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## Light-Controlled Conductance Using Molecular Switches

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## Chapter 1

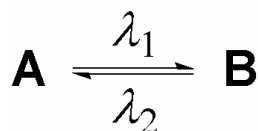
# **Introduction: Light-induced switching of conductance in molecular systems**

*In the first chapter of this thesis an overview is given of the efforts to control conductance by employing light sensitive molecular switches, so-called photochromic switches. The classification of the four most commonly used types of photochromic compounds is given and their conductive properties in solution and on conductive surfaces, as a function of light-induced transformations are described. The light-induced single molecule switching of conductance is discussed to demonstrate the ability of a single molecule to behave as an addressable electronic device. More robust devices that have been realized, based on photochromic molecules (not single molecule devices), having the capability to control conductance are briefly described. Finally, at the end of the chapter an outline of this thesis will be given.*

## 1.1 Introduction

Perhaps, the most basic element of molecular devices is a molecule that can be switched<sup>1,2</sup> between states of low and high conductivity, i.e., can undergo on/off switching. The recent announcement by Stoddart, Heath and coworkers<sup>3</sup> of a 160-kilobit memory based on ‘wired-up’ organic molecular switches has demonstrated the viability of the bottom up approach to molecular components into electronic circuitry promulgated by Richard Feynman almost half a century earlier<sup>4</sup> and popularized by Aviram and Ratner by their pioneering work in 1974.<sup>5</sup> In Stoddart’s and Heath’s system redox stimulation is used to drive changes in molecular states and hence the electronic charge transport properties through the junction.

Photochromic molecular switches are a class of compounds capable of undergoing a reversible photo-induced transformation between two stable states, whose absorption spectra are distinctly different (Scheme 1).<sup>1</sup> The two isomeric forms exhibit different geometries and physical properties such as hydrophobicity, redox chemistry etc. The advantage of photochromic systems are their ease of addressability, reversibility and short response times. Consequently, this offers the possibility of changing local and bulk properties of a molecular based system by irradiation.<sup>6</sup> Indeed the versatile nature of photochromic molecular systems has seen their application in molecular memory devices,<sup>7</sup> molecular electronics,<sup>8</sup> smart surfaces and in the control of supramolecular organization, to name but a few areas.<sup>9</sup>



*Scheme 1* Optical molecular switch that can exist in two different forms and each of them can be selectively addressed by light at a different wavelength.

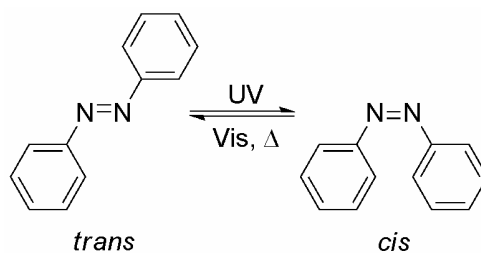
Photochromic molecules represent many challenges as well as opportunities to their application in functioning devices. In particular, the translation of the changes in molecular structure, which accompany photochromism, to changes in molecular conductivity requires that photochromic systems be held as components in electronic circuits and that their charge transport properties change to a measurable degree when the system is addressed with light.

However, to exploit fully the potential of responsive molecular components in electronic devices we need to consider two distinct contributions molecular systems make towards the charge transport across the electrode gap: the effect on tunneling between the metallic contacts, i.e. by modification of the density of states at the surfaces of the metal contacts and the resonant tunneling mediated through the molecular orbitals of the responsive molecule.<sup>10</sup> In the latter case the photochemical changes in the molecule affects either or both the occupied and unoccupied frontier orbitals of the molecule.<sup>11</sup>

## 1.2 Main Classes of Photochromic Switches

Among all organic photochromic compounds there are four most commonly used types of photochromic switches: azobenzenes (Scheme 2), overcrowded alkenes (Scheme 3), spiropyrans (Scheme 4) and diarylethenes (Scheme 5).

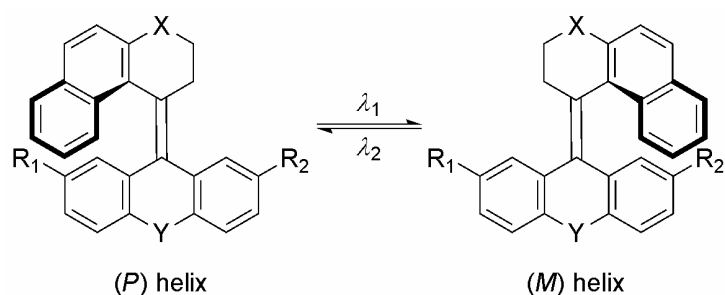
Azobenzenes were among the first photochromic switches used and are still the subject of extensive investigation (Scheme 2). Their *cis*- and *trans*-isomers have a different spatial arrangement of the aromatic moieties, and consequently show significantly different physical and chemical properties.<sup>12</sup> A major advantage of azobenzene switches is that they are easy to synthesize and photoconversion yields are generally high. However, an important drawback is that, depending on the nature of the substituents on the aromatic groups, these switches often undergo thermal *cis* to *trans* isomerization at room temperature.



**Scheme 2** *Trans-cis* isomerization of azobenzene.

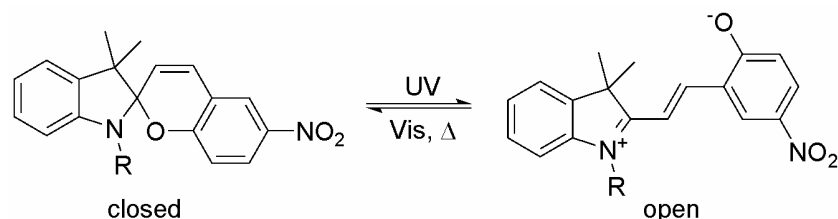
Photochromic interconversions in overcrowded alkenes<sup>13</sup> are based on light-induced isomerization around the central double bond (Scheme 3). The molecular design prevents the notorious photocyclization and other fatigue photochemical pathways common to stilbene-type compounds.<sup>14</sup> The intrinsically chiral structure, based on their helical shape, allows for their use as chiroptical switches *i.e.* the chirality can be controlled by light. This makes them excellent candidates for detection and observation by circular dichroism

spectroscopy or other chiroptical techniques. Their helical shape and possibility of dynamic interconversions between stereoisomers allows them to induce light-driven reversible modifications to supramolecular architectures i.e. liquid crystals.<sup>15</sup> Overcrowded alkenes became the basis for the first light-driven unidirectional molecular motor.<sup>16</sup>



**Scheme 3** Sterically overcrowded alkene undergoing reversible interconversion between a *P* and *M* helix upon irradiation.

