Ultrafast relaxation processes in photoactive heteroleptic copper(I) complexes: insights into the interplay between excited states.


Abstract: The developments made towards increasingly photoactive copper(I) complexes has led to their use in many applications involving light, in particular light emission or photocatalytic activities. Herein, we describe an unprecedented in-depth study of the photophysical properties of two of the most used copper(I) photosensitizers, [Cu(bcp)(DPEphos)]+ and [Cu(bcp)(Xantphos)]+ (bcp = bathocuproine, Xantphos = 4,5,9,9-tetramethylxanthene, DPEphos = Bis[2-diphenylphosphino]phenyl]ether). This study combines traditional spectroscopic techniques with state-of-the-art femtosecond time-resolved transient absorption and fluorescence up-conversion spectroscopy and is further supported by quantum-chemical calculations. This combined analysis hints at the presence of a low-lying ligand-centered dark triplet state which plays a crucial role by acting as a reservoir for the excited heteroleptic copper(I) complexes.

Introduction

Photochemistry is a rapidly growing field of research in many different areas. The most well-known examples of inorganic photoactive complexes are based on ruthenium or iridium. With intense absorption and emission in the visible part of the spectrum, these complexes have dominated most applications in photochemistry such as light harvesting systems,[1–4] OLED applications,[5] photoredox catalysis[6–8] or biomedical applications.[9–12]

However, those metals are some of the least abundant elements on earth. Therefore, attention is shifting towards the design of first-row transition metal based photoactive complexes. Metals such as iron, cobalt or manganese are orders of magnitude more abundant. Nevertheless, despite some recent breakthroughs, most complexes based on these metals are still not competitive with ruthenium and iridium complexes.[13–16]

Photoactive copper complexes are an exception. Indeed, copper complexes are known to be luminescent since the late 1970’s.[17] Due to their high structural versatility,[18–20] photoactive copper complexes have been tailored to meet the requirements of most of the photochemical systems such as OLED’s,[21] DSSC’s[22] or photocatalytic systems.[23–25]

Copper complexes exhibit an intricate photophysical behavior characterized by three main features: (i) a pseudo Jahn-Teller distortion from a tetrahedral ground state geometry to a square-planar geometry in the excited state; (ii) an intersystem crossing from a singlet to a triplet excited state,[26–28] and (iii) a thermally activated delayed fluorescence (TADF) at room temperature originating from a small energy difference between the lowest singlet and triplet excited state.[29–32]

With the continuous developments made in computational and experimental methods, the insight gained into the photophysical scheme of such complexes keeps evolving over time. In this study, we combine state of the art femtosecond time-resolved transient absorption (TA) and fluorescence up conversion (FUC) spectroscopy with Time Dependent Density Functional Theory (TD DFT) computations to yield an in-depth description of the photophysical behavior of [Cu(bcp)(Xantphos)]+ and [Cu(bcp)(DPEphos)]+. These two complexes are amongst the most used heteroleptic copper(I) complexes in photoredox catalysis[33–42] or solar energy conversion[43–57]. Since they are often used as model for this class of complexes, having the most refined description of their excited state dynamics is crucial to further enhance the properties of new derivatives.

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Results and Discussion

The synthesis of the two complexes was performed according to previous reports.\[^{[51]}\] Recrystallization by slow diffusion of diethylether in dichloromethane yielded pure crystals of the complexes, which were characterized and used in this study. The ground state geometry optimized at the DFT level (PBE0, 6-31G(d) basis set for H,C,N and O atoms, 6-311G(d,p) basis set for P atoms and LANL2DZ pseudopotential for the Cu atom) is in good agreement with previously reported geometries obtained by X-ray diffraction spectroscopy.\[^{[51,58]}\] Both complexes adopt a pseudo-tetrahedral geometry in the ground state with calculated dihedral angles between the N-Cu-N and P-Cu-P planes of 85.0° and 88.9° for \([\text{Cu(bcp)(Xantphos)}]^+\) and \([\text{Cu(bcp)(DPEphos)}]^+\), respectively (Figure 1).

