Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 531

www.rsc.org/dalton

PAPER

Polymorph and isomer conversion of complexes based on CuI and PPh_3 easily observed *via* luminescence†

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Received 3rd August 2011, Accepted 15th September 2011
DOI: 10.1039/c1dt11462j

Reactions between copper(I) iodide and triphenylphosphine have been explored in solution and in the solid state and six luminescent coordination complexes have been obtained and characterized by X-ray diffraction and UV-vis spectroscopy and photophysics. Solid-state reactions of CuI with PPh_3 in different conditions (kneading, vapour digestion) and stoichiometries resulted in the formation of high ratio ligand : metal compounds while tetrameric structures could be obtained only by solution reactions. Crystal structures were determined by single crystal X-ray diffraction while purity of the bulk product was checked by powder diffraction (XRPD). Three different tetrameric structures with 1 : 1 stoichiometry have been synthesized: two closed cubane-type polymorphs $[CuI(PPh_3)]_4$ (form **1a**) and $[CuI(PPh_3)]_4$ (form **1b**) and an open step-like isomer $[CuI(PPh_3)]_4$ (form **2**). The conversions between the polymorphs and isomers have been studied and characterized by XRPD. The most stable form $[CuI(PPh_3)]_4$ (form **1b**) can convert into the open step-like isomer $[CuI(PPh_3)]_4$ (form **2**) in a slurry experiment with EtOH or CH_2Cl_2 or AcCN and converts back into $[CuI(PPh_3)]_4$**1b** when exposed to vapors of toluene. At room temperature all the tetrameric compounds exhibit luminescence in the solid state and, notably, the two polymorphs show a dissimilar dual emission at low temperature. The luminescence features in the solid state seem to be peculiarly related to the presence of the aromatic phosphine ligand and depend on the Cu–Cu distance in the cluster.

Introduction

Copper(I) halide aggregates constitute a large family of compounds studied for decades for their photochemical and photophysical properties.[1–11] This class of compounds is attracting renewed interest[12–16] because of its potential applications in high-efficiency OLEDs.[17–19] Coordination systems based on copper halides show a remarkable structural diversity,[15] which arises from the many possible combinations of coordination numbers (two, three and four) available for copper(I) and for the geometries that can be adopted by the halide ions (from terminal to μ_2- and up to μ_8-bridging modes).

Organophosphine copper(I) halides have been extensively studied in the past[20–22] and several species with different metal coordination numbers and metal : ligand stoichiometries (Fig. 1) have been already synthesized and the crystal structure determined, while the luminescence properties have been explored only recently without a clear assignment on the nature of the emission bands. With respect to Cu(I) structures with halogens and amine-based ligands,[5,23,24] when the organic ligand is an aromatic phosphine, further interactions such as back bonding from the metal to the phosphorous system must be taken into account[25,26] and can play a role in the photophysics of the complexes. Since the organophosphine copper(I) iodide complexes could find applications in light emitting diode technology a full comprehension of the emission bands is essential to tune the emission properties.

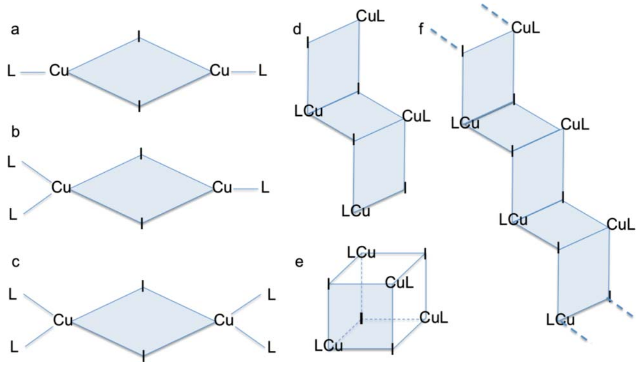

Fig. 1 Schematic representation of some examples of different geometries and stoichiometries for CuI aggregates; a)$[Cu_2I_2L_2]$; b)$[Cu_2I_2L_3]$; c)$[Cu_2I_2L_4]$; d)$[Cu_4I_4L_4]$ step-like; e) $[Cu_4I_4L_4]$cubane-like; f)$[CuIL]_\infty$ coordination polymer.

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† Electronic supplementary information (ESI) available. CCDC reference numbers 838119–838123. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11462j

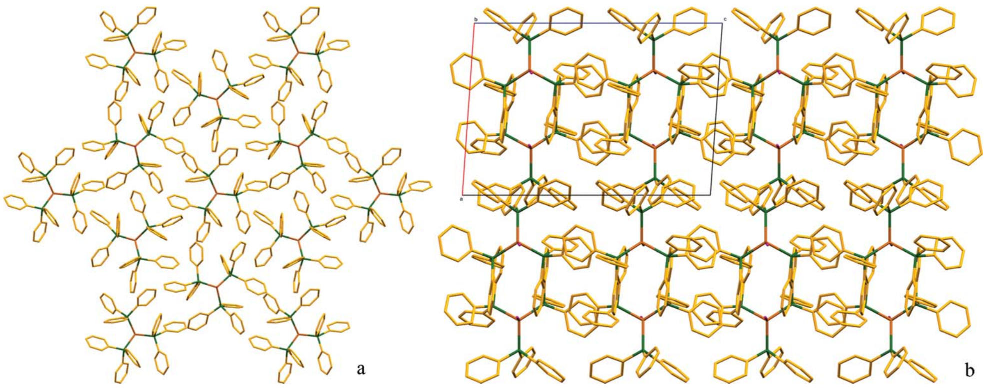


Fig. 2 a) [CuI(PPh$_3$)$_3$] (form **a**) and, b) [CuI(PPh$_3$)$_3$] (form **b**); hydrogen atoms are omitted for clarity.

