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Coordination Chemistry Reviews
171 (1998) 17–41

COORDINATION CHEMISTRY REVIEWS

Design of luminescent polynuclear copper(I) and silver(I) complexes with chalcogenides and acetylides as the bridging ligands

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Received 7 July 1997; accepted 19 November 1997

Contents

Abstract

A number of chalcogenido and alkynyl clusters of copper(I) and silver(I) with various nuclearities have been synthesized and characterized. All these clusters have been found to possess rich photophysical and photochemical properties. The phosphorescent states of the complexes have been shown to undergo facile photo-induced oxidative electron-transfer quenching reactions with a series of pyridinium acceptors, indicative of their highly reducing nature in the excited states. The lowest lying excited states of the clusters have been assigned to be an admixture of ligand-to-metal charge-transfer (LMCT) and metal-centred (d–s) transitions, which have also been supported by Fenske–Hall and *ab initio* molecular orbital

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PII S0010-8545(98)00046-0

calculations. The excited state properties of these clusters have also been probed by nanosecond laser flash photolysis studies.

Keywords: Copper(I); Silver(I); Chalcogenide; Acetylide

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1. Introduction

Polynuclear d^{10} metal complexes display intriguing structural diversity and variable molecular structures. Metal complexes of a d^{10} electronic configuration have commonly encountered coordination numbers varying from two to four and are accompanied by a variety of geometries. Most mononuclear copper(I) complexes are four-coordinated with a tetrahedral geometry, and those of silver(I) and gold(I) being two-coordinated and linear. Polynuclear metal complexes of this kind can have greater complexity owing to the increased number of metal centres and the presence of different bridging ligands. An interesting aspect of these polynuclear d^{10} metal complexes is the common observation of short metal–metal distances present in these clusters. Theoretically, in the absence of metal $(n+1)$s and $(n+1)$p functions, the interaction between the closed-shell d^{10} metal centres would be expected to be 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 atomic orbitals converts this repulsion into a slight attraction between the metal centres, giving rise to a weak metal–metal bonding interaction [1–8].

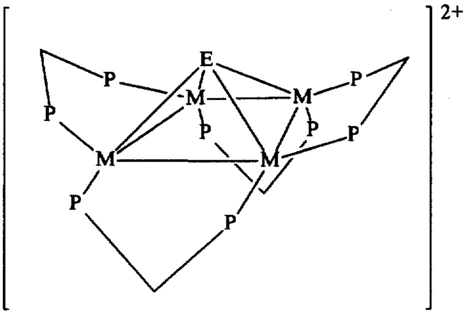
On the other hand, inorganic photochemistry has entered a new era since the rich photophysical and photochemical properties of $[Ru(bpy)_3]^{2+}$ and its analogues have been revealed [9–15]. The idea of metal–metal bond establishment in the excited state of the d^8–d^8 complex $[Pt_2(POP)_4]^{4-}$ [16] has also stimulated the interest on the photochemistry of related polynuclear d^{10} species. In addition to the diverse structural characteristics of polynuclear d^{10} metal complexes, their interesting photophysical and photochemical properties have also attracted increasing attention recently [17–86]. A number of luminescent polynuclear d^{10} metal complexes have been reported to derive their emissions from pure metal-centred d–s or d–p excited states originating from the weak metal–metal interactions [17–20,22,33–35,41,43,44,65–68,71,72,75,76,80,82]. As an electron is promoted from an antibonding dσ* to a bonding sσ or pσ orbital, the bond order between the d^{10} metal centres has been suggested to increase in the excited state, leading to a contraction of the metal core in the clusters [22]. However, in the presence of bridging and/or ancillary ligands, the nature of the excited states of polynuclear d^{10} metal complexes becomes more complicated and the involvement of such ligand contributions in the frontier orbitals cannot be neglected. In accord, a number of luminescent polynuclear d^{10} metal complexes have been suggested to emit from an excited state other than that of a pure metal-centred origin. Examples include those of $[Cu_4I_4(py)_4]$ [22,24–32], $[M_6(mtc)_6]$ (M = Cu, Ag; mtc$^-$ = di-n-propylmonothiocarbamate) [22,23] and $[Hg_4(SPh)_6(PPh_3)_4]^{2+}$ [36], which are thought to originate from metal cluster-centred d–s/XLCT or d–s/LMCT mixed states. In some other systems, the donating and/or accepting orbitals have been assigned to possess significant ligand character [38,39,47,49,69,70,73,74].

As an on-going effort into the investigation of luminescent properties of polynuclear d^{10} metal complexes [43–64], we believe that with the unusual stereochemistry and the highly flexible bonding characteristics of the chalcogenides and acetylides, design of polynuclear transition metal clusters with ligands of this type can be realized, and an exploration into the spectroscopic and photophysical behaviour of these classes of soluble polynuclear d^{10} metal chalcogenide and acetylide complexes would represent a challenging area of research. Despite a large number of transition metal chalcogenide clusters [87] and organometallic aggregates of d^{10} metal centres containing short metal–metal contacts [88–92] are known in the literature, the photophysics and photochemistry of related species remains relatively unexplored. In view of this, a number of chalcogenido and alkynyl clusters of copper(I) and silver(I) with various nuclearities have been synthesized and characterized. In this paper, studies will be focused on a series of tetranuclear copper(I) and silver(I) complexes with μ_4-bridging chalcogenides, $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ [E = S (**1**), Se (**2**)], $[Cu_4(\mu\text{-dtpm})_4(\mu_4\text{-S})]^{2+}$ (**3**), $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ {E = S (**4**), Se (**5**), Te (**6**); dppm = bis(diphenylphosphino)methane; dtpm = bis[bis(4-methylphenyl)phosphino]methane}, and as an extension of our recent work on di-, tri- and tetranuclear copper(I) acetylide complexes [55–58,60–62], a tetranuclear $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1,\eta^2\text{-C}{\equiv}\text{C-})]^{2+}$ (**7**) and two hexanuclear $[M_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C-}C_6H_4\text{-C}{\equiv}\text{C-}p)M_3(\mu\text{-dppm})_3]^{4+}$ acetylide complexes [M = Cu (**8**), Ag (**9**)] will also be described. The structures of the complexes are illustrated in Scheme 1. All these clusters have been found to possess rich photophysical and photochemical properties [50–54,59,64]. Besides, they have also been found to undergo facile photo-induced electron-transfer reactions with a series of pyridinium acceptors, indicative of their highly reducing nature in the excited states. The lowest lying excited states of the clusters have been assigned to be an admixture of ligand-to-metal charge-transfer (LMCT) and metal-centred (d–s) transitions, which have also been supported by Fenske–Hall and *ab initio* molecular orbital calculations. Furthermore, the excited state properties of these clusters have also been probed by nanosecond laser flash photolysis studies.

2. Experimental section

2.1. Materials

All solvents were purified and distilled using standard procedures before use. Organic quenchers for Stern–Volmer quenching experiments and transient absorption spectroscopic measurements were purified by recrystallizing twice using standard procedures.