Absorption and emission spectroscopy

The absorption spectrum of \([\text{Cu(bcp)(Xantphos)}]^+\) in acetonitrile displays two bands (Figure 2.a). According to the TD-DFT calculations of the vertical transitions from the optimized ground state geometry (solvent effects introduced within the Polarizable Continuum Model for acetonitrile), the lowest energy band, peaking at 388 nm (Table 1), corresponds to a metal-to-ligand charge transfer (MLCT) transition, while that at higher energy (284 nm) is composed of multiple ligand centered (LC) transitions. In the case of \([\text{Cu(bcp)(DPEphos)}]^+\) in acetonitrile, the weak band at 470 nm (inset Figure 2.b) is due to the presence of the homoleptic complex \([\text{Cu(bcp)}]^2+\) formed upon dynamic equilibrium, a typical behavior for such kind of Cu(I) complexes.\[^{[51,59]}\] There is no significant change of the absorption spectrum in dichloromethane (Figure S1) except for \([\text{Cu(bc}[0x0]p)(DPEphos)]^+\) which does not exhibit the band of the homoleptic \([\text{Cu(bcp)}]^2+\) complex. Noteworthy, the amount of the homoleptic complex \([\text{Cu(bcp)}]^2+\) in acetonitrile is small enough to have a negligible impact on the transient absorption spectrum shown later. Furthermore, the homoleptic complex is not emissive in acetonitrile.\[^{[20]}\]

The emission spectrum of both complexes is characterized by a broad structureless band around 580 nm in acetonitrile and 570 nm in dichloromethane (Figure 2.c and d). In dichloromethane, both \([\text{Cu(bcp)(Xantphos)}]^+\) and \([\text{Cu(bcp)(DPEphos)}]^+\) show a long luminescence lifetime (15.1 ns and 18.2 ns) and a high luminescence quantum yield (51.6 % and 54.9 %) (Table 1). However, in acetonitrile \([\text{Cu(bcp)(Xantphos)}]^+\) has a shorter luminescence lifetime and a lower luminescence quantum yield of 328 ns and 3.4 %, respectively, when compared to 1100 ns and 11.4 % for \([\text{Cu(bcp)(DPEphos)}]^+\). This is likely due to the additional non-radiative decay pathway via exciplex quenching involving solvent coordination observed in acetonitrile for similar Cu(I) complexes.\[^{[60]}\]

![Figure 1. Optimized ground state geometry of \([\text{Cu(bcp)(Xantphos)}]^+\) and \([\text{Cu(bcp)(DPEphos)}]^+\). Hydrogen atoms are omitted for clarity.](image)

| Table 1. Absorption and emission properties of \([\text{Cu(bcp)(Xantphos)}]^+\) and \([\text{Cu(bcp)(DPEphos)}]^+\) in acetonitrile and dichloromethane under argon atmosphere. |
|------------------|------------------|------------------|------------------|------------------|
| Complex          | \(\lambda_{\text{abs}}\) [nm] | \(\varepsilon_{\text{abs}}\) [M\(^{-1}\).cm\(^{-1}\)] | \(\lambda_{\text{em}}\) [nm] | \(\tau_{\text{em}}\) [ns] | \(\Phi_{\text{em}}\) [%] |
| \([\text{Cu(bcp)(Xantphos)}]^+\) | 388 (5690)       | 392 (5600)       | 578               | 15100            | 3.4              | 51.6             |
| \([\text{Cu(bcp)(DPEphos)}]^+\) | 385 (4840)       | 388 (5790)       | 586               | 18200            | 11.4             | 54.9             |

\(^a\) \(\lambda_{\text{exc}} = 390\) nm, \(^b\) \(\lambda_{\text{exc}} = 405\) nm.
Figure 2: Absorption spectrum of [Cu(bcp)(Xantphos)]⁺ (a) and [Cu(bcp)(DPEphos)]⁺ (b) in acetonitrile; the energy and intensity of the vertical transitions calculated in the optimized ground state geometry are represented by the solid red lines. The inset is a zoom on the MLCT band. Emission spectra of [Cu(bcp)(Xantphos)]⁺ (c) and [Cu(bcp)(DPEphos)]⁺ (d) in acetonitrile and dichloromethane under argon atmosphere (τ_{exc} = 390 nm).

