

# *Incorporation of Molecular Switches in Large-Area Molecular Junctions*

Master Thesis by:  
Auke Jisk Kronemeijer

Supervised by:  
Prof. Dr. Ir. P. W. M. Blom  
Dr. B. de Boer  
Ir. H. B. Akkerman

July 2006



---

## Abstract

In this thesis, large-area molecular junction were processed with two different photochromic switches, entitled the meta-phenyl and the thiophene switch. These switches exhibit two different stable states, a conjugated (ON) and a non-conjugated (OFF) state, with different electronic transport properties. The switches can be turned from one state to the other by exposure to light of specific wavelengths.

The ON/OFF ratio between current densities through devices with the meta-phenyl switch is around a factor 3 at 0.75 V. Both devices with the conjugated and non-conjugated switches resulted in temperature independent  $I$ - $V$  characteristics which indicates tunneling as the dominant transport mechanism for both states. Furthermore, the conductance of these devices can be changed upon UV irradiation and by applying a bias, while devices without switches show no difference after these operations. After VIS irradiation, however, no change was observed, making the meta-phenyl switch optically unidirectional.

Devices with the thiophene switch resulted in similar characteristics as the meta-phenyl switch. The current densities were somewhat higher for both states and the ON/OFF ratio smaller. It was not possible to change the conductance of these devices upon UV and VIS irradiation.

---

# Contents

<b>Abstract</b>	<b>2</b>
<b>Introduction</b>	<b>4</b>
<b>1 Theoretical Background</b>	<b>5</b>
1.1 Molecular Conduction . . . . .	5
1.2 Molecular Switches . . . . .	5
1.3 Self-assembled Monolayers . . . . .	6
1.4 Large-area Molecular Junctions . . . . .	6
<b>2 Experimental</b>	<b>8</b>
2.1 Device Fabrication . . . . .	8
2.2 I-V Measurements . . . . .	9
2.3 Irradiation of the Devices . . . . .	9
<b>3 Experimental Results for the Meta-Phenyl Switch</b>	<b>10</b>
3.1 The Meta-Phenyl Switch . . . . .	10
3.2 Characterisation of the Open State . . . . .	10
3.3 Characterisation of the Closed State . . . . .	12
3.4 Comparison Open and Closed State . . . . .	14
3.5 UV Irradiation of the Devices . . . . .	15
3.6 Capacitance measurements . . . . .	17
3.7 VIS Irradiation of the Devices . . . . .	18
3.8 Electrochemical Switching . . . . .	18
<b>4 Experimental Results for the Thiophene Switch</b>	<b>20</b>
4.1 The Thiophene Switch . . . . .	20
4.2 Characterisation of the Open State . . . . .	20
4.3 Characterisation of the Closed State . . . . .	21
4.4 Comparison Open and Closed State . . . . .	22
4.5 Switching in the Molecular Junctions . . . . .	23
<b>5 Summary and Conclusion</b>	<b>24</b>
<b>Acknowledgements</b>	<b>26</b>
<b>References</b>	<b>26</b>

---

## Introduction

In present day technology, the miniaturization of electronic devices faces a huge challenge since conventional silicon technology is reaching its limits. To ensure that Moore's law is obeyed, which states that the number of transistors on integrated circuits double every 18 months, other solutions have to be exploited. Since the theoretical study of Aviram and Ratner in 1974 predicting a single molecule functioning as a diode<sup>1</sup>, the field of *Molecular Electronics* has received much attention. From that time scientist have been searching to develop methodologies and processing schemes for measurement templates to determine the electronic properties of single molecules or an ensemble of molecules, since molecules are advantageous in their size together with the diversity which can be obtained by chemical synthesis. Yet it has taken around two to three decades since the 1974's publication to develop the first experimental setups to measure the properties of molecules.

One of these methods is based on the development of scanning probe microscopy techniques. By using STM (scanning tunneling microscopy) or CP-AFM (conducting-probe atomic force microscopy) to contact molecules that are self-assembled on a conducting surface (e.g., gold), currents through these molecules can be measured by applying a potential between surface and tip<sup>2</sup>. A disadvantage of these techniques is that the contact area between tip and surface is unknown and thus the number of molecules contributing to the current. Furthermore, in STM an additional tunnel gap is created since the STM tip is hovering above the self-assembled monolayer (SAM). Another method is to use an electrically or mechanically controllable break junction to separate two electrodes from each other in such a way that a gap of the size of a molecule is formed in between<sup>3,4</sup>. A problem with this technique is the reproducibility of one junction. In general, however, statistics can be done to determine the properties of the molecules used.

A very interesting other approach is defining junctions in so-called via holes or vertical interconnects<sup>5</sup>. In these holes, which are determined by (electron beam)lithography, a self-assembled monolayer (SAM) is created on the underlying substrate. Then by special, indirect evaporation of the top contact, molecular junctions are formed with a predetermined area. Direct evaporation of a metal top contact on the SAM is not possible since this results in penetration of the metal into the SAM resulting in shorts<sup>6</sup>.

This concept of via holes has been further exploited more recently<sup>7</sup>. A processing flow chart has been designed to easily make two-terminal devices with a SAM as active component. At the moment, only insulating alkanes and some more conducting molecules have been measured. This research is an extension of the measurements on these alkanes to show proof-of-principle conductance switching to produce devices of which the current in the devices can be altered by means of an external stimulus such as irradiation. For this, devices with molecular switches as an active component have been fabricated and characterized.

## 1.1 Molecular Conduction

As already mentioned in the introduction, only relatively recent measurements are performed on molecules regarding their conduction. General observations conclude that tunneling is the main conduction mechanism, whether the molecule is saturated or conjugated, however in the absolute magnitude of the currents measured are still some discrepancy between the different measurement methods<sup>8</sup>.

Also it is still in debate what is the tunneling pathway. Electrons can tunnel directly from one contact to another through vacuum via the shortest pathway with the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) as the barrier height. Also electrons can tunnel through the molecules, which are not always aligned with the shortest pathway. Tunneling then occurs through HOMO or LUMO.

Theoretically, the description of the conduction through molecules is based on a description of thin dielectric films between two contacts. The most commonly used model is the so called Simmons model, already postulated in 1963<sup>9,10</sup>. Other models are also proposed<sup>11</sup>, however, the biggest challenge in the description of tunneling through molecules seems to be the determination or calculation of the potential barrier shape.

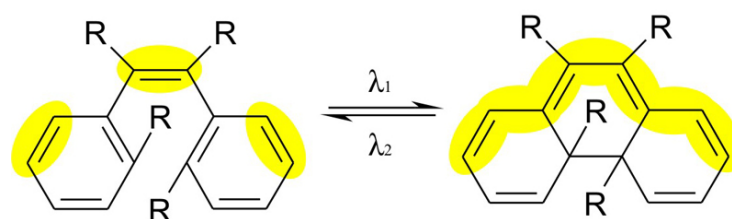
Experimentally, the tunneling current depends exponentially on the applied bias and is independent of temperature<sup>9</sup>. Therefore, temperature dependent measurements are widely used to determine whether an observed current is due to tunneling or caused by another conduction mechanism.

## 1.2 Molecular Switches

The most important part of the molecular electronic devices are of course the molecules. In this study molecular switches are used, which are essentially molecules that are stable in two different states and can be driven externally from one state to another and back. Many different molecular switches are known.