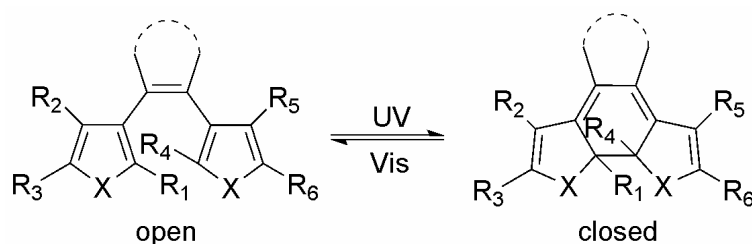
Spiropyrans<sup>17</sup> are molecular switches that can undergo reversible photoisomerization between a stable state and a metastable state using UV and/or visible light. They are well suited to control the interactions within the local environment, since the relatively hydrophobic “closed” spirocyclic isomer can be reversibly converted to a highly polar hydrophilic “open” zwitterionic merocyanine isomer that has a much larger dipole moment as shown in Scheme 4. In addition, the flexibility in the molecule changes considerably going from the rigid closed to the open state. The thermal conversion from the merocyanine isomer back to the closed spirocyclic form occurs typically with a half-life at room temperature of tens of minutes in non-polar media, while the photochemical isomerization with visible light occurs on a much faster timescale.<sup>18</sup>



**Scheme 4** Switching of a spiropyran derivative.

Diarylethenes are reversible molecular switches consisting of conjugated parts connected by a switching element.<sup>19</sup> There are two isomers, i.e., a closed form and an open form of the molecule (Scheme 5). The  $\pi$ -conjugation extends over the entire molecule in the closed

form whereas it is restricted to each half of the molecule in its open form. As a consequence, the closed form is expected to exhibit intrinsically better electrical conductance properties than the open form. The transition from closed to open form takes place for wavelengths  $500 < \lambda < 700$  nm; for the reverse, one requires  $300 < \lambda < 400$  nm. Furthermore, diarylethenes usually exhibit excellent thermal stability and high fatigue resistance.

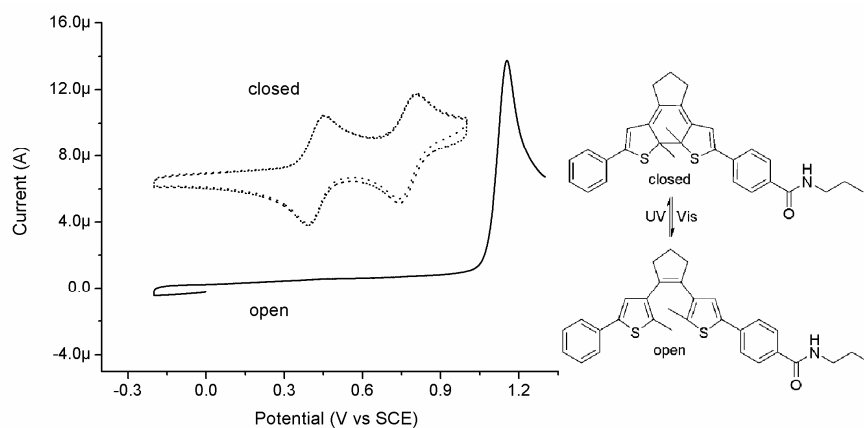


*Scheme 5* Switching cycle of diarylethenes.

### 1.3 Electrochemical Read-Out Following Photochemistry in Solution

The simplest approach to measuring changes in electronic structure, and consequently molecular conductivity (in terms of resonant tunneling), is to examine the changes in the electronic absorption that occur upon photo-switching. In general, a blue or red shift in the lowest electronic absorption band would indicate an increase or decrease in the HOMO/LUMO gap of the molecule, respectively, which can be viewed simplistically as a change in the 'band-gap' of the molecule or as a decrease or increase, respectively in the conjugation pathlength in the molecule. However, this interpretation must be made with caution as the effect of the change in conjugation on 'molecular conductivity' and specifically the change in terms of resonant tunneling requires more detailed information in the absolute changes in the free energy of the HOMO and LUMO orbitals. Cyclic voltammetry offers a powerful tool towards the non-destructive readout of molecular states during photochemical reactions of photochromic molecules (Figure 1). The open and closed forms of diarylethenes give distinguishably different signals.<sup>20</sup> Cyclic voltammetry is a convenient tool to monitor not only the change in the HOMO-LUMO gap (the origin of the change in electronic absorption upon photoreaction) but also provides detailed information as to whether it is the HOMO or LUMO orbital or both which changes in energy – a factor critical to understanding changes in resonant tunneling via these orbitals. For example, two well-known classes of photochromic molecules, the diarylethenes and the spiropyrans show

very similar changes in their electronic absorption spectra upon irradiation, changes which are accompanied by changes in their electrochemical properties.<sup>17,19</sup>

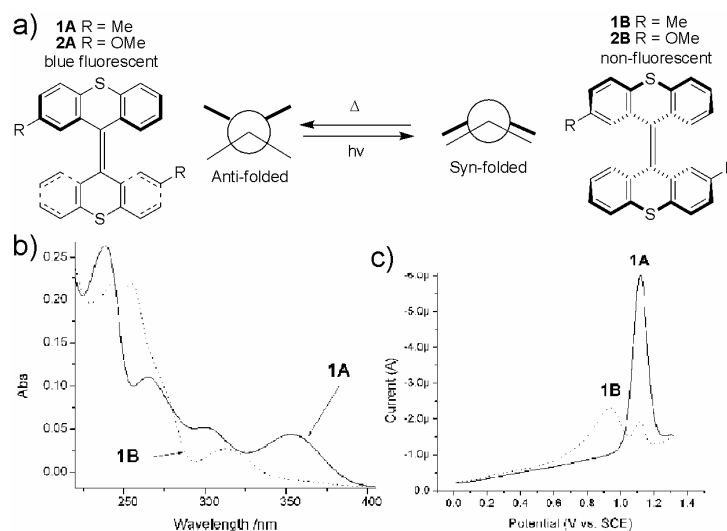


**Figure 1** Cyclic voltammetry and structure of the closed and open diarylethene switch at  $0.1 \text{ V s}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  ( $0.1 \text{ M TBAPF}_6$ ).

The change in redox potential between two photochromic states provides a strong indication of the effect of a photochromic change on the electronic and hence conductive properties of a molecular system. As mentioned above, in the case of the diarylethenes and spiroyrans the dramatic change in the HOMO/LUMO gap is manifested as a bathochromic shift in the absorption spectrum upon irradiation. Based on electrochemical measurements, in the case of the spiroyrans<sup>21</sup> the HOMO levels are essentially unaffected by the ring opening and closing while the LUMO is shifted. In contrast to spiroyrans, for the diarylethenes the increase in conjugation pathlength upon photochemical ring closure results in a lowering of the bandgap by increasing the HOMO energy and decreasing the LUMO energy.<sup>22</sup>

