



Synthesis and structural characterization of three copper coordination polymers with pyridine derivatives from hydro(solvo)thermal *in situ* decarboxylation reactions of 2,5-dicarboxypyridine

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ABSTRACT

The hydro(solvo)thermal self-assembles of CuI, KI and 2,5-dicarboxypyridine [2,5-(COOH)₂py] in different molar ratios in H₂O/alcohol solutions produced three Cu coordination polymers as 2-D [N-C₂H₅py][Cu₃I₄] **1**, 1-D [N-CH₃py][Cu₂I₃] **2** as well as 1-D [Cu(2-COOp₂)]·H₂O **3** (N-C₂H₅py = N-ethylpyridine, N-CH₃py = N-methylpyridine, 2-COOp₂ = 2-carboxypyridine). N-C₂H₅py in **1** and N-CH₃py in **2** derived from the solvothermal *in situ* simultaneous decarboxylation and N-alkylation reactions of 2,5-(COOH)₂py. The semi-decarboxylation reaction of 2,5-(COOH)₂py into 2-COOp₂ occurred in the preparation of **3**. X-ray single-crystal analysis revealed that CuI is transformed into a 2-D [Cu₃I₄]⁻ layer in compound **1** and a 1-D chain in compound **2**, templated by [N-C₂H₅py]⁺ and [N-CH₃py]⁺, respectively. Compound **3** is a divalent Cu compound. The Cu(II) centers with a 4+2 geometry are coordinated by μ₃-mode 2-COOp₂ ligands. All of the title compounds were characterized by CHN analysis, IR spectrum analysis and TG analysis. Compounds **1** and **2** exhibit fluorescence properties with the maximum emissions at 581 nm for **1** and 537 nm for **2**.

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1. Introduction

The study on the design and synthesis of novel metal-organic frameworks (MOFs) has attracted extensive interest due to their various properties such as catalysis, luminescence, magnetism, sorption, ion exchange, nonlinear optics and electricity [1–5]. In the past two decades, a large number of novel MOFs with fascinating topologies have been constructed by the direct interactions between the metal ions and the organic bridging N/O/S-donor ligands. However, most organic ligands in the reported MOFs are pre-synthesized or commercially available. Recently, the *in situ* ligand synthesis provides a new approach towards the crystal engineering of novel MOFs [6–8]. So far, more than ten kinds of ligand *in situ* reactions have occurred under the hydro(solvo)thermal conditions including the alkylation reaction and the decarboxylation reaction [9–14]. Although the carboxyl groups of carboxylic acid ligands could have been released during the reactions, the degree of the decarboxylation reaction is still difficult to be predicted and controlled.

On the other hand, copper(I) halides as the inorganic precursor have been widely employed in the construction of functional coordination polymers material for their excellent photoluminescent properties [15,16] and intriguing topology [17–21]. But most investigations are focused on the reactions of copper(I) halides with aromatic multi-dentate N-heterocyclic ligands or pyridine-monocarboxylate ligands. The study on the reactions between copper(I) halides and pyridinepolycarboxylate ligands is relatively rare to date [22]. Recently, we luckily obtained a novel 3-D network compound [Cu₁₄I₁₄(dabco)₅(py)] [23] (dabco = 1,4-diazabicyclo[2,2,2]octane) with **sqp** (with the Schläfli symbol of (4⁴,6⁶)) net from the simple hydrothermal self-assemble of CuI with 2,6-dicarboxypyridine [2,6-(COOH)₂py] in the presence of dabco. Obviously, the *in situ* full-decarboxylation reaction of 2,6-(COOH)₂py into py ligand occurred during the reaction. As further work of extending the system to the reactions of CuI with 2,5-(COOH)₂py, we herein report the structural characterization of three Cu coordination polymers 2-D [N-C₂H₅py][Cu₃I₄] **1**, 1-D [N-CH₃py][Cu₂I₃] **2** as well as 1-D [Cu(2-COOp₂)]·H₂O **3**. In them, 2-COOp₂ in **3** derived from the hydrothermal *in situ* semi-decarboxylation reactions of 2,5-(COOH)₂py. The full-decarboxylation reaction of 2,5-(COOH)₂py into py occurred in the preparation of **1** and **2**. The simultaneous N-alkylation reactions of py with C₂H₅OH/CH₃OH solvent lead to the formation of [N-C₂H₅py]⁺ cation in **1** and [N-CH₃py]⁺ cation in **2**.

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2. Experimental

2.1. Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Elemental analysis (C, H and N) 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 cm⁻¹ region using a powdered sample on a KBr plate. Thermogravimetric (TG) behavior was investigated on a Perkin-Elmer TGA 7 thermogravimetric analyzer. The luminescence property was measured on a Perkin-Elmer LS55 spectrometer.

2.2. Synthesis of the compounds

The reactions were carried out in 30 mL Teflon-lined stainless steel vessels under autogenous pressure. The single crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature.

