The Effect of Ligand Constraints on the Metal-to-Ligand Charge-Tranfer Relaxation Dynamics of Copper(I)−Phenanthroline Complexes: A Comparative Study by Femtosecond Time-Resolved Spectroscopy

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Two geometrically constrained Cu(I)−monophenanthroline complexes were investigated spectroscopically to study the effects that ligand constraints have on the excited-state dynamics of copper−phenanthroline complexes. Room temperature steady-state absorption and emission spectra were obtained for the two complexes and time-resolved fluorescence spectra of the Cu(I) complexes in dichloromethane were collected using time-correlated single photon counting. The effect of the ligands on the excited-state dynamics of the two complexes was monitored by femtosecond pump−probe spectroscopy. Transient absorption spectroscopy with femtosecond resolution enabled the direct observation of the relaxation in the photoinduced metal-to-ligand charge-transfer (MLCT) state of the complexes, where the tetrahedral Franck−Condon Cu(II) complex undergoes vibrational relaxation to form the energetically favorable square planar conformation. The flattening relaxation was found to have two lifetime components of 8−10 and 40−52 ps for the rearrangement of the 1:1 copper−phenanthroline complexes, which is likely related to the flattening around the metal center and the subsequent rearrangement of the methylphenyl-pyrazole backbone according to the more planar conformation, respectively. The excited-state dynamics correlate with the measured UV−vis absorption and emission properties of the complexes and are discussed in the light of steric constraints on the photophysics of the Cu(I)−monophenanthroline complexes. The higher quantum yield, longer emission lifetime, and faster relaxation dynamics of the dimethyl-substituted pyrazole-based complex compared with the unmethylated analogue agree with the steric arguments that in a 1:1 ligand framework, addition of alkyl substituents in the ligand hinders the flattening relaxation. This investigation is complementing photophysical studies performed over the past two decades on the effect of substitutents on the photophysics of the structurally related 1:2 Cu(I)−phenanthroline complexes by providing a time-resolved spectroscopic observation of the excited-state relaxation in geometrically constrained Cu(I)−phenanthroline complexes following the photoinduced MLCT.

Introduction

Copper−phenanthroline complexes have attracted great interest over the past years due to their potential in technologically important applications, such as solar energy conversion,[1] molecular sensing,[2] and photocatalysis.[3,4] Of particular interest is the capability of Cu(I)−phenanthroline complexes to act as probes for biological structures.[5−7] Owing to the large reducing tendency of the metal center,[8] Cu(I) complexes display charge-transfer transitions in the form of metal-to-ligand charge-transfer (MLCT) bands, which occur in the visible region of the electronic absorption spectrum.[8] The presence of low-lying MLCT excited states causes the luminescence of these complexes to become very sensitive to their environment, making them ideal probes for studying protein structures and nucleic acid interactions.

Over the last two decades, research on Cu(I) complexes has focused on developing a deeper understanding of the photophysics of their excited states.[9−18] For applications involving photoinduced electron-transfer processes, the excited-state life-

times and emission quantum yields of these metal complexes are important parameters and a good understanding of the controlling factors is crucial. One area of emphasis in studying the photophysics of copper metal complexes is the investigation of the structural distortions that occurs in the excited state of the complexes.[22] Copper complexes with substituted phenanthrolines as ligands exhibit particularly strong metal-to-ligand charge-transfer (MLCT) absorption bands in the visible spectral range. However, their emission is compromised by short excited-state lifetimes and low quantum yields, which is often attributed to the flattening relaxation of the excited CT state.[22−24] This relaxation phenomenon can be rationalized by the increase in formal charge on the copper metal center in the emissive CT state, which is stabilized by a square planar coordination environment. The consequences of the torsional relaxation include reduction of the excited-state lifetime that results in poor emission.[23] Coordination of a fifth ligand further stabilizes the CT excited state relative to the ground state, which inevitably promotes quenching.[25] This excited-state complex (exciplex) quenching is frequently observed in the presence of donor solvents such as acetonitrile, water, and methanol. In the following study, we have performed optical measurements using the weakly coordinating dichloromethane as solvent to prevent

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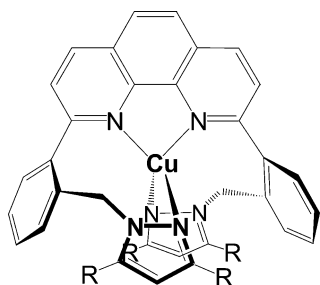‡ Georgia Institute of Technology.
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Figure 1. Molecular design of the 1:1 copper(I)−phenanthroline complex.

exciplex quenching of the emissive CT state[26] to isolate the effect of the constraining ligands from solvent effects on the dynamics of the monophenanthroline−Cu(I) complexes.

