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Review

Improving the photophysical properties of copper(I) bis(phenanthroline) complexes

Aurélie Lavie-Cambot[a], Martine Cantuel[a], Yoann Leydet[a], Gediminas Jonusauskas[b],
Dario M. Bassani[a], Nathan D. McClenaghan[a,*]

[a] Groupe Nanostructures Organiques, Institut des Sciences Moléculaires, University of Bordeaux 1/CNRS, UMR 5255, 33405 Talence cedex, France
[b] Centre de Physique Moléculaire Optique et Hertzienne, University of Bordeaux/CNRS, UMR 5798, 33405 Talence cedex, France

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ABSTRACT

Homoleptic copper(I) bis(2,9-dialkyl-1,10-phenanthroline) units, as well as a range of related heteroleptic species, represent popular choices for building blocks in the construction of supramolecular edifices and photo- and electroactive devices. The photophysical properties of these traditionally underperforming luminescent complexes can be dramatically modified in a qualitatively predictable fashion through ligand design, the use of bichromophoric ligands, and by reconstitution of the primary coordination sphere. An overview of key excited-state processes established in these complexes is presented, with particular emphasis on recent developments and insights, as well as ramifications for developing successful strategies to prolong luminescence lifetimes and increase quantum yields.

1. Introduction

For several years copper(I) bis(2,9-dialkyl-1,10-phenanthroline) complexes have been known to present certain desirable properties which are similar to the popular ruthenium(II) tris(2,2′-bipyridine) and analogous phenanthroline-based complexes [1–7]. The similarity of these properties is notably in terms of MLCT absorption bands located in the visible spectral region and emission in the red. Despite the greater abundance, lower toxicity and lower cost of copper with respect to ruthenium, these analogous complexes have been much less studied than their ruthenium-based cousins. This is perhaps due to certain drawbacks/parameters which can be improved upon or circumvented with subtle structural modifications of the ligands in the primary coordination sphere. Judicious ligand choice and design can now give a diversity of copper-based structures being mononuclear or clusters which can outperform more traditionally popular analogues based on other transition metals [7]. One aspect of this review will focus on guiding principles for instilling designer properties in novel photoactive molecules/supramolecular architectures in a predictable fashion. This is achieved principally through ligand modification, increasing (or decreasing) the bulkiness of substituents (see Section 2), which can also direct the formation of heteroleptic species, or by adding supplementary chromophores (see Section 4). Copper(I) bis(phenanthroline) moieties can be considered cornerstones in the development of supramolecular self-assembling systems, and the

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* Corresponding author. Tel.: +33 540 00 3321; fax: +33 540 00 6158.
E-mail address: n.mc-clenaghan@ism.u-bordeaux1.fr (N.D. McClenaghan).

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diversity of bi-/polynuclear architectures reported to date include helicates, rotaxanes, catenanes, grids and dendrimers [8–13].

The scope of the current article will primarily be dedicated to mononuclear species comprising at least one phenanthroline chelating unit, as such promising species based on recent P–N chelators or bisquinolines will not be discussed in detail [14–18]. The ground-state pseudo-tetrahedral four-coordinate environment around the copper(I) metal centre offers a complementary alternative geometry to octahedral or square planar geometries obtained with, for example, ruthenium(II) and palladium(II) (or platinum) ions, in the construction of molecular edifices [19–21]. Ground and excited-state structural aspects are considered in Section 2, with a particular emphasis on designing highly luminescent copper complexes, including heteroleptic and homoleptic species.

An overview of the photophysical behaviour of copper phenanthroline complexes is given in Section 3, with an emphasis on excited-state dynamics and developments in this area in the last 5 years which, judging from the literature, is stimulating more and more interest. Indeed the understanding of these systems is under constant reevaluation as more sophisticated techniques are applied. As a consequence, many elaborations on the established picture describing the photophysical processes elucidated largely through the pioneering work of McMillin have been reported. For a more detailed description of this traditional picture, interested readers are referred to some excellent reviews [1–3,5]. Certain more recent insights have been gained into the rich photophysical behaviour of copper-based systems due to improved instrumentation and developing techniques, such as time-resolved X-ray-based spectroscopies, and certain time-resolved fluorescence techniques. Until recently, a major obstacle for direct observation of excited-state structures has been the lack of pulsed X-ray sources that provide enough photons. New generation synchrotron sources offer 100 ps pulses with 10^4 times more photons than previous sources [22].

In Section 4 a new approach to change luminescence properties in copper-based bichromophoric systems, not directly related to the nature and size of the primary coordination sphere is presented. This relies on the intervention of triplet–triplet electronic energy transfer in designer systems where energy is temporarily stored on an auxiliary chromophore which plays the role of energy reservoir, while subsequent emission is from the metal-containing centre. A summary of prerequisite kinetic and thermodynamic properties is given which can be satisfied with a relatively high degree of planning. This represents another strategy to change excited-state properties, particularly in increasing the luminescence lifetime.

Clearly, an in-depth comprehension of photophysical processes governing the properties of copper(I) bis(phenanthroline) complexes is desirable. However, even consideration of a few key points and implementation of some straightforward strategies allows the development of luminescent species with a relatively high degree of planning.

2. Ground state and excited-state structural aspects

Copper is a redox-active metal, whose complexes comprise notably Cu(I) and Cu(II). Owing to the facile oxidation of Cu(I), complexes such as those described herein are predisposed exhibit MLCT states with ligands such as 1,10-phenanthroline and their derivatives. The MLCT absorption bands in the visible have been attributed to at least three types of electronic transition (I, II, III with the intermediate transition $e(xy,yz) \rightarrow e(\psi)$ being dominant in a D_{2d} environment) [23]. The specific spectral shape is dictated by the substitution of the ligands which, in turn, affects the dihedral angle between the two phenanthroline ligand planes and the extent of π-delocalization of the accepting orbital. As a result the MLCT electronic transitions are affected giving complexes of various colours (orange, deep red, magenta) [24]. Considering the copper(I) oxidation state, as represented in Fig. 1a, ground-state complexes with bidentate phenanthrolines tend to exhibit a 4-coordinate pseudo-tetrahedral ligating environment around the metal with two 1,10-phenanthroline ligands. This structure is anticipated to be subject to geometrical changes such as wagging, as well as flattening and rocking distortions, represented in Fig. 1a [25].

The overall distortion from the ideal tetrahedral geometry (ζ) is considered to receive contributions in the x, y and z-planes (θ) such that:

$$\zeta = \frac{(90+\theta_x)(90+\theta_y)(90+\theta_z)}{180^3} \quad (1)$$

Recent X-ray crystallographic studies on $[\mathrm{Cu(dmp)_2}]^+$, dmp = **2** = 2,9-dimethyl-1,10-phenanthroline, with various counter anions have been reported (tetrafluoroborate, hexafluorophosphate, nitrate, perchlorate and tetraphenylborate), showing a distorted tetrahedral primary coordination sphere varying with different counter anions [26,27]. Interligand dihedral angles vary with values of 88.1°, 79.4°, 84.7°, 82.4°, and 77.6°, respectively, while bite angles are less than 90° due to ligand rigidity (e.g. 82.75° and 82.54° for the tetraphenylborate dichloromethane solvate). Average Cu–N bond lengths are consistently around 2.032 Å. Studies on a photoexcited heteroleptic copper complex (λ_{ex} = 355 nm) have also been recently reported, where a bidentate

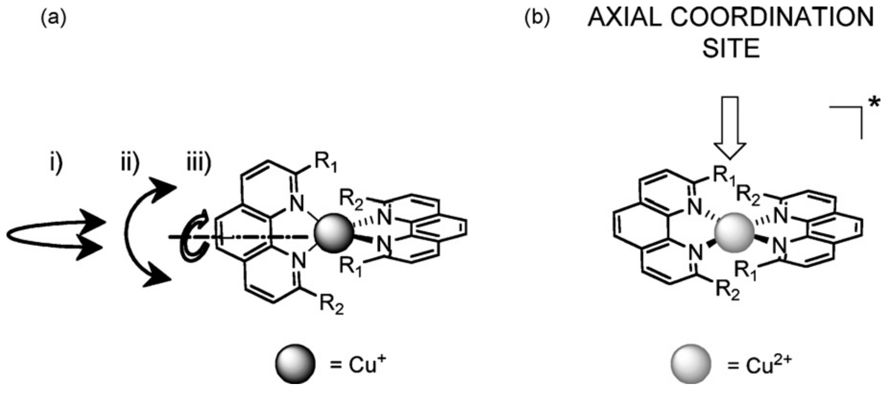


Fig. 1. (a) Pseudo-tetrahedral ground state geometry of homoleptic copper(I) bis(1,10-phenanthroline) complexes. (One of the two possible enantiomers, when $R_1 \neq R_2$, is shown.) Deviations from the ideal tetrahedral geometry are due to: (i) wagging; (ii) rocking and (iii) flattening. (b) Excited-state geometry where an additional coordination site is made available due to flattening via ligand reorganisation around the formally copper(II) ion.

