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Novel Phenanthroline Ligands and Their Kinetically Locked Copper(I) Complexes with Unexpected Photophysical Properties

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The new, sterically encumbered phenanthroline ligands **1a**,**b**, both characterized by the presence of bulky aryl substituents (3,5-di-*tert*-butyl-4-methoxyphenyl, 2,4,6-trimethylphenyl) in the 2,9-position, were prepared along with their homoleptic $[Cu(\mathbf{1a,b})_2]^+$ and heteroleptic complexes $[Cu(\mathbf{1a,b})(phen)]^+$ (phen = parent 1,10-phenanthroline). Due to the pronounced steric shielding, particularly effective in ligand **1a**, the formation of the homoleptic complex $[Cu(\mathbf{1a})_2]^+$ becomes very slow (5 days). Once formed, the homoleptic complexes $[Cu(\mathbf{1a,b})_2]^+$ do not exchange ligands even with phen added in excess because they are kinetically locked due to the large *tert*-butylphenyl substituents at the phenanthroline unit. The electronic absorption spectra of the homoleptic complexes $[Cu(\mathbf{1a})_2]^+$ and $[Cu(\mathbf{1b})_2]^+$ evidence a strongly different ground state geometry of the two compounds, the former being substantially more distorted. This trend is also observed in the excited-state geometry, as derived by emission spectra and lifetimes in CH_2Cl_2 solution. The less distorted $[Cu(\mathbf{1b})_2]^+$, compared to $[Cu(\mathbf{1a})_2]^+$, is characterized by a 15- and over 100-fold stronger emission at 298 and 77 K, respectively. Noticeably, the excited-state lifetime of $[Cu(\mathbf{1a})_2]^+$ in solution is unaffected by the presence of molecular oxygen and only slightly shortened in nucleophilic solvents. This unusual behavior supports the idea of a complex characterized by a "locked" coordination environment.

Introduction

1,10-Phenanthroline and its substituted derivatives represent a widely investigated class of chelating agents.[1] Some intrinsic properties of phenanthroline ligands (e.g. structural rigidity and luminescence) make them attractive as analytical probes, e.g. in proton and cation sensing[2−5] or DNA intercalation and groove binding.[6] Interestingly, suitably engineered phenanthroline ligands can even operate as rudimentary molecular machines simply by varying the ambient acid concentrations.[3,7] However, by far, the most fruitful field of exploitation of these ligands is coordination chemistry, which has received a major impetus through the pioneering work of Sauvage and Dietrich-Buchecker et al. constructing topologically spectacular architectures such as catenates, knots, rotaxanes, etc.[8−10] Some of these coordination compounds were even designed to perform motions at the molecular level via chemical, photochemical, or electrochemical stimulation.[11−15] More recently, further develop-

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ments in the supramolecular chemistry of these systems have been achieved by some of us via the assembly of nanoscale racks,[16] grids,[17] boxes,[18] and baskets[19] based on heteroleptic Cu(I)−bis(phenanthroline) complexes, which are potentially interesting as photoactive units.[20−22] Control of the sophisticated heteroleptic architectures had been achieved by the use of the HETPHEN (HETeroleptic bis(PHENanthroline)) concept.[23] This approach employs bulky aryl substituents at the bis(imine) coordination site to control the metal complexation equilibrium.

Tetrahedral Cu(I)−bis(phenanthroline) complexes (here to after indicated as $[Cu(NN)_2^+]$) are characterized by a relatively long-lived metal-to-ligand-charge-transfer (MLCT) emission in the vis spectral region, and in recent years, they have emerged as potential alternatives to the very popular Ru(II)−polypyridine complexes[24−27] in view of practical applications (e.g. light harvesting and solar energy conversion devices), thanks to lower price, larger abundance, and smaller environmental impact.[22] The MLCT absorption bands of $[Cu(NN)_2^+]$ cover a wide spectral range (380−700 nm), as a result of an envelope of at least three different electronic transitions.[22,28] The corresponding spectral intensities are strictly related to the symmetry of the complex that itself is affected by the distortion from the tetrahedral geometry. The distortion is largely dictated by the position and chemical nature of the substituents on the chelating ligand.[22] For instance, complexes of 2,9-diarylphenanthroline are characterized by π-stacking interactions between the aryl groups of one ligand and the phenanthroline moiety of the other ligand,[29] which brings about a strongly distorted ground-state tetrahedral geometry (D_2 symmetry).[20,22] This explains the very different MLCT absorption profile characterizing complexes of 2,9-diarylphenanthroline ligands compared to those of 2,9-dialkylphenanthroline type.[22]

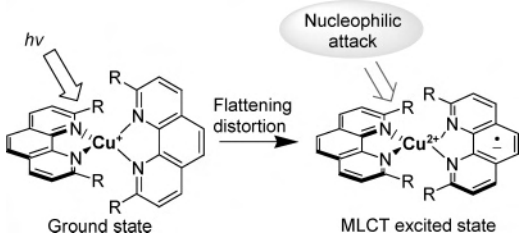

Figure 1. Light excitation into the lowest MLCT excited state(s) of Cu(I)−bis(phenanthroline)s leads to a flattening distortion of the coordination environment, thus exposing the metal center to nucleophilic attack by external molecules such as solvent or counterions.

