Molecular switches in nature and technology: An introduction

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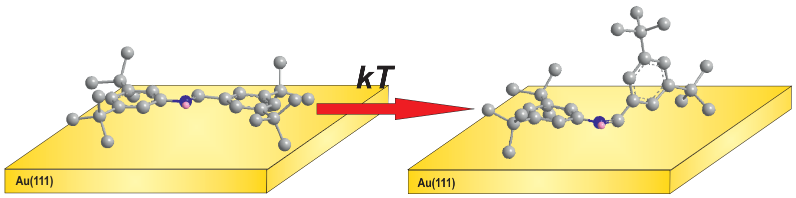
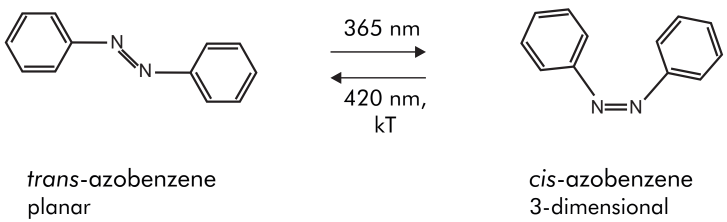


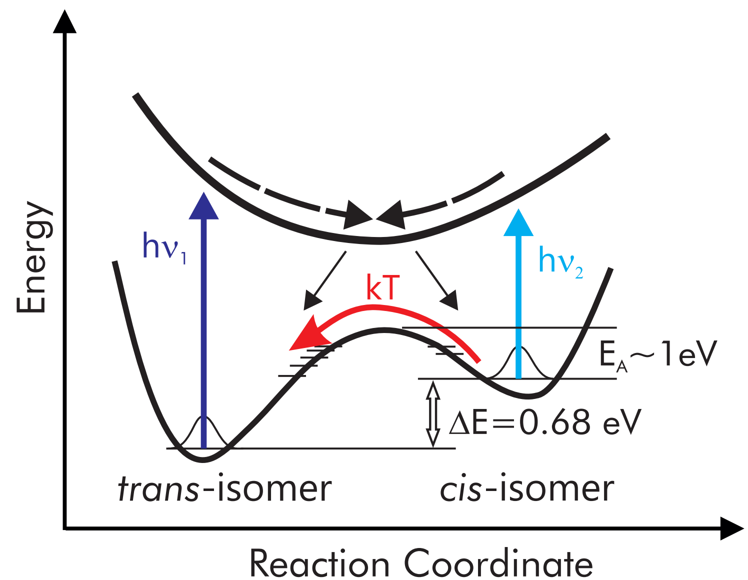
F. Leyssner, PhD thesis, 2011

What are molecular switches?

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

Ben L. Feringa





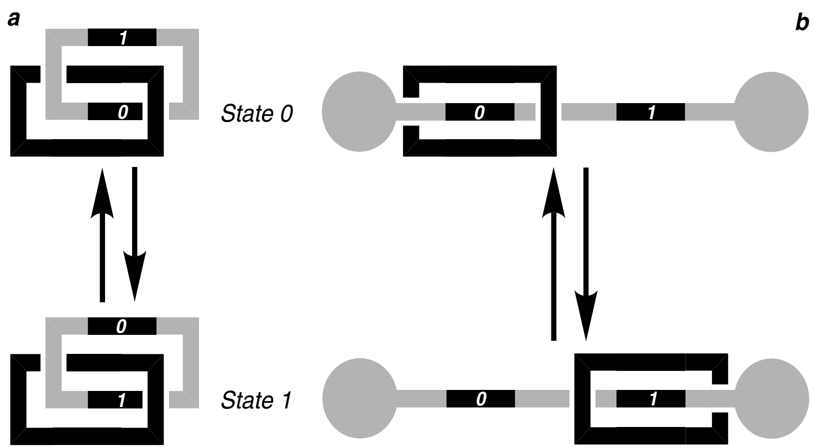
Requirements:

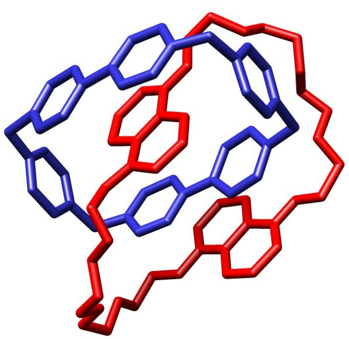
- Two stable/meta-stable states
- Reversibly switchable
- Switch is activated by an outside stimulus