1,2-bis(diphenylphosphino)ethane occupies the primary coordination sphere in addition to the dmp ligand [28]. Subtle structural distortions in the excited state with respect to theoretical predictions are ascribed to confinement effects in the solid-state which in turn are anticipated to have significant effect on reorganisation energies and hence back electron transfer on application of Marcus theory.

The ground-state tetrahedral environment of copper(I) bis(phenanthrolines) has been previously exploited as a templating ion, for example in highly efficient catenane synthesis [29], while the preferential 5-coordinate environment for Cu(II) ions with respect to the 4-coordinate Cu(I) was used as the impetus to operate molecular machines via ring-gliding following a redox process [30,31]. Exception to the tetrahedral structure for copper phenanthrolines may be anticipated when additional chelating groups are introduced in the 2,9-positions; however, in the current examples the 1,10-phenanthroline ligands are devoid of supplementary chelating groups. Passing from ground-state copper(I) bis(phenanthroline) to its structurally relaxed excited state (represented in Fig. 1b) involves changing the oxidation state of the copper to a formally copper(II) species concomitant with metal-to-ligand charge-transfer. Previous Raman experiments conducted by McGarvey and coworkers on the MLCT excited-state of $[Cu(dmp)_2]^+$ imply that the transferred electron, available through metal oxidation giving Cu(II), is localized on a single phenanthroline ligand [32], in analogy with the case of $[Ru(bpy)_3]^{2+}$. Concerning the degree of charge transfer, the structurally equilibrated excited system was probed using an X-ray beam to give information on the oxidation state of the metal ion. This experiment performed by Chen and coworkers on the complex $[Cu(dmp)_2]^+$ in toluene solution (with non-coordinating counteranion—terakis(3,5-bis(trifluoromethylphenyl)borate) gave compelling evidence for essentially discrete electron transfer from the copper ion to the ligand, lending weight to the idea of a formally Cu(II) ion in the excited state [33]. Indeed, copper K-edge X-ray absorption near edge spectra (XANES) of the ground-state compared to the excited metal complex showed a 3-eV transition edge shift for Cu(II) relative to Cu(I), corresponding well to model species including those generated by electrolysis [34]; a shoulder representing a $1s \rightarrow 4p_z$ transition pronounced in Cu(I) but not Cu (II), typically observed for a transition from four to five (or six) coordinate geometry was present, in addition to a pre-edge feature attributed to a $1s \rightarrow 3d$ transition, present only for Cu(II) which has one vacancy in the 3d orbitals.

Due to a different structural preference of copper(II) compared to copper(I) the change in oxidation state forces a significant geometry change between the ground and excited states, with an additional axial coordination site being available for nucleophilic attack by solvent, counteranion or other Lewis bases present in solution. Excited five-coordinate geometries are anticipated to be akin to distorted square pyramidal or trigonal bipyramidal geometry, with a susceptibility to a Jahn–Teller distortion as shown by single crystal X-ray crystallography studies on Cu(II) bipyridine and phenanthroline complexes with an associated counteranion or solvent molecule [35]. Increased coordination number is expected to promote quenching of copper excited states. In a series of papers, McMillin demonstrated that Lewis base addition onto the copper (in non-competitive dichloromethane) forms a 5-coordinate exciplex (excited-state complex) [36–40]. Exciplex quenching can be ascribed to stabilization of the excited-state, which decreases the energy gap between ground and excited-states and promotes non-radiative decay (which increases exponentially with decreasing energy). Direct information on excited state structure via X-ray absorption fine structure (XAFS) experiments showed that the average Cu–N bond distance in the excited state was increased to 2.13 Å from the ground state value of 2.06 Å. Excited state coordination number could not be unambiguously ascribed through XAFS experiments, but XANES features (smooth transition edge, being often associated with ligation) and increase of the Cu–N peak height support the increase in copper coordination number, even with a low coordinating toluene solvent and a bulky, non-nucleophilic counteranion.

The exact pathway describing passage from the initially formed Franck–Condon excited state to the structurally relaxed excited-state geometry has been recently subject to debate (particularly with regard to ligand reorganisation and intersystem crossing) and will be further detailed in Section 3; in this section we look principally at the consequences of excited-state structural distortions with respect to the ground-state geometry and accompanying solvent attack and their influence on the emission properties.

2.1. Enhancing luminescence through steric effects

Firstly we will consider three similar copper(I) bis(phenanthroline) complexes, $[Cu(\mathbf{1})_2]^+$, $[Cu(\mathbf{2})_2]^+$ and $[Cu(\mathbf{2})(\mathbf{3})]^+$ (ligands shown in Fig. 2) where the difference between ligands resides in the identity of the substituents in the 2- and 9-positions (R_1 and R_2 in Fig. 1), which are a proton (**1**), methyl (**2**) and *tert*-butyl (**3**) groups, respectively. The observed luminescence properties are strikingly different. For $[Cu(\mathbf{1})_2]^+$, essentially no luminescence is observed in fluid solution at room temperature. Finally the quest for luminescence from this molecule was fructuous, but only in specific conditions in the solid [27]. For the $[Cu(\mathbf{2})_2]^+$, where protons are replaced by methyl groups, relatively short-lived luminescence ($\tau_{em} = 70$ ns; $\Phi_{em} = 4 \times 10^{-4}$) is recorded in degassed dichloromethane [41]. In more strongly coordinating solvents such as acetonitrile further quenching is observed. It is interesting to note that even toluene was found to participate in filling the fifth coordination site of the excited $[Cu(\mathbf{2})_2]^+$ to some degree by Chen (*vide supra*). The complex $[Cu(\mathbf{2})(\mathbf{3})]^+$ is by far the most luminescent among the three complexes, with a luminescence quantum yield around 25 times higher than that of $[Cu(\mathbf{2})_2]^+$ as well as a prolonged luminescence lifetime ($\tau_{em} = 730$ ns; $\Phi = 1 \times 10^{-2}$), thus having properties comparable to those of $[Ru(bpy)_3]^{2+}$ [42]. Some Hammet substituent effects may have some role to play here [43], but the steric effects invoked are more marked. The ground state structure, obtained through X-ray crystallographic analysis, is best described as trigonal pyramidal with molecular C_s symmetry, where the dmp ligand is canted from D_{2d} symmetry along a mirror plane. (It should be noted that the authors found, on reacting copper(I) with **3** followed by **2**, only traces of the homoleptic complex $[Cu(\mathbf{2})_2]^+$ in the reaction mixture. This is experimental evidence for the pertinence of the steric bulk on these copper(I) bis(phenanthroline) complexes. Indeed, attempts to isolate homoleptic complexes with *tert*-butyl or mesityl substituents have typically proved unsuccessful by traditional methods, although the trifluoromethyl-substituted analogue has been reported [44–46]. Most recently Burstyn and colleagues reported a straightforward oxidation-based synthesis of the elusive $[Cu(\mathbf{3})_2]^+$ from Cu(0) with Ag^+ as the oxidant [47]. Single crystal X-ray studies show a distorted trigonal coordination geometry with very long Cu–N bonds of 2.11 Å, due to steric interactions. However, applicability of this new synthetic strategy towards multichromophoric (electron rich) systems may prove problematic.

On passing from a proton to bulkier aliphatic substituents, it may be anticipated that ligand reorientation would be impeded, which would inhibit movement from a pseudo-tetrahedral geometry to one with a vacant site for solvent coordination and viable deexcitation pathway, thus increasing emission. Fig. 2 shows a range of recently reported ligands, many of which were typically developed in the pursuit of conformationally locked and highly luminescent complexes.

The extent of flattening that occurs in a CT excited state is a critical element in describing the nature of the copper(I) bis(phenanthroline) complex, which can be summarized as follows. The driving force for distortion derives from the increase in the overlap of the σ-donating orbitals of the nitrogens with the formally half-occupied d(*xy*) orbital of the metal. The double-minimum potential energy surface (in Fig. 3) illustrates how the energy of the CT excited-state depends on the dihedral angle between phenanthroline ligands. In the ground state the complex has a pseudo-tetrahedral structure and so will the initially populated Franck–Condon excited state. However, subsequent geometric relaxation within the excited-state manifold can profoundly alter the emission energy and the lifetime. The steric demands of the substituents in the 2,9-positions ultimately limit the extent of flattening. In accord with this model, the emission energy increases with the size of the substituents in the 2,9-positions while the log of the decay rate varies linearly with the energy [48].

