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Ultrafast dynamics of Cu(I)-phenanthrolines in dichloromethane

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Transient absorption spectrometry of Cu(I)-phenanthrolines in CH_2Cl_2 reveals ligand-independent dynamic processes lasting 15 ps, which are associated with the peculiar structural rearrangements occurring for this class of compounds upon photoexcitation.

The photochemistry and photophysics of coordination compounds have been the object of large interest among a few generations of inorganic photochemists.[1] Nowadays the gain of fundamental knowledge related to these disciplines is not disconnected by stimulating perspectives in terms of practical applications which include solar energy conversion[2] and information technology.[3] By far, the most popular family of coordination compounds on the photochemical stage is that of $[Ru(bpy)_3]^{2+}$'s (bpy = 2,2′-bypyridine)[1] however, in more recent years, cheaper and simpler Cu(I)-phenanthrolines ($[Cu(NN)_2]^+$) have emerged as promising competitors.[4]

The photophysics of tetrahedral $[Cu(NN)_2]^+$ has been the object of intensive investigations.[4–8] These complexes exhibit metal-to-ligand-charge-transfer (MLCT) absorption bands in the Vis spectral region and, in poorly donor solvents, they may exhibit MLCT luminescence. It was anticipated by McMillin and coworkers that, since the metal ion is formally Cu(II) in the MLCT excited state, it may assume a larger coordination number (5) than in the ground state.[9] The new coordination site is occupied by the counterion or a solvent molecule, giving rise to a 5-coordinated excited complex (exciplex). Once the exciplex is formed, non-radiative deactivations to the ground state are promoted and the excited state lifetime shortened.[10,11] Thus protection of the metal centre from external contacts must be provided to limit the exciplex stability and disfavour non-radiative deactivations.[12] Upon light excitation, initial evolution of the instantaneous "Franck–Condon" (F–C) ^{1}MLCT excited state to a lower ^{3}MLCT level is considered to occur in the hundred of femtosecond timescale,[13] in analogy with rigid octahedral $[Ru(bpy)_3]^{2+}$-type compounds.[14] Excited state structural rearrangements of Cu(I)-phananthrolines, namely (i) flattening distortion of the initial pseudo-tetrahedral geometry and (ii) expansion of the coordination number are reasonably expected to occur on a longer, *e.g.* ps, timescale.[13]

Very recently Chen *et al.* have shown by means of X-ray nanosecond pulsed spectroscopy that the emissive excited state of $[Cu(dmp)_2]^+$ is pentacoordinated both in poorly donor (toluene)[12] or highly donor (CH_3CN)[13] solvents. In the latter case, by means of optical time-resolved spectroscopy, they have also observed spectroscopic features in the ps timescale, which were associated to excited state structural rearrangements, possibly flattening distortion.[13]

We report here the ultrafast transient absorption spectra of complexes **1** and **2** in CH_2Cl_2 which are characterized by, respectively, alkyl- and more cumbersome phenyl- residues in the 2 and 9 position of the phenanthroline ligand. These features make them rather different for virtually all the photophysical properties (*i.e.* shape of UV-VIS absorption, luminescence spectra, excited state lifetime, Table 1).[4,15] However identical dynamic processes are found on the picosecond timescale upon light excitation, giving important information on excited state structural rearrangements.

The synthesis and characterization of the two Cu(I) complexes here investigated, **1** and **2** (Scheme 1), have been already reported.[15]

The ground state absorption spectra of **1** and **2** are substantially different. In particular **2** exhibits weaker and broader MLCT absorption bands, which are typical for phenyl- *vs.* alkyl- phenanthroline-type ligands.[4,15]

