

## University of Groningen

### Photochromic molecular switches

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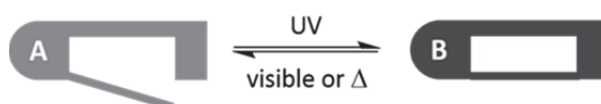
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# Summary

Molecular switches function just like common switches, *i.e.* they have the opportunity to be switched between two states, for example on and off or A and B. In everyday life switches are often controlled by hand, however, there are also switches that are sensitive to light, movement or temperature. Just like commonly used switched molecular switches can be controlled using various stimuli. The switches described in this thesis are controlled by light. The energy contained in light is used to switch the molecules from state A to state B, such a change in state is called an isomerisation. As for everyday switches, molecular switches can also be returned to their original state (A). Switching from A to B generally costs more energy than switching from B to A. When switching from A to B the molecule is brought to a higher energetic state. This could be compared to pushing a kart up a hill. Pushing the kart up the hill takes more energy, than pushing the kart down the hill. Generally ultraviolet (UV) light is used to switch from state A to state B and visible light is used to switch from B to A, as UV light contains more energy than visible light. Molecular switches often don't perfectly remain in their B state but slowly thermally revert back to their A state. Just as the kart on the top wants to roll down the hill without being pushed, so do the switches. Where the kart is forced down by gravity, the molecular switches in state B are reverted to their native state (A) by temperature ( $\Delta$ ).



**Figure 1:** Schematic representation of a light sensitive molecular switch.

The isomerisation from A to B, results in changes in the character of the molecule. Among such changes are changes in color, length or polarity. When it is possible to

observe such changes are observed, the molecular switches can be used in nanoscale materials, for example as data storage, to change the polarity of a surface or in electronic circuits.

One of the most studied molecular switches are the azobenzenes. Azobenzenes can exist in two states the *E*-isomer of which the two halves are distant from each other or the *Z*-isomer in which the two halves are in close proximity. In the *E*-isomer azobenzenes undergo isomerisation to the *Z*-isomer as a result of irradiation with UV light. The *Z*-isomer can be switched back to the *E*-isomer by irradiation with visible light or heating. The stability of the switches is of particular importance, for example when switches are used for data storage, it is essential that the switch remains in the chosen state, else the stored data will be erased.

It is advantageous to combine several switches in one system, for example in data storage this can result in an increase of the data storage capacity. Chapter 3 describes a system made up of two coupled azobenzene units and whether the switching of one of the units influences the switching of the other. However it was discovered that in spite of the proximity of the two azobenzene units it could be determined that the azobenzene switching units operate independently.

In Chapter 4 hemithioindigo (HTI) switches are described. Hemithioindigo switches are made up of half a stilbene switch and half a thioindigo switch. HTI switches can be switched from *Z* to the *E* isomer by light. As for the azobenzene switches the thermal properties of the unstable *E*-isomer of HTI switches were studied. The isomerisation of HTI switches was found to be sensitive to the polarity of its environment. In a polar environment the *E*-isomer reverts back to the *Z*-isomer up to 50 times faster than in an apolar environment.

Both stilbene- and thioindigo switches can be switched by the application of an electrochemical potential. It was expected that Hemithioindigo which are a combination of both these switches would show a similar electrochemical behavior. In Chapter 5 the electrochemical characteristics of HTI switches were studied. It was discovered that application of an electric potential results in a complex mixture of new states of the switch. So far the exact structures of these new states could not be determined. To achieve electrochemical switching of HTI switches this subject will have to be investigated further in the future.

Nanoparticles are particles in the order of 1 to several hundred nanometers. Today nanoparticles have found many practical uses in commercial and medical products. When such particles are used they eventually end up in the environment, where organisms are exposed to them. It is vital to understand the effects nanoparticles can have on organisms. However, studying nanoparticles in living cells is difficult as a result of their diminutive size. However, it is possible to visualize such particles with a

$\pm 10$  nm resolution in living cells by microscopy techniques such as photoactivated localization microscopy (PALM). PALM uses fluorescent molecules (or probes) of which the fluorescence can be switched on and off by irradiation. The position of the probe can be determined with high accuracy by alternating between the dark and fluorescent state of a probe. When such a fluorescent probe is connected to a non-fluorescent particle, this particle can be tracked within the cell. Chapter 6 described the synthesis and properties of a fluorescent switch which can be anchored to gold nanoparticles. The fluorescence of switches internalized by living cells remains active and can be switched on and off using light. However, anchoring the fluorescent switch to the surface of a gold nanoparticle has not been successful to date.

During the synthesis of the molecular switches in chapter 6 an efficient method for the transformation of *t*-butylthioethers to their thioacetates was discovered. Juggling the reactivity of several functional groups in one molecule is common practice in organic synthesis. Protecting groups are commonly used to prevent the wrong functional groups from reacting. Such protecting groups block the functionality to render it unreactive. There are many robust protecting groups, however, the removal of such groups often need harsh reaction conditions (for example high pH or temperature). Such conditions are often not compatible with complex molecules bearing several functional groups, which can result in side reactions. Therefore its often useful to replace a robust protecting group for one that can be removed more easily under mild conditions. Chapter 7 describes the efficient transformation from robust *t*-butylthioethers tot their thioacetates by use of titanium(IV)chloride. Often these transformations could be completed within several seconds and could even be performed with catalytic quantities of titanium(IV)chloride.