When alkyl groups are present in the 2,9-positions such as in the homoleptic complexes of **4**, **7** and **8**, subtle variations in the room temperature behaviour compared to the parent $[Cu(dmp)_2]^+$ are observed in terms of quantum yield and luminescence lifetime (10×10^{-4} and 8×10^{-4} and lifetimes of 132 and 107 ns for **4** and **7**, respectively) [49]. Lowering the temperature decreases the emission intensity and induces a red-shift, for as long as excited state distortion can occur (fluid medium). Below 120 K, when a solid glass is obtained (CH_2Cl_2/MeOH), this trend is lost. McMillin previously investigated differences between members of a homologous series of homoleptic copper(I) complexes with 2,9-disubstituted 1,10-phenanthrolines (dsbp = $-CH(CH_3)CH_2CH_3$; dnpp = $-CH_2C(CH_3)_3$; dop = $CH_2(CH_2)_6CH_3$; dbp = $-CH_2(CH_2)_2CH_3$; dmp = $-CH_3$). The absorption wavelength maxima in the same solvent vary according to the series: dnpp < dsbp < dop = dbp = dmp [50]. The emission maximum wavelengths vary according to: dsbp < dnpp < dop = dbp < dmp. Globally, they found from absorption, emission and electrochemical data that spatial distribution of

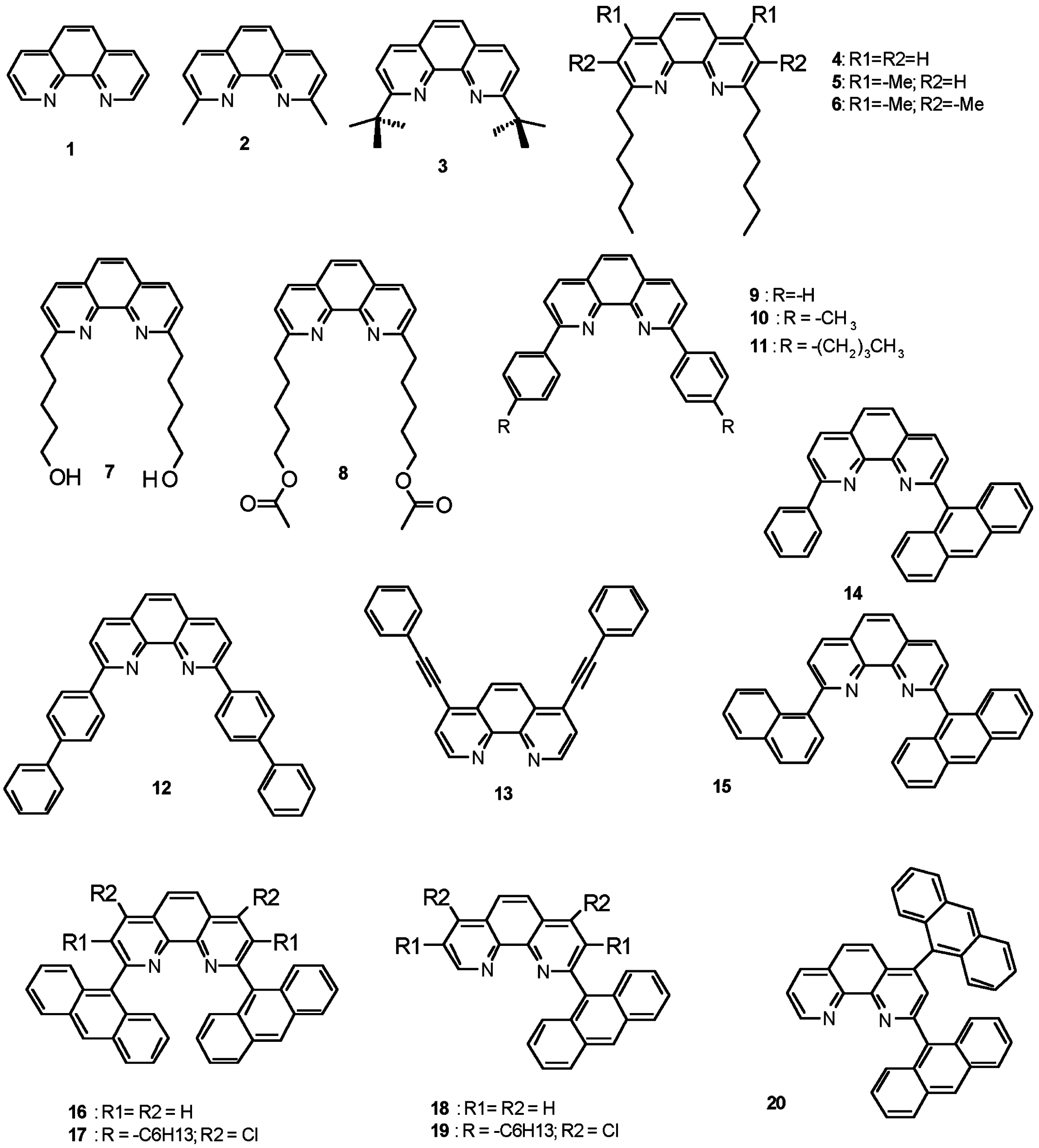


Fig. 2. Mono- and bi-chromophoric ligands of varying bulkiness influencing conformational-locking in their copper(I) complexes.

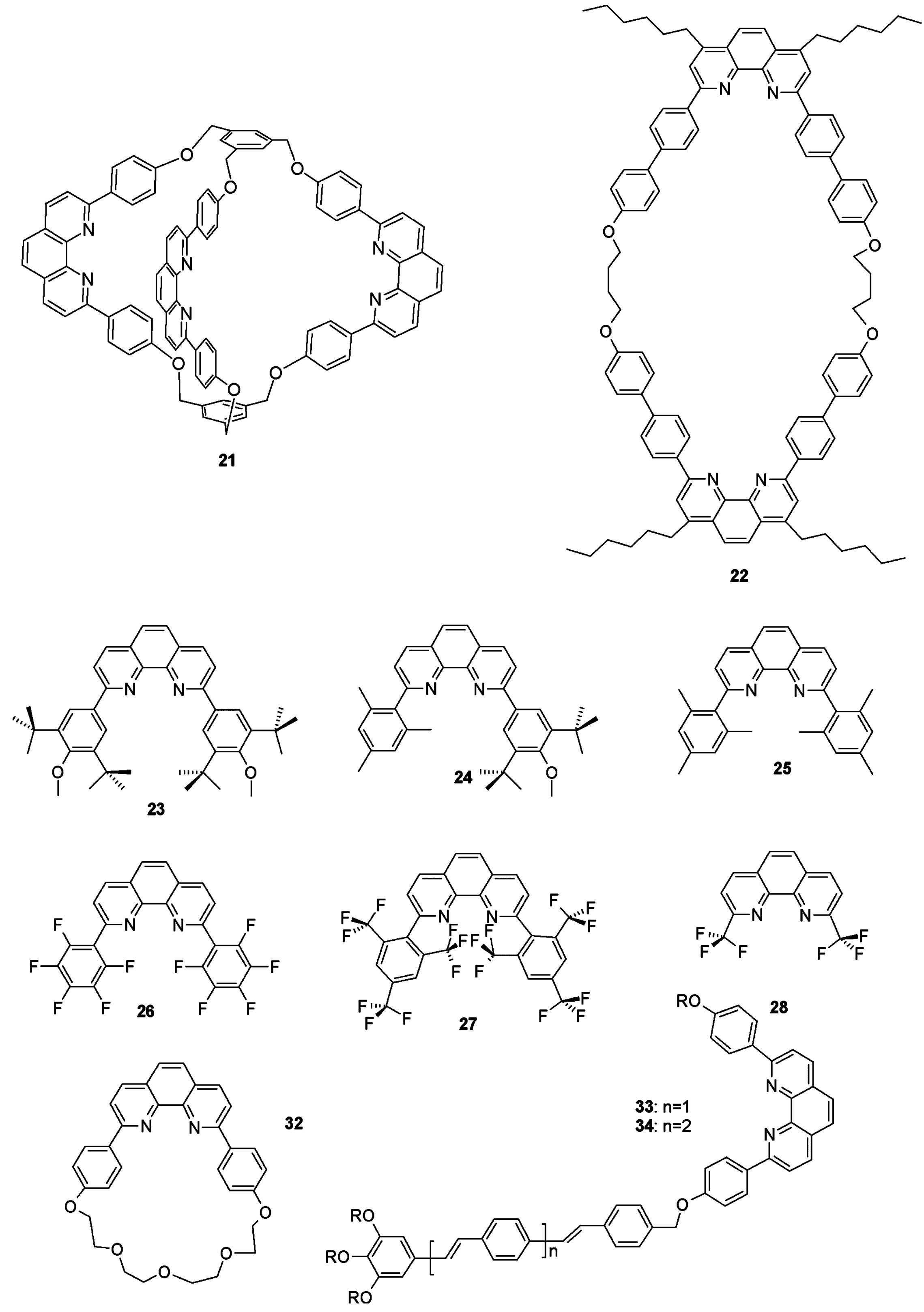
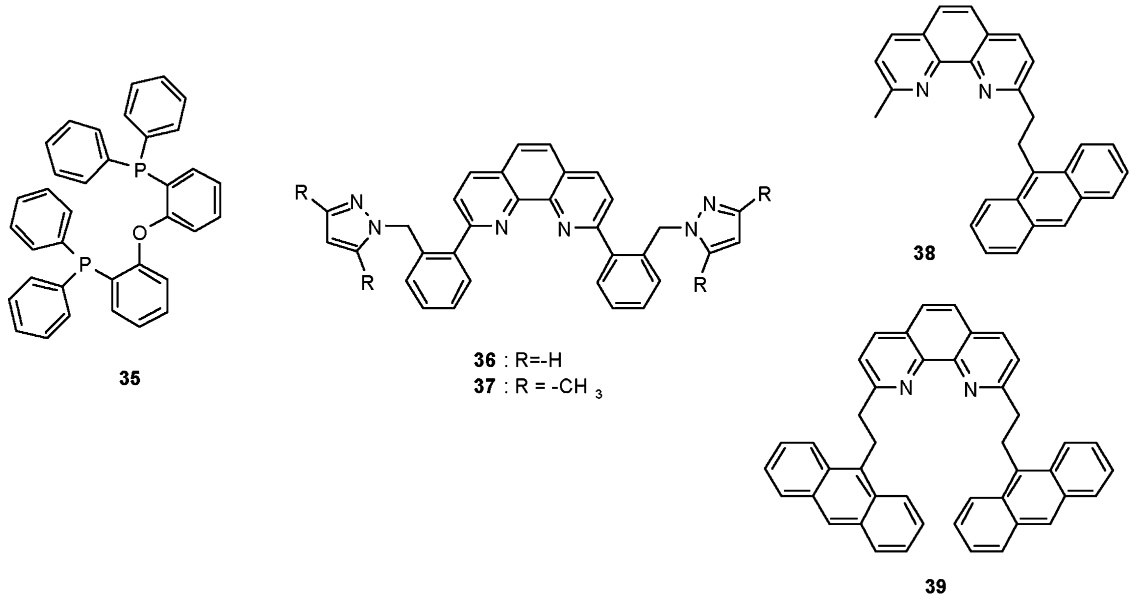


