MOLECULAR FUNCTIONALITY
IN NANOELECTRONIC DEVICES
MOLECULAR FUNCTIONALITY IN NANOELECTRONIC DEVICES

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# Contents

1 Introduction
   1.1 Electronics at the nanoscale ............................................. 2
   1.2 Anatomy of a molecule ................................................... 2
   1.3 Molecular electronics ................................................... 3
   1.4 Thesis outline ........................................................... 3
   References ........................................................................... 4

I Single-molecule electronics ............................................... 7

2 Room-temperature stability of Platinum-nanogaps ................. 9
   2.1 Introduction ................................................................. 10
   2.2 Results and Discussion .................................................. 10
   2.3 Conclusions ................................................................ 15
   References ........................................................................... 16

3 Platinum-nanogaps for single molecule electronics ............... 19
   3.1 Introduction ................................................................. 20
   3.2 Results ........................................................................... 20
   3.3 Discussion ...................................................................... 26
   3.4 Conclusions ................................................................... 28
   References ........................................................................... 28

4 Molecular junctions using few-layer graphene nanogap electrodes 31
   4.1 Introduction ................................................................. 32
   4.2 Results and discussion .................................................... 34
   4.3 Conclusions ................................................................... 40
   References ........................................................................... 40

5 Design for an all-electric single-molecule motor ...................... 45
   5.1 Introduction ................................................................. 46
   5.2 Results and discussion .................................................... 48
   5.3 Conclusions ................................................................... 54
   References ........................................................................... 54
II  Nanoparticle-based electronics  57

6  Electrical addressing of a spin-crossover nanoparticle  59
  6.1  Introduction ................................................. 60
  6.2  Results and discussion ..................................... 62
  6.3  Conclusion .................................................. 69
  References ....................................................... 70

7  Photoconductance in quantum-dot junctions  75
  7.1  Introduction .................................................. 76
  7.2  Results ....................................................... 76
  7.3  Discussion ................................................... 80
  7.4  Conclusion ................................................... 82
  References ....................................................... 83

Appendices  87

A  Appendix: Supplementary information ch.4  89
  A.1  Simmons model ............................................... 90
  A.2  Deposition characterization ................................ 91
  References ....................................................... 91

B  Appendix: Supplementary information ch.6  93
  B.1  Low temperature characterisation .......................... 94
  B.2  Temperature dependence of conductance .................. 94

Summary  97

Samenvatting  99
INTRODUCTION
1.1 **Electronics at the Nanoscale**

One of the major goals of the semiconductor industry is to overcome the inevitable size limit of silicon based technology. Device components have been shrinking at a steady pace for the past decades, motivated by the improved performance in terms of speed, capacity, and efficiency. However, the downscaling of silicon is now approaching the atomic limit and alternative strategies to achieve further performance gain are required.[1]

New strategies are being explored where the performance gain is not focused on downscaling but on for instance higher functionality of each component through more complexity. The semiconductor industry relies on charge-carriers (electrons and holes) as the information carriers. Using light to manipulate or carry information has the advantage of high speed and low loss of energy.[2, 3] Alternatively, using the spin of an electron (spintronics) as additional information increases the functionality[4–7] or mechanical systems as information storage devices or logic operators.[8]

To accommodate this higher functionality, new platforms are required that go beyond the conventional bulk semiconductor technology. Molecular electronics is one of the important candidates for this purpose, providing a variety of functions through the structural diversity of individual molecules.[9, 10] The challenge lies in the incorporation of molecules in electronic circuitry and over the past 20 years many efforts have been made in this direction.[11] To date, however, most work has been focussed on the semi-conducting properties of molecules. In the next steps, the unique functionality that the molecules can provide, will play a central role.

1.2 **Anatomy of a Molecule**

In semiconductors like silicon, the electronic properties are a result of the bulk properties. Changing one atom or dopant does not drastically influence the electronic properties of the system. In a molecular structure on the other hand, the electronic properties are a direct result of the positions of each individual atom in the structure. The relative positions of the atoms in the molecular structure and the overlap between their orbitals determine the potential energy landscape of the electrons. Hence, a strong correlation between the electronic and atomic structure exists; small perturbations of one can have major implications on the other. The result is a complex potential-energy spectrum consisting of (possibly meta-stable) vibrational and electronic states. Transitions between these states can be induced through absorption of a phonon or photon of sufficient energy.

Through the sophisticated toolbox of synthetic chemistry, an almost infinite number of molecular structures can be achieved nowadays and specific properties
can be designed. For instance, unsaturated carbon-carbon bonds (or even conjugation) can be used to create low-lying electronic excited states that give optical absorption and emission in the visible spectrum.[12] Metal centers or radicals can be included to create a magnetic spin on the molecule, giving it specific magnetic properties.[13] Mechanical properties can be included through rotational centers or isomerizable double bonds, which has led to considerable advances in the field of molecular motors and molecular switches.[14–22] Importantly, a molecule is not limited to one of the properties described here: multifunctionality and even interplay between the properties can be achieved.[23]

1.3 MOLECULAR ELECTRONICS

The aim of molecular electronics is to address molecules electronically and in that way profit from their functionality. To do so, nanoscale electrical probes are required to make contact. Different techniques have been developed over the past decades, each with its own advantages and disadvantages. Common techniques include scanning tunneling microscopy (STM), the mechanically controllable break junction (MCBJ) and the electromigrated break junction (EMBJ).[11]

To address the properties of a molecule in such a device geometry, different external stimuli can be used, the most obvious one in this context being the electronic probes themselves. The energy provided by applying a voltage across a molecular system can cause transitions between different states in the system, resulting in for instance phonon or photon-emission or driving the system into a meta-stable configuration. Related to the electronic probes are electric fields that can be applied to the molecule via a gate-electrode. The gate-field can be used for instance to change the chemical potential of the molecule with respect to the Fermi-level of the electrodes it is connected to, leading to changes in the level alignment and possible reduction or oxidation reactions to occur. Electric fields can moreover exert a force on an electric dipole in a molecule which can be used to create mechanical movement in a molecule. Beyond electronic means, light and heat can also be used to induce excitations in a molecule. The absorption of a photon or phonon with enough energy can cause photon or phonon emission of a lower energy, or bring the molecule in a meta-stable state. Alternatively, magnetic fields can be used to manipulate the spin of a molecule.

1.4 THESIS OUTLINE

In this thesis, different strategies to address molecular functionality in nanoelectronic devices will be presented, ranging from technological, conceptual and application driven approaches. The chapters have been divided over two sections;
the first deals with devices on the single molecule scale, the second with nanoparticle-based electronics.

Chapter 2, the first chapter of Part I, describes the formation of nanometer separated electrodes based on Platinum. The electrodes are fabricated using a combination of feedback controlled electromigration and a self-breaking scheme. We will show that nanogaps formed in this way are stable at room temperature, in contrast to the commonly used Au-electrodes.

Chapter 3 follows up on the stability of the Pt-nanogaps and describes their applicability for contacting single porphyrin molecules. The stability of the electrodes allows for a comparison between the empty gap characteristic and the characteristics after molecule deposition. Observed changes can then be attributed directly to molecular features in the transport.

In Chapter 4 we present an alternative strategy for the formation of nanogaps that are stable at room temperature, based on few-layer graphene as the electrode material. The fabrication is based on feedback controlled electroburning and typically yields nanometer separated electrodes. We will show that molecules contacted between these electrodes show gateable Coulomb-blockaded transport at room temperatures. These results are an important step towards potential applications based on single molecules which can benefit from room-temperature functionalities.

To conclude Part I, we present a design for an all-electric single molecule motor in Chapter 5. The design is based on a conjugated backbone of the molecule, which simultaneously provides the potential landscape of the rotor orientation and a real-time measure of that orientation through the modulation of the conductivity. Using quantum chemistry calculations, we show that this approach provides full control over the speed and continuity of motion.

Part II deals with nanoparticle-based electronics. In Chapter 6 we present a new way of contacting individual nanoparticles based on a self-alignment fabrication method. The nanoparticles are based on spin-crossover molecules which can undergo a phase-transition as a function of temperature. This nanoscale device exhibits switching and memory effects near room temperature as a consequence of the intrinsic bistability of the spin-crossover nanoparticle. The magnetic bistability is interesting from the perspective of spintronic applications.

In Chapter 7, the second chapter of Part II and the last of this thesis, we use the same device architecture to make contact to one-dimensional arrays of PbSe quantum dots to construct a highly efficient photodetector. Placing the electrodes directly onto the quantum dots has two advantages: first it allows for highly efficient exciton extraction, and second it acts as a optical antenna which concentrates the incident light into the nanogap area. This demonstrates the potential of plasmonics for photo-induced effects in nanoparticles, but also single molecules.
REFERENCES


1. Introduction


I

SINGLE-MOLECULE ELECTRONICS
We present a method to make Pt nanometer-spaced electrodes that are free of metallic particles and stable at ambient conditions. The nanogaps are fabricated using feedback controlled electromigration to form few-atom contacts. When performing this procedure at elevated temperatures (> 420 K), the Pt-contacts undergo self-breaking so that nanometer separated electrode pairs are formed. Once cooled down to lower temperatures, the nanogaps stabilize and can be characterized in detail. We find that current-voltage characteristics can be well fitted to a Simmons model for tunneling and gap-size fluctuations at room-temperature determined from these fits stay within 0.6 Ångström for at least 50 hours.

Parts of this chapter have been published: F. Prins, T. Hayashi, B. J. A. de Vos van Steenwijk, E. A. Osorio, B. Gao, K. Muraki and H. S. J. van der Zant, Applied Physics Letters, 2009
2. **INTRODUCTION**

Fabrication of three-terminal device architectures for single-molecular electronics has been performed by electromigration (EM) of thin Au wires. EM is the directed migration of atoms by momentum transfer from electrons when a large current density is applied to a wire. This process requires sufficient atomic mobility and is therefore assisted by Joule heating. The planar geometry of the EM-devices results in a relatively large gate-to-molecule coupling and great stability at low temperatures for systematic studies as a function of temperature and magnetic field. However, Au electrodes are not stable at room temperature due to the high mobility of Au and residual stress on the wire after EM. As shown by O’Neill et al., the instability of Au at room temperature can be used advantageously when wires narrowed by feedback-controlled EM to a few atoms “self-break” without an applied voltage. After formation of the gap, the self-breaking continues to widen the gap up to several nanometers unless the device is cooled down and the atomic mobility is frozen. The formation of metallic clusters is largely avoided with this method, a problem often observed in traditional EM techniques.

By performing experiments at different temperatures we show in this chapter that self-breaking of Au and Pt few-atom contacts follows a temperature activated behavior. The activation barrier is higher for Pt, so that self-breaking is not possible at room temperature, but does occur at a temperature roughly hundred degrees higher. Based on these results we have developed a method in which we perform electromigration and self-breaking of Pt nanowires at elevated temperatures after which a cool down to room temperature suffices to freeze the atomic mobility. This process results in nanogaps that are free of metallic clusters and that are stable at room temperature.

2.2 **RESULTS AND DISCUSSION**

Fabrication of the few-atom constrictions is done by feedback-controlled EM of nanowires. The nanowires are fabricated by evaporating Au or Pt thin wire bridges, with a cross section of $100 \times 13 \text{ nm}^2$ and a length of 300 nm. Evaporation of the bridges is done on two different substrates: a SiO$_2$ substrate or SiO$_2$ substrate with a Al/Al$_2$O$_3$ gate structure on top. The latter (see Fig. 2.1) is used for three-terminal transport measurements. Contact to the nanowires is made through large Au contact pads, resulting in an initial wire resistance in the order of a few hundred Ohms. Right before use, the samples are UV/ozone cleaned for 10 minutes. EM is done under ambient conditions while the temperature is regulated by a heater ($300 - 460 \text{ K}$ range). The active feedback mechanism stops EM once a target conductance is reached; in these experiments set at $300 \mu$S. Using this feedback-controlled method, the yield for obtaining $300 \mu$S constrictions is 100%.
2.2. Results and Discussion

After reaching the target conductance, the evolution of the conductance is determined by least squares fitting of current-voltage characteristics between ±100 mV measured at 250 ms intervals. Control experiments in which the conductance was not monitored showed that these applied voltages did not influence the self-breaking. In each experiment, EM and self-breaking are performed at the same temperature. Fig. 2.2a (top panel) shows selected time-traces of the conductance of Au at different temperatures, representative of the overall behavior. As mentioned before, Au readily undergoes self-breaking at 300 K. At elevated temperatures the self-breaking proceeds faster, indicating a temperature activated character of this process.