1: M = Cu, E = S; $\mathrm{P}^\wedge\mathrm{P}$ = dppm

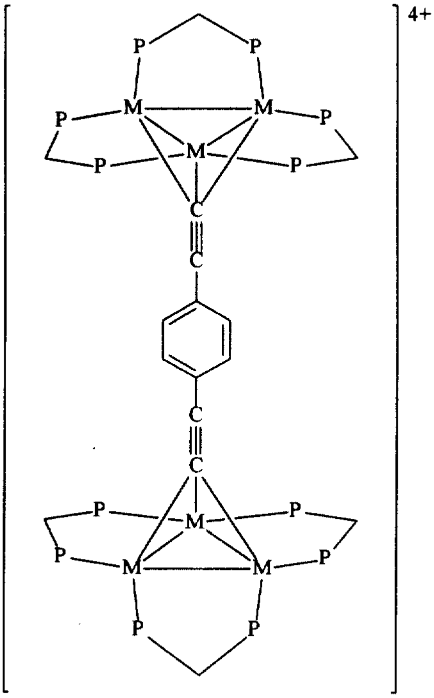
2: M = Cu, E = Se; $\mathrm{P}^\wedge\mathrm{P}$ = dppm

3: M = Cu, E = S, $\mathrm{P}^\wedge\mathrm{P}$ = dtpm

4: M = Ag, E = S, $\mathrm{P}^\wedge\mathrm{P}$ = dppm

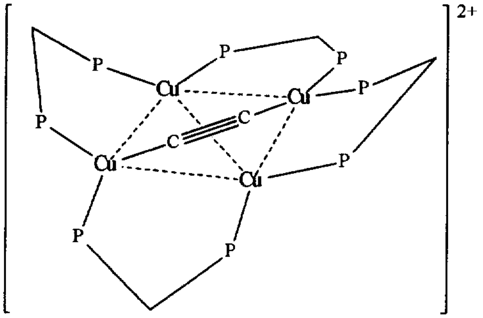
5: M = Ag, E = Se, $\mathrm{P}^\wedge\mathrm{P}$ = dppm

6: M = Ag, E = Te, $\mathrm{P}^\wedge\mathrm{P}$ = dppm



8: M = Cu; $\mathrm{P}^\wedge\mathrm{P}$ = dppm

9: M = Ag; $\mathrm{P}^\wedge\mathrm{P}$ = dppm



7: $\mathrm{P}^\wedge\mathrm{P}$ = dppm

Scheme 1. Structures of complexes **1**–**9**.

2.2. *Synthesis of polynuclear copper(I) and silver(I) complexes*

All reactions were carried out under anaerobic and anhydrous conditions using standard Schlenk techniques. The metal complexes **1**–**9** were prepared according to procedures reported previously [50–54,59,64].

2.3. Physical measurements and instrumentation

UV-vis spectra were obtained on a Hewlett Packard HP8452A diode array spectrophotometer, IR spectra as Nujol mulls on a Bio-Rad FTS-7 Fourier-transform infrared spectrophotometer (4000–400 cm^{-1}), Raman spectra on a Bio-Rad FT-Raman spectrometer with the 1064 nm line of a Nd:YAG laser as the excitation source and steady-state excitation and emission spectra on a Spex Fluorolog-2 111 spectrofluorometer. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser. Luminescence decay signals were recorded on a Tektronix model TDS 620A digital oscilloscope, and analyzed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a 10-cm^3 round bottom flask equipped with a side-arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

Time-resolved transient absorption spectroscopy was performed using the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser as the excitation source, with the monitoring light beam generated from a 250 W quartz–tungsten–halogen lamp placed perpendicular to the excitation beam. The output of the quartz–tungsten–halogen lamp was wavelength selected by passing through two monochromators (Oriel 77250, 1/8 metre and 77200, 1/4 metre). The transient absorption signals were detected by a Hamamatsu R928 photomultiplier tube and amplified using a Tektronix AM502 differential amplifier, and digitized on a Tektronix model TDS 620A digital oscilloscope, interfaced to an IBM-compatible personal computer for data acquisition and analysis. The transient absorption difference spectra were generated using the point-to-point method. The back-electron-transfer (bet) rate constants (k_{bet}) were obtained from a knowledge of the slope (m) of a plot of the reciprocal of absorbance change ($1/\Delta A$) versus time (t) for the transient signal with $k_{bet} = (\Delta\epsilon)bm$ where $\Delta\epsilon$ is the extinction coefficient difference between products and reactants at the monitored wavelength and b is the pathlength of the cell.

2.4. Molecular orbital calculations

Non-parameterized Fenske–Hall MO calculations [93] were carried out on the model complexes $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}E)]^{2+}$ [E = S (**4a**), Se (**5a**) and Te (**6a**)] in terms of the orbital interactions between the fragments $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4]^{2+}$ and E. This non-parameterized model is based on a self-consistent-field method which is an approximation of the Hartree–Fock–Roothaan procedure. The molecular geometry and the atomic basis sets used completely determine the resulting eigenvalues and eigenvectors. The geometry of each complex was taken directly from that crystallographically determined for complexes **4**–**6** [52] with hydrogen atoms replacing the phenyl groups on the dppm ligand (P–H taken to be 1.41 Å and C–H to be

0.95 Å) and idealized to C_{2v} point group. The relative positions of four silver atoms were adjusted to form a rectangle. The basis sets used were those provided with the Fenske–Hall program package (version 5.1). All calculations were carried out on a VAX 780 computer at The University of Hong Kong.

On the other hand, *ab initio* molecular orbital calculations were performed on an IBM9076 computer using the GAMESS package [94]. Similarly, in order to simplify the calculations, the molecules were idealized to C_{2v} symmetry and all the phenyl groups were replaced with hydrogen atoms. The model complexes $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}E)]^{2+}$ [E = S(**4a**), Se(**5a**) and Te(**6a**)] were calculated on the RHF/3-21G level. The 11 valence-electron quasi-relativistic (QR) pseudopotentials of Hay and Wadt [95] for P, C, Ag, S, Se and Te were employed. In order to check the validity of the RHF/3-21G calculations, we have also carried out an MP2 calculation for the $[Ag_4(\mu_4\text{-}S)]^{2+}$ core on a larger double-ζ valence basis set, (3s3p)/[2s2p] for S and (8s6p4d)/[3s3p2d] for Ag. The symmetry orders and compositions of the frontier orbitals for both basis sets were found to be similar.

3. Results and discussion

3.1. Copper(I) and silver(I) chalcogenides

The chalcogenido complexes **1**–**6** were prepared from the reactions of $[Cu_2(\mu\text{-}Ar_2PCH_2PAr_2)_2(CH_3CN)_2]^{2+}$ [Ar = Ph (dppm), C_6H_4–Me-*p* (dtpm)] or $[Ag_2(\mu\text{-dppm})_2]^{2+}$ and sodium sulphide, lithium selenide or sodium telluride in a mixture of acetone/methanol [50–54], all of which gave satisfactory elemental analyses and were well characterized by various spectroscopic techniques. The structures of which have also been established by X-ray crystallography.

In general, all these tetranuclear chalcogenido copper(I) and silver(I) clusters adopt a similar molecular structure, with the four metal centres arranged in a distorted rectangular array and bridged by an unsubstituted μ_4-chalcogenido ligand. Such a bonding mode of the chalcogenide has been observed in complexes of other transition metals [87]. However, the occurrence with copper(I) and silver(I) is extraordinarily rare. The four diphosphine ligands are arranged in a manner such that two of them opposite to each other are located above the M_4 plane while the remaining two below it. The M···M distances (Table 1) observed in these tetranuclear copper(I) and silver(I) complexes are in the ranges of 2.869(1) to 3.271(4) Å and 3.038(2) to 3.357(1) Å, respectively. The Cu···Cu distances in complex **1** are slightly shorter than those found in complex **2** owing to the increased size of the chalcogenide ligand. A similar increase in Ag···Ag distances has been observed for the silver(I) series upon going from the sulphido to the selenido and to the tellurido complex.

