



New organically templated photoluminescence iodocuprates(I)

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ABSTRACT

Two types of organic cyclic aliphatic diamine molecules piperazine (pip) and 1,3-bis(4-piperidyl)propane (bpp) were used, respectively, to react with an inorganic mixture of CuI and KI in the acidic CH₃OH solutions under the solvothermal conditions, generating finally three new organically templated iodocuprates as 2-D layered [(Hpip)Cu₃I₄] **1**, 1-D chained [tmpip][Cu₂I₄] **2** (tmpip = N,N,N',N'-tetramethylpiperazinium) and dinuclear [H₂bpp]₂[Cu₂I₅] · 2H₂O **3**. Note that the templating agent tmpip²⁺ in compound **2** originated from the *in situ* N-alkylation reaction between the pip molecule and the methanol solvent. The photoluminescence analysis indicates that the title compounds emit the different lights: yellow for **1**, blue for **2** and yellow–green for **3**, respectively.

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1. Introduction

Hybrid organic–inorganic materials offer an important opportunity to combine useful properties of inorganic and organic system within a single molecular scale composite. Due to the structural diversity [1–3] and the potential applications in optics [4–8] and catalyst [9,10], as an important member of this family, the study on the design and synthesis of novel organically templated halocuprates(I) has been paid much attention to. Based on a simple strategy of applying various organic amine molecules as the templating agents, lots of 0-D, 1-D, 2-D and 3-D halocuprates(I) with the novel frameworks have been obtained in the acidic solutions during the past three decades. The organic templating agents have an obvious impact on the structures of the obtained halocuprates by means of the size, charge and form as well as the weak interactions between the organic amine cations and the inorganic halocuprates frameworks. Although so many organically templated halocuprates(I) have been structurally characterized, and some significant conclusions about the structures have been drawn, it is still difficult to predict the structure of the obtained halocuprates when a new organic templating agent is used.

Due to the existence of multikinds of potential charge transfer (CT) paths in the structures, the study on the photoluminescence properties of copper(I)-halo coordination polymers with the

composition of (CuX)_mL_n (X = Cl[−], Br[−], I[−]; L = N-heterocyclic molecule) has attracted considerable attention [11–20]. Based on the reported literature, the possible assignment of CT is considered as (i) ligand-to-metal (LMCT), (ii) halide-to-metal (XMCT), (iii) halide-to-ligand (XLCT), (iv) Cu^I d¹⁰–d⁹s¹ transition and (v) a combination of a triplet “cluster center” (³CC*) exited state having mixed XMCT and Cu^I d¹⁰–d⁹s¹ transition. However, the study on the photoluminescence properties of organically templated iodocuprates(I) are still limited, although these charge transfer paths also exist in their structures [4–6]. In this paper, the structural characterization and photoluminescence properties of three organically templated iodocuprates(I) [(Hpip)Cu₃I₄] **1**, [tmpip][Cu₂I₄] **2** and [H₂bpp]₂[Cu₂I₅] · 2H₂O **3** will be reported.

2. Experimental

2.1. Materials and general methods

All chemicals are of reagent grade quality, obtained from commercial sources without further purification. Elemental analysis was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum 1 spectrophotometer in 4000–400 cm^{−1} region using a powdered sample on a KBr plate. Thermogravimetric (TG) behavior was investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of 10 °C min^{−1} in air. Fluorescence spectrum in solid state was obtained on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature.

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2.2. Synthesis of the title compounds

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

[(Hpip)Cu₃I₄] 1: The yellow block crystals of **1** were obtained by a simple solvothermally self-assembly of CuI (0.076 g, 0.4 mmol), KI (0.05 g, 0.3 mmol) and pip · 6 H₂O (0.04 g, 0.2 mmol) in a 10 mL CH₃OH solution (pH=6 adjusted by dilute HCl) at 170 °C for 3 days. Yield: ca. 25% based on Cu(I). Anal. calcd. C₄H₁₁N₂Cu₃I₄ **1**: C, 6.13; H, 1.47; N, 3.57. Found: C, 6.08; H, 1.39; N, 3.65. IR (cm⁻¹) 3220 m, 1553 m, 1389 m, 1369 m, 1094 s, 1052 m, 981 s, 867 s.

