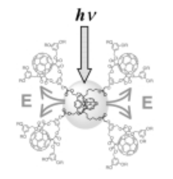
Photoactive mono- and polynuclear Cu(I)–phenanthrolines. A viable alternative to Ru(II)–polypyridines?



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Over the past two decades the photochemical and photophysical properties of Cu(I)–phenanthrolines ($[Cu(NN)_2]^+$) have been investigated in detail. A high degree of control of the metal-to-ligand charge-transfer (MLCT) absorption and luminescence properties of $[Cu(NN)_2]^+$ is now possible, by means of a thorough choice and positioning of the phenanthroline ligand substituents. Exchange of Cu(I) with a variety of metal ions (M^{n+}) allows tuning of the electrochemical and photophysical properties of the $[M(NN)_2]^{n+}$ motif. This has prompted the design of fascinating multicomponent molecular architectures (catenates, knots, rotaxanes, dendrimers) in which photoinduced intercomponent processes like energy- and electron-transfer occur. The possibility of a fine tuning of the absorption and emission properties, long excited state lifetimes, and a characteristic structural flexibility, suggest Cu(I)–phenathrolines as interesting alternatives to Ru(II)–polypyridines, still the most popular family of complexes among inorganic photochemists.

1 Introduction

The study of the photochemical and photophysical properties of coordination compounds has received a great deal of attention since the 1960s.[1] It can be truely asserted that, over four decades, the most extensively investigated family of complexes is that of the Ru(II)–polypyridines ($[Ru(PP)_m]^{2+}$), thanks to the work of numerous groups worldwide, such as those of T. J. Meyer and Balzani.[2] Even those familiar with chemistry literature might be surprised by the impressive number of reports on $[Ru(PP)_m]^{2+}$ regularly appearing in many journals. The main reason for such a success is based on the fact that *most* of these complexes combine remarkable features like: (i) ease of preparation; (ii) reversible electrochemical behaviour; (iii) light absorption in the visible spectral region (VIS); (iv) long-lived electronically excited states; (v) intense luminescence. All these characteristics make them attractive for the study of fundamental processes such as photoinduced energy- and electron-transfer under diffusional (bimolecular) conditions[1,2] or within multicomponent (supramolecular) arrays.[3] Developments in these fields have been of great interest from the practical point of view since various applications can be envisaged, including solar energy conversion.[4]

The search for new molecules able to modify or implement well-known chemical processes remains one of the most stimulating challenges of our activity. In this regard, one could wonder about families of metal complexes, other than Ru(II)–polypyridines, that are comparable with, or even surpass them, in terms of the above (i)–(v) properties. Starting from the late 1970s, thanks to the pivotal work by the group of McMillin,[5] Cu(I)–bis-phenanthrolines ($[Cu(NN)_2]^+$) have emerged as promising candidates. A key feature that distinguishes them from the exacoordinated octahedral Ru(II)–polypyridines is their lower coordination number (4), as a result of a (nearly) tetrahedral arrangement (Fig. 1).

The simpler structure has probably played an important role in encouraging groundbreaking synthetic strategies towards unconventional architectures like catenanes, rotaxanes and knots, as testified by the pioneering work of Sauvage and Dietrich-Buchecker.[6] On the other hand, it turns out that the less demanding coordination environment of Cu(I)–phenanthrolines allows extended structural distortions in the ground and excited states, thus affording a fine tuning of the photophysical and electrochemical properties (*vide infra*).

This review illustrates some of the basic electronic properties of $[Cu(NN)_2]^+$ and tries to show how these complexes, throughout the years, have been increasingly exploited in molecular and supramolecular chemistry. Particular attention will be given to their interaction with UV-VIS light, that has proved to be particularly fruitful for the triggering of a variety of photoinduced phenomena, sometimes quite novel.

2 Photophysical properties of mononuclear $[Cu(NN)_2]^+$ complexes

The parent compound of the $[Cu(NN)_2]^+$ family, *i.e.* $[Cu(phen)_2]^+$ (phen = 1,10-phenanthroline), has been little studied as it is not luminescent in solution. Therefore $[Cu(NN)_2]^+$ are typically intended to be complexes of *substituted phenanthro-*

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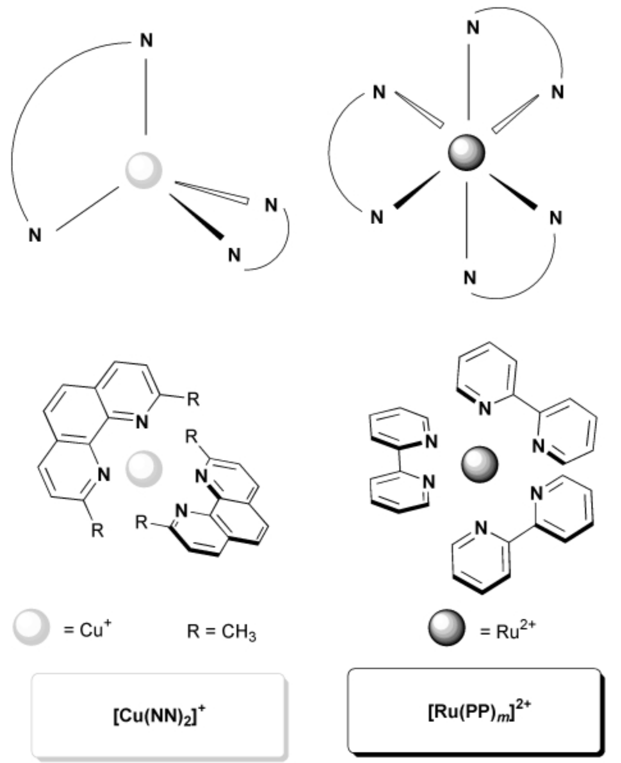


Fig. 1 Different coordination geometry of Cu(I)–phenathrolines ([Cu(NN)$_2$]$^+$) and Ru(II)–polypyridines ([Ru(PP)$_m$]$^+$). A reference complex for each family is shown, namely [Cu(2,9-dimethyl-1,10-phenanthroline)$_2$]$^+$ ([Cu(dmp)$_2$]$^+$) and [Ru(2,2′-bypiridine)$_3$]$^{2+}$ ([Ru(bpy)$_3$]$^{2+}$).

lines (see Fig. 1); the 4,7 and, more often, 2,9 positions are the most common choices. Fig. 2 shows the numbering of the 1,10 phenanthroline ring atoms.

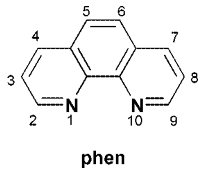


Fig. 2 Numeration of the phenanthroline ring atoms.

The most extensively investigated Cu(I)–bisphenanthroline complexes are those whose ligands are given in Fig. 3.

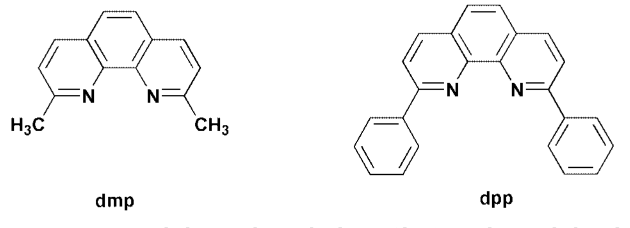


Fig. 3 2,9-Dimethyl-1,10-phenanthroline (dmp) and 2,9-diphenyl-1,10-phenanthroline (dpp) ligands.

A relevant characteristic of [Cu(NN)$_2$]$^+$ complexes is the wide range of attainable modulation of their absorption and luminescence properties, probably higher than that observed among Ru(II)–polypyridines. This property is related to the role played by structural factors. In other words the *chemical nature, the size*, and the *position* of the substituents of the phenanthroline rings can influence not only the geometry of the ground state (affecting the absorption spectra) but also that of the excited state, thus influencing the emission properties. In practice, the ground state geometry of Cu(I)–phenanthrolines can range from nearly tetrahedral (D_{2d} symmetry) to flattened tetrahedral (D_2 symmetry), the degree of distortion being dictated by steric effects of the ligand substituents. In addition, for all complexes, additional distortion is achieved in the excited state, as a consequence of the changes in electronic distribution (see below).

2.1 Nature of the electronic excited states and absorption spectra

In Fig. 4 are reported the absorption spectra of [Cu(dmp)$_2$]$^+$ and [Cu(dtp)$_2$]$^+$ (dtp = 2,9-ditolyl-1,10-phenanthroline) which, having the chelating ligands with alkyl- and aryl-type substituents, can serve as paradigmatic cases.