In contrast to Au, Pt constrictions at 300 K are stable around the 300 μS conductance value at which EM is stopped (light grey curve in Fig. 2.2a; bottom panel). At temperatures above 420 K the constrictions start to show self-breaking. However, whereas Au shows a nearly full self-breaking percentage, for Pt it stays around 70 – 80 % even though the average time-scale of self-breaking is decreasing over orders of magnitude with increasing temperature. Apparent from the Pt conductance traces when compared to the case of Au is the absence of well defined conductance plateaus. This can be attributed to the outer shell electrons, which in case of Pt are located in the anisotropically shaped d-shell making the conductance more susceptible to changes in the atomic arrangement.[8]

In order to quantify the (in)stability of the few-atom contacts, we define the mean time to failure ($\tau_{MTF}$) as the average time it takes for the conductance to drop from 300 μS down to a value below the conductance quantum $G_0 = 2e^2/h \approx 77 \mu S$. At four different temperatures, $\tau_{MTF}$ is determined for both Au and Pt from a min-
Figure 2.2: (a)(top) Time-evolution of the conductance for four Au-nanowires initially narrowed to 300 $\mu$S by electromigration, and held at four different temperatures as indicated. (bottom) Same as top but for four Pt-nanowires. The measurements were performed on substrates without the Al/Al$_2$O$_3$ gate structure. (b) The natural logarithm of the mean time to failure ($\tau_{MTF}$) versus inverse temperature for Au and Pt few-atom contacts electromigrated to 300 $\mu$S. Lines are linear fits to the data.
2.2. Results and Discussion

A maximum of 7 different time traces for each temperature as the ones shown in Fig. 2.2a. The traces of Pt few-atom contacts which do not undergo self-breaking are omitted. Despite the variation in the individual failure times, an exponential temperature dependence is observed for both materials as shown in Fig. 2.2b which depicts \( \ln(\tau_{MTF}) \) as a function of \( T^{-1} \). Assuming a temperature activated process we can write:

\[
\tau_{MTF} = A \exp\left(\frac{E_a}{k_B T}\right),
\]

in which \( A \) is a constant, \( E_a \) the activation energy, \( k_B \) the Boltzmann constant, and \( T \) is the temperature. From the slopes of the linear fits (drawn lines in Fig. 2.2b) we find: \( E_a^{Au} = 0.81 \pm 0.08 \text{ eV} \) and \( E_a^{Pt} = 1.69 \pm 0.48 \text{ eV} \). The activation energy for Au is close to the literature value for the activation energy of grain boundary self diffusion (0.88 eV).[9] This observation suggests that atomic diffusion along grain boundaries is controlling the self-breaking in our few-atom constrictions. This assumption is supported by TEM studies of the self-breaking in Au few-atom contacts, in which a grain boundary was visible up to the point of breaking.[10]

We now turn to the Pt junctions and the main point of this chapter. As Pt few-atom constrictions are stable at room temperature (see Fig. 2.2a, bottom), junctions self-broken at elevated temperatures may be cooled down to form stable nanogaps. To characterize the three-terminal transport of the junctions in detail we use samples with a Al/Al\(_2\)O\(_3\) gate. EM is done consecutively on 32 devices on a chip at 430 K (\( \tau_{MTF} \approx 100 \text{ s} \)). We note that the self-breaking rates of the constrictions on the Al\(_2\)O\(_3\) substrate are comparable to those on SiO\(_2\). After self-breaking with a yield of approximately 70 %, the temperature is lowered by turning off the heater. Within a minute the temperature drops below 400 K and the gap stabilizes. Typically within one chip, this method yields a range of room-temperature nanogap resistances between 100 k\( \Omega \) and infinite (> 100 G\( \Omega \)). Before a detailed characterization by three-terminal measurements, the devices are once again subjected to a UV/ozone cleaning for 10 minutes, after which they are transferred to the vacuum chamber of a low temperature probe station (10\(^{-5}\) mbar).

Current-voltage characteristics between \( \pm 500 \text{ mV} \) of 172 self-broken junctions on 8 different chips were measured at room temperature. Of these, 70 showed current levels below the detection limit of our setup (a few pA) within the applied voltage range; these junctions are disregarded in the rest of the chapter. The remaining 102 junctions show parabolic-like current-voltage curves and were cooled to 77 K. No gate dependence in the current-voltage characteristics was found within the limits of set by the leakage currents (which are lower than 50 pA when applying gate-voltages smaller than \( \pm 2.5 \text{ V} \)). The absence of gate-dependent features suggests that these junctions are free of metallic clusters. This observation is supported by comparing the current-voltage characteristics to a single-barrier tunnel-
Figure 2.3: (a) Current-voltage characteristic of a self-broken Pt junction at 77 K in vacuum (solid red line). After a UV/ozone cleaning step of 10 minutes at room temperature the current-voltage characteristic of the same sample was measured again at 77 K (solid blue line). A least squares fit to the generalized formula for tunneling through a rectangular barrier with image charges included is displayed for both curves (dashed grey lines). For this fit, the junction cross section is fixed at 100 nm$^2$. The fit-parameters are before cleaning: $d = 1.40$ nm, and $\phi = 3.4$ eV, and after cleaning: $d = 1.37$ nm, and $\phi = 3.4$ eV. (b) (bottom) Two-dimensional color plot of the current (negative: blue, zero: white, positive: red) as a function of voltage and time at room temperature. (top) Electrode-separation ($d$) from the fit of each individual current-voltage characteristic to the Simmons model for tunneling. For this fit, the junction cross-section was fixed at 100 nm$^2$, and the barrier height at 3.9 eV.
2.3. Conclusions

We have fitted the current-voltage characteristics to the generalized formula for tunneling through a rectangular barrier with image forces included.\[11\] The junction cross-section is fixed at 100 nm\(^2\), based on a rough estimate of the actual size of the interface from TEM inspection on similar devices (see below). Using the gap-size \((d)\) and barrier height \((\phi)\) as fit parameters, we find a good agreement to this model for all 102 junctions to the parabolic curvature. Fit parameters range from 3.0 to 3.9 eV for \(\phi\) and from 0.5 to 2.1 nm for \(d\). Fig. 2.3a shows two examples of such fits. Note that the fit-parameters are not very sensitive to the cross-section. For instance when taking a cross-section of 10 nm\(^2\) we find \(\phi = 3.2\) eV, and \(d = 1.32\) nm for the sample displayed by the red curve in Fig. 2.3a, instead of 3.4 eV and 1.40 nm for a 100 nm\(^2\) cross-section.

We find that the nanogaps show long-term stability in vacuum at room temperature, undergoing only minor changes in their resistance for periods up to 3 months. This stability was investigated in more detail by taking current-voltage characteristics of one of the junctions over a time span of 50 hours with 2 minute intervals (see Fig. 2.3b, bottom panel). The low-bias resistance in this figure stays within one order of magnitude. This can be translated to atomic scale rearrangements on the sub-Ångström scale, as deduced from fitting each current-voltage characteristic to the above mentioned formula for tunneling (see Fig. 2.3b, top panel, with \(\phi\) fixed at 3.9 eV and the junction cross-section at 100 nm\(^2\)). We also note that the changes in resistance and therefore the electrode spacing stay within the same limits upon repeated thermal cycling between room temperature and 4 K. Furthermore, this stability is maintained when taking the devices out of vacuum and performing a UV/ozone cleaning step of 10 minutes (see Fig. 2.3a, blue curve).

Finally, thanks to the stability of the nanogaps, it was possible to perform transmission electron microscopy (TEM) studies on Pt-nanogaps prepared on SiN\(_4\) membranes. The electrodes display a high degree of crystallinity due to re-crystallization during the electromigration process as a result of Joule-heating. The self-breaking results in symmetric electrodes with steep edges at the gap area (see Fig. 2.4). This information is very useful to develop an intuitive picture of how a molecule can be contacted in the gap.

2.3 Conclusions

In conclusion, we have presented a method for the fabrication of Pt-based nanogaps that are free of metallic clusters and that are stable at room temperature. The Pt-based gaps are interesting candidates for molecule deposition as their stability provides them with a number of advantages as compared to the traditional Au-based nanogaps. Molecule deposition can be performed after the gaps are formed,
which avoids exposure of the molecules to the exceedingly high local temperatures which are generated during the electromigration process.[12–14] Prior to molecule deposition, the bare gaps can be UV/ozone-cleaned and characterized in detail at low temperature. The presented fabrication method therefore opens up a route towards single molecule three-terminal transport at room temperature and possibly single-molecule device applications at ambient conditions. In the next chapter, first studies on molecular junctions based on Pt-nanogaps will be presented.

REFERENCES


We present the formation of single-molecule devices based on nanometer-spaced platinum electrodes. The electrodes are fabricated using a self-breaking electromigration method which yields nanogaps with long-term stability at room temperature, as described in chapter 2. The stability at room temperature allows for detailed comparison of the device electrical properties before and after deposition of the molecules. In this way, conductance as a result of direct tunneling between the electrodes can be distinguished from conductance through the molecule. After molecule deposition, some devices display transport in the strong coupling regime while others are in the weak-coupling Coulomb blockade regime. Gated transport is observed in the latter case.

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3. **INTRODUCTION**

A popular technique to fabricate single-molecule three-terminal devices uses electromigration of thin metal wires on top of Al/Al$_2$O$_3$ gate structures (see Fig. 2.1a). [1–6] To date, three-terminal measurements on single molecules have been limited to low temperatures due to the instability of the commonly used gold electrodes. Although gold is the preferred electrode material because of its superior noble character, at room temperature the atomic mobility is so high that the electrodes retract and the separation between them becomes too large for a molecule to bridge.

In the previous chapter, we have reported the fabrication of platinum-based electrodes with nanometer separations that are stable at room temperature. The advantages of the stable Pt-electrodes are that they can be plasma-cleaned, reused, and repeatedly cycled to low temperature without significant changes in the gap-resistance. The time-variations in these gap-size are determined to be less than 0.5 Å over a time span of at least 50 hours, but we found that devices generally are stable for months. Thanks to the stability of Pt, extensive studies of the formation of the nanogaps and the resulting geometries were possible using TEM microscopy of devices fabricated on SiN$_4$ membranes. [7] The self-breaking results in symmetric, crystalline electrodes with steep edges at the gap area (see Fig. 2.4). This information is very useful to develop an intuitive picture of how a molecule can be contacted in the gap.

Perhaps the most important advantage of the stable contacts is the possibility to perform electrical characterizations of the gap prior to molecule deposition. In this way, changes in the current-voltage characteristics after molecule deposition can be unambiguously attributed to the molecule. In this chapter, we report on the first studies on single molecules contacted in these devices, making use of a porphyrin derivative. Porphyrins are an important class of molecules as they play a central role in many biological processes, such as photosynthesis and fixation and transport of oxygen in the respiratory system. Studies on the single molecule scale could lead to better insights in the mechanisms involved in these processes. Over the past years several reports have been made in this direction, based on Scanning Tunneling Microscopy (STM) and break junction techniques. [8–10] Three-terminal studies have not yet been performed on these systems. The derivative we use is a free base porphyrin functionalized with four amino anchoring groups which have a high affinity for the Pt-electrode surface (5,10,15,20-tetrakis(4-aminophenyl)porphyrin, or H$_2$-TAPP, see Fig 3.1a).

3.2 **RESULTS**

Nanogaps were prepared by feedback controlled electromigration followed by self-breaking according to the process described in in the previous chapter. [11] In short,
FIGURE 3.1: a) Structure of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (H$_2$TAPP). b) Schematic representation of the three-terminal measurement setup.
using standard electron-beam lithography and evaporation a thin Pt-wire (10 x 100 nm cross-section, 300 nm long) is defined on top of an Al/Al₂O₃ electrode (see Fig 2.1a). Feedback controlled electromigration is performed at 420 K until a few-atom contact with a resistance of about 3 kΩ is created. The strain in the wire then causes the contact to break and a nanometer sized separation between the two metal contacts is formed. Cooling down to room temperature suffices to stabilize the nanogap. On two different chips, out of a total of 56 devices, 29 (52 %) underwent self-breaking to form nanometer separated electrodes. The resistance of the other devices remained in the kΩ range. A device yield of 50 % - 70 % is typical for this scheme of nanogap formation.[11] After gap-formation the devices are UV/Ozone cleaned for 10 minutes at room temperature and placed in a vacuum probe station (10⁻⁴ mbar). To make optimal use of the stability of the nanogaps, the empty gaps were characterized electrically at room temperature and at low temperature (10 K). In this way, changes that occur after molecule deposition can be distinguished from the background conductance due to direct tunneling between the electrodes.

After the detailed empty-device characterization, molecules are introduced into the gap from solution. The porphyrin H₂-TAPP was synthesized according to ref. [12]. The electrodes are immersed in a 0.1 mM solution of H₂-TAPP in acetone for 5 minutes after which they are rinsed with pure acetone, blow-dried, and placed back in the probe station vacuum chamber. After deposition, 8 out of 29 devices (28 %) show a clear change in the current-voltage characteristic which is an indication that molecules have been trapped in the nanogap; we will refer to these devices as molecular junctions. It should be noted that control experiments (15 devices) with the solvent only did not show any significant changes in the current-voltage characteristics.

Figure 3.2 displays four characteristic current-voltage characteristics before and after deposition. The conductance before deposition (black lines in Fig. 3.2) is a result of direct tunneling between source and drain and can be seen as an intrinsic background signal of the device. After deposition two types of current increase are observed (red lines in Fig. 3.2). The first, and predominant type (6 devices, see Fig. 3.2a and b for examples), displays an increase in conductance across the entire voltage range. The increases in the low-bias conductance range from two-fold up to ten-fold. The second type, which was observed in two molecular devices (see Fig. 3.2c and d), shows increased conductance only at higher bias values whereas the low-bias region superimposes with the background conductance of the device before deposition. This suggests that at low bias only direct tunneling contributes to the conductance while the conductance via the molecular levels is only possible at higher bias.

Cooling the devices down to low temperature shows that some of the molecular devices display features in the current-voltage characteristics. Broad resonances
3.2. Results

**Figure 3.2**: Room-temperature current-voltage characteristics of four devices, before (black curves) and after (red curves) deposition of H$_2$-TAPP molecules. The clear increases in conductance after deposition show that transport is through one or more molecules.
are observed in the devices that showed increased conductance across the entire voltage range (see Fig. 3.3a for an example). In the other device category, we see that also at low temperature the low-bias conductances before and after molecule deposition are the same (see Fig. 3.3b for an example). Only at high bias clear differences are seen; in Fig. 3.3b only at negative bias voltage, as the red curve shows. At low temperature the increase in conductance is more abrupt, as can be expected since the thermal broadening is decreased.

Besides the two-terminal current-voltage characteristics we have also performed three-terminal characterization using the Al/Al₂O₃ gate electrode. Most of the molecular junctions do not show gate-dependent transport. For example, the current-voltage characteristic of Fig. 3.3a does not change when the gate voltage (V₉) is varied between +/- 2.5 V (the maximum range in our devices). In the sample of Fig. 3.3b however, a clear gate-dependent onset in conductance is observed (see Fig. 3.3b, green and blue lines).

To characterize the gate-dependent transport of the device in Fig. 3.3b in more detail, we construct a conductance map (see Figure 3.4). Before and after molecule deposition current-voltage characteristics are taken at low temperatures at different gate voltages, with the bias voltage ranging from -0.5 to 0.5 V and the gate voltage ranging from -2 to 2 V before deposition and -2.5 to 2.5 V after deposition. On the left panel a color-scale plot of the differential conductance (dI/dV) of the device as a function of bias voltage and gate voltage before deposition is displayed (V₉ = / pm 2 V). The current-voltage characteristics are smooth and therefore the corresponding dI/dV curves do not show any features (Fig. 3.4, left panel). Furthermore, no gate dependence is observed. After deposition, part of what is known as a Coulomb diamond becomes visible.[13] As Fig. 3.4 (right panel) indicates, in the dark blue region transport through the molecule is blocked due to Coulomb repulsion, while in the red regions a molecular charge state has entered the bias window and transport occurs via single electron tunneling through a double barrier potential (incoherent, resonant transport). The presence of only one (partial) Coulomb diamond indicates that transport occurs through a single molecule.

