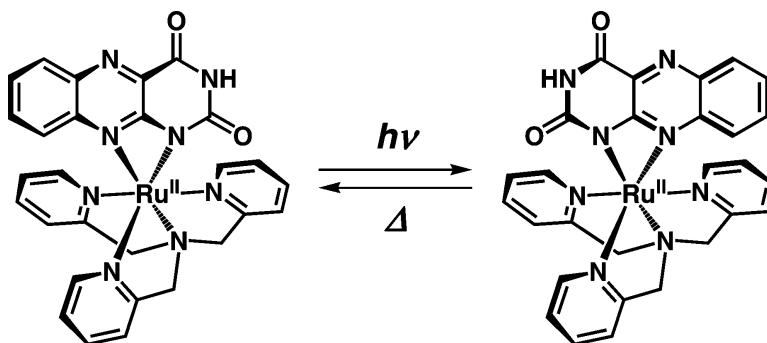Communication

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Photochemical and Thermal Isomerization of a Ruthenium(II)−Alloxazine Complex Involving an Unusual Coordination Mode

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Bistability at the molecular level is a fundamental and indispensable requirement for the control of functionality and properties of the molecule in living cells.[1] Thus far, cis−trans isomerization with photoirradiation and heating, as represented by that observed for 1,2-bisaryl ethene such as stilbene[2] and also azo compounds,[3] has frequently been utilized for the construction of functional molecules and devices.[4]

On the other hand, photochemical structural changes in transition-metal complexes have been well-known, especially in Ru(II)−polypyridyl complexes.[5] However, they undergo ligand dissociation reactions, which have been postulated to proceed via the triplet excited state of metal-to-ligand charge transfer (^{3}MLCT) followed by the metal-centered d−d triplet state (^{3}MC).[5] Such photoinduced ligand dissociation in the Ru(II) complexes is not reversible in most cases.

Among photochemically active components, flavins merit special attention, because flavins are not only a well-known redox-active cofactors[6] but also a photochemically active species to perform photoinduced electron transfer as observed in DNA photolyase.[7] In addition, flavins can bind to various metal ions through 4-oxygen and 5-nitrogen to form a five-membered chelate ring.[8] The redox behaviors of metal−flavin complexes have been studied extensively.[8,9] In contrast to well-established photochemistry of flavins,[10] however, little is known about the photodynamic behaviors of metal−flavin complexes.[11]

We have recently reported the synthesis and characterization of a ruthenium(II) complex [Ru(Hallo)(TPA)]ClO$_4$ (**1**) (H$_2$allo = alloxazine; TPA = tris(2-pyridylmethyl)amine).[12] In this complex, the alloxazine ligand coordinates to the ruthenium center by forming an unusual four-membered chelate ring, in contrast to the other flavin complexes involving the five-membered chelate ring. We report herein that the unique coordination mode in **1** enables for the first time the attainment of a reversible photochemical and thermal isomerization between complex **1** and **2** (Scheme 1).

The absorption spectrum of **1** in CH$_3$CN shows absorption maxima at 315, 400, 450, and 520 nm. Photoirradiation at 400 nm to a CH$_3$CN solution of **1** leads to increase of absorption at 315 nm and decrease of absorption at 450 nm with four isosbestic points (377, 404, 423, and 536 nm) as shown in Figure 1a. ESI-MS spectra exhibited identical peaks before and after the photoreaction, indicating **1** was converted to an isomer with a different configuration. The quantum yield of this photoreaction in deaerated CH$_3$-CN was determined to be 34% by using a standard actinometer (Supporting Information (SI)). The reaction occurs with photoirradiation at any wavelength in the range of 400−600 nm, which includes an MLCT transition.

