

## 論文の内容の要旨

論文題目 Synthesis of New Ruthenium Chelating Sulfoxide Complexes  
and Their Photo- and Electrochemical Linkage Isomerization  
(新規ルテニウムキレートスルホキッド錯体の合成と光・電気化学的結合異性化反応)

氏名 鈴木 翔子

### Introduction

Molecular bistability controllable with external stimuli is one of the most important properties in the realization of molecule-based devices. Especially, photo-controllable systems are appreciated as i) no elaborate contact guide to molecules is required, ii) specific chromophores can be excited by the selection of the wavelength of light, and iii) repetitive operations free from chemical contamination are possible.

Bistable molecular systems based on coordination compounds and organometallics have been studied intensively. Especially, ruthenium complexes with ambidentate sulfoxide ligands, such as dimethylsulfoxide (dmsO), have been reported to show both photochromism and electrochromism based on the linkage isomerization. Both oxidation from Ru<sup>II</sup> to Ru<sup>III</sup> and photoirradiation of the S-bound complex give rise to the O-bound isomer. On the other hand, both reduction from Ru<sup>III</sup> to Ru<sup>II</sup> and irradiation with another wavelength of light open a channel to reproduction of the original S-isomer. Of noteworthy is that the isomerization behavior is accompanied by a large negative shift of the formal potential ( $E^{0'}$ ) of the Ru<sup>3+</sup>/Ru<sup>2+</sup> couple. These complexes are, however, often unstable in the course of isomerization reactions due to dmsO replacement by solvent molecules. To improve the shortcoming, those with polydentate sulfoxide ligands have been synthesized in this decade. However, most of them lack an O- to S- photochemical channel.

### Molecular design

Under the circumstance noted above, we synthesized several new Ru<sup>II</sup>-sulfoxide complexes. Their

isomerization activities are influenced by their electronic and steric factors, which are, for example, distortion of the ground or excited state, reorganization energy, trans effect among ligands, and solvent effect. In my research, I focused on the distortion and trans effects. The trans effect has been thought to strongly promote isomerization. I designed ruthenium complexes with bi- or tri-dentate sulfoxide ligand considering their electronic and steric effects in order to manage stable and effective isomerization reaction. Herein, I will report the results of photo- and electro-triggered isomerization of the designed complexes.

Next, I designed a functional Ru complex which responds to light and redox energy. I selected a functional moiety so that its redox potential exists between S- and O- isomer. It means that the excited electron will be caught to the functional moiety and the excited isomer expected to be stabilized. I will report the photo- electro-chemical reaction property of the complex with electron accepting moiety.

### Photo- and electro-chromic properties of Ru-sulfoxide complexes with a bi- and tridentate sulfoxide ligand

A new photochromic complexes with a bidentate ligand  $[\text{Ru}(\text{bpy})_2(\text{pySO-Tol})]^{2+}$  (pySO- 2-((phenylsulfinyl)methyl)pyridine )

(Fig 1) was prepared. Its isomerization behaviors were compared with  $[\text{Ru}(\text{bpy})_2(\text{pySO-Me})]^{2+}$  (bpy 2,2'-bipyridine, pySO-Me 2-(isopropylsulfinylmethyl)pyridine)<sup>1</sup> to understand the electronic effect of  $\pi$ -conjugating substrates on the sulfur to isomerization.

The ground state complexes (S-isomers) featured a low energy absorption maximum in the electronic spectrum at 360 nm and 380 nm for  $[\text{Ru}(\text{bpy})_2(\text{pySO-Me})]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{pySO-Tol})]^{2+}$ , respectively. Irradiation of S-isomer by 365 nm light caused intramolecular S $\rightarrow$ O isomerization of the sulfoxide moiety. During the irradiation, the intensity of the absorption corresponding to S-isomer diminished, while a new peak corresponding to O-isomer at 470 nm increased. Both complexes showed thermal reversion (Fig. 2), but the one with distorting ligand seems to be unstable compared to  $[\text{Ru}(\text{bpy})_2(\text{pySO-Me})]^{2+}$ .

