

Solvent effect for ruthenium porphyrin

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Relaxation of electronic excited-state and vibrational dynamics in the electronic excited state in Ru^{II}(TPP)(CO) [TPP=tetraphenylporphyrin] dissolved in N₂ bubbled benzene, O₂ bubbled benzene, N₂ bubbled chloroform and N₂ bubbled acetone were clarified using a sub-5fs laser pulse. The result showed that the transition energy from the ¹Q_x states, consisting of the ¹Q_{x(1,0)}(π, π^*) state (existing at 18800 cm⁻¹) and ¹Q_{x(0,0)}(π, π^*) state (existing at 17800 cm⁻¹), to the ¹M state of six-coordinated ruthenium complex is lower than that of the five-coordinated ruthenium complex. The intersystem crossing ¹Q_{x(0,0)}(π, π^*) → ³(d, π^*) in the five-coordinate Ru^{II}(TPP)(CO) in the solution was found to take place in about 1 ps.

femtosecond laser, ruthenium porphyrin complex, real-time spectroscopy

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1 Introduction

Recently, metal complex compounds are gaining attention as a new material for display and memory, which makes the photochemistry of the metal complexes to be one of the hottest topics in the recent study of chemistry field. Especially, the transition metal complex, which emits phosphorescence at room temperature, is attracting attention as electro-luminescent material. Therefore, it is important to clarify the excited state dynamics of the transition metal complex. Among those transition metal complexes, Ru^{II} complex has been studied extensively because of its high reactivity. For example, there were many studies of [Ru(bpy)₃]²⁺ [bpy = bipyridine] for the development of sensitizer to decompose water by solar energy [1,2] and the development of dye-sensitized solar cell [3]. Those studies showed that the lowest excited triplet state of the [Ru(bpy)₃]²⁺ is metal-

to-ring charge-transfer state ³(d, π^*), whose lifetime is about 600 ns, and quantum yield of the phosphorescence are $\Phi_{ph}=0.04$ at room temperature [4]. Moreover, lifetime of singlet lowest excited state was reported to be 40–100 fs from ultrafast time-resolved experimental results using femtosecond laser pulses [5,6]. On the other hand, various study for Ru^{II} porphyrin complexes were reported as model complex of hemoglobin for a long time in biology. In the case of Ru^{II} carbonyl porphyrin complex, the lowest excited triplet state was reported to be ³(π, π^*) of porphyrin ring [7–9]. For example, the phosphorescence lifetime, quantum yield of phosphorescence and fluorescence lifetime in Ru^{II}(TPP)(CO)(py) [TPP=5,10,15,20-tetraphenylporphyrine, py=pyridine] were found to be 35 μ s $\Phi_{ph}=10^{-3}$, and of ~1 ps, respectively, at room temperature [10–13]. However, the excited-state dynamics has not yet been clarified well. In this work, the solvent effects of electronic excited-state dynamics of Ru^{II}(TPP)(CO) were analyzed using a sub-5-fs laser pulse. The result showed that the transition energy

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from the ^1Q_x states (existing at 18800 cm^{-1} and 17800 cm^{-1}) to the ^1M state of six-coordinated ruthenium complex is lower than that of five-coordinated ruthenium complex.

Being the most important part of an article, the introduction introduces the relevant research background and the progress in 2 or 3 years, with references cited in numerical order, then presents the problem to be solved in this article, and finally briefly describes the method adopted in this work. Before the end, the aim of the research should be mentioned. Subtitle is forbidden in this part, and introduction of the article structure is considered unnecessary.

2 Materials and method

2.1 Broadband visible pulse generation by NOPA

Ultra-broadband visible pulse was generated using a non-collinear optical parametric amplifier (NOPA) as shown in Figure 1. Sub-5-fs visible ultrashort pulse was obtained compressing the output of NOPA to be used for the ultrafast pump-probe measurement.

Pump and seed beams of NOPA were generated by using a Ti:sapphire regenerative amplifier (Spectra-Physics, model Spitfire with pulse duration of 100 fs, central wavelength of 790 nm, and repetition rate of 5 kHz). A single-filament white light continuum generated from a 1-mm-thick sapphire plate was used as the seed pulse and non-collinearly amplified in a NOPA crystal (type I-BBO, $\theta = 31.5^\circ$). The NOPA crystal was pumped by a second harmonics (100 μJ) of the laser source. A 0.4-mm-thick BBO crystal was used to obtain the second harmonics with broad enough spectral width to obtain broad gain bandwidth in the pumping process of NOPA.