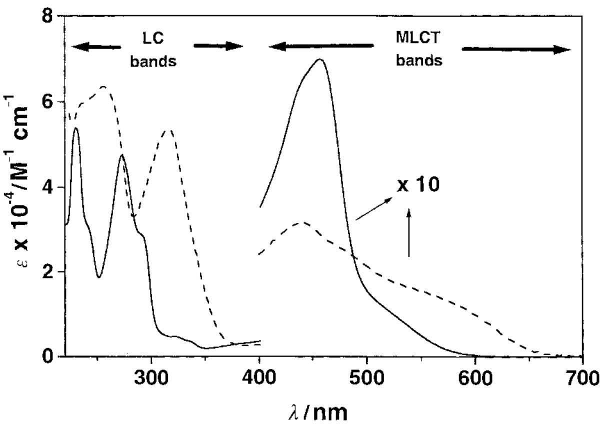


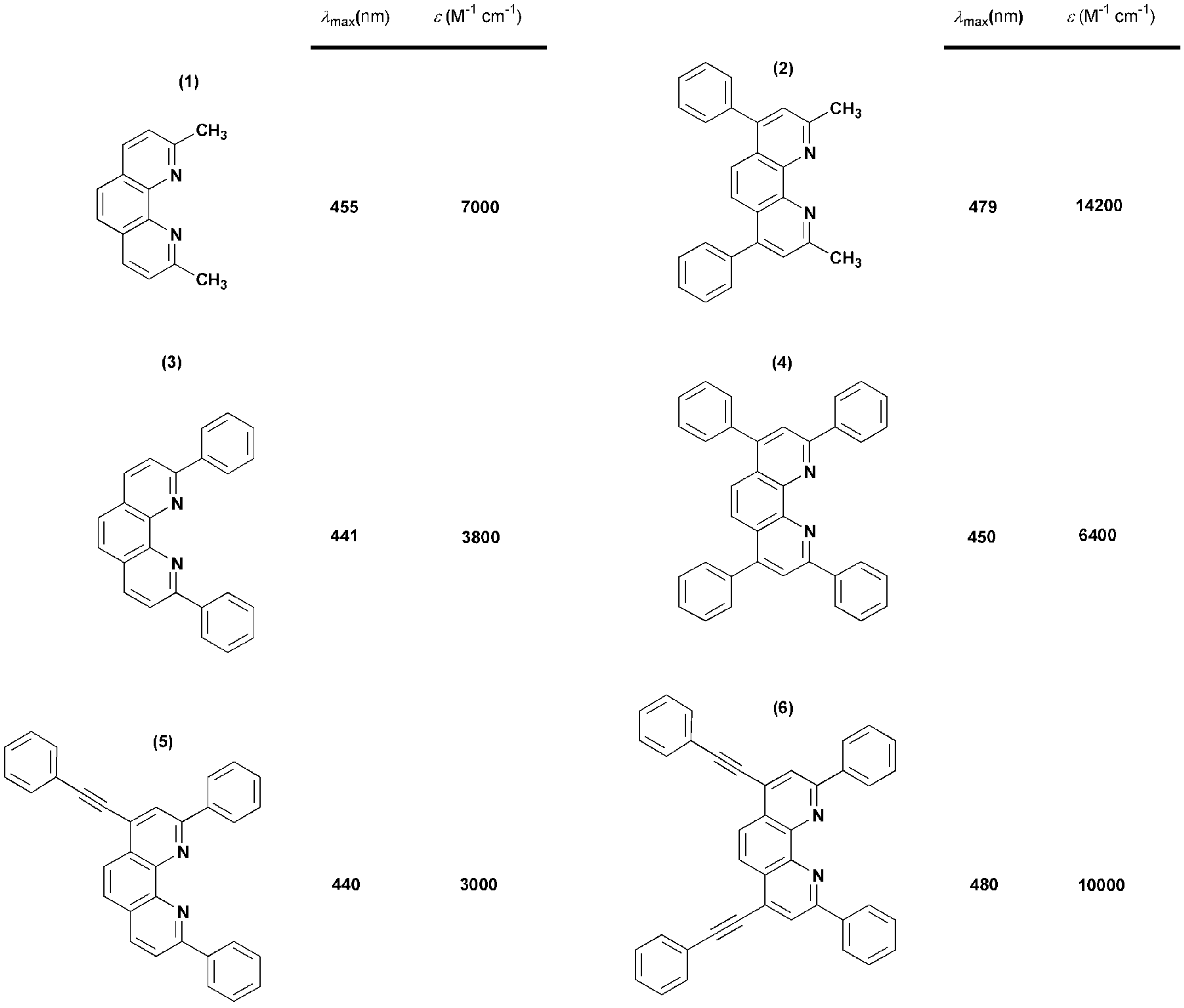
Fig. 4 Absorption spectra of [Cu(dmp)$_2$]$^+$ (full line) and [Cu(dtp)$_2$]$^+$ (dashed line) in CH$_2$Cl$_2$ solution at room temperature. dtp = 2,9-di-*p*-tolyl-1,10-phenanthroline.

The UV portion of the spectra is characterized by the intense ligand-centred (LC) bands typical of the $\pi\pi^*$ transitions of the phenanthroline ligands;[7] the molar absorption coefficients (ε) are of the order of 50 000–60 000 M^{-1} cm^{-1}. The bands lying in the VIS spectral region are much weaker than those in the UV (ε's of the order of 3000–15 000 M^{-1} cm^{-1}) and are assigned to metal-to-ligand charge-transfer (MLCT) electronic transitions.[5] These occur at low energy because the Cu$^+$ ion can be easily oxidized and the phen-type ligands possess low energy empty π^* orbitals. Direct evidence of the localized nature of the lowest-lying MLCT state of Cu(I)–phenanthrolines was achieved by Gordon and McGarvey *via* resonance raman experiments[8] and by Rodgers *et al. via* transient absorption spectroscopy.[9]

In a number of papers McMillin *et al.*[10–13] and, more recently, Karpishin *et al.*[14,15] have presented and discussed the absorption spectra of several mononuclear Cu(I)–phenanthrolines. In general, at least three MLCT bands can be seen in the VIS spectral region.[11] They are termed band I (above 500 nm), band II (maximum around 430–480 nm, the most prominent), and band III (390–420 nm), often hidden by the onset of band II). The envelope of such MLCT bands defines the shape of the VIS absorption spectrum (400–700 nm). Spectral intensities are strictly related to the symmetry of the complex that, in its turn, is affected by the distortion from the tetrahedral geometry.

A simple picture describing the MLCT absorption patterns of these complexes in solution is difficult. Nevertheless, some general trends can be obtained by analyzing the MLCT absorption maxima and ε values (CH$_2$Cl$_2$ solution, room temperature) of the selected complexes whose ligands are reported in Scheme 1.[10,15]

Complexes of 2,9-diarylphenantholines exhibit less intense absorption maxima than those of 2,9-dialkylphenantholines (see **1** *vs*. **3**); addition of phenyl rings to the 4,7 positions strongly

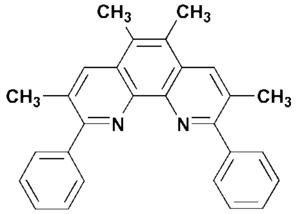


Scheme 1 Selected ligands with MLCT absorption maxima and molar absorption coefficients (ε) of the corresponding $[Cu(NN)_2]^+$ complexes (see ref. 10 and 15).

enhances the absorption[10] and red-shifts the maximum (see **1** *vs.* **2** and **3** *vs.* **4**). Ligand asymmetry substantially affects the absorption features, in particular spectral blue-shift and marked intensity decrease are observed (**5** *vs.* **6**).

As far as the shape of the MLCT absorption bands is concerned, the inspection of the spectra of Fig. 1 is quite instructive. From these spectra and a number of literature reports one can deduce that the presence of a pronounced shoulder around 550 nm (band I, see above) is a fingerprint for 2,9-aryl substitution of the phenanthroline ring. For such complexes, π-stacking interactions between the phenyl groups of one ligand and the phenanthroline moiety of the other ligand occur;[16] this leads to a strongly distorted tetrahedral geometry (D_2), under which the transition corresponding to band I is made allowed. Intriguingly, McMillin *et al.* have recently found a very weak band I for the ligand of Fig. 5,[13] despite the presence of phenyl rings in the 2 and 9 positions.

This is an interesting confirmation for the above model: the methyl groups in the 3 and 8 position prevent the flattening distortion, leading to a coordination geometry (and a spectrum) very similar to that of the much simpler $[Cu(dmp)_2]^+$ complex.



dptm

Fig. 5 2,9-Diphenyl-3,4,7,8-tetramethyl-1,10-phenanthroline (dptm). The corresponding $[Cu(NN)_2]^+$ complex displays an absorption spectrum lacking a pronounced shoulder around 550 nm, a unique case among diphenylphenanthroline complexes.

2.2 Luminescence spectra and excited state lifetimes

The first report on $[Cu(NN)_2]^+$ luminescence in fluid solution dates back to 1980, when Blaskie and McMillin showed that, upon excitation into the MLCT band region, $[Cu(dmp)_2]^+$ exhibits a luminescence spectrum peaking around 700 nm and an excited state lifetime (τ) of 54 ns in air-equilibrated CH_2Cl_2.[17] Interestingly, the luminescence from Cu(I)–phenanthrolines arises from two MLCT excited states in thermal equilibrium, *i.e.* a singlet (^{1}MLCT) and a triplet (^{3}MLCT).[12] The energy gap between these states is about 1500–2000 cm^{-1} and, at room temperature, the population of the lower lying ^{3}MLCT level largely exceeds that of ^{1}MLCT, though the minority ^{1}MLCT excited molecules are responsible for most of the observed room temperature luminescence.[12]

Since 1980, the emission properties of a large variety of Cu(I)–phenanthrolines have been reported, showing that the luminescence behaviour (*i.e.* spectral position, emission quantum yield, excited state lifetime) is quite changeable. The modification of the ground state geometry following light absorption accounts for this characteristic conduct, Fig. 6.

