

Probing the excited state dynamics of a new family of Cu(I)-complexes with an enhanced light absorption capacity: excitation-wavelength dependent population of states through branching†

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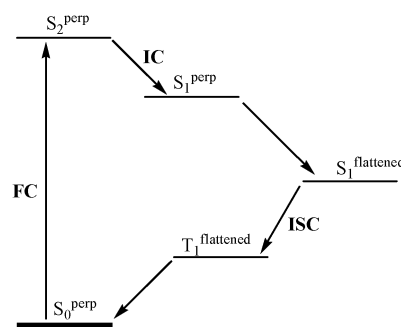
The ultrafast dynamics of six homoleptic Cu(I)-complexes and their respective ligands was examined through time-resolved electronic absorption spectroscopy in the subpicosecond time domain, in a variety of solvents, and at different excitation wavelengths. Results indicate that after excitation of the complexes in the blue part of the spectrum, the initially formed intraligand (IL) singlet excited state decays via two pathways yielding simultaneously both the lower-lying MLCT excited state and the ligand locally excited triplet state. The latter is also observed in the case of the free ligands and relaxes back to the ground state in a timescale of 40 ps. Excitation in the red part results in the formation of the MLCT excited state of the complexes which decays to the ground state through the same intraligand triplet excited state. The solvent viscosity does not affect the overall relaxation kinetics. The short time constant observed for the intersystem crossing of the MLCT singlet excited state is discussed in terms of the contribution of the d-orbitals of copper to the wavefunction of these states.

Introduction

Cu(I)-bisdiimine complexes have recently attracted the interest of the photochemistry community because of their potent application as alternatives to the heavier metal polypyridyl systems in light exploitation.¹ While these compounds belong to one of the most well studied families of photoactive molecules, the processes that take place after the complex excitation and lead to the population of the lowest lying triplet metal to ligand charge transfer (³MLCT) state have only recently been studied through a number of time-resolved techniques, though these are reactions of major interest determining efficiency of light to energy conversion in practical applications. In this framework, several works of different groups have been published

recently which are focused on the ultrafast dynamics of the excited states of Cu(I)-bisphenanthroline complexes.^{2–6} The obtained results are rather controversial but seem to converge finally to the following relaxation scheme (Scheme 1).⁶

According to this scheme, excitation of Cu(I)-bisphen systems at their MLCT absorption band populates the corresponding singlet excited state maintaining the pseudotetrahedral ground state geometry. Depending on the excitation wavelength, a very fast internal conversion (IC) may occur transforming the initially formed second ¹MLCT excited singlet state, ¹S₂, to the lowest singlet MLCT state (S₁) in a timescale of 45 fs retaining the almost undisturbed perpendicular conformation of the complex



Scheme 1

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† Electronic supplementary information (ESI) available: Tables of time constants for the ligands and the complexes under study at all the excitation wavelengths and in solvents used (Tables S1–S5), absorption spectra of ligands and complexes in DCM (Fig. S1), absorption spectra of complexes [Cu(2)₂]BF₄ and [Cu(5)₂]BF₄ in a variety of solvents and thermal stability of [Cu(5)₂]BF₄ (Fig. S2), decay associated spectra for the ligands and the complexes in both solvents and at excitation wavelengths (Fig. S3–S7). See DOI: 10.1039/c3cp50838b

in the ground state. This is followed by a $D_{2d} \rightarrow D_2$ structural change (flattening distortion) within 700–900 fs while inter-system crossing (ISC) takes place in the flattened S_1 state with a time constant of around 10 ps to give rise to the corresponding triplet state, $^3\text{MLCT}$ (T_1), which then decays back to the ground state. Tahara *et al.*⁶ concluded that it is more preferable to excite these complexes directly to their 1S_1 state corresponding to the low energy shoulder of their MLCT absorption band. In the case of the S_2 photoexcitation, a minor ISC directly from this initially formed FC state could result in a mixture of singlet and triplet states even before the structural change takes place. In addition, different vibrational energy content of the S_1 state populated either by direct excitation or by deactivation of the S_2 state might render things complicated and make the interpretation of the transient absorption data unambiguous.

We have recently been involved in the synthesis and the characterization of a new group of homoleptic Cu(I)-bisdiimine coordination compounds^{7a} bearing the Ar-BIAN ligands, well known for their application in a variety of catalytic systems.^{8–14} Complexes of these exocyclic diimines with heavy metals were also tested in photovoltaic device applications.^{15–17} An interesting property of the respective Cu(I)-compounds is their capacity to absorb light in the whole visible part of the spectrum.^{7a,18} Additionally, the tendency of these molecules to stabilize radical species, such as their monoanionic form,^{19–30} could give rise to a potentially long-lived MLCT excited state despite the fact that no emission was detected for the Cu(I)-complexes.

In this paper we present an effort to elucidate the excited state dynamics of this group of molecules and gain insight into their overall photophysics. For this reason we performed femto-second time-resolved absorption measurements for both the ligands and the complexes by varying the solvent medium and the excitation wavelength. Although the timescales of the flattening distortion and the intersystem crossing of the Cu(I)-bisphenanthroline systems appear to be well separated and independent of the substitution pattern on the phenanthroline moieties^{3,6} and despite the similarities in the absorption spectra and the general character of our systems and the Cu(I)-bisphenanthroline complexes, the aforementioned decay path (Scheme 1) does not seem to directly apply in the present case.

