ESRF	**Experiment title:** Investigation of the photoreaction of cyclic tri-nuclear gold complex in solution using pump-probe X-ray solution scattering	**Experiment number**: CH-4933
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Names and affiliations of applicants (* indicates experimentalists):

Hyotcherl Ihee (*), Department of Chemistry, KAIST, Daejeon, Republic of Korea
Michael Wulff (*), ESRF, Grenoble, France
Norman Kretzschmar (*), ESRF, Grenoble, France
Hosung Ki (*), Department of Chemistry, KAIST, Daejeon, Republic of Korea
Youngmin Kim (*), Department of Chemistry, KAIST, Daejeon, Republic of Korea
SungJun Park (*), Department of Chemistry, KAIST, Daejeon, Republic of Korea
Chi Woo Ahn (*), Department of Chemistry, KAIST, Daejeon, Republic of Korea
Yunbeom Lee (*), Department of Chemistry, KAIST, Daejeon, Republic of Korea

Report:

We performed a time-resolved X-ray solution scattering (TRXSS) experiment on [$(AuPz)_3$] (Pz = pyrazolate) at ID09 beamline (Figure 1). It is known that in solid state, the gold complex forms an excimer with the eclipsed conformation due to the aurophilic interaction between gold atoms. However, it is not clear whether the same excimer formation occurs in solution. By revealing the structural dynamics of the gold complex using TRXSS, we aimed to clarify the structure of the possible excimer, as well as origin of photophysical properties of the gold trimer.

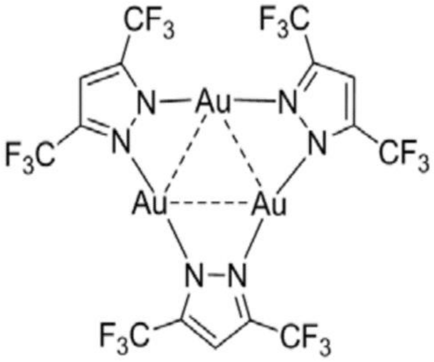

Figure 1. The molecular structure of [$(AuPz)_3$] (Pz = pyrazolate)

A typical pump-probe setup installed in the beamline was used for the experiment. The third harmonic (λ = 267 nm) of 800 nm fundamental pulses which were generated from a femtosecond CPA amplifier were used to excite the gold complex. Following a laser pulse, a hard X-ray pulse (E_{photon} = 18.0 keV and 100 ps temporal width) was delivered to probe the structural change of the solute and solvent molecules. The sample was dissolved in cyclohexane until the solution was saturated (~ 0.4 mM). X-ray scattering patterns were collected at the time delay ranging from 100 ps to sub-microseconds.

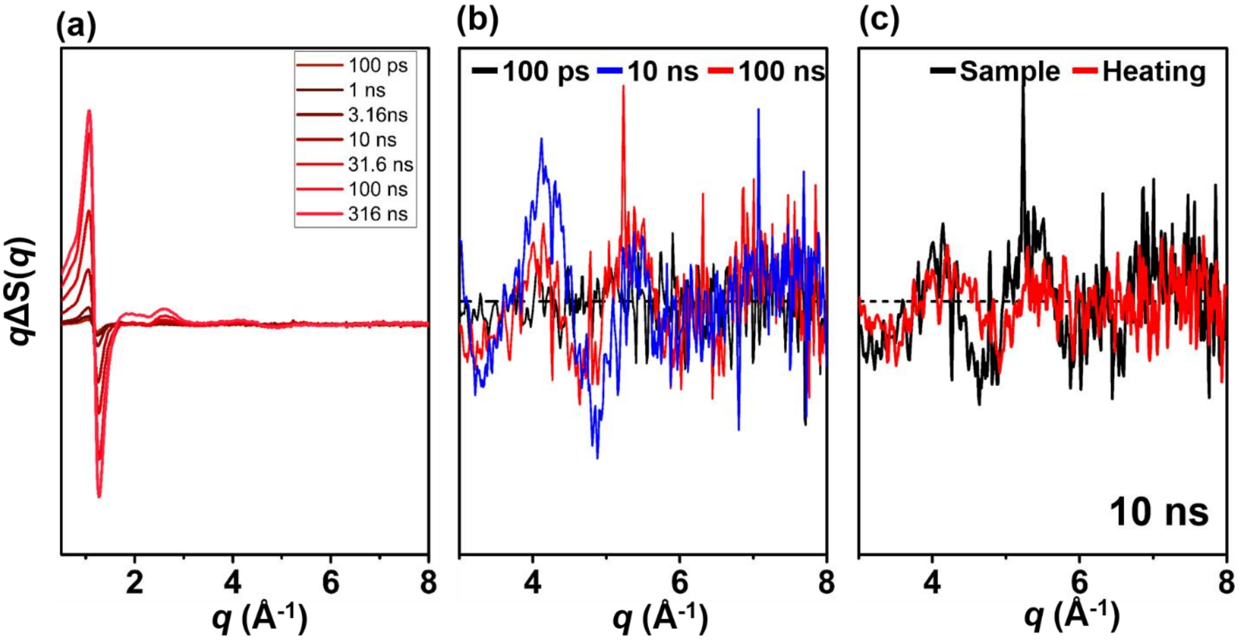

Figure 2. (a) The difference scattering curves, $q\Delta S(q)$, of $[(AuPz)_3]$ in cyclohexane at various time delays. (b) $q\Delta S(q)$ of $[(AuPz)_3]$ at selected time delays (100 ps, 10 ns, and 100 ns). (c) Comparison of $[(AuPz)_3]$ and heating $q\Delta S(q)$ at 10 ns.

From the experiment, we succeeded in obtaining the difference scattering curves ($q\Delta S(q)$) of the gold complex (Figure 2(a)). As shown in Figure 2(b), the oscillatory features at high q region ($q > 3.0$ Å^{-1}) start to rise after 10 ns. To confirm whether those oscillatory features are originated from the structural change of gold complex, $q\Delta S(q)$ of gold complex and heat are plotted together in Figure 2(c) for comparison. It is clearly shown that the gold complex exhibit distinct oscillatory features compared to heat signal, especially at 3 Å^{-1} < q < 6 Å^{-1} region (Figure 3(c)). These findings provide two key insights. First, considering the size of the difference signal, excimer formation was not observed at 100 ps to 10 ns timescale. Thus, the excimer of gold complex might be all dissociated before 100 ps or might not be formed at 0.4 mM condition. Second, the distinct oscillatory features shown after 10 ns indicate that the gold complex is involved in photoreaction associated with a certain structural change. By considering the timescale of that reaction, we expect the structural change of gold complex is originated from a diffusion-controlled bimolecular reaction.

In conclusion, we successfully collected TRXSS data of $[(AuPz)_3]$ at various time delays. Oscillatory features are not observed in the time range from 100 ps to 3.16 ns but start to emerge after 10 ns. Those oscillatory features shown after 10 ns are clearly distinguishable from the solvent heating signals, indicating the sturcutural change of gold complex occurs after 10 ns. Currently, we are analyzing the data to extract the structural dynamics of the gold complex.