Luminescent complexes beyond the platinum group: the d^{10} avenue

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Luminescent metal complexes are key materials for several applications such as lighting, analytical probes, and lasers. In many cases compounds based on precious (*i.e.* platinum group) and rare earth metals are utilized, which are often rather expensive and environmentally problematic. In recent years, interest is growing in luminescent complexes based on less traditional but more abundant and cheaper metal elements. In this scenario compounds of metals with a d^{10} electronic configuration are playing a prominent role, also thanks to the versatility of their luminescent levels which can be of ligand centred, charge transfer or, in the case of polynuclear compounds, even metal-centred nature. Here we focus on some selected examples of Cu(I), Ag(I), Au(I), Zn(II) and Cd(II) luminescent complexes to suggest some possible routes towards promising and unprecedented emitting materials.

1. Introduction

In the mind of most photochemists the quintessential luminescent coordination compound is probably $[Ru(bpy)_3]^{2+}$. The early detailed studies on the charge transfer orange luminescence of this complex dates back to almost 50 years ago[1,2] and the popularity of $[Ru(bpy)_3]^{2+}$ and its derivatives, testified by a wide and virtually relentless flow of scientific papers over the last decades,[3] is the consequence of a unique combination of chemical stability, redox and luminescence properties, excited state lifetime and reactivity.

The lowest electronic excited states of Ru(II)-polypyridines are of metal-to-ligand-charge-transfer (MLCT) nature, involving electronic transitions from a metal d orbital to a π* antibonding orbital centred on the diimine ligand. Such transitions, which occur in the visible spectral region with a wide absorption envelope around 450 nm, can be viewed as a partial oxidation of the metal centre and a concomitant reduction of the chelating ligand.[3] Luminescence of these Ru(II) complexes originates from the lowest lying ^{3}MLCT level at $\lambda_{max} \approx 610$ nm. It is important to point out that the MLCT states of second and third row transition metal complexes are lower-lying than dissociative, non-emissive d–d metal centred (MC) levels, but this ordering is completely reversed for first row elements (Fig. 1). Accordingly, complexes of Fe(II) (as well as Ni(II) and Co(II)) are far less stable than Ru(II) analogues and not luminescent.

Studies on Ru(II) coordination compounds have been logically extended to other platinum group metals such as Os(II),[4] Pd(II),[5] Pt(II)[6] and Rh(III)[7] and, sometimes, intense luminescence can be obtained, especially for Pd(II) and Pt(II) complexes. In relatively recent years cyclometalated Ir(III) compounds have emerged as a new class of outstanding and tunable photo- and electroluminescent materials.[8–10] The emissive excited state of these complexes can be either MLCT or ligand centred (LC) depending on the ligand environment but, whatever the electronic nature, they are invariably triplet

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From left to right, Nicola Armaroli, Gianluca Accorsi and Andrea Barbieri.

The authors met some years ago when AB joined the Molecular Photoscience Group at CNR-ISOF, where NA and GA had been active since the 1990s. Their complementary skills and educational backgrounds are the basis for an effective scientific cooperation. Andrea Barbieri received his PhD in Chemical Sciences in 1992 at the University of Ferrara. Since 1997 he is a Researcher at the Italian National Research Council (CNR). Gianluca Accorsi received his PhD in 2007 at the University of Bologna. Since 2006 he is a research associate at CNR-ISOF. Nicola Armaroli obtained a PhD in Chemistry from the University of Bologna in 1994. He carried out post-doctoral research at the Center for Photochemical Sciences at Bowling Green State University (USA) and later at CNR, becoming senior researcher there in 2002. The researchers' scientific interests include luminescent materials as well as photoinduced energy- and electron transfer processes in supramolecular systems.

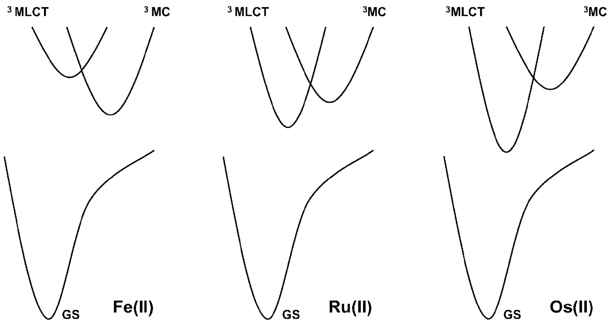


Fig. 1 Schematic representation of the relative position of potential energy curves for the ground state (GS) and the lowest electronic excited states of Fe(II), Ru(II), and Os(II) polypyridine complexes, to notice the change of the MLCT–MC energy gap and ordering.

