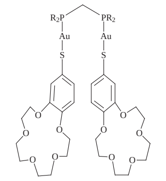
Luminescent polynuclear d^{10} metal complexes



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A number of polynuclear d^{10} transition metal complexes have been found to exhibit interesting luminescence properties. The photoluminescence properties of polynuclear d^{10} metal complexes are highly diversified. In the presence of a wide range of bridging and ancillary ligands, the excited states of such complexes have been suggested to range from metal-to-ligand charge-transfer, ligand-to-metal charge-transfer, metal-centred to ligand-centred in nature. Recent work on the photophysical and photochemical properties, as well as the applications of this class of luminescent polynuclear d^{10} metal complexes will be described in this review article.

1 Introduction

Since the early reports on the observation of phosphorescence of a variety of phosphine, arsine and pyridine complexes of d^{10} metal centres appeared in the seventies,[1,2] work in the area of luminescent d^{10} complexes, especially polynuclear systems, has been developing rapidly and gaining a lot of attention over the past almost thirty years. An important factor which accelerated this subject was the discovery of the interesting photophysical and photochemical properties of dinuclear d^8–d^8 systems such as $[Pt_2(POP)_4]^{4-}$ (**1**) (POP^{2-} = pyrophosphite) in the early eighties.[3] The electronic structures of dinuclear d^8 complexes of this kind have been discussed in terms of a simple molecular orbital model. Interactions between the two filled $5d_{z^2}$ orbitals lead to the formation of d_σ and $d_{\sigma*}$ orbitals while those between the two empty $6p_z$ orbitals yield p_σ and $p_{\sigma*}$ (Pt–Pt vector is taken as the *z*-axis). Promotion of an electron from the anti-bonding $d_{\sigma*}$ (HOMO) to the bonding p_σ (LUMO) results in the formation of a single bond between the platinum(II) centres in the excited state of the complex. This transition ($d_{\sigma*} \rightarrow p_\sigma$) is metal-localised and leads to the contraction along the metal–metal coordinate as well as the formation of a highly reactive diradical species. Investigations on the photophysical and photochemical properties of these photoluminescent d^8–d^8 systems not only provided the fundamental understanding on the photochemistry of polynuclear late-transition metal complexes, but also stimulated interest in the photophysical and photochemical studies of related polynuclear d^{10} systems.

The observation of luminescence from a number of semiconducting materials with d^{10} metal centres such as zinc(II) and cadmium(II) represents an important factor leading to the development of luminescent polynuclear d^{10} metal complexes. The luminescence properties of the semiconductor ZnO have been studied using the molecule $[Zn_4O(CH_3COO)_4]$ (**2**) as a molecular model.[4] This molecule is composed of a central oxygen atom coordinated by four zinc centres in a tetrahedral array. Each zinc ion is also tetrahedrally coordinated by four oxygen atoms. The structure is very similar to the 3-dimensional array of Zn^{2+} and O^{2-} ions in the semiconductor ZnO. The tetranuclear zinc(II) molecule absorbs at a higher energy (216 nm) than the absorption onsets of the smallest quantum size

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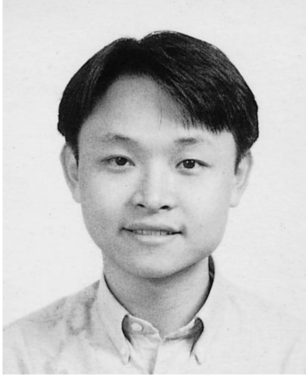

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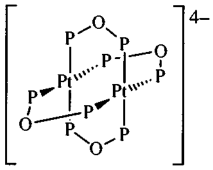

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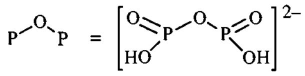


ZnO particles (310 nm) and bulk ZnO material (≤ 365 nm). The decrease of the particle size is associated with a blue shift in the absorption energy and this has been correlated to a phenomenon commonly observed with semiconductors called the quantum size effect.[5] The ligand-to-metal charge-transfer (LMCT) emission of **2** occurs at 372 nm which coincides with the valence-to-conduction band gap emission of ZnO material (the smallest quantum size ZnO particles, λ_{em} = 320 nm; bulk ZnO, λ_{em} = 380 nm). Besides, photophysical studies on $[Zn_4(SPh)_{10}]^{2-}$ (**3**), $[Cd_4(SPh)_{10}]^{2-}$ (**4**) and $[Cd_{10}S_4(SPh)_{16}]^{4-}$ (**5**) also showed that the absorption edges exhibit higher energies with decreasing crystallite size.[6] These polynuclear species, together with their mononuclear analogues $[Zn(SPh)_4]^{2-}$ (**6**) and $[Cd(SPh)_4]^{2-}$ (**7**), exhibit LMCT absorptions, which have also been considered to be the molecular analogues of valence-to-conduction band transitions observed in bulk ZnS and CdS materials.

Luminescence of polynuclear d^{10} metal systems also occurs in many biological species. The most well known is the luminescence of a class of metal–sulfur proteins called metallothioneins.[7] Metallothioneins are proteins of relatively low molecular mass (6–10 kDa) and high cysteine residues (up to 33% by number). The lack of aromatic amino acid residues and the inducibility by some metals are also remarkable features of these proteins. This kind of protein can bind 7, 12 or even 18 Group 11 and 12 metals such as copper(I), cadmium(II), mercury(II) and zinc(II) by their cysteine residues. Copper(I), silver(I) and gold(I) metallothioneins display photoluminescence in the 500–700 nm region with lifetimes in the microsecond range. The luminescence has been suggested to result from LMCT absorptions [cysteines → Cu(I), Ag(I) or Au(I)].

In this review article, we would like to summarise the important work on the luminescence properties of polynuclear d^{10} metal complexes and to discuss the current trend in this rapidly growing area. In the second section, we will describe different approaches in the design of luminescent polynuclear d^{10} systems that lead to our fundamental understanding of the photoluminescence properties of these complexes. In sections three and four, the photophysical and photochemical investigations on the polynuclear copper(I), silver(I) and gold(I) chalcogenide and acetylide complexes essentially carried out in our laboratory will be described. In section five, we will highlight some recent work on the utilisation of luminescent polynuclear d^{10} complexes as a DNA photocleavage agent, chemical probe and cation-induced photoswitch. Finally, a short summary and a future outlook will conclude this review article.

2 Different approaches in the design of luminescent polynuclear d^{10} metal systems

2.1 Polynuclear d^{10} systems with di- and tri-phosphines as bridging ligands

In 1988, Gray and Harvey reported in detail the spectroscopy, photophysics and the resonance Raman spectroscopy of d^{10}–d^{10} metal complexes $[M_2(dppm)_3]$ [M = Pd (**8**), Pt (**9**)].[8] The photophysical properties of these complexes have been correlated to their electronic structures. For mononuclear ML$_3$ complexes with D_{3h} symmetry, the relative energies of the highest occupied orbitals are d_{xz}, d_{yz} < d_{z^2} < d_{xy}, $d_{x^2-y^2}$, while the lowest unoccupied orbital is p_z. A molecular orbital diagram for mononuclear d^{10} ML$_3$ and dinuclear d^{10}–d^{10} (ML$_3$)$_2$ complexes is shown in Fig. 1. Owing to the more significant σ-interactions between the two d_{z^2} orbitals, the splitting of d_σ and $d_{\sigma*}$ is much greater than that of d_δ and $d_{\delta*}$. Therefore, it is likely that [$d_{\sigma*} \rightarrow p_\sigma$] and [$d_{\delta*} \rightarrow p_\sigma$] transitions would occur at similar energies. The spin-allowed and spin-forbidden [$d_{\sigma*} \rightarrow p_\sigma$] and [$d_{\delta*} \rightarrow p_\sigma$] transitions have been identified in the low temperature electronic absorption spectra of these two complexes. The emissions of **8** (694 nm) and **9** (787 nm) in 2-methyltetrahydrofuran glass at 77 K have been assigned to originate from a metal-centred $^3[(d_{\sigma*})^1(p_\sigma)^1]$ excited state. This report highlighted the importance of d^{10} metal–metal interactions to the photophysical properties of this class of complexes.

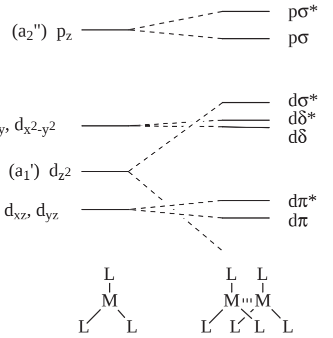


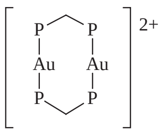
Fig. 1 A molecular orbital diagram for mononuclear d^{10} ML$_3$ and dinuclear d^{10}–d^{10} (ML$_3$)$_2$ complexes. Reprinted with permission from P. D. Harvey and H. B. Gray, *J. Am. Chem. Soc.*, 1988, **110**, 2145. Copyright 1988 American Chemical Society.