Experimental

Samples and steady-state measurements

All of the compounds used in this study were synthesized according to a previously published procedure.^{7a} Steady-state absorption spectra were recorded in 1 cm cuvettes on a Shimadzu UV-3600 spectrophotometer with a resolution of 1 nm. All solvents were of spectroscopy grade and bought from Aldrich. The absorption of the samples used in time-resolved measurements was kept close to unity and solutions were used without degassing.

Time resolved spectroscopy measurements

Femtosecond time-resolved absorption spectra were collected using a pump-probe technique. The femtosecond pulses of the

Ti:sapphire generator were amplified using a multipass amplifier (CDP-Avesta, Moscow, Russia) pumped by a second harmonic of the LF114 Nd:YAG Q-switched laser (Solar TII, Minsk, Belorussia). The amplified pulse energy was ~ 0.5 mJ and the repetition rate was 10 Hz. Two excitation wavelengths of 780 and 390 nm were obtained from the fundamental and the second harmonic of the Ti:sapphire amplifier output, respectively. A part of amplifier output was also used to generate white continuum by focusing light on a 5 mm water cuvette. The white continuum pulse was used as a probe. The probe beam was split into two beams. The first beam was used for the transient absorption measurements and it crossed the sample on the same spot as the excitation beam. The second beam was used as a reference beam; it passed the sample across a non-excited area. Finally the two beams were directed onto an input slit of a monochromator (Shamrock, Andor Technology) coupled with a cooled CCD detector (Newton DU920N, Andor Technology). Each beam produced one stripe on the CCD image. The stripes were used to calculate intensity spectra for the signal, $I_{\text{sig}}(\lambda)$, and for the reference, $I_{\text{ref}}(\lambda)$, pulses. The sample cuvette path length was 1 mm. The recorded transient absorption changes were analyzed by fitting the data to a multi-exponential kinetic model with a Gaussian instrument response function.

Results and discussion

As already mentioned in a previous work we referred to the synthesis and the characterization of a new family of homoleptic Cu(I)-coordination compounds presented in Fig. 1. One of their features that drew our attention is the enhanced absorption they reveal in the visible part of the spectrum extending to the NIR (Fig. 2). This property was assigned to the extended π -system of the Ar-BIAN ligands and the resulting mixing of the FMOs of these compounds in conjunction with a significant flattening distortion that appears to occur in solution as was revealed by ground state geometry optimizations assuming a dichloromethane medium. The lack of emission in the visible part of the spectrum after excitation of the complexes at the MLCT band was initially attributed to the energy gap law.^{7b–d} In this work we proceed with the study of the ultrafast dynamics of both the ligands and their Cu(I)-compounds in order to unravel the details of their excited states behavior.

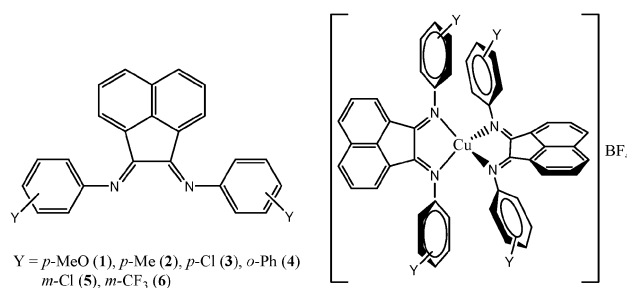


Fig. 1 Schematic representation of the Ar-BIAN ligands and the corresponding homoleptic tetrafluoroborates studied. The position of the substitution on the phenyl rings is referred to the imine nitrogen atoms.

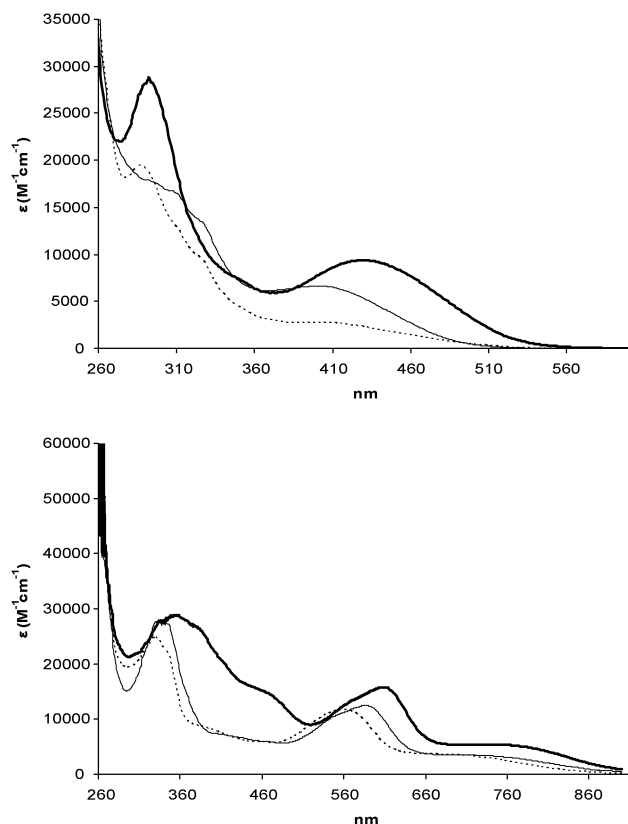


Fig. 2 UV-Vis spectra of representative Ar-BIAN ligands (top) and the corresponding complexes (bottom) in dichloromethane solution. The compounds presented correspond to the *p*-MeO (—), *p*-Cl (---) and *o*-Ph (····) substituted BIAN molecules.