Upon light excitation the lowest ^{3}MLCT excited state is populated, thus the metal centre changes its formal oxidation state from Cu(I) to Cu(II); the latter tends to assume a more flattened coordination geometry.[16] In this 'open' structure a fifth coordination site is made available for the newly formed d^9 ion, that can be attacked by nucleophilic species such as solvent molecules and counterions, leading to pentacoordinated excited complexes (exciplexes), that deactivate *via* non-emissive deactivation paths. Direct spectroscopic evidence for these exciplexes is still lacking, however convincing clues for their formation have been given by McMillin *et al.* in a variety of investigations where the effect of the solvent, of the counterion, and of external molecules on the excited state lifetime of several $[Cu(NN)_2]^+$ was examined.[18] Clearly, any factor which can limit the formation of the exciplexes is able to increase the luminescence quantum yield and excited state lifetime of Cu(I)–phenanthrolines. Practically, one can act on three factors: (i) solvent nature; (ii) chemical nature, size, and number of the substituents; (iii) type of counterion. In order to maximize the luminescence performances, poor donor solvents, numerous and/or cumbersome substituents (which physically prevent the undesired nucleophilic attack), and poor donor counterions must be utilized. As a matter of fact, most of the photophysical investigations on copper phenanthrolines are reported in CH_2Cl_2, phenyl or long alkyl substituents are usually appended to the chelating unit, and BF_4^- or PF_6^- counterions are employed.

In Schemes 2 and 3 a series of selected ligands along with the lifetimes of the corresponding $[Cu(NN)_2]^+$ complexes in

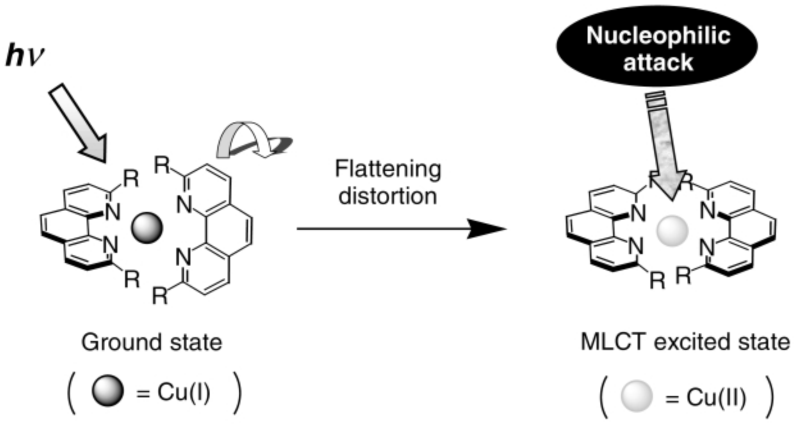
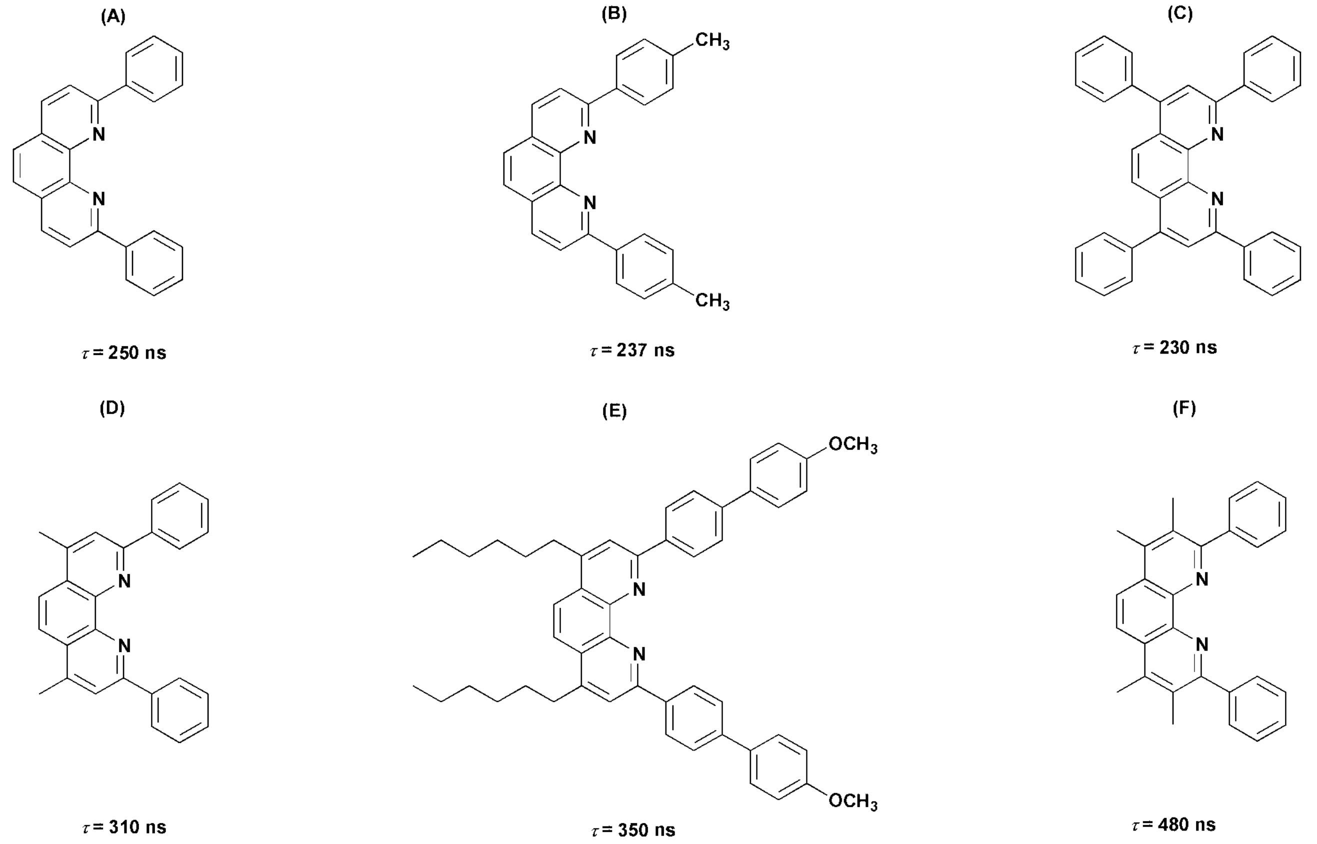
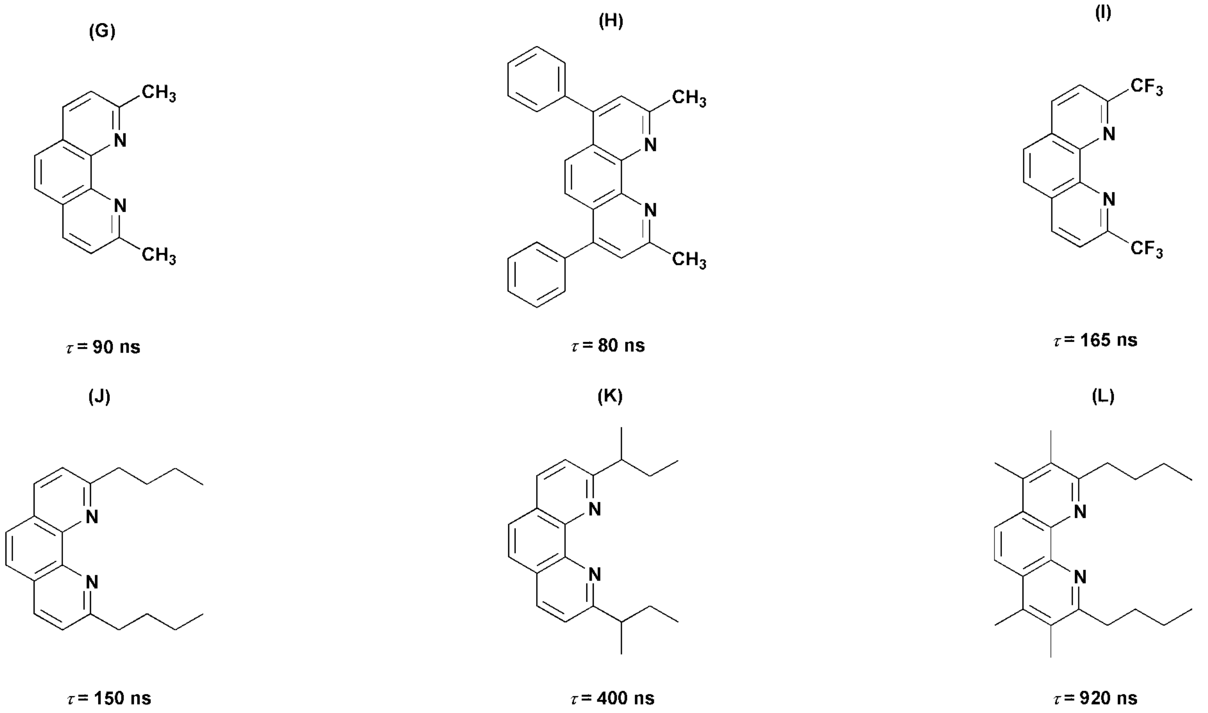


Fig. 6 Flattening distortion and subsequent nucleophilic attack by solvent, counterion, or other molecules following light excitation in Cu(I)–phenanthrolines. The size of the R substituents is of paramount importance in determining both the extent of the distortion and the protection of the newly formed Cu(II) ion from nucleophiles.



Scheme 2 Selected 2,9-diarylphenanthroline ligands and lifetimes (CH_2Cl_2 oxygen-free solution) of the corresponding homoleptic (two identical ligands) $[Cu(NN)_2]^+$ complexes. The lifetime values for the various complexes were obtained from ref. 11 (**A** and **C**), ref. 19 (**B**), ref. 13 (**D** and **F**), and ref. 20 (**E**).