The time resolved absorption spectrum of **1** is depicted in Fig. 1; at $t = 0$ it exhibits a broad band with maximum at 570 nm.† Very neat spectral changes are recorded over time with isosbestic points at 538 and 572 nm. The decay kinetics at 520 and 590 nm, where the absorbance variations are maximized (inset of Fig. 1), yield identical lifetimes of 15 ps. The final spectral shape with maxima at 524 and 562 nm ($t = 1000$ ps) is very similar to that recorded for $Cu(dmp)_2{}^+$ on the tens of ns timescale.[12]

As discussed above, spectral variations in the ps domain are associated with the peculiar structural rearrangements occurring for this class of compounds upon photoexcitation, namely flattening distortion and/or fifth ligand pick-up.[12]

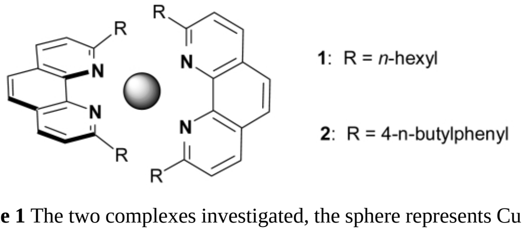
The time resolved absorption spectrum of the phenyl–phenanthroline type complex **2** is reported in Fig. 2; at $t = 0$ it exhibits a broad band with maximum at 615 nm.

Unlike the data for compound **1** (Fig. 1), no isosbestic points could be discerned. This is probably on account of the lower

Table 1 Relevant absorption and luminescence data in CH_2Cl_2 (298 K) and CH_2Cl_2/MeOH (1 : 1 v/v) matrix at 77 K.

	298 K				77K	
	$\lambda_{max, abs (MLCT)}$/nm[a] ε/M^{-1} cm^{-1})	$\lambda_{max, em}$/nm[b]	τ_{AER}/ns[c] (Φ_{em})	τ_{DEA}/ns[d] (Φ_{em})	$\lambda_{max, em}$/nm[b]	τ/μs
1	458 (7300)	724	98 (0.0007)	139 (0.0008)	676	2.40
2	438 (3200)	718	132 (0.0010)	224 (0.0012)	772	[e]

[a] Maximum of the MLCT absorption envelope in the VIS spectral region. [b] Corrected for the photomultiplier response. [c] Air-equilibrated samples. [d] Oxygen-purged samples. [e] Too weak signal to detect luminescence decay.



Scheme 1 The two complexes investigated, the sphere represents Cu(I), the counterion is $BF_4{}^-$.

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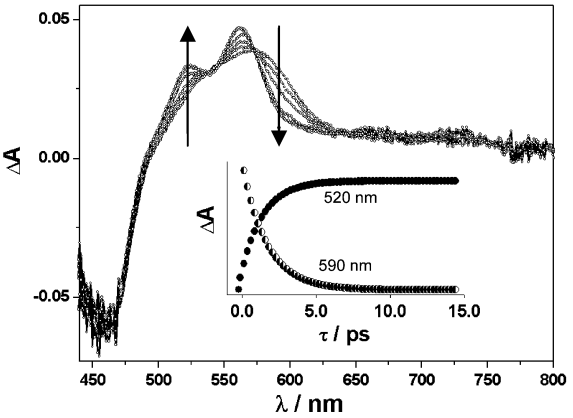

Fig. 1 Time resolved spectra changes observed for **1** in CH_2Cl_2 at λ_{exc} = 400 nm. The spectra were recorded at delays of 2, 5, 10, 25, 100, 1000 ps following the excitation pulse.