Time resolved spectroscopy results

Six homoleptic Cu(I)-BIAN complexes, namely $[\text{Cu}(\mathbf{1})_2]\text{BF}_4$, $[\text{Cu}(\mathbf{2})_2]\text{BF}_4$, $[\text{Cu}(\mathbf{3})_2]\text{BF}_4$, $[\text{Cu}(\mathbf{4})_2]\text{BF}_4$, $[\text{Cu}(\mathbf{5})_2]\text{BF}_4$ and $[\text{Cu}(\mathbf{6})_2]\text{BF}_4$, along with the corresponding free ligands were investigated by femtosecond transient absorption spectroscopy. Free ligands were excited at 390 nm. In the case of the complexes, the same excitation could directly populate both a ligand centered (IL) and a higher lying MLCT state. Therefore the complexes were also excited at 780 nm, in which case only the lowest MLCT state is assumed to be populated. Fig. 3 and 4 illustrate the decay associated spectra for two of the free ligands, namely **3** and **5**, and the corresponding complexes after 390 nm photoexcitation in dichloromethane (DCM). The stability of solutions in all cases was verified by comparing the absorption spectra before and after each measurement. No photodegradation was observed for the reported measurements. A global fitting analysis of the transient absorption spectra of the free ligands reveals two time-constants which are depicted in Table S1 (ESI†). The decay associated spectrum (DAS) of the fast decaying component appears as a strong absorption covering the whole monitoring window with a maximum at around 550 nm and is characterized by a 0.2–0.3 ps time constant. The second component corresponds to a 29–46 ps process and also appears in all the ligands as a weak absorption in the blue part of the spectrum.

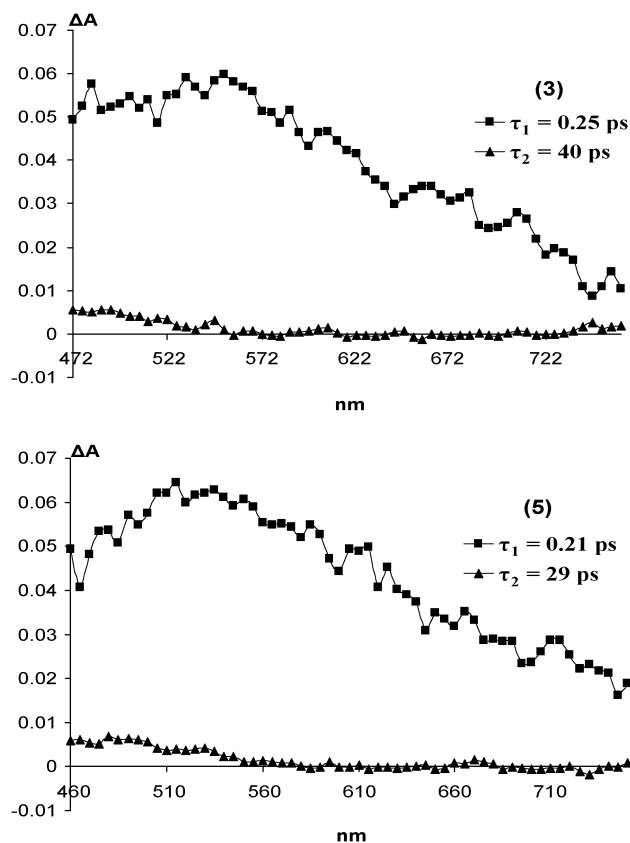


Fig. 3 Decay associated spectra of the ligands **3** (top) and **5** (bottom) in DCM after excitation at 390 nm. The symbol (■) corresponds to the first time component and the (▲) to the second one.

Excitation of the homoleptic Cu(I)-complexes at 390 nm results in all cases in a similar behavior. As can be seen in the following, the global fit gives three time-constants. With the exception of $[\text{Cu}(\mathbf{1})_2]\text{BF}_4$ and $[\text{Cu}(\mathbf{4})_2]\text{BF}_4$, the other four compounds reveal an ultrafast component which cannot be resolved using the instrument (0.05–0.09 ps) corresponding to a transient absorption covering the whole spectrum and maximizing in the region 560–590 nm. The second time constant for these four complexes varies between 2.0 and 2.4 ps (Table S2, ESI†) corresponding to a DAS showing a weak absorption in the blue part of the spectrum and a shallow bleaching of the ground state MLCT absorption at around 600 nm. In the case of $[\text{Cu}(\mathbf{2})_2]\text{BF}_4$ and $[\text{Cu}(\mathbf{3})_2]\text{BF}_4$ this DAS also reveals a positive part over 610 nm maximizing at around 650–660 nm. The third DAS of the complexes has a time-constant of 30–50 ps and reveals a weak absorption in the blue side of the spectrum up to 510 nm accompanied by an intense bleaching of the ground state MLCT absorption covering the whole spectral window over 510 nm. The bleaching also maximizes at around 600 nm but is slightly red-shifted in comparison to the second DAS. For $[\text{Cu}(\mathbf{1})_2]\text{BF}_4$ and $[\text{Cu}(\mathbf{4})_2]\text{BF}_4$ the first time constant and the second of the former complex differ substantially in value from the respective constants of the other complexes. At the same time the first DAS reveals a quite weaker absorption in the region 530–610 nm as compared to the respective DAS of the