Controlling the geometry at a metal ion site is of fundamental importance in many areas of chemistry.[27] The development of ligands that force metal ions into unusual geometries or stabilize specific oxidation states are of interest in designing catalytic systems or biological probes. In particular, to prevent Jahn−Teller distortions in copper−phenanthroline complexes, steric constraints are built into the ligands by introducing bulky substituents.[23] Here we report on the photodynamics study of geometrically constrained Cu(I)−phenanthroline complexes, which have 1:1 metal-to-ligand stoichiometry. The 1:1 copper complex framework was achieved by attaching two pyrazole donor groups to the phenanthroline core ligand,[28] as depicted in Figure 1. Molecular modeling studies of complexes of the type shown in Figure 1 suggest that the steric requirements of the 2-tolyl-pyrazole substituents enforce a C_2-symmetric complex with a pseudo-tetrahedral coordination geometry.[28] Additionally, the rigid ligand framework imposed by the biaryl linker in the complex is anticipated to introduce changes in the structural reorganization pathway of the photoexcited copper complexes.

Recently, Chen et al. have used femtosecond pump−probe techniques to investigate the early relaxation dynamics of [Cu-(dmp)$_2$]$^+$, dmp = 2,9-dimethyl-1,10-phenanthroline, in acetonitrile. They monitored the evolution of the photoexcited Franck−Condon MLCT state to the thermally equilibrated MLCT state and measured lifetime components of 500−700 fs and 10−20 ps, which they assigned to kinetics of the formation of the triplet MLCT state and the structural relaxation, respectively.[29] In this study, we have extended the use of femtosecond spectroscopy as a tool to elucidate the influence of geometrically constraining ligands on the excited-state photodynamics of Cu-(I)−phenanthroline complexes.

To date, most dynamic measurements have been obtained by nanosecond time-resolved emission spectroscopy, which monitors the overall decay of the MLCT excited state. With femtosecond laser spectroscopy, it is possible to observe the earlier nonradiative relaxation processes in metal complexes such as internal conversion, singlet−triplet intersystem crossing, and vibrational or torsional relaxation.[30−32] In these experiments, the complex is excited by a 120 fs laser pump pulse, and its relaxation is monitored by probing absorption changes with a second optical probe pulse. For the presented transient absorption spectroscopy measurements, a femtosecond white-light continuum (delivered by all-reflective optics to avoid chirp) is used as probe pulse.[33,34] Its broad-band spectrum enables the measurement of the transient absorption dynamics over the entire visible range. This is ideal for monitoring the MLCT excited-state dynamics of the investigated Cu(I)−phenanthroline complexes.
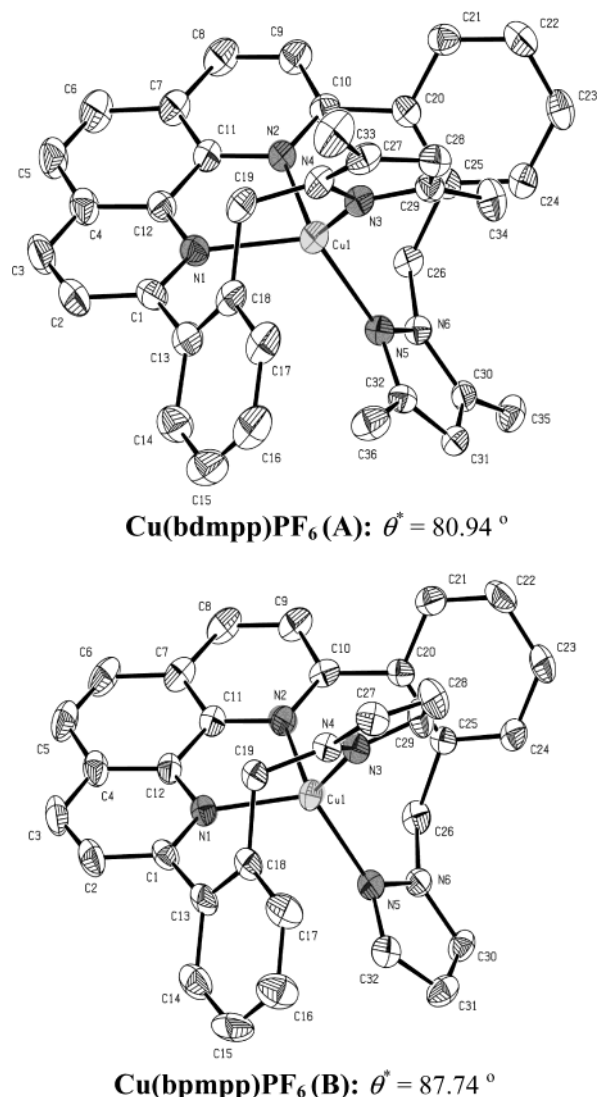

