ESRF	**Experiment title:** Investigation of the wavelength-dependent excimer formation pathways of a platinum complex by using pump-probe x-ray solution scattering	**Experiment number**: CH-6003
Beamline: ID09	**Date of experiment**: from:08 DEC 2021 to:14 DEC 2021	**Date of report**:
Shifts: 18	**Local contact(s)**: Matteo LEVANTINO	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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

Hosung Ki, Center for Advanced Reaction Dynamics, Institute for Basic Science, Daejeon, Republic of Korea

Yunbeom Lee, Center for Advanced Reaction Dynamics, Institute for Basic Science, Daejeon, Republic of Korea

***Minseo Choi, Department of Chemistry, KAIST, Daejeon, Republic of Korea**

***Seonggon Lee, Department of Chemistry, KAIST, Daejeon, Republic of Korea**

Jungmin Kim, Department of Chemistry, KAIST, Daejeon, Republic of Korea

***Jain Gu, Department of Chemistry, KAIST, Daejeon, Republic of Korea**

***Yongjun Cha, Department of Chemistry, KAIST, Daejeon, Republic of Korea**

***Kyung Won Lee, Department of Chemistry, KAIST, Daejeon, Republic of Korea**

Report:

We performed the time-resolved x-ray liquidography (TRXL) experiment on planar platinum (II) complex, platinum terpyridine chloride (Pt(tpy)Cl) at ID09 beamline. From our previous TRXL study (CH-4732), we identified that large structural changes occur upon the metal-to-ligand charge transfer (MLCT) transition as the complexes form excimers. The previous TRXL experiment was performed using an excitation wavelength of 400 nm. After that, we performed a transient absorption spectroscopy experiment to examine whether the reaction shows excitation-wavelength dependency. The result showed that the excimer formation dynamics of Pt(tpy)Cl exhibits wavelength-dependent behavior. Specifically, we observed a significant difference in the dynamics upon metal-metal-to-ligand charge transfer (MMLCT) transition with 500 nm excitation and MLCT transition with 400 nm excitation. Nevertheless, due to the lack of structural sensitivity of the transient absorption spectroscopy, we were not able to identify the structural origin of the different behaviors following two different electronic transitions. The central goal of this experiment (CH-6003) was to gain detailed insights into the wavelength-dependent structural dynamics of the excimer formation of Pt(tpy)Cl by monitoring the structural changes following the MMLCT transition by using TRXL.

We used a typical pump-probe setup installed at ID09 for the experiment. Two excitation wavelengths, 400 nm and 500 nm, were used for the experiment to investigate the wavelength-dependent excimer formation dynamics. A solution of 20 mM platinum terpyridine chloride in water, of which concentration was sufficient to allow the excimer formation, was used in the experiment. The scattering x-ray was collected using an area detector. We collected the data at the following time delays: -3 ns, 50 ps, 100 ps, 178 ps, 316 ps, 562 ps,1 ns, 1.78 ns, 3.16 ns, 5.62 ns, 10 ns, 17.8 ns, 31.6 ns, 56.2 ns, 100 ns, 178 ns, 316 ns, 562 ns, 1 μs.

From the experiment, we successfully obtained a TRXL signal originating from the structural change of Pt(tpy)Cl. First, we confirmed that the signal obtained with 500 nm excitation is different from the signal originating from the heating of solvent, as shown in Figure 1. This comparison shows that the TRXL signal undoubtedly encodes the structural change of Pt(tpy)Cl after the photoexcitation. Prior to the analysis, the TRXL signals were divided into isotropic and anisotropic signal components. The isotropic and anisotropic signals contain information regarding the structural change of the molecule and additional information regarding the orientation of the molecules, respectively. As Figure 2 shows, while the overall shape of the transient TRXL signal is almost the same for the two different excitation wavelengths, there is a difference in the amplitude of the signal components. Notably, while the signal amplitude of the isotropic signal component is about 30% higher for 500 nm excitation, the amplitude of the anisotropic signal component is about two times higher for 400 nm excitation. While the detailed numbers are not shown in this report, we also observed that the exponential time constants representing the rate of the decay of each signal component also differed at the two wavelengths. Currently, we are analyzing the data to extract the details of the structural dynamics of Pt(tpy)Cl following the two different transitions.