Fig. 3 shows a cyclic voltammogram of  $[\text{Ru}(\text{bpy})_2(\text{pySO-Tol})]^{2+}$  in  $\text{Bu}_4\text{NPF}_6$ -acetone at a scan rate of  $0.1 \text{ V s}^{-1}$ . The first scan shows one electron oxidation at around 1.30 V assignable to the  $\text{Ru}^{3+/2+}$  couple of the each S-isomer. By reversing the polarity and scanning in the negative direction, no reduction wave was observed while a new peak at around 0.40 V was appeared after the irradiation. This new wave is ascribed to the O-isomer. Here I can conclude that both steric and electronic effects at the S atom have little influence, and the chelation effect disturbs the electrochemical isomerization.

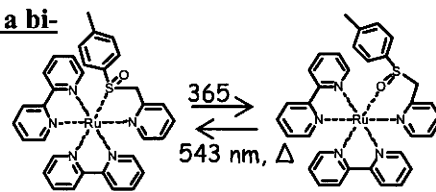


Fig 1. isomerization reaction of Ru complex with bidentate SO ligand

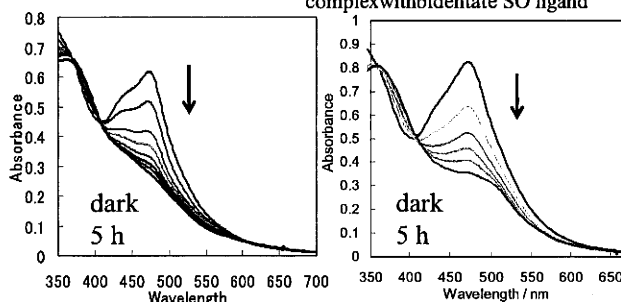


Fig 2. Thermal reversion of  $[\text{Ru}(\text{bpy})_2(\text{PySO-Me})]^{2+}$  (left) and  $[\text{Ru}(\text{bpy})_2(\text{pySO-Tol})]^{2+}$  (right) in acetone

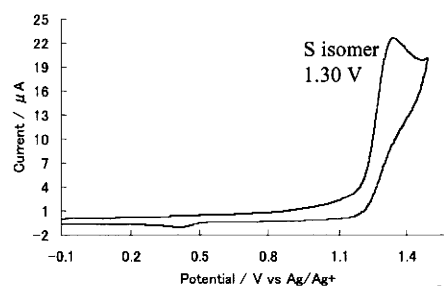


Fig 3. Cyclic voltammogram of  $[\text{Ru}(\text{bpy})_2(\text{PySOTol})]^{2+}$  in  $\text{Bu}_4\text{NPF}_6$ -acetone

Based on the results noted above, I prepared two new complexes with tridentate sulfoxide ligand  $[\text{Ru}(\text{tpy})(\text{bpySO})]^+$  (tpy terpyridine, bpySO 2-((methylsulfinyl)methyl)-6-(pyridine-2-yl)pyridine),  $[\text{Ru}(\text{tpy})(\text{picSO})]^{2+}$  (picSO ((methylsulfinyl)methyl)pyridine-2-carboxylic acid). (Fig 4) They were designed with consideration of their steric structure. Here, I focus on the trans effect. The trans effect is the electronic effect between the ligands that are trans - directing. Ruthenium complexes form octahedral coordination structure and the sulfoxide moiety in the complexes are trans directed to nitrogen ( $[\text{Ru}(\text{tpy})(\text{bpySO})]^+$ ) or oxygen ( $[\text{Ru}(\text{tpy})(\text{picSO})]^{2+}$ ). I compared spectroscopic and electrochemical properties using these rigid complexes with tridentate ligand to discuss steric effect for isomerization.

The initial absorption maximum in the electronic spectrum could be associated with the ground state complex (S-isomer) (420 nm ( $[\text{Ru}(\text{tpy})(\text{bpySO})]^{2+}$ ) (Fig 5), 425 nm ( $[\text{Ru}(\text{tpy})(\text{picSO})]^+$ ). Irradiation to the S-isomer with 405 nm light caused intramolecular S→O linkage isomerization of the sulfoxide moiety. (480 nm  $[\text{Ru}(\text{tpy})(\text{bpySO})]^{2+}$  Fig 5), 525 nm  $[\text{Ru}(\text{tpy})(\text{picSO})]^+$ ).

