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Strong Luminescent Copper(I)-halide Coordination Polymers and Dinuclear Complexes with Thioacetamide and N,N-donor ligands†

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Direct reactions between copper(I) halides, thioacetamide (TAA) and 4,4'-bipyridine (4,4'-bpy) or pyrazine (pyz) in MeCN lead to the formation of mixed ligand compounds $[\text{Cu}_2\text{Cl}_2(\text{TAA})_2(4,4'\text{-bpy})]_n$ (**1**), $[\text{Cu}_2\text{X}_2(\text{TAA})_4(4,4'\text{-bpy})] \cdot (4,4'\text{-bpy})$ (X = Cl (**2**), Br (**3**) and I (**4**)) and $[\text{Cu}_2\text{Cl}_2(\text{TAA})_2(\text{pyz})]_n$ (**5**), and the binuclear complex $[\text{Cu}_2\text{I}_2(\text{TAA})_4]$ (**6**). The formation of these compounds strongly depends on both the ratio of the reactants and the halide. The structure of these compounds has been determined by X-ray diffraction showing interesting intermolecular interactions based on hydrogen bonding. The physical properties of these compounds shows that **1-5** are strongly luminescent with a red emission (500–750 nm) at room temperature in solid state, while compound **1** behaves as a semiconductor and **5** as an insulator.

Introduction

Coordination polymers (CPs) have attracted increasing attention in recent years due to their interesting architectures and physico-chemical properties.¹ In particular, those with Cu(I) are relevant because of their structural diversity, electrical conductivity²⁻⁵ and luminescent properties.⁶⁻⁸ Among these systems, Cu(I) halides represent a versatile type of building blocks that have been successfully used for the synthesis of CPs in combination with different neutral ligands.^{2, 3, 9-11} Many efforts have been devoted to the judicious selection of ligands in the construction of novel functional materials since they play an important role in tuning the final architecture of the products, and their physico-chemical properties.¹² Additionally, the selection of the halide¹³ or/and the metal-to-ligand stoichiometry¹⁴ may affect to both the final structure and properties of the CPs. In this context, it is well-known that N,N'-ditopic ligands are able to generate coordination networks with fascinating supramolecular structures, which can be extended by combining one or several of these organizing forces such as coordination bonds, hydrogen bonds and/or π - π stacking interactions.¹⁵⁻¹⁷ This kind of ligands have strong coordination ability through the nitrogen atoms, and can act as rigid-linear linkers between metal ions¹⁸⁻²⁷ or as multitopic donor building blocks for the construction of more intriguing networks that include 1D, 2D and 3D coordination polymers.²⁸⁻³⁰ Additionally, aromatic nitrogen-donor ligands can improve

photoluminescence properties of Cu(I) halides.³¹⁻³⁴ On the other hand, organosulfur-containing ligands have demonstrated their potential as linkers in the synthesis of metal-organic networks showing interesting electrical and luminescence properties.³⁵ In particular, it has been observed that the incorporation of thiolate-S bridging ligands between adjacent transition-metal centres is highly desirable in terms of magnetic, electrical and optical properties. This is due to the fact that the metal orbital energies are better matched for sulphur, leading to a higher delocalization of spin/charge density through the bridging atoms. We have reported multifunctional CPs based on Cu(I) and S,N-ligands such as pyrimidinedisulfide, 2-dipyridyldisulfide and thioacetamide, showing luminescent emission and electrical conductivity.^{4, 5, 36} It seems that CPs based on the combination of mixed ligands³⁷ enhance the structural diversity, and may produce some remarkable physical properties compared to the ones obtained using only one type of ligand.³⁸⁻⁴⁰ However, design and structure prediction still remain a challenge. Despite the fact that there are some examples of Cu(I) halide coordination polymers based on ligands which contain at once hard N and soft S donor atoms,^{5, 41-45} or organosulfur ligands and acetonitrile,^{46, 47} to the best of our knowledge, the combination of organosulfur and N-heteroaromatic ligands to obtain Cu(I) halide coordination polymers remains still unexplored. Introduction of N,N'-ditopic ligands such as 4,4'-bipyridine and pyrazine to CuX-thioacetamide system, might lead to new compounds with intriguing structures and improve their electrical and luminescent properties. Due to competition between both kind of ligands in the reaction mixture, it is possible in principle to tune the system depending on the ratio of them.⁴⁸

In this work, we have investigated the coordination chemistry of copper complexes involving copper(I) halides, thioacetamide and 4,4'-bipyridine or pyrazine with the aim to produce multifunctional materials with electrical conductivity and photoluminescence.

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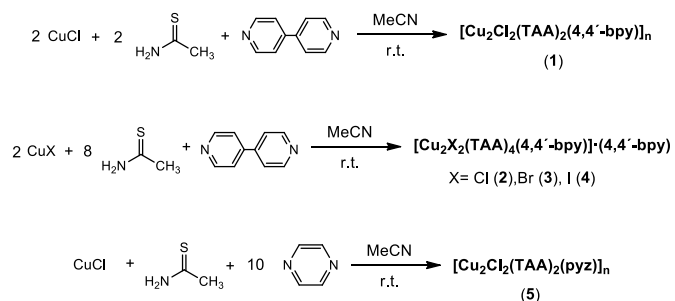
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Results and discussion

Synthesis

Mixed ligand compounds **1-5** were synthesized in acetonitrile at room temperature on air, as shown in Scheme 1.



Scheme 1 Synthesis of mixed ligand compounds **1-5**.