[N-C₂H₅py][Cu₃I₄] 1. The orange pillar crystals of **1** were obtained by a solvothermal self-assembly process of CuI (0.38 g, 2 mmol), 2,5-(COOH)₂py (0.34 g, 2 mmol), KI (0.17 g, 1 mmol) and ethanol (10 mL) at 160 °C for 4 days (pH=4 acidified by dilute HCl). Yield: 25% based on Cu. Anal. Calcd C₇H₁₀Cu₃I₄N **1**: C 10.43, H 1.25, N 1.74. Found: C 10.38, H 1.42, N 1.52%. IR (cm⁻¹): 3052 w, 2918 w, 2843 w, 1625 m, 1480 s, 1445 w, 1355 m, 1316 m, 1238 w, 1177 m, 1154 w, 1087 w, 1063 w, 768 m, 684 s, 477 w (Fig. S1).

[N-CH₃py][Cu₂I₃] 2. The orange pillar crystals of **2** were obtained by another solvothermal self-assembly process of CuI (0.19 g, 1 mmol), 2,5-(COOH)₂py (0.08 g, 0.5 mmol), KI (0.17 g, 1 mmol) and methanol (10 mL) at 160 °C for 4 days (pH=4 acidified by dilute HCl). Yield: 35% based on Cu. Anal. Calcd C₆H₈Cu₂I₃N **2**: C 11.97, H 1.34, N 2.32. Found: C 11.88, H 1.56, N 2.12%. IR (cm⁻¹): 3046 w, 1632 s, 1579 m, 1481 m, 1384 w, 1308 w, 1282 m, 1184 m, 1148 w, 762 s, 676 s, 646 w, 442 w (Fig. S1).

[Cu(2-COOp_y)₂]·H₂O 3. The blue strip crystals of **3** were obtained by a hydrothermal self-assembly process of CuI (0.38 g, 2 mmol), 2,5-(COOH)₂py (0.67 g, 4 mmol), KI (0.66 g, 4 mmol) and H₂O (10 mL) at 160 °C for 4 days (pH=4 acidified by dilute HCl). Yield: 45% based on Cu. Anal. Calcd C₁₂H₁₀CuN₂O₅ **1**: C 44.24, H 3.09, N 8.60. Found: C 43.39, H 3.21, N 8.94%. IR (cm⁻¹): 3075 m,

1643 s, 1604 s, 1475 w, 1448 w, 1371 w, 1348 s, 1286 m, 1267 w, 1169 w, 1152 m, 1096 w, 1048 m, 850 m, 776 s, 712 w, 695 s, 660 w, 459 m (Fig. S1).

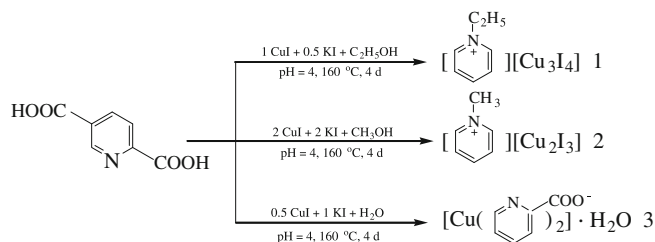
2.3. X-ray crystallography

Data were collected at 293 K with Mo K α radiation ($\lambda=0.71073$ Å) on a Siemens SMART CCD diffractometer for **1**, **3** and on a Rigaku R-Axis RAPID IP diffractometer for **2**. The structures were solved by direct methods and refined with the full-matrix least-squares on F^2 using SHELXL-97 program. Anisotropic thermal parameters were applied to all non-hydrogen atoms; the hydrogen atoms were set in calculated positions except those on lattice water molecules in compound **3**. CCDC numbers of compounds **1**, **2** and **3** are 745631–745633. The crystallographic data and pertinent information are listed in Table 1. The selected bond lengths and angles are listed in Table S1.

3. Results and discussion

3.1. Synthesis

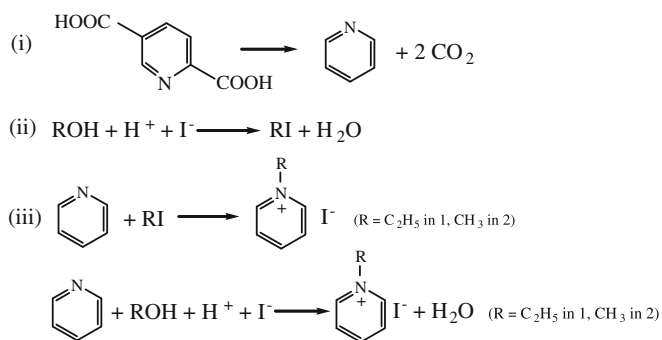
Our original attempt was to synthesize novel cluster polymers using multi-dentate ligand 2,5-(COOH)₂py and CuI. Unexpectedly *in situ* decarboxylation and alkylation reactions of the ligand were detected, which lead to the formation of compounds **1–3**. As shown in Scheme 1, compounds **1** and **2** were obtained by the *in situ* CuI/2,5-(COOH)₂py decarboxylation and *N*-alkylation reactions under the alcohol conditions. While in hydrothermal condition, semi-decarboxylation reaction of 2,5-(COOH)₂py



Scheme 1. Simplified routes of synthesizing compounds **1–3**.