The 1 : 1 : 1 Cu : halogen : ligand complexes CuX(PR$_3$) have tetrameric structures which may either be cubane-like (with all copper atoms *pseudo*-tetrahedral and all X atoms serving as μ$_3$-bridges) or step-like (with the tetramer containing two *pseudo*-tetrahedral and two three-coordinated copper atoms and two μ$_3$- and two μ$_2$- iodides). The 1 : 1 : 2 adducts CuX(PR$_3$)$_2$ may have either monomeric three-coordinate structures or dimeric pseudo-tetrahedral structures. The dimer compounds Cu$_2$X$_2$(PR$_3$)$_y$ (y = 2–4) nicely illustrate the propensity of the organophosphine copper(I) systems to form different polynuclear complexes with similar stabilities with different copper geometries of coordination.[27] At last the 1 : 1 : 3 adducts all seem to have monomeric pseudo-tetrahedral coordination.[28]

In solution, different complexes are simultaneously present due to the high constant of dissociation of the PPh$_3$ligand.[25] Despite the presence of a plethora of complexes in solution, pure compounds can be obtained as precipitates: the stoichiometry ratio determines the nuclearity of the compounds, while the polymorph or isomer outcome can be influenced by the choice of solvent or by the procedure used.

In this work we report on the synthesis and characterization (both structural and photophysical) of different Cu(I) coordination compounds with the PPh$_3$ ligand. All compounds have been obtained either by methods described in literature[29–32] and/or *via* solvent-free reactions such as kneading or vapor digestion.[33,34] It is well known that these approaches can be a valid alternative to traditional synthetic methods, since they reduce the amount of solvent required and are usually quantitative in yields. Sometimes, non-solution methods also allow the synthesis of different compounds which are not found *via* solvent synthesis.[35] As previously reported in the literature, the synthesis with a CuI : PPh$_3$ ratio of 1 : 3 yielded upon crystallization the monomer [CuI(PPh$_3$)$_3$] (form **a**),[29] but we observed also a new polymorph [CuI(PPh$_3$)$_3$] (form **b**) which is a metastable form. A CuI : PPh$_3$ ratio of 1 : 2 yielded the dimer [CuI(PPh$_3$)$_{1.5}$]$_2$[32] and, finally, a CuI : PPh$_3$ ratio of 1 : 1 yielded the crystallization of the cubane-like compounds [CuI(PPh$_3$)]$_4$ (form **1a**),[30] [CuI(PPh$_3$)]$_4$ (form **1b**)[36] and the step-like compound [CuI(PPh$_3$)]$_4$ (form **2**).[30] The conversions within the isomers and polymorphs were studied in solution and *via* vapor digestion.

We focused our attention on the luminescence properties of the dimer and the tetramers, which exhibit remarkably different emission features depending on the nature of the compound, which make these complexes interesting as sensor-like materials. The photophysical characterization was carried out in the solid and in solution and the results were interpreted on the basis of current theories on the luminescence of Cu(I) cubane clusters[4,37,38] with new indications for the specific case of organophosphine based complexes, whose properties have been scarcely investigated up to now.

Results and discussions

Synthesis and structure of [CuI(PPh$_3$)$_3$] (form a) and [CuI(PPh$_3$)$_3$] (form b)

Monomeric coordination compounds with a 1 : 3 molar ratio stoichiometry of CuI salt and PPh$_3$ were synthesized utilizing the experimental instructions previously reported.[29] The product obtained was a mixture of two concomitant polymorphic forms: [CuI(PPh$_3$)$_3$] (form **a**), which corresponds to a known structure and [CuI(PPh$_3$)$_3$] (form **b**) whose structure was determined by us. [CuI(PPh$_3$)$_3$] (form **b**) (Fig. 2b) crystallizes in the monoclinic $P2_1/c$ space group while [CuI(PPh$_3$)$_3$] (form **a**) (Fig. 2a) crystallizes in a denser structure in the trigonal $P3$ space group (1.39 g cm^{-3} and 1.42 g cm^{-3} respectively) which suggests that [CuI(PPh$_3$)$_3$] (form **a**) is the stable form at room temperature, according to the Kitaigorodskii's density rule.[39] The stability of [CuI(PPh$_3$)$_3$] (form **a**) was confirmed by an overnight slurry experiment in chloroform where the polymorph **b** converted into form **a**. No further analyses were performed on these two monomeric forms because of the difficulty to obtain them as a pure powder.

Synthesis and structure of [CuI(PPh$_3$)$_{1.5}$]$_2$

Dimeric compound [CuI(PPh$_3$)$_{1.5}$]$_2$ has been synthesized following the experimental procedure previously reported in the literature.[32] The [CuI(PPh$_3$)$_{1.5}$]$_2$ structure consists of a 4-atom ring (Cu$_2$I$_2$), in which the halogen atom acts as a bridge between copper atoms. Different copper coordination numbers are observed in this complex as shown in Fig. 3: one copper atom binds two P-based ligands and it has a distorted tetrahedral geometry while the other copper atom has a trigonal geometry. The distance between the two metal atoms is 3.044(5) Å; luminescence features linked to Cu–Cu distances are reported in the following section. We obtained also the solvate species [CuI(PPh$_3$)$_{1.5}$]$_2$·CH$_2$Cl$_2$ from the crystallization process (see ESI†) which shows a Cu–Cu distance

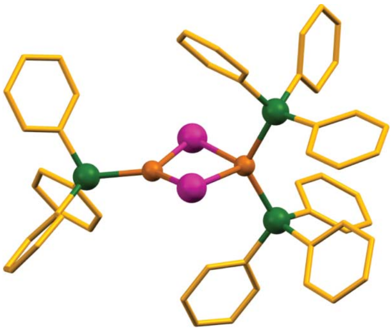


Fig. 3 The $[CuI(PPh_3)_{1.5}]_2$unit; hydrogen atoms are omitted for clarity.