Fig. 6 shows a cyclic voltammograms of  $[\text{Ru}(\text{tpy})(\text{bpySO})]^{2+}$  and  $[\text{Ru}(\text{tpy})(\text{picSO})]^+$  in  $\text{Bu}_4\text{NPF}_6$ -acetone solution at a scan rate of  $0.1 \text{ V s}^{-1}$ . The first scan of both complexes showed a one electron oxidation assigned to the  $\text{Ru}^{3+/2+}$  couple of the S-bonded species (1.30 V  $[\text{Ru}(\text{tpy})(\text{bpySO})]^{2+}$  and 0.10 V  $[\text{Ru}(\text{tpy})(\text{bpySO})]^{2+}$ ). By reversing the polarity and scanning in the negative direction, different reduction wave was observed. S-isomers of both complexes seems to be lost during isomerization, but O-isomer of  $[\text{Ru}(\text{tpy})(\text{bpySO})]^{2+}$  did not appeared. On the other hand, the case of  $[\text{Ru}(\text{tpy})(\text{picSO})]^+$  was different. One oxidation wave appeared near 1.00 V in the fast scan rate and obvious reductive wave at around 0.30 V which assigned to O-isomer appeared. The differences in the redox potential and electro-isomerization reaction should be derived from the trans effect.

### Photo- and electro-chromic properties of Ru-sulfoxide complex with Electron accepting moiety

Next, I designed a functional Ru complex which responds to light and redox energy. Electron migration between the excited state O-isomer and the electron accepting moiety will be expected. N,N,N-triphenylamine (TPA) was selected as an electron accepting moiety. A new complex  $[\text{Ru}(\text{tpyTPA})(\text{bpySO})]$  was synthesized. TPA moiety will be activated to be amine radical by one electron oxidation.

The ground state S-isomer features absorption maximum in the electronic spectrum at 486 nm. Irradiation of S-isomer by 432 nm light caused S→O isomerization of the sulfoxide moiety. This absorption change for O-isomer is shown in Fig. 8. During irradiation, the intensity of the absorption assigned to S-isomer diminished,

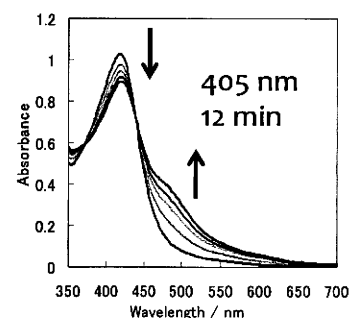


Fig 5. UV-Vis spectra of  $[\text{Ru}(\text{tpy})(\text{bpySO})]^+$  in acetone

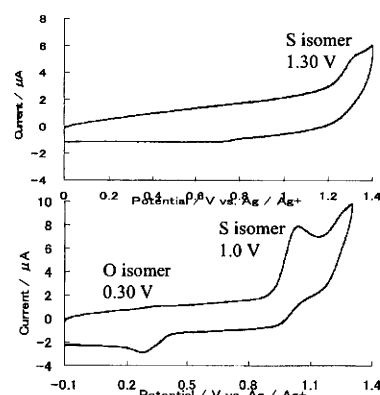


Fig 6. Cyclic voltammogram of  $[\text{Ru}(\text{tpy})(\text{bpySO})]^{2+}$  (top),  $[\text{Ru}(\text{tpy})(\text{picSO})]^+$  (bottom) in  $\text{Bu}_4\text{NPF}_6$ -acetone

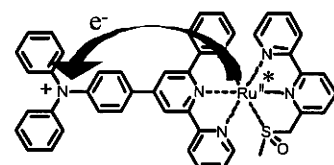


Fig 7. A proposed electron transfer system

while absorption at 543 nm increased.

In Fig. 9 are shown voltammogram obtained in  $\text{Bu}_4\text{NPF}_6$ -acetone of  $[\text{Ru}(\text{tpy-TPA})(\text{bpySO})]^{2+}$  at a scan rate of  $2.0 \text{ V s}^{-1}$ . The first scan shows one-electron oxidation near 0.75 V assigned to TPA moiety and one-electron oxidation near 1.30 V assigned to the  $\text{Ru}^{3+/2+}$ , S-bonded couple. And an obvious reductive wave which assigned to O-isomer appeared instead of reductive wave of S-isomer. Linkage isomerization occurred upon electrical oxidation of the TPA moiety, which was proved by a scan at a range of 0.0-1.0 V in cyclic voltammetry. This behavior also suggests that an electron transfer took place from the S isomer to the activated acceptor.