Also excited-state characteristics of $[Cu(NN)_2^+]$ (e.g. emission spectra and excited-state lifetimes) strongly depend on the substitution pattern of the phenanthroline ligands.[22] The effects on the luminescence intensity and lifetime can be attributed to a distortion occurring in the MLCT excited state, since the metal center changes its formal oxidation state from Cu(I) to Cu(II), thus assuming a more flattened coordination geometry (Figure 1).[30] In the flattened structure a fifth coordination site is made available at the newly formed d^9 ion,[31] allowing for attack by nucleophilic species such as solvent molecules and counterions. The resultant pentacoordinated excited complexes (exciplexes) deactivate via nonemissive deactivation paths.[22] This deactivation mechanism via the formation of an intermediate species, hypothesized a long time ago,[32,33] has been recently demonstrated experimentally via ultrafast spectroscopic techniques, such as time-resolved X-ray[31,34−36] and electronic absorption[37,38] spectroscopies.

To disfavor the formation of nonemissive pentacoordinated exciplexes of $[Cu(NN)_2^+]$ described in Figure 1, the strategy is 2-fold: (i) choose bulky substituents R at the phenanthroline ligands that shield the metal site from intermolecular attack;[39,40] (ii) work in poor donor solvents.[22] The latter constraint has practically limited the solvent choice to CH_2Cl_2 since in other media (methanol, acetonitrile, acetone) there is virtually no luminescence from $[Cu(NN)_2^+]$.

In an attempt to further elucidate the role of the ligand structure in defining the photophysical properties of [Cu-

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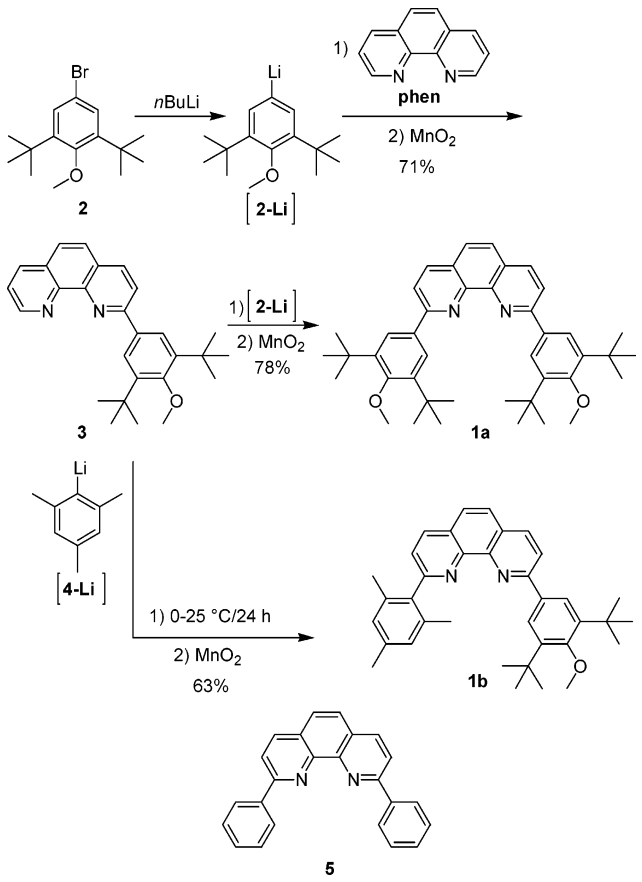
Scheme 1. Synthesis of Ligands **1a**,**b** and Structure of Ligand **5**



$(NN)_2^+$] complexes, we present herein the synthesis of two novel complexes of this family, which turn out to exhibit quite interesting kinetic and photophysical properties.

Results and Discussion

Synthesis and Kinetic Studies. Phenanthrolines **1a,b** are prepared according to known procedures (Scheme 1).[41] The aryllithium compound **2-Li**, obtained from **2** (2 equiv) and *n*-BuLi (2.1 equiv), is added to the parent phenanthroline (phen) affording **3** in 71% yield after oxidative rearomatization. Following the same procedure, ligand **1a** is prepared from **3** and **2-Li**, while **1b** is formed from **3** and **4-Li**. Ligand **5** is well-known from the literature.[2,30,42,43]

The new copper(I) complexes $[Cu(\mathbf{1a})_2]^+$ and $[Cu(\mathbf{1b})_2]^+$ are obtained quantitatively by treatment of **1a,b**, respectively, with $[Cu(CH_3CN)_4]PF_6$ (1:0.5 equiv) in CH_2Cl_2 at ambient temperature (eqs 1−3), as was the known $[Cu(\mathbf{5})_2]^+$.[30,43] It is important to note that the formation of $[Cu(\mathbf{1a})_2]^+$ is very slow (25 °C/5 d), whereas $[Cu(\mathbf{1b})_2]^+$ and $[Cu(\mathbf{5})_2]^+$ form immediately. Complex $[Cu(\mathbf{1a})_2]^+$ exhibits a magenta color, whereas $[Cu(\mathbf{1b})_2]^+$ and $[Cu(\mathbf{5})_2]^+$ show a dark red hue, the color expected for a typical bis(phenanthroline)copper(I) complex. These preliminary observations suggest peculiar