3.1.1. Electronic absorption and emission spectroscopy

All the tetranuclear copper(I) and silver(I) chalcogenide clusters are soluble in common organic solvents to give orange-yellow solutions. The electronic absorption spectral data for these complexes are listed in Table 2. In general, the electronic

Table 1
Metal–metal distances for copper(I) and silver(I) chalcogenides and acetylides

Complex	M···M distance (Å)	Reference
1	2.869(1), 3.128(1)	[50]
2	2.908(4), 3.271(4)	[51]
3	2.955(2), 3.144(2)	[53]
4	3.038(2), 3.160(2)	[52]
5	3.055(2), 3.222(2)	[52]
6	3.071(1), 3.357(1)	[52]
7	3.245(2), 3.264(2)	[59]
8	2.862(2), 2.885(1), 3.243(1)	[64]
9	3.079(1), 3.163(1), 3.338(1)	[64]

Table 2
Electronic absorption spectral data for complexes **1**–**9**

Complex	λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})[a]
$[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})](PF_6)_2$ (**1**)	265 sh (41 490), 285 sh (34 650)[b]
$[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})](PF_6)_2$ (**2**)	262 sh (42 670)[b]
$[Cu_4(\mu\text{-dtpm})_4(\mu_4\text{-S})](PF_6)_2$ (**3**)	272 sh (49 645), 362 sh (4175), 430 sh (930)[b]
$[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-S})](OTf)_2$ (**4**)	246 sh (91 745), 400 sh (970)[b]
$[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-Se})](OTf)_2$ (**5**)	256 sh (53 985), 402 sh (1445)[b]
$[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-Te})](OTf)_2$ (**6**)	254 sh (67 075), 440 sh (1475)[b]
$[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1,\eta^2\text{-C}{\equiv}\text{C-})](BF_4)_2$ (**7**)	262 (62 580), 374 sh (6900)[b]
$[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C-C}_6\text{H}_4\text{-C}{\equiv}\text{C-}p)Cu_3(\mu\text{-dppm})_3](BF_4)_4$ (**8**)	260 sh (83 190), 294 sh (44 050), 370 sh (16 900), 390 (23 150), 416 (24 600)[c]
$[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C-C}_6\text{H}_4\text{-C}{\equiv}\text{C-}p)Ag_3(\mu\text{-dppm})_3](BF_4)_4$ (**9**)	258 sh (55 180), 324 (14 000), 340 (14 680), 364 (16 370)[c]

[a] From Refs. [50–53,59,64].

[b] In MeCN at 298 K.

[c] In CH_2Cl_2 at 298 K.

absorption spectra of these clusters in acetonitrile at 298 K reveal a high-energy absorption shoulder at *ca.* 240–260 nm with an extinction coefficient in the order of 10^4 dm^3 mol^{-1} cm^{-1}, and a lower energy absorption tail in the 350–450 nm region. The high-energy absorption band is assigned as an intra-ligand IL(phosphine) transition.

Excitation of these tetranuclear d^{10} metal chalcogenido clusters in the solid state and in fluid solutions with $\lambda > 350$ nm results in intense long-lived orange luminescence for the copper(I) complexes and green to orange emissions for the silver(I) analogues [50–54]. The photophysical data for these complexes are summarized in Table 3. The room-temperature solid-state emission spectra of complexes **1**–**2** and **4**–**6** are depicted in Figs. 1 and 2, respectively.

The emission lifetimes in the microsecond range suggest that the emissions are associated with a spin-forbidden transition. The emission energies of all the clusters

Table 3
Photophysical data for complexes **1**–**9**[a]

Complex	Medium (T/K)	λ_{em}/nm (τ_o/μs)
1	Solid (298)	579 (3.6 ± 0.1)
	Solid (77)	606
	MeCN (298)	618 (7.8 ± 0.2)
	Me_2CO (298)	622 (8.1 ± 0.2)
2	Solid (298)	595 (3.9 ± 0.2)
	Solid (77)	619
	MeCN (298)	622 (6.9 ± 0.2)
	Me_2CO (298)	626 (7.1 ± 0.2)
3	Solid (298)	604 (3.5 ± 0.3)
	Solid (77)	658
	MeCN (298)	620 (7.7 ± 0.4)
	Me_2CO (298)	622 (8.8 ± 0.4)
4	Solid (298)	516 (1.0 ± 0.1)
	Solid (77)	536
	MeCN (298)	628 (1.5 ± 0.2)
	Me_2CO (298)	628 (1.2 ± 0.1)
5	Solid (298)	527 (0.9 ± 0.1)
	Solid (77)	552
	MeCN (298)	572 (3.4 ± 0.3)
	Me_2CO (298)	570 (1.3 ± 0.1)
6	Solid (298)	574 (3.1 ± 0.2)
	Solid (77)	588
	MeCN (298)	626 (3.3 ± 0.3)
	Me_2CO (298)	615 (1.4 ± 0.1)
7	Solid (298)	509 (9.8 ± 0.9)
	Solid (77)	551
	MeCN (298)	560 (2.9 ± 0.3)
	Me_2CO (298)	562 (16 ± 1)
8	Solid (298)	583 (222 ± 10)
	Solid (77)	582
	CH_2Cl_2 (298)	596 (40 ± 2)
	EtOH/MeOH (v/v 4:1) (77)	579
9	Solid (298)	513 (351 ± 10)
	Solid (77)	515
	CH_2Cl_2 (298)	515 (426 ± 15)
	EtOH/MeOH (v/v 4:1) (77)	510

[a] From Refs. [50–53,59,64].

in the solid state are significantly higher than those in fluid solutions. Similar findings have also been observed in other luminescent copper(I) and silver(I) clusters [22,23].

The origin of these emissions does not appear to be derived from an excited state of pure d–s origin modified by metal–metal interactions. Upon going from sulphido to selenido tetranuclear copper(I), and from sulphido to selenido and to tellurido silver(I), the metal–metal distances increase gradually. An elongation of M···M distance would predict a blue shift in the emission energies owing to the increasing separation of the d–s HOMO–LUMO energy gap. However, such a trend is not

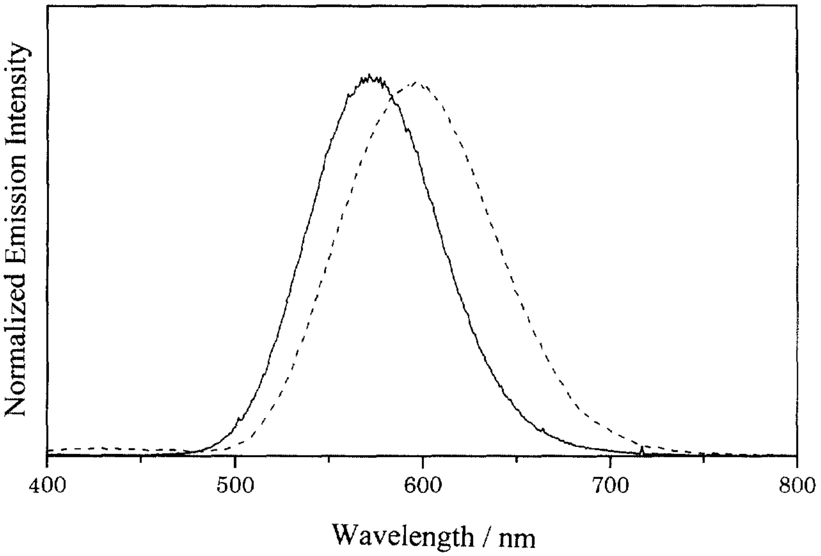


Fig. 1. Solid-state emission spectra of complexes **1** (———) and **2** (- - -) at room temperature. Excitation wavelength at 350 nm.

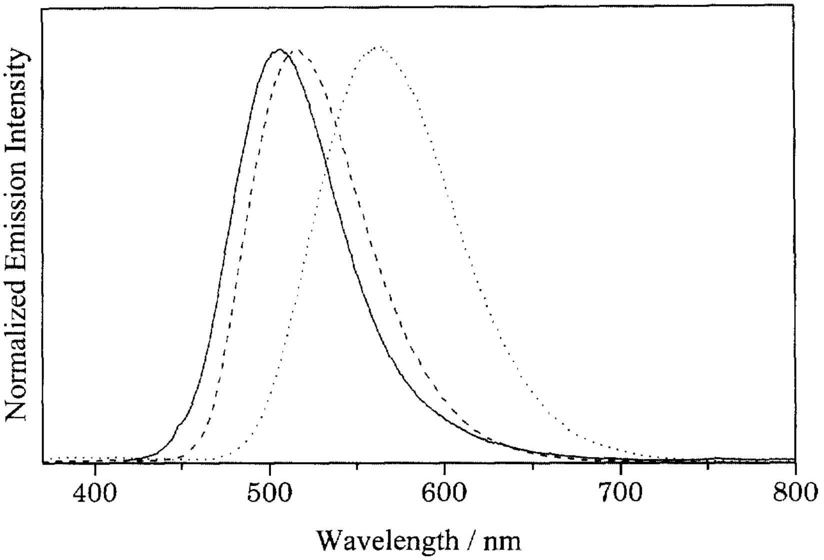


Fig. 2. Solid-state emission spectra of complexes **4** (———), **5** (- - -) and **6** (· · ·) at room temperature. Excitation wavelength at 350 nm.

observed and the assignment of a pure d–s metal-centred excited state resulting from metal–metal interactions is therefore not favoured.

