



## Structure characterization of two new three-dimensional piperazine-bridged metal–halo coordination polymers

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### ABSTRACT

By the simple hydro/solvothermal reaction, two new 3-D metal–halo cluster polymers,  $[\text{NiCl}_2(\text{pip})]$  (pip = piperazine) (**1**) and  $[\text{Cu}_2\text{I}_2(\text{pip})]$  (**2**) were obtained and characterized by IR spectroscopy, CHN analysis and TG analysis. Single-crystal X-ray analysis reveals that, the 3-D network of compounds **1** and **2** are constructed from the 1-D zigzag  $\text{NiCl}_2$  chains and the 1-D castellated  $\text{Cu}_2\text{I}_2$  chains bridged by pip molecules respectively. The  $\mu_{\text{eff}}$  versus  $T$  curve indicates that compound **1** is ferromagnetic when  $T > 14$  K. The photoluminescent spectrum shows that compound **2** possesses the fluorescent property with a broad emission peak at 567 nm upon excitation at 397 nm.

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### 1. Introduction

In the past decade, the study on the design and synthesis of novel cluster polymers achieved considerable attention due to the structural unpredictability (i.e., which cluster will form and what is the linking mode between the clusters and organic moieties) and potential functional properties in some fields as optics (containing groups IB, IIB or rare-earth metal), electrochemistry based on the metals with many oxidation states, catalysis (poly-acid, zeolite or zeolite-like materials), electrical conductivity (containing group IVA metal) and magnetism [1–6]. As far as the construction of cluster polymers is concerned, on the one hand, the inorganic salts being prone to form the clusters, such as oxides, halides or sulfides are usually used as the inorganic precursors to form inorganic subunits (SUs) [7–15]. On the other hand, the literature show that three types of bridges can extend the inorganic SUs into polynuclear or high-dimensional (D) cluster polymers: (i) inorganic bridge. With various organic amines as guest species or organic templating agents, the SUs interact with each other through covalent M–O (X or S) bonds (or through sharing the corner, edge or/and face) between the SUs, producing new polymeric clusters. This is the basic constructing conception of zeolite and zeolite-like materials [16–19]. (ii) Organic bridge, the most common method. Up to now, lots of bridging organic ligands with N/O/S donors have been chosen to extend the SUs into the 1-D, 2-D, 3-D cluster polymers via covalent interactions or a combination of covalent and non-covalent interactions [20–26]. (iii) Metal complex bridge. This

strategy has been extensively adopted when preparing high-D poly-acids [27–31]. Some recent reports show that it is being extended to the construction of metal–halo cluster polymers [32–36].

Since 2001, one of the investigations in our group is focused on the synthesis and property of metal–halo cluster polymers based on these three construction strategies stated above. Some interesting compounds such as the 3-D  $[\text{CuX}_2(1,4\text{-btzb})]$  [ $\text{X}^- = \text{Cl}^-, \text{Br}^-$ ; 1,4-btzb = 1,4-bis(tetrazol-1-yl)butane] [37], 2-D  $[\text{Cu}_4(\text{OH})_4(\text{-phen})_4][\text{Cu}_8\text{Br}_{12}]$  (phen = 1,10-phenanthroline) [38] and decanuclear  $[\text{Ni}(\text{phen})_3]_2[\text{Cu}_{10}\text{HI}_{15}]$  [39] have been obtained. Herein, we report the syntheses and characterization of two new 3-D metal–halo cluster polymers:  $[\text{NiCl}_2(\text{pip})]$  **1** and  $[\text{Cu}_2\text{I}_2(\text{pip})]$  **2** obtained by the simple hydro/solvothermal technique.

### 2. Experimental

#### 2.1. Materials and general methods

The chemicals used to prepare the title compounds include  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , CuI, KI, pip  $\cdot 6\text{H}_2\text{O}$ ,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , succinic acid and ethanol without further purification. The synthesis was carried out in 30 mL Teflon-lined stainless steel vessels under autogenous pressure. Elemental (CHN) analysis was performed with a Perkin–Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded with a Perkin–Elmer Spectrum 1 spectrophotometer in the 4000–400  $\text{cm}^{-1}$  region using a powdered sample on a KBr plate.