[tmpip][Cu₂I₄] 2: The yellow block crystals of **2** were obtained by a similar reaction to that of **1** except that the CuI amount (0.019 g, 0.1 mmol) and the pH level (pH=4 adjusted by dilute HCl) are different. Yield: ca. 20% based on Cu(I). Anal. calcd. C₈H₂₀N₂Cu₂I₄ **2**: C, 11.05; H, 2.32; N, 6.44. Found: C, 10.95; H,

2.35; N, 6.51. IR (cm⁻¹) 3010 m, 1464 s, 1448 m, 1339 m, 1029 m, 1007 m, 980 w, 923 s, 860 w, 846 w.

[H₂bpp]₂[Cu₂I₅] I · 2H₂O 3: The yellow block crystals of **3** were obtained by a simple solvothermally self-assembly of CuI (0.19 g, 1 mmol), KI (0.83 g, 5 mmol) and bpp (0.42 g, 2 mmol) in a 10 mL CH₃OH solution (pH=6 adjusted by dilute HCl) at 170 °C for 3 days. Yield: ca. 30% based on Cu(I). Anal. calcd. C₂₆H₆₀N₄O₂Cu₂I₆ **3**: C, 23.14; H, 4.48; N, 4.15. Found: C, 24.23; H, 4.52; N, 4.13. IR (cm⁻¹) 2917 s, 1443 s, 1415 m, 1365 m, 1154 m, 1085 m, 1019 s, 959 s, 869 s, 835 m.

2.3. X-ray crystallography

Data were collected with MoK α radiation ($\lambda=0.71073$ Å) on a Siemens SMART CCD diffractometer for compounds **1** and **3** and on a Rigaku R-AXIS RAPID IP diffractometer for compound **2**. With SHELXTL program, the compounds were solved using direct methods and refined by full-matrix least-squares techniques. The non-H atoms were assigned anisotropic displacement parameters in the refinement, and the H atoms bound to the C atoms were treated using a riding model. The structures were then refined on F^2 using SHELXL-97. CCDC numbers for **1**, **2** and **3** are 809,404, 809,405 and 809,406, respectively. Basic information pertaining to the crystal parameters and structure refinement of the compounds is shown in Table 1.

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

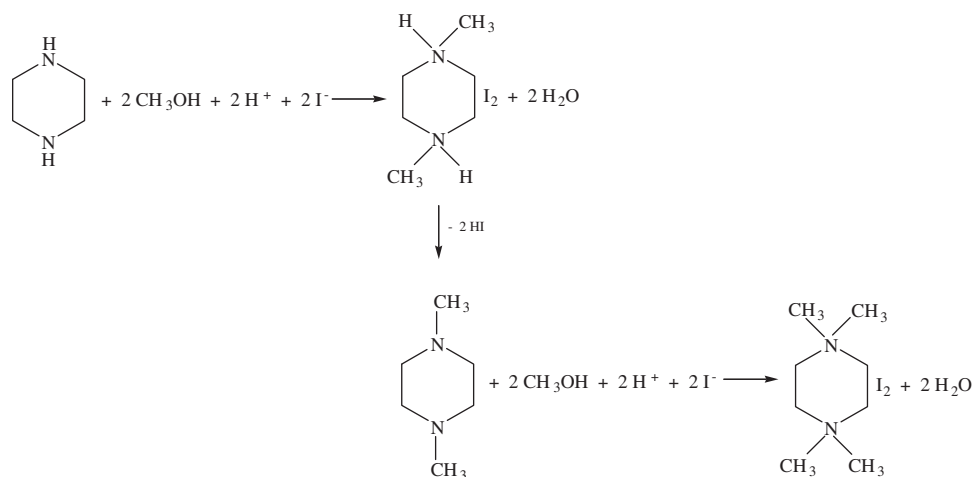
	1	2	3
Empirical formula	C ₄ H ₁₁ N ₂ Cu ₃ I ₄	C ₈ H ₂₀ N ₂ Cu ₂ I ₄	C ₂₆ H ₆₀ N ₄ O ₂ Cu ₂ I ₆
<i>M</i>	785.37	778.94	1349.28
<i>T</i> (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>m</i>	<i>C</i> mc2 ₁
<i>a</i> (Å)	7.1863(2)	14.527(3)	22.960(3)
<i>b</i> (Å)	8.8115(4)	7.1551(14)	15.693(3)
<i>c</i> (Å)	12.2602(6)	9.804(2)	11.7964(19)
α (deg)	108.737(3)		
β (deg)	99.642(3)	122.83(3)	
γ (deg)	97.262(3)		
<i>V</i> (Å ³)	711.18(7)	856.3(3)	4250.4(12)
<i>Z</i>	2	2	4
<i>D_c</i> (g cm ⁻³)	3.668	3.021	2.109
μ (MoK α) (mm ⁻¹)	13.091	9.675	5.385
<i>F</i> (000)	696	704	2544
Total data	5200	4221	5669
Unique data	3506	1060	3309
<i>R</i> _{int}	0.0613	0.0364	0.0365
Data <i>I</i> > 2 σ (<i>I</i>)	2677	1002	2728
GOF	1.040	1.122	0.996
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0473	0.0198	0.0438
<i>wR</i> ₂ [all data]	0.1448	0.0430	0.1195