=> Azobenzene simple example for a photochromic switch

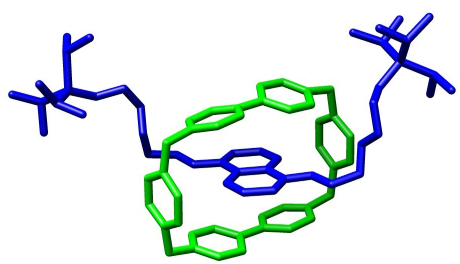
F. Leyssner, PhD thesis, 2011

Mechanically interlocked switches





[2]catenane

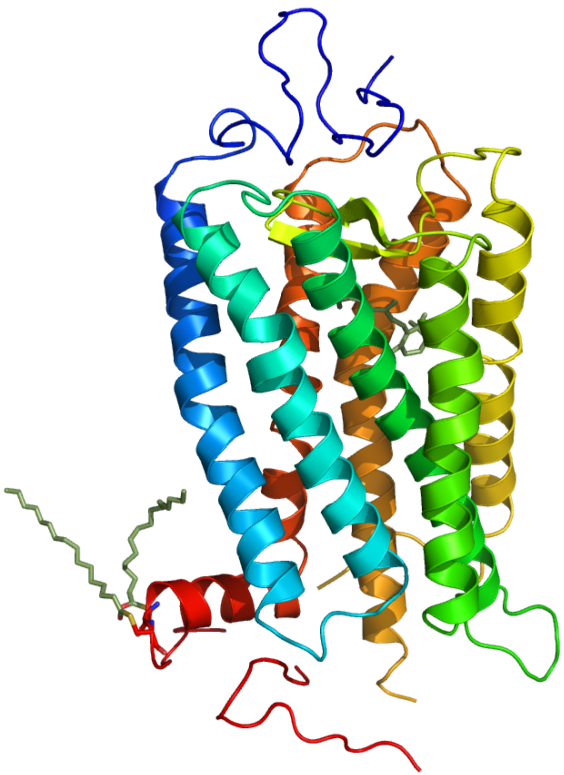


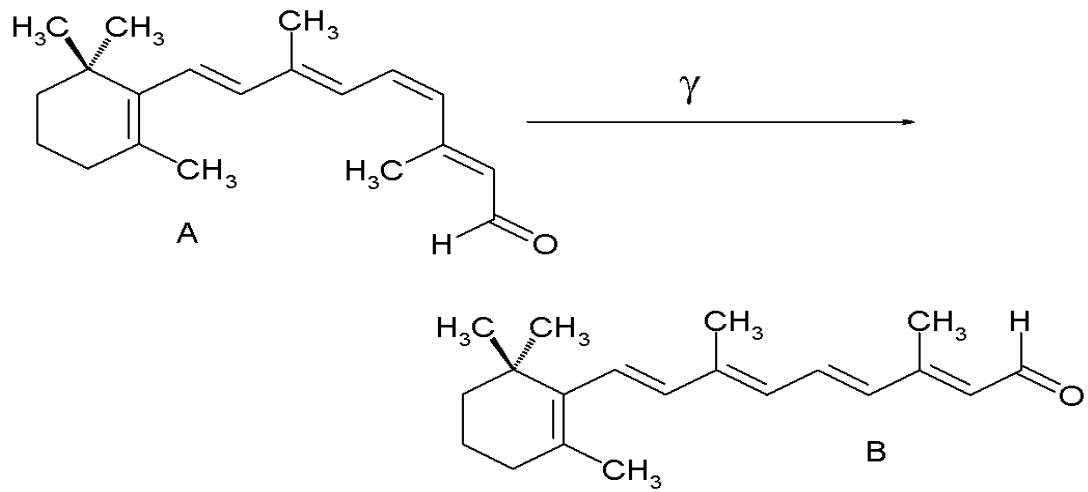
[2]rotaxane

- 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





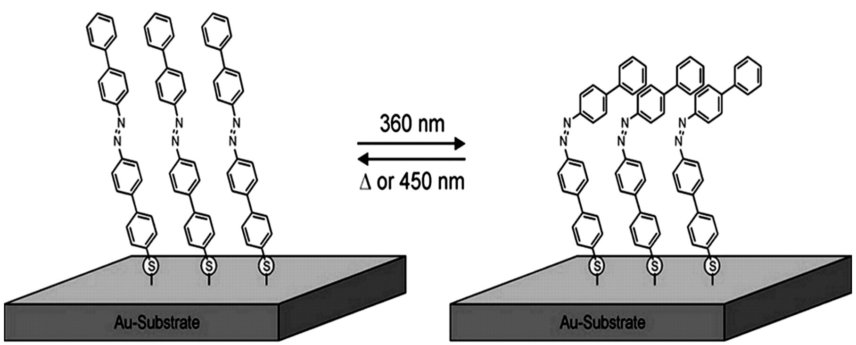
- Cis-trans-isomerisation triggered via the influence of visible light
- Conformation change activates the rhodopsin, in which it is embedded
- Rhodopsin breaks down into several compounds and forms metarhodopsin (activated rhodopsin)
- Protein is able to send electrical impulses to the brain