Fig. 2. (*Continued*)

the atoms is more important than the total molecular volume in determining the influence of a substituent, and that three contributions to the steric demands on the ligand field could be discerned. These may be ascribed to: (a) blocking of excited-state flattening via interactions between substituents on different phenanthrolines; (b) steric interactions with a highly branched substituent leading to destabilization of the ground state; (c) bulky groups impeding an increasing coordination number. Additional substitutions in the



35

36 : R=-H
37 : R = -CH_3

38

39

Fig. 2. (*Continued*).

3,4,7- and/or 8-positions (e.g. **5** and **6**) can also lead to remarkable differences for example when a methyl group is introduced in all four of these supplementary positions [Cu(**6**)$_2$]$^+$, the luminescence lifetime is prolonged from 150 to 920 ns, compared to the parent [Cu(**4**)$_2$]$^+$, while the quantum yield is 7-fold higher. This effect is largely attributed to the steric contribution linked with increased coordination number, blocking solvent-induced exciplex quenching [51].

Replacing the 2,9-dialkyl substituents with phenyl groups (e.g. **9**, **10**, **11**), results in a significant variation in absorption and luminescence properties. Copper(I) complexes based on these ligands exhibit π-stacking interactions between the phenyl groups of one ligand and the phenanthroline sub-unit of the other, bringing about a distorted, flattened tetrahedral geometry. X-ray studies helped elucidate this interaction, which also appears to be significant in solution [52]. This interaction (which is conversely insignificant for analogous Cu(II) species) would go someway towards explaining the different behaviour compared with 2-9-alkyl species, for example with regard to observed luminescence in a coordinating solvent such as methanol. This motif is particularly popular in the construction of mechanically interlocked structures (such as catenates), presumably for synthetic reasons, where phenol-like groups can be easily substituted compared with, for example, the allylic methyl groups of dmp [53]. As with the dialkyl species luminescence decreases and is red-shifted as temperature is decreased (in CH_2Cl_2/MeOH). However, below 120 K, in contrast to 2,9-dialkyl-1,10-phenanthroline complexes, emission intensity continues to drop [49].

Electronic effects govern the complexation of **12** in the presence of **13**. Due to π–π interactions (as well as the increased σ-basicity of **12**) the order of most thermodynamically stable complexes is: [Cu(**12**)$_2$]$^+$ > [Cu(**12**)(**13**)]$^+$ > [Cu(**13**)$_2$]$^+$ [45]. In a strategy developed by Schmittel, the incorporation of steric effects (kinetically impeding formation of the homoleptic species) as well as electronic effects (*vide supra*) assured the formation of heteroleptic complexes in a rational fashion. A whole series of bulky ligands were synthesised by the group including **14**–**20**, and the absence of the (orange) homoleptic complexes was noted in favour of (yellow) complexes comprising one ligand [54]. Combination with a derivative of **13** smoothly gave the corresponding heteroleptic compound. This strategy can be seen as means to generate (in a commutative fashion) potentially interesting photoactive heteroleptic compounds with MLCT absorption, reported maxima in the range 457–496 nm according to the degree of distortion from D_{2d} symmetry. (For details of photophysical properties of copper(I) bis(phenanthroline) species covalently linked to anthracene see Section 4.) A different but related approach to generate heteroleptic compounds relies on endotopic binding with the use of large macrocyclic ligands such as **21** or **22** [55,56].

Further sterically encumbered ligands were developed by Schmittel and co-workers with aryl groups in the 2,9-positions, **23**–**25** [24]. Significantly different behaviour was observed compared to complexes based on ligand **9**, where rapid complex formation and subsequent exchange with a different competitive ligand such as 1,10-phenanthroline was found. [Cu(**23**)$_2$]$^+$ was slow to form (5 days) and the kinetically inert species thus formed proved, uniquely, not to be subject to ligand exchange, even when stirred with 10 equivalents of **1** for 15 days. Equally, due to the steric bulk provided by the *tert*-butyl groups, the weak luminescence ($\Phi_{em} = 10^{-4}$ at room temperature, unemissive at 77 K) is only slightly affected by the presence of oxygen or coordinating solvents. On the other hand, [Cu(**24**)$_2$]$^+$ is 15 times more emissive at ambient temperature and over 1000 times more emissive at 77 K. The authors consider this unusually emissive complex as evidence that