3. Results and discussion

3.1. Synthetic analysis

In the process of preparing compound **2**, pip was selected to act as the templating agent, but the product was proved to be the tmpip²⁺ templated iodocuprate(I). Obviously, the solvothermal *in situ* *N*-alkylation reaction between pip and CH₃OH occurred. Scheme 1 shows reaction process in details. In the acidic KI solution, two methanol molecules *N*-alkylated first to the pip molecule to form *N,N'*-dimethylpiperazinium diiodide. Then *N,N'*-dimethylpiperazinium diiodide lost two hydrogen iodide to produce *N,N'*-dimethylpiperazine. *N,N'*-dimethylpiperazine was further *N*-alkylated by two methanol molecules, forming finally *N,N,N',N'*-tetramethylpiperazium diiodide. Obviously, H⁺ and I⁻ play the important role in the reactions.

A series of parallel experiments indicate that the pH level of the system is the most important factor in the reactions, and the stoichiometry of the reagents only influences the yield and the



Scheme 1. Solvothermal *in situ* *N*-alkylation reaction between pip and CH₃OH in acidic KI solution.

purity for the products. For CuI–KI–pip–CH₃OH system, three different compounds were obtained, respectively, at the different pH levels: [Cu₂I₂(pip)] at pH > 7; [(Hpip)Cu₃I₄] **1** at pH = 6; [(tmpip)][Cu₂I₄] **2** at pH = 4. At pH < 3, no product was obtained. At pH = 4, the optimum CuI:KI ratio for obtaining [(tmpip)][Cu₂I₄] **2** is 1:3 or 1:4. Increasing CuI amount or decreasing KI amount, the yield will decline. By the way, compound [Cu₂I₂(pip)] has been reported before [21]. Unfortunately, we could not obtain the suitable single crystals in other alcohol system as ethanol, propanol and isopropanol.