(3.0444(5) Å) comparable to $[CuI(PPh_3)_{1.5}]_2$ and it is isomorphic to $[CuCl(PPh_3)_{1.5}]_2{\cdot}CH_2Cl_2$ reported in literature.[40]

Synthesis and structure of $[CuI(PPh_3)]_4$

Compounds with 1 : 1 : 1 ratio have been obtained only as in the form of tetrameric units; however it was possible to isolate two polymorphs of $[CuI(PPh_3)]_4$: a cubane-like cluster and a step-like cluster, as shown in Fig. 1d–e.

The first synthesis was carried out by following the reported procedure[30] resulting in the expected $[CuI(PPh_3)]_4$ (form **1a**); however on repeating the synthesis, a second phase appeared which we characterized as form **1b** of $[CuI(PPh_3)]_4$.[36,41]

Interestingly, once form **1b** had been obtained, a mixture of **1a** and **1b** was subsequently obtained on repeating the synthesis. At each repetition step, the percentage of form **1b** became predominant and increasing at each reaction, until only form **1b** could be obtained (see Fig. 4).

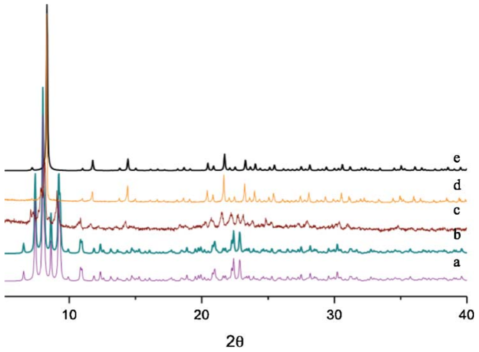


Fig. 4 a) calculated X-ray powder pattern of $[CuI(PPh_3)]_4$ (form **1a**); b) X-ray powder diffractogram of compounds obtained from the first synthesis corresponding to $[CuI(PPh_3)]_4$ (form **1a**); c) X-ray powder diffractogram of compounds obtained from the second synthesis where both form **1a** and **1b** of phases $[CuI(PPh_3)]_4$ could be recognized; d) X-ray powder diffractogram of compounds obtained in subsequent syntheses corresponding to form **1b**; e) calculated X-ray powder pattern of form **1b**.

The metastable $[CuI(PPh_3)]_4$ (form **1a**) product could no longer be obtained as a pure form in our laboratory, and mixtures of forms **1a** and **1b** were obtained when the synthesis was carried out in a different laboratory and with a fast crystallization process. This complex can be counted as a new example of disappearing polymorphs.[42]

$[CuI(PPh_3)]_4$ (form **1a**) is therefore the metastable form at RT, as also suggested by the lower density compared to **1b** (1.72 g cm^{-3} *versus* 1.77 g cm^{-3} at RT).[39]

Diffraction data for both polymorphs **1a** and **1b** were collected at RT and 90 K and structures were found to be in agreement with those previously reported.[29,36] The cubane-like clusters of $[CuI(PPh_3)]_4$ form **1a** and **1b** (Fig. 5 and Fig. 6) are distorted (Table 1) with the shortest Cu–Cu distance equal to 2.839(3) Å and 2.945(4) Å respectively at RT which are longer than the van der Waals distance (2.80 Å)[43] All Cu–Cu distances show a dramatic decrease on lowering the temperature with minima Cu–Cu distances equal to 2.7427(8) Å and 2.828(2) Å for **1a** and **1b** at 90 K. On the basis of the copper distances, only **1a** at low temperature should shows features ascribable to cluster-centered interactions while the luminescence data suggests the presence of such interactions also at RT for both compounds.

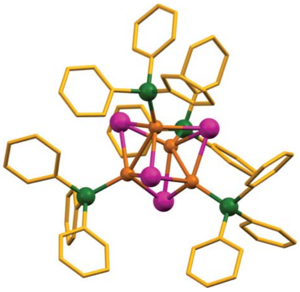


Fig. 5 The $[CuI(PPh_3)]_4$cubane-like unit; hydrogen atoms are removed for clarity and in shorter distances Cu atoms are bonded together.

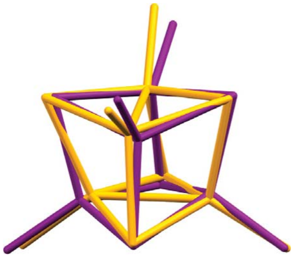


Fig. 6 Overlap between Cu_4I_4 clusters in$[CuI(PPh_3)]_4$**1a** (yellow) and $[CuI(PPh_3)]_4$ **1b** (purple); phenyl rings are removed for clarity.

The step-like cluster $[CuI(PPh_3)]_4$ form **2** (Fig. 7) has been obtained according to the reported synthesis.[30] However no single crystals could be obtained and X-ray powder diffraction data was measured at 90 K to ascertain that the crystal structure was retained. (Fig. S6, ESI† .)

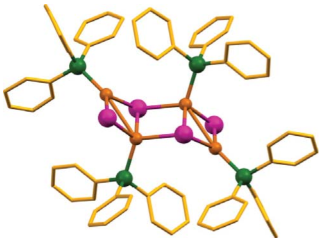


Fig. 7 The $[CuI(PPh_3)]_4$ form **2** unit; hydrogens are removed for clarity.