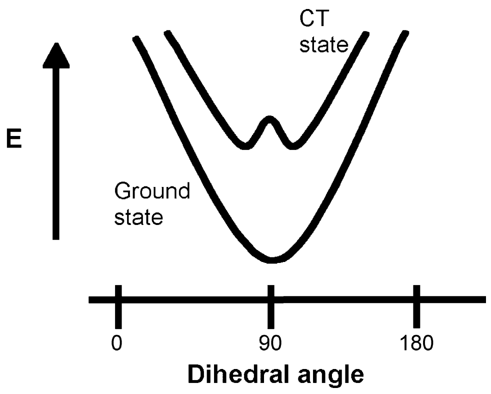
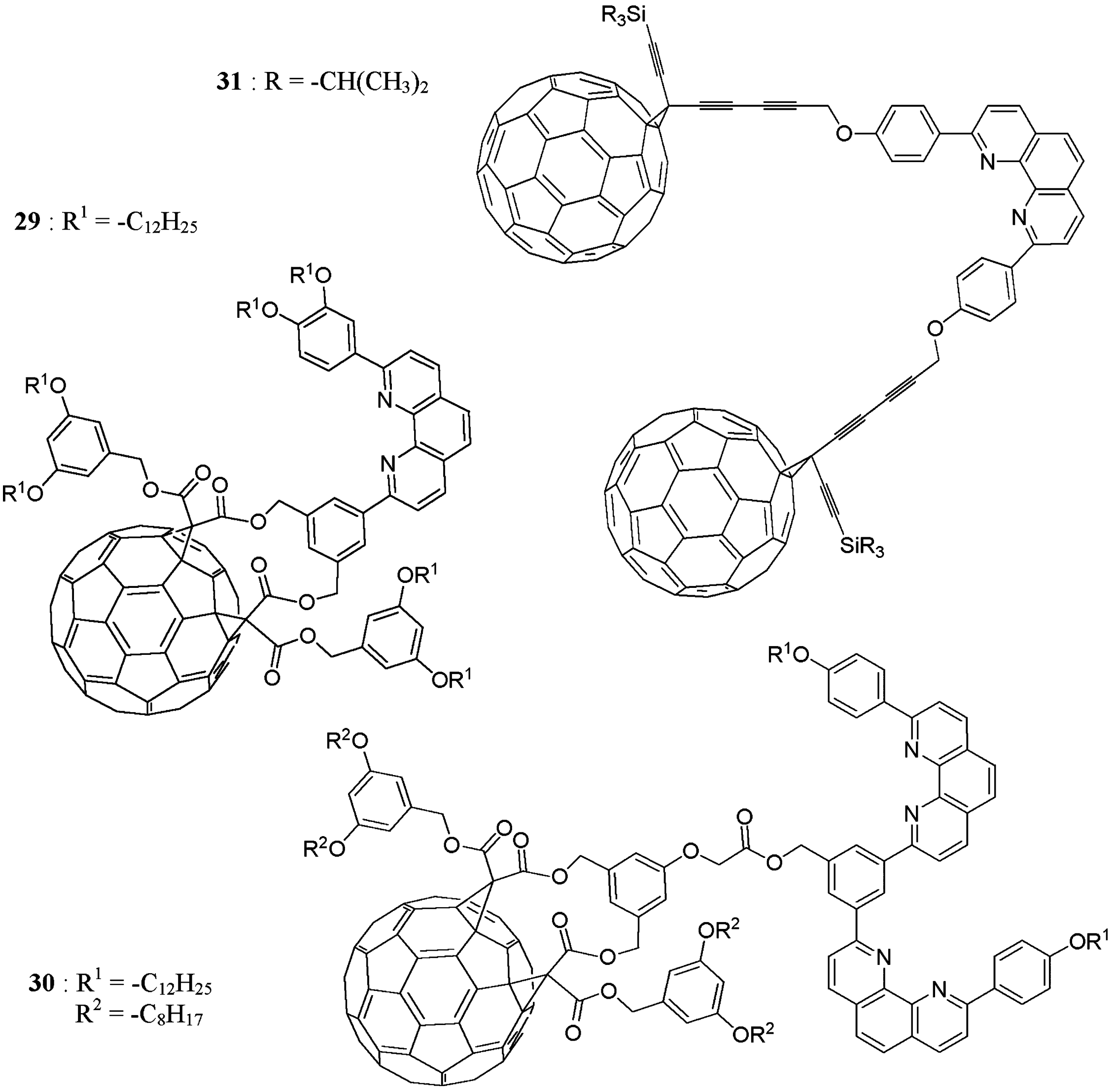


Fig. 3. Representation of the potential energy surface for a copper(I) bis(1,10-phenanthroline) complex with changing interligand dihedral angle.



31 : R = -CH(CH$_3$)$_2$

29 : R^1 = -C$_{12}$H$_{25}$

30 : R^1 = -C$_{12}$H$_{25}$
R^2 = -C$_8$H$_{17}$

Fig. 4. 1,10-Phenanthroline ligands bearing electron-acceptor fullerene units.

structural rather than electronic factors dictate the luminescence behaviour of these compounds in rigid matrices.

Copper complexes comprising ligands **26** and **27**, based on fluorinated versions of parent ligand **9**, have also been reported and are particularly resistant to oxidation [57]. The more encumbered 2,4,6-(CF$_3$)$_3$C$_6$H$_2$-substituted ligand **27** supports the formation of a reactive copper(I) cation which catalyses nitrene transfer to the C–H bonds of an electron-rich arene, while **26** forms preferentially mononuclear complexes comprising two ligands. The fluorous version (**28**) of dmp (**2**), with two perfluorinated methyl groups shows somewhat different behaviour than its non-fluorous counterpart. Recent work by Kovalevsky and Coppens showed that the distortion parameter described by Eq. (1) is smaller for [Cu(**28**)$_2$]$^+$ than for [Cu(**2**)$_2$]$^+$, particularly with respect to flattening due to the bulkier 2,9-substituents. Varying the bulkiness of counter anion of [Cu(**28**)$_2$]$^+$ in solid samples gave phosphorescence lifetimes at 17 K correlating linearly with the combined distortion parameter (with the exception of BF$_4$$^-$) [58].

A fruitful collaboration between the groups of Nierengarten and Armaroli produced a series of copper phenanthroline complexes comprising fullerene units, such as **29** and **30**, programmed to assemble into a range of electron donor–acceptor architectures (see Fig. 4). Indeed, Cu^{I} oxidation is facile while C$_{60}$ acts as a potent electron acceptor, with a first reduction potential approaching that of methylviologen [59]. This fact coupled with the vanishingly low reorganisation energy associated with the 3D ball-like architecture ensures effective photoinduced electron transfer reactions [60].

As well as a photoinduced electron transfer reaction, complex [Cu(**29**)$_2$]$^+$ also shows ground state interaction between the fulleroid subunits due to their proximity (*ca.* 4.3 Å) as evidenced by changes in the electronic absorption spectrum around 430 nm [61]. Engineering donor–acceptor interactions in a hydrogen bonded fullerene-based architecture has been shown in other recent reports [62]. The copper phenanthroline–fullerene system was further elaborated to give ligands capable of forming fullerohelicates of type [{Cu(**30**)}$_2$]$^{2+}$, which equally participate in photoinduced electron transfer reactions, but lack the ground-state interactions present in simpler analogues [63]. In an older report, fullererodendrimers bearing peripheral fullerenes in first, second and third generation structures were described [64]. Here it appears that all MLCT emission from the core unit, located in what the authors describe as a dendritic black box, is quenched and that the lowest lying ^{3}C$_{60}$ state is efficiently populated. Another example of a supramolecular photoactive architecture comprising a copper phenanthroline motif and fullerenes were developed through a collaboration between the Armaroli, Diederich and Sauvage groups.

The rotaxane $[\mathrm{Cu}(\mathbf{31})(\mathbf{32})]^+$ with a central copper-containing unit and terminal fullerene stoppers shows rich photophysical processes including intercomponent singlet energy transfer, intersystem crossing and photoinduced electron transfer. Fast back electron transfer would explain the lack of spectroscopic evidence for the charge separated state [65]. Combining two electron rich, common donor units was achieved on incorporating oligophenylene vinylene units to a copper(I) bis(phenanthroline) motif in $[\mathrm{Cu}(\mathbf{33})_2]^+$ which shows efficient energy transfer when a short trimeric motif ($n = 1$) is employed. When a longer motif is used (**34**), the emission from the inorganic unit was extinguished due to an electron transfer process, showing the tuning of properties that can be achieved on coupling with different members of a homologous series such as oligophenylene vinylenes [66].

Concerning heteroleptic compounds, in addition to those described above which rely on combinations of kinetic and thermodynamic effects based on different phenanthrolines, particularly encouraging results have been obtained on combining phosphino chelators with phenanthrolines. In this regard a recent popular choice of a bulky ligand is the DPEphos, bis[2-(diphenylphosphino)phenyl]ether, **35**, originally implemented in catalytic systems based on Pd(0) and Pd(II) [67]. McMillin incorporated it into heteroleptic complexes, including $[\mathrm{Cu}(\mathbf{2})(\mathbf{35})]^+$, thereby obtaining extraordinary luminescent properties [68,69]. In degassed dichloromethane $[\mathrm{Cu}(\mathbf{2})(\mathbf{35})]^+$ has a high quantum yield (0.15) and a long excited-state lifetime of 14.3 μs. In analogy with $[\mathrm{Cu}(\mathbf{9})_2]^+$ even in coordinating solvents (acetone, methanol and acetonitrile) a relatively long lifetime (>1 μs) is measured.

Previously-reported mixed ligand systems comprising two monodentate triphenylphosphine units gave long lived luminescence in the solid state and frozen solution [70,71]. However, studies of $[\mathrm{Cu}(\mathbf{2})(\mathrm{PPh}_3)_2]^+$ showed significant exciplex quenching in methanol despite the presence of bulky phosphines and changing speciation in dichloromethane [72]. Moving to a bidentate system (the central oxygen atom does not appear to participate in the coordination) gave much better performance (1000-fold enhancement in luminescence; 50-fold enhancement in lifetime). As well as changes in lifetime and quantum yield, absorption and emission are significantly blue-shifted ($\lambda_{\mathrm{max.abs.}} = 383$ nm; $\lambda_{\mathrm{max.em.}} = 570$ nm). In the mixed ligand complex, the MLCT is shifted to higher energy (and is therefore less prone to non-radiative deexcitation) due to differences in bite angles as well as donor types. In homoleptic copper(I) phenanthroline complexes with bulky groups on the 2,9-positions, σ-antibonding interactions between the substituents and the lone pair orbitals of the phenanthroline destabilize the high energy d-orbitals of the $D_{2\mathrm{d}}$ ground-state and inevitably reduce the energy of the CT excited state [5].

