



Influence of synthesis condition on product formation: hydrothermal auto-oxidated synthesis of five copper halides with ratio of Cu(I)/Cu(II) in 1:1, 2:1, 3:1, 4:1 and 1:0

Shuai Zhang^a, Yanning Cao^a, Hanhui Zhang^{a,b,*}, Xiaochuan Chai^a, Yiping Chen^a, Ruiqing Sun^a

^a Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, PR China

^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

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ABSTRACT

The hydrothermal synthesis and structural characterization of five copper iodides derived from chelated ligands, 1, 10-phenanthroline (phen), ethylenediamine (en) and 1, 3-propanediamine, are reported. Except monovalent copper compound **1** ((phen)Cu₃I₃ **1**), other four compounds ([Cu(phen)₂][CuI₂] **2**, [Cu(phen)₂][Cu₃I₄] **3**, [Cu(en)₂][Cu₄(phen)₂I₆] **4** and [Cu(1, 3-propanediamine)₂][CuI₂] **5**) are mixed-valent Cu(I)–Cu(II) compounds by partially auto-oxidated from Cu(I). Supramolecular frameworks of these compounds can be assembled by C/N–H...I hydrogen bonds, Cu(I)–Cu(I) interaction, weak Cu–I semicoordinate interaction, C–H...π and π–π stacking interactions. It's noteworthy that we find hydrothermal synthesis under higher pH value, higher synthesis temperature and longer reaction time can obtain higher ratio of Cu(I)/Cu(II) copper iodides and organic ligand with lower steric hindrance is prone to coordinated with divalent copper to form cation unit. Finally, the fluorescent study shows **1** exhibits intense orange–red luminescence with long lifetime at 293 K and more intense emission and longer lifetime at 77 K. Moreover, the room temperature EPR spectra of above five compounds not only show the valence of copper but demonstrate the coordination environment of Cu(II) centre.

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1. Introduction

Nowadays, the synthesis of inorganic–organic hybrid materials has attracted more and more people's attention, in which the research on metal-oxo cluster has gone through a long period with many vanadium-oxo clusters [1,2], molybdenum-oxo clusters [3,4], tungsten-oxo clusters [5] and hetero-polyacid clusters [6–8]. Though as a burgeoning field, metal-haloid cluster has aroused chemists' much attention for the reasons as follows: monovalent copper compounds showing strong fluorescence [9] and electrical-conductivity [10], divalent copper compounds displaying magnetic property [11] and mixed-valent Cu(I)–Cu(II) copper compounds with biological importance [12] and electronic properties [13]. So, Cu(I) halides have been widely employed as inorganic components in the construction of inorganic–organic hybrid coordination polymers [14,15]. It's known to all that Cu(II) halides have the tendency to be reduced to Cu(I) in the presence of organic species, particularly the compounds containing activated pyridine ring are involved [16,17]. Compared with chlorine (Cl) and bromine (Br), iodine (I) behaves more versatile bridging

modes ranging from μ_1 - to μ_7 -I [18–22], which can exhibit rhomboid dimers [23], zigzag chains [24], double-stranded ladders [16], cubane-like and stepped Cu₄I₄ tetramers [25,26], hexagonal grid chains [27], Cu₆I₆ hexamers including banded ribbons [28], Cu₆I₆ cores [27] and Cu₆I₆ clusters with two copper atoms in trigonal coordination environment etc. [15]. In comparison with coordination bonds, supramolecular interactions (hydrogen bond [29], C–H...π and π–π stacking interactions [30,31], metal–metal interaction [32] and weak coordinative interaction etc. [33]) can construct diversiform structure with novel topologies and potential application in host–guest chemistry, catalysis etc. [34]. Then, taking the advantages of forementioned factors, we are interested in obtaining mixed-valent Cu(I)–Cu(II) copper iodides originating from CuI by auto-oxidation under hydrothermal condition [35]. Herein, we have successfully combined phen, en and 1, 3-propanediamine with copper iodides to build five inorganic–organic hybrid compounds under similar hydrothermal conditions, which assemble to supramolecular architecture by various supramolecular interactions. Except monovalent compound **1**, other four are mixed-valent Cu(I)–Cu(II) compounds (with the ratio of Cu(I)/Cu(II) in 1:1, 3:1, 4:1, 2:1, respectively) by partially auto-oxidated from Cu(I). Meanwhile, we find that hydrothermal synthesis under higher pH value, higher synthesis temperature and longer reaction time can get

* Corresponding author at: Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, PR China. Tel.: +86 591 87893235; Fax: +86 591 87893239.
E-mail address: zhanghh1840@hotmail.com (H. Zhang).

higher ratio of Cu(I)/Cu(II) copper iodide compounds and organic ligand with lower steric hindrance is prone to coordinated with divalent copper to form the cation unit, all of which are beneficial to our future design and synthesis via hydrothermal method to some extent. Besides single crystal X-ray diffraction (XRD) analysis, these five compounds are characterized by elemental analyses, powder XRD analysis, IR spectra, ultraviolet-visible diffuse reflection integral spectra (UV-vis DRIS), fluorescent spectra and EPR spectra analysis. The fluorescent study shows **1** exhibits intense orange-red luminescence with long lifetime ($\tau = 1.25 \mu\text{s}$) at 293 K and more intense emission and longer lifetime ($\tau = 6.95 \mu\text{s}$) at 77 K. Moreover, the room temperature EPR spectra of above five compounds not only show the valence of copper but demonstrate the coordination environment of Cu(II) centre.

2. Experimental

2.1. General procedures

All analytical reagent grade chemicals were commercially purchased and used without purification. The elemental analyses of C, H, and N were performed with an Elementar Vario EL III elemental analyzer. The powder XRD patterns of solid-state samples were recorded on a PANalytical X'pert Pro diffractometer equipped with Cu-K α radiation ($\lambda = 0.1541 \text{ nm}$) at room temperature. The IR spectra were recorded with a Perkin-Elmer Spectrum 2000 FT-IR spectrometer in the range of 400–4000 cm^{-1} using the KBr pellet technique. UV-Vis DRIS was measured by a Perkin-Elmer Lambda 900 UV-Vis spectrometer with BaSO₄ as the reference sample. The solid-state fluorescent spectra were recorded on an Edinburgh Instrument FL/FS-920 fluorescent spectrometer using Xe lamp for steady fluorescent and H₂ nanose-

cond flash lamp for transient fluorescence. EPR spectra of compounds **1**, **3**, **4** and **5** were recorded on a Bruker EMX-10/12 spectrometer at room temperature with a frequency modulation of 100 KHz except compound **2** recorded on a Bruker ER-420 spectrometer.

