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Ultrafast electronic and vibrational dynamics of a ruthenium porphyrin complex in intersystem crossing

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Abstract

Using sub-5fs visible laser pulses, ultrafast time-resolved absorption change was observed for $Ru^{II}(TPP)(CO)$ (TPP=5,10,15,20-tetraphenylporphirine) solved in chloroform. Exponential fitting of the time traces estimated decay life times of intermediates as 230±70 fs, 1150±260 fs, 2150±360 fs, and »4.8 ps for $^1Q_{x(1,0)}(\pi,\pi^*)$, $^1Q_{x(0,0)}(\pi,\pi^*)$, $^3(d,\pi^*)$, and $^3(\pi,\pi^*)$, respectively. Real-time change of instantaneous molecular vibration frequency was studied by spectrogram analysis, which reflects gradual vibration mode change in the intersystem crossing from singlet state to triplet state.

Keywords: absorption change, metallo-porphyrin, intersystem crossing, pump-probe measurement, femtosecond dynamics, ruthenium porphyrin.

1. Introduction

Recently, the metal complex makes a mark as a new material, which can be used for display and memory, therefore the photochemistry of the metal complex is one of the most important topics to be studied in chemical field in recent years. Especially, the transition metal complex that generates phosphorescence at the room temperature is attracting attention as electro luminescent (EL) material. Therefore, it is very important to clarify the excited state dynamics of the transition metal complex. In such a transition metal complex, Ru^{II} complex has been often especially researched because of their good reactivity. For example, $[Ru(bpy)_3]^{2+}$ (bpy = bipyridine) has been many especially researched for the development of sensitizer to decompose water by the sun light energy [1,2,3] and the development of Dye-sensitized solar cell [4,5]. In case of $[Ru(bpy)_3]^{2+}$, the lowest excited triplet state is metal-to-ring charge-transfer state $^3(d,\pi^*)$, whose lifetime is about 600ns, and quantum yield of the phosphorescence are Φ_{ph}=0.04 at room temperature [6]. Moreover, lifetime of singlet lowest excited state was reported to be 40-100fs from ultrafast time-resolved experimental results using femtosecond laser pulses [7,8]. On the other hand, various

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studies for Ru^{II} porphyrin were reported as model complex of very important iron porphyrin for a long time in biology. In case of Ru^{II} carbonyl porphyrin, the lowest excited triplet state is $^3(\pi,\pi^*)$ of porphyrin ring [9,10]. For example, in case of $Ru^{II}(TPP)(CO)(py)$(TPP=5,10,15,20-tetraphenylporphirine, py=pyridine), the phosphorescence lifetime is 35 µs and quantum yield of the phosphorescence is $\Phi_{ph}=10^{-3}$ at the room temperature [11,12]. However, lifetime of fluorescence is only reported to be shorter than 30ps 1999 [11], and 1ps or less in 2005 [12]. Then, we analyzed the excited state dynamics including the lifetime of fluorescence of the $Ru^{II}(TPP)(CO)$ by using sub-5fs pulse laser. The correlation between electronic states and molecular vibrations in the five-coordinate complex of $Ru^{II}(TPP)(CO)$ shows that the transition of $^1Q_{x(1,0)}(\pi,\pi^*) \rightarrow {}^1Q_{x(0,0)}(\pi,\pi^*)$ takes about 230fs and the lifetime of inter crossing of $^1Q_{x(0,0)}(\pi,\pi^*) \rightarrow {}^3T(\pi,\pi^*)$ or emission (fluorescence) lifetime of $^1Q_{x(0,0)}(\pi,\pi^*) \rightarrow S_0$ were about 1060fs. On the other hand, in the case of six-coordinate complex of $Ru^{II}(TPP)(CO)$(acetone), the transition of $^1Q_{x(1,0)}(\pi,\pi^*) \rightarrow {}^1Q_{x(0,0)}(\pi,\pi^*)$ takes about 90fs and the lifetime of inter crossing of $^1Q_{x(0,0)}(\pi,\pi^*) \rightarrow {}^3T(\pi,\pi^*)$ or emission (fluorescence) lifetime of $^1Q_{x(0,0)}(\pi,\pi^*) \rightarrow S_0$ were about 500fs. Moreover, it was clarified that the inter crossing between singlet state and triplet state proceeds not suddenly but gradually. In addition, the stimulated emission of the phosphorescence from $^3T(\pi,\pi^*)$ and $^3T(d,\pi^*)$ was observed for the first time.

