Structural and Electronic Properties of the Triplet State of Ruthenium (II)-*tris*-2,2'-bipyridine Observed by Picosecond Time-Resolved Ru *K*-Edge X-Ray Absorption Fine Structure

Time-resolved X-ray absorption fine structure (TR-XAFS) measurements of ruthenium (II)-*tris*-2,2'-bipyridine ($[Ru^{II}(bpy)_3]^{2+}$) in the triplet metal-to-ligand charge transfer (^{3}MLCT) excited state were conducted and analyzed to investigate transient structural changes directly related to the photophysical properties of the complex. The results from visible (400 nm) and UV (267 nm) excitation indicate that electrostatic interaction between the oxidized Ru atom and the reduced bipyridine ligand is the dominant factor affecting the Ru-N bond contraction. An increase of the Debye-Waller factor from the EXAFS analysis suggests that fast localized structural distortion due to electron hopping exists in the ^{3}MLCT excited state.

Ruthenium (II)-*tris*-2,2'-bipyridine ($[Ru^{II}(bpy)_3]^{2+}$) is a key transition metal complex that acts as a photosensitizer. Because $[Ru^{II}(bpy)_3]^{2+}$ shows high photosensitivity in the visible region originating from a characteristic metal to ligand charge transfer (MLCT) transition, its long-lived triplet MLCT (^{3}MLCT) state, which is the lowest excited state, serves as an extremely efficient photocatalyst [1, 2]. The intramolecular energy transfer reaction combined with the molecular structural transformation of the ^{3}MLCT state directly determines the energy level of $[Ru^{II}(bpy)_3]^{2+}$ and has important consequences for the character of the photocatalytic reaction [1, 2]. Thus, it is essential to investigate the molecular structure of the ^{3}MLCT state. However, such studies have mainly been performed using optical spectroscopic methods [3, 4], with which it is difficult to estimate the molecular structure with atomic resolution. Therefore, a detailed structural study of the ^{3}MLCT state of $[Ru^{II}(bpy)_3]^{2+}$ at atomic resolution in the hard X-ray region is crucially important.

X-ray absorption fine structure (XAFS) measurements reveal the atomic distance between the absorbing atom and coordinated atoms via extended X-ray absorption fine structure (EXAFS) measurements. This is suitable for the structural analysis of disordered systems such as the solution phase. XAFS yields not only structural information but also the energy level of molecular orbitals by X-ray absorption near edge structure (XANES) analysis. Recently, time-resolved XAFS (TR-XAFS) measurements of the excited structure andthe electronic state of metal complexes, using pulsed X-rays from synchrotron radiation for the probe and a laser pulse for excitation, have been developed and are becoming a powerful method to investigate the photochemical reactions of metal complexes [5-7].

TR-XAFS measurements were conducted at the undulator beamline NW14A of the Photon Factory Advanced Ring (PF-AR) [8]. The black circle in Fig. 1 shows the XANES spectrum of the ground state. The difference spectra between the ground and transient states at 50 ps after photoexcitation at 400 and 267 nm are presented in the bottom of Fig. 1 by solid red circles and empty blue circles, respectively. Both difference spectra show the edge-shift to higher energy relative to the ground state. These edge-shifts are due to the change of the oxidation state from Ru(II) to Ru(III). This result indicates that the initial excited state formed at 267 nm is mainly converted to the ^{3}MLCT state in the subnanosecond time scale. This photochemical property is particularly important for an efficient photosensitizer with a wide absorption band.

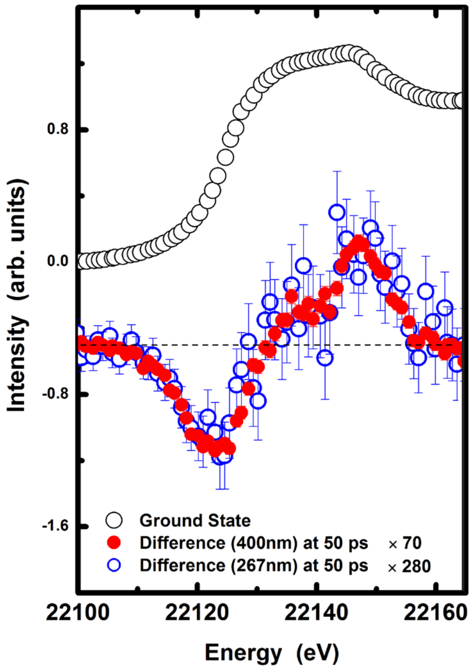

Figure 1: Ground-state Ru *K*-edge XANES spectrum of $[Ru^{II}(bpy)_3]^{2+}$ (black) and the transient difference spectra with 400 nm excitation (red) and 267 nm excitation (blue) at 50 ps. The dotted line indicates zero difference.