Data were collected with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Rigaku R-AXIS RAPID IP diffractometer for **1** and on a Siemens SMART CCD diffractometer for **2**. With SHELXTL program, compound **1** was solved with heavy-atom method and compound **2** with direct methods. Then both were refined by full-matrix least-squares

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**Table 1**  
Crystal data and structure refinement for the title compounds.

Compound	1	2
Formula	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> NiCl <sub>2</sub>	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> Cu <sub>2</sub> I <sub>2</sub>
Formula weight	215.75	467.02
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
T (K)	293(2)	293(2)
a (Å)	9.2889(19)	9.309(2)
b (Å)	12.895(3)	15.436(4)
c (Å)	6.3072(13)	7.0974(16)
β (°)	92.48(3)	103.604(4)
V (Å <sup>3</sup> )	754.8(3)	991.3(4)
Z	4	4
D (g cm <sup>-3</sup> )	1.899	3.129
μ (mm <sup>-1</sup> )	3.189	10.456
F(000)	440	848
θ Range for data collection (°)	3.16–27.47	3.52–28.37
Reflections (measured)	3652	3259
Goodness-of-fit (GOF) on F <sup>2</sup>	1.124	1.027
R <sub>int</sub>	0.0315	0.0883
R <sub>1</sub> /wR <sub>2</sub>	0.0258/0.0509	0.0298/0.0601
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.332, -0.447	1.052, -1.645

[a]  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . [b]  $R_w = [\sum w(|F_o|^2 - |F_c|^2)|^2] / [\sum w(F_o^2)^{1/2}]^{1/2}$ , where  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ .  $P = (F_o^2 + 2F_c^2) / 3$ .

techniques. The non-hydrogen atoms for both were assigned anisotropic displacement parameters in the refinement. For compound **1**, the hydrogen atoms were obtained from difference Fourier map, and for compound **2**, the hydrogen atoms were treated with a riding model except ones on N atoms being obtained from difference Fourier map. The structures were then refined on F<sup>2</sup> using SHELXL-97. Basic information pertaining to the crystal parameters and structure refinement of the title compounds is summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

## 2.2. Synthesis of complex

**[NiCl<sub>2</sub>(pip)] (1)**. To a 16 mL ethanol, NiCl<sub>2</sub> · 6H<sub>2</sub>O (0.24 g, 1 mmol), pip · 6H<sub>2</sub>O (0.19 g, 1 mmol) and succinic acid (0.12 g, 1 mmol) were added in succession. After being stirred for 4 h, the mixture (pH = 6) was sealed in a 30 mL Teflon-lined autoclave, and then heated in an oven at 170 °C. After 3 days, green needle crystals were obtained, being washed with ethanol and dried in ambient temperature. Yield: ca. 30% based on Ni. IR (cm<sup>-1</sup>): 3206 s, 2976 w, 2942 w, 1447 w, 1421 m, 1136 s, 1085 w, 1027 m, 1002 w, 855 s, 664 w, 397 w. Anal. Calc. for C<sub>4</sub>H<sub>10</sub>N<sub>2</sub>NiCl<sub>2</sub>: C, 22.27; H, 4.67; N, 12.98. Found: C, 22.35; H, 4.59; N, 12.90%.