Excited state geometry

To assess the accessibility of the metal center to the coordinating solvent in the excited state, the geometry of the first singlet (S₁) and triplet (T₁) excited states were optimized (Figure S2 and Table 2). The S₁ state adopts a flattened geometry as illustrated by the smaller dihedral angle of 71.1° and 77.7° for [Cu(bcp)(Xantphos)]⁺ and [Cu(bcp)(DPEphos)]⁺, respectively. The greater extent of flattening distortion in [Cu(bcp)(Xantphos)]⁺ is fully consistent with the shorter excited state lifetime and lower luminescence quantum yield in acetonitrile as this complex is expected to be more prone to exciplex quenching due to solvent coordination. Interestingly, the optimized geometry of the T₁ state of both complexes is very similar to the ground state geometry, showing almost no flattening distortion (angles of 85.4° and 86.3°). Using natural transition orbitals (Figure 3 and S3) to analyze the hole and electron localization shows that the S₁ state of both complexes is described by a MLCT state (with the hole localized on the metal and the electron on the bcp ligand) whereas the T₁ state is a LC state (with both the hole and electron localized on the bcp ligand).

Table 2: Structural parameters of the optimized geometry in the ground (S₀), excited singlet (S₁) and excited triplet (T₁) state of [Cu(bcp)(Xantphos)]⁺ and [Cu(bcp)(DPEphos)]⁺:

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<tr>
<td>[Cu(bcp)(Xantphos)]⁺</td>
<td>2.13</td>
<td>2.26</td>
<td>85.0</td>
<td>2.03</td>
<td>2.42</td>
<td>71.1</td>
<td>2.11</td>
<td>2.31</td>
<td>85.4</td>
<td></td>
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<tr>
<td>[Cu(bcp)(DPEphos)]⁺</td>
<td>2.10</td>
<td>2.31</td>
<td>88.9</td>
<td>2.02</td>
<td>2.40</td>
<td>77.7</td>
<td>2.08</td>
<td>2.31</td>
<td>86.3</td>
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Temperature dependent measurements

Copper(I) complexes are known to have close lying $S_1$ and $T_1$ states, making their luminescence mainly dominated by TADF.\cite{61} We measured both the emission spectrum and luminescence lifetime of the complexes in acetonitrile and dichloromethane under argon atmosphere at various temperatures. As expected, the emission of $[Cu(bcp)(Xantphos)]^+$ in both solvents (Figure 4) is intense and centered at lower wavelength (570 nm) at higher temperature (340 K). On the other hand, at low temperature (240 K), the emission is centered at higher wavelength (585 nm), about five times less intense and characterized by a fivefold longer luminescence lifetime. The second complex, $[Cu(bcp)(DPEphos)]^+$ shows the same kind of behavior (Figure S4).

The energy difference between the $S_1$ and $T_1$ state ($\Delta E_{S_1-T_1}$) can be extracted from the luminescence lifetime as a function of temperature (Table 3). Plotting $\ln(k_{obs})$ in function of $1/T$ should give a linear graph with a slope of $\Delta E_{S_1-T_1}k_b$ according to the following equation:\cite{62}

$$\ln(k_{obs}) = \ln\left(\frac{k_{1SC}}{3k_{fl}}\right) \left(1 - \frac{k_{1SC}}{k_{fl} + k_{ISC}}\right) - \frac{\Delta E_{S_1-T_1}}{k_b} \frac{1}{T}$$

where $k_{ISC}$ is the intersystem crossing rate constant $k_b$ and the fluorescence rate constant.