Although the Coulomb diamond is incomplete, we can deduce some important parameters. First, from the slope of the diamond edge we deduce that the crossing point of the diamond lies at positive gate voltage, estimated around V₉ = 3.5 V. At positive gate voltages, molecular levels are shifted downwards in energy with respect to the Fermi level, which means that transport in the red regions occurs through the lowest unoccupied molecular orbital (LUMO) of the porphyrin molecule. Second, from the slopes of the diamond edges (α⁻ = 0.2 V and α⁺ = 0.1 V) we can derive the gate-coupling parameter β = (α⁻ α⁺) / (α⁻ + α⁺) = 0.067, a value consistent with earlier reports in single-molecule transistors based on electromigration.[4] The asymmetry observed in the current-voltage charac-
Figure 3.3: a) Current-voltage characteristic of a molecular device (the one from Fig. 3.2a) at low temperature (10 K) before (black line) and after (red line) deposition of H$_2$-TAPP. The bottom panel shows the first derivative of the current, dl/dV after deposition. b) Same for a second molecular device (the one from Fig. 3.2c). In the bottom panel dl/dV curves at different gate-voltages are displayed illustrating the gate dependent nature of the transport.
3. Platinum-nanogaps for single molecule electronics

3.3 Discussion

When the conductance only increases at higher bias, while at low bias the current is Coulomb-blockaded, transport occurs through a double-barrier potential and sequential tunneling is the main transport mechanism. A likely configuration that may establish such a double barrier is a porphyrin molecule bridging the source and drain electrodes through the amino-groups (see Fig 3.5, right hand side). In contrast, an overall change of the current-voltage characteristic (Fig 3.2a and b) indicates a (partial) lowering of a single tunnel barrier. This can be understood as follows: in the absence of a molecule bridging the gap, the transport mechanism is direct tunneling through the vacuum barrier. In the presence of a molecule, a molecular level with an energy lower than the vacuum level results in a lower effective barrier. Off-resonant transport (i.e. superexchange) is then the main transport mechanism; the current at any non-zero voltage will be larger than in the absence of molecular levels. At higher bias resonances may be present if a molecular level is included in the bias window (resonant transport).

A single barrier configuration can be obtained if the molecule is very strongly coupled (and hybridized) to one electrode only (for example if it lies flat on one of the electrodes, see Fig. 3.5, middle). This situation is then very similar to an STM-like configuration where the molecule interacts with the conducting substrate. The strong coupling to one of the electrodes would also explain the absence of gate-dependence in these devices where hybridization pins the molecular level to the Fermi-level of the metallic electrode. In this respect, it is interesting to compare the current-voltage characteristics of the gate-independent molecular junctions in our setup with previous STM experiments on porphyrin derivatives. Indeed resemblances can be seen between our results and the results obtained by Qiu et al., [8] although it is difficult to compare these results directly because of the differences in the experimental setup and the fact that a thin oxide spacer (5 Å) is present in their experiment.

Finally, in view of room-temperature operation it is interesting to compare the low-temperature and the room-temperature current-voltage characteristics of the gate-dependent device. For both temperatures we find that the low-bias conductance is equal to the one before molecule deposition, while an onset in conductance is observed at higher bias. This suggests that even at room temperature Coulomb blockade is maintained in this device. Although this is a promising as-
3.3. Discussion

**Figure 3.4:** Color-scale plots of the first derivative of the current (dI/dV) vs. bias (V) and gate voltage (V_g) before (left panel) and after (right panel) molecule deposition, at 10 K (same sample as displayed in Fig. 3.2c and Fig. 3.3b). Before deposition the conductance map is featureless whereas after deposition clear gate-dependent onsets of conductance are visible.

**Figure 3.5:** Top: Barrier landscapes of the observed transport mechanisms; direct tunneling (left), off-resonant tunneling (middle) and single electron tunneling (right). Bottom: sketch of the empty gap and two possible configurations of the porphyrin molecule between electrodes, which can lead to the corresponding barrier landscapes.
pect when looking for room temperature single-molecule transistors, the preferred strong coupling of the body of the H$_2$-TAPP molecule to the electrodes suggests that this system is not the ideal candidate for this purpose. Modifications to the molecular system that would decouple the pi-conjugated ring structure from the surface could help to improve the yield of weakly coupled molecules.

### 3.4 Conclusions

In conclusion, we have presented a method to contact single molecules in a three-terminal geometry. The stability of Pt enables operation at room temperature for which initial experiments have been performed with porphyrin molecules. A comparison between the current-voltage characteristics before and after deposition allows to distinguish molecular transport from background-tunneling conductances. This information is important in the understanding of transport through single molecules. We have found that the H$_2$TAPP-porphyrin derivative prefers to be situated flat on one of the electrodes, very similar to the situation studied in a scanning tunneling microscopy setup; gate-dependent transport is absent in this case. In some cases the molecule couples weakly to the electrodes and gate-dependent measurements shows Coulomb-blockaded transport. Further studies will be directed towards new molecular systems with less electrode-molecule interaction, promoting a single-molecule to bridge source and drain electrodes. The final goal is a single-molecule, single-electron transistor at room temperature.

### References


We report on a method to fabricate and measure gateable molecular junctions which are stable at room temperature. The devices are made by depositing molecules inside a few-layer graphene nanogap, formed by feedback controlled electroburning. The gaps have separations on the order of 1-2 nm as estimated from a Simmons model for tunneling. The molecular junctions display gateable IV-characteristics at room temperature, reminiscent of Coulomb-blockaded transport.

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4. Molecular junctions using few-layer graphene nanogap electrodes

4.1 Introduction

Molecular electronics has been the subject of extensive research over the past decade[1, 2], motivated by the appealing concept that molecules can be used as ultimate downscaled functional units in electronic circuits performing a variety of specific electronic functions, including rectifiers,[3, 4] switches, [5] transistors,[6, 7] or sensors.[8] To date, three-terminal experiments have mostly been carried out at low temperatures, whereas for applications room-temperature operation is desirable. Device-stability is a first requirement for this but at the same time remains one of the great challenges in this field. Gold, the preferred electrode material because of its noble character, has such high atomic mobility that at room temperature the nanoelectrodes are unstable.[9] In chapter 1 and 2 we have shown that electrodes made from the more stable Pt can be used to overcome this issue,[9, 10] although gated transport at room temperature was not demonstrated yet. Here, we present an alternative strategy for the fabrication of stable electrodes with nanometer separation, based on few-layer graphene as the electrode material. We will show that molecules contacted between these electrodes are gateable, even at room temperature.

The use of (sp\textsuperscript{2}-)carbon-based materials as electrodes has important advantages over conventional metallic electrodes. First, the covalent bond-structure gives stability up to high temperatures, far beyond room temperature. Second, it allows for a large variety of possibilities to anchor the molecule as compared to metallic electrodes. While with the latter thiol and amine linkage is widely used [2], the carbon-based materials can not only be functionalized covalently through organic chemistry techniques[8] but also via \( \pi-\pi \) stacking interactions of aromatic rings. A third advantage is the fact that extremely thin electrodes can be prepared, ranging from (few-layer) graphene to carbon nanotubes. Compared to the more bulky metallic electrodes, the carbon-based electrodes reduce the screening of an applied gate-field and therefore enhance the gate coupling.

Motivated by the advantages stated above, carbon nanotube based nanogap electrodes have previously been constructed by oxygen-plasma etching where the gap is defined by a PMMA mask [8, 11, 12] or through electrical breakdown. [13–15] To date however, control over the gap-size below 10 nm has not been demonstrated, making it difficult to contact single molecules. Other approaches that could potentially lead to nanogap electrodes include AFM nanolithography of graphene[16], anisotropic etching catalyzed by nanoparticles [17, 18], graphene nanogaps formed by mechanical stress[19], or through electrical breakdown of graphene.[20]

Here, we report on the formation of nanometer-separated few-layer graphene electrodes using feedback-controlled electroburning. The process of electroburning is related to the chemical reaction of carbon atoms with oxygen at high tem-
FIGURE 4.1: a) Schematic of the feedback-controlled electroburning process, before (top) and after (bottom), the formation of nanometer sized gaps in few-layer graphite flakes. b) Current-voltage (I-V) traces of the evolution (green arrow) of the feedback-controlled electroburning. The first I-V trace is displayed in red.
peratures, induced by Joule heating at high current densities. This technique has also been utilized to controllably remove shells of multi-walled carbon nanotubes [21–23], to form nanogaps in single-walled carbon nanotubes (SWNTs) [13–15] and to fabricate narrow graphene constrictions and quantum dots.[24, 25] An important motivation for our choice for few-layer graphene (as opposed to single layer graphene or carbon nanotubes) is that it is thin, yet its conductance largely gate-independent. In particular, the gate-dependence of single-layer graphene can be sensitive to its edge structure which is difficult to control in the fabrication. By selecting few-layer graphene devices which are gate-independent we avoid such problems.

4.2 RESULTS AND DISCUSSION

We start by briefly describing our fabrication technique. Few-layer graphene flakes (between 3 - 18 nm thick) are deposited by mechanical exfoliation of kish graphite (Toshiba Ceramics) on degenerately doped silicon substrates coated with 280 nm of thermal silicon oxide. We use standard wafer protection tape as it leaves little adhesive residue on substrates. Cr/Au electrodes are patterned on top of selected few-layer graphene flakes by electron-beam lithography and subsequent metal evaporation, followed by a lift-off in cold acetone and dichloroethane. Figure 4.1a shows a schematic of the few-layer graphene device used for electro-burning and nanogap formation. Initial device resistances at low bias are in the order of 200 Ω - 3 kΩ.

The feedback controlled electroburning is performed in air at room temperature. The feedback control scheme is based on similar methods used for electromigration of metallic nanowires.[9, 26] Typically, a voltage (V) ramp is applied to the graphite flake (1 V/s), while the current (I) is continuously recorded with a 200 µs sampling rate. The variations in the conductance (G = I/V) are monitored, with a feedback condition set at a >10 % drop in G within the past 200 mV of the ramp. Upon the occurrence of such a drop, the voltage is swept back to zero in 10 milliseconds. Immediately after, a new sweep starts from zero voltage and the process is repeated, in this way gradually narrowing down the flake.

Figure 4.1b shows a typical evolution of feedback-controlled electroburning. Generally, during the first voltage ramp (red trace in figure 4.1b) non-linear I-V characteristics are observed, likely due to removal of contaminants on the flake by current annealing.[27] Increasing the voltage further induces the first electroburning event, as can be seen from the downward curvature in the I-V characteristic, here at V = 4.8 V and I = 15 mA. The feedback then sweeps the voltage back to 0 V and a new voltage ramp is started. As the electroburning process evolves, the conductance decreases in steps and the voltage at which the electroburning occurs
4.2. Results and discussion

**Figure 4.2:** 

a) Left: AFM image of a typical graphite nanogap. Right: aerial view of a zoom in on the gap area. 

b) Representative current-voltage characteristic of a graphite nanogap (black solid line) with a fit to the Simmons model for tunneling (red dashed line). Fit parameters are: gap size: 1.25 nm, crosssection: 494 nm$^2$, barrier height: 0.49 eV, asymmetry: 0.078 (see also appendix A).
decreases (see green arrow in Fig. 4.1b). In total we have performed electroburning on 38 samples of which 35 (92 %) underwent the electroburning process down to a low-bias resistance in the range of 500 MΩ - 10 GΩ. In the other cases the feedback was not fast enough to respond, resulting in gaps with infinite resistance (> 100 GΩ).

Analyzing the cross-section of the device in figure 4.1b by atomic force microscopy we calculate the critical current density at which the first electroburning event occurs, to be 5.3 x 10⁷ A/cm². For all the devices on which we have performed the electroburning the critical current densities are comparable; between 3.8 x 10⁷ and 7.6 x 10⁷ A/cm², independent of the thickness of the flakes and similar to the current densities of 10⁸ A/cm² at which single layer graphene breaks down.[28]

To characterize the gap geometry, we have performed atomic force microscopy on several devices after electroburning, a representative example of which is shown in Fig. 4.2a. This graphite flake has a height of 12 nm, corresponding to ca. 35 layers of graphene. The image suggests that the electroburning starts from the edges in the central region of the flake, predominantly at one side. The evolution of the thinning can be understood by considering that the electroburning is a temperature activated process, relying on the reaction of carbon atoms in the lattice with oxygen. The highest temperature in the flake as a result of Joule heating at large current densities is reached in the central region since heat is evacuated mainly to the Au-leads, while the edge-carbon atoms are the most reactive sites due to the incomplete sp²-hybridization.[29, 30] After the first carbon atoms have been removed on the site of highest reactivity, the electroburning will likely propagate from there as the current density and therefore the temperature is the highest near this point.

Because it is difficult to obtain an accurate gap size from AFM characterization, we turn to the electrical characteristics of the nanogaps. Current-voltage characteristics between +/- 400 mV of 34 electro-burned samples with finite resistance were recorded at room temperature in a vacuum probe station (see Fig. 4.2b for an example). The junctions show current-voltage curves indicative of tunneling behavior through a single barrier. The fact that we observe tunnel currents at these low biases shows that the gaps are in the order of a few nanometers. The Simmons model can be used to estimate the gap-size[31] using the gap-size and cross-section, the barrier height and the asymmetry in the bias-voltage response as fit parameters (see appendix A for the implementation). Fits of the IV-characteristics to this model yield typical gap sizes between 1 and 2 nm. The fitted barrier heights (< 1 eV) are lower than one would typically expect for bulk graphite. However, low barrier heights have also been observed for nanometer sized Au electrodes.[32]

Our few-layer graphene nanogap electrodes are remarkably stable and display
4.2. Results and discussion

Figure 4.3: (a) Chemical structure of the anthracene terminated curuminoid wires (1,7-(di-9-anthracene)-1,6-heptadiene-3,5-dione) (b) Schematic representation of the measurement set-up for the few-layer graphene nanogaps bridged by 9-Accm molecules. (c) IV-characteristics of the nanogapped electrodes before and after being bridged by the 9-Accm molecules at 300K. While the conductance at low bias superimposes with the empty gap characteristic, at higher bias a clear current increase is observed. (d) IV-characteristic of the device in (c) after subtracting the parallel direct-tunneling contribution of the empty-gap IV-characteristic (black curve in (c)) from the IV-characteristic with molecules (red curve in (c)).
only small variations in the tunneling characteristics after several weeks when stored in vacuum (current-levels stay within 10% variation)[33]. We have also carefully measured the conductance as a function of the backgate voltage ($V_{g}$) at low temperature (10 K) at different low bias voltages of e.g. 100 and 200 mV. For most of the devices the conductance does not vary within our experimentally accessible range of $V_{g}$ between +/- 40 V.[34] The small electrode-separations and long-term stability of the nanogaps, combined with the absence of gate-dependent transport across the gap imply that they can be used to contact small molecules and measure their three-terminal transport characteristics.

