

1 Title of the project

The influence of metal-molecule coupling on charge transport in a single molecular switch.

2 Applicants

Everardus Hendrik Huisman

References

Bachelor thesis

$Y_{1-x}Ca_xVO_3$; The influence of Ca-doping on orbital ordering?
Rijksuniversiteit Groningen, The Netherlands 2002

Paper

Light-driven molecular motors
Rijksuniversiteit Groningen, The Netherlands 2003

Intership thesis

Electrical Spin Injection in an InGaAs 2-DEG
Basic Research Laboratories, NTT, Atsugi, Japan 2004

Master thesis

Towards Spin Injection in Pentacene Thin Films
Rijksuniversiteit Groningen, The Netherlands 2005

3 FOM-researchgroup

G-08

4 Institute

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5 Abstract

We propose to investigate the electronic properties of both photochromic and redox-driven molecular switches. We aim to make a molecular junction with a *single* molecule using the mechanical controllable break junction (MCBJ) technique and scanning tunneling microscopy (STM). Focus of our research will be the influence of coupling between the molecule and the metallic leads on electronic transport properties. The coupling with the leads will be systematically changed by chemically modifying our molecules. Transport measurements include conductance measurements and inelastic electron tunneling spectroscopy (IETS). Both MCBJ and STM allow measurements of a large number of molecular junctions, such that statistical analysis of data is possible. In our project, we will strongly profit from collaborations with chemistry and physics groups within and outside our institute.

6 Duration of the project

4 years, starting October 2005.

7 Personnel

7.1 Senior-scientists

Name	Task in project	Time
Prof. Dr. Ir. B.J. van Wees	Supervision and management	5%
Dr. Ir. S.J. van der Molen	Supervision and analysis	20%
Prof. Dr. J.C. Hummelen	Supervision and management	5%
Prof. Dr. B.L. Feringa	Supervision and management	5%

7.2 Junior-scientists and technicians

Name	Task in project	Time
drs. E.H. Huisman	Experiments and analysis	90%
drs. T. Kudernac	Synthesis light-driven switches	20 %
Hummelen based researcher	Synthesis redox-driven switches	10 %
B. Wolffs	technical support	10%
Ing. S. Bakker	technical support	5 %

8 Cost-estimates

8.1 Personnel positions

One 'onderzoeker in opleiding' position for four years.

8.2 Running Budget

15 k€/year

8.3 Equipment

In order to measure the redox-driven switches, we need syringe pumps and a MCBJ setup in solution. Also, we would like to purchase a probe station with a microscope to contact and inspect the break junctions.

Equipment	Costs
MCBJ set-up in solution	5 k€
3 Syringe pumps	1 k€
Probe station	10 k€
TOTAL	16 k€

8.4 Other support

The project is part of a larger research programme of the MSC^{plus}. Except for the 'onderzoeker in opleiding' position, personnel described above is employed via the MSC^{plus} or with money from associated research programmes.

8.5 Budget summary (in k€)

	2005	2006	2007	2008	2009	TOTAL
Personnel (positions)						
PhD students	0.25	1	1	1	0.75	4
postdocs	-	-	-	-	-	-
technicians	-	-	-	-	-	-
guests	-	-	-	-	-	-
personnel(costs)	10.25	41	41	41	30.75	164
running budget	3.75	15	15	15	11.25	60
equipment FOM-part	16	-	-	-	-	16
TOTAL(requested from FOM)	30	56	56	56	42	240

9 Research programme

9.1 Introduction

Recent advances in nanolithographic techniques and self-assembly have made it possible to measure the electronic properties of a single molecule. Molecules are the smallest building blocks thinkable for electronic devices and allow a true bottom-up design of electronic circuits. Organic chemistry allows tune ability of electronic properties at the smallest scale. Therefore, single molecule electronics provides an alternative route for designing electronic circuits. Recently, the field of single molecule electronics has gained a lot of research activity. However, the successful integration of a single functional and addressable molecule in an electronic device is still unaccomplished and will be an important step forward. We propose to realize such a device.

9.2 Goal of the project

Our group focuses on molecular switches, *i.e.* molecules that can reversibly switch between a conductive and a non-conductive state. In solution, switching between the two states can be controlled by applying external stimuli. However, few is known about the operation of molecular switches when attached to metal surfaces. Attaching *one* molecule to two electrodes is challenging. Recently, our group showed reversible switching of a photochromic switch attached to a gold surface [1] and one-way switching of the same kind of switch when attached to two gold electrodes in a break junction [2]. Our first aim is to obtain reversible switching in a molecular junction, such that electrical transport measurements can be performed. Our second aim is to investigate the influence of the metal-molecule coupling on the conductance of a single molecule.