Surprisingly, both complexes in both solvents show a bi-linear variation of these plots (Figure 4). This indicates that in the studied temperature range, three excited states seem to be involved in the emission of these complexes. At this stage we suspect to have one high lying $1\text{MLCT}$, one low lying $3\text{LC}$ and a $3\text{MLCT}$ transition. Optimization of the second triplet state ($T_2$) yielded a second $3\text{LC}$ state lying above the $S_1$ state. In the flattened geometry of the $S_1$ state the $T_1$ excited state shows a $3\text{MLCT}$ transition with an energy lying between the $1\text{MLCT}$ and $3\text{LC}$ state. Therefore, two energy gaps can be extracted from fitting the plots of $\ln(k_{obs})$ vs. $1/T$. One at high temperatures for the difference between the $1\text{MLCT}$ and $3\text{MLCT}$ state and the second one at low temperatures for the difference between the $3\text{MLCT}$ and the $3\text{LC}$ states.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solv.</th>
<th>$1\text{MLCT}$</th>
<th>$3\text{MLCT}$</th>
<th>$3\text{LC}$</th>
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<tr>
<td>$[Cu(bcp)(Xantphos)]^+$</td>
<td>ACN</td>
<td>0.08</td>
<td>0.17</td>
<td>0.25</td>
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<td></td>
<td>DCM</td>
<td>0.04</td>
<td>0.07</td>
<td>0.11</td>
</tr>
<tr>
<td>$[Cu(bcp)(DPEphos)]^+$</td>
<td>ACN</td>
<td>0.20</td>
<td>0.09</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>DCM</td>
<td>0.09</td>
<td>0.04</td>
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</table>

Table 3: Experimental values of $\Delta E$ for $[Cu(bcp)(Xantphos)]^+$ and $[Cu(bcp)(DPEphos)]^+$ in acetonitrile and dichloromethane.
Both complexes show a different trend for these energy gaps. Indeed, [Cu(bcp)(Xantphos)]+ shows a smaller gap between the 1MLCT and the 3MLCT (0.08 eV and 0.04 eV in acetonitrile and dichloromethane) than between 3MLCT and the 3LC (0.17 eV and 0.07 eV in acetonitrile and dichloromethane). On the other hand, [Cu(bcp)(DPEphos)]+ shows a bigger gap between the 1MLCT and the 3MLCT (0.20 eV and 0.09 eV in acetonitrile and dichloromethane) than between 3MLCT and the 3LC (0.09 eV and 0.04 eV in acetonitrile and dichloromethane). The overall energy difference of [Cu(bcp)(Xantphos)]+ is also smaller in both solvents than that of [Cu(bcp)(DPEphos)]+. Since the room temperature lifetime is controlled by the population of the 1MLCT state, the lower energy difference observed for [Cu(bcp)(Xantphos)]+ between the 1MLCT and the 3MLCT, combined with the greater extent of the flattening distortion in this complex as described above, might explain the shorter luminescence lifetime.

Femtosecond time resolved spectroscopy

The relaxation pathway from the Franck-Condon excited state generated right after photo-excitation down to the formation of the fully relaxed triplet state was investigated by using femtosecond time resolved transient absorption (TA) and broadband fluorescence up conversion (FUC) spectroscopy. The spectra obtained for [Cu(bcp)(Xantphos)]+ in acetonitrile are shown in Figure 4: Emission spectrum (λexc = 410 nm) (a and b) and temperature dependance of the luminescence lifetime (λexc = 405 nm) (c and d) of [Cu(bcp)(Xantphos)]+ in acetonitrile (left) and dichloromethane (right) under argon atmosphere.

Figure 4. The spectra obtained in dichloromethane for [Cu(bcp)(Xantphos)]+ (Figure S6) and in both solvents for [Cu(bcp)(DPEphos)]+ (Figure S5 and S7) are in the supplementary files. The time components obtained with both methods are in good agreement (Table 4).

Table 4: Time components of the femtosecond time-resolved transient absorption (red) and broadband fluorescence up conversion spectroscopy (green) (obtained via global analysis) of [Cu(bcp)(Xantphos)]+ and [Cu(bcp)(DPEphos)]+ in acetonitrile and dichloromethane at room temperature (λexc = 400 nm).

