

Ultrafast Excited-State Dynamics of Copper(I) Complexes

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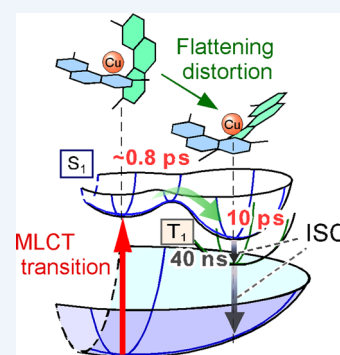
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CONSPECTUS: Bis-diimine Cu(I) complexes exhibit strong absorption in the visible region owing to the metal-to-ligand charge transfer (MLCT) transitions, and the triplet MLCT (³MLCT) states have long lifetimes. Because these characteristics are highly suitable for photosensitizers and photocatalysts, bis-diimine Cu(I) complexes have been attracting much interest. An intriguing feature of the Cu(I) complexes is the photoinduced structural change called "flattening". Bis-diimine Cu(I) complexes usually have tetrahedron-like D_{2d} structures in the ground (S_0) state, in which two ligands are perpendicularly attached to the Cu(I) ion. With MLCT excitation, the central Cu(I) ion is formally oxidized to Cu(II), which induces the structural change to the "flattened" square-planar-like structure that is seen for usual Cu(II) complexes.

In this Account, we review our recent studies on ultrafast excited-state dynamics of bis-diimine Cu(I) complexes carried out using femtosecond time-resolved optical spectroscopy. Focusing on three prototypical bis-diimine Cu(I) complexes that have 1,10-phenanthroline ligands with different substituents at the 2,9-positions, i.e., $[\text{Cu}(\text{phen})_2]^+$ (phen = 1,10-phenanthroline), $[\text{Cu}(\text{dmphen})_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline), and $[\text{Cu}(\text{dpphen})_2]^+$ (dpphen = 2,9-diphenyl-1,10-phenanthroline), we examined their excited-state dynamics by time-resolved emission and absorption spectroscopies with 200 fs time resolution, observed the excited-state coherent nuclear motion with 30 fs time resolution and performed complementary theoretical calculations. This combined approach vividly visualizes excited-state processes in the MLCT state of bis-diimine Cu(I) complexes.

It was demonstrated that flattening distortion, internal conversion, and intersystem crossing occur on the femtosecond–early picosecond time scale, and their dynamics is clearly identified separately. The flattening distortion predominantly occurs in the S_1 state on the subpicosecond time-scale, and the precursor S_1 state retaining the initial undistorted structure appears as a metastable state before the structural change. This observation indicates that the traditional understanding based on the Jahn–Teller effect appears irrelevant for realistically discussing the photoinduced structural change of bis-diimine Cu(I) complexes. The lifetime of the precursor S_1 state significantly depends on the substituents in the three complexes, indicating that the flattening distortion requires a longer time as the substituents at 2,9-positions of the ligands become bulkier. It is suggested that the substituents are rotated to avoid steric repulsions to achieve the flattened structure at the global minimum of the S_1 state, implying the necessity of discussion based on a multidimensional potential energy surface to properly consider this excited-state structural change. After the flattening distortion, the S_1 states of $[\text{Cu}(\text{dmphen})_2]^+$ and $[\text{Cu}(\text{dpphen})_2]^+$, which have bulky substituents, relax to the T_1 state by intersystem crossing on the ~ 10 ps time scale, while the flattened S_1 state of $[\text{Cu}(\text{phen})_2]^+$ relaxes directly to the S_0 state on the ~ 2 ps time scale. This difference is rationalized in terms of the different magnitude of the flattening distortion and relevant changes in the potential energy surfaces. Clear understanding of the ultrafast excited-state process provides a solid basis for designing and using Cu(I) complexes, such as controlling the structural change to efficiently utilize the energy of the MLCT state in solar energy conversion.



1. INTRODUCTION

Transition metal complexes play unique roles in a variety of systems, including biological systems, because they have various redox states, magnetic properties, and structures that are never seen in organic compounds.¹ They have also been attracting much interest in applications, such as solar energy conversion and photodevices. To fully utilize the unique properties of metal complexes, a good understanding of their elementary

photochemical processes is indispensable. Transition metal complexes show fast and complicated excited-state dynamics owing to strong spin–orbit coupling and a high density of states.^{2,3} Therefore, the excited-state dynamics of metal complexes are still far less understood than those of organic

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compounds.^{3–10} However, recent advances in femtosecond spectroscopy now allow us to thoroughly examine the excited-state processes from different perspectives, which make it possible to clearly visualize the complicated ultrafast dynamics of metal complexes.

Bis-diimine Cu(I) complexes such as $[\text{Cu}(\text{dmphen})_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) exhibit strong visible absorption owing to the metal-to-ligand charge transfer (MLCT) transition, and the triplet MLCT ($^3\text{MLCT}$) states have long lifetimes.^{11,12} Because these characteristics are highly suitable for photosensitizers and photocatalysts, bis-diimine Cu(I) complexes have attracted special attention as an alternative to the $[\text{Ru}(\text{bpy})_3]^{2+}$ derivatives that are widely used for these applications.¹³ An intriguing feature of the Cu(I) complexes is the photoinduced structural change called “flattening”. Bis-diimine Cu(I) complexes usually have tetrahedron-like D_{2d} structures in the ground (S_0) state, in which two ligands are attached perpendicularly to each other on the Cu(I) ion. With MLCT excitation, the central Cu(I) ion is formally oxidized to Cu(II), inducing the structural change to the “flattened” square-planar-like structure that is seen for usual Cu(II) complexes (Figure 1). It is considered that this phenomenon can be used in ultrafast molecular switches.^{14,15}

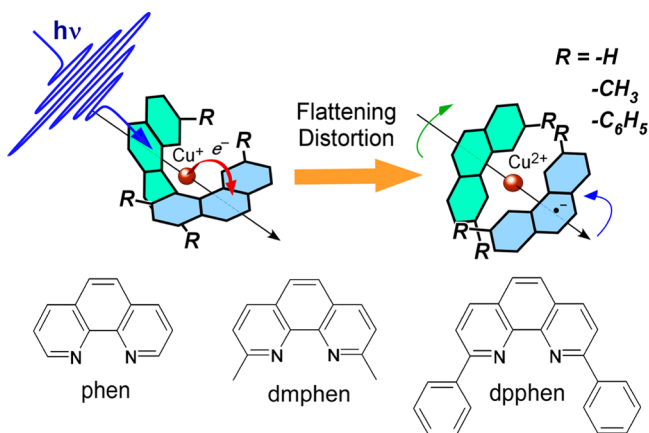


Figure 1. Photoinduced structural change of bis-diimine Cu(I) complexes. The ligands of the three Cu(I) complexes to be discussed are also shown.