Strong coupling, meaning strong overlap between the wave functions of the molecule and the metal electrodes, leads to broadening of the molecular energy levels. The electrical properties of a molecule are expected to be dependent on the coupling. For example, it has been shown that by changing end groups of molecules one can go from tunneling (strong coupling) to Coulomb blockade (weak coupling) [3]. To change coupling, one can either change the electrode materials, the molecule itself or the anchor groups connecting the molecule with the electrodes. It is our aim to obtain a set of molecular junctions in which the coupling is systematically changed. Below we discuss several approaches to come to such a set.

9.3 Molecular switches

Other approaches for determining electronic properties of a single molecule often focus on molecules without any functionality. From electrical measurements alone it is hard to judge whether one has contacted several molecules or just one. Therefore, contacting of just one single molecule between two electrodes has proved to be delicate. Using addressable switching gives an excellent way of verifying

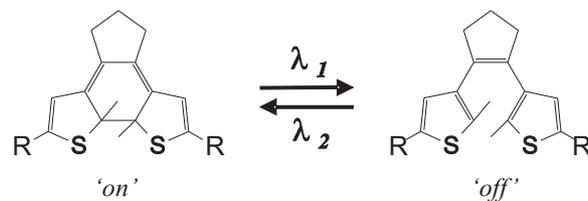


Fig. 1: Diarylethene photochromic switch, also called an Irie switch [4]. The molecule can be switched from the closed form (left) to the open form (right) by applying light of different wavelengths. By switching, the conjugated path of the molecule is changed from fully conjugated (left) to cross-conjugated (right). R denotes a chemically adjustable group.

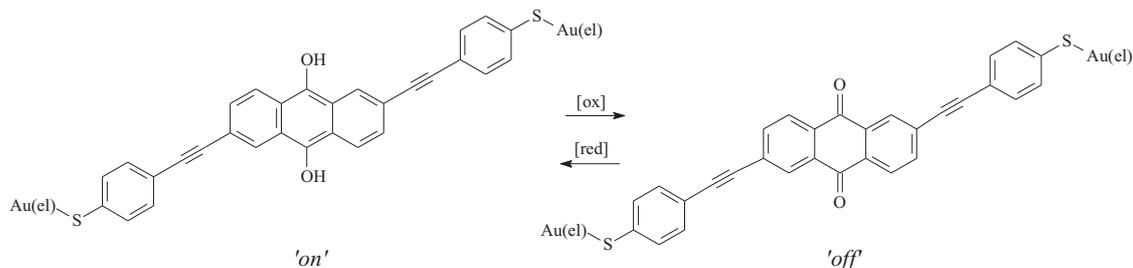


Fig. 2: Example of a redox-driven switch. Note that the conjugated path is broken again upon switching. The ethyn spacers between the redox active central part and the spacers provide rigidity. Switching can only be addressed by redox agents in solution.

the presence of only one molecule in between contacts, since one molecule should give rise to switching between two states only. When switching between multiple states is observed, multiple molecules are contacted.

We aim to investigate two kinds of switches: photochromic and redox-driven switches. Photochromic switches can be addressed both in solution and in vacuum. Redox-driven switches can only be addressed in solution. An example of a photochromic switch is given in figure 1. This diarylethene switch is known for its robustness and excellent reversible switching behavior in solution. Our group already has a lot of experience with this kind of switch [1] [2]. In the so-called 'ON' state, the molecule is fully conjugated. Conjugation is the alternation of single and double carbon-carbon bonds which results in delocalization of π -electrons over the molecule. The resistance of this switch is about $1\text{M}\Omega$ in the 'ON' state and several hundred $\text{M}\Omega$ in the 'OFF' state [2]. In the 'OFF' state, the molecule is cross-conjugated and two successive single carbon bonds are present. The molecule can be switched between the two thermodynamically stable forms by applying light of different wave lengths. The two thiophene units of the switch in the 'ON' state lie in the same plane. In the 'OFF' state the two groups are slightly tilted with respect to each other.

