotch-tape exfoliation* (or micromechanical cleavage). By pressing and pulling an adhesive tape on a pure sample of graphite (HOPG, Highly Oriented Pyrolytic Graphite, commonly used as reference flat surface for STM) it is possible to exfoliate a few layers of graphene. Iterating the process on the residua on the tape, one can obtain crystals of graphene (flakes) of the purest quality. The

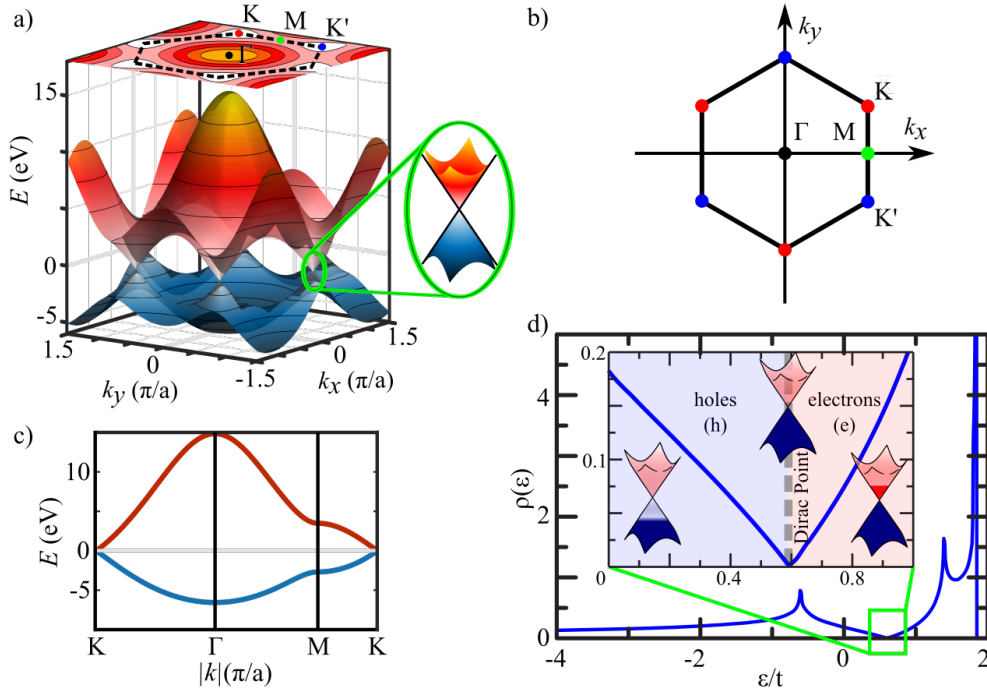


Figure 2.11: Graphene, Band Dispersion.

(top left) Conductance π^* -band (red) and valence π -band (blue) as calculated with Eq. (2.36) in k -space. The two bands touch at the Dirac points, and the electronic dispersion in their proximity is conical with linear slopes in first approximation (inset).

(bottom left) Extract of the electronic dispersion along the highest symmetry lines.

(top right) First Brillouin zone with the 6 Dirac points, of which only two are independent (K and K').

(bottom right) Density of states around the singularity. At the Fermi level the valence band is full and the conductance band empty, so that no free carriers are available (plot reworked from [98]).

drawback of this technique is that the yield of single layer flakes and their dimensions are too low to meet the needs of an industrial-scale production.

In the last few years though, huge steps have been made with the Chemical Vapour Deposition (CVD) technique: a vapour of hydrocarbons, typically methane (CH_4), decomposes when in contact of a transition metal substrate. The carbon atoms stick on the metallic surface and start growing in hexagonal flakes as single crystals up to a few centimetres wide [99]. Once grown up to the desired scale, the flakes can then be transferred to a different substrate, usually silicon (di)oxide (SiO_2), and finally post processed.

2.5.4 Graphene Nanoribbons

Modern electronic devices are based on semiconducting materials, whose characteristic is the existence of a band gap. A band gap is of crucial importance to create (micro)transistors, for example. However, as we have seen in Section 2.5.3.1 pristine graphene lacks a band gap. Nevertheless, it can be obtained by nanostructuring, for example in form of graphene nanoribbons (GNRs). GNRs prove to be extraordinary versatile, considering their tunable properties defined by their chemical structures. They can be created with either a metallic or semiconducting nature, depending on the edge geometry and the width of the ribbon itself.

Edge Geometry and Electronic Structure Even though it is possible to cut graphene in stripes following any direction, the geometry of the edges is of paramount importance in determining the electronic properties of the created nanostructure. Only two geometries present straight regular edges, namely zigzag(ZGNR) and armchair (AGNR) (Fig. 2.12). The cutting angle between the two different geometries is 30° in the graphene plane. Given a geometry, the band structure is then strongly related to the width w of the ribbon, measured in numbers of atoms N in the di-

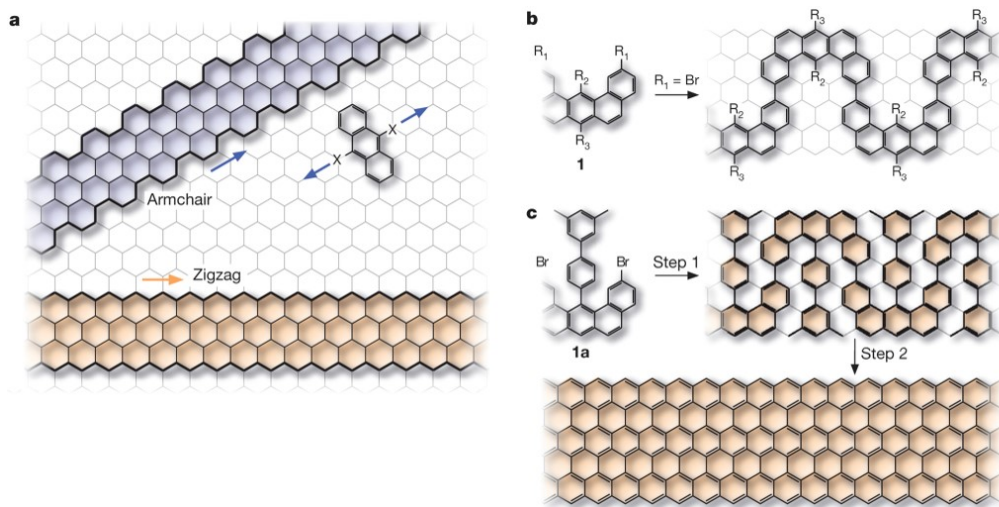


Figure 2.12: **Molecular GNRs.**

(left) An anthracene-based molecular precursor can be used for the production of GNRs with armchair or zigzag edges ($w=2$).

(right) Example with a U-shaped dibenzo[a,j]anthracene monomer precursor. Polymerisation (step 1) and cyclisation (step 2) result in a ZGNR with 6 carbon zigzag lines. (figure from [100]).

rection perpendicular to the length of the ribbon itself. The band structure for both geometries can be obtained via theoretical calculation with a tight-binding approach [101].

For ZGNRs the lowest energy bands are degenerated at the K-points ($k = \pm\pi$) creating a spike in the density of states (DOS) around the Fermi level E_F , giving the ribbon a characteristic metallic behaviour (no band gap). On the contrary, AGNRs show a mixed metallic\semi-conducting behaviour, depending on the width. In particular, whenever the width is $N = 3m - 1$ with m an integer number, the conductance and valence bands meet at the Γ point and the ribbon behaves like a metal.

Synthesis As we have seen, the physical and chemical properties of GNRs are determined by the edges and width of the ribbons. To create GNRs with the desired features require, a control in the fabrication down to the atomic scale is necessary. Huge efforts have been made to improve the top-down production of ribbons since the first synthesis of graphene in 2004, but the resolution of the traditional patterning

methods, namely e-beam and photon lithography, makes them unsuitable for the production of structures with features below 10 nm. Considering that carbon atoms in graphene are 0.14 nm apart, it is clear that this resolution would not permit a deterministic production of narrow GNRs, let alone grant the type of the edge. On the other hand, if such a control is not crucial for the experiment, these methods provide a cheap and fast way to obtain GNRs, even commercially.

Only lately, new bottom up approaches via chemical synthesis became available providing a facile and reliable way of producing large quantities of samples with extremely well-defined and reproducible characteristics [102]. Starting from synthesised organic molecular precursors that undergo polymerisation at first and then a cyclodehydrogenation, the outcoming GNRs not only have a precise edge structure and width, but also the desired doping (Fig. 2.12, right). This can be accomplished both by utilising a metal surface as a catalyst substrate for the reaction, and in solution, providing two complementary methods of synthesis each with its own advantages in terms of functionalisation, sizes and the characterisation processes [100].

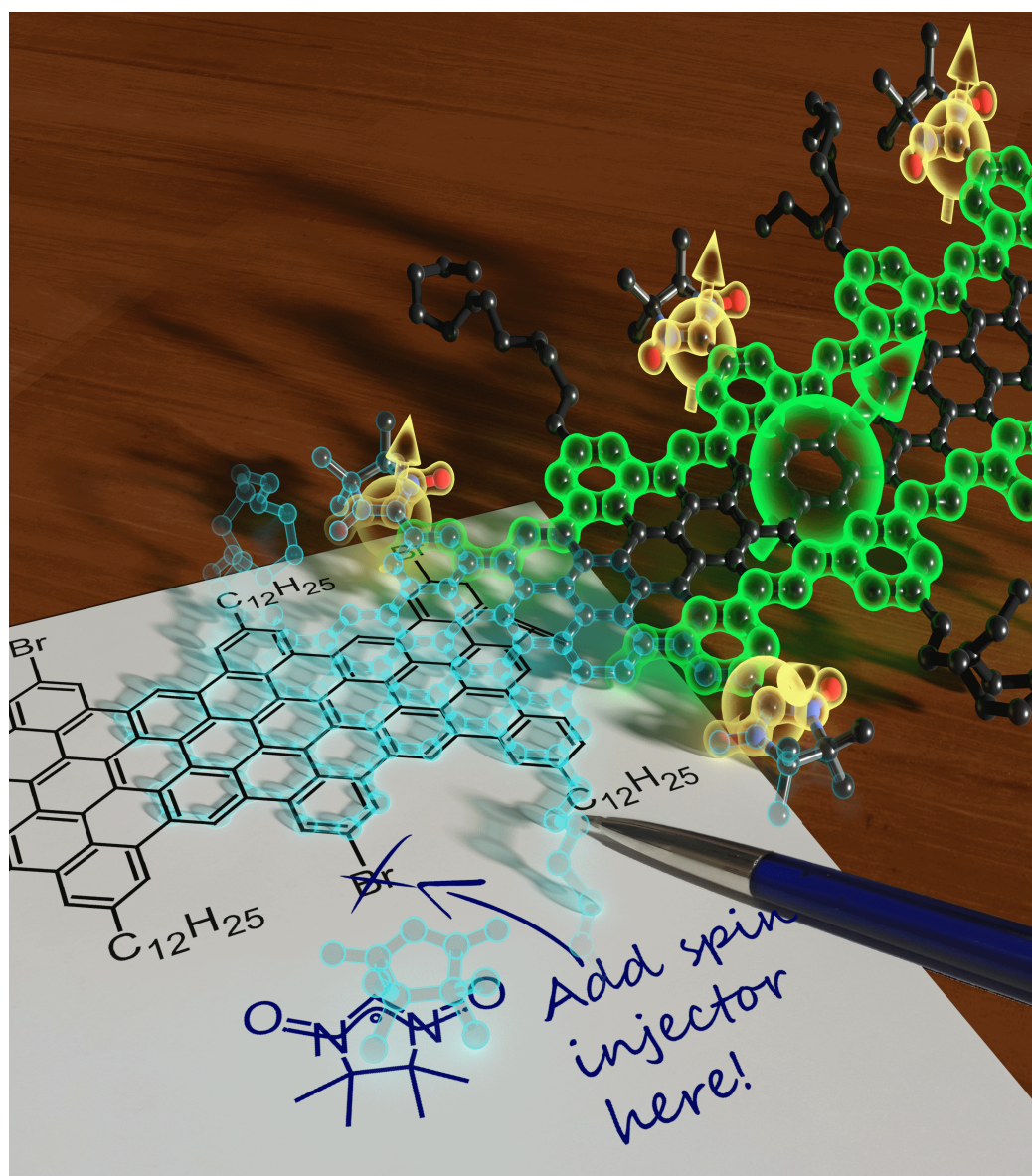


Figure 2.13: **Designing MGNRs**

Artistic view of the processes behind the creation of a functionalised MGNR. Given the molecular building blocks, the scientist designs a molecule prototype. In this case, NIT motifs have been chosen to decorate a ZGNR with the aim of injecting spin densities into the edge states of the ribbon. Concept art created for [28].

Chapter 3

Experimental Methods

If you can not measure it, you can not improve it.

Lord Kelvin

The study of charge transport properties of materials in different dimensionalities requires diverse approaches. This is not only due to the sizes of the analysed samples, but because the different transport channels and phenomena that cause electricity to flow are various. This is particularly important when crossing the boundary between classical and quantum transport.

In this chapter I will present the challenges of measuring electron transport close to the theoretical limits in highly resistive materials (Section 3.1). This is necessary to understand the conduction regimes in molecular crystals (see Chapter 4).

In two dimensions, the analysis of thin-films devices requires a slightly different approach: one of the parameters I was interested in testing is the actual device geometry itself, rather than just the physical properties of the molecules (Section 3.2).

Finally, when the dimensions of the physical object under study are comparable to the electron wavelength in more than two directions (1D and 0D systems), quantum effects not only affect the macroscopic flow of a continuous current, but they introduce interference processes highly dependant on the molecular nature of the conductive

vehicle, providing a method to perform spectroscopy at the ultimate scale of a material (Section 3.3).

3.1 3D: Electrical Characterisation of micro-crystals

When dealing with transport measurements in highly-resistive systems, i.e. above the $G\Omega$ threshold, there are theoretical limits of sensitivity which are bound to the intrinsic noise generated by resistances in the circuit under investigation (Section 3.1.1), and hence their characterisation usually requires advanced setups (Section 3.1.2). This is the case for organic semiconductors (OS). Besides the high-end electronics involved, I used a custom-built probe station with micropositioners that allowed me to measure the microscopic crystals typical of our NIT-R samples (Section 3.1.2).

3.1.1 Low-level Current Measurements

While for the most common transport measurements (DC currents, voltages and resistances), digital multimeters (DMMs) show the sensitivity required (~ 1 nA), different approaches, fixtures and instrumentation are required in our case (Fig. 3.1). Electrometers and picoammeter have a sensitivity as low as 1 fA (10^{-15} A), and the lower input burden decrease the relative error in the measurements, which make them the instruments of choice when measuring ion beam currents, gate leakage checks, insulating materials, or, as in our case, for studying different conduction regimes in a highly-resistive material.

When measuring low currents, there is a variety of error sources which may seriously impact on the accuracy. Particular care has to be taken in realising proper connections, avoiding ground loops and triboelectric or piezoelectric effects that, for high impedance DUTs (*Device Under Test*), may have a significant impact on the

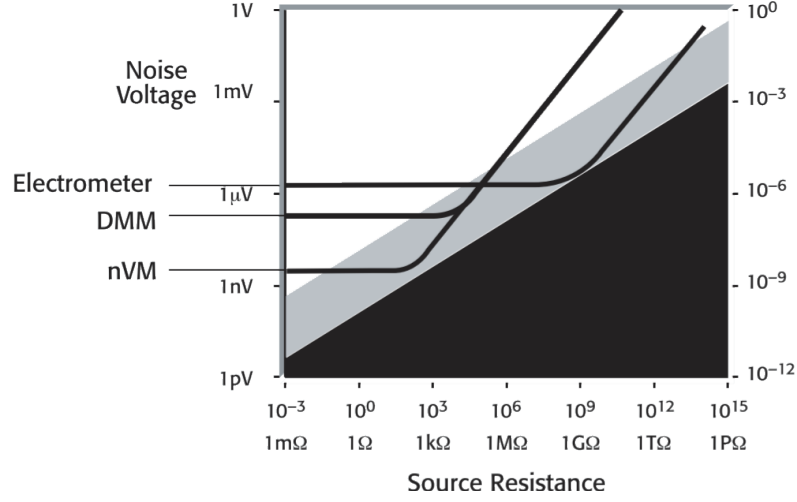


Figure 3.1: **Low-Level, Theoretical Limits.**

Theoretical limits for measuring voltage as a function of the load resistance at room temperature. Black lines represent the ranges covered by Digital Multimeters (DMM), nano Voltmeters (nVM) and Electrometers. (figure from [103])

measurements. Furthermore, cables and fixtures must have a sufficient insulation resistance to have a total leakage current negligible compared to the one measured by the ammeter. In some cases a metal shielding may be necessary to avoid high frequency noise from ambient and thermallight control may be required for sensitive materials.

3.1.2 Probe Station for Surface Currents

Transport experiments on highly resistive crystals in the sub-millimetre range can be performed with a two-point probe high-impedance setup. I used a custom-built probe station (Fig. 3.2) build by Dr. Christian Cervetti at the University of Stuttgart. The measurement setup is constituted by four 3D micro-manipulators (Cascade Microtech), each one fitting a tungsten micro-tip (radius of $10 \mu\text{m}$), a microscope for precise positioning (Leica M60) and, for the electrical measurements, a set of two source meters (Keithley 2400) and an electrometer (Keithley 6517A). The source meters are able to provide $V_{sd,g}$ up to 200 V while reading currents I_{sd} up to 1 A, with

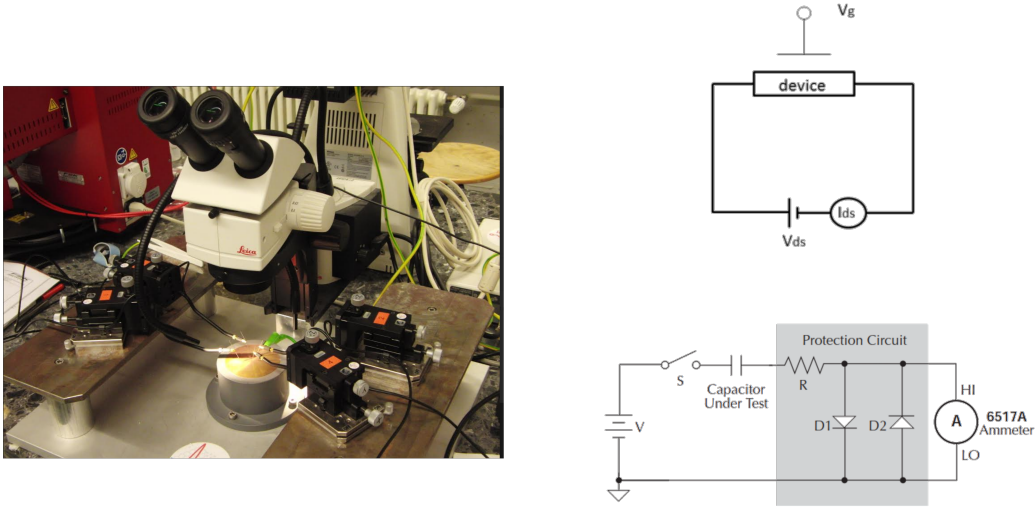


Figure 3.2: **Probe Station.**

(left) The probe station used for my measurements.

(right, top) Electrical scheme for a classic measurement with a source meter, sourcing a V_{sd} up to 200 V and reading the current I_{sd} , while a second one is providing the gate V_g .

(right, bottom) Electrical scheme of the input protection box for the electrometer, used to prevent shock damage in case of a sample electrical breakdown. The box is constituted by two diodes 1N3595 and a resistance $R = 100 \text{ k}\Omega$ (scheme from the instrument manual).

a basic measure accuracy of 0.012%. The electrometer is able to provide voltages up to 1 kV and at the same time measure either the output current, with a sensitivity of 1 fA, or the circuit resistances up to $10^{16} \Omega$.

The sample is positioned on a copper plate that can either be grounded or set to a desired potential useful to provide a back gate, while being electrically isolated from the rest of the stand. Two iron plates accommodate the four manipulators, which are magnetically anchored on top of them allowing for a full customizable positioning on the horizontal plane. The rest of the stand is made of steel, with a sturdy and heavy manufacture to minimise vibrations; furthermore, the whole setup is positioned on a vibration-damped table.

3.2 2D: Thin Film Transport

3.2.1 Thin Film Deposition and Crossbar Devices

The production of electronic devices based on layered thin films of materials with a controlled width may rely on three major techniques.

- **Spin Coating.** This technique can be used with a material that can be uniformly dissolved in a solution. By fixing the substrate on a spinning plate with controlled speed, the solution can be dropcasted in the centre of the sample. Centrifugal forces will then spread the solution evenly on the substrate, with a final thickness that depends on the spinning speed and time, and on the solution concentration and density. I used this technique to create thin film devices based on NIT-R radicals.
- **Physical Vapour Deposition (PVD).** This technique is suited to thermally stable materials. The material is placed in a crucible under vacuum and heated until evaporation starts. The vapour will diffuse and condense on a desired substrate, which is kept at a lower temperature. The layer thickness depends on the temperatures involved and the duration of the evaporation. Furthermore, the deposition can be patterned using a *shadow mask*, designed to cover desired areas of the substrate. In the scope of this work, we used this technique to create the top and bottom contacts for all of our thin film devices, using either cobalt or gold depending on the sample nature. The deposition of the contacts has been made by the technicians of the 1. Physikalisches Institut at the University of Stuttgart. Furthermore, the Dy₂bpym molecules for the devices studied in Chapter 6 have been deposited using PVD by Dr Junfeng Wang at the University of Stuttgart.
- **Chemical Vapour Deposition (CVD).** This technique is used to create thin

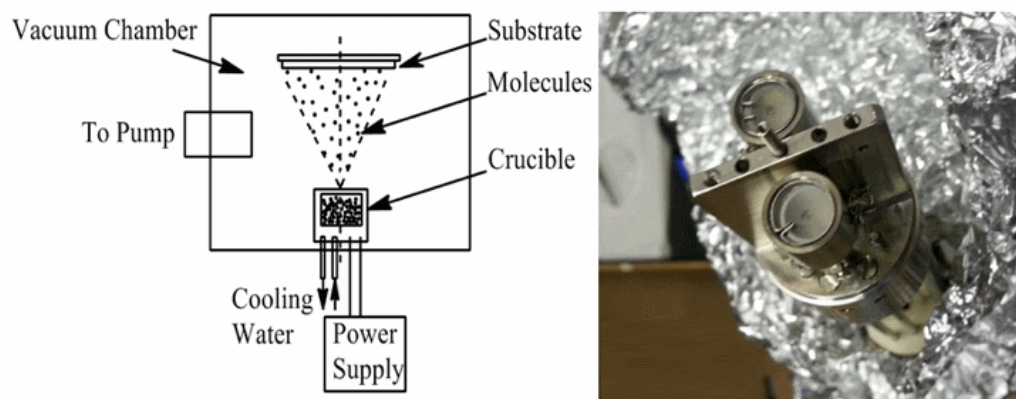


Figure 3.3: **Molecule Deposition.**

(left) Scheme of the molecular evaporation system, with the different elements that can be tuned.

(right) Image of the evaporator with two quartz crucibles used for evaporation process. Figure from [105].

layers of a material that results from a chemical reaction. This may happen between two or more precursors deposited in subsequent steps, from decomposition on the substrate or by means of an external agent (e.g light, heat or plasma waves). In my project I used CVD to grow a thin layer of CoO barrier on top of the Co electrodes, by simple exposure to air. This is known in literature to create a layer of oxide within few seconds, with thickness increasing with the total exposition [104]. The oxide acts both as a tunnel barrier for the electrons and as a contact barrier at the electrodes/active layer of molecules interface, to avoid chemical reactions.

To measure the electrical properties of thin films of magnetic molecules, metal contacts have to be deposited on either side. I decided to deposit the contacts in a crossbar geometry, with the final aim to investigate the potential use of different magnetic molecules as memory elements (similar to [81]). Furthermore, to investigate the potential spin-filtering effect of a magnetic layer, we fabricated also devices with magnetic contacts made of cobalt. Fig. 3.4 shows the two different approaches I used, described hereafter.

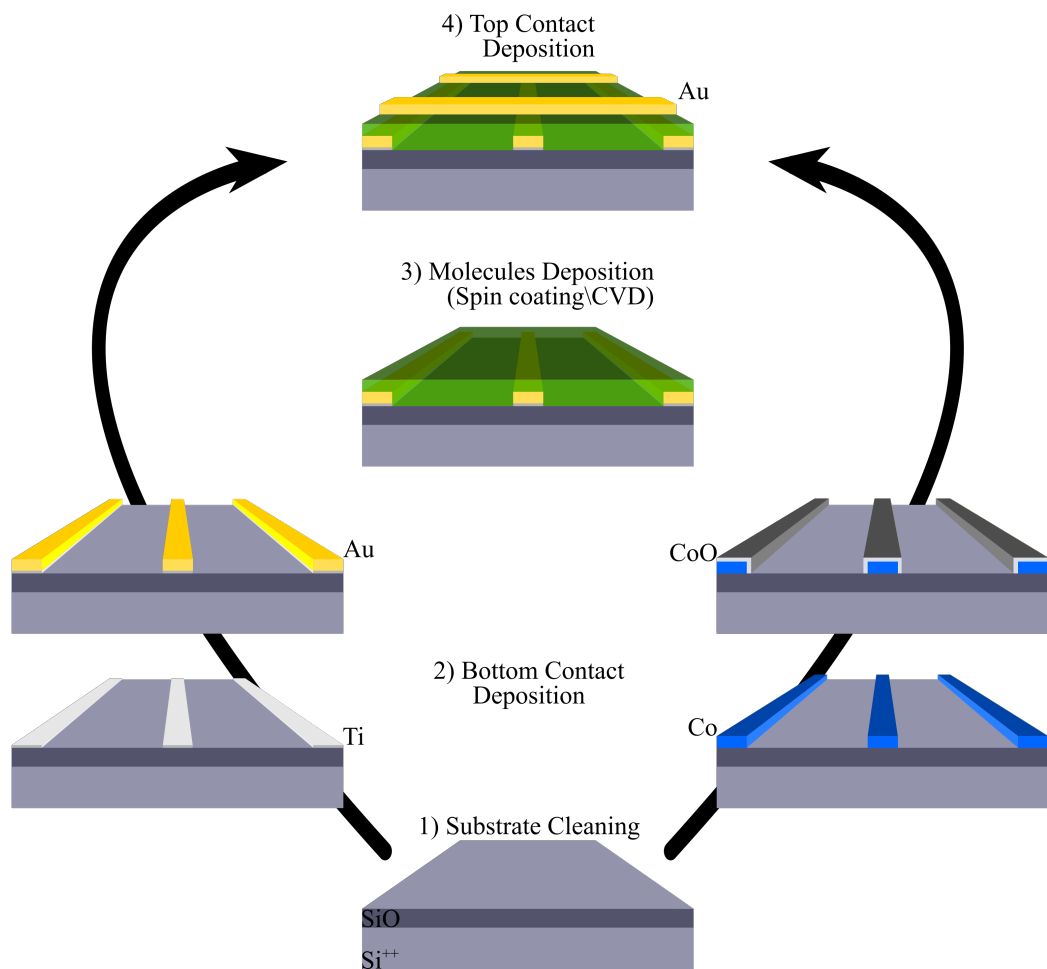


Figure 3.4: **Thin Films - Sample Preparation**

Process flow for the preparation of my thin film devices, with and without magnetic contacts. Process description in the text.

The typical substrate consists in doped silicon (Si^{++}) with an oxide (SiO) insulating layer on top (Siltronix). This allows one to apply a gate potential V_g directly contacting the substrate.

The first layer of contacts is thermally evaporated (PVD) on the substrate as an array of 12 parallel linear contacts using a mask. Width and thickness of the stripes is 50 μm and 60 nm, respectively. The metal used is either Au (in which case a Ti adhesion layer between metal and oxide is necessary), or Co (in which case, the contacts are oxidised in air for 72 hours to create a CoO tunnel barrier). The next step is the deposition of a thin film of molecules, either via spin-coating or PVD. Finally, a perpendicular array of either 1 or 12 golden contacts can be deposited with the same width and thickness of the bottom ones. This allows us to have either an array of 12 devices in line or a crossbar sample with a total of $12 \times 12 = 144$ devices.

