



	<b>Experiment title:</b> Exploring the excited-state dimer of bipyridine dichloro-platinum(Pt(bpy)Cl <sub>2</sub> ) using pump-probe X-ray solution scattering	<b>Experiment number:</b> CH-4129
<b>Beamline:</b> ID09B	<b>Date of experiment:</b> from: 30/04/2014 to: 06/05/2014	<b>Date of report:</b> 02/03/2015 <i>Received at ESRF:</i>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Gemma Newby	

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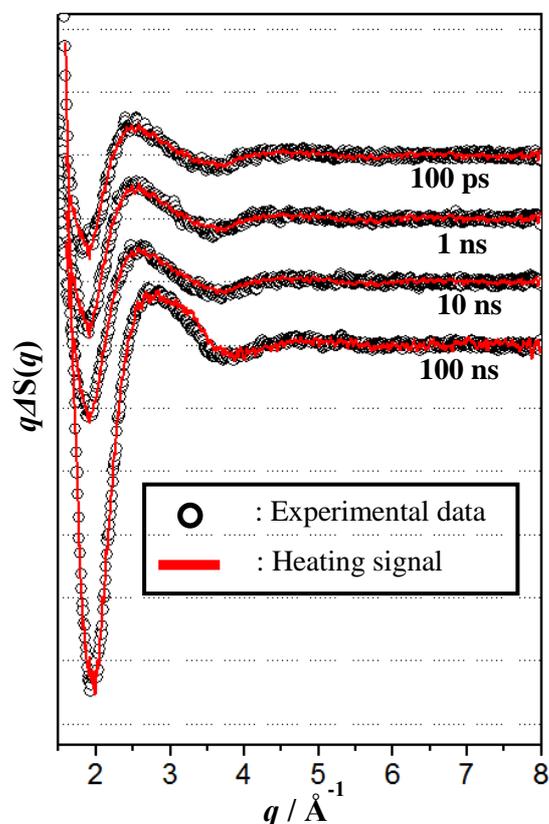
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**Report:**

We proposed to reveal the structure of Pt complex, bipyridinedichloro-platinum(II) (Pt(bpy)Cl<sub>2</sub>), and the kinetics related to the formation of the excited-state dimer, so-called excimer, by using pump-probe X-ray solution scattering. We used a pump-probe device installed at ID09B for this purpose. A total of 12 shifts were allocated during 30<sup>th</sup> of April to 6<sup>th</sup> of May, 2014. The pulses from a femtosecond CPA amplifier ( $\lambda = 800$  nm) was converted to desired wavelength (400 nm) and used excite the sample. And the structural dynamics of the Pt(bpy)Cl<sub>2</sub> after the excitation such as formation of the excimer was investigated. To follow the whole process of the reaction, we collected the scattering data at the following times: -3 ns, 100 ps, 1 ns, 10 ns and 100 ns.

The reaction was probed with hard X-ray pulses ( $E_{\text{photon}} = 18.0$  keV). We used 3.3 mM Pt(bpy)Cl<sub>2</sub> solution in acetonitrile as a sample. This solution was circulated by an open jet system to make a stable liquid sheet. Scattering patterns were detected with FReLoN CCD detector. Collected data was analyzed by several steps. Experimental curves were obtained by radial integration of 2D images to 1D curves followed by subtracting reference curve (diffraction curve obtained at negative time point, -3 ns).

