

# Observation of the Dark State in Ruthenium Complexes Using Femtosecond Infrared Vibrational Spectroscopy

Ken Onda<sup>1,2</sup>, Tatsuhiko Mukuta<sup>1</sup>, Sei'ichi Tanaka<sup>1</sup>, Kei Murata<sup>3</sup>, and Akiko Inagaki<sup>2,4</sup>

<sup>1</sup>Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

<sup>2</sup>PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

<sup>3</sup>Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

<sup>4</sup>Graduate School of Science and Engineering, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan  
onda.k.aa@m.titech.ac.jp

**Abstract:** We comprehensively studied the excited states of prototypical ruthenium complexes using time-resolved infrared vibrational spectroscopy and found a band assigned to the dark <sup>3</sup>MC (metal centered) state, which plays an important role for their photofunctions.

**OCIS codes:** (300.6530) Spectroscopy, ultrafast; (300.6340) Spectroscopy, infrared

## 1. Introduction

Ruthenium complexes are used in a wide variety of photo-functional materials, such as photocatalysts, artificial photosynthesis and organic solar cells because they absorb visible light efficiently and also play a role as a reaction center. Thus, the fundamental process in the excited state has been intensively studied for several decades and elucidated as follows [1,2]. The irradiation of visible light excites the complexes to <sup>1</sup>MLCT (singlet metal to ligand charge transfer state) and subsequently the intersystem crossing to <sup>3</sup>MLCT takes place within 100 fs. The lifetime of <sup>3</sup>MLCT is more than a hundred nanoseconds, and this meta-stable <sup>3</sup>MLCT play a key role in photo-functional materials by transferring the excited electron to a reactive state or another molecule. One of the most important processes here is the electron back transfer from <sup>3</sup>MLCT to <sup>3</sup>MC (metal centered state) because the excited electron in <sup>3</sup>MC weakens the bonds between the center metal and ligands, and most of photochemical reactions are considered to take place via this state. However, <sup>3</sup>MC has never directly observed to date because it does not emit a luminescence, that is, a dark state. We found a vibrational band involved in <sup>3</sup>MC by comprehensive study on the vibrational bands of the excited state in the finger print region (1000-1700 cm<sup>-1</sup>) for the prototypical ruthenium complexes, [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(bpm)]<sup>2+</sup> (bpy = 2,2'-bipyridine, bpm = 2,2'-bipyrimidine) (structures shown in Fig.1), and succeeded in following the photochemical reaction process through this bands.

## 2. Experimental

Time-resolved infrared (TR-IR) vibrational spectra were measured by the pump-probe method using a femtosecond Ti:sapphire chirped pulse amplifier (CPA) (wavelength = 800nm, pulse duration = 120 fs, repetition rate = 1 kHz). A tunable mid-infrared pulse was generated by optical parametric amplification (OPA) and difference frequency generation (DFG) from the output of the CPA. The bandwidth of the IR pulse was 150 cm<sup>-1</sup>. The 400 nm pulse was obtained by doubling the output of the CPA. The probe pulse passed through the IR cell and was subsequently dispersed by a 19 cm polychromator and acquired with a 64-ch. MCT detector. The spectral resolution was ~3 cm<sup>-1</sup> and the detectable absorbance change ( $\Delta$ abs) was ~5 x 10<sup>-5</sup>. Details of the TR-IR system and the sample preparation

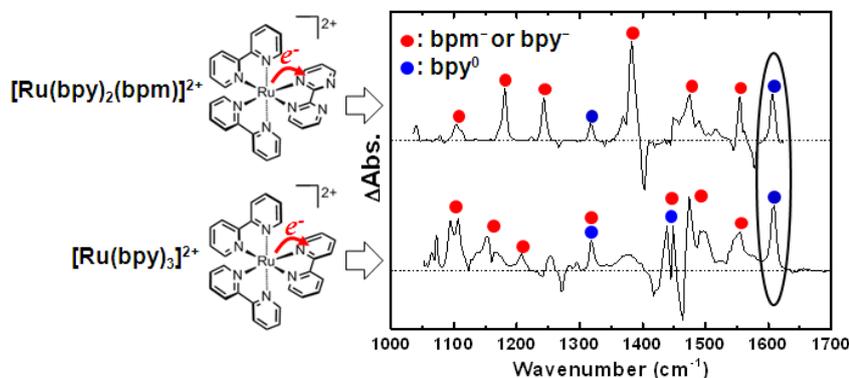


Fig 1. Structures of the complexes investigated and their time-resolved infrared spectra at 500 ps. Red and blue solid circles represent bands associated with vibrations localized on bpm<sup>-</sup> or bpy<sup>-</sup> and bpy<sup>0</sup>, respectively.

were reported in previous papers [3, 4].