3.2. Crystal structure

[(Hpip)Cu₃I₄] 1: Compound **1** is the monoprotonated Hpip⁺ templated 2-D layered iodocuprate(I). It crystallizes in space group *P*-1, and the asymmetric unit is found to be composed of three monovalent Cu(I) ions, four I⁻ ions as well as one monoprotonated Hpip⁺ cation. Fig. 1 shows the 2-D layer structure of compound **1**. Both Cu1 and Cu2 are in the tetrahedral sites, but the detailed coordination environments are different. Cu1 is surrounded by three I⁻ ions (I1, I2, I2A) and one Hpip⁺ N atom, whereas Cu2 is coordinated by four I⁻ ions (I2, I1A, I1B, I3). Different from the usual planar triangular geometry, the 3-fold coordinated Cu3 is in a trigonal pyramidal site, and surrounded by three I⁻ ions (I3, I4, I4C). The distance from the apical Cu3 to the three I⁻ plane is 0.556 Å. The special geometry for Cu3 derives actually from the tetrahedral one. Due to the severe distortion of the tetrahedron, the distance between Cu3 and I2A is elongated to 3.103 Å, indicating that no interaction exists between Cu3 and I2A. Both the Cu1–I range of 2.6640(10)–2.7173(11) Å and the Cu2–I range of 2.6780(14)–2.7151(15) Å are comparable with each other. The Cu3–I bond lengths of 2.5740(14)–2.6361(16) Å are slightly shorter than those associated with Cu1 and Cu2. The reason is that all of the I⁻ ions around Cu1 and Cu2 are double-bridged, whereas most of the I⁻ ions around Cu1 and Cu2 are triple-bridged. The Cu1–N1 bond length is normal [2.104(6) Å]. Four I⁻ ions adopt two types of coordination modes including the triple-bridged I1, I2 and the double-bridged I3, I4. Two μ₃-mode I⁻ ions I1 and I2 bridge two tetrahedral Cu(I) ions Cu1 and Cu2 into a Cu–I double-chain with a castellated arrangement. This kind of chain arrangement has been observed in the reported compounds [Cu₂I₂(pip)] [21]. The alternate arrays of the rhomboid Cu₂I₂ rings form this castellated chain. The short Cu···Cu contact is that between Cu1 and Cu1A (2.707 Å). Via sharing the edge, two symmetric related Cu3 centers form a dinuclear Cu cluster with the Cu···Cu contact of 2.932 Å. The dinuclear clusters act as the bridges, linking the 1-D castellated chains together into a 2-D layer with the 20-membered ring. The Hpip⁺ cations protrude from the layer, and distribute regularly on both sides of the layer. Compared with the discrete and 1-D iodocuprates(I), the reported halocuprates with the 2-D layer

structures are sporadic. The examples have [(*N*-C₂H₅)py][Cu₃I₄] (*py* = pyridine) [6], [C₅H₇N₂O][Cu₃Br₄] (C₅H₇N₂O = 2-amino-3-hydroxypyridinium) [22], [dams][Cu₅I₆] (dams = *trans*-4-(4-dimethylaminostyryl)-1-methylpyridinium) [23] and [A46][Cu₂Br₄] (A46 = 4,6-dibromo-3-chloroanilinium) [24].

[(tmpip)][Cu₂I₄] 2: Compound **2** is the tmpip²⁺ templated 1-D chained iodocuprate(I). It crystallizes in space group *C2/m*, and the asymmetric unit is found to be composed of one Cu(I) ion (occupancy ratio: 0.5), two I⁻ ions (occupancy ratio: 0.5 for each) as well as 0.25 tmpip²⁺ cation. The templating agent tmpip²⁺ originated from the solvothermal *in situ* *N*-alkylation reaction between pip and methanol (see Scheme 1). Templated by tmpip²⁺, the [Cu₂I₄]²⁻ anion exhibits a 1-D chain structure as shown in Fig. 2. The crystallographically unique Cu(I) center (Cu1) with a tetrahedral geometry is coordinated by four I⁻ ions. The Cu1–I2 distance of 2.6661(5) Å is slight shorter than that of the Cu1–I1 [2.6804(8) Å]. Two I⁻ ions (I1, I2) adopt the μ₂-modes, bi-bridging the Cu(I) centers into the 1-D chain of compound **2** based on the rhomboid Cu₂I₂ rings. Each ring is planar with the Cu···Cu contacts of 3.539–3.616 Å. The dihedral angle between two adjacent Cu₂I₂ rings is 91.5°. This 1-D chain can also be described as a linkage of the Cu₄ tetrahedra by sharing the edges.

