Reversible conductance and surface polarity switching with synthetic molecular switches

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This chapter gives a brief introduction to molecular machines and molecular switches as well as to the development of molecular electronics. The working principle of a molecular tunneling junction with gold as bottom electrode and a liquid metal as top electrode is discussed.
1.1. **Molecular Machines (Design and Development)**

Molecular machines can be defined as devices that can produce useful work with the interaction of individual molecules at the molecular length scale. Balzani *et al.*, [1, 2] defined a molecular device as "An assembly of a discrete number of molecular components designed to achieve a specific function. Each molecular component performs a single act, while the entire supramolecular assembly performs a more complex function, which results from the cooperation of the various components." Molecular machines are nanoscale devices, whose movement is governed by statistical mechanics and not by Newtonian mechanics as for macroscopic machines [3]. Since at room temperature the molecular components are constantly in motion, the supramolecular architecture needs to control the directionality of the movement and restrict the degrees of freedom. Mother Nature developed different types of molecular machines for biological systems such as those for ATP [4] synthesis and DNA [5, 6] replication. The pioneering work of Jean-Pierre Sauvage, J. Fraser Stoddart and Ben L. Feringa in the area of molecular machines was awarded the Noble prize 2016. Noble committee member Olof Ramström [7] indicates "In a sense, we are at the dawn of a new industrial revolution of the twenty-first century, and the future will show how molecular machinery can become an integral part of our lives. The advances made have also led to the first steps towards creating truly programmable machines, and it can be envisaged that molecular robotics will be one of the next major scientific areas."

The group of T. Ross Kelly [8] developed a molecular machine (Figure 1.1) where the direction of the rotary motion can be controlled with the help of chemical reactions. These molecular machines only rotate by 120° around the axis. In the same year the Feringa group published an article in *Nature*, describing an overcrowded alkene molecule which rotates unidirectionally around the alkene axis [9–11] under irradiation.

![Figure 1.1 Chemically powered 120° directional rotation of a triptycene residue.](image)
1.1. MOLECULAR MACHINES (DESIGN AND DEVELOPMENT)

Figure 1.2 (a), Light power 360° (a), 1st generation rotatory motor model Copyright © 1999, Springer Nature[9], (b), 2nd generation motor which helps the rotation of (c) microscopic object[13] Copyright © 2006, Springer Nature.

with light. The rotation occurs by first an energetically uphill photoisomerization (stable -> unstable) followed by an energetically favourable helix inversion (unstable -> stable) resulting in a 360° rotation. Repeating these steps results in a biased unidirectional rotation of the upper half (arbitrarily termed rotor) relative to the bottom half (stator) as illustrated in Figure 1.2 (a) In practice the motor continues turning as long as the compound is irradiated with photons and kept above a critical temperature. Over the next decade, different functionality and different generations of motor molecules, dramatically[12] increased the rate of rotation and potential candidates for applications such as rotating a macroscopic object[13] (Figure 1.2 (b)), switching the chirality[14] of an organocatalyst, and acting as the “motorized wheels” of a “nanocar”[15]. Besides molecular motors, over the years scientists have developed a wide range of molecular devices for practical applications, which include tubes, wires, shuttles, switches and ratchets. The following section presents some examples of molecular switches.

1.1.1. MOLECULAR SWITCHES 1 : SPIROPYRANS

Molecular switches are molecules that can exist in two or more stable states. The molecules may be reversibly switched from one state to the other by external stimuli such as heat[16] light[17], or a change in pH[18, 19]. These molecules commonly change their conformation in such a way that the properties of the new structure
are different from the parent one. The light-active switches are interesting for their wide range applications, e.g. spiropyrans have been suggested for optical[20, 21], sensor[22], and electronic[23] applications. Spiropyran was discovered in the early twentieth century and its photochromic reaction described by Fischer and Hirshberg[24] for a “photochemical erasable memory”. The possible pathway of photochemical and thermal isomerization of spiropyran is represented in Figure 1.3. The molecule comprises an indoline N and a chromene moiety, bound together via a spiro carbon. UV (365 nm) irradiation of SP gives rise to the open-ring isomer merocyanine (MC; Figure 1.3) in a first-order process. The ring-opening reaction can be represented either as a heterolytic C–O bond cleavage or as a 6π electrocyclic ring opening, leading to the zwitterionic (MC) or the quinoidal resonance forms, respectively.[25] The MC-SP reverse isomerisation usually occurs spontaneously, and can be accelerated by visible light.