Photochromic behavior is not limited to changes in molecular structure, as also changes in molecular shape can drive changes in electronic structure. This is exemplified in two recent examples. In the case of bis-thiaxylylidene<sup>23</sup> the steric crowding between the four phenyl rings forces the molecule to adopt one of several conformations (Figure 2). In this case the anti-folded state is most stable and is the only state observed at room temperature. Irradiation of this compound in solution at 263 K results in the change of the geometry and a pronounced hypsochromic shift in the absorption spectrum and a complete loss in fluorescence. However, in contrast to spiroyrans and diarylethenes, this change is not due to a change in bonding, but instead in a change in the conformation of the molecule, i.e. to a

syn-folded state. Importantly, the formal conjugation in this system is not affected. However, the electrochemical properties of the molecular change also with a cathodic shift in the first oxidation process upon irradiation (Figure 2). As would be expected, the conversion to a conformationally less stable state implies that the ground state of the molecule is destabilized, i.e. the HOMO rises in energy. The blue shift in the absorption spectrum, however, shows that the destabilization of the LUMO is much more pronounced than that of the HOMO. This is remarkable as there is no simple change in conjugation involved in this transformation but only a change in conformation. Furthermore, the blue shift in the absorption spectrum could be expected to indicate a decrease in conjugation, however, in this case HOMO mediated superexchange process would be enhanced rather than reduced.<sup>24</sup> This is again in stark contrast to the diarylethenes. Hence, a frontier orbital approach i.e. drawing double bonds says little about the charge transport ability of a system. Besides the described photochemical addressing, electrochemical addressing of this compound is also possible. Oxidation of the anti-folded state leads to a dicationic species where the upper and lower halves are oriented perpendicularly to each other. After re-reduction of the dicationic species, the molecule thermally relaxes to the syn-folded state.<sup>23</sup>

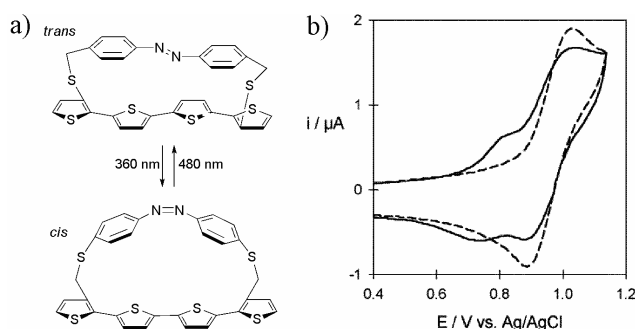


**Figure 2** a) Changes in conformation between the anti-folded and syn-folded states. b) UV/Vis spectrum showing the anti-folded and syn-folded states. c) Differential pulse voltammetry of the anti-folded and syn-folded states.

In the previous example the change in electronic properties was driven by a change in molecular conformation. However, changes in electronic properties driven by



conformational changes can be effected by using photochromic units, which are electronically separated from the unit of interest (Figure 3).<sup>25</sup> The photochromic azobenzene unit in this system is covalently linked to a tetrathiophene moiety. The switching of HOMO level energy is modest but is due to the change in conformation imposed on the tetrathiophene by the photochromic azobenzene unit. The mechanically induced distortion results in the reversible variation of the HOMO/LUMO gap of the tetrathiophene as indicated by cyclic voltammetry (Figure 3a). These effects of mechanical distortions in conductance are known<sup>26</sup> and have important implications for molecular junctions.



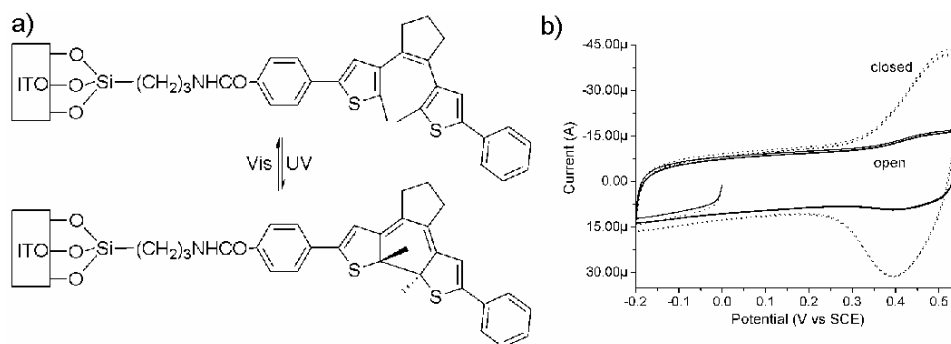
**Figure 3** a) Photomechanical manipulation of the electronic properties of linear  $\pi$ -conjugated system. b) Cyclic voltammogram of the trans form before irradiation (dashed line) and after 2 h of irradiation at 360 nm (solid line).

## 1.4 Electrochemical Read-Out Following Photochemistry on Surfaces

Electronics based on molecular systems can be defined as technology exploiting the properties and functionality of molecules as components in electronic devices.<sup>1,27</sup> However, the molecular component must be “wired up” using other functional units (e.g., thiol or thioacetate groups used for anchoring on gold surfaces, etc.) and must be addressable independently of other switch molecules and functional units in its surroundings.

The electrochemical properties of many of photochromic systems on surfaces have been noted for some time, in particular with respect to the change in surface conductivity which accompanies changes in molecular state.<sup>28</sup> Recently, electrochemistry has been applied as

both complimentary switching method as well as a read-out method for immobilized photochromic switches.<sup>20,29,30</sup>



**Figure 4** a) The open (top) and closed (bottom) form-modified ITO electrode. b) Cyclic voltammetry of the open and closed form covalently attached to ITO electrodes.

However, in immobilizing photochromic switches it is essential to understand that in addition to direct electronic interactions between the surface and the molecule (which can quench photochemistry, change the molecular orbital structure, etc.), other effects can be important, including packing and steric effects, *i.e.* decreases in conformational freedom, intermolecular interactions – changes to rates of intermolecular electron and energy transfer. For example, in the case of dithienylcyclopentenes, in solution the state can be switched in both directions by UV and visible irradiation, but only in one direction by electrochemical stimulation.<sup>22</sup> When immobilized on an ITO surface (Figure 4), no changes in the photochemical properties of the dithienylcyclopentene moiety occur, however it can be switched in both directions electrochemically.<sup>20</sup> The change from solution to surface is not due to changes in intrinsic properties of the molecular species or by orbital interactions with the surface, but rather by a change in observed intermolecular electron transfer rates between the individual molecules, now held closely together on the surface instead of diffusing randomly in solution.

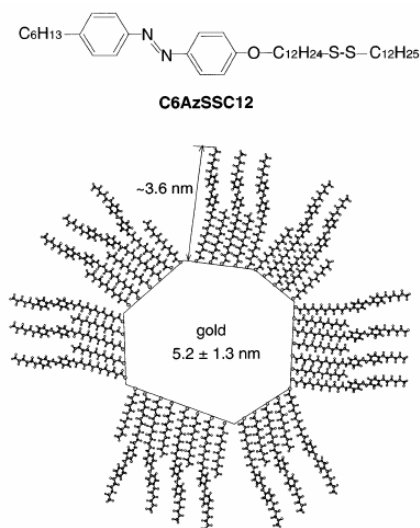
## 1.5 Photochromism on Metallic Nanoparticles

Metallic nanoparticles offer tremendous opportunities for understanding of molecular surface interactions due to the range of nanoparticle sizes which can be accessed uniformly.<sup>31</sup> As such, they offer a convenient model system for mimicking properties of bulk solids, with the additional benefit of being able to tune size-dependent properties, in particular surface plasmon energies.<sup>32</sup> Of particular interest are SAMs of photoactive

molecules formed on the surface of gold nanoparticles. Due to the high surface-to-volume ratio, the concentration of photoactive compounds compared to the number of gold atoms allows for standard characterization techniques such as UV/Vis or FTIR spectroscopy to be employed to detect photochromic switching. Metallic nanoparticles can be easily synthesized from cheap starting materials and thus might serve as a fast screening technique for evaluation of photochromic properties of organic molecules grafted on metallic surfaces.

