

## Ultrafast Vibronic Processes in a Ru–Porphyrin Complex

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The excited-state dynamics of Ru<sup>II</sup>(TPP)(CO)(acetone) (TPP = tetraphenylporphyrin) was investigated by using a sub-5-fs pulse. In previous studies, the fluorescence lifetime of Ru<sup>II</sup>(TPP)(CO) could not be resolved and was reported to be <1 ps. Analysis of the six-coordinate complexes of Ru<sup>II</sup>(TPP)(CO)(acetone) showed that <sup>1</sup>Q<sub>x</sub>( $\pi, \pi^*$ ) had a lifetime of

140 ± 20 fs and the lifetime of <sup>3</sup>(d, $\pi^*$ ) was 560 ± 150 fs. Stimulated emission due to a spin-forbidden transition from <sup>3</sup>( $\pi, \pi^*$ ) to the ground state was observed for the first time.

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## Introduction

Ru<sup>II</sup> complexes have attracted attention, because they have electroluminescent properties and are model complexes for many important biological systems. For example, [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (bpy = bipyridine) has been studied extensively for the development of sensitizers to decompose water by solar energy<sup>[1]</sup> and for the design of dye-sensitized solar cells.<sup>[2]</sup> For [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, the lowest excited triplet state is the metal-to-ring-charge-transfer state <sup>3</sup>(d, $\pi^*$ ), whose lifetime is about 600 ns at room temperature.<sup>[3]</sup> The lifetime of the lowest excited singlet state was found to be 40–100 fs by an ultrafast time-resolved pump-probe measurement with a femtosecond laser.<sup>[4]</sup> Ru<sup>II</sup>-porphyrin complexes were studied as model complexes for hemoglobin. The oxidation reaction of Ru<sup>II</sup>(TPP)(CO) (TPP = tetraphenylporphyrin) was investigated<sup>[5]</sup> to clarify the mechanism of oxidation and deoxidation of Fe<sup>II</sup>(por) (por = porphyrin), which is a key component of the oxygen transport function of hemoglobin in living systems. The phosphorescence lifetime was reported to be 30  $\mu$ s at room temperature in Ru<sup>II</sup>(TPP)(CO)(py) (py = pyridine),<sup>[6]</sup> but the fluorescence lifetime

could not be resolved and was reported to be <30 ps in 1999<sup>[6a]</sup> and  $\leq$ 1 ps in 2005.<sup>[6b]</sup> In this work, we analyzed the excited-state dynamics with a much higher time resolution (<5 fs) and resolved the decay process of the excited singlet state of Ru<sup>II</sup>(TPP)(CO).

## Results and Discussion

The behavior of Ru<sup>II</sup>(TPP)(CO) in deoxidized acetone solution after ultrashort-pulse excitation was probed by using a sub-5-fs pulse<sup>[7]</sup> from a noncollinear optical parametric amplifier (NOPA) system. This system was designed to satisfy all the matching conditions of pulse front, phase velocity, and group velocity.<sup>[8]</sup> An acetone molecule is bound to Ru<sup>II</sup>(TPP) as an axial ligand, forming the six-coordinate complex Ru<sup>II</sup>(TPP)(CO)(acetone).<sup>[9]</sup> It is well known that  $\pi$  back-donation in d $\pi$ →CO( $\pi^*$ ) lowers the energy of the d $\pi$  orbital in Ru<sup>II</sup>, resulting in an increase in the energy of the (d, $\pi^*$ ) state. The lowest excited state, S<sub>1</sub>, in Ru<sup>II</sup>(TPP)(CO) is therefore ( $\pi, \pi^*$ ).<sup>[10]</sup> The ultraviolet/visible (UV/Vis) absorption spectrum of Ru<sup>II</sup>(TPP)(CO) in deoxidized acetone has a Q<sub>x</sub>(1,0) band at  $\lambda_{\max}$  = 531 nm (18832 cm<sup>-1</sup>) and a Q<sub>x</sub>(0,0) band at  $\lambda_{\max}$  = 562 nm (17794 cm<sup>-1</sup>; Figure 1). The lower-energy band, Q<sub>x</sub>(0,0), is the ground vibrational level in S<sub>1</sub>, and the higher-energy band, Q<sub>x</sub>(1,0), is the first excited vibrational level in S<sub>1</sub>.<sup>[10a,10b]</sup> The laser spectrum extending from 525 nm to 725 nm covers both of these bands (Figure 1); therefore, Ru<sup>II</sup>(TPP)(CO)(acetone) was coherently excited into Q<sub>x</sub> states. Real-time vibration traces (from -100 to 3500 fs) of the change in absorbance,  $\Delta A(t)$ , averaged over 16 probe channels corresponding to a spectral range of 23.6 nm are shown in Figure 2a. The probe wavelength dependence of  $\Delta A(\lambda)$  in the full probe wavelength range, 525–725 nm, is shown in Figure 2b. The signal of  $\Delta A(\lambda)$  was positive in the wavelength regions 525–580 nm and 610–700 nm; it was negative in the wavelength ranges 580–610 nm and 700–

