CHIMONO Report UBONN for Deliverable 10: Functionalization of molecular ensembles

Summary
In this report we review the recent progress of switching photochromic molecules physically adsorbed on optical nanofibers.

Photochromic molecules can be switched by irradiation with light between two forms having different absorbance spectra. Typically only one form absorbs light in the visible wavelength range and is therefore called the colored form, the other form is called transparent, and both forms absorb light in the UV wavelength range. Switching from the transparent to the colored form occurs by illumination with UV light, the back switching from colored to transparent by illumination with white light.

We detect the two conformational states of these molecules via ultra-sensitive surface absorption spectroscopy on our optical nanofibers. The molecules are switched using very low powers (nW) of white light and UV light guided by the nanofiber. We have performed time-resolved measurements of the switching processes and modeled these with a rate equation model. This has allowed us to extract the ratios of the two switching rate constants. We have also characterized the cyclability of our photochromic system in two different ways, by repeatedly switching the molecules as well as by determining the ratio between photoswitching and photodestruction sensitivities.

Photochromic molecules on optical nanofibers

Molecules used
The photochromic (photoswitchable) molecules in this project were chosen according to the criteria:

- stable at ambient conditions, especially in an oxygen-containing atmosphere,
- switchable not only in solution but also in the "dry" state on a glass surface,
- absorption in the visible spectrum measurable with existing spectrometers and detectors,
- switching by near UV light which can still be guided in optical fibers.

SpiroOH
In the most experiments we used the fluorescent spiropyran 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-'nitrobenzopyrylospiran which we will call "spiroOH". Spiropyranes belong to the oldest and most studied photochromic molecule classes. The closed-ring form of a spiropyran is transparent in the visible wavelength range and the open-ring form, also called merocyanine, is colored. The molecular structure of both spiroOH forms is shown in Fig. 1.

![Molecular structure of spiroOH](image)

Fig. 1: Molecular structure of spiroOH in the closed/transparent form (left) and the open/colored form (right).
The polarity of spiroOH is high due to the charged N’O’-group on the right and the polar OH-group on the bottom. The open form provides additional polarity because of the charged open-ring section.

**XTPA**

The second molecule we used is the diarylethane XTPA provided to us by the group of Prof. Meerholz from the Institut für Physikalische Chemie, Universität Köln. XTPA provides small polarity and little shape changes due to switching. It is thermally stable up to 80°C.

**Deposition method**

The experimental setup for deposition and detection of organic molecules is shown in Fig. 2. The molecules are dissolved in a spectroscopic-grade solvent and a drop of this solution is dripped onto the nanofiber using a pipette. A thin film of the solution covers the fiber surface. Subsequently, the solvent evaporates and the molecules remain adsorbed at the nanofiber surface. We have found that the polarity of the solvent strongly influences the number of molecules deposited on the fiber surface, with less polar solvents (heptane, toluene) leaving much more molecules on the fiber compared to more polar solvents (acetone, ethanol).

![Deposition and detection organic molecules on optical nanofibers.](image)

In order to deposit spiroOH on the nanofiber, a solution of 10 mg spiroOH in 50 ml toluene was used. For XTPA, a solution of 1.5 mg XTPA in 4 ml heptane was diluted for deposition by a factor 1000.

**Detection**

In our measurements we use optical nanofibers with a diameter of 0.3 - 0.5 μm and a length of 5 mm. Due to their extremely small diameter the light propagating through the nanofiber is very tightly confined. Moreover, up to 50% of the light propagates outside the nanofiber as the evanescent field. This allows strong interaction of light with the surrounding medium, e.g. with surface-adsorbed molecules.

In order to detect the organic molecules we couple white light into the nanofiber. The white light propagating through the nanofiber is partially absorbed by the surface-adsorbed molecules. The remaining white light is detected after the nanofiber by a spectrometer, see Fig. 2. This makes it possible to measure the absorption spectra of the molecules already at a very low surface coverage of less than 1% of a mono layer [1].

**Switching of photochromic molecules**

**Optical setup**

Figure 3 shows the experimental setup of the photoswitching experiment. White light from a halogen lamp is coupled into the fiber sample. The molecules are exposed to the white light during all measurements continuously, so they tend to be in the transparent form. UV light of 365 nm from an
LED can be additionally coupled to the fiber. In order to transmit the UV light, a special doubly-spliced fiber was produced and pulled at JOGU-MAINZ: A UV-guiding fiber using fluorine-doped cladding was used to guide the UV (and visible) light to the fiber taper. A germanium-doped core single-mode fiber, which somewhat absorbs UV but is chemically stable under flame pulling, was used to fabricate the taper and waist to adiabatically transfer the guided modes through the taper into the nanofiber waist.

The UV switches molecules to the colored form and the UV exposure is controlled using a computer-controlled beam shutter. We monitor the white-light transmission through the fiber and obtain the absorbance of the colored form. For monitoring we use either a spectrometer which gives spectral information with slow acquisition time or a photomultiplier providing good time resolution but no spectral information.

