Molecular conductance
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Chapter 5
The Influence of the π-Conjugation Pattern on Conductance

In this Chapter we investigate the influence of the pattern of π-conjugation on conductance, using a series of three molecular wires with different conjugation patterns and nearly identical lengths. The anthracene-based molecular wire is linear conjugated, the anthraquinone-based wire is cross-conjugated, and the dihydroanthracene-based wire has a broken conjugation pattern. We have investigated the formation of self-assembled monolayers from these molecular wires and contacted these monolayers with different top-contacts to study their conductance. Conductive Probe Atomic Force Microscopy (CP-AFM) measurements, measurements with a top electrode of eutectic gallium indium (EGaIn), and Mechanically Controllable Break Junction (MCBJ) measurements showed that the conductance of the cross-conjugated wire is about two orders of magnitude lower compared to the linear conjugated wire. The conductance of the cross-conjugated wire is also lower than that of the wire with a broken conjugation pattern, which is attributed to the destructive quantum interference in the transmission function of the cross-conjugated wire.
5.1 Introduction

In Chapter 2 we have introduced molecular wires in which the conjugation pattern varies from linear conjugated to cross-conjugated and broken conjugation by changing the degree of oxidation of the central anthracene-based unit. Having investigated the growth of high quality self-assembled monolayers from dithioacetates (Chapter 3) and the influence of length and the HOMO-LUMO gap on the conductance of linear conjugated molecules (Chapter 4), we will in this chapter investigate the influence of the conjugation pattern on the conductance, by studying three rigid dithiolated molecular wires with identical length and different conjugation patterns: an anthracene-based linear conjugated wire (26AC = 2.6A), an anthraquinone-based cross-conjugated wire (AQ = 2.1A), and a dihydroanthracene-based wire with broken π-conjugation (H2AC = 2.7A), as shown in Figure 5.1. The synthesis and characterization of these molecules is described in Chapter 2. We will use various junction geometries in this study: CP-AFM, EGaIn, LAMJ, and MCBJ, as shown schematically in the top row of the "Matrix Approach" (Figure 1.15).

![Overview of the molecular wires that are discussed in this chapter.](image)
5.1.1 Conductance of Cross-conjugated Molecular Wires

Cross-conjugation is present in molecules that have “three unsaturated groups, two of which, although conjugated to a third unsaturated center, are not conjugated to each other” (see Chapter 1.3). The cross-conjugated groups do show electronic communication, although less than linear conjugated molecules. Therefore, cross-conjugated molecules are expected to have a lower conductance, as indicated by the about hundred-fold lower current (at 1 V) that was measured for a molecular wire with meta-phenylene linkers by Mayor and Weber et al., compared to the same wire with para-linkers (Figure 5.2). Similar results were reported for STM Break Junction experiments on para- vs. meta-substituted benzenedithiols and benzenediamines, and also found in computational studies.

However, meta-linked phenylene groups have been proposed as interconnects for molecular wires. Alternatively, omniconjugated molecules were designed as interconnects that provide linear conjugated pathways between all substituents. Furthermore, these omniconjugated molecules open the way to perform all 16 Boolean logic operations electrically in relatively compact single molecules, so-called \( \pi \)-logic. This \( \pi \)-logic is based on the difference in conductance between cross-conjugated and linear conjugated pathways through a molecule. Electrical transport measurements that confirm this difference are rare. In the experiment of Mayor and Weber shown in Figure 5.2, in which meta-substituted phenylene linkers were compared with para-substituted phenylene linkers, not only the conjugation pattern of the two molecular wires is different, but also their length and the orientation of the thiol varies. Another example is conductance switching in diarylethene switches, as observed in various junctions. The core of these diarylethene switches is linear conjugated in the closed state and cross-conjugated in the open state (Figure 2.2). Indeed, the closed (linear conjugated) state is measured to have a higher conductance than the open (cross-conjugated) state. However, not only the conjugation pattern, but also the geometry of these

![Figure 5.2 Mayor et al. found higher currents for the linear conjugated para-substituted molecular wire (left) than for the cross-conjugated meta-substituted one (right).]
Ch\chapter{Chapter 5}
molecules and the framework of $\sigma$-bonds changes dramatically upon switching. For that reason, we have designed a cross-conjugated anthraquinone-based redox switch ($AQ$), which becomes linear conjugated upon reduction to its hydroquinone state (Figure 2.1).\textsuperscript{20} The great advantage of this switch is that the cross-conjugated and linear conjugated state have an identical length and geometry and only differ in their electronic properties. This results in a low reorganization energy, which opens opportunities for high frequency switching.

\subsection{5.1.2 Quantum Interference Effects}

Very recently, the conductance of this redox switch was studied by several computational methods and the transmission curve of the cross-conjugated anthraquinone wire showed a quantum interference effect:\textsuperscript{21} at certain energy, the transmission probability of the electrons drops sharply due to destructive interference.\textsuperscript{22} For our anthraquinone-based molecular wire, bound to two gold electrodes, this dip in the transmission curve was found at the Fermi energy (Figure 5.3). No quantum interference effect was found for the hydroquinone state of the molecule.\textsuperscript{21} The quantum interference effect for the anthraquinone-based wire originates from the cross-conjugated nature of the pathway through the molecule, which can be concluded from a computational study in which the topology of the molecular wire was varied.\textsuperscript{23} Though quantum interference effects are generally found for cross-conjugated pathways,\textsuperscript{4,24-26} they are not limited to the class of cross-conjugated molecules only and have for instance been calculated for linear conjugated molecules with nitro-substituents.\textsuperscript{27,28} Quantum interference effects can be tuned by molecular structure and gating (in a three-terminal device), opening the way to functional molecular devices as transistors\textsuperscript{29,30} and rectifiers.\textsuperscript{31}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{transmission_curve.png}
\caption{Transmission curves from DFT-based transport calculations through our cross-conjugated anthraquinone-based molecular wire (AQ) and the corresponding hydroquinone wire (HQ), adapted from ref. 21.}
\end{figure}

