Molecular switches in nature and technology: An introduction

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What are molecular switches?

„[Molecules, which] exist in two different states that can be reversibly switched from one to another [...]“. 

Ben L. Feringa

Requirements:
- Two stable/meta-stable states
- Reversibly switchable
- Switch is activated by an outside stimulus

=> Azobenzene simple example for a photochromic switch

Mechanically interlocked switches

- Rotation (catenane) or linear movement (rotaxane) of the macrocyclic component
- Switching induced by chemical, electrochemical or photochemical stimuli
- Components are held together mechanically and additional non-covalent bonding interactions
- Catenane can be built up to a \([n+1]\)-part chain as well as rotaxane can have \([n]\) compounds cycling the linear part

Feringa, Molecular Switches, 2001
The retinal molecule

Cis-trans-isomerisation triggered via the influence of visible light
Conformation change activates the rhodopsin, in which it is embedded
Rhodopsin breaks down into several compounds and forms metarhodopsin (activated rhodopsin)
Protein is able to send electrical impulses to the brain

Krzysztof Palczewski et al., Science 289, 2010
From solution to the surface

Opportunities

• Benefiting from geometrical properties
• Allowing charge transport
• Self-assembly

Feringa, Molecular Switches, 2001

Difficulties

• Conformation change due to molecule-surface-interaction ranging from physisorption (e.g. van-der-Waals-forces) to strong chemical bonds
• Energy levels can be shifted significantly
• Switching ability is no longer guaranteed
Azobenzene revisited (adsorption on coinage metals)

- Cu(111)-Surface induces strong bond with azo-bridge
- Phenyl-rings get bent out of the surface plane
- Trans-isomer is now 0.3eV higher in energy

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\[ E_A \approx 1 \text{ eV} \]

\[ \Delta E = 0.68 \text{ eV} \]

\[ h\nu_1, h\nu_2 \]

\[ kT \]

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McNellis et al., Phys. Rev. B 80, 2009
Diarylethene derivates

- Ring opening/closing mechanism
- Switching exhibits colorization/decolorization
- Thermally irreversible (P-type chromophore)
- High durability (up to $10^4$ repetitions possible)
- Photoisomerization leads (besides a geometrical change) to a change in electronic structure and the refractive index

*Feringa, Molecular Switches, 2001*
Photoelectrochemical switching

- Pyridinium-ion-groups are electrically separated from each other in the open isomer
- Ring-closing leads to delocalized $\pi$-electrons connecting the ions
- Voltammogram exhibits switched behavior of electric current
- Realization of molecular electrical switch

Feringa, Molecular Switches, 2001
Spiropyran is built up from an indoline and one benzopyran molecule with an additional NO$_2$. Drastic difference in reactivity as well as dipole moment. Due to the large change in molecular properties various applications are proposed.
Photoswitching of fluorophores

- Special spiropyran derivates with a fluorophore donor are synthesized
- Fluorescence wavelength matches the absorption wavelength of the merocyanine
- Radiation-less Förster resonance energy transfer (FRET) instead of emission
- Successful construction of an optical molecular switch

Seefeldt et al., Photochemical & Photobiological Sciences 2, 2010
**Logic operations with molecular switches**

- The purple merocyanine exhibits strong absorption at 563 nm and can completely block an incoming signal.
- The colorless spiropyran allows the beam to pass through.

- Building logic operations possible
- Attractive foundation for digital processing at the molecular level

Raymo et al., PNAS 99, 2002
Simple logic operations

Not-gate

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Research in the Sfb 856

- **Azobenzene**
  AG Weinelt / AG Tegeder: Switching abilities of azobenzene derivates on noble metals

- **Spiropyran**
  AG Franke / AG Kuch / AG Tegeder: Thermal stability of nitro-spiropyran an a gold surface

AG Reich/Setaro: Investigating the switching dipole moment of spiropyran on carbon nano tubes