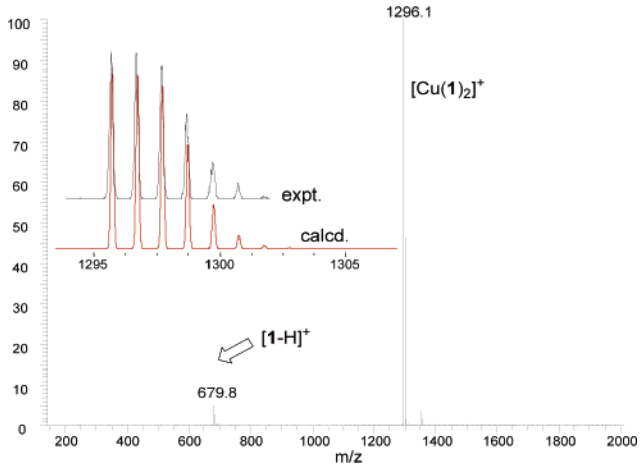


Figure 2. ESI MS of $[Cu(\mathbf{1a})_2]^+$ and its isotopic distribution (dark, experimental; red, calculated). The signal of $\mathbf{1}-H^+$ is due to residual traces of acid in the instrument.

ground-state electronic properties for $[Cu(\mathbf{1a})_2]^+$, compared to analogous homoleptic $[Cu(NN)_2^+]$complexes.

$$\mathbf{1a} \xrightarrow[25\ °C/\sim 5\ d]{[Cu(MeCN)_4]PF_6} [Cu(\mathbf{1a})_2]^+ \quad (1)$$

$$\mathbf{1b} \xrightarrow[immediately]{[Cu(MeCN)_4]PF_6} [Cu(\mathbf{1b})_2]^+ \quad (2)$$

$$\mathbf{5} \xrightarrow[immediately]{[Cu(MeCN)_4]PF_6} [Cu(\mathbf{5})_2]^+ \quad (3)$$

The structures of $[Cu(\mathbf{1a})_2]^+$ and $[Cu(\mathbf{1b})_2]^+$ were confirmed by ^1H NMR, ^{13}C NMR, ESI MS, and elemental analysis. The ^1H NMR spectrum of $[Cu(\mathbf{1a})_2]^+$ shows a single sharp set of signals with a spectral pattern being typical for copper(I) bis(phenanthroline) complexes.[23,44] It reveals an upfield shift of 0.64 ppm for the phenyl protons (from δ 8.12 to 7.48 ppm). Equally, the methoxy and *tert*-butyl protons experience significant upfield shifts (from δ 3.77 to 3.20 and 1.55 to 0.90 ppm, respectively). All assignments are confirmed by COSY. The ^{13}C NMR shows a single set of 13 expected signals for $[Cu(\mathbf{1a})_2]^+$, further supporting the suggested structure. ESI MS (electrospray ionization mass spectroscopy) provides conclusive evidence for the complex structure exhibiting a singly charged signal at $m/z = 1296.1$ assigned to $[Cu(\mathbf{1a})_2]^+$ after the loss of hexafluorophosphate as the counterion (Figure 2). No other signals could be detected up to 4000 Da. It is noteworthy to mention that under ESI MS conditions copper(I)−bis(phenanthroline) complexes normally undergo extensive fragmentation through loss of ligands (>30%).[45] In contrast, $[Cu(\mathbf{1a})_2]^+$ and $[Cu(\mathbf{1b})_2]^+$ do not show any significant fragmentation (<5%) suggesting an excellent kinetic stability.

The dynamics of ligand binding in $[Cu(\mathbf{1a,b})_2]^+$ and for comparison in $[Cu(\mathbf{5})_2]^+$ is probed by adding the parent 1,-10-phenanthroline (phen) in various amounts (1:0.5−10 equiv). In $[Cu(\mathbf{5})_2]^+$, similar to other homoleptic complex-

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Table 1. Formation of Homoleptic and Heteroleptic Cu(I)−Bis(phenanthroline) Complexes with **1a**[a]

expt no.	sequential additn	obsd species by ESI MS
I	$[Cu(\mathbf{1a})_2]^+$ + phen (0.5−10 equiv)	only $[Cu(\mathbf{1a})_2]^+$ and phen detected (analyzed after 15 min and after 15 d)
II	$[Cu(phen)_2]^+$ + **1a** (0.25−1.0 equiv)	mixed complex $[Cu(\mathbf{1a})(phen)]^+$ formed (detected after 15 min)
III	**1a** + phen + Cu(I)	mixed complex $[Cu(\mathbf{1a})(phen)]^+$ formed (detected after 15 min)
IV	$[Cu(phen)]^+$ + **1a** (0.25−1 equiv)	while $[Cu(\mathbf{1a})(phen)]^+$ forms instantly, $[Cu(\mathbf{1a})_2]^+$ is only detected after longer times; $[Cu(\mathbf{1a})_2]^+$ increases with time (10% to 60% over a period of 18 h)

[a] There is a time delay of about 15 min until the ESI measurement.

es,[16,46] ligand exchange is instantaneous, as indicated by ^{1}H NMR and ESI MS through the emergence of new signals corresponding to $[Cu(\mathbf{5})(phen)]^+$ and $[Cu(phen)_2]^+$.

With $[Cu(\mathbf{1a,b})_2]^+$, however, the situation is drastically different. As indicated by ESI MS and ^{1}H NMR, not a single trace of the heteroleptic complex $[Cu(\mathbf{1a,b})(phen)]^+$ is detectable at RT (room temperature) over a period of 15 days from a mixture of phen (0.5 equiv) and $[Cu(\mathbf{1a,b})_2]^+$ (1 equiv). Even upon addition of an excess of phen (10 equiv), no signals of $[Cu(\mathbf{1a})(phen)]^+$ are detected. The same result is obtained after refluxing the reaction mixture for 1 week in dichloromethane or acetonitrile, pointing to a marked kinetic inertness of $[Cu(\mathbf{1a})_2]^+$.