**Table 2**  
Selected bond lengths (Å) and angles (°) for the title compounds.

Compound 1			
Ni(1)–N(1)	2.118(2)	Ni(1)–Cl(1)	2.4455(9)
Ni(1)–Cl(1)#2	2.5050(8)		
N(1)#1–Ni(1)–Cl(1)	94.48(6)	Cl(1)–Ni(1)–Cl(1)#3	84.33(2)
Cl(1)–Ni(1)–Cl(1)#1	176.87(3)	Cl(1)–Ni(1)–Cl(1)#2	93.40(2)
Cl(1)#2–Ni(1)–Cl(1)#3	87.50(4)	N(1)–Ni(1)–N(1)#1	105.73(12)
Ni(1)–Cl(1)–Ni(1)#3	95.67(2)	N(1)–Ni(1)–Cl(1)	87.41(6)
Compound 2			
Cu(1)–N(1)	2.088(3)	Cu(1)–I(1)	2.6569(8)
Cu(1)–I(1)#1	2.6636(7)	Cu(1)–I(1)#2	2.6876(8)
Cu(1)–Cu(1)#2	2.7294(10)	Cu(1)–Cu(1)#1	2.7707(11)
N(1)–Cu(1)–I(1)	104.38(9)	N(1)–Cu(1)–I(1)#1	106.10(8)
I(1)–Cu(1)–I(1)#1	117.23(2)	N(1)–Cu(1)–I(1)#2	103.52(9)
I(1)–Cu(1)–I(1)#2	117.373(19)	I(1)#1–Cu(1)–I(1)#2	106.74(2)

**[Cu<sub>2</sub>I<sub>2</sub>(pip)] (2)**. To a mixture of CuI (0.24 g, 1.2 mmol) and KI (0.2 g, 1.2 mmol) in 10 mL water, a solution of pip · 6H<sub>2</sub>O (0.12 g, 0.6 mmol) and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O (0.04 g, 0.3 mmol) in 5 mL ethanol was added. The following process is similar to that **1**, but before the autoclave being sealed, the mixture was adjusted to pH 9 with dilute KOH. After being washed with water, the orange crystals were obtained with a yield of ca. 25% based on Cu. IR (cm<sup>-1</sup>): 3230 m, 2942 w, 1445 w, 1413 w, 1243 w, 1095 m, 1046 m, 1002 w, 989 s, 866 s, 369 w. Anal. Calc. for C<sub>4</sub>H<sub>10</sub>N<sub>2</sub>Cu<sub>2</sub>I<sub>2</sub>: C, 10.29; H, 2.16; N, 5.99. Found: C, 10.35; H, 2.10; N, 5.91%.

## 3. Results and discussion

### 3.1. Structural description

So far, the report on nickel–halo coordination polymer with the bridging N-donor ligand is rather rare. The classical cases are compounds [NiX<sub>2</sub>(4,4'-bpy)] (X<sup>-</sup> = Cl<sup>-</sup>, Br<sup>-</sup>; bpy = bipyridine) [40], which show a 2-D layered topology consisting of the 1-D NiX<sub>2</sub> chains bridged by 4,4'-bpy ligands.

Using the pip in place of the 4,4'-bpy, the title 3-D compound **1** with a different topology from the former was synthesized. With the pip, NiCl<sub>2</sub> · 6H<sub>2</sub>O forms a 1-D chained SU. The Ni(II) center with an octahedral geometry is coordinated by four Cl<sup>-</sup> ions and two N atoms from the different pip. The Ni–N bond length [2.118(2) Å] and the average Ni–Cl bond length [2.475 Å] are similar to those found in reported [NiCl<sub>2</sub>(4,4'-bpy)] [40]. Through the μ<sub>2</sub>-Cl bridges, all of the Ni(II) centers are linked into a zigzag chain, which can be described as an infinite extension of edge-shared NiCl<sub>4</sub>N<sub>2</sub> octahedra. The Ni(pip)<sub>2</sub><sup>2+</sup> unit adopts a *cis*-type arrangement. It is noticeable that compound **1** displays the different porous shapes in different directions. As shown in Fig. 1, in [100] direction, it takes on a trigonal channel with base 6.3 Å and height 6.6 Å. While in [001] direction, it displays a square hydrophobic channel with the size of 7.9 × 7.9 Å<sup>2</sup>.