Quantum interference effects result in very small conductances at low bias
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voltages. According to calculations based on Hückel methods (which only consider the π-system), the conductance of cross-conjugated molecular wires at low bias voltages could be even lower than that of wires that contain saturated (sp\(^3\)-hybridized) carbon atoms. Though at larger voltages (~1 V), the conductance of cross-conjugated molecules increases rapidly, which causes the I-V curves of the cross-conjugated wire and the wire with broken conjugation to cross.\(^4\) However, when transport through σ-bonds is taken into account in DFT-based calculations, then the conductance of (short) cross-conjugated molecules is at least the conductance of molecules with broken conjugation, since at energies where the transmission through the π-system approaches zero, the σ-system will provide the main channel for the transmission.\(^{10,24}\)

No direct experimental evidence for quantum interference effects in charge transport through molecular junctions with cross-conjugated molecular wires has been reported until now. Recent charge transfer experiments show slower transfer through a cross-conjugated bridge compared to a linear conjugated bridge.\(^{32}\)

5.2 Formation of Self-Assembled Monolayers

5.2.1 Deprotection by Et\(_3\)N

In Chapter 3 we have described how high quality Self-Assembled Monolayers (SAMs) from conjugated dithioacetates can be grown. It is important to generate a small amount of monothiolate anion in a solution of bisacetyl-protected dithiols, which was achieved by addition of around ten volume percent of triethylamine (Et\(_3\)N) to a 0.5 mM solution of the acetyl protected molecular wires in THF. We have applied this optimized procedure for the growth of SAMs from molecular wires 26AC, AQ, and H2AC. We found that the solubility of 26AC and AQ is lower than that of OPE3 and only 0.3 mM solutions in THF could be obtained. A precipitate was observed in these solutions about two days after the addition of Et\(_3\)N, which gave tailing at the low-energy end of the UV-Vis spectra. Since the solubility of these molecular wires is higher in chloroform, we have made 0.5 mM solutions in chloroform, with 10% (v/v) Et\(_3\)N added. In the UV-Vis spectra of these solutions we did not observe any tailing or other changes, compared to the spectra without Et\(_3\)N.
We immersed samples of gold on mica upside down in 0.5 mM solutions of 26AC, AQ, H2AC, and OPE3 in chloroform with 10-13% Et3N for two days and analyzed the resulting SAMs by ellipsometry (see Table 5.1). The length of all anthracene-based compounds is 24 Å. We would therefore expect their SAMs to be slightly thicker than that of OPE3, which has a length of 20 Å. Only for AQ we found a SAM that was slightly thicker than OPE3, as predicted. For H2AC we found a thinner SAM, which is most likely due to the nod (max. 30°) in the backbone of H2AC, caused by the sp3 hybridized carbon atoms, which could result in a different packing to optimize the π-π stacking. For the SAM of 26AC we measured a thickness that is larger than expected for a monolayer. This could originate from the assumptions that we make in the fitting of our ellipsometry measurements (see Chapter 3.8.3); we assume that the index of refraction (n) is 1.55 for all π-conjugated thiols and that the SAMs do not absorb between 300-800 nm. As depicted in Figure 2.7, all molecular wires do absorb above 300 nm. Even though these assumptions did not give any problems for the OPE molecules discussed in Chapter 3, 26AC shows transitions around 400 nm and could therefore obfuscate the ellipsometry measurements. The high reproducibility of the measured large thickness indicates that this is not due to the formation of multilayers.

<table>
<thead>
<tr>
<th>Molecular Wire</th>
<th>Length (^a) (Å)</th>
<th>Ellipsometry (Å)</th>
<th>XPS method A (Å)</th>
<th>XPS method B (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26AC</td>
<td>24.20</td>
<td>28.6</td>
<td>24.1</td>
<td>27.1</td>
</tr>
<tr>
<td>AQ</td>
<td>24.25</td>
<td>21.7</td>
<td>20.1</td>
<td>26.9</td>
</tr>
<tr>
<td>H2AC</td>
<td>24.06</td>
<td>19.1</td>
<td>18.3</td>
<td>20.1</td>
</tr>
<tr>
<td>OPE3</td>
<td>19.83</td>
<td>19.7</td>
<td>17.5</td>
<td>17.8</td>
</tr>
</tbody>
</table>

\(^a\) The distance from S- to S-atom as calculated with Hyperchem™ Release 7.52 for Windows Molecular Modeling Systems. Structures were optimized using the AM1-RHF method. We used methyl-substituted thiols in the calculations.

We performed X-ray Photoelectron Spectroscopy (XPS) measurements to determine the thickness and composition of the SAMs. We determined the thicknesses of the SAMs from our XPS measurements by two different methods: A) from the ratio between the carbon and the gold signals\(^33\) and B) from the attenuation of the gold signal\(^34\) (details are given in Chapter 3.8.4). In Chapter 3 we
found method A to be more reliable compared to method B, since method B is more sensitive to experimental errors (as alignment of the sample and intensity of the X-ray beam). However, the equation that we used to determine the thickness by method A has been derived for hydrocarbon compounds and does not take into account heteroatoms as oxygen and sulfur. The error caused by not considering unbound sulfur is the same in all four SAMs. The thickness of the SAM of AQ is further underestimated, because of the oxygen atoms at the anthraquinone core, which can explain the relatively low value that we found for the thickness of AQ by method A, where the thicknesses of AQ is nearly identical to the thickness of 26AC when we use method B. Even though different methods gave different values for the thicknesses of the SAMs from our anthracene-based molecular wires, the trend is clear: the SAM of 26AC has the largest thickness (25 Å), directly followed by that of AQ (24 Å), while the SAM of H2AC has a similar thickness as that of OPE3 (19 Å).35

