PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Substituent Effect on the MLCT Excited State Dynamics of Cu(I) Complexes Studied by Femtosecond Time-Resolved Absorption and Observation of Coherent Nuclear Wavepacket Motion

Linqiang Hua[1†], Munetaka Iwamura[1§], Satoshi Takeuchi[1,2], Tahei Tahara[1,2*]

[1]Molecular Spectroscopy Laboratory, RIKEN, and [2]Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics (RAP), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

* Author to whom correspondence should be addressed.
Tel: +81-48-467-4592; Fax: +81-48-467-4539; e-mail: tahei@riken.jp

† Current address: State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, P. R. China

§Current address: Department of Chemistry, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan

Abstract

The substituent effect on the excited-state dynamics of bis-diimine Cu(I) complexes was investigated by femtosecond time-resolved absorption spectroscopy with the $S_1 \leftarrow S_0$ metal-to-ligand charge transfer (MLCT) photoexcitation. The time-resolved absorption of $[Cu(phen)_2]^+$ (phen = 1,10-phenanthroline) showed a slight intensity increase of the S_1 absorption with a time-constant of 0.1 – 0.2 ps, reflecting the flattening distortion occurring in the S_1 state. The transient absorption of the 'flattened' S_1 state was clearly observed, although its fluorescence was not observed in the previous fluorescence up-conversion study in the visible region. The flattened S_1 state decayed with a time constant of ~2 ps, and the S_0 bleaching recovered accordingly. This clarifies that the S_1 state of $[Cu(phen)_2]^+$ is predominantly relaxed to the S_0 state by internal conversion. The time-resolved absorption of $[Cu(dpphen)_2]^+$ (dpphen = 2,9-diphenyl-1,10-phenanthroline) showed a 0.9-ps intensity increase of the S_1 absorption due to the flattening distortion, and then exhibited a 11-ps spectral change due to the intersystem crossing. This excited-state dynamics of $[Cu(dpphen)_2]^+$ is very similar to that of $[Cu(dmphen)_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline). In the ultrafast pump-probe measurements with 35-fs time resolution, $[Cu(phen)_2]^+$ and $[Cu(dpphen)_2]^+$ exhibited oscillation due to the nuclear wavepacket motions of the initial S_1 state, and the oscillation was damped as the structural change took place. This indicates that the initial S_1 states have well-defined vibrational structures and that the vibrational coherence is retained in their short lifetimes. The present time-resolved absorption study, together with the previous time-resolved fluorescence study, provides a unified view for the ultrafast dynamics of the MLCT excited state of the Cu(I) complexes.

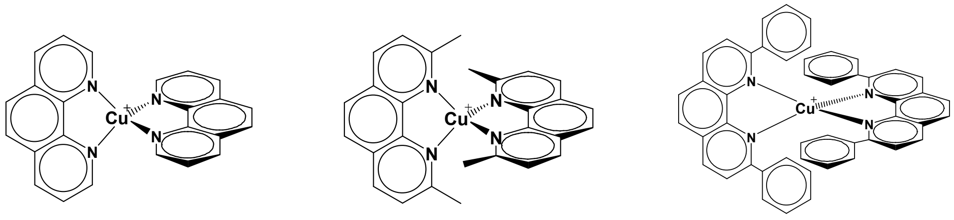
1. Introduction

The photophysical and photochemical properties of bis-diimine copper(I) complexes have attracted a great deal of fundamental interest, because they exhibit a characteristic photoinduced structural change in the metal-to-ligand charge transfer (MLCT) excited state.[1-4] As a prototype of such Cu(I) complexes, $[Cu(dmphen)_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) has been studied extensively.[5-15] This complex has a D_{2d} structure in the electronically ground (S_0) state, where two phenanthroline ligands are attached to the central copper ion perpendicularly to each other.[16, 17] As the copper ion is formally oxidized with the MLCT transition, the conformation of this complex changes from the initial tetrahedral-like D_{2d} structure toward the square-planar structure that is preferred for the Cu(II) complexes. Time-resolved X-ray absorption fine structure (XAFS) measurements experimentally showed that the structure is flattened in the ^{3}MLCT state.[11, 15] Quantum chemical calculations also supported such flattening distortion in the excited state.[10-12, 14, 18]

Because structural changes in the metal complexes are usually very fast processes, the flattening distortion can compete with other fast processes such as internal conversion (IC) and/or intersystem crossing (ISC). To obtain proper understanding about the dynamics and mechanism of photochemical/physical processes of $[Cu(dmphen)_2]^+$, various time-resolved methods have been applied, including picosecond time-correlated single photon counting,[10] femtosecond fluorescence up-conversion,[13, 19, 20] and femtosecond time-resolved absorption spectroscopies.[11, 14, 20-23] Although there was initial controversy for the interpretation of the transient data,[10, 11] we now have a consensus about the dynamics occurring on the femto to picosecond time scale.[13, 14] In particular, our femtosecond time-resolved emission study in solution clarified that the ^{1}MLCT (S_1) state having the perpendicular structure is generated with photoexcitation, and that it stays undistorted for a short time (~0.7 ps) before undergoing a flattening distortion in the S_1 state.[13] The ISC process occurs from the 'flattened' S_1 state to the T_1 state (^{3}MLCT state) with a time constant of ~7 ps. Furthermore, the coherent nuclear wavepacket motion of the initial perpendicular S_1 state was clearly observed by pump-probe spectroscopy performed with time resolution as high as 30 fs.[14] The coherent nuclear motion is induced in the initial S_1 state by MLCT excitation, and it decays as the flattening distortion takes place.

The methyl substituents introduced at the 2- and 9- positions of the phenanthroline ligands sterically hinder [Cu(dmphen)$_2$]$^+$ from achieving the complete square-planar structure with the structural change in the S$_1$ state. This implies that the dynamics and magnitude of the flattening distortion are affected by the substituents and hence that the photochemical properties of the complex are altered by the substituents. Actually, early studies found that the steady-state emission in solution is observed only for the complexes that have bulky substituents at 2- and 9- positions of the phenanthroline ligands.[24] [25] [26]

To clarify the substituent effect on the photochemical/photophysical properties of Cu(I) complexes, it is crucial to examine how excited-state dynamics is influenced by the substituents using time-resolved spectroscopy. Recently, the Chen group studied the effects of the substituents at the 3-, 8-positions and 2-, 9-positions of the phenanthroline ligands by femtosecond time-resolved absorption spectroscopy.[23] [27] They found that the substituents at the 3-, 8-positions do not affect the excited-state properties including the ISC rate, while those at the 2-, 9-positions substantially alter them. We also carried out a systematic femtosecond fluorescence up-conversion study of the substituent effect and compared the fluorescence dynamics of three bis-phenanthroline Cu(I) complexes that have different substituents at the 2-, 9-positions (Figure 1).[19] It was found that bulkier substituents make the structural change in the S$_1$ state slower. We discussed the relevant mechanism from a viewpoint of excited-state trajectories on the multi-dimensional potential energy surface, taking account of the nuclear degrees of freedom of the substituents.



[Cu(phen)$_2$]$^+$ [Cu(dmphen)$_2$]$^+$ [Cu(dpphen)$_2$]$^+$

Figure. 1 Molecular structures of three bis-phenanthroline Cu(I) complexes.

Although these studies have been reported, the coherent view of the substituent effects on the ultrafast dynamics of bis-phenanthroline Cu(I) complexes has not been fully clarified yet. In fact, femtosecond fluorescence up-conversion measurements provided rich quantitative information (e.g. the energy and oscillator strength of the fluorescent states) but they can detect only emissive states. On the other hand, femtosecond time-resolved absorption can detect non-emissive states, but it is not easy to interpret the data taken with $S_2 \leftarrow S_0$ photoexcitation because all the competing processes (e.g. the ISC from the initial S_2 state) other than major relaxation process contribute to the signal. Therefore, to obtain a unified clear view about the substituent effect on the ultrafast relaxation process of Cu(I) complexes, it is desirable to carry out a femtosecond time-resolved absorption study with direct $S_1 \leftarrow S_0$ photoexcitation and interpret data in comparison with information obtained by complementary fluorescence up-conversion experiments.