The dinuclear gold(I) complex $[Au_2(dppm)_2]^{2+}$ (**10**) displays strong luminescence with an emission maximum at 570 nm (τ_o = 21 ± 1 μs) in acetonitrile at 298 K.[9,10] For a linear P–Au–P unit with $D_{\infty h}$ symmetry, the relative energies of the occupied 5d orbitals of Au(I) are in the order: d_{xz}, d_{xy} < d_{z^2}, d_{yz} < $d_{x^2-y^2}$ (P–Au–P vector is taken as the *y*-axis). The lowest unoccupied orbital is 6p$_z$. The formation of (P–Au–P)$_2$ (under D_{2h} symmetry) from two P–Au–P units is associated with the interactions between these two sets of orbitals. Interactions between the two 5d_{z^2} orbitals and two 6p$_z$ orbitals result in the formation of d_σ, $d_{\sigma*}$, p_σ and $p_{\sigma*}$, respectively (Au–Au vector is taken as the *z*-axis). Besides, two sets of d_π and $d_{\pi*}$ orbitals are also generated by the interactions between the two 5d_{xz} and the two 5d_{yz} orbitals. Similarly, the interactions among the two 5d_{xy} and two 5$d_{x^2-y^2}$ orbitals also result in the formation of two sets of d_δ and $d_{\delta*}$ orbitals. Although the energy level of 5$d_{x^2-y^2}$ is higher than that of 5d_{z^2} in the P–Au–P building block, the interaction between two 5d_{z^2} is much more efficient and the splitting between d_σ and $d_{\sigma*}$ is larger than that between d_δ and $d_{\delta*}$ (from two 5$d_{x^2-y^2}$). The electronic absorption spectrum of **10** displays two absorption bands at 267 nm (ε = 19870 dm^3 mol^{-1} cm^{-1}) and 292 nm (ε = 29120 dm^3 mol^{-1} cm^{-1}). The latter has been assigned to the $^1[d_{\sigma*} \rightarrow p_\sigma]$ transition. This absorption occurs at a lower energy than that of the mononuclear species and this is in line with the short Au···Au distance of 2.931(1) Å observed in $[Au_2(dppm)_2](BF_4)_2$.[9]

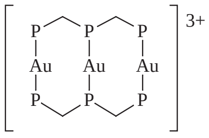
The origin of the phosphorescent state of complex **10** is controversial. From SCF-Xα-SW molecular orbital calculations, Fackler and co-workers suggested that the HOMO of the model compound $[Au_2(H_2PCH_2PH_2)_2]^{2+}$ is $d_{\sigma*}$ and the emission of **10** originates from a $^3[(d_{\sigma*})^1(p_\sigma)^1]$ excited state.[9]

However, based on the large Stokes shift between the $^1[d_{\sigma*} \rightarrow p_\sigma]$ transition (292 nm) and the emission energy (570 nm), Che and co-workers proposed that the HOMO should be the $d_{\delta*}$ orbital and the lowest-lying phosphorescent state of **10** to be $^3[(d_{\delta*})^1(p_\sigma)^1]$ in nature.[10]

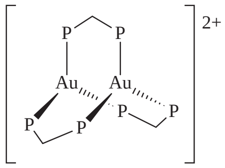
As gold(I) centres can adopt a three-coordinate geometry, a related system using an additional bidentate phosphine ligand has been studied. Complexes of this kind are structural analogues of **8** and **9**. Besides, the effects of the Au–Au interactions have also been examined by the addition of an extra P–Au–P unit and the triphosphine ligand bis(dimethylphosphinomethyl)methylphosphine, dmmp, was chosen to serve this purpose by binding three Au(I) centres together. The photophysical and photochemical properties of the dinuclear $[Au_2(dmpm)_n]^{2+}$ [n = 2 (**11a**),[11] 3 (**11b**)[12]] [dmpm = bis(dimethylphosphino)methane] and trinuclear $[Au_3(dmmp)_n]^{3+}$ [n = 2 (**12a**),[11] 3 (**12b**)[12a]] have been reported. The electronic absorption spectra of **11a** and **12a** exhibit intense absorption bands at 269 and 315 nm, assigned to spin-allowed $^1[d_{\sigma*} \rightarrow p_\sigma]$ transitions. A red shift (*ca.* 0.67 eV) in the transition energy from the dinuclear to trinuclear species is in line with the decreasing energy gap between the $d_{\sigma*}$ and p_σ orbitals upon addition of a P–Au–P unit. A similar observation has also been found for the corresponding three-coordinate species (**11b** and **12b** absorb at 258[12b] and 301 nm,[12a] respectively), with a red shift of *ca.* 0.69 eV from the dinuclear to the trinuclear species.



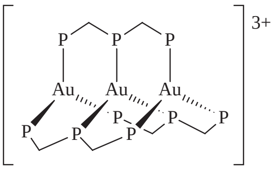
11a



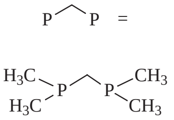
12a

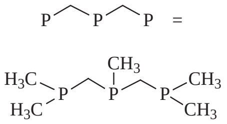


11b



12b





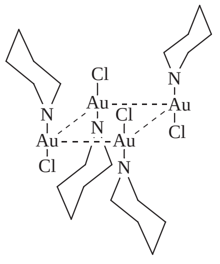
These four polynuclear gold(I) phosphine complexes are strongly luminescent. The two-coordinate complexes show dual luminescence in acetonitrile solution. High-energy emission bands at 455 nm (τ_o = 1.2 ± 0.2 μs) for **11a** and 467 nm (τ_o = 1.6 ± 0.2 μs) for **12a** are observed. In addition, the complexes also show long-lived emission bands at lower energy. The emission bands of **11a** (555 nm, τ_o = 2.8 ± 0.2 μs) and **12a** (580 nm, τ_o = 7.0 ± 0.5 μs) have been suggested to be derived from the $[(d_{\delta*})^1(p_\sigma)^1]$ triplet state. The emission spectra of the three-coordinate complexes **11b** and **12b** in acetonitrile show a single emission band at 588 nm (τ_o = 0.85 ± 0.10 μs) and 625 nm (τ_o = 2.2 ± 0.2 μs), respectively. The relatively small red shift (0.13 eV) from the dinuclear to trinuclear complexes is thought to be supportive of a $^3[(d_{\delta*})^1(p_\sigma)^1]$ excited state.

It is interesting to note that the lifetime and the luminescence quantum yield of the low-energy emission of the two-coordinate $[Au_2(dppm)_2]^{2+}$ complex show a strong solvent dependence.[10] Recent resonance Raman studies and MO calculations showed that the analogous complex $[Au_2(dcpm)_2](ClO_4)_2$ exhibits interactions with the solvent or anion weakly in the ground state but strongly in the excited state.[10d] The involvement of an exciplex formation in the luminescence behaviour of dinuclear Au(I) complexes with bridging phosphine ligands has been suggested.

2.2 Effects of d^{10} metal–metal interactions

A remarkable feature of the molecular structures of polynuclear d^{10} metal complexes is the observation of a short metal–metal distance. Theoretically, in the absence of (n + 1)s and (n + 1)p functions, interactions between the closed-shell d^{10} centres are repulsive in nature. However, configuration mixing of the filled nd-orbitals with the empty orbitals derived from higher energy (n + 1)s and (n + 1)p orbitals has been proposed to establish some weak metal–metal interactions. In 1988, Hoffmann and co-workers examined the presence of Cu–Cu interactions in the model complex $[Cu_3(H\text{–}NNNNN\text{–}H)_3]$ (**13**) using extended Hückel molecular orbital (EHMO) calculations.[13] The overlap population between the copper(I) centres was +0.127 when 4s and 4p orbitals of copper were included in the calculations. It has been concluded that there are attractive interactions between the metal centres as a result of $3d_{z^2} + 4s + 4p_z$ mixing.

The photophysical properties of polynuclear d^{10} metal complexes have been correlated to their electronic structures based on similar arguments. This can be exemplified by a system reported by Vogler and Kunkely.[14] The four gold(I) centres in $[Au_4Cl_4(piperidine)_4]$ (**14**) are arranged in a square array, with a Au···Au separation of 3.301 Å. A qualitative molecular orbital diagram for the tetranuclear gold(I) moiety with a D_{4h} symmetry is outlined in Fig. 2. Each gold atom contributes one 5d and one 6s orbital to the σ-interactions with its closest neighbours. Configuration mixing between the e_u orbitals derived from the filled 5d orbitals and those derived



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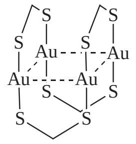

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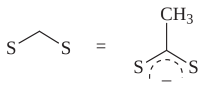


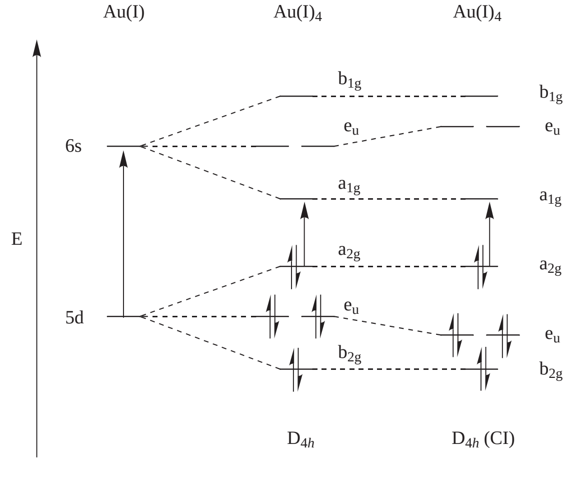


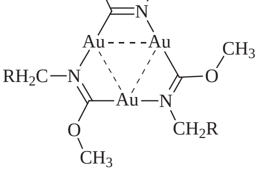
Fig. 2 A qualitative molecular orbital diagram for the tetranuclear gold(I) moiety with a D_{4h} symmetry. Reprinted from *Chem. Phys. Lett.*, **150**, A. Vogler and H. Kunkely, p. 135, Copyright 1988, with permission from Elsevier Science.

from the empty 6s orbitals has been suggested to establish some metal–metal bonding character. The 77 K EtOH glass emission of this complex (700 nm) occurs at a higher energy than that of another tetranuclear Au(I) complex $[\mathrm{Au_4(dta)_4}]$ (**15**) ($\mathrm{dta^-}$ = dithioacetate) (743 nm) in which the Au(I) centres are also arranged in a square geometry. This observation has been explained by a shorter metal–metal distance in the dithioacetate complex (3.01 Å) and hence stronger Au–Au interactions. The emissions of the complexes have also been assigned to be derived from a $^3[(a_{2g})^1(a_{1g})^1]$ d-s state.