A more detailed analysis of the different peaks in the XPS spectra (Figure 5.4 and Table 5.2) gave information about the composition of the three SAMs of the anthracene-based molecular wires. For all three SAMs we found two sulfur signals, of which the smallest (162 eV) corresponds to sulfur bound to gold and the larger one (164 eV) to either free thiol or acetyl protected thiol (we will refer to this signal as “unbound” sulfur). As for the OPEs (Chapter 3.4), we did not find any indications of oxidized sulfur (S=O, 168 eV). Furthermore, we found an intensity per carbon atom that approaches the average of the intensities of bound and unbound sulfur signals. These are clear indications of a SAM comprised of molecular wires that are standing instead of laying flat on the gold surface.

<table>
<thead>
<tr>
<th>Molecular Wire</th>
<th>Integrated Intensities a</th>
<th>Normalized Intensities per C-atom b</th>
</tr>
</thead>
<tbody>
<tr>
<td>26AC</td>
<td>7515 1343 39 19 84 57</td>
<td>43</td>
</tr>
<tr>
<td>AQ</td>
<td>7564 1017 73 18 55 102</td>
<td>36</td>
</tr>
<tr>
<td>H2AC</td>
<td>9919 1228 0 24 55 12</td>
<td>41</td>
</tr>
</tbody>
</table>

a. These areas are divided by the sensitivity factor: 1 for Cls, 1.79 for S2p, 2.49 for O1s, and 1.68 for N1s.
b. The total area of the CxHy Cls signal is divided by the number of C-atoms in the core of the molecular wire. We correct for the presence of carbonyl C-atoms.
In the C1s spectrum of AQ we found a relatively large peak at 288 eV, which is attributed to the carbonyl carbon atoms of the anthraquinone core. We found a smaller signal at 288 eV for the SAM of 26AC, which we attribute to acetyl protecting groups at the unbound sulfur atom. On comparing its area to that of the unbound sulfur signal (164 eV), we can conclude that half of the sulfur atoms that are not bound to gold bear an acetyl protecting group, in good agreement with our results for OPE3 (see Chapter 3.4). In contrast, we have not detected any remaining acetyl groups in the SAM of H2AC, while we cannot draw any conclusions on that for the SAM of AQ. We have not observed any signals from nitrogen or chlorine atoms, indicating that no solvent or base is incorporated in the SAM.36
5.2.2 Deprotection by Bu₄NOH

We have investigated the deprotection of the anthracene-based molecular wires by tetrabutylammonium hydroxide (Bu₄NOH, see Chapter 3.3.2), which is commonly used to apply bis acetylprotected dithiols in STM break junctions. However, in contrast to the molecular wires that were studied by this approach in Chapter 4, anthraquinone and dihydroanthracene units are more reactive than acene units and could react with the hydroxide. For that reason, we compared the changes in UV-Vis absorption spectra of solutions of acetyl protected dithiols (suffix A) AQ and H2AC to those of tert-butyl protected dithiols (suffix B) upon addition of Bu₄NOH.

Figure 5.5 a and c show the UV-Vis absorption spectra of a solution of diSAc-anthraquinone-wire AQ (2.1A) and its tert-butyl protected analogue (2.1B) in THF. The color of the solution of 2.1B changed from yellow to green upon addition of Bu₄NOH, as indicated by the changes in its UV-Vis spectrum. While tert-butyl thioethers are rather inert to strong bases and nucleophiles, the hydroxide anion could easily attack the carbonyl groups of the anthraquinone unit. The obtained spectrum from 2.1B with Bu₄NOH is similar to that shown in Figure 2.10, in which 2.1B was reduced electrochemically to the hydroquinone dianion, indicating

![Figure 5.5 UV-Vis absorption spectra of 0.15 mM solutions of 2.1A=AQ (a) and 2.1B (b), and 0.30 mM solutions of 2.7A=H2AC (c) and 2.7B and 2.6A=26AC (d) in THF, with and without Bu₄NOH, showing not only the conversion of thioacetate into free thiolate, but also reactions of hydroxide with the anthraquinone and dihydroanthracene cores.](image-url)
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that also under the conditions used here the anthraquinone is reduced to the hydroquinone dianion.

In Chapter 3 we observed a shift of 100-120 nm in the UV-Vis absorption spectrum of OPEs upon the reaction of a conjugated thioacetate with Bu4NOH to its thiolate anion. The UV-Vis spectra of AQ (2.1A) did not only show this new absorption with a redshift of about 100 nm, but also a new absorption band around 650 nm appearing upon addition of Bu4NOH. This additional absorption is similar to that found for 2.1B upon addition of Bu4NOH and it is already observed upon addition of 2 eq. Bu4NOH. This indicates that the reaction of Bu4NOH with the thioacetates of AQ is not selective and competes with the reaction with the anthraquinone units, or that the formed thiolate anions give rise to a similar reduction of the anthraquinone unit as Bu4NOH does.