The involvement of the diphosphine ligand orbitals in the nature of the lowest-lying excited state has been considered. The comparatively low emission energies of all the complexes eliminate an intra-ligand IL(phosphine) excited state. Besides, the observation of a very similar emission energy for $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})](PF_6)_2$ (**1**) and its dtpm analogue $[Cu_4(\mu\text{-dtpm})_4(\mu_4\text{-S})](PF_6)_2$ (**3**) [53] also excludes the possibilities of an emission origin to be derived from either a metal-to-ligand charge-transfer MLCT ($M_4 \rightarrow$phosphine) or a ligand-to-ligand charge-transfer LLCT ($E^{2-} \rightarrow$phosphine) transition. The presence of electron-donating methyl groups on the dtpm ligand would destabilize its π^* orbital, thereby increase the MLCT ($Cu_4 \rightarrow$phosphine) or LLCT ($E^{2-} \rightarrow$phosphine) transition energy. However, such an increase in emission energy is not observed and the solid-state emission energy for $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})](PF_6)_2$ is even higher than that of the dtpm counterpart, suggesting that the π^* of the diphosphine is not likely to be the acceptor orbital. Moreover, copper(I) is much more easily oxidized than silver(I), given the higher energy of the Cu(I) 3d orbitals relative to those of the Ag(I) 4d orbitals. The ionization energy of $Ag^+(g)$ ($173.30 \times 10^3\ cm^{-1}$) [96] is almost $10^4\ cm^{-1}$ larger than that for $Cu^+(g)$ ($163.67 \times 10^3\ cm^{-1}$) [97]. The observation that the tetranuclear copper(I) and silver(I) complexes with the same chalcogenido ligand (i.e. **1** and **4**, **2** and **5**) emit at fairly similar energies with a blue shift of only *ca.* 0.27 eV from Cu to Ag does not appear to be compatible with a metal-to-ligand charge-transfer excited state assignment.

In view of the σ-donating capability of chalcogenides, the transitions associated with the emissions of these copper(I) and silver(I) clusters are assigned to originate predominantly from a ligand-to-metal charge-transfer LMCT ($E^{2-} \rightarrow M_4$) triplet excited state, and probably with mixing of a metal-centred MC (d–s or d–p) state of Cu(I) or Ag(I). Similar assignments have also been suggested in other luminescent polynuclear thiolato–copper(I) [22,23,85], silver(I) [22,23], gold(I) [42,48, 77,78,83,84] and mercury(II) [36] complexes. The excited states of a number of polynuclear d^{10} metal complexes containing halides [22,24–32] and acetylides [55–64] as bridging ligands have also been suggested to originate from a similar LMCT/MC mixed state.

The solid-state emission energies of the clusters at 298 K follow the orders:

1 (579 nm) > *2* (595 nm);

and *4* (516 nm) > *5* (527 nm) > *6* (574 nm)

This is in line with the changes in the ionization potentials of the chalcogens [98], and implies that the donor orbital would bear a high parentage of chalcogenide character. It is also interesting to note that the ionization energies of atomic copper and silver are similar (6.232×10^4 and $6.111 \times 10^4\ cm^{-1}$, respectively) [99], with copper(I) being slightly easier to reduce than silver(I), which also agrees well with the observation that the emission of the silver(I) tetramer occurs at a higher energy than the corresponding copper(I) analogue with the same chalcogenido ligand.

Although similar emission energy trends were not observed for the complexes in fluid solutions, it is unlikely that decomposition or structural changes have occurred, as evidenced by positive-ion electrospray ionization-mass spectrometry (ESI-MS) and NMR spectroscopic data.

3.1.2. Molecular orbital calculations

The electronic structures of many polynuclear d^{10} systems have been focused on with considerable attention [1–8,26,40]. Not only are the bonding pictures in these systems interesting, but also insights into the electronic transitions as well as the nature of the excited states could be provided with the help of molecular orbital calculations [26,40]. In order to seek further information on the nature of the excited states of these coinage metal chalcogenido clusters, Fenske–Hall [100] and *ab initio* [101] molecular orbital calculations have been performed on the silver(I) series.

The compositions of the frontier molecular orbitals for the three model complexes **4a**–**6a** from the Fenske–Hall molecular orbital calculations are summarized in Table 4. The calculation results reveal that the three highest occupied molecular orbitals are mainly of Ag–E bonding character (between the 4d orbitals of the four silver(I) centres and the 3p, 4p and 5p orbitals of S, Se and Te, respectively), while the LUMOs of all these clusters are almost metal-localized. The calculated HOMO–LUMO energy gaps of $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}E)]^{2+}$ decrease from **4a** to **6a**, which is in line with the trend observed in the solid-state luminescent energies of the tetranuclear silver(I) clusters. The frontier molecular orbital energy diagrams of **4a**–**6a** are shown in Fig. 3.

In addition, similar results have also been obtained from the *ab initio* studies. A representative summary of the energy levels and compositions of the frontier orbitals of **4a** from *ab initio* MO studies are listed in Table 5. These results suggest that the transitions associated with the emissions of the silver(I) clusters originate essentially from a ligand-to-metal charge-transfer LMCT ($E^{2-} \rightarrow Ag_4$) excited state, with mixing of a metal-centred MC (d–s/d–p) silver(I) state. *Ab initio* molecular orbital calculations have also been carried out on a tetranuclear cuprous iodide complex $[Cu_4I_4(py)_4]$ and the lowest-energy excited state has also been found to be an admixture of metal-centred and halide-to-metal charge-transfer parentages [26].

Table 4
Energies and per cent compositions for the frontier orbitals of $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}E)]^{2+}$ from Fenske–Hall MO studies[a]

Complex	Molecular orbital	Energy (eV)	E (%)	4Ag (%)	$4H_2PCH_2PH_2$ (%)
E=S	LUMO 65(a_2)	−4.14	0.00	96.54	3.46
	HOMO 64(b_1)	−11.08	46.12	42.00	11.88
E=Se	LUMO 65(a_2)	−4.52	0.00	96.52	3.48
	HOMO 64(b_1)	−10.75	50.16	39.26	10.58
E=Te	LUMO 65(a_2)	−5.16	0.00	96.30	3.70
	HOMO 64(b_1)	−10.55	51.64	38.40	9.96

[a] Data taken from Ref. [100].

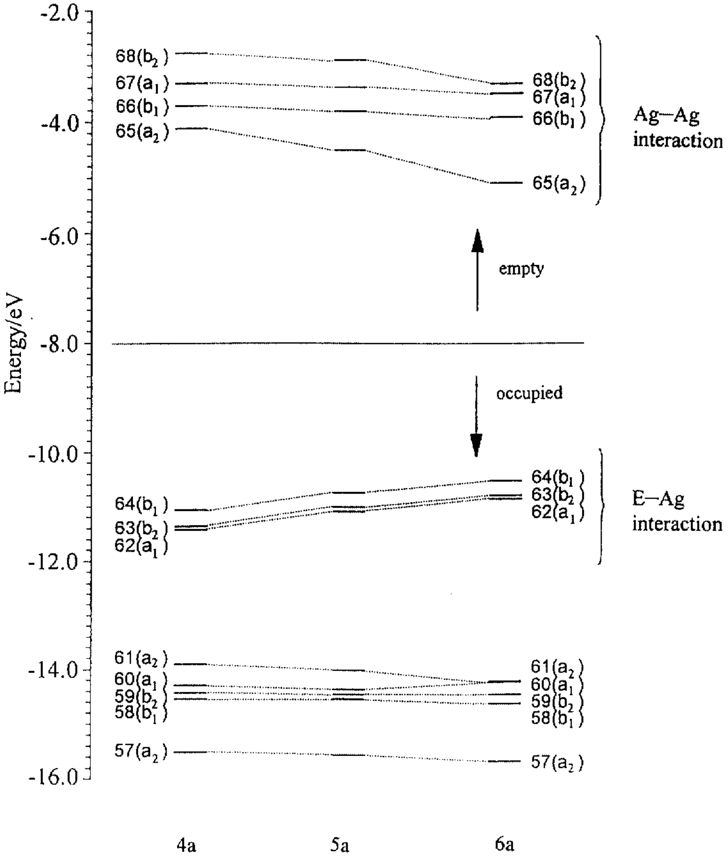


Fig. 3. Molecular orbital energy diagrams showing the frontier molecular orbitals of complexes **4a**–**6a** from Fenske–Hall molecular orbital calculations.