2.2. Synthesis of compounds

Synthesis of (phen)Cu₃I₃ 1: The aqueous solution (2 cm^3) of CuI (0.19 g, 1 mmol) and NaI (0.30 g, 2 mmol) was stirred with adding [Mn(phen)₂I₂] (0.07 g, 0.1 mmol) and ethanol (1 cm^3). [Mn(phen)₂I₂] was prepared in advance according to the Ref. [36]. Then the mixture was stirred for another 30 min and pH value was adjusted to 5.8 with drops of 10% HCl and 10% NaOH solution. Finally, the mixed solution was sealed in a 15 cm^3 Teflon-lined stainless autoclave and heated at 170 °C for 4 d under autogenous pressure and then cooled to room temperature unaffectedly. Red rod crystals of **1** suitable for X-ray analysis were obtained in about 41% yield (based on Cu). Anal. calc for C₁₂H₈Cu₃I₃N₂: C, 19.18; H, 1.07; N, 3.73 wt%; found: C, 19.20; H, 1.04; N, 3.81 wt%. IR (KBr, cm^{-1}): 3042 (vw), 1616 (w), 1574 (w), 1502 (m), 1418 (s), 1134 (w), 834 (s), 761 (w), 722(s), 632 (vw).

Synthesis of [Cu(phen)₂I][CuI₂] 2: The synthesis method of **2** was similar to that of **1** except that pH was adjusted to 6.0 with 10% HCl and 10% NaOH solution and the reaction temperature of 150 °C instead. Black thick sheet crystals of **2** were obtained in about 34% yield (based on Cu). Anal. calc for C₂₄H₁₆Cu₂I₃N₄: C, 33.20; H, 1.86; N, 6.45 wt%; found: C, 33.42; H, 1.83; N, 6.37 wt%. IR (KBr, cm^{-1}): 3042 (vw), 1619 (w), 1579 (w), 1514 (m), 1422 (s), 1138 (w), 843 (s), 775 (w), 718(s), 643 (w).

Synthesis of [Cu(phen)₂I][Cu₃I₄] 3: The synthesis sources of **3** were the same as that of **1** except pH = 7.4 without adjusting. And the mixture was sealed in 15 cm^3 autoclave and heated at 130 °C for 2 d under autogenous pressure. Black square block crystals of **3**

Table 1
Crystallographic data for compounds **1**, **2**, **3**, **4** and **5**

Compounds	1	2	3	4	5
Empirical formula	C ₁₂ H ₈ Cu ₃ I ₃ N ₂	C ₂₄ H ₁₆ Cu ₂ I ₃ N ₄	C ₂₄ H ₁₆ Cu ₄ I ₅ N ₄	C ₁₄ H ₁₆ Cu _{2.50} I ₃ N ₄	C ₃ H ₁₀ Cu _{1.50} I ₂ N ₂
Formula mass	751.52	868.19	1249.07	779.86	423.24
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	4.1844(8)	7.8881(16)	14.081(4)	8.297(6)	6.896(6)
<i>b</i> (Å)	13.460(3)	9.5501(19)	14.006(5)	9.424(5)	8.685(8)
<i>c</i> (Å)	15.998(3)	17.346(4)	16.146(5)	13.985(6)	9.016(6)
α (deg)	113.74(3)	85.75(3)	90.00	83.46(2)	110.42(3)
β (deg)	92.58(3)	77.75(3)	113.957(12)	79.90(2)	98.87(3)
γ (deg)	98.12(3)	77.10(3)	90.00	64.82(2)	110.39(3)
<i>V</i> (Å ³)	811.3(3)	1244.3(4)	2909.9(16)	973.3(9)	450.4(6)
D _c (g/cm ³)	3.076	2.317	2.851	2.661	3.121
<i>Z</i>	2	2	4	2	2
<i>F</i> (000)	680	810	2276	719	383
λ (MoK α) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
θ Range (deg)	3.06–27.48	3.09–27.48	3.12–27.48	3.29–27.48	3.28–27.48
Limiting indices	–5 ≤ <i>h</i> ≤ 5, –17 ≤ <i>k</i> ≤ 17, –20 ≤ <i>l</i> ≤ 20	–10 ≤ <i>h</i> ≤ 9, –12 ≤ <i>k</i> ≤ 11, –22 ≤ <i>l</i> ≤ 22	–16 ≤ <i>h</i> ≤ 18, –18 ≤ <i>k</i> ≤ 18, –20 ≤ <i>l</i> ≤ 17	–10 ≤ <i>h</i> ≤ 10, –10 ≤ <i>k</i> ≤ 12, –18 ≤ <i>l</i> ≤ 18	–8 ≤ <i>h</i> ≤ 8, –11 ≤ <i>k</i> ≤ 11, –11 ≤ <i>l</i> ≤ 11
Goodness-of-fit on <i>F</i> ²	1.132	1.039	1.036	1.018	1.049
Collected reflections	7907	11853	27550	9620	4477
Independent reflections (<i>R</i> _{int})	3627(0.0270)	5537(0.0417)	6544(0.0391)	4417(0.0275)	2042(0.0854)
Observed reflections (<i>I</i> > 2 σ (<i>I</i>))	3044	4037	5327	3983	1811
Final <i>R</i> factors (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ ^a = 0.0329, <i>wR</i> ₂ ^b = 0.0760	<i>R</i> ₁ = 0.0379, <i>wR</i> ₂ = 0.0676	<i>R</i> ₁ = 0.0295, <i>wR</i> ₂ = 0.0613	<i>R</i> ₁ = 0.0240, <i>wR</i> ₂ = 0.0567	<i>R</i> ₁ = 0.0472, <i>wR</i> ₂ = 0.1100
Final <i>R</i> factors (all data)	<i>R</i> ₁ = 0.0416, <i>wR</i> ₂ = 0.0791	<i>R</i> ₁ = 0.0625, <i>wR</i> ₂ = 0.0753	<i>R</i> ₁ = 0.0418, <i>wR</i> ₂ = 0.0645	<i>R</i> ₁ = 0.0278, <i>wR</i> ₂ = 0.0581	<i>R</i> ₁ = 0.0503, <i>wR</i> ₂ = 0.1123
Largest diff. map peak and hole e Å ^{–3}	1.043 and –1.237	0.856 and –0.682	1.634 and –1.599	0.757 and –0.849	1.579 and –2.311

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2}$.

were obtained in about 37% yield (based on Cu). Anal. calc for $C_{24}H_{16}Cu_4I_5N_4$: C, 23.08; H, 1.29; N, 4.49 wt%; Found: C, 23.01; H, 1.33; N, 4.38 wt%. IR (KBr, cm^{-1}): 3046 (vw), 1622 (w), 1579 (w), 1513 (s), 1422 (s), 1136 (w), 841 (s), 771 (w), 717(s), 642 (w).

Synthesis of $[Cu(en)_2][Cu_4(phen)_2I_6]$ **4**: For synthesizing **4**, 4 cm^3 aqueous solution substituted for 2 cm^3 in synthesizing **1**. Besides this, we also introduced 0.2 cm^3 ethylenediamine as another resource. 10% HCl solution was used to adjust the pH to 5.5. Finally, the mixture was sealed in 23 cm^3 autoclave and heated at 160 °C for 1 d under autogenous pressure. Dark red parallelepiped crystals of **4** were obtained in about 44% yield (based on Cu). Anal. calc for $C_{14}H_{16}Cu_{2.5}I_3N_4$: C, 21.56; H, 2.07; N, 7.18 wt%; Found: C, 21.49; H, 2.11; N, 7.23 wt%. IR (KBr, cm^{-1}): 3278 (m), 3210 (s), 3047 (vw), 2935 (w), 2873 (vw), 1617 (w), 1569 (s), 1504 (m), 1448 (m), 1418 (m), 1162 (m), 1034 (s), 965 (m), 847 (s), 769 (w), 725(s), 672 (w).

