ESRF	**Experiment title:** Direct Observation of Structural Dynamics in Photoinduced Ligand Distortions of a Copper Complex	**Experiment number**: CH-5108
Beamline: ID09B	**Date of experiment**: from: 25/5/2017 to: 31/5/2017	**Date of report**: 16/1/2018
Shifts: 18	**Local contact(s)**: Michael Wulff	*Received at ESRF:*

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Report:

We performed a time-resolved X-ray solution scattering (TRXSS) experiment on a copper complex ($[Cu(dmphen)_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline)) at ID09B beamline. According to previous spectroscopic studies, the copper complex exhibits structural change in which the molecular structure flattens from tetrahedral to planar structure upon irradiation (Figure 1). Although the electronic dynamics of the copper complex has been revealed by time-resolved spectroscopy, the details of the structural information of reaction intermediates remain elusive. Hence, we desired to unravel the structural dynamics and the structures of the reaction intermediates of $[Cu(dmphen)_2]^+$ using TRXSS.

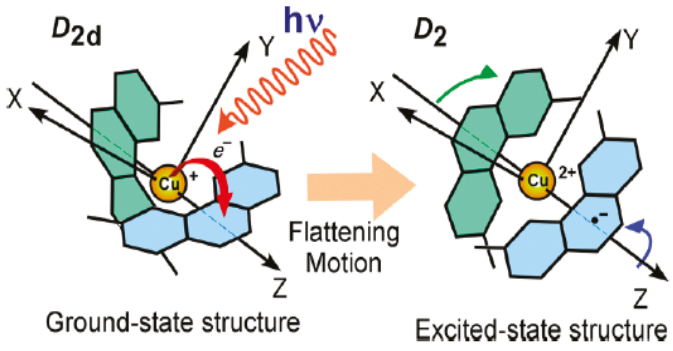

Figure 1. A schematic figure illustrating the photoreaction of $[Cu(dmphen)2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline).

We used a typical pump-probe setup implemented at the beamline. A fundamental laser pulse (λ = 800 nm) from a CPA amplifier was converted to 400 nm, and was used to excite the copper complex. An X-ray pulse with ~100 ps temporal width followed the laser pulse to produce a scattering pattern of the target system. The scattering patterns of the sample were collected using a Rayonix CCD. The time delays in which we collected the scattering patterns were -3 us (for reference), 100 ps, 178 ps, 316 ps, 562 ps, 1 ns, 3.16 ns, 10 ns,

31.6ns, 50 ns, 100 ns, 316 ns, 1 μs. The salt of $[Cu(dmphen)_2]^+$ was dissolved in acetonitrile (MeCN) at 20 mM concentration and used for the experiment.

Figure 2 shows the difference scattering curves of $[Cu(dmphen)_2]^+$. To distinguish the signal produced by the structural change of solute molecules from that originated from heat, the difference scattering curves of $[Cu(dmphen)_2]^+$ and heat are plotted together in Figure 3 for comparison. Even though the difference scattering curves of the copper complex and the heat are similar, one can observe clear difference between them in low q region ($q < 0.3$ ($Å^{-1}$)) especially at early time delays (Figure 4). This indicates that the structural change of $[Cu(dmphen)_2]^+$ complex undoubtedly occurred during the photoreaction.

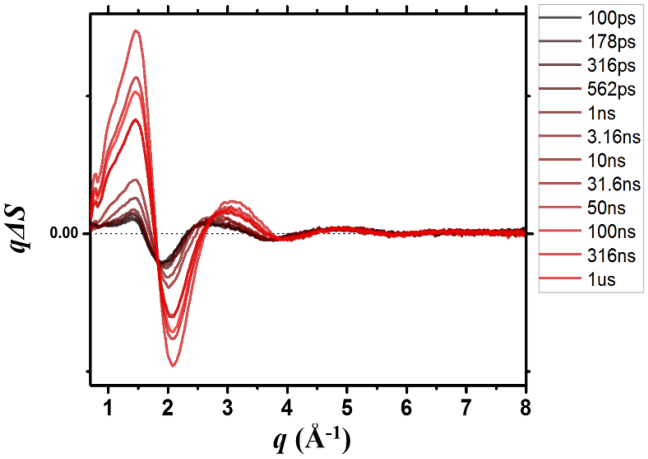

Figure 2. The difference scattering curves of $[Cu(dmphen)_2]^+$ in acetonitrile sovlent.

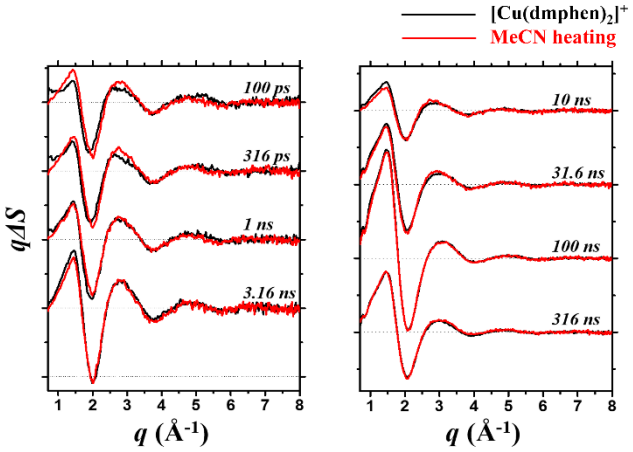

Figure 3. The difference scattering curves of $[Cu(dmphen)_2]^+$ (black) and the heat of acetonitrile solvent (red).

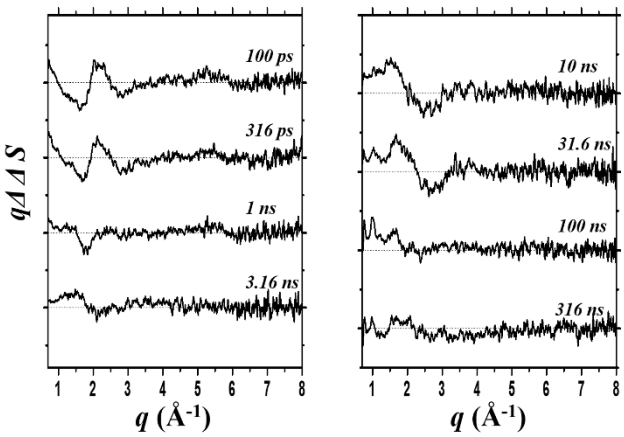

Figure 4. The difference between the difference scattering curves of $[Cu(dmphen)_2]^+$ and the heat of acetonitrile solvent.

In conclusion, we successfully collected TRXSS data of $[Cu(dmphen)_2]^+$ at several time delays to reveal the structural dynamics of the flattening of the copper complex. Currently we are analysing the data to extract the detailed molecular structures of reaction intermediates associated with the signal change.