One interesting class of molecular switches are the diarylethenes<sup>12</sup>. These class of molecules are photochromic compounds. Photochromic compounds can be reversible turned from one state to another by exposure to light of specific wavelengths. The transition in the diarylethenes is ring opening or closure in the middle of the molecule, shown in Figure 1.1.

An interesting other feature of this group of molecules is that during the transition, the conjugation between both ends of the molecules is changed. In the open form, there is no complete conjugation while it is present in the closed form. The consequence of this is that the electrical conductance of the molecules (if there is anything like molecular conduction) is changed or at least the conductance of a junction containing the molecules since the tunnel barrier is changed. The kinetics of both transitions differs in terms of their quantum yields. This quantity illustrates how efficient the transition is. The quantum efficiency specifies the chance that the transition



**Figure 1.1:** Photochromic moiety diarylethene. Ring closure and opening can be achieved by exposure to two different wavelengths. The conjugation throughout the molecule is also switched during the ring closure and opening.

occurs when one photon is absorbed by the molecule. Since there is always a chance that the molecule returns to its original state, the efficiency is always smaller than one. In general the quantum efficiency of the ring closure is higher than the ring opening<sup>13,14</sup>. This means that ring closure is more easily achieved than ring opening. In general, when the transition energy is lower, the efficiency is decreased. The transition energy from closed to open state is lower, because an initially excited state of the molecule has to be reached. Since the closed form is conjugated, the energy gap between the HOMO and LUMO is smaller and so it takes less energy to send an electron from this HOMO into the LUMO, producing an excited molecule.

### 1.3 Self-assembled Monolayers

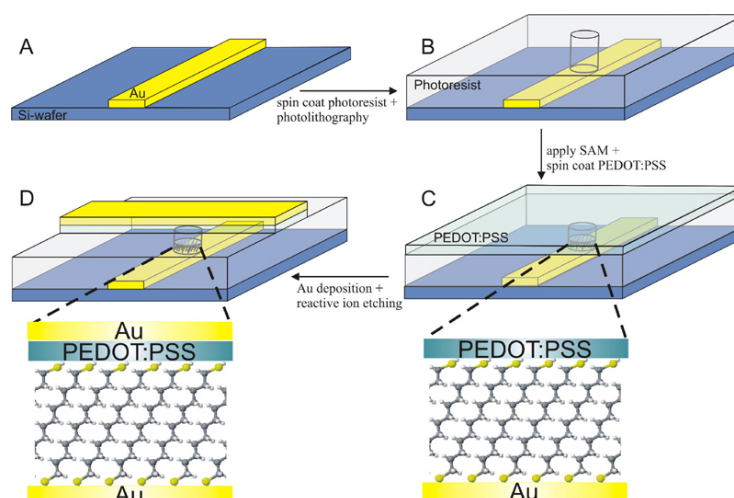
Two key components in molecular junctions are the formation of molecular monolayers and making contacts to these layers. Self-assembled Monolayers (SAMs) are ordered structures which consist of a single layer of molecules attached to a substrate. Often, these substrates are metals, e.g. , gold. The two key ingredients for molecular devices are intrinsic to SAMs. Also, SAMs are easy to produce since the molecules assemble themselves on the surface. A substrate in a solution with the desired molecules is enough to grow a SAM. Also SAMs can have a wide range of properties since the molecular structure can be easily altered. Many different combinations of substrates and molecular endgroups are known to produce ordered SAMs<sup>15</sup>.

A very widely used system is gold – thiolate bonding. Alkanedithiols (length  $< C_{14}$ ) with one thiol endgroup attached to gold form large regular domains with the chain tilted from the surface of the metal<sup>16</sup>. In this configuration the thickness of the SAM is almost equal to the length of the molecules due to a tilt angle of  $\sim 30^\circ$ . However, longer alkanedithiol chains seem to show less order with increasing chain length.

This indicates that making SAMs of large molecules is more difficult and molecular alignment is not always such that the thickness of the SAM is close to the length of the molecule. Also it is possible that nicely ordered domains are interspersed with large amorphous domains.

### 1.4 Large-area Molecular Junctions

The devices in this study, which have been processed with molecules as active components, are based on self-assembled monolayer formation on fabricated metallic contacts. The molecules are self assembled in small vertical interconnects or via holes of which the diameter can be fabricated within a range of  $6 \mu\text{m} - 100 \mu\text{m}$ . This means that the area of the junctions can be varied over almost three orders of magnitude. This already offers a nice check if good devices are produced, since the current through the devices per unit area (current density) should be constant.

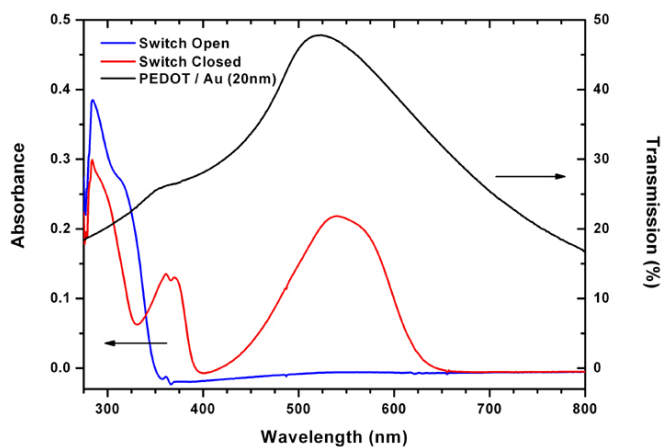


**Figure 1.2:** Processing scheme for the fabrication of the large area molecular junctions.

The processing scheme for the large-area molecular junctions is shown in Figure 1.2<sup>7</sup>. All steps used are conventionally and industrially used processes such as spincoating and photolithography. First, gold bottom contacts are thermally evaporated on a silicon wafer with a thermally grown oxide (500 nm). Then with standard lithography via holes are processed in photoresist. In these holes the molecules are self assembled. Now a monolayer of molecules is formed in the open holes. Evaporation of a top metal contact on top of this monolayer will damage it or penetrate to form shorts<sup>6</sup>. So the key step in the processing is the formation of the top contact. This key step in the processing is done by spincoating the conducting polymer PEDOT:PSS on top of the SAM. The idea is that since the polymer molecules are large, they do not penetrate the SAM but instead form a layer on top of it. Furthermore, PEDOT:PSS is hydrophilic, which prevents penetration of the hydrophobic core of the SAM. Because of this extra layer, direct evaporation of the auxiliary top metal contact is possible, since now the metal will only penetrate to some extent into the polymer but leaving the SAM intact. After the spincoating of the conducting polymer and the evaporation of gold metal top contact, the surrounding, excess polymer is etched away using reactive ion etching, leaving a photoresist encapsulated molecular junction between two contacts, Au and PEDOT:PSS/Au.

## 2.1 Device Fabrication

Devices were fabricated following the processing scheme as shown before (Figure 1.2 and Ref. [7]). Standard bottom contact thickness used was 60 nm. For the self assembly, 0.5 - 1.0 mmol/L solutions of the switches were used and 3 mmol/L solution for alkanedithiols. On top of the molecules, PEDOT:PSS (Baytron®PH 500) was used as conduction layer and standard top contacts used were 20 nm thick. This thickness was used to ensure that light could reach the molecules in the devices. The transmission of PEDOT:PSS and 20 nm Au was measured and is shown in Figure 2.1. It shows that light is transmitted over the wavelengths which are needed to switch the photochromic molecules (312 nm UV and 500-600 nm VIS).