3.2.2 Measurement Setup

The electronic transport measurements were performed on a home-made setup created on an Oxford Instruments Sprecromag cryostat, to allow low temperature characterisation of the devices. I performed the transport measurements using a Keithley 4200 Source Meter, both to provide a voltage source V_{sd} and to measure the current I_{sd} flowing in a device. Furthermore, I set up a Keithley 7100 Switch System that allowed me to perform automatic measurements on multiple devices on the same chip by switching the 12×12 combination between the top and bottom contacts.

3.3 1D, 0D: Single Molecule Transistors

3.3.1 Graphene Break Junctions for Molecular Electronics

Recently, the use of graphene leads has emerged as an alternative to metals. These show an improved capability of contacting organic ligands and carbon based materials

thanks to $\pi - \pi$ stacking bonds, and enhancement of the coupling with a back gate given the 2-D dimensionality of the contacts [106, 107, 108].

For our devices we used an n-doped Si substrate capped with a 300 nm SiO_2 insulating layer pre-patterned with 540 pairs of metal electrodes (Cr 10 nm / Au 70 nm). The CVD graphene was transferred using a standard wet transfer technique above the substrate by Pr. J. Warner’s group at the Materials Department of Oxford. The graphene can then be etched using e’beam technology in a bow-tie geometry that bridges the metal contacts, using standard electron beam lithography and O_2 -plasma etching (Fig. 3.5). The central part of the bow-tie cannot be successfully patterned in a nm-size gap suitable for molecule bridging via standard lithographic procedure. Therefore, we proceeded using feedback-controlled electroburning in air, as reported in [106]. The I - V characteristics for each device are automatically recorded, and then checked to identify successfully burned gaps. The yield of the burning process may be as high as 71% [106], but in most cases a yield around 30-40% is expected. due to the fact that devices may not burn properly (due to the quality of the graphene or the presence of multiple layers) or they blow up due to an excess of current, forming a gap too wide to be bridged efficiently by single molecules. If a sufficiently high number of good gaps is present on a chip (at least 15%), the substrate can then be used for molecule deposition. The graphene e-beam lithography and the room characterisation of the break junctions used for the samples in this thesis have been carried out by Dr P. Gehring or Dr T. Pei at the Materials Department of Oxford.

When it comes to functionalise the gap with a molecule, the final yield per chip will be low (usually around 2-3% of the 540 patterned pairs). This number is not purely due to the efficiency of the deposition, but also a trade-off between the need to trap a molecule and the one to avoid having two or more molecules bridging or shorting the contacts. The electro-burning, the room temperature characterisation and the search for good devices is automated.

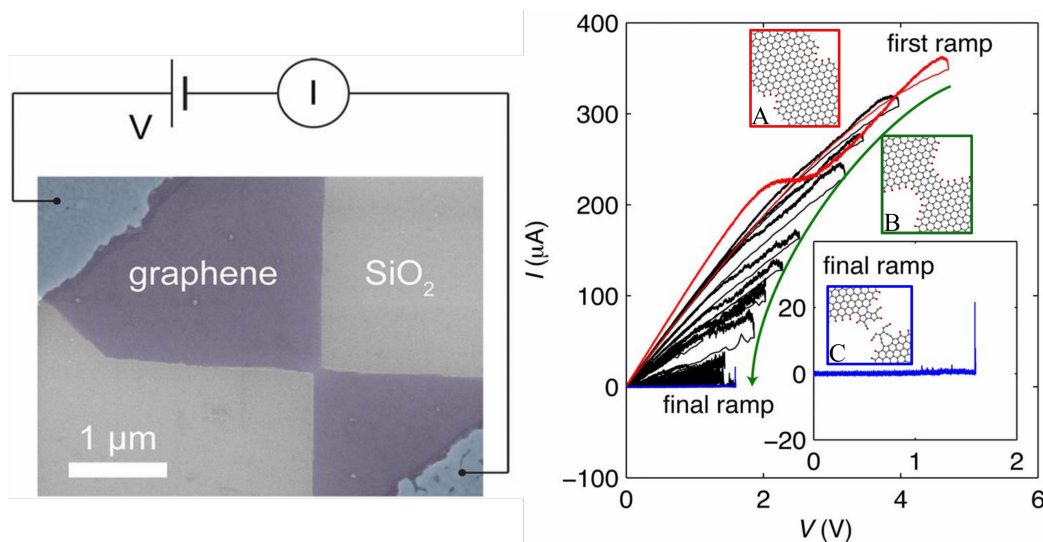


Figure 3.5: **Electroburning Process.**

(left) SEM image of a graphene bow-tie on a silicon substrate. By applying a bias (right) IV curves of subsequent electro-burning processes: once a break-down is detected, the applied bias is quickly ramped down, and the process re-start. Every cycle the intensity of the current decrease, indicating a narrowing of the conduction channel. Finally, when the nanogap is created, only tunnelling current can be detected, allowing for an estimation of the channel width and the barrier height via Simmons fits (Eq. (2.10)). Figure adapted from [109].

In the scope of this work, the following molecules have been used.

Dy₂bpym. The Dy₂bpym molecules were deposited on the graphene electrodes via thermal evaporation Section 3.2.1 by Dr. Junfeng Wang of the University of Stuttgart. This procedure has proved to keep intact the structure of the molecules in thin films, in particular their magnetic properties, as we will see in Chapter 6. The final yield for these molecules is rather low if we compare it with other similar devices fabricated using the same graphene electrodes [110]. This is likely due to the lack of anchor groups in the Dy₂bpym molecules.

Molecular Graphene Nanoribbons (MGNR). MGNRs were deposited via dropcasting a dispersion of substance in powder sonicated in chlorobenzene (PhCl) for about 30 min. Dr P. Gehring and Dr T. Pei, of the Materials department of

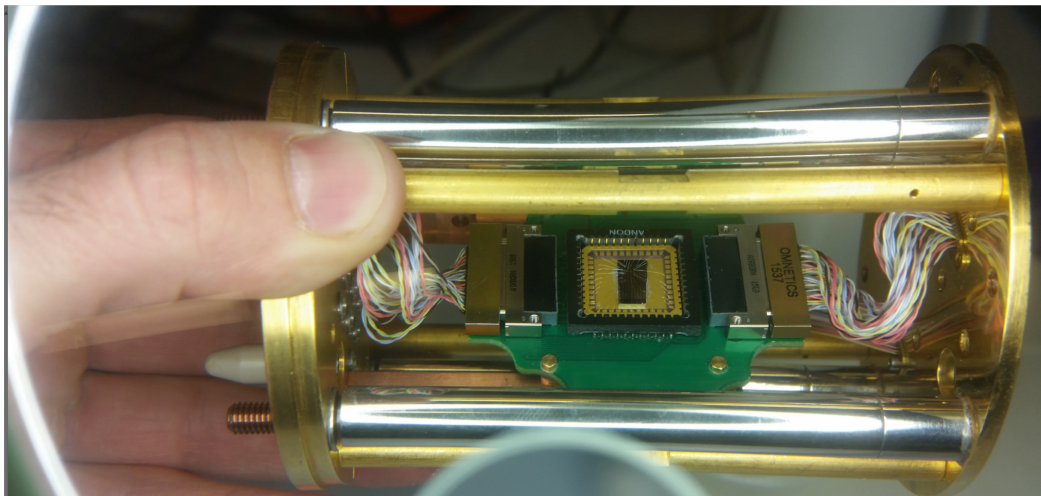
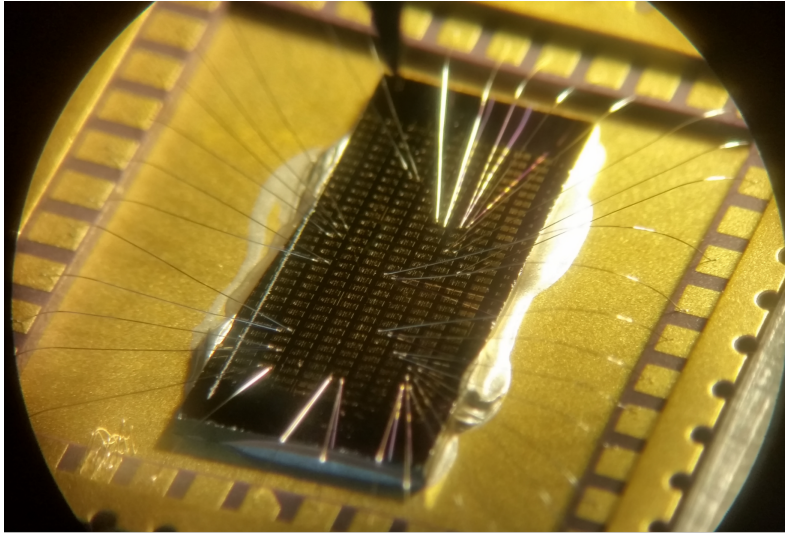


Figure 3.6: **Dy₂bpym sample, bonded.**

(top) One of my samples during the wire bonding process.

(bottom) Sample in the sample holder ready to be inserted in the cryostat. A cylindrical shield still needs to be mounted to complete the puck before the insertion.

Oxford took care of building the devices measured.

After the deposition, each sample is tested to look for promising devices, i.e. devices that show a net increase in conductance respect the trace recorded in precedence. At this point I took responsibility of the samples, preparing them for the characterization I later on carried at low temperatures. The samples are glued with silver paste to a chip carrier, allowing the application of a back gate to all the devices. After that, any promising device is electrically connected with Al microwires with a wire bonding machine (Fig. 3.6).

3.3.2 Dilution Refrigerator with Vectormagnet

Experiments on electrical QDs require temperatures below the typical energy spacing between the dot levels in order to avoid thermal excitations of charges and line-broadening that could hinder their resolution. To work on molecular quantum dots the typical range of temperatures required is in the range of tens of mK. The only machine able to achieve these temperatures at present is the *dilution refrigerator*.

3.3.2.1 Dilution Refrigerator

Dilution refrigerators (DRs) are amongst the most powerful and versatile cryo-machines at our disposal since their first implementation in 1964 [111]. Capable to reach a few mK base temperature, these systems show an impressive cooling power of tens of μW even below 100 mK and the ability to remain at base temperature for months.

The cooling effect is due to a particular property of an isotopic mixture of He_3 and He_4 that, below 0.867 K (*tricritical point*), separates in two non-mixable phases: a fluid one, rich in He_3 (hereafter *concentrated* mixture) and a super-fluid one rich in He_4 (hereafter *diluted*). If the separation was complete, nothing particular would be expected. Instead, keeping an eye on the phase-diagram in Fig. 3.7 (left), we may

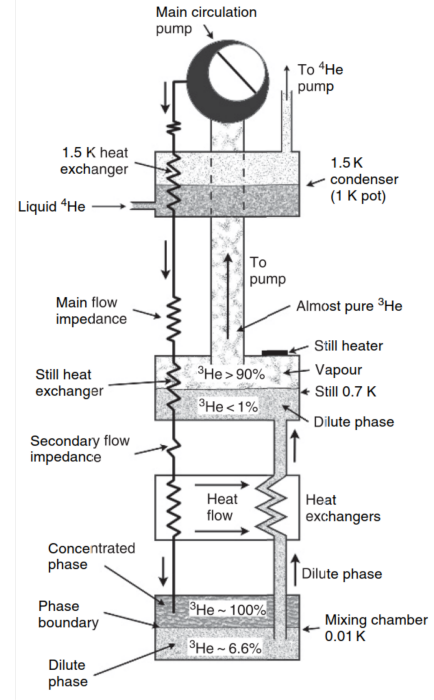
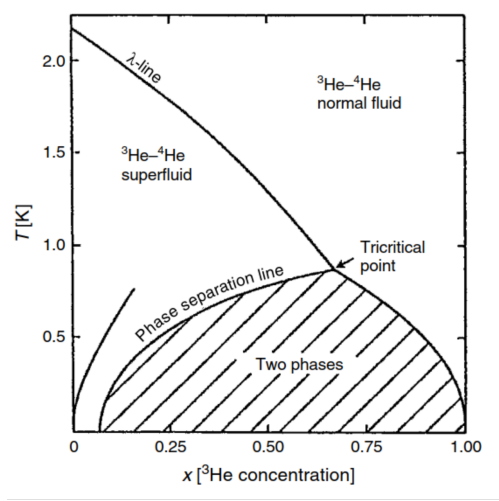


Figure 3.7: **Dilution Principle.**

(left) Phase-diagram for an isotopic mixture of He_3 and He_4 . At temperatures above the *tricritical point* the mixture is either in the superfluid state or in the normal fluid, depending on the relative concentration of the two isotopes (the x-axis). The line that separates the two phases is called λ -line, from the particular shape it takes. Following the line down to the tricritical point, we may say that there is a forbidden region where the mixture separates in the two different phases and how, close to 0 K, the diluted one still has a 6.6% of He_3 isotopes.

(right) Typical scheme for a DR. In a dry DR the *1K pot* is substituted with a pulse-tube refrigerator. Figures from [112].

see that close to 0 K only the concentrated phase is composed of $\sim 100\%$ He_3 while the diluted one still has a 6.6% He_3 component. This means that at the interface between the two phases, He_3 atoms may diffuse from the concentrated to the diluted mixture till the latter will not saturate in a process analogous to evaporation. By keeping the diluted phase below the saturation level (*diluting* it, hence the principle name), the continuous diffusion of He_3 extracts kinetic energy from the concentrated phase, providing cooling power.

To liquefy the mixture and reach sufficiently low temperatures to induce the phase separation, two different implementations are available: a *wet* one, where the mixture

is cooled down to 1K by cryo-baths (liquid nitrogen and helium), and a *dry* (or *cryo-free*) configuration that employs a pulse tube refrigerator (PTR). The *wet/dry* names come from the fact that while the former relies on the cooling power of evaporating cryoliquids in which the setup is bathing, the *cryo-free* alternative implement the cryoliquid in a closed circuit which doesn't come in direct contact with the rest of the refrigerator [112].

For measurements on the single molecule transistors discussed in Chapters 5 and 6, and for other side projects, I personally set up an Oxford Instrument Triton 200 dilution refrigerator fitting different sets of custom made DC and AC lines. This was possible thanks to the instructions and the experience in similar apparatus of Dr N. Ares and Dr. E.A. Laird of the Materials Department of Oxford.

Furthermore, the fridge comes with a 3D vector-magnet with a main bore that provides up to 6 T in the vertical axis of the fridge, and two perpendicular split-pair that allow us to apply H up to 1 T in the horizontal plane.

The typical base temperature is 20 mK with a loaded idle sample and 23-24 mK during usual electrical characterisation experiments with low currents ($\sim$ pA). However, the presence of Eddy currents could lead to an increase in temperature, up to a few hundreds mK, requiring its constant monitoring and adjustments on the data collection protocol.

3.3.2.2 Magnetic Protocols

Our dilution refrigerator is provided with a 6-1-1 T vector-magnet, allowing us to explore the magnetic anisotropy of a sample in different ways. The main parameters that I worked with are the bias potential V_{sd} and the back gate V_G applied to a single device, the magnetic field H and the output current measured I_{sd} . I chose four main ways of electrical investigation for my samples:

- **Field rotations, bias traces:** keeping the intensity of H constant, I varied its

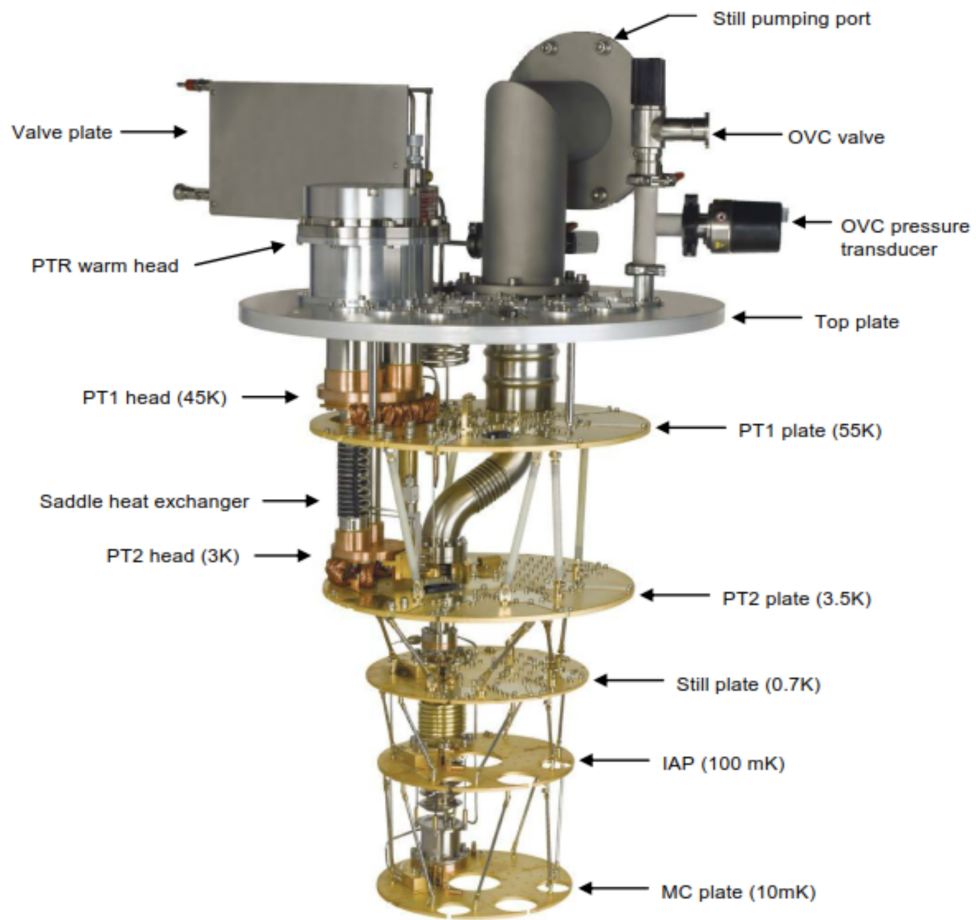


Figure 3.8: **Dilution Refrigerator and Measurement Lines.**

The interior of the OI Triton 200 dilution refrigerator, with the main parts highlighted (figure from the instrument manual).

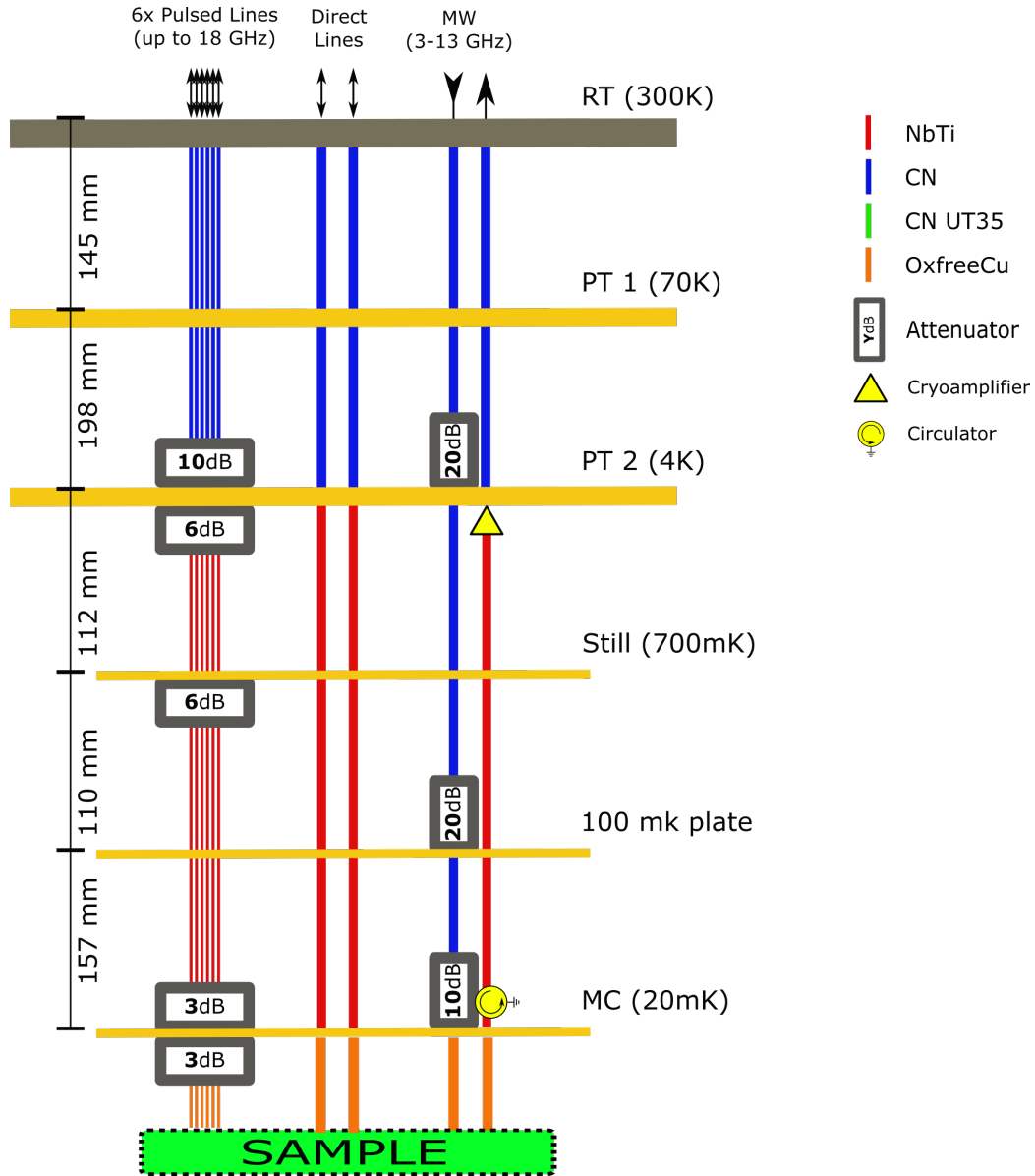


Figure 3.9: **Measurement Lines.**

Measurement lines I personally fitted in the fridge for the studies in Chapters 5 and 6. AC lines were fitted for a side project which is not actually presented in this thesis.

direction as rotations in one of the three principal axes of the sample. I performed the rotation in a pre-defined number of steps, and every step I recorded I_{sd} as function of the applied V_{sd} (a bias I - V trace). V_g was fixed with a potential close to the coulomb peak. The readings gave directly the energy shifts of the levels.

- **Field rotations, gate traces:** manipulating the field as described above, this time I recorded for each magnetic step an I - V trace at a fixed bias V_{sd} , varying the gate V_g . In this case, to read the energy it is necessary to consider the lever arm as a scaling factor for the real potential applied to the molecule. This influences also the resolution, which will be lower compared to a bias measurement. On the other hand, by keeping V_{sd} sufficiently low, it is possible to limit I_d , usually increasing the device stability.
- **Field Sweep, bias traces:** the direction of H is constant and the H field is swept up to the maximum intensity available in that direction. Also in this case, H is varied in discrete steps, and, at each step, a bias I - V trace is recorded. The sweep is usually performed in a hysteretic loop, starting with H at its maximum and then $H_{max} \rightarrow 0 \rightarrow H_{min} \rightarrow 0 \rightarrow H_{max}$, to allow the detection of bistability in the sample. The direction of maximum anisotropy is used as a preferential direction for the field sweep.
- **Field Sweep, gate traces:** H is controlled as described in the previous point, and at every step a gate I - V trace is acquired.

Chapter 4

The Conduction Mechanisms in Organic Radicals

Our journey through different dimensionalities starts with the analysis of the charge transport properties of one of the most studied families of organic radicals: the Nitronyl Nitroxides. Organic radicals, as introduced in Section 2.5, are a particular interesting family of materials for spintronics applications, thanks to their unpaired, generally localised, electron. This allows us for example to perform a full set of spectroscopic analysis of electronic resonances (EPR, *Electron Paramagnetic Resonance*; or ESR, *Electron Spin Resonance*). Further more, the electronic transport through such systems is expected to show a strong interaction with an external magnetic field, making them interesting for building spintronics devices exploiting the high tailorability that organic compounds grant.

We synthesised five different compounds made with a NIT base and an aromatic -R group, as described in Section 4.1. Then, to properly study the compounds, we used a combination of low-energy(sub-THz) spectroscopy to investigate the bulk properties of powder pressed-pellets of crystallised NIT-Rs (Section 4.2), theoretical modelling to unveil the electronic band structure properties (Section 4.3) and finally

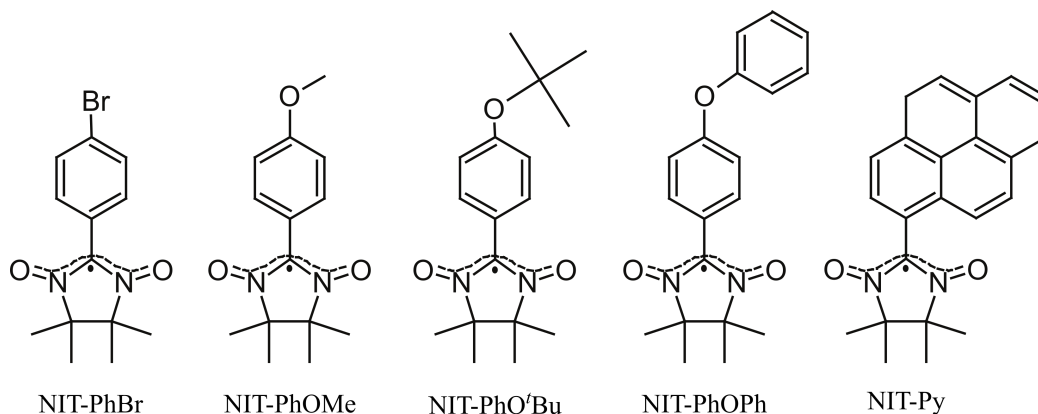


Figure 4.1: **NIT, the Molecules.**

Chemical representation with relative acronyms for the five compounds studied in this project. Figure adapted from [113].

high-voltage transport measurements (Section 4.4) to fully characterise the current response of macroscopic crystals.

4.1 The Molecules

The five compounds of the NIT-R family studied are shown in Fig. 4.1. Their synthesis has been carried out by Dr. Ralph Hübner, at the 1.Physikalisches Institut of the University of Stuttgart. All synthetic operations were performed under an argon atmosphere using standard Schlenk-line techniques. All solvents (ethanol, methanol, dichloromethane, diethyl ether and water) were purified with the standard procedures and degassed via repeated freeze-pump method [114]. The reagents 2-nitropropane, zinc (powder, $< 10\mu m$), ammonium chloride, 4-methoxybenzaldehyde, 4-phenoxyaldehyde, 4-bromobenzaldehyde, 4-*tert*-butoxybenzaldehyde, 1-pyrenecarboxyaldehyde and sodium (meta)periodate were purchased from Sigma Aldrich and beside zinc, which was activated by washing with diluted hydrochloric acid and afterwards acetone, used without further purification.

The starting material 2,3-dimethyl-2,3-dinitrobutane was synthesised by published procedure and purified by crystallisation from hot methanol [115]. The nitronyl ni-

Table 4.1: **List of Measurements and Samples.**

Number of measurements used for statistical analysis. Several I-V cycles were performed on the indicated number of crystals, usually varying contact configuration. It should be noticed that each curve contributed four points to the statistical analysis shown in Fig. 4.6 (forward and backward sweeps, positive and negative bias).

NIT-R	Number of Crystals	Total I-V curves
NIT-PhBr	2	15
NIT-PhOMe	3	23
NIT-PhO ^t Bu	2	27
NIT-PhOPh	3	45
NIT-Py	1	5

troxides were prepared according to the published method by Ullman [79] and purified via column chromatography on silica gel (60 Dm, 0.04 - 0.07 mm, $\varnothing = 5$ cm, d = 20 cm) with diethyl ether as eluent ($R_f = 0.6$). The purity of the organic radicals was verified by CHN elemental analysis of powders and crystals, which were obtained by solvent evaporation from a 1 M dichloromethane solution of the radicals in stopper sealed glass tubes ($\varnothing = 2.5$ mm, d = 10 cm) within ten days. No incorporation of the solvent in the structure was observed.