Comparing the topology of **1** with one of [NiX<sub>2</sub>(4,4'-bpy)], we can find that the different organic ligands lead to the different topologies. The reason is that NiL<sub>2</sub><sup>2+</sup> unit adopts the different geometric configuration due to the different bulk of organic ligand. In compound **1**, Ni(pip)<sub>2</sub><sup>2+</sup> is *cis*-pattern, which helps to extend NiCl<sub>2</sub> chains into a 3-D network, while in [NiX<sub>2</sub>(4,4'-bpy)], Ni(4,4'-bpy)<sub>2</sub><sup>2+</sup> is *trans*-pattern. In addition, the different NiL<sub>2</sub><sup>2+</sup> type has an effect on NiX<sub>2</sub> chain arrangement: zigzag type in **1**; linear-type in [NiX<sub>2</sub>(4,4'-bpy)].

Compared with the Ni(II), the structure of copper–halo clusters is richer due to the diversity of coordination geometry of Cu(I). With bridging N-donor ligands, CuX can form various neutral oligomeric and polymeric clusters, namely so-called SUs. The most reports are rhombic dimer, cubane tetramer, zigzag-type and staircase chains [41]. Further, these SUs are extended by organic bridges into the 1-D, 2-D or 3-D networks. It was reported that the size of organic ligands determines the mode of the SUs. In general, the bulky ligands as 4,4'-bpy favor the formation of discrete SUs, whereas the small ones favor the polymeric SUs. In compound [Cu<sub>2</sub>Br<sub>2</sub>(tri)] (tri = 1,3,5-triazine) [41], the castellated CuI single chain was reported, while in compound **2**, a new castellated CuI double chain was observed in reaction with the pip.

X-ray analysis reveals that the structure of compound **2** features a new 3-D framework constructed from the 1-D Cu<sub>2</sub>I<sub>2</sub> chains bridged by the pip molecules. With the pip, CuI forms a 1-D castellated Cu<sub>2</sub>I<sub>2</sub> chain as shown in Fig. 2a. The Cu(I) ion adopts a distorted tetrahedral geometry [the angles around Cu(I) ion being from 103.52(9) to 117.373(19)°] and is coordinated by three equivalent I<sup>-</sup> ions and one N atom from the pip. The Cu–I bond lengths, ranging from 2.6569(8) to 2.6876(8) Å, are comparable with those

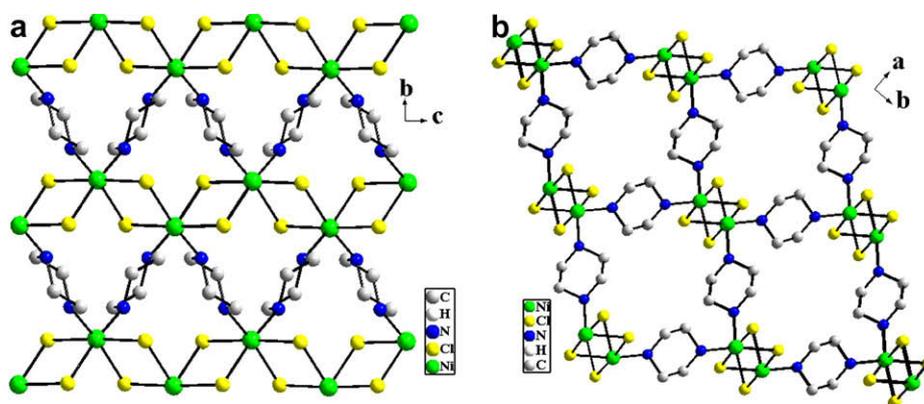


Fig. 1. 3-D networks of  $[\text{NiCl}_2(\text{pip})]$  (**1**) in  $[100]$  (a) and  $[001]$  (b) directions.