[H₂bpp]₂[Cu₂I₅] 1 · 2H₂O 3: Compound **3** is the diprotonated H₂bpp²⁺ templated 0-D iodocuprate(I). It crystallizes in space group *Cmc2₁*, and the asymmetric unit is found to be composed of one Cu(I) ion, four coordinated I⁻ ions (occupancy ratio: 1 for I1; 0.5 for I2, I3, I4), one diprotonated H₂bpp²⁺ cation, one uncoordinated I⁻ ion (occupancy ratio: 0.5) as well as two lattice water molecules (occupancy ratio: 0.5 for each). Fig. 3a gives the [Cu₂I₅]³⁻ anionic cluster structure in compound **3**. The crystallographically unique Cu(I) ion adopts a tetrahedral geometric configuration, and is coordinated by one terminal I⁻ ion (I1) and three double-bridged I⁻ ions (I2, I3, I4). The Cu–I(terminal) bond length of Cu1–I1 = 2.5378(19) Å is obviously shorter than those of the Cu–I(μ₂) [2.692(2)–2.937(3) Å]. To our surprise, the Cu1–I4 bond length [2.937(3) Å] is by far longer than the others. Four coordinated I⁻ ions exhibit two types of coordination modes including the terminal I1 and the μ₂-mode I2, I3 and I4. By sharing the face, two symmetric related Cu1 centers aggregate together into a dinuclear cluster. This cluster structure is similar to that observed in the reported literature [25], but the Cu···Cu contact of 2.514(4) indicates two copper ions are not mixed valent. Via the intermolecular hydrogen bondings, the H₂bpp²⁺ cations, the uncoordinated I⁻ ions together with the lattice water molecules self-assemble into a 2-D supramolecular layer as shown in Fig. 3b. Through the Ow···I interactions, two lattice water molecules (Ow1A, A: *x/a*, *y/b*, *z/c*; Ow2B, B: *x*–1/2, *y*+1/2, *z*+1) link first together by the uncoordinated I⁻ ion (I5A) into a I(Ow)₂ unit with ∠Ow1A···I5A···Ow2B = 122°. The Ow···I separations are Ow1A···I5A = 3.450 Å and Ow2B···I5A = 3.439 Å, respectively. Through the N···Ow interactions, the I(Ow)₂ units are further linked by the H₂bpp²⁺ cations

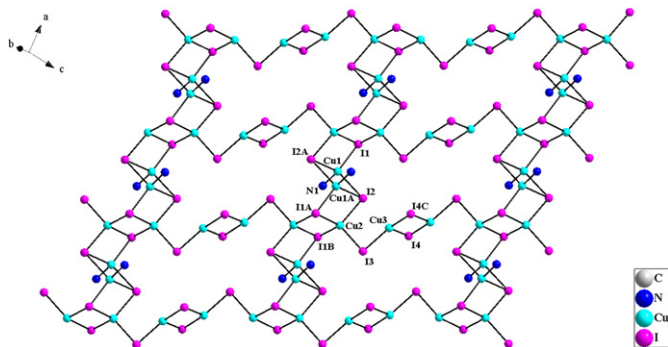


Fig. 1. 2-D layer structure of [(Hpip)Cu₃I₄] (C and one N of pip are omitted for clarity) **1**.

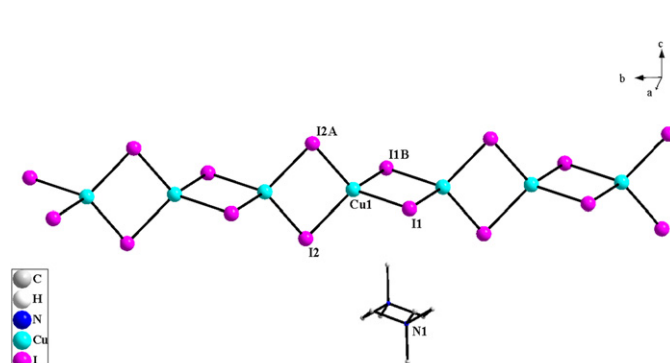


Fig. 2. 1-D chain structure of compound **2**.