To clarify the intriguing properties of bis-diimine Cu(I) complexes, time-resolved spectroscopic studies were performed using time-resolved absorption,^{16–19} time-correlated single-photon counting,²⁰ and time-resolved X-ray^{17,19} techniques. However, clarification of the excited-state processes was difficult because different ultrafast processes, that is, structural change, intersystem crossing, and internal conversion, occur in a competitive manner. Therefore, their ultrafast dynamics was ambiguous or even controversial. One of the problems is that each type of spectroscopy can provide only limited information from one aspect; this is inadequate to unveil the complicated processes taking place in the excited state of the complexes.

In this Account, we review a series of our recent studies on ultrafast excited-state dynamics of bis-diimine Cu(I) complexes. Focusing on three prototypical bis-diimine Cu(I) complexes that have 1,10-phenanthroline ligands with different substituents at 2,9-positions, i.e., $[\text{Cu}(\text{phen})_2]^+$ (phen = 1,10-phenanthroline), $[\text{Cu}(\text{dmphen})_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline), and $[\text{Cu}(\text{dpphen})_2]^+$ (dpphen = 2,9-diphenyl-1,10-phenanthroline) (Figure 1), we examined their

excited-state dynamics by time-resolved emission^{21,22} and absorption spectroscopies^{23,24} with 200 fs time resolution, observed the excited-state coherent nuclear motion with 30 fs time resolution,^{23,24} and also performed complementary quantum chemical calculations.²³ Our challenge was making the obscure ultrafast dynamics of the metal complexes clear by this combined approach. We show how a unified view of the excited-state processes of the Cu(I) complexes is obtained by gathering pieces of information provided from each approach.

2. ELECTRONIC STRUCTURE, STEADY-STATE SPECTRA, AND EXCITED-STATE STRUCTURAL CHANGE OF BIS-DIIMINE Cu(I) COMPLEXES

The photochemical/photophysical properties of bis-diimine Cu(I) complexes are directly related to the low-lying excited states that have MLCT characteristics. We first describe electronic structures, steady-state spectra, and the traditional picture of the excited-state structural change, as the basis for discussing the data obtained by ultrafast spectroscopy.

The bis-diimine Cu(I) complexes usually take a D_{2d} tetrahedron-like structure in the S_0 state, in which two diimine ligands are perpendicularly attached to the Cu(I) ion whose d-orbitals are fully occupied (d^{10}).²⁵ The d orbitals of the Cu(I) are separated into four groups, degenerate d_{xz} and d_{yz} and nondegenerate d_{xy} , $d_{x^2-y^2}$, and d_{z^2} , in the order of energy (Figure 2d). MLCT excitation transfers one electron to the ligands, and the central copper formally becomes Cu(II) (d^9), which has a degenerate electronic state of E symmetry. On the ligand side, one electron is transferred to the LUMO of E symmetry.^{25,26} Consequently, the electronic states of the MLCT excited states have symmetries deduced from $E \otimes E$, which are A_1 , B_1 , B_2 , and A_2 . Among them, only B_2 symmetry is dipole allowed (Figure 2d).

Figure 2 shows steady-state absorption of the three bis-diimine Cu(I) complexes discussed in this Account. Their absorption spectra are characterized by an intense band at ~ 450 nm and a weaker band at ~ 550 nm, both of which are due to the MLCT transition. Hereafter, we call these two absorption bands the $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ transition bands, for convenience. $[\text{Cu}(\text{dmphen})_2]^+$ and $[\text{Cu}(\text{phen})_2]^+$ have perpendicular D_{2d} structures in the S_0 state,²⁷ and the strong $S_2 \leftarrow S_0$ absorption is assignable to the transition to the B_2 state, whereas the weaker $S_1 \leftarrow S_0$ absorption is assigned to the transition to the A_2 state.²⁶ The $A_2 \leftarrow A_1$ transition is dipole forbidden, but it acquires significant intensity through the vibronic coupling with the B_2 state²⁶ or dynamic symmetry lowering due to large amplitude motions such as flattening.²⁷ In the absorption spectrum of $[\text{Cu}(\text{dpphen})_2]^+$, the $S_1 \leftarrow S_0$ absorption band has a much higher intensity, reflecting the distorted structure in the S_0 state. Because of the steric effect of the phenyl substituents, the S_0 structure changes from the perpendicular D_{2d} geometry to a flattened D_2 geometry.²⁸ The B_2 and A_2 point groups of D_{2d} become B_1 in the D_2 geometry, and both $B_1 \leftarrow A_1$ transitions are dipole allowed in $[\text{Cu}(\text{dpphen})_2]^+$ (Figure 2d).

The steady-state emission spectra are also shown in Figure 2. $[\text{Cu}(\text{dmphen})_2]^+$ and $[\text{Cu}(\text{dpphen})_2]^+$, which have bulky substituents in the ligand, exhibit long-lived emission at around 700–800 nm. The emission is attributed to the phosphorescence from the lowest $^3\text{MLCT}$ state with substantial fluorescence from the thermally populated $^1\text{MLCT}$ state (delayed fluorescence).²⁹ The large Stokes shift of the emission indicates that a large structural change occurs in the excited