The synthesised compounds, after crystallisation, resulted mostly in powders composed of micro-crystals. This was suitable for the spectroscopy analysis, since it requires pellets of compressed powder. On the other hand, we obtained only few single crystals big enough for macroscopic transport experiments. In Table 4.1 the number of crystals electrically characterised via our two-points probe setup is listed, together with the number of measurements taken.

4.2 Sub-THz Spectroscopy

As we have introduced in Section 2.1.2, one of the parameters we need to know about a material to understand its electrical properties, is its dielectric constant ϵ_r . In this project, we addressed this issue by performing quasi-optical sub-terahertz (sub-THz)

Table 4.2: **NITs Dielectric Constants.**

Values of ϵ_1 and ϵ_2 as extracted from THz measurements for the NIT-R radicals. The ϵ_1 values are obtained from averaging between 2 and 300 K, while the ϵ_2 ones refer to measurements at 250 K (see text).

NIT-R	ϵ_1	ϵ_2
NIT-PhBr	2.9 ± 0.2	$6.7 \pm 0.2 \cdot 10^{-2}$
NIT-PhOMe	2.8 ± 0.1	$2.9 \pm 0.2 \cdot 10^{-2}$
NIT-PhO ^t Bu	2.79 ± 0.06	$3.97 \pm 0.05 \cdot 10^{-2}$
NIT-Py	2.61 ± 0.07	$8.18 \pm 0.05 \cdot 10^{-2}$

spectroscopy. This technique provides direct access to the optical conductivity of our compounds, with the high accuracy necessary for probing the intrinsic electronic properties of powder-pressed pellets of the samples studied, such as carrier minimum mobility μ_{min} and refractive index n' . All of this, in a contact-less fashion. At such low energies, the sub-THz regime, ϵ_r corresponds to the real part of optical dielectric constant ϵ_1 (Table 4.2) that can be derived via optical spectroscopy.

In Fig. 4.2 the transmission spectra for the analysed compounds are shown, taken by Dr. Michael Slota and Dr. Eric Einze at the 1.Physikalisches Institut of the University of Stuttgart. The values were recorded at a temperature of 10 K and obtained dividing the spectra of the pellets by that of the sources (acquired at exactly the same conditions). A superposition of two oscillations is clearly noticeable, and by fitting them it's possible to extract the imaginary and real part of the refractive index ϵ . The spectra do not show absorptions, except for the NIT-Py radical that has a vibronic excitation at 20 cm^{-1} . The overall transmission decreases with increasing wavenumber, owing to the non-vanishing value of ϵ_2 as reported in Table 4.2. This indicates the presence of underlying mechanisms more complex than those present in pure Mott insulators. The different transmissivity observed are to be ascribed to different ϵ_2 values and pellet thickness. It can be noticed that all NIT-R compounds show roughly the same ϵ_1 value, often within experimental error, and that this defines the range of values to be typically expected for such materials.

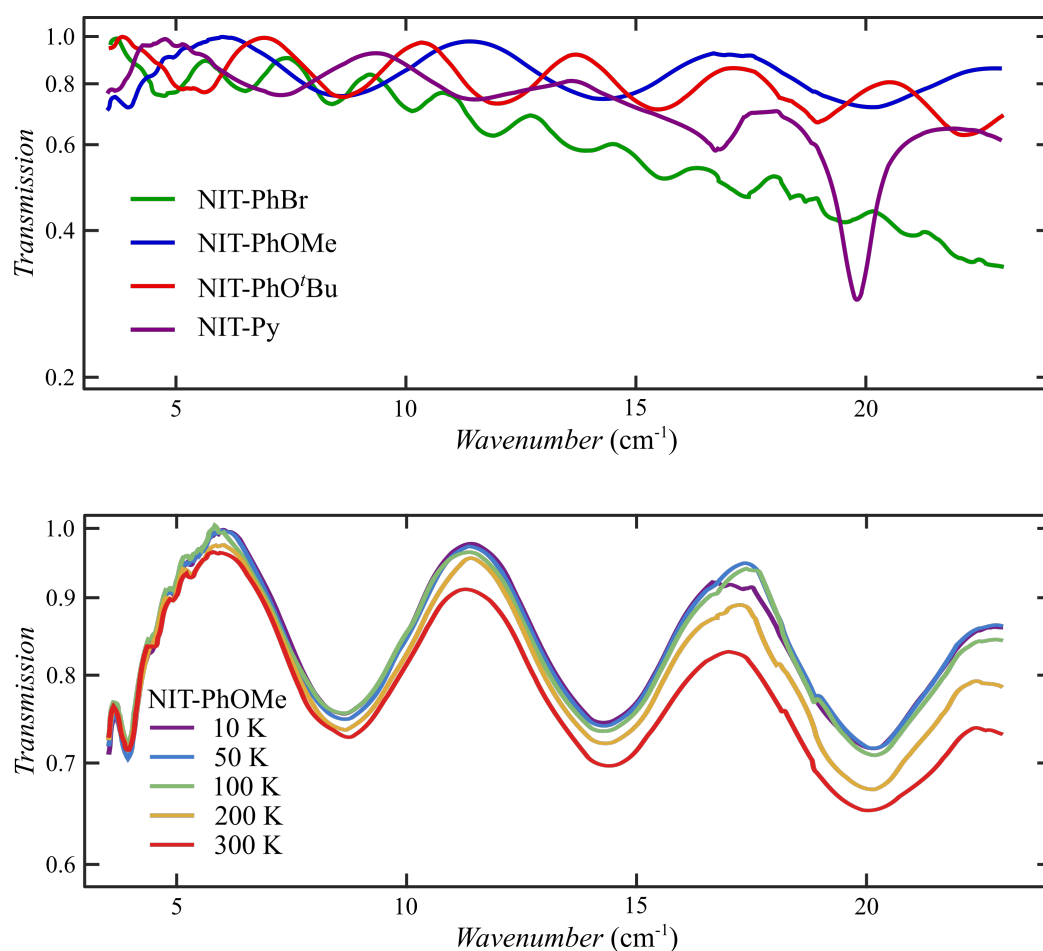


Figure 4.2: **THz Spectroscopy.**

(*top*) THz transmission data for all measured compounds in a range from 3-23 cm⁻¹ at 10 K.

(*bottom*) Temperature and frequency dependence of the transmission spectra of NIT-PhOMe in the 3-23 cm⁻¹ and 10-300 K ranges. For both plots a vertical logarithmic scale is used for clarity. Data collected by Dr M. Slota in Stuttgart, and figures adapted from [113].

4.2.1 Hopping of Small Polarons

The fact that this hopping intermolecular channel is not simply limited by intramolecular properties, but is assisted by intermolecular interactions is also revealed by the analysis of the temperature dependence of the optical conductivity. In Fig. 4.3 we can see the trend of ϵ_2 vs T , which, for low photon frequencies ω , is directly related to the mobility of the carriers μ by the relation $\epsilon_2 = A\mu$, where A is a proportionality constant equal to $\omega/(4e\pi n_{th})$ [116]. The presence of a minimum at low temperatures is clear for all NIT-R radicals and can be understood in the framework of transport theories describing electron hopping among molecules assisted by vibrational effects [117, 118, 119]. According to these models the electron mobility should first decrease, with temperature, because of the progressive decrease of available vibrational modes that can assist the hopping. This implies a decrease of ϵ_2 vs T , as indeed observed in the data down to $T \sim 30$ K.

This trend can be nicely reproduced, for all NIT-R, by considering hopping of small polarons [117], as described by the Holstein model. An analytical form for the mobility is available:

$$\mu_{pol} = \frac{\pi^{1/2} e a^2 J^2 e^{-\frac{W_p}{2k_B T}}}{\hbar (2W_p)^{1/2} (k_B T)^{3/2}} \quad (4.1)$$

where a is the lattice constant of the crystal in which the small polaron occurs, J is the polaron interaction potential and W_p is the thermal activation energy for hopping and is given by half the small-polaron binding energy. All the extracted polaron energies are in the order of 0.4 eV, about the magnitude of the HOMO-SOMO distances calculated (Section 4.3) and much smaller than the molecular level separation of the LUMO. This, again, indicates that the hopping is eased by intermolecular interaction channels.

Below 30 K an increase of ϵ_2 is typically observed. This cannot be accounted by

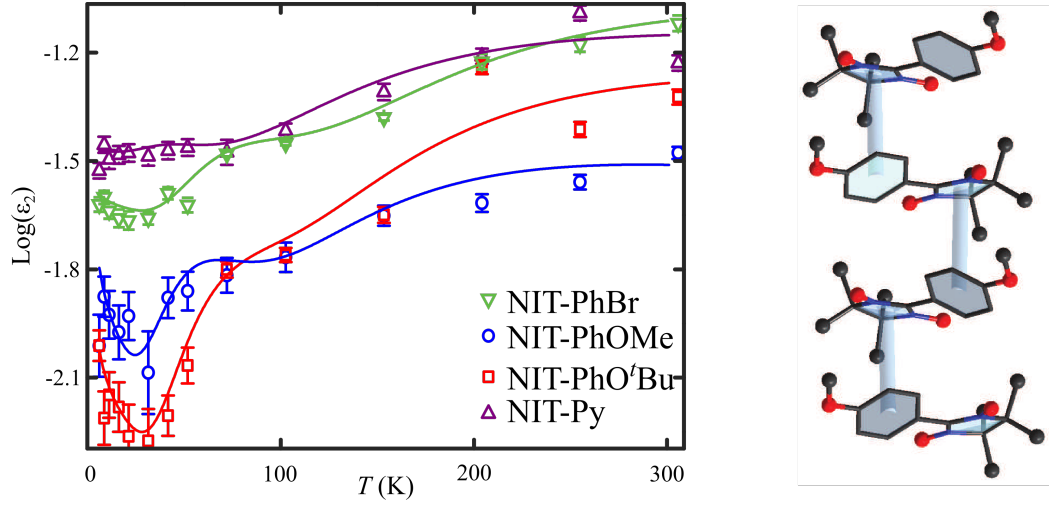


Figure 4.3: **Hopping of Small Polarons.**

(left) Temperature dependence of the logarithm of the optical ϵ_2 values for the studied compound, as marked in the figure. The values are obtained via fitting the THz spectra. Solid lines correspond to fits with the expected behaviour for small polarons and low-temperature residual conductivity, as described in the text.

(right) Model of the crystal and the transport channels. Figures adapted from [113].

simple hopping, and such observations are typically ascribed to the effects of polaron tunnelling and residual band-like conductivity. To account for these effects we can add two terms to Eq. (4.1), accounting for the tunnelling and the band-like conductance:

$$\mu_{LT} = \mu_{tun} + \mu_{BL} = \frac{ea^2}{\hbar\gamma k_B T} e^{\left[-2\gamma \text{csch}\left(\frac{W_p}{2\gamma k_B T}\right)\right]} \left[\frac{\gamma}{\pi} \text{csch}\left(\frac{W_p}{2\gamma k_B T}\right)\right]^{1/2} + dT^{-n} \quad (4.2)$$

where γ is a measure the strength of the electron phonon-coupling and n is an empirical exponential describing the band-like processes. The expression reproduces well all curves for all NIT-R radicals down to 2 K, and the γ term is always found to be between 2 and 3, which still indicates a relatively weak electron-phonon coupling, even though higher than many organic semiconductors. In all cases we could not reproduce the data with the tunnelling term μ_{tun} alone, without including the power-law dependence of μ_{BL} . This, again, can be considered an indication of an important role played by intermolecular interaction channels.

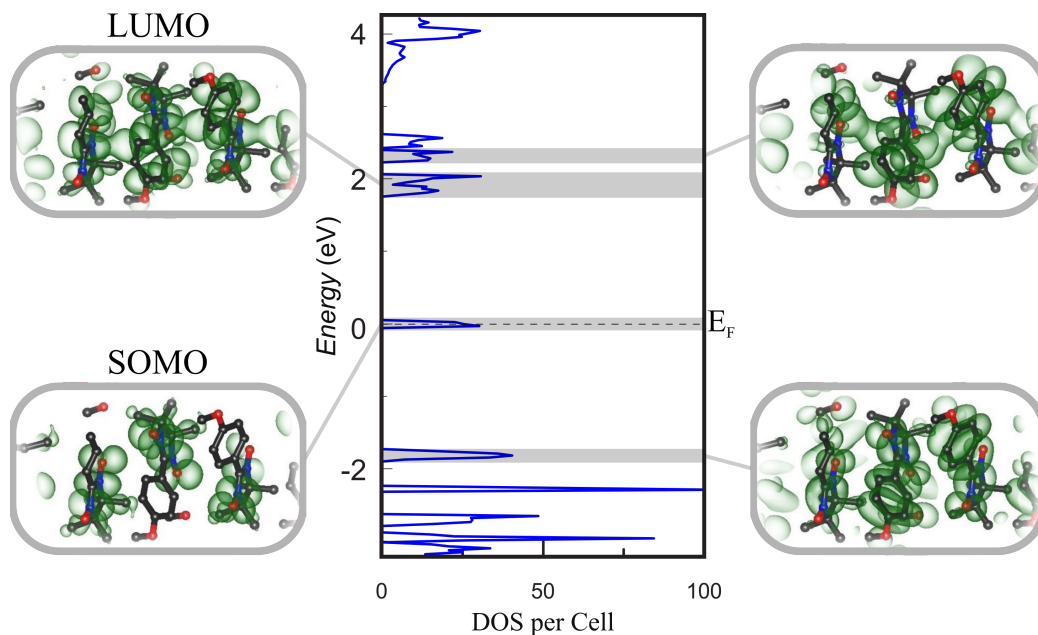


Figure 4.4: **NIT-R DOS.**

Calculated DOS for NIT-PhOMe showing the different densities close to the Fermi level, E_F . The insets contain the charge density maps obtained by projecting in real space the states in different energy intervals, as highlighted by the shaded areas pointed. In particular, on the left there are the SOMO (Singly Occupied Molecular Orbital) which is at the Fermi level, but shows very little overlap of orbitals. Above there is the LUMO (Lowest Unoccupied Molecular Orbital) with the orbital overlap that creates further conduction channel at higher energies. Calculations by Dr. F.Wang from Lund University.

4.3 DFT Modelling

DFT calculations on the crystal structure of NIT-PhOMe were performed by Dr. F.Wang from Lund University. Its unit cell is the smaller amongst the studied compounds, counting only four molecules, and hence it was the only one requiring a reasonable computing power. Numerical calculations were carried out using the density functional theory method (DFT) at the B3LYP level [120] together with All atoms were assigned a 6-311++G** basis set and calculations were performed with Spartan'14 program packages [121]. For the electronic structure calculations of NIT-PhOMe the Vienna *ab initio* simulation package (VASP) has been employed [122, 123, 124, 125], using the projector augmented-wave (PAW) pseudopotentials

[126] and the Perdew-Burke-Ernzerhof generalised gradient approximation (PBE-GGA) [127]. The energy cut-off for the plane wave basis set is 400 eV. The first Brillouin zone was sampled with a 7 x 7 x 7 Monkhorst-Pack k-points mesh [128]. From the calculation results, the density of states (DOS) curve and the charge density maps for the states around the Fermi level are plotted and can be seen in Fig. 4.4. Analysis of the charge density maps, as obtained by projecting in real space all states belonging to specific energy intervals shows the localised characteristic of the states around E_F and the delocalised conduction channels of the states between 1.5 and 2.5 eV.

4.4 Transport Study

I was in charge of the high-resistance charge transport measurements for the samples in this project. I studied the behaviour of single crystals of all the NIT-R introduced earlier using the two point probe setup explained in Section 3.1.2. The typical transport properties of each compound is shown in Fig. 4.5(left), where representative I-V curves obtained averaging on several dataset are displayed. For all the compounds two different transport regimes are clearly detectable: a linear (ohmic) regime, and super-quadratic (SCL) regime. The theory of these two different regimes has been introduced in Section 2.1.1.

To measure such highly resistive materials on the physical scale of few hundreds of microns, several precautions needs to be in place. First of all, even with the sensitivity in the pA range, bias voltages as high as a few hundreds of volts may be necessary to measure samples with a resistance in the order of the T Ω ($V = RI \Rightarrow 1V = 1T\Omega * 1pA$). Since the experiment was run on air, particular attention was taken not to cause electric arcs for dielectric brake-down of the air, which happens at 3 V μm^{-1} in normal humidity conditions. Furthermore, the process of injecting charges at high

voltages in high-resistive materials is known to cause capacitive effects [129] and hence a hysteretic behaviour for the fastest sweep rates. Such effects can be minimised by decreasing the sweep rate, as shown in Fig. 4.5(right), where I plot the dependence of the I-V curves on the bias voltage sweep rate. In all the data used for the transport analysis, such capacitive effects were minimised by sweeping V_{sd} slower than 0.2 V/s.

For each system I can define a crossing voltage V_c , between the ohmic regime and the non-linear one (see Fig. 4.6(left) for an example on each compounds, and Table 4.3 for the values). Below V_c the density of thermally-generated free carriers inside the crystal is dominant with respect to the injected charge carriers. The behaviour is hence given by Ohm's law, which, neglecting diffusive contributions to the current, provides the current density:

$$j_{\Omega} = \frac{I_{\Omega}}{W} = en_{th}\mu_0 \frac{V_{\Omega}}{L} \quad (4.3)$$

where the subscript Ω denotes the ohmic regime, e is the electron charge, n_{th} is the thermal-equilibrium carrier density, W and L are the width and the length of the electronic channel, respectively, and μ_0 the charge carrier mobility at low electric fields. From the linear regime in the I-V curves we can then evaluate the sheet resistance $R_S = V_{\Omega}I_{\Omega}^{-1}WL^{-1}$ where we take $W = 20\text{ }\mu\text{m}$ as the tungsten tip diameter contacting the crystals and $L = 300\text{ }\mu\text{m}$ to $600\text{ }\mu\text{m}$ is the range of distances between the tips as determined during the contacting process. For all substituents -R attached to the NIT-R radical, we obtain R_S values in the T Ω range (Table 4.3). This is as expected for this family of organic semiconductor radicals. The high sheet resistance obtained indicates localised transport processes taking the major role in intermolecular transport rather than delocalised ones.

In order to corroborate this observation, the carrier mobility, which can be derived from the measurements as shown below, is a useful parameter to start distinguishing

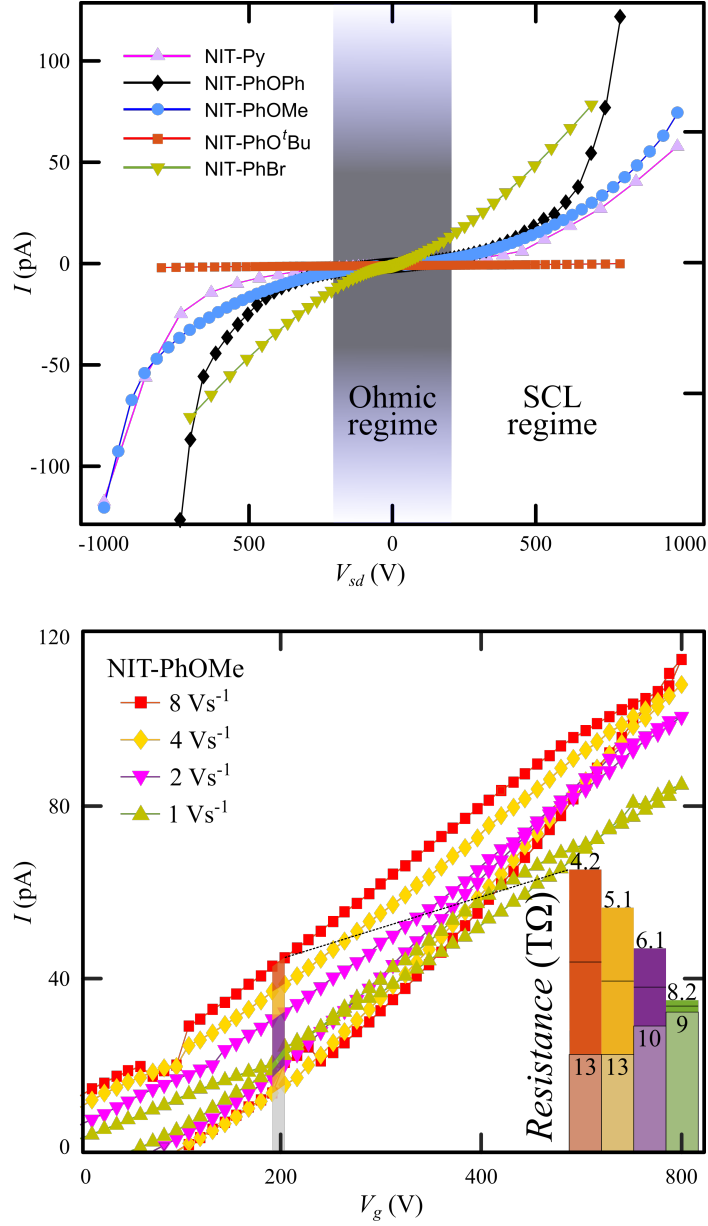


Figure 4.5: **IV Curves.**

(left) Room temperature $I - V_{sd}$ characteristic curves resulting from averaging on multiple sets of measurements collected on my samples.

(right) Dependence of the IV curves on the bias voltage sweep rate, as acquired for the NIT-PhOMe radical. Decreasing the sweep rate, the capacitive effects can be minimised. This can be seen from the narrowing gap between forward and backward sweeps and decreased zero-voltage residual current during the back-sweep. The inset shows the current at 200V for the four different sweeps and the relative range of resistances, with the fastest sweep rate with a maximum measured resistance value more than 300% the lower.

between the different possible transport mechanisms. The boundary between delocalised and localised transport processes, i.e. between band and hopping transport, is commonly considered in the range of $0.1\text{-}1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [130, 118]. For all investigated compounds, extremely low mobilities in the order of 10^{-3} to $10^{-6}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ are obtained, indicating that inter-molecular hopping transport is the dominant mechanism. This means that the electrons move by rapidly passing from one molecule to another.

The non-linear behaviour at high voltages is attributed to Space-Charge Limited (SCL) currents Section 2.1.2. Insulating crystals [131], organic semiconductors (both in crystalline [132] and film [130, 133] form) and even semiconducting nanowires [134, 135, 136] are known to show this phenomenon. In this regime, we have access to many intrinsic properties of a material, such as carrier mobility μ , thermal-equilibrium carrier concentration n_{th} and charge-trap density. In the present case, due to both the high resistance of the bulk material and the contact geometry, the system will follow surface SCL currents, rather than bulk SCL [137] (which would only be possible for contacts on opposite sides of a very extended crystal slab). In this regime, above the crossover voltage V_c , the current is proportional to the squared voltage:

$$I_{\text{SCL}} = \frac{2}{\pi} \frac{\mu_{\text{min}} \epsilon_0 \epsilon_r W}{L^2} V^2 \quad (4.4)$$

where ϵ_r is the dielectric constant of the material and μ_{min} is the minimum carrier mobility, which includes the contact quality and the presence of traps in the electron channel. A common way to identify the presence of SCL current is by plotting the linear conductance $G = I/V$ vs V in a log-log plot, which will yield straight lines which slope is equal to the power-dependence of the current to the voltage (i.e. 1 for ohmic regime, and 2 for typical surface SCL).

Substituting in Eq. (4.4) the optical dielectric constant ϵ_1 to ϵ_r it is possible

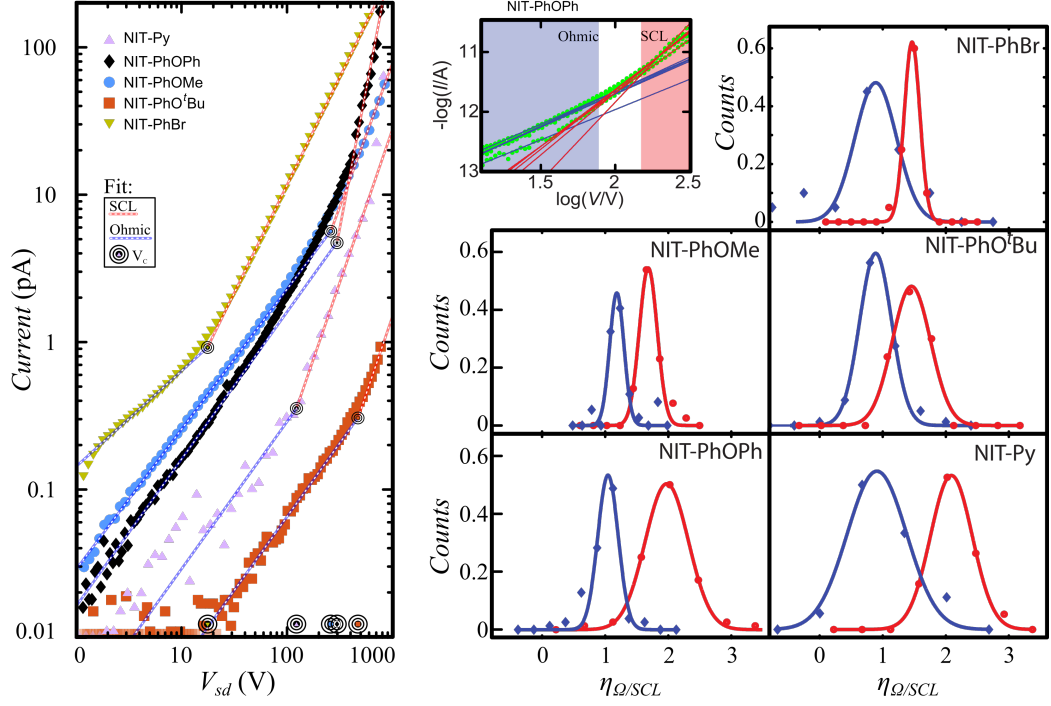


Figure 4.6: **Threshold Voltage and Conduction Regimes.**

(left) Log-log plot of the current vs source-drain voltage for the different NIT-R compounds. The slope of the data curves corresponds to the exponential factor η_i that characterise the relation between current and bias in Eq. (4.6). Linear fits for the ohmic and SCL are highlighted, as well as their crossing point at the threshold voltage V_C

(right) Resulting distribution of the parameter η_i obtained fitting Eq. (4.6) in the ohmic (in blue) and in the SCL regimes (in red). Solid lines correspond to fits with Gaussian curves, providing the values reported in Table 4.3. A value for η_i close to one means that the conduction is in the linear, ohmic regime. A value close to 2 is fingerprint of SCL regime whilst a higher value is attributed to trap-filling SCL regime. The inset shows an example fitting for a number of measurements performed on NIT-PhOMe.

Table 4.3: **NIT-R Parameters.**

Minimum mobility $\mu_{\min}$, surface thermal carrier density n_{th} , sheet resistance R_S , crossover voltage V_c , ohmic conductance and fitting exponent (G_Ω and η_Ω), charge-limited parameters G_{SCL} and η_{SCL} and low-field mobility μ_0 for the different NIT-R radicals, as extracted from the optical and transport measurements.

NIT-R	$\mu_{\min}$ [cm ² V ⁻¹ s ⁻¹]	n_{th} (2D) [10 ¹³ m ⁻²]	R_S [TΩ]	V_c^a [V]	G_Ω^a [fS]	η_Ω^a	G_{SCL}^a [fSV η^{-1}]	η_{SCL}^a	μ_0 [cm ² V ⁻¹ s ⁻¹]
NIT-PhBr	3.0±0.5·10 ⁻²	1.0±0.5	0.9±0.3	40±20	55±10	0.9±0.3	6.3±0.9	1.5±0.1	6±4·10 ⁻³
NIT-PhOMe ^b	4±3·10 ⁻³	4.2±0.8	2.2±0.3	170±30	23±3	1.2±0.1	0.9± 0.6	1.7±0.1	7±1·10 ⁻⁴
NIT-PhO ^t Bu	7±4·10 ⁻⁴	17±2	75±4	510±40	0.89±0.03	0.9±0.3	0.2±0.1	1.5±0.3	5.0±0.5·10 ⁻⁶
NIT-PhOPh	6±3·10 ⁻³	3±1	3±1	130±40	18±8	1.1±0.2	1.2±0.7	2.0±0.3	7±4·10 ⁻⁴
NIT-Py	1.4±0.9·10 ⁻⁴	0.9±0.4	5±3	60±30	6±3	0.9±0.5	1±0.9·10 ⁻²	2.1±0.3	1.4±0.9·10 ⁻³

^aErrors represent the widths of the statistical distributions

^bValues refer to $\epsilon_1 = 2.8 \pm 0.2$, see text

to combine the optical and transport measurements and obtain information on the *minimum mobility* ($\mu_{\min}$). This is valid since at the frequencies used the two are comparable within the overall error estimation. It should also be noticed that all NIT-R compounds show roughly the same ϵ_1 value, and that even variations much larger than those observed in the series do not introduce important variations in the extracted $\mu_{\min}$. This comes useful, to have an estimation of the missing measure on the dielectric constant of NIT-PhOPh, which can be safely considered to be, for the purposes of the analysis of the conduction, 2.8 ± 0.3 . With reference to Table 4.3, we may see that the *minimum mobility* depends on the radical substituent, with NIT-PhBr exhibiting the highest one, followed by NIT-PhOMe and NIT-PhOPh. Eventually the lowest mobilities are sported by NIT-PhO^tBu and NIT-Py, which show very similar conductivities, at the limit of our detection range.