<table>
<thead>
<tr>
<th>Complex</th>
<th>ACN</th>
<th>DCM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T1</td>
<td>T2</td>
</tr>
<tr>
<td>[Cu(bcp)(Xantphos)]+</td>
<td>0.2</td>
<td>2.4</td>
</tr>
<tr>
<td>[Cu(bcp)(DPEphos)]+</td>
<td>0.2</td>
<td>1.9</td>
</tr>
<tr>
<td>[Cu(bcp)(DPEphos)]+</td>
<td>0.4</td>
<td>2.2</td>
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</table>

The fastest time component of 0.2 ps for [Cu(bcp)(Xantphos)]+ in acetonitrile is assigned to the relaxation of the solvent as well as to the geometry relaxation of the complex. The pristine TA spectrum is characterized by a band at 570 nm and a shoulder around 630 nm. The flattening distortion of the complex, due to the pseudo Jahn-Teller distortion of the S=1 MLCT excited state, is accompanied by the attenuation of the shoulder. The FUC spectrum associated with this the unrelaxed state shows an emission maximum at 520 nm.
The second component of about 2.0 ps is assigned to the conversion of the relaxed \(^1\)MLCT to the \(^3\)MLCT state. The timescale of such an intersystem crossing process is in good agreement with previously published studies for sterically hindered copper(I) complexes.\[^{[61]}\] The TA spectrum associated with the relaxed \(^1\)MLCT shows one band centered at 560 nm. The solvation and relaxation of the complex is accompanied by a significant redshift of the emission spectrum from 520 nm to 575 nm.

A third component of about 10 ps, which is not typically reported for such copper(I) complexes, is also observed. We assign this time component to the relaxation of the \(^3\)MLCT to the \(^5\)LC excited state. Indeed, right after the intersystem crossing from the \(S_1\) to the \(T_1\) excited state, the complex lies in a flattened geometry. However, as discussed previously, the optimized geometry of the \(T_1\) state is tetrahedral and therefore different from the optimized \(S_1\) geometry. This time component is also characterized by the reappearance of the shoulder around 630 nm in the TA spectrum which is reminiscent of the starting TA spectrum. This shoulder is thus observed initially when the complex is still in its tetrahedral geometry, disappears when the complex adopts a flattened geometry in the relaxed \(S_1\) state and finally reappears again, thus indicating that the \(T_1\) state also acquires a pseudo-tetrahedral geometry, in full agreement with the calculations. The emission spectrum in the FUC associated with the complex in the \(^3\)MLCT state is further red shifted from 560 nm to 585 nm.

The second complex, [Cu(bcp)(DPEPhos)]\(^+\) shows the same behavior in acetonitrile with very similar time components (Figure S5). In dichloromethane, both complexes show almost the same relaxation pathway as in acetonitrile with a slightly longer time component for the third relaxation process (Table 4, Figures S6 and S7). However, one main difference between the relaxation pathway in the two solvents is that a fourth time component of 1260 ps for [Cu(bcp)(Xantphos)]\(^+\) and 800 ps for [Cu(bcp)(DPEPhos)]\(^+\) is present in acetonitrile but not in dichloromethane. This relaxation process does not have an important weight in the fitting procedure and might be linked to the formation of an exciplex between the excited complex and acetonitrile. Indeed, the formation of an exciplex could explain the shorter luminescence lifetime and quantum yield observed for both complexes in acetonitrile.

A long-lived species is formed in all cases at the end of the cascade of relaxation processes. This last species is likely the fully relaxed excited triplet state. However, this relaxed triplet state is not visible in the FUC experiment indicating its low radiative decay rate. This behavior is consistent with the LC nature of the fully relaxed triplet state which should have a low emission quantum yield.

During the ultrafast relaxation processes, the FUC emission spectrum associated with the transient species shows a significant red shift. This parallels the evolution of the emission spectrum as a function of temperature. Accordingly, Figure 6 displays both the normalized time-resolved emission spectrum at room temperature and steady-state spectrum at various temperatures for [Cu(bcp)(Xantphos)]\(^+\) (see Figure S8 for the spectrum of [Cu(bcp)(DPEPhos)]\(^+\)).
Figure 6: Normalized fs time resolved emission spectrum ($\tau_2$, and $\tau_3$) and steady state emission spectrum as a function of temperature (at 340 K and 240 K) of [Cu(bcp)(Xantphos)]$^+$ in deaerated acetonitrile.