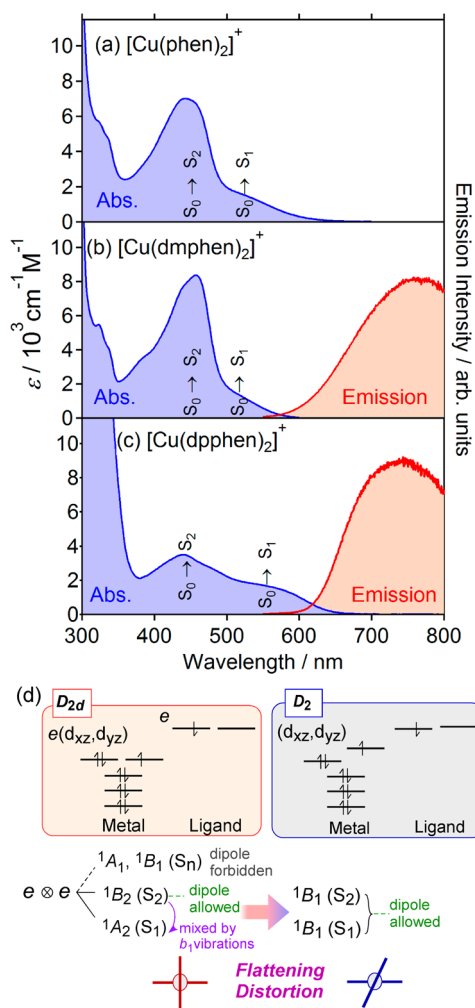


Figure 2. (a–c) Steady-state absorption and emission spectra of $[\text{Cu}(\text{phen})_2]^+$, $[\text{Cu}(\text{dmphen})_2]^+$, and $[\text{Cu}(\text{dpphen})_2]^+$ in dichloromethane. Reference 22 - Reproduced by permission of the PCCP Owner Societies. (d) Electronic configurations of Cu(I) complex in D_{2d} and D_2 structures.

states.³⁰ In sharp contrast, $[\text{Cu}(\text{phen})_2]^+$ does not show any long-lived emission. This difference has been explained by a larger structural change in the excited state of $[\text{Cu}(\text{phen})_2]^+$, which is possible owing to the absence of the steric effect.^{30,31}

The excited-state structural change of bis-diimine Cu(I) complexes has been discussed in terms of Jahn–Teller distortion. The simplest explanation would involve the first-order Jahn–Teller effect because the central Cu(I) ion formally becomes Cu(II) with MLCT excitation, and the Cu(II) ion has the degenerate electronic state at the perpendicular structure. However, the MLCT excited state is not degenerate from the viewpoint of the molecular orbital of the whole molecule. Thus, the structural change in the MLCT state was considered in terms of a pseudo-Jahn–Teller effect (the second-order Jahn–Teller effect)³¹ that is based on the following expansion of the excited-state potential curve with respect to a nuclear coordinate:³²

$$E(Q) = E_e + \left(\frac{1}{2} \left\langle \psi_e \left| \frac{\partial^2 \hat{H}}{\partial Q^2} \right| \psi_e \right\rangle + \sum_{n \neq e} \frac{\left| \left\langle \psi_n \left| \frac{\partial \hat{H}}{\partial Q} \right| \psi_e \right\rangle \right|^2}{E_e - E_n} \right) Q^2 \quad (1)$$

$$= E_e + fQ^2 \quad (2)$$

As seen, when the f value becomes negative ($f < 0$), the potential curve has a parabolic feature opening downward. This gives rise to the structural instability at the initial $Q = 0$ geometry and induces a structural change. Although the theory of the Jahn–Teller effect does not predict the direction of the distortion, absorption and emission studies of crystals indicated that a flattening distortion determines the spectroscopic properties of bis-diimine Cu(I) complexes.³¹ The flattening distortion in the MLCT state was also supported by time-resolved XAFS¹⁷ and quantum chemical calculations.^{17,20,33}

3. EXCITED-STATE DYNAMICS CLARIFIED BY FEMTOSECOND TIME-RESOLVED FLUORESCENCE AND ABSORPTION SPECTROSCOPY WITH 200 fs TIME RESOLUTION

The steady-state electronic spectra indicate that a structural change occurs in bis-diimine Cu(I) complexes after photoexcitation. However, they do not indicate what actually happens in the excited state, that is, when and how the change takes place in competition with other relaxation processes such as internal conversion and intersystem crossing. Because these processes occur on a very short time scale, femtosecond time-resolved spectroscopy is necessary to elucidate the excited-state dynamics. In this section, we describe, for $[\text{Cu}(\text{dmphen})_2]^+$, how clearly the excited-state processes are observed and identified by femtosecond time-resolved spectroscopy with a time resolution of ~ 200 fs.

Figure 3a shows femtosecond time-resolved fluorescence spectra of $[\text{Cu}(\text{dmphen})_2]^+$ measured with $S_2 \leftarrow S_0$ excitation at 420 nm.²¹ These spectra have been reconstructed from the temporal fluorescence traces measured at different wavelengths by up-conversion. The three time regions that correspond to three distinct relaxation processes are separately shown. In the 0–0.3 ps region, intense fluorescence appears at around 500 nm, which is attributed to the fluorescence from the S_2 state generated by photoexcitation. This S_2 fluorescence decays with a ~ 50 fs time constant by $S_2 \rightarrow S_1$ internal conversion, leaving a weak fluorescence ascribable to the S_1 state. In the next 0.3–1 ps region, a drastic spectral change of the S_1 fluorescence is observed. The S_1 fluorescence initially exhibits a peak at 550 nm, and then a new peak appears at around 700 nm in accordance with the decay of the 550 nm fluorescence. The initial 550 nm fluorescence appears in the region of the $S_1 \leftarrow S_0$ absorption of the S_0 state that has the perpendicular structure, and the 700 nm fluorescence appears in the region close to the phosphorescence of the flattened ${}^3\text{MLCT}$ state. Therefore, the drastic S_1 fluorescence change is attributed to the flattening structural change. This dynamics becomes slower in a more viscous solvent, confirming this assignment.²¹ The area-integrated time-resolved fluorescence intensity is kept almost constant during this change, showing that the structural change occurs on a single electronic state (i.e., the S_1 state). The fluorescence of the flattened S_1 state decays on the 10 ps time scale, leaving the long-lived phosphorescence. The quantitative