states even if, for LC levels, some residual singlet character can still be present.[11,12] This is a consequence of the high spin–orbit coupling of the iridium atom (ζ_{Ir} = 3909 $\mathrm{cm^{-1}}$).[13] In addition, Ir(III) cyclometalated complexes can be prepared so as to neutralize the metal ion positive charge, *i.e.* without the need of electrostatically bound counteranions. The availability of neutral strongly luminescent triplet emitters in the visible spectral region has made these compounds excellent candidates as materials for organic light emitting devices (OLED).[14,15] An impressive flow of scientific papers in the fields of chemical and physical science related to OLEDs for flat "cold light" sources has been observed in the last 6–7 years[16–18] and this technological perspective is particularly appealing in the current situation where end-user efficiency is considered one of the key strategies to cope with the impending energy crisis.[19]

The interest in luminescent molecules and materials is not only limited to lighting technologies but there are several fields of research such as imaging, lasers, sensors, switches,[20] *etc.* where substantial progress and real breakthroughs can be made in the near future if novel UV-Vis-NIR emissive molecules will be made available. Widespread diffusion of novel "luminescent" technologies that make use of platinum group metals might be hampered by their prohibitive cost, which is related to their scarcity in the Earth's crust; curiously, they are several orders of magnitude less abundant in the Earth's crust than the so-called "rare earth" elements. It is thus highly desirable to pursue more affordable alternatives to metal emitters, out of the range of the platinum group. In recent years there has been increasing attention towards less conventional luminescent metal compounds made from d^{10} metal ions. The main advantages of these complexes over the corresponding derivatives made from d^6 metal ions can be summarized in two points: (i) the lack of non-emissive low-lying MC levels that would quench the luminescent excited states by thermal equilibration or energy transfer; and (ii) a large variety of coordination geometries, with respect to the almost ubiquitous octahedral geometry of d^6 metals, which make them ideal building blocks for the synthesis of complex molecular architectures.

In the following sections, classified according to the central metal ion, the most recent advances in the design of luminescent d^{10} metal complexes, particularly Cu(I),[21] Ag(I),[22–26] Au(I),[27] Zn(II) and Cd(II),[18,28,29] will be illustrated.

2. Cu(I)

Cu(I) complexes and clusters are currently the largest class of luminescent metal compounds based on a relatively abundant element. Copper in solution may exhibit two oxidation states: +1 and +2. Cu(II) complexes are characterized by a d^9 electronic configuration and show relatively intense metal-centred (MC) absorption bands in the Vis-NIR spectral window, which deactivate *via* ultrafast non-radiative pathways. Accordingly, Cu(II) complexes do not have any interest for luminescence-related applications; likewise Fe(II), Co(II) and Ni(II), as mentioned above, which are characterized by d^6, d^7 and d^8 electronic configurations, respectively.

The most extensively investigated family of Cu(I) complexes has the general formula $[\mathrm{Cu(N{^\wedge}N)_2}]^+$, where N^N indicates a chelating bisimine ligand, typically a substituted 1,10-phenanthroline (Fig. 2).[21,30–32] In recent years increasing attention has been paid to heteroleptic $[\mathrm{Cu(N{^\wedge}N)(P{^\wedge}P)}]^+$ compounds (where P^P denotes a bisphosphine ligand) because they exhibit greatly enhanced emission performance compared to $[\mathrm{Cu(N{^\wedge}N)_2}]^+$. Two examples of P^P ligands, POP and dppb, are illustrated in Fig. 2.[33–36] The impressive performance of $[\mathrm{Cu(N{^\wedge}N)(P{^\wedge}P)}]^+$ heteroleptic complexes is found also in neutral amidophosphine derivatives with the general formula $[\mathrm{Cu(P{^\wedge}N)(P{^\wedge}P)}]$, Fig. 2.[37,38] Recently, the first example of a luminescent $[\mathrm{Cu(P{^\wedge}P)_2}]^+$ complex was also finally reported.[39]

In Fig. 3 are depicted the absorption and luminescence spectra of three prototypical $[\mathrm{Cu(N{^\wedge}N)_2}]^+$, $[\mathrm{Cu(N{^\wedge}N)(P{^\wedge}P)}]^+$ and $[\mathrm{Cu(P{^\wedge}P)_2}]^+$ complexes.