Scheme 3 Selected 2,9-dialkylphenanthrolines and lifetimes (CH_2Cl_2 oxygen-free solution) of the corresponding homoleptic (two identical ligands) $[Cu(NN)_2]^+$ complexes. The lifetime values for the various complexes were obtained from ref. 11 (**G** and **H**), ref. 21 (**I**), ref. 22 (**J**, **K**), and ref. 13 (**L**).

deaerated CH_2Cl_2 solution are reported;[11,13,19–22] the emission band maxima are located in the range 650–750 nm. As expected, an increase (decrease) in lifetime value is accompanied by an increase (decrease) in emission quantum yield, even though this trend is not strictly parallel for Cu(I)–phenanthrolines,[22] opposite to what happens for ($[Ru(PP)_m]^{2+}$ complexes.[2] The trends in lifetime values will be commented on below even if, as in the case of absorption spectra (see above), a simple picture able to fully explain the observed behaviour is not available. Some important points deserve attention:

(a) For both series of Scheme 2 and 3, an increase in substituent *size* and *number* leads to longer lifetimes. The size increase is very effective in the 2 and 9 positions (see **G** *vs*. **I**), but not in the 4 and 7 positions (see **A** *vs*. **C** and **G** *vs*. **H**);
(b) The range of lifetime variation for 2,9-diaryl-type complexes (Scheme 1) is 250–480 ns (less than a twofold change);
(c) The range of lifetime variations for 2,9-dialky-type complexes (Scheme 2) is 90–920 ns (a greater than tenfold increase).

For both series, by *sterically* preventing the formation of pentacoordinated exciplexes (Fig. 6), a remarkable τ prolongation is achieved. In particular, occupation of the 3 and 8 positions (when the 2 and 9 positions are also occupied) seems to be very effective[13] (see **F** and **L**), as well as the alkyl ramification (see **J** *vs*. **K**). An important role in determining the lifetimes is probably also played by (i) electronic factors such as interligand (phenyl/phenanthroline) π-stacking interactions and larger electronic delocalization for arylphenanthrolines;[14,16] (ii) the thermal equilibrium between the lowest ^{1}MLCT and ^{3}MLCT levels (see above);[12] (iii) specific energy location(s) of the emitting excited state(s), that affects the ratio between radiative and non-radiative deactivation rates.[13] Probably, detailed temperature-dependent luminescence experiments[23] on large series of complexes could provide more insight into these issues.

In conclusion, the absorption spectra and the luminescence properties of $[Cu(NN)_2]^+$ are affected by a series of factors, as a direct or indirect result of their relatively loose coordination geometry. The prolongation of the excited state lifetimes that has been pursued over the years *via* ligand modifications can be considered a quite remarkable achievement. The longest lifetime value reported to date (920 ns in deoxygenated CH_2Cl_2, see Scheme 3)[13] is quite comparable to that of the very popular $[Ru(bpy)_3]^{2+}$ in air-free CH_3CN.[2] This result has probably gone beyond the most optimistic expectations, and now makes Cu(I)-phenanthrolines competitive with Ru(II)–polypyridines for a series of applications.

2.3 Comparing $[Cu(dpp)_2]^+$ and $[Ru(bpy)_3]^{2+}$

In photochemistry, the *excited state* electrochemical potentials are important parameters to quantify the 'abilities' of a given excited state. These quantities can be obtained from the *ground state* electrochemical potentials and the spectroscopic energy ($E^{\circ\circ}$, in eV units, to be considered divided by a unitary charge) related to the involved transition:[1,2]

$$E(A^+/{}^*A) = E(A^+/A) - E^{\circ\circ} \quad (1)$$

$$E({}^*A/A^-) = E(A/A^-) + E^{\circ\circ} \quad (2)$$

Hence the variation of the electron-donating or accepting capability of a given molecule A, upon light excitation, can be assessed. In eq. (1) and (2) *A denotes the lowest-lying electronically excited state; $E^{\circ\circ}$ can be estimated from emission spectra.[1,2]

Unfortunately, the electrochemistry of Cu(I)–phenanthrolines has been less extensively investigated than the photophysics, and the electrochemical potentials of many complexes (including some related to Schemes 2 and 3) are not available. To date no systematic compilation of electrochemical data for $[Cu(NN)_2]^+$ has been reported. Consequently, in an attempt to compare the absorption, emission, and electrochemical properties of Cu(I)–phenanthrolines and Ru(II)–polypyridines, the choice of a suitable paradigm for the former family is limited. We opted for $[Cu(dpp)_2]^+$ because it has been largely studied and it is a good emitter. In Fig. 7 are reported a series of photophysical and electrochemical parameters for $[Cu(dpp)_2]^+$ and $[Ru(bpy)_3]^{2+}$.

As expected,[1,2] both complexes are better oxidant *and* reductant in the excited state than in the ground state.

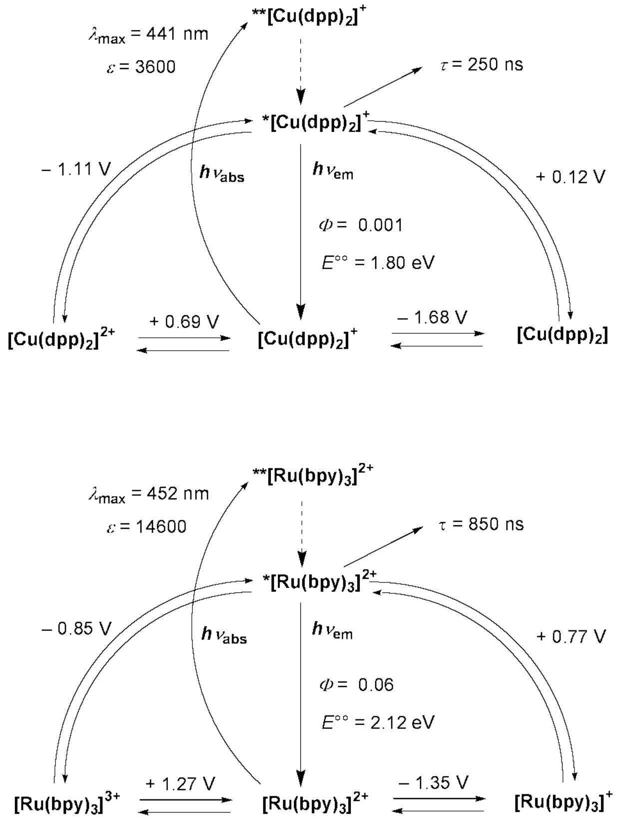


Fig. 7 $[Cu(dpp)_2]^+$ and $[Ru(bpy)_3]^{2+}$. Comparison between the photophysical and electrochemical properties. The latter are as measured in deaerated CH_2Cl_2 (ref. 11), the former in deaerated CH_3CN (ref. 2). Electrochemical potentials are in CH_3CN for both complexes ($[Ru(bpy)_3]^{2+}$, ref. 2; $[Cu(dpp)_2]^+$, P. Federlin, J.-M. Kern, A. Rastegar, C. O. Dietrich-Buchecker, P. A. Marnot and J.-P. Sauvage, *New J. Chem.*, 1990, **14**, 9). Two asterisks denote species with spin-allowed MLCT excited states populated by exciting in correspondence of the absorption maxima; one asterisk indicates the species with the lowest-lying luminescent MLCT excited states.

Importantly, $*[Cu(dpp)_2]^+$ is a more powerful reductant than $*[Ru(bpy)_3]^{2+}$ (A+/A* = −1.11 and −0.85 V, respectively) owing to its more favourable ground state 2+/+ potential (+0.69 *vs*. +1.27 V), that largely compensates for the lower content of excited state energy (1.80 *vs*. 2.12 eV). Other parameters (*e.g.* ε, excited state energy and lifetime, emission quantum yield) seem to disfavour $[Cu(dpp)_2]^+$ *vs*. $[Ru(bpy)_3]^{2+}$. However, as already pointed out here, it is now clear how to modify the phenanthroline ligands in order to improve photophysical performances like excited state lifetimes. This progress, together with some other peculiar properties, suggests that Cu(I)–phenanthrolines can be an interesting alternative to Ru(II)–polypyridines for a variety of purposes, as we will see in the next sections.

3 $[Cu(NN)_2]^+$ complexes at work: interactions with other species

The interactions of Cu(I)–phenanthrolines with other species has been the object of recent reviews. In particular G. J. Meyer *et al.* reported on bimolecular photoinduced energy- and electron-transfer processes,[24] McMillin and McNett discussed DNA interactions,[25] whereas Linton and Hamilton showed how to exploit them as molecular receptors.[26] A brief survey on these issues is provided below.

3.1 Photoinduced energy transfer

As mentioned earlier (section 2.2), at room temperature a thermal equilibrium is established between the lowest-lying ^{1}MLCT and ^{3}MLCT excited states in Cu(I)–phenanthrolines. However, since the ^{3}MLCT population largely exceeds that of ^{1}MLCT, for bimolecular quenching processes one can only consider the participation of the ^{3}MLCT level.

In Fig. 8 the two possible energy transfer processes involving Cu(I)–phenanthrolines are schematically represented.