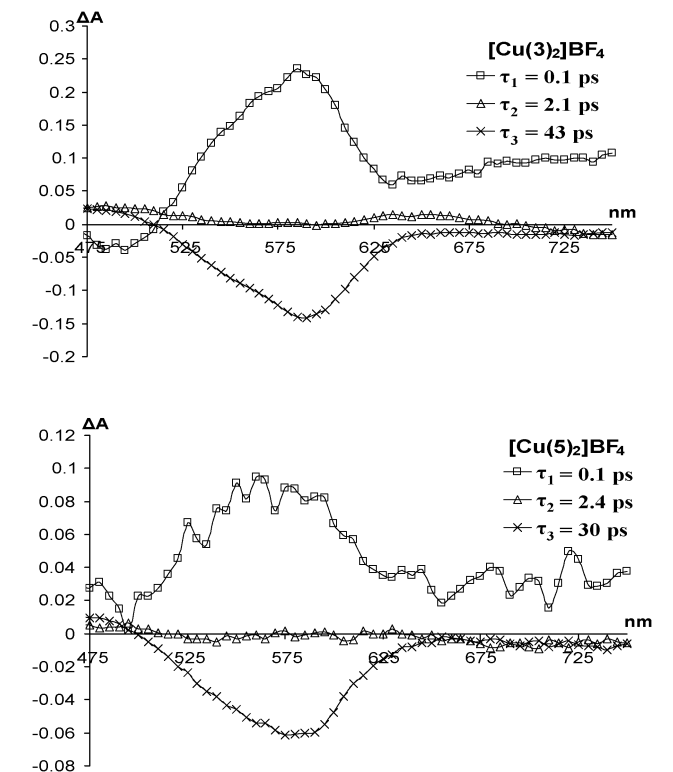


Fig. 4 Decay associated spectra of complexes $[\text{Cu}(\mathbf{3})_2]\text{BF}_4$ (top) and $[\text{Cu}(\mathbf{5})_2]\text{BF}_4$ (bottom) in DCM solution after excitation at 390 nm. The symbol (\square) corresponds to the fast decaying component (<0.1 ps), the (Δ) to the component with 2.0–2.4 ps lifetime and the (\times) to the long-lived component (30–50 ps).

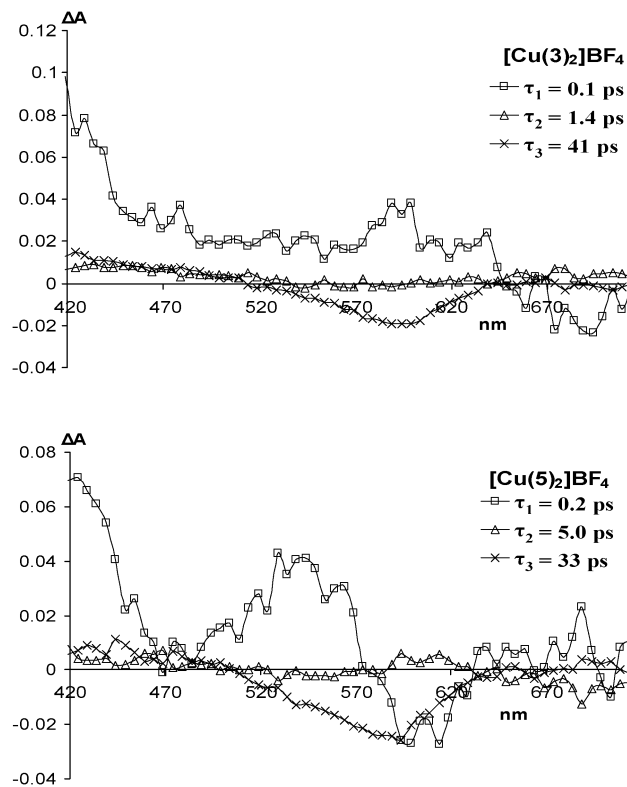


Fig. 5 Decay associated spectra of complexes $[\text{Cu}(\mathbf{3})_2]\text{BF}_4$ (top) and $[\text{Cu}(\mathbf{5})_2]\text{BF}_4$ (bottom) in *o*-DCB solution after excitation at 390 nm. The symbol (\square) corresponds to the first time component (0.1–0.19 ps), the (Δ) to the second (1.4–5.0 ps) and the (\times) to the third time component (30–50 ps).

rest of the complexes. An additional feature stemming from the fitting analysis is that the longer-lived components of the complexes seem to be characterized by a time constant analogous to the τ_2 value of the respective ligands.