Interestingly, the heteroleptic $[Cu(\mathbf{1a})(phen)]^+$ complex is cleanly obtained when we add ligand **1a** to $[Cu(phen)_2]^+$ or $[Cu(phen)]^+$ (Table 1, experiments II and III, observed over several days at RT). In experiment IV both $[Cu(\mathbf{1a})(phen)]^+$ and $[Cu(\mathbf{1a})_2]^+$ are formed, with the amount of $[Cu(\mathbf{1a})_2]^+$ increasing over time. These results indicate that once the $[Cu(\mathbf{1a})_2]^+$ complex is formed it is kinetically "locked" due to the large substituents at the 2,9-positions of the phenanthroline. To the best of our knowledge this is the first Cu(I)−bis(phenanthroline) complex that does not exchange with added 2,9-unsubstituted phenanthrolines thanks to a peculiar kinetic inertness.

To understand the marked kinetic behavior of $[Cu(\mathbf{1a})_2]^+$, we calculated its energy minimized structure by ZINDO/1 semiempirical self-consistent field (SCF) calculations[47] (Figure 3). From the structure it appears that the 3,5-di-*tert*-butylphenyl groups at the phenanthroline are responsible for the kinetic locking of the ligands at the Cu(I) ion. Both in the association and dissociation process, the *tert*-butyl groups of one ligand **1a** will have to slip by the *tert*-butyl groups of the second ligand **1a**, a process that is clearly accompanied by large steric repulsions. As a consequence, the association process $[Cu(\mathbf{1a})]^+ + \mathbf{1a} \rightarrow [Cu(\mathbf{1a})_2]^+$ becomes rather slow (about 5 days at RT for completion), while the reverse process must be even slower by many orders of magnitude ($k_{diss} = k_{ass}K^{-1}$). Practically, the slow dissociation process means that the complex is kinetically locked. Unfortunately, all attempts to obtain the solid-state structure of $[Cu(\mathbf{1a})_2]^+$ have been unsuccessful.

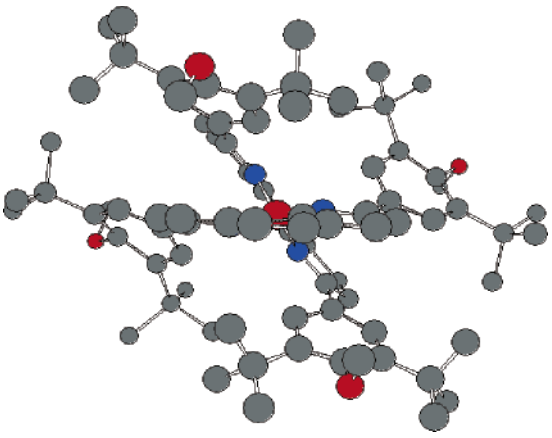

Figure 3. Model structure of $[Cu(\mathbf{1a})_2]^+$ optimized by ZINDO/1 semiempirical self-consistent field (SCF) calculations.

Photophysical Properties. Electronic Absorption Spectra. The absorption spectra of $[Cu(\mathbf{1a})_2]^+$ and $[Cu(\mathbf{1b})_2]^+$ are depicted in Figure 4. In the UV region, where the ligand-centered ($\pi-\pi^*$) transitions of the phenanthroline ligands are dominant,[22] the difference recorded for the two complexes are mainly attributable to the difference in the phenyl fragments, in particular the chemical nature and the position of their substituents.[22] The absorption bands in the vis spectral region are ascribed to an envelope of MLCT electronic transitions.[20−22]

The complex $[Cu(\mathbf{1a})_2]^+$ exhibits a quite peculiar MLCT absorption profile if compared to previously investigated Cu(I)−bis(phenanthroline) complexes with aryl substituents in the 2 and 9 ligand positions.[22] In a number of complexes with such ligands reported so far a pronounced maximum has been found in the range 440−470 nm, with molar extinction coefficients between 3000 and 5000 M^{-1} cm^{-1}.[40,48−50] On the contrary, the most prominent absorption band of $[Cu(\mathbf{1a})_2]^+$ is the one centered at 560 nm, while the band peaked at 444 nm appears as just a weak shoulder. This is a rather unusual behavior for Cu(I) homoleptic complexes with

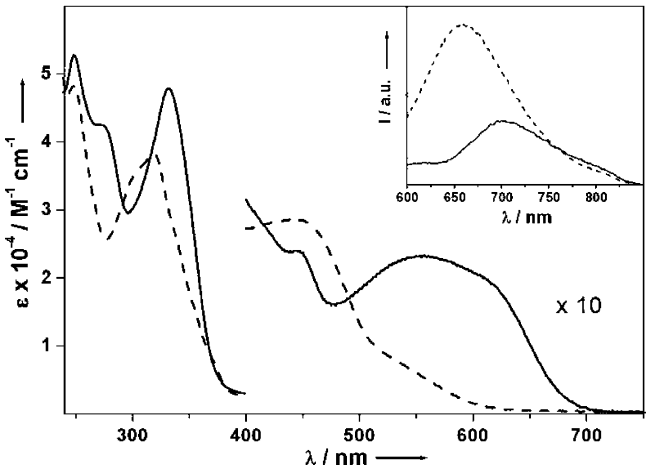

Figure 4. Absorption and (inset) luminescence spectra of $[Cu(\mathbf{1a})_2]^+$ (full line) and $[Cu(\mathbf{1b})_2]^+$ (dashed line) in CH_2Cl_2 at 298 K. The region above 400 nm is multiplied by a factor of 10. Luminescence spectra are taken at identical absorbance values (0.20) and upon excitation at 550 and 422 nm for $[Cu(\mathbf{1a})_2]^+$ and $[Cu(\mathbf{1b})_2]^+$, respectively.