In case (a) the energy stored in $*[Cu(NN)_2]^+$ (about 1.8–1.9 eV, see Fig. 7) is transferred to a nearby molecule that possess lower-lying (energy below 1.8–1.9 eV) electronically excited levels. In case (b), the process has an opposite direction and originates from the excitation of a molecule displaying electronically excited states above 1.8–1.9 eV, followed by sensitization of $[Cu(NN)_2]^+$ to its lowest (^{3}MLCT) excited state. In both cases, the excited molecule formed by light absorption must live ‘long enough’ to meet the partner at suitable distance and interact with it.[1,2]

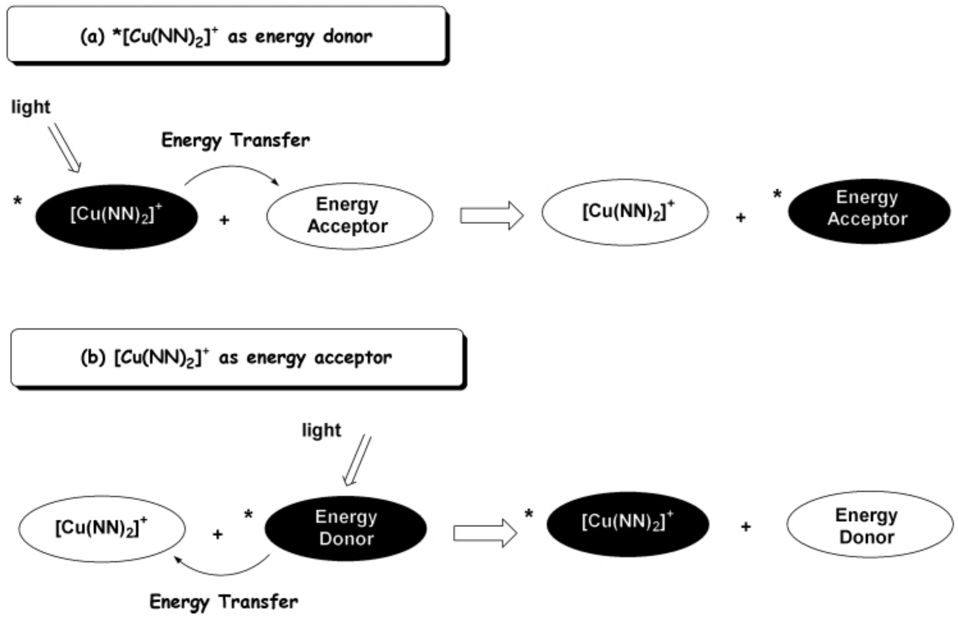


Fig. 8 Schematic representation of bimolecular photoinduced energy transfer process involving (a) $*[Cu(NN)_2]^+$ as energy donor and (b) $[Cu(NN)_2]^+$ as energy acceptor. Black ovals represent molecules in the *excited state* either obtained by direct light excitation or following sensitization; white ovals indicate *ground state* molecules.

An elegant example of type (a) energy transfer (Fig. 8) was reported by G. J. Meyer *et al.*, that chose anthracene (An) as energy acceptor.[24] The reaction is the following and was carried out in CH_2Cl_2 solution:

$$^*[Cu(dpp)_2]^+ + An \rightarrow [Cu(dpp)_2]^+ + {}^3An \qquad (3)$$

^{3}An indicates the anthracene lowest triplet state, slightly lower-lying than $^*[Cu(dpp)_2]^+$. Unambiguous demonstration of energy transfer was obtained by transient absorption spectroscopy; upon selective excitation of $[Cu(dpp)_2]^+$ the diagnostic band of the anthracene triplet is observed.

The sensitization of Cu(I)–phenanthroline MLCT excited states *via* bimolecular processes has been scarcely investigated. In contrast, several interesting cases in multicomponent systems have been reported and will be described in section 5.

3.2 Photoinduced electron transfer

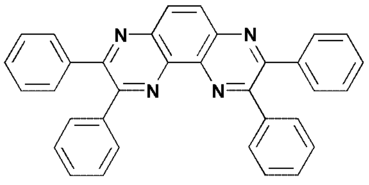
A scheme of oxidative and reductive quenching involving $^*[Cu(NN)_2]^+$ complexes is reported in Fig. 9.

From the data of Fig. 7 it is clear that the lowest MLCT excited state of Cu(I)–phenanthrolines is typically a potent reductant and a modest oxidant; in fact, oxidative quenching (Fig. 9a) of $^*[Cu(NN)_2]^+$ has been more extensively investigated than reductive quenching (Fig. 9b).

As for oxidative quenching, viologens have been the most utilized electron acceptors, since transient absorption allows easy detection of the reduced viologen species.[24,27] Interestingly, in the case of methyl viologen, the yield of electron-transfer reaction is significantly larger for $[Cu(dpp)_2]^+$ than for $[Ru(bpy)_3]^{2+}$.[24]

A potentially interesting application of the oxidative quenching of $^*[Cu(NN)_2]^+$ is related to the sensitization of large band gap semiconductors in photovoltaic devices. By coating the semiconductor surface with $[Cu(NN)_2]^+$, it has been observed that illumination with VIS light causes electron injection from the Cu(I) complex to the semiconductor material.[24,28]

Only a couple of reports on reductive quenching (Fig. 9b) of $^*[Cu(NN)_2]^+$ have been published. For instance the MLCT excited state of $[Cu(tptap)_2]^+$ (Fig. 10) can be reduced by ferrocenes, thanks to the much lower +/0 electrochemical potential with respect to ‘conventional’ $[Cu(NN)_2]^+$ such as $[Cu(dpp)_2]^+$; the potential difference between the two complexes is 0.6 V.[29]



tptap

Fig. 10 The ligand 2,3,6,7-tetraphenyl-1,4,5,8-tetraazaphenanthrene (tptap).

3.3 Dioxygen quenching

Molecular oxygen (dioxygen) is a potent quencher of excited states.[2] The concentration of dioxygen in the most common (air equilibrated) solvents is of the order of 10^{-3} mol l^{-1}, namely as much as 10 or 100 times the typical concentration of the molecule to be photochemically investigated. Hence dioxygen removal is essential to avoid undesired interfering processes during photochemical experiments.

Dioxygen possesses low-lying (<1 eV) electronic energy levels, and is also an outstanding electron acceptor. Consequently, it is able to quench the MLCT excited states of Cu(I)–phenanthrolines *both* by energy (Fig. 8a) *and* by electron transfer (Fig. 9a). It is thus not surprising that, for instance, the excited state lifetime of $[Cu(dpp)_2]^+$ in oxygen-free CH_2Cl_2 solution (250 ns, Scheme 2) is reduced to 140 ns in air-equilibrated samples. Unfortunately, no systematic investigations of dioxygen quenching in mononuclear $[Cu(NN)_2]^+$ complexes have been reported. In contrast, more detailed studies are available for the polynuclear systems discussed in section 5.

3.4 $[Cu(NN)_2]^+$ as receptors and substrates

Suitably designed substituted phenanthrolines afford Cu(I) complexes that are able to bind dicarboxylic acid *via* hydrogen bonding.[26] Effectively, the complexes are molecular tweezers that catch the substrate between two binding arms located on each phenanthroline ligand. The binding reaction can be followed by absorption spectroscopy, since in the supramolecular aggregate the coordination geometry is modified relative to the starting complex, thereby affecting the absorption pattern. Conversely, $[Cu(NN)_2]^+$ complexes have also been used as

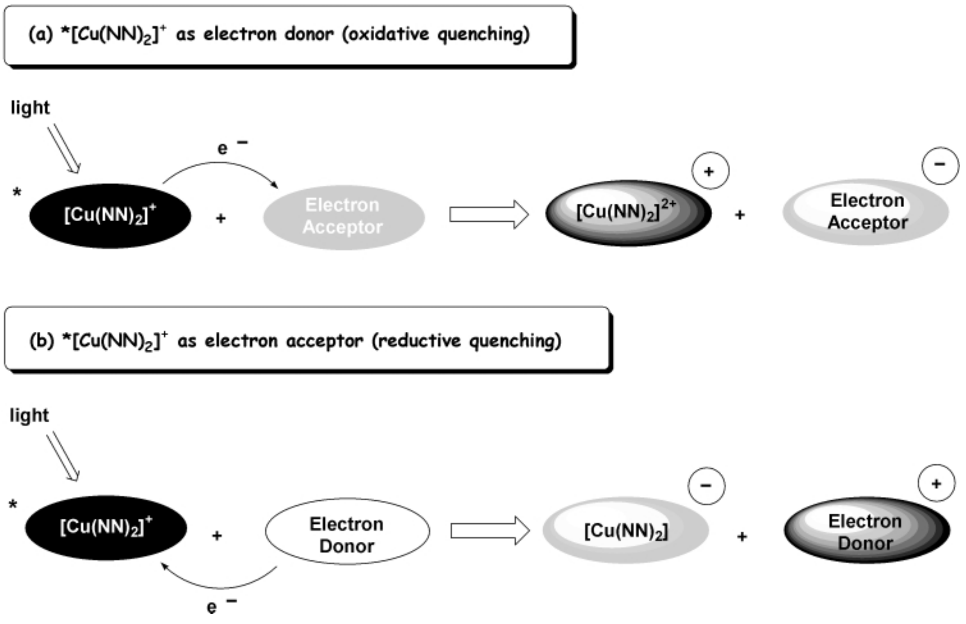


Fig. 9 Schematic representation of bimolecular photoinduced electron transfer process involving $^*[Cu(NN)_2]^+$; (a) oxidative quenching, (b) reductive quenching.

