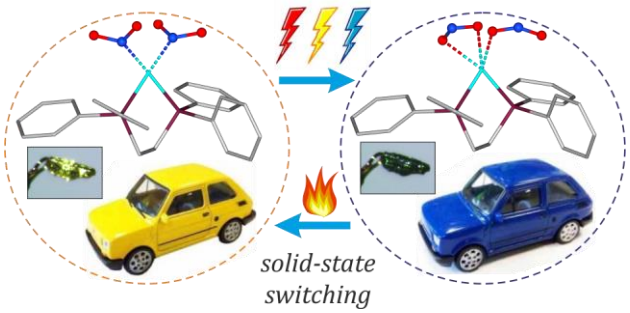
NO2-SWITCH: Photocrystallographic studies of new photoswitchable 4th-row transition-metal nitro complexes

Currently, one of main goals of chemistry and physics is to develop new materials that are able to respond rapidly and reliably to changes in local environment, and send out signals that let us know what is happening. Transition metal switchable complexes, thanks to the specific interactions and presence of the groups that can exist in many isomeric forms, as well as, their interesting optoelectronic and magnetic properties, very often fulfil these criteria. The unique properties of such complexes have important consequences in both materials science and biology.

The aim of this project is to comprehensively investigate the dynamics and nature of molecular switching which occurs upon light irradiation. We will focus on structural changes (bond breaking, bond formation) which will be examined mainly through application of the advanced photocrystallographic techniques supported by theoretical computations. In such a way we will study the relationships between the material behaviour (switching properties, percentage conversion), its appearance changes (*e.g.* colour) under external stimuli and its structure in the microscopic scale.



Light-induced structural switching in NO_2-group-containing solid-state materials.

The project is dedicated to investigations of 4th-row transition metal complexes having the NO_2 group attached to the metallic centre. The metals we have selected, *i.e.* Ni, Co or Cu, are relatively cheap and abundant. NO_2 can be linked to the metal species in various ways using the nitrogen atom only (M–N(O)$_2$), the oxygen atom only (M–O–NO), *etc.* Complexes differing by the binding mode of the same molecular fragment are called linkage isomers. To switch the system between the isomers, if feasible, one can use either light or heat. In the former case, the light can bring the system to the state which is essentially short-lived and hard to observe. For that reason we will apply *in situ* photocrystallographic techniques, which allow for tracing of structural changes occurring when the NO_2 is transformed from one isomer (*e.g. nitro*) to another (*e.g. nitrito*) or *vice versa*, determine the conversion percentage, and see how this phenomenon is dependent on the light wavelength and temperature.

The overall scheme of the project is as follows: synthesis and crystallisation → crystallographic and quantum chemistry modelling → physicochemical measurements (including photocrystallographic approaches) → understanding of the phenomena. The knowledge of the nature of the NO_2 group switching processes, as well as, about the impact of the metal centre and ligands on it, shall contribute to our conscious and rational design of new controllable materials of desired features for applications in optoelectronics, high-capacity storage devices, as colour-changing materials, *etc*. Furthermore, the outcomes of the project may also have important consequences for our better understanding of complex biological systems, in which the light-matter interactions and nitrite ions play a crucial role.