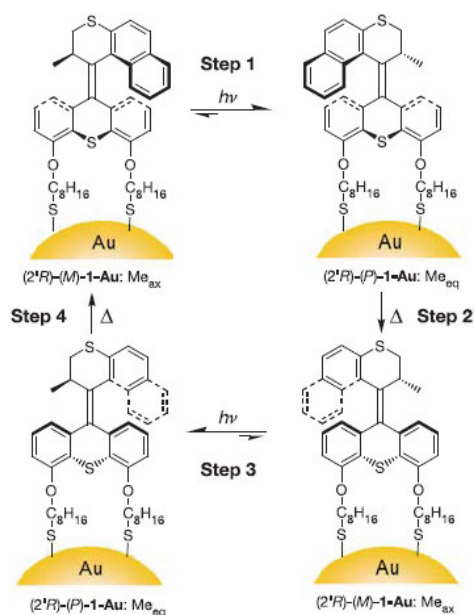
The effect of self-assembly of photoswitches on metallic nanoparticulate surfaces can be seen in two major contributions. Firstly, a direct electronic coupling of a nanoparticle core with a chromophore due to their proximity,<sup>31b</sup> which might result in complete quenching of the photoreaction (see Chapter 4). Secondly, effects of steric constraints, which limit conformational freedom of the molecular entities.

*Trans-cis* isomerization of azobenzenes and stilbenes chemisorbed on gold nanoparticles via alkythiol linkers with a range of spacer lengths has been reported.<sup>33</sup> The quantum yields for the photoisomerization from *trans* to *cis* isomers were found to be dependent on the length of the alkyl chain and were attributed to distance-dependent quenching of the excited state by the metallic core. By contrast, *trans* to *cis* isomerization of an analogous stilbene monolayer on planar gold was not observed because of high crystallinity and dense packing of the monolayer.<sup>34</sup> These observations demonstrate the importance of conformational restrictions on the photoreactivity of photochromic molecules. More recently, unsymmetrical azobenzene disulfides were employed in an attempt to realize highly efficient isomerization on colloidal gold surfaces.<sup>35</sup> In the SAMs formed, the free volume for photoreaction of azobenzenes was guaranteed by a 50% dilution due to the presence of the second alkyl unit used for surface assembly of the disulfide (Figure 5). As a result of this dilution effect both *trans* to *cis* and the *cis* to *trans* isomerizations occur as they were relatively free of steric restrictions in contrast to that obtained on the planar gold surface.<sup>36</sup>



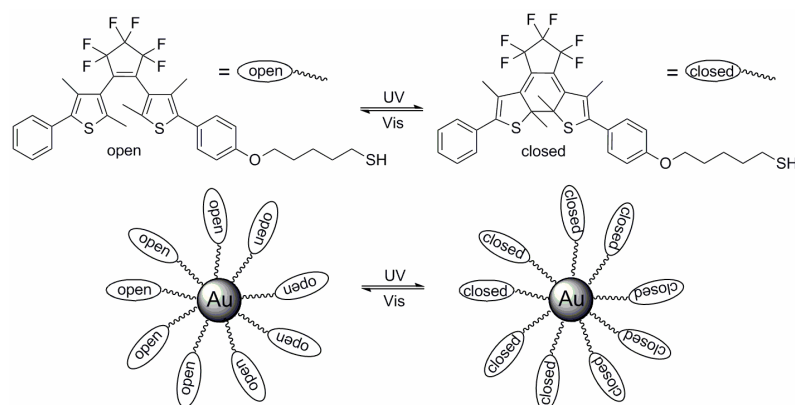
**Figure 5** Molecular structure of the azobenzene disulfide and schematic drawing of the azobenzene-capped gold nanoparticle (adopted from reference 34).

The *cis-trans* isomerization on gold nanoparticles has been studied recently in the so-called light-driven unidirectional molecular motors<sup>37</sup> (Figure 6). A sequence of two energetically uphill photochemical isomerization steps each followed by an energetically downhill irreversible thermal helix inversion step result in a full 360° rotation of a rotor part with respect to a stator part around the central double bond (axis of rotation). Separation of the motor molecules from the gold surface by two eight-methylene-unit linkers was chosen to ensure that the function of the motor observed in solution is retained upon grafting to the gold surface. The barrier for thermal isomerization of molecules grafted on gold nanoparticles was found to be slightly higher than for the molecules in solution, a change which was attributed to the decrease in the molecules' degrees of freedom.



**Figure 6** The four-state unidirectional rotation of a motor-functionalized nanoparticle is shown ( $h\nu$ , photochemical step;  $\Delta$ , thermal step). The photoisomerizations were induced by irradiation at  $\lambda \geq 280$  nm or  $\lambda = 365$  nm.  $Me_{ax}$  indicates the pseudo-axial orientation of the methyl substituent,  $Me_{eq}$  indicates the unstable pseudo-equatorial orientation of the methyl substituent.

In the previous examples, direct electronic coupling and steric restrictions contributed to the change in photochemistry observed upon immobilization. For diarylethenes, however, steric effects arising from close packing in SAMs should not significantly alter photochemistry, since the photoswitching is not accompanied by dramatic geometrical changes and photochemistry is preserved even in crystalline states.<sup>38</sup> An early attempt to investigate photoswitching of diarylethenes self-assembled on a surface of gold nanoparticles showed that when the switching unit is isolated from the surface by a linker based on pentamethylene alkyl chain (Figure 7), the photochromic behavior stays intact.<sup>39</sup> Both ring closure and ring opening processes of molecules grafted on gold nanoparticles resembled those of free molecules in solution.



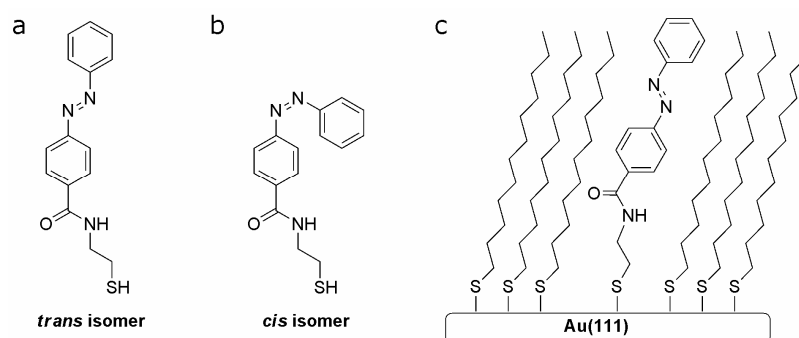
**Figure 7** Photochromic interconversions of unbound (top) and bound to gold nanoparticles (bottom) thiol-terminated diarylethene derivative.

As discussed above an easy way to preserve photochemistry upon grafting on metallic surfaces is to isolate the switching unit by non-conjugated linker. However, this might have negative implications on charge transport properties, since a certain level of communication between switching unit and metallic surface is essential in order to make molecular switching devices feasible. Hence, it is of great interest to study photochromic behavior of diarylethenes with their switching unit connected to the surface of gold nanoparticles directly *via* conjugated spacers (see Chapter 4).