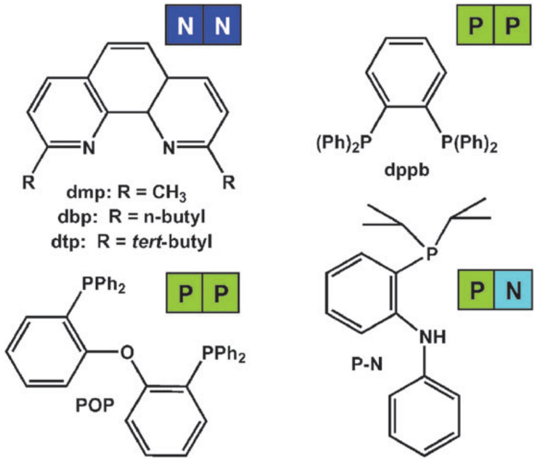


Fig. 2 Examples of ligands utilized to make luminescent Cu(I) complexes with general formulas $[\mathrm{Cu(N{^\wedge}N)_2}]^+$, $[\mathrm{Cu(N{^\wedge}N)(P{^\wedge}P)}]^+$, $[\mathrm{Cu(P{^\wedge}N)(P{^\wedge}P)}]$, or $[\mathrm{Cu(P{^\wedge}P)_2}]^+$. dmp = 2,9-dimethyl-1,10-phenanthroline; dbp = 2,9-di-*n*-butyl-1,10-phenanthroline; dppb = 1,2-bis-(diphenylphosphino)-benzene; POP = bis[2-(diphenylphosphino)-phenyl]ether; PN: 2-(diisopropyl-phosphino)diphenylamide. In the case of P^N compounds, "N" refers to an amide and not to an imine ligand, as for N^N.

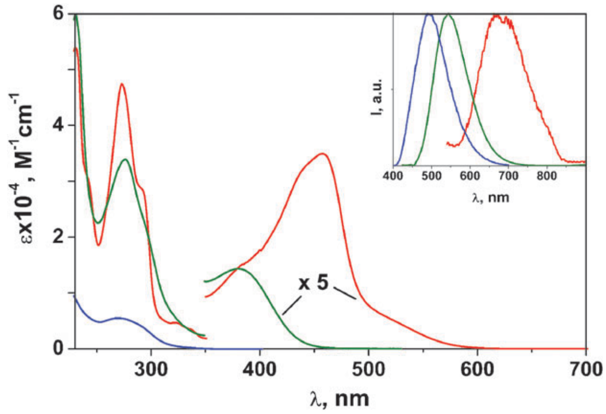


Fig. 3 Absorption and (inset) normalized emission spectra of $[Cu(dmp)_2]^+$ (red), $[Cu(dbp)(POP)]^+$ (green) and $[Cu(POP)(dppb)]^+$ (blue) in CH_2Cl_2 at 298 K. The intense UV absorption of the former two compounds compared to $[Cu(POP)(dppb)]^+$ is mainly due to π,π* ligand centred transitions of the phenanthroline ligand(s). The noisy trace of the emission spectrum of $[Cu(dmp)_2]^+$ is a clear indication of signal weakness. The structures of the ligands are reported in Fig. 2.

2.1 $[Cu(N^\wedge N)_2]^+$, recent advances in the rationalization of the photophysics

Upon light excitation, tetrahedral $[Cu(N^\wedge N)_2]^+$ compounds undergo extensive molecular rearrangements to square planar geometry, possibly with the pick-up of external nucleophiles (solvent molecules or counteranions) to form a five-coordinated exciplex.[21,30,40] This is a consequence of the generation of relatively long-lived (ns–μs timescale) thermally equilibrated MLCT excited states in which the metal centre is formally Cu(II) and thus prefers a "flattened" geometry. Very recently, extensive work by several groups has somewhat clarified the details of such ultrafast events and this will be of great benefit in the design of Cu(I) complexes with optimized luminescence performance. Such an important result has been made possible thanks to a combination of theoretical (DFT)[41–44] and experimental techniques such as ultrafast transient absorption,[43,45–47] time-correlated single photon counting,[42] fluorescence upconversion,[47,48] light-initiated time-resolved X-ray absorption spectroscopy (LITR-XAS) in solution[43,45,49,50] and in the solid state (photocrystallography).[51,52] Work is still in progress and certainly viable of further refinements, also because so far only the very simple complex $[Cu(dmp)_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) has been investigated in depth. The picture that stems from the latest results[47,48] indicates molecular rearrangements (and perhaps ligand pickup) occurring on an ultrafast timescale (hundreds of fs), following light excitation. At later times (7–15 ps), ^{1}MLCT → ^{3}MLCT intersystem crossing takes place, which can be followed either by time resolved luminescence[42] or transient absorption spectral changes which are independent from the molecular structure or solvent viscosity.[46,47] The emission band of $[Cu(N^\wedge N)_2]^+$, which peaks around 700 nm, is due to the deactivation of the lowest ^{3}MLCT state[48] in equilibrium with the slightly higher lying singlet (ΔE *ca.* 1500 cm^{-1})[53–55] and occurs on the timescale of tens to hundreds of nanoseconds, depending on the ligand environment.[30]