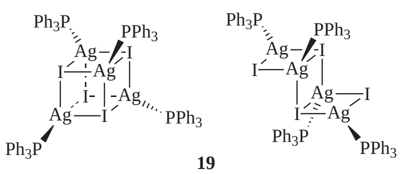
Fackler and co-workers reported another system illustrating the importance of metal–metal separation to the photophysical properties of this class of complexes. The solid-state emissions of a series of mononuclear gold(I) thiolate complexes [L–Au–SR] with phosphine ligands L at 77 K occur over a wide energy range (413–702 nm).[15] The origin of the emission has been ascribed to a LMCT $[\mathrm{RS^-} \rightarrow \mathrm{Au}]$ triplet state. Lower emission energy is observed for those with electron-donating substituents on the phenyl ring of the thiolate ligand and those with short intermolecular Au···Au distances. The excited state for those complexes with short Au···Au contacts has been best described as ligand-to-metal–metal charge-transfer (LMMCT) in nature.

Eisenberg and co-workers reported an interesting example that also demonstrates the influence of gold–gold separations on the photophysical properties of this class of complexes. The bright orange crystals of $[\mathrm{Au_2\{S_2CN(C_5H_{11})_2\}_2}]\cdot\mathrm{DMSO}$ (**17a**) show strong photoluminescence with a broad emission peak at 631 nm.[16] After this solid was left in air for several days or *in vacuo* for several hours, it became colourless and non-emissive. This colourless crystal (**17b**) has also been prepared by crystallisation of the orange complex in *n*-propyl alcohol–benzene. The X-ray crystal structures of these two crystals revealed a similar gold(I) dimer with intramolecular Au···Au separation of *ca*. 2.9617(7) and 2.7653(3) Å for the orange and colourless crystals, respectively. The most remarkable difference is the intermolecular Au···Au distance. The orange crystal shows an intermolecular Au···Au separation of 2.7690(7) Å and the colourless one 8.135 Å. The orange colour of the solvated crystal and its luminescence have been suggested to arise from short intermolecular Au···Au contacts. Thin films of the gold(I) complex have been prepared by coating a $\mathrm{CH_2Cl_2}$ solution of the complex onto quartz disks. The emission of the orange film saturated with $\mathrm{CH_2Cl_2}$ occurs at 630 nm. When the film is heated to 50 °C for 10 seconds, the orange colour and the emission properties of the film disappear. Exposure of the dried film to $\mathrm{CH_2Cl_2}$ or acetone vapours reverts the orange colour and the luminescence.

Balch and co-workers reported the interesting solvent-induced luminescence properties of the organometallic complex $[\mathrm{Au_3(\mu\text{-}CH_3N{=}COCH_3)_3}]$ (**18a**).[17] When a solvent such as chloroform is in contact with the solid sample of the complex which has been irradiated with UV light, intense and long-lived yellow luminescence is observed. X-Ray crystallographic studies reveal a triangular array of gold(I) centres with a Au···Au separation of 3.308(2) Å. The triangular units also exhibit some stacking interactions with an intermolecular Au···Au distance of 3.346(1) Å. A related complex $[\mathrm{Au_3(\mu\text{-}C_6H_5CH_2N{=}COCH_3)_3}]$ (**18b**) with Au···Au separation > 3.6 Å does not show similar solvent-induced luminescence behaviour. The supramolecular aggregation has been proposed to be important for the liquid contact triggered luminescence behaviour of **18a**.



18a: R = H
18b: R = Ph



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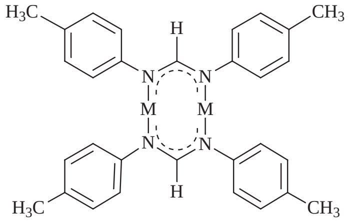
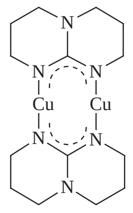
Apart from metal–metal separations, the arrangement of the metal centres and the structure of the excited state molecule are also important to the photoluminescence behaviour of polynuclear $\mathrm{d^{10}}$ metal complexes. The luminescence of the cube and chair isomeric forms of $[\mathrm{Ag_4I_4(PPh_3)_4}]$ (**19**) has been assigned to originate from a 4d → 5s silver-centred state modified by metal–metal interactions.[18] Interestingly, the solid sample of the cube form (455 nm) emits at a lower energy than that of the chair form (418 nm) at 12 K, although the former (3.12 Å) has a slightly longer Ag–Ag separation than the latter (3.09 Å). The lower emission energy of the cube isomer has been attributed to the higher delocalisation over the 4d and 5s orbitals of the silver(I) centres, as each silver has three silver centres as its closest neighbours.

The existence of a metal–metal bond between two $\mathrm{d^{10}}$ metal centres has been the subject of increasing attention. Cotton and co-workers recently carried out SCF Xα-SW molecular orbital calculations to investigate the possibility of metal–metal bonding in the complexes $[\mathrm{M_2(form)_2}]$ [M = Cu (**20a**), Ag (**20b**)] ($\mathrm{form^-}$ = *N*,*N*′-di-*p*-tolylformamidinate), both of which have short metal–metal separations [$d_{\mathrm{Cu\cdots Cu}}$ = 2.497(2) Å; $d_{\mathrm{Ag\cdots Ag}}$ = 2.705(1) Å].[19] The calculations have been performed on the model complex $[\mathrm{Cu_2(HNCHNH)_2}]$ (**21**), and it was concluded by these authors that there is no net metal–metal bond formation in this complex and the silver(I) counterpart. Recently, the same group also reported the very short Cu–Cu distance [2.4527(10) Å] observed in the complex $[\mathrm{Cu_2(hpp)_2}]$ (**22**) {$\mathrm{hpp^-}$ = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate}.[20] The density functional theory (DFT) calculations revealed five Cu–Cu bonding orbitals (essentially d character with negligible s and p characters) and their anti-bonding counterparts in **21**. It was concluded that there is no Cu–Cu bond and the short Cu–Cu distance is a result of the strong Cu–N bonds and the small bite angle of the bridging ligand.



20a: M = Cu
20b: M = Ag



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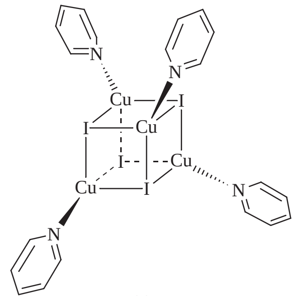

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The observation of short d^{10}–d^{10} separations does not necessarily mean that there is a bond established between the metal centres and the effects of the bridging ligands should be taken into account. However, for gold(I) systems, short Au–Au separations are very commonly observed. This has been coined as 'aurophilicity' by Schmidbaur.[21] The strong and unique tendency for gold to form dimers, oligomers and polymers originates from the relativistic effects. For detailed comparisons of different calculation methods and experimental data on closed-shell interactions, readers are referred to an exhaustive review by Pyykkö.[22]

2.3 Polynuclear d^{10} systems with halides and thiolates as bridging ligands

The photoluminescence properties of the tetranuclear copper(I) halide complex $[Cu_4I_4(\text{pyridine})_4]$ (**23**) and its analogues have been extensively studied by Ford and co-workers.[23,24] In general, these complexes reveal a low energy emission at 678 to 698 nm and a weaker higher energy emission at 473 to 537 nm in toluene solution at 294 K. The high-energy emission is only observed for the complexes with aromatic amine ligands but not with aliphatic amine or tri-*n*-butylphosphine ligands. This, together with the energy trend observed for the substituted pyridine ligands, suggests that the high-energy emission is associated with a metal-to-ligand $[Cu \rightarrow \pi^*(\text{pyridine})]$ or ligand-to-ligand $[I^- \rightarrow \pi^*(\text{pyridine})]$ charge-transfer excited state. The low energy emission of this class of complexes is characteristic of the Cu_4I_4 core and independent of the identity of the pyridine or amine ligands. This low energy emission has been suggested to originate from a cluster-centred excited state in which metal–metal interactions are enhanced by depopulation of a d_{σ^*}(Cu–Cu) anti-bonding orbital and population of a s_{σ}(Cu–Cu) bonding orbital. In other words, the complex undergoes a significant shrinking upon excitation. This is in line with a very large Stokes shift from the excitation maximum to the low energy emission maximum. For example, the Stokes shift is 1.64 μm^{-1} for **23** in toluene.

Ab initio molecular orbital calculations indicated that the highest occupied molecular orbitals in **23** and the model compound $[Cu_4I_4(NH_3)_4]$ (**23a**) are largely composed of iodide p orbitals,[25] suggestive of a ligand-to-ligand charge-transfer $[I^- \rightarrow \pi^*(\text{pyridine})]$ XLCT excited state for the high-energy emission (XLCT = halide-to-pyridine ligand charge transfer). The results of more thorough calculations which include the factors arising from the electronic reorganisation showed that the origin of the emitting state for the low energy emission is an admixture of Cu_4 [3d $\rightarrow$ 4s] and XMCT [halide $\rightarrow$ Cu_4] character delocalised over the Cu_4I_4 core.

Recently, the interesting luminescence response of the polynuclear material $[CuI(4\text{-picoline})]_x$ [x = 4 (**24a**) or ∞ (**24b**)] to volatile organic compounds has been reported.[26] The polymer **24b** emits at 426 nm at room temperature. Addition of a very small amount of toluene to this solid results in the disappearance of the blue luminescence but the appearance of yellow luminescence from the solid with an emission maximum at 578 nm (Fig. 3). This low energy luminescence has been assigned to arise from a mixed iodide-to-copper charge-transfer and (3d $\rightarrow$ 4s/4p) cluster-centred excited state, characteristic of the tetranuclear cubane molecule **24a**. The reversibility of this system has also been justified by the appearance of blue luminescence when **24a** is exposed to a small amount of liquid pentane over the course of 2 hours at room temperature. This colour change in the photoluminescence also occurs when the solid samples of the polymer and cubane are exposed to toluene and pentane vapours, respectively. Therefore, the structural changes of this material in contact with two different organic solvents can be monitored by luminescence measurements.