To demonstrate this, we have deposited anthracene-functionalized curcuminoid molecules (1,7-(di-9-anthracene)-1,6-heptadiene-3,5-dione, abbreviated as 9Accm, see Fig. 4.3a) on the nanogap devices.[35] The anthracene-groups are extended $\pi$-conjugated systems that interact strongly with the $\pi$-system of the top-graphene layer, providing a strong anchor to the electrodes, while the curcuminoid wire has a high $\pi$-electron density which can mediate charge transport. We deposit the molecules by placing the devices overnight in a chloroform solution containing 0.1 mM of 9Accm. After taking the devices out of the solution they are blow-dried by a flow of $N_{2}$. AFM characterization of the deposition on a reference sample shows that a sub-monolayer of molecules is formed on the devices. The devices are then electrically characterized in a vacuum probe station (see fig. 4.3b for a schematic representation).

An important advantage of stable nanogap electrodes is that the current-voltage characteristics after deposition can be compared with the characteristics before deposition. Changes in the transport-characteristics can then be attributed to the presence of molecules in the gap. In our case, 14 out of 35 devices displayed an increase in conductance after deposition. Figure 4.3c shows a typical device in which such changes in the IV-characteristic are observed. While the conductance at low bias superimposes with the empty gap characteristic, at higher bias a clear current increase is observed. At this point it is interesting to note that the empty-gap IV-characteristic represents a parallel, direct-tunneling conductance path. Subtracting this parallel contribution from the IV-characteristic after deposition yields the molecular contribution to the current through the device. For the curve in Fig. 4.3c, the result is shown in Fig. 4.3d. The complete suppression of current at low bias is reminiscent of Coulomb-blockaded transport.

Importantly, the conductance in this device is dependent on the gate-voltage at room temperature, as illustrated in Fig. 4.4a. Taking current-voltage characteristics at different gate-voltages between -10 and 10 V, the conductance increases towards more positive gate-values; i.e. the blue curve in Fig. 4.4a displays the highest currents. Because the empty-gap characteristic is gate-independent, we subtract the parallel direct-tunneling contribution from the IV-characteristics at different
4.2. Results and discussion

**Figure 4.4:** (a) Dependence of the I-V characteristics of the nanogapped electrodes bridged by 9Accm molecules on the applied back-gate voltage measured at 300K, (same device as Fig. 4.3) (b) I-V characteristics from (a) at different back-gate voltages, corrected for the parallel direct-tunneling contribution from the empty-gap IV-characteristic of Fig. 4.3c.

**Figure 4.5:** (a) Conductance as a function of the applied back-gate voltage of the nanogapped electrodes bridged by 9Accm molecules at 10 K (same device as Fig. 4.3 and 4.4). While the empty nanogap electrodes show no dependence of the applied back-gate voltage, a clear conductance modulation as a function of $V_g$ is observed after deposition of 9Accm molecules. (b) Current map of the same device at 10 K. IV's are taken between $V_{sd} = +/-300$ mV while the backgate voltage is swept between $-/+30$ V at 100 mV intervals. In the green regions, transport is blocked due to charge quantization in the molecule, while in the red and blue regions the blockade is lifted and single-electron tunneling occurs. Although the signatures may originate from a few molecules in parallel, the single electron tunneling nature of the transport is apparent from the current map.
gate-voltages (see Fig. 4.4b). The gap decreases at more positive values of the gate-voltage, eventually almost disappearing at $V_g = 10\, \text{V}$, suggesting the alignment of the molecular state with the Fermi-energy of the leads. The gate-dependent characteristics are robust, showing only minor variations in the conductance (<10 %) for a period up to a week when stored in vacuum, and even after thermal cycling to low temperatures (10 K, see below). In total we observed gate-modulated transport in 4 out of the 14 junctions that displayed an increase in conductance after deposition.

At low temperature (10 K), the gate-dependent transport becomes more apparent and we can moreover compare it to the empty-gap gate-dependence taken before deposition. In figure 4.5a the conductance at $V_{sd} = -200\, \text{mV}$ is plotted as a function of gate voltage before and after deposition (same device as Fig. 4.3 and 4.4). While the conductance is gate-independent before deposition, after deposition a clear modulation of the conductance is present towards more positive values of $V_g$, consistent with the room temperature IV-characteristics. For a full characterization, we construct current maps at 10 K, in which IV’s are taken between $V_{sd} = +/-300\, \text{mV}$ while the backgate voltage is swept between -$+/+30\, \text{V}$ at 100 mV intervals. An example is shown in Fig. 4.5b. In the green regions, transport is blocked due to charge quantization in the molecule, while in the red and blue regions the blockade is lifted and single electron tunneling occurs. Although the signatures may originate from a few molecules in parallel, Coulomb-blockaded transport and the single-electron tunneling nature of the transport is apparent from the conductance map.

### 4.3 Conclusions

In conclusion, we report on a new method to controllably form nanogaps in few-layer graphene with nanometer separations based on feedback controlled electroburning of few-layer graphene. Gateable Coulomb-blockaded transport through molecules contacted between the electrodes demonstrates the potential of room-temperature operation of molecular devices. Combined with the observed stability in time, our study shows that few-layer graphene nanogaps are an interesting alternative to metal electrodes. We further note that the fabrication technique is not limited to the use of exfoliated graphene but could also be applied to CVD-grown few-layer graphene over large areas, paving the path to more complex, integrated devices involving multiple molecular devices integrated on the same chip.

### References


4. Molecular junctions using few-layer graphene nanogap electrodes


[33] *Once the gaps are successfully formed, it is important to avoid high bias voltages (> 1.5 V) to prevent that the device switches back to a high conductance state, as described in ref. 22. (????).*

[34] *Occasionally we find a dependence of G on V_g, indicating that the sample is not fully electroburned and there still is a connection between the source and drain electrodes. The connection can be removed by performing an additional electroburning step, after which also for these devices we obtain few-layer graphene nanogap electrodes that do not show a response to the applied gate voltage. (????).*

Many types of molecular motors have been proposed and synthesized in recent years, displaying different kinds of motion, and fuelled by different driving forces such as light, heat, or chemical reactions. We propose a new type of molecular motor based on electric field actuation and electric current detection of the rotational motion of a molecular dipole embedded in a three-terminal single-molecule device. The key aspect of this all-electronic design is the conjugated backbone of the molecule, which simultaneously provides the potential landscape of the rotor orientation and a real-time measure of that orientation through the modulation of the conductivity. Using quantum chemistry calculations, we show that this approach provides full control over the speed and continuity of motion, thereby combining electrical and mechanical control at the molecular level over a wide range of temperatures. Moreover, chemistry can be used to change all key parameters of the device, enabling a variety of new experiments on molecular motors.

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5.1 Introduction

Motivated by examples found in nature, and propelled by recent advances in synthetic chemistry, the field of molecular motors is rapidly developing into a major area of research [1–12]. Molecular motors are (supra-)molecules that are able to convert energy into continuous directional motion of one molecular component relative to another. For a molecule to be able to function as a motor, at least two (meta)stable conformations are required, separated by energy barriers. The height of these barriers should be several times larger than $k_B T$, to prevent thermal fluctuations from setting the molecule into random motion. In order to perform work, the transitions between the states should be unidirectional, which has so far been achieved in a few systems [3–5, 7]. Most experiments to date have been performed on large assemblies of molecules [1–5, 7], although some examples have been studied where scanning tunneling microscopy was used to either manipulate or detect the motion on the single-molecule scale [6, 8, 10, 12].

Here, we propose a conceptually new design for a molecular motor, which enables the simultaneous driving and detection of the motion of a single-molecule motor at the nanoscale (see Fig. 5.1a). The rotating moiety is equipped with a permanent electric dipole moment and is part of a conjugated molecule, which is suspended between two metallic contacts above a gate electrode. By modulating the electric field generated by the gate, the dipole rotor can be driven to rotate with a speed controlled by the frequency of the gate field [13]. As it rotates, the rotor repeatedly switches between two stable states, each corresponding to a planar conformation where the molecule is fully conjugated. The unique aspect of this design is that by applying a small bias between the metallic contacts and measuring the current through the molecule, we can determine the position of the rotor, since a lowering of the conjugation during rotation has a dramatic effect on the conductance.

Structure 1 (see Fig. 5.1b) is a simple example of a molecular dipole motor. It consists of three basic components: a dipole rotor, axles, and anchoring groups. The bidentate mercaptothiophene anchoring groups connect the molecule to the source and drain electrode, and are designed to provide good conductance and to limit conformational changes near the contact surface[14] The ethynyl groups connected to the anchoring groups act as an axle about which the central anthracene moiety can rotate. The chemical design of these axles determines the height and shape of the rotational barrier potential. Finally, the anthracene rotor in between the axles interacts with an external electric field through the cyano ($\delta^-$) and methoxy ($\delta^+$) substituents, which induce a dipole moment $p$. The dipole moment can be tuned by choosing different combinations of electron-withdrawing or electron-donating substituents and varying the distance between them.
FIGURE 5.1: a) Design of a molecular motor with a permanent electric dipole moment. The motor consists of anchoring groups connecting the conjugated backbone to the leads, allowing the measurement of the low-bias conductance, and a dipole rotor which can be driven by the oscillating gate field underneath. b) Proposal for a molecular dipole motor: structure 1 (9,10-bis((5-mercapto-3-thiophen-3-yl)ethynyl)-6,7-dimethoxyanthracene-2,3-dicarbonitrile). The blue $\delta^-$ and red $\delta^+$ symbols denote the partial charges inducing the dipole moment of the rotor, and the green arrow shows the axis facilitating a rotation of the rotor with an angle $\alpha$. c) The rotational barrier potential (bottom) and normalized zero-bias off-resonance conductance (top) of structure 1 obtained from DFT calculations as a function of the rotation angle $\alpha$ of the dipole rotor. The red lines illustrate the $\sin^2(\alpha)$ and $\cos^4(\alpha)$ behavior of the barrier potential and conductance, respectively.
We note that, in principle, it is also possible to use a magnetic field to drive a molecule with a magnetic dipole moment. However, the energy range accessible to a high-spin molecule ($S = 5$) in a large magnetic field ($|B| = 10$ T) is limited to about $U = -\mu \cdot B = \pm 3$ meV, whereas the energy range of a molecule with a large electric dipole moment ($|p| = 10$ D) in a large electric field ($|E| = 1$ V nm$^{-1}$) can be as large as $U = -p \cdot E = \pm 200$ meV. Moreover, electric fields can easily be applied locally in a molecular junction via a gate electrode. Solving Poisson’s equation for a typical geometry in an electromigrated break junction (EMBJ) with a gap separation of 2 nm yields an electric field of $|E| \approx 1$ V nm$^{-1}$ at the position of a molecular dipole due to the gate electrode for a gate range of $\pm 5$ V. The calculated gate coupling at that position ($\beta = 0.1$) corresponds well to typical values in measurements on single-molecule devices [15].

### 5.2 Results and Discussion

In order to analyze the behavior of the motor and to check whether its motion is detectable through current measurement, we have performed quantum chemistry calculations and classical Langevin simulations.

Using density functional theory (DFT, ADF-package) and the Green’s function method, the rotational barrier potential and the zero-bias off-resonance conductance have been calculated as a function of the rotation angle of the rotor ($\alpha$) and the anchoring groups ($\theta$), where $\alpha$ and $\theta$ are defined with respect to the direction of the electric field (vertical in the figures in this paper). For a conjugated molecule, conductance takes place primarily via the HOMO or LUMO, which consist of a hybridization of the $p_z$-orbitals on the carbon and sulfur atoms of the backbone. Since the dipole rotates around the ethynyl ‘axles’, we expect the conductance to be proportional to the overlap between the $p_z$-orbitals on the backbone. Therefore, since a dipole motor has two axles, the conductance is expected to be proportional to $\cos^4(\alpha - \theta)$, or, when $\theta_l \neq \theta_r$:

$$G(\alpha) \sim \cos^2(\alpha - \theta_l) \cdot \cos^2(\alpha - \theta_r),$$

where each axle contributes a factor of $\cos^2(\alpha)$ to the conductance.

For $\theta = 0^\circ$, the results in Fig. 5.1c show the $\sin^2(\alpha - \theta)$ dependence of the barrier potential $U^r(\alpha)$ for structure 1, while the conductance is proportional to $\cos^4(\alpha - \theta)$. This strong dependence of the conductance on the rotation angle, which has also been observed in measurements [16–18], allows it to be used as a measure of the rotation. Note that the minima of the conductance correspond to the maxima of the barrier potential.

Since the peaks in $G(\alpha)$ become narrower when $\theta_l \neq \theta_r$, the conductance is slightly more sensitive to the rotation angle. However, the overall behaviour of
the potential and the conductance do not change when \( \theta_l \neq \theta_r \) and the proposed actuation and detection principle should work for a large variety of experimental configurations. It should be noted that a gate field could influence the conductance by shifting the HOMO and LUMO with respect to the Fermi energy, but since the molecule is strongly coupled to the leads, this effect is expected to be much smaller than the change in conductance due to the lowering of the conjugation.