**Figure 2.1:** Absorbance of the meta-phenyl molecular switch (See section 3.1) measured in toluene and transmission of PEDOT:PSS with 20 nm Au on top. 20% transmission is obtained for 312 nm and almost 50% transmission for the visible light.



## 2.2 I-V Measurements

Measurements were performed in vacuum ( $\sim 10^{-6}$  mBar) in a home-built probe station. A Keithley 4200 was used to measure the currents as a function of the applied voltage. A back and forth voltage sweep was always performed with forward bias on the Au bottom contact. The measurements were done in vacuum to avoid any influence of remaining water in the PEDOT:PSS on the measurements.

## 2.3 Irradiation of the Devices

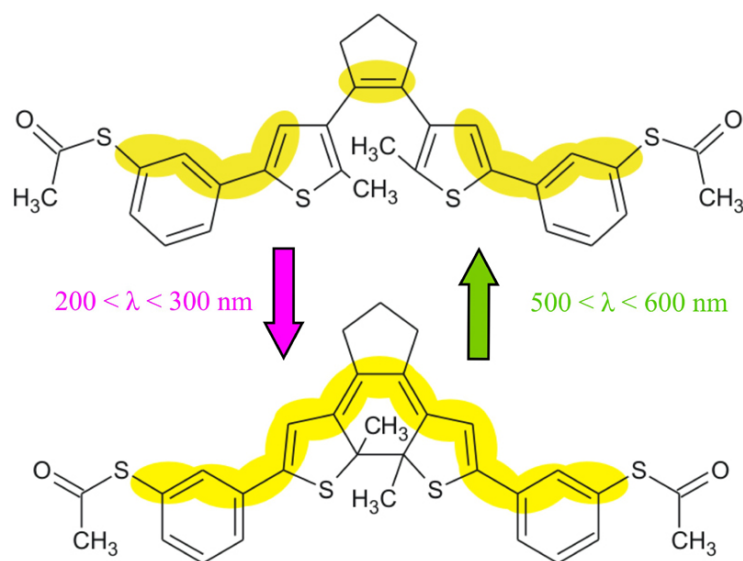
Irradiation of the devices was performed outside vacuum. In the ultraviolet spectral region, an UV lamp with specific wavelength of 312 nm was used. For the visible irradiation part, this was a Xe-lamp with a 420 nm cut-off. Immediately after irradiation, the devices were put in vacuum again. In general, the pump time of the probe station was around 3 hours to reach the desired low pressure ( $\sim 10^{-6}$  mBar). Consequently, a delay between the irradiation of the devices and the  $I$ - $V$  sweep is obtained.

## Chapter 3

# Experimental Results for the Meta-Phenyl Switch

### 3.1 The Meta-Phenyl Switch

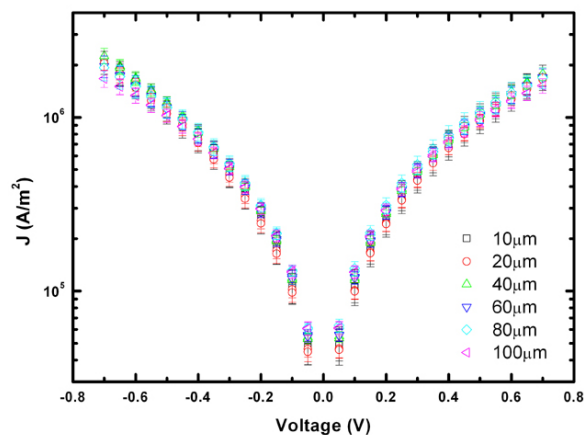
Different switches have been used in the large-area devices. The photochromic part of the molecules (the core) is often the same, while the remainder of the molecules (the electrical leads) differs. One of the molecules used is shown in Figure 3.1. The specific orientation of the two substitutions on the benzene ring in this molecule are called meta substitutions. Therefore the molecule is entitled the meta-phenyl molecular switch. The meta substitution on a phenyl ring is known for electronic decoupling of the two substituents with its metal contacts<sup>17</sup>. In this way, it is made sure that the photochromic moiety is not very much influenced by the coupling of the sulfur atom to the gold which, of course, changes the electronic energy levels of the molecule at the interface.



**Figure 3.1:** Molecular structure and conjugation of the meta-phenyl switch. The meta substitution is used to decouple the photochromic moiety electronically from the contacts.

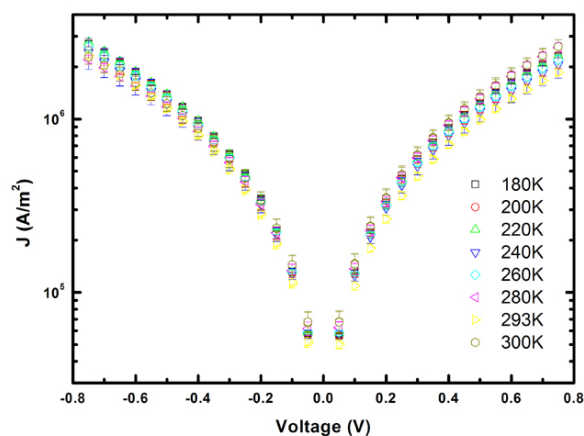
### 3.2 Characterisation of the Open State

The molecules have been assembled in the open, low conducting state. It is expected that because the molecule is not conjugated in this state, tunneling through an insulator is observed. The results of the  $I$ - $V$  measurements of these devices are shown in Figure 3.2. It shows that the current densities for the different device areas are the same. Although not clear on a logarithmic scale, the current density depends exponentially on the applied bias.



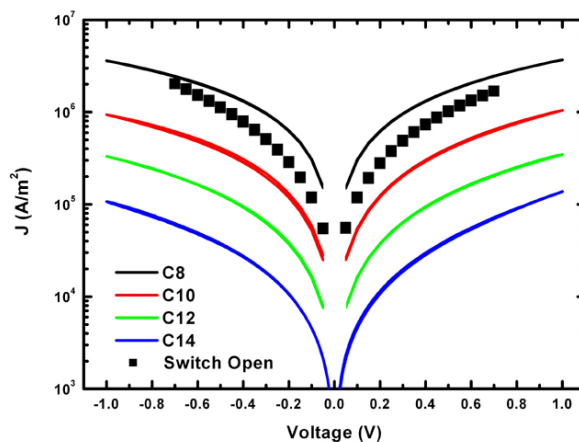
**Figure 3.2:** Current densities obtained from devices in which the open form of the meta-phenyl switch was self-assembled. The current densities of the devices with varying areas are the same, which shows that good devices are produced. At least 11 devices of each diameter are measured.

The temperature dependence of the currents through the open form of the switches has been determined to check the transport mechanism of the devices (Figure 3.3). The current through the devices is temperature independent in the temperature range 180 K - 200 K. Furthermore, when enlarging the figure, no trend is observed in the current as a function of temperature. Because of this temperature independence, the conduction mechanism through the open switch is determined to be tunneling.



**Figure 3.3:** Temperature (in)dependence of the current densities obtained for 60  $\mu\text{m}$  devices with the open form of the meta-phenyl switch self-assembled. No trend is observed as a function of temperature. Similar results were obtained for other device sizes where at least 4 devices were measured for every diameter.