![Diagram](image)

**Fig. 3**: Setup of the absorbance spectroscopy and photoswitching experiment.

**Basic switching**

After deposition of spiroOH we expose the molecules on the nanofiber for 5 min to white light with a power of 10-20 nW between 435 and 600 nm in order to switch all molecules to the transparent form. Subsequently, they are additionally exposed to 1.5 nW of UV light for 1 s. The absorbance increase due to switching to the colored form is shown in the left plot of Fig. 4. After the UV exposure has stopped, the absorbance decreases since the white light switches the molecules back to the transparent form (right plot of Fig. 4).

Due to the high sensitivity of our nanofiber spectroscopy [1], the measured absorbance levels correspond to surface coverages on the order of only 0.01 monolayer of molecules. This would in principle allow to observe isolated, non-interacting adsorbed molecules. However, do not know whether the deposition from solution yields isolated molecules, such as the sublimation method, or rather islands, clusters or nanocrystals.
**Photoswitching dynamics**

In order to obtain the temporal behavior of the photoswitching process we monitor the white-light transmission through the fiber with the photomultiplier. This makes it possible to measure the spectrally integrated white-light absorbance \( A = \log(P_{\text{transmitted}}/P_{\text{reference}}) \) with a high time resolution. The absorbance \( A \) is proportional to the number of colored molecules \( N_{\text{col}} \). The time-resolved absorbance of spiroOH during and after exposure to UV light is illustrated in Fig. 5.

![Fig. 4: Switching on and off absorption. Absorbance spectra of spiroOH on the nanofiber during exposure to visible white light and UV (a) and visible white light only (b).](image)

During the UV exposure, the absorption approaches a limiting maximum value, indicating that the number of colored molecules reaches a (dynamic) equilibrium of UV photocoloration and visible light photodiscoloration, the so-called photostationary state.

**Mathematical modeling and rate extraction**

The light-induced switching dynamics of the molecules is modeled in a rough approximation as a rate equation system. This simple model neglects different couplings of different molecules to the fiber-guided light, e.g. due to light absorption along the fiber, multi-mode light propagation in the fiber, and inhomogeneous local molecule adsorption sites. In this way we avoid dependence of various unknown parameters and lengthy numerical calculations, while being able to approximately extract the important and intuitive main properties of the systems. Thermal (dark) switching has not been observed in our system at relevant timescales (seconds or minutes).
In the rate-equation model, the colored molecules \(N_{\text{col}}\) are switched to the transparent state by the visible light with a rate \(k_{\text{vis}}\) whereas the transparent molecules \(N_{\text{tr}}\) are switched by UV light with a rate \(k_{\text{UV}}\) to the colored state:

\[
\frac{dN_{\text{col}}}{dt} = -k_{\text{vis}}N_{\text{col}} + k_{\text{UV}}N_{\text{tr}}
\]

\[
\frac{dN_{\text{tr}}}{dt} = -k_{\text{UV}}N_{\text{tr}} + k_{\text{vis}}N_{\text{col}}
\]

In the photostationary equilibrium state we get

\[
\frac{N_{\text{col}}}{N_{\text{col}} + N_{\text{tr}}} = \frac{k_{\text{UV}}}{k_{\text{UV}} + k_{\text{vis}}}.
\]

Since the fraction of colored molecules is proportional to the measured absorbance \(A\) and the UV switching rate \(k_{\text{UV}}\) is proportional to the UV power, we can vary the UV power, fit the measured photostationary absorbance with this model and thus obtain the ratio of the switching rates. Fig. 6 shows a clever way to take into account also the parasitic photodestruction of molecules over the course of the measurement.

![Fig. 6: Left plot: Absorbance in the photostationary state for several switching cycles. In each cycle the molecules were exposed to 7.5 nW of UV light for 100 ms. The absorbance decreases due to the photodestruction of switchable molecules. The red line shows the corresponding linear fit. Right plot: Absorbance in the photostationary state for 10 cycles with varying UV power (1.5, 3, 4.5, 6, 7.5) nW and backwards. The exposure time of each cycle was varied inversely to keep the UV dose, and thus the photodestruction per cycle, constant. This allows us to fit a model (red curves) taking photodestruction (dashed line) into account.](image)

From this measurement we find that the photocoloration rate \(k_{\text{UV}}\) for 1.5 nW of UV light coupled into the nanofiber is 6.9 times faster than the photodiscoloration rate \(k_{\text{vis}}\) due to the 10-20 nW of visible light used for the absorbance measurement. This means that in the photostationary state we have switched 87\% of the molecules into the colored form. With the highest available UV power of 7.5 nW even 97\% of the molecules are switched into the colored form.

**Cyclability**

Photochromic molecules lose their ability to switch upon illumination. The switching process itself is non-destructive, but photodestructive side reactions lead to non-switchable photoproducts. A
parameter to quantify how often a system with photochromic molecules can be switched is the cyclability $Z_{50}$. It is defined as the number of switching cycles to reduce the initial absorbance at by 50% \[2\]. The cyclability of a photochromic system is an important parameter to characterize the practicability of photochromic applications.