Table 1
Crystal data and structure refinement parameters of compounds **1–3**.

	1	2	3
Empirical formula	C ₇ H ₁₀ Cu ₃ I ₄ N	C ₆ H ₈ Cu ₂ I ₃ N	C ₁₂ H ₁₀ CuN ₂ O ₅
Formula weight	806.38	601.91	325.77
Crystal system	<i>Ima</i> 2	<i>Pnma</i>	<i>P</i> -1
Space group	Orthorhombic	Orthorhombic	Triclinic
<i>T</i> (K)	293(2)	293(2)	293(2)
<i>a</i> (Å)	18.559(14)	18.182(4)	5.1329(2)
<i>b</i> (Å)	11.908(9)	6.2834(13)	7.6410(4)
<i>c</i> (Å)	6.910(5)	11.200(2)	9.2397(4)
α (°)	90	90	74.918(2)
β (°)	90	90	84.368(2)
γ (°)	90	90	71.469(2)
<i>V</i> (Å ³)	1527(2)	1279.6(4)	331.71(3)
<i>Z</i>	4	4	1
<i>D</i> (g cm ⁻³)	3.507	3.124	1.631
μ (mm ⁻¹)	12.197	10.517	1.666
<i>F</i> (000)	1432	1072	165
Data collected/unique	6283/1536	12080/1598	2428/1636
GOF	1.067	1.178	1.199
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ =0.0363, <i>wR</i> ₂ =0.0962	<i>R</i> ₁ =0.0256, <i>wR</i> ₂ =0.0705	<i>R</i> ₁ =0.0538, <i>wR</i> ₂ =0.1717
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0400, <i>wR</i> ₂ =0.0982	<i>R</i> ₁ =0.0286, <i>wR</i> ₂ =0.0720	<i>R</i> ₁ =0.0547, <i>wR</i> ₂ =0.1729



Scheme 2. The possible formation mechanisms of compounds **1** and **2**.

happened in compound **3**. The semi-decarboxylation in compound **3** may be due to the first chelation of 2,5-(COOH)₂py to the copper center, fixing the *ortho*-position carboxyl and preventing the *ortho*-position carboxyl further decarboxylation. Another interesting phenomenon is that the oxidation from Cu(I) to Cu(II) is observed in compound **3**, which is rare under the hydrothermal conditions [24]. The oxidation may be due to the instability of tetrahedral intermedial [Cu^I(2-COOHpy)₂]⁺ (similar to [Cu^I(en)₂]⁺) from the reaction between 1 CuI and 2 2,5-(COOH)₂py. The [Cu^I(2-COOHpy)₂]⁺ is further oxidized to stable octahedral [Cu^{II}(2-COOp₂)] by air. Although the decarboxylation of carboxylic acids can happen both by homolytic and heterolytic cleavage of the C–C bond by a variety of mechanisms [25], we have not determined the mechanism of the decarboxylation which takes place on the ligand 2,5-(COOH)₂py.

In the ethanol/methanol system, 2,5-(COOH)₂py ligands converted into [N-C₂H₅py]⁺ and [N-CH₃py]⁺ by the decarboxylation and *N*-alkylation reactions, which are further assembled into compounds **1** and **2**. The mechanisms of producing compounds **1** and **2** are similar and the possible formation mechanisms are shown in Scheme 2. Based on the above and previous results, the *in situ* metal–ligand reactions from 2,5-(COOH)₂py to [N-C₂H₅py]⁺ and [N-CH₃py]⁺ are suggested to be a two-step procedure containing the decarboxylation and *N*-alkylation reactions. It is easy for 2,5-(COOH)₂py to decarboxylate in the first step in a higher temperature. In the second step, [N-C₂H₅py]I and [N-CH₃py]I are important intermediates which directly resulted in the formation of compounds **1** and **2**, according to the literature [13]. The indirect and direct alkylation reagents are ethanol/methanol and C₂H₅I/CH₃I, respectively. Unfortunately, we could not obtain the suitable single crystals in other alcohol system such as propanol, isopropanol and 2-methyl-2-propanol.

In order to investigate the relationship between the structure, the stoichiometry of the reagents and the solvent used. A series of parallel experiments have been done. In C₂H₅OH solvent, we can obtain [N-C₂H₅py][Cu₃I₄] (**1**) with the CuI:KI ratios of 1:1, 1:2, 2:1, 1:3, 3:1, different only in purity and yield, which can be validated by IR spectra. The same argument has been made in CH₃OH solvent. With CuI:KI ratios of 1:1, 2:1, 1:3, 3:1, we can also obtain [N-CH₃py][Cu₂I₃] (**2**). From the above results, we can see that there is no inevitable relationship between the structure and the stoichiometry of the reagents in preparing compounds **1** and **2**, while the organic ligands exert a significant templating effect.