Cu(bdmpp)PF$_6$ (A): $\theta^* = 80.94\,^\circ$

Cu(bpmpp)PF$_6$ (B): $\theta^* = 87.74\,^\circ$

Figure 2. ORTEP plots and atom numbering scheme for Cu(I)−monophenanthroline complexes **A** (bdmpp = 2,9-bis-[2-(3,5-dimethylpyrazol-1-ylmethyl)-phenyl]-1,10-phenanthroline) and **B** (bpmpp = 2,9-bis-[2-pyrazol-1-ylmethyl-phenyl]-1,10-phenanthroline). Hydrogen atoms are omitted for clarity. θ^* is the angle between the two intersecting planes of the coordination tetrahedron, N(1)−Cu−N(2) and N(3)−Cu−N(5).[28]

We herein present the femtosecond time-resolved spectroscopic study of the flattening dynamics of two geometrically constrained 1:1 Cu(I)−phenanthroline complexes with pyrazole ligand donors. The excited-state dynamics, steady-state UV−vis absorption, and emission spectral properties of the complexes are discussed and correlated with the recently published[28] structural and electrochemical data of the investigated Cu(I)−monophenanthroline complexes.

Experimental Section

Materials and Reagents. All chemicals used were reagent grade unless otherwise specified. Dicholoromethane used for photophysical studies was Fisher optima grade and was used as received. The two Cu(I)−monophenanthroline complexes were available from a previous study.[28] The structure of the complexes and the corresponding intersecting plane angles are presented in Figure 2. Ligand abbreviations used are as follows: bpmpp = 2,9-bis-[2-pyrazol-1-ylmethyl-phenyl]-1,10-phenanthroline; bdmpp = 2,9-bis-[2-(3,5-dimethylpyrazol-1-ylmethyl)-phenyl]-1,10-phenanthroline.

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Steady-State Absorption and Fluorescence Spectroscopy. The UV−vis absorption spectra and steady-state emission spectra of the Cu(I)−phenanthroline complexes were recorded at room temperature using a Varian Cary Bio50 and a Varian Eclipse Fluorescence spectrophotometer, respectively. Quantum yields were determined using $[Ru(bpy)_3](PF_6)_2$ as standard ($\Phi_f(H_2O) = 0.042$). The refractive indices of water and dichloromethane were taken as 1.333 and 1.424, respectively. For absorption and emission measurements, spectrophotometric grade dichloromethane was used as solvent.

Time-Resolved Emission Spectroscopy. Time-resolved fluorescence spectra of the copper(I) complexes were measured by time-correlated single photon counting. The excitation source used was a Spectra-Physics (SP) Tsunami Ti-sapphire laser pumped with a SP Millennia diode-pumped Nd−YVO_4 laser. The repetition rate was set at 4 MHz with 2.2 ps pulse width. The output was frequency doubled by a SP GWU HG flexible harmonic generator and used as the excitation source for the sample measurements. The fluorescence emission was detected by a cooled Hamamatsu R3809U-50 microchannel plate photomultiplier (Hamamatsu, Japan), while a SPC-330-12 PC module (Becker & Hickl GmbH Intelligent Measurement and Control Systems, Berlin, Germany) was used for the photon counting electronics. The excitation wavelength used was 400 nm, and the emission was monitored at 650 nm. Fluorescence decays were acquired simultaneously with a lamp profile in 1024 channels of 9.8 ps/channel. Decay curves were deconvoluted using the Beechem global program. Goodness of fit was judged by reduced chi-square, χ_r^2, and the autocorrelation function of the weighted residuals.

Femtosecond Transient Absorption Laser Spectroscopy. Femtosecond time-resolved transient absorption measurements were measured using a Clark MXR 2001 femtosecond laser and a pump−probe system that has been described previously.[33,34] Samples were excited at 390 nm with a laser pulse of 120 fs duration (fwhm) and 0.8 mJ/cm² output energy per pulse. The excitation beam is focused to a spot diameter of about 500 μm and the probe beam to 100 μm. The samples were measured in a quartz cuvette of 2 mm path length and stirred by a cell stirrer to avoid permanent bleaching of the pump−probe volume element in the solution. All pump−probe experiments were carried out under ambient conditions. The samples were nitrogen-purged 15 min prior to measurements, and UV−vis spectra were obtained before and after the laser measurements to ensure that no significant photodecomposition occurred during the experiments.