To a first approximation this tunneling depends on the thickness and height of the barrier, respectively the length of the molecule and its energy levels. Because of this, the currents which were obtained for the open form have been compared to currents which were obtained for alkanedithi-



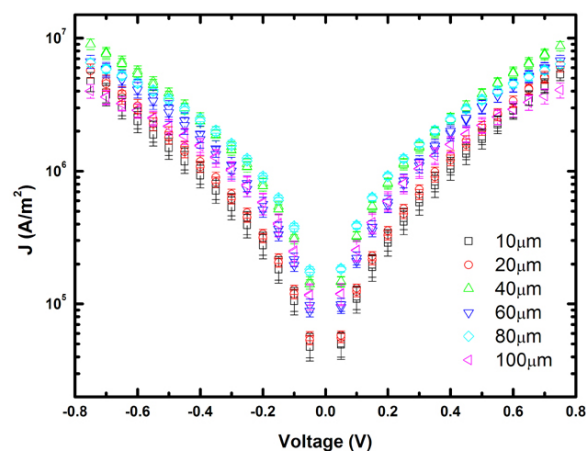
**Figure 3.4:** Comparison of the different average currents obtained for different molecules which are used. The currents obtained for the switches reasonably fit in, resulting in the conclusion that really the molecular switches are measured.

ols (Ref. [7]). If only a comparison is made involving the length of the molecules, the currents of the molecular switches, which are around 18 Å in length, should be comparable to the ones measured for decanedithiol, which is 17.4 Å. The currents obtained are somewhat higher (Figure 3.4), but this can be explained qualitatively since only a small part of the open form of the molecular switch is insulating and both ends are conjugated. This effectively results in a smaller tunnel barrier and a higher current through the molecules. Although the shape of the  $I$ - $V$  curve differs for unclear reasons, since the magnitude of the current is comparable to the current obtained for the alkanedithiols, it is concluded that indeed the current through the molecular switches is measured.

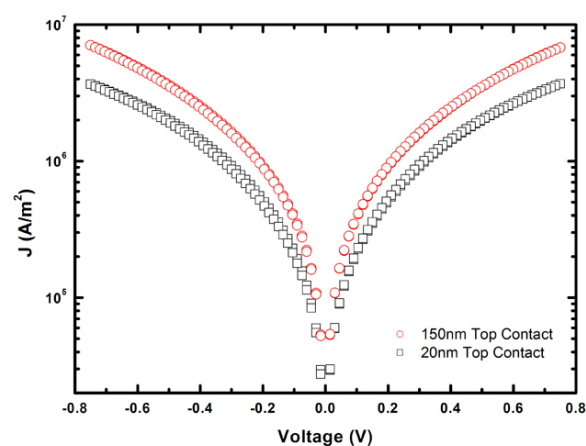
### 3.3 Characterisation of the Closed State

Similar to the investigation of the open form, the closed form of the molecule has been self assembled in the devices and characterised. Because the molecular switch is turned from non-conjugated to conjugated, an increase in the currents through the devices is expected. Results obtained from the devices are shown in Figure 3.5.

The scaling of the currents for these devices is not as good as for the low conducting form of the molecule. The reason for this is the influence of the 20 nm thick top contact. Devices have been processed with the standard 20 nm top contact and, after measuring, an extra 130 nm Au was evaporated on top of the 20 nm, resulting in a 150 nm top contact. It is seen that the current for almost all device areas was increased, the effect most pronounced for the largest, 100 μm in diameter (Figure 3.6). Furthermore, the scaling of the currents with area improved drastically. This shows that the 20 nm top contact is limiting the current through the larger devices. As the diameter of the molecular junctions increases, the resistance of the monolayer junction decreases and the thin top contacts become the limiting resistance. Therefore, the current through the device is increasingly more limited with increasing device area. Therefore, scaled to the area of the devices, the current density decreases for the larger diameter devices.



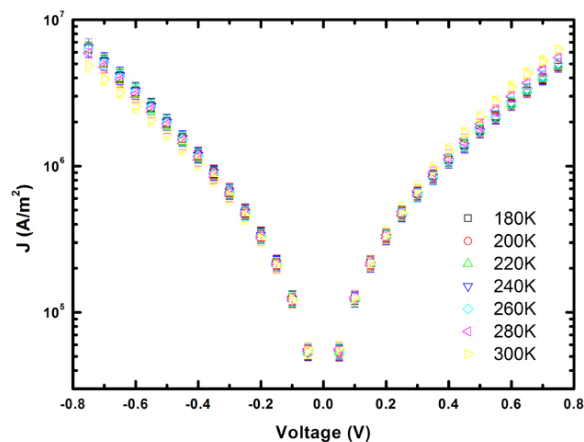
**Figure 3.5:** Average current densities of devices in which the closed state of the molecular switch is self assembled. The current densities for different areas are not exactly equal, as observed for the open state. At least 9 devices of each device diameter have been measured.



**Figure 3.6:** Current densities obtained from 4 devices with 20 nm top contacts and 130 nm extra, resulting in 150 nm top contacts. The currents are higher for the devices with thicker top contacts, demonstrating that the 20 nm top contacts limit the current through the larger devices with the closed form of the molecular switch assembled.

To determine the conduction mechanism, also the temperature dependence of these currents has been measured. A priori, it could be reasoned that because the molecule is completely conjugated, temperature dependent semiconducting behavior is expected. However, because the distance between the electrodes is so small, tunneling could still be the dominant conduction mechanism.

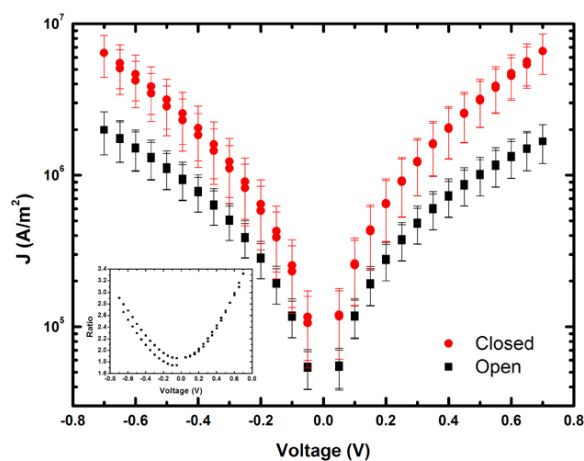
Results of the temperature dependent measurements are shown in Figure 3.7. It is demonstrated that the current through the closed form is also temperature independent. This leads to the conclusion that the transport mechanism through the closed form is also tunneling.



**Figure 3.7:** Temperature dependence of  $20\ \mu\text{m}$  devices in which the closed form of the meta-phenyl switch has been self-assembled. Similar results are found for other device sizes.

### 3.4 Comparison Open and Closed State

Since both forms of the molecular switch have been characterised, a comparison can be done between the currents obtained from both types of devices. In Figure 3.8, the averages of the current densities are plotted for both devices with the open and the closed switch. It is shown that the currents through the closed state are higher than the open state.



**Figure 3.8:** Average current densities obtained from devices with the open and closed switch self-assembled. At least 34 devices have been used in the average per state of the molecule. A difference in current density through the devices is observed between both forms. As a function of voltage, the ratio between the current is not constant (inset).