$[Cu(N^\wedge N)_2]^+$ complexes absorb throughout the whole visible spectral window due to an envelope of MLCT transitions. The specific spectral shape of a given complex is dictated by the substitution pattern of the ligands which affect the dihedral angle between the two phenanthroline planes and the extent of π-delocalization of the accepting orbital. These peculiar features dramatically influence the probabilities of MLCT electronic transitions and result in complexes exhibiting a variety of brilliant colours (*e.g.* orange, deep red or magenta).[56] Unfortunately, the emission performance of $[Cu(N^\wedge N)_2]^+$ complexes is generally poor. In nucleophilic solvents luminescence is often barely detectable. In CH_2Cl_2 at ambient temperature a wide emission band, centred between 680 and 740 nm, is usually recorded but the emission quantum yield is typically below 0.001 (lifetimes between 50 and a few hundred ns).[30] To our knowledge the highest value reported to date is 0.01 for $[Cu(dmp)(tbp)]^+$ (tbp = 2,9-di-*tert*-butyl-1,10-phenanthroline).[57] Interestingly 2,9-substituted phenanthrolines with long alkyl chains exhibit a bright orange intense luminescence at 77 K, related to specific structural constraints in the low temperature matrix.[54] As far as the engineering of excited state lifetimes is concerned, the "energy reservoir effect"[58] *via* an appended organic chromophore possessing a low-lying triplet state (anthracene), enabled the prolongation of the MLCT lifetime of a $[Cu(dmp)_2]^+$-like complex from 70 to 1200 ns.[55]

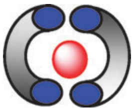
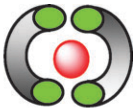
Several review articles presenting extensive photophysical data on simple $[Cu(N^\wedge N)_2]^+$ luminescent complexes, also as part of sophisticated supramolecular architectures, have been published recently.[21,30,59–62] We suggest that the reader refers to these papers for a comprehensive and updated overview of this topic.

2.2 Stronger emitters: $[Cu(N^\wedge N)(P^\wedge P)]^+$ and $[Cu(P^\wedge P)_2]^+$

Heteroleptic Cu(I) complexes containing both N- and P- coordinating ligands ($[Cu(N^\wedge N)(P^\wedge P)]^+$) have been studied since the late 70s by McMillin *et al.*[63,64] For two decades they have been rather neglected but a revived interest is found in current literature and this is mostly due to the fact that, with tailored imine and phosphine ligands, they may exhibit intense green emission[33,65] attributable to MLCT excited states.[66,67]

The first example of a highly emissive $[Cu(N^\wedge N)(P^\wedge P)]^+$ complex was $[Cu(dmp)POP]^+$;[33] its emission quantum yield and lifetime in deaerated CH_2Cl_2 are reported to be 0.15 and 14.3 μs, respectively. In this compound, a favourable combination of structural and electronic factors contribute to the high emission output: (i) alkyl substituents in the N^N ligand (much weaker emission is detected with unsubstituted 1,10-phenanthroline);[33] (ii) a chelating P^P ligand (very little emission is found with two individual phosphine residues); (iii) higher-energy MLCT excited states, compared to $[Cu(N^\wedge N)_2]^+$ systems, which disfavours non-radiative deactivations. The former two factors impart the structural rigidity[68] and steric protection which is needed to increase luminescence yield, as discussed in the previous section. Following the seminal report of McMillin *et al.* several papers have been published in recent years by many groups dealing with

Table 1 Top performing Cu(I) luminescent complexes with four different coordination environments (see Fig. 2 for ligand formulas, dmdpp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline). a = oxygen-free solution at 298 K; b = 77 K rigid matrix; c = solid state at 298 K

N Cu^+ P	 $[Cu(dmp)(tbp)]^+$	 $[Cu(POP)(dppb)]^+$	 $[Cu(POP)(dmdpp)]^+$	 $[Cu(PN)(PPh_3)_2]$
a	$\Phi_{em} = 0.01^a$	$\Phi_{em} = 0.02^b$	$\Phi_{em} = 0.28^c$	$\Phi_{em} = 0.70^d$
a	$\tau = 1.5\ \mu s^a$	$\tau = 2.4\ \mu s^b$	$\tau = 17.3\ \mu s^c$	$\tau = 6.7\ \mu s^d$
b	Very intense orange[e]	Intense green[f]	Very intense blue-greenish	Not reported
c	Very weak	Intense green[g]	Very intense green[h]	Not reported