We developed a pulse compressor to compensate the residual chirp, which exists in the output pulse of NOPA. The pulse compressor is composed of the ultra-broadband chirped mirror (Hamamatsu Photonics) pair, a 45° fused-silica prism pair. The parameters of the compressor are designed to compensate the measured group delay across the whole spectral range. The best compression is attained in

the case of a 1-m separation and a 6.0-mm intraprism path length of the prism pair at 650 nm and the net four round trips of the ultra-broadband chirped mirror pairs. The throughput of the compressor is about 80%, whose loss is mainly caused by Fresnel loss at the prism surfaces. Nearly Fourier transform limited sub-5-fs pulse was obtained by compressing the NOPA output pulse, which has broad spectrum extending from 525 to 725 nm.

2.2 Pump-probe measurement

An equation is numerically numbered (Arabic numeral), and has the number put on its right side.

We used a sub-5-fs pulse [14] to observe the dynamics of the electronic excited states of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ in N_2 bubbled benzene, O_2 bubbled benzene, N_2 bubbled chloroform and N_2 bubbled acetone. Benzene and chloroform are non-coordinating solvents, and acetone is a coordinating solvent [15,16]. In the case of O_2 bubbled benzene, O_2 coordinates to Ru complex as an axial ligand [17]. The spectrum of the sub-5-fs laser pulses extended from 525 to 725 nm (Figure 2). All measurements were performed at room temperature using a 1-mm solution cell. A polychromator (300 grooves/mm, 500 nm blazed) was coupled to avalanche photodiodes through a 128-channel fiber bundle to observe time-resolved difference transmittance ΔT in the spectral range extending from 525 to 725 nm simultaneously with spectral resolution of $\sim 1.57\text{ nm}$. Laser intensity was relatively low at the 16 probe channels (from 700 to 725 nm) compared with other channels in the 128-channel detectors. We did not show the data of those 16 channels on the figure since the low signal intensity did not provide enough signal-to-noise ratio. The probe spectrum that transmitted through the sample was recorded by averaging 50000 laser shots without injecting the pump pulse. The transmission difference of the probe was accumulated every 3,000 laser shots taking difference between the cases of with and without excitation by the pump pulse.

2.3 Spectroscopy

Ultraviolet/Visible (UV/Vis) spectra were recorded on a Shimadzu model UV-3101PC spectrometer. Emission spectra were recorded on a HITACHI model F-4500 fluorescence spectrophotometer.

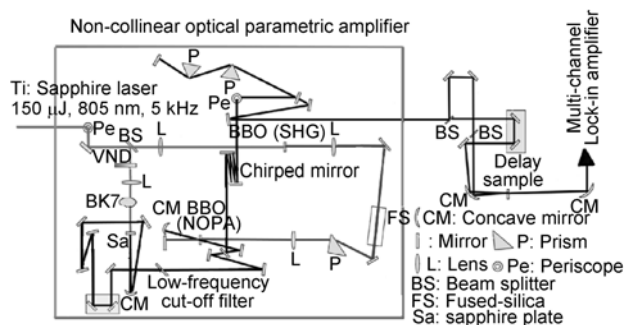


Figure 1 Non-collinear optical parametric amplifier for sub-5-fs generation and the pump-probe measurement system.

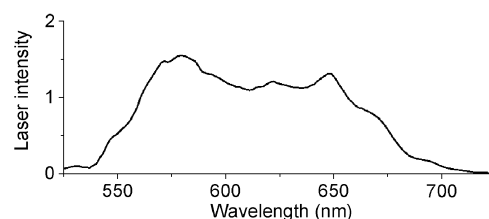


Figure 2 Spectrum of the sub-5 fs laser pulses.

2.4 Computational methods

$\text{Ru}^{\text{II}}(\text{por})(\text{CO})$ complex [por = porphyrin] without four phenyl group was used for the model complex instead of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ for simplicity of the theoretical calculation. The Gaussian 03 program [18] was used for the theoretical calculations. Geometry optimizations were performed with B3LYP/6-31G*//B3LYP/6-31G*. (The 3-21G* basis set was substituted for 6-31G* in the case of the ruthenium atom.) Geometry optimizations were performed without assuming any symmetry. As for the d orbital, $5d$ functions were used. The frequency calculations were performed for all of the obtained structures at the same level. It was confirmed that all the frequencies were real valued for the ground states.