Krzysztof Palczewski et al., Science 289, 2010

From solution to the surface

Opportunities

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



trans-form of immobilized **1**

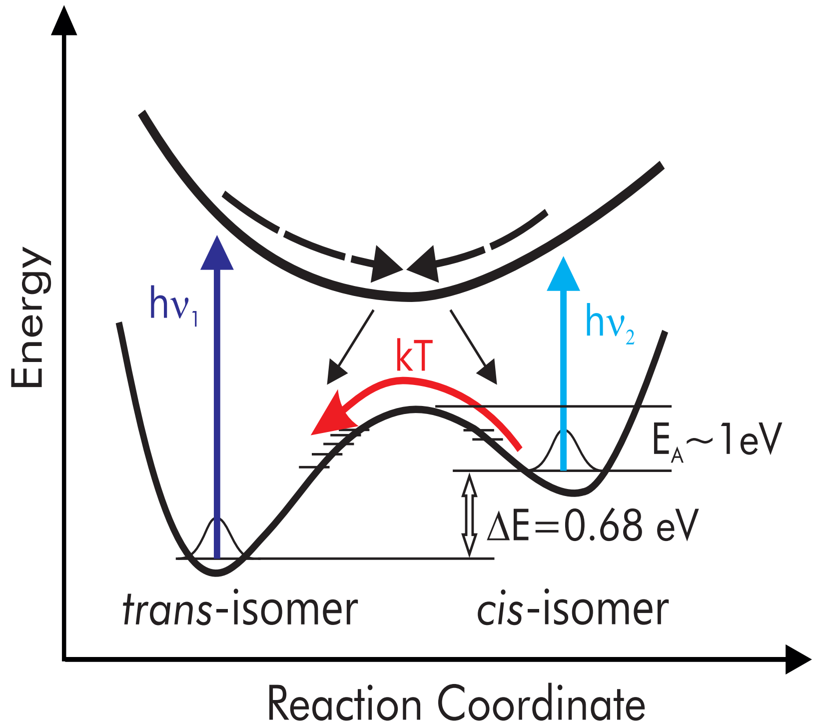
cis-form of immobilized **1**

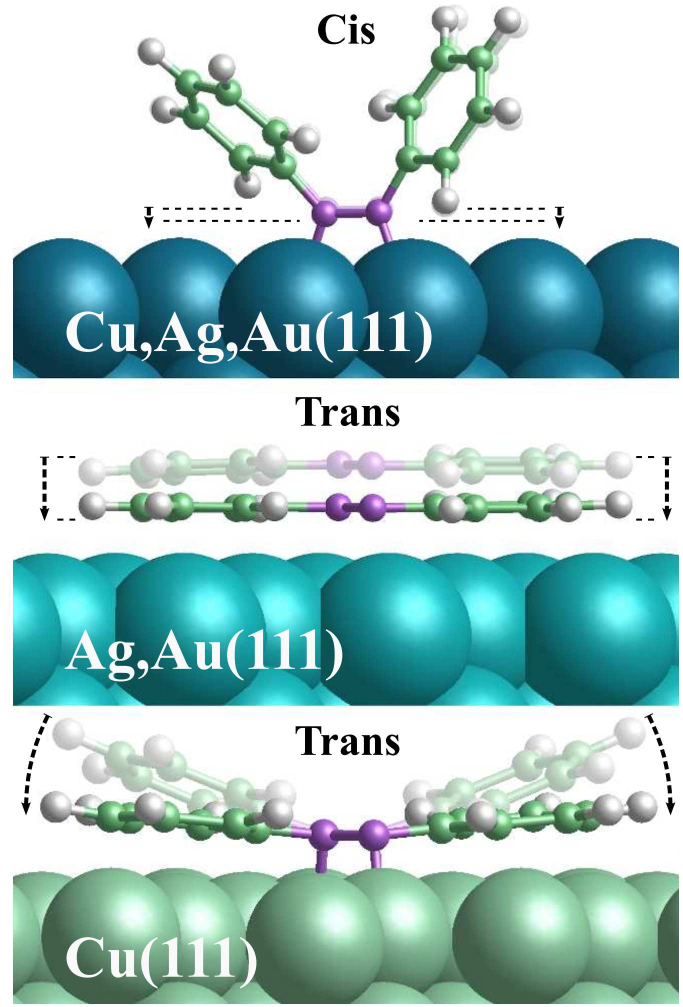
Difficulties

- 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

Feringa, Molecular Switches, 2001

Azobenzene revisited (adsorption on coinage metals)

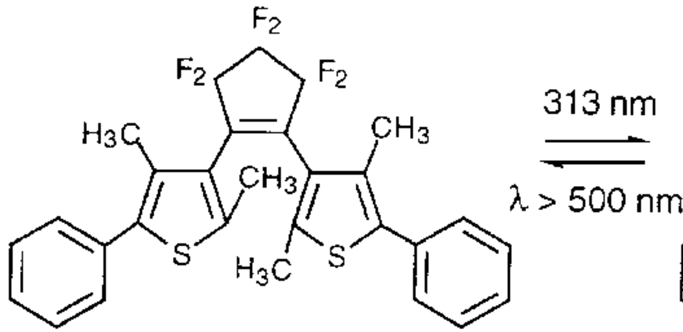




- Cu(111)-Surface induces strong bond with azo-bridge
- Phenyl-rings get bent out of the surface plane
- Trans-isomer is now 0.3eV higher in energy