At 340 K in acetonitrile, the emission occurs mostly from the singlet state through TADF. The emission maximum at 340 K in acetonitrile (572 nm for [Cu(bcp)(Xantphos)]$^+$) matches very well with the emission maximum of the second transient species. This second species which relaxes to the third one in about 2.0 ps is thus the complex in the geometrically relaxed $S_1$ excited state. At the lowest temperature (240 K) in liquid acetonitrile, the emission mostly occurs from the $^3$MLCT excited state. This last emission maximum (585 nm for [Cu(bcp)(Xantphos)]$^+$) matches well with the emission maximum of the third transient species. Therefore, the third emitting transient species corresponds to the complex in its $^3$MLCT excited state. In the FUC no signal is observed once the $^3$MLCT relaxes down to the $^3$LC.

However, the absence of emission after this third relaxation process is contradictory with the steady-state luminescence observed for these complexes. This showcases that both triplet excited states (the $^3$LC and $^3$MLCT) are likely in a fast dynamic equilibrium. The proposed revision of the photophysical scheme for heteroleptic copper(I) complexes resulting from this study is shown in Figure 7. The $^3$LC excited state is proposed as being responsible for the long excited state lifetime of heteroleptic copper(I) complexes as it could act as a long-lived reservoir for the emissive MLCT states. Such behavior has already been used to extend the emission lifetime of ruthenium(II) complexes. However, this study is the first to provide direct evidence for the presence of a $^3$LC excited state. Furthermore, it shows that introducing a separate organic chromophore on purpose (i.e. perylene, anthracene or pyrene moiety) is not essential for a $^3$LC state to play a key role in the excited state properties of heteroleptic copper(I) complexes.

Figure 7: Proposed photophysical scheme of [Cu(bcp)(Xantphos)]$^+$ in acetonitrile.

Taking this $^3$LC excited state into account should play a key role in the design of novel copper(I) complexes as destabilizing it above the $^3$MLCT should drastically reduce the luminescence state lifetime of the resulting complexes. However, stabilizing it too much could prevent the repopulation of the $^3$MLCT state and therefore kill the luminescence of the complex. One last possibility would be to enhance the radiative decay from this $^3$LC state in order to get even longer luminescence lifetimes. Further investigation into the structural impact on both the MLCT and LC states is crucial for the development of a new generation of heteroleptic copper(I) complexes.

Conclusion

In this study, we combined theoretical and experimental approaches to shed light into the ultrafast photophysical behavior of [Cu(bcp)(Xantphos)]$^+$ and [Cu(bcp)(DPEphos)]$^+$, two commonly used photoactive copper(I) complexes. Overall, the theoretical results are found to be in very good agreement with the experimental data. Their combination allows for a deep understanding of the photophysical properties and excited-state dynamics of the studied copper(I) complexes to be gained.
Small structural changes can lead to substantial differences in photophysical properties such as the excited state lifetime. These differences are mainly due to the geometry adopted by the complexes at each stage of the ultrafast relaxation processes. As shown here, the excited singlet state tends to be more flattened since it is a pure MLCT transition. On the other hand, the triplet state appears to adopt a pseudo tetrahedral geometry close to the ground state geometry due to its more pronounced LC character. The use of state-of-the-art ultrafast spectroscopic setups has further deepened the understanding of the relaxation processes of copper(II) complexes in their excited state. Using these advanced methods allows to nicely picture all key relaxation processes occurring from the pristine photogenerated singlet excited species down to the final relaxed triplet excited state. Besides applying this unique panel of approaches to prototypical copper(II) complexes, the present work should stimulate similar efforts on new generations of complexes to help in the design of structures with enhanced performances.

Experimental Section

1. Materials

Synthesis and characterization of [Cu(bcp)(Xantphos)]PF$_6$ and [Cu(bcp)(DPEphos)]PF$_6$ were carried out according to previously described methodology in our laboratory. All solvents are of spectroscopic grade and used without further purification. The solvents were degassed using the freeze-pump-thaw method.

