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Molecular conductance

Valkenier-van Dijk, Elisabeth Hendrica

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Summary

This thesis describes how the molecular structure determines the conductance of rigid π -conjugated molecules: molecular wires. We developed a library of molecular wires, synthesized by a general scheme, and studied molecular conductance by the "Matrix Approach". In that, we study *trends* in the molecular conductance of several *series of molecular wires* in five different *junction geometries*. The resulting matrix allows to compare these trends for different junctions and separate technical influences from the influence of molecular structure on conductance.

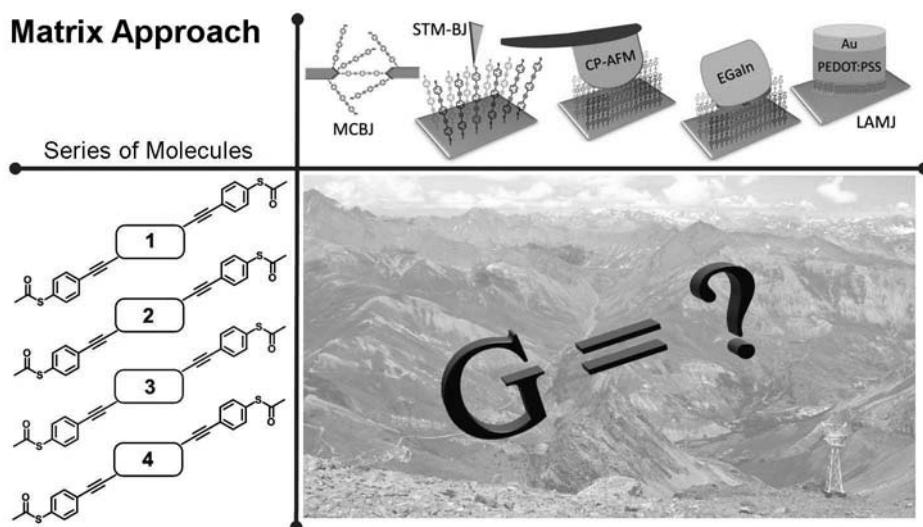


Figure 1 The Matrix Approach, in which the trends in molecular conductance of several series of molecular wires are studied in different junction geometries.

Determining the molecular conductance is a first step. Controlling molecular conductance by means of switching is an important requirement on the road towards functional molecular electronic devices. In Chapter 2 we present an anthraquinone-based redox-switch. This molecule is cross-conjugated in its stable state, and turns linear conjugated upon (electro)chemical reduction. Oxidation of the linear conjugated state returns it to the cross-conjugated state. This cross-conjugated state is expected to have a lower conductance compared to the linear conjugated state, due to the reduced electronic coupling in cross-conjugated π -systems. Reduction and oxidation are, in principle, electronic tools that allow fast and complete switching of the molecular switch between these high and low

conductance states.

Before measuring the conductance of our molecular wires and switches, we describe in Chapter 3 the formation of contacts between the molecules and the electrodes. The molecular wires discussed in this thesis have thiol groups on both ends of the molecular wire, to anchor the molecules to gold electrodes via thiolate-gold bonds. These thiol anchoring groups are protected with acetyl groups, to prevent the conjugated thiols from degradation (by oxidation on air). When these π -conjugated dithioacetates bind to gold, the acetyl groups disappear and the molecules form a self-assembled monolayer (SAM). However, this SAM did not have the maximum packing density. Densely-packed and high-quality SAMs were obtained when a small fraction of the thioacetate groups was deprotected to form thiolate anions. We have shown in Chapter 3 that this can be realized upon immersion of a gold surface for two days in a solution of π -conjugated dithioacetates, to which $\sim 10\%$ triethylamine was added. Alternatively, dithioacetates can be deprotected with a stronger base or nucleophile as we illustrated with tetrabutylammonium hydroxide. Addition of four equivalents resulted in solutions of molecules with two thiolate anions, which formed monolayers of molecules laying flat on the gold surface. The addition of one to two equivalents tetrabutylammonium hydroxide as deprotecting agent allowed the formation of SAMs in less than one hour. However, these SAMs have more defects than those formed with triethylamine and have tetrabutylammonium counter ions incorporated. The conditions used for the formation of SAMs have a major influence on charge transport properties of the SAMs, as we have shown in Large Area Molecular Junction (LAMJ) devices.

