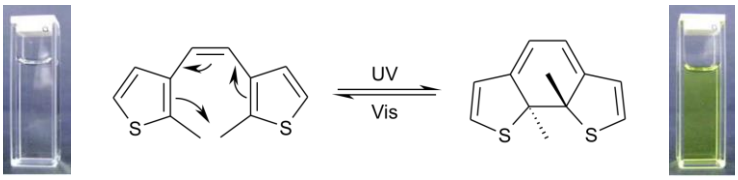
THIO-SWITCH: towards novel photo-active switchable materials – exploration of dithienylethene-based transition-metal complexes via advanced in situ photocrystallographic and spectroscopic approaches

Interaction of light with matter is one of the most important processes occurring in nature. Deep understating of its character and other associated phenomena is crucial as far as the conscious design of new functional materials with desired properties is concerned. Regarding applications in optoelectronics, solar energy conversion/storage devices, or medicine, photo-switchable systems are particular. Controlling the chemical systems via external stimuli has an unprecedented value. One can easily imagine novel materials which can be applied as various coatings (e.g. car body, contact lenses, etc.) properties of which (e.g. colour) are controlled by external perturbation. This is truly the future of technology. Therefore, such vision constitutes grounding for our project. We will concentrate on systems in which the molecule contains the dithienylethene (DTE) fragment that can work as two-direction switch using light of various wavelengths. Such switching is often accompanied by the material's colour changes or other properties (e.g. luminescence decay).

Example potential application of light- or heat-switchable systems.



Light-induced switching of dithienylethene (DTE) core (example sample colour change is shown for one of the literature-known systems).

The aim of our project is to better understand the switching process in transition-metal complexes containing the DTE group. Our choice is supported by the fact that the presence of metallic centre introduces another dimension of change, and thus new interesting optical properties. We plan to synthesise a series of new DTE-based ligands which will serve as new transition-metal complexes' scaffolds. In the syntheses we shall use metal precursors containing for example copper(I), platinum(II) or osmium(II). We will focus most of our attention on the crystalline phase, as it is the relatively poorly explored concerning this class of systems. We plan to determine the crystal structures of all newly-obtained complexes and subject them into comprehensive and systematic studies of various properties.

Photocrystallographic and spectroscopic investigations of DTE-based ligands and their complexes constitute the core of the presented project. We would like to learn how the optical properties of crystals of these compounds depend on their structure, temperature and/or applied external pressure. Such an approach should enable us to elucidate the mechanism and dynamics of the DTE-fragment switching, as well as to determine the role of environmental conditions on this process. Cutting-edge *in situ* photocrystallographic measurements will be feasible thanks to our home-made device allowing irradiation of samples directly on the single-crystal diffractometer. Results of such dynamical X-ray diffraction measurements will be correlated with spectroscopic data, putting particular emphasis on the UV-Vis absorption and/or luminescence emission spectral changes induced by the form of the DTE fragment (open or closed). All our experiments will be supported by high-level theoretical computations.

The proposed project will constitute the first systematic analysis of the DTE-based compounds and their transition-metal complexes in the solid state. We believe the obtained results will shed some more light on the photochemical processes occurring in such systems and on their nature. Furthermore, the outcomes of the described studies could contribute to future conscious design of new functional materials of desired properties.