In this paper, we report on our femtosecond time-resolved absorption study of $[Cu(phen)_2]^+$ (phen = 1,10-phenanthroline) and $[Cu(dpphen)_2]^+$ (dpphen = 2,9-diphenyl-1,10-phenanthroline) in solution, which was performed with the $S_1 \leftarrow S_0$ photoexcitation. By direct excitation to the S_1 state, we were able to simplify the observed dynamics and make interpretation straightforward. We extended the observation wavelength range to the ultraviolet region to directly monitor the recovery of the ground-state bleaching, which greatly helped us to distinguish the dynamics in the excited state from others. Furthermore, we carried out pump-probe measurements with 35-fs resolution, and observed nuclear wavepacket motions of the initial S_1 state and their dephasing. Combining information obtained by femtosecond time-resolved absorption measurements with that from complementary femtosecond fluorescence up-conversion experiments, we discuss a unified view on how the substituents affect the ultrafast relaxation process of bis-phenanthroline Cu(I) complexes.

2. Experimental section

2.1 Samples

The samples were prepared as reported in the literatures.[28, 29] The purity was checked by absorption spectra and elemental analysis. $[Cu(phen)_2]PF_6$ C: 50.67, H: 2.83, N: 9.85, Cu: 11.17 (Cal.), C: 49.72, H: 2.87, N:9.82, Cu: 11.16 (found); $[Cu(dpphen)_2]PF_6$ C: 66.01, H: 3.96, N: 6.42, Cu: 7.28 (Cal.), C: 66.15 H: 3.76, N: 6.42, Cu: 7.29 (found). All the solvents were purchased from Wako Chemicals (HPLC grade), and were used as received. A fresh sample solution was prepared for each experiment. The absorption spectra of the sample solution before and after measurements were compared to confirm that the sample degradation is negligible during the measurement. All the measurements were carried out under an air-saturated condition.

2.2 Steady-state absorption

Steady-state ultraviolet-visible absorption spectra were recorded using a commercial spectrometer (U-3310, Hitachi).

2.3 Femtosecond time-resolved absorption measurements (200-fs time resolution)

The light source of the apparatus was a Ti:sapphire regenerative amplifier (Legend Elite, Coherent, 800 nm, 80 fs, 1mJ/pulse, 1 kHz). A portion of the amplified pulse was converted to a near-infrared pulse (1760 nm) in an optical parametric amplifier (TOPAS, Light Conversion), and then the 1760-nm pulse was sum-frequency mixed with the fundamental pulse (800 nm) to generate a 550-nm pulse. This 550-nm pulse was used as the pump pulse to photoexcite the sample. A small fraction of the 800-nm pulse was focused into a CaF_2 plate (3 mm thickness, continuously moved) to generate a white-light continuum pulse that covers a wavelength region down to ~320 nm. This white-light continuum pulse was divided into the probe and reference pulses. The pump and probe pulses were focused together into a 1-mm-thick fused-silica flow cell, in which the sample solution was circulated. The pump polarization was set at the magic angle with respect to the probe polarization. The probe and reference spectra of each five laser shots were measured with a spectrograph (500is/sm, Chromex) and a charge-coupled device (TEA/CCD-1024-EM/1-UV, Princeton Instruments) that was read out at 100-Hz. The effect of the chirp of the white-light probe on the time-resolved spectra was corrected on the basis of the optical Kerr effect data of the solvent, which were measured with the same experimental configuration. The time resolution of this transient absorption measurement was evaluated as ~200 fs from the Kerr data.

2.4 Ultrafast two-color pump-probe measurements (35-fs time resolution)

Two-color pump-probe measurements were carried out using a setup with two home-built non-collinear optical parametric amplifiers (NOPAs), which were driven by the output of a Ti:sapphire regenerative amplifier (Legend Elite, Coherent, 800 nm, 80 fs, 1mJ/pulse, 1 kHz).[14] Briefly, the output of the first NOPA was tuned to 550 nm and compressed to 18 fs. It was used as the pump pulse for photoexcitation of the sample. The output of the second NOPA (1000 nm, 19 fs) was divided into two parts, and they were used as the probe and reference pulses. The pump and probe pulses were focused into a 200-μm-thick flow cell, in which the sample solution was circulated. The pump polarization was set at the magic angle with respect to the probe polarization. The intensities of the probe and reference pulses were detected by photodiodes, and the electric signals were processed on a shot-to-shot basis to evaluate the pump-induced absorbance change. The time resolution was evaluated as 35 fs (fwhm) by measuring a cross-correlation between the pump and probe pulses using a 50-μm-thick BBO crystal.

3. Results and Discussion

3.1 Steady-state and femtosecond time-resolved absorption measurements of $[Cu(phen)_2]^+$ in dichloromethane

The steady-state absorption spectrum of $[Cu(phen)_2]^+$ in dichloromethane is shown in Figure 2(a). It exhibits two absorption bands in the 400 – 600 nm region due to the ^{1}MLCT transitions. In this paper, we call the intense band around 450 nm the $S_2 \leftarrow S_0$ transition, whereas the weaker band around 550 nm the $S_1 \leftarrow S_0$ transition. It is known that the relative intensity of the $S_1 \leftarrow S_0$ absorption to the $S_2 \leftarrow S_0$ absorption is correlated with the structure in the S_0 state,[24] and the relative intensity observed for $[Cu(phen)_2]^+$ is similar to that for $[Cu(dmphen)_2]^+$.[19] In solution, these two complexes have a perpendicular structure with D_{2d} symmetry in the S_0 state, where the two ligands are coordinated to the copper ion perpendicularly to each other. With this D_{2d} symmetry, the $S_2 \leftarrow S_0$ absorption is attributed to the optically allowed $B_2 \leftarrow A_1$ transition, whereas the $S_1 \leftarrow S_0$ absorption to the optically forbidden $A_2 \leftarrow A_1$ transition. As already discussed,[19] it is considered that the weak but substantial absorption intensity of the "forbidden" $S_1 \leftarrow S_0$ transition in $[Cu(phen)_2]^+$ (and also in $[Cu(dmphen)_2]^+$) arises from the vibronic coupling with the strong $S_2 \leftarrow S_0$ transition and/or dynamic symmetry lowering due to large amplitude b_1 vibrations such as the flattening motion.

To investigate the excited-state dynamics, we photoexcited $[Cu(phen)_2]^+$ to the S_1 state by the 550-nm pump pulse and measured time-resolved absorption spectra. The time-resolved absorption spectra of $[Cu(phen)_2]^+$ in dichloromethane at selected delays are shown in Figure 2(b)-(d). Immediately after photoexcitation (Figure 2(b)), an intense positive band due to the excited-state absorption is observed at 570 nm. A negative band due to bleaching of the S_0 absorption is also observed around 445 nm. The S_0 bleaching does not change in the early time region from 0.1 ps to 0.4 ps, but the 570-nm absorption band exhibits a slight intensity increase, indicating that ultrafast processes take place in the excited state. In the subsequent time region from 0.4 ps to 10 ps (Figure 2(c)), the 570-nm absorption decays drastically, and at the same time, the S_0 bleaching recovers substantially. The concomitant decrease of the 570-nm absorption and the S_0 bleaching indicates that most of the excited-state molecules are relaxed back to the S_0 state, i.e. occurrence of the $S_1 \rightarrow S_0$ IC process on this time scale. The spectral change shown in Figure 2(c) reveals that the $S_1 \rightarrow S_0$ IC is the major relaxation pathway of the S_1 state of $[Cu(phen)_2]^+$. This is in sharp contrast to the S_1 state of $[Cu(dmphen)_2]^+$ which is relaxed to the T_1 state by efficient ISC.[14] In fact, the transient absorption of $[Cu(dmphen)_2]^+$ showed a spectral change with isosbestic points and turned into a characteristic T_1 spectrum having several peaks at 525, 565, 660, and 725 nm. Such a characteristic T_1 spectrum is not clearly recognized in the transient absorption of $[Cu(phen)_2]^+$ shown in Figure 2, suggesting that formation of the T_1 state is very inefficient in $[Cu(phen)_2]^+$ in dichloromethane. We note that our time-resolved absorption measurements cover a wide spectral region, which allows us to directly observe the $S_1 \rightarrow S_0$ IC by monitoring the recovery of the S_0 bleaching. In the time region from 10 ps to 50 ps, the transient signal gradually decays in the wavelength region shorter than 540 nm, whereas the weak transient signal in the longer wavelength region remains essentially unchanged (Figure 2(d)). The time-resolved absorption spectra after 50 ps do not show any significant changes, at least, in the time range of the present measurements (~60 ps). This suggests that the small transient signal observed at later delays is attributable to the long-lived T_1 state.