Results

Steady-State Absorption Spectra. The room-temperature absorption spectra of $Cu(bdmpp)PF_6$ (**A**) and $Cu(bpmpp)PF_6$ (**B**) solutions in dichloromethane are shown in Figure 3. The absorption bands extend over a broad region of the visible spectrum and correspond to the MLCT transitions involving the π^* orbitals of the disubstituted phenanthroline ligands.

The absorption spectra display maxima at 418 and 428 nm for complexes **A** and **B**, respectively. The position of the maximum of the absorption band, denoted as λ_{max}, appears to be blue-shifted for complex **A**, which reveals an additional destabilization of the Franck−Condon (FC) MLCT state relative to the equilibrium Cu(I) ground state. The introduction of methyl groups on the two pyrazole moieties on complex **A** may have induced steric strain in the complex, which likely leads to a blue shift in the absorption band. The parameters characterizing the MLCT transitions on the copper(I) complexes are summarized in Table 1.
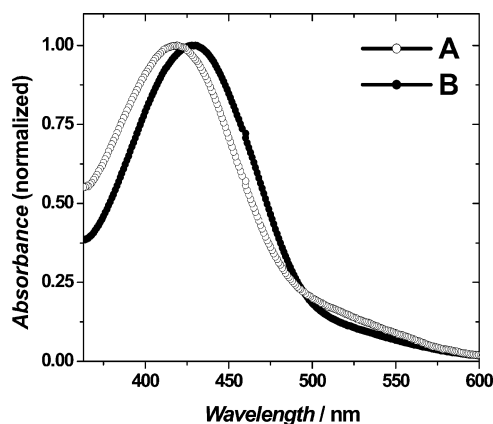

Figure 3. Room temperature steady-state absorption spectra of (A) $Cu(bdmpp)PF_6$ and (B) $Cu(bpmpp)PF_6$ solutions in dichloromethane.
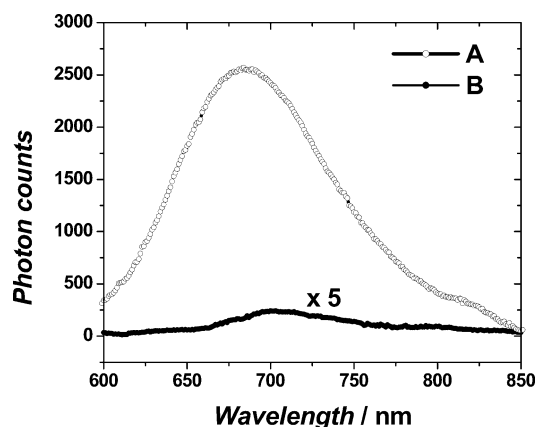

Figure 4. Room temperature steady-state emission spectra of (A) Cu-(bdmpp)PF_6 and (B) Cu(bpmpp)PF_6 solutions in dichloromethane.

TABLE 1. Room Temperature Photophysical and Electrochemical Data for Cu(I)−Monophenanthroline Complexes in Dichloromethane

	Cu(bdmpp)PF_6 (**A**)	Cu(bpmpp)PF_6 (**B**)
absorption λ_{max} (nm)	418	428
ϵ (cm^{-1} M^{-1})	3070	3010
emission λ_{max} (nm)	685	700
quantum yield ϕ_{em}	0.13%	∼0.004%
τ_{em} (ns)	110.5 ± 0.4	5 ± 1
$E_{1/2,ox}$ (V)[28]	0.48	0.33

Steady-State Emission. Shown in Figure 4 are the emission spectra in dichloromethane of samples **A** and **B** recorded after 400 nm excitation. The broad spectrum of Cu(bdmpp)$^+$ has an emission maximum at 685 nm, which is much more intense than the corresponding emission band of the Cu(bpmpp)$^+$ derivative, which peaks around 700 nm. The emission band of the dimethylpyrazole-substituted complex is blue-shifted, suggesting a relatively higher-lying energy level of CT states compared to that of the unmethylated pyrazole derivative. This observation parallels the absorption properties of these compounds.