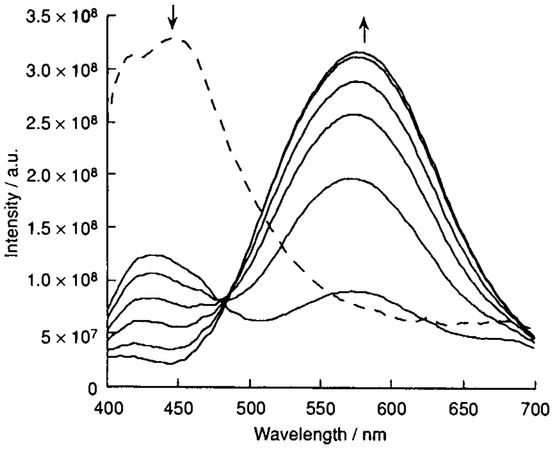
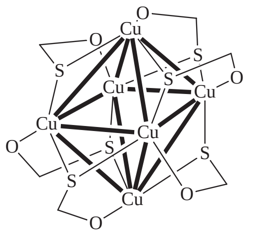


Fig. 3 Temporal emission spectra of solid **24b** at ambient temperature before (---) and after (—) exposure to liquid toluene. Spectra were collected every 5 min (arrows indicate sequence of data collection). Reproduced with permission from ref. 26.

Thiolates are well known to possess a variety of bonding characteristics and there have been a number of polynuclear d^{10} metal complexes with thiolates as the bridging ligands. Ford and Vogler reported the photophysical properties of hexanuclear copper(I) and silver(I) thiolate clusters, $[Cu_6(\text{mtc})_6]$ (**25**), $[Ag_6(\text{mtc})_6]$ (**26**) and $[Ag_6(\text{dtc})_6]$ (**27**) (mtc$^-$ = di-*n*-propylmonothiocarbamate, dtc$^-$ = di-*n*-propyldithiocarbamate).[23] At 77 K, the solid samples of **25**, **26** and **27** emit at 767, 644 and 545 nm, respectively. An assignment of intraligand (IL) π–π^*(mtc or dtc) for the excited state has been excluded on the basis of their emission at such a low energy region. Also, the π^* levels for the thiolate ligands are too high to justify a MLCT assignment for the lowest-lying excited state. A blue shift of only *ca.* 0.31 eV in the solid-state emission of the complexes **25** to **26** also precludes a MLCT excited-state assignment. The excited state of these luminescent hexanuclear copper(I) and silver(I) thiolate complexes has been assigned to a LMCT [mtc$^-$/dtc$^-$ $\rightarrow$ Cu_6 or Ag_6] mixed with a cluster-centred Cu_6 or Ag_6 (d-s) triplet state.



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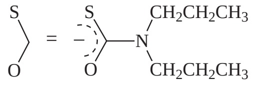


3 Polynuclear copper(I), silver(I) and gold(I) chalcogenides

Transition metal chalcogenides exist in a huge variety of molecular structures. The bonding modes of chalcogenides are very diverse. They commonly act as a μ_2-, μ_3- and μ_4-bridging ligand but a μ_8-bridging mode has also been observed. In view of this, we believe that chalcogens are attractive candidates in the preparation of polynuclear d^{10} metal systems. Although the photophysical properties of semiconducting insoluble d^{10} metal chalcogenide materials have been receiving a lot of attention, related studies on the photoluminescence behaviour of soluble molecular species are extremely limited.

In 1993, we successfully isolated the first luminescent tetranuclear copper(I) sulfido complex $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$ (**28a**).[27] The X-ray crystal structure of the complex reveals a μ_4-bridging sulfido ligand (Fig. 4). The four copper(I) centres form a distorted rectangle with Cu···Cu separations of 2.869(1) and 3.128(1) Å.

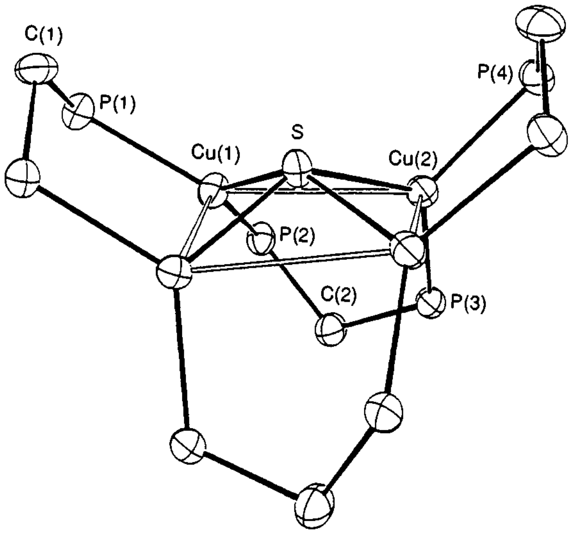


Fig. 4 The X-ray crystal structure of **28a**. Reproduced with permission from ref. 27.

The complex displays extremely strong and long-lived emissions in the solid state and in fluid solutions under ambient conditions. For example, the solid sample emits at 579 nm with a lifetime of 3.6 ± 0.3 μs at 298 K. In acetone solution, the complex also displays a very intense and long-lived emission at 622 nm ($\tau_o = 8.1 \pm 0.4$ μs, $\Phi = 0.22$) at 298 K. The large Stokes shifts and the long lifetimes suggest that the emission is phosphorescence. In view of the strong σ-donating properties of the sulfido ligand, we tentatively suggested that the photoluminescence properties arise from a ligand-to-metal charge-transfer LMCT $[S^{2-} \rightarrow Cu_4]$ excited state. Although the relatively long Cu···Cu distances exclude the possibility of substantial metal–metal interactions, the mixing of a copper-centred (3d → 4s) state into the LMCT excited state is also possible.

In order to gain more insight into the nature of the excited state of this complex, the photophysical studies on structurally related complexes were explored. Recently, we successfully isolated the copper(I) selenide analogue $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+}$ (**28b**) as well as the dtpm analogue $[Cu_4(\mu\text{-dtpm})_4(\mu_4\text{-S})]^{2+}$ (**28c**) {dtpm = bis[bis(4-methylphenyl)phosphino]methane}.[27,28] The silver(I) counterparts with different chalcogenide ligands $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$ (**29a**), $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-Se})]^{2+}$ (**29b**) and $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-Te})]^{2+}$ (**29c**) have also been synthesised and structurally characterised.[27]

The occurrence of the room-temperature solid-state emission of **28b** (595 nm) at a lower energy than that of the sulfide analogue **28a** (579 nm) supports the assignment of an excited state with substantial LMCT character. A similar trend in the solid-state emission energies of the silver(I) analogues has also been observed. At 298 K, the solid samples of the complexes $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ emit at 516 (E = S), 527 (E = Se) and 574 nm (E = Te). This energy trend is in line with the ionisation energies of the chalcogens and further supports the excited-state assignment of large LMCT $[E^{2-} \rightarrow Ag_4]$ character.

Owing to the presence of low-lying empty π^* orbitals of the phenyl rings on the phosphine ligands, the possibility of a MLCT $[M_4 \rightarrow \text{phosphine}]$ and LLCT $[E^{2-} \rightarrow \text{phosphine}]$ excited state has also been considered. However, the fact that the presence of electron-donating methyl groups on the phenyl rings of the phosphine ligands in **28c** does not cause a shift of the emission to the blue compared with the dppm counterpart **28a**, disfavours the assignment of a MLCT or LLCT excited state. In addition, the small blue shift of *ca.* 0.27 eV in emission energy from $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ to $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ (E = S, Se) does not support the assignment of a MLCT state, for which the shift should be more significant.

The assignment of an excited state with a high degree of ligand-to-metal charge-transfer LMCT $[E^{2-} \rightarrow M_4]$ triplet character, mixed with a metal-centred (ds/dp) state is supported by *ab initio* molecular orbital calculations.[27] However, one should be aware that the assignments of electronic transitions between metal and/or ligand localised orbitals are only oversimplified descriptions owing to the fact that the states are usually highly mixed in nature as a result of the possible extensive orbital mixing in these complexes.

A series of oxidative quenching experiments was carried out to determine the excited-state reduction potential, $E°\{[Cu_4]^{3+}/[Cu_4]^{2+*}]\}$ of the complexes. We used a series of structurally related pyridinium ions as the quenchers. These compounds do not react with the complexes thermally under ambient conditions. The triplet states of these pyridinium ions are relatively high and the possibility of an energy-transfer quenching pathway can be excluded. These factors make them ideal candidates as oxidative quenchers. The phosphorescent state of **28a** undergoes facile electron-transfer reactions with these pyridinium acceptors. From the Stern–Volmer equation (1),

$$\tau_0/\tau = 1 + k_q\tau_0[Q] \quad (1)$$

where τ_0 and τ are the lifetimes of the excited complex in the absence and in the presence of quencher at concentration [Q], respectively, and k_q is the bimolecular quenching rate constant, we obtained a series of bimolecular quenching rate constants for the photo-induced electron-transfer reactions between the excited complex and various quenchers. The excited-state reduction potential of the complex can then be estimated by eqn. (2), where k_q' is the bimolecular quenching rate constant

$$(RT/F) \ln k_q' = (RT/F) \ln K\kappa\nu - (\lambda/4)\,[1 + (\Delta G°'/\lambda)]^2 \quad (2)$$

corrected for diffusional effects, $K = k_D/k_{-D}$, k_D and k_{-D} are the diffusion-limited rate constants, κ is the transmission coefficient, ν is the nuclear frequency, and λ is the reorganisation energy for electron transfer.

For oxidative quenching, $\Delta G°' = E°\{[Cu_4]^{3+}/[Cu_4]^{2+*}]\} - E°[Q^+/Q^0] + \omega_p - \omega_r$, where ω_p and ω_r are the respective coulombic work terms to separate the products and to bring the reactants together.

The reorganisation energy, λ, is assumed to be constant based on the consideration that the quenchers are structurally related analogues. We can determine the unknowns $E°\{[Cu_4]^{3+}/[Cu_4]^{2+*}]\}$, λ and $\ln K\kappa\nu$ by a three-parameter, non-linear least-squares fit to eqn. (2). From the oxidative quenching experiments, excited-state reduction potentials, $E°\{[Cu_4]^{3+}/[Cu_4]^{2+*}]\}$, of −1.71(10), −1.55(10) and −1.56(10) V *vs.* saturated sodium chloride calomel electrode (SSCE) have been estimated for **28a**, **28b** and **28c**, respectively. The highly negative excited-state reduction potentials suggest that the excited complexes are strongly reducing. It is interesting to note the reorganisation energies associated with these electron transfer reactions are comparatively small compared with that of the tetranuclear copper(I) iodide cluster **23**. For example, a reorganisation energy of 1.12(10) eV has been estimated for **28b**.