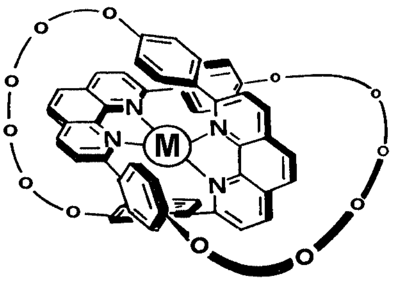
substrates for DNA binding, in attempts to take advantage of the sensitivity of the luminescence of Cu(I)–phenanthrolines to the local environment.[25] The structure of the associates is not yet available: both electrostatic binding and intercalation of the aromatic ligands between adjacent bases are possible. At the moment Cu(I)–porphyrins seem to be more promising substrates for DNA than Cu(I)–phenanthrolines.[25]

In conclusion, Cu(I)–phenathrolines can be exploited for molecular recognition processes. Quite intriguingly, their chemical and structural features make them appealing both as receptors and substrates.

4 Towards multicomponent systems: tuning the properties of the bis-phenanthroline chelating unit

The preparation of $[Cu(NN)_2]^+$ complexes is typically simple and is carried out under mild conditions.[6] A key feature of the bis-phenanthroline complexes thus obtained is that the ligands are arranged in a specific (pseudo tetrahedral) geometry. Such an oriented gathering, dictated by the outstanding affinity of Cu(I) for phenanthroline ligands, is known as a *template effect*. The reactions to obtain $[Cu(NN)_2]^+$ are the starting point for a brand new chemistry towards fascinating molecular architectures like catenanes and knots, as originally developed by Sauvage, Dietrich-Buchecker *et al.* over nearly two decades.[6]

One of the simplest series of molecules that can be obtained by templated synthesis is that reported in Fig. 11. These complexes are made of two macrocycles interlocked around a cation M^{n+} (M = H^+, Li^+, Cu^+, Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Pd^{2+}, Cd^{2+}). They are called [2]-catenates,[6] and the complexing core is a $[M(dap)_2]^{n+}$ unit (dap = 2,9-dianisyl-1,10-phenanthroline).



[2]-M

Fig. 11 [2]-M catenates (M = H^+, Li^+, Cu^+, Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Pd^{2+}, Cd^{2+}) where two 30-membered rings are interlocked around the M ion. The line connecting the oxygen atoms represents $–(CH_2)_2–$ groups. The structure of the Pd catenate is slightly different, see ref. 30.

The availability of a coordination environment able to bind protons, alkaline ions, as well as first and second-row transition metals is certainly quite unusual; furthermore, the electrochemical potentials can be varied within a large window.[6]

The photophysical investigations performed by us on this family of **[2]-M** catenates showed that not only the electrochemical but also the photophysical properties can be finely tuned.[30] The absorption spectra in the UV-VIS, depending on the type of metal ion, present a variety of bands including ligand-centred (LC), metal-centred (MC), ligand-to-metal charge-transfer (LMCT), and metal-to-ligand charge-transfer (MLCT).

The wide tuning of the electronic properties of **[2]-M**, as observed from the electrochemistry and UV-VIS absorption, also causes modulation of the luminescence spectra in CH_2Cl_2 solution or 77 K rigid matrix. Upon changing the metal ion the luminescence bands are spread across the whole visible spectral region,[30] Fig. 12.

The luminescence of the Li^+, Cd^{2+}, Zn^{2+}, H^+ catenates is of LC character. For **[2]-Ag** only a spin-forbidden (phosphorescence) LC band at 77 K is observed. The 77 K band of **[2]-Pd** is difficult to attribute, but a substantial MLCT character can be deduced from the lifetime value. Finally, **[2]-Cu** shows the typical MLCT band (τ = 175 ns). No luminescence is observed for **[2]-Ni** and **[2]-Co** owing to the presence of low-lying non-emissive MC excited states which offer a fast radiationless decay path to the upper-lying LC levels.[30]

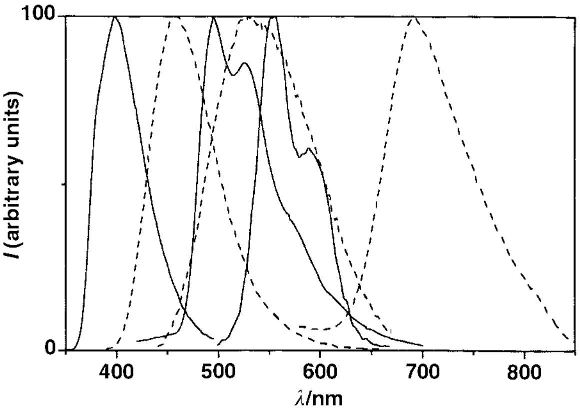


Fig. 12 Luminescence spectra of some **[2]-M** catenates in CH_2Cl_2. From left- to right-hand-side, maxima correspond to M = Li^+, Zn^{2+}, Ag^+, H^+, Pd^{2+}, Cu^+ (alternate full and dashed line). The spectra of the Ag^+ and Pd^{2+} catenates are recorded at 77 K, all the others at 298 K.

The sum of the absorption, emission, and electrochemical properties now presented makes the **[2]-M** molecular unit quite unique. As we will see in the next sections, in suitably assembled *multicomponent* systems containing **[2]-M** moieties, a variety of *intercomponent* processes and structural rearrangements can be induced by light input.

5 Multicomponent arrays containing Cu(I)–phenanthrolines

5.1 Coupling two tetrahedral moieties: [3]-catenates and knots

The assembling of polynuclear systems containing two [2]-M-type units was first accomplished by Sauvage *et al.* with the synthesis of [3]-catenates (three interlocked rings), Fig. 13.[31]

This family of complexes (**[3]-CuM**) includes, among others, one mononuclear (**[3]-Cu**) and five dinuclear (**[3]-CuCu, [3]-CuH**, **[3]-CuAg, [3]-CuZn,** and **[3]-CuCo**) compounds. We examined the spectroscopic properties of these complexes, and the results are summarized below.[31,32]

5.1.1 Absorption spectra. The spectra of **[3]-CuM** match the sum of the spectra of the corresponding **[2]-M** units.[31] In the UV the typical LC absorption bands are detected, whereas in the VIS MLCT features are recorded, due to the ubiquitous $[Cu(NN)_2]^+$-type subunit. Interestingly, for the mono- and dinuclear **[3]-Cu** and **[3]-CuCu** complexes, the MLCT spectral shapes are very similar to those of **[2]-Cu** and identical to each other, suggesting that in the dinuclear system the ground state geometry is unaffected.

5.1.2 Luminescence and excited state intercomponent processes. Upon excitation in the MLCT absorption bands, **[3]-Cu**, **[3]-CuCu**, **[3]-CuAg**, **[3]-CuZn** and **[3]-CuH** exhibit the typical MLCT $[Cu(NN)_2]^+$ luminescence around 700 nm. However, differences in the luminescence properties are observed. For instance, the emission quantum yield (0.0011) and excited state lifetime (210 ns) of **[3]-Cu** are larger relative to **[3]-CuCu** (Φ = 0.00059; τ = 168 ns), suggesting that the excited state distortion (Fig. 6) is somewhat different in the two

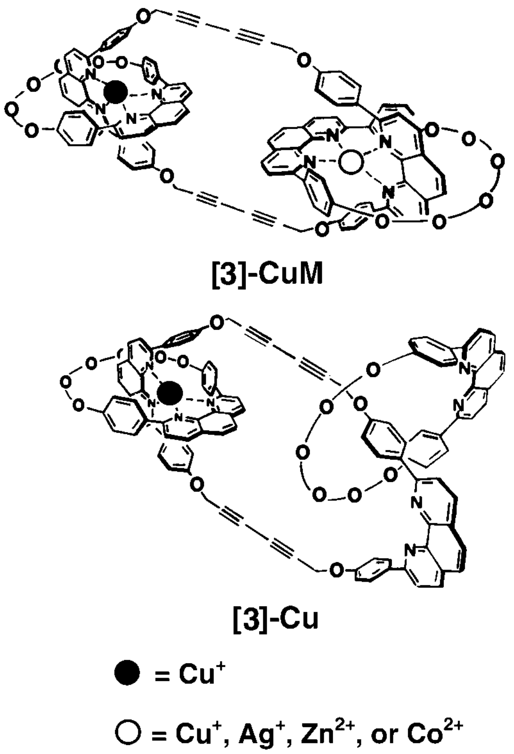


Fig. 13 Dinuclear **[3]-CuM** (M = Cu^{+}, Ag^{+}, Zn^{2+}, Co^{2+},) and mononuclear **[3]-Cu** catenates.

cases. Quite peculiarly, **[3]-CuCo** does not exhibit MLCT luminescence. In fact, the potentially luminescent MLCT level of the Cu-complexed moiety is quenched by the Co-based one; both energy- or electron transfer quenching mechanisms are thermodynamically allowed.[31]

When excitation is addressed to the ligand-centred UV bands of **[3]-Cu, [3]-CuAg**, **[3]-CuZn** and **[3]-CuH**, dramatic quenching of the typical luminescence of the **[2]-M** moieties (Fig. 12) is observed. In all cases a detailed discussion of the quenching mechanism (energy- or electron-transfer) has been reported.[31] In Fig. 14 a schematic picture of the intercomponent processes taking place in this family of [3]-catenates is drawn.

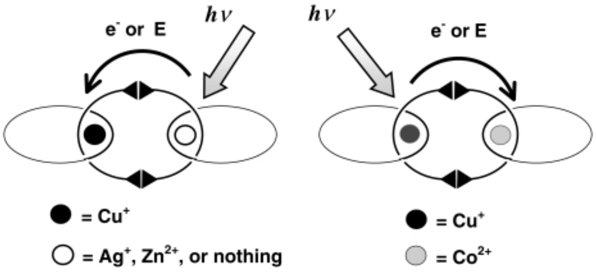


Fig. 14 Direction of photoinduced processes in **[3]-CuM** catenates; e^{-} indicates electron transfer, E denotes energy transfer.