### 3. Results and discussion

Although the complexes are important materials for many applications, the vibrational bands in the excited state have never been comprehensively assigned because of their weak infrared absorptions; thus, we have first measured the transient absorption spectra of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{bpm})]^{2+}$  and assigned all the observed bands to the normal vibrational modes using deuterium substitution and quantum chemical calculation [4]. Figure 1 shows the spectra at 500 ps after photoexcitation, and at this delay time it is known that the complexes are the vibrational ground state in  $^3\text{MLCT}$  and the excited electron is localized at a single ligand named  $\text{bpy}^-$  or  $\text{bpm}^-$  [2]. As shown in Fig. 1, most of the transient absorption bands are assigned to the modes associated with vibrations of charge localized ligands,  $\text{bpy}^-$  or  $\text{bpm}^-$ . However, we found two or three exceptional bands assigned to neutral ligand,  $\text{bpy}^0$ , indicating that transient moment of these modes are largely changed by oxidation (loss of electron) of the center metal without a change in charge of the ligands. Intriguingly, one of these bands at approx.  $1600\text{ cm}^{-1}$  (indicated by an oval in Fig. 1) is found to show a spectral shift with increasing delay time. Figure 2 shows the expanded view of the TR-IR spectra around  $1600\text{ cm}^{-1}$ . The center wavenumber of the left band clearly increases as a function of delay time. In general, a wavenumber shift of a vibrational band indicates potential change due to charge and/or structural variations; however,  $^3\text{MLCT}$  is stable so we expected an influence of another excited state. Most probable such state is  $^3\text{MC}$  as mentioned in Introduction. To confirm this, we varied the excitation wavelength because  $^3\text{MC}$  is known to be located at  $\sim 3000\text{ cm}^{-1}$  above  $^3\text{MLCT}$  [1, 2] and found that the band showing a spectral shift disappears when the excitation wavelength is longer than  $480\text{ nm}$ , indicating that the band is attributed to a potential located at more than  $2000\text{ cm}^{-1}$  than the bottom of  $^3\text{MLCT}$ . This result is in good agreement with the expectation because the longer wavelength cannot reach  $^3\text{MC}$  as shown Fig. 2. If the band at  $1600\text{ cm}^{-1}$  is assigned to  $^3\text{MC}$ , it should be affected by photochemical reaction because such reaction is believed to take place via  $^3\text{MC}$ . We compare the temporal variations of the band under non-reactive and reactive conditions. One  $\text{bpy}$  ligand is substituted by  $\text{Cl}$  if the counter anion is chlorine ( $\text{Cl}$ ) and solvent is  $\text{CH}_2\text{Cl}_2$  [5]. As clearly seen in Fig. 2, the band at  $1600\text{ cm}^{-1}$  disappears up to 20 ps only under reactive condition probably because the population in this state has gone to a reaction path. On the other hand, the band at  $1610\text{ cm}^{-1}$  is assigned to  $^3\text{MLCT}$  because no spectral shift is observed. Considering some more experimental results, we concluded that the band at  $1600\text{ cm}^{-1}$  is assigned to the dark  $^3\text{MC}$  or at least a mixing state with  $^3\text{MC}$ , which has never observed despite of its importance for photochemistry and photophysics.

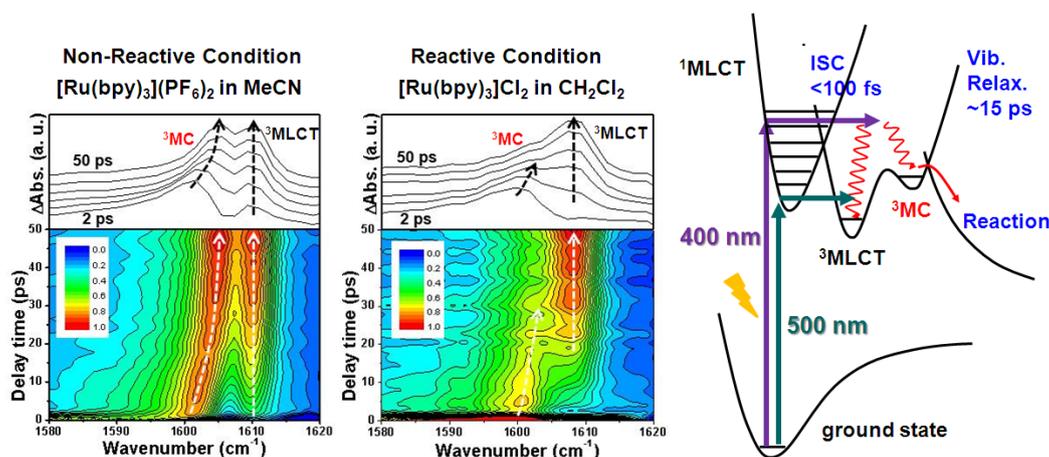


Fig. 2. Temporal variations of the bands at around  $1600\text{ cm}^{-1}$  under non-reactive and reactive conditions (left). Schematic of the excited states of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (right)

### References

- [1] D.W. Thompson, et al. "[Ru(bpy)<sub>3</sub>]<sup>2+</sup> and other remarkable metal-to-ligand charge transfer (MLCT) excited states" *Pure Appl. Chem.* **85**, 1257-1305 (2013).
- [2] S. Campagna, et al. "Photochemistry and Photophysics of Coordination Compounds: Ruthenium" *Top. Curr. Chem.* **280**, 117-214 (2007).
- [3] N. Fukazawa, et al. "Time-Resolved Infrared Vibrational Spectroscopy of the Photoinduced Phase Transition of Pd(dmit)<sub>2</sub> Salts Having Different Orders of Phase Transition" *J. Phys. Chem. C* **117**, 13187-13196 (2013).
- [4] T. Mukuta, et al. "Infrared Vibrational Spectroscopy of [Ru(bpy)<sub>2</sub>(bpm)]<sup>2+</sup> and [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in the Excited Triplet State" *Inorg. Chem.* in press.
- [5] B.D. Durham, et al. "Photochemistry of Ru(bpy)<sub>3</sub><sup>2+</sup>" *J. Am. Chem. Soc.* **104**, 4803-4810 (1982).