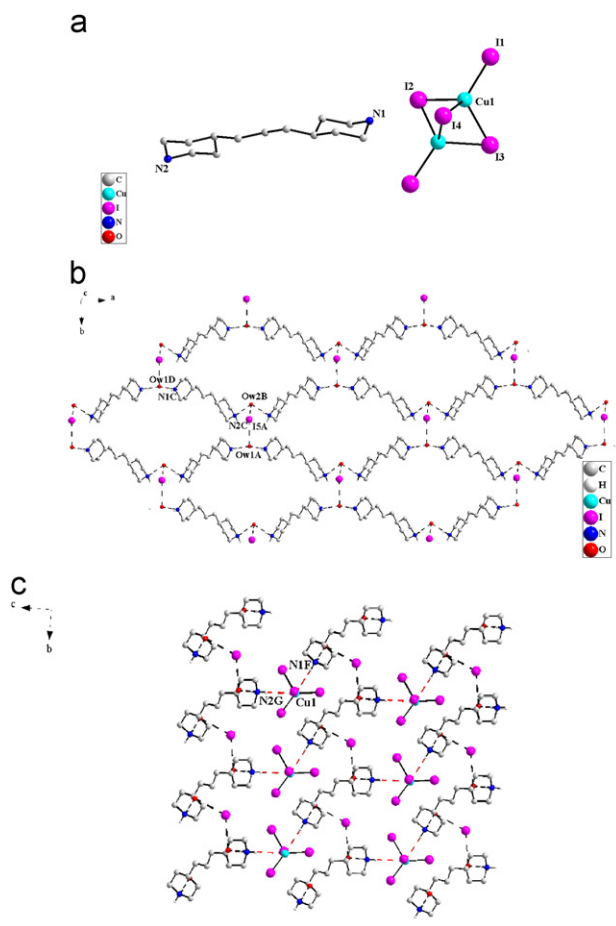


Fig. 3. $[\text{Cu}_2\text{I}_5]^{3-}$ cluster structure (a), 2-D supramolecular layer constructed up from the $\text{H}_2\text{bpp}^{2+}$ cations, the uncoordinated I^- ions as well as the lattice water molecules (b) and the projection plot in the (100) direction for compound **3**.

into a 2-D supramolecular layer with the hydrogen-bonded cyclic rings. The formation of the ring can be described as an alternate linkage of four $\text{H}_2\text{bpp}^{2+}$ cations, two $\text{I}(\text{Ow})_2$ units as well as two Ow molecules. The $\text{N}\cdots\text{Ow}$ separations are $\text{N}2\text{C}\cdots\text{Ow}2\text{B}=2.897 \text{ \AA}$ (C: $-x+1/2, y-1/2, z$) and $\text{N}1\text{C}\cdots\text{Ow}1\text{D}=2.868 \text{ \AA}$ (D: $x-1/2, y-1/2, z$), respectively. Fig. 3c is the projection plot of compound **3** in (100) direction. The supramolecular sheet is not planar. The $[\text{Cu}_2\text{I}_5]^{3-}$ cluster units occupy the space between the supramolecular layers. Interestingly, the Cu(I) center (Cu1) form the hydrogen bonds to the bpp N atoms (N1F, F: x, y, z ; N2G, G: $-x+3/2, y-1/2, z-1$) with the $\text{Cu}\cdots\text{N}$ contacts of $\text{Cu}1\cdots\text{N}1\text{F}=3.853 \text{ \AA}$ and $\text{Cu}1\cdots\text{N}2\text{G}=3.764 \text{ \AA}$, respectively.

3.3. IR and TG analyses

In the previous reports, we ever draw a conclusion that the existing form of the pip molecule in the compound can be preliminarily known by the IR spectrum. The sharp $\nu(\text{N-H})$ peak for the pip molecule appears at 3210 cm^{-1} . If the pip molecule exists in nonprotonated or monoprotonated form, this sharp peak still appears in the IR spectrum, and only some red or blue shifts occurred. Once the pip molecule is diprotonated, this sharp peak will disappear [26]. Now, another possibility must be considered. If the sharp peak disappeared in the IR spectrum, maybe the *N*-alkylation reaction for the pip molecule occurred, and two H atoms were replaced by alkyl groups. As shown in Fig. 4, the peak at 3224 cm^{-1} in the IR spectrum of compound **1** indicates the pip molecule in compound **1** is nonprotonated or monoprotonated.