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

Diarylethene derivates

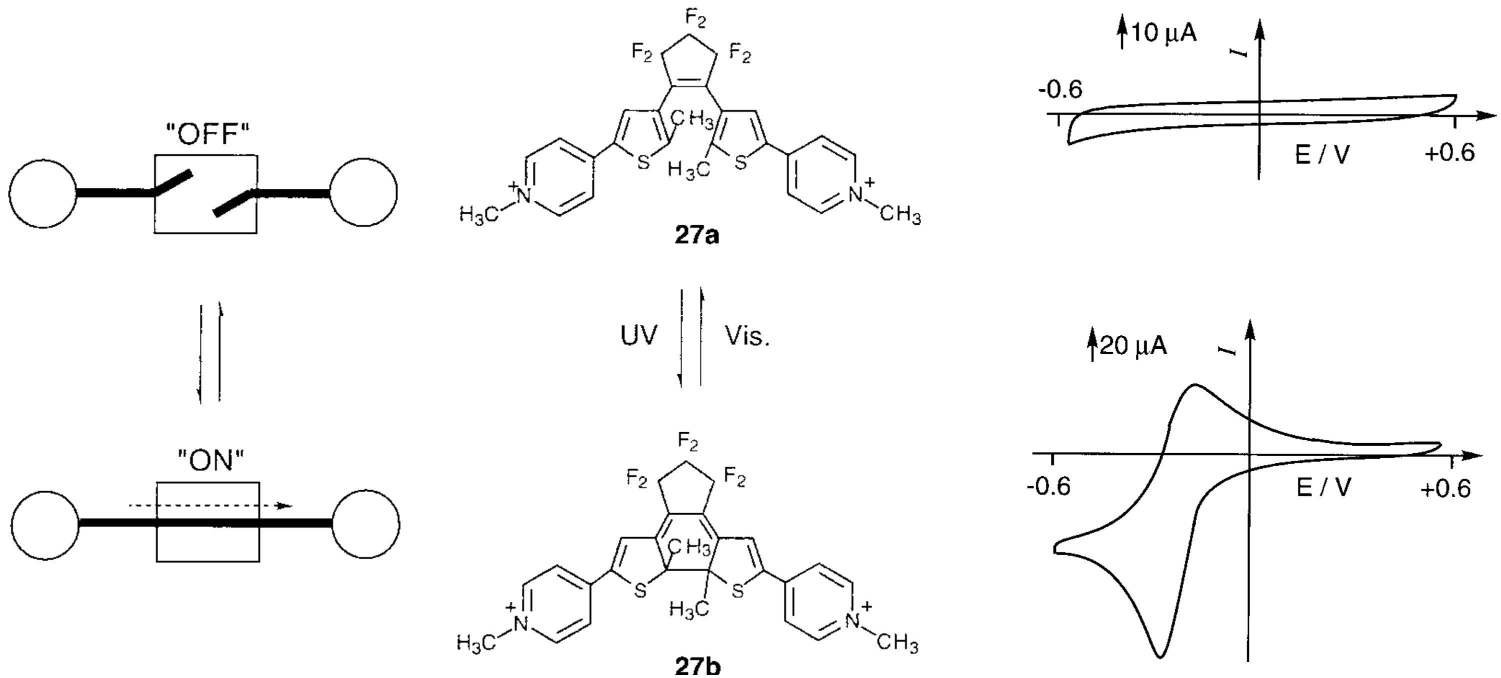


1a **1b**

- 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

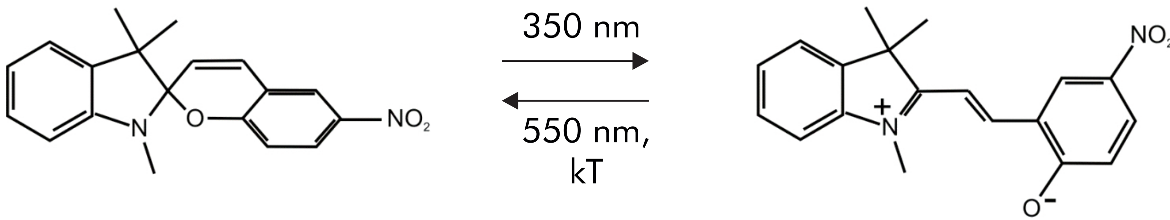
Photoelectrochemical switching



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

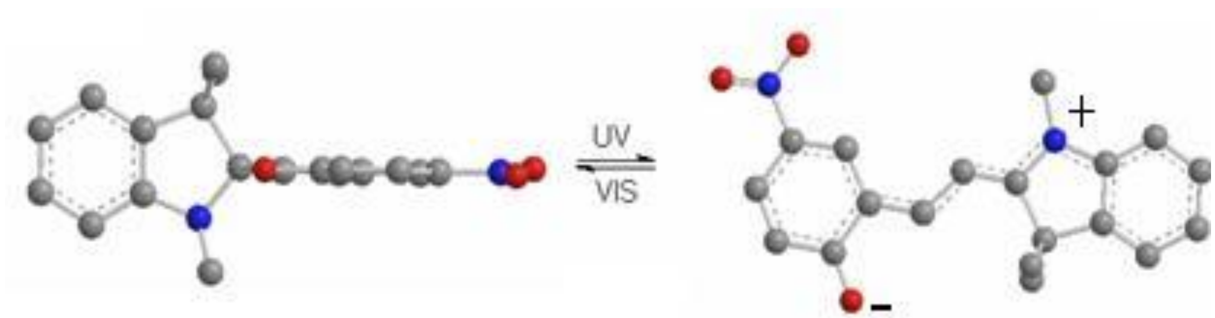
Feringa, Molecular Switches, 2001

Spiropyran