Substituent effects have come to play an important role in the development of the chemistry of copper(I) complexes with 1,10-phenanthroline ligand derivatives. Several studies reveal that the presence of moderately bulky substituents in the 2,9-positions enhance the ligand's selectivity for copper(I) binding and stabilize the resulting copper(I) complexes against oxidation.[14,18,35] Subsequent work has shown that the same sterically active substituents increase the energy, the intensity, and the lifetime of the emission from the lowest excited MLCT state.[36,37]
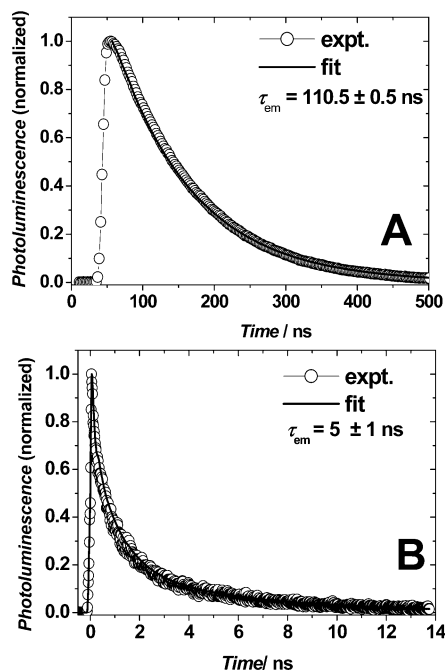
Figure 5. Lifetime measurements, τ_{em}, of the emission of the excited CT state in (A) Cu(bdmpp)PF$_6$ and (B) Cu(bpmpp)PF$_6$ complexes in dichloromethane.

Part of the explanation was that bulky substituents inhibit flattening distortion that would otherwise promote nonradiative decay. It was also shown that bulky substituents suppress solvent-addition reactions, which are possible in the relaxed excited state due to the opened coordination site and the increase in the oxidation state of the metal ion.[15] Although the two compounds **A** and **B** have a similar ligand backbone, it is interesting to note that the presence of the methyl groups in the pyrazole rings seems to impart a shielding to the copper complex **A**, resulting in an increased rigidity of the molecular framework and rendering it less susceptible to flattening relaxation. This can explain the higher emission quantum yield of complex **A** compared to that of complex **B**. Complex **B** seems to be a more flexible complex and therefore is able to relax to a lower excited state with almost completely quenched emission. The opening of additional nonradiative relaxation channels in complex **B** helps to explain the trend in the measured emission quantum yields of the two copper complexes relative to Ru(bpy)$_3{}^{2+}$, 0.13% for the Cu(bdmpp)PF$_6$ complex (**A**) and 0.004% for the Cu(bpmpp)PF$_6$ complex (**B**).

Emission Lifetimes. The copper complexes exhibit detectable emission in dichloromethane at room temperature upon irradiation into their MLCT band, and lifetime measurements (Figure 5) have been performed to determine the CT lifetimes. In the study of copper(I)–phenanthroline complexes, the extent of flattening that occurs in the CT excited state is a critical element in the emission dynamics. From Table 1, we see that the charge-transfer excited-state lifetime, τ_{em}, of complex **A** is appreciably longer than the excited-state lifetime of complex **B**. The lifetime of the CT excited state of Cu(bdmpp)$^+$ is 22× longer than that of the Cu(bpmpp)$^+$ analogue. Both complexes have similar 2-tolyl-donor substituents in the 2,9-positions of the phenanthroline ligand that are expected to enforce a C_2-symmetric complex with a pseudo-tetrahedral coordination geometry.[28] However, the introduction of methyl groups into copper complex **A** may have lead to steric constraints that resulted in a increased ligand framework rigidity and less nonradiative relaxation from the MLCT excited state. On the other hand, without the methyl
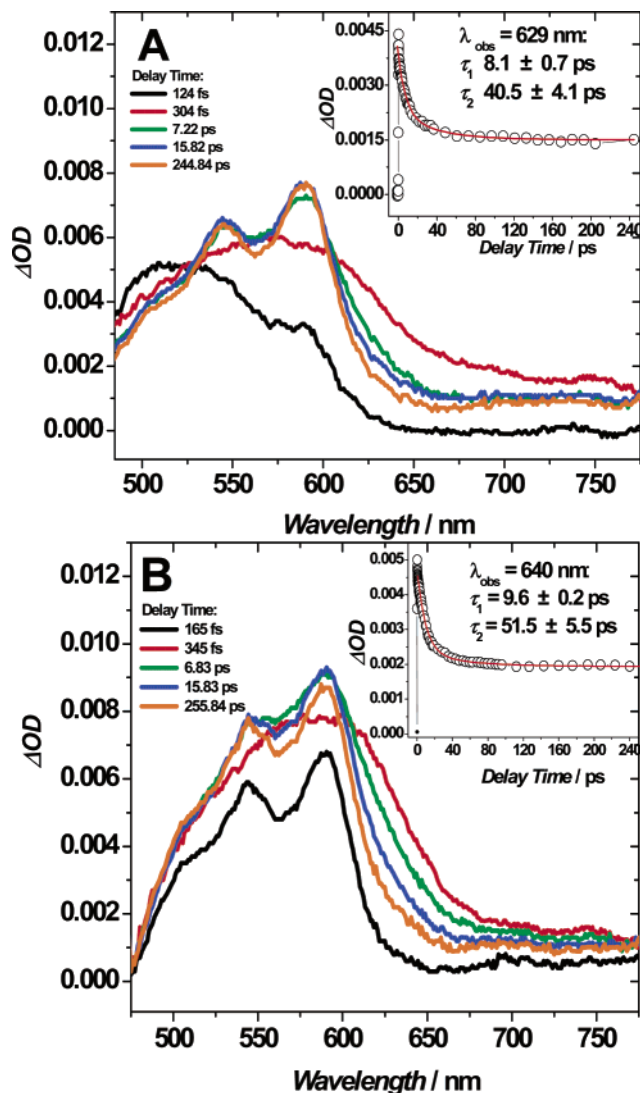