Following on from the discovery that the DPEphos ligand could greatly improve the luminescence properties of copper(I) complexes, several analogous systems have been reported. Feng, Ma and co-workers studied a series of heteroleptic complexes where phenanthroline or 2,2′-bipyridine ligands were present in addition to the DPEphos. Through time-dependent density functional theory (TDDFT) calculations, they showed that while certain changes in orbitals and energies may be anticipated, relative ordering and character is not changed in mixed-ligand systems. A greater influence in observed properties derives from substitution on the 2,9-positions compared with the 4,7-positions (e.g. Hs replaced by phenyls) [73].

Copper(I) complexes based on the DPEphos ligand have also attracted interest for electroluminescent applications including light-emitting electrochemical cells (LEC), of interest for large area lighting applications. LEC devices which emit green light on applying a voltage were constructed through spin-coating a conducting polymer and metal complex on ITO-coated glass substrates, annealing and deposition of a silver electrode [74–76]. Resulting LEC device efficiencies are moderate, but comparable to those produced with Ru(II)-analogues. Heteroleptic copper(I)–DPEphos complexes, where bisquinoline ligands replace phenanthrolines were shown to produce red-emission (orange-red to red) in light emitting diode devices [75]. With a multilayer device architecture, the highest current efficiency of 6.4 cd A^{-1} and external quantum efficiency

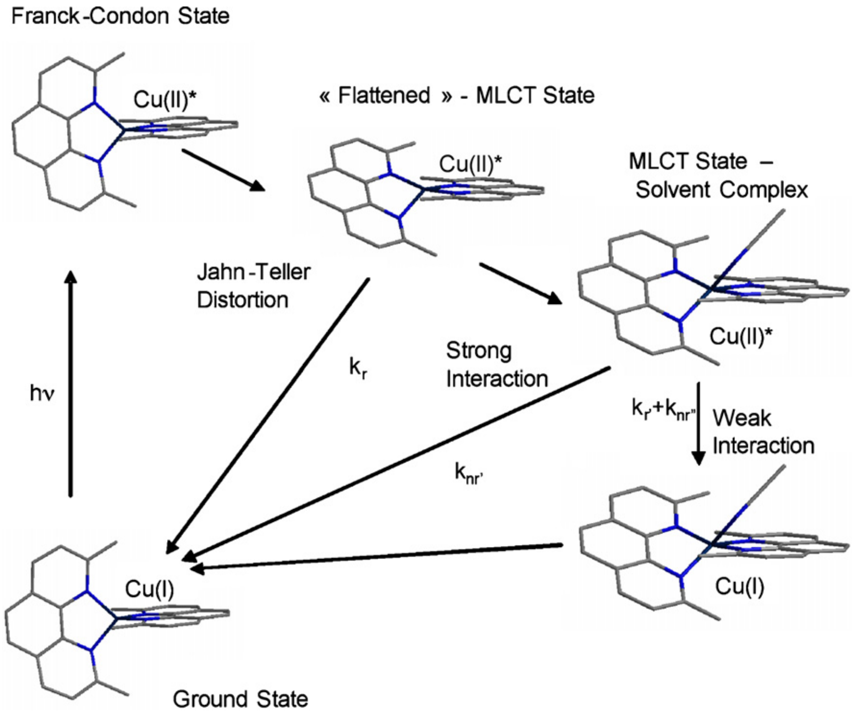


Fig. 5. Representation of dynamic excited-state processes in $[\mathrm{Cu(dmp)}_2]^+$-like complexes including interaction with a coordinating (acetonitrile) solvent molecule. Protons are omitted for clarity.

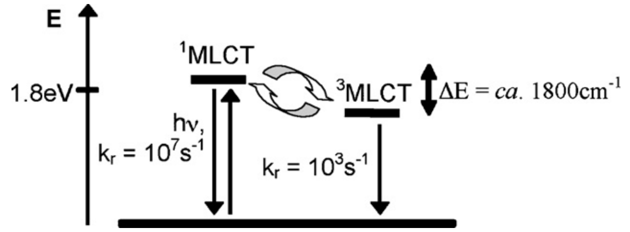


Fig. 6. Jablonski diagram showing the two-state model describing the excited-state behaviour of typical copper(I) bis(phenanthroline) complexes.

of 4.5% was obtained. For comparison, these systems are less performant than Ir(III)-based OLEDs [77,78], but better than devices based on Pt(II) [79,80] or Os(II) [81,82]. Several groups have also reported green and white OLEDs based on these Cu(I) complexes [73,74,83–86]. Development of charge-neutral copper complexes is a major challenge in this area for certain device architectures.

3. Dynamic excited-state processes

The behaviour of copper(I) bis(phenanthroline) complexes is rather distinctive, both in terms of excited-state structural variations as well as the role and interplay of specific excited-states. Recent spectroscopic measurements have allowed further insights into these aspects and deepened understanding of the pertinent processes. The sequence of structural variations upon irradiating a copper(I) bis(1,10-phenanthroline) in its ground state are summarized in Fig. 5, with the pseudo-tetrahedral Franck–Condon excited state being subject to ligand flattening following photooxidation of the metal centre. Solvent attack and exciplex formation can subsequently serve to non-radiatively quench the excited-state to varying degrees as a function of the coordinating nature of the solvent and bulkiness of substituents in the 2,9-positions. Increased interaction is consistent with an increased non-radiative rate constant (k_{nr}) for deexcitation. The sequence of events shown is implied through the coordination requirements of copper(I) and copper(II) elucidated through X-ray crystallographic data as well as experimental evidence with different solvent and quenchers (see Section 2).

Concerning the photophysical processes, for around 20 years it was generally accepted that the photophysical properties and observed luminescence of molecules such as $[\mathrm{Cu(dmp)_2}]^+$ can best be described through a two-state model taking into account singlet and triplet MLCT states. The relative energy levels of these lowest-lying states (^{1}MLCT and ^{3}MLCT) are represented in Fig. 6. In a series of variable temperature measurements, McMillin provided compelling evidence for a subsequently widely adopted model based on two thermally equilibrated MLCT excited states, with the ^{3}MLCT state being somewhat lower in energy ($\Delta E \approx 1800\,\mathrm{cm}^{-1}$ [48] later evaluated at $1500–2000\,\mathrm{cm}^{-1}$ [23]). In this case, the radiative rate constants for the ^{1}MLCT and ^{3}MLCT states are very different, $10^7\ \mathrm{s}^{-1}$ *cf.* $10^3\ \mathrm{s}^{-1}$, respectively. Thus while the majority of excited states would be anticipated to be formally triplet in nature, it may be expected that for kinetic reasons the prompt emission may result from fluorescence from the small proportion of higher-lying ^{1}MLCT state, constantly replenished by thermal activation [23,48,49]. Due to the predominant population of excited triplet states, it may be expected that many intercomponent processes such as energy and electron transfer may be adequately described by considering principally the ^{3}MLCT state.

Different ultrafast spectroscopies as well as DFT calculations have been employed in an attempt to reconcile the sequence of processes and role of excited-states in Figs. 5 and 6. Pioneering ultrafast transient absorption measurements in dichloromethane with $[\mathrm{Cu}(\mathbf{9})_2]^+$ and the hexyl derivative of $[\mathrm{Cu(dmp)_2}]^+$ showed changes in the red part of the absorption spectrum (around 615 nm, red-shifted to 625 nm for $[\mathrm{Cu}(\mathbf{9})_2]^+$) in the sub-picosecond regime which rapidly evolved in 15 ps to give a species stable in the time window of the experiment (1 ns) [87]. The rapid processes are insensitive to the solvent environment and substituent, similar results being obtained in acetonitrile (a further time constant of 1.6–1.7 ns was ascribed to exciplex emission [37]) with methyl, *n*-hexyl and phenyl substituents [33,88]. In analogy with the $[\mathrm{Ru(bpy)_3}]^{2+}$ complex, one might anticipate that this behaviour could be attributed to ultrafast intersystem crossing (singlet to triplet MLCT states), followed by a slower ligand reorganisation process and resulting expansion of the coordination number following the formal oxidation of the copper centre [89]. Indeed, spin-orbit coupling values of 990 and $829\,\mathrm{cm}^{-1}$ are associated with the 4d-electrons of ruthenium and 3d-electrons of copper, respectively [90,91]. Density functional studies on $[\mathrm{Cu}(\mathbf{2})_2]^+$ indicate that structural changes of this type occur on the way from the ^{1}MLCT Frank-Condon state to the lowest ^{3}MLCT level, suggesting that structural distortion occurs prior to the formation of the long-lived emitting state [92]. It was proposed that the optical absorption of the MLCT state could also be a function of the dihedral angle between the two dmp planes, or could vary with ligation. However, judging from the invariance of the transient absorption signature in different solvents, differences in ligation alone cannot explain transient absorption spectral changes [88]. Previous calculations showed that the energy gap between the HOMO and LUMO in the ground state of a model compound for $[\mathrm{Cu^I(dmp)_2}]^+$ decreased with a dihedral angle between the two ligand planes due to simultaneous increase of the HOMO and decrease of the LUMO energies [93]. This argumentation was applied to spectra to determine ligand reorganisation via an observed blue shift.