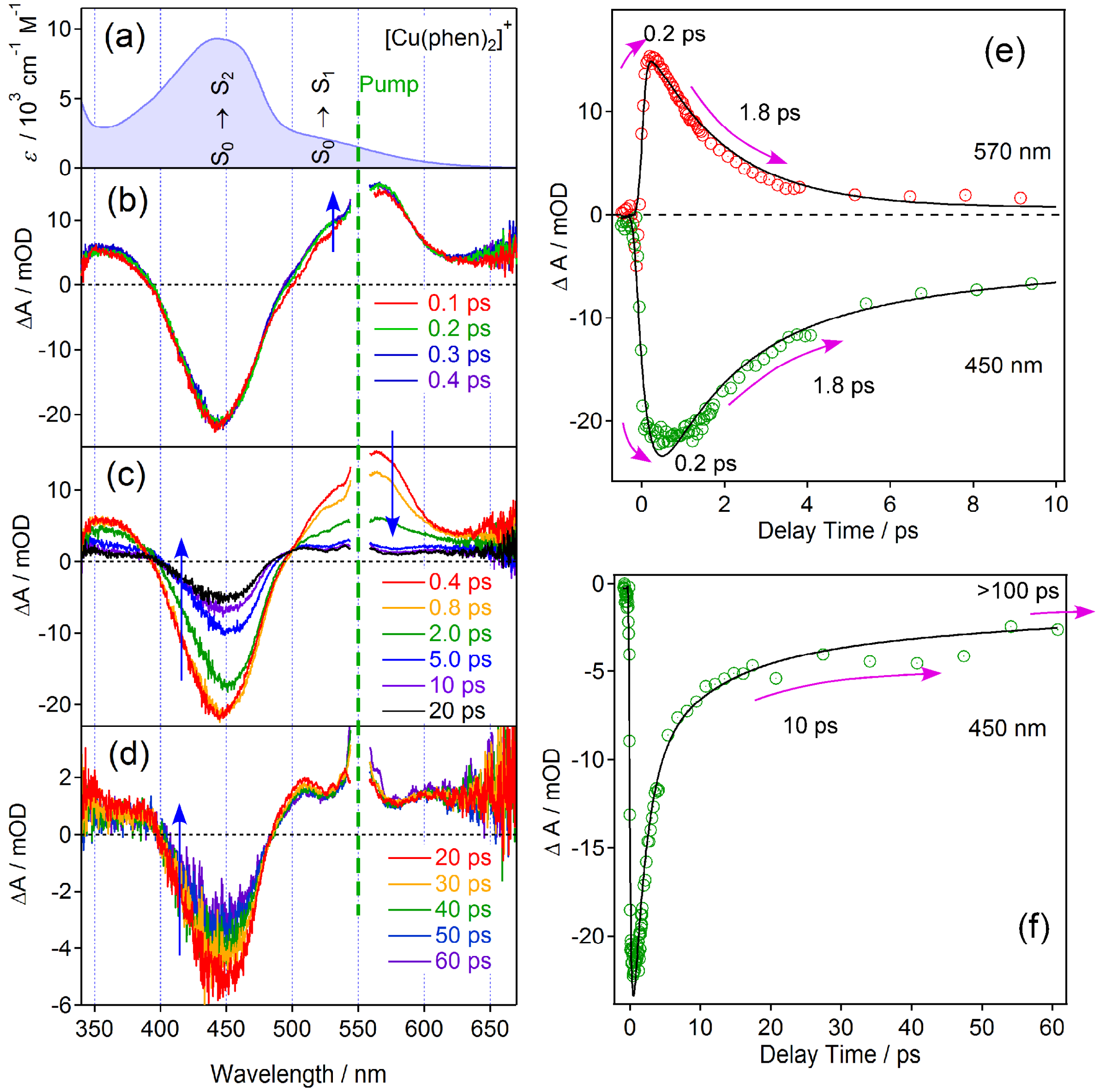


Figure 2. (a) Steady-state absorption spectrum of [Cu(phen)$_2$]$^+$ in dichloromethane. (b-d) Time-resolved absorption spectra of [Cu(phen)$_2$]$^+$ in the delay time range of (b) 0-0.4 ps, (c) 0.4-20 ps and (d) 20-60 ps. (e) Time-resolved absorption traces at 570 and 450 nm up to 10 ps. (f) Time-resolved absorption trace at 450 nm up 60 ps. (Pump 550 nm; 2 × 10^{-3} mol/dm^3)

To examine the excited-state dynamics more quantitatively, we performed a global fitting analysis. Figure 2(e) and (f) show temporal traces of the transient signals and the best fits at 450 nm and 570 nm, where the S_0 bleaching and the excited-state absorption are predominantly observed, respectively. As shown, we needed at least four exponential components to reproduce the temporal behaviors of the transient signals observed in the wide wavelength region, and the corresponding four time constants were 0.2 ps, 1.8 ps, 10 ps, and >100 ps (see Figure S1 in Supplementary Information (SI) for the fitting results at all the wavelengths). The longest time constant was too long to be determined in the time range of the present experiments, and hence it was treated as a temporally-flat component.

The 0.2-ps component recognized as a rising feature of the transient signal at 570 nm corresponds to the slight intensity increase of the excited-state absorption (Figure 2(b)). This 0.2-ps dynamics was also observed in our recent femtosecond time-resolved fluorescence measurements using the up-conversion method.[19] Actually, the up-conversion data of $[Cu(phen)_2]^+$ in dichloromethane obtained with $S_2 \leftarrow S_0$ excitation showed a 47-fs decay due to the $S_2 \rightarrow S_1$ relaxation, which is then followed by the 0.2-ps decay. Because the oscillator strength of the 0.2-ps fluorescence component was comparable to that obtained for the $S_1 \leftarrow S_0$ absorption band, this fluorescence component was assigned to the fluorescence of the S_1 state having the initial perpendicular structure. Because the time constant of this S_1 fluorescence varied depending on the solvent viscosity, it was concluded that the S_1 state is relaxed through the structural change. Therefore, it is natural to attribute the 0.2-ps component observed in the present transient absorption measurements to the structural change in the S_1 state, i.e. the flattening distortion process in the S_1 state from the initial perpendicular structure to a flattened structure. We note that the fluorescence in the 400 - 700 nm region completely decays with the 0.2-ps time constant, and no fluorescence from the flattened S_1 state was observed in our previous fluorescence study.[19] On the other hand, the present time-resolved absorption data only exhibits a slight change of the S_1 absorption with this time constant, implying that the transient absorption spectra of the initial perpendicular S_1 state and flattened S_1 state are very similar. The present data also clarified that the flattened S_1 state is certainly populated after the structural change and that its fluorescence highly likely appears in the wavelength region outside of the detection window (400 - 700 nm) of the previous fluorescence up-conversion study. This means that the fluorescence of the flattened S_1 state appears in the near infrared/infrared region and that the energy gap between the S_1 and S_0 state becomes small at the flattened geometry of $[Cu(phen)_2]^+$. This argument is very reasonable because the unsubstituted phenanthroline ligand of $[Cu(phen)_2]^+$ gives less steric hindrance than those of $[Cu(dmphen)_2]^+$ and $[Cu(dpphen)_2]^+$, which is expected to lead to a greater structural change toward the square-planar structure. It is noted that, also in the case of $[Cu(dmphen)_2]^+$, the structural change in the S_1 state only induces a very small spectral change (i.e., a slight intensity increase) in transient absorption whereas it causes a drastic red shift of the S_1 fluorescence.[14]

As shown in Figure 2(e), the 1.8-ps dynamics is clearly observed as a dominant decay component in the transient signals at both 450 nm and 570 nm, which corresponds to the concomitant decrease of the S_0 bleaching and the S_1 absorption, respectively. The fact that the S_0 bleaching recovers in accordance with the decay of the S_1 absorption unequivocally indicates that the flattened S_1 state undergoes a rapid IC to the S_0 state with the time constant of 1.8 ps.