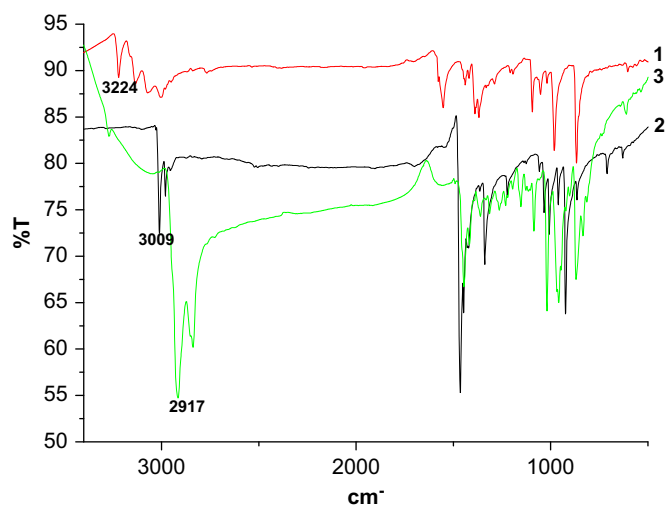


Fig. 4. IR curves of the title compounds.

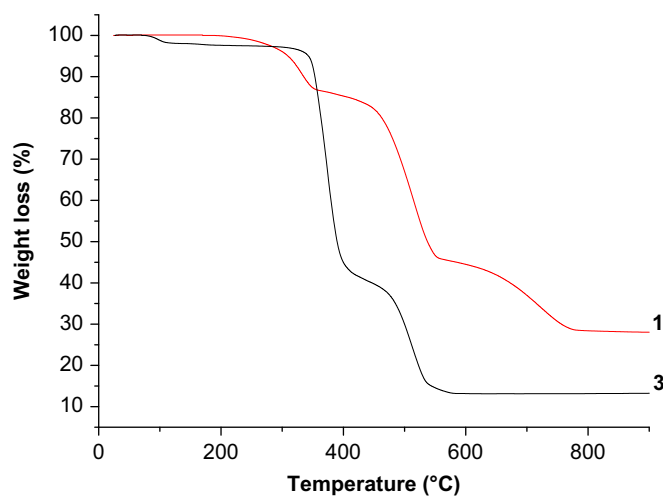


Fig. 5. TG curves of compounds **1** and **3**.

That no peak around 3210 cm^{-1} in the IR spectrum of compound **2** is found suggests that the pip molecule is either diprotonated or *N*-alkylated. The peaks at 3009 cm^{-1} in the IR spectrum of compound **2** should be attributed to that of the $\nu(\text{C-H})$.

The TG behaviors of compounds **1** and **3** were investigated, and their temperature ($^{\circ}\text{C}$) vs. weight loss (%) curves are shown in Fig. 5. From the TG curves of compounds **1** and **3**, we can know that (i) compound **1** is more stable, and it is thermal stable up to ca. $250 \text{ }^{\circ}\text{C}$, whereas the stability of compound **3** is not good due to the existence of the lattice water molecules in the crystal, (ii) both compounds underwent three steps of weight losses, (iii) the first-step weight loss for compounds **1** and **3** could be well assigned: for compound **1**, the initial weight loss should be ascribed to the removal of the organic pip molecule (calcd. 11.0; found 12.1%), while for compound **3**, the first step weight loss corresponds to the loss of the lattice water molecules (calcd. 2.66%; found 2.15%), (iv) the final residues for both compounds are proved to be CuO, because the calculated results of 30.1% for **1** and 11.8% for **3** are well comparable with those of the found ones of 29.3% for **1**, 12.9% for **3** and (v) although the second and third steps could not be well assigned, the removal of the organic bpp molecule for compound **3** should occur in the second step, and the decomposition of the