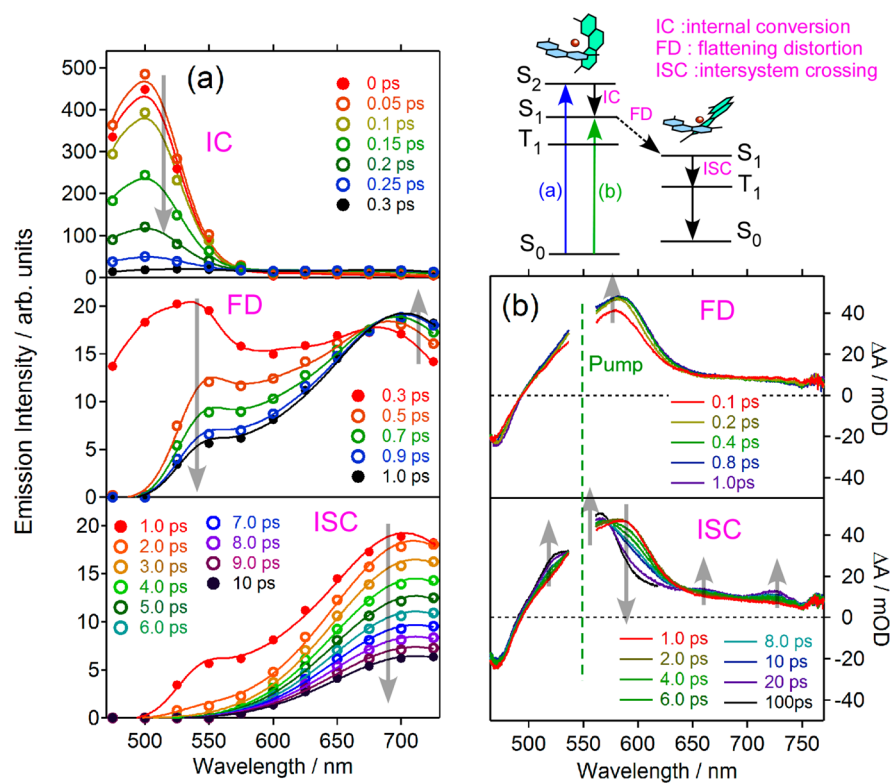


Figure 3. Femtosecond time-resolved fluorescence spectra (a) and absorption spectra (b) of $[\text{Cu}(\text{dmphen})_2]^+$ measured with 200 fs time resolution in dichloromethane. Reprinted with permission from refs 21 and 23. Copyright 2007 and 2011 American Chemical Society.

analysis of the time-resolved fluorescence spectra provides information about the oscillator strengths of each fluorescence component,^{34–36} which supports the above assignments.²¹ Femtosecond time-resolved fluorescence spectra clearly show that the $S_2 \rightarrow S_1$ internal conversion, the flattening distortion in the S_1 state, and the $S_1 \rightarrow T_1$ intersystem crossing occur sequentially after $S_2 \leftarrow S_0$ excitation of $[\text{Cu}(\text{dmphen})_2]^+$, and the time scales of the three processes are well separated.

We note that there is another minor pathway from the S_2 state in addition to the above-described major relaxation pathway. The difference in the S_1 fluorescence yield obtained with the $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ excitations indicated that 30% of the S_2 state directly generates the triplet state, which is relaxed to the flattened $^3\text{MLCT}$ state bypassing the S_1 state.^{21,22}

Time-resolved absorption spectroscopy is another powerful method for investigating ultrafast excited-state dynamics. It can detect all the transient species including the bleaching of the S_0 state, although time-resolved fluorescence spectroscopy only monitors the emissive singlet excited states. However, time-resolved absorption measurements with S_2 excitation were not able to clarify the excited-state dynamics of the bis-diimine Cu(I) complex well.^{16–18} A reason is that the S_2 state directly generates some triplet state, which makes time-resolved absorption spectra complicated. More importantly, the spectral change of the S_1 absorption accompanying the flattening distortion is very small, as seen in the time-resolved absorption spectra measured with direct S_1 excitation.

Figure 3b shows femtosecond time-resolved absorption spectra of $[\text{Cu}(\text{dmphen})_2]^+$ obtained by $S_1 \leftarrow S_0$ photoexcitation with 200 fs time resolution. Direct S_1 excitation gives rise to a transient absorption peak at 580 nm, which is assigned to the S_1 state that retains the perpendicular geometry. This S_1 absorption exhibits a very small intensity change in the

subpicosecond time region when time-resolved fluorescence shows a drastic spectral change due to the flattening distortion. In other words, the S_1 absorption spectra before and after flattening distortion are very similar. This makes it difficult to identify the flattening distortion using only the time-resolved absorption data, although the time-resolved absorption spectra show a clear spectral change with $S_1 \rightarrow T_1$ intersystem crossing in the early picosecond time region.

As shown, the flattening distortion in the S_1 state is unambiguously identified as a drastic red shift of the time-resolved fluorescence, whereas the $S_1 \rightarrow T_1$ intersystem crossing at the flattened geometry is more readily recognized in time-resolved absorption data. This demonstrates that the complementary use of time-resolved fluorescence and absorption spectroscopy is critically important to gain a proper understanding of the excited-state dynamics.

In the femtosecond time-resolved measurements, the transient spectrum of the S_1 state before the flattening distortion is clearly captured. Furthermore, time-resolved fluorescence spectra exhibit a clear isoemissive point at 675 nm while the structural change is taking place (Figure 3a). This means that the S_1 state before the structural change is a metastable state that has an intrinsic lifetime and that the flattening distortion is considered to be a decay of the perpendicular S_1 state and the corresponding rise of the flattened S_1 state. This finding was surprising because it looked to contradict the simple picture based on the pseudo-Jahn–Teller effect. The Jahn–Teller effect causes the instability of the perpendicular geometry so that an immediate structural change is expected without the appearance of any metastable precursors.

4. OBSERVATION OF EXCITED-STATE COHERENT NUCLEAR MOTION

Femtosecond time-resolved fluorescence and absorption data of $[\text{Cu}(\text{dmphen})]^+$ clarified that flattening distortion occurs in the S_1 state and indicated that the metastable perpendicular S_1 state appears before the structural change. Because the Jahn–Teller effect is not expected to generate any precursors of the structural change, it was crucially important to clarify the properties of this precursor S_1 state. Particularly, we thought that the key was whether this state has a well-defined vibrational structure like an ordinary “bound” state.