The very fast IC time of 1.8 ps generates a substantial population of vibrationally excited S_0 molecules because this time constant is much smaller than the vibrational cooling time in solution. The hot S_0 molecules usually show a red-shifted absorption spectrum compared to that of the 'cooled' S_0 molecules. Thus, the hot S_0 state can be recognized as a dispersive shape in the region of the S_0 absorption, i.e. a positive feature in the red side and a negative feature in the blue side of the S_0 absorption. As shown in Figure 2(c)-(d), the transient absorption spectra in the 400 – 540 nm region exhibit such a feature, and it vanishes with the time constant of ~10 ps, as evaluated by the fitting analysis. Because the decay time constant of 10 ps is a typical vibrational cooling time in organic solvents,[30] [31] we attribute the ~10-ps dynamics to the vibrational cooling process of the hot S_0 molecules that are generated by the rapid $S_1 \rightarrow S_0$ IC process.

Although the decay time constant of the last component was too long (>100 ps) to be determined in the present measurements, it is most likely assignable to the T_1 state generated from the flattened S_1 state via the (inefficient) ISC process that occurs in parallel to IC to the S_0 state. This assignment is consistent with the reported T_1 lifetime (143 ps) of $[Cu(phen)_2]^+$ in dichloromethane. [23] This assignment is further supported by the following estimation of the quantum yield and rate of ISC: Assuming that the transient absorption signal observed after 50 ps is due to the T_1 state, we can estimate the quantum yields of the ISC (ϕ_{ISC}) and IC (ϕ_{IC}) processes from the recovery of the S_0 bleaching. As shown in Figure 2(f), the S_0 bleaching signal at 450 nm is ~3 mOD at 60 ps when the T_1 state is populated, whereas it is ~21 mOD at 1 ps when the flattened S_1 state is populated. Therefore, assuming that the transient absorption signal at 450 nm is solely due to the S_0 bleaching, we can estimate the ISC yield as $\phi_{ISC} = 0.14$ (= 3 mOD / 21 mOD) and the IC yield as $\phi_{IC} = 0.86$ (= 1 – 0.14). From this ISC yield ($\phi_{ISC} = 0.14$) and the lifetime of the flattened S_1 state (1.8 ps), the rate constant of the ISC process is evaluated as $0.14 \times (1.8\ \mathrm{ps})^{-1} = (14\ \mathrm{ps})^{-1}$. This value is close to a typical rate constant of the ISC process in bis-diimine Cu(I) complexes, ~ $(10\ \mathrm{ps})^{-1}$.[10, 13, 19] This estimation also indicates that the ISC of $[Cu(phen)_2]^+$ is inefficient not because the ISC rate is small but because the competing IC process to the S_0 state is much faster.

The relaxation scheme that we conclude for $[Cu(phen)_2]^+$ in dichloromethane is significantly different from a recent report by the Chen group.[23] They measured transient absorption of $[Cu(phen)_2]^+$ in dichloromethane with $S_2 \leftarrow S_0$ excitation at 415 nm, and observed the excited-state absorption over the entire wavelength region of their measurement (490 – 750 nm).[23] They claimed that the excited-state absorption around 550 nm includes three decay components having time constants of 0.3, 1.5 and 143 ps. These three components seem to correspond to those observed in the present measurement (0.2, 1.8, >100 ps), but they assigned the second 1.5-ps component to the ISC process from the S_1 state to the T_1 state. As clearly observed in this study, the S_0 bleaching shows a recovery corresponding to the 1.8-ps decay of the 570-nm S_1 absorption, which indicates that the flattened S_1 state predominantly relaxes to the S_0 state with this time constant. The observation of the S_0 bleaching recovery unambiguously shows that the IC process from the flattened S_1 state to the S_0 state takes place in the early picosecond region. We also note that their transient absorption data were measured with the $S_2 \leftarrow S_0$ excitation. Therefore, other processes such as the IC and

ISC processes from the initially populated S_2 state contribute to the signal, which makes the observation complicated. We think that this is the reason why the spectra and dynamics of their time-resolved absorption measurements are deviated from the data obtained in the present work, although they also attributed their first 0.3-ps component to the structural change in excited $[Cu(phen)_2]^+$ as we do in the present study.

3.2 Femtosecond time-resolved absorption measurements of $[Cu(phen)_2]^+$ in acetonitrile

To examine solvent dependence of the excited-state dynamics, we also measured time-resolved absorption of $[Cu(phen)_2]^+$ in acetonitrile. As shown in Figure S2 of SI, the overall feature of the time-resolved absorption spectra is very similar to that observed in dichloromethane: With $S_1 \leftarrow S_0$ photoexcitation at 550 nm, the excited-state absorption around 570 nm and the bleaching of the S_0 absorption around 450 nm appear, and both bands rapidly decay in the early picosecond range. Nevertheless, there are several noticeable differences between the time-resolved absorption data in the two solvents. First, the transient signal in acetonitrile completely vanishes by 50 ps, indicating that the formation of the T_1 state is negligible. A possible reason for this is a rapid quenching of the T_1 state by the ligation of solvent acetonitrile, and/or lowering of the energy of the T_1 state in polar acetonitrile which accelerates the $T_1 \rightarrow S_0$ relaxation process (vide infra). Second, the time constant of each process looks slightly different, as compared in Table 1. It is consistent with our previous femtosecond fluorescence up-conversion study which showed that the structural change occurs with a time constant of 0.20 ps in dichloromethane and 0.13 ps in acetonitrile.[19] The faster structural change in acetonitrile is rationalized by a difference in solvent viscosity (0.44 mPa·s for dichloromethane and 0.37 mPa·s for acetonitrile), because the structural change is expected to occur faster in a less viscous solvent. The time constant of the $S_1 \rightarrow S_0$ IC process is also shorter in acetonitrile (1.4 ps) than in dichloromethane (1.8 ps). It is expected that the S_1 state having a charge-transfer character is more stabilized in the polar environment. Thus, the energy gap between the flattened S_1 state and the S_0 state likely becomes even smaller, which can accelerate the $S_1 \rightarrow S_0$ IC process.

Table 1. Time constants of the dynamics and their assignments.

	Solvent	Structural change / ps	IC / ps	ISC / ps	Vibrational cooling / ps	T_1 / ps
$[Cu(phen)_2]^+$	CH_2Cl_2	0.2	1.8	-	~10	>100
	CH_3CN	~0.1	1.4	-	11	-
$[Cu(dpphen)_2]^+$	CH_2Cl_2	0.9	-	11	-	1.35×10^{5} (a)
	CH_3CN	0.5	-	11	-	-

(a) ref. 19

3.3 Steady-state and femtosecond time-resolved absorption measurements of $[Cu(dpphen)_2]^+$

The steady-state absorption spectrum of $[Cu(dpphen)_2]^+$ in dichloromethane is shown in Figure 3(a). As in the cases of $[Cu(phen)_2]^+$ and $[Cu(dmphen)_2]^+$, it exhibits two bands in the visible region, and we refer to the bands peaked at 440 nm and 550 nm as the $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ transitions, respectively, in this paper. The relative intensity of the S_1 absorption to the S_2 absorption is significantly larger than those of $[Cu(phen)_2]^+$ and $[Cu(dmphen)_2]^+$, which is considered to reflect a distorted structure of $[Cu(dpphen)_2]^+$ in the S_0 state. It was argued that the dihedral angle between the two ligands is smaller than 90 degrees in the S_0 state of $[Cu(dpphen)_2]^+$, owing to π-electron interaction between the phenyl substituent of one ligand and the phenanthroline moiety of another ligand. [16, 24, 32] The lowered symmetry in the S_0 state (i.e. from the D_{2d} perpendicular structure to the D_2 flattened structure) makes the $S_1 \leftarrow S_0$ transition optically-allowed, causing the intensity increase of the S_1 absorption.