^{1}H NMR spectrum of **1** in CD$_3$CN showed drastic change upon photoirradiation (Figure 2). After photoirradiation at 400 nm for 4 h, the original peaks decreased, accompanied by the appearance of new peaks assigned to one set of TPA and alloxazine ligands. Since no other peak was observed, the percentage of conversion was determined to be 87% on the basis of peak integration. The NMR spectrum of a new species **2** generated by photoirradiation indicates

Scheme 1.
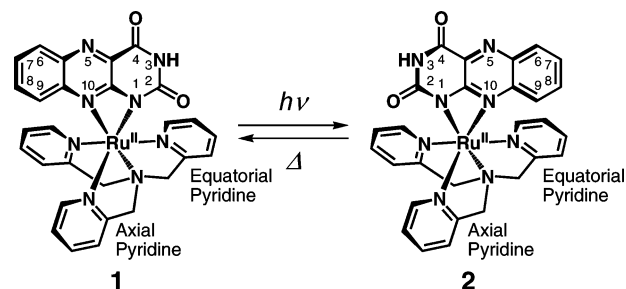
its σ_h symmetry[13] in solution and the structural change without ligand dissociation and change of symmetry.

To obtain geometrical information of the isomer **2**, we examined differential NOE experiments in the ^{1}H NMR spectroscopy. The crystal structure of **1** clarified the close vicinity between the H9 of alloxazine and the H6 of the axial pyridine.[12] An NOE between the axial pyridine H6 (9.65 ppm) and the alloxazine H9 (8.23 ppm) was observed for **1**, suggesting their close contact even in solution. In sharp contrast, the NOE between the axial pyridine H6 and the alloxazine H9 could not be observed for **2**. Instead, a large downfield shift ($\Delta\delta = 1.1$ ppm; arrow in Figure 2) was observed for the signal assigned to H6 of the axial pyridine. This downfield shift can be ascribed for nonclassical CH···O hydrogen bonding interaction between the axial py-H6 and the carbonyl oxygen of the alloxazine ligand. These observations suggest that the **2** should be an isomer accompanying a rotation of the alloxazine ligand as depicted in Scheme 1.

Next, we examined the thermal reaction of the isomer **2**. When the solution of **2** was heated, the NMR spectrum was changed to recover that of **1**. Thus, it was revealed that the isomerization reaction is reversible and the direction of the reaction can be controlled by external stimuli. The thermal isomerization rate obeys first-order kinetics and the rate constants of the conversion of **2** to **1** were determined to be $(9.5 \pm 0.2) \times 10^{-5}$ s^{-1} at 318 K, $(1.6 \pm 0.1) \times 10^{-4}$ s^{-1} at 323 K, $(3.0 \pm 0.1) \times 10^{-4}$ s^{-1} at 328 K, $(4.6 \pm 0.1) \times 10^{-4}$ s^{-1} at 333 K, and $(8.1 \pm 0.4) \times 10^{-4}$ s^{-1} at 338 K. On the basis of these data, a linear Eyring plot was obtained to determine the activation enthalpy and the activation entropy to be 22 kcal mol^{-1} and −9 cal K^{-1} mol^{-1}, respectively (SI, Figure S3). The large activation enthalpy suggests the involvement of the rupture of the coordination bond, whereas the negative activation entropy suggests the bond rupture may be associated with coordination of CH$_3$CN (vide infra).

The complexes **1** and **2** show no luminescence in CH$_3$CN at room temperature. We examined femtosecond laser flash photolysis to detect a transient species of the photochemical process. The femtosecond laser excitation of **2** at 420 nm affords transient spectra as shown in Figure 3. We assigned a broad absorption at 750 nm to that of an MLCT excited-state of **2** (Ru^{III}-Hallo$^{-\bullet}$).[14] The decay of absorption at 750 nm coincides with the recovery of bleaching at 520 nm (SI, Figure S4). In the MLCT excited-state of **2**, the
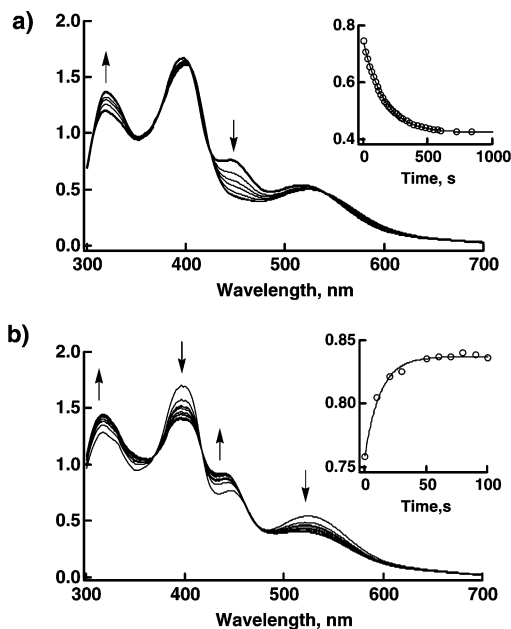
Figure 1. Absorption spectral changes of **1** under photoirradiation at 400 nm: (a) at room temperature; (b) at −40 °C.
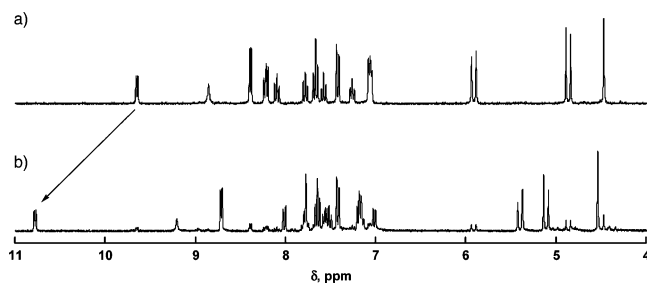