3.2. Crystal structures

[N-C₂H₅py][Cu₃I₄] 1. Compound **1** crystallizes in the space group *I*ma2. The asymmetric unit of compound **1** consists of 1.5

copper cations (Cu1, Cu2), 2 iodine anions (I1, I2) and 0.5 [N-C₂H₅py]⁺ cation. Both Cu1 and Cu2 ions with the tetrahedral geometries are coordinated by four iodine ions with the Cu(1)–I bond lengths of 2.660(2)–2.683(2) Å and Cu(2)–I bond lengths of 2.655(3)–2.722(2) Å, respectively. The Cu(1)–I distances are in agreement with those observed in the reported Cu(I) iodides [26]. The I–Cu(1)–I angles and the I–Cu(2)–I angles vary in the ranges of 98.37(11)–118.83(4)° and 97.87(7)–119.30(7)°, respectively, indicating that the Cu(1)I₄ and the Cu(2)I₄ tetrahedra are seriously distorted. I1 and I2 adopt the different μ₃-bridging modes. I2 takes on a common trigonal pyramidal geometry with a distance of 2.081 Å above the plane of three copper ions and the acute Cu–I2–Cu of 66.90(9)–67.23(7)°, whereas I1 takes on a special trigonal-planar geometry with the Cu–I1–Cu angles of 117.88(9)°, 118.59(7)° and 119.26(7)°.

Templated by the [N-C₂H₅py]⁺ cation, the Cu^I ions and the I[−] ions aggregate to form [Cu₃I₄][−] anionic layer (Fig. 1a). The basic building block of [Cu₃I₄][−] layer is [Cu_{2.5}I₂]^{0.5+} subunit. This subunit exhibits a trigonal bipyramidal shape with three Cu atoms on the equatorial plane and two iodine atoms on the axial position. The Cu1 (0.5, 0, 0.449) atom in the cluster is located on a

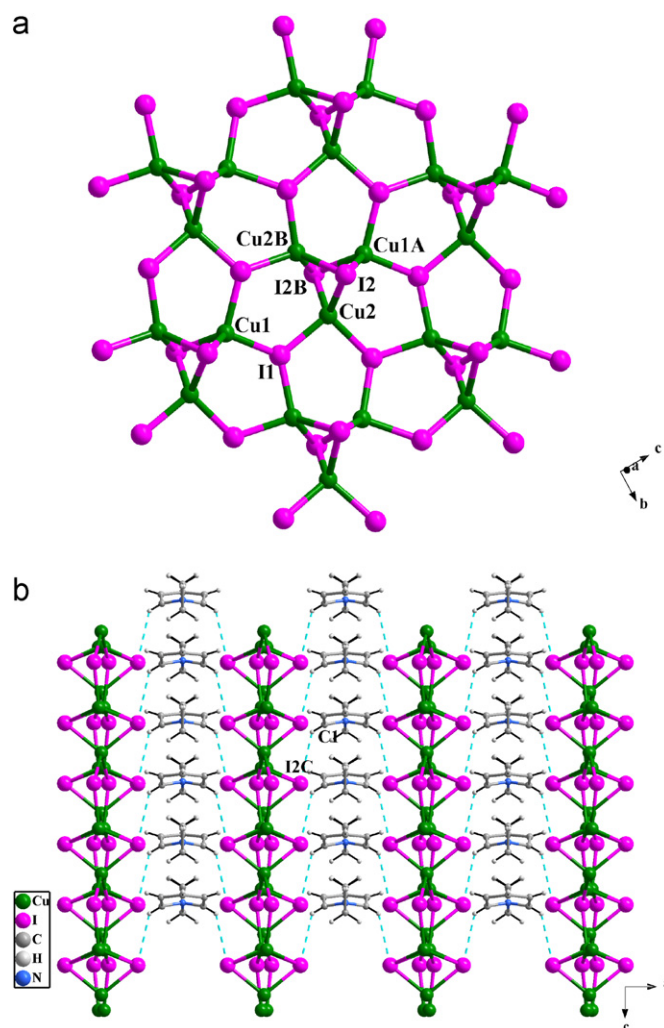


Fig. 1. The 2-D [Cu₃I₄][−] anionic layer templated by [N-C₂H₅py]⁺ (a) and the 3-D supramolecular network constructed by C–H...I hydrogen bondings (b) in [N-C₂H₅py][Cu₃I₄] **1** (symmetry code: A: x, y, 1+z; B: 1−x, −y, z; C: 1.5−x, 0.5−y, −0.5+z).