In order for an electric field to rotate a dipole, the torque exerted by the field,

\[
\tau^P(\alpha) \equiv -\frac{dU^P(\alpha)}{d\alpha} = |p| |E(t)| \sin(\alpha),
\]

should exceed the restoring torque in the molecule,

\[
\tau^R(\alpha) \equiv -\frac{dU^R(\alpha)}{d\alpha} = -U^R_0 \sin(2(\alpha - \theta)),
\]

for all values of \( \alpha \) before the rotor crosses the maximum of the rotational barrier potential:

\[
|p| |E| \sin(\alpha) \geq U^R_0 \sin(2(\alpha - \theta)). \tag{5.2}
\]

In the case where \( \theta = 45^\circ \) the critical field is lowest (\( |E_c| = \frac{U^R_0}{|p|} \)), while for \( \theta = 0^\circ \) or \( \theta = 90^\circ \) it is twice as large.

Since thermal fluctuations are important, and can even be dominant for nanoscale devices, the dynamics of a molecular motor at temperatures above the quantum level splitting are most appropriately described by the Langevin equation [19–21]:

\[
I \frac{d^2 \alpha(t)}{dt^2} = \tau^R(\alpha) + \tau^P(\alpha, t) - \gamma \frac{d\alpha(t)}{dt} + R(t), \tag{5.3}
\]

where \( \alpha \) is the rotation angle of the dipole rotor, \( I \) is the moment of inertia, \( \gamma \) is a friction coefficient due to the coupling of the molecular motion to the phonon bath of the electrodes and the interaction between the dipole and the metallic surfaces [22], and \( R(t) \) is a Gaussian distribution describing the thermal fluctuations, with a width of \( 2k_B T \gamma \) [20].

In eq (5.3), the moment of inertia, height of the rotational energy barrier, and the dipole moment of structure 1 are calculated using DFT, leaving only the friction coefficient \( \gamma \) as a free parameter. In the limit of small oscillations around the potential minima, \( \gamma \) enters into the solution of eq (5.3) as an exponential decay factor of \( e^{-\frac{t}{\gamma I}} \). This suggests defining \( k_v = \frac{I}{\gamma} \), where \( k_v \) is the vibrational relaxation rate. For structure 1, we find \( I = 2.66 \cdot 10^{-7} \) a.u. \((6.77 \cdot 10^{-44} \text{ kg m}^2)\), \( U^R_0 = 139 \text{ meV} \) (or 3.21 kcal mol\(^{-1}\), corresponding to a torque of at most \( 2.23 \times 10^{-20} \text{ Nm} \)), and \( |p| = 12.6 \text{ D} \). The vibrational relaxation rate \( k_v \) is chosen to be \( 10^9 \text{ Hz} \). Although it
is possible to estimate certain contributions to the relaxation rate [22], this rather slow rate has been chosen because it represents a worst-case scenario from a device standpoint (slow relaxation amplifies thermal fluctuations). The results in this chapter show, however, that even in this case the molecular motor can be driven and its motion be measured.

The position of a molecular dipole rotor as a function of an oscillating electric field is shown in Fig. 5.2. The anchoring groups are taken to bind under an angle of $\theta = 45^\circ$ with respect to the direction of the field, as this results in the smallest gate voltage required to drive the motor. It is clear from this figure that the motor is unidirectional, and can therefore perform work. This holds even when $\theta \neq 45^\circ$, although the critical field may then be larger (by at most a factor of two). The only two cases where the motor would not be unidirectional are $\theta = 0^\circ$ and $\theta = 90^\circ$ (within about 5$^\circ$ at 15 K due to thermal fluctuations), as the rotor is then in the top (or bottom) dead center corresponding to the minimum or maximum of the barrier potential, where the direction of motion is random. Though unidirectional, the direction of motion will of course depend on the orientation of the molecule in the junction. For example, when $\theta = -45^\circ$ the direction of motion will be counterclockwise.

To show how the rotational motion can be unambiguously detected, we have calculated the rotation angle $\alpha$ and conductance due to an oscillating gate field as a function of time. For $T = 15$ K, the rotation angle and the conductance for

**Figure 5.2:** Dynamics of a dipole rotor in an electric field. (a)–(h) The position $\alpha$ of the dipole rotor as a function of time (top) due to an oscillating gate field (bottom). The rotor has been depicted schematically as seen along the rotation axis (see Fig. 5.1a for comparison), where the anchoring groups are shown in yellow, and the positive and negative partial charges of the dipole are shown in red and blue, respectively. When the field is zero, the rotor is in the equilibrium position (a) ($\alpha = 45^\circ$). As soon as the field is turned on, the rotor feels a torque and starts to rotate (b). For this particular configuration, the torque becomes maximal at $\alpha = 90^\circ$, precisely when the restoring torque in the molecule is also maximal (c). The rotor now accelerates and flips (d), ending up in the next equilibrium position when the field has vanished (e). The gate field then changes sign, and the process repeats (f)–(h).
FIGURE 5.3: a) The gate field, rotation angle, and normalized conductance as a function of time for structure 1 in the configuration of Fig. 5.2. The red line corresponds to the situation where the field is too weak to drive the motor into rotation, and the green line to when it is just strong enough. For the first 0.5 ms the field is in the ‘wrong’ direction, pushing the rotor counter-clockwise instead of clockwise, and the conductance traces overlap since no rotation takes place. After that, the field is in the ‘right’ direction, the motor starts to rotate, and the conductance traces start to deviate from each other. The dashed line indicates the amplitude of the critical field (∼0.4 V nm⁻¹). In the case of a rotating motor, the conductance has a period that is half that of the driving field, and is no longer symmetric under time reversal. b) The rotation angle and normalized conductance as a function of the applied gate field. The red line corresponds to the forward sweep of the field (negative to positive), and the green line to the backward sweep. Both the rotation angle and the conductance clearly show hysteresis.
structure 1 are shown in Fig. 5.3a for a gate field with an amplitude just below (red line) and just above (green line) the critical value (∼0.4 V nm⁻¹ for θ = 45°), which is well within the range accessible in current three-terminal devices. The rapid flip of the rotor (Fig. 5.2c–d) is visible as a vertical line in the rotation angle and as a switch in the conductance. While the potential changes with time, at any instance the rotor executes a Brownian motion around the equilibrium position, with the exception of the (nearly instantaneous) switch. The characteristics of Fig. 5.3a therefore do not change if the driving frequency is different, as long as it is lower than the relaxation rate (> 10⁹ Hz). This means that we have full control over the speed of motion, and therefore over the power output of the molecular motor, up to the GHz regime. At very low frequencies, the motor can even be driven statically as a switch.

Two features in the conductance plots in Fig. 5.3a enable us to distinguish between a rotating and a non-rotating molecular motor: the period and the time-reversal symmetry. While the period of the conductance is equal to that of the driving field for a merely oscillating motor, for a rotating motor it is half as long. More importantly, the conductance for a rotating motor is not symmetric under time-reversal. The reason for this can be seen in Fig. 5.3b, which shows hysteresis in the conductance as a function of the applied field: after the rotor flips, the field has to change sign for the rotor to return to its original position. Although the gate field may have an influence on the conductance besides the rotation of the dipole rotor, the time-reversal asymmetry in the conductance will still be present, and is therefore the hallmark of a molecular dipole motor.

The temperature of 15 K used in the calculation of Fig. 5.3 should be compared to the quantum-mechanical level splitting of the rotor vibrations (∆E = ℏ√(2U₀₀/₀, where ₀ is the moment of inertia). For the structure 1 the level-splitting is 0.533 meV (6.19 K). As long as kₜ T is higher than the level splitting, the motor behaves classically, but at lower temperatures a quantum mechanical description becomes necessary. For example, at liquid helium temperatures, the motor will exhibit temperature-independent zero-point oscillations with an estimated amplitude of 2.5°. This leads to variations in the conductance which may be observable in the current noise.

At higher temperatures, thermal fluctuations cause the rotor to flip at a lower value of the gate field, making the difference between the conductance of the rotating and non-rotating motor less pronounced. Our calculations show that structure 1 should still be operational at 77 K, but at room temperature it will rotate freely, even in the absence of a driving force. To allow operation at room temperature, a molecule with a higher rotational barrier potential is required. An example of such a design is shown in Fig. 5.4a (structure 2). Compared to structure 1, we
5.2. Results and discussion

Figure 5.4: Design of a molecular dipole motor capable of room temperature operation. a) Structure 2 (2,7-bis((E)-2-(5-mercaptothiophen-3-yl)vinyl)-9,10-dimethoxy pyrene-4,5-dicarbonitrile). The pyrene rotor has a dipole moment \( p \) of 9.8 D. b) Normalized conductance as a function of time at temperatures of 15, 77, and 300 K. The driving frequency is the same as in Fig. 5.3a, but the amplitude of the field is 1.75 V nm\(^{-1}\) at 300 K, 2.75 V nm\(^{-1}\) at 77 K, and 3.25 V nm\(^{-1}\) at 15 K.
have substituted the ethynyl groups in the axles for ethenyl and the anthracene rotor for a pyrene analogue. The axis of rotation is now located on the single bond between the ethenyl groups and the pyrene rotor. We have chosen pyrene instead of anthracene to minimize the steric hindrance between the rotor and the axles. These changes result in a fivefold increase of the rotational barrier potential \( U_0' = 691 \text{ meV or } 15.9 \text{ kcal mol}^{-1} \), preventing the motor from rotating freely at room temperature. The normalized conductance as a function of time for this molecule is shown in Fig. 5.4b for different temperatures. It is clear from this figure that the motor can still be driven and measured at temperatures up to 300 K, although the critical field at this temperature \( (1.75 \text{ V nm}^{-1}) \) may be challenging for current three-terminal devices.

### 5.3 CONCLUSIONS

In conclusion, we have shown that the use of an electric field to drive a molecular dipole motor provides unidirectionality and complete control over the speed of rotation, while the conductance provides a real-time measure of the motion. The proposed molecule is easily synthesized and the parameters are such that it should be measurable in current electromigrated break junction setups. An important aspect of our design is the versatility offered by chemical synthesis. In particular, the barrier height, the dipole moment, and the moment of inertia of the rotor can all easily be changed. Our motor therefore constitutes a well-defined nanoelectromechanical system suitable for studying molecular motion over a wide range of temperatures, encompassing both the classical and quantum regime.

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NANOPARTICLE-BASED ELECTRONICS
We report a switchable molecular device made by contacting individual nanoparticles based on spin-crossover molecules between nanometer-spaced electrodes. This nanoscale device exhibits switching and memory effects near room temperature as a consequence of the intrinsic bistability of the spin-crossover nanoparticle. Interestingly for molecular spintronics, the spin crossover in this molecular nanodevice can also be induced by applying a voltage, showing that its magnetic state is controllable electrically.

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6. Electrical addressing of a spin-crossover nanoparticle

6.1 Introduction

Molecular switches have continuously inspired the scientific community working on molecular electronics.[1–7] Switching between different magnetic states of a molecule is of particular interest, especially when it involves interplay between molecular spin and electric transport. Many potential candidates have appeared over the years,[8] but addressing these systems electronically is challenging, especially at the nanoscale.[9] The design of switchable nanodevices based on magnetic molecules has therefore remained a theoretical topic.[10–12] Here, we report a switchable molecular device made by contacting individual nanoparticles based on spin-crossover molecules between nanometer-spaced electrodes. This nanoscale device exhibits switching and memory effects near room temperature as a consequence of the intrinsic bistability of the spin-crossover nanoparticle. Thus, a sharp increase in the conductance is observed upon heating above $\sim 350 \text{ K}$, together with the presence of a thermal hysteresis as large as 30 K for a single-particle device, after which the conductance switches back to the original value. This is a long-sought for result, as it confirms the existence of hysteretic spin crossover effects in a single nano-object. [13–17] Interestingly for molecular spintronics, the spin crossover in this molecular nanodevice can also be induced by applying a voltage, showing that its magnetic state is controllable electrically.

Spin crossover metal complexes are one of the paradigmatic examples of magnetic molecular materials showing switching and bistability at the molecular level.[18] In these systems low-spin to high-spin transitions can be triggered through a variety of external stimuli (temperature, illumination or pressure)[19] and in contrast to the other classes of magnetic molecular materials, they may exhibit bistability near room temperature.[20] This magnetic state switching has been studied extensively in bulk samples, both in the solid state and in solution. The idea that molecular electronics could profit from these properties was recognized at an early stage,[21, 22] but attempts to realize an electronic spin-crossover device have to date been limited to reports using thin film transistors[23, 24] and scanning tunnelling microscopy.[25]

In this work we place nanoparticles based on the Fe(II) coordination polymer $[\text{Fe(trz)}_3(\text{BF}_4)_2]_2$ (trz = triazole) in between two nanometer-spaced electrodes (see Fig. 6.1). The particles of ca. 11 nm in diameter consist of a spin-crossover Fe(II) core, coated with a surfactant shell. The spin-crossover properties of large collections of these particles have been studied in detail through magnetic susceptibility measurements in solid samples after solvent removal and also by the change in color of an octane suspension containing the nanoparticles. A cooperative spin transition from Fe(II) low spin, $S_{LS} = 0$, to high spin, $S_{HS} = 2$, has been detected, exhibiting a thermal hysteresis loop above room temperature with a width in ex-
6.1. Introduction

**Figure 6.1:**  
a) Ligand-field splitting and filling of the five d-orbitals in Fe(II) octahedral centers, in which the spin-crossover is defined by a transition between a low-spin state, $S_{LS} = 0$, and a high-spin state $S_{HS} = 2$.  
b) Magnetic susceptibility as a function of temperature of aggregates of the nanoparticles showing hysteresis above room temperature.  
c) Schematic side view of the device geometry with the nanoparticle placed on top of the electrodes. In purple the spin-crossover core is represented, in blue the surfactant shell.
6.2 Results and Discussion

Planar electrodes of different widths are fabricated using a self-alignment fabrication scheme (see Fig. 6.2a). In short, a nanometer thick chromium-oxide shadowmask is used to define a gap between two Au electrodes. After a selective wet-etching to remove the shadowmask, the gap is exposed, giving an electrode-separation typically in the order of 5 - 10 nm, small enough for a single nanoparticle to bridge the gap. The electrode widths are either 100 nm or 1 µm. While the broader devices allow the contacting of several particles in parallel, in the 100 nm wide devices only a few, or even a single particle, are expected to be trapped. Devices are electrically characterized before deposition to determine the empty gap resistance, typically exceeding 100 GΩ (see green lines in Fig. 6.2b). An important advantage of the device architecture is the good thermal stability, as was confirmed by repeating this electrical characterization as a function of temperature up to 400 K.