3 Discussion and conclusions

3.1 The UV/Vis absorption spectrum and fluorescence spectrum of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$

Previous study [19,20] reported that π -back donation in $d\pi \rightarrow \text{CO}(\pi^*)$ lowers the energy of the $d\pi$ orbital in Ru^{II} , resulting in energy increase of the (d, π^*) state. Therefore, they concluded that the lowest excited state S_1 in $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ is (π, π^*) state. As seen in Figure 3, the UV/Vis absorption spectrum of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ has a $Q_x(1,0)$ band peak at $\lambda_{\text{max}} = 528 \text{ nm}$ (18939 cm^{-1}) and a $Q_x(0,0)$ band peak at $\lambda_{\text{max}} = 560 \text{ nm}$ (17897 cm^{-1}). The lower and higher energy band, $Q_x(0,0)$ and $Q_x(1,0)$, are vibrational ground level in S_1 and first vibrational excited level in S_1 , respectively [19,20]. Figure 4 shows that the fluorescence spectrum has a peak around 600 nm [19,21]. The laser spectrum extends from 525 to 725 nm covering both of the absorption bands, which causes coherent excitation of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ into both of the $^1Q_{x(0,0)}(\pi, \pi^*)$ and $^1Q_{x(1,0)}(\pi, \pi^*)$ states. The signals due to $^1Q_{x(1,0)}(\pi, \pi^*)$ and $^1Q_{x(0,0)}(\pi, \pi^*)$ are thought to decay in a sequential order from the higher energy states to the lower energy states following the sequences of $^1Q_{x(1,0)}(\pi, \pi^*) \rightarrow ^1Q_{x(0,0)}(\pi, \pi^*) \rightarrow ^3(d, \pi^*) \rightarrow ^3(\pi, \pi^*)$ and $^1Q_{x(0,0)}(\pi, \pi^*) \rightarrow ^3(d, \pi^*) \rightarrow ^3(\pi, \pi^*)$, respectively.

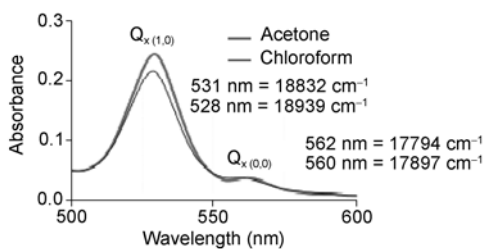


Figure 3 UV/Vis absorption spectra of $Q_x(1,0)$ and $Q_x(0,0)$ of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ in N_2 bubbled chloroform (gray line) and N_2 bubbled acetone (bold line).

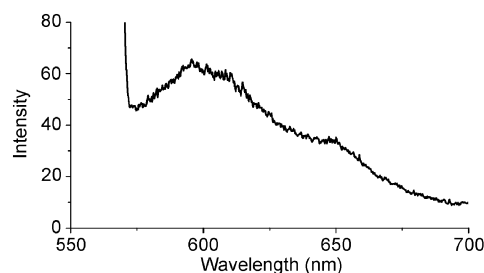


Figure 4 Fluorescence spectrum of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ in N_2 bubbled chloroform with 550 nm excitation.

3.2 Pump probe experiment

Ultrafast dynamics of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ was studied by pump-probe method using sub-5-fs pulse laser. Figure 5 shows two-dimensional display of the time-resolved absorbance (ΔA) change traces obtained in the pump-probe measurement.

Figures 5(a) and (c) shows that ΔA is negative for the five-coordinated $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ in all spectral region. However, six-coordinated one showed positive ΔA from 525 to 580 nm (see Figures 5(b) and (d)). Moreover, when six-coordinated $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ was solved in acetone, positive ΔA was also observed from 610 to 700 nm as shown in Figure 5(d). The signal of positive $\Delta A(\lambda)$ was due to induced absorption. The signal of negative $\Delta A(\lambda)$ was due to stimulated emission from the excited state or to bleaching induced by ground-state depletion. In any solvent studied, ΔA has the minimum value at $\sim 600 \text{ nm}$. The fluorescence spectrum shown in Figure 4 has the peak at $\sim 600 \text{ nm}$, which implies that the negative ΔA signal reflects stimulated emission. Positive ΔA observed for six-coordinated $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ between 525 and 580 nm is thought to be reflecting the induced absorption for the transition from the ^1Q_x state (existing at 18800 cm^{-1} and 17800 cm^{-1}) to the ^1M state with an absorption peak around 215 nm [11]. Peak energies of $Q_x(1,0)$ band and $Q_x(0,0)$ band maintain the same among five-coordinated $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ and six-coordinated one (Figure 3), however positive ΔA does not appear for the five-coordinated one. It shows that energy level of ^1M state of the five-coordinated $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ is higher than that of the other.