## 1.6 Light Switching of Conductance of Individual Molecules and Monolayers

In the frame of development of optoelectronic molecular devices a crucial milestone would be a direct observation of photo-induced conductance switching under the conditions similar to those that molecules will be confronted with in real devices, i.e. molecules assembled on nanoscopic metallic electrodes at ambient pressures in air. Fundamental questions related to charge transport in molecules (i.e. stability of molecule-electrode contact versus conductance, random conformational changes versus conductance changes, random switching versus controlled switching) can be addressed in setups allowing measurements of individual molecules (scanning tunneling microscopy<sup>40</sup> (STM), mechanically controlled break-junction<sup>41</sup> (MCBJ)). Understanding of these issues will help to design future suitable molecular candidates for switchable devices.

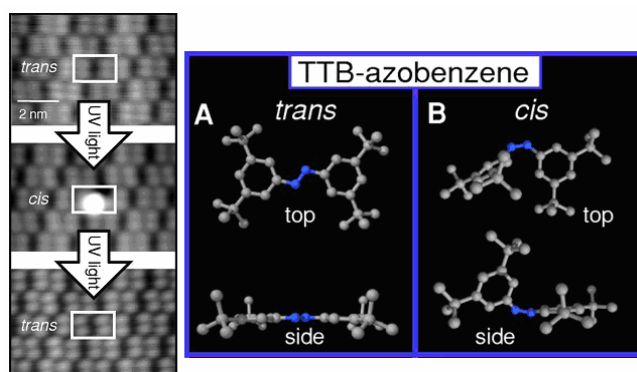
In one of the first reported experiments correlating photochromic switching and changes of conductance for individual molecules, the azobenzene derivatives were embedded in *n*-dodecanethiol SAMs formed on Au(111).<sup>42</sup> The STM tip was used as a nanoscale probe for the charge transport properties of the switch. Direct evidence of light-induced switching for individual azobenzene molecules was achieved by comparing unequal apparent STM heights for *trans* respectively *cis* isomers during irradiation. When azobenzenes undergo a *cis-trans* isomerization, the physical height of the molecules is altered (Figure 8). This does not significantly change the conductance of the molecule itself but does significantly change its height. The apparent changes in conductivity observed by STM thus can be attributed to the switching of height of the molecules rather than to an internal structural modification leading to a modification of resistance. Additionally, it was shown that even in the absence of light, conductance switching was observed and attributed to the reversible *trans-cis* isomerization driven by external electric field and current flow. By varying potentials this voltage-induced switching could be suppressed.



**Figure 8** Schematic structures of an azobenzene derivative which can be grafted on a surface through a S–Au bond. (a) *trans* isomer, (b) *cis* isomer. (c) The *trans* isomer was inserted in a SAM of *n*-dodecanethiol, forming a mixed azobenzene/*n*-dodecanethiol monolayer. The state of the embedded azobenzenes was characterized by their apparent height as seen by STM, which measures a convolution of real physical height and of local density of states.

In the aforementioned case the photoactive unit was isolated from Au(111) surface by the linker composed of two non-conjugated  $sp^3$  carbon atoms terminated by a thiol group providing chemical bonding to the Au(111) surface. More recently, light-induced switching of individual azobenzenes physisorbed on Au(111) was investigated under ultra-high vacuum conditions.<sup>43</sup> *Tert*-butyl groups lift the switching unit away from the substrate (Figure 9), thereby increasing molecular photomechanical activity by decreasing molecule-surface coupling. If the molecule contained zero or two *tert*-butyl legs no isomerization

could be observed, due to the stronger electronic coupling of the switching unit with the substrate. The “transition” that was observed from quenched to active photomechanical behavior reveals the importance of electro-mechanical coupling between a molecule and substrate in determining single molecule photoswitching capability.



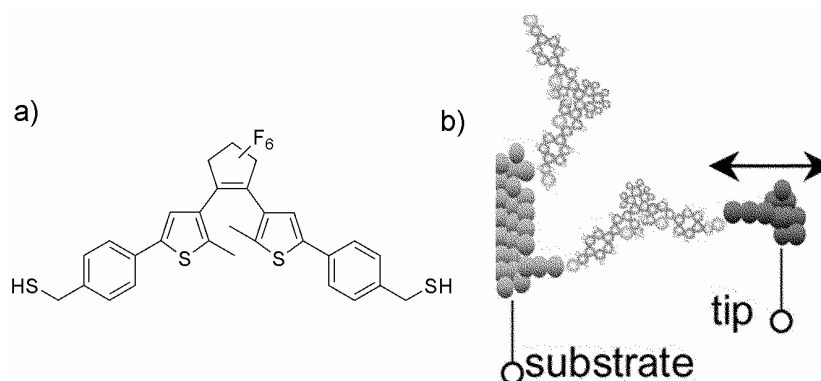
**Figure 9** (left) Reversible photo-induced switching is observed for a single azobenzene molecule. The same individual azobenzene molecule (identified by white boxes in three successive panels) is shown before and after two successive exposures to UV light. The molecule starts out in the *trans* state (top panel), is then switched to the *cis* state after the first exposure to UV light (middle panel), and is then switched back to the *trans* state after a second exposure to UV light (bottom panel). (right) Simulated *trans*- and *cis*- azobenzene structures compared to experiment. (A) Calculated *trans* geometry. (B) Calculated *cis* geometry.

Both examples of conductance switching of azobenzene derivatives relied inherently on switching of height rather than direct switching of intrinsic conductance of the molecules. This means that a setup, sensitive to height switching (as is STM) would have to be employed if azobenzenes are to be used for switching devices. On the other hand, in case of diarylethene photochromic switches rearrangement of double and single bonds after photoswitching should be accompanied by significant modification of conductance, while their physical height is not dramatically altered. Confirmation of the tremendous potential of 1,2-dithienylethenes for molecular electronics was obtained by studying the conductivity of a dithienylethene switch with thiophene groups as spacers and functionalized by two thiol functions chemisorbing on each side of a MCBJ electrode (for the detailed results see Chapter 2).<sup>44</sup> These experiments revealed that switching a molecule from the closed to the open form results in a significant resistance increase of three orders of magnitude. This constitutes an additional indication that closed and open forms are characterized by



intrinsically different charge transport properties. However, once the switch is connected to gold via the Au–S bond, it could only be switched from the closed to the open form. These results were subsequently corroborated by measuring a monothiol analogue of the switch in a STM setup (Chapter 2).<sup>45</sup> Additionally to one-way photoswitching, an extensive analysis of random (stochastic) switching was carried out exhibiting a voltage-dependent behavior. An important consequence of such studies is immediately obvious since both effects, light-induced or stochastic switching, are of the same order of magnitude. The lack of reversibility in those systems (the same behavior was observed for the monothiol derivative on gold nanoparticles) was theoretically investigated and attributed to the quenching of the excited state of the open form by gold.<sup>46</sup> More specifically, density functional theory (DFT) calculations suggested that the observed quenching may result from the alignment of the Fermi-level of gold with the open isomers. The deep-lying HOMO level at a high metal density of states offers the opportunity for many possible electron transfer events, thus reducing the lifetime of the hole created after an excitation. In contrast, the HOMO of the closed isomer is higher in energy within the low density of states of gold and the ring opening can take place (for more details see Chapter 2).