Photoexcitation using extremely short optical pulses can populate the excited state that has the initial S_0 structure at the Franck–Condon region. This state is not a stationary state, and hence, the nuclei start moving (or vibrating) immediately. Thus, coherent nuclear motion is induced in the excited state, which can be monitored through the oscillation of the transient signal. This oscillation directly reflects the vibrational structure of the excited state generated by photoexcitation, and its Fourier transform provides the vibrational spectrum. Using this time-domain approach, we attempted to catch the vibration of the precursor state of the structural change.²³

Figure 4a shows the temporal trace of the transient absorption of $[\text{Cu}(\text{dmphen})_2]^+$ measured with $S_1 \leftarrow S_0$

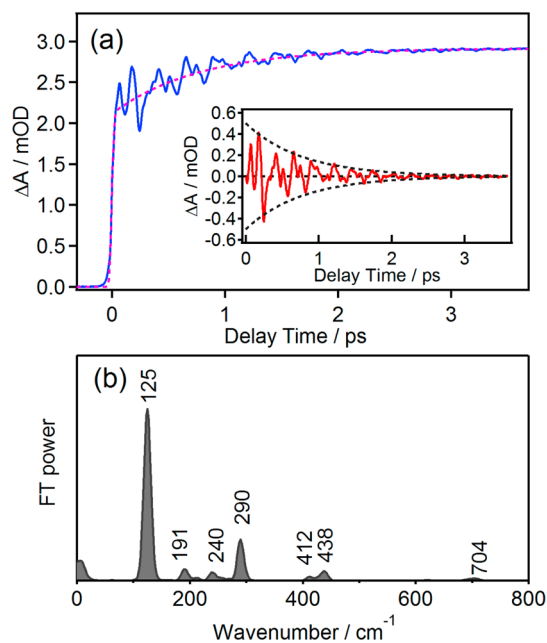


Figure 4. (a) Temporal trace of the S_1 transient absorption of $[\text{Cu}(\text{dmphen})_2]^+$ measured with 30 fs time resolution in dichloromethane. Inset: Extracted oscillatory component and the exponential fit drawn with a time constant of 770 fs (dashed line). Pump = 540 nm; probe = 650 nm. (b) Fourier transform power spectrum of the oscillation component. Reprinted with permission from ref 23. Copyright 2011 American Chemical Society.

photoexcitation using ~ 15 fs pulses for the pump (~ 540 nm) and probe (~ 650 nm). In this experiment, the total intensity of the probe pulse is detected to measure the intensity change of the transient absorption at ~ 650 nm (i.e., the two-color pump–probe experiment). The molecular vibrations that have longer periods than the time resolution of the measurement are observed as intensity oscillations of the transient signal. As clearly seen, the transient absorption signal exhibits a clear

oscillation on the population component. The observed oscillation is attributable to the coherent nuclear motion of the perpendicular S_1 state that is generated by photoexcitation. This observation of coherent nuclear motion reveals that the precursor of the flattening distortion has well-defined vibrational structures. In other words, the S_1 state retains the initial perpendicular structure while vibrating during its short lifetime before the structural change. The oscillation of the transient absorption decays with a time constant of ~ 0.8 ps, which agrees with the time constant of the flattening distortion.

Figure 4b shows the Fourier transform of the oscillation of the transient absorption signal. Several vibrations contribute to the oscillation, and the contribution of the 125 cm^{-1} vibration is the largest. The normal coordinate analysis of the perpendicular S_1 state by TD-DFT calculations indicates that this 125 cm^{-1} vibration is assignable to the “breathing” vibration of the complex (Figure 5a). Actually, it is natural

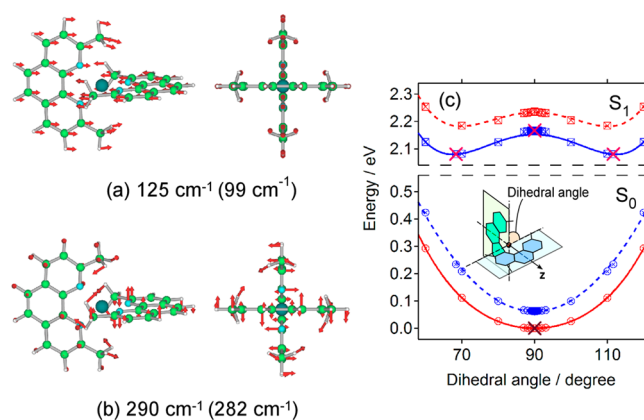


Figure 5. Two predominant coherent nuclear motions induced by direct $S_1 \leftarrow S_0$ photoexcitation of $[\text{Cu}(\text{dmphen})_2]^+$. The assignments are based on TDDFT calculations that reproduce the perpendicular and flattened structures of the S_0 and S_1 states, respectively, as shown in (c). Reprinted with permission from ref 23. Copyright 2011 American Chemical Society.

that this breathing motion is induced by photoexcitation. With MLCT excitation, one electron in the HOMO having some antibonding character of the Cu–N bonds is excited to the LUMO, and the electrostatic attraction between copper and ligands increases. Thus, the complex feels sudden compaction forces that shorten the Cu–N bond, and coherent breathing vibration is induced. The vibrations at 191, 412, 438, and 704 cm^{-1} in the Fourier power spectrum are also attributable to the totally symmetric vibrations that contain Cu–N stretch motions. The second largest 290 cm^{-1} vibration is exceptional, and it is assigned to a ligand-twisting b_1 vibration (Figure 5b). This coherent b_1 motion is intriguing because flattening motion also has b_1 symmetry. The energy most probably flows efficiently from the coherently excited ligand-twisting b_1 vibration to the flattening motion because motions having the same symmetry can be coupled with anharmonicity.

5. SUBSTITUENT EFFECT ON THE EXCITED-STATE DYNAMICS AND RELAXATION PATHWAY

In the previous two sections, we described how the combined use of femtosecond spectroscopies can clarify the ultrafast excited-state processes of $[\text{Cu}(\text{dmphen})_2]^+$. As described in section 2, the steady-state electronic spectra are significantly