Time-resolved absorption spectra of $[Cu(dpphen)_2]^+$ in dichloromethane measured with photoexcitation at 550 nm are shown in Figure 3(b)-(c). Immediately after photoexcitation, the excited-state absorption peaked at 620 nm and a bleaching of the S_0 absorption around 445 nm are observed. The relative amplitude of the S_0 bleaching to the excited-state absorption is smaller compared to the data of $[Cu(phen)_2]^+$, indicating the greater intensity of the excited-state absorption of $[Cu(dpphen)_2]^+$. In the first picosecond, the 620-nm band gradually grows up, while the S_0 bleaching remains unchanged. Then, the 620-nm band decays on the 10-ps time scale in accordance with appearance of a new peak around 590 nm while exhibiting a clear isosbestic point at 600 nm. After this spectral change, the transient absorption signal, including the S_0 bleaching, does not show any significant changes in the time range of the present measurement (60 ps). The spectral shape and dynamics of the time-resolved absorption data are markedly different from those of $[Cu(phen)_2]^+$ but are very similar to the data of $[Cu(dmphen)_2]^+$.[14]

The global fitting analysis showed that the temporal behavior of the transient signals is well reproduced by three exponential functions with time constants of 0.9 ps, 11 ps, and > 100 ps (see Figure S3 in SI for the fitting results at all the wavelengths). The best fits for two typical temporal traces are shown in Figure 3(d). These three time constants agree well with the time constants obtained in our previous time-resolved emission study of $[Cu(dpphen)_2]^+$ (0.92 ps, 9.4 ps, 135 ns).[19] The 0.9-ps component corresponds to the rise of the 620-nm absorption, and it is safely assigned to the structural change in the S_1 state based on the previous time-resolved fluorescence data: With this time constant, time-resolved fluorescence spectrum exhibited a red-shift keeping the integrated time-resolved emission intensity unchanged, and this time constant showed solvent viscosity dependence. (Note that the structural change in the S_1 state of $[Cu(dpphen)_2]^+$ is a 'further' flattening distortion because the molecule is already flattened in the initial S_0 state.[16]) The 11-ps component is attributable to the spectral change due to ISC from the flattened S_1 state to the T_1 state (Figure 3(c)) because this process yields a long-lived transient signal without any recovery of the S_0 bleaching. The transient spectrum observed after the spectral change shows a relatively sharp peak at 590 nm and it resembles the T_1 spectrum of $[Cu(dmphen)_2]^+$,[14] which further supports this assignment. The 590-nm absorption due to the T_1 state as well as the associated bleaching of the S_0 absorption does not change within the time range of the present measurement, and it is consistent with the reported T_1 lifetime of $[Cu(dpphen)_2]^+$ in dichloromethane (135 ns [19]). The time constants of the dynamics of $[Cu(dpphen)_2]^+$ are listed in Table 1.

We also measured time-resolved absorption spectra of $[Cu(dpphen)_2]^+$ in acetonitrile. The spectral change in acetonitrile is very similar to that observed in dichloromethane (Figure S4 in SI), and the time constants of the dynamics are listed in Table 1. A noticeable difference between the data in the two solvents was found in the time constant of the structural change, which is shortened from 0.9 ps in dichloromethane to 0.5 ps in acetonitrile. This change can be rationalized by the solvent viscosity effect on the structural change.[19] The ISC time of $[Cu(dpphen)_2]^+$ does not noticeably change in the two solvents, as in the case of $[Cu(dmphen)_2]^+$.[13]

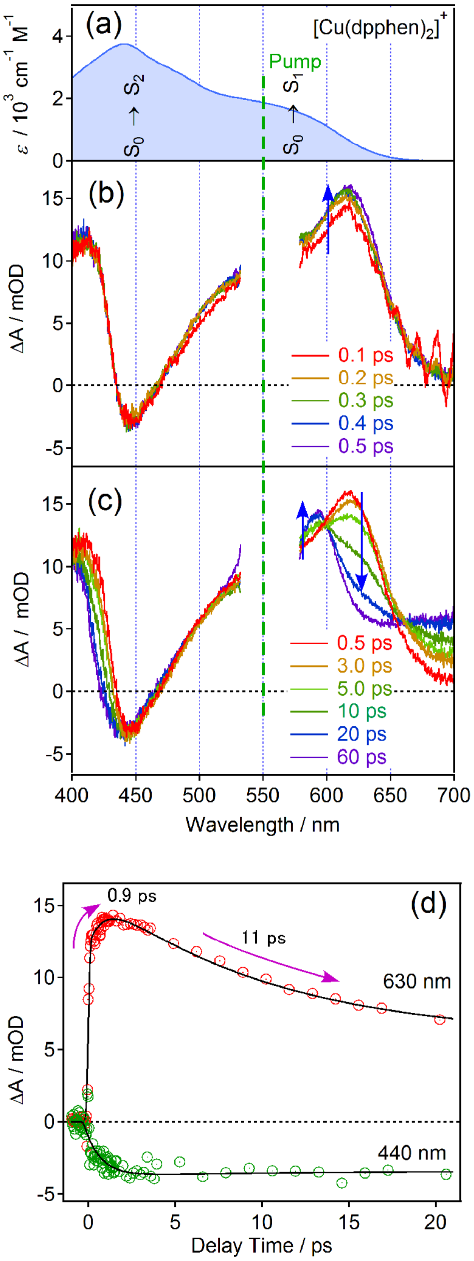


Figure 3. (a) Steady-state absorption spectrum of $[Cu(dpphen)_2]^+$ in dichloromethane. (b, c) Time-resolved absorption spectra of $[Cu(dpphen)_2]^+$ in the delay time range of (b) 0.1~0.5 ps and (c) 0.5~60 ps. (d) Time-resolved absorption signals at 630 and 440 nm. (Pump 550 nm; 2×10^{-3} mol/dm^3)

3.4 Observation of coherent nuclear dynamics by ultrafast pump-probe measurements

To investigate the initial nuclear dynamics and vibrational structure of the S_1 state, we carried out two-color pump-probe measurements with time resolution as good as 35 fs. The obtained time-resolved absorption traces of $[Cu(phen)_2]^+$ in dichloromethane and acetonitrile are shown in Figure 4(a) and (b), respectively. In these measurements, the pump wavelength was set at 550 nm to photoexcite the complex directly to the S_1 state. To exclusively monitor the nuclear wavepacket motion of the S_1 state, the probe wavelength needs to be resonant with the S_1 absorption but should be off-resonant from the S_0 absorption. From the steady-state and time-resolved spectral information shown in Figure 2, we thought that a wavelength region longer than 700 nm can safely meet this requirement, because the red side of the S_1 absorption extends to this wavelength but the S_0 absorption does not. However, because it is difficult to tune the 800-nm-driven NOPA in the wavelength region around 800 nm, we operated it in the longer wavelength region and carried out the experiments with the probe pulse having a center wavelength of 1000 nm.

As shown in Figure 4(a), the pump-probe trace of $[Cu(phen)_2]^+$ in dichloromethane exhibited a week but noticeable positive signal. The overall temporal behavior of the signal can be reproduced by the 0.2-ps rise, 1.6-ps decay, and residual longer-lived component, as indicated by the blue curve. Although this fitting is somewhat ambiguous due to strong oscillatory features as well as a strong coherent spike around the time zero, this temporal behavior is consistent with the dynamics observed in the transient absorption in the visible region (Figure 2). Very strong oscillation observed for $[Cu(phen)_2]^+$ in dichloromethane is mostly attributed to the solvent vibrations but the nuclear wavepacket motion in the S_1 state also contributes to it (vide infra). A contribution of the nuclear wavepacket motion of the S_0 state is negligibly small because the probe wavelength (1000 nm) is far from the S_0 absorption and is only resonant with the S_1 absorption. To examine this oscillatory component quantitatively, we extracted it by subtracting the population component from the raw trace and calculated Fourier transform. As shown in Figure 5(a), Fourier transform shows several vibrations at 183, 255, 285, 407, and 703 cm^{-1}. We also performed a control experiment for the solvent only, and found that the two intense bands at 286 cm^{-1} and 700 cm^{-1} originate from the solvent (dichloromethane). In fact, these two solvent vibrations dominate the oscillation observed in the pump-probe trace in Figure 4(a). It is noteworthy that the non-resonant oscillatory signal due to the solvent is not usually observed as the absorptive change in this type of experiments. We consider that the spectrum of the probe pulse is modulated by the non-resonant refractive change (i.e., the real part of the third order susceptibility) of the solvent, and it changes the detected signal intensity because the sensitivity of the Si photodiode drastically changes around the probe wavelength of 1000 nm (i.e., the spectral filtering effect).

