



	Experiment title: Investigation of Irreversible Photoreactions of Organometallic Complexes Using Serial X-ray Crystallography	Experiment number: MI-1310
Beamline: ID09B	Date of experiment: from: 22/02/2018 to: 28/02/2018	Date of report: 25/02/2020
Shifts: 18	Local contact(s): Norman Kretschmar	<i>Received at ESRF:</i>
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Report:

We performed a serial crystallography at ID09B beamline on the dinuclear silver complex $[\text{Ag}_2(4\text{-stilbz})_4][\text{CO}_2\text{CF}_3]_2$ (4-stilbz = trans-1-(4-pyridyl)-2-(phenyl)ethylene, $\text{Ag}_2(\text{stilbz})_4$) to investigate the irreversible photoreaction of the organometallic complex. It was previously reported that the molecule in crystal undergoes [2+2] photodimerization reaction upon photoexcitation (See Figure 1). In this beamtime, our primary goal was to investigate whether a sufficient fraction of the molecules in the crystal undergoes the reaction even with an excitation using a single laser pulse. In other words, we were to confirm whether the structural change induced by the single laser pulse is large enough to be detected by using serial crystallography. To confirm this, we collected the x-ray diffraction images at two time delays which correspond to before (-3 ns) and after the reaction (100 ps time delay), respectively.

A typical pump-probe scheme using an optical laser pump pulse and an x-ray probe pulse was used to identify the structures of the molecule before and after the photoreaction. A 360 nm pump pulse was generated by using optical parametric amplifier (OPA) on a fundamental pump pulse (800 nm). The laser pulse was converted to the desired wavelength (360 nm) and focused to a spot of $150 \mu\text{m} \times 190 \mu\text{m}^2$ at the sample position (laser fluence = $1.1 \text{ mJ}/\text{mm}^2$). After excitation, the reaction was probed by an x-ray pulse ($E = 15 \text{ keV}$) with the x-ray energy bandwidth of $\sim 3 \%$. Single crystals of $\text{Ag}_2(\text{stilbz})_4$, with the size from 300 to 500 μm , were loaded on fixed target holders and subjected to x-ray pulses to obtain diffraction images from the crystals. To apply a serial experimental scheme, where each fresh crystal is exposed to only a single x-ray pulse and then discarded, the fixed target holder was translated continuously during the measurement. Ten X-ray diffraction images were collected for every second using the Rayonix MX 170-HS CCD.

Initially, the x-ray diffraction images were collected for the negative time delay, i.e., for the crystal before laser excitation. As shown in Figure 2, it can be confirmed that a sufficient number of diffraction spots can be captured by using a single x-ray probe pulse. The collected x-ray diffraction

images were manually indexed by using Lauetools (Figure 3). We also collected the diffraction images for the crystal after the photoexcitation, i.e., at 100 ps time delay.

In conclusion, we successfully collected sufficient numbers of x-ray diffraction images of $\text{Ag}_2(\text{stilbz})_4$ for the crystals before and after the photoexcitation. Now we are analyzing the diffraction images to retrieve the exact molecular structures of $\text{Ag}_2(\text{stilbz})_4$ in the crystal.

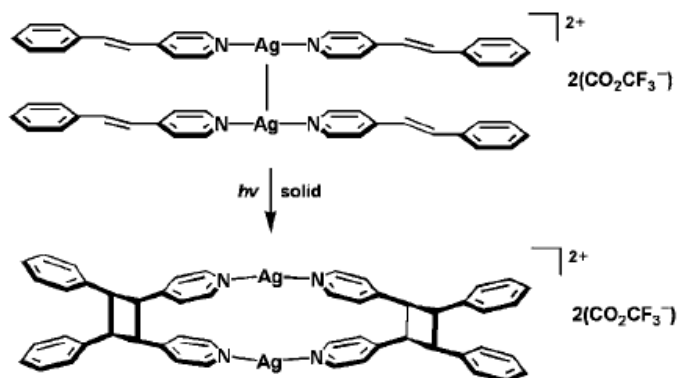


Figure 1. A schematic drawing of the [2+2] photodimerization of $\text{Ag}_2(\text{stilbz})_4$ [1].

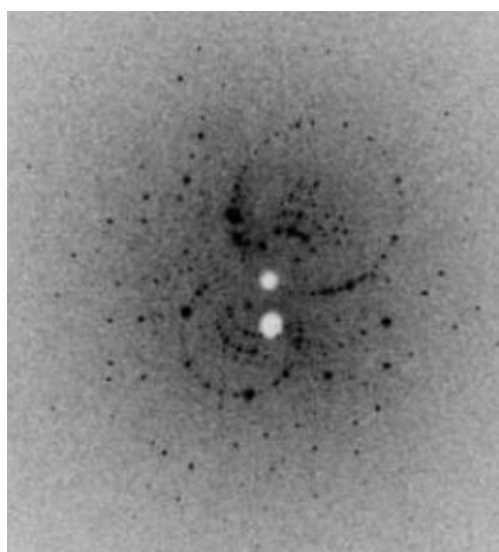


Figure 2. A representative x-ray diffraction image of $\text{Ag}_2(\text{stilbz})_4$ for the negative time delay ($\Delta t = -3$ ns).

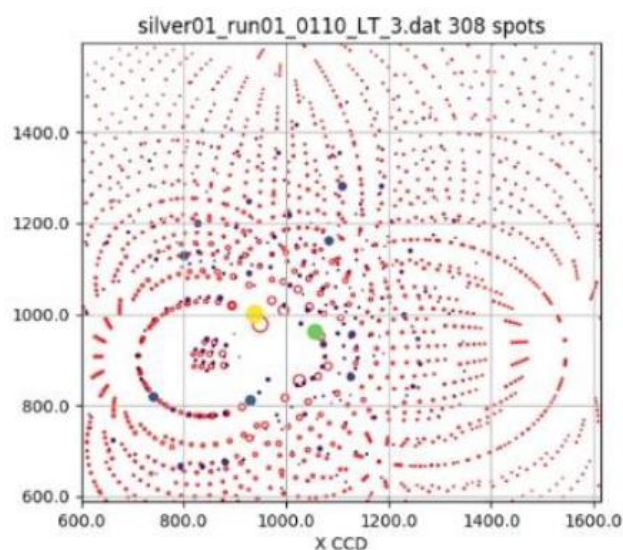


Figure 3. An example image showing the result of indexing of a diffraction image of $\text{Ag}_2(\text{stilbz})_4$. The blue spots are the experimentally detected diffraction spots and the red spots are theoretically predicted diffraction spots using Lauetools for a certain crystal orientation and the cell parameters.

References

[1] Q. Chu et al., *Angew. Chem. Int. Ed.* **2005**, 44, 3569-3572