Nozaki and co-workers gave further insight into the pertinent photophysical processes associated with $[\mathrm{Cu}(\mathbf{2})_2]^+$ (as well as the 2,2′-bipyridine analogue and a phenanthroline ligand bearing butyl chains instead of methyls) via DFT calculations as well as picosecond time-correlated photon counting measurements in dichloromethane ($\lambda_{\mathrm{ex}} = 400\,\mathrm{nm}$) [94]. These latter measurements allowed detection of a surprisingly long fluorescence emission (13–16 ps) of similar magnitude to that of the short-lived component previously observed in transient absorption measurements, suggesting this time constant is associated with an extremely sluggish intersystem crossing (ISC) process. This slow intersystem crossing was rationalized on the basis of the large flattening reorganisation in the excited state resulting in a large splitting between HOMO and HOMO-1 levels (associated largely with copper $3d_{yz}$ and $3d_{xz}$ electrons, respectively), negating its role in the ISC process. As a consequence the authors believe the ISC to be promoted by weakly interacting ligand-centred molecular orbitals (*ca.* $30\,\mathrm{cm}^{-1}$), accounting for the slowness of the process. This analysis could lead to another way of modulating excited-state properties by regulating ISC rates to give, for example, inexpensive sensitizers for Graetzel-type cells. In their kinetic analysis, the authors went on to suggest that from an initially formed Franck–Condon state ($2^1\mathrm{B}_1$), population of the ^{3}MLCT and ^{1}MLCT states are in competition, with 10% going to the low-lying ^{1}MLCT ($1^1\mathrm{B}_1$).

Another approach to constraining the primary coordination sphere relies on the incorporation of chelating groups in the 2- and 9-positions in addition to the N-chelators of the central phenanthroline unit, giving ligands **36** and **37** and complexes $[\mathrm{Cu}(\mathbf{36})]^+$ and $[\mathrm{Cu}(\mathbf{37})]^+$ [95,96]. The supplementary chelating groups used are reminiscent of the coordinating nature of histidine associated with Cu(II) in the blue copper site inside plastocyanin, which links Photosystems I and II, [97] and equally in the mixed $\mathrm{Cu_A}$ mixed-valence binuclear site in cytochrome *c* oxidase [98] in the presence of S-ligating groups. While the properties strongly resemble those

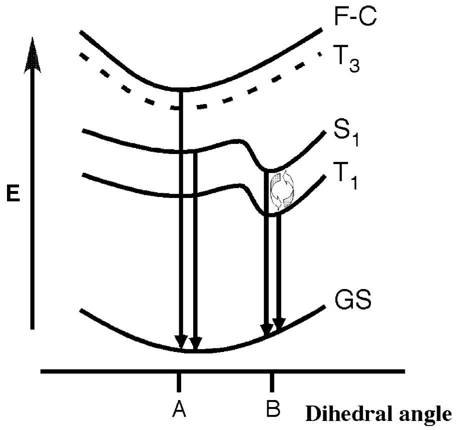


Fig. 7. Simplified potential energy surface diagram showing radiative deexcitation processes with different time constants (45 fs to 45 ns) associated with $[Cu(\mathbf{2})_2]^+$ [100,101]. 'A' corresponds to a pseudo-tetrahedral geometry while 'B' corresponds to a flattened structure.

of other copper(I) bis(phenanthroline) complexes, significantly different photophysical behaviour was observed between these two complexes. In the case of $[Cu(\mathbf{36})]^+$ a 5-ns lifetime is measured with a quantum yield of 4×10^{-5}. In contrast, for $[Cu(\mathbf{37})]^+$ a 110-ns luminescence lifetime and a quantum yield of 1.3×10^{-3} was measured. Different properties may be anticipated on incorporating other coordinating groups within the same molecular design framework.

Most recently, femtosecond fluorescence upconversion experiments have shed further light on the ultrafast processes observed, allowing spectroscopic determination of internal conversion processes, with $[Cu(\mathbf{2})_2]^+$ and $[Cu(\mathbf{9})_2]^+$ [99]. An ultrafast biexponential decay whose relative weights are excitation wavelength dependent was recorded with longer wavelength excitation similar to previous TCSPC results. The short time constant is ascribed to an ultrafast flattening reorganisation (80 fs) of the Franck–Condon tetrahedral geometry which would result in the slowing down of the ISC process. Spectral evolution in the 10–15 ps timescale appears to be independent of solvent polarity, viscosity and thermal diffusivity (acetonitrile, ethylene glycol and toluene) which the authors ascribe to ISC from ^{1}MLCT state towards the ^{3}MLCT manifold, rather than an inner sphere reorganisation process.

In parallel, Tahara independently reported similar ultrafast fluorescence results for $[Cu(\mathbf{2})_2]^+$ in dichloromethane [100]. These results which are largely similar to those of Castner Jr. and Chen are illustrated and summarized in Fig. 7, further elaborating on the initial model of McMillin. The authors found that the initial Franck–Condon state evolves (45 fs) to the S$_1$ state in its perpendicular geometry, and that the flattening distortion occurs with a time constant of 660 fs. Subsequent ISC (7.4 ps) is found to occur following structural flattening. The authors went on to identify an isoemissive point (675 nm) in the temporal spectral evolution, implying a shallow potential minimum at the perpendicular S$_1$-geometry, which is retained for up to 660 fs prior to further structural distortion. The authors ascribe the slow emission components to ^{1}MLCT and ^{3}MLCT states.

4. Prolonging MLCT luminescence through excited-state equilibration with an organic auxiliary

A recently developed strategy to prolong luminescence lifetimes of d^6-transition metal-polypyridine complexes relies on rapid reversible interchromophore energy transfer in supramolecular bi-/multichromophoric systems following light absorption [101–106]. The pertinent low-lying excited states of the prototype bichromophoric complex comprising an emissive $[Ru(bpy)_3]^{2+}$-type unit described by Ford and Rodgers are represented in Fig. 8a [107,108]. In this case an inert hydrocarbon spacer assures that the two tethered chromophores retain their specific properties, where the lowest lying excited-state (^{3}LC) localized on the pyrene lies at a very similar energy to that of the emissive ^{3}MLCT local-

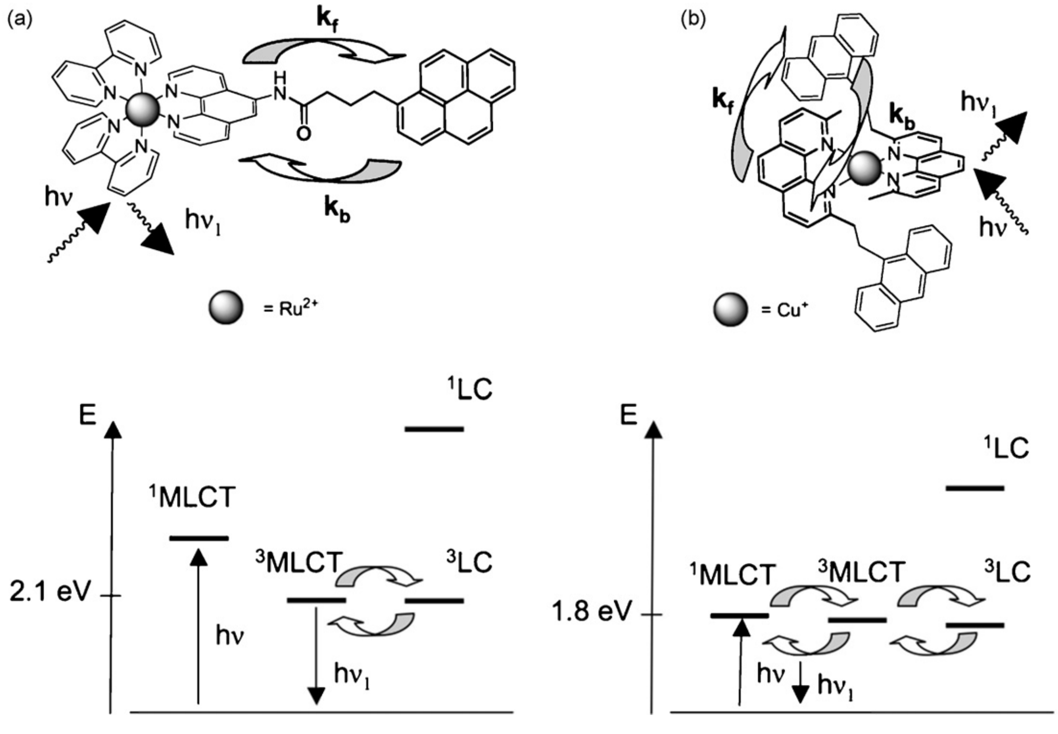


Fig. 8. Prototype luminescent bichromophoric ruthenium(II) polypyridine (a) and copper(I) bis(phenanthroline) (b) systems showing excited-state equilibration along with corresponding simplified Jablonski diagrams.