Figure 6. Femtosecond transient absorption spectra of (A) Cu(bdmpp)-PF$_6$ and (B) Cu(bpmpp)PF$_6$ complexes in dichloromethane. The insets show the flattening relaxation dynamics of the MLCT excited states of the respective complexes.

groups, copper complex **B** seems to allow for a strong nonradiative deactivation component and enhanced quenching of the emission.

Femtosecond Transient Absorption. The question arises whether the differences in nonradiative relaxation dynamics between **A** and **B** can be resolved using ultrafast spectroscopy. The transient absorption spectra of the Cu(I)–monophenanthroline complexes in dichloromethane were recorded at different delay times after photoexcitation with 390 nm femtosecond laser pulses (Figure 6). Immediately following laser excitation, formation of the two characteristic absorption maxima of the phenanthroline radical anion[38] was observed. The formation of the radical anion also indicates the formation of the MLCT state, where the copper metal center is oxidized to the +2 state. The absorption maxima of the free radical ion of the ligand in solution are reported at 604 and 657 nm.[38] For the coordinated ligand, these peaks are blue-shifted, according to the electron-withdrawing influence of the Cu(II) metal cation, to 545 and 590 nm, respectively. These are the wavelengths where the formation and decay of the CT state can be observed (Figures 6 and 7). The observation that the MLCT state is formed immediately after the laser pulse excitation was not surprising, since the excitation occurs directly into the MLCT
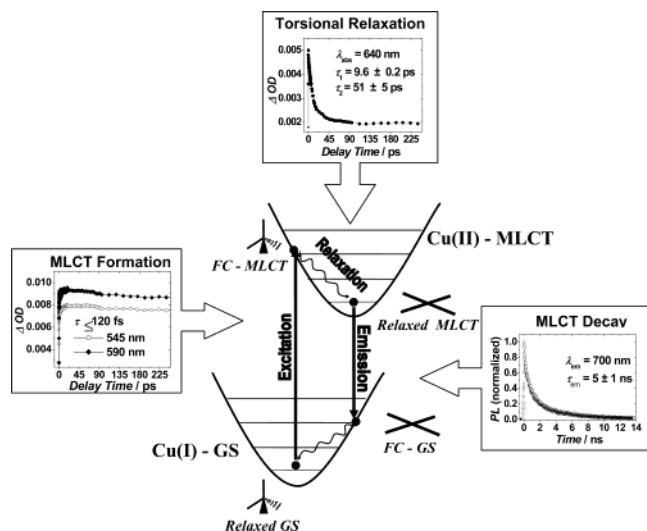
Figure 7. Schematic diagram of the photophysical processes in Cu-(I)−monophenanthroline complexes and the kinetic traces of the MLCT excited state lifetime components derived from femtosecond transient absorption measurements shown in Figure 6.

absorption band. Furthermore, the femtosecond time resolution allows for the direct observation of the subsequent flattening dynamics discussed in these types of geometrically constrained copper(I)−phenanthroline compounds for over two decades.[9−14] The MLCT lifetimes were longer than the time window of the femtosecond experiment and therefore were not measured via transient absorption but via the lifetime of the MLCT emission (Figure 5).