More recently, a new diarylethene derivative with one CH<sub>2</sub> group separating the aromatic part of the switch from the gold surface was investigated using a repetitive break junction method based on a STM setup (Figure 10).<sup>47</sup> Extensive statistical analysis of conductance properties of the single switch is possible as repeatedly a gold probe is pushed into a gold surface and pulled out again to form a thin gold filament in the solution of switch. Markedly different resistances of 526 MΩ in the open form and 4 MΩ in the closed form were found. The isolation of the switching unit by a not fully conjugated linker allowed for the perseverance of reversible photoisomerizations.

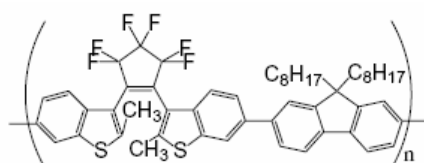


**Figure 10** a) Dithiolated diarylethene switch. b) Schematic representation of the apparatus for conductance measurements. A break junction is formed by pushing a gold probe tip into a gold surface covered with dithiolated switches and retracting it. Molecules become transiently trapped in the gap.

## 1.7 Switching Devices Based on Photochromic Molecules

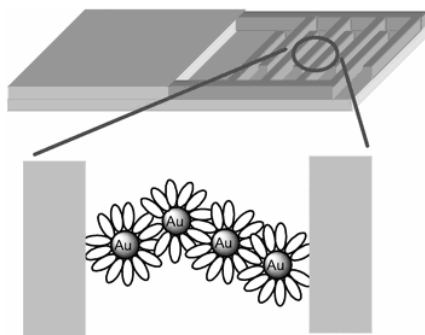
The most obvious objective of molecular electronics is to create fully functioning devices based on molecules. The first “macroscopic” switching device based on diarylethene photochromic molecules has been previously realized.<sup>48</sup> A conductive polymer based on diarylethenes (Figure 11) was sandwiched between metallic (Al and Au) and ITO electrodes. The sets of experiments with different metals as an electrode showed dramatic changes in conductance. If an Al electrode was used devices containing the open form showed rectifying behavior due to the significant junction barrier at the Al/polymer interface, in contrast to the ohmic Au/polymer interface, which in combination with the ohmic polymer/ITO interface results in symmetric IV characteristics of the device. The lower workfunction of Al was responsible for this difference in the junction properties. After ring closure, induced by UV light irradiation, larger currents were observed and IV curves became symmetric. This was attributed to the loss of the junction barrier at the Al/polymer interface because of new electronic states at the previously forbidden area in the original polymer. This highlights the importance of the material that is used as an electrode. The overall reversibility of current switching was found to be poor. However, this was not a direct consequence of a loss of reversibility in photochemical switching judging from the reversible changes in the fluorescence emission intensity. Instead, it was attributed to the instability of the junction or interface structure upon the photochromic reaction. This is not surprising since the surface morphology for a single crystal of

diarylethenes can be changed following photoreactions.<sup>49</sup> The problems with the instability of the interface in the sandwiched photoswitching polymer devices can be overcome by using a non-photochromic polystyrene polymer doped with diarylethene molecules.<sup>50</sup> The domination of photochromic dopants in charge transport in non-conductive polymers was emphasized by the fact that the switch molecule with a donor-acceptor structure exhibited the highest conductance profile (the conductance increases by factor of two changing from the closed to the open form).



**Figure 11** Chemical structure of the diarylethene based polymer from ref. 48.

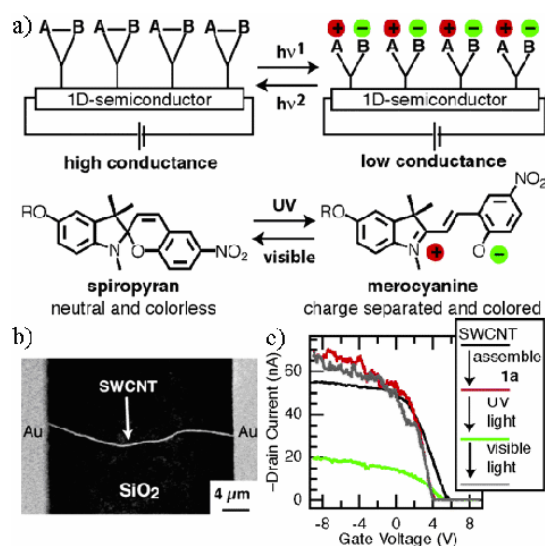
More recently, a  $\mu\text{m}$ -sized device based on a network of nanoparticles deposited in between interdigitated nanogapped Au electrodes (Figure 12) was reported.<sup>51</sup> Nanoparticles were encapsulated by switchable diarylethene molecules connecting pairs of nanoparticle cores. Fully reversible conductance switching was achieved by a sequence of UV and visible irradiation cycles. Switching times were, however rather long (10 h for the maximum ON/OFF ratio).



**Figure 12** Schematic drawing of the diarylethene-Au nanoparticle network on an interdigitated nano-gap Au electrode.

A field effect transistor (FET) based on isolated single-walled carbon nanotubes (SWCNTs) functionalized with spiropyran photochromic molecules was also constructed (Figure 13).<sup>52</sup> Pyrene- or alkane-tethered spiropyran molecules were self-assembled on a SWCNT. The single nanotube was contacted on each side to Au electrodes (Figure 13b).

Using alternating UV and visible light as an external trigger the observed low and high conductance of the devices could be switched back-and-forth. The reversible switching in the functionalized SWCNT FETs was attributed to the photoswitching of the tethered molecules. Two explanations of the phenomenon were provided. One possibility is that the charge-separated state of the merocyanine (Figure 13a) introduces scattering sites for the carriers by creating localized dipole fields around the tubes. These sites then scatter charge when it flows in the nearby SWNT channel and thereby lower the mobility in the devices. Another possibility is that the nearby phenoxide ion quenches the p-type carriers in the tubes and behaves like a charge trap.



**Figure 13** a) Schematic of a carbon nanotube based semiconductor that has spiropyran molecules assembled on its surface (adapted from reference 52). b) Scanning electron micrograph image of a gold-contacted single carbon nanotube. c) Change in drain current of an individual SWCNT device as a function of  $V_g$ . Black curve is device before assembly; red curve is device after assembly of the spiropyran; green curve after irradiation with UV light for ~10 min; blue curve after irradiation with visible light.

## 1.8 Conclusions and Contents of this Thesis

The future of molecular electronic systems based on photoswitchable components looks increasingly bright. However, many challenges remain in achieving the goal of making the leap from fundamental science to applied technologies. The demonstration of a working

## *Chapter 1*

redox based device based on assemblies of switchable molecules by Stoddart, Heath and coworkers<sup>3</sup> and the demonstration of single molecule photoswitching of conductance<sup>47</sup> (see also Chapter 2 and Chapter 5) have paved the way for this transition. However, to realize the full potential of photochromic systems key issues in device assembly, in particular interfacing molecular systems with the macroscopic world, stability, and the understanding of the relative contributions of photochromic responses to changes in tunneling and resonant tunneling contributions to charge transport over the gap bridged by these systems remain to be resolved.