Synthesis of $[Cu(1,3\text{-propanediamine})_2][Cu_2]$ **5**: 1, 3-propanediamine was used instead of en of **4**. Then after adjusting the pH value to 7.4 with 10% HCl solution, the mixture was sealed in 23 cm^3 autoclave and heated at 150 °C for 1 d under autogenous pressure. Black block crystals of **5** were obtained in about 53% yield (based on Cu). Anal. calc for $C_3H_{10}Cu_{1.5}O_2N_2$: C, 8.51; H, 2.38; N, 6.62 wt%; Found: C, 8.46; H, 2.34; N, 6.70 wt%. IR (KBr, cm^{-1}): 3249 (m), 3193 (s), 3109 (vw), 2929 (w), 2873 (vw), 1572 (vs), 1560 (m), 1449 (m), 1390 (m), 1309 (m), 1281 (s), 1172 (s), 1152 (s), 1009 (vs), 937 (w), 909 (s), 878 (m), 660 (s), 612 (m), 489 (s).

2.3. X-ray crystallography

The reflection intensities for these five crystals were collected on a Rigaku Weissenburg IP diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $298 \pm 2 \text{ K}$. Lp correction and a ψ empirical absorption correction were made for the intensity data. The

structures of these five crystals were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. The remaining hydrogen atoms were generated geometrically and not refined. The isotropic displacement parameters of all hydrogen atoms were defined as $U_{iso}(H) = 1.2U_{eq}(C)$. In compound **2**, the I3 atom is disordered and possesses two positions with occupancies given in parentheses: I3A (66.2%), I3B (33.8%). And Cu4 in compound **3** is disordered as well: Cu4A(48%), Cu4B(52%). Further details of the crystallographic data and structure refinement for five compounds are tabulated in Table 1. Selected bond lengths and angles are listed in Tables 2–6. All calculations were performed on a computer with SHELXTL-PC program package [37,38].

Table 4
Selected bond lengths (Å) and angles (deg) for **3**

I(1)–Cu(3)	2.5438(9)	I(1)–Cu(1)	2.6617(10)
I(2)–Cu(2)#1 ^a	2.6038(10)	I(2)–Cu(2)	2.6105(11)
I(3)–Cu(2)	2.6037(10)	I(3)–Cu(3)	2.6763(13)
I(3)–Cu(4)	2.729(8)	I(4)–Cu(3)	2.6497(11)
I(4)–Cu(4)	2.660(4)	I(5)–Cu(4)#2	2.555(4)
I(5)–Cu(3)	2.8486(12)	Cu(3)–Cu(4)	2.471(4)
I(5)–Cu(4)	2.919(11)	Cu(1)–N(1)	1.989(4)
Cu(1)–N(4)	1.993(4)	Cu(1)–N(3)	2.103(4)
Cu(1)–N(2)	2.129(4)	Cu(2)–I(2)#1	2.6038(10)
Cu(2)–Cu(2)#1	2.6754(15)	Cu(2)–Cu(3)	2.7582(13)
Cu(3)–I(1)–Cu(1)	93.56(3)	Cu(2)#1–I(2)–Cu(2)	61.74(3)
N(4)–Cu(1)–N(3)	81.06(15)	N(1)–Cu(1)–N(2)	80.67(15)
I(2)–Cu(2)–Cu(3)	122.54(4)	I(1)–Cu(3)–I(4)	116.05(4)
I(1)–Cu(3)–I(3)	126.07(3)	I(1)–Cu(3)–Cu(2)	72.41(3)
I(4)–Cu(3)–I(5)	100.68(3)	I(3)–Cu(3)–I(5)	103.42(3)
I(5)#2–Cu(4)–I(5)	112.1(3)	I(4)–Cu(4)–I(3)	101.4(2)
I(3)–Cu(4)–I(5)	100.29(13)	I(4)–Cu(4)–I(5)	98.7(3)

^a #1 $-x+1, -y+2, -z+1$; #2 $-x, -y+2, -z+1$.

Table 2
Selected bond lengths (Å) and angles (deg) for **1**

I(1)–Cu(1)	2.4940(12)	I(1)–Cu(2)	2.6008(11)
I(1)–Cu(1)#1 ^a	2.6630(12)	I(2)–Cu(2)#1	2.6640(15)
I(2)–Cu(2)	2.6747(13)	I(2)–Cu(3)#2	2.6773(12)
I(2)–Cu(3)	2.6791(13)	I(3)–Cu(2)	2.6283(12)
I(3)–Cu(3)	2.6383(13)	I(3)–Cu(3)#3	2.6433(15)
Cu(1)–N(1)	2.058(5)	Cu(1)–N(2)	2.067(6)
Cu(1)–I(1)#3	2.6630(12)	Cu(2)–I(2)#3	2.6640(15)
Cu(2)–Cu(3)#3	2.9244(15)	Cu(2)–Cu(3)	2.9333(16)
Cu(3)–I(3)#1	2.6433(15)	Cu(3)–I(2)#2	2.6773(12)
Cu(3)–Cu(2)#1	2.9244(15)	Cu(3)–Cu(3)#2	2.963(2)
Cu(1)–I(1)–Cu(2)	112.68(4)	Cu(2)–I(2)–Cu(3)	66.44(4)
Cu(2)–I(3)–Cu(3)	67.69(4)	Cu(3)–I(3)–Cu(3)#3	104.80(4)
N(1)–Cu(1)–N(2)	81.1(2)	N(1)–Cu(1)–I(1)	127.36(15)
N(2)–Cu(1)–I(1)	130.02(16)	N(1)–Cu(1)–I(1)#3	98.81(15)
N(2)–Cu(1)–I(1)#3	105.29(17)	I(1)–Cu(2)–I(3)	109.07(4)
I(1)–Cu(2)–I(2)#3	109.97(4)	I(3)–Cu(2)–I(2)	113.17(4)
I(1)–Cu(2)–I(2)	107.54(4)	I(3)–Cu(3)–I(2)	112.70(4)

^a #1 $x+1, y, z$; #2 $-x+4, -y+2, -z$; #3 $x-1, y, z$.