Information on the thermal-equilibrium carrier density n_{th} can be extracted from the voltage threshold V_c , when $I_\Omega = I_{\text{SCL}}$. Combining Eq. (4.3) and Eq. (4.4), we obtain:

$$n_{\text{th}} = \frac{2}{\pi} \frac{\epsilon_0 \epsilon_r}{e} \frac{V_c}{L} \quad (4.5)$$

To extract the threshold voltages we can plot the current in both the ohmic and the SCL regimes in a double logarithmic plot. In Fig. 4.6 I plotted the current in a double logarithmic plot. The threshold voltages are clearly visible as crossing points between the two regimes, and their values can be extracted using the function:

$$I = G_i V^{\eta_i}, \quad (4.6)$$

where the i index stands for the ohmic ($i=\Omega$) or charge-limited ($i=\text{SCL}$) regions and the exponent η varies between the two regimes as already discussed. V_c is then obtained from the intercept between the fits of the high and low voltage regions. In order to account for the variability amongst the different sample geometries and measurements, a statistical analysis was performed by acquiring several measurements for each compound, and then performing the fitting procedures on all of them (see the inset in Fig. 4.6 for an example on a small subset of measurements). The resulting statistical analysis provided a Gaussian distribution for each η , as shown in Fig. 4.6(left), which results are then listed in Table 4.3 using the full-widths-half-maxima of the Gaussians to provide the statistical errors. All compounds with the higher mobilities show a value of the SCL exponent slightly below the predicted value of 2, while the two systems with the lowest conductance and the least efficient intermolecular channels provide exactly 2, within experimental error. These compounds also display a wider dispersion of behaviours, with a few cases showing exponents up to 3, as expected when other mechanisms, such as traps, become particularly relevant. All compounds show an effective thermal carrier density in the order of 10^{13} m^{-2} at the crystal surface, with only a small dependence on the -R group and only small variations observable, in perfect compatibility with the expected variability in the quality of the crystal-electrodes contacts.

4.4.1 Charge Traps

As shown in Fig. 4.7(left), the typical SCLs quadratic behaviour of I vs V is not able to describe the conduction at higher voltage for some of my measurements. We have already seen in Section 2.1.3 that defects in the crystal lattice of a (semi)conducting material can lead to charge traps and recombination centres. In the case of molecular radicals, defects that act as charge traps can be easily created close to the contacts and interface layers, localised at defective molecule sites or introduced by impurities in the compounds (presence of side-products of synthesis). This lead to new states in the band gap of the semiconductor, either localised, or diffused.

In my studies, I was able to identify both of these mechanism in a set of measurements on NIT-PhOMe and NIT-Py. As can be seen in Fig. 4.7(left), a set of measures on NIT-Py showed an abrupt increase in current when a certain voltage threshold V_t has been reached. This super-quadratic behaviour is typical for diffused electron traps below the LUMO, and very common in organic materials. The energy distribution is described by $\rho_t(E)=(\delta_t/E_t)\exp(-E/E_t)$ [138] where δ_t is the trap density, E_t the characteristic trap depth and E the energy relative to the conduction or valence band. While gradually filling the traps, the intensity of the current keep increasing faster than a quadratic rate, until eventually all the trap levels are filled. In this case, the current will follow:

$$I \propto V^{m+1}/d^{2m+1} \quad (4.7)$$

where the distance between the electrodes appears as d and m is given by $m=E_t/k_B T > 1$. We can see from this relation how the current only depends on the trap depth but it is independent of the device geometry: when an IV trace show such a behaviour it can be regarded as indication for trap-limited SCL processes. Exponentially-distributed traps with lower density can also explain deviations from

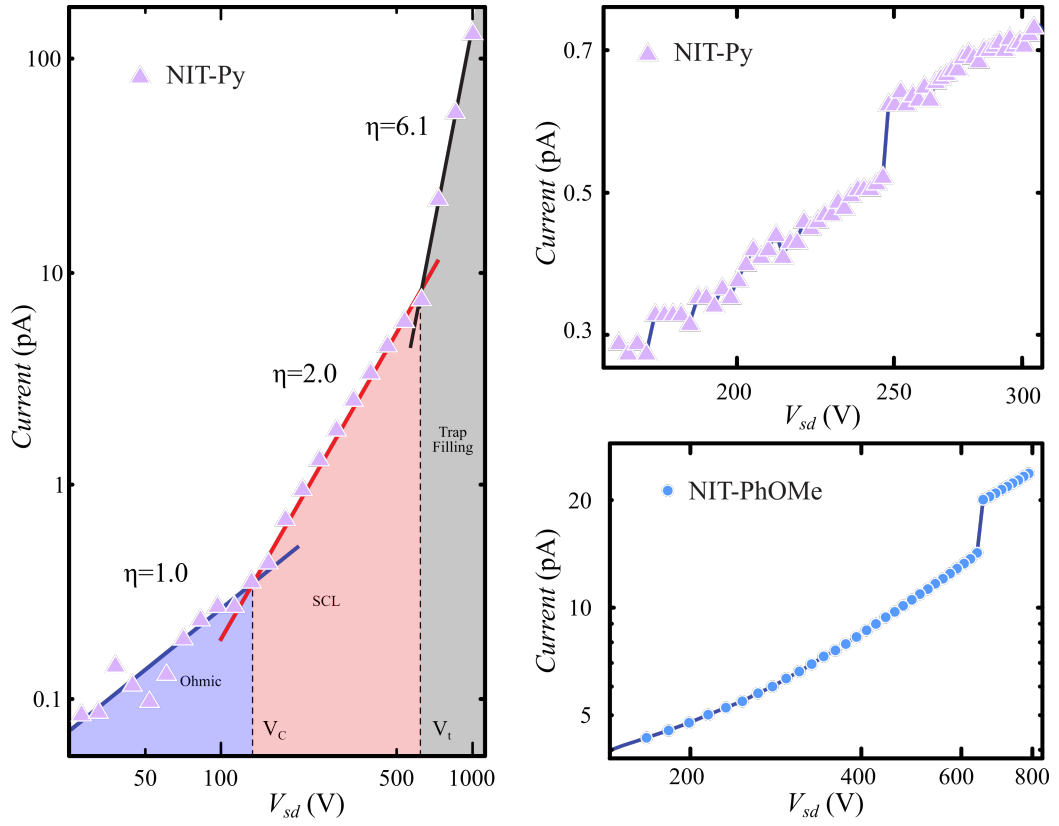


Figure 4.7: **Electronic Traps.**

(left) Evidence of distributed traps within the SOMO-LUMO gap for NIT-py, as observed on a log-log plot. The three different regimes and their respective linear fit are highlighted: ohmic (blue), SCL (red), distributed Trap Filling (black).

(right) Examples of localised traps for NIT-Py and NIT-PhOMe.

the typical quadratic I vs V SCL behaviour wherever $\eta > 2$ is observed, as, for example, in NIT-Py in Fig. 4.7.

Nevertheless, the NIT-R systems show far better agreement with the ideal SCL regime than most other molecular conductors: for example values of $6 < m < 10$ have been found in AlQ₃, with trap energies $E_t = 0.15$ eV [139, 140].

Before the publication of our work on the NIT-R conduction mechanisms, the theoretical models for distributed traps were not considering neither hopping transport nor surface conductance [19]. Using a similar approach to the ones applied on AlQ₃ and PPV devices [141], we may introduce a field-dependent mobility via the Poole-Frenkel mechanism [16]:

$$\mu(E) = \mu_0 \exp \left(\frac{e^{3/2}}{k_B T} \sqrt{\frac{E}{\pi \epsilon_0 \epsilon_r}} \right) \quad (4.8)$$

where μ_0 is the low-field mobility. The value of μ_0 can be extracted using the previous results on the thermal charge carrier density (n_{th}) and Eq. (4.3), and substitute μ_{min} by the Poole-Frenkel mobility $\mu(E)$ in Eq. (4.8). The result gives an $I - V$ dependence that describes well superquadratic behaviour at voltages higher than a certain critical level V_C , like some of our compounds do (Fig. 4.7a).

The second kind of traps I described in Section 2.1.3 are energetically localised in deep levels in the band gap. Two examples of such traps for NIT-Py and NIT-PhOMe are shown in Fig. 4.7(right), with clear signatures of conductance jumps in the current at a well defined applied bias (trap-filling voltage V_{tfl}). Once the traps are filled, the transport continues at the *trap-filled limit* and the SCL quadratic voltage characteristic is restored.

At voltages higher than V_{tfl} transport is in the so-called trap-filled limit and continues to follow the quadratic voltage dependence. In the case of surface SCL

currents, these traps are filled by the injected charge at:

$$V_{tfl} = \frac{\pi}{4\epsilon_0\epsilon_r}eL\delta_d \quad (4.9)$$

from which the trap density per unit surface area, δ_d can be evaluated. Here, the subscript d denotes that we are dealing with deep-traps, located at energies several times $k_B T$ from the valence band. This is also visible from the presence of the current jumps due to trap filling, which would otherwise be absent in the presence of a dense distribution of traps close to the conduction band. The presence of such deep traps, which are typically filled close to 0.4 eV, is very likely in systems with very wide band-gaps, and would match with a gap width close to the 3 eV that separate the SOMO and LUMO orbitals. The typical densities of localised traps observed for the NIT-R radicals is around $\delta_d=3.5\pm0.3\cdot10^{10} \text{ cm}^{-2}$, which compares very favourably to known trap densities in organic conductors [142, 143, 144, 145, 146] and, in particular, to experiments on surface-limited charge transport in rubrene single crystals [147].

4.5 Conclusions

In this chapter I discussed the conduction regimes of organic radicals of the NIT-R family, by combining optical measurements at THz frequencies and charge transport data. The analysis shows the presence of a low-voltage conductance channel that relies on intermolecular hopping mechanisms. This is largely unrelated to the intramolecular level structure but actually relies on the presence of sizeable interactions between the π electronic cloud of the phenyl appendix and the delocalised NIT motif. Structure-property relations could then be established, by considering the effect of the orientation and distance of the two delocalised system.

The analysis shows how different steric substituents in the -R moiety may weaken the intermolecular channel, leading to more insulating systems. Using high-resistance

transport measurements I could then identify, for the first time, space-charge limited currents in NIT-R compounds and evidence of strong effect of traps on the hopping mechanism, with the resulting trap densities comparing favourably to those of well-known molecular conductors.

My findings show that NIT-R organic radicals that contain aromatic substituents do not behave as pure Mott insulators, in contrast to what conjectured up to now. The rationalisation of the different transport regimes, and the identification of structure-properties correlations provide the essential indications for the rational tuning of the NIT-R electronic properties via chemical means. These results will constitute the experimental and theoretical backbone for the study of electron transport in magnetic complexes based on NIT-R systems, which are attracting particular interest for their slow-relaxing behaviour [148] and the possibility of controlling them with light [149]. The combination of optical and transport measurements, demonstrated here, sets the methodological basis for the investigation of molecular magnetic materials, and holds particular promise for the systematic investigation of magnetic coordination compounds [150].

Furthermore, this work sets the ground for the exploitation of organic magnets in electronic devices. In particular, the observed charge limited transport and the hopping processes can be exploited in latch memory and field-effect devices (2D systems). Finally, these results are of great importance for the exploitation of NIT-R radicals in nanoscale (1D - 0D) electronics and spintronics [151, 25, 152, 153, 154], demonstrating the important role of defects and traps for charge transport, as well as the relevance of intact conduction channels. Moreover, they show that the mobilities of aromatic NIT-R radicals fall in the correct range for the creation of memristive devices, and that charge-limiting effects will play a dominant role at the nanometre scale, in the proximity of nanostructured electrodes. Such effects, which have been ignored until now, will thus be essential for the proposed switching devices [155] at

the nanoscale.

Chapter 5

Transport through Molecular Graphene Nanoribbons

Amongst the family of carbon-based nano-materials, graphene nanoribbons (GNRs) lately emerged as one of the most promising ways to achieve electronic devices tailored deterministically down to the single atom level. Part of this interest is due to the outstanding mechanical and electronic properties of these nanostructures (sec:2.5-Materials). Furthermore, the chemical approach opens ways to functionalise the edges of a quasi-one dimensional system like the GNRs are, for instance introducing charge and spin dopants or optically and magnetically active centres in key positions.

In this study I used chemically-derived molecular GNRs (MGNRs), grown with a bottom-up chemical process described in Section 5.1. The molecules have been deposited on GBJs to build single-molecule transistors, as described in Section 3.3.1. I studied the room temperature (RT) electrical characterisations in order to make sure of the successful creation of the molecular bridge between the graphene electrodes (Section 5.3). Once the presence of suitable devices had been proved, the samples are cooled down to mK temperature regime in a dilution refrigerator, a Triton 200 from Oxford Instruments, demonstrating the successful creation of SETs and proceeded

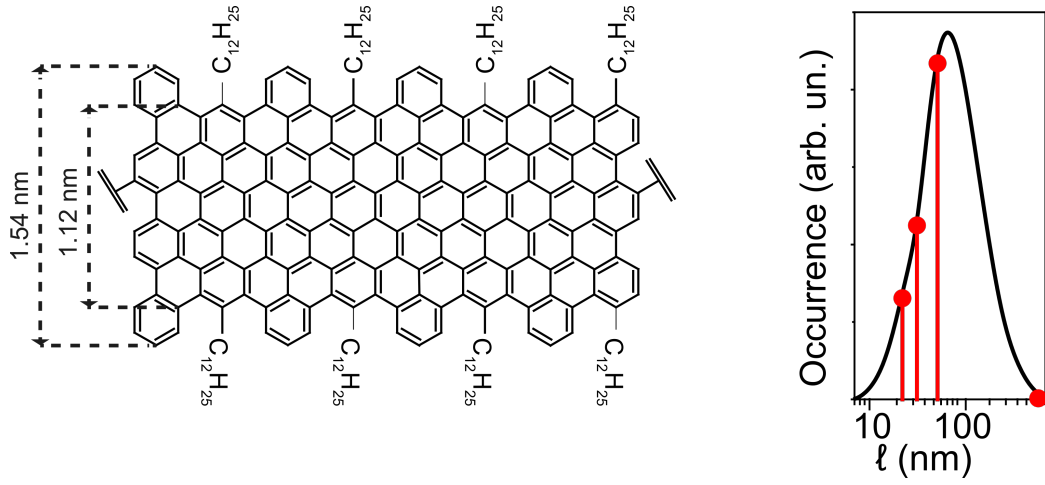


Figure 5.1: **The Ribbons.**

(left) Molecular structure of an MGNR segment, showing the atomically-precise width of the graphene backbone and the alkyl groups that decorate the edges.

(right) Distribution of MGNR lengths, as obtained from size-exclusion chromatography on the polymerised molecular precursor (black), and MGNR l obtained from the electronic properties (red).

analysing their electronic transport properties (Section 5.4). In particular, I will show that the hybridisation of a 1D system like a GNR with a GBJ introduces a second potential barrier in the electronic channel, creating a system that behaves like a double quantum dot. Furthermore, I studied the devices behaviour in a magnetic environment, presented in Section 5.5, by analysing the Coulomb peaks modulation when an external magnetic field is applied, gathering useful information on the spin current through the MGNR. Finally, I will show the capability of "burning" the devices, showing how it is possible to selectively lift the blockade for one of the barriers Section 5.6.

5.1 The Molecule: Chemically-Derived Molecular Graphene Nanoribbons

I chose for this project a 12-atom-wide MGNRs with a total width $w=1.12$ nm, much narrower than just the edge roughness obtained by classic methods (e.g. 5 nm in

graphene quantum dots). The edges are chemically defined, and the only variable parameter in the MGNR geometry is the length, ℓ , which shows a distribution that ranges from a few tens to a thousand nanometers. For the samples used in my project, the measured distribution of lengths is shown in Fig. 5.1, where the red dots mark the four devices which measurements are discussed in this chapter. The numerically-calculated bandgap is $E_{gap} \approx 1.7$ eV, as obtained via density functional theory (DFT).

5.2 The Samples: Graphene Break Junctions and Graphene Nanoribbons

Even though the synthesis of MGNRs allows one to tailor their properties for a number of different applications, integrating them into devices has proved extremely challenging. The use of metal contacts, typically Pd, Au or Pt, is common for SETs, but they are largely irreproducible, atomically unstable at room temperature and induce a large screening of the gate electric field due to the intrinsic thickness imposed by the production procedure.

Recently the use of bulk graphene leads is emerging as an alternative to metals, and it has been demonstrated the improved capability of contacting organic ligands and carbon based materials thanks to $\pi - \pi$ stacking bonds, and an enhancement of the coupling with a back gate given the 2-D dimensionality of the contacts [106].

As common practice in our labs, the devices substrate is an n-doped Si chip capped with a 300 nm SiO₂ insulating layer pre-patterned with metal electrodes (Cr 10 nm / Au 70 nm). The transfer of the CVD graphene has been done by Pr. Warner's group, at the Materials Department, using a standard wet transfer technique above the substrate. The graphene contacts have been etched in a bow-tie geometries that bridge the metal contacts using standard electron beam lithography and O₂-plasma

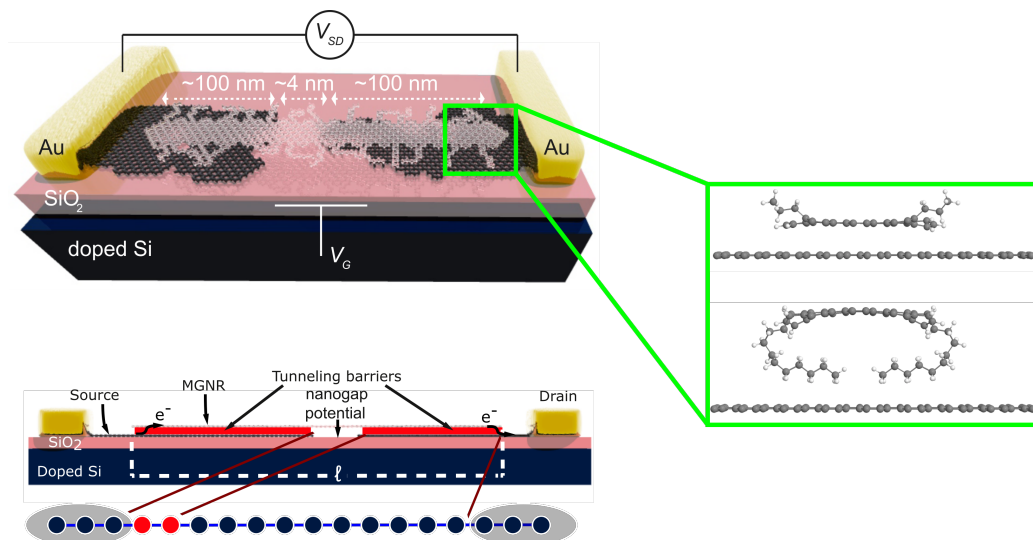


Figure 5.2: **Device Geometry.**

(*left*) Artistic view of the device geometry, with a single GNR sitting in a graphene break-junction. The different regions related to the gap induced potential and the tunnelling barrier to the leads are highlighted.

(*inset*) Different configurations of the alkyl groups may strongly tune the tunnelling barrier to the leads when they roll below the MGNR (see also Fig. 5.4)

etching. The central part of the bow tie can not be successfully patterned in a nanometre size gap suitable for molecule bridging via standard lithographic procedure, so we proceeded using feedback-controlled electroburning in air as reported in [106]. The I-V characteristics for every device are automatically recorded, and then checked to identify successfully burned gaps (one example in Fig. 5.3). The yield of the burning process is quite low, with most of the devices that either do not burn properly a useful gap (due to the quality of the graphene or a deposition of multiple layers that actually do not electroburn) or due to an excess of current they blow up in a gap too wide to be bridged efficiently by single molecules. If a sufficiently high number of good gaps is present on a chip, the substrate can then be used for molecule deposition. The processes above are usually common practice in our group, as the substrates can be used for the characterisation of a diverse set of molecules. For this reason, several persons may be involved in the creation with the workload shared and tasks exchanged to optimise preparation times.

	ℓ (nm)	C_g (aF)	C_s/C_g	C_d/C_g	E_{add} (meV)	α
Dev680	680	22	25	170	(4,8)	0.005
Dev20	20	0.6	8	5	(70,80)	0.12
Dev35	35	1.1	6	20	(30 , 40)	0.05
Dev60	60	1.9	5	5	(100 , 110)	0.05

Table 5.1: **List of the devices described in this work.**

ℓ is the length of the nanoribbon, C_g is the gate coupling and $C_{s,d}/C_g$ are the coupling ratio between source (drain) capacitance and the gate one. These parameters are calculated as described in Section 2.4. The Addition Energy (E_{add}) and the lever arm (α) are extracted from the stability diagrams presented in the following section.

The MGNRs studied in this work have been dropcasted on the substrate after being dispersed with sonication in a tri-chlorobenzene solution (PhCl). The concentration of the dispersion was variable, but usually contained about 60 mg/l of MGNR powder, sonicated for about 30 min. After that, 10 μ l of light blue GNR dispersion is dropcasted on the chip. The final yield is usually low (around 2-3% of the devices show and increased conductance), due to the fact that the concentration of molecules applied to the substrate has to be high enough to get the chance to trap at least one of them in a device, but not so high to risk and have multiple molecules bridging or shorting the majority of them. Luckily both the electro-burning and the room temperature characterisation and hunt for good devices can be done with the automatic probe station, working on chips with up to 250 patterned pristine contact devices at the same time.

During this project, we have produced up to 651 graphene break junctions (GBJ) that showed a tunnelling current compatible with a gap size in the nanometer range. Of these, 56 showed an increase of current after molecule deposition, and were then tested at baste temperature. Signs of coulomb blockade, and then the successful creation of a quantum dot, was detected in 8 devices, of which four were thoroughly studied and the results are to be presented in this chapter. In the following they will be called Dev(ice)A-D, and their main properties, as calculated using the models introduced in Section 2.4, are resumed in Table 5.1.

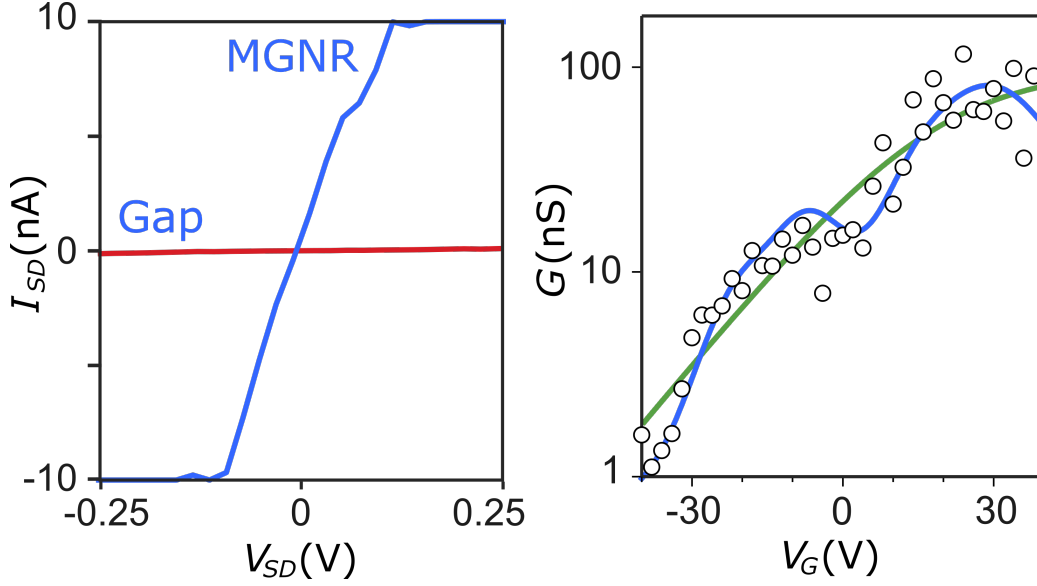


Figure 5.3: **Bias and Gate Traces, Dev20, room temperature.**

(left) Room-temperature dependence of the current vs source-drain potential before (orange) and after (blue) a successful deposition of a MGNR bridging the graphene leads ($V_G = 0$).

(right) Gate dependence of the conductance of the device ($V_{sd} = 10\text{mV}$). Lines represent the behaviours expected for an MGNR with perfectly-defined edges (blue) and a structurally-disordered n-doped GNR transistor (green), resulting from the calculations made by Hatef Sadeghi, from the Physics Department of Lancaster University.

The additional energy E_{add} ranges from 4 meV to 200 meV. This large interval of energies is mainly due to the large statistical variation of ribbons length (Fig. 5.1).

5.3 Room Temperature Characterisations

Fig. 5.3 (left) shows the typical transport characteristic of a junction, before and after deposition of a MGNR. With no MGNR bridging the leads the source-drain current I_{SD} is almost undetectable and the weak current is exclusively due to electron tunnelling between the graphene leads. When a MGNR comes resting across the electrodes, the conductance $G = dI_{SD}/dV_{SD}$ is about 100 nS, even without any gate voltage applied (channel always ON). The device behaves as an n-channel field effect transistor (FET, Fig. 5.3 right), with an ON-state $I_{SD} \approx 1\text{ nA}$ at 10mV, and a

subthreshold swing comparable to that of non-molecular GNR devices (≈ 4 V/dec). The MGNR-FET response shows excellent agreement with numerical calculations made using the exact MGNR structure, with features unobserved in non-molecular GNRs that are predicted to vanish when moderate edge disorder is introduced.

Considering the nature of the device, built bridging two graphene contacts with an intrinsic conductor that in principle should have a good electrical contact via π -staking bonds, the conductance is actually particularly low. The reason is that the alkyl groups that decorate the edges of the ribbons have a considerable chance to roll up below the ribbon, creating in fact an insulating barrier towards the graphene leads. Theoretical calculation performed on two different configuration of the groups respect the ribbon and the graphene contacts confirm this hypothesis. Fig. 5.4 shows the calculated conductance of a GNR with the same dimensions as Dev680, in the two configuration shown on the right. Nine orders of magnitude separates the two configurations, and this device sits in between these two regimes, as expected for a random configuration between the two extreme cases calculated.