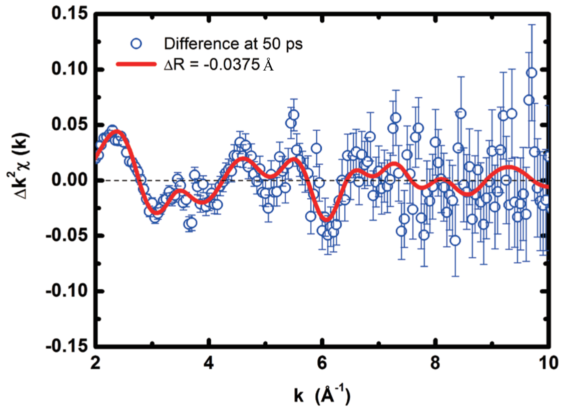

Figure 2: The experimental data at 50 ps (blue circle) and the EXAFS fitting result (red line).

Table 1: Structural parameters obtained from the EXAFS analysis

	shell	R (Å)	σ^2 (Å)
Graound State	Ru-N	2.06 (1)	0.004 (1)
^{3}MLCT State	Ru-N	2.02 (1)	0.014 (1)

Figure 2 shows the transient difference spectrum at +50 ps and the EXAFS fitting result. In order to obtain the photo-excited EXAFS spectrum, a quantum yield of 3% was assumed by a reduced chi square value in the EXAFS analysis [7]. The Ru-N bond lengths and Debye-Waller factors of the ground and excited states are presented in Table 1. TR-EXAFS analysis at the Ru *K*-edge revealed a 0.04 Å contraction in the Ru-N bond lengths in the ^{3}MLCT state compared with the ground state. EXAFS analysis showed that the Debye-Waller factor slightly increased in the ^{3}MLCT state compared with that in the ground state. The increase of the Debye-Waller factor suggests that a structurally distorted state exists in the ^{3}MLCT state with a shorter lifetime than the X-ray pulse duration of 60 ps.

A schematic summary of this study is shown in Fig. 3. Transient structure analysis suggested that the decreasing Ru-N bond lengths provided stability in the ^{3}MLCT excited state. Therefore, the bpy ligand, where hopping electrons localize, will be a long-lived, optically-active center in the photocatalyzed reaction of $[Ru^{II}(bpy)_3]^{2+}$. Our results provide a better understanding of photocatalytic reactions by providing structural information for the theoretical calculation of the reorganization energy of electron transfer reactions beginning with the ^{3}MLCT state, and will be useful for designing artificial photochemical systems.

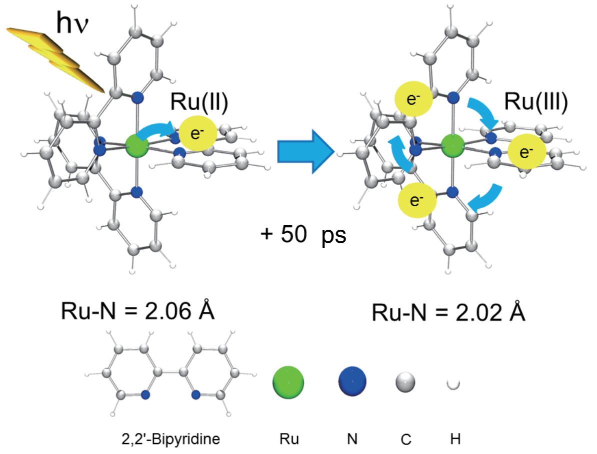

Figure 3 : A schematic summary of this study.

REFERENCES

[1] J. Ferguson, F. Herren, E.R. Krausz, M. Maeder and J. Vrbancich, *J. Coord. Chem. Rev.* **64**, 21 (1985).

[2] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. Von-Zelewsky, *Coord. Chem. Rev.* **84**, 85 (1988).

[3] N.H. Damrauer, G. Cerullo, A. Yeh, T.R. Boussie, C.V. Shank and J.K. McCusker, *Science* **275**, 54 (1997).

[4] T.A. Yeh, V.V. Shank and J.K. McCusker, *Science* **289**, 935 (2000).

[5] T. Sato, S. Nozawa, K. Ichiyanagi, A. Tomita, M. Chollet, H. Ichikawa, H. Fujii, S. Adachi and S. Koshihara, *J. Synchrotron. Rad.* **16**, 110 (2009).

[6] S. Nozawa, T. Sato, M. Chollet, K. Ichiyanagi, A. Tomita, H. Fujii, S. Adachi and S. Koshihara, *J. Am. Chem. Soc.* **132** (1), 61 (2010).

[7] T. Sato, S. Nozawa, A. Tomita, M. Hoshino, S. Koshihara, H. Fujii and S. Adachi, *J. Phys. Chem. C* **116**, 14232 (2012).

[8] S. Nozawa, S. Adachi, J. Takahashi, R. Tazaki, L. Guérin, M. Daimon, A.Tomita, T. Sato, M. Chollet, E. Collet, H. Cailleau, S. Yamamoto, K. Tsuchiya, T. Shioya, H. Sasaki, T. Mori, K. Ichiyanagi, H. Sawa, H. Kawata and S. Koshihara, *J. Synchrotron Rad.* **14**, 313 (2007).

BEAMLINE

AR-NW14A

T. Sato[1], S. Nozawa[1], A. Tomita[1], M. Hoshino[2], S. Koshihara[2], H. Fujii[3] and S. Adachi[1] ([1]KEK-PF, [2]Tokyo Inst. of Tech., CREST-JST, [3]IMS)