For all of the probe wavelengths, lifetime of stimulated emission was determined fitting the ΔA traces by eq. (1). Figure 6 shows the obtained lifetimes. For the error estimation of lifetimes, their standard deviations were calculated for the obtained values. The results in N_2 bubbled benzene, O_2 bubbled benzene, N_2 bubbled chloroform, and N_2 bubbled acetone are shown in Figures 6(a)–(d), respectively. For the four cases, lifetimes were determined “ $\tau_1 = 1030 \pm 400 \text{ fs}$ ”, “ $\tau_1 = 116 \pm 39 \text{ fs}$ ”, “ $\tau_1 = 230 \pm 70 \text{ fs}$, $\tau_2 = 1100 \pm 100 \text{ fs}$ ”, and “ $\tau_1 = 90 \pm 35 \text{ fs}$, $\tau_2 = 500 \pm 110 \text{ fs}$ ”, respectively. It shows that lifetime of six-coordinated $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ is shorter than

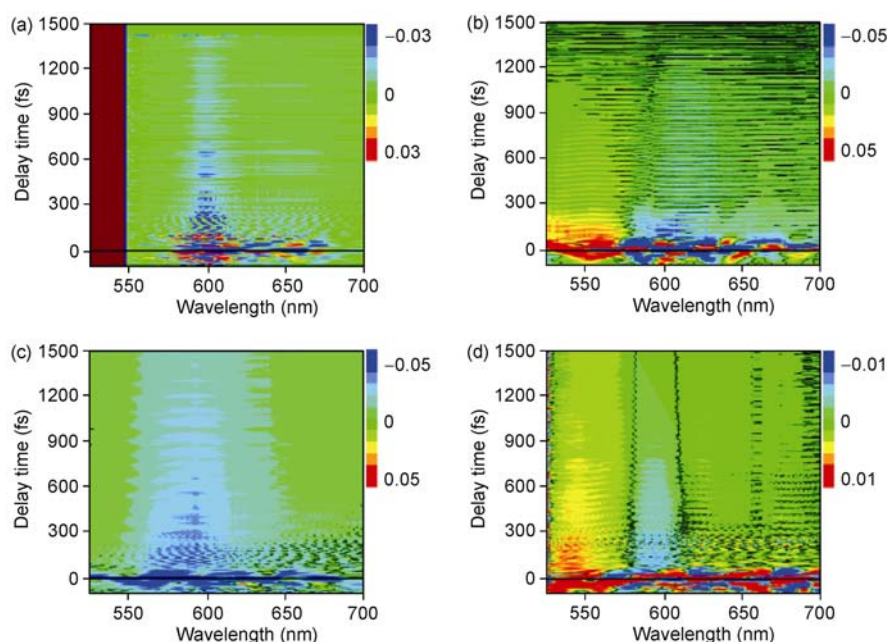


Figure 5 2D-real-time trace. (a) N_2 bubbled benzene; (b) O_2 bubbled benzene; (c) N_2 bubbled chloroform; (d) N_2 bubbled acetone.

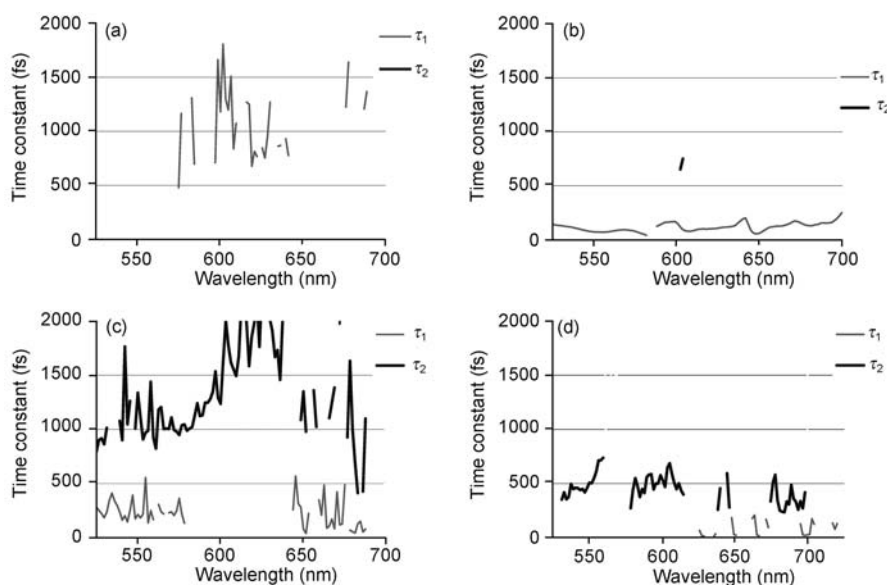


Figure 6 Time constants obtained in exponential fit using eq. (1) for $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ in (a) N_2 bubbled benzene, (b) O_2 bubbled benzene, (c) N_2 bubbled chloroform, and (d) N_2 bubbled acetone.

