


Experiment title:

Investigation of the exciplex of square-planar Au(III) terpyridine using pump-probe X-ray solution scattering

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CH-5274

Beamline:

ID09B

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Shifts:

18

Local contact(s):

Martin nors Pedersen

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

Hyotcherl Ihee, Department of Chemistry, KAIST, Daejeon, Republic of Korea

Hosung Ki, Department of Chemistry, KAIST, Daejeon, Republic of Korea

Sungjun Park*, Department of Chemistry, KAIST, Daejeon, Republic of Korea

Chiwoo Ahn*, Department of Chemistry, KAIST, Daejeon, Republic of Korea

Yunbeom Lee, Department of Chemistry, KAIST, Daejeon, Republic of Korea

Siin Kim*, Department of Chemistry, KAIST, Daejeon, Republic of Korea

Min Seo Choi*, Department of Chemistry, KAIST, Daejeon, Republic of Korea

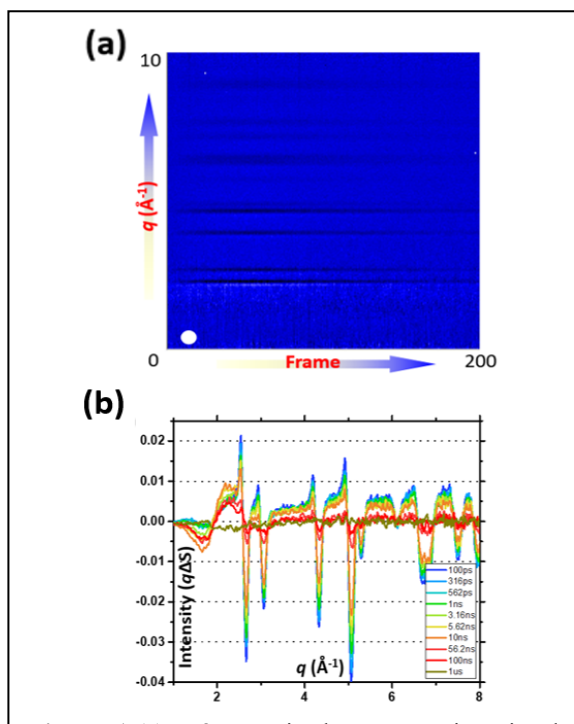
Report:


Figure. 1 (a) A 2D matrix shows a transient signal to increase and decrease soon as repeated measurements are accumulated for the 100 ps time delay. (b) 1st ISV obtained by SVD of matrix (a) according to each time delay. (100 ps ~ 1 μ s for 20 mM of $[\text{Au}(\text{terpy})\text{Cl}]^{2+}$ solution in water)

In the previous beamtime (CH-4732), the time-resolved X-ray liquidography (TRXL) experiment was carried out to investigate the excimer formation of the chloro-(terpyridine)platinum(II) $[\text{Pt}(\text{terpy})\text{Cl}]^+$. The $[\text{Au}(\text{terpy})\text{Cl}]^{2+}$, which is the target molecule of this experiment, has a very similar structure and electron configuration to that of the $[\text{Pt}(\text{terpy})\text{Cl}]^+$. It was predicted that the excimer-forming mechanism of $[\text{Au}(\text{terpy})\text{Cl}]^{2+}$ will be differ from that of $[\text{Pt}(\text{terpy})\text{Cl}]^+$ due to different oxidation numbers in the central metal. Comparison of the two systems may reveal how the charge of the building unit affects the excimer formation. The sample was dissolved in water to a final concentration of 20 mM. We used a pump-probe setup installed at ID09B for the experiment. The pulses from a femtosecond CPA amplifier (800 nm) was converted to desired wavelength (400 nm) and used. In order to avoid multiphoton excitations, the pulses were stretched with silica prisms to the pulse length of ~ 2 ps before

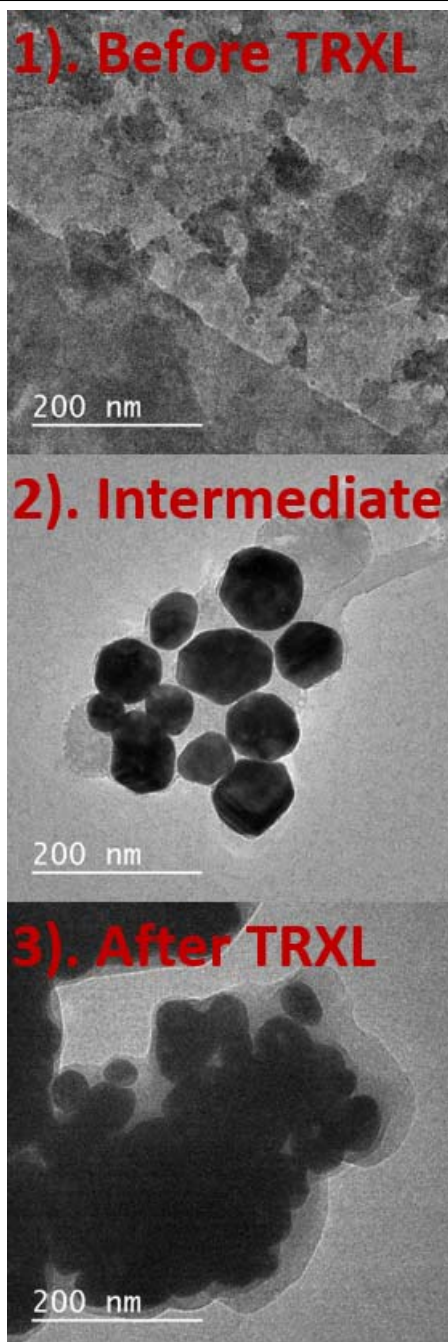


Figure. 2 TEM images ; Prior to TRLX measurements, no special structures were observed. And then, in the case of reaction intermediate, nanostructure is shown to form. Finally, we observed that there were relatively small nanostructures after the measurements.

reaching the sample. After excitation, the reaction was probed by hard X-ray pulses (18.0 keV) with the X-ray energy bandwidth of 1.89 %. The sample solution was circulated through an open-jet sapphire nozzle and scattering patterns were collected using Rayonix CCD. The measured data showed that the initial expected excimer-forming photoreaction was not observed. However, as the measurement continued, the transient signal appeared slowly, indicating a tendency to increase and decrease again as the time of repeated measurement (**Figure 1(a)**). The difference scattering curves of $[\text{Au}(\text{terpy})\text{Cl}]^{2+}$ from 100 ps to 1 μs showed clear oscillatory features with superb S/N ratio (**Figure 1(b)**).

The data provide two key insights. First, through an irreversible process, gold complex in an initial solution produces a side product (intermediate) after first response to photoreaction. Second, because of the circulated liquid jet system, the intermediate accumulate and a secondary photoreaction occurs and it's also irreversible photoreaction. To confirm these hypothesis, TEM measurements were carried out on three different samples: 1). A sample of the solution before measurement, 2). Side product (intermediate), 3). A sample of the solution after measurement (**Figure 2**). Indeed, the TEM images of the side and final products clearly show formation of nanoparticles whereas the initial solution does not show any nanoparticles. Considering the TEM data, the observed X-ray transient signal seems to indicate that the initially formed nanoparticles by photoexcitation of the gold complex is converted into smaller nanoparticles by the further photoreaction. Although

this type of reaction is not what we originally planned to study, the unexpectedly observed reaction may be worth further investigation. We plan to further analyze the lattice structure and its time-dependent changes of nanoparticles.