5.4 Base Temperature Transport Properties

The weak coupling of the MGNRs to the leads makes them good candidates for well-defined quantum dots at lower temperatures. The 1.7 eV bandgap that the models predict for undoped ribbons is much wider than the applicable gate range in our low-T setup. As a consequence, only highly-doped GNRs with energy states close to the Fermi level are suited for such experiments. This again explains why only four devices, out of the 651 junctions tested, showed signs of conductance. Single-electron transistor (SET) behaviour, as explained in Section 2.4, appears below 30 K, with electrons charging the QD from the leads in a quantised way. The typical regions of blocked conductance due to Coulomb repulsion clearly appear during a full

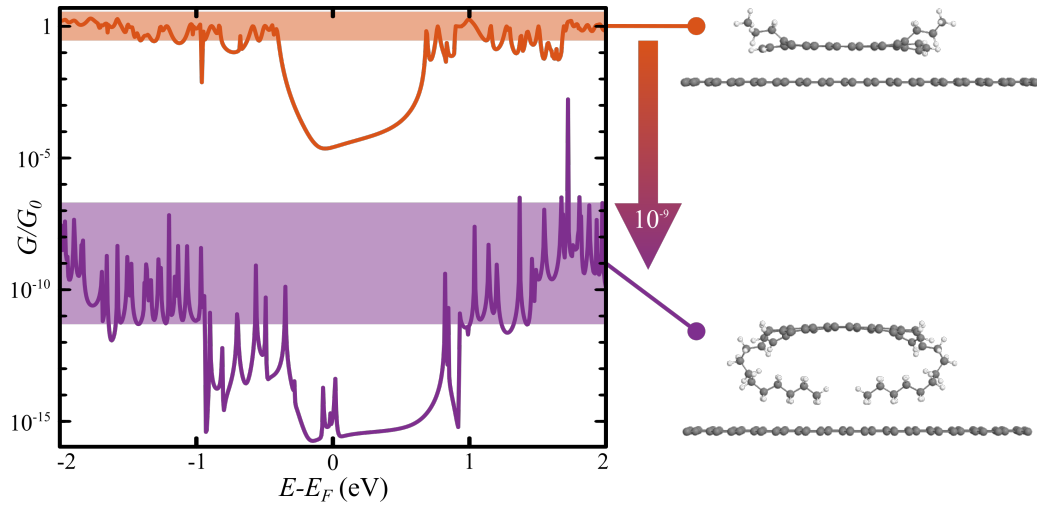


Figure 5.4: **Calculated conductance of MGNRs.**

Calculated conductance of a device made with a GNR with the same length as Dev680 ($\ell = 620$ nm) with the two possible dispositions of the alkyl chains shown on the right: side-way, with direct MGNR-graphene stacking (*top*) and sandwiched between the graphene and the ribbon (*bottom*). Nine order of magnitudes in the conductance separates these two opposite configurations, and my devices sit halfway with a typical conductance in the order of 10^{-4} G/G_0 . Calculations made by Hatef Sadeghi, from the Physics Department of Lancaster University.

transport characterisation of all the devices in function of the Gate and Bias applied, the so-called Stability Diagram (SD).

5.4.1 Stability Diagrams

For all the four devices I am presenting, we can clearly see evidence of Coulomb blockade (CB) in the stability diagrams. Furthermore, there is no saw-tooth edges, indicating that a single MGNR is bridging the channel. For 2-3 nm nanogaps, the geometry of the gap itself can lead to spurious effects explaining the different behaviours amongst the four samples, but the MGNRs features remain recognizable in all of them.

In certain cases, the edge of the MGNR bandgap is visible as a large region of blocked current, where Coulomb diamonds are absent and the tunnelling current is modulated by interference effects between graphene electrode states. This can

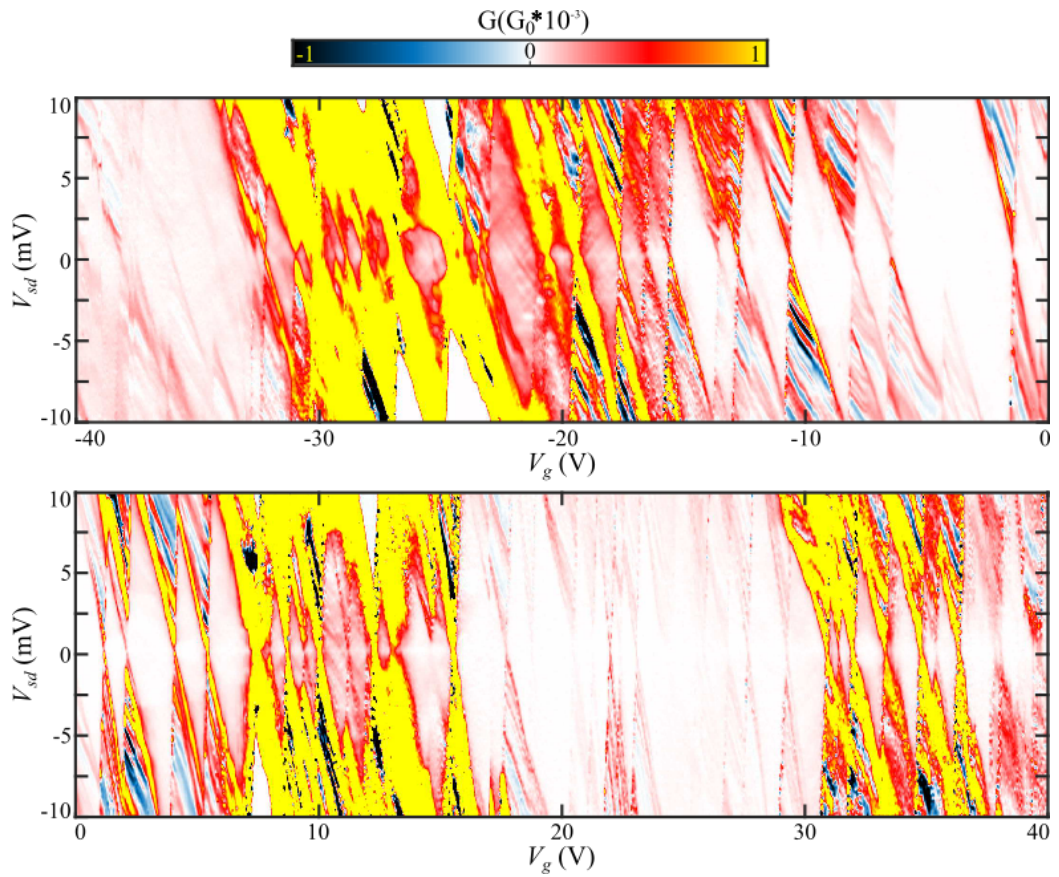


Figure 5.5: **Dev680, Stability Diagram.**

One of the charge stability diagrams taken on Dev680 at 25 mK. This particular one has been taken after the device was thermally cycled from base temperature to 70K and then back to BT again. The two plots are part of a unique measurement, split in positive and negative gate voltage for clarity.

be clearly seen in Fig. 5.5, where an overlaying pattern of blockade diamonds is superposed to smaller ones.

In the following I will propose a selection of stability diagrams taken on the devices I studied and characterised throughout the whole project. Even if some of them may seem redundant, given the lack in bibliography of good collections of Stability Diagrams of molecular quantum dot (especially with such a resolution), I decided to include them in this work.

Dev680 Dev680 is the very first sample based on MGNR that was characterised at low temperature. Out of 105 devices suitable for molecular transistors on the chip, this was the only one which conductance increased noticeably after drop casting the ribbons. This device demonstrated to be very resistant to use: it has been continuously measured for over a month, applying gate voltages up to $\pm 40V$, bias up to $|1V|$ and currents flowing in the device up to 5 nA. Furthermore, this device has been thermally cycled from base temperature up to 77K and back again at base temperature. The main electronic properties of the device stayed the same, demonstrating that even after a thermo-mechanical adjustment the intrinsic properties of the SET are dictated by the nature of the MGNR that constitute it.

Dev20 A wide stability diagram taken on an 80V gate windows (Fig. 5.7, top) showed at once the presence of multiple coulomb diamonds, proving the device to be an electric QD able to be charged several times. Measuring such a wide interval of gates and large bias window make it impossible to have an effective high resolution though, since fluctuation during gate and bias sweep and the presence of electronic traps that can be filled, make the single traces shift slightly in energy one respect to the others.

Narrowing down the measurement window though, it is possible to appreciate the regular pattern of the blockades that gave us an estimation for the addition

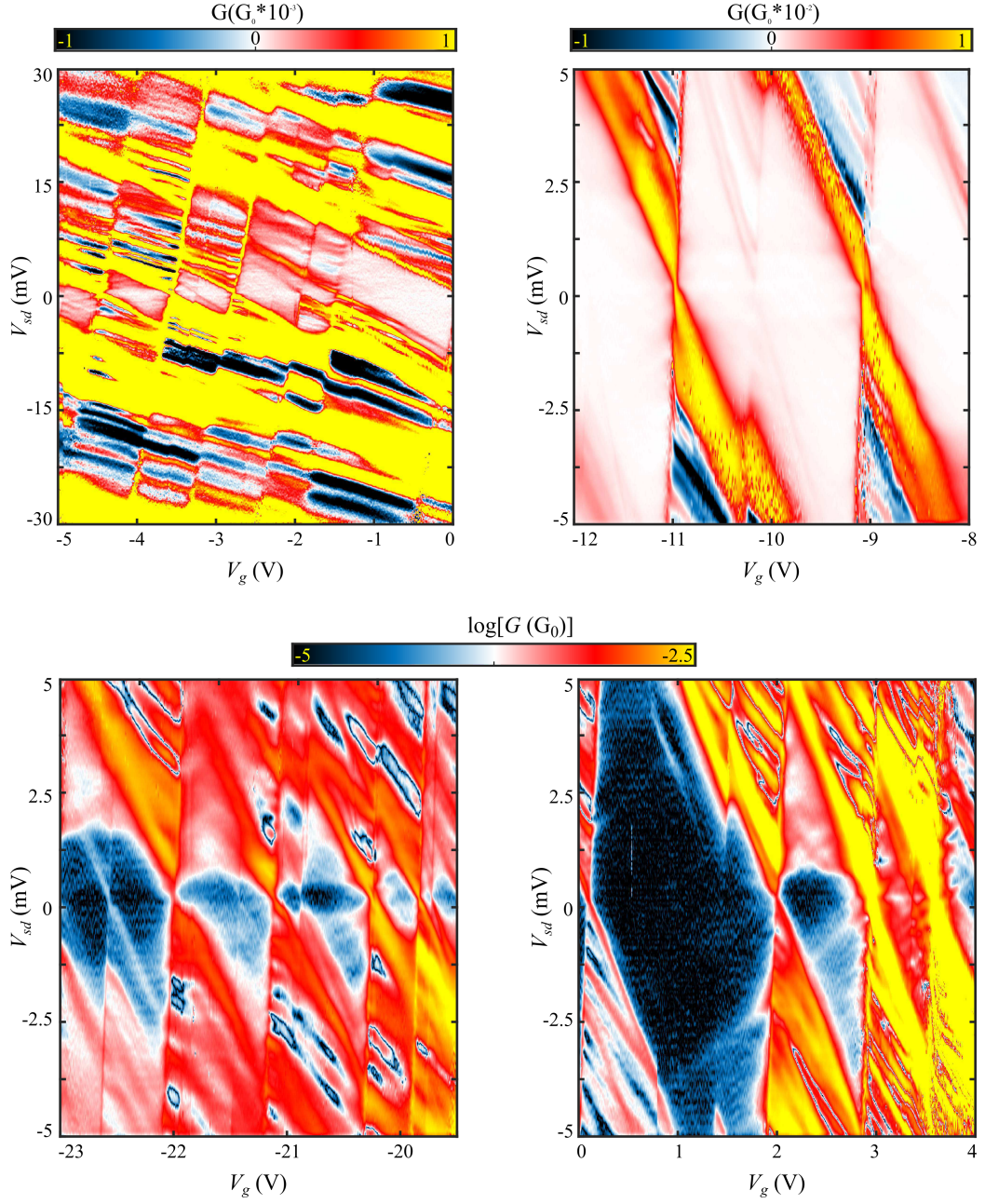


Figure 5.6: Dev680, Graphene states and cotunnelling.

(top) Charge stability diagrams on Dev680 taken at 25 mK that show the graphene lead interference states as wide alternating bands of higher conductance and negative differential conductance (NDC).

(bottom) Again Dev680, zoom-in in different gate ranges, where there is evidence of cotunnelling. In these maps I am displaying the logarithm of the data, to enhance the effect.

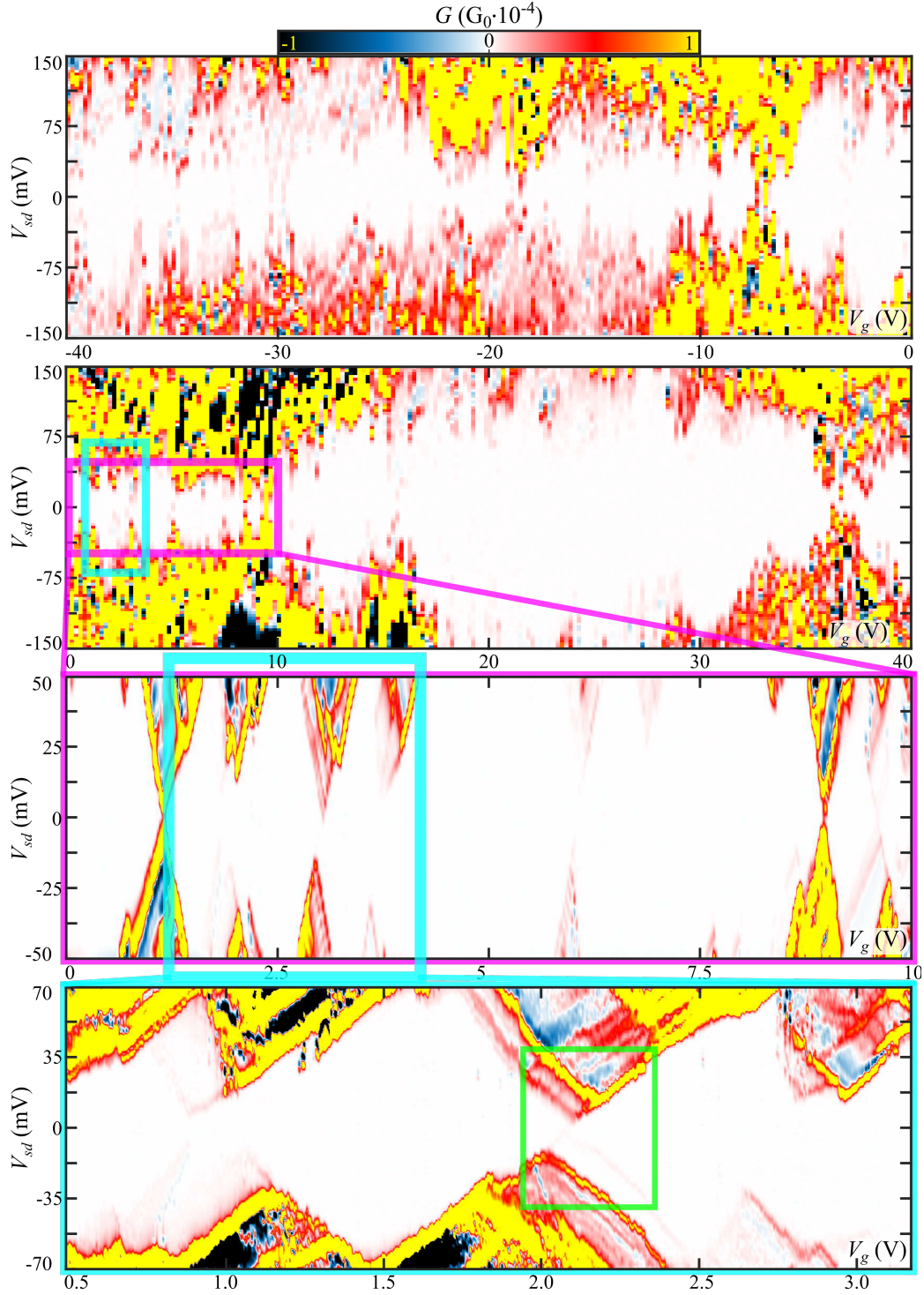


Figure 5.7: **Dev20, Stability Diagrams.**

(top two) Wide map that covers 80V in Gate for Dev20. The resolution only allows us to see wide areas where conductance is blocked alternated to areas with higher conductance like in the previous device.

(bottom two) Two different SDs on Dev20 taken with progressively higher resolution in the areas highlighted in the map above. The peak at 2.0 V is the one which excited states are studied in Section 5.4.5 and the green box highlights the area where the SD in Fig. 5.14 was measured.

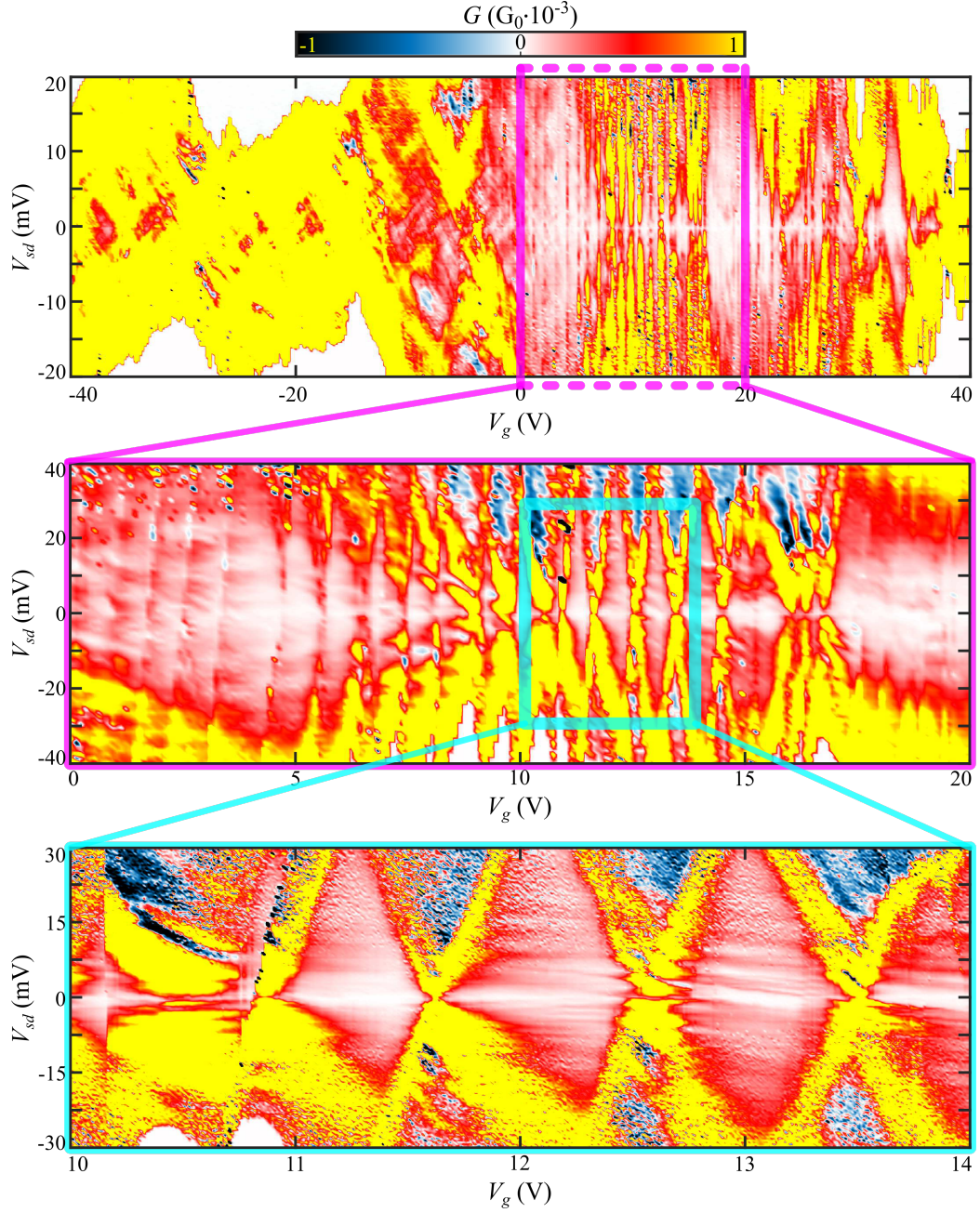


Figure 5.8: **Dev35, Stability Diagrams.**

(top) Wide map that covers 80V in Gate for Dev35.

(center and bottom) Two SDs taken with increasingly higher resolution to resolve the Coulomb peaks features. This device showed strong cotunnelling, as the bottom panel shows.

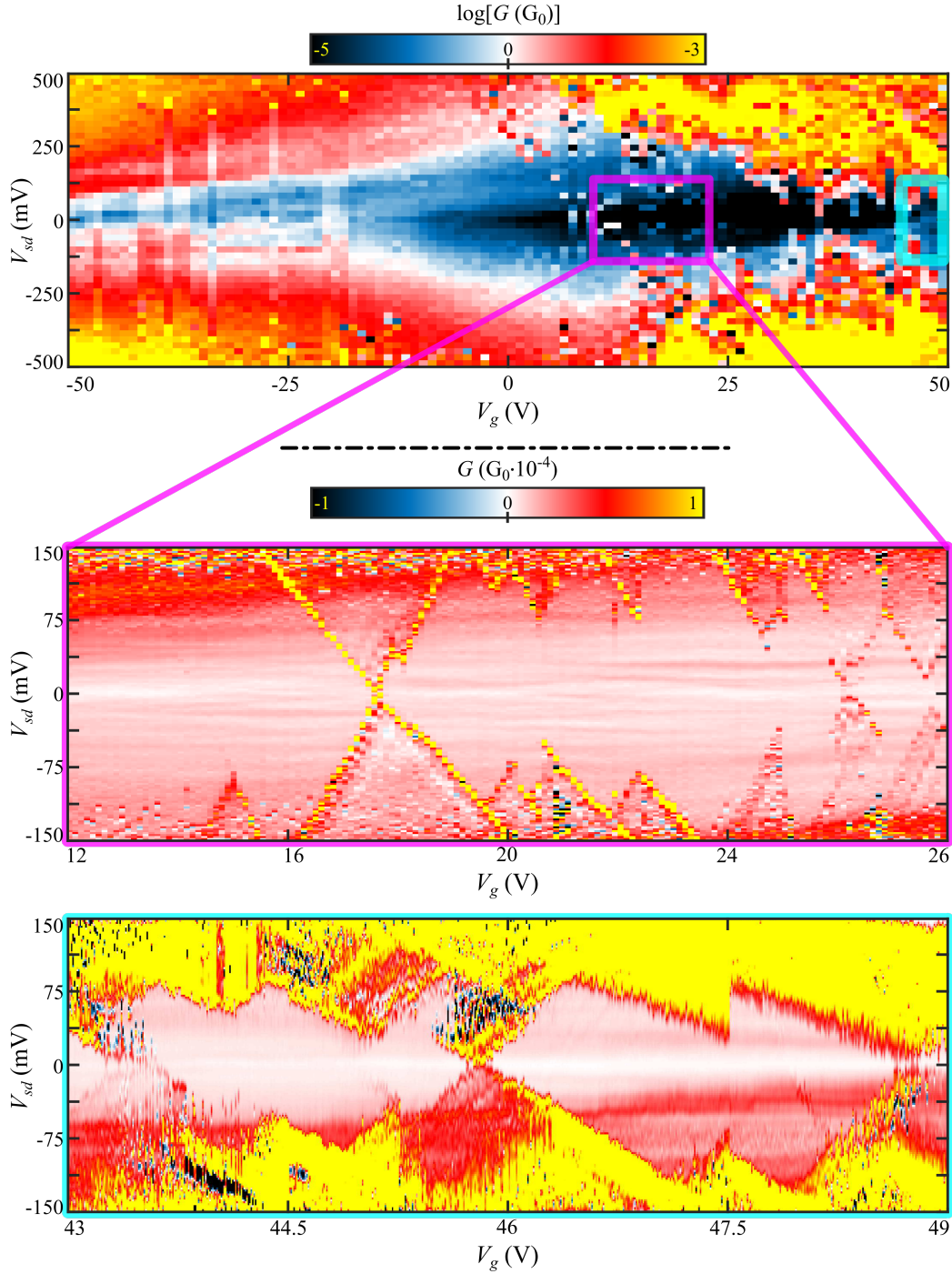


Figure 5.9: **Dev60, Stability Diagrams.**

(top) Wide map that covers 50V in Gate for Dev35. This is the widest gate range I measured on the MGNR devices, and shows how robust they are.

(center and bottom) Two SDs taken with increasingly higher resolution to resolve the Coulomb peaks features in the regions highlighted in the diagram above.

energy $E_{add} \approx 60\text{meV}$ and a lever arm approximately of 0.12 (Fig. 5.7, bottom). Conductance modulation can be detected in the conductive regions, but the resolution in this case is not enough to attribute them either to interference in the graphene leads or to MGNR excited states. At the very bottom of the same figure, a SD that shows a rich pattern of excited states in three different coulomb peaks is displayed. The peak at $V_g = 2.1\text{V}$ has been thoroughly studied for it's abundant information on excited states, and it is discussed in Section 5.4.5.

Dev35 The overall look of the SD is like a typical p-doped device with high conductance (ON) state at negative gate voltages and a blocked region at positive ones. In the positive voltage range, though, multiple interference features are visible that, with a closer look, can be easily ascribed to Coulomb Blockade. As we have previously seen in Dev680, also here we may notice a superposition of two CB patterns with different periodicity: a larger one with approx 15 V step in gate, induced by narrow gap between the graphene leads, and a finer one with ~ 1 V step that we can attribute to the MGNR, as it is a larger confining potential.

The conductance of this device is approximatively one order of magnitude higher than the previous one. This is due to a narrower gab between the leads, which lead to an overall higher background tunnelling current superimposed at the blockade regions. The charging energy that we can deduce from the diagram is approximately 30 – 40 meV. Cotunnelling can be seen in the blockade region (Fig. 5.8, bottom), indication of a strong coupling of the dot with the leads.

This device also showed a peculiar behaviour: intentionally applying larger bias (and hence higher current), it has been possible to remove the ribbon from the channel, lifting the Coulomb blockade. The results is a device with similar overall features, This will be further discussed in S3: Burning of an MGNR in a junction

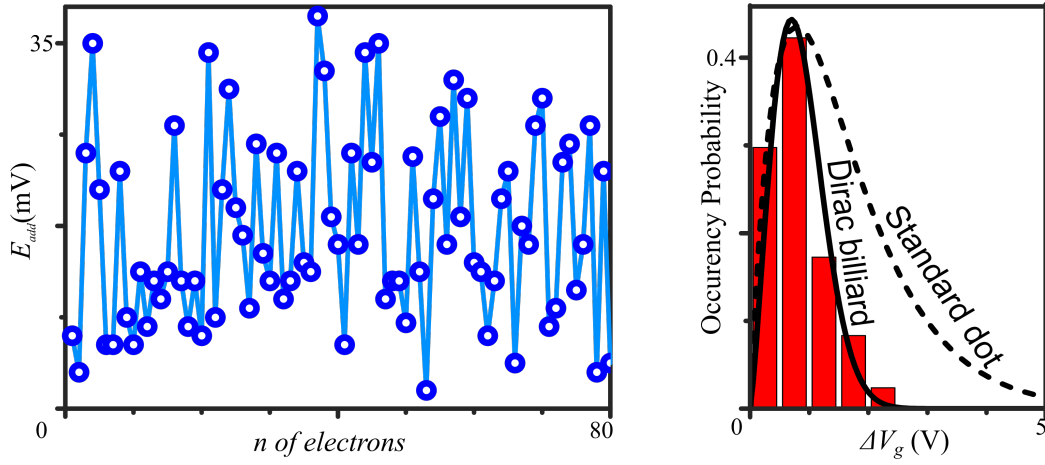


Figure 5.10: **Dev680, level spacing statistics.**

(left) Zero-bias diamond spacing at $V_{sd} = 0$ at base temperature.

(right) Dirac billiard: histogram of the peak-to-peak spacings using the diamonds spacing for Dev680 both before and after the thermal cycling, showing non-Poissonian level statistics even for $\ell=680$ nm.

Dev60 The last device that I will present (Fig. 5.9) shows again the major features of the others: an underlying pattern with a large step ascribed to the potential barrier induced by the break junction gap, and a pattern of narrow blockade diamonds ascribed to the full ribbon. In this case we can appreciate the extreme electric robustness of the device, that worked over an interval of 100V in gate for several sets of measurements.