The two isomers (zwitterionic, quinoidal) have different properties in different solvents, and react differently to metal ions, acids and bases, temperature, redox potential, and mechanical force. The vastly different physiochemical properties of SP and MC derive firstly from the charge separation in MC, which gives rise to a large electric dipole moment. Density functional theory along with experimental results suggest that the dipole moment of the parent SP is in the range of 4–6 D, whereas it amounts to 14–18 D for the MC form[25]. Secondly, SP occupies less volume than MC and thirdly the electronic structure related to each conformation implies that SP is optically transparent in the visible region, whereas MC strongly absorbs at $\lambda = 550–600$ nm[22]. Fourthly, protonation of MC in presence of acid leads to MCH+$^{[23]}$.

1.1.2. Molecular switches 2: A switchable host-guest system based on cucurbit[8]uril

Supramolecular host–guest systems with reversible non covalent interactions such as hydrogen[26, 27], electrostatic[28], van der Waals[29] and hydrophobic[29] bonding between macrocyclic hosts and suitable guests are good candidates for surface functionalization [30–32]. The binding and dissociation processes for the host-guest chemistry are often reversible. Cucurbiturils constitute a unique class of macrocyclic hosts, because of the strong charge-dipole and H-bonding interactions as well as the hydrophobic effect derived from the negative portals and rigid cavity which help to
form stable host-guest complexes, with binding constants ranging up to $10^{10} \, M^{-1}$ \cite{33} with cationic or electro-positive guest molecules \cite{34–36}. Cucurbit[8]uril (CB[8]) is the largest member of the Cucurbit[n]uril family, and capable of encapsulating two different guest molecules at the same time, an electron-deficient molecule (which serves as the first guest) and an electron-rich molecule (as the second guest), inside the cavity to form a stable 1 : 1 : 1 heteroternary complex. The complex formation is driven by the hydrophobic effect and exhibits an enhanced charge-transfer (CT) interaction between the guest pair inside the hydrophobic cavity of CB[8] \cite{37, 38}. A photo-responsive complex can be formed between CB[8] and azobenzene photo-switches with methyl viologen (MV$^{+2}$) \cite{39} as shown in Figure 1.4. The trans-1 (azobenzene), MV$^{+2}$ together with CB[8] leads to formation of 1 : 1 : 1 heteroternary complex (MV$^{+2}$.trans−1)$\subset$CB[8] spontaneously. The complex was irradiated with UV light to promote ‘trans’ to ‘cis’ isomerisation, and hence a new complex of (MV$^{+2}$)$\subset$CB[8] forms. Similarly, under visible light the ‘cis’ to ‘trans’ isomerization leads to formation of the reverse complex.

1.2. MOLECULAR ELECTRONICS

The performance of electronic devices over the past half-century follows Moore’s law, which resulted from the miniaturization of ‘top-down’ manufactured components. The device manufacturers are interested in the development of more economical, faster and smaller devices for next-generation computing technology. The ‘bottom-up’ fabrication of molecular electronic components, using single molecules (especially organic molecules) would push the limit of miniaturization. The field of molecular electronics started with one of the most fundamental questions: how do electrons move through molecules? Understanding the movement of electrons through a single molecule is central to the field of molecular electronics, but presents a significant experimental and theoretical challenge. In single-molecule electronics, one of the most popular transport measurements techniques is based on either the electrochemical break junction\cite{40, 41} or the mechanical break junction\cite{42}. Both techniques produce extensive data sets because measurements can be made rapidly, and therefore statistical theoretical analysis on the basis of the information in histograms and the distributions of data can be carried out, which allows mechanistic insight tunneling on the tunneling...
of an electron in the junction.

1.2.1. LARGE AREA JUNCTION
Integration of single-molecule junctions[40] into a device is an almost impossible task since stability and reproducibility are major issues. In order to measure molecular charge transport through the molecule in a “metal // molecule // metal” device architecture millions of molecules in between two electrodes can be used. First a one molecular thick (equivalent to molecular length) film is formed on the electrode surface, which can be metal or another conducting material. In 1971, Kuhn and Mann reported conductivity measurements through monolayers of cadmium salts of fatty acids[43]. The conductivity of these organic monolayers was exponentially decreasing with thickness, a demonstration of electron tunneling through the organic monolayer.