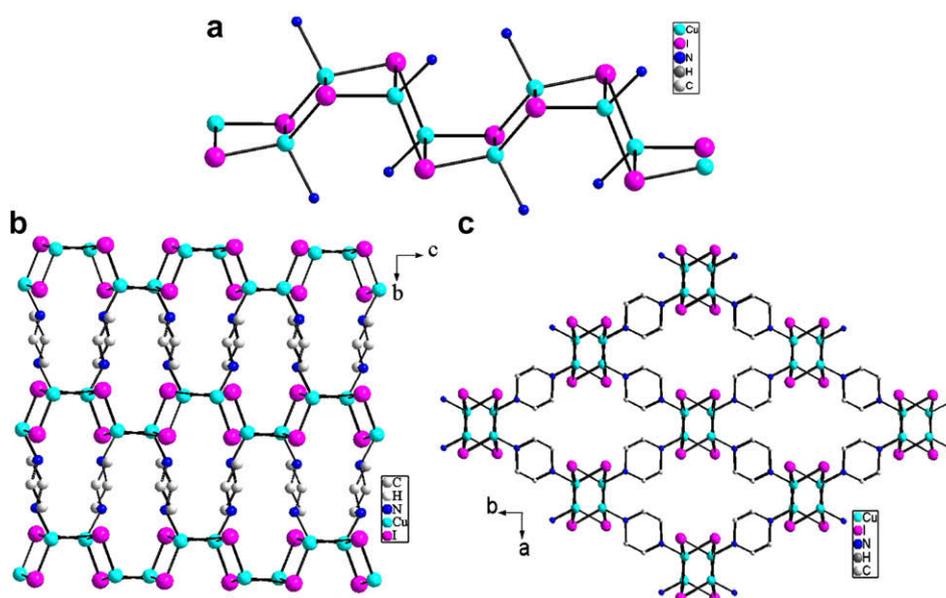


Fig. 2. A 1-D castellated  $\text{Cu}_2\text{I}_2$  SU (a) together with 3-D networks in  $[100]$  (b) and  $[001]$  (c) directions in **2**.

observed in the reported similar compounds [8,23,42,43]. The distances of  $\text{Cu}\cdots\text{Cu}$  [2.7294(10)–2.7707(11) Å] are less than twice the van der Waals radius of the Cu (2.8 Å), which implies that there exist the weaker  $\text{Cu}\cdots\text{Cu}$  interactions within the inorganic chains. The  $\text{I}^-$  ions with a trigonal pyramidal geometry link the tetrahedral Cu(I) to form a castellated  $\text{Cu}_2\text{I}_2$  chain, which is obviously different from the known zigzag chain and the staircase chain. Next, the pip molecules protrude out from the inorganic chains, bridging them into a 3-D framework with the 1-D channels in different directions. In  $[100]$  direction, the channel is rectangular with the size of  $2.7 \times 9.0 \text{ \AA}^2$  (see Fig. 2b), while in  $[001]$  direction the channel is a diamondoid structure with the size of  $7.5 \times 13.9 \text{ \AA}^2$  (see Fig. 2c).

Based on the title compounds and the documents, it is easy to find that the structure of copper(I)-halo cluster is richer than that of nickel-halo cluster. Perhaps it is due to the flexibility of the metal ion. Generally, the  $\text{X}^-$  ion has a tendency to exhibit the multi-types of bridging-modes with the flexible metal. For example, in the reported Cu(I)-X cluster compounds, the  $\text{X}^-$  ions take on the  $\mu_2$ -,  $\mu_3$ -,  $\mu_4$ - and  $\mu_5$ -bridging modes with linear, trigonal pyramidal, tetrahedral, planar rectangular, tetragonal pyramidal, pentagonal pyramidal and umbrella-like ( $\mu_4$ -) geometric configurations [38].

### 3.2. Synthetic analysis

It deserves to note that the pH level of the system plays a key role in the course of crystal growth. The optimal pH values are 6 for **1** and 9 for **2**, respectively. The reasonable explanation may be: (i) in a acid condition, the  $\text{Cu}^+$  ion will be disproportionated to the  $\text{Cu}^{2+}$  ion and the Cu metal. (ii) In a basic condition, the  $\text{Ni}^{2+}$  ion exists in the  $\text{Ni}(\text{OH})_2$  form.