To evaluate further the nature of the photophysical processes taking place after excitation of the complexes, we performed a second series of measurements in a solvent of different viscosity and of similar polarity. The solvent of choice in this case is *o*-dichlorobenzene (*o*-DCB).[‡] As is generally accepted, any process involving severe molecular motion or structural rearrangement after photoexcitation is largely affected by the surrounding environment with the corresponding time constant being slowed down in a more viscous medium. Therefore a significant increase in the lifetime of any of the kinetic components of the complexes would be indicative of photoinduced geometrical changes associated with the decay of the respective excited species. Table S3 (ESI[†]) summarizes the results of a multi-exponential global fitting analysis of the transient absorption

spectra of the six complexes recorded after excitation at 390 nm in *o*-DCB. The DAS of the complexes for the same excitation in *o*-DCB are shown in Fig. 5. By comparing the lifetimes of the relative components in the two solvents (DCM and *o*-DCB) it can be seen that no drastic changes in any of the time constants occur upon increasing the solvent viscosity. The only case for which an increase in the lifetime is observed is for the second kinetic component of the $[\text{Cu}(\mathbf{5})_2]\text{BF}_4$ complex but this on its own cannot be directly connected to the higher viscosity of *o*-DCB. The calculated time constants seem to remain unaffected by the change of solvent indicating that no pronounced or detectable structural changes occur during the deactivation of the excited molecules. Additionally the change of the solvent has no strong impact on the shape of the DAS corresponding to the second and the third time-constant of the coordination compounds as can be seen by comparing the respective panels in Fig. 4 and 5.

In order to check for any dependence of the excited state dynamics on the excitation wavelength, the ¹MLCT state of the complexes was excited directly by switching the pump wavelength to 780 nm in both DCM and *o*-DCB. The results of the analysis for this excitation are summarized in Fig. 6 and 7 and Tables S4 and S5 (ESI[†]), respectively. Comparison of the shapes of the DAS for the two photoexcitations in DCM reveals that the change in the pump wavelength does not lead to any striking differences in the shape of the second and third DAS of these

[‡] The complexes appear to decompose after a few minutes in a coordinative environment^{7a} and this did not allow for time-resolved studies in other solvents. Despite this the ground state absorption spectra could be recorded right after dissolution although in some cases like *e.g.* in MeCN, the dissociation is almost immediate as is depicted in Fig. S2 (ESI[†]). However, the complexes remain stable for at least 48 hours in DCM and *o*-DCB (see Fig. S2 (ESI[†]), the last spectrum). The poor solubility of the complexes in more innocent solvents like toluene or hexane also did not allow for similar studies.

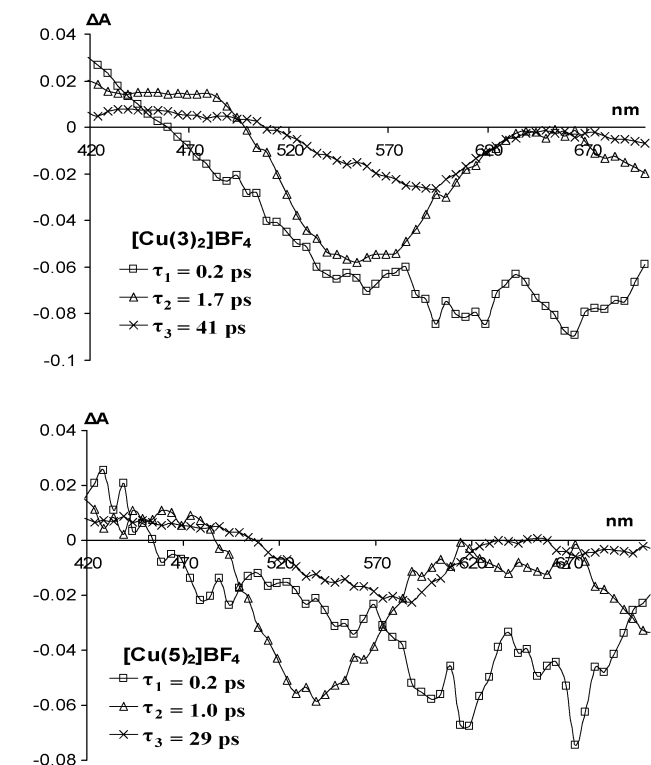


Fig. 6 Decay associated spectra of complexes $[\text{Cu}(\mathbf{3})_2]\text{BF}_4$ (top) and $[\text{Cu}(\mathbf{5})_2]\text{BF}_4$ (bottom) in DCM solution after excitation at 780 nm. The symbol (\square) corresponds to the first time component, the (Δ) to the second and the (\times) to the third time component.

systems indicating that the decay kinetics for both excitations arises from the same MLCT excited states.³¹ When exciting the sample at 780 nm, these states are directly populated while excitation at 390 nm leads to their population after a fast IC from the initially pumped locally excited IL state. This rapid conversion probably originates from a close resemblance of the geometries of these two states and according to the small value of the first time constant it could occur even from a vibrationally excited level of the IL state that is from the FC state produced by 390 nm excitation.

By inspecting the time constants in Table S4 (ESI[†]) it can be seen that the lifetime for the first DAS ranges now between 0.03 and 0.36 ps and except for $[\text{Cu}(\mathbf{2})_2]\text{BF}_4$ differs in shape from the DAS of the corresponding compound excited at 390 nm. The second time constant instead takes values close to those obtained with 390 nm pumping, ranging between 1.0 and 2.7 ps. Also the DAS shapes of this component remain virtually independent of the excitation wavelength. The same also holds true for the longer-lived component which again agrees with the time constant of the corresponding free ligand (τ_2). Despite the close resemblance both in spectral shapes and time constants for the second and the third kinetic component obtained with excitation at 390 and 780 nm in DCM there is a significant difference in their relative intensities. The excitation at 390 nm results in a stronger third component while the second DAS gains intensity when the samples are excited at 780 nm.