Molecular monolayers on metal surface can also be obtained by self-assembly in solution. Self-assembled monolayers (SAMs) were discovered in the early 1980s by Nuzzo and Allara[44] and later popularized by Whitesides[45] and Chidsey[46]. When the SAM is grown on a metal surface, another electrode on top of the molecular film creates a junction where the distance between two electrodes is defined by molecular length. Such junctions can easily be fabricated with \( \text{cm}^2 \) areas and are hence referred to as large area junctions.

A liquid metal contact is ideal as top electrode in such a large area junction because it is relatively stable and does not damage the soft layer below. This technique effectively solved problems that are encountered with the direct evaporation of metal top contacts, where metal atom diffusion into the SAM is often encountered. Slowinski et al., first[47] introduced liquid metal electrodes in molecular junctions[48, 49] in the form of a clean mercury (Hg) drop delivered with a microsyringe to mechanically contact a multilayer molecular film. The principle used to form the Hg/SAM1 // SAM2/Metal or Hg/SAM//Si, where / symbolizes a covalent bond and // a Van-der-Waals interaction) is relatively simple[49], as illustrated in Figure 1.5. It is a slow and laborious technique only applicable for multilayers of molecules on metal electrodes.

1.2.2. EUTECTIC GALLIUM INDIUM (EGaIn) SOFT CONTACT
The toxic nature of Hg motivated the search for other liquid metals and in 2008 Chiechi et al., [50] used a eutectic alloy of Ga and In (EGaIn) (75% In and 25% Ga by weight, melting point= 15.5 ° C) as top electrode in a large area junction. At the ambient conditions EGaIn, is a non-Newtonian fluid protected by a very thin skin of Ga\(_2\)O\(_3\) (0.7 nm)[51]. This layer guarantees for shear-thinning, i.e. its viscosity decreases under shear stress such that it can be molded into non-spherical shapes that allow for electrical contact area down to the micrometer scale. The EGaIn junction can be defined as EGaIn/Ga\(_2\)O\(_3\) // SAM/Au, where the SAM is connected to the Ga\(_2\)O\(_3\) Van-der-Waal (//) forces[52].

There is some major concern about the data accumulation and interpretation to extract the J/V characteristics of a molecular tunneling junction. The molecular monolayers or SAMs are not perfect systems as shown in Figure 1.5(b), and hence these junctions have two classes of defects. First, the defects that preserve the basic (Au\(^{TS}\)-SAM//Ga\(_2\)O\(_3\)/EGaIn) structure, even while changing the tunneling distance, like
1.2. Molecular electronics

Figure 1.5 How to measure electron transport through the large area molecular junction by using top contact (a) Schematic representation of an EGaIn/Ga2O3//SAMs/Ag junction[51] Copyright © 2012 American Chemical Society. b) Schematic representation of the formation of a Hg drop junction for thiol-molecules on a hydrogen-terminated Si substrate[49]. Copyright © 2014 American Chemical Society.

domain boundaries, pinholes, disordered regions, and physisorbed contaminations on the SAM. This type of defect follows the Simmons model[53, 54] because charge is transported through the junction. The second type of defect is the defect due to artifacts, such as the area in which the Ga2O3/EGaIn electrode penetrates the SAM, or the impurities between the two electrodes. These artifacts not only change the tunneling distance but also change the mechanism of charge transport, in other words they don’t follow the Simmons model of charge transport through the junction. Reus et al., [55], solved this problem by using statistical analysis. In their article, these authors used the normally distributed log|J| (current density) histogram and statistically calculated the population mean, µJ, and the standard deviation, σJ. There are two ways of estimating µlog and σlog for a non-ideal distribution; first, taking the arithmetic mean and
slandered deviation of $\log|J|$; or second, fitting the histogram of $\log|J|$ with a Gaussian function\cite{52, 55} - the mean value of the Gaussian peak gives $\mu\log$ and the width of the peak or fitting parameter is considered as standard deviation $\sigma\log$. The first one is sensitive to outliers and shorts, but insensitive to noise. The Gaussian method\cite{52} is not only taking into account the noise of measurement but also solving the problems of outliers and shorts in the histogram.