Figure 5.5 b and d show the UV-Vis absorption spectra of solutions of diSAc-dihydroanthracene-wire H2AC (2.7A) and its tert-butyl protected analogue (2.7B) in THF. Upon addition of Bu4NOH to H2AC we observed a change of the color from colorless to orange and found a new absorption around 400 nm that grows when increasing the amount of Bu4NOH from a halve to five equivalents. We attribute this absorption to the formation of the thiolate anion. However, after having measured these spectra, we observed that the solution in the cuvette (with Teflon stopper and sealed with parafilm) slowly turned red, starting from the gas/liquid interface. After 30 minutes we measured the UV-Vis absorption spectrum again and found a completely different spectrum, which is identical to that of a solution of diSAc-2,6-anthracene-wire 26AC (2.6A) with over four equivalents of Bu4NOH added (Figure 5.5d), which shows the common 100 nm redshift due to the formation of thiolate anion. The solutions of H2AC with Bu4NOH in the glove box did not change color upon time. This teaches us that Bu4NOH with a trace amount of oxygen converts the dihydroanthracene unit of H2AC into an anthracene unit as present in 26AC. The thiolate anions could also play a role in this reaction. Addition of one equivalent of Bu4NOH to the tert-butyl protected dihydroanthracene wire also gave rise to change of the color (from colorless to blue) as shown in its UV-Vis spectrum, showing that Bu4NOH indeed reacts with the dihydroanthracene core. From these UV-Vis studies on AQ and H2AC we can conclude that Bu4NOH is not a suitable deprotecting agent to facilitate the formation of SAMs from these molecules.
5.3 Conductance Measurements using Conductive Probe Atomic Force Microscopy\textsuperscript{37}

We have grown SAMs of molecular wires 26AC, AQ, and H2AC on gold coated silicon samples (using Et$_3$N as deprotecting agent, Section 5.2.1) and contacted these SAMs with a gold coated contact mode AFM tip (Figure 5.6a). The current through these junctions was measured as function of the bias voltage and the conductance was obtained from the slope of the linear regime of the $I-V$ curves at low bias (-100 mV to 100 mV). From the measurements of about 200-1000 $I-V$ curves per spot and 3-6 spots per sample, we obtained the conductance histograms shown in Figure 5.6b. Since the geometry of the contact and thus the number of molecules contacted varies from measurement to measurement, a distribution of conductance values is obtained.\textsuperscript{38}

Linear conjugated 26AC clearly shows the largest conductance. The Gaussian fit of the histogram is centered around $10^{-2.5}$ $G_0$ (221 nS). The conductance of the SAM of 26AC is lower than the conductance found for a SAM of OPE3 (841 nS) and larger than for a SAM of OPE4 (63 nS, see Chapter 7), in agreement with the single molecule conductance studies discussed in Chapter 4.

We measured significantly lower conductance values for cross-conjugated wire AQ ($10^{-4.1}$ $G_0$, 7 nS) than for linear conjugated 26AC. This difference of a factor 32 between the centers of the histograms reflects the reduced electronic coupling caused by the cross-conjugation. These measurements unambiguously show the
influence of \( \pi \)-conjugation on conductance, supporting the assumptions made when developing the \( \pi \)-logic concept (Chapter 1.3).

Reference compound \( \text{H}_2\text{AC} \) gave conductance values around \( 10^{-3.4} \, G_0 \) (32 nS), in between those of \( \text{AQ} \) and \( \text{26AC} \). This result is counterintuitive, since the \( \pi \)-conjugation pattern in \( \text{H}_2\text{AC} \) is completely broken (which is reflected by its UV-Vis absorption, see Chapter 2.3 and Figure 5.5), whereas the \( \pi \)-conjugation in \( \text{AQ} \) and \( \text{26AC} \) extents over the full carbon framework, resulting in identical optical HOMO-LUMO gaps for these two molecules. For that reason, we had expected the conductance of \( \text{H}_2\text{AC} \) to be below that of \( \text{AQ} \) (and \( \text{26AC} \)). However, when we look at the HOMO levels (Chapter 2.5) of this series of molecules with identical length and use the simple model for tunneling through a rectangular barrier (see Section 4.5.2) to predict the trends in the conductance values of this series, we would indeed expect \( \text{AQ} \) to have the lowest conductance, \( \text{26AC} \) to have the largest conductance, and \( \text{H}_2\text{AC} \) to be in between. However, according to this model, the difference between \( \text{AQ} \) and \( \text{26AC} \) would be no more than a factor four. Thus, the relatively low HOMO level of \( \text{AQ} \) cannot account for its much lower conductance and the simple model for tunneling through a rectangular barrier is not sufficient to explain the trends shown in Figure 5.6. For that reason, DFT-based transport calculations were performed.

### 5.4 DFT-NEGF Transport Calculations

The transmission functions of molecular wires \( \text{26AC}, \text{AQ}, \) and \( \text{H}_2\text{AC} \) were calculated by Troels Markussen and Kristian Thygesen, Technical University of Denmark, using Density Functional Theory (DFT) in combination with non-equilibrium Green's function (NEGF)\(^{40-42} \) (see Figure 5.7). Both thiolate anchoring groups were bound to the gold surface of the electrodes at a bridge site slightly displaced towards the hollow site, which was found to be energetically most favorable. The transmission functions approach unity at energy values that correspond to the energies of the molecular orbitals, though standard DFT calculations are known to underestimate the HOMO-LUMO gap. For linear conjugated molecular wire \( \text{26AC} \) we found a transmission maximum that corresponds to transport through the HOMO level around \(-0.6 \, \text{eV} \), whereas the LUMO related maximum is located around \(1.3 \, \text{eV} \). Since the maximum related to
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The HOMO is found closer to the Fermi energy, this calculation suggests that the HOMO is the main orbital to contribute to the charge transport through molecular wire 26AC. We found a maximum in the transmission through cross-conjugated molecular wire AQ at 0.9 eV. This LUMO-related maximum is located closer to the Fermi energy than the LUMO-related maximum of wire 26AC, in agreement with strong electron accepting character of the anthraquinone unit, caused by the electron withdrawing carbonyl groups, resulting in frontier orbitals that are lower in energy than those of wire 26AC. The transmission maxima calculated for wire H2AC (-0.7 eV and 2.0 eV) are located much further from the Fermi energy than for the other two wires, all in good agreement with its broken conjugation pattern and with the wider HOMO-LUMO gap that we found for this molecule in the optical experiments.

