

Structural dynamics of photoinduced charge transfer in a dicopper(I)-disulfide complex

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Photoexcited states of transition metal complexes have long been in the focus of research attention due to both fundamental interest in their properties and their various applications. Copper compounds, in particular, are cheaper, more abundant and more environmentally friendly than the noble metal analogues, and are investigated as both photosensitizers and light emitters (*Armaroli, 2007*). In the chemistry of life copper is a part of many essential metalloenzymes. In particular, copper-sulfur centres in some enzymes take part in unusually rapid electron transfer (ET) (*Solomon, 2014*). Many efforts have been undertaken to study and reproduce properties of active sites of enzymes in small synthetic compounds. Photoinduced charge transfer in such complexes may model the ET in biochemical systems. The object of this study is a biomimetic dicopper complex coordinated with disulfide and guanidine ligands (*Neuba et al, 2012*). A combination of pump-probe optical and X-ray techniques supported by theoretical calculations was applied to study the structural dynamics of this complex upon photoinduced metal-to-ligand charge transfer (MLCT).

DFT and TD-DFT calculations were used to predict the geometric and the electronic structures of the ground state (S_0) and excited states with singlet ($^1\text{MLCT}$) and triplet ($^3\text{MLCT}$) multiplicities. The ultrafast evolution of the photoexcited system was studied with the transient absorption spectroscopy in UV/vis. The structural dynamics of the excited triplet state was followed with a combination of pump-probe X-ray absorption spectroscopy (*Görries et al, 2016*) and pump-probe wide-angle X-ray scattering (WAXS) (*Wulff et al, 2002*) with 100 ps resolution.

The calculations show that MLCT bands are the lowest energy absorption bands in the spectrum, with transitions happening from orbitals having strong contribution of Cu $3d$ to a σ^* orbital of a disulfide bridge $-\text{S}-\text{S}-$. Upon photoexcitation to one of higher singlet states, the complex undergoes internal conversion (IC) to the ground state with $\tau = 650$ fs and intersystem crossing (ISC) to the triplet state $^3\text{MLCT}$ with $\tau = 11$ ps. DFT predicts that due to the population of the σ^* orbital in the triplet state one of the two disulfide bridges is cleaved. The structure of the triplet state was studied with pump-probe X-ray techniques: PP-XAS revealed changes in the local structure around the copper atoms, whereas PP-WAXS was sensitive to the changes in the global shape of the molecule arising due to rotation of two halves of the molecule relative to each other upon the disulfide bond cleavage.

In this work (*Naumova et al, 2018*) we demonstrate that combining pump-probe XAS and WAXS has a big potential for investigation of photoinduced electronic and structural changes in molecular systems in solution. The investigated molecule represents a Cu-S system where biologically relevant disulfide-thiolate conversion can be achieved both chemically by addition of chloride ions (*Neuba et al, 2012*) and, as we show in this work, *via* photoexcitation

of a MLCT band. Good air and radiation stability make this system a suitable model to study photoinduced disulfide bond cleavage and recombination.