2. Experimental

A sub-5fs pulse laser developed in our group [13,14] was used to observe Ru^{II} porphyrin complexes. Pump and probe pulses were generated by a NOPA (Non-collinear Optical Parametric Amplifier) seeded by a white-light continuum with a sub-5 fs pulse compressor system. The pump source of the NOPA is a regenerative amplifier (Spectra-Physics, model Spitfire), whose pulse duration, central wavelength, and repetition rate are 100 fs, 790 nm, and 5 kHz, respectively. The spectrum of the pulses covered from 525 to 725 nm with a nearly constant phase. 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 2580 and 480 GW cm^{-2}, respectively. The focus areas of the pump and probe pulses are 100 and 75 µm^2, respectively with a common center on a back surface of the front wall plate of a cell of 1mm-optical path length. All measurements were performed at room temperature (295 ± 1 K). Time-resolved difference transmittance ΔT at 128 wavelengths in the spectral range extending from 525 to 725 nm was measured simultaneously using a multi-channel lock-in amplifier coupled to a polychromater.

The Gaussian 03 program [15] was used for the theoretical calculations. Geometry optimizations were performed with B3LYP/6-31G*//B3LYP/6-31G* [16,17] and CIS/6-31G*//CIS/6-31G*. (The 3-21G* basis set was substituted for 6-31G* in the case of the ruthenium atom.) As for the d orbital, $5d$ functions were used. The calculation was performed without assuming any symmetry. The frequency calculations were performed for all of the obtained structures at the same level. It was confirmed that all the frequencies were real for the ground states. $Ru^{II}(por)(CO)$ complex (por = porphyrin) without four phenyl group was used for the model complex instead of $Ru^{II}(TPP)(CO)$ for simplicity of the calculation.

3. Results and discussion

Chloroform does not coordinate to $Ru^{II}(TPP)(CO)$, but acetone coordinates to $Ru^{II}(TPP)(CO)$ [18,19] generating six-coordinate Ru^{II} porphyrin. Figure 1 shows UV absorption spectrum of the five-coordinate $Ru^{II}(TPP)(CO)$ solved in deoxidized $CHCl_3$ consisted of two bands of $Q_x(1,0)$ band at λ_{max}=528.5 nm and $Q_x(0,0)$ band at λ_{max}=559.5 nm.
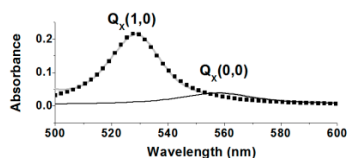

Figure 1. Visible absorption spectra of $Q_x(1,0)$ and $Q_x(0,0)$ of $Ru^{II}(TPP)(CO)$ (gray curves) obtained from the absorption spectrum of the sample fitted by two Lorentzian functions ($Q_x(1,0)$: black dots, $Q_x(0,0)$: black line).

3.1. Time-resolved spectroscopy of $Ru^{II}(TPP)(CO)$

3.1.1. Electronic state dynamics

We have used a sub-5fs pulse laser developed in our group to observe the real-time dynamics of $Ru^{II}(TPP)(CO)$ in the delay time region from -100 to 3500 fs with 1fs step. The signal of ΔA was observed to be negative in all of the probe wavelength area of 525-720nm and it has a peak at λ_{max}=593nm. The spectrum of ΔA is similar to simulated spectrum of stimulated emission (λ_{max}=595nm) of $Ru^{II}(TPP)(CO)$. The stimulated emission spectrum was calculated from the emission spectrum of the sample excited at λ_{exc}=515 nm ($Q_x(1,0)$ band) and that of the sample excited at λ_{exc}=550 nm ($Q_x(0,0)$ band) using the Einstein coefficients A_{nm} (spontaneous emission) and B_{nm} (stimulated emission) in the equation of $A_{nm}=(2hc/\lambda^3)B_{nm}$.