Table 3
Selected bond lengths (Å) and angles (deg) for **2**

I(1)–Cu(1)	2.7259(10)	I(1)–Cu(2)	2.6204(10)
I(2)–Cu(2)	2.5165(11)	I(3)–Cu(2)	2.526(4)
Cu(1)–N(2)	1.992(4)	Cu(1)–N(4)	1.980(4)
Cu(1)–N(3)	2.112(4)	Cu(1)–N(1)	2.075(4)
Cu(2)–I(1)–Cu(1)	92.82(4)	N(2)–Cu(1)–N(1)	81.34(16)
N(4)–Cu(1)–N(3)	81.37(16)	N(4)–Cu(1)–I(1)	92.14(13)
N(2)–Cu(1)–I(1)	91.55(13)	N(1)–Cu(1)–I(1)	127.59(11)
N(3)–Cu(1)–I(1)	118.23(13)	I(2)–Cu(2)–I(3)	128.66(12)
I(2)–Cu(2)–I(1)	115.18(4)	I(3)–Cu(2)–I(1)	115.73(12)

Table 5
Selected bond lengths (Å) and angles (deg) for **4**

I(1)–Cu(2)	2.5929(12)	I(1)–Cu(3)	2.7261(15)
I(1)–Cu(1)	3.2132(18)	I(2)–Cu(2)	2.6111(15)
I(2)–Cu(3)	2.6962(15)	I(3)–Cu(3)#1 ^a	2.6441(13)
I(3)–Cu(3)	2.6608(13)	Cu(1)–N(1)	2.014(3)
Cu(1)–N(2)	2.013(3)	Cu(2)–N(3)	2.086(3)
Cu(2)–N(4)	2.106(3)	Cu(3)–I(3)#1	2.6441(13)
Cu(2)–Cu(3)	2.7238(13)	Cu(3)–Cu(3)#1	3.0359(15)
Cu(2)–I(1)–Cu(3)	61.55(4)	Cu(2)–I(1)–Cu(1)	143.53(2)
Cu(3)#1–I(3)–Cu(3)	69.82(3)	Cu(2)–I(2)–Cu(3)	61.73(4)
N(2)–Cu(1)–N(1)	84.69(14)	I(1)–Cu(1)–I(1)#2	180.0
N(3)–Cu(2)–N(4)	80.44(12)	I(1)–Cu(2)–I(2)	114.11(4)
I(3)#1–Cu(3)–I(3)	110.18(3)	I(3)–Cu(3)–I(2)	111.14(5)
I(3)–Cu(3)–I(1)	104.03(3)	I(2)–Cu(3)–I(1)	107.30(4)

^a #1 $-x+1, -y, -z+1$; #2 $-x, -y+1, -z+1$.

Table 6
Selected bond lengths (Å) and angles (deg) for **5**

I(1)–Cu(2)	2.6658(17)	Cu(1)–N(2)#3 ^a	2.017(4)
Cu(1)–N(1)#3	2.047(5)	I(2)–Cu(2)	2.659(3)
Cu(1)–N(2)	2.017(4)	Cu(1)–N(1)	2.047(5)
Cu(2)–I(1)#1	2.6821(19)	Cu(2)–I(2)#2	2.6839(19)
I(2)–Cu(1)	3.3069(19)	I(2)–Cu(1)–I(2)#3	180.000(11)
N(2)#3–Cu(1)–N(2)	180.0	N(2)–Cu(1)–N(1)#3	89.3(2)
N(2)–Cu(1)–N(1)	90.7(2)	N(1)#3–Cu(1)–N(1)	180.0(3)
I(2)–Cu(2)–I(1)	116.45(7)	I(2)–Cu(2)–I(1)#1	113.39(7)
I(1)–Cu(2)–I(1)#1	96.46(7)	I(2)–Cu(2)–I(2)#2	102.79(8)
I(1)–Cu(2)–I(2)#2	111.64(6)	I(1)#1–Cu(2)–I(2)#2	116.81(7)

^a #1 $-x+1, -y+1, -z+2$; #2 $-x, -y+1, -z+2$; #3 $-x, -y, -z+1$.

3. Results and discussion

3.1. Structural description and discussion

Structural description of **1**: X-ray crystal structure analysis reveals that compound **1** crystallizes in space group $P-1$. The asymmetry unit is shown in Fig. 1a which contains three independent tetrahedrons coordinated monovalent copper atoms, one phen molecular and three iodine atoms two of which adopting μ_3 -bridging mode and I2 in μ_4 -mode. Both Cu2 and Cu3 are coordinated to four iodine atoms while two nitrogen atoms of one phen take part in the coordination of Cu1. The selected Cu–N, Cu–I bond lengths and N–Cu–N, I–Cu–N, I–Cu–I, Cu–I–Cu bond angles are listed in Table 2 which agree with similar reported literatures [27]. The distance between Cu2 and Cu3 with $d_{\text{Cu2-Cu3}} = 2.9333(16) \text{ \AA}$ and $d_{\text{Cu2-Cu3}\#3} = 2.9244(15) \text{ \AA}$ ($\#3 x-1, y, z$) is a little longer than twice the sum of the van der Waals radii of Cu atoms of 2.80 \AA , which indicates weak Cu(I)–Cu(I) interactions [32]. Viewing from the direction shown in Fig. 1b, compound **1** displays one dimensional ribbon like structure and there are two kinds of Cu_3I_3 hexagon units, A and B, sharing a axis. Each two antiparallel B hexagon units form Cu_6I_6 hexagon prism cluster

units which propagate along a axis through one mutual flank to form a $(\text{CuI})_6$ chain. And the Cu_6I_6 hexagon prism cluster units in this chain is similar to the double six-membered (D6R, hexagonal prism) rings found in zeolites, which is an important and attractive unit in zeolites [27,39]. When taking a closer look at these two hexagon units A and B, it's worth noting that they present two interesting skeleton motifs for Cu(I) halides which seem like boat and chair conformations of cyclohexane, respectively (Fig. 1b). Taking one with another, there are more Cu_3I_3 units B than A, which is in accordance with the fact that chair cyclohexane is more stable than boat cyclohexane. Compared with **1**, the Cu_3I_3 units of Cu_6I_6 hexagon prism cluster in reported compound (2, 2'-bipyridine) Cu_3I_3 were in boat form [27]. This kind of phenomena illustrates that though both phen and 2, 2'-bipyridine are chelated ligands, the distinction between two can induce interesting structural difference of final compounds. Obviously, in the ribbonlike chain of compound **1**, there are π – π stacking interactions [40,41] during phen six-membered rings and metal chelated five-membered rings with the centroid–centroid distance ($d_{\text{c-c}}$) ranging from 3.6831 to 4.2836 \AA (Table 8).

Structural description of **2**: X-ray diffraction analysis shows the molecular structure of **2** contains two independent copper