Linear conjugated 26AC clearly has the largest transmission around the Fermi energy of the gold electrodes, in good agreement with the largest conductance values found for 26AC in the CP-AFM experiments. The transmission function of cross-conjugated anthraquinone wire AQ shows a destructive quantum interference at 0.25 eV (Section 5.1.2). Due to this interference it crosses the transmission function of dihydroanthracene wire H2AC, of which the π-conjugation is broken by sp³-hybridized methylene groups in the center of the molecule. The exact position of the quantum interference dip depends on parameters such as the basis set, binding site, and structure used in the calculations. This quantum interference effect causes the transmission of AQ at the Fermi energy of the electrodes (and thus the conductance) to be smaller than that of H2AC. The order of this difference cannot be calculated exactly, due to the relatively large uncertainty in the position of the dip with respect to the Fermi energy.

Figure 5.7 Transmission functions of AQ (red), 26AC (blue), and H2AC (black). (Denmark, note 39)
energy. Quantum interference convincingly explains the lower conductance of AQ compared to H2AC.

5.5 Conductance Measurements in EGaIn Junctions\textsuperscript{43}

SAMs of AQ, 26AC, and H2AC on gold on mica were contacted with tips of the eutectic alloy of gallium (75%) and indium (25%) (EGaIn) as described in Section 1.4.4 (inset in Figure 5.8a).\textsuperscript{44} The current was measured as function of the applied bias between the EGaIn tip and the (grounded) gold surface of the sample. The contact area was estimated from the image of a high magnification camera and used to calculate the current densities. Around 200 $I-V$ curves were recorded for each SAM and current density histograms were obtained for each voltage (Figure 5.8b). The centers of the Gaussian fits\textsuperscript{45} of these histograms are plotted in Figure 5.8a.\textsuperscript{46}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.8}
\caption{a. Mean values of the current densities from Gaussians fits of the current density histograms versus the bias voltage, obtained for EGaIn contacted SAMs of AQ, 26AC, and H2AC on gold on mica. b. Histograms of the current densities measured through EGaIn contacted SAMs of 26AC (blue, 782 $I-V$ curves), H2AC (black, 268 $I-V$ curves), and AQ (red, 232 $I-V$ curves) on gold on mica at 100 mV bias voltage. (note 43)}
\end{figure}

In this setup, the conductance of linear conjugated 26AC is significantly larger than the conductance of AQ (cross-conjugated) and of H2AC (broken
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conjugation). The current densities as obtained from Gaussian fits were slightly larger for H2AC than for AQ. However, when comparing the distributions of the current densities measured for these SAMs, we find a similar spread of the current densities of AQ and H2AC. The histograms of 26AC clearly depict a larger population at higher current densities, compared to AQ and H2AC.

A main cause of the spread in the data is the roughness of the annealed mica surface, which is known to have large flat terraces of gold (111), but also very steep trenches, making the overall roughness relatively large.47 Samples for EGaIn measurements are generally prepared by template stripping a metal film from a Si/SiO₂ surface,44,48,49 by which ultraflat polycrystalline surfaces are obtained, compared to evaporated metal layers.50 The use of these ultraflat metal surfaces significantly reduces the error in charge transport measurements on SAMs.51 However, the technique of template stripping (and especially the commonly used optical adhesive) is not compatible with organic solvents as chloroform and THF, which are required to dissolve our rigid π-conjugated dithioacetates. Other parameters influencing the spread in the data and influencing the reproducibility are for instance the shape of the tip, the gallium oxide layer, temperature, and humidity.52,53

A subtle asymmetry is visible in the J-V curves in Figure 5.8a, which reflects the asymmetry in the contact geometry: the molecules are bound with one thiolate anchoring group to the gold substrate (with a work function of around -5.0 eV), while the other thiolate (or thioacetate) group is in contact with the EGaIn tip (work function around -4.1 eV).43 Such an asymmetry was not found in the CP-AFM measurements.

The difference between AQ and H2AC is not significant in these EGaIn measurements, which could be caused by the different Fermi energy of the Ga₂O₃/GaIn electrode compared to the gold coated AFM tip, which influences the position of the interference minimum in the transmission function (and thus the position where the transmissions of AQ and 26AC cross). Strikingly consistent with the CP-AFM measurements, linear conjugated 26AC gave one to two orders of magnitude higher current densities than AQ and H2AC.
Large Area Molecular Junctions (LAMJ) devices were made with molecular wires 26AC, AQ, H2AC, and OPE3. These devices were fabricated on 4-inch wafers and consist of a gold bottom contact on which a SAM is grown in a lithographically defined pore (5-100 μm in diameter). The top contact is made by spin coating the conducting polymer PEDOT:PSS (~90 nm) and subsequent evaporation of gold (see inset Figure 5.9a, details are reported in Section 5.9.4). We measured the currents through these devices as function of the voltage and found a good scaling of the currents with the device areas. The averaged current densities are plotted in Figure 5.9a and the distributions of the current densities at 100 mV are shown in Figure 5.9b.

In these LAMJ experiments we found the current densities (or conductance) of broken conjugated H2AC to be a factor six lower than those of linear conjugated 26AC. This difference is less pronounced than in the CP-AFM and EGaIn junction, but the trend is the same. However, cross-conjugated AQ gave current densities in between those of 26AC and H2AC. We attribute this difference to the special nature of the top contact in LAMJs: the PEDOT:PSS has a dominant role.
on the charge transport (see Chapter 7),\textsuperscript{56} which is not yet understood. For that reason, it is hard to predict the influence of quantum interference on the conductance of LAMJs containing \textit{AQ}. It could be that the minimum in the transmission curve is shifted away from the Fermi energy, resulting in a larger currents for \textit{AQ} than for \textit{H2AC}.\textsuperscript{46} Alternatively, quantum interference effects could be absent in LAMJs, resulting in a trend that follows the relative degree of conjugation of the three molecular wires.

