

## Time-resolved X-ray absorption spectroscopy to study molecular photocatalytic systems for H<sub>2</sub> evolution

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Recent developments and applications of time-resolved X-ray absorption spectroscopy (XAS) at SLS synchrotron will be presented. To study photochemical reaction in solution, we have developed the setup that uses pulsed laser source for photoexcitation and continuous synchrotron X-ray beam for probing<sup>[1]</sup>. The instrument covers the time range from 20 ns to 500  $\mu$ s and it is optimized for systems with sub-mM concentrations typical for photocatalytic reactions. Quantitative analysis of time-resolved X-ray absorption spectra allows determining the structure of intermediates of catalysts during photochemical reactions and excited state structure of photosensitizers.

Applications of time-resolved XAS to study components of photocatalytic systems for H<sub>2</sub> evolution will be shown. Cobalt complex with pentadentate pyridine-based ligand is the promising H<sub>2</sub> evolving catalyst that efficiently works in water<sup>[2]</sup>. The structure of Co(I) intermediate of this catalyst has been determined using the approach that we have demonstrated previously for cobaloxime<sup>[3]</sup>. We have found that one pyridine ligand dissociates from Co and the metal center remains 4-coordinated without any strong bonds with the solvent. In such configuration, the protonation of both metal center and pyridyl is possible which opens perspectives for rational design of more efficient catalyst based on computational predictions.

The structure of Cu phenanthroline-based photosensitizers in the triplet excited state has been also determined with time-resolved XAS. We previously demonstrated that the Cu center in the excited state is coordinated by solvent molecule if groups at 2,9 positions of phenanthroline are small<sup>[4]</sup>. Substitution by bulky sec-butyl groups blocks the access of solvent to the metal and reduces the flattening distortions of the complex. As a result, the excited state lifetime of such complex is long ( $\sim 1\mu$ s). The review of our other recent time-resolved XAS results in the field of artificial photosynthesis can be found in<sup>[5]</sup>

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### References:

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