Direct reactions between CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), TAA and 4,4'-bpy were carried out in acetonitrile in a 2:2:1 stoichiometry, resulting in the formation of microcrystalline solids that were characterized by FT-IR, elemental analysis and X-ray powder diffraction (Fig. S1-S6). These results revealed that when the reaction was carried out with CuCl, the mixed-ligand coordination polymer $[\text{Cu}_2\text{Cl}_2(\text{TAA})_2(4,4'\text{-bpy})]_n$ **1**, was formed. However, the analogous reactions carried out with CuX ($\text{X} = \text{Br}, \text{I}$), yielded the previously reported coordination polymers $[\text{CuX}(4,4'\text{-bpy})]_n$.^{10, 14, 17} The lack of thioacetamide observed in these compounds prompted us to test reactions increasing the TAA:4,4'-bpy ratio. The Table 1 shows that reactions tested in a 2:4:1 stoichiometry gave rise to the formation of the same compounds, while when the reactions were carried out in a larger excess, 2:8:1 ratio, the dinuclear complexes $[\text{Cu}_2\text{X}_2(\text{TAA})_4(4,4'\text{-bpy})]_n \cdot (4,4'\text{-bpy})$ ($\text{X} = \text{Cl}$ (**2**), Br (**3**) and I (**4**)) were synthesized. Unfortunately, in the case of CuBr and CuI, we were unable to isolate mixed ligand polymers analogous to **1** and only rich thioacetamide complexes **2-4** were obtained by increasing the TAA:4,4'-bpy ratio.

Table 1 Compounds obtained from the direct reactions between CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), TAA and 4,4'-bpy in acetonitrile using different $\text{CuX}:\text{TAA}:4,4'\text{-bpy}$ ratios.

	2:2:1	2:4:1	2:8:1
CuCl	1 *	1 *	2 *
CuBr	$[\text{CuBr}(4,4'\text{-bpy})]_n$ ^{14, 17}	$[\text{CuBr}(4,4'\text{-bpy})]_n$ ^{14, 17}	3 *
CuI	$[\text{CuI}(4,4'\text{-bpy})]_n$ ^{10, 17}	$[\text{CuI}(4,4'\text{-bpy})]_n$ ^{10, 17}	4 *

* this work

Reactions with pyrazine in a $\text{CuX}:\text{TAA}:\text{pyz}$ 2:2:1 stoichiometry led to $[\text{CuCl}(\text{TAA})_3]$ and $[\text{CuBr}(\text{TAA})_n]$, containing only thioacetamide as coordinated ligand, for CuCl and CuBr, respectively, while $[\text{Cu}_2\text{I}_2(\text{pyz})]_n$ for CuI.^{10, 46} The $[\text{CuX}(\text{TAA})]$ ($\text{X} = \text{Cl}, \text{Br}$) compounds have been previously reported from the direct synthesis between copper(I) or copper(II) halides and TAA^{36, 49} (Table 2). In order to obtain mixed ligand compounds

containing both TAA and pyz as ligands, we followed the same strategy to that used for 4,4'-bpy derivatives. Thus, in the case of CuCl and CuBr, reactions increasing the pyz:TAA ratio were tested (Table 2). For CuCl, using a 1:1:10 stoichiometry, the coordination polymer $[\text{Cu}_2\text{Cl}_2(\text{TAA})_2(\text{pyz})]_n$ **5** was isolated as a pure solid, while mixtures of $[\text{CuCl}(\text{TAA})_3]$ and **5**, were obtained using lower ratio of TAA. Reactions between CuBr and thioacetamide in the presence of an excess of pyrazine yielded known coordination polymers $[\text{Cu}_2\text{Br}_2(\text{pyz})]_n$ ⁵⁰ and $[\text{CuBr}(\text{pyz})]_n$ ⁹, depending on the ratio of pyz. On the contrary, in the case of CuI, only the dinuclear complex $[\text{Cu}_2\text{I}_2(\text{TAA})_4]$ **6** was isolated for higher ratios of thioacetamide (Table 2).

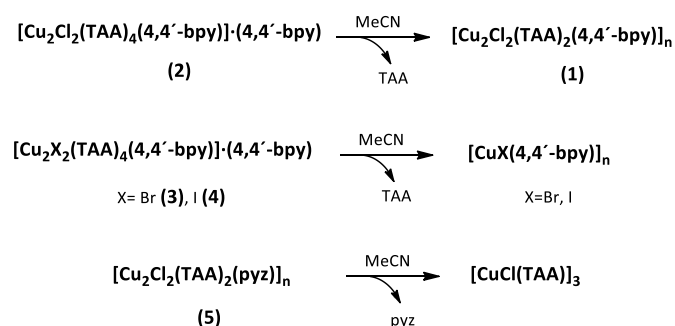
Table 2 Compounds obtained from the direct reactions between CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), TAA and pyz in acetonitrile using different $\text{CuX}:\text{TAA}:\text{pyz}$ ratios.

