



MMCT-XRAY: Communication between metallic centres in selected bridged mixed-valence coordination complexes – photocrystallographic studied combined with ultrafast spectroscopy

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. Multicentre transition metal complexes, thanks to the specific interactions and metal centres communication, 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.

Among transition metal coordination compounds, bridged mixed-valence transition metal coordination complexes (*i.e.*, complexes with two or more metallic centres on different oxidation states connected via molecular linkers) are of particular importance. Examples include the (photo)magnetic behaviour of mixed-valence polycyanometalates, with the best-known Prussian blue, which are also usually temperature-dependent, making the compounds excellent in applications regarding optical storage materials, molecular switches, or even photoresponsive mechanical devices. On the other hand, in biology the mixed-valence enzyme reaction centres are present in, for example, terminal oxidases (heme- a_3 /Cu_B sites = Fe/Cu moieties) and are important for the cell respiration process. Many of these properties are directly linked to inherently unstable metal-to-metal charge transfer (MMCT) states, and therefore the structure and dynamics of the latter should be comprehensively explored.

The aim of this project is to thoroughly investigate the dynamics of light-induced processes, which occur both in crystals and in solution, with the emphasis put on the direct determination of structural changes (bond distance changes, breaking or forming new bonds) via cutting-edge experimental methods supplemented by theoretical computations. The project is dedicated to studies of molecular mixed-valence transition-metal complexes with the general structure of L_nM_1 -bridge- M_2L_m ($M_1, M_2 = \text{Fe, Co, Cu, Mn, etc.}$, bridge = CN, SCN, pyrazine etc.; $L_n, L_m = \text{ligands}$), including the heme-based complexes. The choice of these complexes is dictated by their relatively easy modification facilitated by exchanging various ligands and rich spectroscopic properties (most importantly the existence of unique metal-to-metal charge transfer (MMCT) bands: *e.g.* light-induced $\text{Fe}^{\text{II}}/\text{Co}^{\text{III}} \rightarrow \text{Fe}^{\text{III}}/\text{Co}^{\text{II}}$; see figure). Detailed study and interpretation of signal related to atomic rearrangements taking place during chemical reactions or other processes induced by light pulse constitutes a great experimental challenge. In this project we take up this challenge and aim at investigations of nature and dynamics of charge transfer processes both in solution and in the solid state. We plan to utilise the newest and most advanced time-resolved spectroscopic and photocrystallographic methods. The spectroscopic part of the project will be realised with the aid of ultrafast time-resolved absorption spectroscopy (transient absorption). In turn, structural changes occurring upon irradiation will be studied at the X-ray free-electron sources (XFELs). It has to be stressed that such studies are very difficult, technically advanced and, thus, still very rare worldwide. However, only studies of this complexity will provide direct experimental information about photochemistry of molecules in crystals, and are thus well-suited for the proposed project.

The overall scheme of the project is as follows: synthesis and crystallization \rightarrow crystallographic and quantum chemistry modelling \rightarrow physicochemical measurements (including TR X-ray diffraction) \rightarrow understanding of the phenomena. The knowledge of the nature of charge transfer processes and metal centres communication and their role, as well as, about the impact of the bridge type and the ligands on such properties, shall contribute to conscious and rational design of new materials of desired optoelectronic and magnetic features. 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 play a crucial role.