that of five-coordinated one. Figure 7 shows the obtained A'_1 , A'_2 and A'_3 . The results obtained for N_2 bubbled benzene, O_2 bubbled benzene, N_2 bubbled chloroform, and N_2 bubbled acetone are shown in Figures 7(a)–(d), respectively. The stimulated emission from the $^1\text{Q}_{\text{x}(0,0)}(\pi, \pi^*)$ state were found as negative absorption change in A'_1 , A'_1 , A'_2 and A'_1 , respectively. Therefore, the lifetime of the $^1\text{Q}_{\text{x}(0,0)}(\pi, \pi^*)$ state were determined 1030 ± 400 fs, 116 ± 39 fs, 1100 ± 100 fs and 90 ± 35 fs, respectively. It shows that lifetime of $^1\text{Q}_{\text{x}(0,0)}(\pi, \pi^*)$ state of six-coordinated $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ is shorter than that

of five-coordinated one.

$$f(t) = A'_1(\exp(-t/\tau_1)) + A'_2(\exp(-t/\tau_2)) + A'_3. \quad (1)$$

Spectrogram analysis was performed to study instantaneous frequency change of porphyrin ring stretching mode (ν_{por}), which appears $\sim 1040 \text{ cm}^{-1}$. Benzene and acetone are not suitable for this purpose because these solvents have strong vibration modes around the porphyrin mode; benzene has benzene ring stretching mode around 1000 cm^{-1} and acetone has C-C stretching mode around 1066 cm^{-1} . We

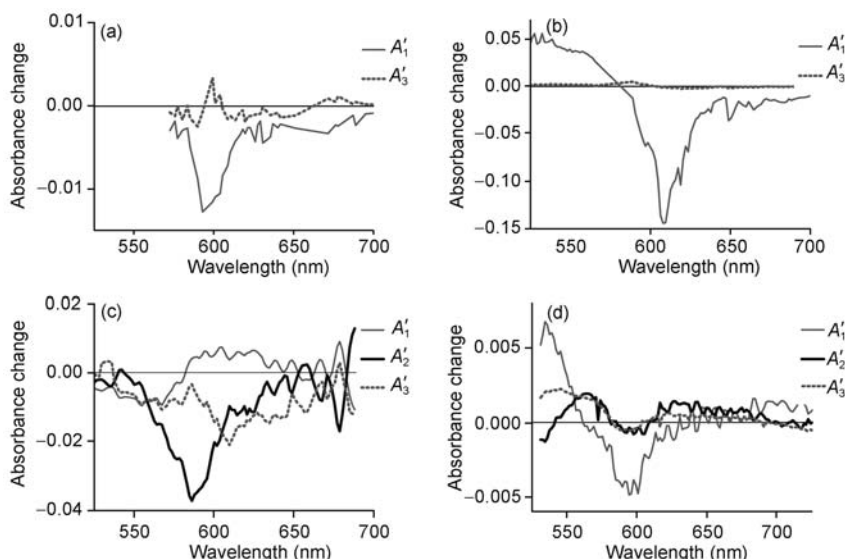


Figure 7 Spectra of each lifetime component in (a) N_2 bubbled benzene, (b) O_2 bubbled benzene, (c) N_2 bubbled chloroform, and (d) N_2 bubbled acetone.

performed the spectrogram analysis of five-coordinated $Ru^{II}(TPP)(CO)$ solved in chloroform, since the solvent has no vibration modes in the frequency region that we are going to study in the spectrogram analysis of this work (800 to 1200 cm^{-1}).