	2:4:1	2:2:1	1:1:2	1:1:10
CuCl	$[\text{CuCl}(\text{TAA})_3]$ ⁴⁹	$[\text{CuCl}(\text{TAA})_3]$	5 *	
CuBr	$[\text{CuBr}(\text{TAA})_n]$ ³⁶	$[\text{Cu}_2\text{Br}_2(\text{pyz})]_n$ ⁵⁰	$[\text{CuBr}(\text{pyz})]_n$ ⁹	
CuI	6 *	$[\text{Cu}_2\text{I}_2(\text{pyz})]_n$ ^{10, 51}		

* this work

Solution studies

The stability in solution of the mixed ligand compounds **1-5** was also investigated. In these experiments, acetonitrile suspensions of **1-5** were allowed to stand undisturbed for one day. Finally, the products were identified by X-ray powder diffraction. In all the experiments, with the exception of compound **1**, a transformation takes place. Thus, for **2-4** the loss of thioacetamide and, the subsequent formation of **1** together with $[\text{CuX}(4,4'\text{-bpy})]_n$ ($\text{X} = \text{Br}, \text{I}$)^{10, 14, 17} was observed. The same procedure was employed for **5**, but in this case the release of pyrazine and the formation of $[\text{CuCl}(\text{TAA})_3]$ ⁴⁹ took place (Scheme 2).



Scheme 2 Mixed ligand compounds **1-5** transformations after 24 h in acetonitrile.

Taking into account these results, the formation and the stability in solution of compounds **1-5** seem to be governed by the competition between TAA and N,N'-ditopic ligands. Therefore, the synthesis of the mixed ligand compounds can only be achieved by controlling the ligands ratio. Once the complexes are formed, the suspension of these solids in acetonitrile implies a transformation because the ratio required for the stabilization is not reached. Only for **1** the stoichiometry

employed for the synthesis corresponds to the final product composition, and no transformation occurs in solution.

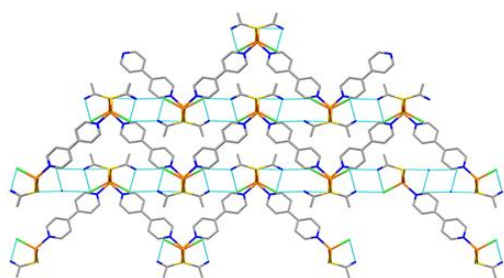
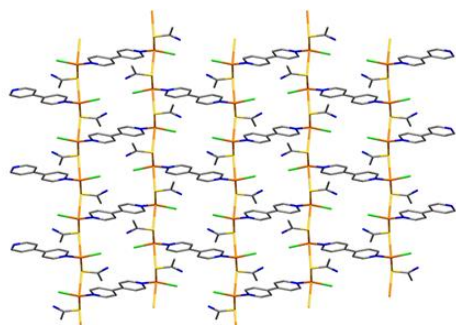


Fig 1 View of a $[\text{Cu}_2\text{Cl}_2(\text{TAA})_2(4,4'\text{-bpy})]_n$ layer in compound **1** (top) and packing of the layers with inter- and intralayer hydrogen bonds shown in blue (bottom). In both representations hydrogen atoms have been omitted for clarity.

Description of crystal structures

The crystal structures of compounds **1-6** were solved by single crystal X-ray diffraction. Complete data collection and refinement information is collected in the SI, and Fig. S7-S12 depict the asymmetric units with atoms labelled for compounds **1-6** respectively. Bond distances and angles for compounds **1-6** (Table 3) were found to be within the expected ranges and similar to the values presented by other similar compounds previously published.^{17, 34, 36}

Compound **1** crystallizes in the monoclinic $P2_1/c$ space group. The asymmetric unit consists of one copper(I) atom, one TAA, one chlorine and one half of 4,4'-bpy ligand, to give the formula $[\text{Cu}_2\text{Cl}_2(\text{TAA})_2(4,4'\text{-bpy})]_n$. The copper centre is coordinated to two sulphur atoms from TAA fragments, a chlorine terminal ligand and a nitrogen from the 4,4'-bpy ligand in a tetrahedral CuS_2ClN geometry. Both the TAA and 4,4'-bpy ligands act as ditopic μ_2 bridging ligands to yield a 2D polymeric structure with zigzag layers stacked by $\text{N-H}\cdots\text{Cl}$ hydrogen bonds in the [100] direction, as depicted in Fig. 1 and S13. The distance between copper atoms is 4.025 Å in the [001] direction (atoms joined by sulphur atoms from TAA ligands), and 11.252 Å for centres bridged by the full length of the 4,4'-bpy ligands.

Compound **2** crystallizes in the triclinic $P-1$ space group. Its structure consist of $[\text{Cu}_2\text{Cl}_2(\text{TAA})_4(4,4'\text{-bpy})]$ bimetallic molecules, interacting with interstitial 4,4'-bpy molecules (Fig. 2). The asymmetric unit comprises of one copper(I) atom, two TAA ligands, one half of a 4,4'-bpy coordinated molecule and another half of interstitial free 4,4'-bpy. The coordination CuS_2ClN environment of the copper atom displays a tetragonal

geometry and consists of the chlorine atom, two sulphur atoms from monotopic terminal TAA ligands and a nitrogen atom from a bridging μ_2 4,4'-bpy ligand.

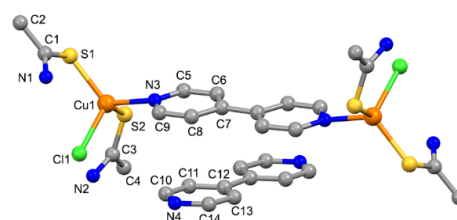


Fig 2 View of the two types of molecules present in the crystal structure of **2**, with labelled atoms in the asymmetric unit. Hydrogen atoms have been omitted for clarity.

The supramolecular network shows interactions between coordinated and free 4,4'-bpy ligands *via* $\text{N-H}\cdots\text{N}$ hydrogen bonds between NH_2 groups and nitrogen atoms from the pyridine rings (Fig. S14), and π - π stacking interactions between the pyridine rings (centroid distance 3.651 Å).