3.1.3. Electrochemical properties

The electrochemistry of complexes **1**–**6** in MeCN (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$) was studied. The cyclic voltammograms showed ill-defined irreversible oxidation waves while no reduction waves were detected within the acetonitrile solvent window. The electrochemical data are summarized in Table 6.

3.1.4. Photo-redox reactivities

The phosphorescent states of the copper(I) clusters have been found to be quenched by pyridinium acceptors [50,51]. In order to gain more understanding into the photo-redox behaviour of these complexes, a study of electron-transfer quenching of the phosphorescent states of **1** and **2** by a series of pyridinium acceptors of variable reduction potentials has been carried out. Excited-state reduction potentials $E^{\circ}[Cu_4^{3+/2+*}]$ of −1.71(10) and −1.55(10) V for **1** and **2**, respectively, vs saturated sodium chloride calomel electrode (SSCE) have been estimated by three-

Table 5
Energy levels and atomic contribution for the frontier molecular orbitals of $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}S)]^{2+}$ (**4a**) from *ab initio* MO studies[a]

MO	E (eV)	Composition								Orbital description
		Ag			S				$H_2PCH_2PH_2$	
		4d	5s	5p	3s	$3p_x$	$3p_y$	$3p_z$	(total)	
$17a_2$	−13.48	16.6	1.3	2.7	0	0	0	0	79.4	Ag (d)
$20b_2$ (HOMO-2)	−12.85	14.9	2.1	12.3	0	0	38.8	0	31.9	σ(Ag–S)
$23a_1$ (HOMO-1)	−12.81	18.0	0.5	6.1	1.3	0	0	56.1	18.0	σ(Ag–S)
$20b_1$ (HOMO)	−12.04	21.2	2.0	5.3	0	31.0	0	0	40.5	σ(Ag–S)
$24a_1$ (LUMO)	−3.61	0.8	47.9	15.7	0	0	0	0.5	35.1	Ag (s,p)

[a] Data taken from Ref. [101].

Table 6
Electrochemical data for complexes **1**–**6**[a]

Complex	Oxidation E_{pa} (V) vs Fc^+/Fc
1	+0.27 +1.25 +1.39
2	+0.24 +1.05 +1.24
3	+0.29 +0.84 +1.20 +1.35
4	+0.33 +0.82 +1.63
5	+0.34 +0.75 +1.07
6	+0.14 +0.80 +1.57

[a] Working electrode, glassy carbon; scan rate 100 mV s^{-1}.

parameter, non-linear least-squares fits to the equation

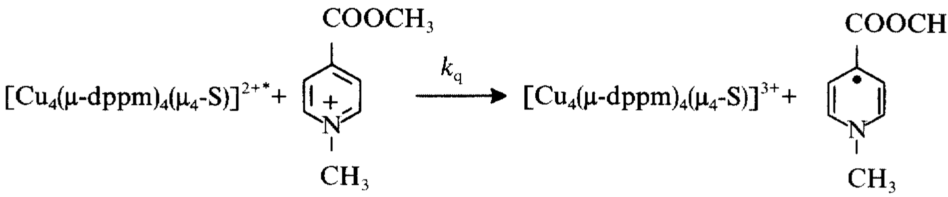
$$(RT/F)\ln k'_q = (RT/F)\ln K\kappa\nu - (\lambda/4)[1 + (\Delta G/\lambda)]^2$$

where k'_q is the rate constant corrected for diffusional effects, $K = k_d/k_{-d}$ which is approximately 1–2 $dm^3\,mol^{-1}$, k_d is the diffusion-limited rate constant which is taken to be 1.0×10^{10} dm^3 mol^{-1} s^{-1}, κ is the transmission coefficient, ν is the nuclear frequency, λ is the reorganization energy for electron-transfer and ΔG is the standard free energy change of the reaction. A reorganization energy of 1.12(10) eV and a RTlnKκν of 0.61(10) V vs. SSCE have been obtained for **2**.

A plot of ln k_q' vs $E(A^{+/0})$ for the oxidative electron-transfer quenching of **2*** by pyridinium acceptors is shown in Fig. 4. The close agreement between the theoretical curve and the experimental data suggests that the mechanism of the photo-reactions is outer-sphere electron-transfer in nature. It is envisaged that both **1** and **2** are strongly reducing in the excited state in view of their highly negative excited-state reduction potentials.

In order to gain more direct spectroscopic evidence into the mechanism of the photo-reactions between these luminescent clusters and pyridinium acceptors, a nanosecond transient absorption spectroscopic study has been carried out [53]. The transient absorption difference spectrum of the laser flash photolysis of a degassed acetone solution of **1** (0.27 mM) and 4-(methoxycarbonyl)-*N*-methylpyridinium hexafluorophosphate (7.93 mM) is shown in Fig. 5. A sharp absorption band is observed at *ca.* 390 nm, concomitant with the growth of a lower intensity band at *ca.* 484 nm and a broad absorption band at *ca.* 693 nm with a larger extinction coefficient. The high-energy absorption band at *ca.* 390 nm is characteristic of the pyridinyl radical and matches very well with the reported spectrum of the 4-(methoxycarbonyl)-*N*-methylpyridinyl radical [102]. The reaction mechanism is likely to be:

$$[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+} \xrightarrow{h\nu} [Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+*}$$



The 484 nm absorption band and the much lower-energy broad band at *ca.* 693 nm which are not characteristic of the pyridinyl radical, are likely to arise as a result of the oxidized form of the copper(I) cluster, $[Cu^ICu^ICu^ICu^{II}(\mu\text{-dppm})_4(\mu_4\text{-S})]^{3+}$. Although the ligand-field (d–d) transitions for the copper(II) metal centre in an unsymmetric environment can occur at such a low-energy region [103], such an assignment for both the 484 and 693 nm absorption bands in the transient absorption difference spectrum is not favoured, given that the extinction coefficients for the bands are estimated to be 1200 and 6700 dm^3 mol^{-1} cm^{-1}, respectively, assuming that both $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$ and $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{3+}$ do not have significant absorption at *ca.* 390 nm. Another possible assignment is the ligand-to-metal charge-transfer LMCT [$S^{2-} \rightarrow Cu(II)$] absorption which is commonly suggested in many mixed-valence copper(I,II) thiolate [104–107] and copper(II) thioether complexes [108,109] to occur at *ca.* 400–500 nm. However, such an assignment for the

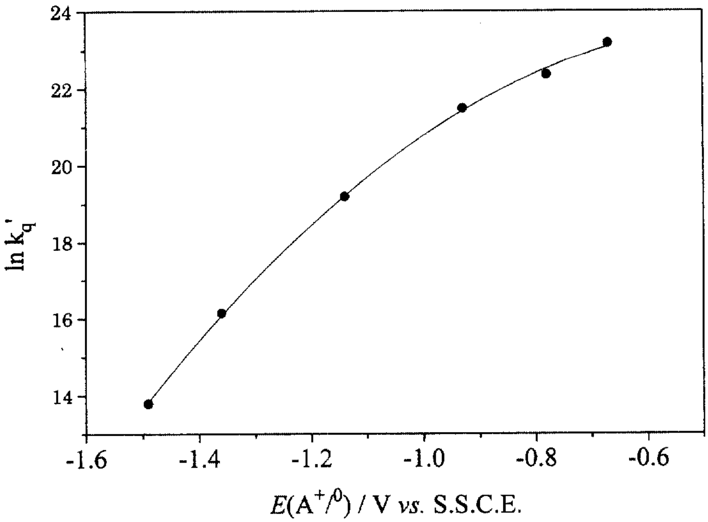


Fig. 4. Plot of ln k_q' vs $E(A^{+/0})$ for the oxidative electron-transfer quenching of **2*** by pyridinium acceptors in degassed acetone (0.1 mol dm^{-3} $^nBu_4NPF_6$): (●) experimental, (———) calculated.