Spiropyran (SP)
neutral closed form
3-dimensional

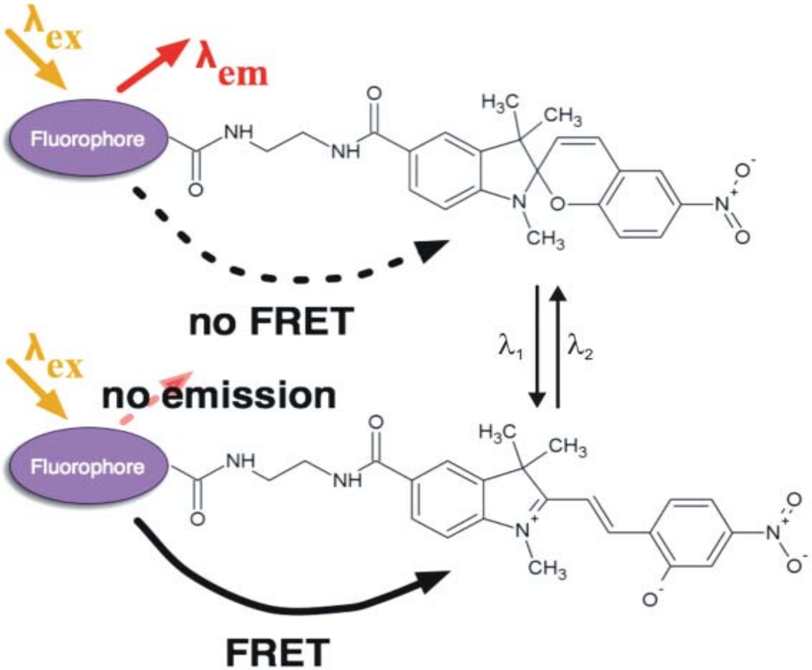
Merocyanine (MC)
zwitteriomic open form
planar

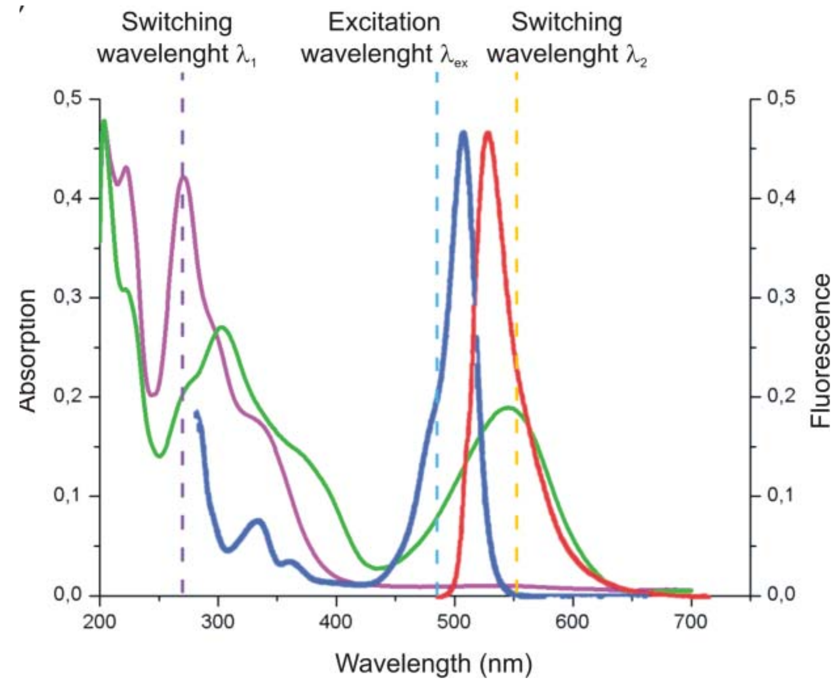


- Spiropyran is built up from on indoline and one benzopyran molecule with an additional NO_2
- Drastic difference in reactivity as well as dipole moment
- Due to the large change in molecular properties various applications are proposed