An example of a redox-driven switch is given in figure 2. The molecule can be reversibly switched in solution by applying redox agents. Oxidation of the hydroxy group to a ketone group will change the conjugated path from fully conjugated ('ON') to cross-conjugated ('OFF') without changing the length of the molecule. The ethyn ($\text{R-C}\equiv\text{C-R}$) bridges between the central 'anthracene' unit and the phenyl groups are introduced to facilitate contacting and are well known for their rigidity. The usage of redox-processes provides an alternative approach and can circumvent problems specific for light induced switching, such as light absorption of the gold-plasmon and low quantum yields of molecules in molecular junctions.

Chemistry provides an excellent way to tune the coupling of a molecule to the metal electrodes. Figure 3 shows a series of photochromic switches in which the coupling to the electrodes is changed by modifying the side group of the photochromic switch. Our 'standard' photochromic switch **1** consists of a switching central part with a thiophene ring ($\text{R-C}_4\text{SH}_3$) on each side. This molecule shows one-way switching when connected to gold surfaces [2]. By replacing the thiophene moieties by phenyl rings ($\text{R-C}_6\text{H}_5$), switch **2** is obtained. This molecule switches reversibly between the closed and open

form when attached to gold [1]. The thiophene and phenyl rings also tune the frequency of absorption. The observation of reversible switching upon changing the side group might indicate that the molecule gets less coupled to the gold. By introducing additional phenyl spacers in between the molecule and the electrodes, we obtain switch **3** which is slightly decoupled with respect to **2**. Two phenyl rings connected via a single carbon-carbon bond are weakly tilted with respect to each other due to sterical hindrance caused by the hydrogens present on the phenyl rings. The tilting might even be enhanced by substituting a hydrogen by a methyl (R-CH₃) group on the phenyl rings. Another mild way of decoupling is to introduce an ethyn group in between the photochromic central part and the phenyl group. Switch **4** is expected to be slightly more decoupled than switch **3**, since the ethyn spacer will induce a bigger angle between the plane of the phenyl group and the plane of the central part. Decoupling in this way will probably affect the optical absorption of the switch as well. Switch **5** uses a more rigid way of decoupling and completely destroys the conjugated path by introducing single bonds by alkyl spacers. Switching of **5** with a fluorinated central cyclopentene has been reported by Lindsay *et al* [5]. Decoupling in this way can be extended by introducing more alkyl spacers, see switch **6**. The influence of side groups on the on-off conductance ratios has been theoretically investigated by Sankey *et al.* [6]. Sankey reported a maximum on-off ratio of 109, 47 and 16 for switch **1**, **2** and **6**, respectively.

An alternative approach to change the coupling is to fabricate junctions with different metal-anchor groups. A wide spectrum in molecule-electrode coupling can be obtained by choosing the right combination of metal and anchor groups. So far, we fixed the anchor group metal combination to gold and thiols (R-S-H). The dynamics and physics of this self-assembly are well known and have been studied extensively, also within our institute. Alternative metals such as platinum, silver and palladium change the coupling due to a change in work function and different binding energies with the anchor groups. Alternative anchor groups such as the selenols (R-Se-H) [7] and the tellurols (R-Te-H) [8] are alternatives for thiols (R-S-H) with similar chemistry (though very toxic!). Also, the amine group (R₁R₂NH₂) [9] and the isocyanides (R-NC) [10] [11] provide alternatives. The exact influence of different anchor groups on the conductance is not completely known. However, two independent theoretical studies predict a significant increase in the conductance while replacing thiol anchor groups by selenol and tellurol anchor groups [12] [13]. The latter even predicted conductance close to the quantum limit ($2e^2/h$) in the case of a relatively simple molecule (benzeneditellurol). We would like to determine the influence of changing the anchor groups experimentally. Figure 4 gives a series of redox-driven switches in which the coupling is decreased due to the anchor groups. These anchor groups can also be attached to the photochromic switch.

9.4 Measurement techniques

Our group has expertise in electrical lock-in measurements, which allow accurate measurements of the first and second derivative of the current to the voltage. The first derivative of current to voltage, or differential conductance, can be used to study the influence of coupling to the charge transport properties. The second derivative of current to voltage gives direct information on the vibrational modes of the molecular junction. This technique is also known as inelastic electron tunneling spectroscopy (IETS). By using theoretical modeling we can contribute the peaks to specific vibration modes. By comparing these spectra with vibrational spectra of the molecules on a surface (Raman spectroscopy and IR-spectroscopy) or in solution (IR-spectroscopy) we can determine the influence of the gold electrodes and extract indications for selection rules for IETS vibrational modes.