[a] CH_2Cl_2, ref. 57. [b] CH_2Cl_2, ref. 39. [c] CH_2Cl_2, ref. 36. [d] Benzene, neutral complex, ref. 37. [e] CH_2Cl_2–MeOH (1 : 1) ref. 54 and 56. [f] Ref. 39. [g] Unpublished results from our group. [h] Ref. 36.

emissive $[Cu(N^\wedge N)(P^\wedge P)]^+$ complexes,[34,35,65,66,69–73] and these compounds are also increasingly considered as active materials in electroluminescent devices both in multilayer OLED stacks[74,75] and in simpler light emitting electrochemical cell (LEC)[76] configurations.[36,77] They exhibit good current-to-light efficiency and even colour tuning, but the device lifetime, likely to be related to chemical stability of the complex under working conditions, is still an issue.[36] A very promising class of Cu(I) complexes appears to be that of amidophosphine derivatives $[Cu(P^\wedge N)(P^\wedge P)$, which exhibit luminescence quantum yields as high as 0.7 in benzene solution and excited state lifetimes around 10–20 μs.[37,38] They exhibit a tunable green to blue emission and have therefore the chance to rival widespread Ir(III) cyclometalated emitters in electrooptical devices.

Application perspectives in optoelectronics are a major driver in the search for novel luminescent Cu(I) d^{10} complexes and several routes have been attempted. For instance the typical $N^\wedge N$ phenanthroline-type chelator in $[Cu(N^\wedge N)(P^\wedge P)]^+$ has been replaced by halides[78] or other diimine ligands,[70] and this afforded blue to red colour tuneability[79] and high emission quantum yields (17% at 77 K).[80] Very interestingly, it has been demonstrated recently that even $[Cu(P^\wedge P)_2]^+$ emissive compounds are obtainable. $[Cu(POP)(dppb)]^+$ (dppb = 1,2-bis(diphenylphosphino)-benzene, Fig. 2) exhibits a relatively intense emission band in solution (Φ_{em} = 2% CH_2Cl_2, τ = 2.4 μs), tentatively assigned as MLCT, and it has been employed to fabricate a simple white light electroluminescent device.[39]

In Table 1 are summarized luminescence data, under different experimental conditions, of top performing Cu(I) complexes exhibiting different coordination spheres. A substantial improvement of luminescence performance is clearly observable. Thus it is not daring to foresee further progress in the synthesis and exploitation of luminescent d^{10} Cu(I) complexes in the near future, even with unconventional coordination environments or structures. Clear signs of these trends are being found in current literature.[81–87]

3. Ag(I)

Photoactive silver compounds have been known for a long time; for instance, the use of silver halides was of capital importance for the development of photography. They were discovered as light sensitive compounds at the end of the eighteenth century by C. W. Schiele and J. Senebier. The pioneering experiments on silver halide layers on metal plates by J. Herschel, J. N. Niepce and L. Daguerre gave birth to the first photographic images at the beginning of the nineteenth century. The photographic "emulsion" is, in fact, a suspension of AgBr and/or AgI microcrystals in natural gelatine and the spectral sensitivity of silver halides is extended through the whole visible range by organic dyes absorbed to the crystal surfaces.[88,89]

Ag(I) forms stable d^{10} complexes with several organic ligands, which are rather appealing for their emissive properties.[24] Very often these compounds are polynuclear (cluster-type) and the nature of their emitting states strongly depends on the number of metal centres and on the interactions between them. In fact metal–metal bonding typically occurs providing cluster-centred emission (MC nature), often accompanied by ligand-to-metal-charge-transfer (LMCT) bands.[90–92] Furthermore, Ag(I) has the ability to form even larger two- and three-dimensional architectures (*e.g.* coordination networks), made *via* self-assembly, with tunable optical and electronic properties.[26,92–94] On the other hand, when the complex structure does not allow a close contact between the metal centres, ligand centred (LC) emissions are generally observed. Here we will mainly focus on this last case.

As discussed above, the emitting states of Cu(I) complexes are assigned to the MLCT deactivations, favoured by the low oxidation potential of Cu(I). In the case of Ag(I) complexes, the redox inert metal ion does not allow low-energy charge

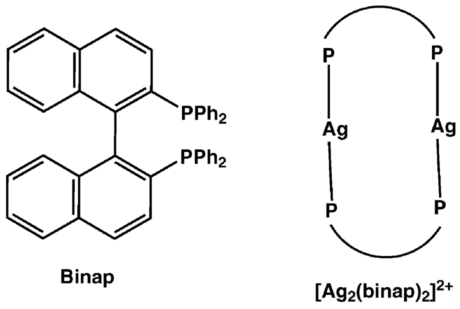


Fig. 4 Chemical structure of binap (left) and schematic representation of the related Ag(I) complex (right).