The figure shows two important aspects; first, it is possible to observe the difference in conduction between the different states of the molecules. The difference in current (density) through the devices is a factor  $\sim 3$  at  $0.75\ \text{V}$ . This encourages the fact that the conduction through the devices

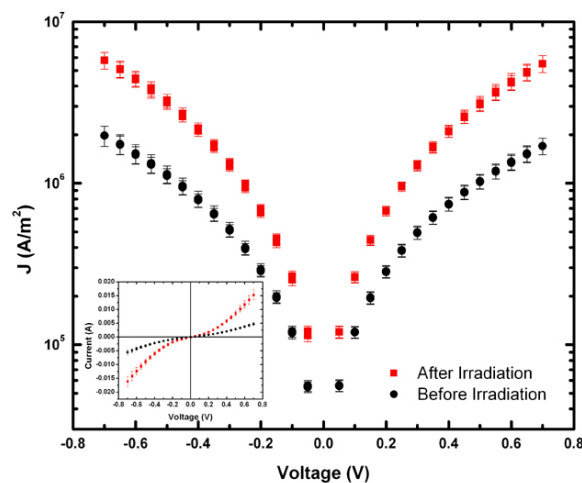
can really be changed upon irradiation and observed with conventional  $I$ - $V$  measurements. Second, the ratio between the currents obtained is not constant as a function of voltage (inset Figure 3.8). If this aspect can be reproduced upon irradiation, it verifies that the molecules are responsible for the conductance switching and it is not due to a change in contact area in the device.

The difference in conductance through the devices is, however, not as large as expected. Similar molecules have been measured using the breakjunction technique. A difference in resistance of orders of magnitude was determined between the open and closed state<sup>4</sup>. An explanation can be that the molecules have different surroundings in both cases, e.g. cooperative effects in self-assembled monolayers could be of importance in the large-area junctions while this is not the case in the break junctions<sup>18</sup>.

Of course, a larger ratio between the currents is desirable. However, first of all, it should be demonstrated that in the large-area devices the molecules can be switched from ON to OFF and vice versa, thereby changing the conductance of the devices upon irradiation.

### 3.5 UV Irradiation of the Devices

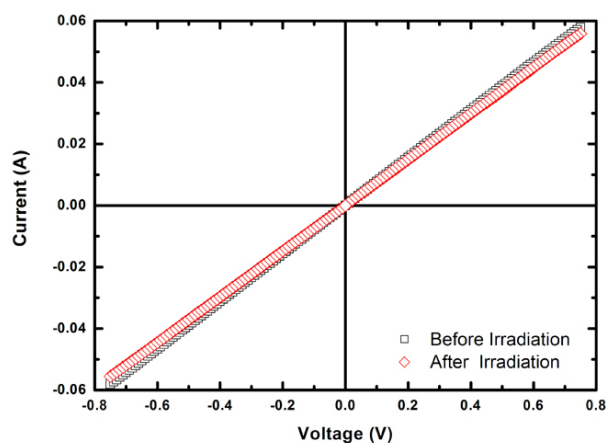
Since both forms of the molecules have been characterised and it has been demonstrated that it should be possible to switch the conductance of the devices around a factor 3, devices have been irradiated to convert the switches from one state into the other. Figure 3.9 shows the current densities obtained from  $60\ \mu\text{m}$  devices with the open form assembled and irradiated for 15 minutes with UV light of 312 nm wavelength.



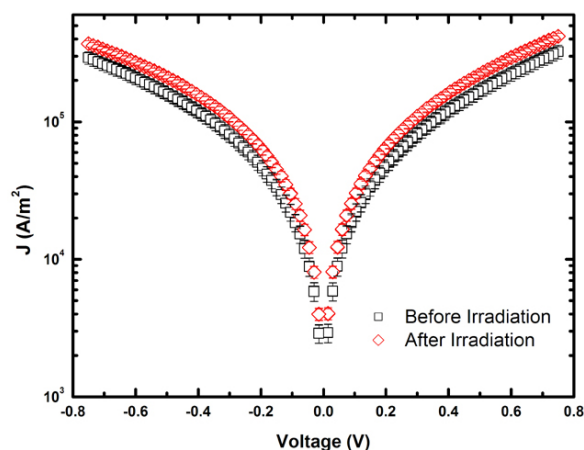
**Figure 3.9:** Current densities (inset: currents) obtained from  $60\ \mu\text{m}$  devices with the open state of the molecule assembled ( $\bullet$ ) and after irradiation with UV light for 15 minutes in air ( $\blacksquare$ ). After irradiation, the currents through the devices are essentially the same as for devices with the closed form of the molecule assembled in the device (Figure 3.8).

The currents obtained from the irradiated devices are compared with the currents obtained for devices based on the assembled closed switch. The currents are essentially the same which is a first indication that the switches in the devices have been turned from the ring open to the ring closed state. However, to check whether this is not a property of the Au contacts or the

PEDOT:PSS, devices have been processed without molecules (Au-PEDOT-Au) and with tetradecanedithiol molecules assembled. When it is assumed that the currents obtained in Figure 3.9 are indeed caused by switching of the meta-phenyl switch, irradiation of the PEDOT and tetradecanedithiol devices should not lead to an increase in the currents through the devices.



**Figure 3.10:** Average currents obtained from  $20\ \mu\text{m}$  Au-PEDOT-Au devices before and after UV irradiation for 15 minutes. No change in current is measured for these devices, concluding that the Au-PEDOT contacts are not responsible for the increase in current which is observed for irradiation of devices with molecular switches.



**Figure 3.11:** Current densities obtained from  $20\ \mu\text{m}$  devices with tetradecanedithiol before and after UV irradiation. The devices nearly produce the same currents after irradiation. The ratio between the two curves is around 1.3 on average but not constant. It is concluded that UV irradiation has no influence on the devices since this difference in curves is in the error margin of the measurement.



Currents obtained before and after irradiation of Au-PEDOT-Au devices are shown in Figure 3.10. Since PEDOT is a heavily doped semiconductor, ohmic behavior is observed for the current – voltage characteristics.

After irradiation of these devices, no increase in the current is observed as was seen for devices with the meta-phenyl switches assembled. This leads to the conclusion that the device structure with PEDOT:PSS as contact is not responsible for the observation of the increase of the conductance of the devices after UV irradiation. To verify that devices based on non-switching molecules exhibit the expected characteristics, tetradecanedithiol molecules ( $\text{HS-C}_{14}\text{H}_{28}\text{-SH}$ ) were used since these are simple molecules exhibiting no special behavior with respect to their electrical transport properties (Figure 3.11). After irradiation of the tetradecanedithiol devices, the currents obtained do not significantly differ from the currents obtained before the irradiation. Therefore, it is deduced that not some interface interaction between the thiol endgroup and gold or PEDOT is responsible for the switching upon irradiation in the large-area junctions. Thus, the molecular photochromic moiety, which is present in the molecular switches and absent in the other devices, is responsible for the switching of the currents through the devices as observed in Figure 3.9. Therefore it is concluded that the meta-phenyl switch can be switched in the large-area molecular junction from the open to the closed state using UV irradiation, resulting in an increase in current through the devices of around a factor 3.

### 3.6 Capacitance measurements

Capacitance measurements were performed on a series of devices processed on a quartz wafer with smaller bottom contacts. Quartz was used to avoid any parasitic capacitances and small contacts were used to reduce the overlap of the top and bottom electrodes and consequently to reduce the extra capacitance of the photoresist which is also measured. Results of the measurements are only indicative because of the low resistance of the SAM, resulting in the observation of the influence of the capacitance at high frequencies only and the large contribution of the capacitance of the photoresist to the total capacitance, resulting in a rather crude determination of the capacitance of the SAM. However, it is expected that due to a change of the dielectric constant of the monolayer after irradiation, the capacitance of the devices should change. Although the measurements are not very accurate, capacitance measurements on devices before and after illumination result, for both the 10 and 20  $\mu\text{m}$  devices, in higher capacitance values together with the observation of the change in current (Table 3.1).