Table 2. Luminescence Properties of $[Cu(\mathbf{1a})_2]^+$ and $[Cu(\mathbf{1b})_2]^+$ in CH_2Cl_2

	298 K			77 K	
compd	λ_{max},[a] nm	$10^4\Phi_{em}$[b]	τ,[c] ns	λ_{max},[a] nm	τ,[c] μs
$[Cu(\mathbf{1a})_2]^+$	704 (750)	1 (1)	87 (87)	*d*	*d*
$[Cu(\mathbf{1b})_2]^+$	660 (690)	15 (18)	266 (285)	673 (685)	2.9

[a] Emission maxima from spectra uncorrected and (in parentheses) corrected for the photomultiplier response. [b] Emission quantum yields in air-equilibrated and (in parentheses) deoxygenated solutions. [c] Excited-state lifetimes in air-equilibrated and (in parentheses) deoxygenated solutions. [d] Very weak signal, hardly distinguishable from instrumental noise.

symmetrically substituted phenylphenanthrolines, which has to be related to the presence of the cumbersome *tert*-butyl groups on the ligands, that strongly affect the ground-state coordination geometry of the complex and, accordingly, have an effect on electronic transition probabilities.[22] Notably, the MLCT absorption spectral shape of $[Cu(\mathbf{1a})_2]^+$ is similar to that of a Cu(I)−catenate complex made of two interlocked 27-membered ring containing a phenanthroline moiety.[51] This suggests that the above-mentioned locked structure of $[Cu(\mathbf{1a})_2]^+$ is rather similar, in terms of ground-state geometric distortion, to that of the catenate complex. This latter compound is characterized by a low-symmetry strongly distorted tetrahedral geometry, and its absorption spectrum is scarcely affected by temperature decrease,[51] which also supports the view of a fairly rigid coordination environment.

The electronic absorption spectrum of $[Cu(\mathbf{1b})_2]^+$ is substantially different from that of $[Cu(\mathbf{1a})_2]^+$ (Figure 4). In particular, a dramatic decrease of the lowest energy MLCT bands is observed. This effect, normally observed in Cu(I) complexes of 2,9-dialkylphenanthroline-type ligands, has been related to negligible distortions from the D_{2d} tetrahedral symmetry.[22] In the present case, in analogy with Miller et al.,[49] the reduced distortion is most likely driven by the $-CH_3$ groups present in one phenyl unit, *ortho* to the C atom connected to the phenanthroline fragment. Such methyl groups prevent extensive $\pi\pi^*$ stacking interactions between their phenyl ring and the phenanthroline of the other ligand, which is typical for these compounds.[22,29] Thus, it is confirmed that little variations in ligand structures result in dramatic effect on the ground-state geometry of Cu(I)−phenanthrolines. This is reflected in the electronic absorption profiles of $[Cu(\mathbf{1a})_2]^+$ and $[Cu(\mathbf{1b})_2]^+$ which, in CH_2Cl_2 solution, turn out to be magenta and deep red, respectively.

Emission Spectra. The luminescence data and lifetimes of $[Cu(\mathbf{1a})_2]^+$ and $[Cu(\mathbf{1b})_2]^+$ at 298 and 77 K in CH_2Cl_2 are collected in Table 2. The two metal complexes show a broad luminescence band centered around 700 nm, attributable to deactivation of MLCT excited states (Figure 4).[21,22]

$[Cu(\mathbf{1a})_2]^+$ is a very poor luminophore (Table 2) and exhibits a relatively short lifetime of only 87 ns, comparable to that of $[Cu(dmp)_2]^+$ (73 ns, dmp = 2,9-dimethyl-1,10-phenanthroline).[52] The short lifetime of $[Cu(dmp)_2]^+$ is related to the small size of the methyl substituents on the phenanthroline ligand, which cannot contrast effectively excited-state geometric distortion and subsequent nucleophilic attack (Figure 1). Clearly, in our present case, the small size of the substituent cannot be invoked to rationalize the weak luminescence signal. This can be explained, instead, assuming that the strong ground-state geometric distortion, derived from the analysis of the absorption spectrum (see above), is kept in the excited state. The distorted $[Cu(\mathbf{1a})_2]^+$ complex emits at relatively low energy and due to the energy-gap law[50,53] nonradiative deactivations, always largely prevailing over radiative transitions in Cu(I)−phenanthrolines, are further strengthened. At 77 K the MLCT emission band of $[Cu(\mathbf{1a})_2]^+$ is hardly distinguishable over the instrumental noise. The substantial decrease of luminescence observed on passing to low-temperature rigid matrix is in line with the behavior of virtually all the Cu(I)−diphenylphenanthroline complexes investigated to date. This behavior has been rationalized assuming that emission in $[Cu(NN)_2]^+$ stems from a low-lying poorly emitting MLCT triplet (^{3}MLCT), whose population is depleted at higher temperatures as a consequence of a thermal equilibrium with an upper lying singlet (^{1}MLCT) exhibiting stronger luminescence and mainly responsible for emission at room temperature (two-level model).[50,54]