The progress towards the development of light switchable electronic devices based on diarylethene photochromic molecular switches is described in this thesis. The main focus is on fundamental aspects that have to be solved before a fully operational device can be constructed. The central questions of the research are: synthetic availabilities and costs of the molecules of interest, fundamental aspects of the photochemical switching (reversibility, fatigue efficiency), influence of the surface anchoring on the reversibility of the switching processes, effects of different surfaces on the organization of molecules, charge transport properties, scaling down to nanoscale as small as single molecule and finally, can conductivity switching be realized with a single molecule? The investigation on several of these aspects is described in the following chapters.

In Chapter 2 the first attempt towards single molecule light-induced switching of the conductance is described. Two independent techniques (MCBJ and STM) were used to follow changes of conductance of individual molecules upon irradiation. Important limits in light switching were found for molecules chemisorbed on gold surfaces.

Chapter 3 deals with the synthesis of new diarylethene derivatives capable of chemisorption on gold surfaces. Subsequently, their photochromic properties in solution are studied. Suppression of the photochemical reaction at low temperatures is discussed in detail, indicating the existence of a thermal activation barrier involved in the photochemical ring opening.

Chapter 4 focuses on photochromic properties of SAMs of diarylethenes on the surface of gold nanoparticles and bulk gold electrodes. Both approaches seem to provide key methods to rapidly assess switching behavior of photochromic compounds on surfaces. The main finding is that the switching behavior of diarylethenes is strongly influenced by a spacer unit which connects the central switching unit with the gold surface. Equally important is the investigation of redox properties of the SAMs with implications on non-destructive read-out.

Reversible light induced single molecule switching of conductance is described in Chapter 5. The molecule which was found to preserve its photochromic behavior upon chemisorption on gold (Chapter 4) is investigated using STM. Irradiation of photochromic molecules inserted in an insulating matrix of alkanethiols results in modulations of their conductivity.

Finally, Chapter 6 focuses on molecular monolayers formed spontaneously at the interface between a series of atomically flat surfaces and a solution containing N-salicylideneaniline based photochromic molecules. The effect of a systematic variation of substrates on the geometry of SAMs is discussed. The polymorphism observed on Au(111), is rationalized by a consideration of the substrate-induced intermolecular interactions, suggesting that a simplified view on separated effects of molecule/molecule interactions and molecule/substrate interactions is not always sufficient enough to explain the self-assembly properties of organic molecules.

## 1.9 References and Notes

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- <sup>1</sup> a) B.L. Feringa (Ed.), *Molecular Switches*, Wiley-VCH, Weinheim, **2001**. b) J. C. Crano, R. Guglielmeti, *Organic Photochromic and Thermochromic Compounds Vol. 1*, Plenum Press, New York, **1999**
- <sup>2</sup> R. L. Carroll, C. B. Gorman, *Angew. Chem. Int. Ed.* **2002**, *41*, 4378-4400; b) C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541-548.
- <sup>3</sup> J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. DeIonno, Y. Luo, B. A. Sheriff, K. Xu, Y. S. Shin, H. -R. Tseng, J. F. Stoddart, J. R. Heath, *Nature* **2007**, *445*, 414-417.
- <sup>4</sup> R. P. Feynman, *The Pleasure of Finding Things Out*; Perseus Books: Cambridge, MA, **1999**; Chapter 5. Richards Feynman's original lecture "There's plenty of room at the bottom" can read at [www.its.caltech.edu/~feynman](http://www.its.caltech.edu/~feynman).
- <sup>5</sup> A. Aviram, M. Ratner, *Chem. Phys. Lett.* **1974**, *29*, 277-283.
- <sup>6</sup> a) W. R. Browne, B. L. Feringa, *Nature Nanotechnology* **2006**, *1*, 25-35; b) M. Irie (guest editor), Photochromism: Memories and Switches, *Chem. Rev.* **2000**, *100*, 1683-1890 and references therein.
- <sup>7</sup> K. Uchida, M. Saito, A. Murakami, T. Kobayashi, S. Nakamura, M. Irie, *Chem. Eur. J.* **2005**, *11*, 534-542, b) M. Irie, *Applied Photochromic Polymer Systems* (Ed.: C. B. McArdle), Blackie, Glasgow, **1991**, pp. 174-206; c) T. Ikeda, O. Tsutsumi, *Science* **1995**, *268*, 1873-1875; d) S. Shinkai, *Pure Appl. Chem.* **1987**, *59*, 425-430.
- <sup>8</sup> S. L. Gilat, S. H. Kawai, J. -M. Lehn, *Chem. Eur. J.* **1995**, *1*, 275-284.

- 
- <sup>9</sup> a) J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch, B. L. Feringa, *Science* **2004**, *304*, 278-281; b) R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. M. Bastiaansen, D. J. Broer, B. L. Feringa, *Nature* **2006**, *440*, 163-163.
- <sup>10</sup> X.-Y. Zhu, *Surf. Science Reports* **2004**, *56*, 1-83.
- <sup>11</sup> T. Albrecht, A. Guckian, A. M. Kuznetsov, J. G. Vos, J. Ulstrup, *J. Am. Chem. Soc.* **2006**, *128*, 17132-17138.
- <sup>12</sup> H. Rau, Photoisomerization of azobenzenes, in: J.F. Rebek (Ed.), *Photochemistry and Photophysics*, CRC Press, Boca Raton, **1990**.
- <sup>13</sup> B. L. Feringa, R. A. van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789-1816.
- <sup>14</sup> H. Meier, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1399-1420.
- <sup>15</sup> B. L. Feringa, N. P. M. Huck, H. A. van Doren, *J. Am. Chem. Soc.* **1995**, *117*, 9929-9930.
- <sup>16</sup> a) N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada, B. L. Feringa, *Nature* **1999**, *401*, 152-155; b) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem. Int. Ed.* **2007**, *46*, 72-191; c) R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. M. Bastiaansen, D. J. Broer, B. L. Feringa, *Nature* **2006**, *440*, 163-163.
- <sup>17</sup> G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.* **2000**, *100*, 1741-1753.
- <sup>18</sup> R. Rosario, D. Gust, M. Hayes, J. Springer, A. Garcia, *Langmuir* **2003**, *19*, 8801-8806.
- <sup>19</sup> a) M. Irie, *Chem. Rev.* **2000**, *100*, 1683-1684; b) H. Tian, S. Yang, *Chem. Soc. Rev.* **2004**, *33*, 85-97.
- <sup>20</sup> J. Areephong, W. R. Browne, N. H. Katsonis, B. L. Feringa, *Chem. Commun.*, **2006**, 3930-3932.
- <sup>21</sup> a) M. Campredon, G. Giusti, R. Guglielmetti, A. Samat, G. Gronchi, A. Alberti, M. Benaglia, *J. Chem. Soc. Perkin. Trans. 2* **1993**, 2089-2094; b) A. S. Saraç, B. Ustamehmetoglu, A. Leiminer, B. Stephan, A. Mannschreck, *Electrochimica Acta* **1997**, *42*, 3629-3635; c) J. F. Zhi, R. Baba, K. Hashimoto, A. Fujishima, *Ber. Bunsenges. Phys. Chem.* **1995**, *99*, 32-39.
- <sup>22</sup> a) 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.* **2005**, *11*, 6414-6429 and references therein; b) 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.* **2005**, *11*, 6430-6441 and references cited therein.
- <sup>23</sup> W. R. Browne, M. M. Pollard, B. de Lange, A. Meetsma, B. L. Feringa, *J. Am. Chem. Soc.* **2006**, *128*, 12412-12413.
- <sup>24</sup> W. R. Browne, N. M. O'Boyle, J. J. McGarvey, J. G. Vos, *Chem. Soc. Rev.* **2005**, *34*, 641-663.