To extract the oscillatory component purely due to the S_1 state, we filtered out the two solvent bands in the Fourier transform spectrum and then converted the filtered spectrum into the time domain by the inverse Fourier transform. (Details are given in Figure S5 in SI.) The oscillatory component due to the S_1 state obtained by this procedure is shown in the inset of Figure 4(a). Unlike the oscillation seen in the raw pump-probe trace, the oscillation due to the S_1 state rapidly decays within a picosecond. An exponential fit to the envelope of the oscillation gives a dephasing time constant as short as 0.3 ps. This dephasing time of the S_1 nuclear motion well matches the time constant of the structural change in $[Cu(phen)_2]^+$ in spite of a large error in the evaluated dephasing time constant. This agreement indicates that the nuclear wavepacket motion observed is surely ascribable to the initial perpendicular S_1 state and that it dephases in accordance with the structural change. It means that the initial S_1 state having the perpendicular structure has a well-defined vibrational structure, which allows the coherent nuclear motion during its lifetime. The agreement between the dephasing time of the coherent nuclear motion and the time constant of the structural change was also observed for $[Cu(dmphen)_2]^+$.[14]

As shown in Figure 4(b), the pump-probe trace of $[Cu(phen)_2]^+$ in acetonitrile also exhibits a positive signal due to the S_1 absorption with oscillatory features arising from the nuclear wavepacket motion induced by photoexcitation. Unlike the case in dichloromethane, however, the oscillatory component observed in acetonitrile predominantly arises from the S_1 state, and the contribution of the solvent is negligibly small. Therefore, the population component is readily recognized in the raw data, and it was well fitted using the time constant listed in Table 1. (The fit is shown with the blue curve in Figure 4(b).) The oscillatory component was extracted from the raw data by subtracting the population component, and it is shown in the inset of Figure 4(b). Fourier transform of the extracted oscillation (red line in Figure 5(a)) does not exhibit any noticeable peak at 380 cm^{-1} due to solvent acetonitrile, but shows peaks at 184, 249, and 410 cm^{-1}. These three frequencies agree well with the vibrational frequencies that we assigned to the S_1 state in the Fourier transform in dichloromethane. Therefore, the oscillatory component extracted from the raw trace (inset of Figure 4(b)) is solely attributed to the nuclear wavepacket motion in the S_1 state. An exponential function was fit to the envelope of the oscillatory component (the blue dashed curve), and the dephasing time was estimated to be 0.2 ps. This dephasing time agrees fairly well with the time constant of the structural change of $[Cu(phen)_2]^+$ in acetonitrile (~0.1 ps), assuring that the observed oscillation is attributed to the S_1 state.

We also carried out pump-probe measurements of $[Cu(dpphen)_2]^+$ in both dichloromethane and acetonitrile, and the obtained signals are shown in Figure 4(c) and (d), respectively. The same combination of the pump (550 nm) and probe (1000 nm) wavelengths were used to photoexcite the complex to the S_1 state and to monitor the transient absorption. The transient signal exhibits a small decay in the first few picoseconds, and then shows a very slow decay. The time constant of the initial small decay was determined to be 0.95 ps and 0.67 ps for the dichloromethane and acetonitrile solutions, respectively, and they agree very well with the time constants of the structural change of $[Cu(dpphen)_2]^+$ in dichloromethane (0.9 ps) and acetonitrile (0.5 ps), respectively. We note that the pump-probe traces in Figure 4(c) and (d) exhibit an additional ultrafast (< 100 fs) rise immediately after photoexcitation, which can be recognized only with the present high time resolution. The origin of this rise component is not clear at the moment, but it likely reflects the early dynamics in the initially populated S_1 state.

As seen in Figure 4(c) and (d), the pump-probe signals of $[Cu(dpphen)_2]^+$ also exhibit oscillatory features clearly in both dichloromethane and acetonitrile, reflecting the nuclear wavepacket motion induced by photoexcitation. The oscillatory component was extracted by subtracting the population component (blue curves) from the raw signal, and its Fourier transform was calculated (Figure 5(b)). The Fourier transform in the two solvents show two common bands at 170 cm^{-1} and 250 cm^{-1} which are assignable to the nuclear wavepacket motion of the S_1 state of $[Cu(dpphen)_2]^+$. An additional band at 286 and 700 cm^{-1} observed in dichloromethane are attributable to the solvent. Thus, we filtered out these 286- and 700-cm^{-1} bands from the Fourier spectrum in dichloromethane and converted the filtered spectrum back to the time domain by inverse Fourier transformation (inset of Figure 4(c)). The Fourier transform of the oscillation observed in acetonitrile does not contain solvent bands, so that this oscillation is solely due to the nuclear wavepacket motion of the S_1 state (inset of Figure 4(d)). The dephasing time of the oscillation was evaluated to be 1.1 ps in dichloromethane and 0.9 ps in acetonitrile by the exponential fit to the envelope of the oscillation. These dephasing times agree fairly well with the time constants of the structural change in each solvent, indicating that the coherent nuclear wavepacket motion dephases as the structural change takes place in the S_1 state.

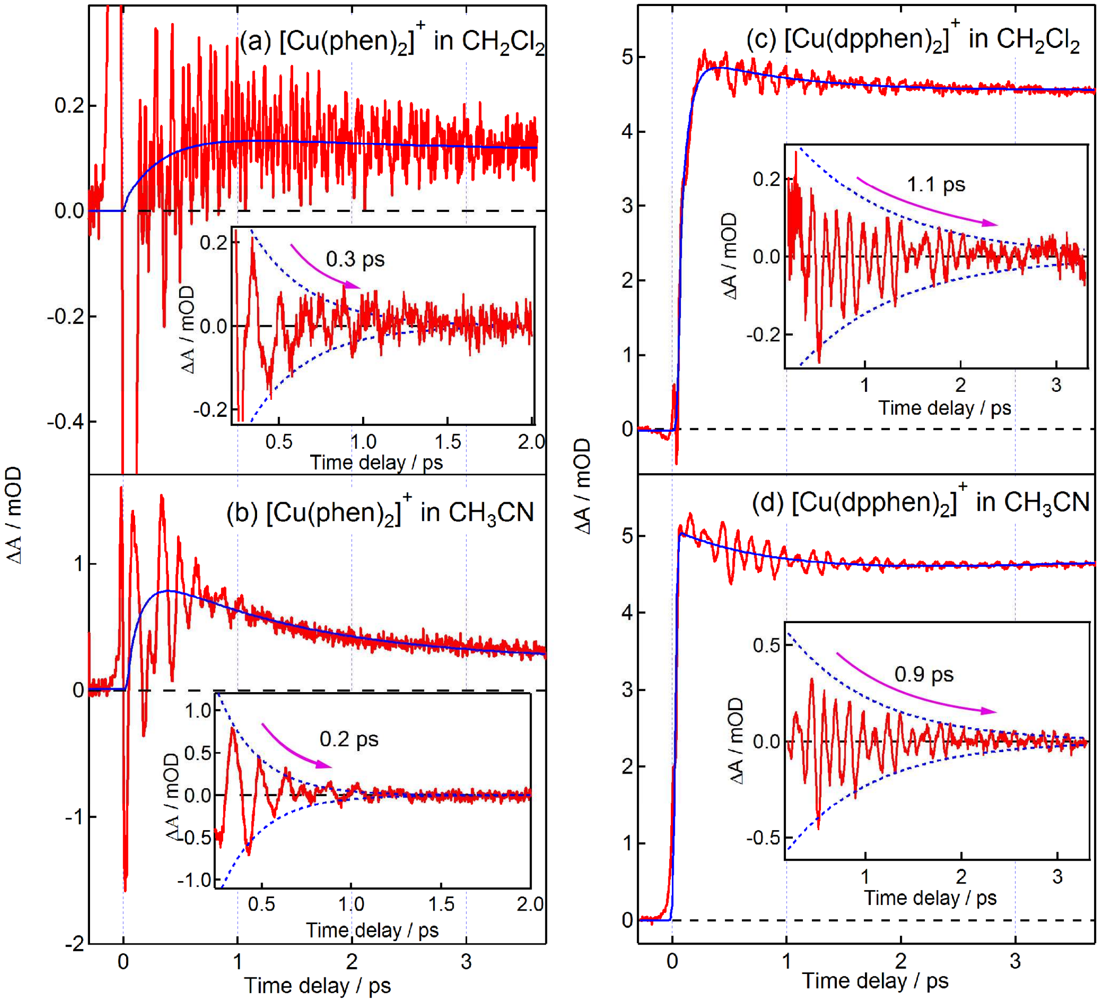


Figure 4. Pump-probe traces of $[Cu(phen)_2]^+$ and $[Cu(dpphen)_2]^+$. Left: $[Cu(phen)_2]^+$ in (a) dichloromethane (8×10^{-3} mol/dm^3) and (b) acetonitrile (22×10^{-3}mol/dm^3). Right: $[Cu(dpphen)_2]^+$ in (c) dichloromethane (15×10^{-3} mol/dm^3) and (d) acetonitrile (20×10^{-3} mol/dm^3). (Pump: 550 nm; Probe: 1000 nm;) Red line: experimental data. Blue line: fit to the population component. Insets: oscillatory component due to the nuclear wavepacket motion of the S_1 state. Blue dashed line: exponential fits to the envelope of the oscillation.