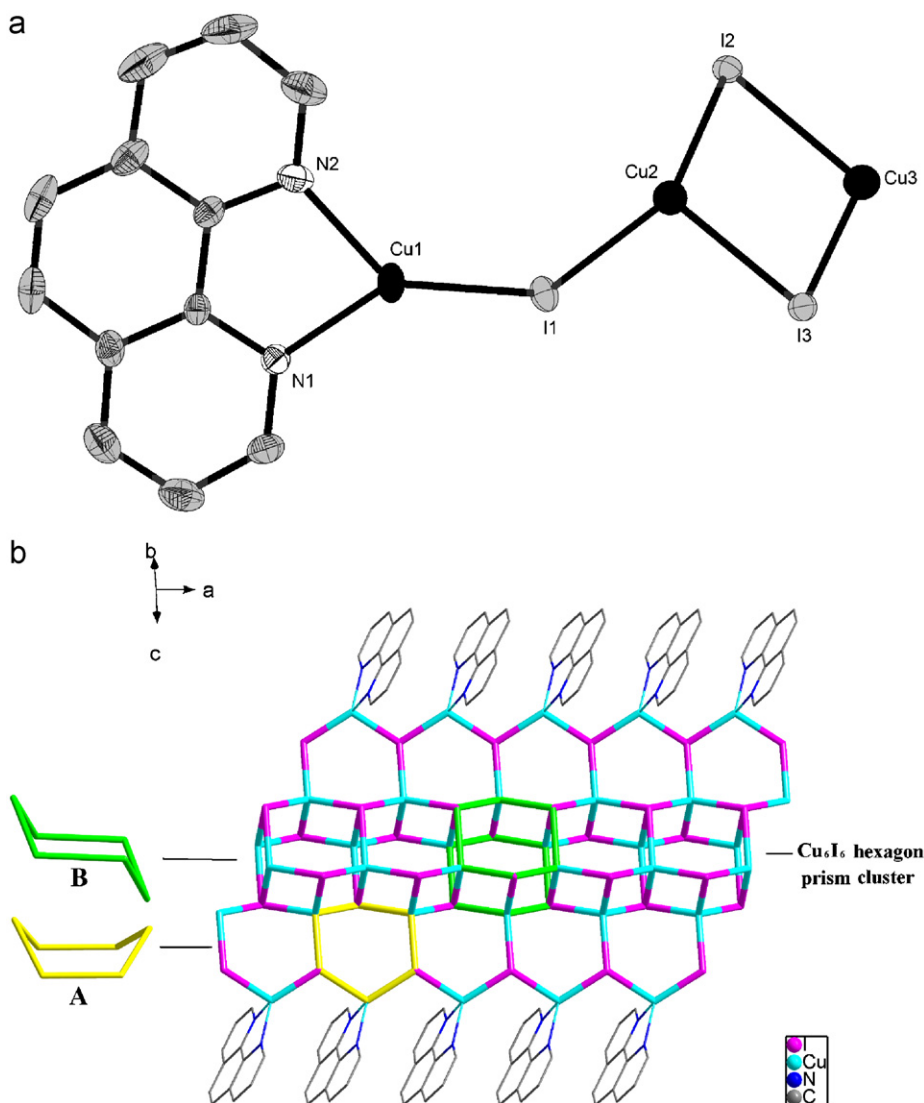


Fig. 1. Structure of **1**: (a) thermal ellipsoid plot (30%) showing the asymmetry unit; (b) one dimensional ribbonlike chain along a axis showing the connection of two different Cu_3I_3 units marked as A (yellow) and B (green). Hydrogen atoms are omitted for clarity.

atoms: one monovalent copper atom Cu2 which is trigonally coordinated to one bridging and two terminal iodine atoms with a little deviation of 0.096(6) Å and one distorted trigonal bipyramid coordinated divalent copper atom Cu1 coordinated to four nitrogen atoms from two phen and one μ_2 -I (Fig. 2a). As for trigonal bipyramid, two axial sites are occupied by N2 and N4 with the Cu–N bonds of 1.992(4) and 1.980(4) Å, the N1, N3 and I1 atoms construct the equatorial plane with longer Cu–N bonds of 2.075(4) and 2.112(4) Å, and Cu–I1 of 2.7259(10) Å. All of the Cu–I bonds of trigonal plane vary from 2.5165(11) to 2.6204(10) Å and I–Cu2–I bond angles cover the range of 115.18(4)–128.66(12)°. All of these bond lengths and bond angles are comparable to other similar compounds [42,43]. The most remarkable structural feature of compound **2** is diverse π – π stacking interactions during six-membered rings of phen (d_{c-c} varying from 3.6238 to 3.9008 Å) and the parameters of which are listed in Table 8 in detail. These π – π stacking interactions induce the construction of a novel three dimensional supramolecular framework (Fig. 2b).

Structural description of **3**: X-ray diffraction analysis of compound **3** indicates it's a mixed-valent Cu(I)–Cu(II) compound as well. Among four independent copper atoms, Cu2, Cu3 and Cu4 adopt tetrahedral coordination while Cu1 is in trigonal bipyramid environment. Though the structure is similar to $[\text{Cu}_4\text{Br}_2\text{I}_3(\text{C}_{12}\text{H}_8\text{N}_2)_2]_n$ reported by Yu et al. [43] before, the substitution of I1 and I4 for two bromine atoms brings several interesting results. Firstly, the distance of Cu2–Cu3 (2.7582(7) Å)

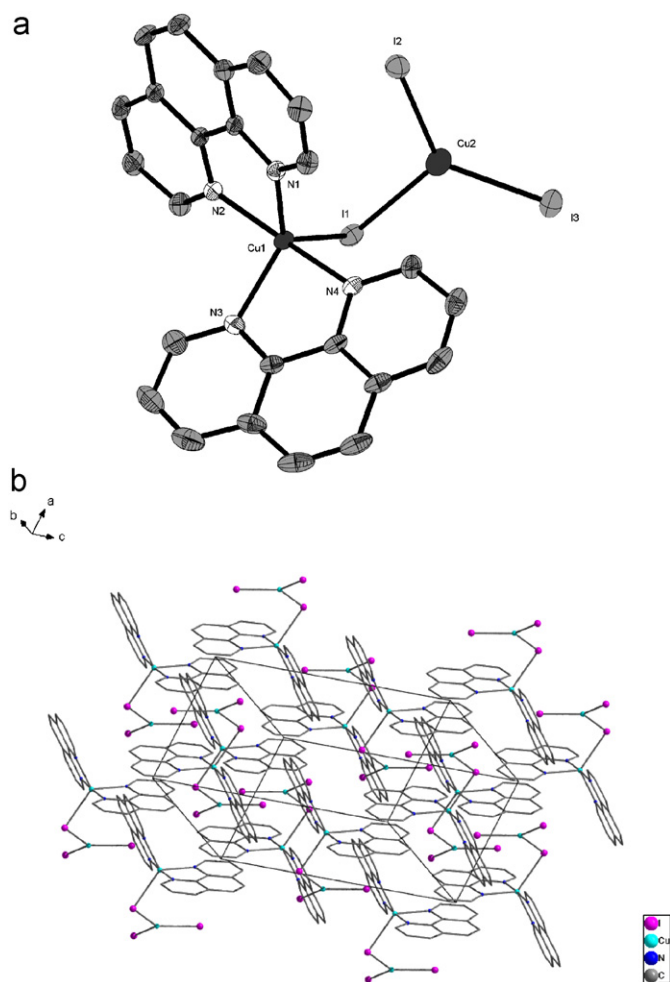


Fig. 2. Structure of **2**: (a) view of molecular structure; (b) view of three dimensional packing structure. Hydrogen atoms are omitted for clarity.