When using the Simmons model with the dielectric constant incorporated<sup>9,10</sup>, the current densities for devices with the open state can be modelled reasonably well. However, if only the change in dielectric constant of the monolayer is taken into account, the current densities for devices with the closed state cannot be modelled anymore, since the influence of an increased dielectric con-

Diameter	$C_{Open}$ (pF)	Determined $\epsilon_{Open}$	$C_{AfterUV}$ (pF)	Determined $\epsilon_{AfterUV}$
10 $\mu\text{m}$	1.692	5.1	1.886	5.7
20 $\mu\text{m}$	5.310	3.8	6.790	4.9

**Table 3.1:** Capacitance and dielectric constant values obtained from devices processed on quartz before and after UV irradiation. The values are at least averaged over 12 devices. The change in capacitance / dielectric constant of the monolayer indicates that the molecular switches are converted from the open to the closed state.

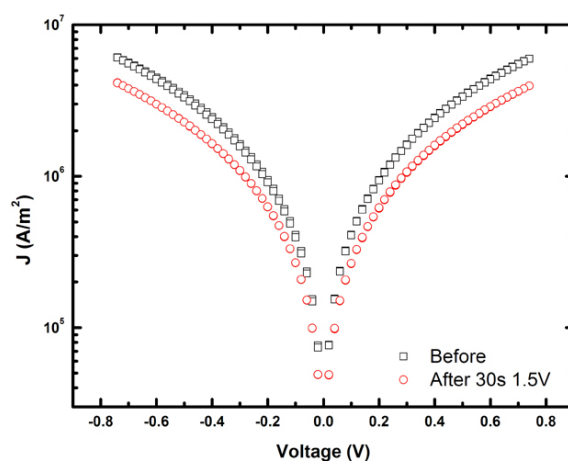
stant is to reduce the current density by the reduction of image charges at the contacts. Therefore, other properties than only the dielectric constant change upon irradiation, e.g., the electronic energy levels. The change in dielectric constant of the monolayer together with the change in other properties of the system supports the conclusion that the molecular switches changing states are indeed responsible for the change in current.

### 3.7 VIS Irradiation of the Devices

After the conclusion that the switches can be turned from the open to the closed state, it was investigated if the opposite transition takes place using VIS irradiation. However, it was observed that the currents through the molecules did not return to their lower values after 25 minutes of irradiation. Therefore, it is determined that the switching from the closed to the open state is quenched. A possible explanation is that this is caused by the interaction of the molecules with the gold, via the thiolate bond. One-way switching is also observed for similar molecules in a breakjunction geometry<sup>4</sup>. Furthermore, specific properties of the whole class of diarylethenes seem to be intimately related to the specific substitution on the various positions around the photochromic moiety (Figure 1.1)<sup>19,20</sup>. Therefore, it is not trivial to choose a photochromic diarylethene and know a priori if it will switch in both directions under illumination while it is in the large-area molecular junction. In the junctions, the molecules are connected to gold and are maybe even more hindered for the switching because of the PEDOT:PSS top contact.

### 3.8 Electrochemical Switching

Recently, it has been shown that different diarylethenes can be turned from one state into the other electrochemically in solution<sup>19,20,21</sup> and in the bulk<sup>22,23</sup>. In the quest to observe the switching from the closed to the open state, which was impossible to observe with visible irradiation, it was proposed to turn the closed molecules into the open state by applying a rather



**Figure 3.12:** Average current densities obtained before ( $\square$ ) and after 30 seconds 1.5 V bias ( $\circ$ ) over  $80\ \mu\text{m}$  devices with meta-phenyl switches assembled in the closed state. Similar results are obtained for devices with other diameters. The ratio between the curves is around 1.5 at 0.75 V.

large potential to the molecules. Results of these experiments are shown in Figure 3.12.

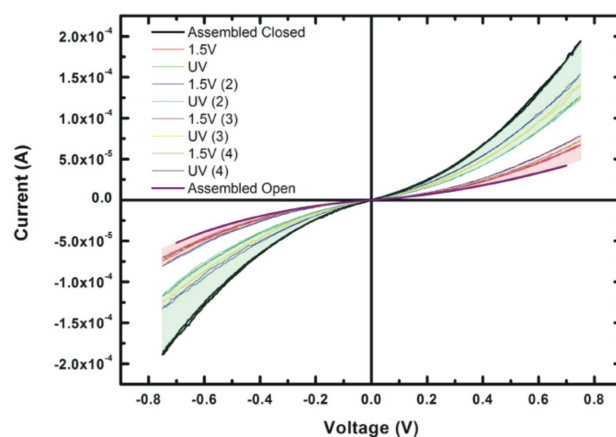
The figure shows that the current through the devices decreases after biasing the devices with 1.5 V. This indicates that the molecular switches are converted from the closed to the open state inside the junctions.

However, it is possible that the large bias destroys the devices and therefore a lower current is observed. Because of this, a series should be performed of UV irradiation followed by biasing for several times consecutively. This has been done on 6  $\mu\text{m}$  devices resulting in the characteristics shown in Figure 3.13.

It is determined from the consecutive operations that the molecular junctions are not destroyed by the 1.5 V bias. If the molecules are destroyed, the current can not increase again after UV irradiation, since this is the manifestation of the photochromic moiety. However, from the  $I$ - $V$  characteristics it is concluded that the monolayer is not fully transformed into the open and the closed state as the absolute value of the currents remain within the window given by 3.8. This is confirmed by the determination that the currents obtained after the operations are all related to the maximum achievable current of the closed switch devices by a constant factor ( $<1$ ). This shows that the monolayer in the devices is partly switched from one state to the other.

In conclusion, the measurements show that both the open (OFF) and closed (ON) state can be assembled on Au and further processed to make large-area molecular junctions. The ON/OFF ratio of these devices is  $\sim 3$ . Switching from the open (OFF) to the closed (ON) state with UV irradiation is possible, but the reverse operation with VIS irradiation is not observed, making the meta-phenyl switch a unidirectional optical switch.

However, switching from the closed (ON) state to the open (OFF) state is feasible by an electrical stimulance of 1.5 V with an ON/OFF ratio of  $\sim 1.5$ . This implies that the SAM of the closed state switches only partially to the open state with voltage, after which the monolayer switches optically, again partially, back to the closed form.



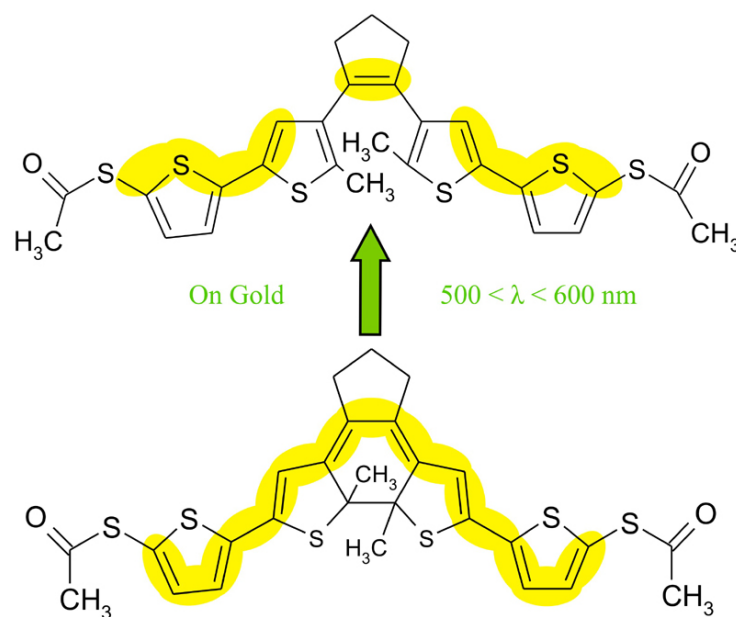
**Figure 3.13:** Consecutive UV and biasing operations performed on a 6  $\mu\text{m}$  device with the closed state of the meta-phenyl switch assembled. UV irradiation and 1.5 V biasing results in an alternation between a higher (greenish area) and lower (bright red area) conductance state, respectively. The ratio between the currents is at least 1.5 at 0.75 V.