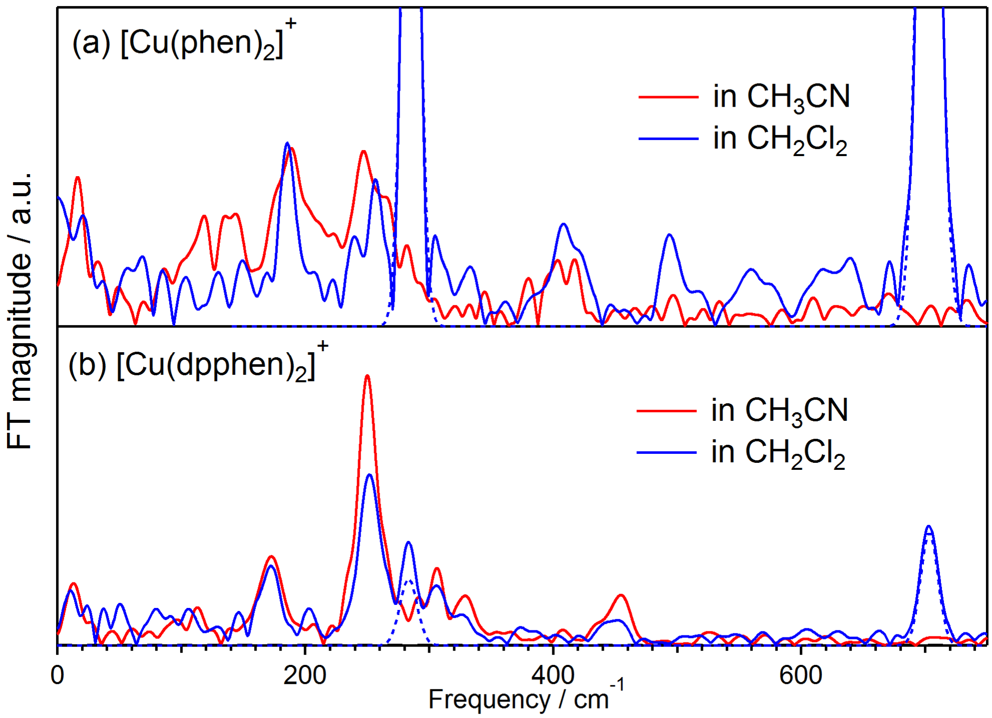


Figure 5. Fourier transform magnitude spectra of the oscillatory components of (a) [Cu(phen)$_2$]$^+$ and (b) [Cu(dpphen)$_2$]$^+$. Red line: in acetonitrile. Blue line: in dichloromethane. Solvent bands are shown with dotted lines.

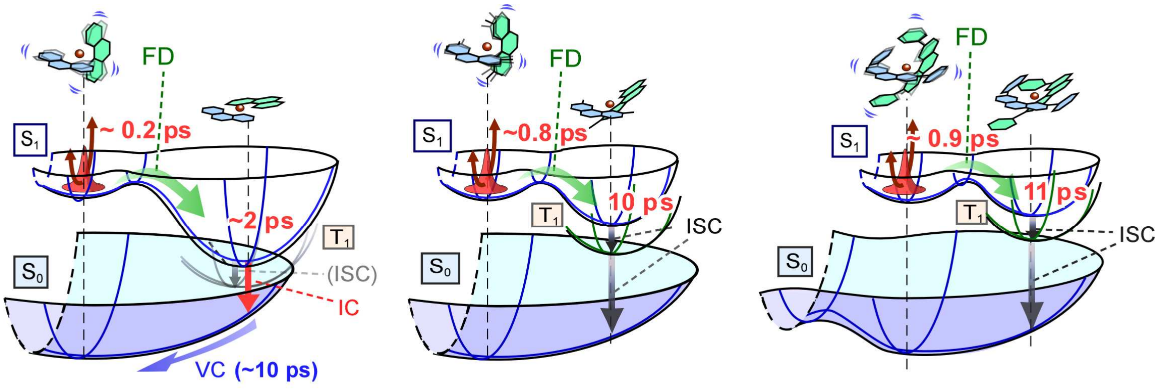
3.5. Substituent effect on the relaxation process of Cu(I) complexes

Figure 6 illustrates the comparison of the ultrafast relaxation processes of [Cu(phen)$_2$]$^+$ and [Cu(dpphen)$_2$]$^+$, together with those of [Cu(dmphen)$_2$]$^+$. The conclusion obtained by the present time-resolved absorption study is very consistent with that obtained by our recent femtosecond fluorescence up-conversion study, and they make a coherent view of the substituent effect on the relaxation process of the Cu(I) complexes.

[Cu(dmphen)$_2$]$^+$ and [Cu(dpphen)$_2$]$^+$ exhibit quite similar dynamics, although their initial structures in the S_0 state are substantially different: [Cu(dmphen)$_2$]$^+$ has a perpendicular structure whereas [Cu(dpphen)$_2$]$^+$ has a substantially distorted structure. These two complexes undergo the flattening structural change in the S_1 state on the sub-picosecond time scale, and then relax to the T_1 state by ISC with the time constant of ~10 ps. The time constant of the structural change becomes longer as the substituent becomes bulkier ($[Cu(dmphen)_2]^+$ < $[Cu(dpphen)_2]^+$) whereas the time constant of ISC is insensitive to the substituent.

On the other hand, the flattening structural change in $[Cu(phen)_2]^+$ occurs on a much shorter time scale (~0.2 ps). Moreover, the present time-resolved absorption measurements directly showed that the flattened S_1 state is populated after the structural change, which could not be detected by the fluorescence up-conversion measurements in the visible region.[19] The lifetime of the flattened S_1 state of $[Cu(phen)_2]^+$ is much shorter (1-2 ps) than those of $[Cu(dpphen)_2]^+$ and $[Cu(dmphen)_2]^+$ (~10 ps). This difference arises from much faster IC from the flattened S_1 state to the S_0 state in $[Cu(phen)_2]^+$. Actually, the flattened S_1 state of $[Cu(phen)_2]^+$ does not efficiently produce the T_1 state by ISC like the other two complexes, and it predominantly relaxes to the S_0 state. This fast IC generates a substantial population of the vibrationally hot S_0 molecule, and hence the vibrational cooling process in the S_0 state is observed on the 10-ps time scale for $[Cu(phen)_2]^+$. We consider that the different relaxation schemes between $[Cu(phen)_2]^+$ and the other two complexes arise from the different magnitude of the structural change occurring in the S_1 state. Because $[Cu(phen)_2]^+$ has the ligands with no substituents, the steric hindrance between the two ligands is minimum. Therefore, it is natural to think that $[Cu(phen)_2]^+$ can change its structure largely in the S_1 state, becoming close to the square planar structure. As a result, the potential energy surfaces of the S_0 and S_1 states energetically become close at the flattened structure, which significantly accelerates the $S_1 \rightarrow S_0$ IC process. Consequently, the $S_1 \rightarrow S_0$ IC process becomes faster than other competing relaxation pathways such as ISC to the T_1 state, which makes the flattened S_1 state relax predominantly through the $S_1 \rightarrow S_0$ IC process. In the other $[Cu(dpphen)_2]^+$ and $[Cu(dmphen)_2]^+$, such an extensive flattening distortion is prohibited by the steric hindrance due to the substituents at the 2- and 9- positions of the ligands. Thus, the IC rate is much smaller than the rate of ISC so that the flattened S_1 state relaxes predominantly to the T_1 state. This picture is consistent with the result of our previous femtosecond fluorescence up-conversion study, in which the fluorescence signal from the flattened S_1 state of $[Cu(phen)_2]^+$ was not observed in the visible region although those of $[Cu(dmphen)_2]^+$ and $[Cu(dpphen)_2]^+$ were clearly observed.