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725 nm. The positive signal of  $\Delta A(\lambda)$  was due to induced absorption. The positive  $\Delta A(\lambda)$  signal in the range 525–580 nm had two minima at  $\lambda_{\min} = 528$  nm and  $\lambda_{\min} = 558$  nm, which are due to Q-band photobleaching caused by ground-state depletion. The negative signal of  $\Delta A(\lambda)$  was due to stimulated emission from the excited state or to bleaching induced by ground-state depletion.

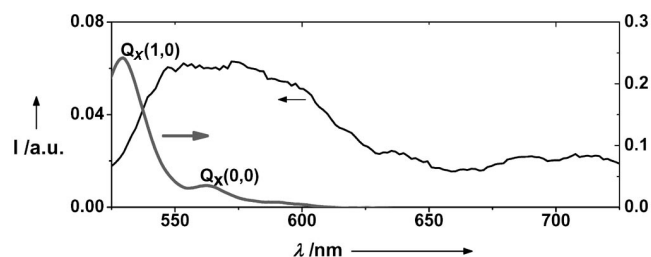


Figure 1. Sub-5-fs laser pulse spectrum (black line) and ground-state absorption spectrum (gray line) of Ru<sup>II</sup>(TPP)(CO) (TPP = 5,10,15,20-tetraphenylporphyrin) in acetone.

The observed real-time  $\Delta A(t)$  was analyzed with the single-valued decomposition (SVD) method to evaluate the dynamics of the excited states in Ru<sup>II</sup>(TPP)(CO). Figure 3 shows the values of  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ , obtained by SVD analysis of time traces at 128 probe wavelengths. These values were  $\tau_1 = 140 \pm 20$  fs,  $\tau_2 = 560 \pm 150$  fs,  $\tau_3 = 1.7 \pm 0.3$  ps, and  $\tau_4 = 4.5 \pm 2$  ps. Each one is the average of the corresponding data measured at 128 probe channels except for the highest and lowest five values. Time-resolved  $\Delta A$  traces up to a delay time of 3.5 ps were used for discussion in this work; therefore, a signal whose lifetime was 4.5 ps was assumed to be constant.

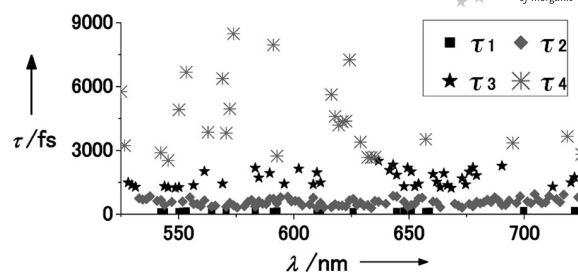


Figure 3. Time constants of Ru<sup>II</sup>(tpp)(CO)(acetone) obtained with SVD analysis:  $\tau_1$  (black square),  $\tau_2$  (gray diamond),  $\tau_3$  (black star), and  $\tau_4$  (gray asterisk).