special position with the occupancy factor of 0.5. The shortest Cu...Cu contact in the cluster is 2.982 Å. Each $[\text{Cu}_{2.5}\text{I}_2]^{0.5+}$ cluster interacts with six adjacent clusters via the trigonal-planar I1 bridges, finally resulting in the formation of 2-D $[\text{Cu}_3\text{I}_4]^-$ layer. Although a variety of CuI subunits has been well documented, the CuI motifs with a 2-D layer are scarce [17,27–29]. $[\text{Pr}_4\text{N}][\text{Cu}_3\text{I}_4]$ [30], $[\text{C}_3\text{H}_8\text{NO}][\text{Cu}_3\text{I}_4] \cdot \text{DMF}$ [31], $[(\text{C}_6\text{H}_5)_4\text{P}][\text{Cu}_3\text{I}_4]$ [32] and $[\text{ebq}]_2[\text{Cu}_3\text{I}_4][\text{CuI}_2]$ [33] (ebq = *N*-ethylbenzo[*f*]quinolium) also have the same composition form of $[\text{Cu}_3\text{I}_4]^-$, but all of the $[\text{Cu}_3\text{I}_4]^-$ anions in the reported compounds are 1-D infinite chains which are different only in the linkage modes.

The anionic $[\text{Cu}_3\text{I}_4]^-$ layers in compound **1** interact with $[\text{N}-\text{C}_2\text{H}_5\text{py}]^+$ cations via the C–H...I hydrogen bondings with the $\text{C1}\cdots\text{I2C}=3.704$ Å (C: $1.5-x, 0.5-y, -0.5+z$) into a 3-D supramolecular network as shown in Fig. 1b.

$[\text{N}-\text{CH}_3\text{py}][\text{Cu}_2\text{I}_3]$ 2. Compound **2** was obtained as further work by using methanol instead of ethanol. Compound **2** consists of the $[\text{N}-\text{CH}_3\text{py}]^+$ cation and the 1-D $[\text{Cu}_2\text{I}_3]^-$ chain (Fig. 2a). The shortest Cu...Cu separation of 2.949 Å in $[\text{Cu}_2\text{I}_3]^-$ chain is slightly shorter than that observed in compound **1**. The molecule structure of compound **2** has been found in the literature [30]. Compared with the literature, the $[\text{N}-\text{CH}_3\text{py}]^+$ cation in compound **2** was *in situ* synthesized via the simultaneous decarboxylation and *N*-alkylation reactions of 2,5-(COOH)₂py. As shown in Fig. 2b, the 1-D $[\text{Cu}_2\text{I}_3]^-$ chain interact with $[\text{N}-\text{CH}_3\text{py}]^+$ cations through the C–H...I hydrogen bonds forming a 3-D

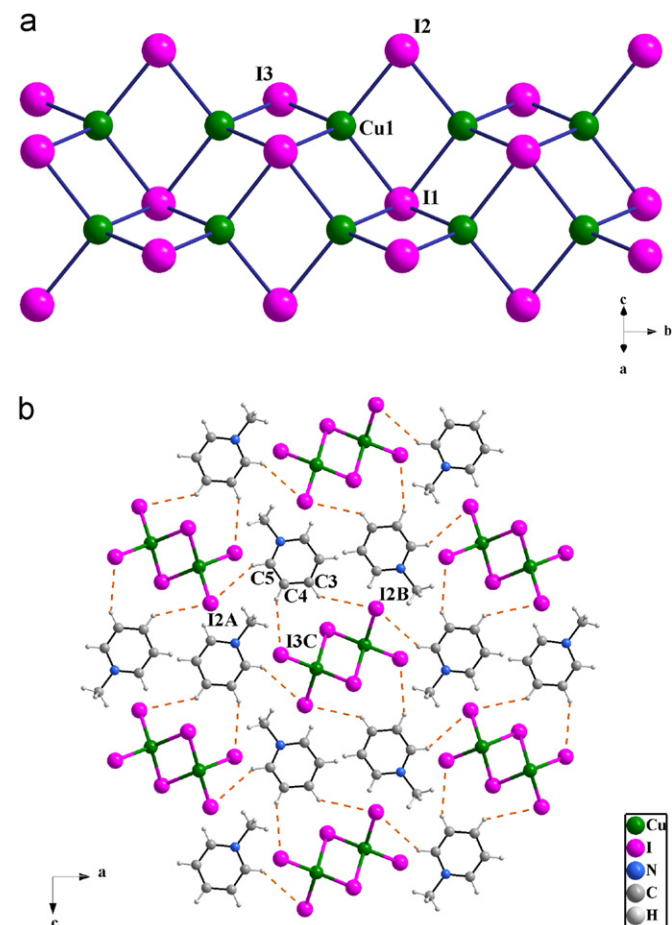


Fig. 2. The 1-D $[\text{Cu}_2\text{I}_3]^-$ chain (a) and the 3-D packing diagram with C–H...I hydrogen-bonded interactions in $[\text{N}-\text{CH}_3\text{py}][\text{Cu}_2\text{I}_3]$ (b) (symmetry code: A: $0.5+x, 0.5-y, 0.5-z$; B: $x, y, -1+z$; C: $1-x, 0.5+y, -z$).

structure with $\text{C5}\cdots\text{I2A}=3.933$ Å, $\text{C3}\cdots\text{I2B}=3.954$ Å and $\text{C4}\cdots\text{I3C}=3.901$ Å (A: $0.5+x, 0.5-y, 0.5-z$; B: $x, y, -1+z$; C: $1-x, 0.5+y, -z$).

