

A comprehensive study of molecular switches

Henrieta Volfová¹, Alina Khodko², Qi Hu¹, Roland Wilcken¹, Eberhard Riedle¹

¹ Lehrstuhl für BioMolekulare Optik, LMU München, Oettingenstr. 67, 80538 München

² Institute of Physics, National Academy of Sciences of Ukraine, Prospekt Nauky 46, Kyiv

E-mail: Henrieta.Volfova@campus.lmu.de

We report a comprehensive study of the ultrafast switching processes in molecular switches with optimized structure, performed over a broad spectral and time range. In order to understand the switching process in detail, we use different conceptual measurement strategies.

We use a quantum yield determination setup (QYDS) based on high power LEDs for analysis of the kinetics. QYDS is a novel opto-electronic device that allows rapid and facile determination of absolute quantum yields for visible as well as for UV light photoreactions under the conditions of a chemical synthesis laboratory.^[1] We investigate the effect of different illuminations wavelengths on the switches (figure 1 a)). Hereby the switches from the diarylethene family can be completely closed by illumination with 346 nm and ultimately reopened using 537 nm. However, according to our results the ring opening and closing reactions are not equivalent in efficiency. As demonstrated in figure 1 b) and c) the molecules require for the opening process two order of magnitude more light than for closing.

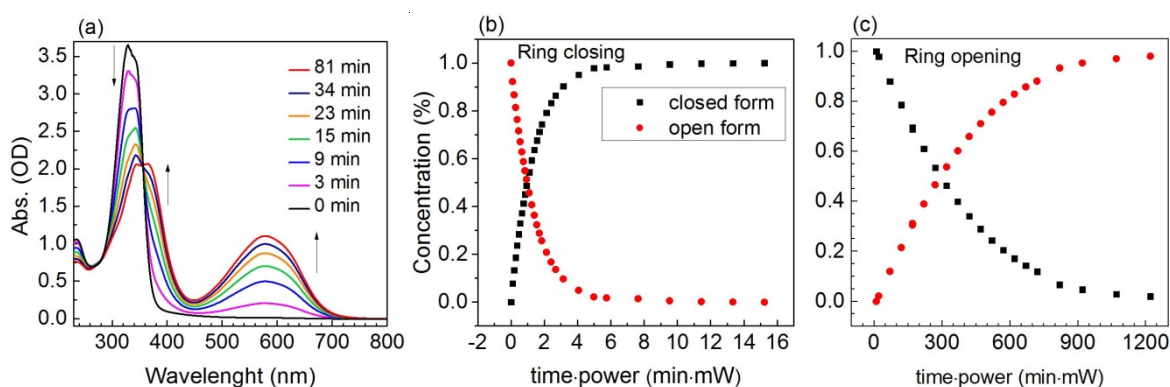


Figure 1. a) Typical QYDS measurements for a diarylethene based molecule in ethanol illuminated by 346 nm light. The determined quantum yield is 48 %. b) Kinetics of the ring closing and ring opening process in c).

Measurements with UV-C excitation at 265 nm show that the switching efficiency goes down by more than a factor of 2. In addition, the deep UV light leads to additional photochemical processes that lead to a fairly rapid deterioration of the switches. For the proper investigation, in particular with pulsed light, the proper choice of the switching wavelength is essential.

The information about the molecular dynamics of the switches is provided by femtosecond transient absorption measurements. A measurement of a donor substituted HemiThioIndigo (HTI) photoswitch^[2,3] is shown in figure 2a. The molecule can undergo a Z/E isomerization via a conical intersection or can go to a suggested charge transfer (CT) state in the first picosecond.