\section*{5.7 Single Molecule Conductance Measurements\textsuperscript{57,58}}

In Section 5.2.2 we have described the problems that arose when deprotecting molecular wires \textit{AQ} and \textit{H2AC} with the strong base and strong nucleophile \textit{Bu$_4$NOH}, which was used to deprotect the conjugated dithioacetates for the Scanning Tunneling Microscopy Break Junction (STM-BJ) experiments described in Chapter 4. For this reason, the conductance of \textit{AQ} and \textit{H2AC} was not studied by STM-BJ. In the single molecule conductance studies presented in this Section no deprotecting agent was used to hydrolyze the thioacetate groups, since thioacetate groups can bind to gold and spontaneously form thiolate-gold bonds (see Chapter 3). The lower coverages obtained without deprotection do not hinder the single molecule studies in Mechanically Controllable Break Junctions (MCBJs).

Wenjing Hong measured conductance histograms of \textit{26AC}, \textit{AQ}, and \textit{H2AC} by repeatedly opening and closing of notched gold wire-based MCBJs in the presence of solutions of the molecular wires, at the University of Bern (Figure 5.10). The blank measurement with solvents only shows a conductance peak at $10^{-8.8} \, G_0$, which is attributed to the noise level of the setup. The conductance histograms of the molecular wires all show clear peaks at 1 $G_0$ (single gold atom contact) and a noise peak below $10^{-8} \, G_0$. Apart from these peaks, the histogram of \textit{26AC} shows a very clear peak at $10^{-4.6} \, G_0$ (1.95 nS), which is close to the conductance value of 3.6 nS as determined by STM-BJ (Chapter 4, wire \textit{4.7}). The less pronounced peak around $10^{-7} \, G_0$ could be caused by an alternative binding geometry of the molecular wires (see Chapter 4.7) or by $\pi-\pi$ stacking of molecules (see Section 7.2.3). The conductance histogram of \textit{AQ} shows a peak at $10^{-7.0} \, G_0$ (0.0078 nS),
indicating that the most probable single molecule conductance value of this cross-conjugated molecular wire is 250 times lower than that of linear conjugated 26AC. The histogram of H2AC shows a conductance peak at $10^{-6.3} G_0 (0.039 \text{ nS})$, which is fifty times lower than 26AC, though five times larger than AQ. This trend is the same as that found in the CP-AFM and EGaIn experiments, although the differences between the conductance values are larger.

![Figure 5.10](image)

**Figure 5.10** Conductance histograms of 26AC (blue), AQ (red), and H2AC (black) measured in notched gold-wire MCBJ experiments in a liquid cell at room temperature (450 traces each). The conductance histogram obtained in decane/THF (4:1) in the absence of molecules wires is shown for comparison (green, 200 traces). The main conductance peaks are indicated by their values in log ($G/G_0$). (Bern, note 57)

The conductance of molecular wires AQ and 26AC was investigated in lithographically defined MCBJs (operated in vacuum and at room temperature) by Mickael Perrin and Diana Dulić at Delft University. The 2D histograms of the opening conductance-distance traces are depicted Figure 5.11 and show plateau-like features for both molecules. The plateaus in the 2D histogram measured for 26AC (Figure 5.11a) are mainly found between $10^{-4}$ and $10^{-5} G_0$, resulting in a peak
around $2 \cdot 10^5 \, G_0$ (1.6 nS) in the conductance histogram, in good agreement with the values found in the STM-BJ and MCBJ experiments at Bern. The plateaus observed in the 2D histograms measured for cross-conjugated AQ are located between $10^5$ and $10^6 \, G_0$, which is at the low current limit of the setup (as indicated by the noise in the histograms). Although a clear conductance value cannot be determined for AQ, these measurements support the conclusion that the linear conjugated anthracene wire (26AC) has a higher conductance than the cross-conjugated anthraquinone wire (AQ). More detailed investigations at low temperatures are ongoing at the moment of writing this thesis.

![Figure 5.11](image)  
**Figure 5.11** Normalized 2D histograms (left panel, logarithmic color scale) and conductance histograms (right panel) of the conductance-distance traces from MCBJ experiments on a. 26ACQ and b. AQ. The junctions were closed to a conductance of $10 \, G_0$ and opened with a speed of 1.5 nm/s in vacuum at a bias voltage of 150 mV. (Delft, note 58)

### 5.8 Conclusions

We have investigated the influence of the $\pi$-conjugation pattern on conductance by measuring the electrical transport properties of three molecules with similar length and different conjugation patterns in various junctions. We were able to grow SAMs of the three molecular wires, following the methodology described in Chapter 3.

Electrical measurements through these SAMs using a conductive probe AFM tip or an EGaIn tip as top contact showed that linear conjugated anthracene-based wires had an almost two orders of magnitude higher conductance than the cross-conjugated anthraquinone-based wires. The dihydroanthracene-based wire with a
broken conjugation pattern had a slightly higher conductance than the cross-conjugated anthraquinone-based wire. This is best explained by DFT-based transport calculations, which revealed a destructive quantum interference for the cross-conjugated anthraquinone wire, resulting in a very low transmission close to the Fermi energy of the electrodes. This quantum interference effect causes the transmission functions of the cross-conjugated and broken-conjugated wires to cross, resulting in a lower conductance of the cross-conjugated anthraquinone-wire compared to the broken-conjugated dihydroanthracene wire. This order could be altered by a small change in the Fermi energy of the electrodes. This might explain why in Large Area Molecular Junctions the anthraquinone-based wire had a larger conductance than the dihydroanthracene wire, though still lower than the linear conjugated anthracene-wire. However, the presence of PEDOT:PSS makes these junctions complicated to understand and quantum interference could be absent.