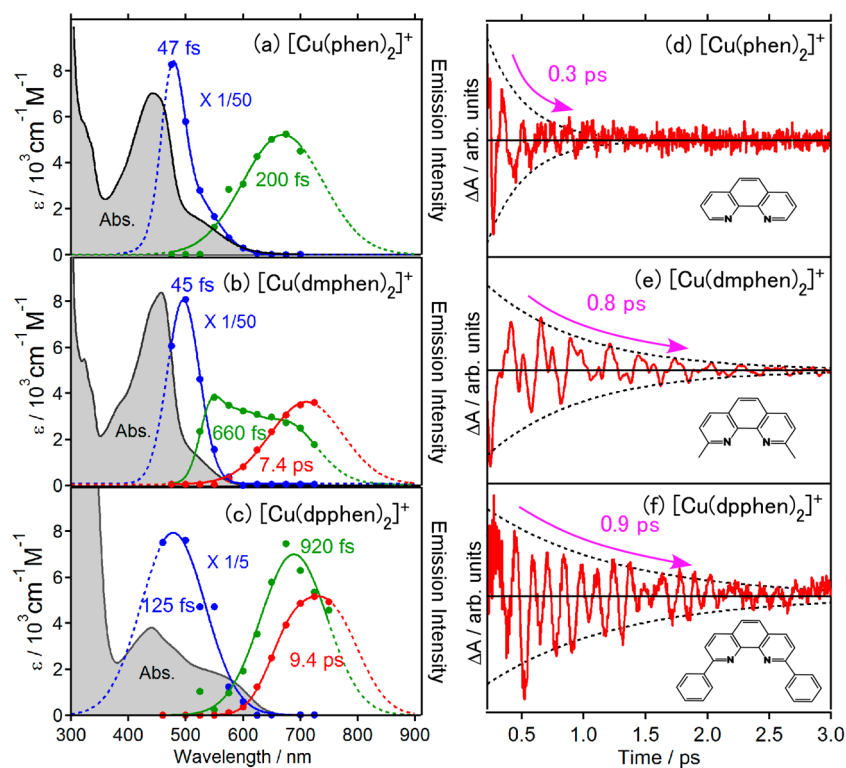


Figure 6. Fluorescence spectra of the S_2 (blue), precursor S_1 (green), and flattened S_1 (red) states of (a) $[\text{Cu}(\text{phen})_2]^+$, (b) $[\text{Cu}(\text{dmphen})_2]^+$, and (c) $[\text{Cu}(\text{dpphen})_2]^+$ in dichloromethane. The oscillatory component of the S_1 time-resolved absorption signal of (d) $[\text{Cu}(\text{phen})_2]^+$, (e) $[\text{Cu}(\text{dmphen})_2]^+$, and (f) $[\text{Cu}(\text{dpphen})_2]^+$ measured with direct $S_1 \leftarrow S_0$ photoexcitation. References 22 and 24, Reproduced by permission of the PCCP Owner Societies.

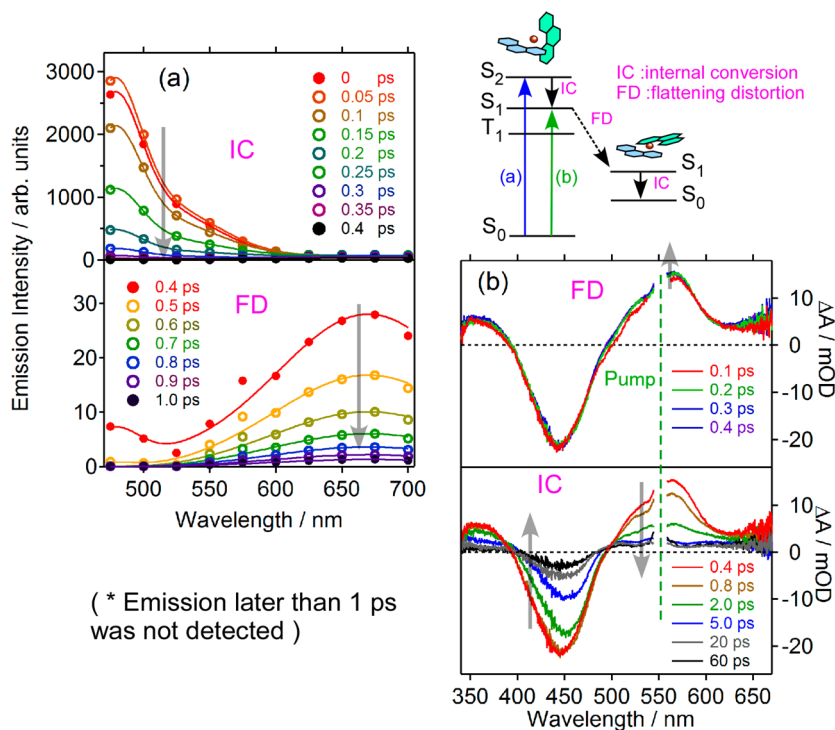


Figure 7. Femtosecond time-resolved fluorescence spectra (a) and absorption spectra (b) of $[\text{Cu}(\text{phen})_2]^+$ measured with 200 fs time resolution in dichloromethane. References 22 and 24 - Reproduced by permission of the PCCP Owner Societies.

changed by the substituents introduced to the 2,9-positions of the phenanthroline ligand through the steric effect. To clarify the substituent effect on the excited-state dynamics, we carried

out femtosecond time-resolved measurements for $[\text{Cu}(\text{phen})_2]^+$ and $[\text{Cu}(\text{dpphen})_2]^+$ and compared the excited-state dynamics of the three Cu(I) complexes.^{22,24}

The analysis of time-resolved fluorescence data provides the fluorescence spectra of the S_2 state, precursor S_1 state, and flattened S_1 state and their lifetimes of the three Cu(I) complexes, as shown in Figure 6a–c. With the $S_2 \leftarrow S_0$ photoexcitation, it is common for the strong S_2 fluorescence (blue) to appear immediately, and the fluorescence of the precursor S_1 state (green) is observed after the decay of the S_2 fluorescence on the 50–100 fs time scale. Because the fluorescence of the precursor S_1 state appears in the wavelength region close to the $S_1 \leftarrow S_0$ absorption, it is safe to consider that the S_1 state initially retains the structure of the S_0 state in all three Cu(I) complexes. The precursor S_1 state is a well-defined metastable state, and the coherent nuclear motion is observed with direct S_1 excitation in the two-color pump–probe measurements using ultrashort pulses (Figure. 6d–f).^{23,23} The lifetime of this precursor (i.e., the time constant of the structural change) shows a clear dependence on the substituents. It becomes longer as the substituents become bulkier: 200 fs ($[\text{Cu}(\text{phen})_2]^+$) < 660 fs ($[\text{Cu}(\text{dmphen})_2]^+$) < 920 fs ($[\text{Cu}(\text{dpphen})_2]^+$). It is noted that $[\text{Cu}(\text{dpphen})_2]^+$ can retain the initial structure in the S_1 state for ~ 900 fs although it is already distorted in the S_0 state.