Compounds **3** and **4**, with formula $[\text{Cu}_2\text{X}_2(\text{TAA})_4(4,4'\text{-bpy})]$ ($\text{X} = \text{Br}, \text{I}$ for **3** and **4**, respectively) are isostructural. Their crystal structure are very similar to that of compound **2**. Although both compounds crystallize in the monoclinic $C2/c$ space group, these crystals also contain $[\text{Cu}_2\text{X}_2(\text{TAA})_4(4,4'\text{-bpy})]$ dimeric molecules joined by hydrogen bonds and π - π interactions to the interstitial 4,4'-bpy molecules (Fig. 3). The asymmetric unit contains one copper(I) atom, two TAA ligands, one half of a 4,4'-bpy coordinated molecule, and one half of free 4,4'-bpy. The supramolecular network is defined by $\text{NH}\cdots\text{X}$ ($\text{X} = \text{Br}, \text{I}$) and $\text{N-H}\cdots\text{N}$ hydrogen bonds between the NH_2 groups of the dimers and the free 4,4'-bpy molecules (Fig. S15 and S16), and additional π - π stacking interactions between rings of coordinated and free 4,4'-bpy (centroid distance 3.629 Å in **3** and 3.667 in **4**). The two pyridine rings in the interstitial bipyridine molecules are not coplanar in this case, as happened in compound **2**, and display an angle of 34.79° and 33.42° for **3** and **4**, respectively.

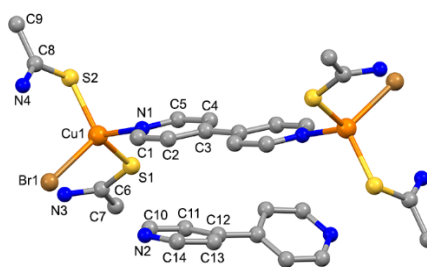


Fig 3 View of the two types of molecules present in the crystal structure of **3**, with labelled atoms in the asymmetric unit. Hydrogen atoms have been omitted for clarity.

Table 3 Selected distances and angles for compounds 1-6.

	1	2	3	4	5	6
	Distances (Å)					
Cu-X	2.372(1)	2.4215(6)	2.5392(5)	2.6900(5)	2.3518(5)	2.6370(5)
Cu-N	2.042(2)	2.099(2)	2.089(3)	2.081(2)	2.044(1)	3.0016(6)
Cu-S	2.257(1)	2.2711(7)	2.2769(9)	2.2803(7)	2.2741(5)	2.246(1)
	2.696(1)	2.3140(7)	2.2954(9)	2.3036(8)	2.5052(5)	2.2579(9)
Cu-Cu					2.7481(5)	
	Angles (°)					
S-Cu-S	108.52(4)	108.02(3)	113.97(3)	113.50(3)	109.99(2)	110.26(4)
N-Cu-S	95.23(7)	101.71(6)	113.17(8)	97.44(6)	106.33(4)	100.81(3)
	126.40(6)	119.39(3)	100.06(7)	115.68(6)	118.00(5)	102.88(4)
X-Cu-S	93.79(3)	111.27(2)	110.62(3)	111.09(2)	100.43(2)	118.02(3)
	119.40(3)	115.08(3)	112.01(3)	111.10(2)	116.50(2)	121.38(3)
N-Cu-X	105.55(7)	101.30(6)	106.18(7)	107.20(6)	130.15(5)	
X-Cu-X						98.85(2)

Polymeric compound **5**, with formula $[\text{Cu}_2\text{Cl}_2(\text{TAA})_2(\text{pyz})]_n$, crystallizes in the monoclinic $P2_1/n$ space group with an asymmetric unit that contains one copper(I) atom, one TAA ligand, one chlorine atom and one half of pyrazine (Fig. 4). It displays a monodimensional coordination polymeric structure with the copper atoms in a CuS_2ClN tetrahedral environment. Both the TAA and the pyz ligands are linking copper atoms to form chains parallel to the [001] direction, with the halogen atoms acting as terminal ligands. Within the chains, two TAA molecules form a double bridge with the sulphur atoms joining copper atoms located at 2.748 Å, and the pyrazine ligands also join two copper atoms (Cu-Cu distance 4.839 Å) coordinating by the two opposed nitrogen atoms. The chains are packed in the crystal by N-H...Cl hydrogen bonds (Fig. S17).

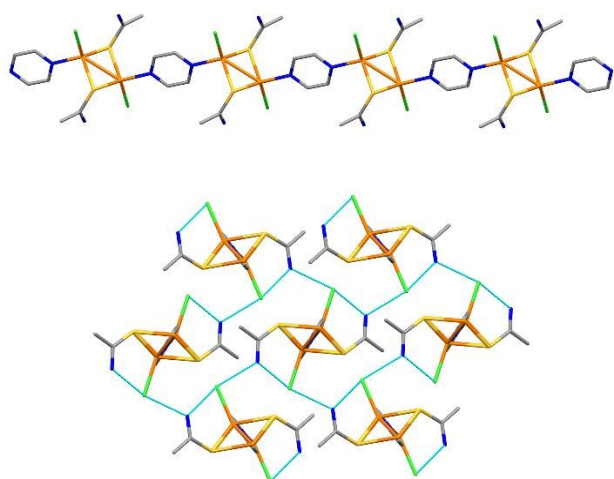


Fig 4 View of a $\text{Cu}_2\text{Cl}_2(\text{TAA})_2(\text{pyz})_n$ chain in compound **5** (top) and packing of the chains with inter- and intra-chain hydrogen bonds shown in blue (bottom). In both representations hydrogen atoms have been omitted for clarity.

