

Visualizing photoinduced intramolecular electron transfer

Photosynthesis designates the intricate chain of chemical reactions by which plants capture and store solar energy into chemical bonds [1]. Understanding this process would enable scientists to devise artificial supramolecular assemblies capable of mimicking splitting water to produce clean fuels [2]. Among the various key steps which have been delineated so far, the intramolecular conversion of an incident photon into an activated electron has remained one of the most challenging to date [3]. This work shows how novel analytical methods that utilize intense femtosecond X-ray pulses can provide unique information about this process [4].

The large molecule shown in Fig. 1 consists of a bimetallic ruthenium (Ru) antenna linked to a cobalt (Co) center. The photoinduced electron transfer from the photoexcited Ru to the optically-dark Co was studied at beamline BL3 of SACLA XFEL using the combined techniques of X-ray emission spectroscopy (XES) and X-ray diffuse scattering (XDS). The Ru center was selectively excited using 400 nm optical laser pulses (60 fs pulse length), and the induced dynamics were probed using 8 keV X-ray laser pulses (10 fs pulse length, 0.3% bw, 10^{10} photons per pulse) generated by SACLA. The fluorescent X-ray photons of a specific energy (CoK α) were selected using a bent crystal in the Johan geometry and detected using a MultiPort Charged Coupled Device (MPCCD) area detector. The XDS signal was detected directly behind the sample using a secondary MPCCD area detector.

Figure 2(a) shows the transient X-ray emission signal detected at 6.93 keV, which probes the valency and spin state of the Co center. The analysis of the time

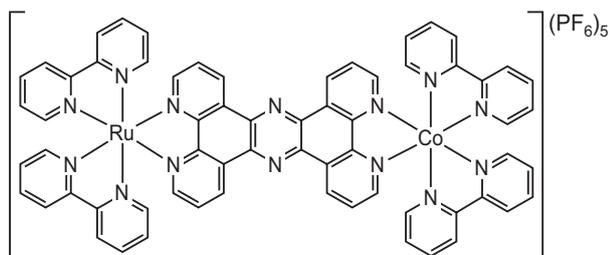


Fig. 1. The bimetallic photoactive molecule investigated, consisting of a ruthenium (Ru) antenna linked to a cobalt (Co) center.

trace indicates that the electron crosses the bridge in less than half a picosecond (i.e. half a trillionth of a second), and that a second electronic relaxation step in the form of a spin state transition, occurs at the Co center with a 1.9 picosecond time constant, following the electron transfer.

Figure 2(b) shows the transient X-ray diffuse scattering signal, which is sensitive to global structural changes of the solute and the solvent. The analysis of this pattern allows not only to retrieve the internal changes of the molecular structure as the electron localizes at the Co center, but also the amount of energy dissipated into the surrounding solvent as heat. The internal structural dynamics are dominated

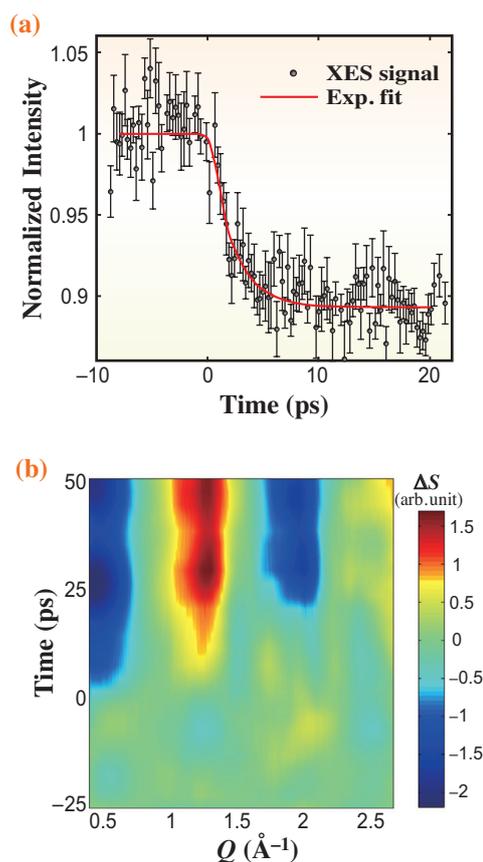


Fig. 2. (a) The transient X-ray emission signal detected at 6.93 keV (black circles), with standard error (black lines) and the description of the data resulting from the proposed electronic transfer pathways. (b) The transient X-ray diffuse scattering signal measured simultaneously with the X-ray emission signal.

by a 0.2 Å expansion of the Co-N bonds, induced by the electron transfer and spin state transition at the Co center.

Figure 3 summarizes the fundamental timescales and processes, as obtained from these combined X-ray measurements delivering the complete picture of the photoinduced electron transfer process.

In conclusion, this experiment shows that it is now possible to track all the stages of electron transfer through a large photoactive molecule. This will contribute to elucidate at the atomic level the various

factors that govern the efficiency of functional systems, such as photocatalysts or photovoltaic solar cells.

Another important finding of this study is that molecules, where photoconversion and electron transduction are so fast that they proceed with minimal energy loss as heat, can indeed be constructed under the fumehood of the chemistry lab. Such photochemical molecular devices are of great potential for future sustainable production of fuel or electricity.

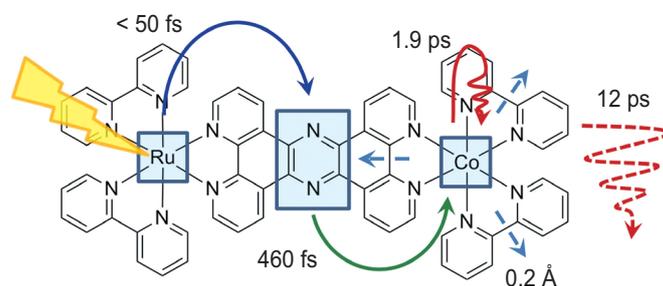


Fig. 3. Summary of the fundamental timescales and processes following photoexcitation, obtained from the combined X-ray measurements described here. Full arrows show electronic dynamics, dashed arrows show structural dynamics. Dark blue arrow shows the initial electron transfer from the photoexcited Ru center to the bridge, and green arrow shows electron transfer from the bridge to the Co center. The red arrow shows the spin state transition at the Co center induced by the electron transfer. Dashed lines show the structural dynamics, consisting of a 0.2 Å bond length expansion of the Co-N bonds (blue), and a reorganization of the solvent as it is heated by the transfer of excess excitation energy from the excited molecule (red).

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