$[\text{Cu}(\text{2-COOp})_2] \cdot \text{H}_2\text{O}$ 3. Compound **3** is a 2-COOp-bridged chained Cu coordination polymer. As shown in Fig. 3a, the crystallographically unique Cu(1) center in the chain exhibits a 4+2 geometry, suggesting that the copper atom is in a +2 oxidation state. This is further confirmed by the bond valence Sums (BVS) of 1.85 around the Cu(1) center [34]. The equatorial plane of the Cu(II) octahedron is occupied by two 2-COOp ligands with the pyridyl nitrogen atom (N1) and one carboxyl oxygen atom (O1) chelating to the Cu(II) center. The axial positions are occupied by two symmetric related O2 atoms (O2B and O2C) from adjacent two planar $\text{Cu}(\text{2-COOp})_2$ units. The equatorial Cu–O bond length of 1.948(2) Å and Cu–N bond length of 1.964(3) Å are normal, similar to those observed in other copper(II) complexes [35]. The axial Cu–O distance of 2.754(2) Å is far longer than that in the equatorial plane, which is ascribed to the John Teller effect. Although the axial Cu–O bond is weaker, it is non-negligible [36–38]. The 2-COOp ligands with a μ_3 -coordinated mode bridge the copper octahedra into a 1-D endless chain based on 8-membered $\text{Cu}_2(\text{-CO}_2)_2$ macroporous rings, extending along the *a*-axis. This macroporous ring exhibits a chair-type configuration if the carboxyl C atoms are omitted, further stabilizing the 1-D chain structure of compound **3**.

The lattice water molecules link to each other to form a 1-D zigzag-type water chain through the O–H...O hydrogen bondings, also extending along the *a*-axis. The average O...O distance of 2.816 Å in the water chain is slightly shorter than that observed in liquid water of 2.854 Å [39,40], but comparable with those observed in the ice II phase of 2.77–2.84 Å [41]. This distance is also comparable to those of the other water chain examples [42]. As shown in Fig. 3b, two types of chains arrange alternately in *bc* plane. The axial carboxyl O atoms form the hydrogen bonds to the water molecules (O1w) with the hydrogen-bonded parameter of $\text{O1w}\cdots\text{O2C}=2.916$ Å (C: $1+x, y, z$), linking two types of chains together into a 2-D supramolecular layer. As shown in Fig. 3c, the 2-D hydrogen-bonded layers are further propagated into a 3-D supramolecular network via the C–H...O hydrogen bondings with a $\text{C}\cdots\text{O}$ separation of 3.229 Å. The existence of such hydrogen-bonded interactions makes compound **3** more stable.

3.3. IR spectroscopy

As shown in Fig. S1 of the Supporting Information, the IR spectra of compounds **1–3** display some difference. The asymmetrical and symmetrical stretching frequencies in the carboxylate complexes, $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, in compound **3** are at 1645 and 1348 cm^{-1} , respectively. The absence of strong bands ranging from 1690 to 1730 cm^{-1} in **3** attributed to the protonated carboxyl indicates that the carboxyl of 2-COOp ligand in **3** has been deprotonated [43]. While in compounds **1** and **2**, there are no characteristic absorption of the carboxyl, so full-decarboxylation reaction of 2,5-(COOH)₂py happened.

3.4. Thermal analysis

Thermogravimetric (TG) behaviors of compounds **1, 2** and **3** were investigated in the temperature range of 40–800 °C with a heating rate of 10 °C min^{-1} in air (Fig. 4). Compounds **1–3** all exhibit two steps of weight losses. In compounds **1** and **2**, from 254 to 390 °C and 200–430 °C, respectively, corresponding to the loss of the iodide of the organic amine (Calcd: 29.15%; Found: 30.61% for **1**, Calcd: 36.72%; Found: 35.27% for **2**). The loss of the I[−] ion and the oxidation of the Cu(I) exist in the second step. The