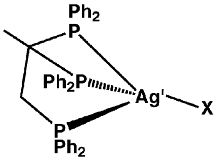


Fig. 5 Chemical structure of Ag(I) complexes with luminescent LLCT states (X = Cl$^-$ or I$^-$).

transfer processes to the organic ligands.[23] As a consequence, the role played by the Ag(I) ion in dictating the luminescence properties of the complexes is essentially promotion of intersystem crossing (ISC) between the lowest singlet (^{1}LC) and triplet (^{3}LC) ligand-centred excited states (*heavy atom* effect, $\zeta_{Ag} = 1779\ cm^{-1}$).[13,24,95]

As reported by Vogler and Kunkely,[24] a common organic ligand such as binap (2,2′-bis(diphenylphosphino)-1,10-binaphthyl), also used for Cu(I) coordination,[72] forms a dinuclear complex with Ag(I) (Fig. 4) which exhibits a strong phosphorescence band in the green spectral region at room temperature. By contrast, the free ligand emits only in 77 K rigid matrix.

Similar compounds containing binap derivatives (2,2′-dimethoxy-1,10-binaphthyl-3,3′-bis(4-vinylpyridine)) have been studied, however no phosphorescence was observed.[96] Hence, the heavy atom effect is most likely driven by intermetal electronic interaction, and slight changes of the chemical structure limit Ag–Ag contacts and remove phosphorescence at ambient temperature.

The nature of the emitting states in d^{10} Ag(I) complexes can be varied by using two different coordinating units (Fig. 5), *i.e.* a tripod (1,1,1-tris(diphenylphosphinomethyl)ethane, electron acceptor) and a halogen anion X (X = Cl$^-$ or I$^-$, electron donors).[23]

Ag(I) does not contribute to low-energy electronic transitions owing to its high-energy MC levels, while electronic interactions between ligands may result in charge transfer processes. Thus the luminescence spectra detected for the Ag(I) complexes in Fig. 5 at both low and room temperature, peaking at 464 (X = Cl$^-$) and 482 (X = I$^-$) nm, are attributed to ligand-to-ligand charge transfer (LLCT) transitions.

Another factor that can influence the emission intensity of Ag(I) complexes is represented by the dihedral angles between the ligands and the metal ion. As shown by Duan *et al.*,[25] three different dinuclear structures are originated by the use of the ligand depicted in Fig. 6 coupled with three different ancillary ligands (NO_3^-, $SO_3CF_3^-$, and H_2O) to complete the coordination sphere of the Ag(I) ions.

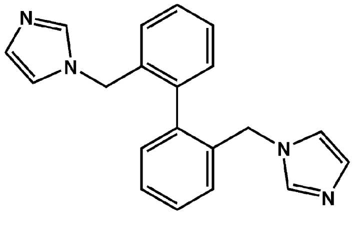


Fig. 6 Chemical structure of the ligand 2,2′-bis(imidazol-1-ylmethyl)-biphenyl.

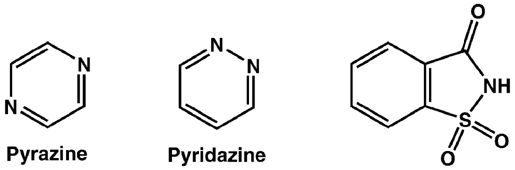


Fig. 7 Chemical structures of ligands utilized in Ag(I) luminescent complexes.

The LC luminescence intensities of these complexes are remarkably affected by the local environment around the metal ion (Φ_{em} up to 5%). In particular, the co-planarity of the two imidazole rings induces an enhancement of π-conjugation leading to self-quenching of the excited states. When this effect is prevented by different geometrical arrangements, an emission increase is detected, and the luminescence output is stronger than that of the free ligand. Thus, in the case of Ag(I) complexes, geometrical factors normally play a rather different role compared to those observed in Cu(I) complexes (see section 2).

Pyridyl-type diazabenzenes (pyrazine and pyridazine) as bidentate (N^N) bridging ligands in tandem with saccarinate (Fig. 7) have been employed recently in the coordination of Ag(I).[97] For these compounds formation of a MLCT emitting state is not compatible with the experimental observations and Ag–Ag interactions are not possible due to distance reasons. Therefore, once again, the detected luminescence is ascribed to intraligand transitions, as also suggested by DFT calculations.