9.5 Fabrication techniques

We consider two techniques to fabricate molecular junctions: the molecular controllable break junction (MCBJ) technique and Scanning Tunneling Microscopy (STM). Both techniques will be discussed below. In figure 5, a scanning electron micrograph of a home-made MCBJ is displayed. When the substrate containing this device is bent, the central bridge elongates and breaks, resulting in two gold contacts. The distance between these nanocontacts can in principle be tuned within 10 pm, so that molecules can be inserted in between (see below) [14]. Thanks to a collaboration with Prof. Van

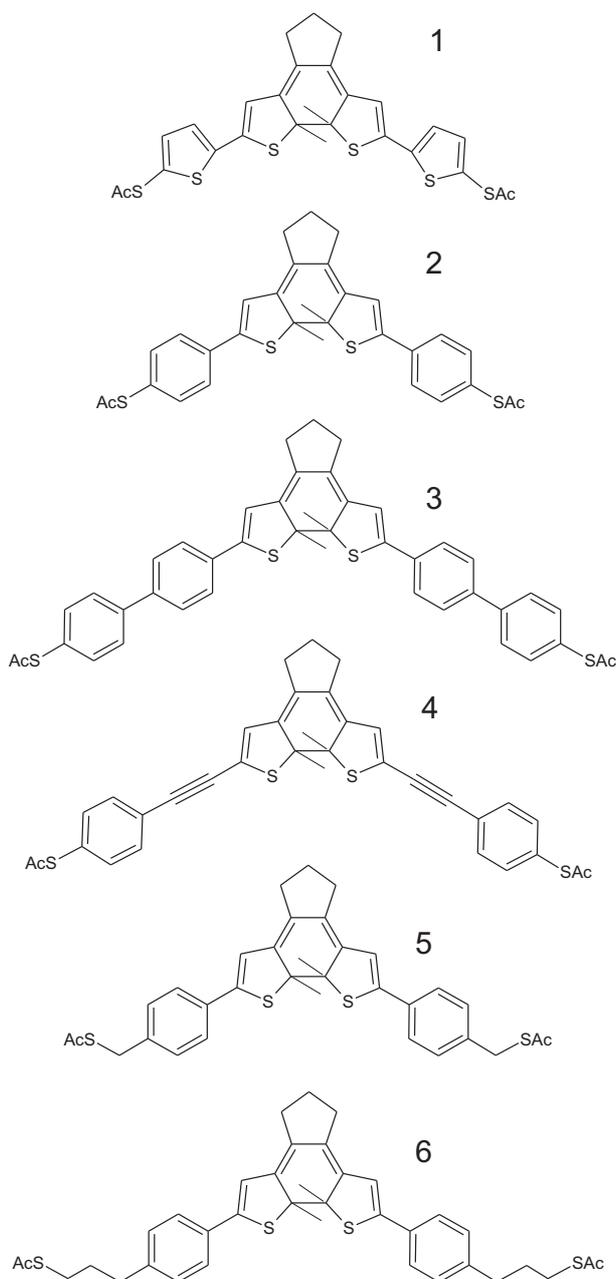


Fig. 3: Chemical modification of a diarylethene switch in the closed ('ON') state in order to modify the coupling of the switch to the electrodes. Coupling is expected to decrease in this series. **1**) The standard switch with thiophene side groups. **2**) The standard switch with phenyl side groups. **3**) Weakly decoupled switch by introducing an additional phenyl group. Steric hindrance of hydrogen atoms on the phenyl groups might cause tilting of the two groups with respect to each other. **4**) Other way of decoupling, the ethynyl group is placed in between the switching central unit and the phenyl moiety. This way of decoupling will probably affect the light absorption of the photochromic unit, but is expected to decouple less than **5**). **5-6**) Standard switches with increased decoupling due to alkyl spacers, which are expected to strongly decouple from the electrodes. NB: Ac means an acetyl group (R-COCH₃).