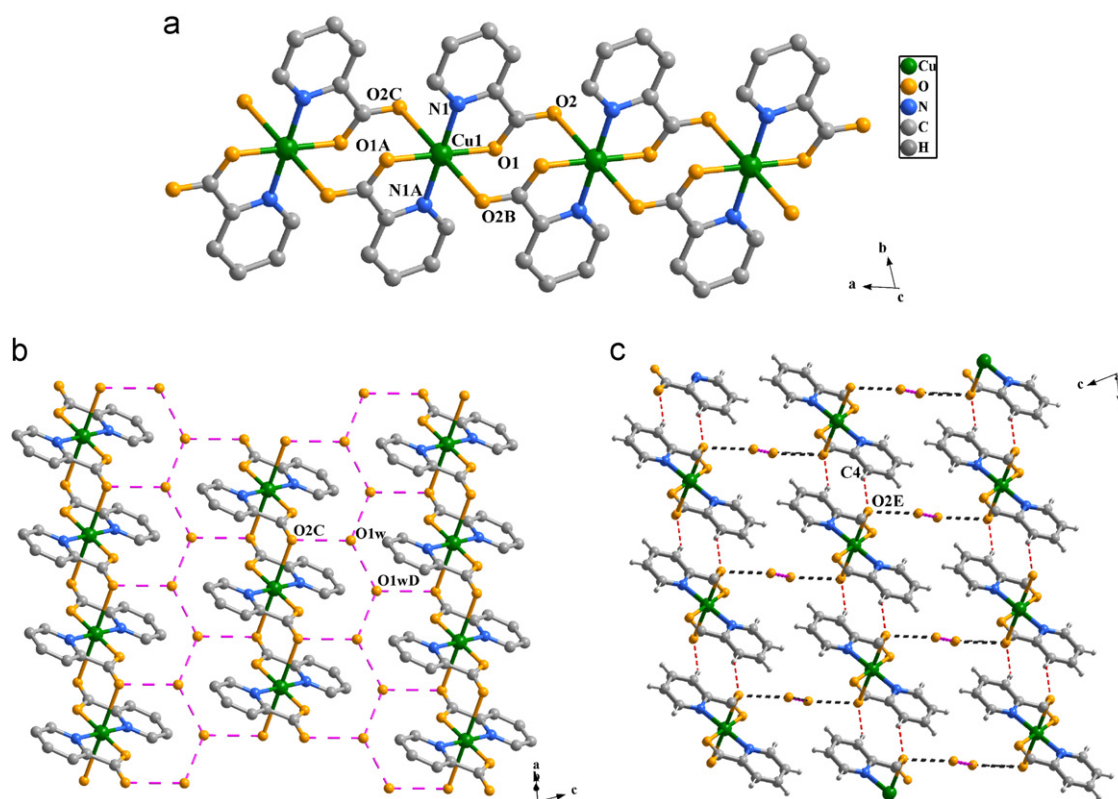


Fig. 3. The 1-D chain extending along the *a*-axis (a), 2-D supramolecular layer constructed by O–H...O hydrogen bonds (b) (H atoms on carbons are omitted for clarity) and 3-D supramolecular network constructed by O–H...O hydrogen bonds and C–H...O hydrogen bonds (c) in [Cu(2-COOpPy)₂] \cdot H₂O **3** (H atoms on oxygens are omitted for clarity (symmetry code: A: 1–*x*, 1–*y*, 1–*z*; B: –*x*, 1–*y*, 1–*z*; C: 1+*x*, *y*, *z*; D 1–*x*, 1–*y*, 2–*z*; E: –3–*x*, 1–*y*, 1–*z*).

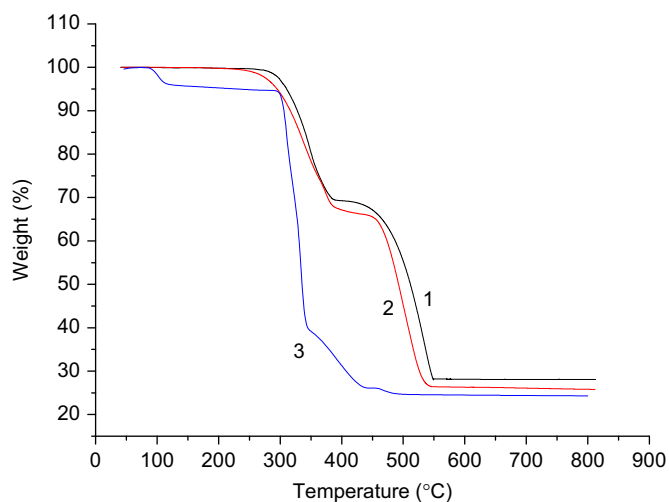


Fig. 4. TGA curves of compounds **1**, **2** and **3**.

final residues are proved to be CuO (Calcd: 29.59%; Found: 28.23% for **1**, Calcd: 26.43%; Found: 26.15% for **2**). In compound **3**, the first weight loss between 90 and 130 °C is due to the loss of the lattice water molecules (Calcd: 5.53%; Found: 4.73%). The second significant weight loss from 290 to 500 °C corresponding to the decomposition of 2-COOpPy ligands (Calcd: 74.96%; Found: 73.25%). Finally, the sample converts to CuO (Calcd: 24.4%; Found: 24.6%), which is stable in air.