Compound **6** displays a dimeric $[\text{Cu}_2\text{I}_2(\text{TAA})_4]$ molecular structure. It crystallizes in the triclinic $P-1$ space group with an asymmetric unit comprising one copper(I) centre, one TAA ligand and one iodine atom (Fig. 5). In this case, the TAA moieties do not act as bridging ligands but as terminal ones, and the iodine atoms are the ones that establish a double bridge between copper centres to yield the dimeric entity. Copper atoms are coordinated in a CuS_2I_2 tetrahedral environment and located at a distance of 3.678 Å. The dimers are joined by N-H...I hydrogen bonds to form a dense net of supramolecular interactions (Fig. S18).

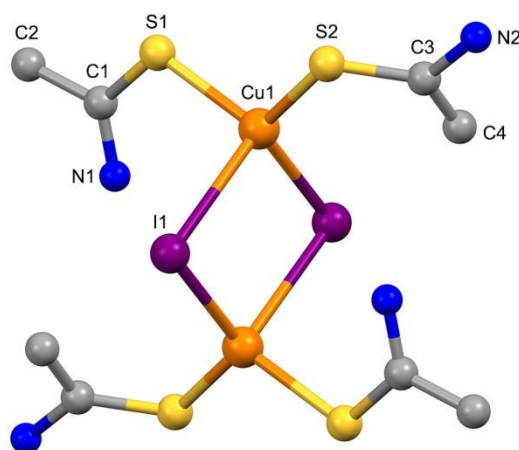


Fig 5 View of the dimeric molecule in the crystal structure of **6**, with labelled atoms in the asymmetric unit. Hydrogen atoms have been omitted for clarity.

Photoluminescence properties

Luminescent coordination polymers have recently undergone a great development due to their potential applications as light emitting diodes.⁵²⁻⁵⁷ Among these CPs based on metal ions with d^{10} electronic configuration^{58, 59} and particularly those of Cu(I) are appropriate since they may show rich structural variety

combined with brightly luminescent emission varying from blue to red light.¹² The solid-state luminescent properties of **1-6** compounds were investigated (solution studies were hindered by their insolubility). The mixed-ligand compounds **1-5** show a strong orange-red luminescence that can be seen with the naked eye when they are excited with a UV lamp at $\lambda = 365$ nm (Fig. 6). The excitation of solid samples at $\lambda = 402$ nm (at room temperature) produced a strong red-orange band emission with maximum values ranging from 589 nm for **1** up to 629 nm for **2** (Fig. 7). The determined values of the photoluminescence quantum yields (Φ_{PL}) were 0.12, 0.06, 0.19, 0.98, and 1.55% for **1-5**, respectively. In the case of coordination polymers **1** and **5**, these values are similar to those found in other copper(I) halide based coordination networks.³⁴ Generally, the electronic transitions responsible for photoluminescence properties of copper(I)-halide molecular and polymeric complexes with N-donor ligands can be assigned to ligand centered (LC), ligand-to-metal (LMCT) or metal to ligand charge transfer (MLCT) or metal-centered $d^{10} \rightarrow d^9s^1$ (MCC). The presence of a halide atom in complexes also enables the halide to metal charge transfer (XMCT).^{7,8} It has been already mentioned that **1-5** have a similar coordination environment where the metal center is bonding to a terminal halide, an N-donor ligand and two S-sulfur atoms of two different thioacetamide ligands. Ligand-centered $\pi \rightarrow \pi^*$ transitions could be discarded because the thioacetamide as well as the N-aromatic ligands (4,4'-bipy or pyz) show weak photoluminescence in the blue region.

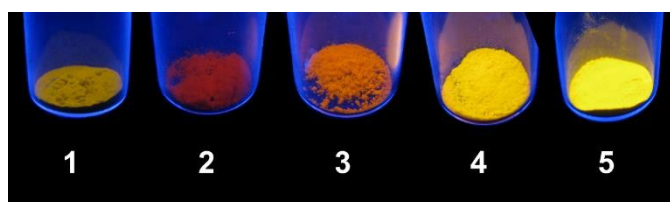


Fig 6 Photographs of **1-5** under UV light ($\lambda = 365$ nm).

The metal-centered transition $d^{10} \rightarrow d^9s^1$ (MCC) is only significant when the distance between the metal ions does not exceed than sum of van der Waals radii (2.8 Å) and this only takes place for compound **5** [$d(\text{Cu-Cu}) = 2.748$ Å]. On the other hand, the similarities observed in the luminescence of compounds **1** and **5** ($\lambda_{em} = 589$ and 609 nm for **1** and **5**, respectively) suggest that although pyrazine has relatively different physical properties than those observed for 4,4'-bipyridine, a change of the ligand has no significant contribution in the luminescence indicating that the structure of the organic ligand does not play an important role in luminescence behavior. However, the halide size seems to influence in the emission maximum, because a decrease of the energy value is observed when halide size increases ($\lambda_{em} = 629, 613$ and 604 nm for **2-4**, respectively) together with a stretching in the Cu-X distances (2.42, 2.54 and 2.69 Å for **2-4**, respectively). Taking into account the observation of the clear dependence between the Cu-X distance and luminescent emission, we assume that XMCT is the dominating transition in all compounds. For **5**, this XMCT transition is probably mixed with a contribution of metal-

centered $d^{10} \rightarrow d^9s^1$ (MCC). The maximum emission values observed are similar to other [CuXN-donor] coordination polymers.³⁴ Dimer **6** displays scarce luminescence in the blue region, showing a photoluminescence spectrum similar to thioacetamide (Fig. S19), suggesting that these transitions could be assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions and/or intraligand transitions.