Figure 2. ¹H NMR spectral change before (a) and after (b) photoirradiation of **1** in CD₃CN at room temperature.
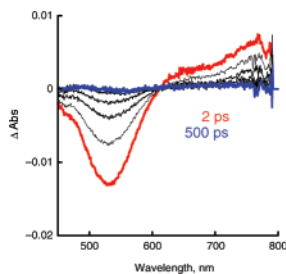

Figure 3. Femtosecond laser flash photolysis of **2** in CH₃CN with excitation at 420 nm.

negative charge on the oxygen atoms of the alloxazine ligand can be enhanced,[15] and thus, the intramolecular CH···O interaction can be strengthened to hold the structure of **2**, thereby prohibiting the back reaction to **1**.

The absorption spectral change upon photoirradiation at −40 °C revealed the formation of a metastable intermediate (**I**) as shown in Figure 1b. The ESI-MS spectrum (SI, Figure S6) exhibited a peak cluster assigned to [Ru(Hallo)(TPA)(CH₃CN)]⁺ (I) (m/z = 646.1). Thus, CH₃CN is coordinated to the Ru center in the intermediate (**I**). The ¹H NMR signals of the intermediate suggest the stronger CH···O interaction reflected on the larger downfield shift of H6 of the axial pyridine (SI, Figure S7).

On the basis of the results described above, a mechanism of the pseudorotation of the alloxazine ligand is proposed as shown in Scheme 2. The photoexcitation of **1** affords a ³(MLCT)* state which undergoes coordination bond rupture via ³(MC)* to give a five-

Scheme 2.
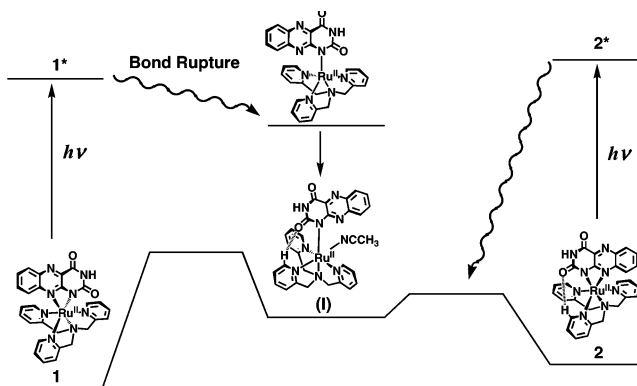
coordinate transition state.[16,17] The five-coordinate species accepts CH₃CN as a ligand to form the intermediate (I). In this intermediate, a monodentate alloxazine ligand forms a four-membered chelate ring and the CH···O interaction results in formation of the isomer **2** that can go back to the isomer **1** thermally (not photochemically).

In summary, the ruthenium−alloxazine complex shows reversible photochemical and thermal isomerization. The isomerization reaction occurs by pseudorotation of the alloxazine ligand via bond rupture due to the unusual four-membered chelation of the alloxazine ligand. This bistable molecular system provides a new concept for a MLCT-based reversible structural regulation and efficient mechanical motions of coordination compounds due to the novel bistability.

Supporting Information Available: Experimental details, an Eyring plot, time profiles of the transient absorptions, ESI-MS and ¹H NMR spectra of the intermediate (**I**). This material is available free of charge via the Internet at http://pubs.acs.org.

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