The UV/Vis absorption spectrum shows that visible pulse irradiation excites Ru<sup>II</sup>(TPP)(CO)(acetone) into the  $^1Q_x(\pi, \pi^*)$  state (Figure 1). The photoexcited  $^1Q_x(\pi, \pi^*)$  state was assumed to follow the sequential decay process  $^1Q_x(\pi, \pi^*) \rightarrow ^3(d, \pi^*) \rightarrow ^3(\pi, \pi^*) \rightarrow \text{ground state}$ . Since the energy spacings are small, it is expected that the photoexcited Ru(por)CO relaxes to the neighboring lower level very efficiently by the energy gap law.<sup>[11]</sup> The energy gap between  $^1Q_x(\pi, \pi^*)$  and  $^3(d, \pi^*)$  was  $110 \text{ cm}^{-1}$ , that between  $^1Q_x(\pi, \pi^*)$  and  $^3(\pi, \pi^*)$  was  $3070 \text{ cm}^{-1}$ , and that between  $^1Q_x(\pi, \pi^*)$  and the ground state was  $16860 \text{ cm}^{-1}$ . The ratio of relaxation rates for  $^1Q_x(\pi, \pi^*) \rightarrow ^3(d, \pi^*)$ ,  $^1Q_x(\pi, \pi^*) \rightarrow ^3(\pi, \pi^*)$ , and  $^1Q_x(\pi, \pi^*) \rightarrow \text{ground state}$  was roughly estimated to be about 17:6:1. The contribution to the relaxation from  $^1Q_x(\pi, \pi^*)$  was dominated by the first process. The energy gap between  $^3(d, \pi^*)$  and  $^3(\pi, \pi^*)$  was  $2960 \text{ cm}^{-1}$ ; and that between  $^3(d, \pi^*)$  and ground state was  $16750 \text{ cm}^{-1}$ . The ratio of relaxation rates between  $^3(d, \pi^*) \rightarrow ^3(\pi, \pi^*)$  and  $^3(d, \pi^*) \rightarrow \text{ground state}$  was roughly estimated to be about 5:1, which indicates that the former was dominant. Ru(por)CO therefore relaxes

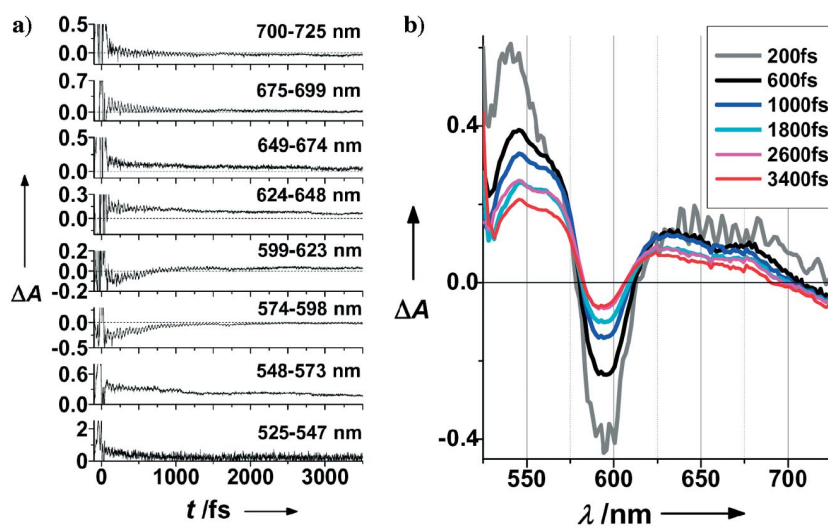


Figure 2. (a) Real-time vibration traces of induced absorbance changes of Ru<sup>II</sup>(tpp)(CO)(acetone) in the delay time range from  $-100$  fs to  $3500$  fs averaged over  $23.6$  nm. (b) Probe wavelength dependence of induced absorbance changes of Ru<sup>II</sup>(tpp)(CO)(acetone). The six curves show absorbance changes in the delay time region  $100$ – $300$  fs (gray),  $500$ – $700$  fs (black),  $900$ – $1100$  fs (blue),  $1700$ – $1900$  fs (cyan),  $2500$ – $2700$  fs (pink), and  $3300$ – $3500$  fs (red).