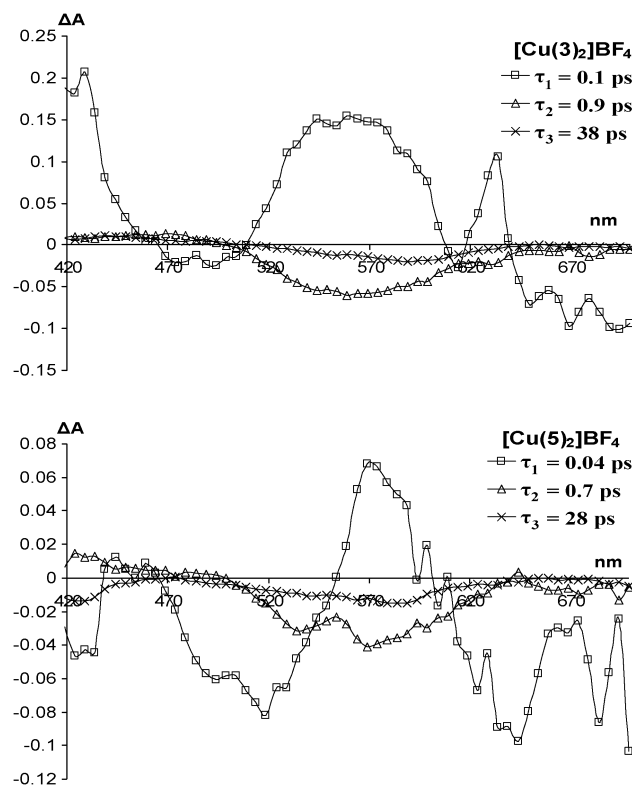


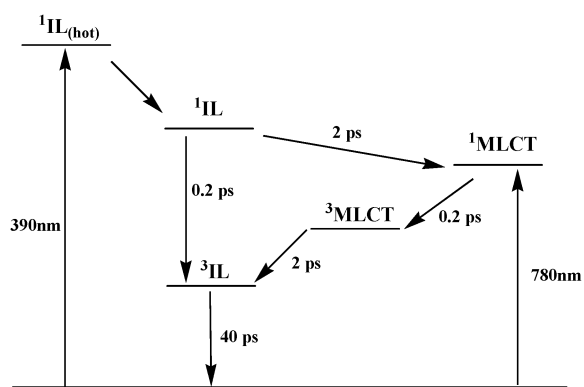
Fig. 7 Decay associated spectra of complexes $[\text{Cu}(\mathbf{3})_2]\text{BF}_4$ (top) and $[\text{Cu}(\mathbf{5})_2]\text{BF}_4$ (bottom) in *o*-DCB solution after excitation at 780 nm. The symbol (\square) corresponds to the first time component, the (Δ) to the second and the (\times) to the third time component.

Fig. 7 and Table S5 (ESI[†]) summarize the results of the global fitting analysis for the 780 nm excitation of the complexes in *o*-DCB. Again it can be seen that the first kinetic component differs both in shape and value when compared to the corresponding component for 390 nm excitation in the same solvent and for the 780 nm excitation wavelength in DCM but resembles more the case of 390 nm photoexcitation in DCM. The second DAS, corresponding to the process with the time constant in the range 0.7–2.6 ps, correlates well in shape and time constant values with the respective DAS for the same excitation in DCM. The third DAS and corresponding time constants are also similar for both excitations at 390 and 780 nm and both solvents. In addition, its time constant is close to the second time constant of the corresponding free ligand. The obvious result is that again the second component appears to have a stronger intensity than the third DAS as opposed to the 390 nm photoexcitation in both solvents.

In conclusion, it can be said that considering the second and third kinetic component at each pumping wavelength and in both solvents, the results for spectral shapes and time constant values are quite similar for each of the complexes while for the same excitation the solvent viscosity does not impose any important differentiation on the kinetic components of the decay. The difference between the results obtained at the two excitation wavelengths is the relative intensity of the two DAS with the second component becoming the major one

when the samples are excited in the red part of the spectrum while the longer lived component is characterized by higher intensity after blue photoexcitation. This variation can be assigned to a difference in the population of the respective excited states participating in the decay scheme when the samples are excited at these two wavelengths. In contrast, the first DAS reveals differences both in its value and dispersion when the pumping wavelength or the solvent changes. Possible explanation for this finding is that when the complexes are excited at 390 nm, the transient spectrum is dominated by the absorption of the locally excited IL state while the excitation at 780 nm results in the direct population of the respective $^1\text{MLCT}$ states besides the fact that the 390 nm excitation can also result in the simultaneous population of higher lying MLCT states resulting in a more complicated deactivation path. Additionally the small value of this constant does not allow a good time resolution and its evaluation may contain errors. All of the aforementioned can be explained by Scheme 2 comprising the energy level diagram and transitions between different states. As has already been reported, the only difference observed for exciting the samples at the two edges of the spectrum is a change in the relative intensities of the second and the third kinetic component and this can be attributed to a different population of the states that correspond to each of the DAS. Additionally, the longer lived component of all of the complexes displays a time constant which agrees with the τ_2 value of the respective free ligand. The third important factor is the relative intensity and the shapes of the DAS. With direct excitation of the MLCT band the initial bleaching of the band is almost completely recovered after a few picoseconds and the third DAS shows only minor spectral perturbations in this wavelength range. This indicates that the final state from which de-excitation occurs is the same for both ligands and complexes assigned as a ^3IL in nature.