Particles are deposited by contact-printing of a monolayer of particles formed on top of a droplet of diethyleneglycol. Atomic force microscopy on flat surfaces confirms a homogeneous sub-monolayer coverage of approximately 70 %. After deposition, seven out of thirteen devices of 1 µm width (55 %) and three out of twelve devices of 100 nm width (25 %) display a clear increase in conductance as compared to the empty gap measurement (see red lines in Fig. 6.2b), indicating that one or several particles in parallel are contacted between the electrodes. The increase in the conductance after deposition is generally larger for the wider electrode devices, although the resistance does not scale with the electrode width. We note that exposure of the empty devices to solvent alone does not lead to observable changes in the conductance.

At low temperatures (10 K), two of the 100 nm wide electrode devices show equidistant step-like features in the current-voltage characteristics and peaks in the corresponding derivative (dI/dV), reminiscent of a Coulomb staircase (see Fig. 6.3). The transport mechanism is therefore sequential single-electron tunnelling through an asymmetric double-barrier junction in which the nanoparticle core is the island, isolated from the electrodes by tunnel barriers defined by the surfactant layer. In this geometry, electrons first tunnel onto the particle, remain there for some time, before tunnelling off again. The conductance through the junction is therefore fully determined by the probabilities of tunnelling through the surfactant layer, i.e. the barrier material and width determine the device resistance.

The fact that the Coulomb-steps in Fig. 6.3 are equidistant indicates that trans-
6.2. Results and discussion

**Figure 6.2:** a) Left: Schematic of the device before Cr wet-etching showing the different layers in the fabrication and the Cr$_2$O$_3$ shadow mask. Right: Scanning electron micrograph of a device illustrating the different dimensions ($d = 5 - 10$ nm, $W = 100$ nm or 1 $\mu$m). b) Left: Room-temperature current-voltage characteristics before (green) and after (red) deposition of the particles on a device with 1 $\mu$m wide electrodes. Right: Same for a device with 100 nm wide electrodes. In both cases a clear increase in the current is observed.
port occurs through a single particle. The peak separation in the dI/dV vs. V plot of this single-particle device then equals e/C, where C is the island capacitance; for the two devices with equidistant Coulomb staircase features, e/C is found to be 240 and 210 meV (see Fig. 6.3 and Appendix B.1 respectively). These values can be compared to a simple estimate obtained from the self-capacitance of a sphere given by $C = \frac{2\pi\varepsilon_r\varepsilon_0 d}{d}$. With a core-diameter d of 8 nm and taking the dielectric constant $\varepsilon_r$ to be 2 as a typical value for the organic surfactant layer, we find e/C to be equal to 181 meV, which is in close agreement with the experimental values considering the uncertainty in the parameters. Note that if several particles would be present in parallel, the peaks of each individual particle should occur at different voltages due to a different electrostatic environment; as a result, they would be superimposed, leading to an irregular pattern of more closely spaced peaks.

After this basic device characterization we turn to the temperature dependent measurements. Current-voltage characteristics of the devices in the temperature range of 300 - 400 K were recorded. In Fig. 6.4, we plot the conductance (I/V) at 0.4 V as a function of temperature for two devices, one with 1 µm and one with 100 nm wide electrodes (Fig. 6.4a and b, respectively). Although for the 1 µm device transport may be through several particles in parallel, from the low-temperature characterization of the 100 nm device we infer that transport occurs through a single particle (see Appendix B.1). Increasing the temperature from 300 K, the conductance of the 1 µm device is stable until it jumps between 360 and 370 K to a value that is two times higher than the original state. The single-particle 100 nm device shows a similar behavior with a transition to a higher conductance between 350 and 355 K. When subsequently lowering the temperature, a clear hysteresis is observed for both devices. For the 1 µm device, a hysteresis loop opens after a slight initial decrease in conductance. The system switches back to the original low-conductance state between 320 and 300 K. For the single-particle 100 nm device the high-conductance state is maintained down to 330 K. We have checked that the bistability is preserved in a second thermal cycling, although the absolute values of the conductance can vary. In total five out of ten samples exhibit an increase in conductance in the 350 - 390 K range. For three of these a clear hysteresis is observed, while for the other two the change in conductance is (partially) irreversible (see Appendix B.2).

The thermal hysteresis in the conductance resembles that observed in the magnetic susceptibility measured in aggregates, suggesting that the intrinsic spin-crossover properties of the particles is at the origin of the observed electrical bistability. Although the mechanism responsible for the conductance response to the spin transition is not clear, we can speculate on the origin considering the spin-crossover phenomenon. Upon switching between low and high spin, the Fe-N bond-length of the compound changes by 0.2 Å. This expansion is followed by an
Figure 6.3: Top: Current-voltage characteristic of the 100 nm wide device of Fig. 6.2b at 10 K. The equidistant step-like features indicate Coulomb staircase behavior and transport through a single particle. Bottom: Corresponding first derivative (dI/dV) of the current. Grey arrows are equally spaced at 240 mV and coincide with peaks that exhibit equidistant spacing.
overall lattice expansion, giving the high-spin state a larger volume than the low-spin state. Taking into account the single electron tunnelling behavior that we described earlier, the increase in the nanoparticle size can reduce the tunnel-barrier width, and consequently lead to an increase of the conductance. This would explain why we consistently see an increase in conductance for the transition to the high temperature state. It must be stated that other mechanisms, such as rearrangements in the electron density, changes in the level alignment, or changes in the self-capacitance can also be at the origin of the conductance increase. However, it is not a priori clear how these would consistently lead to an increase in the conductance.

In this context it is interesting to note that Alam et al. have also observed switching in a spin crossover system using Scanning Tunnelling Microscopy (STM).[25] In their case a lower conductance (with a factor 3) is observed upon switching to the high-spin state which is attributed to a decrease in hybridization inside the molecules. In STM the molecular levels are strongly hybridized with the surface and lowering the hybridization in the molecule will therefore have a large influence which in their case leads to a conductance decrease. In single electron tunnelling, where the coupling is weak and the hybridization low, the size expansion of the nanoparticle has to be taken into account as it influences the barriers (see above), leading to a conductance increase.

Another interesting point, when comparing the thermal hysteresis of the conductance with the spin crossover behavior of the particles in the bulk, is the observation that the transitions have been shifted towards room temperature. It is well known that the transitions sensitively depend on the local environment of the Fe(II)-centres. The observed shift is therefore not surprising given the differences between the solid obtained after solvent removal and the single-nanoparticle in a device geometry (solvent and/or surfactant loss, interaction with the electrodes, change in the internal pressure of the nanoparticle, etc.).

Finally, we have found a new phenomenon in the spin-crossover particles, namely that the applied bias voltage can also induce a transition between the low- and the high-conductance state. This effect is most pronounced at low temperatures. In Fig. 6.5a we show an example in a 1 µm wide device. The voltage is swept up and down while recording the current which at high bias instantaneously switches to the high-conductance state. Interestingly, we found that at higher temperatures this change in conductance is the same as the one induced thermally. Thus, for the 100 nm device discussed in Fig. 6.4b, the voltage induced transitions between the low- and the high-conductance states correspond to the conductance values (I/V at 0.4 V) of the thermal hysteretic cycle of the same device (see Fig. 6.5b). Generally, the onset-voltage and the lifetime of this high-conductance state varies, both at low and high temperatures, but in some cases can be cycled repeatedly (see Fig.
FIGURE 6.4: a) Conductance (I/V) as a function of temperature for a device with 1 \( \mu \)m wide electrodes. Each point represents the average of the conductance at 0.4 V of 30 individual current-voltage characteristics. b) Same for a device with 100 nm wide electrodes. The low temperature current-voltage characteristic of this device is shown in Appendix B.1, and displays coulomb staircase behavior, indicative of a single particle between the electrodes. Similar hysteresis curves have been obtained for other bias voltages, however, if the bias voltage is chosen too high (> 0.4 V) the electric field can also induce transitions (see Fig. 6.5).
Figure 6.5: a) Current-voltage characteristic of a 1 µm wide electrode device at low temperature. b) Current-voltage characteristic of a 100 nm wide electrode device at 340 K. The conductance (I/V) at 0.4 V coincides with the values observed in the thermal hysteresis of the same device, showing that the bistability can be probed with an applied voltage. c) Repetitive cycling of the voltage between 0 and 1 V at low temperature (10 K) of the device displayed in Fig. 6.5a. In cycle 1 - 3 the switch to higher conductance (green arrows) reproducibly occurs between 0.6 and 0.8 V, after which it is maintained until the voltage returns to 0 V. In cycle 4 the high conductance state is maintained throughout the cycle while in cycle 5 the switch only occurs for a short time before switching back (red arrow) to the low conductance state. Cycle 6 shows again similar behavior as cycle 1 - 3.
6.3. Conclusion

Note that if the high-conductance state is maintained when returning to low bias, the following sweep can begin in the high-conductance state and can switch back to the low-conductance state at higher bias. The voltage-induced switching could have various origins. For instance, electric field polarization can influence the stability of the two states. Also, intersystem crossing through excited state population by the electric field may play a role, analogous to light induced excited spin state trapping (LIESST) known in spin crossover compounds. In this perspective it is interesting to note that following the work presented here, a recent report of photoconductance was presented by Etrillard et al. using a nanocrystal-transistor of a similar spin crossover material. Yet another possibility is local resistive heating due to inelastic processes which produce a higher effective temperature in the nanoparticle, thereby triggering the spin transition.

6.3 Conclusion

In conclusion a molecular device exhibiting switching near room temperature has been fabricated by contacting a bistable spin-crossover nanoparticle to two electrodes. By measuring the conductance, we have shown that it is possible to send current through these particles, and that they show bistability in the conductance as a function of temperature. The observed thermal hysteresis loop at room temperature makes this bistable system attractive as a memory element. Furthermore, a novel voltage-induced conductance switching has been demonstrated which is promising for electrical addressing of this memory function, and more generally for the field of molecular spintronics; it should enable the construction of molecular devices in which the magnetic state can be controlled electrically.

Experimental

Electrodes were fabricated in three steps by standard electron-beam lithography techniques. On top of a Si/SiO$_2$ substrate, the first electrode is defined and deposited by electron-beam evaporation, consisting of a 2 nm thick Ti adhesive layer, with on top 24 nm of Au as the electrode material, and 10 nm of Cr. Upon removal from the evaporation chamber, the Cr forms a natural Cr$_2$O$_3$ layer which overhangs the Au as a shadow mask. In the second step, the second electrode of 2 nm Ti with 20 nm Au on top is defined, overlaying the first Ti/Au/Cr/Cr$_2$O$_3$ electrode, while the shadow masks protects a few nanometers around the first electrode. In the third step, a selective wet Cr-etchant (Cyantek, Cr-10, 5 minutes immersion) is used to remove the shadowmask, exposing a nanometer sized separation between the first and second electrode. Before use, the samples are O$_2$-plasma cleaned.

Particles were synthesized by a previously described procedure. Fe(BF$_4$)$_2$ · 6H$_2$O (1 g, 2.96 mmol) was dissolved in water (6 mL), and added to a mixture
of sodium dioctyl sulfosuccinate (10 g, 98%), in 100 mL of octane. After a few
minutes of stirring, behenic acid (2 g) was added to this suspension. 1,2,4-1H-
Triazole (0.614 g, 0.0089 mol) was dissolved in ethanol (3 mL), and added to a mix-
ture of sodium dioctyl sulfosuccinate (10 g, 98%) in 100 mL of octane. The two
suspensions were mixed and stirred for 4 hours. Afterwards, the mixture was fil-
tered to yield a stable purple suspension of \( \text{[Fe(Htrz)}_2(\text{trz})](\text{BF}_4) \) nanoparticles in
octane. The size of the particles was determined through transmission electron
microscopy and dynamic light scattering giving a value for the particle diameter of
11 ± 5 nm.

Particles were deposited by use of a stamping technique. In a Teflon cup, 2 mL
of diethylene-glycol is used to form a convex meniscus. On top of the diethylene-
glycol, 250 \( \mu \)L of a 1000 times diluted stock solution of nanoparticles in octane
was carefully placed, forming a concave meniscus in the hydrophobic Teflon. Slow
evaporation of the octane brings the two oppositely shaped meniscuses together.
At the point of contact, a monolayer of nanoparticles is formed, driven by surface
tension. The substrate with the electrodes is carefully brought into contact with
the monolayer film, transferring the film to the substrate. The sample is dried un-
der a flow of \( \text{N}_2 \)-gass.

All measurements were performed in a vacuum (10\(^{-5}\) mbar) flow cryostat probe
station (Desert Cryogenics) with home-built low-noise electronics. Temperature
dependence studies (10 - 400 K) were done using a built-in heater element with
a Lakeshore temperature controller and liquid nitrogen and helium for cooling
power. Temperature dependent measurements of the conductance between 300
and 400 K was done by using a calibrated thermistor (TE-tech, MP-3011) posi-
tioned on the sample stage.

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6. Electrical addressing of a spin-crossover nanoparticle


We present an efficient photodetector based on a one-dimensional array of PbSe quantum dots. In this new device-architecture, the electrodes act as optical nano-antennae which concentrate incident light into the nanoparticle junction where they are converted into electron-hole pairs. The excitons are extracted with high efficiency due to the fact that the quantum dots are in direct contact with both source and drain electrodes, in contrast to previous studies which employed large assemblies of quantum dots.

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7. Photoconductance in quantum-dot junctions

7.1 Introduction

The band-structure of colloidal quantum dots exhibits phenomena such as size-based spectral tuning, broad-band absorption,[1] and multi-exciton processes.[2] In combination with the possibility of solution phase processing, this makes these materials interesting for photodetection applications and considerable advances have been made in this direction using colloidal quantum dot solids as the photosensitive layer. [3] Here we present an efficient photodetector based on a one-dimensional array of PbSe quantum dots. In this new device-architecture, the electrodes act as optical nano-antennae which concentrate incident light into the nanoparticle junction where they are converted into electron-hole pairs (see Fig 7.1a). The excitons are extracted with high efficiency due to the fact that the quantum dots are in direct contact with both source and drain electrodes, in contrast to previous studies which employed large assemblies of quantum dots. An overall device efficiency in terms of electrons/photon of over 6 % is achieved. The device-architecture is promising as a broadband photodetector and as a platform for the study of exciton dynamics in colloidal quantum dots.