5.4.2 SET Characterisation

For molecular quantum dots I have discussed the addition energy E_{add} in Section 2.4. In particular, from Eq. (2.31) and considering the molecular level energies negligible compared to the Coulomb repulsion between the electrons that populates the ribbons, we have:

$$E_{add} = \Delta E + E_c \approx E_c = e^2/C = e^2 \frac{\ln(4h/w)}{(2\pi\epsilon_0\epsilon_r)} \quad (5.1)$$

(where ΔE is the MGNR level-spacing, E_c the charging energy, e the electron charge, ϵ_0 the electric constant and ϵ_r the relative permittivity of SiO_2). The last part of the equation is the electrical capacitance calculated for a ribbon sitting on a conductive plane [156]. The calculated values for ℓ are much larger than the width of the nanogap, with the longest and shortest values being 680 and 20 nm Fig. 5.10. This is consistent with the idea that the full ribbon is the active dot, and that the tunnelling barrier that defines the SET sits between the graphene and MGNR planes, in opposition to what commonly happens in other nanoelectronic devices, where it is the spacing between the metal leads that determines the dot dimension.

The MGNR-graphene tunnel coupling, Γ , is relatively low, and values of $\gamma = \Gamma_S + \Gamma_D = 100 - 400 \text{ eV}$ are obtained by fitting the peaks with a Breit-Wigner type resonance Eq. (2.35). The capacitive couplings to the source and drain, obtained from the slopes of the Coulomb diamonds, are comparable to each other for short MGNRs, while a sevenfold asymmetry is present in the $\ell=680$ nm device ($C_s = 24C_g$, $C_d = 169C_g$). This, again, is statistically expected when the length of a ribbon is far longer than the width of the graphene gap, at which point the two sections that rest on the leads on either side of the gap will most probably have very different lengths. In agreement with a larger electrode-MGNR overlap, the lever arm $\alpha = C_G/(C_G + C_S + C_D)$ of Dev680 is also a hundred times smaller than for the other shorter MGNRs devices (Table 5.1).

The side-groups lower the inter-ribbon stacking interactions and make MGNRs soluble, and they are thus likely to fold between the MGNR and graphene. The MGNRs mostly rest over the leads, but experience a different environment, and a local confinement potential, in the nm-sized gap of the junction. This situation can be modelled by including in the same one-dimensional tight-binding model the spectral features of the GNR region overlapped with graphene electrodes, and the local spectrum arising from the region inside the nano-gap (Fig. 5.2). The beating between

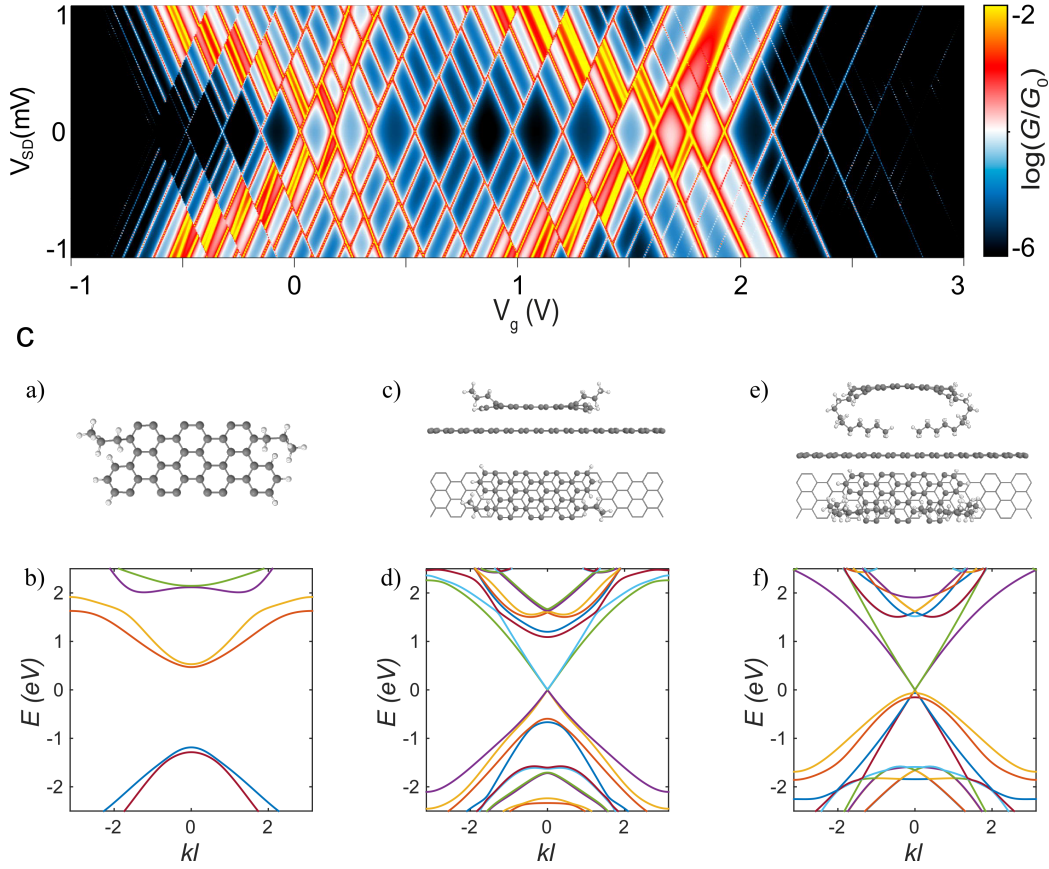


Figure 5.11: **Dev680, Tight Binding Calculations.**

(top) Examples of stability diagrams obtained using a tight-binding model consisting of two one-dimensional leads connected to a scattering region containing two one-dimensional dots. (bottom) 3D modelling and relative band calculation for a free infinite GNR (left), a GNR with alkyl side groups on top of graphene leads (center), and a GNR with the alkyl groups folding below the ribbon (right). These calculations have been performed in Dr. Hatef Sadeghi, Physics Department, Lancaster University.

the two spectra yields a conductance map with widely-spaced regions of high and low differential conductance, as calculation done by Dr Hatef Sadeghi of the university of Lancaster show (Fig. 5.11). This pattern is indeed observed in all devices, with the predicted long-period modulation of the Coulomb diamonds ($30\text{-}40\text{ V} \Rightarrow 150\text{-}200\text{ meV}$).

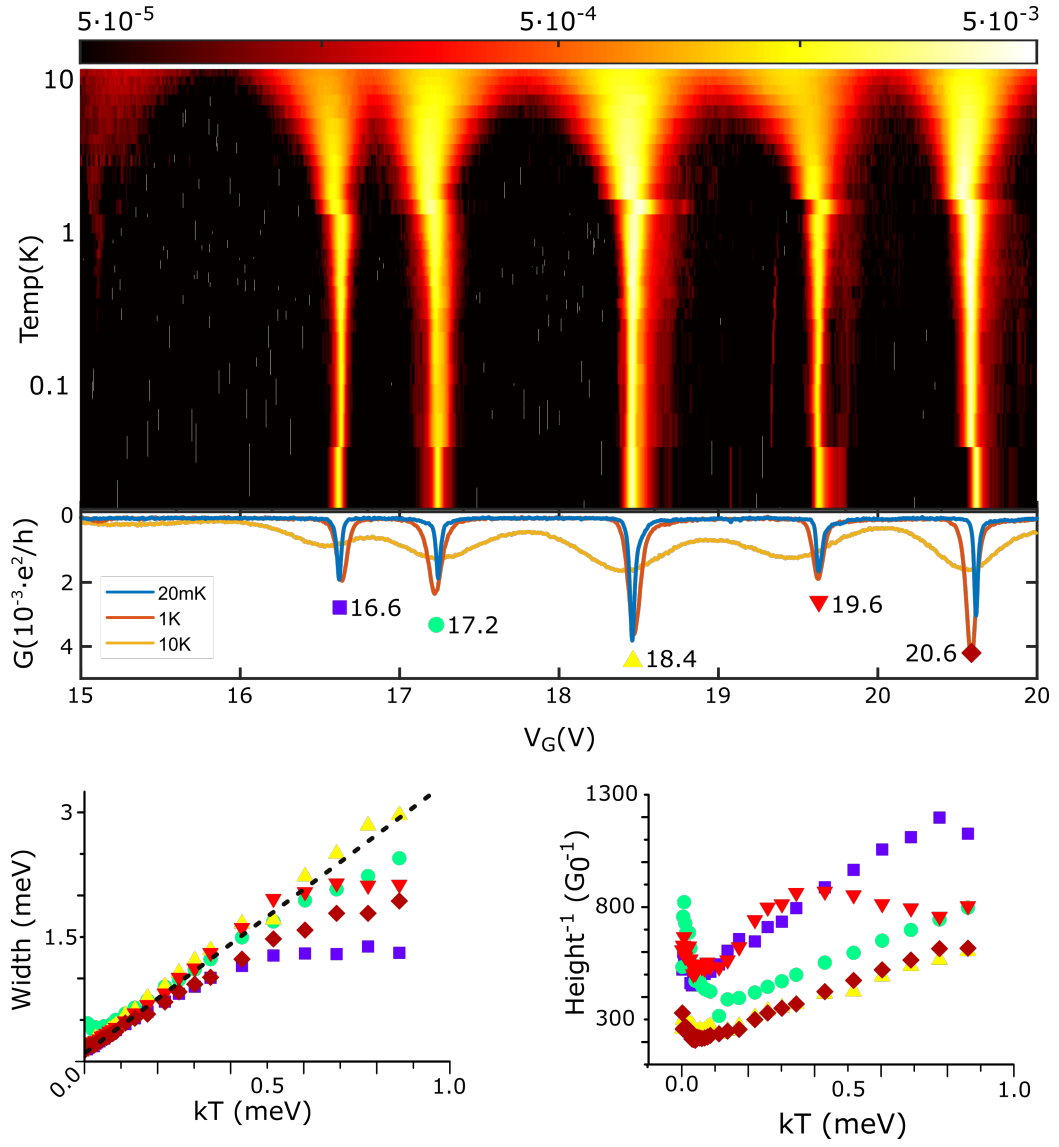


Figure 5.12: **Dev680, Temperature Dependence of the Coulomb Peaks.**

(top) Conductance on five Coulomb peaks of Dev680 plotted against temperature, from 25 mK to 10K.

(bottom) plots of the peak widths (left) and inverse height (right) for the five peaks, as labelled above.

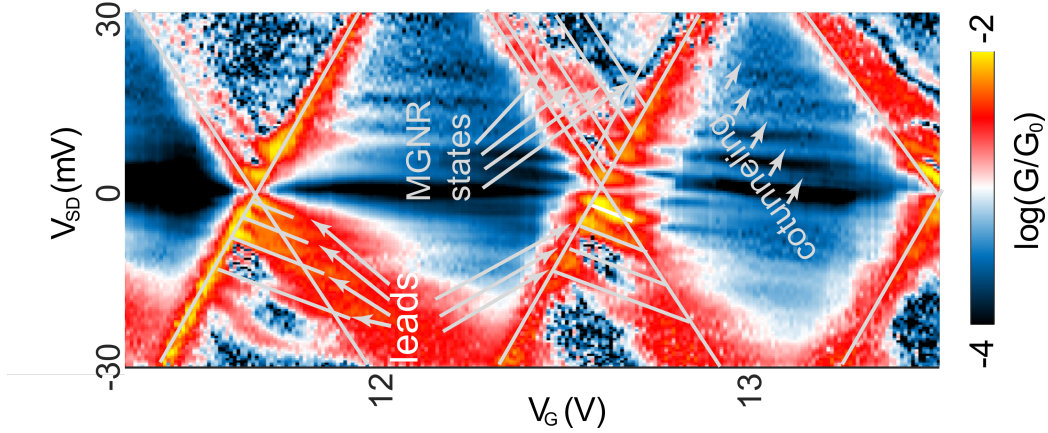


Figure 5.13: **Dev35, Cotunnelling.**

Another SD measured on Dev35, with higher details on the cotunnelling regions. The guides for the eyes are on the edges of cotunnelling zones in the blockade region that follow on excited states in the conductive one. We can also see leads states, recognizable from MGNR states for the fact that they do not run parallel to the sides of the Coulomb diamonds.

5.4.3 Lifetime and Temperature Dependence

I performed a temperature dependence study on four Coulomb Peaks in Dev680 (Fig. 5.12), that demonstrate that this device operates in a typical Quantum Coulomb Blockade regime (QCB). In this regime $\hbar\Gamma \ll k_B T \ll \delta E, e^2/C$ and tunnelling occurs through a single orbital state. Using the relation $G(V_G) = G_\infty \frac{\Delta E}{4k_B T} \cosh^{-2} \left(\frac{\xi_i - \alpha V_G}{2k_B T} \right)$, with $G_\infty \approx 0.001e^2/h$ the high-T conductance, and assuming that T-independent tunnel couplings, we can extract $\delta E \approx 4 - 7 meV$, close to the value of $\Delta E \approx 1 meV$ extracted from the conductance spectroscopy of this device. Analysis of the temperature dependence of the peaks shows that the transition between lifetime-broadened ($k_B T \ll \hbar\Gamma, \delta E, e^2/C$) and thermally-broadened weak coupling regimes happens at $T_C \approx 400$ mK Fig. 5.12. Above T_C , the peak widths increase linearly with a slope ≈ 3.3 , as predicted for QCB [157].

5.4.4 Cotunnelling

Cotunnelling of carriers is clearly visible in several of the maps showed in this chapter as very pronounced conductance lines inside the Coulomb-blocked regions. These lines typically intersect the edges of the Coulomb diamonds and go on in the conduction region as excited states (Fig. 5.13). We observed both elastic and inelastic cotunnelling, depending on the particular device, with typical co-tunnelling energies $\Delta E_{CT} \approx 1$ meV. Cotunnelling is another important fingerprint that we are dealing with a single quantum dot, being an intrinsic second order process that interest a single conductive island between the leads.

5.4.5 Excited States

Inside the conductive region of most of the SDs I discussed in this chapter, several different modulations of the conductance can be spotted. Discrete lines that do not run parallel to the diamonds edges indicate quantum interference-induced changes in the barriers, promoted by the graphene leads (Fig. 5.6, top). These interference patterns are much better resolved than in previous graphene quantum-dots, potentially paving the way to its use in electron interferometric techniques.

On the other hand, excited states of the MGNR are also clearly visible as multiple lines running parallel to the Coulomb edges, and several excitation energies can be extracted, as Fig. 5.14 shows on Dev20. A theoretical study with tight-binding approach performed in collaboration with the Physics Department in Lancaster, showed us that the spectrum of these excited states is in accordance with the discrete energy level spectrum for a $\ell=20$ nm MGNR with alkyl chains between the graphene and the ribbon.

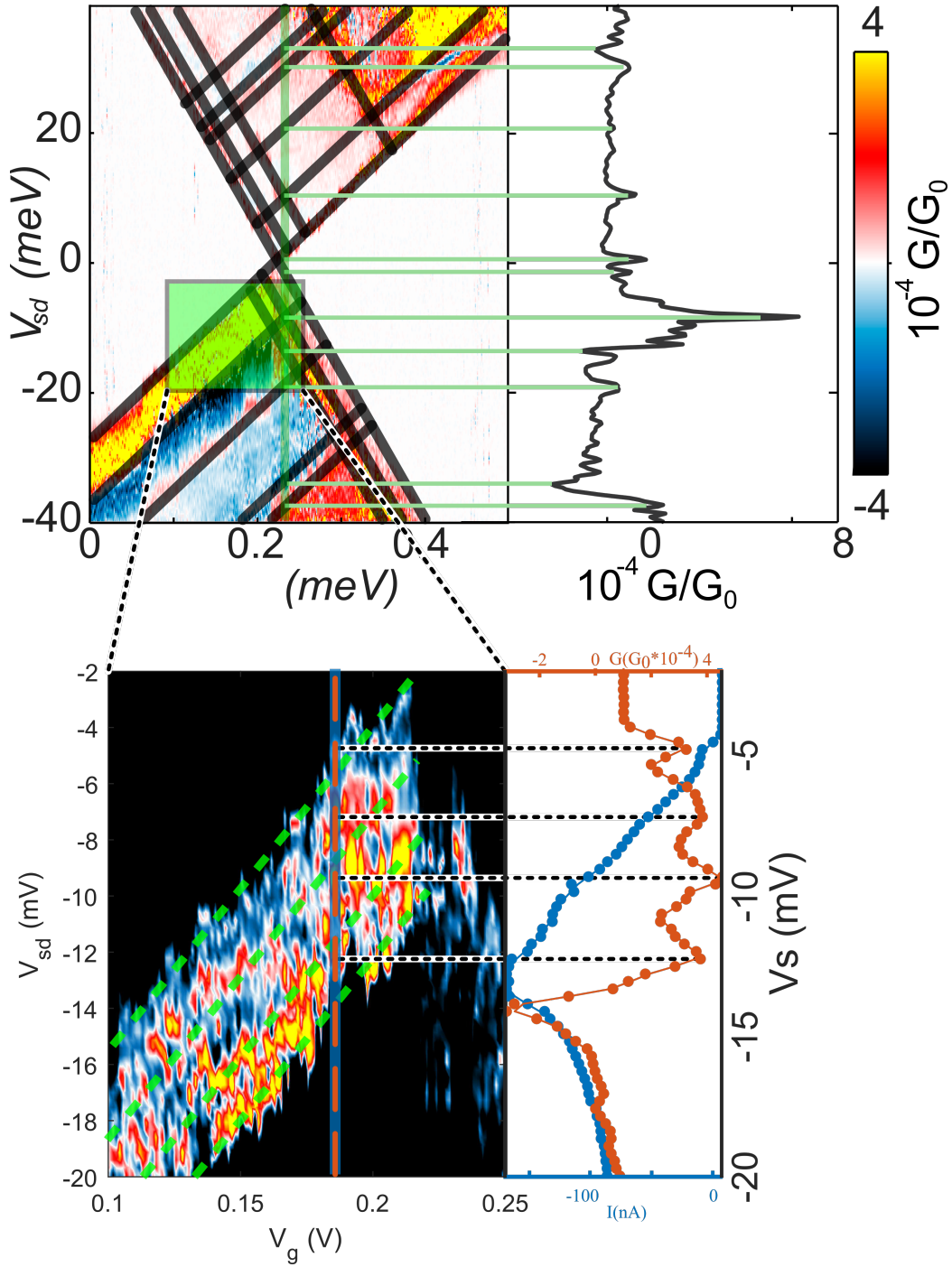


Figure 5.14: **Dev20, Excited States.**

(top) High resolution SD measured on Dev20 on the peak highlighted in green in Fig. 5.7. There is a shift of $\approx -2V$ respect that map, which is due local electronic traps that shift the potential of the gate in proximity of the dot. bottom Close-up of the highlighted region, with a colormap that enhances the summit of the conductance peaks.

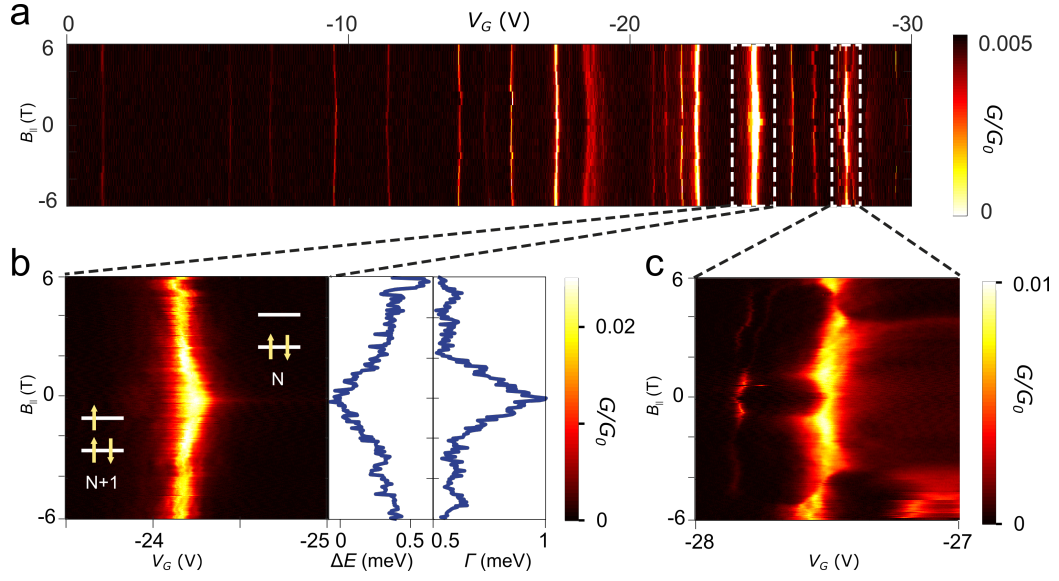


Figure 5.15: **Dev680, Magnetic Properties.**

(top) Dependence of the conductance of Dev680 Coulomb peaks to an external magnetic field with a direction parallel to the graphene substrate.

(bottom) Higher definition scans of the conductance for two peaks.

5.5 Magnetic Effects on GNRs

Fig. 5.15 shows maps of Coulomb peaks at positive bias, as a function of back gate voltage V_g and in-plane magnetic field B , measured on Dev680.

On the peak centred at -24.3 V two effects can be observed: the peak shifts towards higher (positive) gate voltages; and the width of the peak decreases. The plots besides the map show the energy shift of the peak with respect to the peak position at $B_{||}=0$ as a function of magnetic field. The linear shift at low magnetic fields ($B_{||} < 3.5$ T) is attributed to Zeeman splitting. From a linear fit to the low-field data using $\Delta E_{N+1} = (S_{N+1} - 2S_N + S_{N-1})\mu_B g^* \cdot B_{||}$, where μ_B is the Bohr magneton and S_N is the spin quantum number along the $B_{||}$ direction of the quantum dot with N electrons, an effective g-factor of $g^* = 1.95$ can be extracted. Here I am assuming that

$$\Delta S_{N+1} = (S_{N+1} - 2S_N + S_{N-1}) = 1 \quad (5.2)$$

with $S_{N+1} = 1/2$, $S_N = 0$ and $S_{N-1} = 1/2$. This means that the difference between three successive spin states is equal to one. The extracted value for g^* is very close to the value of 2 found for bulk graphene and suggests low spin-orbit coupling in the graphene nanoribbons.

In addition, we observe that the tunnel coupling $\Gamma = \Gamma_L + \Gamma_R$ decreases with increasing $B_{||}$ and levels off to a constant value of about 0.6 meV at $B_{||} > 2$ T (see Fig. 5.15). I attribute this to the magnetic field changes induced in the spatial distribution of the quantum dot wave function, and consequently its overlap with the leads, with a direct effect on the coupling. A more detailed description was suggested for carbon nanotubes [158]: spin and pseudo-spin (K,K' valleys) lead to four-fold degenerate states, which can form two doublets due to disorder induced valley mixing and spin-orbit interaction. A finite intrashell coupling $\Delta_{KK'}$ can lead to valley mixing which changes the tunnel coupling of the doublets resulting in a strongly and a weakly coupled state. However, this effect gets lifted when $B \gg \|\Delta_{KK'}\|$ which results in a decrease (increase) of the tunnel coupling of the strongly (weakly) coupled doublet.

5.6 Electrical "burning" of an SET

I have shown SDs measured on Dev35 in Fig. 5.8. This device showed a very peculiar behaviour: I was able to change its electrical properties by applying a relative large bias (and hence a relative high current). This allowed us to better understand the transport properties of the hybridisation between a molecular quantum dot and a graphene break junction. In Fig. 5.16 I show a comparison of SDs taken before and after such a "burning" process. In the wide gate range diagram, on top, we may recognise the same main features that I already ascribed to the graphene gap potential: a blockade with 20-30 V periodicity in gate. I should be noticed though, on the left diagram, that there is a fine interference pattern between 0 and 20 V. With a

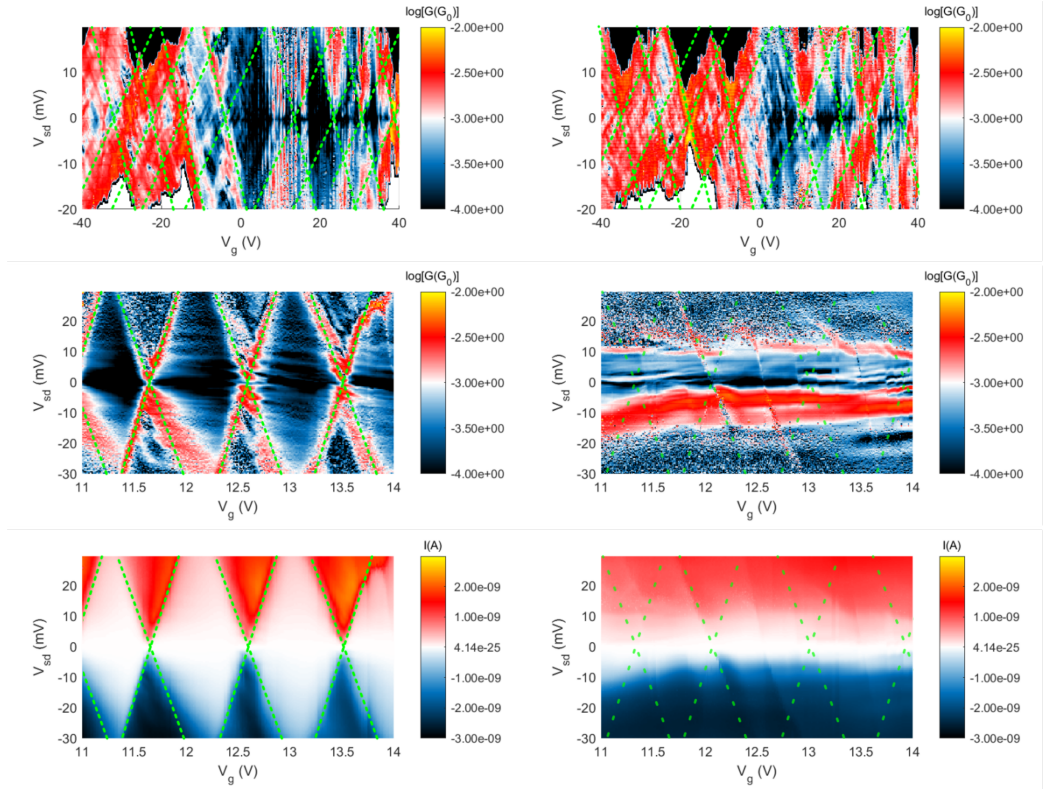


Figure 5.16: **Dev35, "Burning" a Device.**

A comparison of stability diagrams taken at base temperature on Dev35 before (*left*) and after (*right*) we "burned" the MGNR from the graphene leads.

closer look in that range, a periodic Coulomb Blockade pattern has been detected, as shown in the central and bottom diagrams of Fig. 5.8. After the "burning", though, in these regions the blockade is lifted, as shown in the current plots of Fig. 5.16. Nevertheless, a close look at the conductance plots, at the bottom of the same figure, shows a very faint interference pattern with a similar pace, before and after the burning. This confirms again that the alkyl groups are responsible of tuning the barrier between the ribbon and the leads. Furthermore, I showed that their configuration is sensitive to the current that pass through the device, most probably for Joule heating that induce a reconfiguration of the alkyl chains.

5.7 Conclusions and perspectives

In this project I have shown how MGNRs can be integrated in nanodevices to be used as single-molecule transistors. As we can see in Fig. 5.17, the quantum transport of the MGNRs can be compared to the ones of other carbon-based devices by defining different transport regions on a map of the conductance against the ratio between the level spacing and the charging energy. The MGNR-SETs fall considerably close to the Kondo regime region, similarly to many single- and multi-walled carbon-nanotube devices. Furthermore, the localisation is much weaker than in all reported molecular devices that use graphene leads, since they do not usually show cotunnelling effects. This enables encouraging perspectives for the study of magnetic states using MGNRs: both Kondo features and closed-dot states appear to be accessible. The observed cleanliness of the transport features is encouraging for a possible observation of topologically-protected magnetic states, and for the use of MGNRs in superconducting nanodevices. The non-negligible contrast ratio obtained in the lead-MGNR interference patterns opens the perspective of using it as potential spectroscopic tool, and to create hybrid states between bulk graphene and MGNRs.