Finally, the photoluminescence properties of Ag(I) complexes, coordinated by a different family of chelating ligands, have been investigated by Yilmaz *et al.*[98] In this work, they show that, although non-aromatic coordinating ligands are present, significant luminescence at room temperature is detected. The photoluminescence was attributed to the presence of relatively strong Ag–Ag interactions. This confirms that intermetal contacts can strongly affect the luminescence behaviour of polynuclear structures, whereas in mononuclear complexes the emission pattern is essentially dictated by ligand-related transitions (LC and LLCT).

4. Au(I)

One prominent feature of Au(I) complexes is the tendency to form weak metal–metal bonds, attributed to the stabilisation of filled 5d metal orbitals by the interaction with empty 6s/6p based molecular orbitals, which come close in energy because of the strong relativistic effect possessed by gold.[99] The energy of this interaction (*ca.* 10 kcal mol^{-1})[100] is comparable to that of a hydrogen bond and provides an extra stabilisation to Au(I) polynuclear complexes. This effect has been termed by Schmidbaur "aurophilicity".[101] For mononuclear Au(I) complexes, the most common coordination geometries observed are linear and trigonal planar, thus resulting in quite different structures with respect to the homologue Cu(I) or Ag(I) complexes.[102]

The intriguing photophysical properties showed by gold complexes have been extensively studied since the 1970s, when Dori and coworkers first reported the luminescence of Au(I) (and other d^{10} metal ions) phosphine complexes;[103] several extensive review articles on their luminescence properties have been published.[18,27,100,104–106] As for other d^{10} transition metals, LMCT and IL transitions dominate the photophysics of Au(I) complexes. Gold exhibits the highest spin–orbit coupling constant (ζ_{Au} = 5104 cm^{-1})[13] among metals, providing effective access to the low-lying emissive triplet state by ISC. Consequently, luminescent gold complexes normally exhibit a lowest excited state that is phosphorescent in nature. In most cases, the emission has been attributed to ^{3}LMCT levels, with aurophilic interactions strongly affecting the luminescence properties in a number of ways.[107] Such interactions are usually observed only in the solid state, and do not necessarily require the formation of formal bonds between the metal centres; short Au–Au distances between neighbouring molecules can yield the same effect. Thus, many Au(I) complexes may display phosphorescence in the solid state (at room temperature or 77 K), and no detectable luminescence in dilute solution. For example,[107] in heteroleptic mononuclear Au(I) phosphine arylthiolate complexes, the photophysical properties depend both on the presence of gold–gold interactions between neighbouring molecules in the solid state and on the nature of the substituents attached to the phenyl ring of the thiolate ligand. In particular, lower emission energy is observed with appended electron-donating groups as well as with complexes exhibiting short intermolecular gold–gold distances.

In dinuclear Au(I) complexes containing thiolate and phosphine ligands the ^{3}LMCT excited states originating from the two types of ligands are close in energy, and for those complexes with short Au–Au contacts the excited states originate from a ligand-to-metal/metal charge-transfer state (LMMCT).[105] Then, through a systematic variation of the substituents on the thiolate and phosphine ligands it is possible to control the luminescence properties of the complexes, and the origin of the emission can be switched from the phosphine to the thiolate ^{3}LMCT excited state.[105]

A notable exception to the LMCT or LMMCT nature of the excited states in Au(I) complexes is represented by the phosphine alkynyl derivatives, where the presence of low energy π* orbitals of the $-C\equiv C-$ ligand imparts a metal perturbed ^{3}IL character to the luminescence, with some contribution from metal-to-alkynyl ^{3}MLCT excited states.[106]

With a judicious choice of auxiliary ligands, coordination geometry, and extent of metal–metal interaction, it is possible to tune the emission energies of Au(I) complexes over a wide spectral range. This feature, coupled with lifetimes of the order of microseconds, raised interest in the use of Au(I) complexes as active materials in OLED devices.[108–110] Interestingly gold complexes have found important applications also in catalysis[111] and in medicine, for instance as antiarthritic, antiviral, cytotoxic and antiinfective drugs.[112]

5. Zn(II) and Cd(II)

In the last few years, there has been growing interest in the photophysics of luminescent Zn(II) and Cd(II) coordination complexes, and several reviews have appeared on monomeric and multinuclear Zn(II)/Cd(II) coordination compounds,[28] Zn(II) coordination polymeric structures,[113] fluorescent detection of Zn(II) in biological systems,[114,115] and Zn(II)/Cd(II) coordination complexes as electroluminescent materials applied in OLEDs.[18,29]

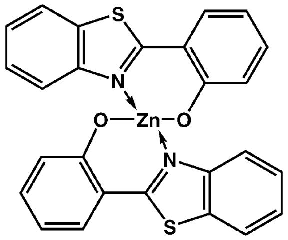


Fig. 8 Chemical structure of the white emitting $[Zn(btz)_2]^+$ complex.