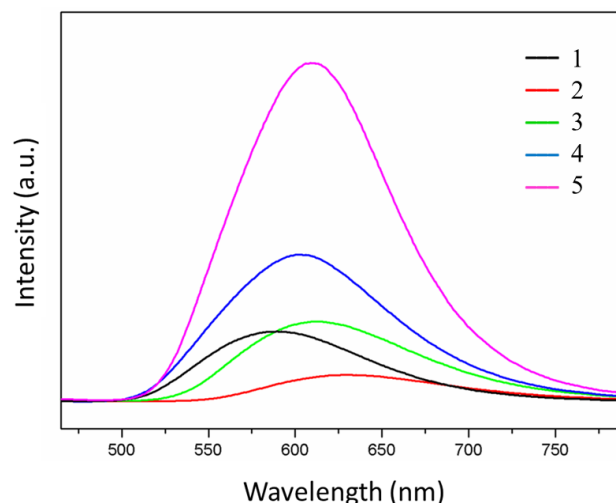


Fig 7 Photoluminescence emission spectra of **1-5** in the solid state at $\lambda_{exc} = 402$ nm.

Electrical properties

We have previously reported that CPs based on Cu(I) with organosulfur ligands are especially suitable to produce electrical conductive materials.^{4, 60, 61} Therefore, the structures of compounds **1** and **5** showing S atoms bridging metallic centres suggest their potential in terms of electrical conductivity. We have evaluated the electrical conductivity of single crystals of both compounds using the two-probe method at 300 K.

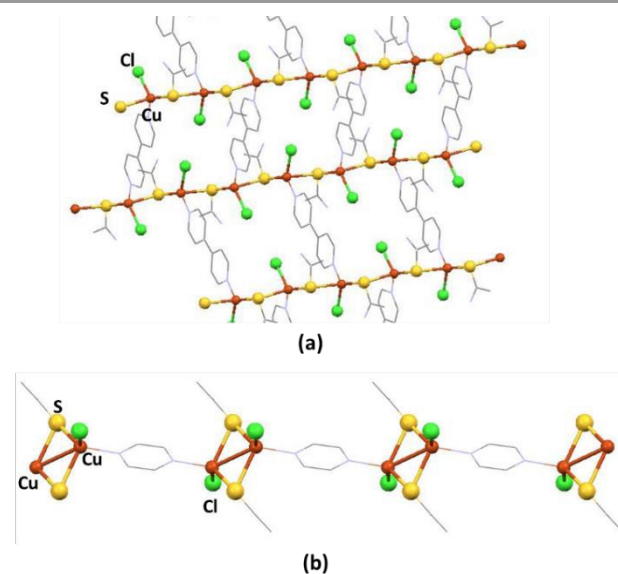


Fig 8 (a) Representation of the possible pathway to the electrical conductivity across the S-Cu-S zig-zag chains in compound **1**. (b) Representation of the bimetallic Cu-S-Cu units, linked by pyrazine ligands to explain the insulator behaviour of compound **5**.

For compound **1**, an electrical conductivity value of $1 \times 10^{-8} \text{ S cm}^{-1}$ was estimated from their IV curves suggests a semiconductor behaviour (Fig. S20). However, compound **5** shows a very low electrical conductivity value of *ca.* $7 \times 10^{-12} \text{ S cm}^{-1}$ therefore suggesting a pretty insulator behaviour. Probably, this is consequence of the crystal structure of **1** that shows Cu-S-Cu zig-zag chains parallel to the *c*-axis, with short Cu-S distances (2.257 and 2.696 Å, respectively) and the connections between the Cu-S-Cu zig-zag chains via 4,4'-bpy ligands (Cu-4,4'-bpy-Cu distance 11.252 Å). Taking this into account, the conductivity could probably be more favoured by the Cu-S-Cu pathway (Fig. 8a). In the case of **5**, the polymer chain is building by repeating Cu-Cu-pyz units along the *c* axis. Although the Cu-Cu distance in the bimetallic units (2.748 Å), is slightly shorter than twice the van der Waals radius (1.40 Å), the longer distance between these bimetallic units joined by the pyrazine molecule (6.883 Å) can explain the non-conducting behaviour of **5** (Fig. 8b).

Experimental

Materials and methods

All the reagents were purchased from Sigma-Aldrich and used as received. FTIR spectra (KBr pellets) were recorded on a Perkin-Elmer 1650 spectrophotometer. C, H, N, S elemental analyses were performed by the Microanalysis Service of the Universidad Autónoma de Madrid on a Perkin-Elmer 240 B microanalyser. Powder X-ray diffraction experiments were carried out on a Diffractometer PANalyticalX'Pert PRO theta/2theta primary monochromator and detector with fast X'Celerator. The samples have been analysed with scanning theta/2theta. Direct current (DC) electrical conductivity measurements were performed on four different single crystals of compounds **1** and **5**, connected with graphite paint to platinum wires (25 µm diameter). The samples were measured at 300 K applying an electrical current with voltages from +10 to -10V. Luminescence excitation and emission spectra of the solid compounds were performed at 25 °C on a 48000s (T-Optics) spectrofluorometer from SLM-Aminco. A front face sample holder was used for data collection and oriented at 60° to minimize light scattering from the excitation beam on the cooled R-928 photomultiplier tube. Appropriate filters were used to eliminate Rayleigh and Raman scatters from the emission. Excitation and emission spectra were corrected for the wavelength dependence of the 450 W xenon arc excitation but not for the wavelength dependence of the detection system. UV-vis spectroscopic properties were measured by reflection (front face mode) on finely ground samples and placed in quartz cells of 1 mm path length. No attempt was made to remove adsorbed or dissolved molecular oxygen from the materials. Reference samples that do not contain any fluorescent dopant were used to check the background and optical properties of the samples. The overall quantum yields (Φ) were measured at r.t. using a method for powdered samples described by Brill *et al.*⁶² The selected method involves the use of a standard phosphor (Sodium Salicylate) which quantum yield at the excitation wavelength is estimated in 60%.