The photo-induced electron-transfer reactions have also been studied with nanosecond transient absorption spectroscopy. The optical arrangements for spectroscopic and kinetic measurements consist of a linear monitoring beam passing through an absorption cell with photolysis light irradiating the cell normally (Fig. 5). The transient absorption difference spectrum is obtained by the point-to-point method through the selection

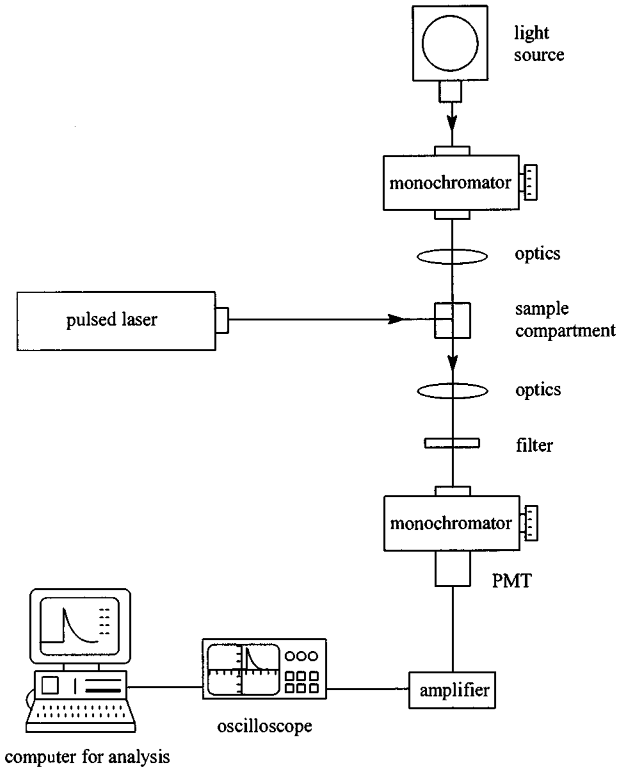


Fig. 5 The schematic layout of the instrumentation for transient optical difference spectral measurements.

of wavelength of the monitoring monochromators. The transient absorption difference spectrum for the reaction of **28a*** and 4-(methoxycarbonyl)-*N*-methylpyridinium acceptor is characterised by a sharp intense absorption at *ca.* 390 nm, a lower intensity band at 484 nm and an intense broad absorption band at *ca.* 693 nm (Fig. 6).[28] The intense band at *ca.* 390 nm is characteristic of pyridinyl radical absorption. The reaction mechanism is depicted in Scheme 1.

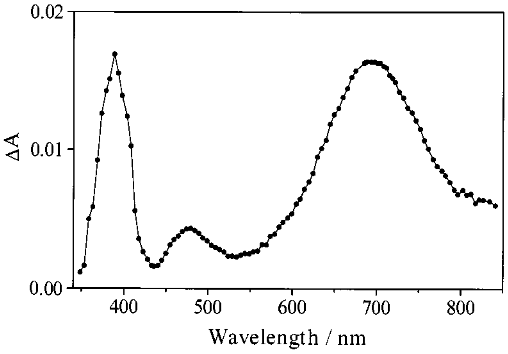
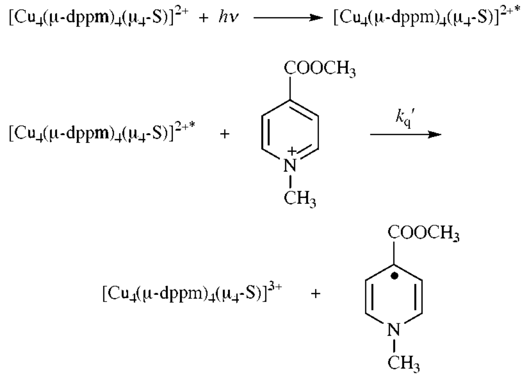


Fig. 6 A transient absorption difference spectrum recorded 10 μs after laser flash excitation of **28a** (0.27 mM) and 4-(methoxycarbonyl)-*N*-methylpyridinium hexafluorophosphate (7.93 mM) in degassed acetone (0.1 M ^{n}Bu$_4$NPF$_6$). Reprinted with permission from V. W. W. Yam, K. K. W. Lo, C. R. Wang and K. K. Cheung, *J. Phys. Chem. A*, 1997, **101**, 4666. Copyright 1997 American Chemical Society.



Scheme 1

The 484 nm and 693 nm absorption bands are characteristic of the one-electron oxidised form of the copper cluster. As the photo-induced electron-transfer reactions result in the formation of the pyridinyl radical and the oxidised form of the copper species in equal amounts, with a knowledge of the extinction coefficient of 4-(methoxycarbonyl)-*N*-methylpyridinyl radical, the extinction coefficients of the 484 nm and 693 nm bands are estimated to be 1200 and 6700 dm^3 mol^{-1} cm^{-1}, respectively. The possibility of ligand-field transitions of Cu(II) is excluded owing to the high extinction coefficients of these absorption bands. The 484 nm band is assigned to a ligand-to-metal charge-transfer LMCT [S^{2-} → Cu(II)] transition which is commonly observed for mixed-valence Cu(I,II) thiolate and Cu(II) thioether systems. The low energy absorption is assigned to an intervalence-transfer IT transition, eqn. (3).

$$\mathrm{Cu(I)Cu(I)Cu(I)Cu(II)} + h\nu \longrightarrow \mathrm{Cu(I)Cu(I)Cu(II)Cu(I)}^* \quad (3)$$

Similar intervalence-transfer transitions have also been observed in a variety of mixed-valence copper(I,II) systems. Such a transition has also been observed for **28b** and **28c** at very similar energies. This indicates that the selenide and phosphine ligands have no significant effects on this metal-centred absorption and further supports the assignment of an IT transition. The occurrence of such absorption bands at fairly high energies has also been reported in dinuclear copper complexes in which an assignment of a Cu–Cu centred [σ → σ*] transition which resulted from extensive electron delocalisation across the two copper centres has been made.

As a continuation of our efforts in the photophysical and photochemical studies of polynuclear d^{10} metal chalcogenide systems, we recently isolated a novel luminescent gold(I) sulfido complex $[Au_{12}(\mu\text{-dppm})_6(\mu_3\text{-}S)_4]^{4+}$ (**30**).[29] This high-nuclearity gold(I) sulfido complex was prepared from the reaction of $[Au_2(\mu\text{-dppm})Cl_2]$ with H_2S. X-Ray crystallographic studies show that the complex cation contains four $Au_3(\mu_3\text{-}S)$ units linked together by six bridging dppm ligands (Fig. 7). Most of the Au···Au distances are short [3.001(1) to 3.342(1) Å]. The complex displays strong luminescence upon photoexcitation in the solid state and in fluid solutions. The solid-state emissions occur at 648 and 634 nm at 298 and 77 K, respectively. In acetonitrile solution, the complex emits at 546 nm. The emission is tentatively assigned to result from a LMCT (S^{2-} → Au) excited state, which is probably mixed with a metal-centred (5d → 6s/6p) state modified by Au···Au interactions.

4 Polynuclear copper(I), silver(I) and gold(I) acetylides

Acetylides are also well known to possess widely diverse bonding modes. Apart from σ-bonding, they can also exhibit π-bonding with different metal centres. A number of coinage metal acetylide complexes have been structurally characterised and their chemical properties studied to date. However, the photophysical and photochemical properties of these compounds are yet to be fully explored. In view of this, together with the recent reports on the potential applications of transition metal acetylides as non-linear optical materials and molecular wires, we carried out photophysical and photochemical studies of a number of polynuclear copper(I), silver(I) and gold(I) acetylide complexes.

The trinuclear copper(I) acetylide complexes $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{–}Ph)_2]^+$ (**31a**) and $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}$

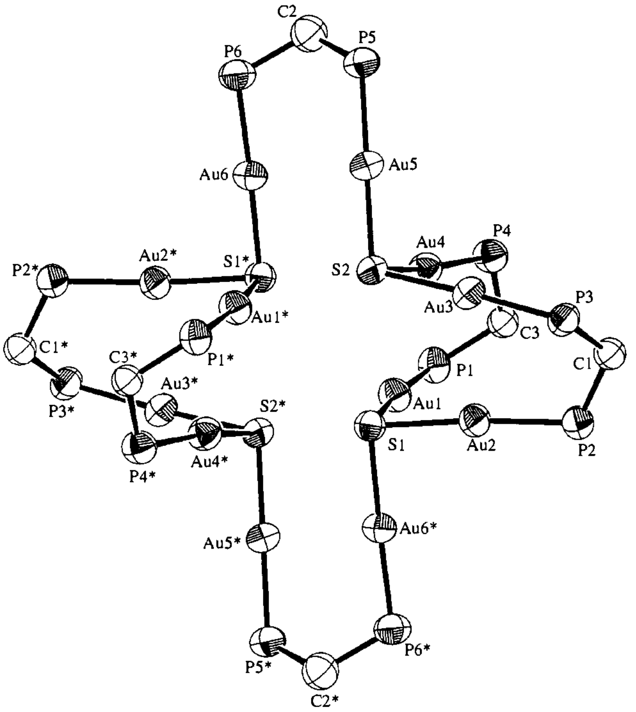
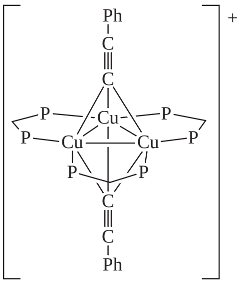
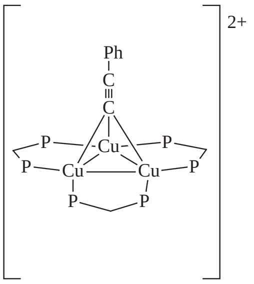


Fig. 7 The X-ray crystal structure of **30**. Reprinted with permission from V. W. W. Yam, E. C. C. Cheng and K. K. Cheung, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 197. Copyright 1999 Wiley-VCH.