Despite its small emission yield $[Cu(\mathbf{1a})_2]^+$ allows an evaluation of the importance of bulky phenanthroline ligands to prevent interactions of the Cu(I) ion with external molecules and, thus, exciplex deactivation (Figure 1). The emission yield and MLCT lifetime of $[Cu(\mathbf{1a})_2]^+$ is insensitive to the presence of O_2 in solution (Table 2), and to the best of our knowledge, this is an unprecedented finding for Cu(I)−phenanthrolines. Moreover $[Cu(\mathbf{1a})_2]^+$ exhibits MLCT luminescence also in solvents with a more nucleophilic character than CH_2Cl_2, such as THF, DMF, and MeOH. In the latter case the lifetime is 62 ns and the luminescence quantum yield is 7.0×10^{-5}, to be compared with 87 ns and 1.0×10^{-4} in CH_2Cl_2. This result is particularly interesting because most Cu(I)−phenanthrolines lack any luminescence in MeOH[32] and confirms that $[Cu(\mathbf{1a})_2]^+$ possesses an extremely rigid and protected coordination environment, giving support to the notion of a locked complex (see above).

The MLCT emission spectrum of $[Cu(\mathbf{1b})_2]$ has an emission maximum at 690 nm and is much more intense than the corresponding spectrum of $[Cu(\mathbf{1a})_2]^+$ (Table 2). The emission band of $[Cu(\mathbf{1b})_2]$ is substantially blue shifted, suggesting a relatively higher lying MLCT state, less affected by nonradiative deactivations[50] (energy-gap law). Clearly,

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the higher lying MLCT levels of this compound are the result of a less distorted excited-state geometry compared to [Cu(**1a**)$_2$]$^+$; a similar trend has been observed for the ground state (see above). Unlike the case of [Cu(**1a**)$_2$]$^+$, the lifetime of [Cu(**1b**)$_2$]$^+$ is sensitive to the presence of molecular oxygen, with a lifetime of 266 and 285 ns in air equilibrated and oxygen-free solutions, respectively. However the effect is small if compared to similar simpler compounds such as [Cu(dtp)$_2$]$^+$ (dtp = 2,9-ditolyl-1,10-phenanthroline), whose lifetimes are 139 and 237 ns under the same conditions.[52] Also some effect of solvent nucleophilicity is found for [Cu(**1b**)$_2$]$^+$, but nevertheless the compound is emissive in MeOH with a respectable lifetime of 182 ns. These results demonstrate that also the coordination environment of [Cu(**1b**)$_2$]$^+$ is well protected from external contacts, though not locked as much as [Cu(**1a**)$_2$]$^+$.

At 77 K [Cu(**1b**)$_2$]$^+$ exhibits a very strong emission band, as only rarely observed for [Cu(NN)$_2$]$^+$,[50] which tend to become very poor emitters in low-temperature rigid matrixes. The bright orange luminescence observable under these conditions, though a quantitative measure in a rigid matrix is difficult, can be roughly estimated at least 100 times more intense than that of [Cu(**1a**)$_2$]$^+$ and comparable to that of [Cu(dhp)$_2$]$^+$ (dhp = bis(2,9-hexyl-1,10-phenanthroline)) reported earlier.[50]

So far, to the best of our knowledge, only Cu(I) complexes of (some) alkylphenanthroline ligands have turned out to be highly luminescent at 77 K,[50] and this is likely to be the first example where such a behavior is found for compounds of phenylphenanthroline-type ligands. The shape of the absorption spectrum and the position of the emission band of [Cu(**1b**)$_2$]$^+$ are similar to those of alkylphenanthroline Cu(I) complexes, pointing to little distortion from the ground-state induced by the specific substituent onto the chelating agents (see above). These findings and the low-temperature behavior of [Cu(**1b**)$_2$]$^+$ support our previous hypothesis[50] that the occurrence of strong luminescence at 77 K in Cu(I)−phenanthrolines depends on electronic (i.e. alkyl vs phenyl substituents) and structural (i.e. distortion from the ground state) factors, with the latter likely to play a predominant role.

Conclusions

In this paper we present the synthesis of two novel phenanthroline ligands (**1a**,**b**) and the preparation of the corresponding homoleptic Cu(I)−bis(phenanthroline) complexes [Cu(**1a**)$_2$]$^+$ and [Cu(**1b**)$_2$]$^+$, whose photophysical properties turn out to be extremely different from each other due to dramatic variations in the ground- and excited-state geometries. Due to geometric constraints brought about by the bulky *tert*-butyl ligands on the phenyl rings, the homoleptic phenanthroline complexes [Cu(**1a,b**)$_2$]$^+$ are kinetically locked and do not exchange with added ligands. In agreement with the calculated structure, the results of kinetic and luminescence studies suggest that [Cu(**1a**)$_2$]$^+$ has an extremely blocked and shielded coordination environment. Finally, [Cu(**1b**)$_2$]$^+$ turns out to be, to the best of our knowledge, the first example of a [Cu(NN)$_2$]$^+$ complex with phenylphenanthroline ligands strongly emitting at 77 K; this confirms that structural rather than electronic factors mainly dictate the luminescence performances of these compounds in rigid matrix.

The results presented here give further insight into the rationalization of the photophysical properties of phenanthroline ligands and related [Cu(NN)$_2$]$^+$ complexes and provide valuable information for understanding the behavior of more sophisticated architectures including such molecular motifs as key building blocks.[19,45]

Experimental Section

^{1}H NMR and ^{13}C NMR were measured on a Bruker AC 400 (400 MHz) unless specified otherwise. ESI MS spectra were measured on a LCQ Deca Thermo Quest instrument. Typically, each time 25 scans were accumulated for one spectrum. Phenanthrolines **1a,b** and **3** were prepared according to known procedures (Scheme 1).[41] All compounds were characterized by ^{1}H and ^{13}C NMR, ESI MS, IR, and elemental analysis.