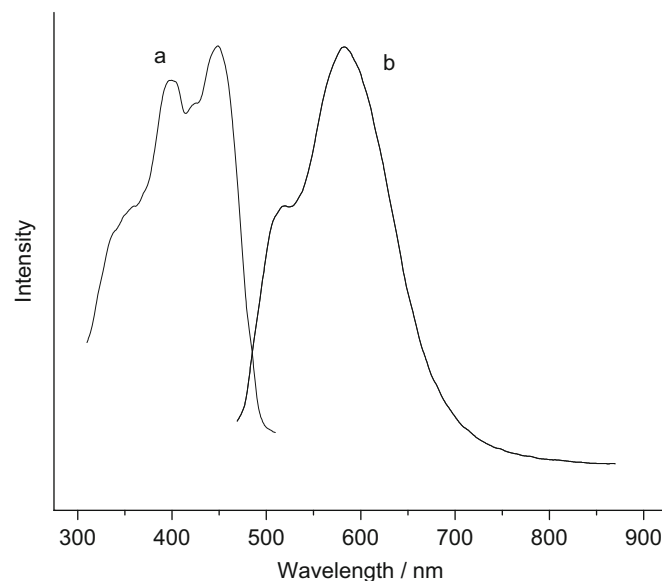


Fig. 5. Solid-state fluorescence spectra of **1**: (a) excitation spectrum ($\lambda_{\text{max}}=448$ nm) and (b) emission spectrum ($\lambda_{\text{max}}=581$ nm).

3.5. Photoluminescent properties

It is well known that copper(I) halide compounds with both discrete or multi-dimensional structures exhibit luminescence

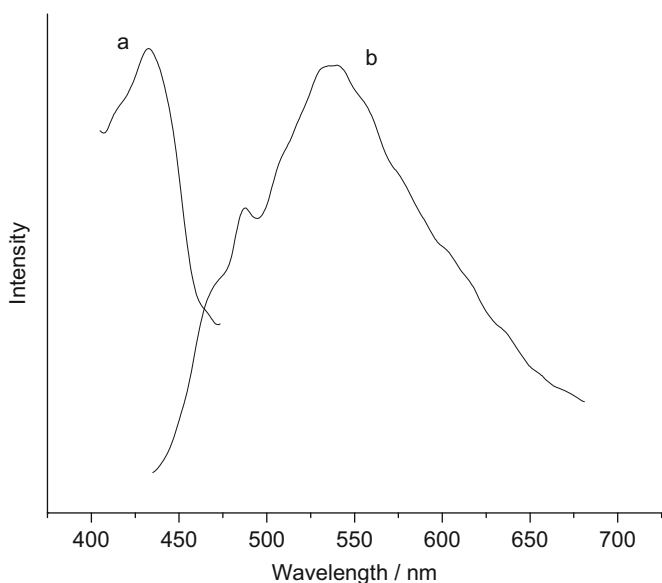


Fig. 6. Solid-state fluorescence spectra of **2**: (a) excitation spectrum ($\lambda_{\text{max}}=432$ nm) and (b) emission spectrum ($\lambda_{\text{max}}=537$ nm).

properties. Hence, we have studied the luminescence properties of compounds **1** and **2** (Figs. 5 and 6). The emission spectra in the solid state at room temperature with powder have a maximum at 581 nm ($\lambda_{\text{ex}}=448$ nm) and 537 nm ($\lambda_{\text{ex}}=432$ nm) for **1** and **2**, respectively. On the basis of experimental and theoretical results for the $\text{Cu}_4\text{L}_4\text{L}_4$ system ($\text{L}=\text{pyridine}$) [17,18,44,45], the low energy luminescence is assigned to a combination of a triplet “cluster centered” (${}^3\text{CC}^*$) excited state having mixed iodide-to-metal charge-transfer (XMCT) and “metal cluster centered” [MCC*, $d_{\text{Cu}} \rightarrow (s,p)_{\text{Cu}}$] transition by $\text{Cu}\cdots\text{Cu}$ interaction.

4. Conclusions

In summary, we have successfully isolated three compounds via the *in situ* metal–ligand hydro(solvo)thermal reactions of 2,5-(COOH) $_2$ py with CuI. Three types of *in situ* reactions occurred for 2,5-(COOH) $_2$ py in the reactions: decarboxylation *N*-ethylated, *N*-methylated and semi-decarboxylation. The results show that hydro(solvo)thermal *in situ* metal–ligand reaction is a forceful approach in crystal engineering of coordination polymers. On the other hand, it is well known that alkyl halides are a class of alkylation reagents in organic synthesis. These results demonstrate that ethanol or methanol can not only act as the solvents during solvothermal synthesis but also provide an interesting route to alkylation by using ethanol/methanol and haloids instead of alkyl halides. Work is in progress on extending this method to synthesize the derivatives of piperazine.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.04.033.

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