Our device consists of nanometer separated Au-electrodes, fabricated by a self-aligned fabrication scheme (for details, see the methods section).[4–6] This method produces 5 nm separations between source and drain electrodes, small enough for a single particle to bridge them. Devices can be prepared over almost arbitrary widths, here from 50 nm up to 10 µm, in order to make contact to either a small number of particles or to many particles in parallel (see figure 7.1b). PbSe quantum dots (QDs) of 4 nm in size are placed on top of the electrodes using dipcoating (see methods section for details). The deposition is completed by a short dip in a MeOH solution containing a short organic linker molecule (ethylenedithiol) in order to replace the original thick surfactant layer (oleylamine) of the PbSe QDs and in that way improve the electronic coupling between the particles and the electrodes.

7.2 Results

Electrical contact of the particles to the electrodes is confirmed by performing electrical characterization before and after deposition. Before deposition the resistance in all 300 devices studied is infinite (> 100 GΩ at V up to 2.5 V), whereas after deposition a clear onset in conductance is observed at biases that overcome the addition energy (= level spacing + charging energy) of the PbSe-QDs. In Fig. 7.1c an example is shown of a 10 µm device for which the onset occurs roughly at V > 0.5 V. Irradiating the devices with green light (λ = 532 nm, 200 µW, 150 µm spot size) induces a strong photoconductive effect, which scales roughly linearly with the applied bias until it merges with the dark-current at high bias (typically...
Figure 7.1: (a) Schematic representation of the device geometry (side view). Inset: schematic representation of the exciton extraction after light absorption in the PbSe quantum dot. (b) Schematic of the device architecture illustrating the one-dimensional array of particles contacted between source and drain electrodes. (c) Current-voltage characteristics of a 10 µm wide device before deposition (grey), after deposition (black), and under light irradiation ($\lambda = 532$ nm, $P = 200 \, \mu$W, spot size = 150 µm).
Photoconductance in quantum-dot junctions

around 2 V, see green line in Figure 7.1c). Of the 300 devices of different widths, all display onsets in conductance after deposition and photoconductive effects. Even though some variation in the (photo-)conductance values exists, a linear scaling of the average conductance as a function of device width (i.e. number of particles contacted in parallel) is present.

Looking at the efficiency of the photocurrent generation, 8 nA (5 x 10^{10} electrons /second) of current is produced at -1 V at 200 µW optical power (3 x 10^4 photons/s/nm²) in the device of Fig. 7.1c. Since a maximum of 2000 particles can be deposited along the 10 µm wide junction, the combined physical cross-section is 25 x 10^3 nm². With the numbers above, we can place a lower limit on the efficiency, in the order of 65 electrons for each photon that hits one of the particles in the junction. This is a lower limit since it assumes a maximally covered junction and does not take the optical cross-section into account.[7] This can be understood by considering the optical antenna-function of the electrodes, which enhances the field due to the incident light in the nanogap. Field-enhancement in nanometer spaced electrodes has previously been employed in the study of Surface Enhanced Raman Scattering (SERS)[8–11] and has recently been reported to enhance photoconductive effects in graphene photodetectors.[12]

We record photoconductance maps by scanning a diffraction limited laser beam (λ = 532 nm, spot size of ≈ 800 nm) across the device and measuring the current as a function of the position of the spot. The maps, recorded at 0.75 V with varying optical power, show a high photoconductive response when the laser spot is placed directly on top of the area of the nanogap (see Fig. 7.2a and b, white dotted lines in 7.2b are guides to the eye to illustrate the electrode edges). The response along this area is consistently above a nA, with only small variation in the current, probably the result of a non-homogeneous distribution of PbSe QDs or a variation in the electronic coupling of the particles to the electrodes (see inset of Fig. 7.2a). Interestingly, the region of photoconductive response extends far across the electrode area, suggesting extensive propagation optical energy along the electrode structure.

The non-local photoconductive response along the electrodes becomes more apparent from Figure 7.2c which shows a line trace taken perpendicular to the nanogap area (see green arrow in Fig. 7.2b). Comparing the photocurrent (green line) with the dark current (black line), even when the laser is positioned at a distance as far as 10 µm from the nanogap area, photoconduction is still present. Two effects could be at the origin of the non-local photoconductance. First, surface plasmon polaritons can be generated at the Au/SiO₂ interface, where they can propagate towards the nanogap area and excite the QDs. However, for light of 532 nm wavelength the plasmon propagation length in Au has been reported to be only in the order of a micron. Although it could play a role in the non-local response at
Figure 7.2: (a) Three-dimensional color plot of the current through the device as a function of laser position (spot size = 800 nm, $\lambda = 532$ nm, $P = 1 \mu W$, $V = 0.75 V$). (b) Same as (a), but now as a two-dimensional color plot which illustrates the electrode edges. (c) Line trace taken perpendicular to the gap (see green arrow in (b)) with laser on (green line) and off (black line).
short distances, it is unlikely that the observed enhancement at 10 µm distance is due to surface plasmon polaritons. A second possibility is waveguiding of light between the Au film and the Si-backgate. A detailed description of the influence of the two effects, and the optical antenna-function of the electrodes in general, requires finite-difference time domain simulations which will be subject of forthcoming studies.

We have also recorded the line trace of Fig. 7.2c at different optical powers (between 0.45 and 15 µW, see Fig. 7.3a). A clear power-dependence is observed, both at the position of the nanogap itself, as well as along the electrode surface. In Fig. 7.3b the maximum observed photocurrent ($I_{\text{light}} - I_{\text{dark}}$) is plotted as a function of incident power. Saturation behavior is present towards high powers, which may be related to the finite number of states available within the PbSe QDs. In terms of number of electrons per number of incident photons, the same saturation behavior shows up as an exponentially increasing efficiency towards lower powers (see Fig. 7.3c). An efficiency of 6% is obtained at $\lambda = 532$ nm at the minimum measured optical power of 10 nW at 0.75 V. Although this value is still an order of magnitude lower than the state-of-the-art QD-based photodetectors,[3] the current device geometry allows for considerable improvements in terms of the antenna-function. In particular, interdigitated electrodes, where the nanogaps are closely spaced will enhance the density of active particles and should therefore allow for a more efficient capture of the incident light.

Similar exponential dependencies of the efficiency as a function of power are observed at different wavelengths (see Fig. 7.3d), though the efficiency itself decreases with increasing wavelength. The wavelength dependence at a constant power at the hot-spot can be compared to the absorption spectrum of the PbSe QDs, as determined from UV/Vis spectroscopy on particles in solution. The spectral dependence of the photoconductance roughly follows the trend in the absorption spectrum of the PbSe QDs. It should be noted though that the spectral dependence in this system is a complex combination of different factors of which the absorption spectrum of the PbSe QDs is only one. For example, the wavelength dependence in the plasmon propagation-length,[13] the possible occurrence of multi-exciton processes,[2, 14] and metal-surface induced changes in the level spacing of the QDs[15] could all have influence on the spectral dependence.

## 7.3 Discussion

The unique feature of our configuration as compared to QD-photodetectors to date is the direct contact of the source and drain to the particles. Conventional QD-photodetectors that use large assemblies of particles require a large multiple of hopping events before the electron or hole reach either source or drain, resulting
Figure 7.3: (a) Line traces at the same position as Fig. 7.2c at different optical powers. (b) Power dependence of the photocurrent ($I_{\text{light}} - I_{\text{dark}}$) at the gap-position taken from the line-traces shown in (a). (c) Power dependence of the efficiency (electrons/photon) at the gap-position at three different wavelengths. (d) Wavelength dependence of the photocurrent at a constant incident optical power of 2.5 $\mu$W (red dots) and the optical absorption spectrum of the PbSe quantum dots in solution as determined by UV/Vis absorption spectroscopy.
in a large probability for charge recombination along the way. In our device, on the other hand, only a single tunnel barrier separates each particle from both source and drain resulting in a very efficient charge separation. The charge-transport mechanism is therefore of very different nature.

As a first approximation, the charge separation can be explained by a simple model describing a two-level system separated from the leads by tunnel barriers (see figure 7.4a). The key parameter in this model is the effective barrier height. Applying a bias creates an asymmetry in the heights of the barriers to the left and right lead. This asymmetry is more strongly felt by the electron in the excited state, as it is closer to the top of the barrier, than by the hole. The electron therefore has a stronger directional preference than the hole, resulting in a net flow of current. Using a rate equation method, where the tunnel rates are obtained from the WKB-approximation, we can model the current-voltage characteristics displayed in figure 7.1b, as can be seen in figure 7.4b. Even though the model is simple in nature and far from complete, the resemblance between experiment and model is striking.

### 7.4 Conclusion

We have presented a new device architecture for photodetection, based on a one-dimensional array of colloidal quantum dots between nanometer-separated electrodes. This novel geometry achieves two major advances in the electrical detec-
tion of photons: First, the optical cross-section of the quantum dots is strongly enhanced by the plasmonic antenna function of the electrodes. Second, these same electrodes provide direct contact to each quantum dot enabling highly efficient exciton extraction. This dual function of the electrode structure yields a total efficiency of photon-to-electron conversion as high as 6%. It moreover provides a new platform for the study of exciton dynamics and near-field detection of optical plasmons. Our flexible approach is based on a combination of standard lithography and solution processing, gives high yields, making it potentially scalable. Even though the parameters in this proof-of-concept device are still behind on the state of the art, further optimization should allow for considerable advances and perhaps eventually competitive operation with commercial photodetectors.[3]

**EXPERIMENTAL**

Electrodes were fabricated in three steps by standard electron-beam lithography techniques. On top of a Si/SiO₂ substrate, the first electrode is defined and deposited by electron-beam evaporation, consisting of a 2 nm thick Ti adhesive layer, with on top 15 nm of Au as the electrode material, and 10 nm of Cr. Upon removal from the evaporation chamber, the Cr forms a natural Cr₂O₃ layer which overhangs the Au as a shadow mask. In the second step, the second electrode of 2 nm Ti with 10 nm Au on top is defined, overlaying the first Ti/Au/Cr/Cr₂O₃ electrode, while the shadow masks protects a few nanometers around the first electrode. In the third step, a selective wet Cr-etchant (Cyantek, Cr-10, 5 minutes immersion) is used to remove the shadowmask, exposing a nanometer sized separation between the first and second electrode. Before use, the samples are O₂-plasma cleaned.

PbSe particles of appr. 4 nm in diameter are deposited on the electrodes by a dipcoating technique under N₂-atmosphere. First, the devices are immersed in a MeOH solution of ethylenedithiol for 3 hours to mediate a chemical linkage between the Au and the PbSe particles. After this the devices are subsequently immersed in MeOH (1 min), a hexane solution of oleylamine-coated PbSe nanoparticles (1 min). Finally, the devices are once more immersed in a MeOH solution of ethylenedithiol (1 min, followed by 1 min in pure MeOH), to substitute the long oleylamine ligands and minimize the barrier between the particles and the electrodes.

Photoconductance maps were recorded using a confocal microscope with a NA = 0.8 objective illuminated by a λ = 532 nm laser beam or by a supercontinuum laser. The diffraction limited spot is scanned using a combination of two galvo-mirrors and a telecentric lens system while the dc photoconductance signal and the reflected light intensity are recorded simultaneously in order to determine the absolute position of the detected photoconductance features.
REFERENCES


APPENDICES
APPENDIX: SUPPLEMENTARY INFORMATION CH.4
A. Appendix: Supplementary information ch.4

A.1 Simmons model

![Simmons model diagram](image)

Figure A.1: Asymmetric tunnel junction with different work functions on the left ($\phi_L$) and right ($\phi_R$) leads. The barrier potential is assumed to vary linearly with the distance $x$ in the gap.

The current density in a tunnel junction with a barrier in the $x$-direction ($\phi(x)$), see Fig. A.1 is given by[1]

$$j = e \frac{4\pi m}{\hbar^3} \int_0^\infty d\epsilon \left[ f_L(\epsilon) - f_R(\epsilon) \right] \int_0^\epsilon d\epsilon_x T(\epsilon_x),$$  \hspace{1cm} (A.1)

where

$$f(\epsilon) = \frac{1}{e^{\frac{\epsilon - \mu}{k_B T}} + 1}$$  \hspace{1cm} (A.2)

is the Fermi distribution on leads with chemical potential $\mu$, and $T(\epsilon_x)$ is the tunnel probability of an electron with a kinetic energy $\epsilon_x$ in the $x$-direction. In the low-temperature limit, i.e., $k_B T \ll \mu_L, \mu_R, \phi(x)$, the Fermi distribution effectively becomes a step-function and eq A.1 reduces to

$$j = e \frac{4\pi m}{\hbar^3} \int_{\mu_L}^{\mu_R} d\mu \int_0^\epsilon d\epsilon_x T(\epsilon_x).$$  \hspace{1cm} (A.3)

The tunnel probability can be obtained via the WKB-approximation:

$$T(\epsilon_x) = e^{-\frac{2}{\hbar} \int_{x_1}^{x_2} dx |p_x|} = e^{-\alpha \int_{x_1}^{x_2} dx \sqrt{\phi(x) - \epsilon_x}},$$  \hspace{1cm} (A.4)

where $\alpha = 2\sqrt{\frac{2m}{\hbar}}$. For a barrier with constant height, i.e., $\phi$ is independent of $x$ between $x_1$ and $x_2$,

$$T(\epsilon_x) = e^{-\alpha d \sqrt{\phi - \epsilon_x}}.$$  \hspace{1cm} (A.5)
where \( d = x_2 - x_1 \), and the current density becomes[1]

\[
j \approx \frac{e}{2\pi \hbar d^2} \left[ (\phi - \mu_L) e^{-2d \frac{\sqrt{2m(\phi - \mu_L)}}{\hbar}} - (\phi - \mu_R) e^{-2d \frac{\sqrt{2m(\phi - \mu_R)}}{\hbar}} \right]. \tag{A.6}
\]

This is a good approximation when the work functions of the left and right lead are the same (\( \phi_L = \phi_R \)). When they are different, the barrier height (to first order) changes linearly from \( \phi_L \) at \( x_1 \) to \( \phi_R \) at \( x_2 \):

\[
\phi(x) = \phi_L + (\phi_R - \phi_L) \frac{x - x_1}{x_2 - x_1}, \tag{A.7}
\]

and

\[
\int_{x_1}^{x_2} dx \sqrt{\phi(x) - \epsilon_x} = d \frac{2}{3} \left( \frac{\phi_R - \epsilon_x}{\phi_R - \phi_L} \right)^{\frac{3}{2}} - \left( \frac{\phi_L - \epsilon_x}{\phi_R - \phi_L} \right)^{\frac{3}{2}}. \tag{A.8}
\]

However, this is only valid when \( \epsilon_x < \phi_L, \phi_R \). When \( \phi_L < \epsilon_x < \phi_R \),

\[
\int_{x_1}^{x_2} dx \sqrt{\phi(x) - \epsilon_x} = d \frac{2}{3} \left( \frac{\phi_R - \epsilon_x}{\phi_R - \phi_L} \right)^{\frac{3}{2}}, \tag{A.9}
\]

and similarly for \( \phi_R < \epsilon_x < \phi_L \).