As literature reported, the bridging organic acid can be used as one of the precursors when preparing hybrid metal-halo coordination polymers. Sometimes, organic acid appeared in the final product as the reported  $\text{Na}[\text{Cd}_2\text{Cl}_4(\text{C}_2\text{O}_4)_{0.5}] \cdot 4\text{H}_2\text{O}$  [44] and  $\text{Na}_3[\text{Cd}_5(\text{C}_4\text{H}_4\text{O}_4)_6\text{X}]$  ( $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ ;  $\text{C}_4\text{H}_4\text{O}_4 = \text{succinate}$ ) [45]. Sometimes, organic acid didn't appear in the final product. Just as Rao has ever mentioned, the real role of organic acids is still unclear, but the target products can't be obtained without them [45].

### 3.3. TG analysis

Thermogravimetric (TG) behavior was investigated on a SHIMA-DZU DTG-60 instrument in a temperature range of 25–800 °C with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in air. As shown in Fig. 3, compound **1**

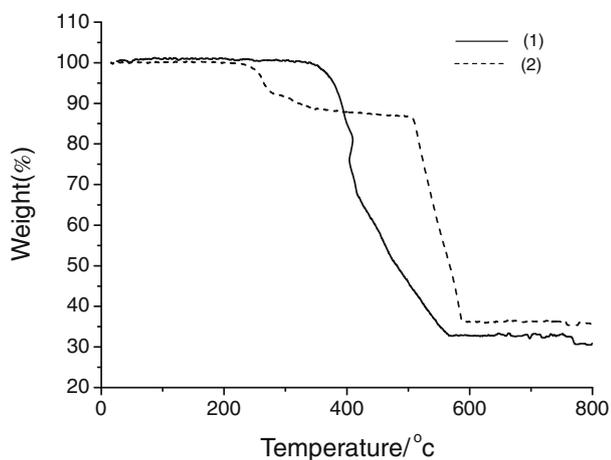


Fig. 3. TGA curves of the title compounds.

exhibits one-step continuous weight-loss in the temperature range of 310–575 °C. The final residue is proved to be NiO (calc.: 34.62%; found: 33.15%), which suggests that the pip molecule and the Cl<sup>-</sup> ion released simultaneously, meanwhile, the Ni(II) ion combined with the O<sub>2</sub> to form the NiO. Compound **2** underwent two steps of the weight loss. The first step from 210 °C to 440 °C should correspond to the loss of the pip, meanwhile, part Cu(I) transformed into CuO (calc.: 18.43%; found: 12.67%). The second stage should correspond to the sublimation of the I<sup>-</sup> ion and the oxidation of the residual Cu(I) (calc.: 54%; found: 51%).

#### 3.4. Magnetic property

Magnetic susceptibility data were determined on the basis of a 10.3 mg sample over the temperature of 2–300 K at a magnetic field of 1 kG on a Quantum Design MPMS-7 SQUID magnetometer. The  $\mu_{\text{eff}}$  versus  $T$  plot is shown in Fig. 4 (left) [ $\mu_{\text{eff}} = 2.83 (\chi_{\text{M}}T)^{1/2}$ ]. The experimental  $\mu_{\text{eff}}$  value at 300 K is 3.11  $\mu_{\text{B}}$ , comparable with the theoretically expected value of 2.83  $\mu_{\text{B}}$  for a d<sup>8</sup> Ni(II) ion with an octahedral geometry. Upon cooling down,  $\mu_{\text{eff}}$  increases continuously up to a maximum of 4.8  $\mu_{\text{B}}$  at 14 K, then drops rapidly down to a value of 1.4  $\mu_{\text{B}}$  at 2 K. The  $1/\chi_{\text{M}}$  versus  $T$  curve is close to be linear when  $T > 150$  K [see Fig. 4 (right)], being well fitted by using the Curie Weiss law with  $C = 1.014$  emu K mol<sup>-1</sup>, and  $\theta = 53.97$  K. On the other hand, zero-field splitting is known to occur for Ni(II) ions, and for isolated ions may induce either an increase or a decrease of  $\mu_{\text{eff}}$  value at rather low temperature due to the site distur-