Very importantly, the direction of the photoinduced intercomponent processes in the **[3]-CuM** catenates can be tuned at wish, *i.e. to* or *from* the [Cu(NN)$_2$]$^{+}$ core, depending on the M ion.

Finally, we have also performed photophysical investigations on two families of complexes made of two [2]-M-type units, *i.e.* the homo-[33] and heterodinuclear[34] knots prepared by Dietrich-Buchecker and Sauvage. In these systems a molecular thread containing four phenanthroline units is closed around two metal ions in a trefoil knot arrangement.[6] For these complexes, substantial variations of the MLCT absorption patterns have been observed upon negligible changes of the chemical structure.[33] Remarkably, a still unique case of Cu(I)–phenanthroline MLCT emission in the IR spectral region ($\lambda_{\max}$ = 950 nm, τ = 11 ns) was reported for a dinuclear Cu(I)–Zn(II) knot in which the Zn(II) ion exerts a strong electrostatic effect on the MLCT transitions of the nearby moiety.[34]

5.2 Coupling a tetrahedral and an octahedral moiety: dinuclear [2]-catenates

Sauvage *et al.* have recently reported the synthesis of [2]-catenates substantially different from that of Fig. 12.[35] One of the two interlocking rings is in fact closed *via* coordinative bonds (Fig. 15).

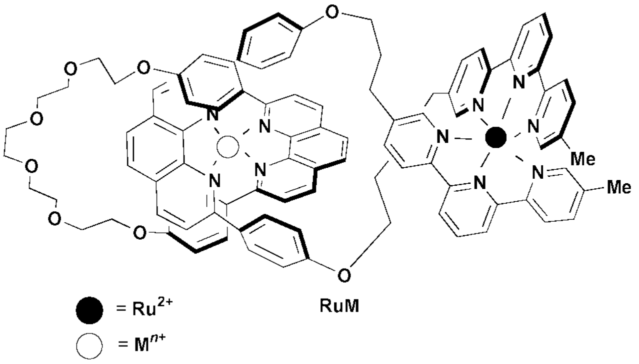


Fig. 15 [2]-catenates **RuM**, (M = Ag^{+}, Cu^{+}, Zn^{2+}, or nothing).

Thus a unique family of dinuclear coordination compounds (**RuM**, M = Cu^{+}, Ag^{+}, Zn^{2+}, or nothing) was obtained, exhibiting two subunits with different coordination geometry, *i.e.* an octahedral ([Ru(tpy)$_2$]$^{2+}$-type) and a tetrahedral ([M(dap)$_2$]$^{+}$-type) moiety; tpy = 2,2′:6′,2″-terpyridine. [Ru(tpy)$_2$]$^{2+}$-type complexes are known to exhibit scarce or no MLCT luminescence at 298 K, but very strong and long-lived MLCT emission at 77 K.[2] The **RuM** complexes were designed in order to obtain multicomponent arrays where the photoinduced interactions between the two different coordination centres could be investigated.

The absorption spectra of the **RuM** catenates match the sum of the spectra of the corresponding model compounds, showing that ground-state intercomponent interactions are weak.[32] In the VIS, the typical MLCT absorption bands of Ru(II)–polypyridines are always observed, superimposed on those of the ([Cu(NN)$_2$]$^{+}$ moiety in **RuCu**. The comparison of the luminescence properties of **RuM** with those of suitable model compounds shows that some sort of luminescence quenching always occurs, as a result of excited state intercomponent interactions. In detail, excitation of **Ru**, **RuAg**, and **RuZn**, in the VIS spectral region at 77 K gives rise to the typical (unquenched) MLCT luminescence of Ru(II)–polypyridine complexes ($\lambda_{\max}$ = 602 nm). By contrast, UV light excitation populates the LC levels of the tetrahedral **[2]-M** moiety, but the corresponding luminescence (Fig. 12) is strongly quenched. This suggests that intercomponent quenching processes take place, due to the presence of a [Ru(tpy)$_2$]$^{2+}$-type unit nearby. In the case of **RuCu** the situation is reversed. The MLCT emission of the **[2]-Cu** subunit is preserved at any excitation wavelength, whereas the Ru(II)-type MLCT luminescence is quenched. The inversion of the direction of the photoinduced processes is related to the position of the luminescent MLCT excited state of the Ru-type moiety. For **Ru**, **RuAg**, and **RuZn** this is the lowest electronic level of the bipartite system. Instead, in **RuCu**, the lowest level is the ^{3}MLCT of the **[2]-Cu** moiety.

A detailed discussion of the luminescence quenching mechanism (energy- or electron-transfer) for all **RuM** complexes appears in ref. 35 In Fig. 16 a schematic picture shows the direction of the observed intercomponent processes; these can occur *either* to the octahedral *or* to the tetrahedral centre, depending on the M ion.

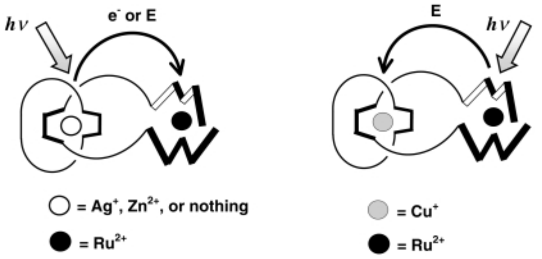


Fig. 16 Direction of photoinduced processes in **RuM** [2]-catenates; e⁻ indicates electron transfer, E denotes energy transfer.

5.3 Coupling $[Cu(NN)_2]^+$ with fullerenes: rotaxanes and dendrimers

C_{60} fullerene is an extremely interesting molecule from the photochemical point of view: it displays fluorescence, is a potent singlet oxygen sensitizer, exhibits quite diagnostic transient absorption singlet and triplet spectra, and is a very good electron-acceptor.[36] This makes it an attractive partner for $[Cu(NN)_2]^+$ in the design of photoactive multicomponent systems.

A few years ago a rotaxane containing a $[Cu(NN)_2]^+$-type core and C_{60} terminal units was prepared and investigated.[36] Remarkably, the typical excited state properties of each moiety are strongly quenched, *e.g.* MLCT emission of the $[Cu(NN)_2]^+$ core, C_{60} fluorescence, and the C_{60} triplet absorption. Also, the singlet oxygen sensitization, typical of both (separated) subunits, is dramatically reduced. It was shown that all the excited states localized on the molecular components are deactivated by means of a sequence of energy- and electron-transfer steps to a low energy charge-separated state which is made available in the multicomponet rotaxane thanks to the complementary electronic character of the $[Cu(NN)_2]^+$ core (electron donor) and of the C_{60} terminals (electron acceptors).[33] In particular, excitation of the MLCT levels of the core is followed by electron transfer to the peripheral fullerene units, as schematically depicted in Fig. 17.

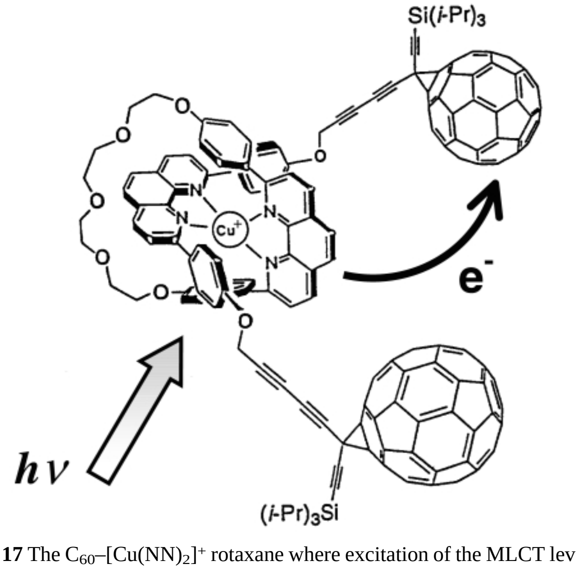


Fig. 17 The C_{60}–$[Cu(NN)_2]^+$ rotaxane where excitation of the MLCT levels of the core is followed by electron transfer to the peripheral fullerene units.

More recently, Nierengarten *et al*. have prepared three fascinating dendrimers in which a $[Cu(NN)_2]^+$-type core is surrounded by 4, 8, or 16 C_{60} terminal units.[37] In Fig. 18 the smaller representative of the series is reported.

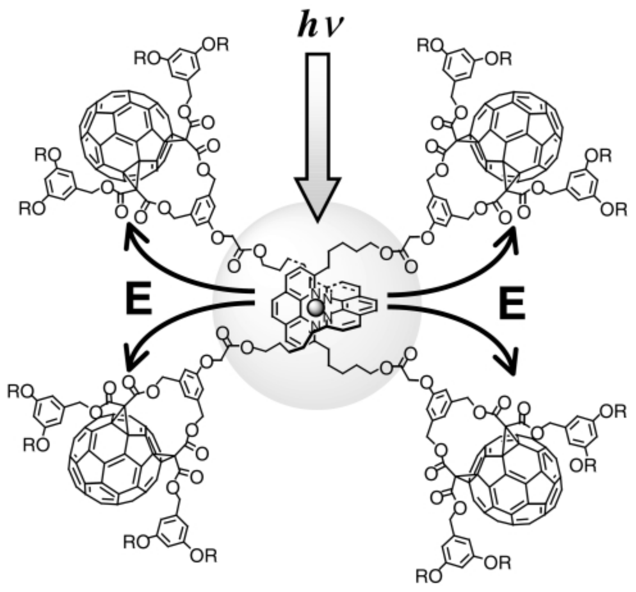


Fig. 18 Energy transfer in a C_{60}–$[Cu(NN)_2]^+$ dendrimer. R indicates $–C_8H_{17}$ groups.