Table 1 Cu–Cu distances in cuprous organophosphine compounds. All distances are reported in Å. Labels are in agreement with those reported in ESI†

$[CuI(PPh_3)_{1.5}]_2$			$[CuI(PPh_3)]_4$ **1a** RT			$[CuI(PPh_3)]_4$ **1a** 90 K			$[CuI(PPh_3)]_4$ **1b** RT			$[CuI(PPh_3)]_4$ **1b** 90 K			$[CuI(PPh_3)]_4$ **2**		
Cu1	Cu2	3.0444(5)	Cu1	Cu2	2.928(8)	Cu1	Cu2	2.7431(4)	Cu1	Cu1	2.945(3)	Cu1	Cu1	2.8281(4)	Cu1	Cu1	2.834(2)
			Cu1	Cu3	2.896(6)	Cu1	Cu3	3.0809(4)	Cu1	Cu2	3.174(5)	Cu1	Cu2	3.1051(4)	Cu1	Cu2	3.404(3)
			Cu1	Cu4	2.873(4)	Cu1	Cu4	2.7971(8)									
			Cu2	Cu3	2.839(3)	Cu2	Cu3	2.9985(7)									
			Cu2	Cu4	3.165(3)	Cu2	Cu4	2.8085(8)									
			Cu3	Cu4	3.109(4)	Cu3	Cu4	2.8080(9)									

The step-like cluster $[CuI(PPh_3)]_4$ form **2** is characterized by two copper atoms *pseudo*-tetrahedral and two three-coordinate copper atoms; although a quite short Cu–Cu distance is observed in the complex (2.834(2) Å at RT) the different coordination around the copper atoms seems to be responsible for the weak luminescence properties of this compound (*vide infra*).

Solvent free reactions

The possibility of obtaining compounds based on $CuI:PPh_3$ *via* solvent free reactions with $CuI:PPh_3$ ratios of 1 : 1, 1 : 2 and 1 : 3 was also explored. Kneading process (i.e grinding the physical mixture with a drop of solvent)[33] produced only $[CuI(PPh_3)]_4$ (form **2**) irrespective of the ratio or solvent used.

The physical mixture between CuI and PPh_3 with different ratios was exposed to the vapor of organic solvents and the final products depended on the starting solvents and ratios. Form **2** was obtained with the $CuI:PPh_3 = 1:1$ molar ratio exposed to vapor of acetonitrile; monomeric $[CuI(PPh_3)_3]$ (form **a**) was obtained with the $CuI:PPh_3 = 1:2$ molar ratio exposed to acetonitrile vapour while in all the other cases only the monomer $[CuI(PPh_3)_3]$ (form **b**) was observed.

Interconversions between isomers

The isomer conversion *via* exposure to solvent vapour was also investigated. It has been observed that the two isomeric forms $[CuI(pic)]_\infty$ and $[CuI(pic)]_4$ interconvert in presence of organic solvent.[24] In our case form **1b**, when exposed to saturated atmosphere of acetonitrile, fully converts into form **2** as confirmed by XRPD measurements (Fig. 8).

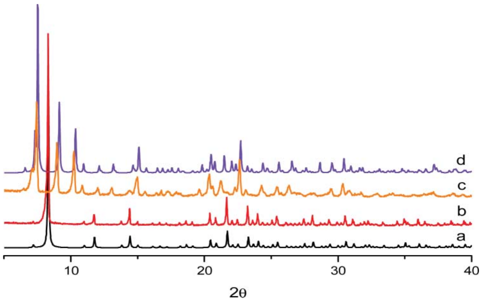
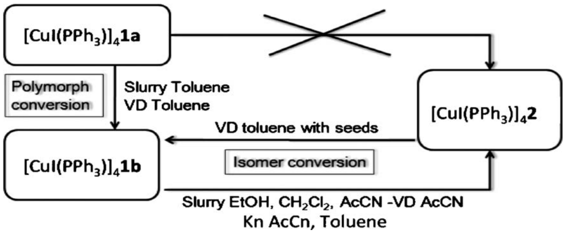


Fig. 8 a) $[CuI(PPh_3)]_4$ (form **1b**) calculated; b) $[CuI(PPh_3)]_4$ (form **1b**) experimental; c) $[CuI(PPh_3)]_4$ (form **2**) experimental after conversion; d) $[CuI(PPh_3)]_4$ (form **2**) calculated.

Since solid form **1b** is characterized by a bright green emission while form **2** shows only a very weak luminescence (*vide infra*), the conversion between the two isomeric forms produces a switch-on/switch-off signal which can be easily detected by naked eyes. When $[CuI(PPh_3)]_4$ (form **1a**) is exposed to vapors of toluene it rapidly converts into form **1b** which subsequently transforms into form **2**. The conversion from **1b** to **2** was observed in other experimental conditions such as in kneading experiments with acetonitrile or toluene or slurry experiments with ethanol, dichloromethane or acetonitrile. The conversion is reversible since it is possible to obtain **1b** from a slurry of form **2** with seeds of form **1b**. All interconversions are summarized in Scheme 1.



Scheme 1 Summary of all interconversions between polymorphic and isomeric forms. (VD = vapour digestion, Kn = kneading).

Photophysical properties

The photophysical properties of compounds $[CuI(PPh_3)]_4$ **1a**, **1b**, **2** and $[CuI(PPh_3)_{1.5}]_2$ and of the free ligand PPh_3 have been investigated in solution and in the solid state, both at room temperature and at 77 K. The main luminescence data are summarized in Table 2.

Toluene has been used as a solvent for **1a**, **1b** and $[CuI(PPh_3)_{1.5}]_2$, to retain the main cluster features of the complexes. For the same reason, acetonitrile was chosen for the solubilization of $[CuI(PPh_3)]_4$ form **2**, but this compound was found to be unstable in solution. It is worth recalling that previous studies on $Cu:Cl:PPh_3$ complexes in solution have highlighted the presence of different equilibria between various complexes due to ease of exchange of the PPh_3 ligand.[25] The absorption spectra of compounds **1a**, **1b** and $[CuI(PPh_3)_{1.5}]_2$ in toluene show absorption features extending up to 350–400 nm, ascribable to CT transitions, while the absorption of the free ligand PPh_3 does not exceeds 320 nm (see Fig. S7, ESI†).[31,44]