The spectrogram was calculated from the ΔA traces averaged over 10 probe wavelengths around 600 nm using the Blackman window function whose FWHM was 240 fs. The result is shown up to 1500 fs in Figure 8. Around the zero delay region (0 to 300 fs), the spectrogram is not shown on the figure because there exists strong interference between the scattered pump pulse and probe pulse. At 300 fs, the porphyrin ring stretching mode was observed around 1036 cm^{-1} , which agrees well with the calculated frequency (1040 cm^{-1}) of singlet state $Ru^{II}(por)(CO)$ (Figure 9(a)). This vibration mode blue shifts to 1150 cm^{-1} with several hundreds fs in the delay region from ~ 600 fs to ~ 1 ps. It implies the appearance of the triplet state, whose ν_{por} was obtained by the quantum chemical calculation to be 1100 cm^{-1} . The mode around 900 cm^{-1} that appears at ~ 1 ps is also considered to be due to the triplet state after the intersystem crossing, because the calculated result suggests the appearance of

the porphyrin ring bending mode at 990 cm^{-1} , characteristic of the triplet state in $Ru^{II}(por)(CO)$ (Figure 9(b)).

From the dynamics observed in the electronic state analysis and the spectrogram, we could thus clarify the ultrafast dynamics of $Ru^{II}(TPP)(CO)$, which shows that the lifetime of the singlet excited state is about 1.2 ± 0.2 ps. Both positive and negative absorbance changes were successfully assigned to the absorption bands of the transition states.

The electronic spin state is thought to convert from the singlet into the triplet state with a certain transition proba-

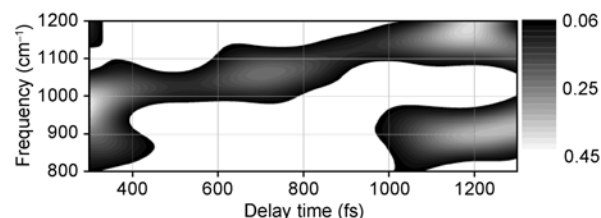


Figure 8 Fourier power spectrogram calculated from the real-time trace probed around 600 nm. The frequency resolution of the spectrogram was estimated to be 30 cm^{-1} .

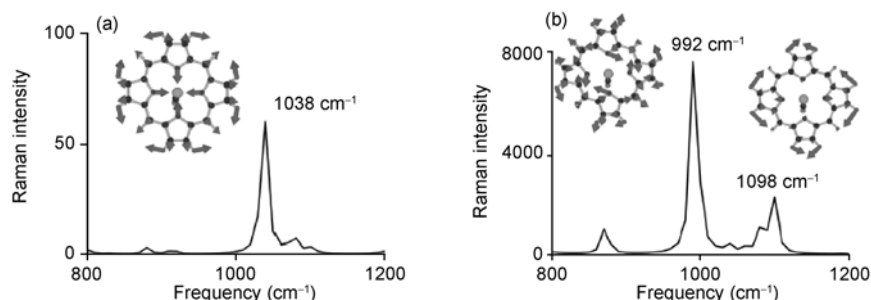


Figure 9 Calculated Raman spectra with the DFT method for (a) the ground singlet state and (b) the triplet state.

bility, therefore we performed a model calculation in which Fourier power of the porphyrin ring stretching mode of 1040 cm^{-1} (singlet) and that of 1150 cm^{-1} (triplet) decays and grows, respectively, both with a time constant of 1.2 ps. The model calculation shows that the two frequency modes keep their original frequencies (Figure 10). Even if their vibration phases are displaced to each other, the two modes appeared on the calculated spectrogram keeping their original frequency. However, in the experimental results, we found the intermixing between the two modes as a gradual blue shift of ν_{por} from 1040 to 1150 cm^{-1} . The signal intensity at 1060 cm^{-1} has a peak at the gate delay time of 640 fs during the course of delay time. This may reflect the existence of the bottleneck in wavepacket passage through the curve crossing point between the excited singlet state and excited triplet state.

Thus, the observed spectrogram reflects the structural change in $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ during the transition from the Franck-Condon state to the curve crossing point between the singlet and triplet followed by the intersystem crossing to the triplet state [22]. The delay of the observed intermixing, $\sim 1\text{ ps}$, reflects the timing of the intersystem crossing during the chemical reaction.

To support the above assignment, we also studied electronic state relaxation dynamics in the chloroform solvent as follows. Experimental results of real-time traces (from -100