The excited-state dynamics of $[\text{Cu}(\text{dpphen})_2]^+$ is very similar to that of $[\text{Cu}(\text{dmphen})_2]^+$. The fluorescence of the flattened S_1 state appears in accordance with the decay of the fluorescence of the precursor S_1 state on the subpicosecond time scale, and it decays with the $S_1 \rightarrow T_1$ intersystem crossing on the time scale of ~ 10 ps. The S_1 fluorescence of $[\text{Cu}(\text{phen})_2]^+$ decays much faster (~ 200 fs), and the fluorescence of the flattened S_1 state is not observed in the visible region. However, the femtosecond time-resolved absorption clearly show that the flattened S_1 state appears after the structural change also in the case of $[\text{Cu}(\text{phen})_2]^+$. Figure 7 compares femtosecond time-resolved fluorescence spectra (measured with $S_2 \leftarrow S_0$ excitation) and femtosecond time-resolved absorption spectra (measured with $S_1 \leftarrow S_0$ excitation) of $[\text{Cu}(\text{phen})_2]^+$. Time-resolved absorption data clearly show the spectral change corresponding to the structural change (i.e., a small intensity increase of the S_1 absorption), and the transient absorption due to the flattened S_1 state remains after the fluorescence of the precursor S_1 state decays. Thus, the flattened S_1 state is surely populated although its fluorescence is not observed in the visible region.

Flattening distortion occurs more or less in a similar manner in the S_1 states of the three Cu(I) complexes, although the time constant of the process is changed by the steric effect. However, it was revealed that the relaxation pathway of the flattened S_1 state of $[\text{Cu}(\text{phen})_2]^+$ is markedly different from those of the other two. As seen in Figure 7b, the flattened S_1 state of $[\text{Cu}(\text{phen})_2]^+$ decays with the time constant of ~ 2 ps. It does not efficiently generate the T_1 state but mainly induces the recovery of S_0 bleaching at ~ 450 nm. This indicates that the major relaxation pathway of the flattened S_1 state of $[\text{Cu}(\text{phen})_2]^+$ is the internal conversion to the S_0 state, while the flattened S_1 states of $[\text{Cu}(\text{dmphen})_2]^+$ and $[\text{Cu}(\text{dpphen})_2]^+$ are relaxed to the T_1 state by intersystem crossing. Note that this difference originates not from the difference in the intersystem crossing rate but from the ultrafast internal conversion of $[\text{Cu}(\text{phen})_2]^+$. The intersystem crossing rate estimated from the triplet yield of $[\text{Cu}(\text{phen})_2]^+$ is $(\sim 10 \text{ ps})^{-1}$, which is not so different from the others. This indicates that there is no large difference in the spin–orbit coupling.²⁴

The time constants of excited-state processes of the three Cu(I) complexes are compared in Table 1.

Table 1. Lifetimes of Low-Lying Excited States of the Copper(I) Complexes in Dichloromethane at Room Temperature

state ^a	τ / ps					
	$[\text{Cu}(\text{phen})_2]^+$		$[\text{Cu}(\text{dmphen})_2]^+$		$[\text{Cu}(\text{dpphen})_2]^+$	
S_2^{IS}	0.047 ^b		0.045 ^b		0.135 ^b	
S_1^{IS}	0.20 ^b	0.2 ^c	0.66 ^b	0.9 ^c	0.92 ^b	0.9 ^c
S_1^{FS}	1.8 ^c		7.4 ^b		9.4 ^b	
T_1^{FS}			4.1×10^{4b}		1.35×10^{5b}	

^aIS denotes the state retaining the initial structure, while FS denotes the state having the flattened structure. ^bTime constants are determined by time-resolved emission spectroscopy. ^cTime constants are determined by time-resolved absorption spectroscopy.

6. EXCITED-STATE PROCESSES AND RELEVANT POTENTIAL ENERGY SURFACES OF Cu(I) DIIMINE COMPLEXES

The ultrafast processes in the MLCT excited states of the three Cu(I) diimine complexes, as well as the substituent effects, are summarized in Figure 8. Photoexcitation through the dipole allowed S_2 absorption generates the S_2 state that essentially keeps the structure of the S_0 state. The S_2 state predominantly relaxes to the S_1 state on the 50–100 fs time scale, although some direct intersystem crossing also occurs. The resultant “precursor” S_1 state holds the initial structure for its subpicosecond lifetime before flattening distortion. The lifetime of the precursor S_1 state significantly depends on the substituents at 2,9-positions of the ligand, and the flattening distortion requires a longer time as the substituents become bulkier. The flattened S_1 states of $[\text{Cu}(\text{dmphen})_2]^+$ and $[\text{Cu}(\text{dpphen})_2]^+$, which have bulky substituents, relax to the T_1 state by intersystem crossing on the ~ 10 ps time scale, while the flattened S_1 state of $[\text{Cu}(\text{phen})_2]^+$ relaxes directly to the S_0 state by the fast internal conversion on the ~ 2 ps time scale. This ultrafast $S_1 \rightarrow S_0$ internal conversion of $[\text{Cu}(\text{phen})_2]^+$ is the reason why long-lived phosphorescence is not observed in the steady-state emission spectrum.

The relaxation pathway of the S_1 state of $[\text{Cu}(\text{phen})_2]^+$ is markedly different from those of the other two complexes. It is considered that this difference arises from the different magnitude of the flattening distortion in the S_1 state. Because $[\text{Cu}(\text{phen})_2]^+$ has no bulky substituent on the ligands, the steric effect is minimum. Thus, $[\text{Cu}(\text{phen})_2]^+$ can change its structure greatly in the S_1 state and becomes close to the square planar structure. Consequently, the energy gap between the S_1 and S_0 states becomes small in the flattened geometry, which accelerates the $S_1 \rightarrow S_0$ internal conversion. Because the rate of the $S_1 \rightarrow S_0$ internal conversion becomes higher than that of intersystem crossing, the flattened S_1 state of $[\text{Cu}(\text{phen})_2]^+$ predominantly relaxes to the S_0 state by internal conversion. This picture is consistent with the fact that fluorescence of the flattened S_1 state of $[\text{Cu}(\text{phen})_2]^+$ is not observed in the visible region. It is expected to appear in the near-infrared or infrared region, reflecting the small S_1 – S_0 energy gap.

Femtosecond time-resolved measurements show that the flattening distortion in the S_1 state takes more time when the Cu complex has bulky substituents at 2- and 9-positions of the ligand ($[\text{Cu}(\text{phen})_2]^+ < [\text{Cu}(\text{dmphen})_2]^+ \lesssim [\text{Cu}(\text{dpphen})_2]^+$).