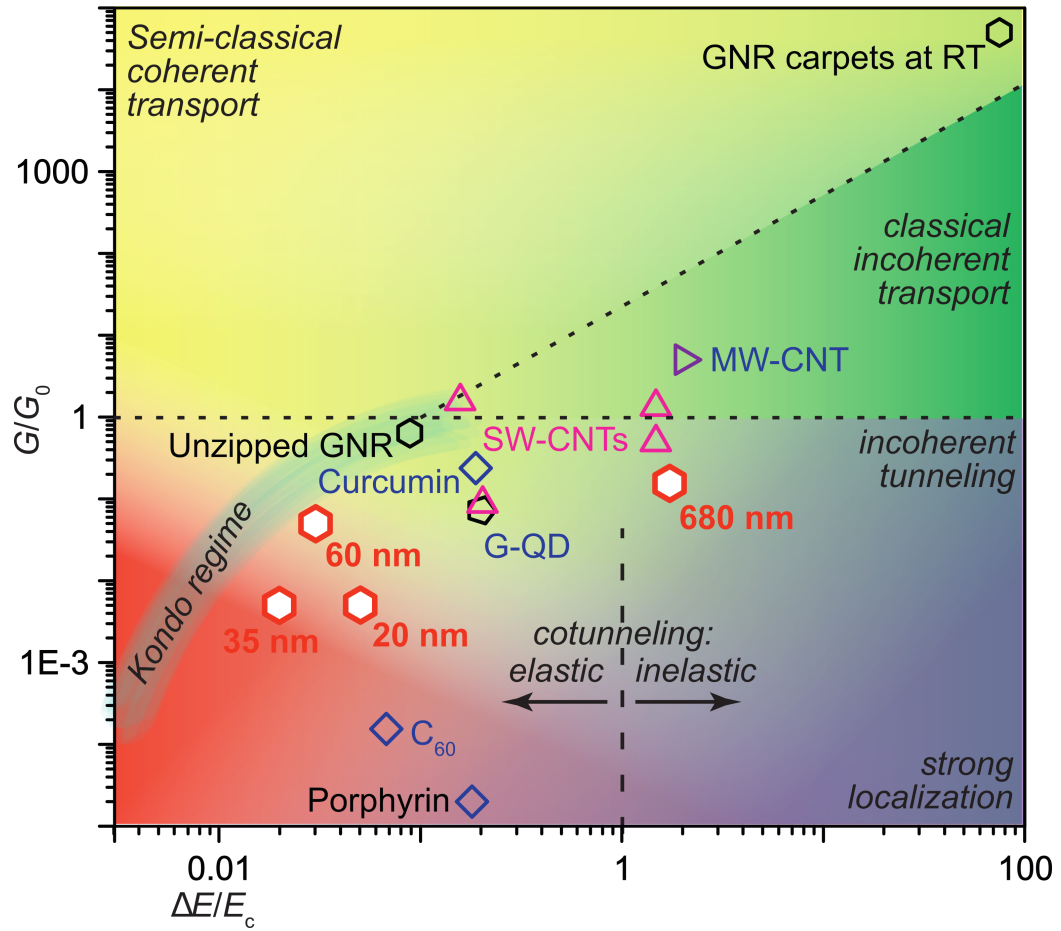


Figure 5.17: **Map of Quantum Devices.**

Map of different transport regimes for molecular devices, plotted in function of their conductance and charging energy. MGNRs devices are in red, while carbon nanotubes are violet, non-molecular graphene dots black and different single-molecule devices measured with graphene leads are displayed in blue.

Furthermore, these results open the path to the precise tuning of graphene quantum dots with the rich means of synthetic organic chemistry: the bandgap and the doping can be engineered using MGNRs with different widths or with electron-injecting side-groups. Multifunctional quantum dots become possible by functionalising the MGNR edges, e.g. with luminescent or magnetic groups. These results thus look promising for the creation of a common research area between synthetic chemistry and quantum transport.

Chapter 6

Magnetic Anisotropy Shaping in Rare-earth based Single-molecule Devices

The aim of molecular spintronics is the control of spin-bearing molecules as building blocks for electronic and spintronic circuits. Using single-molecule magnets (SMMs) then comes natural: their strong magnetic anisotropy and long coherence times enables new potential ways to store data [159], especially for quantum computing [7]. Up to now, SMMs have been studied as spin-ensembles in highly-ordered crystals, where the bonds between the molecules are supposed to not interfere with the magnetic properties of the spin centres [58]. The behaviour of a solitary SMM incorporated in a nanodevice, instead, is still unknown. In particular, the magnetic properties of the molecule may change when coupling them with different substrates or contacts, hindering the deterministic creation of specific quantum-nanodevices just by rational chemistry design. On the contrary, the coupling effects on the molecules may actually prove useful to tune in a completely new way SMMs magnetic anisotropy [160, 161] or even unlock a coherent spin manipulation [162].

For this project, I used the rare-earth based SMM already introduced in Section 2.5.2, the Dy₂bpym. I will start this chapter showing the transport properties of thin film devices based on this compound that I studied during my permanence at the University of Stuttgart. After this initial characterisation, the chapter will focus on a thorough study of the Dy₂bpym behaviour when trapped between two graphene contacts (GBJ, Section 3.3.1). We will see how this will lead to an hybrid device that behaves as a single-molecule transistor [110, 163] at low temperature (mK regime).

6.1 The Molecules: Rare Earth Dimers with a Dysprosium core

The molecules studied in this project have been synthesised in Stuttgart by Dr. Junfeng Wang. He also took care of the PVD of the material both on Si substrates with metal contacts and on top of GBJs. The former lead to the creation of the thin film devices I measured in Section 6.2 The latter enabled the creation of the single molecule transistors characterised later in the chapter.

SMMs based on β -diketonates and heterocyclic aromatic ligands possess magnetic properties that can be tuned by using different bridging ligands and offer the opportunity of introducing high volatilities by using Fluorine-substituted β -diketonates, such as hexafluoroacetylacetonate (hfac). The structural and morphological properties of the thin layers as well as the magnetic response of multilayer films are investigated by means of static and dynamic susceptibility and magnetisation measurements by Dr Wang, and can be found in his PhD thesis [105]. The bulk form of the Dy₂bpym molecules exhibit a strong uniaxial type anisotropy and slow relaxation of magnetisation even after chemical deposition in thin films. Confirming their SMM nature after deposition is an important step toward further miniaturisation, which allowed me to proceed in the study at lower dimensions (Section 6.3).

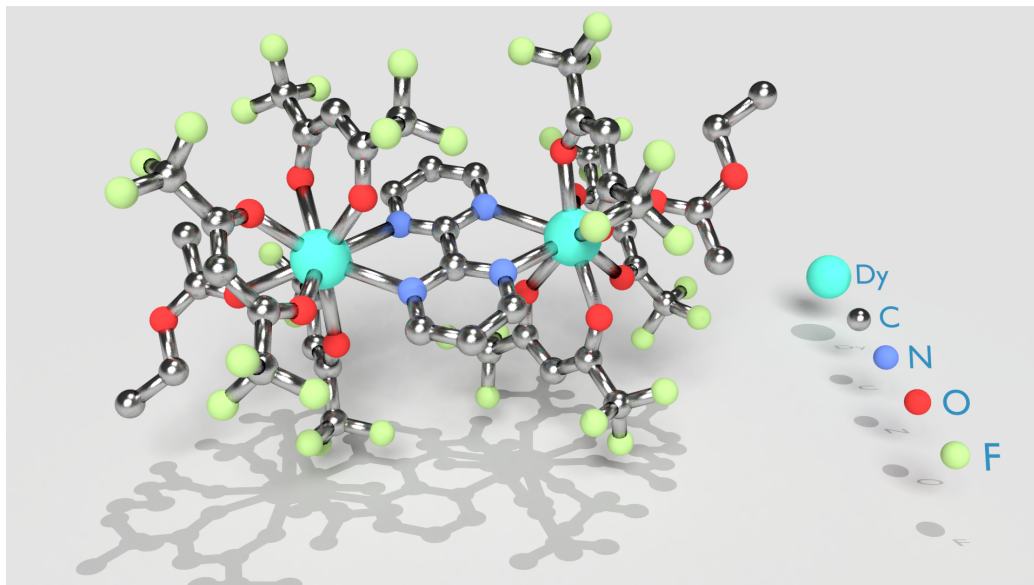


Figure 6.1: **Dy₂bpym Structure.**

3D model showing the structure of Dy₂bpym molecule. This model has been created by me elaborating the X-ray crystallographic data collected by Dr. Wang.

6.2 Electronic Transport of Thin Films

In order to investigate the capability to implement thin films of the investigated compound in electronic devices, both 2D and lower dimensionalities, a first proof of concept device in a vertical cross-bar geometry has been developed and characterised (Fig. 6.2). The figure shows a typical I - V curve for the reference sample, with an exponential dependence of the current to the applied bias. This is typical of tunnelling current, as we discussed in Section 2.1.1, and it is expected for the presence of an insulating CoO layer of approx one nanometer between the golden contacts. As we may see from the I - V curves in Fig. 6.2, both the control sample and the one with the molecular layer suggest that the main transport channel is tunnelling current. Using a Simmons fit [17] to determinate the thickness of the oxide layer we obtain 1.61 ± 0.01 nm, which is consistent with the values found in literature [164], and a barrier height of 1.75 ± 0.03 eV.

Comparing the transport properties of the single devices on the reference sample

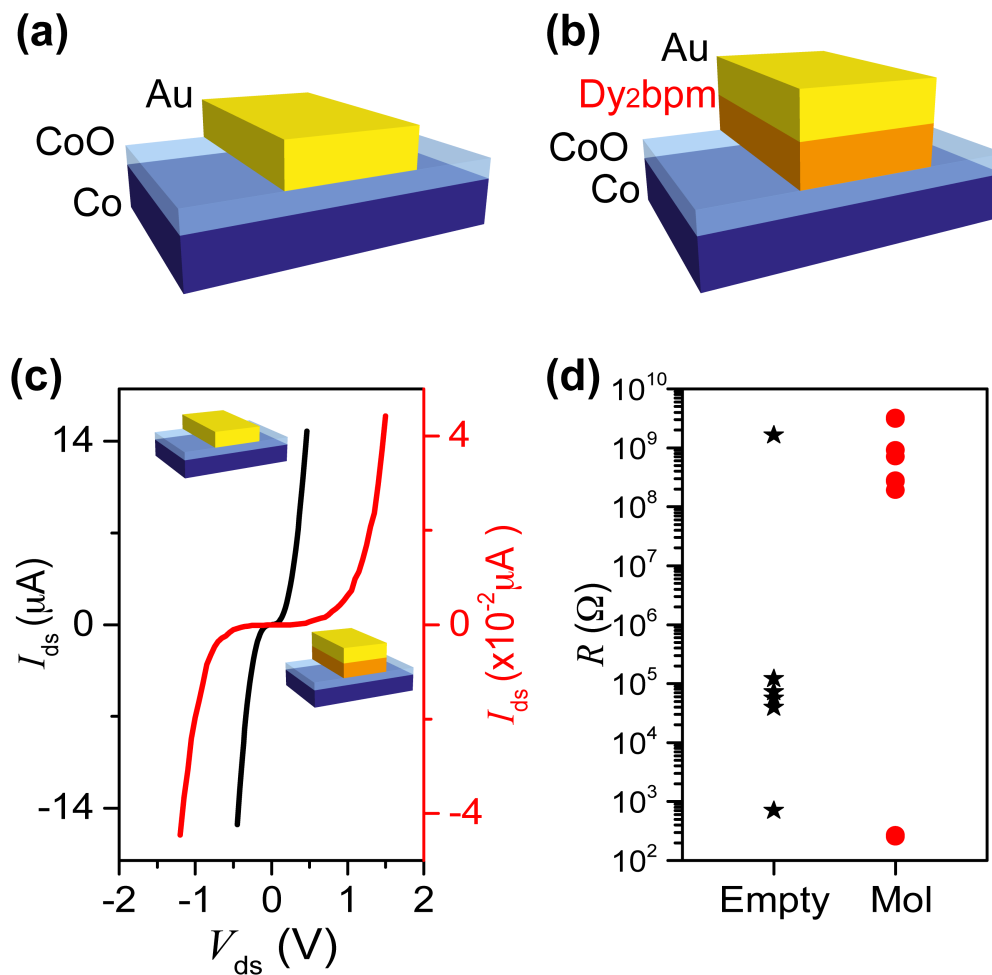


Figure 6.2: **Transport Properties.**

(top) Schematic diagrams of the crossbar device without and with a thin layer of Dy dimers, respectively.

(bottom, left) Typical I-V curves for the stripe device (red) and the reference (black).

(bottom, right) Comparison of resistances (I/V at 500 mV bias) for samples with and without molecular layers: at least 4 order of magnitudes separates the two devices typical resistance.

with the ones on the sample with the Dy dimers layer we can clearly see an increasing of at least 4 order of magnitude in the resistance (Fig. 6.2). At the same time, the I-V curves continue to show a tunnel-like trend, now asymmetric. Using again the Simmons fit to determine the layer properties, we find a barrier a height of 2.14 ± 0.02 eV (with an asymmetry of 0.05 eV) and a layer thickness of 2.07 ± 0.01 nm. Such a small value for the thickness of the molecular layer seems to contradict the AFM measurements, that estimates a thickness of the molecule layer of at least 100 nm. This can be justified with two considerations.

First of all the AFM analysis show that the growth of an homogeneous layer is granted up to 30 nm, then the molecules start to deposit preferably in agglomerates similar to islands. Since the tunnelling current decrease exponentially respect the thickness of the insulating layer ($I \propto d^{-2}e^{-d}$, the growth of island of insulating material will decrease linearly the overall conductance due to the reduction of the conductive area, but the electrons will keep tunnelling preferentially in the thinner zones.

Moreover, it has been observed that layers of bulky molecules can lead to a multi-step tunnelling [165, 166], where the tunnelling distance obtained with Simmmons fitting is related to the sum of the intermolecular distances instead of the overall molecular layer thickness.

Concluding, these measurements demonstrated the successful deposition of intact SMMs on surfaces and the fabrication of electrical thin-film devices with crossbar geometry. This was the first step towards the scaling to 0D and the studies presented in the following sections.

6.3 Low Temperature Spectroscopy of Single Molecule Transistors

Scaling down to 0D, we studied the Dy₂bpym molecules in a device geometry identical to the one used for the MGNR single-molecule transistors seen in the previous chapter. Once a sample shows a successful deposition of molecules in the gap, i.e. a room temperate I-V curve shows an increased conductivity after the deposition of molecules, it gets cooled down in the dilution cryostat. The magnetic properties of the devices are studied by observing the modulation in the charge transport as a function of an external magnetic field. All the measurement, the figures and the data analysis related to the 0D devices are fruit of a close collaboration with Dr Junjie Liu, now at the Physics Department of the University of Oxford.

The stability diagrams for ~ 100 devices have been taken at ~ 20 mK in the Triton 200 system described in Section 3.3. Amongst them four showed well-defined Coulomb diamonds and sharp conductance peaks suitable for studying the magnetic anisotropy, namely DevA-D. The typical addition energies are $E_{\text{add}} > 400$ meV, compatible with what expected given the dimension of the molecular QD. The lever arm *alpha* is ~ 0.02 , very similar to the value found for the MGNR devices. This is expected given the same substrate and contacts geometry.

A selected stability diagram taken on DevA is shown in Fig. 6.3, with an extracted bias I-V trace. The sharp step in current observed is in resonance with the ground state energy level of the molecule. The conductance peak can be fitted with a Lorentzian function (Eq. (2.35)), which indicates that lifetime broadening is dominant respect to thermal broadening. The representative field-bias spectra recorded on device A are shown in Fig. 6.3. The field dependence of the transition energy is calculated and plotted in Fig. 6.4.

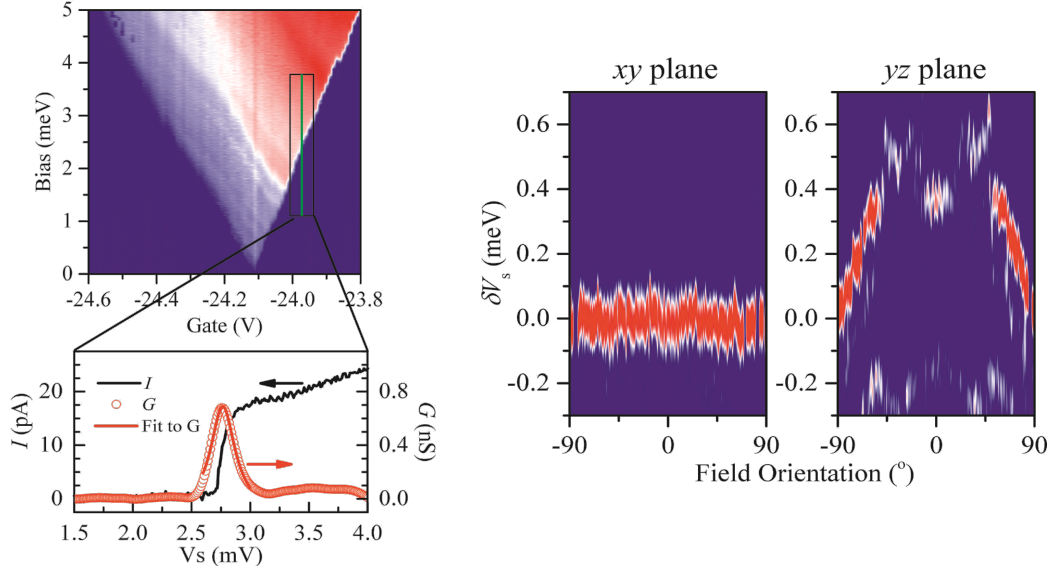


Figure 6.3: **Dy SET, low T characterization.**

(left) Stability diagram taken on devA at 25 mK. The inset shows a typical I-V trace extracted from the data, its numerical differential conductance and the relative Lorentzian fit for the resonance peak.

(right) Conductance maps measured rotating an external magnetic field of 1 T within the graphene plane (xy) and perpendicular to it (yz) while maintaining a constant gate value.

6.4 Magnetic Anisotropy Study

To prove and measure a magnetic anisotropy in my devices, the best way amongst the one I described earlier is to observe the coulomb peak behaviour while rotating a magnetic field with a constant intensity. Fig. 6.3 shows an example of such a measurement. From the measurement, it is clearly observable an isotropic energy value for the coulomb peak when the field is rotated within the graphene plane, namely *xy*. On the other hand, performing the same measurement rotating the field in a perpendicular plane (namely *xz*), a consistent shift in the ground state energy is observed. The plot shows the conductance peak shifting to a higher voltage when the field is rotated out of the graphene plane. The change of the transition energy (δE) is extrapolated fitting the Coulomb peak with a Lorentzian curve, and plotted in Fig. 6.4(a). As the field approaches the normal direction to the graphene plane,

the transition exhibits a slight drop, suggesting that the direction of maximum magnetisation has been crossed and left behind. The maximum energy shift detected is ~ 0.31 meV which, considering the field intensity of 1 T, suggest a g -factor one order of magnitude stronger than the one of a spin 1/2 system (0.0578 meV/T when $g = 2$) The change in δE reaches a maximum value of 600 meV in the 1 T rotation, which is an order of magnitude stronger than the Zeeman energy of a spin 1/2 system.

The g -factor has been measured in the graphene plane, with a field sweep at higher field values. Fig. 6.4 shows the sweeps performed on a device that suggest a Zeeman split of 0.038(4) meV/T, with a corresponding g -factor = 1.32. This value is smaller than the free electron one ($g_e = 2$), but in good agreement with the value predicted with the Hund's rule for a Dy^{3+} atom ($g = 1.33$).

These measurements have been performed on all the devices with similar results: in-plane rotations display an isotropic energy split, while perpendicular rotations show very similar patterns (in Fig. 6.4 I show all of them in single plot). In particular, the energy splitting δE seems to decrease in all the devices at $\sim 30^\circ$ from the direction perpendicular to the graphene plane, with a shift between 0.25 and 0.35 meV from the maximum intensity. This corresponds to a change in the g -factor from 8.3 to 12. It must be noted that the sign of δE varied for individual devices, reflecting that the total spin number either increased or decreased in the relative electron transition. This phenomenon may be understood based on the spin filling order of the bpym bridging ligand and is discussed in more details in the analysis.

As mentioned in the introduction to this chapter, in order to be sure that the anisotropy is solely due to the Dy core of the molecules, I performed analogue measurements on graphene quantum dots (GQD) This has also a double importance: in literature studies on the magnetic properties of graphene dots are related to relatively large dots, made using lithography [167, 168], while the ones on similar geometries [169, 170] do not show results with fields applied. Fig. 6.5 shows the results of this

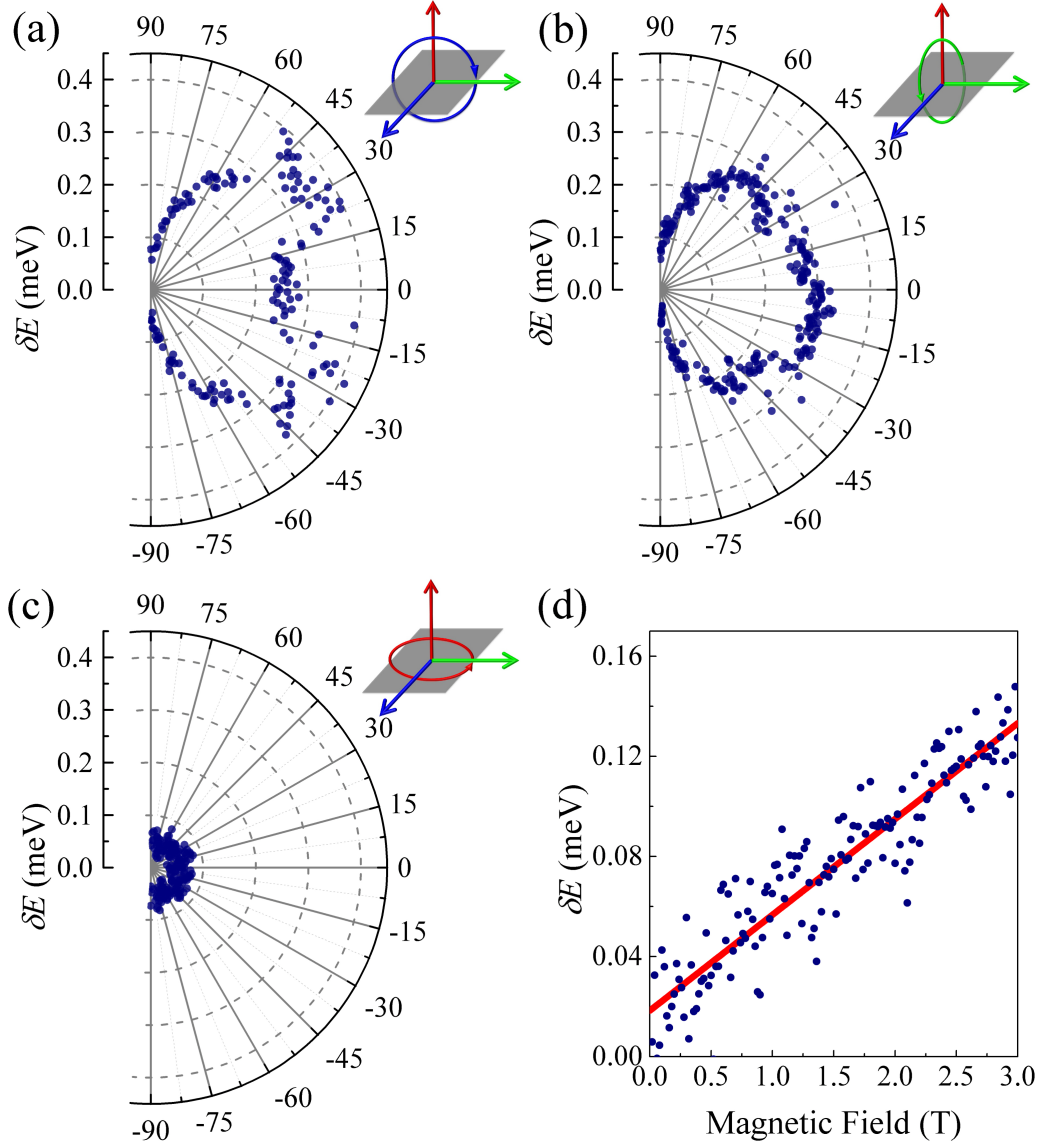


Figure 6.4: **Polar Plots.**

(a)-(c) Polar plots showing the energy shift of E_g as a function of the field orientation, with a constant field intensity of 1 T. Strong shifts are observed in the out-of-plane rotations [(a) and (b)]. (d) Evidence of Zeeman splitting in the charging energy, plotted as a function of the field intensity in a fixed direction in the device plane. The solid line is a linear fit with a 0.038 meV/T slope.

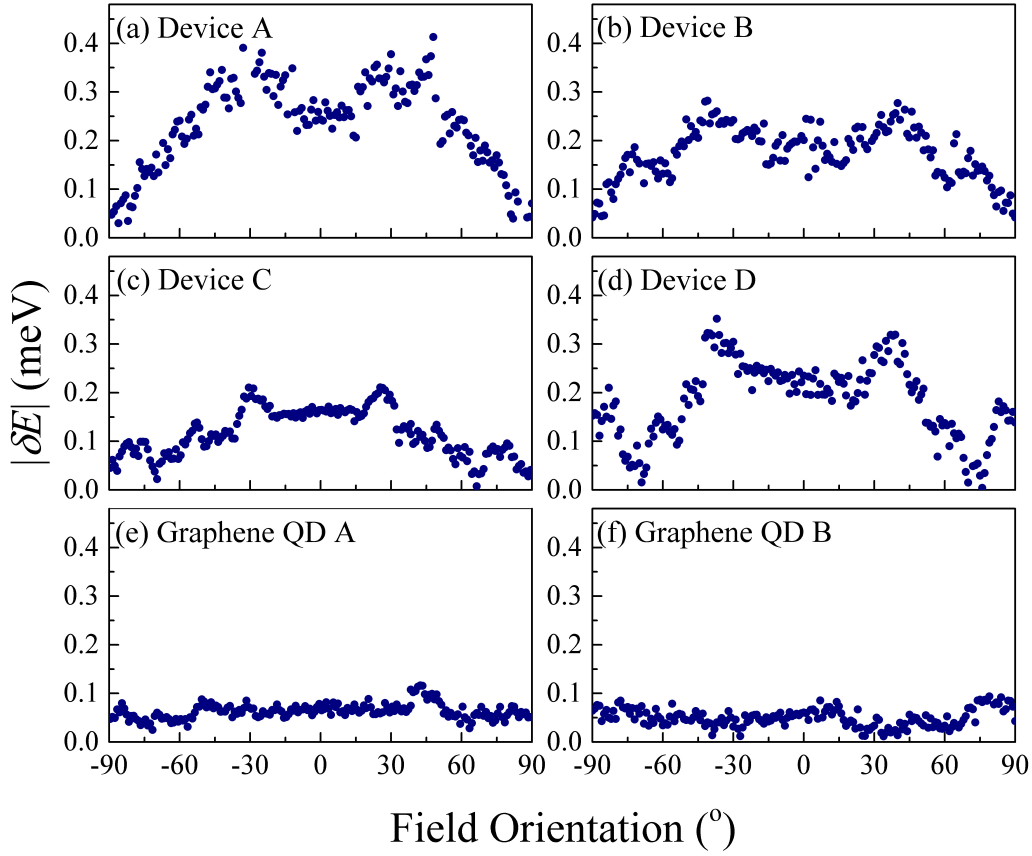


Figure 6.5: **Magnetic Anisotropy, Comparison.**

Transition energy as a function of the field orientation in the 1 T out-of-graphene-plane rotations for the Dy₂bpym devices [(a)-(d)] and the graphene quantum dots [(e) and (f)]. At 90° the field is applied perpendicular to the graphene plane. The vertical axes of all plots are the same for comparison.

comparison. Rotating the field in the plane perpendicular to the graphene, no appreciable anisotropy can be detected in the GQD, whilst the huge Dy₂bpym energy shifts are clear.