We have demonstrated that upon excitation of the $[Cu(NN)_2]^+$ MLCT absorption bands, no MLCT luminescence is detected, thanks to an energy transfer quenching process to the peripheral C_{60} subunits (Fig. 18).[37] It has also been demonstrated that, for the two larger dendrimers, the $[Cu(NN)_2]^+$ core is buried in a sort of C_{60}-made 'black box' hardly accessible or completely inaccessible to external molecules, electrons, and even photons. The much higher absorption coefficient displayed by the (many) C_{60} units relative to the (single) $[Cu(NN)_2]^+$ core, practically prevents excitation of the core, relative to the footballene fragments.[37]

Finally, for completeness, it must be recalled that many authors have also reported on porphyrin-stoppered rotaxanes with $[M(NN)_2]^{n+}$-type cores, in which energy- and electron-transfer processes are in evidence.[38]

6 Photochemically induced molecular motions in $[Cu(NN)_2]^+$

One of the most recent developments in the photochemistry of $[Cu(NN)_2]^+$ systems deals with molecular motions in multicomponent arrays where a chelating ligand is kept free of coordination, but made available 'on demand'. Thus, Sauvage *et al*. have demonstrated that in suitably designed catenates and rotaxanes, reversible molecular motions can be *electrochemically* induced by taking advantage of the different coordination environment of Cu(I) and Cu(II).[39] We have further shown that, in the same molecules, movements can be partially generated by using photons,[40,41] as illustrated in Fig. 19.

In the [2]-catenate (Fig. 19a), one ring contains a phenanthroline-type fragment (phen), whereas the other contains both a phenanthroline and a terpyridine-type unit (tpy).[40] Cu(I) ion prefers a tetrahedral coordination geometry, therefore the two phenanthrolines act as chelating units for the Cu(I) ion. Excitation with VIS light (MLCT bands) of the $[Cu(phen)_2]^+$-type complex, in the presence of an oxidant (*p*-nitrobenzylbromide), leads to oxidative quenching (Fig. 9a) in CH_3CN solution; conversion of Cu(I) into Cu(II) is carried out by about 20 minutes of irradiation and at this stage the Cu(II) is tetracoordinated and still bound to the phen ligands. However,

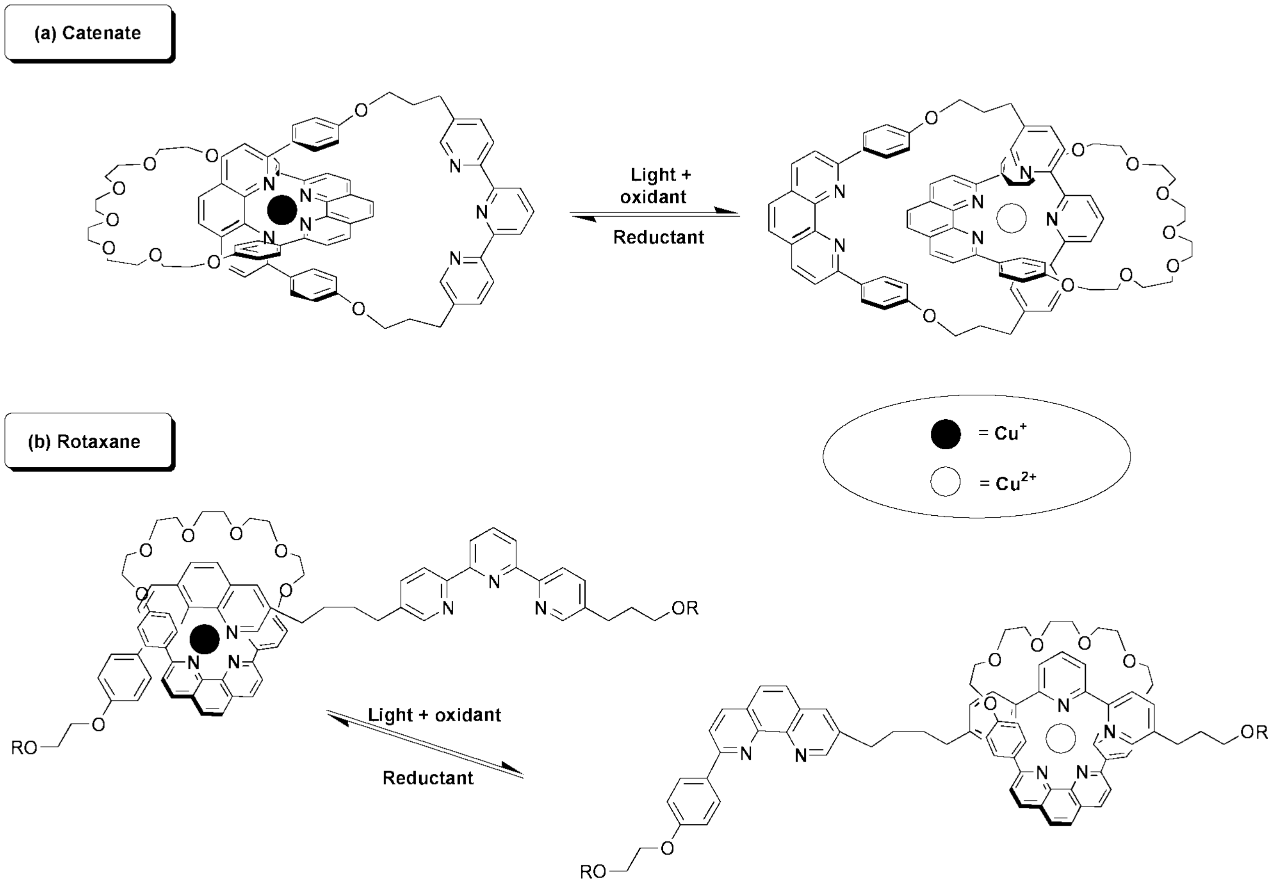


Fig. 19 Photochemically induced molecular motions in a catenate and in a rotaxane containing a $[Cu(NN)_2]^+$ centre and a free tpy ligand.

since Cu(II) prefers a pentacoordinated geometry, the nearby tpy ligand can successfully compete with phen for Cu(II) complexation and a spontaneous ring gliding motion leads to the formation of $[Cu(phen)(tpy)]^{2+}$ (Fig. 19a); the molecular rearrangement is very slow and requires several hours. Unfortunately, a backward reaction *via* photoinduced reductive quenching of the Cu(II) complex is not possible.[40] Nevertheless, by means of a 'dark' reduction with ascorbic acid, the starting Cu(I) compound is recovered with 100% yield. Interestingly, the whole reaction cycle can be followed by naked eye since the various compounds exhibit different colours in solution, namely red ($[Cu(phen)_2]^+$), green ($[Cu(phen)_2]^{2+}$), and yellow ($[Cu(phen)(tpy)]^{2+}$).[40]

A similar process has been carried out for a rotaxane (Fig. 19b).[41] The principle is the same as for the catenate, however a complete reaction cycle can be only accomplished by adding high amounts of inert electrolyte. This suggests that the metal ion is less protected from the interaction with external species in the rotaxane than in the catenate. In the former, the assistance of external ions during the molecular motions to fill temporary empty coordination positions is more important, as expected from structural considerations. These findings are also in agreement with the different (forward and backward) reaction rates observed for the two compounds.[41]

7 Conclusions and perspectives

By means of a suitable choice of the chemical nature, position, and size of the phenanthroline substituent groups, a rigid control of the photophysical properties of Cu(I)–phenanthrolines (UV-VIS absorption shapes and intensities, luminescence spectra, emission quantum yields, excited state lifetimes) has been achieved. For instance it is possible to vary (i) the molar absorption coefficients of the MLCT band maxima from 3000 to over 14 000 M^{-1} cm^{-1}; (ii) the excited state lifetimes from 10 to over 900 ns; (iii) the MLCT luminescence band maxima from 650 to 950 nm. These features are accompanied by a series of other no less important characteristics: (a) an intrinsic synthetic flexibility that allows the preparation of unparalleled sophisticated multicomponent architectures (catenates, rotaxanes, knots, dendrimers, cage compounds); (b) a unique variability of the electrochemical and photophysical properties upon exchange with (a large number) of metal ions; (c) a potent reductive character of the MLCT excited state; (d) a different coordination geometry of the oxidized Cu(II) form that allows, for instance, the design of photochemically driven molecular machines. Furthermore, several studies demonstrate that Cu(I)–phenanthrolines are promising building blocks for the construction of multicomponent arrays in which photoinduced energy- and electron-transfer processes occur.

Indeed, it can be somewhat daring to make a comparison with a different, octahedral class of complexes such as Ru(II)–polypyridines. However, one can assert that all the above listed properties of $[Cu(NN)_2]^+$, though well investigated and tested, have not yet been fully exploited. It is thus conceivable that, in the future, the photochemist's interest in the two classes of complexes, now mainly in favour of Ru(II)–polypyridines, will be somewhat differently balanced. Definitely, if any extensive applications of coordination compounds are ever found (*e.g.* in photovoltaic technology),[4] it will be hard to overlook the fact that many crucial features (abundance, price, environmental care) make copper complexes far more attractive than those of ruthenium.

8 Acknowledgements

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