from the highest level to the lowest level step by step without a short-cut path. This sequential model was used in the present study to express the excited-state dynamics of Ru(por)CO. The three lifetimes  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  obtained in the SVD analysis were attributed to the decay of the  $^1Q_x(\pi,\pi^*)$ ,  $^3(d,\pi^*)$ , and  $^3(\pi,\pi^*)$  states, respectively. Using the lifetimes determined above, real-time  $\Delta A(t)$  traces were fitted in Equation (1) to obtain spectra of the four lifetime components:

$$f(t) = A_1[\exp(-t/\tau_1)] + A_2[\exp(-t/\tau_2) - \exp(-t/\tau_1)] + A_3[\exp(-t/\tau_3) - \exp(-t/\tau_2)] + A_4[1 - \exp(-t/\tau_3)] \quad (1)$$

Figure 4 shows the spectra of the four lifetime components ( $A_1$ ,  $A_2$ ,  $A_3$ , and  $A_4$ ) obtained by using this fitting.

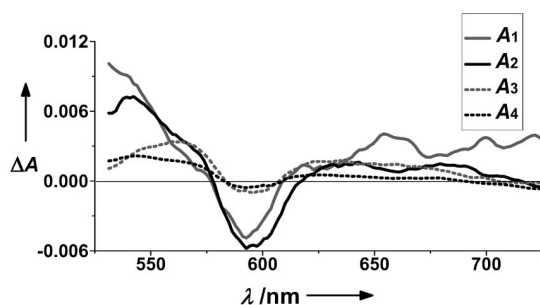


Figure 4. Magnitude of the four spectral components in a sequential model.

The  $A_1$  spectrum, whose lifetime was about 140 fs, had a positive peak in the probe spectral range 525–580 nm (Figure 4). This positive peak was considered to be due to the induced absorption of the  $^1Q_x$  state, which is more intense than the photobleaching induced by ground-state depletion. Induced absorption observed at  $\lambda_{\max} > 525$  nm ( $>19000$   $\text{cm}^{-1}$ ) was thought to be due to the transition from the  $^1Q_x$  state (existing at  $18800$   $\text{cm}^{-1}$  and  $17800$   $\text{cm}^{-1}$ ) to the  $^1M$  state, which had absorption at about 215 nm.<sup>[10b]</sup>

A negative spectral component that broadened in the region 580–607 nm and exhibited a peak at  $\lambda_{\max} = 590$  nm was considered to be due to stimulated emission from the  $^1Q_x$  state. This assignment was supported by the observed emission spectrum with a peak at 601 nm (Figure 5).<sup>[10e,12,13]</sup> The reported fluorescence spectra of Ru<sup>II</sup>(TPP)(CO)(dansylimidazole)<sup>[12]</sup> and Ru<sup>II</sup>(OEP)(CO)(py) (OEP = octaethylporphyrin),<sup>[10e,13]</sup> which had peaks at 560 nm and 556 nm, respectively, also supported the assignment stated above.

A positive spectral component extending from 607 nm to 725 nm may imply the appearance of induced absorption of the excited state, because the ground state did not have any absorption in this range, and hence was not effective. Induced absorption observed from 607 nm to 725 nm had peaks at  $\lambda_{\max} = 654$  nm ( $15300$   $\text{cm}^{-1}$ ),  $\lambda_{\max} = 700$  nm ( $14300$   $\text{cm}^{-1}$ ), and  $\lambda_{\max} > 725$  nm ( $>13800$   $\text{cm}^{-1}$ ), and it