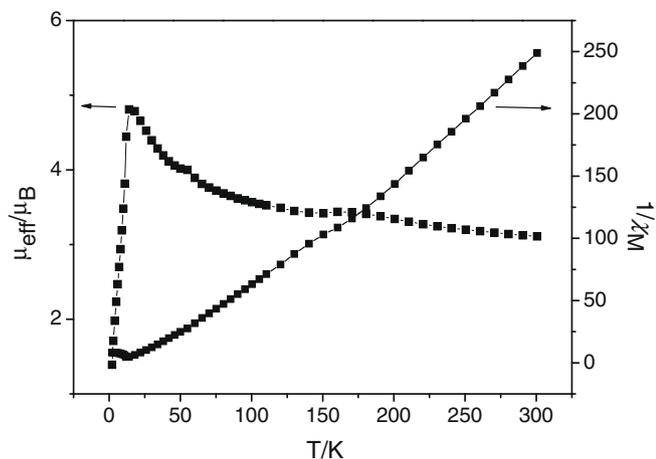


Fig. 4.  $\mu_{\text{eff}}$  vs.  $T$  curve (left) and  $1/\chi_{\text{M}}$  vs.  $T$  curve (right) of **1**.

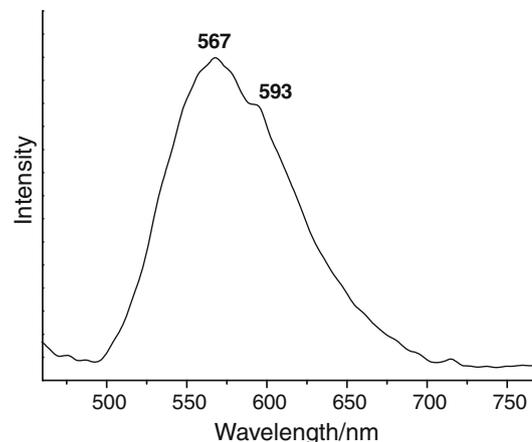


Fig. 5. Solid-state fluorescence emission spectrum of **2** ( $\lambda_{\text{ex}} = 397$  nm).

tion of metal ion. Based on both stated above, the observed behavior is thus characteristic of the occurrence of ferromagnetic interactions within the NiCl<sub>2</sub> chains due to a plus  $\theta$  value, whereas the drop below 14 K can be related to antiferromagnetic coupling between the chains as well as the effect of zero-field splitting. A 1-D chain model was used to fit the magnetic data of compound **1**, unluckily no ideal result was obtained [46].

#### 3.5. Photoluminescent property

The photoluminescent spectrum of compound **2** was measured on a LS 55 fluorescence/phosphorescence in the solid state at room temperature. As displayed in Fig. 5, the emission spectrum of compound **2** shows a strong band at 567 nm with a shoulder at 593 nm when excited at 397 nm. The emission may be from a triplet “cluster centered” (<sup>3</sup>CC<sup>\*</sup>) excited state, which should be assigned to a combination of iodide to copper charge transfer (IMCT<sup>\*</sup>) and “metal cluster centered” [(<sup>3</sup>MCC<sup>\*</sup>), d<sub>Cu</sub> → (s,p)<sub>Cu</sub>] transition. The weak Cu···Cu interactions with an average distance of 2.75 Å within the Cu<sub>2</sub>I<sub>2</sub> chain, as literature reported, will be responsible for a <sup>3</sup>MCC<sup>\*</sup> excited solid [47,48].

#### 4. Conclusion

Two new metal-halo cluster polymers based on the pip ligand have been obtained, which show the 3-D network structures comprising the 1-D zigzag NiCl<sub>2</sub> SUs and the 1-D castellated Cu<sub>2</sub>I<sub>2</sub> SUs, respectively. Compound **1** possesses the ferromagnetism, whereas compound **2** displays the fluorescence due to the existence of the weaker Cu···Cu interaction. The interrelated work is still going on, aiming at getting more compounds and exploring the relationship between the structure and the property.

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#### Appendix A. Supplementary data

CCDC 672190 and 672191 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2008.12.025](https://doi.org/10.1016/j.ica.2008.12.025).

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