6.5 Modelling the Magnetic Anisotropy

6.5.1 Giant-Spin Approximation

To understand how an SMM behaves when placed in an external magnetic field, we use the giant-spin approximation (GSA), described in [46]. Ignoring the internal spin

degrees of freedom of the molecule, we may write its Hamiltonian as:

$$\hat{H} = D\hat{S}_{\text{z,mol}}^2 + B_4^0\hat{O}_{4,\text{mol}}^0 + \mu_B g_{\text{Dy}} \mathbf{B} \cdot \hat{\mathbf{S}}_{\text{mol}} \quad (6.1)$$

where $\mathbf{B}$ is the external field and $\hat{O}_4^0$ is the fourth order uniaxial Stevens operator [171], which describe the magnetic anisotropy of the molecule. We chose to add only this operator from the full set, since its uniaxial symmetry better represents the results of my experiments. In this model, the spins of the two magnetic cores sum up in a single giant spin of 15 ($2 \times 15/2$), for the molecule in a neutral state.

To describe the next charge state ($N + 1$), we can use the same Hamiltonian but with a different set of zero-field splitting (ZFS) parameters (D , B_4^0). The spin will either decrease or increase by 1/2, depending on the orbital the electron will populate. In particular, filling a partially filled orbital will decrease the spin, while populating an empty one will have the spin to increase.

In my analysis, the ZFS parameters are allowed to vary between the N and $N + 1$ states [172], giving as result the fit showed in Fig. 6.6 as black solid line.

As the figure suggests, this model fails to describe the anisotropy in the data, in particular the ripples close to the molecular easy axis ($\theta = 0$).

The analysis suggests that Eq. (6.1) may be inadequate for explaining the experimental result.

6.5.2 Giant-spin Approximation with Graphene Hybridisation

It has been recently demonstrated that the deposition of molecules on a graphene substrate induce an hybridisation between the two, with interesting modifications of the quantum magnetic property of the molecules [173]. In particular, the three-fold

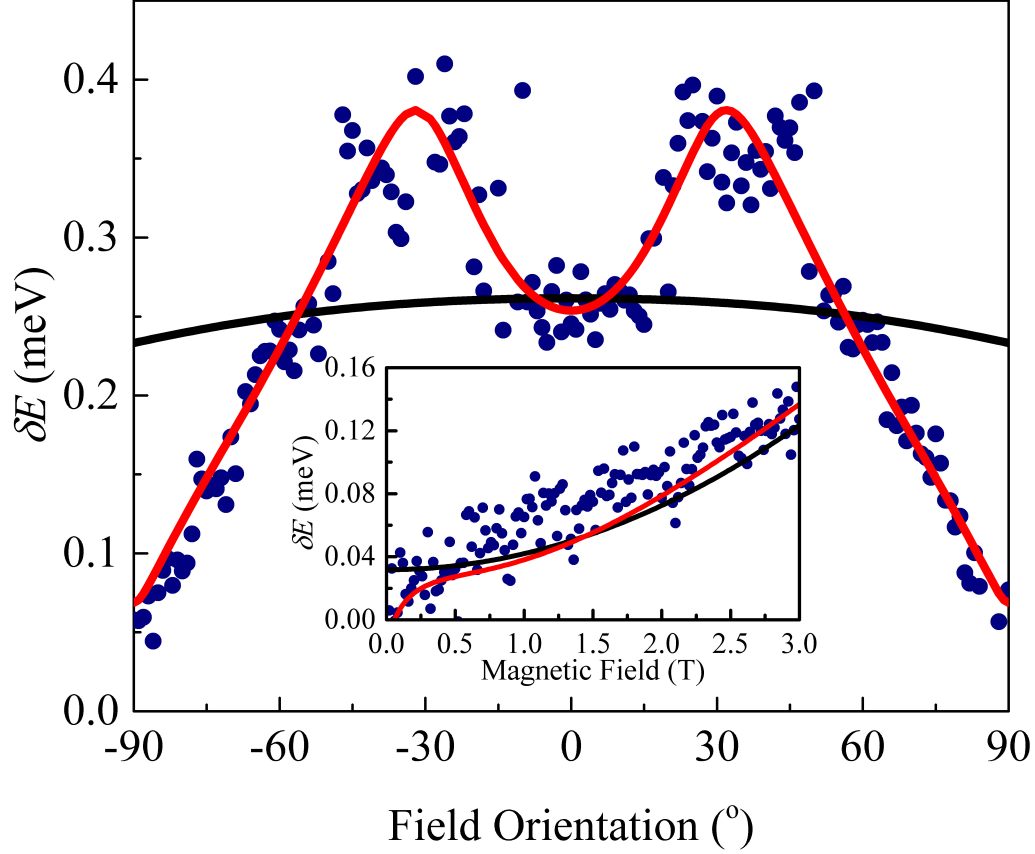


Figure 6.6: **GSA fit.**

The experimental data of the out-of-plane 1 T rotation and the simulations employing the GSA Hamiltonians. The black curve corresponds to the best fit obtained with Eq. (6.1) with $D < 0$ and $B_4^0 < 0$. The red curve is the simulations performed with Eq. (6.2) with the same constriction of the D and B_4^0 parameters. Inset: The field sweep data and the simulations. The red and black lines correspond to the simulations performed with Eq. (6.1) and Eq. (6.2), respectively.

symmetry of the graphene wave function induces a similar symmetry on the molecules, selectively enhancing the anisotropy operators with similar properties. The result is an axial direction of maximum anisotropy that points perpendicular to the graphene plane.

We can take this in account adding to Eq. (6.1) and additional term with a the three-fold symmetry, representing the hybridisation of the two moieties. The first choice is to use the lowest order of Steven operator with that symmetry: $B_4^3 \hat{O}_4^3$ ($\hat{O}_4^3 = [\hat{S}_z, \hat{S}_+^3 + \hat{S}_-^3]_+/2$).

The Hamiltonian can then be written as:

$$\hat{H} = D\hat{S}_{z,\text{mol}}^2 + B_4^0 \hat{O}_{4,\text{mol}}^0 + B_4^3 \hat{O}_{4,\text{mol}}^3 + \mu_B g_{Dy} \mathbf{B} \cdot \hat{\mathbf{S}}_{\text{mol}} \quad (6.2)$$

The best fit to Eq. (6.2) is shown in Fig. 6.6 The inclusion of a strong B_4^3 parameter leads to significant modifications to the simulation. With sizeable B_4^3 parameters, it is possible to fit both the angular dependence data and field sweep simultaneously. The simulation shows a significant difference between the B_4^3/B_4^0 ratios for the N and $N + 1$ states. This suggests that the molecule-graphene hybridisation may strongly depend on the spin state of the molecule due to the symmetry of the graphene wave function. This symmetry selected substrate-spin coupling has been observed recently on the single-atom level. [174]

Finally, we consider the in-plane anisotropy induced by the $B_4^3 \hat{O}_4^3$ term. Surprisingly, even with a strong hybridisation term B_4^3 , the three-fold term only leads to a small ripple when the field is rotated within the graphene plane. The simulations demonstrate that even with a B_4^3 parameter comparable to the axial anisotropy parameters, the in-plane rotation only show a modulation of 0.02 meV, which is within the noise level of the experimental data. This limited in-plane anisotropy can be intuitively understood based on the form of the $B_4^3 \hat{O}_4^3$ operator. The $\hat{O}_4^3$ couples the

S_z and the $S_{x,y}$ components of the molecule and its contribution is proportional to the S_z component. When the field is applied within the hard plane of the molecule ($\perp$ to the z -axis), the S_z component almost vanishes, leading to a small modulation to the inplane rotation caused by $B_4^3\hat{O}_4^3$. In summary, the incorporation of the $B_4^3\hat{O}_4^3$ term allows all experimental results to be fitted with the same set of parameters. The analysis suggests that the hybridisation may play an important role in the magnetic property of the Dy_2bpym molecules embedded in a graphene nanogap.

6.5.3 Dimer Model

The aforementioned GSA model ignores the internal degrees of freedom within the molecule by treating the total spin number of the molecule as a rigid number. An alternative approach, which takes into account the anisotropy of individual Dy spins as well as the coupling between them, is given by the Hamiltonian:

$$\begin{aligned}
\hat{H} = & (d\hat{S}_{z,\text{Dy1}}^2 + b_4^0\hat{O}_{4,\text{Dy1}}^0 + d\hat{S}_{z,\text{Dy2}}^2 + b_4^0\hat{O}_{4,\text{Dy2}}^0) \\
& + (\hat{\mathbf{S}}_{\text{Dy1}} \cdot \bar{\bar{\mathbf{J}}} \cdot \hat{\mathbf{S}}_{\text{bpym}} + \hat{\mathbf{S}}_{\text{Dy2}} \cdot \bar{\bar{\mathbf{J}}} \cdot \hat{\mathbf{S}}_{\text{bpym}}) \\
& + \mu_{\text{B}}g_{\text{Dy}}\mathbf{B} \cdot (\hat{\mathbf{S}}_{\text{Dy1}} + \hat{\mathbf{S}}_{\text{Dy2}}) \\
& + \mu_{\text{B}}g_{\text{bpym}}\mathbf{B} \cdot \hat{\mathbf{S}}_{\text{bpym}}
\end{aligned} \tag{6.3}$$

where interaction J and the g factor take the tensor form of:

$$\bar{\bar{\mathbf{J}}} = \begin{pmatrix} J_{\perp} & 0 & 0 \\ 0 & J_{\perp} & 0 \\ 0 & 0 & J_{\parallel} \end{pmatrix}, \quad \bar{\bar{g}}_{\text{bpym}} = \begin{pmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix} \tag{6.4}$$

The first term in Eq. (6.3) represents the single-spin anisotropy associated with the Dy ions. The second term corresponds to the intra-molecule Dy-Dy interaction mediated

by the bpym bridge. The third and fourth terms are the Zeeman energy of the Dy ions and the bpym ligand, respectively. In the dimer model, the spin of the Dy ions and their single-ion ZFS parameters (d and b_4^0) are independent of the molecule charge state with $S_{\text{Dy1}} = S_{\text{Dy2}} = 15/2$. The spin of the bpym ligand (S_{bpym}) oscillates between 0 and $1/2$, depending on the number of unpaired electrons.

In the dimer Hamiltonian, the spin configurations of three consecutive charge states can be visualised with Fig. 6.7a. In the neutral state (N) of the molecule the bpym ligand carries no charge and the interaction between the two Dy spins is negligible. This can be seen from Eq. (6.3) where $S_{\text{bpym}} = 0$, hence, $\hat{\mathbf{S}}_{\text{Dy}} \cdot \bar{\bar{\mathbf{J}}} \cdot \hat{\mathbf{S}}_{\text{bpym}} = 0$. When an electron is added to the Dy_2bpym molecule, it resides on the the central bpym ligand [175]. The negatively charged bpym bridge has a spin of $S_{\text{bpym}} = 1/2$ and it mediates an interaction between the Dy spins [176] which is characterised by the $\hat{\mathbf{S}}_{\text{Dy}} \cdot \bar{\bar{\mathbf{J}}} \cdot \hat{\mathbf{S}}_{\text{bpym}}$ term in Eq. (6.3). Due to the antiferromagnetic nature of this interaction, the total spin of the molecule decreases from 15 to $29/2$, which is the case for device A and B. When the molecule is in the $N + 2$ charge state, the two extra electrons on the bpym bridge form a singlet spin state, resulting $S_{\text{bpym}} = 0$ and the interaction between the Dy spins is suppressed. In this transition, the total spin of the molecule increases from $29/2$ to 15, which corresponds to the data recorded in device C and D.

The observed anisotropy can be explained with the dimer model by treating the Dy spins classically. Due to the giant Ising type anisotropy of the Dy ions, S_{Dy} prefers to align parallel to its local anisotropy axis. When a small external field is applied ($|\mu_{\text{B}}g_{\text{Dy}}HS_{\text{Dy}}| \ll |DS_{\text{Dy}}^2 + B_4^0\hat{O}_{4,\text{Dy}}^0|$), the magnetic moments of the Dy ions lie parallel to the easy axis of the molecule at 20 mK. In which case, the magnetic contribution (E_{mag}) to the charge transition energy only relies on the intra-molecular Dy-bpym interactions and the Zeeman energy of the bpym ligand. By treating the Dy spins classically $\hat{\mathbf{S}}_{\text{Dy}} = S_{\text{Dy}}\mathbf{n}_z$, where $\mathbf{n}_z$ is the unit vector parallel to the z -axis,

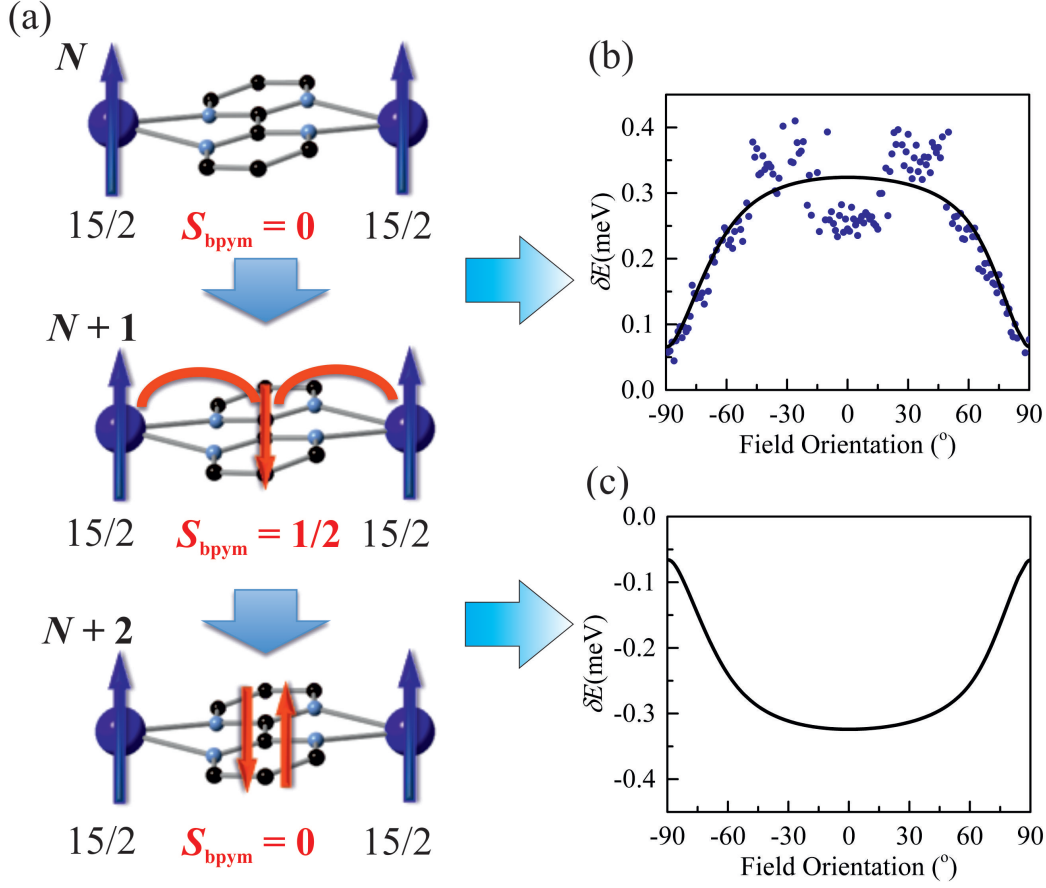


Figure 6.7: **Dimer model.**

(a) Schematic plot showing the Hamiltonian described by the dimer model. The plot shows the magnetic core of the Dy_2bpym molecule and the spin configuration for the neutral state (top) and two consecutive charged states. The spins of the Dy ions and the bpym ligand are indicated by the blue and red arrows, respectively. When an electron is added to the molecule (middle), the bpym ligand is singly charged which has a spin of $1/2$. The anionic bpym bridge mediates an antiferromagnetic interaction between the two Dy spins. If two electrons are added to the molecule (bottom), they form a singlet state on the bpym ligand, leading to $S_{\text{bpym}} = 0$. This effectively "switches off" the magnetic interaction between the Dy centres through the bpym bridge. Therefore, $E_{N+1}(\theta) - E(N)(\theta) = -[E_{N+2}(\theta) - E(N+1)(\theta)]$. (b) The experimental data and the fit employing Eq. (6.3) for the transition energy between the N and $N+1$ states. (c) The prediction for the shift of the transition energy between the $N+1$ and $N+2$ states. Note the polarity of the shift is reversed between (b) and (c).

E_{mag} can be written as:

$$\begin{aligned}
E_{\text{mag}}(\theta) &= (\mu_B g_{\text{bpym}} \mathbf{B} + J_{\parallel} S_{\text{Dy}} \mathbf{n}_z) \cdot \hat{\mathbf{S}}_{\text{bpym}} \\
&= (\mu_B g_{\text{bpym}} B \cos \theta + J_{\parallel} S_{\text{Dy}}) \hat{S}_{z, \text{bpym}} \\
&\quad + \mu_B g_{\text{bpym}} \sin \theta \hat{S}_{x, \text{bpym}}
\end{aligned} \tag{6.5}$$

where θ ($-90^\circ < \theta < 90^\circ$) is the angle between the applied field and the easy-axis of the molecule. When a 1 T field is rotated from the easy-axis to the hard plane of the molecule, the energy shift of the device can be written in the following analytical form:

$$E_{\text{mag}}(\theta) = \sqrt{(\mu_B g_{\text{bpym}} \cos \theta + J_{\parallel} S_{\text{Dy}})^2 + (\mu_B g_{\text{bpym}} \sin \theta)^2} \tag{6.6}$$

Eq. (6.6) gives an analytical solution for the correlation between the observed anisotropy and the physical parameters $J_{\parallel}$ and g_{bpym} .

The experimental results were first fitted to the dimer model by exact diagonalisation of Eq. (6.3). We found it is not possible to obtain a good fit with $J_{\parallel} < 1$ meV. This $J_{\parallel}$ value is consistent with the Dy-bpym⁻ interactions reported in similar SMMs [176]. When $J_{\parallel}$ is above 1 meV, the 1 T rotation data can be explain adequately by Eq. (6.3) and the fit does not show strong dependence on $J_{\parallel}$. However, we found a large g_{bpym} (≈ 8) is required for fitting the experimental result, regardless of $\bar{J}$ and the ZFS parameters for the Dy ions. This large g_{bpym} can be better understood based on Eq. (6.6). The maximum and the minimum values of Eq. (6.6) correspond to $\theta = 90^\circ$ and 0, respectively, with a difference of:

$$\Delta E = (J_{\parallel} S_{\text{Dy}} + \mu_B g_{\text{bpym}}) - \sqrt{(J_{\parallel} S_{\text{Dy}})^2 + (\mu_B g_{\text{bpym}})^2} \tag{6.7}$$

For a given $J_{||}$, the maximum value of Eq. (6.7) is obtained with $J_{||}S_{Dy} \gg \mu_B g_{bpym}$ and $\Delta E_{\max} = \mu_B g_{bpym}$, which indicates that a large g_{bpym} is required for the dimer model to explain a significant shift in the transition energies. This also explains the lower limit of $J_{||}$ found in diagonalising Eq. (6.3) as the maximum shift is achieved with the condition $J_{||}S_{Dy} \gg \mu_B g_{bpym}$.

An important aspect of the dimer model is that it can inherently account for the different types of shifting observed in the experiments. The spin number of the bpym ligand and the interaction through it is determined by its charge state. Effectively, the interaction $\bar{J}$ is switched between "on" and "off" in two adjacent charge states. When the number of unpaired electrons on the bpym bridge is switched from even to odd, the interaction is turned on and ΔE shifts to positive values when the field is rotated to the normal direction of the graphene plane. On the other hand, when the number of unpaired electrons on the bpym bridge is switched from odd to even, the interaction is turned from on to off and ΔE shifts to the opposite direction in the field rotation measurements.

The dimer model explains the observed magnetic behaviour based on the unique bpym bridging ligand and the dimer structure of the molecule. More importantly, the model intrinsically incorporates the different types of energy shifts upon the application of the external field. However, the large g factor remains to be explained. A possible explanation for the g factor may be introduced by considering the orbital angular momentum of the electron on the bpym ligand. Unfortunately, without more information regarding the detailed geometry of the molecule in the nanogap, it is difficult to give a quantitative estimation for this correction.

6.6 Perspectives on Magnetic Anisotropy in Single-Molecule Devices

The reproducible magnetic anisotropy observed in our devices raises an interesting question regarding the origin of the giant-magneto anisotropy. Especially, the lack of graphene anchor groups in the $\text{Dy}_2(\text{bpym})$ molecule means that it is unlikely to obtain a reproducible microscopic control on the device configuration. Therefore, it is somehow surprising to find that the magnetic anisotropy axes of all devices are pointing in the same direction. This raises the question whether the coupling between the molecule and the electrodes/substrate dominates the magnetic anisotropy in the single-molecule devices. In the bulk form, it has been well established that the anisotropy of a SMM is determined by the spin-orbit coupling (SOC) associated with the magnetic ions and the coordination environments surrounding them. However, little is known about the anisotropy mechanisms when the molecules are integrated into nano-devices. A literature survey shows that in most reported SMM-based devices, the anisotropy axes are strongly related to the geometry of the device [177, 172, 178]. Indeed, in most of those cases the anisotropy axis is perpendicular to the substrate of the device. In single molecule devices, the mirror symmetry corresponds to the device is broken due to the different materials on each side of this plane, e.g. silicon oxide versus vacuum. Intuitively speaking, this modifies the molecular orbitals in single molecule devices due to molecule-substrate coupling and/or substrate image charges, leading to a uniaxial type anisotropy. This symmetry-breaking mechanism manifests itself through SOC, raising a magnetic anisotropy axis which is perpendicular to the substrate plane. However, to the best of our knowledge, no experiment has been performed to explicitly study this symmetry breaking mechanism in single-molecule devices.

In addition to experiments conducted with single-molecule devices, several studies

have been performed to investigate the influence of the substrate on the magnetic properties of molecules by measuring a (sub)monolayer of molecules deposited on different substrates (Si, graphene...) [179, 180, 181, 182, 183]. In such studies, it has been found that the orbitals of the molecules can strongly hybridise with the orbitals of the substrate, leading to significant modifications to the physical properties of the molecules. In particular, a scanning tunneling microscope (STM) study for the metal phthalocyanine (MPc , $M = \text{Zn, Cu and Co}$) molecules on a silicon surface shows that the $3d$ orbitals of the spin centre of the MPc molecules can directly hybridise with the p orbitals of the substrate [179]. A separate STM study for single $FePc$ molecule on a CuN substrate demonstrates that the magnetic anisotropy axis of the hybridised system points strictly perpendicular to the substrate plane [180] and a giant out-of-plane effective g factor was found, similar to the observation reported in this study. Besides the direct hybridisation between the molecular spin centre and the substrate, another mechanism for the surface induced anisotropy is studied in Ref. [181]. The magnetic behaviour of $TbPc_2$ SMMs chemically grafted on a silicon surface is investigated by X-ray magnetic circular dichroism (XMCD). It is found that the magnetism of the monolayer of $TbPc_2$ SMMs is significantly modified compared with that for the bulk sample, which includes a strong enhancement of the hysteresis loop in the monolayer form. This effect is attributed to the change of the electron density of the phthalocyanine ring grafted to the substrate, resulting in a modification to the magnetic anisotropy of the compound. The similar process could also happen in the Dy_2bpym devices, which may explain the orientation of the device anisotropy axes.

In principle, the breaking of the mirror symmetry can be generally applied to all devices, not limited to the Dy_2bpym based single-molecule transistors. Therefore, it is worth discussing the lack of magnetic anisotropy in our graphene QDs. The anisotropy observed in the graphene QDs are more than an order of magnitude smaller than the Dy_2bpym devices. We suspect that the out-of-plane type anisotropy is due to the

combination of breaking of the mirror symmetry and strong SOC associated with the Dy ions. Therefore, in the case of the graphene quantum dots where the SOC is weak, the magnetic anisotropy is expected to be much smaller than that for the Dy₂bpym devices.

6.7 Conclusion and Future Work

In this chapter we have seen how it is possible to use Graphene Break Junctions (GBJs) to both tune and investigate the magnetic anisotropy of SMMs based on dysprosium cores. For this we utilised low-temperature charge transport spectroscopy. Our results demonstrate an hybridisation of the molecules with the graphene leads, which induces a strong uniaxial anisotropy perpendicular to the graphene plane. We proposed two different models to justify our observation, which both lead to good fits to our datasets.

The first approach is a more canonical Giant-Spin Approximation (GSA) with a Hamiltonian that stresses on the magnetic anisotropy terms with the same symmetries of the graphene wave function. This model is particularly good in explaining all the modulations we observe in the conductance peaks in the field rotation maps. The second approach considers single electrons tunnelling on the ligand, with their spins coupling with the two dysprosium active centres. The dimer structure of the molecule, as well as the capability of tuning the intra-molecular spin-spin interaction via charging the bpym ligand, makes our device an ideal candidate for realising the architecture proposed by Lehmann *et al.* [184], which allows the quantum $\sqrt{\text{SWAP}}$ operation to be demonstrated in single-molecule devices.

From this study, different directions may be taken to improve the results and get deeper understanding of the physics involved. By using different anchor groups, for instance, we may be able to control the graphene-SMM hybridisation and get a better

understanding on the Hamiltonian of the system. Furthermore, using the same device geometry and similar compounds based on different magnetic cores (e.g. terbium, cobalt, or other metal ions) may be characterised and their magnetic anisotropy unravelled. Finally, considering a configuration where the dimer counts two different magnetic cores, we may think to realise a device able to perform quantum operation at the molecular level, as proposed in [7].

Chapter 7

Conclusions and Outlook

In this thesis we have investigated the charge transport properties of a diverse set of magnetic materials and devices, scaling dimensionalities from microscopic crystals down to single molecules. In this process, we have learned how we can tune the conduction regimes via chemical design.

We began our journey by analysing how different steric substituents in nitronyl-nitroxide radicals affect the conduction channels responsible for charge flow. We have demonstrated that these compounds can no longer be considered as Mott insulators, in contrast to what is known from literature in this matter. These results are important as a theoretical backbone for the implementation of complexes based on NIT-R systems in nanodevices, which are attracting particular interest for their slow-relaxing behaviour, the possibility of light control of the spin states and for next-gen memory switching devices.

When we made the transition to two dimensions, we showed how SMMs can be deposited on different surfaces while maintaining their magnetic properties. In the frame of this work, these results are fundamental to understand the behaviour of these molecules when thermally evaporated on a substrate. In particular, we have found that thermal evaporation allows us to successfully deposit an SMM in a graphene

nanogap, creating a single-molecule transistor.

We then moved on to one-dimensional systems, where we have analysed single-molecule transistors based on molecular graphene nanoribbons, which were produced via bottom-up synthesis. In those systems, we observed an exceptional cleanliness of the transport features at low temperatures. This confirms that molecular bottom-up production of carbon-based nanostructures produces QDs with superior electrical properties. For the first time we were able to detect the excited states of GNRs in transport measurements, which are in exceptional agreement with theoretical calculations. Furthermore, we observed lead-MGNR interference patterns with high contrast ratios, which allows for a use as a potent spectroscopic tool. These results open the path to the precise design of MGNRs by means of synthetic chemistry. In particular, the recently demonstrated capability to decorate the ribbons with spin-injecting side-groups enables exciting perspectives for novel quantum devices implemented on a single nanoribbon.

Finally, when a Dy-dimer SMM is used as building block for a single-molecule transistor, we have seen that strong hybridisations between the molecule and the graphene leads take place. We have proposed two models to explain the strong uniaxial magnetic anisotropy that shows in our measurements. A giant-spin approximation approach has helped us to understand the reason for the direction of the easy axis: the three-fold symmetry of the graphene wave function induces a similar symmetry on the molecules, selectively enhancing the relevant anisotropy operators. On the contrary, the alternative dimer model intrinsically incorporates the different types of energy shifts observed in the Coulomb peaks upon the application of an external magnetic field. These results are paving the way for the implementation of rare-earth dimers SET as quantum devices, in particular to implement the quantum $\sqrt{\text{SWAP}}$ operation in a single-molecule transistor.

Looking at the overall picture, we have shown several tools to manipulate electric-

ity at different dimensionalities, finding how the magnetic properties of the materials have a strong influence in each case. Nevertheless, a lot of research needs to be done at the single-molecule level. The use of carbon-based nanostructures unlocks exciting playgrounds for novel nanodevices, and the field is currently thriving. The results reported here aim to provide future researchers a reference ground to build on, with the goal to finally master the rational design of molecules suited as active cores for next-gen quantum devices.

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