Forms **1a**, **1b** and $[CuI(PPh_3)_{1.5}]_2$ are non emissive in air-equilibrated solutions and display a weak emission centered around 620 nm in air-free toluene at room temperature ($\phi_{em} = 2–3 \times 10^{-3}$), with lifetimes on the order of 200–300 ns (Fig. S7, ESI† and Table 2). The similarities between the emission features of the three compounds point to a loss of the rigid cluster structure in solution in favour of a comparable pseudo-tetrahedral geometry and the observed luminescence can tentatively be assigned to MLCT (metal-to-ligand charge transfer) excited states.[45] In the dimeric

Table 2 Luminescence parameters of the ligand and Cu(I) complexes in air–free toluene solutions and in the solid state, at room temperature and at 77 K

		Emission at RT			Emission at 77 K	
		λ_{max}[a]/nm	ϕ_{em}[b]	τ[c]/μs	λ_{max}[a]/nm	τ[c]/μs
PPh_3	Solution	468	6.0×10^{-3}	0.6×10^{-3}	445	13.6×10^3
	Solid[e]	437		0.8×10^{-3}	434	2.4×10^3
$[CuI(PPh_3)]_4$ **1a**	Solution	628	2.9×10^{-3}	0.26	412	224.8
	Solid	544		4.7	410, 591	117.3, 26.0[d]
$[CuI(PPh_3)]_4$ **1b**	Solution	628	1.7×10^{-3}	0.22	412	190.4
	Solid	518		3.2	434, 516	271.8, —
$[CuI(PPh_3)_{1.5}]_2$	Solution	620	1.9×10^{-3}	0.28	412	185.8
	Solid	482		7.1	414	397.0
$[CuI(PPh_3)]_4$ **2**	Solution	—	—	—	—	—
	Solid	527		3.4	515	11.7

[a] From corrected emission spectra. [b] Emission quantum yields in solution, determined by comparing corrected emission spectra, using quinine sulfate in air-equilibrated 1 N H_2SO_4 ($\phi_{em} = 0.546$)[51] as a standard for PPh_3 and $[Ru(bpy)_3]Cl_2$ in air-equilibrated water ($\phi_r = 0.028$)[51] as a standard for the complexes, excitation at 300 nm for PPh_3 and at 330 nm for the complexes. [c] Excitation at 278 or 300 nm for PPh_3 and at 331 nm for the complexes. [d] A rise time of 7.3 μs is detected, see text. [e] Emission spectra of PPh_3 in the solid state are shown in Fig. S10, ESI.†

compound $[CuI(PPh_3)_{1.5}]_2$, Cu(I) experiences both a trigonal and a tetrahedral geometry, the latter with two phosphine ligands, and the tetrahedral part of the cluster is probably responsible for the emission. Compound **2**, where the tetrahedral coordination of copper includes only one phosphine ligand is instead non stable in solution, since only a weak emission from PPh_3 was observed.

At 77 K in glassy toluene all the three emissive compounds show a luminescence band centered around 415 nm, that is largely hypsochromically shifted in comparison with the room temperature emission, and is blue-shifted also with respect to the low temperature emission of the free PPh_3 ligand (Fig. S7, ESI† and Table 2). The 77 K luminescence of PPh_3, in fact, is centered at 445 nm with a lifetime of 13.6 ms and is attributed to phosphorescence.[31] The spectral features and the lifetimes, on the order of 200 μs, of the luminescence of the complexes at 77 K, suggest a ligand contribution to the emission, that can be tentatively assigned to a mixed MLCT/LC (ligand-centered) phosphorescence. A similar long-lived blue emission in solution at 77 K has been recently reported for Ag(I)-bis(diphosphine) complexes, and has been attributed to ^{3}MLCT/^{3}IL (intra-ligand) states based on tetrahedral geometry.[46]

Reflectance spectra of solid samples of PPh_3 and complexes **1a**, **1b**, $[CuI(PPh_3)_{1.5}]_2$ and **2** (Fig. S8, ESI†), revealed absorption bands below 350 nm for the ligand, with maxima at 212 and 264 nm, ascribable to phenyl-centered and n→ π* phosphorous→phenyl transitions, respectively,[25,47] and a longer extension of the absorption up to 370 nm for the complexes, with the exception of **2** that tails till 420 nm. A clear band at 300 nm is more pronounced for the two solids **1a** and **1b** while solid $[CuI(PPh_3)]_4$ **2** displays a more pronounced absorption around 350 nm.

With respect to the solution case, the solid state luminescence differentiates to a larger extent the four examined complexes. The two polymorphic forms **1a** and **1b**, show different features. Form **1a** displays a bright green–yellow emission at 544 nm at room temperature whereas at 77 K a dual emission is clearly observed, with maxima at 410 and 591 nm (see Fig. 9a and Table 2), that noticeably renders the resultant emission color nearly white. These luminescence features closely resemble the behavior of Cu(I) cubane structures with aromatic amine ligands,[5–8,23] widely studied by Ford and co-workers, where a dual emission from CC (cluster-centered) and XLCT (iodide to ligand charge transfer) poorly coupled triplet excited states occur. The room temperature emission of form **1a** can thus be attributed to ^{3}CC (low energy, LE, emission), and the same band red-shifts at 591 nm at 77 K due to the shortening of the Cu–Cu distance at low temperature.[35,48] The band at 410 nm that appears at 77 K, with a lifetime of 117 μs, can then be ascribed to ^{3}XLCT (high energy, HE, emission). This compound presents a Cu–Cu distance in the cluster of 2.839(3) Å at RT, slightly longer than the sum of the orbital radii (2.80 Å), which markedly shortens up to 2.7427(8) Å at 90 K. Interestingly, the LE band at 591 nm shows a rise of 7.3 μs, followed by a decay of 26.0 μs (see Fig. S9, ESI†). Ford and co-workers also describe LE rise-times considerably shorter than the HE emission lifetime (ns *vs.* μs range) for $Cu_4I_4L_4$ clusters with pyridinic ligands, speculating on a third higher energy state that directly populates the LE state.[5] Excitation spectra monitored at 590 nm and 410 nm at low temperature and that measured at 544 nm at room temperature (Fig. 9a), closely resemble those reported for ^{3}XLCT and ^{3}CC bands of solid $[CuI(py)]_4$.[49] The excitation spectrum measured on the LE band is more confined below 350 nm, even if a clear differentiation is difficult due to the overlap of the two emission bands.