The quantum yield is calculated measuring the luminescent emission of the samples and the standard under the same conditions. To have absolute intensity values, diffuse reflectance of the samples and the standard were estimated.

X-ray data collection and crystal structure determination

Data collection for compounds **1-6** were carried out in the Single Crystal X-Ray Diffraction Laboratory of SIdI (UAM) on a Bruker Kappa Apex II diffractometer, using graphite-monochromated Mo-K radiation ($\lambda=0.71073 \text{ Å}$) and operating at 50 kV and 30 mA. The cell parameters were determined and refined by a least-squares fit of all reflections. A semi-empirical absorption correction (SADABS) was applied for all cases. The structures were solved by direct methods and refined by full-matrix least-square procedures on F^2 (SHELXL-97⁶³). All hydrogen atoms were included in their calculated positions and refined riding on the respective carbon atoms. Further crystallographic details for the structures reported here are collected in the supplementary information and the files containing the deposited structures may be obtained from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC 1427905-1427910 (compounds **1-6**, respectively).

Synthetic procedures

All the compounds were synthesized at room temperature on air. The purity of the samples was checked by X-ray powder diffraction (Fig. S1-S6).

Synthesis of $[\text{Cu}_2\text{Cl}_2(\text{TAA})_2(4,4'\text{-bpy})]_n$ (1**).** To a mixture of TAA (0.114 g, 1.50 mmol) and 4,4'-bipyridine (0.120 g, 0.75 mmol) in 10 mL MeCN, a solution of CuCl (0.150 g, 1.50 mmol) in 5 mL MeCN was added and stirred for 10 min at 20 °C. The resulting orange solid was collected by filtration, washed with MeCN and diethyl ether and dried in air. Yield: 0.272 g, 74% based on Cu. The product was recrystallized from MeCN to afford suitable crystals for single-crystal X-ray diffraction measurements. Anal. Calc. for $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{Cu}_2\text{N}_4\text{S}_2$: C, 33.33; H, 3.60; N, 11.11; S, 12.71. Found: C, 33.34; H, 3.70; N, 11.21; S, 12.51. IR selected data (solid KBr pellet v/cm^{-1}): 3194(s), 3016(s), 1646(m), 1601(s), 1531(m), 1506(m), 1482(s), 1404(s), 1359(s), 1319(m), 1216(m), 1066(m), 1042(m), 975(s), 799(s), 737(m), 724(m), 695(s), 632(m).

Synthesis of $[\text{Cu}_2\text{Cl}_2(\text{TAA})_4(4,4'\text{-bpy})] \cdot (4,4'\text{-bpy})$ (2**).** To a mixture of TAA (0.152 g, 2.00 mmol) and 4,4'-bipyridine (0.080 g, 0.50 mmol) in 15 mL MeCN a solution of CuCl (0.050 g, 0.50 mmol) in 15 mL MeCN was added. After stirring for 10 min at 20 °C, the reaction mixture was filtered through silica gel, then the volume was reduced under vacuum to *ca.* 2 mL and 10 mL diethyl ether was added. The resulting orange crystals were collected by filtration, washed with diethyl ether and dried in air. Yield: 0.091 g, 45% based on Cu. Anal. Calc. for $\text{C}_{28}\text{H}_{36}\text{Cl}_2\text{Cu}_2\text{N}_8\text{S}_4$: C, 41.47; H, 4.47; N, 13.82; S, 15.82. Found: C, 41.49; H, 4.47; N, 13.77; S, 15.67. IR selected data (solid KBr pellet v/cm^{-1}): 3268(s), 3099(s), 2923(m), 1636(m), 1598(s), 1532(m), 1486(m), 1457(w), 1408(s), 1367(w), 1311(m), 1218(w), 1062(w), 976(m), 816(m), 801(m), 711(s), 614(s).

Synthesis of $[\text{Cu}_2\text{Br}_2(\text{TAA})_4(4,4'\text{-bpy})]\cdot(4,4'\text{-bpy})$ (3). Following a procedure similar that used for **2** but using a 1:10:1 ratio of CuBr:TAA:4,4'-bpy respectively, orange crystals were collected by filtration, washed with diethyl ether and dried in air. Yield: 0.119 g, 53% based on Cu. Anal. Calc. for $\text{C}_{28}\text{H}_{36}\text{Br}_2\text{Cu}_2\text{N}_8\text{S}_4$: C, 37.37; H, 4.03; N, 12.45; S, 14.25. Found: C, 37.22; H, 4.05; N, 12.45; S, 14.17. IR selected bands (solid KBr pellet ν/cm^{-1}): 3328(m), 3248(s), 3151(m), 1668(w), 1620(s), 1599(s), 1529(m), 1483(m), 1456(m), 1408(s), 1365(m), 1311(s), 1217(m), 1063(m), 978(m), 854(w), 806(s), 711(s), 613(s).