Chapter 4 presents three series of linear conjugated molecular wires. The trends in the conductance of these wires was investigated by the Wandlowski group with the Scanning Tunneling Microscopy Break Junction (STM-BJ) method. The conductance of the molecular wires was found to be mainly determined by the length of the wires. Wires with a smaller HOMO-LUMO gap (or higher HOMO level) showed a higher conductance, although the influence of length dominates the charge transport, which is described by a non-resonant tunneling model. Transport calculations confirmed the experimental trends.

Chapter 5 discusses the influence of the π -conjugation pattern on the charge transport properties of molecular wires. After analysis of the SAMs grown from this series of molecular wires, the results from conductance studies by several

methods (all performed in collaborations with different groups) are discussed. Electrical measurements through SAMs that were contacted with a gold-coated Atomic Force Microscopy (CP-AFM) tip or with the eutectic alloy of gallium and indium (EGaIn) showed that the cross-conjugated anthraquinone unit reduced the conductance by about a factor fifty, compared to the linear conjugated anthracene unit. A similar reduction of the conductance was found when the conjugation pattern was broken, by incorporation of a dihydroanthracene unit. This trend was less clearly displayed in LAMJs. Single molecule experiments by Mechanically Controllable Break Junction (MCBJ) methods gave about two orders of magnitude lower conductances for the anthraquinone wire than for the anthracene-based wire, in good agreement with the other measurements. Transport calculations revealed a strong minimum in the transmission of the anthraquinone-wire around the Fermi energy. The reduction of the conductance of the cross-conjugated anthraquinone-based wire can be attributed to this quantum interference effect.

In Chapter 6 we have incorporated the aromatic methano[10]annulene unit (10π -electrons) into molecular wires and thiophene-based polymers and compared it to naphthalene, to study the influence of aromaticity on the conductance of molecular wires and on the conductivity of conjugated polymers. We observed a decrease in the optical HOMO-LUMO gap of the methano[10]annulene based wire and polymer, compared to the naphthalene analogues. This study is still in an exploratory state.

In Chapter 7 we return to the Matrix Approach by presenting additional results from conductance measurements by various methods (in several collaborations) on the length dependence of molecular conductance and on the comparison of monothiolated and dithiolated molecular wires. We present an overview of all conductance measurement results on our series of wires, obtained by different collaborating groups in different junctions. The results obtained in Au-molecule-Au junctions (CP-AFM, STM-BJ, and MCBJ) showed an identical dependence of the conductance on the length of the linear conjugated molecular wires, expressed in β values of 0.33 - 0.35 \AA^{-1} . Significant decreases in HOMO-LUMO gap resulted only in a small deviation from this length dependence. The molecular conductance was however changed by about two orders of magnitude when the conjugation pattern was changed into cross-conjugated or broken conjugation. This latter trend was also found in junctions over larger areas that have a more complex top contact (e.g., GaIn/Ga₂O₃ in EGaIn junctions or Au/PEDOT:PSS in LAMJs). In these

junctions the estimated values for the conductance per molecule were lower and the length dependence was less strong than for Au-molecule-Au junctions, which is attributed to the less conductive interlayer between the SAM and the metal electrode. The mentioned dependence of the molecular conductance on the conjugation pattern, which can be described by quantum interference effects, offers an interesting tool to control the conductance of single molecules and SAMs as required for electronic applications. As such, these fundamental studies can contribute to the development of molecular electronic switching and computing.