F. Leyssner, PhD thesis, 2011

Photoswitching of fluorophores

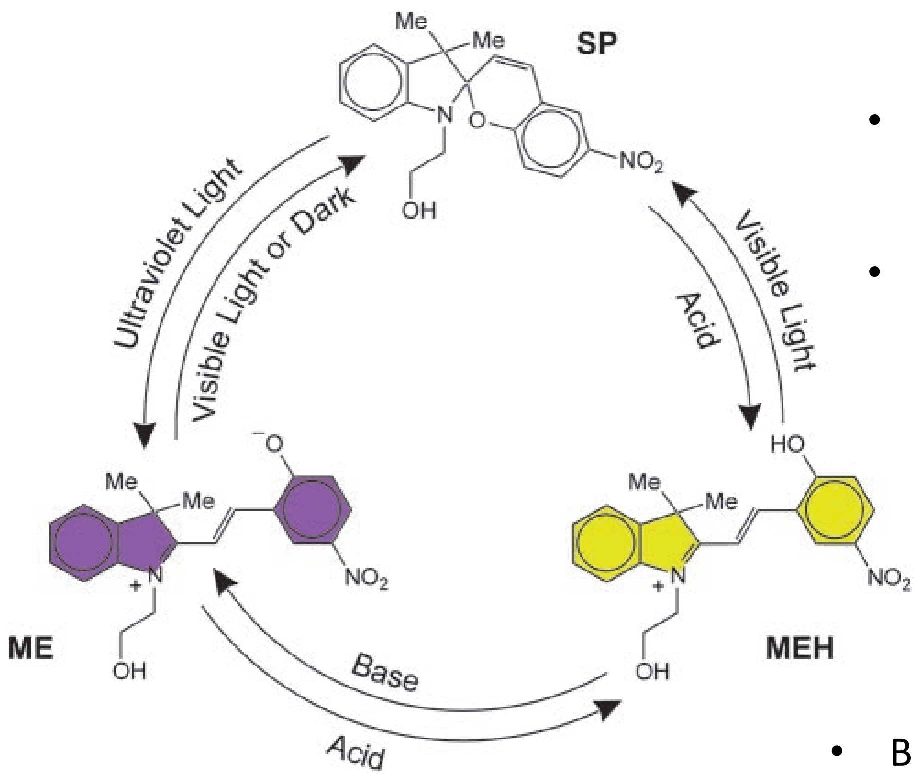




- Special spiropyran derivates with a flurophore donor are synthesized
- Fluorescence wavelength matches the absorption wavelength of the merocyanine
- Radiation-less Förster resonance energy transfer (FRET) instead of emission
- Successful construction of an optical molecular switch

Seefeldt et al., Photochemical & Photobiological Sciences 2, 2010

Logic operations with molecular switches



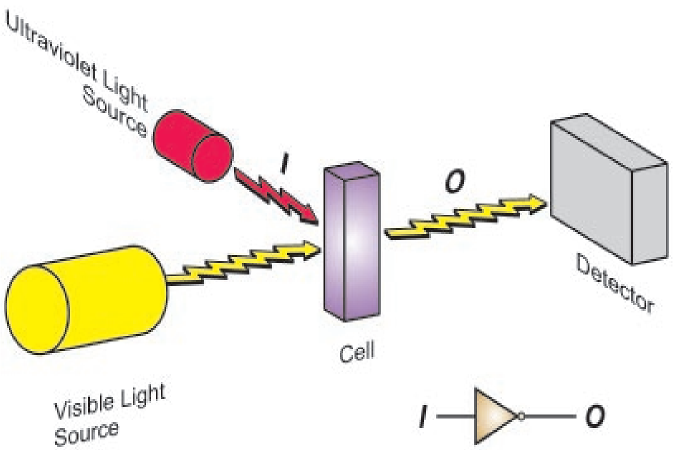