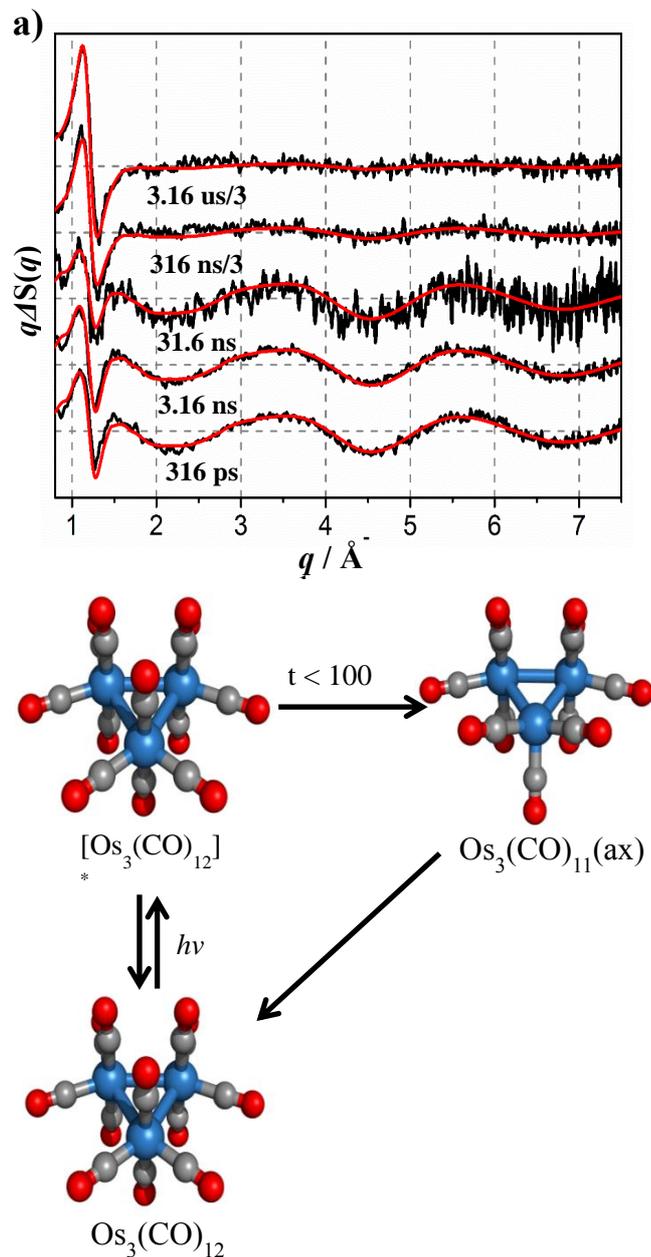


**Figure 1.** The comparison of Time-resolved difference X-ray scattering curves of the Pt(bpy)Cl<sub>2</sub> complex in acetonitrile to the heating signal of pure solvent.

Because the scattering pattern from a solution cannot offer a direct structural information as the pattern from single crystal, other strategy, the global analysis, was used. First, we compare the difference curve obtained from solution of Pt(bpy)Cl<sub>2</sub> to the heating signal of pure acetonitrile (see Figure 1). Strangely, however, the difference scattering curve obtained from solution of Pt(bpy)Cl<sub>2</sub> has no clear difference when compared to the heating signal of pure solvent. This means that there is no observable signal which originates from the structural change of solute. We also tried to increase the power of laser pump. Various laser powers ranging from 0.8 mJ/mm<sup>2</sup> to 4.1 mJ/mm<sup>2</sup> are tried but even at the highest laser power, we failed to get a distinct difference scattering signal of solute.

From the series of trials, we determined that the Pt(bpy)Cl<sub>2</sub> has extremely small quantum yield of formation of excimer in acetonitrile upon 400 nm excitation. To study the structural dynamics related to the formation of excimer, we suggest that the Pt(bpy)Cl<sub>2</sub> should be modified to have higher quantum yield of the formation of excimer.

After the failure, we promptly changed the sample system to triosmium dodecacarbonyl complex which was prepared as a back-up. The structural dynamics of Os<sub>3</sub>(CO)<sub>12</sub> after 400 nm excitation was probed using typical pump-probe solution X-ray scattering scheme. As a consequence, we obtained a series of difference scattering signal at several time delays (see Figure 2a). Global analysis is performed to extract the whole scheme for structural dynamics from the measured difference scattering curves. From the analysis, it was revealed that Os<sub>3</sub>(CO)<sub>11</sub> complex, which has a vacancy at equatorial position, is the major intermediate of the reaction. Now we are organizing the result and preparing manuscript for publication.



**Figure 2.** Time-resolved difference X-ray scattering curves of the Os<sub>3</sub>(CO)<sub>12</sub> scattering curve in cyclohexane measured with 400 nm laser excitation. **a)** Experimental difference scattering curves,  $q\Delta S(q)$ , at various time delays (black) and their theoretical fits (red) are shown together. **b)** Schematic of candidate reaction pathways for photodissociation of the Os<sub>3</sub>(CO)<sub>12</sub> complex.

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