## Chapter 4

# Experimental Results for the Thiophene Switch

### 4.1 The Thiophene Switch

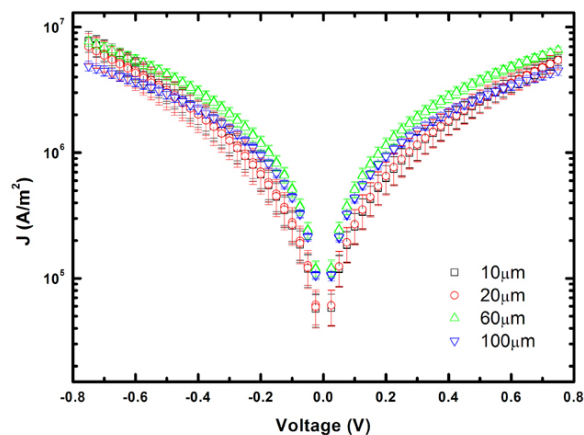
The second molecular switch used in the large area molecular junctions is entitled the thiophene switch. The molecular structure is shown in Figure 4.1. The photochromic moiety of the switch is the same as the meta-phenyl switch, however the moiety is substituted by thiophene rings on both sides. Because of this substitution the coupling to the electrodes is expected to be larger. Possibly this is also the reason why these molecules can only be switched one way, from closed to open, when connected to gold in a breakjunction geometry<sup>4</sup>. Therefore, the aim for using this molecule is to observe this unidirectional switching in the large-area molecular junctions based on the thiophene switch.



**Figure 4.1:** Molecular structure of the thiophene switch. When connected to a gold electrode, this molecular switch can only be switched from the closed to the open state.

### 4.2 Characterisation of the Open State

Similarly as for the meta-phenyl switch discussed in Chapter 3, devices were processed with one of both states self-assembled in the devices. First of all, the open state was assembled. Current densities obtained for these devices are shown in Figure 4.2.

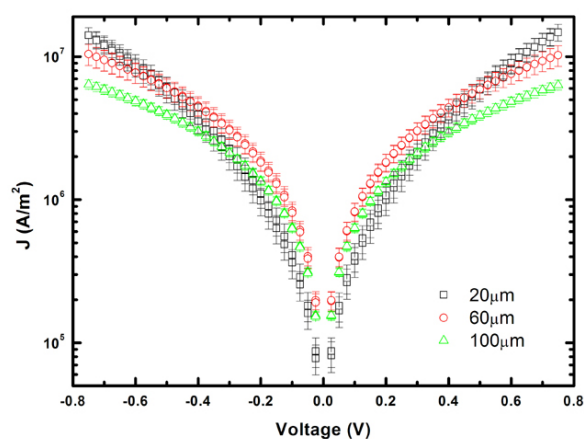


**Figure 4.2:** Current densities obtained for devices with the open thiophene switch self-assembled. Current densities are not exactly equal, which is probably due to the higher currents through the devices.

Apparently, because of the better coupling to the electrodes through the thiophene rings, higher currents are obtained for devices with this molecular switch, compared to the devices with the meta-phenyl switch. Consequently, current densities of devices with different diameters are not the same, since the current is limited by the thin Au top contacts. This can be avoided by using thicker top contacts. (Figure 3.6). However, good devices are obtained also when this specific switch is incorporated.

### 4.3 Characterisation of the Closed State

Also devices were processed with the closed state of the switch. The  $J$ - $V$  characteristics are plotted in Figure 4.3. Since the currents of the open state were already quite high, the in-



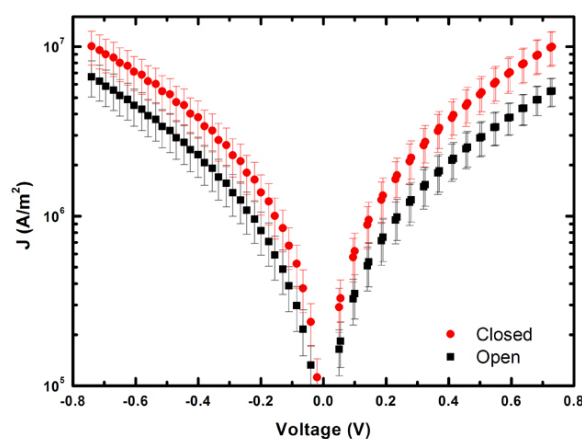
**Figure 4.3:** Current densities for devices with the closed state assembled. The thin Au contacts limit the current density. 10  $\mu\text{m}$  devices were all shorted in this specific measurement.

crease in current (density) is expected to be of the same order or lower than the increase observed for the meta-phenyl switches. Since the thin contacts start to limit the conduction through the devices, an upper limit is present for the current. Although then, probably, the resistance of the monolayer still changes with the same factor, it will not show up in the measurements since it will be dominated by the contacts. Thicker top contacts should be used instead but simultaneously the transmission of the contacts will decrease.

As for the temperature dependence of the devices with this thiophene switch, no measurements have been performed. Because of the similarities in the molecular structure and in the I-V characteristics of both the open and the closed state to the meta-phenyl switch, these devices will probably also show temperature independent behaviour and therefore also the conduction mechanism is believed to be tunneling. However, this still needs to be verified experimentally.

#### 4.4 Comparison Open and Closed State

Both the open and closed state of the thiophene switch have been measured as shown in the previous paragraphs. It is now possible to compare the currents obtained for these devices, which also determines the maxima of current differences which can be obtained in one single device upon irradiation. Both the average current densities measured are shown in Figure 4.4.



**Figure 4.4:** Average current densities obtained from the devices with the thiophene switch assembled in the open (■) and closed (●) state. The difference between the curves is small, but observable.

The difference between both states is smaller in these devices compared to devices fabricated with the meta-phenyl switch. Yet, in every single device a difference in current density can be observed between the open and the closed state. Of course this difference is a consequence of the molecular structure of the switch and coupling to the contacts has already been put forward to explain this qualitatively. However, what exactly determines the properties is not exactly known and remains to be investigated.

## 4.5 Switching in the Molecular Junctions

Even though only a small difference in current density is present between both states, the devices were UV irradiated in an effort to switch from the open to the closed state. This should normally cause the molecules to convert into the closed, higher conducting state but not when connected to gold<sup>4</sup>. This is exactly what has been observed. After illumination, no change in current was observed which confirms the previous measurements on these molecules.