2. Instruments

All spectroscopic experiments were realized using quartz cuvettes with a 1 cm optical path (2 mm for the ultra-fast experiments). UV–vis absorption spectra were recorded with a Shimadzu UV1900i UV-VIS spectrophotometer. Steady state emission spectra were recorded with a Shimadzu RF-5301 PC spectrofluorometer at an absorbance of 0.15 at the excitation wavelength (detection: Hamamatsu R-928 red-sensitive photomultiplier tube, excitation source: xenon lamp 150 W). Luminescence quantum yields were calculated relative to [Ru(bpy)$_3$]$_2$PFS (θ$_{cal} = 5.9\%$ in deaerated acetonitrile). Emission lifetimes at all temperatures were measured by Time-Correlated Single Photon Counting (TC-SPC) using a LifeSpec II Lifetime Spectrometer from Edinburgh Instruments with a Pulsed laser EPL405 as excitation source. Temperature control from 340 K to 80 K as achieved using a liquid nitrogen cryostat OptistatDN-X from Oxford Instruments coupled to a Oxford ITC4 intelligent temperature controller.

Emission spectra in function of temperature were obtained using a nanosecond pulsed laser as excitation source (Nd:YAG Q-switched Surelille laser from Continuum using the 355 nm pulse to pump and a Surelille OPO plus giving a 410 nm pulse to excite the sample). The detector was a PI-MAX (ICCD camera from Princeton Instruments. The five first spectra right after the end of the excitation pulse (from 0 ns to 10 ns) were averaged to give the emission spectra in function of temperature. The experimental setups for femtosecond transient absorption and fluorescence upconversion measurements have been widely described elsewhere.$^{[70–73]}$ In particular, the 400 nm excitation pulses of ca. 40 fs are generated by an amplified Ti:sapphire laser system (Spectra Physics). The transient absorption setup (Helios, Ultrafast Systems) is characterized by a temporal resolution of ca. 150 fs and a spectral resolution of 1.5 nm. Probe pulses are produced in the 450–800 nm range by passing a small portion of 800 nm light through an optical delay line (with a time window of 3200 ps) and focusing it onto a 2 mm thick sapphire window to generate a white-light continuum. In the upconversion setup (Halcyone, Ultrafast Systems), the 400 nm pulses excite the sample, whereas the remaining fundamental laser beam plays the role of the “optical gate” after passing through a delay line. The fluorescence of the sample is collected and focused onto a BBO crystal together with the delayed fundamental laser beam. A CCD detects the upconverted fluorescence. Movements of the crystal through a rotational stage allow for broadband detection of the emission at each delay and thus acquisition of the entire time-resolved fluorescence spectra. The temporal resolution of the upconversion equipment is about 250 fs, whereas the spectral resolution is 1 nm. Ultrafast spectroscopic data were fitted by Global Analysis using Surface Explorer and GloTarAn softwares.$^{[74]}$

3. Molecular modelling

The density functional theory (DFT) calculations were performed with the Gaussian 16 revision A.03 suite. All calculations were obtained using the PBE0 functional $^{[75]}$ with the LANL2DZ pseudopotential for the Cu atom, 6-311G(d,p) basis set for the P atoms and 6-31G(d) basis set for the H, C, N and O atoms, with dispersion included with a Grimme’s correction.$^{[76]}$ Solvent effects were always introduced within the Polarizable Continuum Model for acetonitrile.$^{[77]}$ The ground state geometries were first obtained using DFT and all excited-state properties were obtained with TD-DFT calculations. Molecular structures were visualized using the Mercury software from the Cambridge Structural Database. Natural Transition Orbitals (NTOs) of both singlet and triplet excited states were visualized using the Jmol 14.31 software.

Contributor roles

C.M., J.C. and T.T. defined the research topic. T.T. designed and carried out the experiments and calculations. B.C., F.P., L.L. and S.C. designed the experiments in the ultrafast regime which B.C. and T.T. carried out. T.T. and B.C. analyzed the data. T.T. wrote the first draft. All authors contributed to a critical discussion of the data and revised the manuscript. J.C. and C.M. supervised the project.

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