

## Mechanistic Insights into Photochromic Behavior of a Ruthenium(II)-Pterin Complex

Tomoya Ishizuka,<sup>1</sup> Takuya Sawaki,<sup>1</sup> Soushi Miyazaki,<sup>2</sup> Masaki Kawano,<sup>3</sup> Yoshihito Shiota,<sup>4</sup> Kazunari Yoshizawa,<sup>4</sup> Shunichi Fukuzumi,<sup>\*2,5</sup> and Takahiko Kojima<sup>\*1</sup>

<sup>1</sup>Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571 (Japan)

<sup>2</sup>Department of Material and Life Science, Graduate School of Engineering, Osaka University 2-1 Yamada-oka, Suita, Osaka 565-0871 (Japan)

<sup>3</sup>Division of Advanced Materials Science (WCU Project), POSTECH, Hyojadong, Pohang 790-784, South Korea

<sup>4</sup>Institute for Materials Chemistry and Engineering, Kyushu University, Motooka, Nishi-Ku, Fukuoka 819-0395 (Japan)

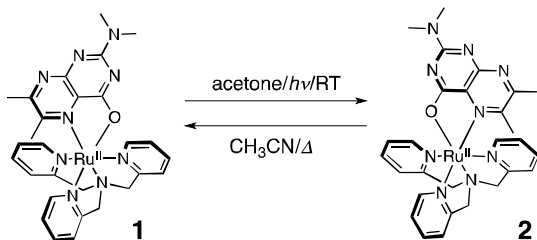
<sup>5</sup>Department of Bioinspired Science (WCU Project), Ewha Womans University, Seoul 120-750 (South Korea)

### Introduction

Molecular bistability is an essential factor to control molecular structures and functionality toward the development of molecular devices. Among a variety of molecular bistability, photochromism of coordination compounds has been reported, however, the number of the examples of photochromic metal complexes is so limited in comparison with that of organic molecules. As a metal center, ruthenium has been useful to exhibit the photochromic structural change due to the formation of metal-centered triplet excited states (<sup>3</sup>MC) derived from triplet metal-to-ligand charge transfer (<sup>3</sup>MLCT) excited states. Ru(II) complexes in the <sup>3</sup>MC state undergoes thermal ligand dissociation to result in drastic structural change.

Ru(II) complexes having heteroaromatic compounds as ligands have been known to show strong MLCT absorption that is essential for photo-excitation. As heteroaromatic ligands, diimine compounds such as 2,2'-bipyridine have been used to photochemical structural change, however, the structural change inevitably reaches to photostationary state to afford mixtures of photoproducts and starting materials.

In this report, we describe a complete photochromic structural change of a Ru(II) complex bearing a pterin derivative, which is a redox-active heteroaromatic co-enzyme, as a bidentate ligand, together with tris(2-



**Scheme 1.**

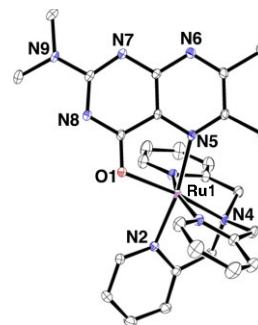
Photochromic structural change between **1** and **2**.

pyridylmethyl)amine (TPA) as an ancillary ligand, as shown in Scheme 1.

### Results

Photoirradiation of a Ru(II)-TPA complex with a deprotonated pterin derivative, dmdmp<sup>-</sup> (Hdmdmp = *N,N*-dimethyl-6,7-dimethylpterin), [Ru(dmdmp)(TPA)]ClO<sub>4</sub> (**1**), at 460 nm in acetone afforded complete conversion to the isomer of **1**, in which the pterin ligand underwent an apparent 180-degree pseudo-rotation relative to the original orientation in **1**. The structure of the isomeric complex **2** was by X-ray crystallography. Diffraction data of the crystal of **2** was collected at Photon Factory-Advanced Ring for Pulse X-rays (PF-AR NW2A) of KEK. The crystal structure is presented in Figure 1.

Thermal recovery of **1** from **2** was completely achieved by heating **1** in CH<sub>3</sub>CN. The thermodynamics of the reverse structural change was established by kinetic analysis.



**Figure 1.**

Synchrotron X-ray structure of **2**. Hydrogen atoms and ClO<sub>4</sub><sup>-</sup> are omitted.

### References

[1] T. Ishizuka *et al.*, Chem.–Eur. J. 2011, 17, 6652 – 6662.

\* kojima@chem.tsukuba.ac.jp