Table 7
Parameters for C/N–H...I hydrogen bonds and C–H... π interaction

Compounds ^a	D–H...A	$d(\text{D–H})(\text{Å})$	$d(\text{H...A})(\text{Å})$	$d(\text{D...A})(\text{Å})$	$\angle \text{DHA}(\text{deg})$
3	C5–H5...I4#7	0.95	3.05	3.943(5)	157.2
	C22–H22...I4#8	0.95	2.91	3.751(5)	147.8
	C13–H13...Cg(1)	—	2.97	3.7349	139
4	N1–H1A...I3#9	0.92	2.89	3.770(4)	159.5
	N2–H2B...I2#10	0.92	2.96	3.723(4)	141.0
	N2–H2A...I3#6	0.92	3.02	3.898(4)	160.9
5	N1–H1A...I1#11	0.92	2.88	3.705(6)	150.0
	N2–H2B...I2#12	0.92	2.94	3.740(6)	145.8
	N2–H2A...I1#5	0.92	2.91	3.677(5)	141.3

^a Symmetry codes: #1 2–x, 1–y, –z; #2 x–1, y, z; #3 –x, 1–y, –z; #4 x, y–1, z; #5 –x, –y, 1–z; #6 –x, 1–y, 1–z; #7 1–x, y–0.5, 1.5–z; #8 x, 1.5–y, z–0.5; #9 1–x, –y, 1–z; #10 x–1, y+1, z; #11 1–x, 1–y, 2–z; #12 –1–x, –y, 1–z; #13 x, y, z–1. Cg(1): N(1), C(1), C(2), C(3), C(4), C(12).

and Cu3–Cu4 (2.4708(5) Å) which are much shorter than 2.80 Å suggest strong Cu(I)–Cu(I) interaction in one dimensional chain; secondly, it seems no obvious Cu(I)–Cu(I) interaction between Cu4 and Cu4#1 for longer distance 3.0719(8) Å compared with 2.652(4) Å in $[\text{Cu}_4\text{Br}_2\text{I}_3(\text{C}_{12}\text{H}_8\text{N}_2)_2]_n$; thirdly, the Cu_4I_4 core in describing $[\text{Cu}_4\text{Br}_2\text{I}_3(\text{C}_{12}\text{H}_8\text{N}_2)_2]_n$ is bridged by additional I4 and I4#1 to form Cu_4I_6 core herein; furthermore, Cu_4I_6 cores are connected by Cu_2I_2 rhombus to form a one dimensional chain along *a* axis which is decorated by $[\text{Cu}(\text{phen})_2\text{I}]^+$ units in each side and strengthened by C13–H13... π interaction [40] ($d_{(\text{H...Cg})} = 2.97$ Å, $\angle \text{CHCg} = 139^\circ$) (Table 7)(Fig. 3a). Last but not the least, three dimensional supramolecular framework is constructed through strong C–H...I hydrogen bonds [44] ($d_{(\text{H...I})} = 2.91$ and 3.05 Å, $\angle \text{CHI} = 147.8$ and 157.2°) (Table 7)(Fig. 3b).

Structural description of **4**: X-ray diffraction analysis shows there are independent $[\text{Cu}(\text{en})_2]^{2+}$ cation unit and $[\text{Cu}_4(\text{phen})_2\text{I}_6]^{2-}$ anion unit in mixed-valent Cu(I)–Cu(II) copper compound of **4**. The existence of mixed ligands: en and phen, is the most attractive character of this structure. Fig. 4a illustrates the asymmetry unit of compound **4** in which Cu1 is seated at the special position with an occupancy of 0.5 and coordinated to four nitrogen atoms from two chelated en molecules to build equatorial plane with all the geometrical parameters are consistent with those observed previously [45,46]. Cu2 and Cu3 in anion unit are in tetrahedron coordination environment with the Cu2–Cu3 distance of 2.7238(13) Å. Such a short intermetallic distance implies strong Cu(I)–Cu(I) interactions (Fig. 4b). All of the iodine atoms in anion adopt the μ_2 -bridging mode and Cu_2I_2 rhombus bridge two CuN_2I_2 tetrahedrons. When taking semicoordination of Cu1–I1 (3.2132(18) Å) into account [47,48], it's interesting to find that Cu1 resides in 4+2 octahedron coordination environment with I–Cu1–I angle of 180.0° and then both the cation and anion units are combined at the same time to build a N-shape chain extending along *b* axis (Fig. 4b). What's more, hydrogen bonding interactions [44] between nitrogen atoms of chelated en and iodide atoms further reinforce this N-shape chain (Table 7)(Fig. 4b). Besides, strong π – π stacking interactions of the intra- and inter-layer phen rings ($d_{c-c} = 3.4403$ –3.6419 Å) cannot be ignored in completing three dimensional supramolecular architecture (Table 8)(Fig. 4c).

Structural description of **5**: The structure of mixed-valent Cu(I)–Cu(II) copper compound **5** is composed of organic $[\text{Cu}(1,3\text{-propanediamine})_2]^{2+}$ unit and inorganic $[\text{CuI}_2]_\infty$ chain along *a* axis (Fig. 5). Herein, 1, 3-propanediamine is used instead of en in $[\text{Cu}(\text{en})_2][\text{CuI}_2]_2$ which has been described in detail in 2002 [48]. The Cu(II) ion in compound **5** resides in the symmetry centre with