The cyclability depends not only the molecule but also on the measurement conditions: Do we try to switch 80% or 99% of the molecules in each cycle? Are all molecules exposed to the same UV power, or does the UV intensity decrease along the nanofiber? Therefore, the experimentally observed cyclability is a system-specific parameter. We measure $Z_{50}$ by switching the molecules back and forth in many subsequent cycles and measure the maximum white-light absorbance in each cycle. This measured absorbance is proportional to the number of still switchable molecules and it decreases with cycling, see fig. 5. The number of cycles after which the peak absorbance has dropped to 50% is then the system's $Z_{50}$. For spiroOH it is on the order of 40.

To study the interplay of system parameters, in two similar experiments we set the switching UV light power to 3.2 nW and 7 nW, respectively (UV pulse time 100 ms). With the higher UV power of 7 nW the photostationary state was reached during each switching cycle, and the absorbance decreased to 50% after 20 cycles, i.e. $Z_{50}(7 \text{ nW}) = 20$. With 3.2 nW the photostationary state was not fully reached in each cycle, and we obtain $Z_{50}(3.2 \text{ nW}) = 41$. From the switching rate analysis we conclude that in both measurements we have switched the majority of molecules to the colored form and back in each cycle. However, the total UV dose accumulated until reaching $Z_{50}$ was very similar in both experiments, 14 nJ and 13.1 nJ for the 7 nW and 3.2 nW experiment, respectively. This confirms that the molecules are destroyed due to the UV light and not due to the switching process itself.

As a comparison to spiroOH, we also measured the cyclability of XTPA adsorbed on the nanofiber. The molecules were switched for 30 ms with 3.2 nW of UV light. The photodiscoloration of XTPA with white light is much slower than for spiroOH such that we had to expose the molecules in each cycle to white light for 15 min. The absorbance was reduced to 50% after $Z_{50} = 14$ cycles, corresponding to a deposited UV energy of 1.4 nJ. This is a factor 10 less than for spiroOH.

**Ideal cyclability**

For characterization and comparison of switchable molecules it would be very useful to define an intrinsic cyclability of the molecules, independent of the optical system. This "ideal cyclability" would specify how often on average a single molecule could be switched before it undergoes a destructive side reaction.

As the photodestruction is only caused by the UV light (see above), the critical switching step is the photocoloration. An principal upper estimate of the ideal cyclability can thus be obtained by measuring the ratio of the UV-induced photocoloration and photodestruction sensitivities of the molecules. For this purpose, we prepare the molecules on the nanofiber in the transparent state with visible light, and then additionally switch on the UV light. As shown in fig. 7, we see a fast onset of absorbance due to photocoloration, reaching the photostationary state, and then slowly decreasing due to photodestruction.
Fig. 7: Fast photocoloration and slow photodestruction of spiroOH under UV exposure (3 nW), used for the determination of the respective sensitivities.

The process is described approximately by the rate equation

\[
\frac{dN_{\text{col}}}{dt} \approx k_{\text{UV}} N_0 - k_{\text{destr}} N_{\text{col}},
\]

where \( N_0 \) is the initial number of (transparent) molecules, and \( k_{\text{destr}} \ll k_{\text{UV}} \) is the photodestruction rate. Here, under continuous UV exposure, the photodiscoloration rate \( k_{\text{vis}} \ll k_{\text{UV}} \) has been neglected, and it has been assumed that in the photostationary state (almost) all molecules are in the colored form.

Fitting the rates from fig. 7, we obtain for spiroOH a principal upper limit of the ideal cyclability limit of

\[
\frac{k_{\text{UV}}}{k_{\text{destr}}} \approx 400.
\]

This means that upon UV exposure, the probability of initiating the switching process is about 400 times higher than the probability of initiating the destructive side reaction.

**Conclusion**

The main finding of our experiment with molecules adsorbed on optical nanofibres is that the functionality which is typically known from macroscopic diluted samples can successfully be transferred to the nanofiber environment. The system has truly nanoscale properties: minute light powers at the nW level are sufficient to switch molecules between conformal states, but at the same time cause photodestruction already. We also find that not all molecules participate in the switching process. As a result, the cyclability obtained so far remains behind the values obtained for macroscopic samples.

**Outlook**

Our experiments point at the measures to be taken to improve the cyclability: changes to the environment, such as excluding oxygen or embedding the molecules in a matrix may improve the chemical stability. State controlled deposition could increase the number of molecules participating in the switching process.
The switching speed could be increased by orders of magnitude by applying tailored laser pulses. The switching process of the molecules themselves seems to happen on a sub-nanosecond timescale (in solution). We expect the dynamics of adsorbed molecules to be governed by a similar time scale.

For reducing the minimum number of detectable molecules at JOGU Mainz, the use of photoswitchable molecules can be a significant advantage: By repeatedly measuring the nanofiber transmission while optically switching the molecules between their state tens of times could improve the signal-to-noise ratio of the detection by a factor of 3-10, similar to using a lock-in amplifier. This technique could help to reach single molecule detection, switching and addressing in the near future.

On the long run, further integration on a chip could be obtained by using nanofibers on a low refractive index substrate, or employing optical waveguides inscribed into a suitable chip material.

References