1.2.3. MECHANISM OF CHARGE TRANSPORT

In the molecular electronics the electrodes are separated by molecules as discussed earlier, and the size of the molecules is in the range of a few nanometers. At this quantum scale the dominant mechanism of charge transport becomes tunneling. The organic molecules are insulators or wide band gap semiconductors, and this is why molecular electronics follows the Simmons model\cite{53} for electrons tunneling through the barrier. The derivation of Simmons model\cite{53} relies on a few assumptions: (i) The barrier is larger than the thermal energy and the probability of electron tunneling through an arbitrary potential barrier can be described by the WKB approximation, named after the scientists Wentzel, Kramers, and Brillouin, and a method to approximate solutions to a time-independent linear differential equation; (ii) the Drude-Sommerfield model for free electron describes the electrons in the metal contacts. The tunneling current $J$ through a rectangular barrier of average height $\phi$ and width $d$ at $V<\phi/e$ can be described by following equation\cite{53}.

$$ J = J_0 \left[ \left( \phi - \frac{eV}{2} \right) e^{-\Lambda\alpha\sqrt{\phi - \frac{eV}{2}}} - \left( \phi + \frac{eV}{2} \right) e^{-\Lambda\alpha\sqrt{\phi + \frac{eV}{2}}} \right] $$

(1.1)

where $J_0 = e/(2\pi\hbar d^2)$ and $\Lambda = 4\pi d\sqrt{2m_e}/\hbar$

$m_e$ = electron mass, $\hbar$ = Plank constant, $\alpha$ = fit parameter, $d$ = barrier thickness

The most useful for molecular electronics however, turned out to be an approximation of Simmons model that describes how the tunneling current scales with the tunneling distance:

$$ J = J_0 e^{-\beta d} $$

(1.2)

Where $J_0$, equals to the tunneling current density at $d=0$, $\beta$ is the tunneling decay coefficient. The tunneling decay coefficient $\beta$, is a very well reproduced parameter and its value for alkanethiols\cite{55, 56} ($\approx 0.75\AA^{-1}$) is used as a benchmark for determining whether the molecules dominate the transport in a given experimental setup\cite{57}.

1.3. THESIS OUTLINE

Aim of this research reported in this dissertation is to study the behaviour of molecular switches on the gold surface. We examine the isomerization of these switches on the surface and their performance as suitable switches in molecular tunnel junctions for electron transport and other switches for the photo-switchable surface. This dissertation is organised as follows:

In Chapter 2, we give detailed information about the experimental procedures employed in this thesis. In this report we included all the steps involved in the sample
preparation necessary to obtained self-assembled monolayers (SAMs) of the switches on gold surface. We also discuss in detail about the instrumental conditions for performing X-ray photoelectron spectroscopy, for contact angle measurements and for determining the current through a molecular tunneling junction.

**Chapter 3** describes how the light-induced structural changes influence the tunneling through the molecular junction made up by a pure spiropyran monolayer on template stripped gold surface (Au$^{TS}$) or by a mixed monolayer of spiropyran and hexanethiol. The monolayers were investigated by X-ray photoelectron spectroscopy (XPS) and conductivity measurements performed by using liquid metal (EGaIn) as top contact. This chapter also puts forward a proposal for the mechanism of electron tunneling trough the spiropyran in a molecular tunnel junction (MTJ).

**Chapter 4** is devoted to a detailed study of the reversible chemical locking of spiropyran switches bound to metallic surfaces to enable the encoding of nonvolatile information. We show how to selectively trap spiropyran moieties in their the merocyanine (MC) form by using a combination of exposure to acid and UV light. A proof-of-concept device of 8 bit ASCII characters for encoding information on the surface is described. Therein information is read by measuring the tunneling charge–transport through the monolayer using eutectic Ga–In top-contacts, erased by the base and rewritten.

**Chapter 5** details the difference between physisorbed (non-covalently bounded S atom to a gold surface) and covalently bound molecules in affecting the tunneling conductance across the metal-molecule-metal junction. In this project $\alpha$-lipoic, a five-membered ring with a disulphide and its derivatives were employed for the analysis of the tunneling coefficient ($\beta$). We also elucidate the role of the co-absorbant, ethanethiol, in mixed SAMs.

**Chapter 6** focusses on reversible surface polarity switching with a host- guest complex on a gold surface. We report on the two step surface immobilization of a supramolecular cucurbit[8]rils (CB[8]) complex with a light-responsive thread, bearing paraquat and azobenzene moieties, connected to surface anchoring group via a tetraethylene glycol linker. Upon exposure to UV light, the paraquat moiety is expelled from the cavitand but upon subsequent visible light irradiation the paraquat moiety threads back into the cavitand. This dynamic behaviour leads to a reversible change in water contact angle ($20^\circ$).
BIBLIOGRAPHY