signal to noise ratio, caused by the low extinction coefficient of **2** at the excitation wavelength (480 nm), stronger ground state absorption of **2** relative to **1**,[15] and perhaps lower extinction coefficient of the product state. Another feature seen in Fig. 2 is an apparent isosbestic point at 660 nm. However, this is most likely not an isosbestic point but the intersection of an absorption spectrum red edge and the blue edge of a stimulated emission signal. Stimulated emission has the same spectrum as spontaneous emission and is generated by the superposition of the white light photons in the probe beam and emissive states generated by the preceding pump beam. That this is not as clearly apparent in Fig. 1 is in part because the absorption signal for **1** is much higher. In fact there is a hint of stimulated emission on Fig. 1 at the red edge of the absorption signal. Decay kinetics of **2** at 635 nm (inset of Fig. 2), yield a lifetime of 15 ps. The final spectral shape (t = 1000 ps) with maxima at 548 and 592 nm is very similar to that recorded for Cu(I)-catenate with diphenyl–phenanthroline type ligands on the hundreds of ns timescale.[16] We attribute the observed spectral changes to excited state structural rearrangements, in analogy with **1**.

For **1** and **2** an identical 15 ps dynamic process is observed which is longer-lived than early events associated F-C excited state evolution (hundreds of fs)[13,14] and much shorter lived than deactivation to the ground state (hundreds of ns).[15] Interestingly, a 10–20 ps time decay is also observed for $[Cu(dmp)_2]^+$ in polar CH_3CN solvent.[13] We associate the processes that are observed in the ps timescale to the peculiar intramolecular rearrangements which Cu(I)-phenanthrolines undergo upon light excitation, leading to an expanded coordination number.[4] Specific assignment of the spectral variation to (i) flattening distortion or (ii) extra ligand pick-up, two processes that might also occur simultaneously, is not straightforward. Access to the fifth coordinating position is likely to be less favoured for the more congested phenyl–phenanthroline ligand of **2**. Hence the identical rate constant observed for **1** and **2** in CH_2Cl_2, as well as in CH_3CN for another $[Cu(NN)_2]^+$ complex,[13] is likely to be associated with the flattening distortion which is expected to be less solvent and ligand dependent than pick-up of an external unit for coordination expansion. Recent density functional studies on $[Cu(dmp)_2]^+$ indicate that structural changes of this type occur on the way from the ^{1}MLCT F–C state to the lowest ^{3}MLCT level, suggesting that structural distortion occurs prior to the formation of the long-lived emitting state.[17]

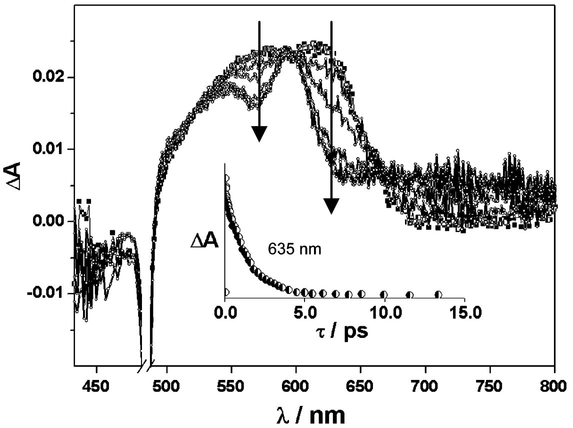

Fig. 2 Time resolved spectra changes observed for **1** in CH_2Cl_2 at λ_{exc} = 480 nm. The spectra were recorded at delays of 2, 5, 10, 25, 60,100, 500 ps following the excitation pulse.

In conclusion picosecond dynamics of Cu(I)-phananthrolines in CH_2Cl_2 have been monitored for the first time. The ligand and solvent independence of the kinetics of this process for $[Cu(NN)_2]^+$ complexes, as shown by the present work in combination with that of Chen *et al.*,[13] suggests that flattening distortion is most likely the process associated with the 15 ps observed decay.

Notes and references

† The basic laser system and pump-probe spectrograph for the ultrafast transient absorption experiments has been described elsewhere.[18] Improvements include replacing the double beam arrangement with a single spectrograph with a chopper in the excitation beam to provide a sequence of pump on/pump off cycles. In the current experiments excitation was at 400 nm (the second harmonic of the Ti-Sapphire output) derived from CSK Super Tripler, or at 480 nm, derived from an optical parametric amplifier (Spectra Physics OPA 800).

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