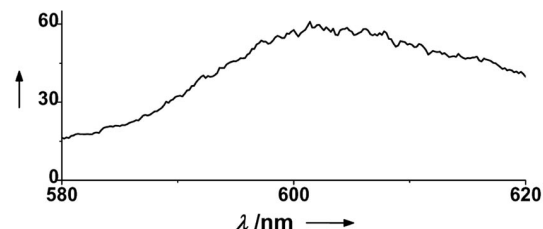


Figure 5. Emission spectrum of Ru<sup>II</sup>(tpp)(CO)(acetone) recorded with a fluorescence spectrometer (HITACHI model F-4500).

was thought to excite the  $^1Q_x$  states (extending from  $18800$   $\text{cm}^{-1}$  and  $17800$   $\text{cm}^{-1}$ ) to the  $^1N$  [extending from about 310–330 nm ( $30300$ – $32260$   $\text{cm}^{-1}$ )] and  $^1L$  [existing at about 270–310 nm ( $32260$ – $37040$   $\text{cm}^{-1}$ )] states.<sup>[10a,10b]</sup>

As mentioned above, the  $A_1$  spectrum was assigned to the induced absorption/emission from  $^1Q_x(\pi,\pi^*)$ , which has a lifetime of 140 fs. The spin-forbidden radiationless transition from  $^1Q_x(\pi,\pi^*)$  to  $^3(d,\pi^*)$  takes 140 fs,<sup>[14]</sup> which agrees well with the reported intersystem crossing time constant of 40–100 fs in [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.<sup>[4]</sup> The ultrafast intersystem crossing time constant can be explained by enhanced spin–orbit coupling caused by the heavy atom Ru and the metal-to-ligand charge transfer in the  $^3(d,\pi^*$  MLCT) transition.

The  $A_2$  spectrum was positive in the spectral range 525–575 nm, which was attributed to induced absorption from the  $^3(d,\pi^*)$  to the M state. A spectral component of negative absorbance change extending in the range 575–622 nm with a peak at  $\lambda_{\max} = 595$  nm was assigned to the stimulated emission from the  $^3(d,\pi^*)$  state, with a decay time of about 500 fs. The observed emission spectrum showing a peak at 601 nm (Figure 5) was thought to include fluorescence from the  $^1Q_x(\pi,\pi^*)$  state together with phosphorescence from the  $^3(d,\pi^*)$  state, because intersystem crossing can take place rapidly from  $^1Q_x(\pi,\pi^*)$  to  $^3(d,\pi^*)$ , when the energy difference between the two states is quite small.<sup>[9,10d]</sup>

A broad positive spectral component extending from 622 nm to 725 nm with peaks at  $\lambda_{\max} = 637$  nm ( $15700$   $\text{cm}^{-1}$ ) and  $\lambda_{\max} = 680$  nm ( $14700$   $\text{cm}^{-1}$ ) may be due to induced absorption from the excited  $^3(d,\pi^*)$  state to the N and L states. The L–N splitting of about 1000–2000  $\text{cm}^{-1}$  reported in ref.<sup>[10a]</sup> supports this assignment.

The spectral shape of  $A_3$  was similar to that of  $A_4$ , having a broader bandwidth and a small blueshift from 627 nm to 621 nm. Spectral narrowing and the blueshift from  $A_3$  to  $A_4$  can be explained by thermal equilibration. A positive  $\Delta A(\lambda)$  component in the spectral region 607–690 nm of  $A_3$  and  $A_4$  was attributed to induced absorption of the  $^3(\pi,\pi^*)$  state. This is supported by the research of Holton et al.,<sup>[10d]</sup> who observed the induced absorption spectrum due to the lowest excited triplet state  $^3(\pi,\pi^*)$  in Ru<sup>II</sup>(TPP)(CO)(py). The spectrum extended from 600 nm to 900 nm with an intense and broad peak at about 850 nm and a weak peak at about 750 nm.