Effective back donation in $d\pi \rightarrow CO(\pi^*)$ lowers the energy of $d\pi$ orbital of Ru^{II}. Therefore, the lowest excited state of $Ru^{II}(TPP)(CO)$ is (π,π^*) [10,20]. The emission spectrum of $Ru^{II}(TPP)(CO)$ excited at λ_{exc}=515 nm and that of the sample excited at λ_{exc}=550 nm have similar spectral shape. It is thought that because of quick relaxation of $^1Q_{x(1,0)}(\pi,\pi^*) \rightarrow {}^1Q_{x(0,0)}(\pi,\pi^*)$ after the photo-excitation at λ_{exc}=515 nm makes $^1Q_{x(0,0)}(\pi,\pi^*)$ to be the main contribution of the emission source. The emission peaked at λ_{max}=590 nm was assigned to fluorescence being main contribution of the ΔA signal. This is because, in the case of, the phosphorescence from the lowest triplet state $^3(\pi,\pi^*)$ of $Ru^{II}(TPP)(CO)(py)$ excited at λ_{exc}=530 nm ($Q_x(1,0)$ band) was observed to be peaked at λ_{max}=726 nm at room temperature [9,11]. The florescence spectrum of $Ru^{II}(TPP)(CO)(dansyl-imidazole)$ was peaked at ca. λ_{max}=560 nm as is reported in [21]. In the case of $Ru^{II}(OEP)(CO)(py)$ (OEP=octaethylporphyrin), the phosphorescence spectrum from $^3(\pi,\pi^*)$ and the florescence spectrum were reported to be peaked at λ_{max}=658 nm and λ_{max}=556 nm, respectively [22,23].

Decay times of the florescence was estimated by fitting the observed real-time ΔA traces with the function of $f(t)=A_1(\exp(-t/\tau_1))+A_2(\exp(-t/\tau_2))+A_3(\exp(-t/\tau_3))+A_4(\exp(-t/\tau_4))$, where $\tau_1<\tau_2<\tau_3<\tau_4$. The parameters τ_1, τ_2, τ_3, and τ_4 are estimated as 230±70 fs, 1150±260 fs, 2150±360 fs, and »4.8 ps, respectively.

3.1.2. Vibrational state dynamics

Theoretical calculation result shows that singlet state of $Ru^{II}(por)(CO)$ has an anti-symmetric porphyrin ring stretching mode observed at 1040 cm^{-1}. On the other hand, in case of triplet state of $Ru^{II}(por)(CO)$, this mode is blue-shifted to 1100 cm^{-1}, and a new peak of porphyrin ring bending mode appears at 990 cm^{-1}. Using the spectrogram analysis, we have detected the transitional change of these molecular vibration modes during the intersystem crossing from singlet state to triplet state. Figure 2 shows the spectrogram calculated from the ΔA trace probed at 600 nm using the Blackman window function whose FWHM is 240 fs. The frequency resolution of the spectrogram was estimated as 30cm^{-1}. About 300fs after the photo-excitation, porphyrin ring stretching mode was observed at around 1036 cm^{-1}, which agrees well with the calculated frequency of 1040 cm^{-1}. This peak is blue shifted to 1150 cm^{-1} in the delay time range from ~600 fs to 1 ps. The peak centered around 900 cm^{-1} that appears at ~1 ps is due to the intercrossing to triplet state. It is consistent with the theoretical calculation result suggesting the appearance of the porphyrin ring bending mode at 990 cm^{-1}. The result of this spectrogram analysis also shows that lifetime of the singlet excited state is about 1ps, and has a good agreement with the results obtained in the electronic state analysis. The observed gradual blue shift of the anti-symmetric porphyrin ring stretching mode to 1150 cm^{-1} shows that the intersystem crossing between singlet state and triplet state proceeds gradually in ~1.0 ps.

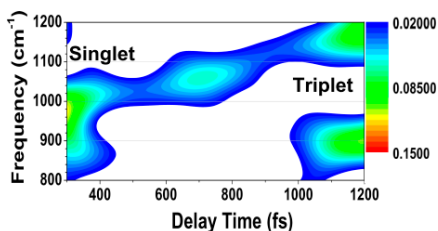Figure 2. Spectrogram calculated from ΔA trace probed at 600 nm.

4. Conclusion

Ultrafast time-resolved absorption change of $Ru^{II}(TPP)(CO)$ solved in chloroform was observed using sub-5fs laser pulses. Fitting the time traces with exponential functions, we determined lifetimes of intermediates in the sequential relaxation after photo excitation of $^1Q_{x(1,0)}(\pi,\pi^*) \rightarrow {}^1Q_{x(0,0)}(\pi,\pi^*) \rightarrow {}^3(d,\pi^*) \rightarrow {}^3(\pi,\pi^*) \rightarrow$ ground state. Spectrogram analysis showed that vibration mode frequency shifts gradually in ~1.0 ps reflecting the intersystem crossing from singlet state to triplet state.

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