The onset of the FC-MLCT state results in the formation of a transient absorption spectrum, which shows the two characteristic peaks[38] of the ligand anion occurring at 545 and 590 nm. The spectral changes in Figure 6 suggest that the transient absorption spectra of the 1:1 Cu complexes initially exhibit a relatively sharp band; then it broadens and afterward sharpens back again. This could suggest that the complex originally has a well-defined equilibrium structure, and then samples a range of geometries before settling into a relaxed geometry. This has been related to the torsional reorganization of the Cu(I)/Cu(II) system undergoing a geometrical transition from the tetragonal to the more planar conformation[29] (as illustrated in Figure 7). The broadening can be monitored with the largest absorption differences at the red wing of the transient absorption spectra around 640 nm, and the kinetics monitored allows for the observation of the conformational changes from tetragonal to quasi-planar geometry. This broadening of the intraligand transient spectra is likely due to a combination of variations in the torsion angles of the pyrazol-1-ylmethyl-phenyl-1,10-phenanthroline ligand backbone and the flattening of the copper complex. It will be interesting to compare the dynamics of these 1:1 complexes with 1:2 Cu(I)−phenanthroline complexes. To date, the only femtosecond time-resolved study on the flattening dynamics of a 1:2 Cu(I)−phenanthroline complex has, however, only been reported in coordinating donor solvents, where the flattening dynamics is influenced by the coordination of the solvent.[29]

The investigated copper coordination compounds possess the interesting property that the Cu(I) ground state and the Cu(II) excited state prefer fundamentally different geometries. Cu(I) as a d^{10} ion generally adapts a four-coordinate tetrahedral geometry. On the other hand, Cu(II) being a d^9 ion prefers a square-planar geometry. The latter, when surrounded by good Lewis bases, like acetonitrile or dimethyl-sulfoxide, tends to expand into a penta- or hexa-coordinated system to undergo a stabilizing Jahn−Teller distortion. In dicholoromethane, however, this solvent coordination is reportedly not found.[15]

Monitoring the dynamics of complex **A** and complex **B** at 629 and 640 nm, respectively, reveals that both Cu(bdmpp)$^+$ and Cu(bpmpp)$^+$ complexes exhibited biexponential relaxation (inset of Figure 6, panels a and b, respectively). The unmethylated pyrazole analogue showed relaxation time constants of 9.6 ± 0.2 and 51.5 ± 5.5 ps. This could indicate that two distinct types of rearrangement motions are taking place during the relaxation process in the MLCT state.

It seems reasonable to picture this as the flattening around the metal center and the subsequent rearrangement of the methylphenyl-pyrazole backbone according to the new more planar conformation. In comparison, the 1:1 pyrazole complex with four additional methyl groups shows a similar but slightly shorter relaxation time with lifetimes of 8.1 ± 0.7 and 40.5 ± 4.1 ps. This observation is in agreement with the results of the absorption and emission lifetime measurements of the two compounds. With the introduction of four methyl groups in the 1:1 complex, the complex needs to adapt a conformation away from the ideal tetrahedral geometry (Figure 2) so as to provide additional room for the added moieties, in effect increasing the steric constraint in the ligand backbone. Consequently, it should become a smaller amplitude motion and therefore a faster process for the Cu(bdmpp)$^+$ to adapt the relaxed MLCT geometry.

It should be noted that internal vibrational energy distribution and singlet−triplet intersystem crossing are also part of the early dynamics. However, due to the similarity of complex **A** and **B**, the two latter processes are not expected to differ considerably. Moreover, based on the involved time scale and the order of the relaxation dynamics, it seems most plausible that the spectral changes are due to the torsional relaxation of the complex. The observed femtosecond dynamics of the 1:1 Cu complexes seem not only to point to the common vibrational modes exhibited by the ligand but also serve as an experimental observation of the motions that follow the known geometrical transition from a distorted-tetrahedral to a more planar Cu complex structure.[15] It has been previously shown that the transients of Cu(dmp)$_2$$^+$ at low temperature arise from closely spaced singlet and triplet MLCT excited states, which behave at room temperature as one state.[20,21] Therefore, since the presented measurements were performed at room temperature, no significant effect from intersystem crossing is expected.

Discussion

It is interesting to note that the observed spectral properties of the 1:1 Cu(I)−phenanthroline complexes follow the same trend as in the case of 1:2 Cu(I)−phenanthroline complexes.[15] Studies on Cu(I)−phenanthroline complexes with the 1:2 binding stoichiometry suggest that substituents in the 2- and 9-positions of 1,10-phenanthroline, when coordinated with Cu-(I), would interact in a destabilizing manner with the 2- and 9-substituents on the opposite ligand in the Cu(II) state.[15] Thus, more bulky substituents in the 2- and 9-positions of the two phenanthroline ligands lead to the complex offering more resistance to flattening toward a planar geometry during the relaxation of the Cu(II) MLCT state. Likewise, in the 1:1 framework, addition of methyl groups on the pyrazole rings seems to hinder flattening and retains some of the steric constraint, thus producing the shorter nonradiative relaxation times for complex **A** compared to those for complex **B**. This is in accordance with the absorption spectra, the blue-shifted emission, and the emission quantum yields.