According to Scheme 2, excitation of the samples at 390 nm results in the direct population of the ^1IL state. In the case of the free ligand this state transforms through ISC to the



Scheme 2 Proposed energy-level diagram and the excited states relaxation pathway of both the free ligands and the corresponding complexes after excitation at the two wavelengths selected for the study. The bold solid line in the bottom represents the ground state of the systems. Time constants given are indicative of each decay step.

short-lived ^3IL state with a time constant of 0.20–0.29 ps, probably residing in the naphthyl-part of the molecule, which then decays back to the ground state in a timescale of 30–46 ps depending on the nature of the organic molecule under discussion. For the complexes, after the ^1IL has been populated by the same excitation, the decay proceeds *via* two pathways simultaneously to yield the ^3IL state and the lower-lying $^1\text{MLCT}$ state. The indirectly populated CT state transforms through a rapid process involving ISC and probably a marginal flattening distortion to the respective $^3\text{MLCT}$ state which then populates back the lower-lying ^3IL state. The depletion of the $^3\text{MLCT}$ state through its decay to the ^3IL can justify its very short lifetime and this is further supported by the results of DFT calculations indicating that the lowest MLCT excited state should involve the diiminic part of the ligand while the naphthyl moiety should participate in higher excited states.^{7a} This allows the two parts of the molecule to be considered as two isolated chromophores with distinct orbital structure. The existence of the two chromophoric moieties at such a close distance results in a very fast energy transfer between them leading to an extremely short lifetime of the $^3\text{MLCT}$ state. This hypothesis also justifies the lack of luminescence from the complexes $^3\text{MLCT}$ state, which depopulates fast towards a non-emissive ^3IL state.[§]

On the other hand, when the complexes are pumped directly to the $^1\text{MLCT}$, the de-excitation follows the pathway involving only the CT states which again leads to the lowest energy ^3IL state. When the samples are excited in the blue part, only a fraction of the excited molecules deactivates through the MLCT states while the 780 nm photoexcitation results in the direct population of the $^1\text{MLCT}$. Based on this model one can explain the differences in the intensities that are observed for the second and the third DAS of the complexes by changing the pumping wavelength. The second DAS, corresponding to the relaxation of $^3\text{MLCT}$, gains intensity when all excited molecules decay only through the CT states, *i.e.* excited at 780 nm, while the 390 nm excitation populates partly these CT states, since the major part of the molecules deactivates directly *via* a $^1\text{IL} \rightarrow ^3\text{IL}$ pathway resulting in the reduction of the intensity of the second DAS relative to the third because of a lower population of the $^3\text{MLCT}$ state. Since the relative intensity of the second DAS at 390 nm excitation is roughly ten times smaller than at 790 nm excitation, the time constant for $^1\text{IL} \rightarrow ^1\text{MLCT}$ transition is expected to be ten times longer than for the $^1\text{IL} \rightarrow ^3\text{IL}$ transition. This gives an estimation for the former time constant to be around ~ 2 ps. Considering that the ISC for the $^1\text{MLCT}$ is much faster, ~ 0.2 ps, the population of $^1\text{MLCT}$ is never higher than a percent and this state is virtually invisible when the sample is excited at 390 nm.

According to the above results and their interpretation, an intriguing point is that the transformation of the $^1\text{MLCT}$ to the $^3\text{MLCT}$ seems to take place in a quite short timescale when

[§] The lack of r.t. emission from the triplet state of an organic molecule is not something uncommon as phosphorescence in these cases usually occurs at low temperatures (77 K).

compared to the respective process of the Cu(i)-bisphenanthroline systems. More precisely, independently of the excitation wavelength, it appears that the decay of the initial FC-state, whether it corresponds to the ^1IL or to the $^1\text{MLCT}$, towards the $^3\text{MLCT}$ occurs faster than it would be expected considering the overall time needed for the flattening distortion and the ISC of the respective Cu(i)-bisphenanthroline molecules. Though the structural change for the latter systems can be a fast process happening in a timescale less than 1 ps, a typical timescale for the ISC is around 10 ps.⁶ In the case of the homoleptic Cu(i)-BIAN complexes the ISC should be quite facilitated in comparison to the corresponding phenanthroline compounds since it takes place in the sub-picosecond time region in analogy to the heavier metal-analogues such as Ru(II). This assumption could be based on a recent report of Chang *et al.*³² according to which an enhanced participation of the d atomic orbitals (AOs) of the metal center in the electronic transition of a complex implies a strong internal heavy atom effect which in turn enhances the ISC from the singlet to the respective triplet state. Additionally the strong participation of the metal d AOs in the MLCT state results in a reduced energy difference between the $^1\text{MLCT}$ and the $^3\text{MLCT}$, and leads to the lowest triplet excited state being an IL $^3\pi-\pi^*$ in nature.³²