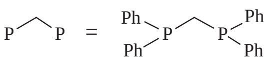
C≡C–Ph)]$^{2+}$ (**32a**) exhibit intense and long-lived luminescence upon photoexcitation.[30] For example, at 298 K, the solid-state emission of **31a** occurs at 493 nm (τ_o = 14 ± 1 μs). In acetonitrile solution, the complex emits at 494 nm (τ_o = 6.5 ± 0.6 μs). In order to gain more understanding of the excited state nature of these acetylide complexes, we prepared a series of structurally related analogues with different acetylides as the bridging ligand. These complexes are represented by the general formulae $[\mathrm{Cu_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–R})_2]^+$ [R = ^{t}Bu (**31b**), $\mathrm{C_6H_4{-}NO_2}$-4 (**31c**), $\mathrm{C_6H_4}$–Ph-4 (**31d**), $\mathrm{C_6H_4{-}OCH_3}$-4 (**31e**), $\mathrm{C_6H_4{-}NH_2}$-4 (**31f**), $^n\mathrm{C_6H_{13}}$ (**31g**)] and $[\mathrm{Cu_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–R})]^{2+}$ [R = ^{t}Bu (**32b**), $\mathrm{C_6H_4{-}NO_2}$-4 (**32c**), $\mathrm{C_6H_4}$–Ph-4 (**32d**), $\mathrm{C_6H_4{-}OCH_3}$-4 (**32e**), $\mathrm{C_6H_4{-}NH_2}$-4 (**32f**), $^n\mathrm{C_6H_{13}}$ (**32g**)].[30] Besides, a series of trinuclear copper(I) acetylide complexes with $(\mathrm{Ph_2P})_2\mathrm{N{-}R}$ (R = $\mathrm{CH_2CH_2CH_3}$, Ph, $\mathrm{C_6H_4{-}CH_3}$-4, $\mathrm{C_6H_4}$–F-4) as the bridging phosphine ligands have also been isolated.[30] They all display intense and long-lived luminescence upon photoexcitation. The complexes with electron-rich acetylides generally emit at a lower energy. For example, the emission energies of $[\mathrm{Cu_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–R})]^{2+}$ in acetone solution occur in the order: R = $\mathrm{C_6H_4{-}OCH_3}$-4 (483 nm) ≈ Ph (499 nm) > $\mathrm{C_6H_4{-}NH_2}$-4 (504, 564 nm) > ^{t}Bu (640 nm) > $^n\mathrm{C_6H_{13}}$ (650 nm). This is in line with the increasing donating ability of the acetylide ligand. Therefore, the origin of the emission has been proposed to involve substantial ^{3}LMCT [acetylide ⟶ $\mathrm{Cu_3}$] character and the possibility of a MLCT excited state has not been favoured. In view of the short Cu···Cu distances found in the trinuclear copper(I) complexes, especially in the case of the bi-capped acetylide species, a mixing of a metal-centred $3d^94s^1$ state into the lowest-lying emissive state is also possible. However, for the complexes containing acetylide ligands with strong electron-withdrawing groups such as 4-nitrophenylacetylide, the emission bands are very similar to those of the free acetylenes. This is suggestive of an involvement of some ligand-centred π–π*(acetylide) character in the emissive state of these complexes.



31a

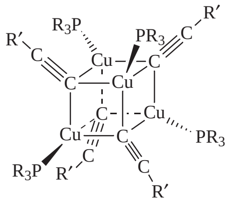


32a



The luminescence properties of the silver(I) counterparts, $[\mathrm{Ag_3}(\mu\text{-P–P})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–R})]^{2+}$ {P–P = dppm, R = Ph (**34a**), $\mathrm{C_6H_4{-}OCH_3}$-4 (**34b**), $\mathrm{C_6H_4{-}NO_2}$-4 (**34c**); P–P = $(\mathrm{Ph_2P})_2\mathrm{N{-}CH_2CH_2CH_3}$, R = Ph (**34d**)} and $[\mathrm{Ag_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–}\mathrm{C_6H_4{-}NO_2}\text{-4})_2]^+$ (**34e**) have been investigated.[31] The complexes are structurally analogous to the trinuclear copper(I) acetylides. The emission spectra of some of the complexes exhibit vibronic-structured bands at both 298 and 77 K. Progressional spacings of *ca.* 1880–2080 $\mathrm{cm^{-1}}$ are observed and attributed to the ground-state stretching frequencies of the acetylide moieties. In some cases, additional vibrational progressions with spacings of *ca.* 1450–1600 $\mathrm{cm^{-1}}$, typical of the ground-state stretching frequencies of the aromatic rings, are also observed. The emission has been assigned to originate from a ^{3}LMCT [acetylide ⟶ $\mathrm{Ag_3}$] state, and probably mixed with a silver-centred (ds/dp) triplet state. A MLCT [Cu/Ag ⟶ π*(acetylide)] excited state is ruled out based on the small blue shift in energy from **32a** and **32e** to the respective **34a** and **34b**, in view of the large difference (1.19 eV) between the ionisation energies of $\mathrm{Cu^+(g)}$ and $\mathrm{Ag^+(g)}$. However, the mixing of an ^{3}IL π–π*(acetylide) state is also possible, particularly in the case of complexes with the less electron-rich acetylides, in view of the exceptionally long lifetime and the low-lying π* orbitals of these acetylides.

A series of tetranuclear copper(I) acetylide complexes $[\mathrm{Cu_4(PR_3)_4}(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–R}')_4]$ (**35**) also exhibit rich photophysical properties.[30] The excited state for the low energy emissions of these complexes at *ca.* 620 nm bears a large copper cluster-centred (d-s) character and is probably mixed with some LMCT [acetylide ⟶ $\mathrm{Cu_4}$] character.



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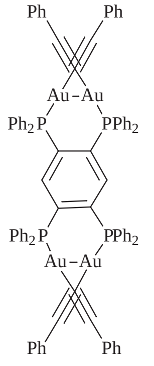

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In an attempt to prepare a trinuclear copper(I) complex with trimethylsilylacetylide as the bridging ligand, which we believed could serve as a precursor for oligomeric and polymeric copper(I) acetylides based on the trinuclear $\mathrm{Cu_3}$ core, we isolated a novel tetranuclear copper(I) complex $[\mathrm{Cu_4}(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1,\eta^2\text{-C}{\equiv}\text{C})]^{2+}$ (**36**) from the reaction of $[\mathrm{Cu_2}(\mu\text{-dppm})_2(\mathrm{CH_3CN})_2]^{2+}$ with trimethylsilylacetylene and *n*-butyllithium.[32] X-Ray crystallographic studies reveal an acetylido ligand bridging four copper(I) centres with both η^1 and η^2 bonding modes (Fig. 8). The tetranuclear copper(I) acetylide complex exhibits strong and long-lived greenish yellow emis-

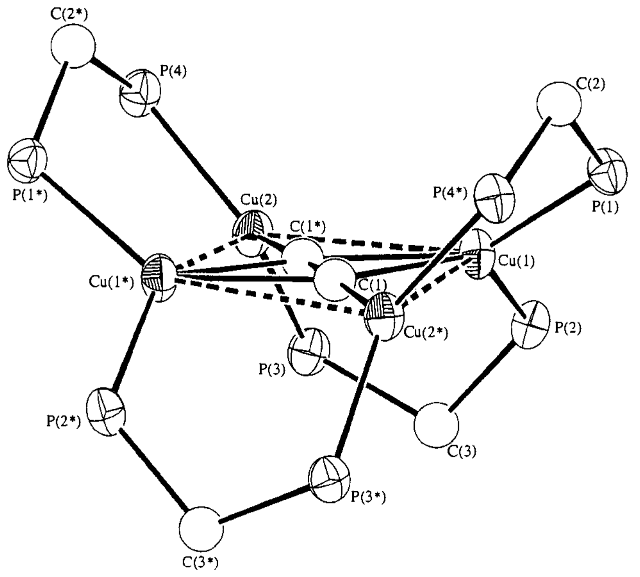


Fig. 8 The X-ray crystal structure of **36**. Reprinted with permission from V. W. W. Yam, W. K. M. Fung and K. K. Cheung, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1100. Copyright 1996 Wiley-VCH.

sion upon photoexcitation. The solid sample emits at 509 nm (τ_o = 9.8 μs) and 551 nm at 298 and 77 K, respectively. In acetone solution, the intense and long-lived emission occurs at 562 nm (τ_o = 16.0 μs, Φ = 0.22). The emission has been assigned to originate from an excited state of substantial ^{3}LMCT [$(C{\equiv}C)^{2-} \rightarrow Cu_4$] character in view of the strong σ-donating properties of the acetylide.

In order to demonstrate that the copper(I) and silver(I) acetylides are attractive building blocks for oligomeric and polymeric luminescent rigid-rod materials, we employed 1,4-diethynylbenzene as the bridging ligand to link two M_3 units together. Hexanuclear copper(I) and silver(I) acetylide complexes [$M_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{–}C_6H_4\text{–}C{\equiv}C\text{-}4)M_3(\mu\text{-dppm})_3]^{4+}$ [M = Cu (**37**), Ag (**38**)] have been synthesised and their photophysical properties studied.[33] The X-ray crystal structure of **37** is illustrated in Fig. 9. Upon photoexcitation, the complexes show strong orange yellow to green luminescence. A blue-shift in the solid-state emission energy at 77 K on going from the copper(I) complex **37** (582 nm) to the silver(I) complex **38** (515 nm) suggests that the excited states of the complexes bear a substantial ^{3}LMCT [acetylide → Cu/Ag] character, probably mixed with a metal-centred d-s triplet state. Besides, owing to the observation of highly structured emission bands and the significantly long lifetimes, an involvement of a ligand-centred π–π*(acetylide) excited state is also possible. Again, one should be aware that the states are usually highly mixed in nature in these complexes as a result of the possible extensive orbital mixing commonly observed in these systems.