For this barrier, the current density can no longer be calculated analytically, but is easily evaluated numerically. For fitting purposes it is generally more convenient to work with an average barrier height \( \phi = \frac{\phi_L + \phi_R}{2} \) and an asymmetry factor \( \alpha = \frac{\phi_L - \phi_R}{\phi_L + \phi_R} \). Apart from \( \phi \) and \( \alpha \), also the gap width \( (d) \) and the cross-section of the tunnel-junction are fitted in the paper. The latter is necessary since the Simmons model gives the current density, but the current is measured. Using the asymmetric Simmons model we can estimate the gap width within 5% accuracy.

### A.2 Deposition characterization

We have deposited 1,7-(di-9-anthracene)-1,6-heptadiene-3,5-dione molecules on the nanogap devices. The anthracene-groups are extended \( \pi \)-conjugated systems that interact strongly with the \( \pi \)-system of the top-graphene layer, providing a strong anchor to the electrodes. We deposit the molecules by placing the devices overnight in a chloroform solution containing 0.1 mM of 9Accm. After taking the devices out of the solution they are blow-dried by a flow of \( \text{N}_2 \). Atomic force microscopy indicates a sub-monolayer coverage of molecules on the graphite surface.

### References

FIGURE A.2: AFM characterization of the deposition on a reference sample shows that a sub-monolayer of molecules is formed on the devices.
APPENDIX: SUPPLEMENTARY INFORMATION CH.6
B.1 Low Temperature Characterisation

Some of the prepared devices display step-like features in the current-voltage characteristics at low temperatures (10 K). Of the 100 nm electrode-width devices, 2 out of 3 show step-like features and from both (see Fig. 6.3 and Fig. B.1) the step size has been determined (240 and 210 meV, respectively).

![Coulomb staircase behaviour](image)

**Figure B.1:** Coulomb staircase behaviour. The first derivative (\(dI/dV\)) of the current of a second 100 nm wide device that displays step-like features in the current-voltage characteristic. Grey arrows are equally spaced at 210 mV and illustrate the equidistant peaks in the differential conductance (most pronounced at positive bias). This spacing closely corresponds to that of the device displayed in Fig. 6.3. The hysteretic temperature dependence of the conductance at higher temperature of this device is displayed in Fig. 6.4b.

B.2 Temperature Dependence of Conductance

The temperature dependence of the conductance has been studied by taking current-voltage characteristics of the devices in the temperature-range of 300 - 400 K. In total five out of ten samples exhibit a sudden increase in conductance in the 350 - 380 K range. As displayed in Fig. 6.4 for two other devices, Fig. S4 shows the conductance (\(I/V\) at 0.4 V) as a function of temperature in the range 300 - 400 K for 3 devices. Similar to the two devices displayed in Fig. 6.4, raising the temperature results in a sudden increase of the conductance in the range 350 - 390 K. When subsequently lowering the temperature, the higher conductance state is
maintained for all three devices. However, only the device in Fig. B.1a recovers its original conductance state at lower temperatures (between 320 and 300 K). In the two other devices the increase in conductance is partially irreversible. Lowering the temperature further (recorded down to 200 K) does not yield the original state either. An irreversible change in conductance can be originating from changes in the nanoparticle itself (degradation) due to solvent- or surfactant-loss. Other possibilities lie in a change in the orientation of the nanoparticle between the electrodes when undergoing the magneto-mechanical switch.

**Figure B.2: Temperature-induced conductance switching.** **a,** Conductance (I/V at 0.4 V) as a function of temperature for a 1 µm wide electrode device. Each point is an average of 50 points taken as individual current-voltage sweeps. **b,** same as a, for a 1 µm device which undergoes a transition to higher conductance around 395 K. Lowering the temperature yields a conductance state higher than the original. Even at temperatures below 200 K (not shown), the original conductance state was not recovered. **c,** same as b, for a 100 nm wide electrode device. The transition to higher conductance is in this case located at 370 K.
The aim of molecular electronics is to address molecules electronically and in that way profit from their functionality. To manipulate and use properties of a molecule in such a device geometry, different probes can be used, including electrical, optical, or magnetic stimuli. In this thesis, different strategies to address molecular functionality in nanoelectronic devices will be presented, ranging from technological, conceptual and application driven approaches.

The first three chapters of this thesis focus on new strategies to address the functionality of a single molecule in an electronic device with an emphasis on room-temperature operation of such devices. To date, single-molecule experiments have mostly been carried using gold as the electrode material. Gold is preferred because of its noble character, but has such high atomic mobility that at room temperature the nanoelectrodes are unstable. For this reason, experiments are generally carried out at low temperatures, whereas for applications room-temperature operation is desirable.

In the first chapter of this section (chapter 2) we present a method to make Pt nanometer-spaced electrodes that are free of metallic particles and stable at ambient conditions. The nanogaps are fabricated using feedback controlled electromigration to form few-atom contacts. When performing this procedure at elevated temperatures (> 420 K), the Ptcontacts undergo self-breaking so that nanometer separated electrode pairs are formed. Once cooled down to lower temperatures, the nanogaps stabilize and can be characterized in detail. We find that current-voltage characteristics can be well fitted to a Simmons model for tunneling and gap-size fluctuations at room-temperature determined from these fits stay within 0.6 Ångström for at least 50 hours.

In chapter 3 we present the formation of single-molecule devices based on nanometer-spaced platinum electrodes, fabricated by the self-breaking electromigration method which was described in chapter 2. The stability of the devices at room temperature allows for detailed comparison of the electrical properties before and after deposition of the molecules. In this way, conductance as a result of direct tunneling between the electrodes can be distinguished from conductance through the molecule. After molecule deposition, some devices display transport in the strong coupling regime while others are in the weak-coupling Coulomb blockade regime. Gated transport is observed in the latter case.
In chapter 4 we conclude on the room temperature stability by using few-layer graphene as the electrode material. The nanogaps in the few-layer graphene are formed by feedback controlled electroburning, similar to the electromigration methodology used in chapter 2. The gaps have separations on the order of 1-2 nm as estimated from a Simmons model for tunneling. Depositing molecules inside the gap results in molecular junctions which display gateable IV-characteristics at room temperature, reminiscent of Coulomb-blockaded transport.

In chapter 5 we propose a new type of molecular motor based on electric field actuation and electric current detection of the rotational motion of a molecular dipole embedded in a three-terminal single-molecule device. The key aspect of this all-electronic design is the conjugated backbone of the molecule, which simultaneously provides the potential landscape of the rotor orientation and a real-time measure of that orientation through the modulation of the conductivity. Using quantum chemistry calculations, we show that this approach provides full control over the speed and continuity of motion, thereby combining electrical and mechanical control at the molecular level over a wide range of temperatures. Moreover, chemistry can be used to change all key parameters of the device, enabling a variety of new experiments on molecular motors.

In the second part of this thesis, we present experiments on nanoparticle-based electronic devices. Chapter 6 describes a new way of contacting individual nanoparticles based on a self-alignment fabrication method. The nanoparticles are based on spin-crossover molecules which can undergo a phase-transition as a function of temperature. This nanoscale device exhibits switching and memory effects near room temperature as a consequence of the intrinsic bistability of the spin-crossover nanoparticle. The magnetic bistability is interesting from the perspective of spintronic applications.

In the final chapter of this thesis, chapter 7, we present an efficient photodetector based on a one-dimensional array of PbSe quantum dots using the same self-aligned fabrication technique. In this new optoelectronic device-architecture, the electrodes act as optical nano-antennae which concentrate incident light into the nanoparticle junction where they are converted into electron-hole pairs. The excitons are extracted with high efficiency due to the fact that the quantum dots are in direct contact with both source and drain electrodes, in contrast to previous studies which employed large assemblies of quantum dots.
SAMENVATTING

Het doel van moleculaire elektronica is om moleculen elektronisch te adresseren om zodoende te profiteren van hun functionaliteit. Verschillende stimuli, van bijvoorbeeld elektrische, optische of magnetische aard, kunnen worden gebruikt om de eigenschappen van een molecuul in zo’n geometrie te kunnen manipuleren en gebruiken. In dit proefschrift worden verschillende strategieën gepresenteerd om de moleculaire functionaliteit in nano-elektronica te gebruiken, zowel op technologisch alsook op conceptueel vlak.

De eerste drie hoofdstukken van dit proefschrift focussen op nieuwe strategieën voor de ontwikkeling van enkele molecuul juncties met de nadruk op werking bij kamertemperatuur. Tot op heden zijn experimenten op enkele moleculen vooral uitgevoerd met goud als het elektrodemateriaal. Goud heeft de voorkeur vanwege zijn nobele karakter, maar heeft ook een hoge atomaire mobiliteit bij kamertemperatuur waardoor de nano-elektrodes instabiel zijn. Experimenten op enkele moleculen worden hierdoor over het algemeen uitgevoerd bij lage temperaturen, terwijl werking bij kamertemperatuur wenselijk is voor eventuele toepassingen.

In het eerste hoofdstuk van dit deel (hoofdstuk 2) presenteren we een methode om nanogaps te fabriceren uit platina, die vrij zijn van metalen deeltjes en stabiel op kamertemperatuur. De methode om de electrodes te maken is gebaseerd op feedback-gecontroleerde elektromigratie waarmee in eerste instantie enkele-atom contacten gevormd worden. Bij het uitvoeren van deze procedure bij verhoogde temperaturen (> 420 K), breken de Pt-contacten uit zichzelf, zodat nanometer afstanden tussen de elektrodes worden gevormd. Deze nanogaps stabiliseren zodra ze worden afgekoeld tot lagere temperaturen en kunnen dan in detail worden gekarakteriseerd. De elektrische karakteristieken kunnen worden gemodelleerd met een Simmons model voor tunneling. De fluctuaties in de elektrode afstand bij kamertemperatuur, bepaald op basis van dit model, blijven binnen 0.6 Angstrom voor ten minste 50 uur.

In hoofdstuk 3 presenteren we de vorming van enkele-molecuul juncties op basis van nanogaps platina-elektrodes, gefabriceerd met behulp van de elektromigratie methode die is beschreven in hoofdstuk 2. Dankzij de stabiliteit van de juncties op kamertemperatuur kunnen we de elektrische karakteristieken van voor en na de depositie van de moleculen in detail met elkaar vergelijken. Op deze manier
kan geleiding als gevolg van directe tunneling tussen de elektrodes worden onderscheiden van de geleiding door het molecuul. Na de molecuuldepositie laten sommige juncties transport in het sterke-koppeling gebied zien, terwijl anderen in het zwakke-koppeling Coulomb blokkade gebied zitten. In het geval van zwakke-koppeling is het transport gate-afhankelijk.

Hoofdstuk 4 vormt het laatste deel over kamertemperatuur-stabiliteit waarin we gebruik maken van enkel-laags grafeen als het elektrode materiaal. De nanogaps in het enkel-laags grafeen worden gevormd door feedback gecontroleerde elektroverbranding, vergelijkbaar met de elektromigratie methode die gebruikt wordt in hoofdstuk 2. De elektrode-afstand is in de orde van 1-2 nm zoals afgeleid op basis van een Simmons model voor tunneling. Depositie van moleculen in de junctie resulteert in gate-afhankelijke IV-karakteristieken bij kamertemperatuur, die doen denken aan transport in het Coulomb-blokkade regime.

In hoofdstuk 5 stellen we een nieuw soort moleculaire motor voor die werkt op basis van een door een elektrisch veld aangedreven moleculaire dipool in een enkel-molecuul junctie. Het belangrijkste aspect van dit volledig elektrische onttwerp is de geconjugeerde backbone van het molecuul, die tegelijkertijd het potentiële landschap van de rotor definiërt en ook een real-time meting van die oriëntatie toestaat door middel van de modulatie van de geleidbaarheid. Met behulp van kwantumchemie berekeningen laten we zien dat deze aanpak een volledige controle over de snelheid en continuïteit van de beweging biedt. Bovendien kan de synthetische chemie worden gebruikt om de belangrijkste parameters van het molecuul te wijzigen, waardoor een groot aantal nieuwe experimenten op moleculaire motoren mogelijk wordt.

In het tweede deel van dit proefschrift presenteren we experimenten met elektronica gebaseerd op nanodeeltjes. Hoofdstuk 6 beschrijft een nieuwe manier om elektrisch contact te maken met individuele nanodeeltjes waarbij gebruik wordt gemaakt van een self-alignment fabricage methode. De nanodeeltjes zijn gebaseerd op spin-crossover moleculen die een fase-overgang als een functie van de temperatuur ondergaan. Dit device vertoont geheugen effecten bij kamertemperatuur als gevolg van de intrinsieke bistabiliteit van het spin-crossover nanodeeltje. De magnetische bistabiliteit is interessant voor toepassingen in de spintronica.

In het laatste hoofdstuk van dit proefschrift, hoofdstuk 7, presenteren we een efficiënte lichtsensor die gebaseerd is op een één-dimensionale rij van PbSe quantum dots waarbij we gebruik maken van dezelfde self-aligned fabricage techniek. In deze nieuwe opto-elektronische architectuur fungeren de elektroden als optische nano-antennes die het invallende licht concentreren op de nanodeeltjes in de junctie waar ze vervolgens worden omgezet in excitonen. De excitonen worden met een hoge efficiëntie geëxtraheerd als gevolg van het directe contact van de quantum dots met beide elektrodes.