- 
- <sup>25</sup> a) B. Jousselme, P. Blanchard, N. Gallego-Planas, J. Delaunay, M. Allain, P. Richomme, E. Levillain, J. Roncali, *J. Am. Chem. Soc.* **2003**, *125*, 2888-2889; b) B. Jousselme, P. Blanchard, M. Allain, E. Levillain, M. Dias, J. Roncali, *J. Phys. Chem. A* **2006**, *110*, 3488-3494; c) B. Jousselme, P. Blanchard, N. Gallego-Planas, E. Levillain, J. Delaunay, M. Allain, P. Richomme, J. Roncali, *Chem. Eur. J.* **2003**, *9*, 5297-5306.
- <sup>26</sup> C. Joachim, J. K. Gimzewski, R. R. Schlittler, C. Chavy, *Phys. Rev. Lett.* **1995**, *74*, 2102-2105.
- <sup>27</sup> Y. Wada, *Pure Appl. Chem.* **1999**, *71*, 2055-2066.
- <sup>28</sup> a) I. Willner, A. Doron and E. Katz, *J. Phys. Org. Chem.* **1998**, *11*, 546-560; b) I. Willner, V. Prado-Yissar, E. Katz, K. T. Ranjit, *J. Electroanal. Chem.* **2001**, *497*, 172-177.
- <sup>29</sup> R. Baron, A. Onopriyenko, E. Katz, O. Lioubashevski, I. Willner, S. Wang and H. Tian, *Chem Commun.*, **2006**, 2147-2148.
- <sup>30</sup> I. Willner, B. Basnar, B. Willner, *Adv. Funct. Mater.* **2007**, *17*, 702-717.
- <sup>31</sup> a) M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293-346; b) K. G. Thomas, P. V. Kamat, *Acc. Chem. Res.* **2003**, *36*, 888-898.
- <sup>32</sup> M. Brust, C.J. Kiely, *Colloids Surf. A: Physicochem. Eng. Asp.* **2002**, *202*, 175-186.
- <sup>33</sup> a) J. Hu, J. Zhang, F. Liu, K. Kittredge, J. K. Whitesell, M. A. Fox, *J. Am. Chem. Soc.* **2001**, *123*, 1464-1470. b) J. Zhang, J. K. Whitesell, M. A. Fox, *Chem. Mater.* **2001**, *13*, 2323-2331.
- <sup>34</sup> M. O. Wolf, M. A. Fox, *Langmuir* **1996**, *12*, 955-962.
- <sup>35</sup> A. Manna, P. -L. Chen, H. Akiyama, T. -X. Wei, K. Tamada, W. Knoll, *Chem. Mater.* **2003**, *15*, 20-28.
- <sup>36</sup> K. Tamada, H. Akiyama, T. X. Wei, *Langmuir* **2002**, *18*, 5339.
- <sup>37</sup> R. A. van Delden, M. K. J. ter Wiel, M. M. Pollard, J. Vicario, N. Koumura, B. L. Feringa, *Nature* **2005**, *437*, 1337-1340.
- <sup>38</sup> a) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778-781; b) M. Irie, S. Kobatake, M. Horichi, *Science* **2001**, *291*, 1769-1772.
- <sup>39</sup> K. Matsuda, M. Ikeda, M. Irie, *Chem. Lett.* **2004**, *33*, 456-457.
- <sup>40</sup> a) P. Jiang, G. M. Morales, W. You, L. Yu, *Angew. Chem. Int. Ed.* **2004**, *43*, 4471-4475; b) J. He, Q. Fu, S. M. Lindsay, J. W. Ciszek, J. M. Tour, *J. Am. Chem. Soc.* **2006**, *128*, 14828-14835; c) L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara, P. S. Weiss, *J. Phys. Chem. B* **1999**, *103*, 8122-8127; d) B. Xu, N. J. Tao, *Science* **2003**, *301*, 1221-1223.
- <sup>41</sup> a) C. Kergueris, J.-P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga and C. Joachim, *Phys. Rev. B* **1999**, *59*, 12505-12513; b) M. Mayor, H. B. Weber, J. Reichert, M.



- 
- Elbing, C. von Hänisch, d. Beckmann and M. Fisher, *Angew. Chem. Int. Ed.* **2003**, *42*, 5834-5838; c) J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. von Lohneysen, *Phys. Rev. Lett.* **2002**, *88*, 176804.
- <sup>42</sup> S. Yasuda, T. Nakamura, M. Matsumoto, H. Shigekawa, *J. Am. Chem. Soc.* **2003**, *125*, 16430–16433.
- <sup>43</sup> M. J. Comstock, N. Levy, A. Kirakosian, J. Cho, F. Lauterwasser, J. H. Harvey, D. A. Strubbe, J. M. J. Fréchet, D. Trauner, S. G. Louie, M. F. Crommie, arXiv: *cond-mat/0612201v2* [*cond-mat.mtrl-sci*] (last revised 8 May **2007**).
- <sup>44</sup> a) 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.* **2003**, *91*, 207402.
- <sup>45</sup> S. J. van der Molen, H. van der Vegte, T. Kudernac, I. Amin, B. L. Feringa, B. J. van Wees, *Nanotechnology* **2006**, *17*, 310.
- <sup>46</sup> a) J. Li, G. Speyer, O. F. Sankey, *Phys. Rev. Lett.* **2004**, *93*, 248302; b) M. Zhuang, M. Ernzerhof, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *72*, 073 104.
- <sup>47</sup> J. He, F. Chen, P.A. Liddell, J. Andreasoon, S.D. Straight, D. Gust, T.A. Moore, A.L. Moore, J. Li, O.F. Sankey, S.M. Lindsay, *Nanotechnology* **2005**, *16*, 695-702.
- <sup>48</sup> T. Kawai, Y. Nakashima, T. Kunitake, M. Irie, *Curr. Appl. Phys.* **2005**, *5*, 139-142.
- <sup>49</sup> a) M. Irie, S. Kobatake, M. Hirichi, *Science* **2001**, *291*, 1769-1772; b) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778-781.
- <sup>50</sup> E. Kim, M. Kim, K. Kim, *Tetrahedron* **2006**, *62*, 6814-6821.
- <sup>51</sup> M. Ikeda, N. Tanifuji, H. Yamaguchi, M. Irie, K. Matsuda, *Chem. Commun.* **2007**, 1355-1357.
- <sup>52</sup> X. Guo, L. Huang, S. O'Brien, P. Kim, C. Nuckolls, *J. Am. Chem. Soc.* **2005**, *127*, 15045-15047.