As stated above, group 12 metal dications (Zn(II), Cd(II), and Hg(II)) contain a d^{10} closed shell electronic configuration, thus d–d transitions are not expected. Consequently the lowest energy excited states of their complexes are mainly of a ligand-centred (LC) and/or ligand-to-ligand charge transfer (LLCT) nature. Many observations of ligand-to-metal charge transfer (LMCT) states have been reported, involving the low-lying s or p empty orbitals of the central metal ion. It should be pointed out that LMCT states usually involve transitions from π(ligand) to d(metal) orbitals. In most cases, however, the ligands are not innocent, but provide their σ*-antibonding orbitals to the LUMO, and the lowest excited level is more accurately described as an admixture of LMCT and LLCT states.

Many Zn(II) complexes are known to exhibit intense fluorescence at room temperature and there has been substantial research assessing the performances of zinc(II) complexes in fluorescence-based OLED devices. The fluorescence emission stems from a π,π* ligand-centred transition and the role of the central atom is to provide stability to the ligand. The modification of the ligand often leads to a change of emission energy, emission intensity and stability of the complex, along with a dramatic change of the structure and bonding. A notable example is represented by $[Zn(btz)_2]^+$,[116] (Fig. 8) which shows a wide fluorescence spectrum extending from 430 to 700 nm, and has been employed in the fabrication of white OLEDs.[117]

Phosphorescence from Zn(II) complexes is generally observed only in low-temperature glasses. Recently, however, two blue phosphorescent Zn(II) complexes have been reported to emit in the solid state at room temperature.[118] The emission is assigned to a ^{3}IL π,π* state, due to the long excited state lifetime.

Room-temperature phosphorescence in both solid state and solution has been observed in a series of dinuclear Cd(II) diimine complexes with bridging chalcogenolate ligands.[119] The emission from these compounds is assigned to ^{3}LLCT, and consequently the emission energy is dependent on the identity of both the chalcogenolate and the diimine ligands.

In multinuclear clusters, current results show that the specific nature of metal centres and ligands of the core governs the nature of the lowest-lying emissive states, thus different types of ligands and coordination structures may result in a variety of radiative deactivation mechanisms.[28]

Besides the use of Zn(II) complexes in electrooptical devices, an area of considerable importance is the design of molecular probes for the spectrofluorimetric detection of Zn^{2+} ions in biological samples *via* coordinative interactions. Zinc is the second-most abundant transition-metal ion in the human body, where it has multiple roles in both intra- and extracellular functions. The reader interested in this topic may refer to several review articles.[114,120,121]

A recent interesting analytical application of fluorescent zinc–acridine derivatives is the selective detection of traces of nonaromatic high explosives 1,3,5-trinitro-1,3,5-triazinane (RDX) or pentaerythritol tetranitrate (PETN).[122]

6. Conclusion

The combination of metal ions with the wide flow of synthetic organic ligands designed by the chemists' ingenuity generates a virtually countless library of coordination compounds. The intrinsic electronic properties of d^{10} transition metal ions make them particularly attractive for the preparation of luminescent complexes, which are characterized by a larger variety of coordination spheres and emitting levels compared to the classical octahedral d^6 complexes with MLCT luminescence. Among them, tetrahedral, square planar, and trigonal geometries are obtainable, as a function of the specific ligands.

The high redox potentials of Zn(II) virtually prevent any type of charge transfer electronic transitions involving the metal centre in Zn(II) complexes; hence their photophysical behaviour is relatively easy to rationalize. Blue and green ligand-centred fluorescence (^{1}LC), also enhanced compared to the bare ligand, are typically found. The emission behaviour of Ag(I) complexes is more complicated to rationalize. Sometimes they exhibit ligand centred emission from the triplet state (^{3}LC), due to heavy atom effect. However, LMCT, LLCT and, for polynuclear compounds, MC cluster-centred bands are detected. A similar intricate behaviour is found for Au(I) complexes. The case of Cu(I) is particularly intriguing, also due to peculiar structural effects on the photophysical properties. MLCT emissions in the red, orange and green are observed, progressively more intense upon shifting to higher energy. Blue-greenish emissions have been found recently with unconventional coordination environments provided by P^P and P^N ligands. In these cases it cannot be excluded that LC levels are involved in radiative deactivations.

We have presented here some examples of d^{10} luminescent complexes in an attempt to highlight some of their unique properties. The tuneability of the emission colour from red to blue, the variety of chemical structures and the significant progress in the emission performance recently observed make them increasingly appealing. We may expect that the persistent quest for performing luminescent metal compounds, to be utilized in a variety of applications, will find reliable answers among these still relatively unexplored classes of metal compounds.

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