Photoexcitation using ultrashort pulses induces the coherent nuclear wavepacket motion in the S_1 state of $[Cu(phen)_2]^+$ and $[Cu(dpphen)_2]^+$, as observed before for $[Cu(dmphen)_2]^+$.[14] In these three Cu(I) complexes, the nuclear wavepacket motion dephases in accordance with the flattening structural change. This implies that the initially populated S_1 state has a well-defined vibrational structure and that the coherent nuclear motion along the coordinates other than the flattening motion persists in its short lifetime before the flattening structural change. This is intriguing, particularly for $[Cu(dpphen)_2]^+$ in which the initial structure is already distorted in the S_0 state. The present study showed that, even if the initially populated S_1 state has a distorted structure, it can hold the structure for a period as short as ~1 ps while vibrating coherently before the further flattening distortion takes place.



(a) $[Cu(phen)_2]^+$ (b) $[Cu(dmphen)_2]^+$ (c) $[Cu(dpphen)_2]^+$

Figure 6. Relaxation pathways of (a) $[Cu(phen)_2]^+$, (b) $[Cu(dmphen)_2]^+$ and (c) $[Cu(dpphen)_2]^+$. In the figure, FD and VC represent the flattening distortion and the vibrational cooling, respectively.

4. Acknowledgement

L. H. thanks Japan Society for the promotion of Science (JSPS) for a postdoctoral fellowship. We are grateful to the RIKEN chemical analysis team for elemental analyses of the samples used in this work. This work was supported by a Grant-in-Aid for

Scientific Research on Innovative Area (No. 25104005) and Grant-in-Aid for Scientific Research (A) (No. 25248009) from JSPS.

The following supplementary information is available free of charge via the Internet at http://www.rsc.org/.

(1) Global fitting of the time-resolved absorption signal of $[Cu(phen)_2]^+$ in dichloromethane.

(2) Time-resolved absorption data of $[Cu(phen)_2]^+$ in acetonitrile.

(3) Global fitting of the time-resolved absorption signal of $[Cu(dpphen)_2]^+$ in dichloromethane.

(4) Time-resolved absorption data of $[Cu(dpphen)_2]^+$ in acetonitrile.

(5) Procedure of extracting the oscillatory component of the S_1 state of $[Cu(phen)_2]^+$ in dichloromethane.

Reference

1. V. Balzani and C. Campagna, *Coordination Compounds I*, Springer, Berlin, 2007.
2. S. Kume, M. Kurihara and H. Nishihara, *Inorg. Chem.*, 2003, **42**, 2194-2196.
3. N. Armaroli, *Chem. Soc. Rev.*, 2001, **30**, 113-124.
4. M. Ruthkosky, C. A. Kelly, F. N. Castellano and G. J. Meyer, *Coord. Chem. Rev.*, 1998, **171**, 309-322.
5. J. J. McGarvey, S. E. J. Bell and K. C. Gordon, *Inorg. Chem.*, 1988, **27**, 4003-4006.
6. D. R. McMillin, M. T. Buckner and B. Ahn, Tae, *Inorg. Chem.*, 1977, **16**, 943-945.
7. M. W. Blaskie and D. R. McMillin, *Inorg. Chem.*, 1980, **19**, 3519-3522.
8. J. R. Kirchhoff, R. E. J. Gamache, M. W. Blaskie, A. A. Delpaggio, R. K. Lengel and D. R. McMillin, *Inorg. Chem.*, 1983, **22**, 2380-2384.
9. W. L. Parker and G. A. Crosby, *J. Phys. Chem*, 1989, **93**, 5692-5696.
10. Z. A. Siddique, Y. Yamamoto, T. Ohno and K. Nozaki, *Inorg. Chem.*, 2003, **42**, 6366-6378.
11. L. X. Chen, G. B. Shaw, I. Novozhilova, T. Liu, G. Jennings, K. Attenkofer, G. J. Meyer and P. Coppens, *J. Am. Chem. Soc.*, 2003, **125**, 7022-7034.
12. K. Shinozaki and Y. Kaizu, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2435-2439.
13. M. Iwamura, S. Takeuchi and T. Tahara, *J. Am. Chem. Soc.*, 2007, **129**, 5248-5256.
14. M. Iwamura, H. Watanabe, K. Ishii, S. Takeuchi and T. Tahara, *J. Am. Chem. Soc.*, 2011, **133**, 7728-7736.

15. T. J. Penfold, S. Karlsson, G. Capano, F. A. Lima, J. Rittmann, M. Reinhard, H. Rittmann-Frank, O. Bram, E. Baranoff, R. Abela, I. Tavernelli, U. Rothlisberger, C. J. Milne and M. Chergui, *J . Phys. Chem. A*, 2013, **117**, 4591–4601.
16. M. T. Miller, P. K. Gantzel and T. B. Karpishin, *Inorg. Chem.*, 1998, **37**, 2285-2290.
17. K. Kalyanasundaram, *Photochemistry of polypyridine and porphyrin complexes*, Academic Press, London, 1992.
18. M. Z. Zgierski, *J. Chem. Phys.*, 2003, **118**, 4045-4051.
19. M. Iwamura, S. Takeuchi and T. Tahara, *Physical Chemistry Chemical Physics*, 2014, **16**, 4143-4154.
20. G. B. Shaw, C. D. Grant, H. Shirota, E. W. CastnerJr., G. J. Meyer and L. X. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 2147-2160.
21. M. Iwamura, H. Watanabe, K. Ishii, S. Takeuchi and T. Tahara, in *Ultrafast Phenomena XVI Springer Series in Chemical Physics*, Springer, Berlin2009, vol. 92, pp. 382-384.
22. T. Gunaratne, M. A. J. Rodgers, D. Felder, J.-F. Nierngarten, G. Accorsi and N. Armaroli, *Chem. Comm.*, 2003, 3010-3011.
23. J. V. Lockard, S. Kabehie, J. I. Zink, G. Smolentsev, A. Soldatov and L. X. Chen, *J. Phys. Chem. B*, 2010, **114**, 14521-14527.
24. A. K. Ichinaga, J. R. Kirchhoff, D. R. McMillin, C. Dietrich-Buchecker and P. A. Marnot, *Inorg. Chem.*, 1987, **26**, 4290-4292.
25. M. l. K. Eggleston, P. E. Fanwick, A. J. Pallenberg and D. R. McMillin, *Inorg. Chem.*, 1997, **36**, 4007-4010.
26. C. T. Cunningham, J. J. Moore, K. L. H. Cunningham, P. E. Fanwick and D. R. McMillin, *Inorg. Chem.*, 2000, **39**, 3638-3644.
27. N. A. Gothard, M. W. Mara, J. Huang, J. M. Szarko, B. Rolczynski, J. V. Lockard and L. X. Chen, *J. Phys. Chem. A*, 2012, **116**, 1984-1992.
28. A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem*, 1959, **9**, 211.
29. M. Ruthkosky, F. N. Castellano and G. J. Meyer, *Inorg. Chem.*, 1996, **35**, 6406-6412.
30. N. Sarkar, S. Takeuchi and T. Tahara, *J. Phys. Chem. A*, 1999, **103**, 4808-4814.
31. T. Elsaesser and W. Kaiser, *Annu. Rev. Phys. Chem.*, 1991, **42**, 83-107.
32. F. K. Klemens, C. E. A. Palmer, S. M. Rolland, P. E. Fanwick and D. R. McMillin, *New J. Chem.*, 1990, **14**, 129-133.

Table of Contents Entry

Ultrafast absorption spectroscopy clarified excited-state dynamics of bis-diimine copper (I) complexes. Photoexcitation induces coherent vibrations in the ^{1}MLCT states, which dephase with flattening distortion. $[Cu(phen)_2]^+$ and $[Cu(dpphen)_2]^+$ then relaxes differently by internal conversion and intersystem crossing, respectively, highlighting the substituent effect.

Graphics for TOC