The extremely red shifted MLCT ground state absorption of the Cu(i)-BIAN complexes as compared to the Cu(i)-bisphenanthroline systems and their relatively strong absorption intensity are strong indications of an enhanced orbital mixing between the d AOs of Cu(i) and the lower lying π^* MOs of the BIAN ligand. Additionally, in the case where it was possible to record the absorption spectra in solvents with polarity different from that of DCM (Fig. S2, ESI[†]), we noticed the absence of any strong impact of this factor on the position of the MLCT band. The lack of solvatochromism is an indication of an extended orbital mixing in the ground state of the systems as has already been reported for a similar compound.^{33a} Finally, DFT calculations^{7a} reveal that the HOMO and HOMO – 1 of these systems comprise an enhanced contribution from the diiminic part of the organic moieties along with the d AOs of the metal center supporting further the orbital mixing and the highly delocalized nature of the lowest MLCT state of these complexes. This strong orbital mixing results in an impure charge-transfer character of what is assigned as a MLCT state of the complexes, meaning that during this type of excitation one should not expect a strong charge depletion from the Cu(i)-center towards the diimines.^{33b} This indicates that the excited electron will still reside in the metal area imposing a substantial participation of the Cu(i) d AOs in this state. All of the aforementioned point towards a strong involvement of the d AOs of Cu(i) in the MLCT electronic transition which results in an enhanced ISC between the $^1\text{MLCT}$ and the $^3\text{MLCT}$ as well as a reduced energy difference between them.

Perkovic and Endicott further showed that the rate of ISC can be related to the ease of structural changes within a molecule^{34a} while orbital mixing through these changes can also promote this type of transformation.^{34b,c} Within the same framework, even a small pseudorotation of a chelate may have a

profound effect on surface crossing.^{34c} Considering the structure of the present ligands which does not seem to provide any steric constraints towards a flattening distortion and the extended tetragonal deformation of the ground state geometry of the complexes in solution,^{7a} a torsion of the two coordinated diimines should be expected in the excited MLCT state of these complexes which could result in a fast ISC.

In conclusion, the lack of steric bulkiness around the metal center as revealed by the crystal structure data^{7a} cannot prevent molecular rearrangements during excitation. This along with the highly distorted ground state geometry predicted by a DFT optimization in solution^{7a} and the strong participation of the d AOs of the metal center in the MLCT state render the transition of the initial singlet states formed by photoexcitation towards the $^3\text{MLCT}$ an ultrafast process. The extended orbital mixing also implies a strong covalent character for the metal-ligand bonding which leads to an enhanced internal heavy atom effect^{35,36} and supports further this assignment. Similar time-scales for the ISC have been reported for other first row transition metal-diimine systems such as Cr(III) and Fe(II), which show an ISC rate constant similar to that of heavier analogues.^{34d,37–39}

A final point to be discussed deals with the assignment of the longer-lived component of the complexes to the same ^3IL state from which the free ligands also decay to their ground states. This state seems to preserve analogous lifetimes in the free diimines and the respective complexes as can be expected. Firstly, the ISC process is already fast in the ligands alone. Then, the lack of participation of the metal's d orbitals in the IL state ($\pi\pi^*$ in nature) preserves this part of complex as a relatively independent chromophore, and considering a rather "light atom" character of the Cu(i) no considerable change in the relaxation rate of the ^3IL state through an internal³² or external heavy atom effect is expected.

Conclusions

This work comprises an attempt to clarify the excited state dynamics of a family of Cu(i)-bisBIAN complexes revealing an enhanced light absorption capacity extending to the NIR region. Two solvents with close polarities but different viscosities and two excitation wavelengths populating different excited states were used in order to elucidate the mechanisms of the excitation relaxation process.

The viscosity of the solvent has no significant impact on the relaxation kinetics of the complexes. This indicates a non-hampered and slight deformation of the already flattened ground state geometry of these compounds in solution after the excitation. On the other hand, the variation of the excitation wavelength affects the decay path of the excited molecules by an alternation of the population of the states that correspond to the second and the third kinetic component of the decay. The measurements revealed the existence of a non-emissive ^3IL state which lies lower in energy than the $^3\text{MLCT}$ state of the complexes and from which the final relaxation to the ground state occurs. This conclusion further supports the lack of

luminescence from the MLCT state as it was observed in our previous study.^{7a} Additionally, a striking feature of the whole relaxation scheme of these Cu(i)-compounds is the short time-scale of the transformation of the ¹MLCT state to the respective ³MLCT through ISC when compared to the relative Cu(i)-bisphenanthroline systems. This fast ISC mainly arises from an enhanced participation of the d AOs of the metal center in the MLCT excited state stemming from its highly delocalized nature. The proposed ease of structural change in the excited state along with the orbital mixing observed in these complexes further support the high rate of this process.

A possible way to improve the photophysical behavior of transition metal complexes is to perturb the excited state dynamics by mixing a low-lying ³ $\pi\pi^*$ IL state with a ³MLCT state.⁴⁰ In the present case the contribution of the triplet IL state shortens the lifetime of the ³MLCT and it solely provides a path for its non-radiative deactivation.

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