These arguments become even more compelling if one compares explicitly the radiative and nonradiative decay rates. The quantum yield, ϕ_{em}, and emission lifetime, τ_{em}, can be used to determine the radiative rate constant, k_r, via $\phi_{em}/\tau_{em} = k_r$, and the nonradiative relaxation rate, k_{nr}, via $k_{nr} = \tau_{em}^{-1} - k_r$. This reveals that the attenuated emission and lifetime of compound **B** relative to compound **A** is due to both an increase in k_{nr} (2×10^8 s^{-1} for compound **B** versus 9×10^6 s^{-1} for compound **A**) and a decrease in k_r (8×10^3 s^{-1} for compound **B** versus 1.2×10^4 s^{-1} for compound **A**). The increase in k_{nr} is expected, but the drop in k_r is somewhat surprising and is likely related to the structural differences.

Femtosecond spectroscopy provides here a unique opportunity to directly observe the effect of ligand constraints on the ultrafast formation of the equilibrated MLCT excited state in copper-(I)−phenanthroline complexes. Coupled with the information obtained from steady-state absorption and emission and time-resolved emission spectroscopy, it provides complementary information on the photophysics of these metal complexes.

We can assume that the excited-state reorganization from the FC-MLCT to the relaxed MLCT (Figure 7) is energetically similar to the ground-state reorganization from the FC-GS after radiative back electron transfer (distorted square planar type) to the relaxed GS (distorted tetrahedral). These are the same motions along the same torsional nuclear coordinate but in reverse direction and with different charge distribution. Therefore, one can roughly estimate the total reorganization energy for the torsional relaxation to be $\Delta E_{reog} \approx \{\Delta E_{abs} - \Delta E_{em}\}/2 = 0.56$ eV. Taking the singlet−triplet energy difference of the MLCT manifold into account, this value would be somewhat reduced. Nevertheless, here the singlet−triplet splittings are not large, and geometry differences between the ground state and the emitting CT state are more important factors determining the Stokes shift.[20]

From Table 1, one can estimate the relaxation energy differences from the FC-MLCT to the relaxed MLCT states and show that they are similar for the two 1:1 copper complexes. $\Delta E_{abs} - \Delta E_{em}$ is 1.125 eV for the unsubstituted and 1.156 for the dimethyl-substituted system. Therefore, the dynamical differences appear to reflect the constraints in the amplitude of the flattening motions. Based on X-ray crystallographic data,[28] the unmethylated 1:1 complex exhibits a nearly perfect tetrahedron at the metal center, the angle between the two coordination planes being 87.7°. This allows an almost undistorted tetrahedral ground-state conformation. On the other hand, the X-ray data for the dimethyl-substituted compound show a different ground-state geometry, the angle between the two coordination planes being 80.9°, which is farther from the ideal 90°. This implies a geometrical distortion toward a more planar configuration, which is in agreement with the trend in the measured absorption spectra. Accordingly, the energies of the ground and excited states of the two complexes are different with the Cu(bdmpp)$^+$ complex exhibiting a more blue-shifted absorption and emission maxima.

The higher quantum yield, long emission lifetime, and fast relaxation dynamics of the Cu(bdmpp)$^+$ complex (**A**) are consistent with the steric arguments that in a 1:1 ligand framework, addition of alkyl substituents in the ligand hinders the flattening relaxation. This observation is consistent with what has been reported for the case of the 1:2 copper(I)−phenanthroline complexes, where the presence of alkyl substituents in the 2- and 9-positions of the two phenanthroline rings has a destabilizing effect in the more planar geometry. In summary, the photophysical measurements suggest that the methyl groups

in the Cu(bdmpp)$^+$ complex introduce ligand constraints to the complex's adaptation of both a tetrahedral and also a planar symmetry causing a smaller amplitude of the torsional motion in the photoinduced MLCT state.

Conclusion

In conclusion, femtosecond transient absorption spectroscopy enables to spectrally and temporally resolve the effect of ligand constraints on the flattening rearrangement dynamics in photoexcited Cu(I)−monophenanthroline complexes. This technique can be extended toward the investigation of more complex systems, such as copper(I)−phenanthroline−DNA[23] conjugates and macrocyclic copper(I) systems,[39] to provide additional information about ligand binding interactions and dynamics. Currently, we are investigating the reorganization dynamics of Cu(I)−monophenanthroline complexes in the presence of coordinating solvents to gain more understanding of the solvent effects in terms of stabilization of the MLCT state and the quenching of the MLCT emission.

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