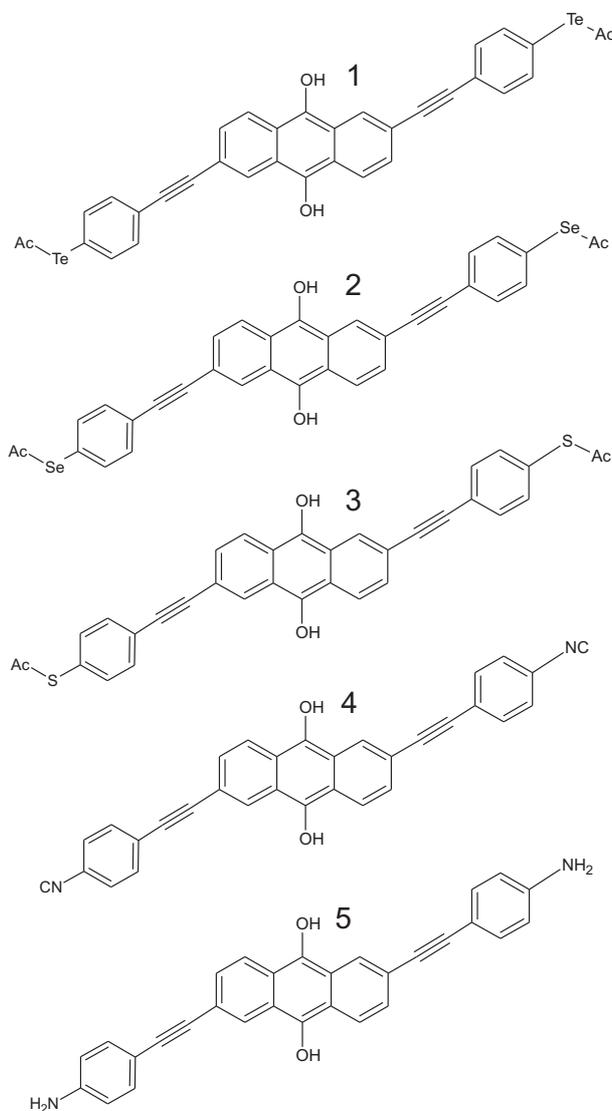


Fig. 4: Modification of the anchor groups in a redox-driven switch in the closed ('ON') state in order to change the coupling of the switch to the electrodes. Coupling is expected to decrease in this series. **1**) Redox switch with sulfur replaced by Te. **2**) Redox-driven switch with sulfur replaced by Se, which is expected to conduct less than **4** [13], but better than **3** [7]. **3**) Standard redox switch. **4**) Switch with isocyanide group, coupling is expected to be weaker than **3** **5**) Switch with primary amine group. The amine-metal bond is expected to be very weak and proper solvents have to be chosen.

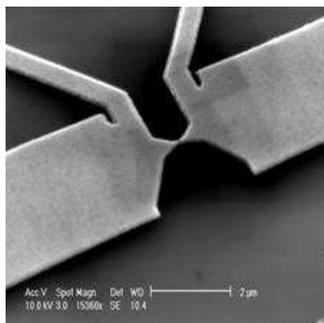


Fig. 5: Scanning electron micrograph of a break junction, showing a free-hanging gold bridge. When the substrate containing this device is bent, the bridge elongates and breaks, so that two contacts are created. The distance between the contacts can be tuned within 10 pm.

der Giessen, the micromechanics of break junctions is well understood, accounting for deviations we observed in previous distance calibration experiments [15]. We will use this knowledge to perfect break junction control in the future. One can apply stress to the molecule in break junction experiments which might be very interesting for IETS measurements to distinguish between backbone and side-group vibrations. Several approaches to implement a gate in break junctions have already been discussed in literature such as the usage of the solvent [16] [17] and the usage of highly doped silicon as gate electrode [18]. We also aim to implement a gate. By repetitively opening and closing break junctions, thereby connecting a (new) molecule each time, one can perform statistics on a larger data set. We are already able to perform break junction experiments at ambient condition in solution and in a vacuum of $p=10^{-6}$ mbar at room temperature and in a cryogenic vacuum at 77K and 4.2K. We are also planning to build a cryostat with an optical setup¹. In order to control switching of the redox-driven switch, we need to build a MCBJ setup in solution in which the concentration of the redox agents can be changed (see section 8.3). Implementation of a break junction in a cryostat enables temperature dependent measurements over a large temperature range. Optical control of switching can be obtained by using a laser or an optical fiber. Frequency doublers can be used to reach the required wavelengths and pulsed signals can prevent heating.