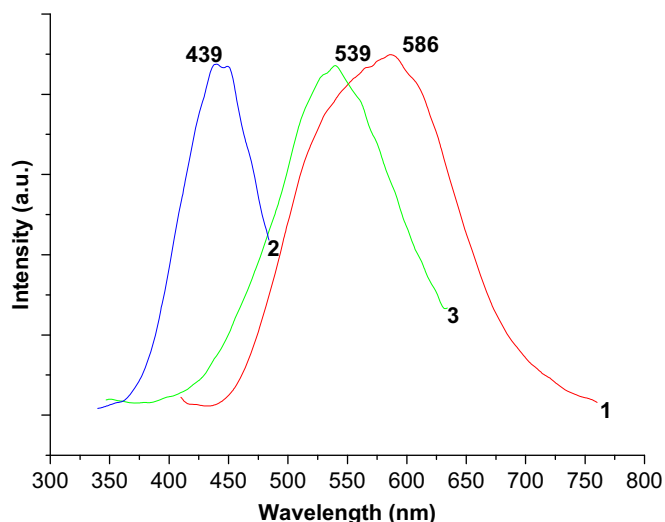


Fig. 6. Luminescence emission spectra of the title compounds.

Γ^- ions, and the oxidation of Cu(I) for both compounds should also occur in these two steps.

3.4. Photoluminescence property

The solid-state luminescence properties of compounds **1–3** were investigated and their luminescence emission spectra are shown in Fig. 6. Obviously, three compounds possess the luminescence properties, and they emit the different lights. Compounds **1** and **3** exhibit the low energy (LE) emissions centered, respectively, at 586 nm for **1** ($\lambda_{\text{ex}}=395$ nm) and 539 nm for **3** ($\lambda_{\text{ex}}=327$ nm) upon excitation, whereas compound **2** exhibits the high energy (HE) emission with the maximum peak at 439 nm when excited at 252 nm. Based on the study on the emission of $\text{Cu}_4\text{I}_4\text{L}_4$ system ($L=\text{py}$ or similar species), this should be due to the different $\text{Cu}\cdots\text{Cu}$ interactions in the structures. The study indicated only those with the short $\text{Cu}\cdots\text{Cu}$ interactions less than 2.8 Å in the structures could exhibit the LE emissions [27,28,29]. The emission of three organically templated iodocuprates(I) obey this rule. The $\text{Cu}\cdots\text{Cu}$ interactions in compounds **1** and **3** are short (2.707 Å for **1**, 2.514 Å for **3**), while that is relatively longer in compound **2** (3.539 Å). The study on the emission of $\text{Cu}_4\text{I}_4\text{L}_4$ system also indicated the electron densities of the highest occupied molecular orbital (HOMO) are distributed mainly on the 5p orbital of I, whereas those of the lowest unoccupied molecular orbital (LUMO) are located at the 4s orbital of Cu. Therefore, XMCT should also be responsible for the LE emissions of the compounds [14,18]. The further study indicated that the $\text{Cu}^1 d^{10}-d^9s^1$ transition also occurred for the LE emissions [14,18]. Therefore, the LE emissions of $\text{Cu}_4\text{I}_4\text{L}_4$ system are generally ascribed to a combination of a triplet “cluster center” (${}^3\text{CC}^*$) excited state having mixed XMCT and $\text{Cu}^1 d^{10}-d^9s^1$ transition based on these significant conclusions. The LE emissions for compounds **1** and **3** should have a similar attribution to that of $\text{Cu}_4\text{I}_4\text{L}_4$ system. As to the emission mechanism of compound **2**, paths (i), (ii), (iii) and (v) mentioned in “Section 1” are impossible, because the $\text{Cu}\cdots\text{Cu}$ interactions are long and the organic molecule is uncoordinated [20]. Therefore the HE emission for compound **2** should be assigned to the $\text{Cu}^1 d^{10}-d^9s^1$ transition. In fact, the HE emission is also similar to that of the inorganic CuI ($\lambda_{\text{max}}=420$ nm) [30].

4. Conclusion

In summary, we reported the structural characterization of three organically templated iodocuprates(I), obtained by the simple solvothermal self-assemblies of CuI, KI and pip/bpp in the acidic CH_3OH solutions. It is worth emphasizing that (i) compound **1** is one example of new 2-D layered iodocuprate(II) with the 20-membered rings, (ii) the templating agent tmpip^{2+} in compound **2** derived from the solvothermal *in situ* N-methylation reaction between pip and CH_3OH , which provides a new approach to prepare the new templating agent and (iii) the title compounds emit the different lights, which is associated with the short $\text{Cu}\cdots\text{Cu}$ interactions in the structures.

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Appendix. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.05.010.

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