Solid **1b** behaves quite differently from its polymorphic form **1a**, showing at room temperature a green emission centered at 518 nm with a lifetime of 3.2 μs, significantly blue-shifted with respect to the room temperature emission of **1a**. At low temperature, then, a dual emission is also observed, but with one band centered at 434 nm and a less intense band at 516 nm, substantially unshifted with respect to the room temperature case (Fig. 9b and Table 2). The description of the dual luminescence of compound **1b** in terms of ^{3}XLCT and ^{3}CC is less straightforward, in consideration of the fact that all the Cu–Cu distances estimated in the cluster are longer than 2.80 Å (2.945(4) Å, see Table 1). It is however emerging from recent examples in the literature that organophosphine copper(I) halides with Cu–Cu distances in the range 2.9–3.0 Å show this type of thermochromism, characterized by a dual emission at low temperature with a LE band almost unshifted with respect to the room temperature emission and a blue HE band.[17,36,50] The

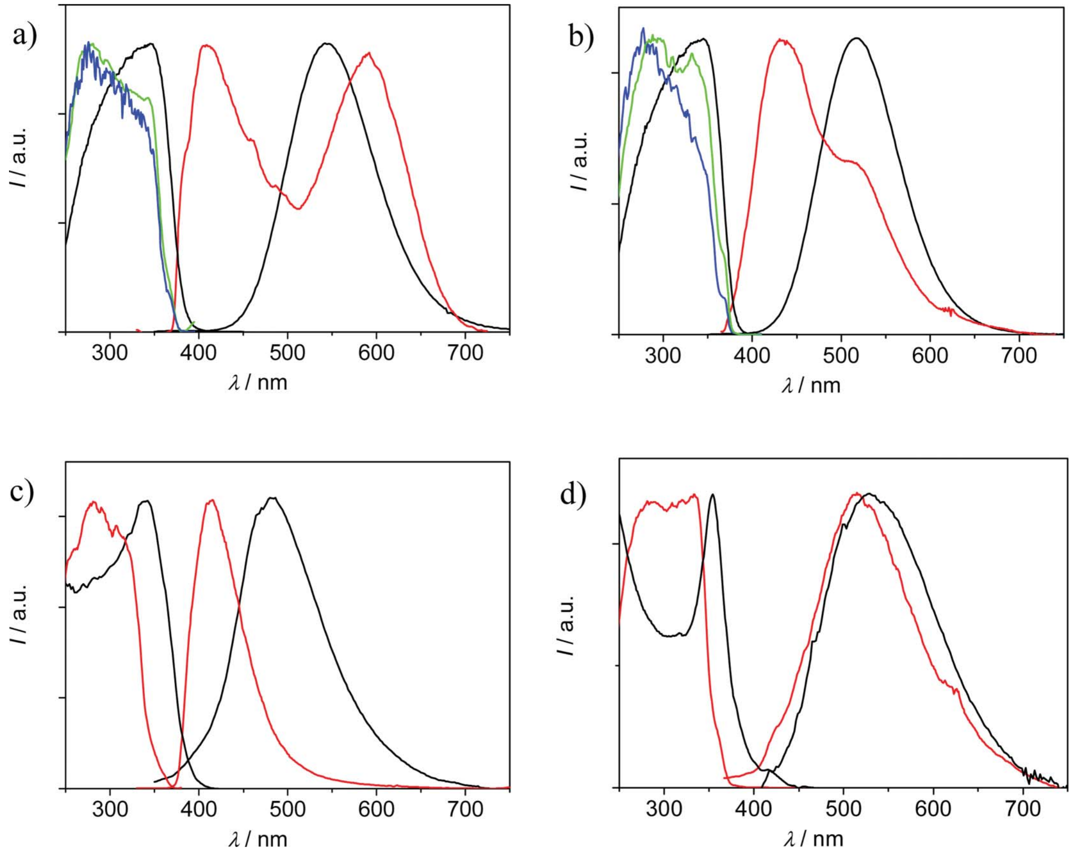


Fig. 9 Normalized emission and excitation spectra of solids (a) $[CuI(PPh_3)]_4$ form **1a**, (b) $[CuI(PPh_3)]_4$ form **1b**,(c) $[CuI(PPh_3)_{1.5}]_2$ and (d) $[CuI(PPh_3)]_4$ form **2**, at room temperature (black lines) and at 77 K (red lines). For (a) and (b) the excitation spectra at 77 K measured on the HE band are reported as green lines whereas those measured on the LE band are reported as blue lines.

excitation spectra measured at both temperature are similar to those observed for $[CuI(PPh_3)]_4$ **1a** (Fig. 9b), indicating a similar nature of the excited states and confirming the CC nature of the LE band. The reduced shift in the position of the LE band with temperature can be interpreted considering that at longer Cu–Cu distances the distortion of the CC state with respect to the ground state is reduced.[49] The occurrence of a CC based emission in clusters with Cu–Cu distances longer than 2.8 Å, however, seems to be correlated to the presence of the aromatic phosphine ligand. It is known that the phosphorous–metal bond of triphenylphosphine–transition metal complexes is not simply describable by the charge donation from the phosphorous lone-pair orbital to the metal, but interactions between the metal d orbitals and the phosphorous–carbon σ orbitals also participate to the bond.[26] We can thus speculate that the involvement of 3d electrons in a "back-bonding" toward the ligand renders the d→s,p metal centered contribution to the CC state less effective: the ^{3}CC emission should be of predominant halide-to-metal charge transfer (XMCT), thus possible also at distances slightly longer than the sum of the van der Waals radii and less sensitive to the contraction of the Cu–Cu cluster occurring when the temperature is decreased. DFT calculations have been performed on $Cu_4X_4L_4$ structures with L = PH_3 or NH_3,[47] indicating a larger X contribution to the HOMO and a larger Cu contribution to the LUMO when L = PH_3, but further calculations are required to investigate the nature of the transitions when the phosphine bear aromatic groups.