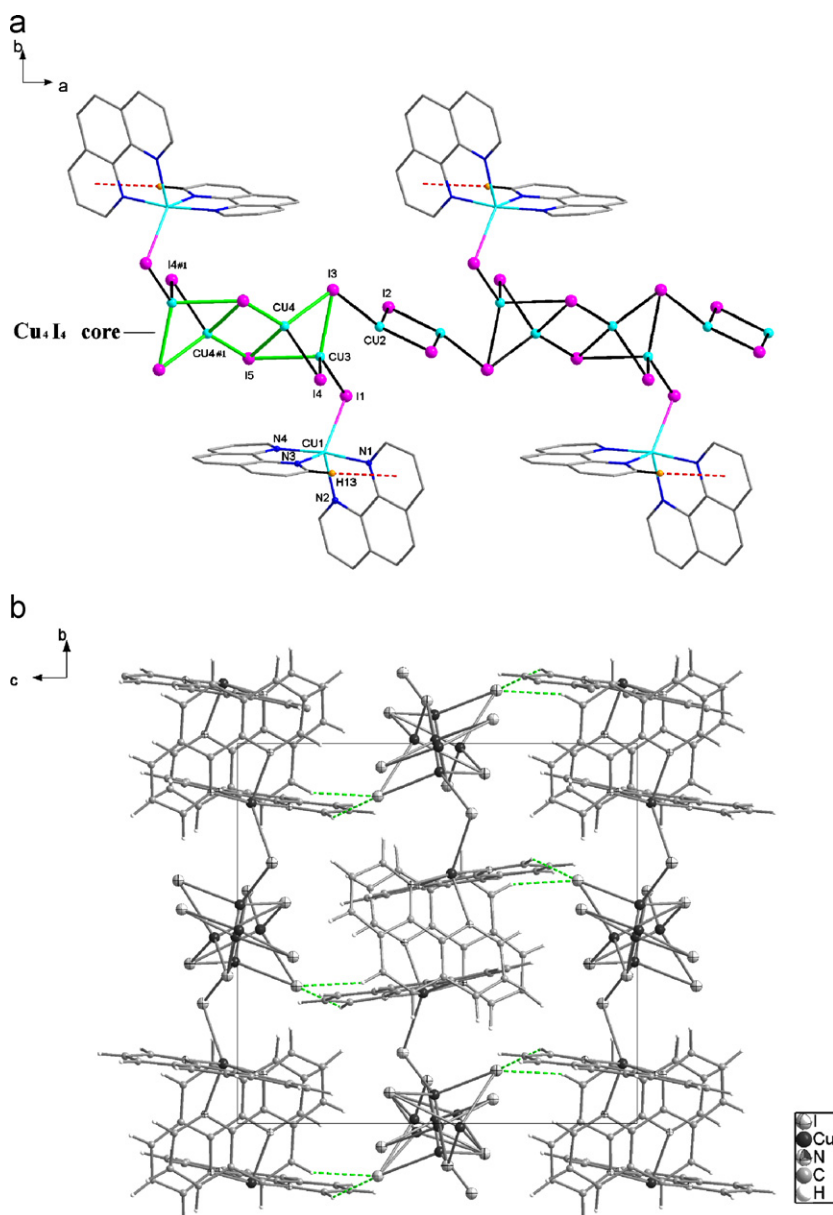


Fig. 3. Structure of **3**: (a) view of one dimensional chain propagating along *a* axis. Symmetry code: #1–*x*, 2–*y*, 1–*z*. Color codes: green solid and red dashed lines stand for Cu_4I_4 core and $\text{C13-H13}\cdots\pi$ interaction, respectively. Except H13, other hydrogen atoms are omitted for clarity; (b) view of three dimensional packing framework down *a* direction. Green dashed lines stand for $\text{C-H}\cdots\text{I}$ hydrogen bonds.

a 4+2 coordination as that of **4**. The axial positions are occupied by two *semicoordinated* iodide atoms: $d_{\text{Cu1-I2}} = 3.3069(19)\text{Å}$, I-Cu1-I angle = $180.000(11)^\circ$. The *semicoordination* of Cu1-I2 not only induces Cu(II) to show 4+2 coordination, but combines the organic unit with inorganic chain to spread the structure into two dimensional inorganic-organic hybrid layer. Just like en in compound **4**, 1, 3-propanediamine acts as a hydrogen bond donor and abundant $\text{N-H}\cdots\text{I}$ hydrogen bonds further strengthen layer structure (Table 7)(Fig. 5).

3.2. Characterizations

Fig. S1 show experimental and theoretically simulated powder XRD patterns for compounds **1-5**. The generally good agreement between the two patterns of each compound shows pure phase.

The IR spectra of compound **1-4** show the characteristic peaks of phen obviously: stretching vibrations of $\text{C}=\text{C}$ and $\text{C}=\text{N}$ bonds

(around $1420, 1500, 1579$ and 1616 cm^{-1}), stretching and bending vibrations of $=\text{C-H}$ (around 3042 cm^{-1} and $830-630\text{ cm}^{-1}$, respectively). As for compounds **4** and **5**, the peaks around $3260\text{ cm}^{-1}, 2935$ and $2873\text{ cm}^{-1}, 1162\text{ cm}^{-1}, 1034\text{ cm}^{-1}, 1448$ and $1418\text{ cm}^{-1}, 1570\text{ cm}^{-1}$, can be ascribed to the stretching vibrations of N-H , $-\text{CH}_2-$, C-N , C-C and the bending vibrations of $-\text{CH}_2-$, N-H , respectively.

In the UV-Vis DRIS (Fig. S2), the sharp peaks less than 260 nm (254 nm for **1** and **4**; 230 nm for **2** and **3**) attribute to $\pi-\pi^*$ transition of phen [49,50]. Two kinds of charge-transfer excitation: one between Cu^+ and I^- , the other between copper ions (Cu^+ or Cu^{2+}) and ligands (phen, en or 1, 3-propanediamine), cover with each other, which can be deduced from the broad peaks in the range of $317-401\text{ nm}$ in **1** and **4**, the sharp peaks at 270 nm and acromion peaks around 367 nm for **2** and **3**, the intense absorption at 254 nm and acromion peak around 320 nm for **5**, respectively [50,51]. Besides, there are extremely weak and broad absorptions around 650 nm in **2** and **3**, which is ascribed to the $d-d$ transition of Cu^{2+} [52].