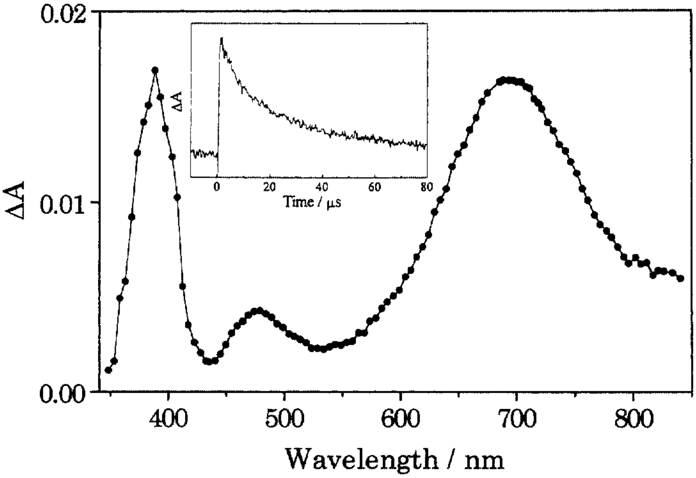


Fig. 5. Transient absorption difference spectrum recorded 10 μs after laser flash excitation for a degassed acetone solution of complex **1** (0.27 × 10^{-3} mol dm^{-3}) and 4-(methoxycarbonyl)-*N*-methylpyridinium hexafluorophosphate (7.93 × 10^{-3} mol dm^{-3}). The insert shows the decay trace of the transient absorption at 390 nm.

broad absorption band at 693 nm is unlikely in view of its occurrence at such a low-energy region.

A more probable assignment for the absorption is the intervalence-transfer (IT) transition:

$$\mathrm{Cu^{I}Cu^{I}Cu^{I}Cu^{II}} + h\nu \rightarrow \mathrm{Cu^{I}Cu^{I}Cu^{II}Cu^{I*}}$$

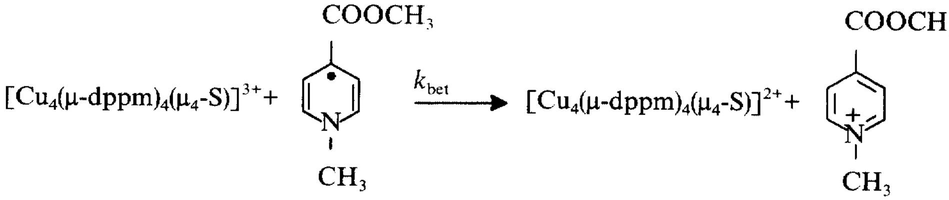
There have been a number of intervalence-transfer transitions reported in a variety of mixed-valence copper(I,II) systems. For example, the 756 nm absorption band ($\epsilon = 5000\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) of a dinuclear complex $[\mathrm{Cu^ICu^{II}L}]^{3+}$ with a macrocyclic ligand $\mathrm{L = N(CH_2CH_2N{=}C{-}C{=}NCH_2CH_2)_3N}$ has been assigned as an intervalence-transfer transition [110]. A similar assignment has also been suggested in other mixed-valence Cu(I)Cu(II) systems with thiolato- [111], halo- [112] and N,O-containing macrocyclic ligands [113,114].

Besides, similar transient absorption difference spectra have also been observed for the photo-induced electron-transfer reactions between **1*** and 4-(aminoformyl)-*N*-methylpyridinium, and **2*** and 4-(methoxycarbonyl)-*N*-methylpyridinium, as well as 4-(aminoformyl)-*N*-methylpyridinium, respectively. There are no significant differences between the spectra of the sulphido- and selenido–copper(I) complexes except that the 480 nm band is less intense for the latter. The broad and intense absorption at 685 nm in the difference spectrum for the reaction between **2*** and 4-(methoxycarbonyl)-*N*-methylpyridinium is also assigned as the absorption of the mixed-valence $\mathrm{Cu^ICu^ICu^ICu^{II}}$ species. The occurrence of this absorption band at similar energy compared with that of the sulphido analogue (693 nm) further supports that these absorption bands are not due to LMCT transitions, as a much lower energy absorption would be expected for the selenido analogue. Instead, an assignment of intervalence-transfer transition appears to be more possible for these low-energy absorption bands.

For **3**, similar photo-induced electron-transfer reactions with different pyridinium acceptors have also been found to occur. In general, all the transient absorption difference spectra are very similar to those of the dppm analogue **1**, indicative of relatively little participation of the bridging phosphine ligand in the absorption characteristics of the transient species.

Similar low-energy transient absorption bands for the mixed-valence copper species have also been observed in the photo-induced electron-transfer reactions between a series of trinuclear alkynylcopper(I) complexes and various pyridinium acceptors [56,57,62]. Intervalence-transfer transitions have also been suggested for the near-infrared absorptions observed in these systems with nanosecond transient absorption spectroscopy.

The transient absorption signals are found to decay with time. A plot of ($1/\Delta A$) vs time yields a straight line, indicating that the decays follow second-order kinetics, attributable to the back-electron-transfer reaction:



A back-electron-transfer rate constant k_{bet} of 9.7×10^9 dm^3 mol^{-1} s^{-1} is determined based on the decay of the intervalence-transfer absorption. This value agrees well with that obtained from the pyridinyl radical decay trace.

In conclusion, characteristic pyridinyl radical absorptions have been observed in all transient absorption difference spectra and therefore the electron-transfer nature of the photo-reactions between the phosphorescent states of these tetranuclear copper(I) chalcogenido clusters and the pyridinium acceptors can be established. The highly reducing capabilities of the excited states of these copper(I) clusters have also been demonstrated.

3.2. Copper(I) and silver(I) acetylide complexes

As an extension of our recent work on di-, tri- and tetranuclear copper(I) and silver(I) acetylide complexes [55–64], attempts have been made to synthesize luminescent rigid-rod oligomers based on the *triangulo*-M_3 building blocks. In an attempt to build higher oligomers employing a trinuclear copper(I) trimethylsilylacetylide $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–SiMe}_3)_2]^+$ as the precursor complex, to our surprise, reaction of the binuclear complex $[Cu_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ with $Me_3SiC{\equiv}CH$ in the presence of ^{n}BuLi in THF afforded a novel tetranuclear complex $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1,\eta^2\text{-C}{\equiv}\text{C–})]^{2+}$ (7) in moderate yield [59]. On the other hand, reaction of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ or $[Ag_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ with 1,4-diethynylbenzene in the presence of ^{n}BuLi in THF afforded the respective diyne-bridged hexanuclear copper(I) and silver(I) complexes, $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–C}_6\text{H}_4\text{–C}{\equiv}\text{C-}p)Cu_3(\mu\text{-dppm})_3](BF_4)_4$ (**8**) and $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–C}_6\text{H}_4\text{–C}{\equiv}\text{C-}p)Ag_3(\mu\text{-dppm})_3](BF_4)_4$ (**9**); each of which contains two triangular M^I_3 units linked *via* an extended conjugated diyne backbone [64]. All these alkynyl complexes have been characterized by elemental analyses and various spectroscopic methods. Their X-ray crystal structures have also been determined.

Complex **7** shows a crystallographic C_2 symmetry, with the four Cu atoms arranged in a distorted rectangular array and the four μ-dppm ligands bridging each of the four Cu–Cu edges in a saddle-like arrangement. Unlike complexes **1**–**6** where the chalcogen atom is projected above the M_4 plane occupying the apex of a distorted rectangular-based pyramid, the C≡C unit in complex **7** is situated in the middle of the rectangular Cu_4 plane, with a C≡C bond distance of 1.26(2) Å. It is interesting to note that the Cu···Cu distances in complex **7** are longer than those found for complexes **1**–**3**, which is understandable on the grounds that the C≡C unit is larger in size and is situated on the plane of the Cu_4 core and inevitably pushes the Cu atoms further apart. These distances are significantly longer than the sum of van der Waals radii for copper (2.8 Å) [115], suggestive of insignificant metal–metal interaction between the four copper atoms. It should be emphasized that this complex represents the first example of a μ_4-η^1,η^2 bridging mode of a C≡C unit occurring with tetranuclear copper(I).