2,9-Bis(3,5-di-*tert*-butyl-4-methoxyphenyl)[1,10]phenanthroline (1a): 78%; mp > 230 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.31 (d, 2H, J = 8.3 Hz, phen), 8.12 (s, 4H, phenyl), 8.04 (d, 2H, J = 8.3 Hz, phen), 7.81 (s, 2H, phen), 3.77 (s, 6H, methoxy), 1.55 (s, 36, *t*-Bu); ^{13}C NMR (CD_2Cl_2, 50 MHz) δ 161.0, 158.1, 146.3, 144.0, 136.7, 134.8, 127.7, 126.3, 125.9, 120.9 (arom), 64.4 (methoxy), 35.9, 32.0 (aliph); IR (KBr) ν 3387, 2960, 2867, 1623, 1607, 1590, 1498, 1466, 1408, 1392, 1359, 1313, 1259, 1225, 1115, 1006, 889, 854, 804, 738, 648; ESI MS *m*/*z* (%) 1296.1, [M + H]$^+$. Anal. Calcd for $C_{42}H_{52}N_2O_2$: C, 81.78; H, 8.50; N, 4.54. Found: C, 81.71; H, 8.89; N, 4.42.

2-(3,5-Di-*tert*-butyl-4-methoxyphenyl)-9-(2,4,6-trimethylphenyl)-[1,10]phenanthroline (1b): 63%; mp 182 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30 (d, J = 8.0 Hz, 1H, phen), 8.28 (d, J = 8.0 Hz, 1H, phen), 8.15 (s, 2H, phenyl), 8.04 (d, J = 8.4 Hz, 1H, phen), 7.83 (m, 2H, phen), 7.63 (d, J = 8.0 Hz, 1H, phen), 7.01 (s, 2H, phenyl), 3.75 (s, 3H, methoxy), 2.39 (s, 3H, benzyl), 2.32 (s, 6H, benzyl), 1.54 (s, 18H, *t*-Bu); ^{13}C NMR (CD_2Cl_2, 50 MHz) δ 161.5, 160.0, 158.5, 146.7, 146.3, 144.3, 138.3, 137.8, 136.9, 136.8, 135.8, 134.9, 129.0, 127.6, 127.4, 126.9, 126.4, 126.1, 125.6, 120.8, 64.9, 36.4, 32.5, 21.6, 21.4; IR (KBr) ν 3417, 2960, 2916, 2867, 1620, 1587, 1540, 1495, 1479, 1410, 1394, 1356, 1313, 1223, 1115, 1099, 1007, 887, 859, 751, 729, 631, 583; ESI MS *m*/*z* (%) 517.5 (100), [M + H]$^+$. Anal. Calcd for $C_{36}H_{40}N_2O$: C, 83.68; H, 7.80; N, 5.42. Found: C, 83.22; H, 8.24; N, 5.15.

2-(3,5-Di-*tert*-butyl-4-methoxyphenyl)[1,10]phenanthroline] (3): 71%; mp 156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.24 (dd, J = 4.3, 1.8 Hz, 1H, phen), 8.33 (d, J = 8.3 Hz, 1H, phen), 8.29 (dd, J = 8.1, 1.8 Hz, 1H, phen), 8.21 (s, 2H, phenyl), 8.11 (d, J = 8.3 Hz, 1H, phen), 7.84 (d, J = 8.6 Hz, 1H, phen), 7.79 (d, J = 8.6 Hz, 1H, phen), 7.67 (dd, J = 8.1, 4.3 Hz, 1H, phen), 3.82 (s, 3H, methoxy), 1,61 (s, 18H, aliph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.0, 159.9, 151.2, 151.1, 147.0, 144.9, 137.6, 136.9, 135.7, 129.9, 128.1, 127.6, 127.3, 126.9, 123.8, 122.2 (arom), 65.5 (methoxy), 36.9, 33.1 (alkyl); IR (KBr) ν 3395, 2959, 1618, 1589, 1547, 1508, 1489, 1445, 1409, 1362, 1226, 1117, 1009, 779, 746, 717, 627; ESI MS *m*/*z* (%) 399.4 (100), [M + H]$^+$. Anal. Calcd for $C_{27}H_{30}N_2O$: C, 81.37; H, 7.59; N, 7.03. Found: C, 81.08; H, 7.86; N, 6.82.

General Procedure for the Copper Complex Formation. Homoleptic complexes were prepared by reacting **1a** or **1b** with

$[Cu(MeCN)_4]PF_6$ (1:0.5 equiv, respectively) in dichloromethane.[55] All complexes were analyzed in solution by NMR and ESI MS without any further purification. However, prior to elemental analysis the copper complexes were recrystallized using dichloromethane and/or diethyl ether. In some cases, the solvents showed up in the elemental analysis.