The trends that were found in CP-AFM junctions and EGaIn junctions were confirmed by single molecule conductance measurements in break junctions: the linear conjugated anthracene wire has a much higher conductance than the cross-conjugated anthraquinone wire, whereas the broken-conjugated wire has a slightly higher conductance than the cross-conjugated wire.

Although we have found different conductances for the cross-conjugated anthraquinone-wire and the linear conjugated anthracene wire independently in this chapter, we have not yet been able to measure in situ conductance switching upon (electro)chemical reduction and subsequent oxidation of the anthraquinone wire as described in Chapter 2 and depicted in Figure 5.3, though various efforts towards this aim are ongoing.

The clearly lower conductance found for the cross-conjugated wire than for the linear conjugated wire provides experimental support for one of the fundamental assumptions made when developing the π-logic concept (Chapter 1.3). This study constitutes the first direct comparison of molecular conductance experiments on a set of fundamentally different π-conjugated systems present in three molecules of nearly identical shape and length.
5.9 Experimental Section

5.9.1 Preparation and analysis of the solutions and SAMs

Dry chloroform was used (Aldrich anhydrous, ≥99%, contains amylenes as stabilizer). Triethylamine (Et\textsubscript{3}N) was purchased from Fisher (HPLC grade) and degassed. Tetrabutylammonium hydroxide 30-hydrate (Bu\textsubscript{4}NOH) was purchased from Sigma-Aldrich and stored under dry nitrogen.

All solutions and SAMs were prepared inside a glovebox filled with nitrogen (<5 ppm O\textsubscript{2}). SAMs were grown in two nights (40-44 h) from 0.5 mM solutions in chloroform, with 10% (v/v) Et\textsubscript{3}N added, unless stated otherwise. The solutions of AQ and 26AC were stirred and heated till 50°C, and -if particles were observed by eye- filtered through a 1 µm PTFE syringe filter by gravity. We used freshly prepared samples of 150 nm gold on mica for the ellipsometry, XPS, and EGaIn studies and freshly prepared samples of 2-5 nm chromium and 200 nm gold thermally deposited on a silicon wafer for the CP-AFM studies. After two days, samples were taken from solution and immersed three times in vials with clean THF, after which the samples were dried in the glovebox or with a nitrogen pistol.

UV-Vis absorption spectra of the solutions were measured on a Perkin Elmer Lambda 900 Spectrometer in a 1 mm quartz cuvette with Teflon stopper.

Ellipsometry measurements were performed using a V-Vase from J. A. Woollam Co., Inc. in air. Measurements were acquired from 300-800 nm with an interval of 10 nm at 65, 70, and 75° angle of incidence. For every set of experiments a fresh gold-on-mica sample was measured at three or four different spots. The data from these measurements were merged and the optical constants were fitted. For every SAM three spots were measured and the thickness of a cauchy layer (n=1.55, k=0 at all λ) on top of the gold layer was fitted and averaged over the three spots.

XPS measurements were performed on a X-PROBE Surface Science Laboratories photoelectron spectrometer with a Al Kα X-ray source (1486.6 eV) and a takeoff angle of 37°. We accumulated 20 scans for S2p, 10 for C1s, 10 for O1s, 15 for N1s, and 5 for Au4f. All reported data are averaged over three different spots per sample. See Chapter 3.8.4 for details on the fitting of the data with WinSpec and calculation methods for the thickness.

5.9.2 CP-AFM Measurements\textsuperscript{37}

The measurements were performed on a Multimode 8 atomic force microscope base using a Nanoscope III controller. The AFM cantilevers (Veeco NP-10 chips, B cantilever, 0.12 N/m and 14-26 kHz) were sputtered with MoGe (4 nm) as an attachment layer prior to the Au layer (80 nm). Before every measurement the tips were cleaned by an oxygen plasma. The samples were prepared by growing SAMs on Au-coated Si/SiO\textsubscript{2} substrates as explained in Section 5.9.1. Subsequently, the sample was electronically connected to the scanner with silver paint and the scanner was connected to the data acquisition card via the AFM breakout box. Using a modified tip holder, the (grounded) cantilever was connected to the I/V converter (Femto DLPAC-200). The AFM was operated in contact mode with the scanning range set to 0 nm in order to contact continuously the same area of the SAM. To insure a soft contact with the molecules, a force of
approximately 2 nN was applied and maintained constantly using feedback on the deflection of the cantilever.

Once the molecules were contacted, the current sensing was switched on as it is externally driven by Labview. A bias voltage was applied to the tip-sample junction and swept from 0 V to 1.2 V to -1.2 V and back to 0 V typically. Simultaneously the current was recorded at a sampling rate of 10 kHz. We recorded 200 to 1000 of such $I$-$V$ curves for each of the three to six spots per sample. For each molecule we computed all the measured $I$-$V$ curves into a linearly averaged $I$-$V$ curve. The conductance histograms were build up from low bias (100 mV) conductances of individual $I$-$V$ curves. Those conductances were logarithmically binned and plotted linearly.

### 5.9.3 EGaIn Junctions

The EGaIn setup was composed of an EGaIn filled 10 μL syringe with a flat needle, a CCD camera with a variable-zoom telescopic lens, a piezo-crystal for high precision motion control of the syringe, and a subfemto-Amperometer with external current amplifier (Keithley 6430). The EGaIn tips were formed by placing a big drop of EGaIn on a surface and subsequent withdrawal the syringe with the piezo. The speed and the step voltages applied to the syringes determined the shape of the EGaIn tip. The sample and the amperometer were grounded and a voltage was applied on the syringe filled with EGaIn. The sample was approached with the EGaIn tip first manually (no contact, 1-5 pA at 100 mV bias voltage), then with the piezo until the current started to increase. Five $I$-$V$ traces were measured per spot, from 0 to 0.4 to -0.4 to 0 V, at ~20 spots per sample.