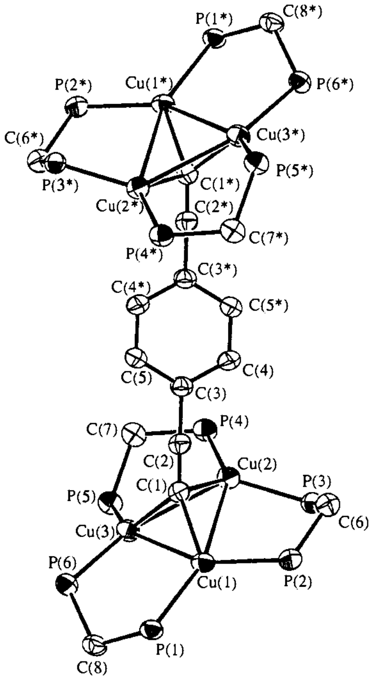


Fig. 9 The X-ray crystal structure of **37**. Reproduced with permission from ref. 33.

These luminescent polynuclear copper(I) acetylide complexes possess rich photoredox chemistry.[30,32,34] For example, the emission of **36** is quenched in the presence of a series of structurally related pyridinium ions.[32] The dependence of the bimolecular quenching rate constants on the reduction potentials of the pyridinium quenchers suggests that the quenching mechanism is oxidative electron-transfer in nature. An excited-state reduction potential, $E°\{[Cu_4]^{3+}/[Cu_4]^{2+*}\}$, of −1.77 V ($\lambda$ = 1.36 eV) *vs.* SSCE has been estimated for **36***, indicative of the strong reducing power of the photoexcited complex.

The photo-induced electron transfer behaviour has also been established by nanosecond transient absorption spectroscopy.[34] A typical transient absorption difference spectrum recorded 10 μs after laser flash excitation of **31a** (0.05 mM) and 4-(methoxycarbonyl)-*N*-methylpyridinium hexafluorophosphate (13 mM) in degassed acetonitrile (0.1 M ^{n}Bu$_4$NPF$_6$) is shown in Fig. 10.

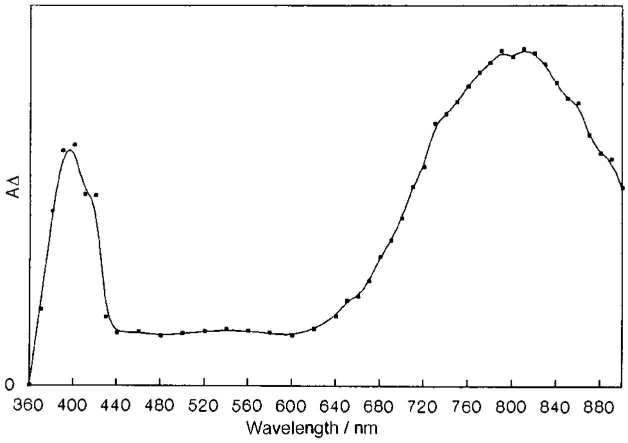


Fig. 10 A transient absorption difference spectrum recorded 10 μs after laser flash excitation of **31a** (0.05 mM) and 4-(methoxycarbonyl)-*N*-methylpyridinium hexafluorophosphate (13 mM) in degassed acetonitrile (0.1 M ^{n}Bu$_4$NPF$_6$). Reprinted with permission from V. W. W. Yam, W. K. Lee, P. K. Y. Yeung and D. Phillips, *J. Phys. Chem.*, 1994, **98**, 7545. Copyright 1994 American Chemical Society.

The 400 nm absorption band is characteristic of the pyridinyl radical. The reaction involves the reduction of the pyridinium cation to the pyridinyl radical, while **31a*** is oxidised to the mixed-valence species [Cu(I)Cu(I)Cu(II)]$^{2+}$. The absorption at *ca.* 810 nm (ε = 9940 dm^3 mol^{-1} cm^{-1}) has been suggested to arise from the intervalence-transfer transition of the mixed-valence Cu(I)Cu(I)Cu(II) species [eqn. (4)]. Similar low

$$\mathrm{Cu(I)Cu(I)Cu(II)} + h\nu \rightarrow \mathrm{Cu(I)Cu(II)Cu(I)}^* \qquad (4)$$

energy absorption bands have also been observed for the other polynuclear copper(I) acetylide complexes as well as the tetranuclear copper(I) chalcogenide complexes **28a**, **28b** and **28c** with different pyridinium acceptors.

Owing to the occurrence of short Au···Au contacts, there are a lot of interesting molecular structures of polynuclear gold(I) acetylides. The diphenylphosphine units of the ligand 1,2,4,5-tetrakis(diphenylphosphino)benzene (tppb) are arranged in a radial orientation. However, X-ray crystallographic studies on [$Au_4(tppb)(C{\equiv}C\text{–}Ph)_4$] (**39**) reveal an intramolecular gold···gold separation of 3.1541(4) Å.[35] This results in the arrangement of the two adjacent Au(C≡C–Ph) units in a crossed geometry. The emission of the solid sample at 298 K occurs at 611 nm ($\lambda_{\text{excitation}}$ = 450 nm, τ_o = 0.57 μs) and has been assigned to originate from a $^3[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{Ph}_{\text{bridge}})]$ excited state.

Dinuclear and trinuclear gold(I) acetylides, $[\text{Au}_2(\text{dmpm})(\text{C}{\equiv}\text{C–R})_2]$ [R = Ph (**40a**), $\text{C}_6\text{H}_4\text{–OCH}_3\text{-4}$ (**40b**)] and $[\text{Au}_3(\text{dmmp})(\text{C}{\equiv}\text{C–R})_3]$ [R = Ph (**41a**), $\text{C}_6\text{H}_4\text{–OCH}_3\text{-4}$ (**41b**)] with bridging phosphine ligands have been reported.[36] The solid-state emissions of the acetylide complexes **40a**, **40b**, **41a** and **41b** occur at 490, 521, 538 and 539 nm, respectively. The emission energy shows a red shift from the dimer to the trimer but is relatively insensitive to the methoxy substituent on the phenylacetylide ligand. In view of this and the large Stokes shifts observed, the excited state has been assigned to be $^3[(d_{\delta^*})^1(p_\sigma)^1]$ in origin. On the other hand, the X-ray crystal structure of $[\text{Au}_2(\text{dppe})(\text{C}{\equiv}\text{C–Ph})_2]$ (**42**) [dppe = 1,2-bis(diphenylphosphino)ethane] revealed an intermolecular Au···Au separation of 3.153 Å.[36] The emission (550 nm) observed for the complex in the solid state at 298 K has been suggested to be derived from a $^3[(d_{\delta^*})^1(p_\sigma)^1]$ excited state.

5 Applications of luminescent polynuclear d^{10} metal complexes

As mentioned in previous sections, one of the most remarkable characteristics of luminescent polynuclear d^{10} metal complexes is their rich photoredox chemistry. In fact, many systems have been found to possess excited states that are highly reducing. This provides a possibility of utilising these complexes as a photoactive reagent in different areas of applied science. The interactions between transition metal complexes and DNA have been the focus of enormous attention. Studies in this area are important in the design of antitumor drugs as well as in the development of photodynamic therapeutic agents. Besides, gold compounds have recently been used clinically for treating rheumatoid arthritis and have been shown to exhibit cytotoxic activities. We envisage that luminescent polynuclear d^{10} metal complexes can be explored as photocleavage reagents for DNA owing to their highly reactive excited state. Recently, we demonstrated the photolytic cleavage of double-stranded pBR322 plasmid DNA by the trinuclear Au(I) complex **12a**.[37] Irradiation of an aqueous solution of the complex and the plasmid DNA at λ > 350 nm in the presence of oxygen causes the photocleavage of the supercoiled form of pBR322 to the linearised form. We proposed that the strongly reducing and long-lived excited complex **12a*** reacts with oxygen, leading to the formation of superoxide radical, reaction (5). Addition

$$[\text{Au}_3]^{3+*} + \text{O}_2 \rightarrow [\text{Au}_3]^{4+} + \text{O}_2^{\cdot-} \qquad (5)$$

of superoxide dismutase to the reaction mixture results in some inhibition of the photocleavage of DNA, suggesting that superoxide radical is responsible for the cleavage. From a series of quenching experiments, it has been found that singlet oxygen formed by the back-electron-transfer reaction is also responsible for the cleavage of the biomolecule, reaction (6). It is

$$[\text{Au}_3]^{4+} + \text{O}_2^{\cdot-} \rightarrow [\text{Au}_3]^{3+} + {}^1(\text{O}_2) \qquad (6)$$

interesting to note that the photocleavage of the plasmid DNA by **12a** can be made to produce either the linearised or the nicked form of the DNA under carefully controlled conditions.

The development of optical sensors for the quantitative detection of oxygen has aroused a lot of interest. Many polynuclear d^{10} metal systems often possess very long-lived phosphorescence that is effectively quenched by oxygen and therefore they are ideal candidates to be utilised as an oxygen sensor. Mills and co-workers reported the fabrication of oxygen sensors using a dinuclear gold(I) complex $[\text{Au}_2\{\mu\text{-}(\text{Ph}_2\text{P})_2\text{N–}{}^n\text{C}_{18}\text{H}_{37}\}_2\text{I}_2]$ (**43**).[38] The polystyrene film incorporated with the complex displays an emission maximum at 530 nm with a lifetime of 9.8 μs. The luminescence is quenched by oxygen with a Stern–Volmer constant of $(5.35 \pm 0.09) \times 10^{-3}$ Torr^{-1}. The change in luminescence intensity in an alternating atmosphere of nitrogen and oxygen is completely reversible (Fig. 11).