Compound $[CuI(PPh_3)_{1.5}]_2$ emits at 482 nm at room temperature and at 414 nm at 77 K with no evidence of dual emission (Fig. 9c). The Cu–Cu distances in this case are much longer than the sum of the orbital interaction radii (3.044(5) Å) and this leads to describe the luminescence at room temperature in terms of ^{3}XLCT phosphorescence; the excitation spectrum recorded at 482 nm is in line with this analysis. The excitation spectrum measured at 414 nm at low temperature, instead, is markedly blue-shifted, suggesting a more pronounced LC nature of the emission, supported also by the long lifetime of 397 μs.

It can be noticed that in all the three previously discussed cases the 77 K solid state emission (considering the HE bands for polymorphs **1a** and **1b**) is very similar for spectral features and lifetime to that registered in solution at the same temperature and this point to a similar nature of the emitting excited state that involves the ligand orbitals.

$[CuI(PPh_3)]_4$ form **2**, that is non-emissive in solution, shows a very weak luminescence also in the solid state. The room temperature emission, centered at 527 nm with a lifetime of 3.4 μs, slightly blue-shifts at 515 nm at low temperature, with a lifetime of 11.7 μs (Fig. 9d and Table 2). The excitation spectrum at room temperature show a sharp peak at 354 nm, responsible of the observed emission (excitation below 300 nm yielded a more broadened and red-shifted emission). In this compound, the crystal data evidenced the presence of only one Cu–Cu distance in the unit cell of 2.83 Å (Table 1), close to the orbital interaction limit, so the observed weak emission can be tentatively interpreted in terms of ^{3}XLCT emission at both temperatures.

Conclusions

Our study confirms the tendency of organophosphine copper(I) iodide compounds to form polynuclear complexes of different structural types but of similar stabilities. On the other hand the observation of the existence of two polymorphs: $[CuI(PPh_3)_3]$ **a** and **b** and $[CuI(PPh_3)]_4$**1a** and **1b** for both species suggests also the propensity of organophosphine copper(I) iodide compounds to afford polymorphic modifications, probably because of the flexibility of copper(I) in coordination systems. Coordinating solvents seem to stabilize complexes with three coordinated copper atoms, while the stoichiometry influences the nuclearity of the complexes.

The extensive photophysical characterization in solution and solid allowed to a deeper understanding on the nature of the luminescence bands. Room temperature emission is postulated to be of ^{3}CC nature also in compound $[CuI(PPh_3)]_4$ (form **1b**) which has Cu–Cu distances longer than 2.80 Å, a behavior not observed in similar complexes with nitrogen based ligands. The experimental evidence suggests that the ^{3}CC excited state has a predominant halide-to-metal charge transfer (XMCT) nature, which is in agreement with the absence of bathochromic shift in lowering the temperature. The contraction of the cubane cluster $[CuI(PPh_3)]_4$ (form **1a**) at low temperature reduces the distances among the Cu atoms till 2.7431(4) Å, which is shorter than the sum of the van der Waals radii. In this case the ^{3}CC emission can be considered of both d → s,p metal centered and XMCT nature, and the red-shift of the LE band at low temperature is indicative of the effect of the shortening of the Cu–Cu distance on the transition. In solution the room temperature emission is described as ^{3}MLCT whereas the blue band registered at 77 K is attributed to mixed ^{3}MLCT/^{3}LC.

In summary, we have prepared and characterized a rather unusual pair of polymorphs and isomers and studied their interconversion and luminescence properties. Our results have established that $[CuI(PPh_3)_3]$ as form **a** is more stable than as form **b** at RT, while in the case of the tetrameric compounds $[CuI(PPh_3)]_4$ form **1b** is more stable than form **1a**. The relative stability of the isomers, on the other hand, depends on the nature of the solvent. $[CuI(PPh_3)]_4$ as form **1b** converts into form **2** in the presence of solvents such as ethanol, acetonitrile and dichloromethane, while the reverse reaction takes place only in slurry in toluene. The conversion can be easily detected by naked eye because forms **1b** and **2** show a dramatic difference in the emission output and the system could be used as a switch-on/switch-off signal.

Experimental section

Synthesis of $[CuI(PPh_3)_3]$ forms a and b

The synthesis of the two forms **a** and **b** of compound $[CuI(PPh_3)_3]$ was carried out by utilizing the experimental instruction as previous reported in the literature.[29] Stoichiometric quantities of CuI (1 mmol, 0,190 g) and PPh3 (3 mmol, 0.786 g) were refluxed for 2–4 h in chloroform and the hot, clear solution has been filtered. On slow cooling and evaporation of the solvent, the products have been separated as colourless crystal. A mixture of polymorphs **a** and **b** was obtained.

A different synthetic strategy has been developed to make $[CuI(PPh_3)_3]$ **b**:

CuI salt (1 mmol; 0.190 g) was dissolved in dimethylchloride under reflux then a solution of PPh_3 (3 mmol; 0,786 g) in *n*-hexane was added. After two days colourless crystals of $[CuI(PPh_3)_3]$ **b** appeared.

Polymorph **b** was also obtained exposing: a) a 1 : 1 molar ratio physical mixture of CuI and PPh_3 to vapour of toluene; b) a 1 : 2 molar ratio physical mixture of CuI and PPh_3 to vapour of toluene, acetonitrile and dichloromethane; c) a 1 : 3 molar ratio physical mixture of CuI and PPh_3 to vapour of toluene and acetonitrile.