The complex cation of **8** consists of two triangular arrays of copper atoms with a dppm ligand bridging each edge to form two roughly planar $[Cu_3P_6]$ cores with interior angles of the Cu_3 triangles ranging from 55.31(3) to 68.71(3)°. The two Cu_3P_6 cores are bridged by a 1,4-diethynylbenzene unit to form a dumb-bell shaped structure. The Cu···Cu distances [2.862(2)–3.243(1) Å] are comparable to those found in other related copper(I) acetylide systems [55,57,116–118], suggestive of very weak to no Cu···Cu interactions. The bridging mode of the μ_3-acetylides is asymmetric. The observed C≡C distance [1.223(9) Å] and the linearity of the acetylide groups indicate a typical C≡C bond, characteristic of metal–acetylide σ bonding. A similar bonding mode has been found in the related trinuclear copper(I) acetylide complexes [55,57]. The complex cation of **9** is isostructural to **8** except the six copper atoms are replaced by silver atoms. The Ag···Ag distances fall within the range of 3.079(1) to 3.338(1) Å and the interior angles of the Ag_3 triangles range from 56.46(4) to 64.65(4)°. The asymmetric bonding mode of the alkynyl group [*d*(C≡C): 1.24(2) Å] is also similar to that observed for **8**.

It is interesting to note that the ν(C≡C) stretch appeared as a strong band in the solid-state FT-Raman spectra of **7**, **8** and **9** at 1788, 1955 and 2015 cm^{-1}, respectively. The lower ν(C≡C) stretching frequency observed in **7** is in line with the longer C≡C bond associated with π-bonding interactions with the copper atoms.

3.2.1. Electronic absorption and emission spectroscopy

The electronic absorption data of complexes **7**–**9** are summarized in Table 2. The electronic absorption spectrum of **7** shows an absorption band at *ca.* 262 nm in MeCN, attributable to the intra-ligand transition of dppm since free dppm also absorbs strongly in this region. The low-energy absorption at *ca.* 374 nm is likely to arise from a $[(C{\equiv}C)^{2-} \rightarrow Cu_4]$ LMCT transition, given the good σ-donating ability of the $(C{\equiv}C)^{2-}$ unit. On the other hand, it is interesting to note that the absorption spectral patterns of solution samples of **8** and **9** are very similar (Fig. 6). The strong absorptions in the UV region at *ca.* 258–324 nm are tentatively assigned as ligand-localized transitions. Longer wavelength absorptions appear as vibronically structured bands at *ca.* 370–416 nm for **8** and *ca.* 324–364 nm for **9** in CH_2Cl_2. The vibrational progressional spacings of *ca.* 1475–1500 cm^{-1} are typical of ν(C=C) stretching modes of the aromatic ring in the excited state.

Upon excitation of complex **7** at $\lambda > 350$ nm at room temperature, intense green and greenish-yellow emissions are observed in the solid state and in fluid solutions, respectively. The long excited-state lifetimes observed at room temperature in both the solid state and in fluid solutions, together with the large Stokes' shift suggest that the emission is most likely associated with a spin-forbidden transition of triplet parentage. The photophysical data of **7** are collected in Table 3. With the good σ-donating ability of the $(C{\equiv}C)^{2-}$ unit, it is likely that the origin of the low-energy emission would be dominated by an acetylide-to-copper charge-transfer LMCT $[(C{\equiv}C)^{2-} \rightarrow Cu_4]$ excited state and probably mixed with a metal-centred d–s excited state [55–62,64].

On the other hand, excitation of a solid sample of complex **8** at $\lambda > 350$ nm at both 298 and 77 K produces intense yellow-orange luminescence. The room-temperature solid-state emission spectrum shows an intense and vibronically structured band at *ca.* 583 nm with progressional spacings of *ca.* 1500–1520 cm^{-1}, characteristic

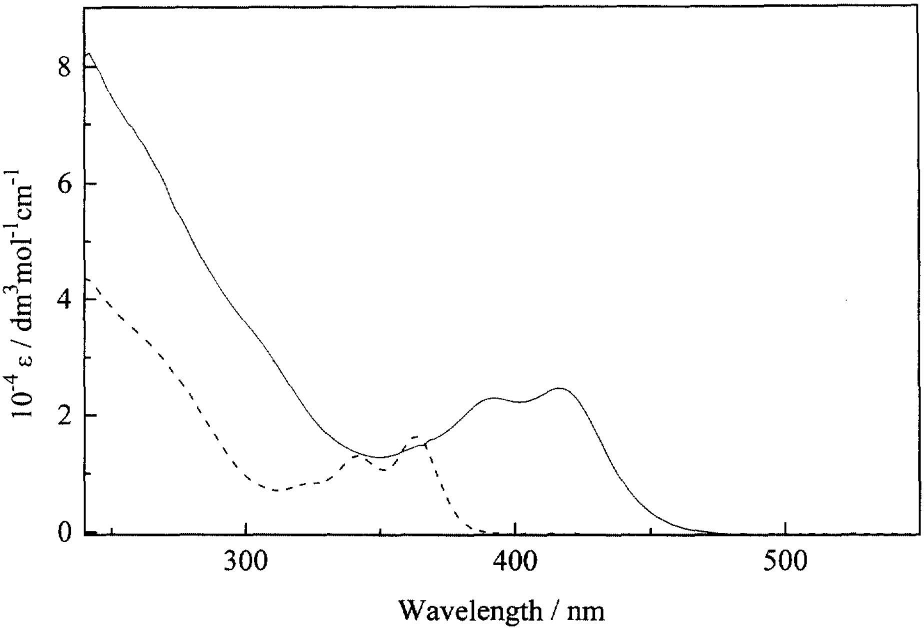


Fig. 6. Electronic absorption spectra of complexes **8** (———) and **9** (- - -) in CH_2Cl_2.

of the aromatic $\nu(C \stackrel{...}{=} C)$ stretch. Upon cooling to 77 K, the structured emission bands become better resolved. Similar emission bands are also observed in fluid solutions. Excitation of a solid sample of **9** at $\lambda > 350$ nm at both 298 and 77 K gives intense greenish-yellow luminescence. The solid-state emission spectra at both temperatures also show an intense vibronically structured band at *ca.* 513 nm. The solid-state emission spectra of **8** and **9** at room temperature are shown in Fig. 7. The excitation spectra of both **8** and **9** show vibronically structured bands at *ca.* 360–420 nm and 320–362 nm, respectively, which coincide with those of their respective absorption spectra. The photophysical data of **8** and **9** are summarized in Table 3.

It is interesting to note that both the absorption and emission bands of **8** occur at lower energy than those of **9**. A possible assignment for the origin of the emission involves emissive states derived from ligand-to-metal charge-transfer (LMCT) transition mixed with d–s character. The blue shift in the 77 K solid-state emission energy of *ca.* 0.28 eV from **8** to **9** is comparable to the value of 0.31 eV reported for the related hexanuclear copper(I) and silver(I) thiocarbamate clusters, $[Cu_6(mtc)_6]$ and $[Ag_6(mtc)_6]$ (mtc^- = di-*n*-propylmonothiocarbamate), where an origin of mixed LMCT and d→s character has been suggested [22,23]. Besides, a similar blue shift in emission energy (*ca.* 0.27 eV) on going from copper(I) to silver(I) chalcogenido clusters **1** to **4** and **2** to **5** has also been observed, in which a mixed LMCT/d–s origin has also been suggested and supported by molecular orbital calculations [50–54,100,101]. The long lifetime of the emissive states of **8** and **9** in the microsecond range is suggestive of a triplet parentage. However, the possibility of the involvement