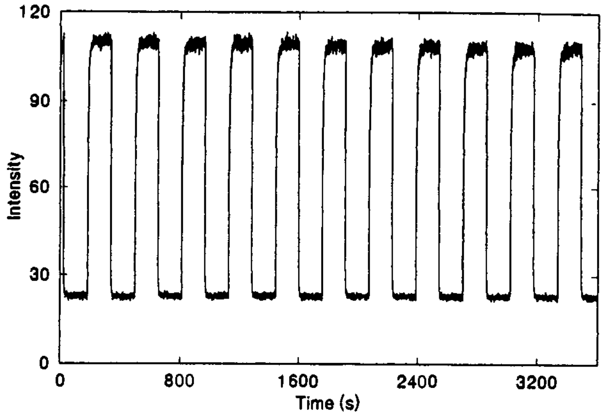
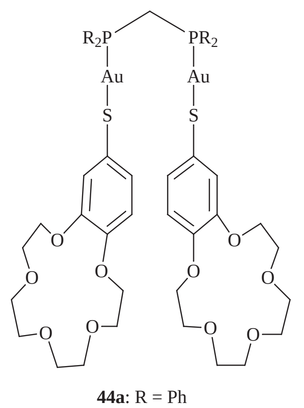


Fig. 11 Luminescence emission intensity of **43** incorporated in a polystyrene film exposed to an alternating atmosphere of 100% oxygen and 100% nitrogen over a period of 1 h. Reprinted with permission from A. Mills, A. Lepre, B. R. C. Theobald, E. Slade and B. A. Murrer, *Anal. Chem.*, 1997, **69**, 2842. Copyright 1997 American Chemical Society.

Apart from oxygen, different organic solvents also have a significant effect on the luminescence properties of polynuclear d^{10} metal systems. For example, the copper(I) iodide materials **24a** and **24b** mentioned in Section 2.3 have very different emission properties in different organic solvents such as toluene and pentane.[26] The photophysical properties of the dinuclear gold(I) dithiocarbamate **17b** also show significant changes in contact with different solvents.[16] The solvent-induced luminescence behaviour of the organogold(I) complex **18a** may also be exploited in sensing different solvents.[17] It is very likely that all these interesting examples and many others will be applied in the development of luminescence sensors of different chemicals in the near future.

As the luminescence properties of polynuclear d^{10} metal complexes, especially those of gold(I), show a strong dependence on the metal–metal interactions, this unique behaviour can be exploited in the development of sensing materials for different analytes. We illustrate this point with a dinuclear gold(I) crown-ether complex which shows a high selectivity towards potassium ions.[39] The electronic absorption spectra of the dinuclear gold(I) crown-ether complexes $[\text{Au}_2(\mu\text{-P–P})(\text{S-B15C5})_2]$ [P–P = dppm (**44a**), dcpm (**44b**) {dcpm = bis(dicyclohexylphosphino)methane}; HS-B15C5 = 4′-mercaptomonobenzo-15-crown-5] exhibit spectral changes upon



44a: R = Ph
44b: R = C_6H_{11}

addition of potassium ions. The absence of such changes for the crown-free complexes [Au_2(μ-P–P){S–$C_6H_3(OCH_3)_2$-3,4}$_2$] [P–P = dppm (**44c**), dcpm (**44d**)] suggests that the spectral changes result from the encapsulation of the potassium ion by the benzo-15-crown-5 units of [Au_2(μ-P–P)(S-B15C5)$_2$]. From electronic absorption titration studies, both complexes **44a** and **44b** have been found to form 1 : 1 adducts with potassium ions with log *K* values of 3.4 and 4.0, respectively. This indicates that one potassium ion is sandwiched between the two benzo-15-crown-5 rings of the dinuclear Au(I) molecule (Fig. 12), which has also been confirmed by electrospray-ionization mass spectrometric (ESI-MS) studies. The emission spectrum of **44a** shows a drop in intensity at *ca.* 502 nm, with the concomitant formation of a long-lived emission band at *ca.* 720 nm (τ_o = 0.2 μs) upon addition of potassium ion (Fig. 13). Such a change in emission spectral traces is absent for the crown-free analogues. Despite the well-known binding of sodium ions by benzo-15-crown-5 compounds, similar emission spectral changes are not observed when sodium ions are used instead of potassium ions. These observations are in line with our expectations when the benzo-15-crown-5 ring was deliberately chosen in the design of these molecules, in that the cavity size of the benzo-15-crown-5 ring is too small to fit a K^+ ion, forcing its binding to the benzo-15-crown-5 to be in a 1 : 2 sandwich binding mode. Thus, it is likely that the binding of K^+ would bring the two gold(I) centres in close proximity to each other, resulting in some weak gold···gold interactions. These intramolecular gold···gold interactions are then reported by the emission properties of the complexes. The low-energy emission band has been proposed to arise from a LMMCT [$RS^- \rightarrow Au_2$] excited state (Fig. 14).

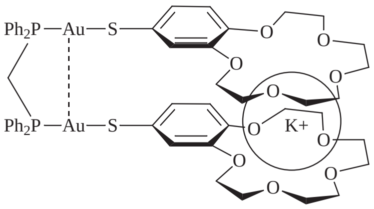


Fig. 12 A proposed binding mode in which a potassium ion is sandwiched between the benzo-15-crown-5 units of the same dinuclear gold(I) complex **44a**.

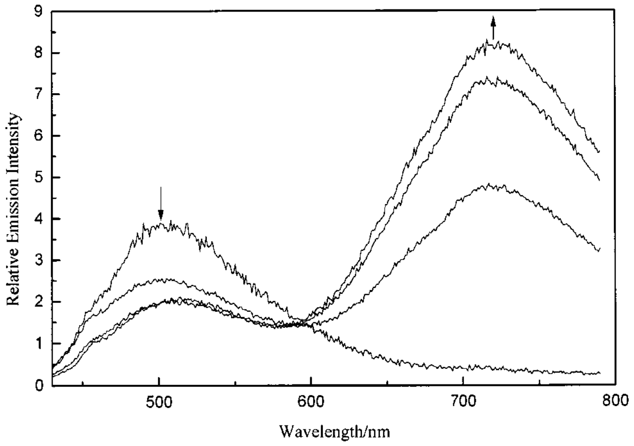


Fig. 13 Emission spectra of **44a** (1.7 mM) upon addition of various concentrations of potassium ions in CH_2Cl_2–MeOH (1 : 1 v/v; 0.1 M ^{n}Bu_4NPF_6). Reprinted with permission from V. W. W. Yam, C. K. Li and C. L. Chan, *Angew. Chem., Int. Ed. Engl.,* 1998, **37**, 2857. Copyright 1998 Wiley-VCH.

Recently, a tetranuclear zinc(II) complex [$Zn_4O(AID)_6$] (**45**) has been used in the fabrication of a blue electroluminescent device.[40] A single-layer light emitting diode (LED) has been prepared by vacuum deposition of the complex onto indium-tin oxide (ITO) to form a homogeneous film. Blue electroluminescence has been observed when the LED was forward biased with the ITO electrode at positive polarity. The electroluminescence resembles the photoluminescence spectrum of the tetranuclear zinc(II) complex. Improved electroluminescence performance has been observed with the incorporation of a hole-transport material in a double-layer device. This work demonstrates the potential of polynuclear d^{10} metal complexes to be utilised in the fabrication of LED devices.

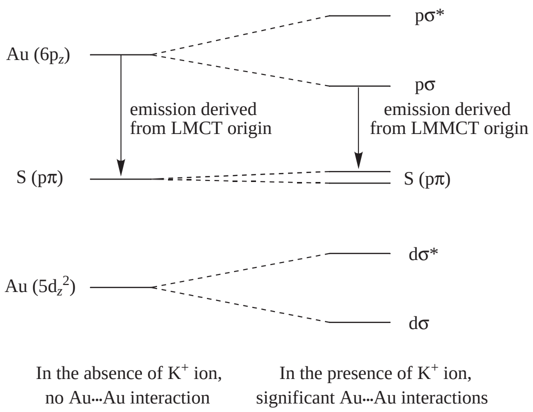


Fig. 14 A schematic representation of the orbital splittings in **44a** in the absence and in the presence of potassium ion binding.

6 Summary and future outlook

Although the luminescence behaviour of polynuclear d^{10} metal complexes was discovered a fairly long time ago, it was only in the last one or two decades that studies on the photophysical and photochemical properties of these systems have grown at a rapid rate. With a more thorough basic understanding of the origins of the luminescence properties of these complexes, it is not impossible for us to design novel systems with desirable emissive behaviour. However, despite the fact that a wide range of bridging and ancillary ligands has been employed to construct polynuclear luminescent d^{10} metal systems, there are still a number of difficulties to be overcome in the design of these complexes. For example, as the nd orbitals are completely filled, many polynuclear d^{10} metal complexes, when dissolved in solution, tend to undergo ligand scrambling and even structural rearrangement due to the high lability of the complexes. Besides, many complexes of this kind may undergo polymerisation during the preparation and recrystallisation stages. Usually, the polymers formed are insoluble in common solvents and the structural information is difficult to obtain.

Despite all these, polynuclear d^{10} metal complexes are still very attractive candidates in the sense that many of them possess very intense and long-lived luminescence with emission energies spanning a wide range in the visible spectrum. Besides, metal–metal interactions may also have a significant effect on the luminescence properties of these systems. The highly flexible coordination number and coordinate unsaturation of a number of d^{10} metal centres may also imply that vacant coordination sites are available for interaction with a wide variety of substrates, with the possibility in some cases of exciplex formation. All these remarkable photophysical characteristics render this class of complexes perfect candidates for the fabrication of different luminescent sensors. With the judicious choice and design of ligand systems and metal complexes, it is very promising that these luminescent polynuclear d^{10} metal systems will be utilised in sensing a wide variety of chemical and biological species.

On the other hand, with the recent advances in the computer hardware and software, theoretical studies on polynuclear d^{10} metal systems can be more accurate and efficient. This allows us to obtain a much clearer and insightful picture of the electronic structures and the photochemical properties of these complexes. The design of luminescent polynuclear d^{10} metal systems with fine-tuned and desirable physical and chemical properties is possible.

Summing up all these factors, it is obvious that research in this area is exciting and development of new polynuclear d^{10} systems with desired luminescence and photochemical properties is very promising. It is conceivable that these systems will be increasingly utilised in different areas of applied science.

7 Acknowledgements

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