Synthesis of $[CuI(PPh_3)_{1.5}]_2$

The synthesis of $[CuI(PPh_3)_{1.5}]_2$ was previously reported in the literature.[32] We report an alternative synthetic strategy. CuI (1 mmol, 0.190 g) was dissolved in 20 mL of acetonitrile stirring at 70 °C. Then, a solution of PPh_3 (2 mmol, 0.524 g) in AcCN (20 mL) was added to the clear solution. The solution was stirred at 70 °C overnight, and crystals with prismoidal shape appeared after two days.

Synthesis of $[CuI(PPh_3)]_4$ form 1a and $[CuI(PPh_3)]_4$ form 1b

The synthesis of compound $[CuI(PPh_3)]_4$ form **1a** has been made utilizing the experimental instruction as previous reported in the literature.[29] CuI (1 mmol, 0.190 g) and PPh_3 (1 mmol, 0.262 g) have been refluxed overnight in toluene. Very slow cooling (overnight) of the resultant clear solution to room temperature resulted in well formed crystals of the complex $[CuI(PPh_3)]_4$.

As described in discussion section, we had some difficulties to re-prepare $[CuI(PPh_3)]_4$ form **1a**; the second time we followed the above described experimental procedure, we obtained a mixture of polymorph **1a** and **1b**, and from the third time on, we obtained always the most thermodynamically stable polymorph **1b**.

Compound $[CuI(PPh_3)]_4$ form **1a** could be re-prepared in drastic kinetic conditions: copper(I) iodide (0.190 g, 1 mmol) was dissolved in toluene under reflux and than a solution in toluene of PPh_3 (0.262 g, 1 mmol) was added. The transparent solution was suddenly evaporated under reduced pressure. The predominant compound was mainly **1a** even if minor quantities of **1b** have been observed.

Synthesis of $[CuI(PPh_3)]_4$ form 2

The synthesis of compound $[CuI(PPh_3)]_4$ form **2** was made utilizing the experimental instruction as previously reported in the literature.[20] Stoichiometric quantities of CuI (1 mmol, 0190 g) and PPh_3 (1 mmol, 0.262 g)were refluxed for 1 h in chloroform and the hot, clear solution filtered. On slow cooling and solvent evaporation, the product separate as colourless crystal

The same compound has been obtained by grinding a physical mixture of CuI and triphenylphosphine in 1 : 1 molar ratio with two drops of toluene or grinding a physical mixture of CuI and triphenylphosphine in 1 : 2 and 1 : 3 molar ratio with two drops of acetonitrile.

Photophysics

Solvents used for photophysical determinations were of spectroscopic grade (C. Erba). Dilute solutions were analyzed in 10 mm path length square optical Suprasil Quartz (QS) cuvettes at room temperature, solid samples were placed inside two quartz slides, while capillary tubes immersed in liquid nitrogen in a home-made quartz Dewar were used for measurements at 77 K of both solids and solutions. The absorption spectra of solutions were obtained with a Perkin-Elmer Lambda 950 UV/vis/NIR spectrophotometer, whereas reflectance spectra of solid samples were acquired on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer equipped with a 60 mm integrating sphere.

Emission and excitation spectra were measured in a SpexFluorolog II spectrofluorimeter, equipped with a Hamamatsu R928 phototube, in right angle mode for solutions and front face mode for solids. Corrected emission spectra are reported, the uncertainty on the band maxima is 2 nm. Luminescence quantum yields in solution were evaluated from the area of the luminescence spectra, corrected for the photomultiplier response, with reference to quinine sulfate in air-equilibrated 1 N H_2SO_4 (ϕ_{em} = 0.546)[51] for PPh_3 and to $[Ru(bpy)_3]Cl_2$ in air-equilibrated water (ϕ_r = 0.028)[51] for the complexes. The samples with absorbances <0.1 were bubbled with Ar for approximately 15 min and sealed in home made 10 mm optical cells. The luminescence tail of toluene emission below 450 nm was previously subtracted from the spectra. The estimated error on the quantum yields is 20%.

Luminescence lifetimes in the range 0.5 ns–100 μs were measured with an IBH 5000 F time-correlated single-photon counting device, by using pulsed NanoLED excitation sources at 278 or 331 nm (pulse width ≤ 0.6 ns). Longer lifetimes were measured on the same IBH 5000 F TCSPC device, by using a pulsed SpectraLED excitation source at 370 nm or on a Perkin-Elmer LS-50B spectrofluorimeter equipped with a pulsed Xe lamp and in a gated detection mode. Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 or with the PHOSDecay Software provided by the manufacturers, with an estimated error on the lifetimes of 10%. In some cases the low temperature luminescence of the solid samples showed multiexponential decays; Table 2 reports lifetimes corresponding to pre-exponential factors >80%.

X-ray powder diffraction

X-ray powder diffractograms were collected on a Panalytical X'Pert PRO automated diffractometer with Cu-Kα radiation and X'Celerator detector without a monochromator equipped with a Anton Paar TK 450 chamber to collect data at low temperature. The program PowderCell[52] was used for calculation of X-ray powder patterns.

Crystal structure determination

Crystal data for **1a** and **1b** were collected on a Oxford Xcalibur S with Mo-Kα radiation, λ = 0.71073 Å, monochromator graphite and equipped with a liquid nitrogen Oxford-Cryostream device.

Crystal data and details of measurements are summarized in Table S1.† SHELX97[53] was used for structure solution and refinement based on **F**^{2}. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were added in calculated positions. Mercury[54] was used for the graphical representation of the results.

Acknowledgements

We thank MIUR, the University of Bologna and CNR (Project PM-P04-010 MACOL) for financial support to this research. PPM thanks the University of Bologna for a PhD grant. We thank Dr Nicola Armaroli for helpful discussion.

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