Finally, we tried to observe the electron transfer triggered by light.

Judging from the result of electrochemical measurement, there can be two types of electron transfers. (Fig. 10) Both of them produce the trivalent Ruthenium

O-isomer, diminishing the TPA cation radical. I observed decreasing rates of the TPA cation radical in the dark and upon photoirradiation: If the photo-induced electron transfer occurs, the decreasing rate should be faster in the case of photoirradiation. This observation suggested the existence of photo-triggered electron transfer. (Fig. 11)

### Conclusion

I discussed the structural and electronic effects of a series of bi- or tri-dentate sulfoxide ligands on the photo- and electrochemical linkage isomerization of their Ru complexes. Chelation of sulfoxide degrade the isomerization abilities, especially the electrochemical response. On the other hand, the trans-effect encourages isomerization. A tridentate ligand stabilizes the Ru complex, although its rigidity disturbs isomerization at the same time. This series of results indicates that it is possible to design photochromic Ru complexes with more stable and more efficient linkage isomerization.

I also designed a photochromic Ru complex with a more sophisticated function. The complex can manage electron migration induced by the linkage isomerization. Furthermore, electron transfer results in stabilizing the metastable state (O-isomer).

The present work will lead to higher functional molecules such as a molecular switch or a photonic sensor by taking advantage of the structural and electronic effects I stated formerly.

[1] B. A. McClure, J. J. Rack, *Angew. Chem., Int. Ed.*, **2009**, 48, 8556

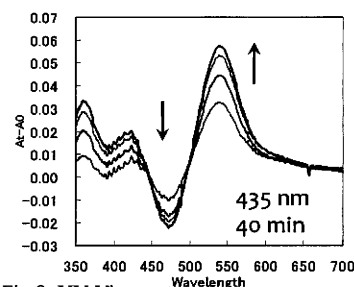


Fig 8. UV-Vis spectra of  $[\text{Ru}(\text{tpy-TPA})(\text{bpySO})]^+$  in  $\text{CH}_2\text{Cl}_2$

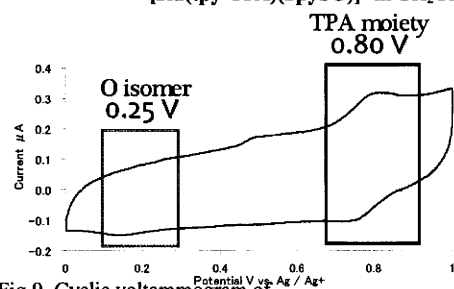


Fig 9. Cyclic voltammogram of  $[\text{Ru}(\text{tpy-TPA})(\text{bpySO})]^+$  in  $\text{Bu}_4\text{NPF}_6$ -acetone

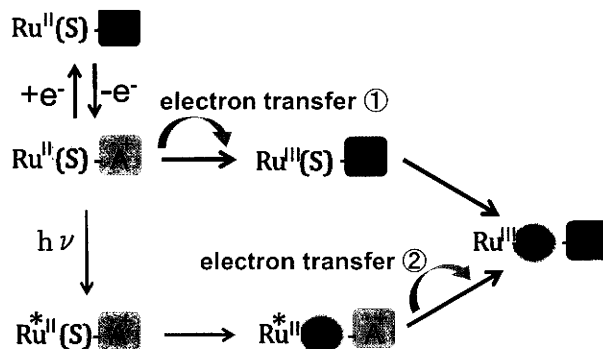


Fig 10. Schematic illustration of the expected electron transfer

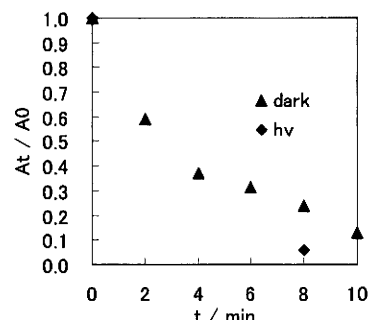


Fig 11. Decreasing ratio of activated acceptor was plotted with time