- The purple merocyanine exhibits strong absorption at 563 nm and can completely block an incoming signal
- The colorless spiropyran allows the beam to pass through

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

Raymo et al., PNAS 99, 2002

Simple logic operations

Not-gate

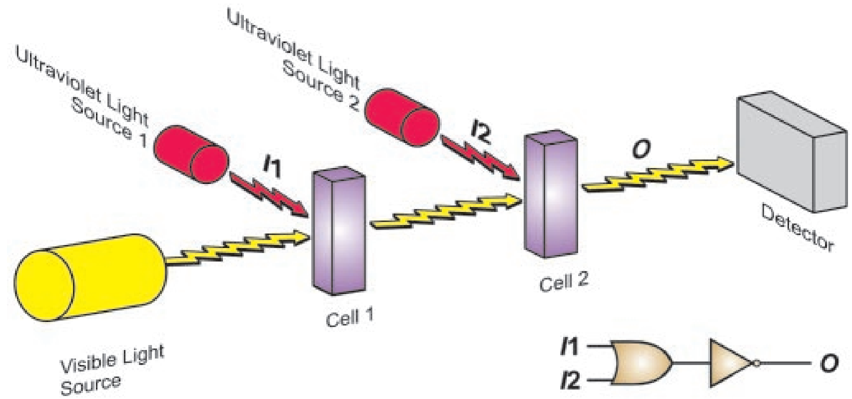


I	O (%)
Off	100
On	3

NOT

I	O
0	1
1	0

Nor-gate



I1	I2	O (%)
Off	Off	100
Off	On	3
On	Off	4
On	On	0

Two-Input NOR

I1	I2	O
0	0	1
0	1	0
1	0	0
1	1	0

Raymo et al., PNAS 99, 2002

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

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