ized on the adjacent inorganic unit, such that one excited-state can be thermally populated from the other at room temperature ($\Delta E \sim 1.7\,\mathrm{kcal\,mol^{-1}}$). Due to the kinetics of the radiative and non-radiative processes, in cases where the interchromophore electronic energy transfer (k_f, k_b) is faster than other quenching processes, excited-state equilibration is established. As the k_f value is superior than k_b, this pushes the equilibrium mixture to a population comprising largely molecules with the excitation energy localized on the organic chromophore. As the deexcitation of the inorganic unit (k_r is typically *ca.* $10^5\,\mathrm{s^{-1}}$) is much faster than the phosphorescence radiative rate constant of an aromatic hydrocarbon (k_p is typically *ca.* $10^3\,\mathrm{s^{-1}}$), the emission results exclusively from the inorganic unit, whose depleting population is replenished form the organic chromophore energy reservoir. Because the interchromophore energy transfer processes are highly efficient, little energy is wasted and the system maintains a luminescence quantum yield similar to that of the parent lumophore, but with a much longer observed luminescence lifetime. In the case of the prototype, a luminescence lifetime of 11.2 μs was recorded compared to 800 ns for the parent complex.

In specific cases the accrued lifetime may be beneficial, particularly in diffusion-controlled bimolecular reactions and may have a role to play in charge separation devices or oxygen sensors [109,110]. Development in the area of intramolecular reversible energy transfer is principally based on two kinetic schemes, largely with regard to aromatic chromophore-appended ruthenium(II) polypyridine based systems but also with osmium based examples, which have been recently reviewed [111,112]. For example, this reversible energy transfer strategy has been recently applied to underperforming copper(I) bis(phenanthroline) based complexes, in analogy with their d^6-ruthenium-containing cousins [113,114]. As mentioned above, while inexpensive copper presents some properties similar to those of luminescent ruthenium(II) complexes, the excited-state lifetimes are generally relatively short. In the case of parent $[\mathrm{Cu(dmp)_2}]^+$, the luminescence lifetime in degassed dichloromethane is of the order of 70 ns. On satisfying the kinetic and energetic rubrics outlined above, the emissive centre was anticipated to participate in reversible energy transfer with an appropriate organic chromophore presenting a slowly deactivating triplet state ($k_p \ll k_r$) of similar energy. The radiative rate constant for deexcitation of the metal core has been estimated at *ca.* $10^7\,\mathrm{s^{-1}}$ compared with *ca.* $10^3\,\mathrm{s^{-1}}$ for aromatic chromophore phosphorescence. Anthracene (whose triplet energy is located at 1.8 eV) satisfies the energetic and kinetic criteria ($\tau_{\mathrm{phoshorescence}} = 350\,\mu\mathrm{s}$), as represented in Fig. 8b [115]. The prototype bichromophoric complex $[\mathrm{Cu}(\mathbf{38})_2]^+$ has two additional covalently appended anthracene units with respect to the parent complex, which are separated by a saturated ethylene spacer. It is noteworthy that a bimolecular system was previously reported comprising $[\mathrm{Cu(dmp)_2}]^+$ and unsubstituted anthracene [116]. While this system served to demonstrate perhaps the first example of a copper phenanthroline in the role of donor component to a separate acceptor in an energy transfer reaction, the repopulation of the emissive $[\mathrm{Cu(dmp)_2}]^+$ from the organic chromophore was not operational in this case. This is presumably due to diffusion of the two components increasing the interchromophore distance beyond the range for a Dexter-type triplet–triplet energy transfer process.

In the case of $[\mathrm{Cu}(\mathbf{38})_2]^+$, a luminescence lifetime of 1.2 μs in degassed dichloromethane solution was recorded at room temperature, representing an enhancement in luminescence lifetime (15-fold) with respect to the 70 ns recorded for the parent $[\mathrm{Cu(dmp)_2}]^+$, and even that of $[\mathrm{Ru(bpy)_3}]^{2+}$ (*ca.* 700 ns in acetonitrile). The analogous complex $[\mathrm{Cu}(\mathbf{39})_2]^+$ gave a somewhat longer lifetime, as anticipated due to the multichromophoric approach using four, rather than two anthracene energy reservoirs. A similar quantum yield (0.04%) in both cases shows the energy transfer processes to be efficient, with low energy wastage, and compatible with their possible incorporation in specific photo-/redox-active devices or applications (using either organic and/or metal-centred triplets taking advantage of a visible light absorbing metal-polypyridine photosensitizer unit).

A closer analysis of the individual photophysical processes by ps time-resolved fluorescence and ultrafast flash photolysis shows a short-lived fluorescent component consistent with the relatively slow intersystem crossing phenomenon (*ca.* 15 ps) in both $[\mathrm{Cu(dmp)_2}]^+$ and $[\mathrm{Cu}(\mathbf{38})_2]^+$ [94,113]. However, in the case of $[\mathrm{Cu}(\mathbf{38})_2]^+$, this initial process is followed by a rapid (*ca.* 60 ps) electronic energy transfer process. Concomitant disappearance of the MLCT absorption signature and grow-in of the $T_n \leftarrow T_1$ absorption band centred on the anthracene further supports this notion. In this case, with three different, potentially interacting excited states (^{1}MLCT, ^{3}MLCT, ^{3}LC), the luminescence lifetime can be qualitatively and quantitatively predicted as a weighted average of deexcitation pathways. The deexcitation of the equilibrated system is described by Eq. (2), where α, β, γ corresponds to the fractional populations of ^{1}MLCT, ^{3}MLCT and ^{3}LC states, respectively, with the sum of these three components totalling 1 and $\alpha, \beta \ll \gamma$. The values $\tau_{1\mathrm{MLCT}}{}^{-1}$, $\tau_{3\mathrm{MLCT}}{}^{-1}$, and $\tau_{3\mathrm{LC}}{}^{-1}$ correspond to the kinetic contributions of each state to the deexcitation of the ensemble.

$$k_{\mathrm{obs}} = \alpha(\tau^{-1}_{^1\mathrm{MLCT}}) + \beta(\tau^{-1}_{^3\mathrm{MLCT}}) + \gamma(\tau^{-1}_{^3\mathrm{LC}}) \qquad (2)$$

A series of other bichromophoric copper(I) complexes and architectures have been subsequently prepared in the author's laboratory which will be reported presently.

5. Conclusion

Copper(I) bis(phenanthroline) complexes can be persuaded to exhibit very varied photophysical properties, particularly in terms of quantum yields and luminescence lifetimes, which can vary over 3 orders of magnitude. Sterically encumbered ligands block excited-state reorganisation of the primary coordination sphere, and thus raise emission energies and lower subsequent unwanted deexcitation resulting from solvent attack and vibrational deexcitation, augmenting emission quantum yields. Other particularly promising systems include those based on π-stacking interactions, fluorous ligands, as well as very recent heteroleptic systems comprising for example both P- and N-donors, assuring a less easily quenched higher energy emissive state. Furthermore, efficient reversible energy transfer involving an appropriate anciliary chromophore playing the role of an energy reservoir, can lead to prolonged luminescence lifetimes, for example 1.2 μs emanating from a $[\mathrm{Cu(dmp)_2}]^+$ centre when appended with an anthracene unit (15-times longer than the parent complex). Recent ultrafast time-resolved measurements have suggested further elaborations of the initial model describing the photophysical behaviour, particularly with regard to relative rates of ligand reorganisation, intersystem crossing (particularly slow passage from ^{1}MLCT to a ^{3}MLCT being suggested by time-resolved fluorescence measurements), and participation of higher excited states of singlet character. Other developments are anticipated in the near future with the availability of a range of ultrafast spectroscopic tools. The unambiguous elucidation and unravelling of the rich photophysical behaviour of even structurally simple complexes such as $[\mathrm{Cu(dmp)_2}]^+$ is an active ongoing research area. However, it is clear that even armed with straightforward ideas, be it in terms of structure, thermodynamics and/or kinetics, significantly different luminescent properties can be instilled in copper complexes in a qualitatively predictable fashion. This holds particular promise for the development of more sophisticated supramolecular architectures or potentially for complexes in applications such as oxygen sensors, light-emitting devices or dye-sensitized wide band gap semiconductor-based devices for photovoltaic applications, as well as for biological applications. Steps in this direction have already been taken [34,117–120].

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