STM measures a convolution of topology and electrical properties of a conductive substrate. By self-assembling switches on a gold surface, a layer of single molecules can be measured with STM. By diluting the switches in a layer of a self-assembled monolayer of non-conductive molecules, one can even observe switching of single molecular switches [1]. So far, our group has been measuring STM at room temperature. By using an STM setup in an ultra high vacuum chamber ($p \leq 10^{-9}$ mbar) and at low temperatures one has better stability and less thermal noise. If one uses a metal colloid attached to the tip or the appropriate metal tip one can really electrically measure a single molecule. Again by repetitive performing measurements, for example by constantly changing the height of the tip, one can obtain large data sets. The implementation of a gate electrode in STM experiments is hard.

9.6 Collaborations

In our project two chemistry groups, the group of prof. Hummelen and the group of prof. Feringa, are responsible for the synthesis and modification of the redox-driven and photochromic molecules, respectively. Our group is responsible for the preparation of the molecular junction and the electronic characterization. The intensive and well defined cooperation between chemistry groups and physics groups within our institute, the Material Science Center^{plus} (MSC^{plus}) of the Rijksuniversiteit Groningen (RuG), defines another strong point of our research. The mission of MSC^{plus} is the design and scientific study of materials for functionality. The MSC^{plus} was selected by the Dutch National Science Foundation (NWO) as a National Research Center. The MSC^{plus} unites chemists, physicists and biologists and research has a strong interdisciplinary character. This is also strongly reflected in

¹ The cryostat with optical control and low temperature STM are part of a broader project than discussed here and will be financed differently.

this project.

We have, and are planning to set up, several collaborations outside our institute. We recently set up a collaboration with the group of professor Schönenberger of the university of Basel, Switzerland. In this project we will focus on the how to implement our photochromic molecular switch in a regular array of gold colloids. Furthermore, there is a collaboration with the group of professor Bourgoin in Saclay, France. This collaboration has focused on low temperature break junction experiments with our photochromic molecular switch. In the future we would like to have a cooperation in theoretical modeling of our molecules to attribute IETS peaks to specific vibration modes [19]. Also, an important issue to consider with theoreticians is the discrepancy between theoretical predictions of the conductance (typically several k Ω s) [6] [13] and the conductance of a molecule measured in experiment (typically 1 M Ω) [2].

10 Infrastructure

The physics of nanodevices group has a variety of processing and measuring facilities. For this project the most important facilities are:

- A clean room equipped with general processing facilities such as a mask aligner, an e-gun evaporator and a reactive ion plasma etcher;
- A Raith e-line electron beam lithography system;
- A JEOL inspection scanning electron microscope;
- A MCBJ setup for experiments in solution at room temperature with measurement equipment such as lock-in amplifiers, multimeters, amplifiers etc.;
- A MCBJ setup for experiments in vacuum at liquid nitrogen and liquid helium temperatures with measurement equipment such as lock-in amplifiers, multimeters, amplifiers etc.;
- A digital instruments Nanoscope IV room temperature scanning probe microscope.

We are planning to extend our measurement facilities by realizing:

- A scanning tunneling microscope at low temperatures in ultra high vacuum with an optical setup (this setup is not included in this proposal and will be financed by other means);
- A MCBJ setup for experiments in solution at room temperature in which the concentration of the solutes can be changed;
- An optical cryostat (4-300K) with atmosphere control and an optical setup (this setup is not included in this proposal will be financed by other means).

11 Application perspective in industry, other disciplines or society

Molecular switches can have all kinds of applications. Switches on surfaces and in liquid crystalline phases can be used to modify properties of surfaces and bulk such as reflectivity, transparency, color and hydrophobicity [20]. Single molecular switches might for example be used in a memory device. Still, for both redox-driven and photochromic switches local addressability of two different switches is a problem. For redox-driven switches this is due to difficulties in creating locally a concentration gradient and in photochromic switches this is due to the wavelength of photons compared to the molecules. However, it has been shown that the switching of our photochromic switch can also be controlled electrically [21].