A negative spectral component in the range 690–725 nm with a peak at  $\lambda_{\max} \geq 725$  nm can be attributed to the stimulated emission from  $^3(\pi,\pi^*)$ , because the phosphorescence of Ru<sup>II</sup>(TPP)(CO)(py) was reported to have a peak at  $\lambda_{\max}$



= 726 nm at r.t.<sup>[6a,10c]</sup> Another negative spectral component in the range 580–607 nm with a peak at  $\lambda_{\text{max}} = 590$  nm ( $\Delta A = -0.0009$ ) is considered to be due to residual (11%) bleaching induced by ground-state depletion, because Ru<sup>II</sup>-(TPP)(CO)(acetone) has an absorption spectrum in this range ( $\Delta A = 0.008$ ). Usually, stimulated emission from the triplet state cannot be observed because of the small cross-section of the spin-forbidden transition. However, strong spin–orbit coupling in the Ru<sup>II</sup> complex makes the singlet-to-triplet (S–T) absorption detectable.<sup>[10c,15]</sup> This is why the induced absorption from the triplet state was observed in this work. This is the first observation of stimulated emission in the pump-probe experiment.

Figure 6 summarizes the dynamics discussed above, showing the lifetimes of  $^1Q_x(\pi, \pi^*)$ ,  $^3(d, \pi^*)$ , and  $^3(\pi, \pi^*)$  to be 140 fs, 560 fs, and 1.7 ps, respectively.

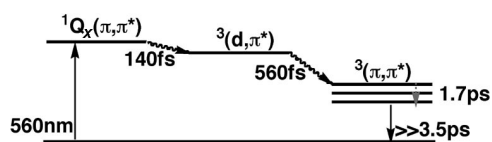


Figure 6. Energy level diagram illustrating the relaxation dynamics after the photoexcitation of Ru<sup>II</sup>(tpp)(CO)(acetone).

## Conclusions

The ultrafast excited-state dynamics of Ru<sup>II</sup>(TPP)(CO) was investigated by using a sub-5-fs pulse. Analysis of Ru<sup>II</sup>-(TPP)(CO)(acetone) shows that the lifetimes of  $^1Q_x(\pi, \pi^*)$  and  $^3(d, \pi^*)$  were  $140 \pm 20$  fs and  $560 \pm 150$  fs, respectively. Stimulated emission due to a spin-forbidden transition from  $^3(\pi, \pi^*)$  to the ground state was observed for the first time.

## Experimental Section

The spectrum of the pulses covered the range between 525 and 725 nm with a nearly constant phase, giving the Fourier-transform pulse. The polarizations of the pump and the probe pulses were parallel to each other. The experiments were performed at intensities of the pump and probe pulses of 3840 and 560 GWcm<sup>-2</sup>, respectively. The focus areas of the pump and probe pulses are 100 and 75  $\mu\text{m}^2$ , respectively.

The probe pulse was dispersed by a polychromator (Ocean Optics, 300 groovesmm<sup>-1</sup>, 500 nm blazed) into a 128-branch bundle fiber, whose other end was separated in 128 branches of fibers and connected to avalanche photodiodes (APDs). Therefore, the time-resolved transmittance difference,  $\Delta T$ , at 128 probe wavelengths was detected at the APDs with a spectral resolution of about 1.57 nm. The signals detected at the APDs were sent to a multichannel lock-in amplifier to obtain the signal with a fine signal-to-noise ratio. A liquid cell of 1 mm optical path length was used. All measurements were performed at room temperature ( $295 \pm 1$  K). The probe spectrum transmitted through the sample was recorded by averaging 50,000 laser shots without injecting the pump pulse. Meanwhile,  $\Delta T$  was measured by accumulating every 3,000 laser shot. The pump-probe experiment was performed with a delay time step of 1 fs in the time range –100 to 3500 fs. Details are shown in the Supporting Information.

UV/Vis spectra were recorded with a Shimadzu model UV-3101PC spectrometer. The emission spectra were recorded with a HITACHI model F-4500 fluorescence spectrophotometer.

**Supporting Information** (see footnote on the first page of this article): Detailed experimental method.

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