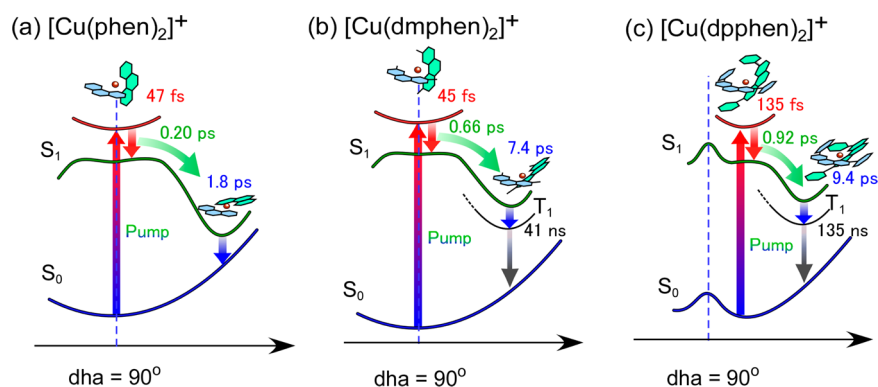


Figure 8. Schematic potential curves and ultrafast relaxation processes of (a) $[\text{Cu}(\text{phen})_2]^+$, (b) $[\text{Cu}(\text{dmphen})_2]^+$, and (c) $[\text{Cu}(\text{dpphen})_2]^+$.

It is tempting to simply rationalize this observation in terms of the difference in the potential barrier along the flattening coordinate on one-dimensional potential curves. However, the argument on only the flattening coordinate is probably not appropriate because other motions, such as rotation of the substituent, also play important roles. In fact, TD-DFT calculation of $[\text{Cu}(\text{dmphen})_2]^+$ shows that the substituents are rotated to avoid steric repulsions in the flattened structure in the S_1 state.²³ This implies that it is necessary to consider the dynamics of the structural change with a *multidimensional* potential energy surface of the S_1 state.

In ultrafast reactions taking place on a short time scale of ~ 1 ps, the excited state generated by photoexcitation (or electronic relaxation) is highly unequilibrated, and the dynamics should be treated as trajectories on the multidimensional potential energy surface (Figure 9). In this view, it is natural that the molecule requires a finite time to change its initial structure by escaping from the initial region on the potential energy surface. The

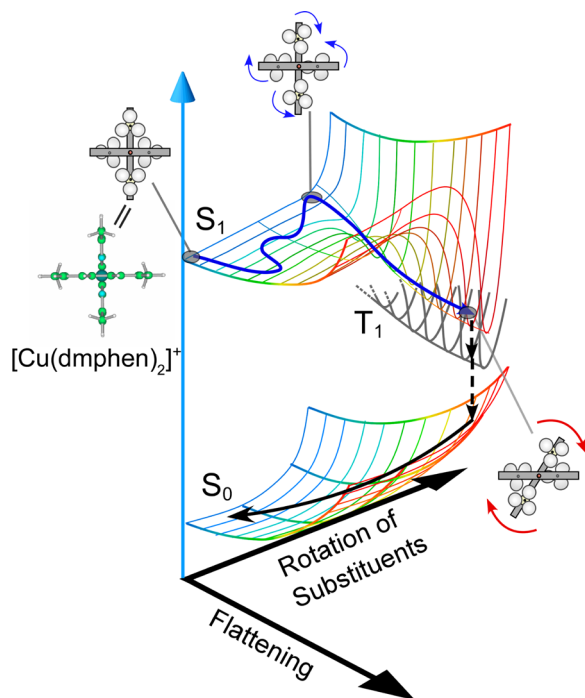


Figure 9. Mechanism of the proposed flattening process of bis-phenanthroline Cu(I) complexes having substituents at 2,9-positions. $[\text{Cu}(\text{dmphen})_2]^+$ is taken as an example.

difference in the lifetime of the initial S_1 state can be considered as the difference in the trajectories that lead to the final flattened structure. As the complex is flattened, the dihedral angle of the two ligands becomes smaller and the pair of substituents at 2,9-positions become close to each other. In the cases of $[\text{Cu}(\text{dmphen})_2]^+$ and $[\text{Cu}(\text{dpphen})_2]^+$, each bulky substituent must rotate on the C–C axis to achieve the flattened structure that has the minimum energy. This makes the trajectories on the S_1 potential energy surface long and complicated. In contrast, $[\text{Cu}(\text{phen})_2]^+$ has no such substituent, and it can change its structure faster without the corresponding motion. Thus, the short lifetime of the precursor S_1 state of $[\text{Cu}(\text{phen})_2]^+$ (200 fs) can be considered as the intrinsic time necessary for the S_1 state to leave the initial region of the potential energy surface directly along the flattening coordinate. We consider the substituent rotation to be the mechanism that makes the structural changes in $[\text{Cu}(\text{dmphen})_2]^+$ and $[\text{Cu}(\text{dpphen})_2]^+$ much slower than that in $[\text{Cu}(\text{phen})_2]^+$. This picture can also explain how the precursor S_1 state of $[\text{Cu}(\text{dpphen})_2]^+$ retains the initial structure for a period as long as ~ 0.9 ps even though the complex is already distorted in the S_0 state. This view of the ultrafast excited-state reactions matches the concept of the *ab initio* MD on the excited-state potential surface.

7. CONCLUDING REMARKS

We have shown how the combined use of different ultrafast optical spectroscopies vividly visualizes excited-state processes occurring in the MLCT state of bis-diimine Cu(I) complexes. The flattening distortion predominantly occurs in the S_1 state on the subpicosecond time scale, but the precursor S_1 state that retains the initial undistorted structure clearly appears before the structural change. Because such precursor states are not expected in the simple picture of the Jahn–Teller distortion, ultrafast spectroscopy showed that the traditional understanding is not appropriate for realistic discussion of the photoinduced structural change of bis-diimine Cu(I) complexes. Substituent effects on the steady-state properties are rationalized from the viewpoint of differences in the excited-state dynamics with relevant changes in the potential energy surfaces. Furthermore, the study indicates the necessity of discussion based on a multidimensional potential energy surface, which is a common important issue in understanding chemical reactions beyond the specific problem for bis-diimine Cu(I) complexes. Clear and proper understanding of the excited-state process provides a solid basis for designing and using Cu(I) complexes, such as controlling the structural

change as well as utilizing the energy of the MLCT state efficiently.

Ultrafast spectroscopy is a powerful tool not only for elucidating fundamental properties of transition metal complexes but also for examining actual processes occurring in real applications such as solar cells. Combinations of suitable ultrafast spectroscopies will unveil the unique phenomena of transition metal complexes and allow us to deepen our fundamental knowledge on transition metal complexes and to utilize them strategically in various purposes.

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