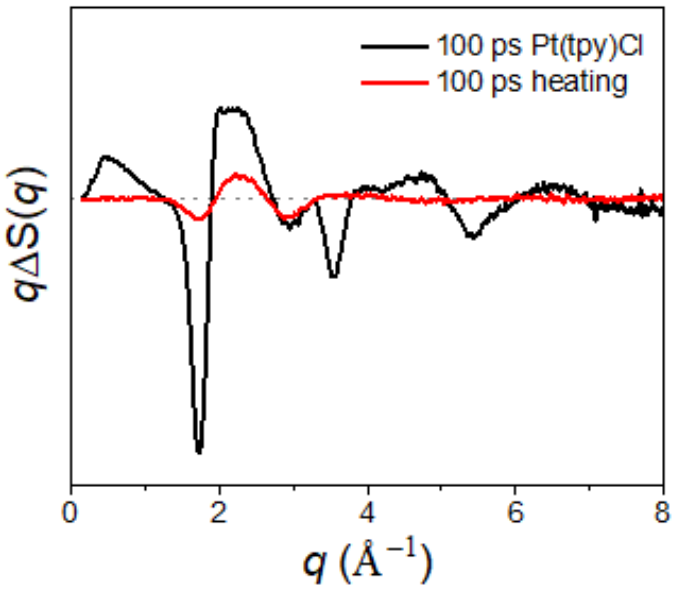

Figure 1. Comparison of the TRXL signal of Pt(tpy)Cl obtained at 100 ps time delay after 500 nm excitation (black) and solvent (water) heating signal obtained at 100 ps time delay after the photoexcitation of a dye molecule dissolved in water (red).

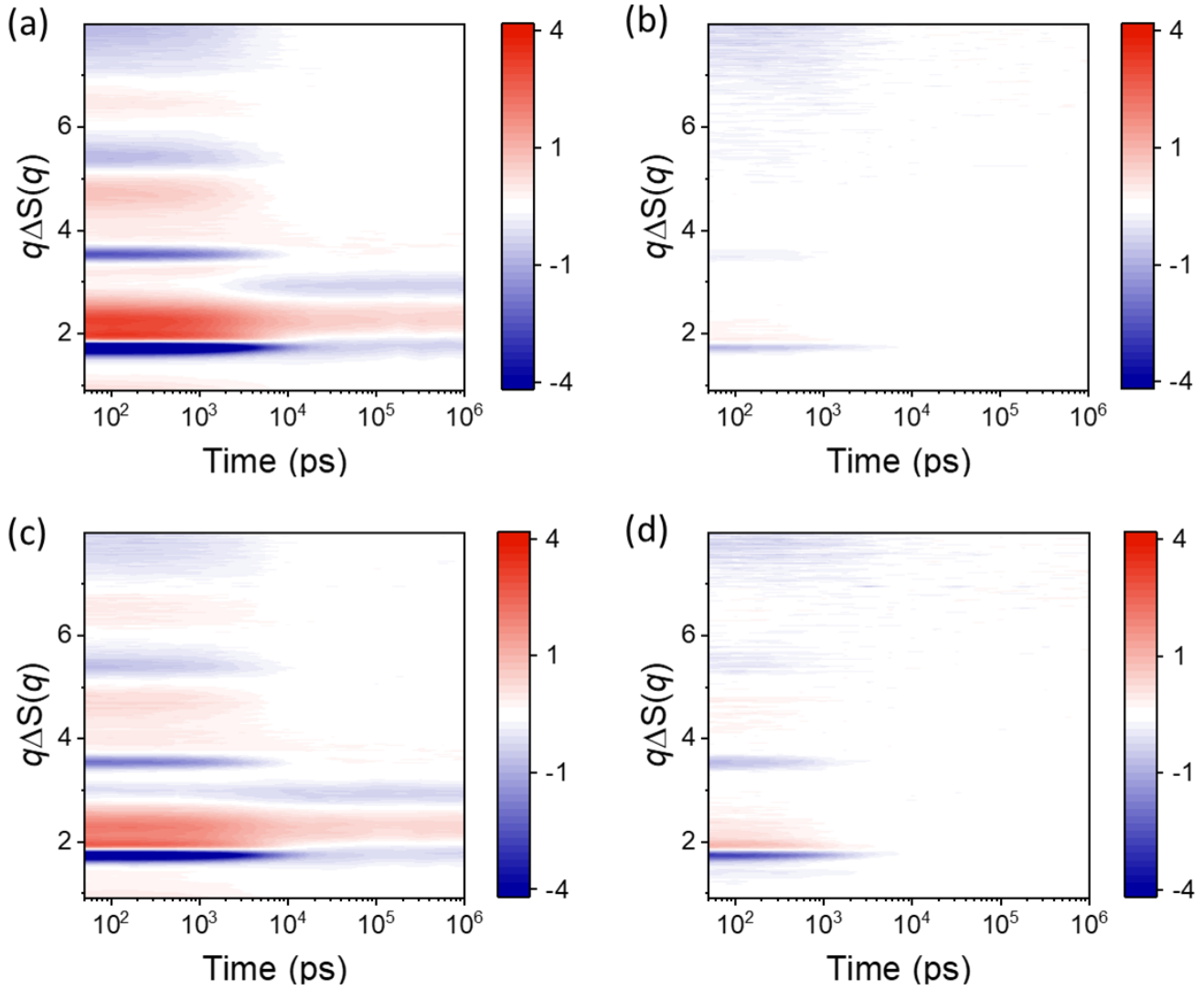

Figure 2. Contour plots of (a) isotropic and (b) anisotropic signal components of the TRXL signal of Pt(tpy)Cl obtained with 400 nm excitation. Contour plots of (c) isotropic and (d) anisotropic signal components of Pt(tpy)Cl obtained with 500 nm excitation.