

# Unravelling details of the excited states in molecular dyads using ultrafast X-ray spectroscopy

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The conversion of sunlight into fuels or chemicals is a key technology for a sustainable future. Hydrogen production via photocatalytic proton reduction with sun light is a prominent example of this strategy. Base metal photoactive compounds are sustainable alternatives to their noble metal counterparts. Bimetallic assemblies of the later are often used for direct conversion of sun light into chemical energy carriers like H<sub>2</sub>. The transition to base metal dyads as active compounds is partially hindered by the so far missing understanding of the working principle of such hetero-bimetallic complexes, which is required to improve their photocatalytic performance. Therefore, more detailed investigation of the ultrafast photoinduced electron transfer (ET) is of utmost importance on the way to active base metal dyads for photocatalytic ET reactions.

Such an ambitious aim requires the knowledge driven design of photoactive complexes, which in turn relies on the application of cutting-edge spectroscopic methods. We will underline the advantages of employing combined ultrafast X-ray and optical probes to obtain simultaneously the transient electronic and geometric structure changes in transition metal-based photosensitizers and functional bimetallic dyads.

We will report on our recent results investigating the novel family of FeCo molecular dyads. We used femtosecond X-ray emission spectroscopy (XES) in combined optical pump/ X-ray probe experiments at various XFEL sources to track the electronic and structural dynamics in a bimetallic assembly, connecting an Fe photosensitizer (PS) to a Co catalyst. Due to the very fast processes, partially unknown excited states at the iron PS and the optically dark states at the cobaloxime catalyst, an ultrafast two-color XES experiment is applied for the first time, detecting simultaneously the Fe and Co X-ray emission on femtosecond timescales to avoid ambiguities about time zero.

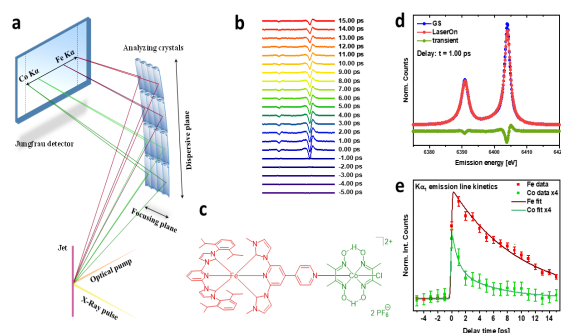


Figure 1: (a) Schematic setup of the experiment; (b) A time series of Fe XES spectra as a function of pump-probe time delay; (c) Structure of the investigated Fe-Co dyad; (d) Fe XES ground and excited state spectra and a corresponding transient spectrum (bottom) at  $\Delta t = 1$  ps; (e) Long timescale XES kinetics of Fe and Co with fitted multiexponential decay functions.

In this manner it is possible to unequivocally correlate the ultrafast excited state dynamics to ET processes within the dyad. The X-ray results are complemented with ultrafast UV-VIS transient absorption data to correlate the observed changes in the electronic and geometric structures of the dyad with the population dynamics derived from optical data.

**Index Terms:** water splitting, electron transfer, X-ray free electron laser, pump-probe spectroscopy

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[2] Nowakowski, M., (...), Gawelda, W., Bauer, M., “Ultrafast two-colour X-ray emission spectroscopy reveals excited state landscape in a base metal dyad”, Nature Communications (in revision) **2022**.