Contrary to the generally used procedure of a global fit, the ultrafast dynamics was deduced by parameterization of each transient spectrum with a set of Gaussian functions. The time dependence of the amplitude of the Gaussians clearly shows the transition to the CT state in ~ 1 ps. The peak position indicates a spectral shift of 500 fs and 2.5 ps exponential time constants, which is assigned to solvation and vibrational cooling. Through the parametrization we can unambiguously separate the electronic relaxation and the solvation/cooling processes, even though the time constants are very similar. The quantum yield is comparably low with 4 %, arguably because of the low lifetime of the excited state. Further analysis will show, if a switching from the CT-state is possible as well, but with low efficiency.

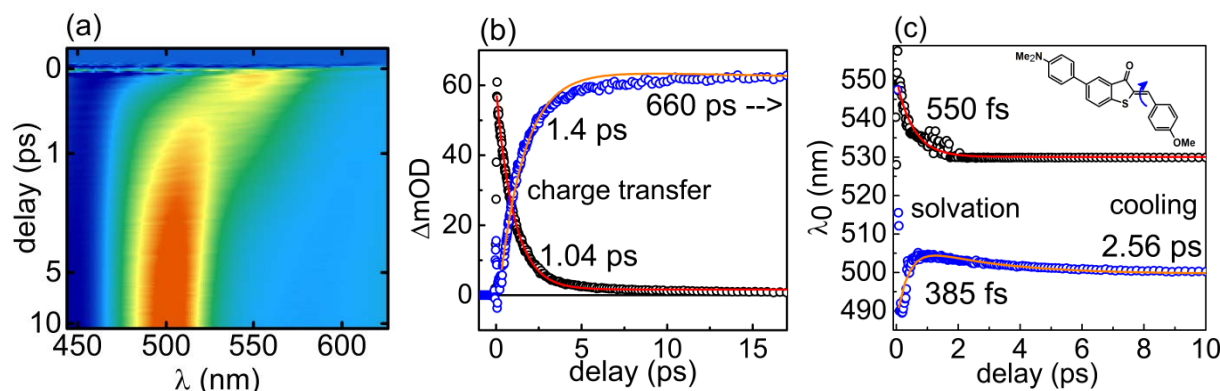


Figure 2. a) Transient absorption measurement of a molecule of a HTI family. b) Amplitude of two Gaussian functions fitted to the data. c) Central wavelength of the two Gaussians.

Steady state and time resolved fluorescence measurements can provide this crucial additional information about the nature of the switching process. An ultrasensitive fluorescence setup of our own design offers the possibility to perform fluorescence measurements from 200-1100 nm. Even fluorescence from an excited state with a sub-1 ps lifetime can readily be observed. The sample is excited by a tunable ns-laser and the fluorescence light is collected to a fiber-coupled spectrometer with TE cooled detector. The HTI switch, e.g. has a dual fluorescence with bands at a normal Stokes shift and with a very large Stokes shift, moving the fluorescence from 500 to 800 nm. This red fluorescence comes from relaxation of the CT state. As a next step we will perform time resolved fluorescence measurements by amplifying the fluorescence light by a noncollinear optical parametric process. The final goal is to determine whether the molecules return to the electronic ground state while switching or stay in the excited state. In the latter case a long lived fluorescence signal should be observed.

Acknowledgement: We thank D. Sysoiev from Prof. Huhn's group in Universität Konstanz and F. Kink from H. Dube's group (LMU München) for providing the molecular samples. We gratefully acknowledge financial support from the DFG through the SFB749, GRK1626 and the excellence cluster 'Munich Center for Advanced Photonics' (MAP).

References:

- [1] U. Megerle, R. Lechner, B. König, E. Riedle, *Photochem. Photobiol. Sci.*, **2010**, 9, 1400.
- [2] S. Wiedbrauk, H. Dube, *Tetrahedron Letters*, **2015**, 56, 4266.
- [3] B. Maerz, S. Wiedbrauk, S. Oesterling, E. Samoylova, A. Nenov, P. Mayer, R. de Vivie-Riedle, W. Zinth, H. Dube, *Chem. Eur. J.*, **2014**, 20, 13984.