### 5.9.4 Large-Area Molecular Junctions

A 4-inch silicon wafer with a 500 nm thermally grown oxide was passivated using hexamethyldisilazane (HMDS). A 1 nm layer of chromium was thermally evaporated through a shadow mask, followed by 60 nm of gold. The rms roughness of the bottom contact was about 0.7 nm over an area of 0.25 μm². The two terminal junctions were photolithographically defined in an insulating matrix of photoresist, ma-N 1410 (Micro Resist Technology GmbH). The negative photoresist was spin cast on the wafer resulting in a layer of 570 nm. After a pre-bake step to remove any remaining solvents, the layer was exposed to UV light with a Karl Süss MA1006 mask aligner, to define the vertical interconnects, ranging from 5 μm to 100 μm in diameter. After development, the film was hard-baked at 200°C for at least 1 hour to render the photoresist insoluble in organic solvents. The wafer was subsequently cut in 4 pieces using a diamond tip pen. This allowed the simultaneous processing of different SAMs on a single wafer, thereby eliminating processing variations that can affect device performance. A last step before self-assembly was cleaning of the bottom gold contacts with a PDC plasma cleaner (Harrick plasma) to remove any photoresist residuals.

The self-assembled monolayers were formed from 0.5 mM solutions in chloroform with 10% Et₃N in 44 hours in a glove box (wafer pieces were immersed upside down in the solutions). After that, the wafer pieces were thoroughly rinsed with chloroform in ambient. Subsequently, the interlayer of PEDOT:PSS, a water-based suspension of poly(3,4-ethylenedioxythiophene) and poly(4-styrenesulfonic acid), was spin cast. PEDOT:PSS acts as a highly conductive buffer layer that protects the SAM during subsequent evaporation of the top gold contact. The
commercially available PEDOT:PSS AGFA® ICP new type, filtered over a 5 µm Whatman® glass filter, was used. The PEDOT:PSS solution was spin cast, resulting in a layer thickness of about 90 nm. The wafer was then immediately transferred to a vacuum oven for at least 1 hour to dry the film. To facilitate contacting the top electrode, approximately 100 nm of gold was evaporated through a shadow mask. This gold layer, apart from ensuring a better contact with the measurement probes, also serves as a self aligned mask for the removal of redundant PEDOT:PSS by reactive ion etching (O₂ plasma). This step eliminates any parasitic currents from top to bottom electrode.

Current-voltage (I-V) measurements were performed in a home-built probe station using a Keithley 4200 Semiconductor Analyzer Characterization System. The probe station was pressurized at 10⁻⁶-10⁻⁷ mbar for at least 6 hours before the measurements, to remove any water absorbed in the PEDOT:PSS layer. Devices were swept in the voltage range of 0 V to 1 V to -1 V and back to 0 V and the recorded current densities were averaged for all devices with different diameters. We measured in total 27-36 devices per SAM and found nearly identical current densities for junctions of 5-100 µm in diameter. We have plotted the median of the current density as function of the voltage.

5.9.5 MCBJ Measurements Bern

A notched gold wire (0.1 mm diameter) was glued on a polyimide-coated stainless steel sample with epoxy glue (stycast 2850ft with catalyst 9) and cleaned in an ozone cleaner. A liquid cell was mounted on the sample and a mM solution of molecular wires in THF/decane (1:4) was placed in the liquid cell under argon atmosphere. The substrate was bend by a pushing rod, controlled by a stepper motor and a piezo stack. After breaking of the junction, current-distance traces were recorded while repeatedly opening and closing.
5.10 References and Notes


35. The thicknesses as obtained by ellipsometry and XPS are averaged: The absolute values obtained from XPS by method A are considered more thrust worthy than those obtained by method B and therefore weighed twice as strong. Identical weights were used for ellipsometry and XPS (methods A and B combined). The value for AC-DT determined by ellipsometry and the value for AQ-DT determined by XPS method A are not included in the average.
36. We have not investigated the quality of these SAMs by electrochemistry. We assume that these SAMs are densely packed and of high-quality, since we used the optimized procedure developed in Chapter 3.
37. CP-AFM measurements were performed by Constant Guédon and Sense Jan van der Molen at Leiden University.
39. DFT transport calculations were performed by Troels Markussen and Kristian Thygesen at the Technical University of Denmark.
43. EGaIn measurements were performed in our group by Davide Fracasso and Ryan Chiechi, University of Groningen.

45. The histograms are automatically fit to a Gaussian distribution using the least-squares fitting routine from GnuPlot.

46. For a detailed discussion on the analysis of the data see: D. Fracasso, H. Valkenier, J.C. Hummelen, G.C. Solomon, R.C. Chiechi, *submitted for publication*


54. Large Area Molecular Junctions were made and analyzed by Ilias Katsouras in the group of Dago de Leeuw, Zernike Institute for Advanced Materials, University of Groningen.


57. MCBJ measurements were performed by Wenjing Hong, in the group of Thomas Wandlowski at the University of Bern.

58. UHV MCBJ studies are in progress by Diana Dulić and Mickael Perrin in the group of Herre van der Zant at Delft University of Technology.

59. We cannot exclude the possibility that some of the relatively unstable $\text{H}_2\text{AC}$ molecules have been converted *in situ* into $26\text{AC}$ and cause the small peak at $10^{-4.7} G_0$ in the histogram of $\text{H}_2\text{AC}$.


61. WinSpec 2.09, developed at Laboratoire Interdépartemental de Spectroscopie Electronique, Namur, Belgium