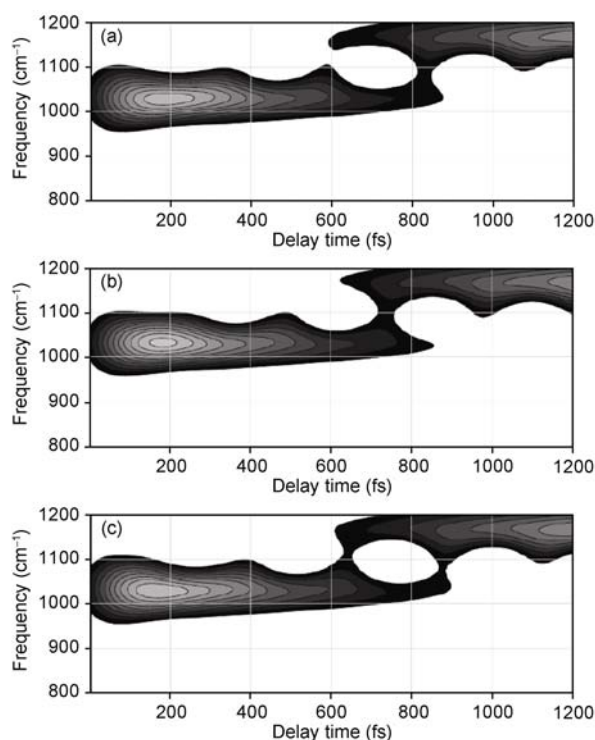


Figure 10 Simulated data of spectrogram assuming that the modes of 1040 and 1150 cm^{-1} decay and rise, respectively, with the same time constant of 1060 fs . (a) Vibration phase = 0π ; (b) Vibration phase = 0.8π ; (c) Vibration phase = 1.6π .

to 3500 fs) of absorbance change (ΔA) and probe wavelength dependency of ΔA ($525\text{--}700\text{ nm}$) are shown in Figure 11. The result shows that the spectrum of ΔA is similar to the simulated spectrum of stimulated emission ($\lambda_{\text{max}}=595\text{ nm}$) of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$. The stimulated emission spectrum was calculated from the fluorescence spectrum of the sample excited at $\lambda_{\text{exc}}=515\text{ nm}$ ($Q_x(1,0)$ band) and at $\lambda_{\text{exc}}=550\text{ nm}$ ($Q_x(0,0)$ band) using the Einstein coefficients A_{nm} (spontaneous emission) and B_{nm} (stimulated emission), and the equation of $A_{\text{nm}}=(2hc/\lambda^3)B_{\text{nm}}$. Since the fluorescence has a peak at $\lambda_{\text{max}}=595\text{ nm}$, the main contribution of the ΔA signal is thought to be due to the stimulated emission from $^1Q_{x(0,0)}(\pi, \pi^*)$.

Figure 12(a) shows the observed real-time trace fitted with the following function $f(t)$,

$$f(t) = A'_1(\exp(-t/\tau_1)) + A'_2(\exp(-t/\tau_2)) + A'_3(\exp(-t/\tau_3)) + A'_4, \quad (2)$$

where A'_1 , A'_2 , A'_3 , and A'_4 are spectral components whose lifetimes are τ_1 , τ_2 , τ_3 , and infinite, respectively. All of the lifetimes were obtained taking average over 112 probe wavelength channels. τ_1 and τ_3 were determined to be $230 \pm 70\text{ fs}$ and $2.8 \pm 0.3\text{ ps}$, respectively. τ_2 in the probe spectral range of “ $525\text{--}600$ and $650\text{--}700\text{ nm}$ ” (τ_2) and that of “ $600\text{--}650\text{ nm}$ ” (τ_2') were different from each other (Figure 12(a)), and determined as $1.1 \pm 0.14\text{ ps}$ and $1.8 \pm 0.3\text{ ps}$, respectively. Real-time ΔA trace to be discussed in this work was obtained up to the delay time of 3.5 ps , therefore the signal whose lifetime is 2.8 ps was assumed to be constant value, which is included in A'_4 in the current discussion. $^1Q_x(\pi, \pi^*)$ is thought to decay into lower energy excited states step-by-step after the photo-excitation, therefore the real-time ΔA traces were fitted with eq. (3) showing the sequential-reaction model.

$$f(t) = A_1(\exp(-t/\tau_1)) + A_2(\exp(-t/\tau_2) - \exp(-t/\tau_1)) + A''_2(\exp(-t/\tau''_2) - \exp(-t/\tau_2)) + A_4(1 - \exp(-t/\tau''_2)). \quad (3)$$

The obtained spectral components A_1 , A_2 , A''_2 and A_4 are shown in Figure 12(b). The signal of A_2 is thought to be due to the stimulated emission from $^1Q_{x(0,0)}(\pi, \pi^*)$, because of its good agreement with the stimulated emission spectrum of $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ ($\lambda_{\text{exc}}=550\text{ nm}$, $\lambda_{\text{max}}=595\text{ nm}$) (Figure 11(b)).