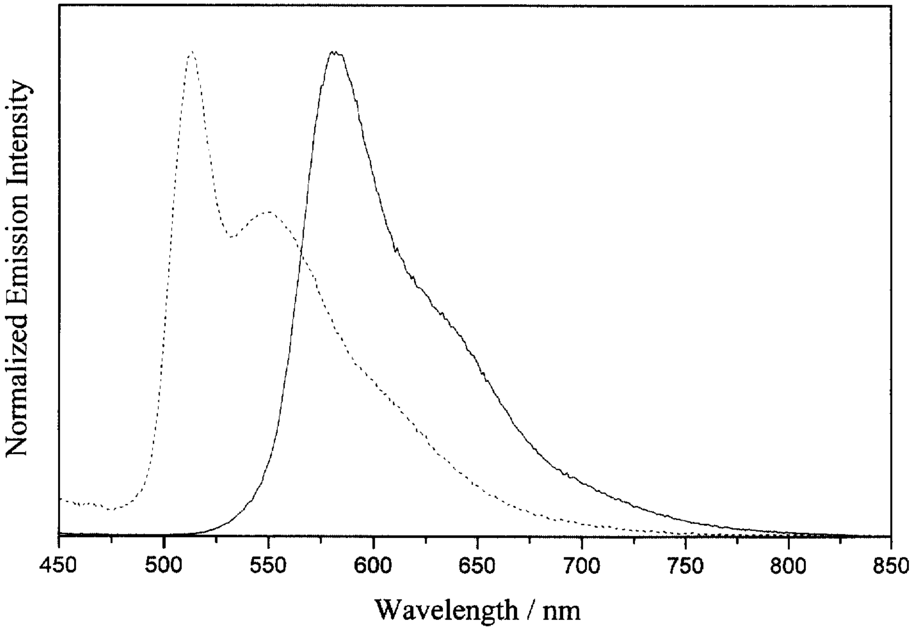


Fig. 7. Solid-state emission spectra of complexes **8** (———) and **9** (- - -) at room temperature. Excitation wavelength at 350 nm.

of an intra-ligand excited state of 1,4-diethynylbenzene should not be overlooked given the unusually long lifetime of the emissive state and the low-lying π* orbital energy of the diynyl unit. The excited states of luminescent polynuclear d^{10} systems may be strongly influenced by the ligands. The emitting states of many polynuclear d^{10} complexes have been suggested to possess intra-ligand character [38,39,47,49,69,70,73,74]. Therefore, it is likely that the low-energy emission for **8** and **9** is derived from states of ligand-to-metal charge-transfer LMCT (acetylide→Cu_4 or Ag_4) parentage mixed with a metal-centred MC (Cu_4 or Ag_4) d–s state, and probably with substantial intra-ligand IL(acetylide) π–π* character.

3.2.2. Photo-redox properties

The phosphorescent state of complex **7** has been found to be quenched by a number of pyridinium acceptors (Table 7). A plot of $\ln k_q'$ vs $E(A^{+/0})$ for the oxidative electron-transfer quenching of **7*** by a series of structurally related pyridinium acceptors is shown in Fig. 8. The triplet state energies of pyridinium ions are too high for any appreciable energy transfer reaction between the excited state of the complex and the quenchers to occur. This, together with the close agreement between the theoretical curve and the experimental data, suggests that the mechanism of the photo-reactions is outer-sphere electron-transfer in nature. An excited-state reduction potential $E^\circ[Cu_4^{3+/2+*}]$ of -1.77 V vs SSCE ($\lambda = 1.39$ eV, $RT\ln K\kappa\nu =$ 0.58 V vs. SSCE) has been estimated for **7** through the oxidative quenching studies.

Table 7
Rate constants for the quenching of 7 by pyridinium acceptors in degassed acetone (0.1 mol dm^{-3} $^nBu_4NPF_6$) at 298 K[a]

Quencher[b]	$E(A^{+/0})$ (V) vs SSCE	k_q' (dm^3 mol^{-1} s^{-1})[c]
3,4-Dicyano-*N*-methylpyridinium	−0.11	4.05×10^9
2-Chloro-*N*-methyl-3-nitropyridinium	−0.37	7.78×10^9
4-Cyano-*N*-methylpyridinium	−0.67	5.23×10^9
4-Methoxycarbonyl-*N*-methylpyridinium	−0.78	2.59×10^9
4-Aminoformyl-*N*-ethylpyridinium	−0.93	9.17×10^8
3-Aminoformyl-*N*-methylpyridinium	−1.14	9.56×10^7
N-Ethylpyridinium	−1.36	1.13×10^7
4-Methyl-*N*-methylpyridinium	−1.49	1.47×10^6

[a] Data taken from Ref. [59].
[b] All the compounds are hexafluorophosphate salts except 3,4-dicyano-*N*-methylpyridinium and 2-chloro-*N*-methyl-3-nitropyridinium which are tetrafluoroborate salts.
[c] k_q' is the rate constant corrected for diffusional effects.

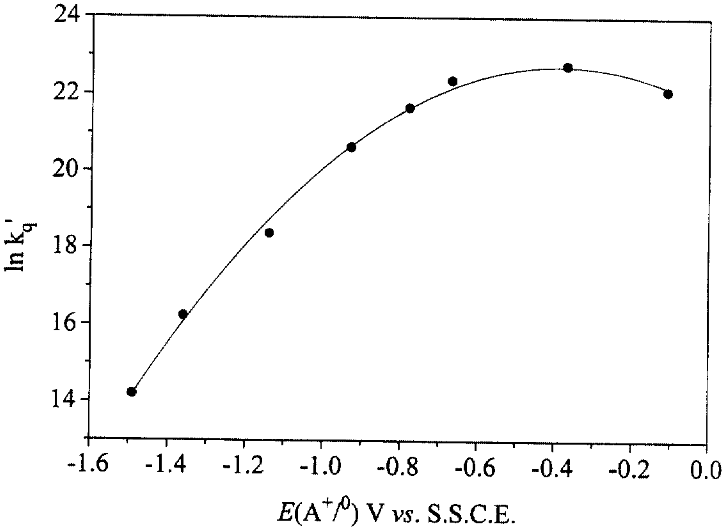


Fig. 8. Plot of ln k_q' vs $E(A^{+/0})$ for the oxidative electron-transfer quenching of 7* by pyridinium acceptors in degassed acetone (0.1 mol dm^{-3} $^nBu_4NPF_6$): (●) experimental, (———) calculated.

This indicates the strong reducing power of the tetranuclear copper(I) acetylide complex in the excited state.

The electron-transfer nature of these quenching reactions was further supported by nanosecond transient absorption spectroscopy. Similar to our previous studies on the photo-induced electron-transfer reactions between a series of trinuclear copper(I) acetylide complexes and various pyridinium acceptors [56,57,62], the transient absorption difference spectrum generated from the laser flash photolysis of a degassed acetone solution (0.1 mol dm^{-3} $^nBu_4NPF_6$) of complex 7 and

4-(methoxycarbonyl)-*N*-methylpyridinium is dominated by a high-energy band at *ca.* 390 nm and a much broader band near the near-infrared region. The 390 nm band is characteristic of pyridinyl radicals and matches well with the literature reported spectrum of the reduced radical of 4-(methoxycarbonyl)-*N*-methylpyridinium [102], while the broad intense band near the near-infrared region is characteristic of the intervalence-transfer (IT) transition in polynuclear copper acetylide clusters [56,57,62].

4. Concluding remarks

This paper summarized our recent efforts on the studies of polynuclear copper(I) and silver(I) clusters with chalcogenides and acetylides as bridging ligands. Very often, complexes of this kind exhibit unique and intriguing photoluminescent properties. It is anticipated that the tetranuclear and hexanuclear d^{10} clusters described in this paper may be utilized as building blocks in the formation of higher nuclearity luminescent materials with desirable physical and chemical properties.

Acknowledgements

V.W.W.Y. acknowledges financial support from the Research Grants Council and The University of Hong Kong, K.K.W.L. the receipt of a Sir Edward Youde Postgraduate Fellowship, administered by the Sir Edward Youde Memorial Fund Council, both K.K.W.L. and W.K.M.F. a Postgraduate Studentship and a Hung Hing Ying Postgraduate Scholarship, administered by The University of Hong Kong, and C.R.W. the receipt of a Postdoctoral Fellowship, also administered by The University of Hong Kong.

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