Synthesis of $[\text{Cu}_2\text{I}_2(\text{TAA})_4(4,4'\text{-bpy})]\cdot(4,4'\text{-bpy})$ (4). The synthetic conditions of compound **4** were analogous to **2**, but using CuI (0.096 g, 0.50 mmol) instead of CuCl. Yield: 0.155 g, 62% based on Cu. Anal. Calc. for $\text{C}_{28}\text{H}_{36}\text{I}_2\text{Cu}_2\text{N}_8\text{S}_4$: C, 33.84; H, 3.65; N, 11.28; S, 12.91. Found: C, 33.69; H, 3.66; N, 11.19; S, 12.80. IR selected bands (solid KBr pellet ν/cm^{-1}): 3298(m), 3248(s), 3150(m), 1661(w), 1615(s), 1596(s), 1527(m), 1482(m), 1452(m), 1404(s), 1361(m), 1301(s), 1216(m), 1062(m), 974(s), 852(w), 805(s), 708(s), 613(s).

Synthesis of $[\text{Cu}_2\text{Cl}_2(\text{TAA})_2(\text{pyz})_n]$ (5). To a mixture of TAA (0.038 g, 0.50 mmol) and pyrazine (0.405 g, 5.00 mmol) in 2 mL MeCN, a solution of CuCl (0.050 g, 0.50 mmol) in 3 mL MeCN was added, and stirred for 10 min at 20 °C. The resulting orange solid was filtered, washed with EtOH and diethyl ether and dried in air. Yield: 0.068 g, 65 % based on Cu. Upon standing the filtered solution at 4 °C for three days, few single crystals suitable for X-ray analysis were formed. Anal. Calc. for $\text{C}_8\text{H}_{14}\text{Cl}_2\text{Cu}_2\text{N}_4\text{S}_2$: C, 22.43; H, 3.29; N, 13.08; S, 14.97. Found: C, 22.11; H, 3.33; N, 13.02; S, 14.99. IR selected bands (solid KBr pellet ν/cm^{-1}): 3152(m), 3030(s), 2968(s), 1667(m), 1541(m), 1480(s), 1409(s), 1373(s), 1305(m), 1276(w), 1157(m), 1117(w), 1053(w), 968(s), 801(m), 763(m), 692(s).

Synthesis of $[\text{Cu}_2\text{I}_2(\text{TAA})_4]$ (6). A solution of CuI (0.096 g, 0.50 mmol) in 12 mL of MeCN was added to a solution of TAA (0.152 g, 2.00 mmol) in 3 mL of the same solvent. The mixture was stirring for 10 min at 20 °C. The volume of the mixture was reduced under vacuum to ca. 1 mL, and 10 mL diethyl ether was added. The resulting white crystals were collected by filtration, washed with diethyl ether and dried in air. Yield: 0.310 g, 91% based on Cu. Anal. Calc. for $\text{C}_8\text{H}_{20}\text{I}_2\text{Cu}_2\text{N}_4\text{S}_4$: C, 14.10; H, 2.96; N, 8.22; S, 18.82. Found: C, 13.95; H, 2.88; N, 8.30; S, 18.29. IR selected bands (solid KBr pellet ν/cm^{-1}): 3354(s), 3265(s), 3178(s), 1606(s), 1456(m), 1398(m), 1307(m), 970(m), 710(m), 573(m).

Conclusions

In this work we have investigated the reactivity of the ternary system based on copper(I) halides (chloride, bromide and iodide), thioacetamide (TAA) and 4,4'-bipyridine (4,4'-bpy) or pyrazine (pyz), finding that the composition of the final products depends strongly on the halide, the N,N'-ditopic ligand, and the stoichiometry employed. Hence, we have synthesized five new mixed ligand compounds, **1-5**, by changing the TAA:N-donor ligand ratio, due to the competition between both of them. Moreover, solvent mediated transformations support the stoichiometric dependence on the construction of these solids.

Due to the use of different N-heteroaromatic ligands and stoichiometries, various supramolecular architectures with different compositions were obtained, with structures ranging from discrete to one- and two-dimensional polymers. Mixed ligand compounds **1-5** display significant red solid-state luminescent emission upon irradiation with UV light at room temperature, where halide atoms play a key role in the photoluminescence properties of these complexes. Additionally, electrical conductivity studies carried out in **1** and **5** suggest a semiconductor and insulator behaviour, respectively. In summary, compound **1** represents an interesting multifunctional two-dimensional coordination polymer showing both significant red photoluminescence and moderated electrical conductivity.

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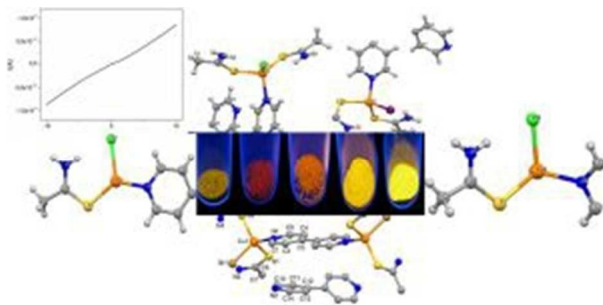
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Text for Graphical Abstract

Ternary compounds based on Copper(I)-halides with thioacetamide and 4,4'-bipyridine or pyrazine have been prepared and characterized showing luminescence and semiconductivity.



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