12 References

References

- [1] N. Katsonis, T. Kudernac, M. Walko, S. J. van der Molen, B. J. van Wees, and B. L. Feringa, "Reversible light-controlled conductance switching of single photochromic molecules on gold," *submitted to Phys. Rev. Lett.*, p. ., 2005.
- [2] D. Dulic, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, and B. J. van Wees, "One-way optoelectronic switching of photochromic molecules on gold," *Phys. Rev. Lett.* **91**, pp. 207402–1, 2003.
- [3] S. Kubatkin, A. Danilov, M. Hjort, J. Cornil, J. Brédas, N. Stuhr-Hansen, and P. Hedegaard, "Single-electron transistor of a single organic molecule with access to several redox states," *Nature* **425**, p. 698, 2005.
- [4] M. Irie and M. Mohri, "Thermally irreversible photochromic systems. reversible photocyclization of diarylethene derivatives," *J. Org. Chem.* **53**, p. 803, 1988.
- [5] J. He, F. Chen, P. A. Liddell, S. D. Andréasson, J. andStraight, D. Gust, T. A. Moore, A. L. Moore, O. F. Li, J. andSankey, and S. M. Lindsay, "Switching of a photochromic molecule on gold electrodes: single-molecule measurements," *Nanotechnology* **16**, p. 695, 2005.
- [6] J. Li, G. Speyer, and O. F. Sankey, "Conduction switching of photochromic molecules," *Phys. Rev. Lett.* **93**, pp. 248302–1, 2004.
- [7] L. Patrone, S. Palacin, J. Bourgoin, J. Lagoute, T. Zambelli, and S. Gauthier, "Direct comparison of the electronic coupling efficiency of sulfur and selenium anchoring groups for molecules adsorbed onto gold electrodes," *Chemical Physics* **281**, p. 325, 2002.
- [8] M. Brust, N. Stuhr-Hansen, K. Nørsgaard, J. B. Christensen, L. K. Nielsen, and T. Bjørnholm, "Langmuir-blodgett films of alkane chalcogenide (s,se,te) stabilized gold nanoparticles," *Nanoletters* **4**, p. 189, 2001.
- [9] J. R. Heath, C. M. Knobler, and D. V. Leff, "Synthesis and characterization of hydrophobic, organically-soluble gold nanocrystals functionalized with primary amines," *Langmuir* **12**, p. 4723, 1996.
- [10] S. L. Horswell, C. J. Kiely, I. A. O Neil, and D. J. Schiffrin, "Alkyl isocyanide-derivatized platinum nanoparticles," *J. Am. Chem. Soc.* **121**, p. 5573, 1999.
- [11] J. I. Henderson, S. Feng, T. Bein, and C. P. Kubiak, "Adsorption of diisocyanides on gold," *Langmuir* **16**, p. 6183, 2000.
- [12] S. Yaliraki, M. Kemp, and M. A. Ratner, "Conductance of molecular wires: Influence of molecule-electrode binding," *J. Am. Chem. Soc.* **121**, p. 3428, 1999.
- [13] M. Di Ventra and N. D. Lang, "Transport in nanoscale conductors from first principles," *Phys. Rev. B.* **65**, pp. 045402–1, 2001.
- [14] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, "Conductance of a molecular junction," *Science* **278**, p. 252, 1997.
- [15] S. A. G. Vrouwe, E. van der Giessen, S. J. van der Molen, D. Dulic, and B. J. van Wees, "Mechanics of lithographically defined break junctions," *Phys. Rev. B.* **71**, p. 35313, 2005.
- [16] B. Q. Xu, X. L. Li, Y. Xiao, X. H. Sakaguchi, and N. Tao, "Electromechanical and conductance switching properties of single oligothiophene molecules," *Nanoletters* **5**, p. 1491, 2005.

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- [17] L. Gruter, M. Gonzalez, M. Calame, and C. Schonberger, “Electrical conductance of atomic contacts in liquid environments,” *aprx*, p. 0410666 v2, 2005.
- [18] A. R. Champagne, A. N. Pasupathy, and D. C. Ralph, “Mechanically adjustable and electrically gated single-molecule transistors,” *Nanoletters* **5**, pp. 305–308, 2005.
- [19] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H. B. Weber, and M. Mayor, “A single-molecule diode,” *PNAS* **102**, p. 8815, 2005.
- [20] J. Bernal, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. Pérez, P. Rudolf, G. Teobaldi, and F. Zerbetto, “Macroscopic transport by synthetic molecular machines,” *Nature Materials on-line* **aug.**, p. doi:10.1038/nmat1455, 2005.
- [21] T. Tsujioka and H. Kondo, “Organic bistable molecular memory using photochromic diarylethene,” *Appl. Phys. Lett* **83**, p. 937, 2003.