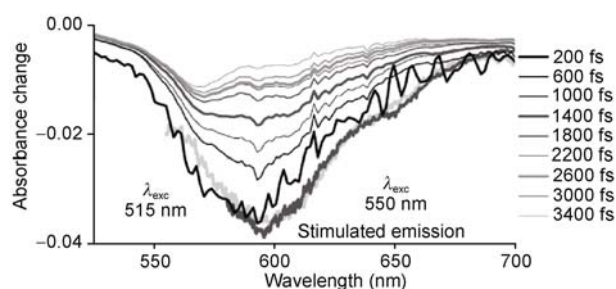


Figure 11 Probe wavelength dependency of ΔA of $\text{Ru}^{\text{II}}(\text{tpP})(\text{CO})$.

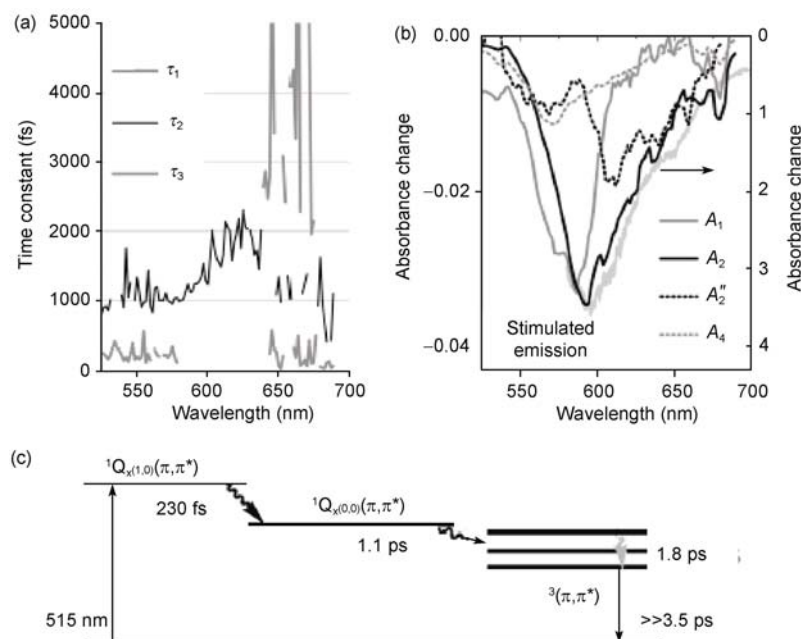


Figure 12 Fitting results give (a) time constants, (b) spectra of those time components in the sequential model, and (c) the energy level diagram illustrating the excited state dynamics.

The lifetime of $^1Q_{x(0,0)}(\pi, \pi^*)$ was estimated to be about 1.1 ps ($=\tau_2$). Lifetime and wavelength of A_1 are shorter and longer, respectively, than those of A_2 . Therefore, A_1 can be attributed to the stimulated emission from $^1Q_{x(1,0)}(\pi, \pi^*)$ with lifetime of 230 fs ($=\tau_1$). A_2'' , which has a negative peak at $\lambda_{\max}=610$ nm and longer lifetime than that of A_2 , is thought to be reflecting the spectrum of the thermal relaxation in the triplet excited state, because the lifetime of τ_2' increases when the probe wavelength increases from 600 to 650 nm. In the thermal relaxation, the population in the higher-energy vibrational levels relaxes to the lower-energy ones, and the dynamics cannot be described with a single lifetime constant, but be represented with wavelength dependent lifetime, which is longer in the longer probe wavelength region.

As a result of above analysis of electronic state, the lifetimes of $^1Q_{x(1,0)}(\pi, \pi^*)$, $^1Q_{x(0,0)}(\pi, \pi^*)$, thermal relaxation of triplet excited state, and $^3(\pi, \pi^*)$ were determined to be 230 fs, 1.1 ps, 1.8 ps, and $>>3.5$ ps, respectively (Figure 12(c)).

3.3 Conclusion

In conclusion, both electronic relaxation and vibrational dynamics in $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ were elucidated simultaneously under the same experimental conditions using a sub-5-fs pulse. The observed result shows that the transition energy from Q_x states ($^1Q_{x(1,0)}(\pi, \pi^*)$ state and $^1Q_{x(0,0)}(\pi, \pi^*)$ state) to ^1M state in six-coordinated $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ is lower than that in five-coordinated one. The lifetimes of both of the Q_π states in six-coordinated $\text{Ru}^{\text{II}}(\text{TPP})(\text{CO})$ were found to be

shorter than those in five-coordinated complex.

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