Next it was tried to convert the closed molecules to the open state, which should actually work with the molecules, as observed previously in breakjunction experiments<sup>4</sup>. Unfortunately, also in this case no change in current was observed. This means that for the thiophene switch, no change has been observed while the molecules were assembled in the molecular junctions. It has, however, not been tried to switch the molecules electrochemically in the junctions. This could still lead to the observation of one-way switching, since it has been also observed in the devices with the meta-phenyl switch.

## Chapter 5

---

### Summary and Conclusion

In this thesis, large-area molecular junctions were processed with two different photochromic switches, entitled the meta-phenyl and the thiophene switch. These switches exhibit two different stable states, a conjugated and a non-conjugated state, with different electronic transport properties. The switches can be turned from one state to the other by exposure to light of specific wavelengths.

The difference in current densities through devices with the meta-phenyl switch in the conjugated (ON) and the non-conjugated (OFF) state is around a factor 3 at 0.75 V. Devices with both states resulted in temperature independent  $I$ - $V$  characteristics, which indicates tunneling as the dominant transport mechanism. Furthermore, the conductance of these devices can be changed upon UV irradiation and by applying a bias, while the reference devices without switches (Au/Alkanedithiol/PEDOT:PSS/Au and Au/PEDOT:PSS/Au) do not show any difference after these operations. After VIS irradiation, however, no change in current density was observed.

Devices with the thiophene switch resulted in similar characteristics as the meta-phenyl switch. The current densities obtained were somewhat higher and the difference in current densities between the ON and the OFF state smaller. It was not possible to change the conductance of these devices upon UV and VIS irradiation. A possible explanation is that, because of the better coupling of the molecules to the contacts, the current densities are higher and the switching is quenched.

In general, reliable large-area molecular junctions with molecular switches incorporated as a self-assembled monolayer can be produced. It has been shown that it is possible to influence the current through devices in which the molecular switch, entitled meta-phenyl switch, has been incorporated. However, some specific properties about this system still remain unclear.

The first observation that stands out is the small difference between the conjugated state of the molecule and the non-conjugated state. It seems that conjugation is not that important when a single layer of molecules is used in an electronic device. This aspect has to be further investigated and is related to the understanding of the conduction through (such) monolayers. As already mentioned in section 1.1, this is still not understood. For this, several different series of molecules have to be measured in the large-area molecular junctions.

Secondly, to understand the relation between the properties of the switches and their molecular structure is of great importance. In literature, many switches have been characterised in several different ways, but still nothing really conclusive can be said about it. Furthermore, it is of course not only needed to know specifically this relation for molecular switches, but more for molecules or a monolayer of them in general. Then eventually other functional devices based on molecules can be produced also, e.g. , diodes.

Furthermore, the properties of the monolayer are yet completely neglected. Specially for these longer, flexible molecules it is important to know what is the structure of the monolayer, because in general the layers are not very ordered. It seems that the environment of a molecule is also



important for the electronic transport properties<sup>8,14</sup>. It is also possible that the molecules do not switch (as good as expected) because of steric hindrance within the monolayer. Therefore, the structure of the monolayer seems to be quite important and should be measured. To determine the structure of the monolayers of the molecular switches, Polarization Modulated Infrared Absorption Spectroscopy has been performed. However, no conclusive data have been obtained so far.

Since many things about these systems are still unknown, more research is needed to determine the important parameters for the conduction through monolayers of molecules and the manifestation of molecular properties in electronic transport junctions. However, though not completely understood, proof-of-principle switching of the conduction of molecular junctions has been demonstrated with the use of photochromic molecular switches.

---

## Acknowledgements

I would like to thank some people without whom this whole research project would not be possible at all.

*Tibor Kudernac*  
*Ben Feringa*  
*Bart van Wees*

Members within the *Materials Science Centre<sup>Plus</sup>*, for providing the molecular switches and the knowledge to work with these molecules.

*Jan Harkema*  
*Frans van der Horst*  
*Minte Mulder*

Technicians, and former technician, of the research group, for providing and maintaining the research equipment used.

*Hylke Akkerman*

Member of the research group and direct supervisor, for the nice social and intellectual cooperation on the project.

*Bert de Boer*  
*Paul Blom*

Leaders of the research group Molecular Electronics / Physics of Organic Semiconductors, for providing a professional environment together with an adequate social atmosphere to perform research in the group, making a nice cooperation possible.

---

## References

- [1] A. Aviram and M. A. Ratner, *Chem. Phys. Lett.* **29** (1974) 277–283
- [2] V. B. Engelkes, J. M. Beebe, C. D. Frisbie, *J. Am. Chem. Soc.* **126** (2004) 14287–14296
- [3] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **278** (1997) 252–254
- [4] 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, B. J. van Wees, *Phys. Rev. Lett.* **91** (2003) 207402
- [5] W. Wang, T. Lee, M. A. Reed, *Phys. Rev. B* **68** (2003) 035416
- [6] B. de Boer, M. M. Frank, Y. J. Chabal, W. Jiang, E. Garfunkel, Z. Bao, *Langmuir* **20** (2004) 1539–1542
- [7] H. B. Akkerman, D. M. de Leeuw, P. W. M. Blom, B. de Boer, *Nature* **441** (2006) 69–72
- [8] A. Salomon, C. Cahen, S. Lindsay, J. Tomfohr, V. C. Engelkes, C. D. Frisbie, *Adv. Mater.* **15** (2003) 1881–1890
- [9] J. G. Simmons, *J. Appl. Phys.* **34** (1963) 1793–1803
- [10] J. G. Simmons, *J. Appl. Phys.* **34** (1963) 2581–2590
- [11] K. Hansen, M. Brandbyge, *J. Appl. Phys.* **95** (2004) 3582–3586
- [11] M. Irie, M. Mohri, *J. Org. Chem.* **53** (1988) 803–808
- [13] K. Kuldova, K. Tsyganenko, A. Corval, H. P. Trommsdorff, A. T. Bens, C. Kryschi, *Synth. Metals* **115** (2000) 163–166
- [14] P. R. Hania, R. Telesca, L. N. Lucas, A. Pugzlys, J. van Esch, B. L. Feringa, J. G. Snijders, K. Duppen, *J. Phys. Chem. A* **106** (2002) 8498–8507
- [15] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **105** (2005) 1103–1169
- [16] L. H. Dubois, B. R. Zegarski, R. G. Nuzzo, *J. Chem. Phys.* **98** (1993) 678–688
- [17] K. P. C. Vollhardt, N. E. Schore, *Organic Chemistry: Structure and Function, 3rd Ed.* Chap. 16, W.J. Freeman and Company, 1999
- [18] D. Cahen, R. Naaman, Z. Vager, *Adv. Funct. Mat.* **15** (2005) 1571–1578
- [19] W. R. Browne, J. J. D. de Jong, T. Kudernac, M. Walko, L. N. Lucas, K. Uchida, J. H. van Esch, B. L. Feringa, *Chem. Eur. J.* **11** (2005) 6414–6429
- [20] W. R. Browne, J. J. D. de Jong, T. Kudernac, M. Walko, L. N. Lucas, K. Uchida, J. H. van Esch, B. L. Feringa, *Chem. Eur. J.* **11** (2005) 6430–6441
- [21] G. Guirado, C. Coudret, M. Hliwa, J. P. Launay, *J. Phys. Chem B* **109** (2005) 17445–17459
- [22] T. Tsujioka, H. Kondo, *Appl. Phys. Lett.* **83** (2003) 937–939
- [23] T. Tsujioka, M. Shimizu, E. Ishihara, *Appl. Phys. Lett.* **87** (2005) 213506