$[Cu(1a)_2]^+$: ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.38 (d, J = 8.5 Hz, 4H, phen), 7.98 (s, 4H, phen), 7.85 (d, J = 8.5 Hz, 4H, phen), 7.48 (s, 8H, phenyl), 3.20 (s, 12H, methoxy), 0.90 (s, 72H, *t*-Bu); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 161.9, 157.6, 144.1, 144.0, 136.7, 133.6, 128.8, 126.9, 126.3, 126.1 (arom), 63.6 (methoxy), 35.3, 31.7 (aliph); IR (KBr) ν 3393, 2961, 1582, 1504, 1451, 1409, 1391, 1349, 1314, 1113, 1004, 862, 841, 753, 557, 526; ESI MS *m*/*z* (%) 1296.1 (100), $(M - PF_6]^+$. Anal. Calcd for $CuC_{84}H_{104}N_4O_4 \cdot PF_6$: C, 69.95; H, 7.27; N, 3.88. Found: C, 69.76; H, 7.58; N, 3.69.

$[Cu(1b)_2]^+$: ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 8.54 (d, J = 8.3 Hz, 2H, phen), 8.50 (d, J = 8.3 Hz, 2H, phen), 8.15 (d, J = 8.3 Hz, 2H, phen), 8.05−8.12 (m, 6H, phen), 7.47 (s, 2H, phenyl), 7.44 (s, 2H, phenyl), 6.29 (s, 2H, MesH), 5.74 (s, 2H, MesH), 3.41 (s, 6H, methoxy), 2.12 (s, 6H, benzyl), 2.09 (s, 12, benzyl), 0.99 (s, 36H, *t*-Bu); ESI MS *m*/*z* (%) 1095.7(100), $[M - PF_6]^+$. Anal. Calcd for $CuC_{72}H_{80}N_4O_2 \cdot PF_6 \cdot 0.5CH_2Cl_2$: C, 67.80; H, 6.36; N, 4.36. Found: C, 67.62; H, 6.49; N, 4.33.

$[Cu(1a)(phen)]^+$: ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 8.66 (d, J = 8.1 Hz, 2H, phen), 8.47 (d, J = 4.3 Hz, 2H, phen), 8.34 (d, J = 8.1 Hz, 2H, phen), 8.16 (s, 2H, phen), 8.04 (d, J = 8.4 Hz, 2H, phen), 7.91 (s, 2H, phen), 7.63 (dd, J = 8.1, 4.3 Hz, 2H, phen), 7.27 (s, 4H, phenyl), 2.98 (s, 6H, methoxy), 0.82 (s, 32H, *t*-Bu); ^{13}C NMR (CD_2Cl_2, 50 MHz) δ 160.2, 158.9, 148.1, 143.9, 143.5, 142.9, 137.0, 136.1, 134.8, 129.4, 128.0, 126.4, 126.3, 126.1, 125.9, 125.1 (arom), 64.1 (methoxy), 35.1, 31.0 (aliph); IR (KBr) ν 3404, 2922, 1586, 1508, 1459, 1408, 1356, 1224, 1115, 1006, 838, 726, 557; ESI MS *m*/*z* (%) 859.5 (100), $[M - PF_6]^+$. Anal. Calcd for $[CuC_{54}H_{60}O_2 \cdot PF_6 \cdot CH_2Cl_2]$: C, 60.58; H, 5.73; N, 5.14. Found: C, 60.51; H, 5.88; N, 5.03.

$[Cu(1b)(phen)]^+$: ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 8.64 (d, J = 8.4 Hz, 2H, phen), 8.46 (m, 3H), 8.17 (m, 4H), 7.92 (s, 2H, phen), 7.70 (m, 3H), 7.45 (s, 2H, phenyl), 5.71 (s, 2H, MesH), 2.80 (s, 3H, methoxy), 1.65 (s, 3H, benzyl), 1.57 (s, 6H, benzyl), 0.83 (s, 18H, *t*-Bu); ^{13}C NMR (CD_2Cl_2, 50 MHz) δ 160.6, 159.5, 158.5, 149.1, 147.9, 146.9, 144.1, 143.7, 143.4, 143.1, 140.8, 139.0, 137.3, 136.5, 136.1, 135.4, 134.4, 133.9, 129.0, 128.0, 126.8, 126.5, 125.8, 124.9, 117.6, 116.7 (arom), 63.4 (methoxy), 35.1, 31.0 (3C) (aliph); IR (KBr) ν 3423, 2965, 1618, 1583, 1509, 1459, 1411, 1223, 1111, 1003, 840, 729, 557, 541; ESI MS *m*/*z* (%) 759.4 (100), $[M - PF_6]^+$. Anal. Calcd for $[CuC_{48}H_{48}N_4O \cdot PF_6]$: C, 63.67; H, 5.34; N, 6.19. Found: C, 63.34; H, 5.53; N, 5.85.

Photophysical Measurements. Absorption spectra were recorded with a Perkin-Elmer λ40 spectrophotometer. Emission spectra were obtained with an Edinburgh FLS920 spectrometer (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185−850 nm) or a Hamamatsu R5509-72 supercooled photomultiplier tube (193 K, 800−1700 nm range). Corrected spectra were obtained via a calibration curve supplied by the instrument manufacturer. Emission quantum yields were determined according to the approach described by Demas and Crosby[56] using air-equilibrated $[Os(phen)_3]^{2+}$ in acetonitrile ($\Phi_{em} = 0.005$)[57] as standard. O_2 removal from CH_2Cl_2 solutions was accomplished by bubbling argon for 10 min. Emission lifetimes were determined with the time-correlated single photon counting technique using an Edinburgh FLS920 spectrometer equipped with a laser diode head as excitation source (1 MHz repetition rate, $\lambda_{exc} = 407$ or 637 nm, 200 ps time resolution upon deconvolution) and an Hamamatsu R928 PMT as detector. All measurements were carried out in spectroscopy grade solvents, used without further purification.

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