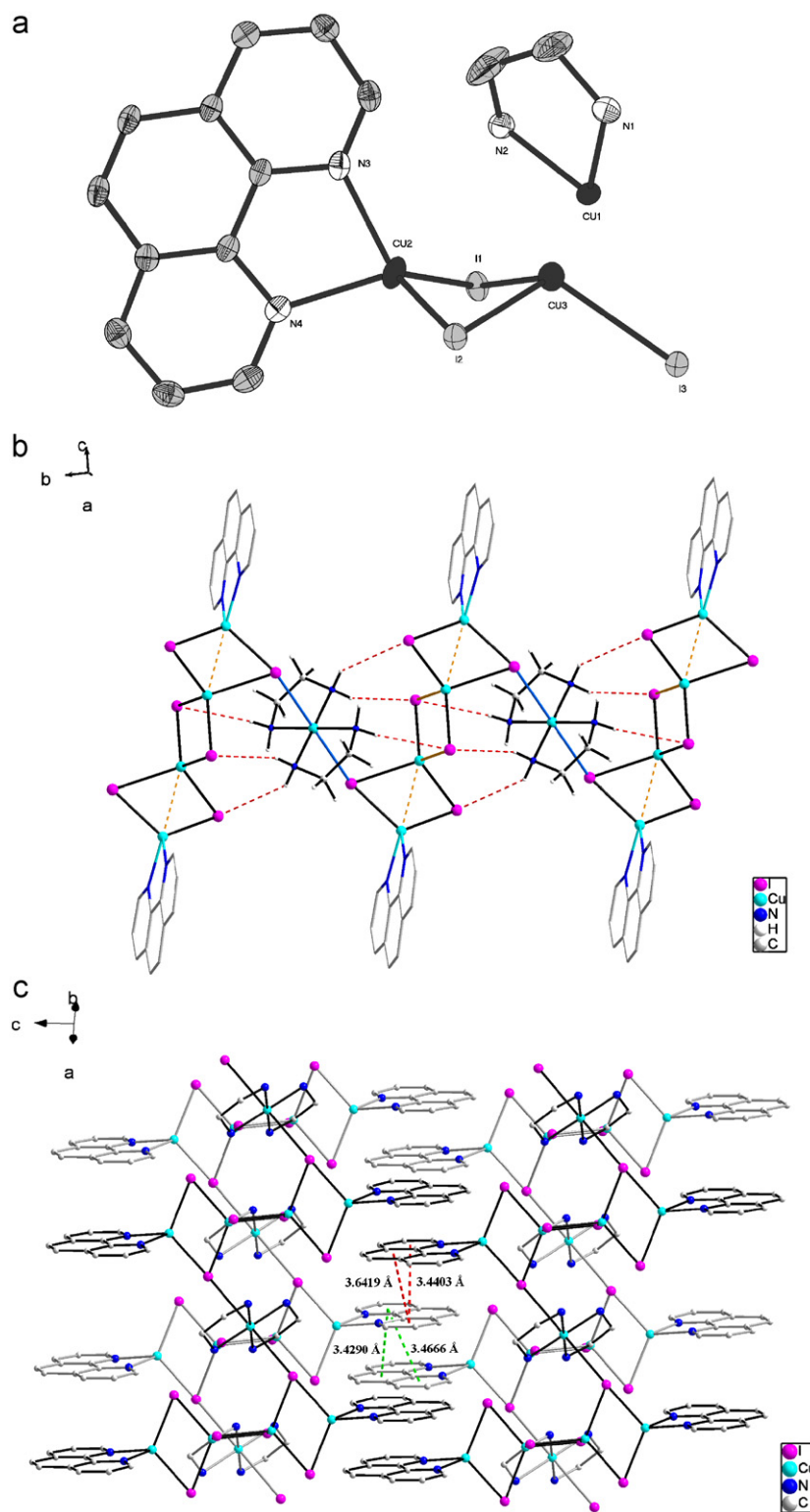


Fig. 4. Structure of **4**: (a) thermal ellipsoid plot (30%) showing the asymmetric unit. Hydrogen atoms are omitted for clarity; (b) view of N-shape chain extending along *b* axis: blue solid, red dashed and yellow dashed lines stand for the *semicoordinate* Cu–I bonds, N–H...I hydrogen bonds and Cu(I)–Cu(I) interaction, respectively. Hydrogen atoms of phen are omitted for clarity; (c) view of three dimensional packing structure via intra- and inter-layer π – π stacking interactions marked as green dashed and red dashed lines, respectively. Hydrogen atoms are omitted for clarity.

Except compound **1**, other compounds didn't show fluorescence under 293 K. The solid-state fluorescent emission spectrum of compound **1** at 293 K was shown in Fig. 6. It exhibits an intense fluorescent emission band with a maximum at 650 nm when

photoexcited at 370 nm, which may be assigned to metal-to-ligand-charge-transfer band (MLCT) and/or iodide-to-metal-charge-transfer band (XMCT) deduced from relatively longer $d_{\text{Cu-Cu}}$ and analogous photoluminescent properties of Cu_4I_4

clusters [9,18,32,53]. What's more, compound **1** exhibits extremely long fluorescence lifetime ($\tau = 1.25 \mu\text{s}$). Meanwhile, **1** show an emission band with a maximum at 655 nm at 77 K as well ($\lambda_{\text{ex}} = 370 \text{ nm}$). Though the emission band just red shifted for 5 nm, it becomes narrower and much stronger. It's noteworthy that fluorescence lifetime increases more obviously with the value of 6.95 μs . These changes happened to the emission spectrum of **1** may induced by an increase of electronic interactions between adjacent copper ions in the excited state with lowering of the temperature [9].

The EPR analysis of compound **1** show no signal, which suggests there is no Cu(II) in **1**. Other four compounds' room temperature EPR spectra were shown in Fig. S3. The spectra of compounds **2** and **3** show a reversal of parallel and perpendicular regions ($g_{\parallel} < g_{\perp}$) as expected for trigonal bipyramid coordination geometry of Cu(II)

Table 8
Parameters for π - π interactions between selected rings

Compounds ^a	Cg(I)→Cg(J)	$d_{\pi,\pi}$ (Å)	d_{c-c} (Å)	α (deg)	β (deg)	γ (deg)
1	Cg(1)→Cg(2) ⁱ	3.713	4.2836	6.80	28.18	31.55
	Cg(1)→Cg(4) ⁱ	3.657	3.6831	6.39	8.37	4.01
	Cg(3)→Cg(4) ⁱ	3.621	4.1433	1.18	28.60	29.53
2	Cg(3)→Cg(3) ⁱⁱ	3.461	3.8518	0.00	26.02	26.02
	Cg(3)→Cg(4) ⁱⁱⁱ	3.449	3.9008	1.53	27.93	27.78
	Cg(6)→Cg(7) ^{iv}	3.377	3.6238	0.46	21.15	21.36
	Cg(4)→Cg(4) ⁱⁱⁱ	3.463	3.7159	0.03	21.28	21.28
	Cg(7)→Cg(7) ^{iv}	3.368	3.8769	0.00	29.68	29.68
4	Cg(8)→Cg(8) ⁱⁱ	3.219	3.4666	0.00	21.79	21.79
	Cg(8)→Cg(10) ⁱⁱ	3.220	3.4920	0.72	22.65	22.88
	Cg(9)→Cg(9) ^v	3.327	3.4403	0.00	14.74	14.74
	Cg(9)→Cg(10) ^v	3.318	3.6419	1.35	24.91	23.77

^a Stacking parameters for the analysis of π - π interactions between two rings: Cg(I) = plane I; α = dihedral angle between planes I and J; β and γ = slipping angles defined by centroid-centroid distance (d_{c-c}) and the normal to the plane I or J, respectively; $d_{\pi,\pi}$ = stacking distance defined as the centroid → normal to the plane averaged distance, $\beta = \gamma$ when $\alpha = 0^\circ$. Definition of rings: Cg(1): Cu(1), N(1), C(12), C(11), N(2); Cg(2): N(1), C(1), C(2), C(3), C(4), C(12); Cg(3): N(2), C(10), C(9), C(8), C(7), C(11); Cg(4): C(4), C(5), C(6), C(7), C(11), C(12); Cg(5): N(3), C(13), C(14), C(15), C(16), C(24); Cg(6): N(4), C(22), C(21), C(20), C(19), C(23); Cg(7): C(16), C(17), C(18), C(19), C(23), C(24); Cg(8): N(3), C(3), C(4), C(5), C(6), C(14); Cg(9): N(4), C(12), C(11), C(10), C(9), C(13); Cg(10): C(6), C(7), C(8), C(9), C(13), C(14). Symmetry codes: i = 1+x, y, z; ii = 1-x, -y, -z; iii = -x, -y, -z; iv = -x, -y, 1-z; v = 1-x, 1-y, -z.

and the main parameters for **2** and **3** are $g_{\parallel} = 2.0671$, $A_{\parallel} = 56.11\text{G}$, $g_{\perp} = 2.1342$ and $g_{\parallel} = 2.0654$, $A_{\parallel} = 76.40\text{G}$, $g_{\perp} = 2.1497$ [54,55], respectively. By contrast, the observed trend of $g_{\parallel} > g_{\perp}$ derived from the spectra of compounds **4** and **5** indicate spectral pattern characteristic of a $d_{x^2-y^2}$ ground state and the occupation of the unpaired d electron in the $d_{x^2-y^2}$ orbital, which demonstrate the Cu(II) of these two compounds reside in 4+2 elongate octahedron coordination position [56]. Meanwhile, due to the interaction between unpaired electron of Cu(II) and Cu(II) nuclear, the hyperfine splitting structure of Cu(II) nuclear exists both in **4** and **5**, the phenomenon of which is more obvious in **5**.

3.3. Discussion

All of five copper compounds in this article were synthesized under hydrothermal condition with similar resource and they displayed various structure and spectral property. As far as the structure is concerned, compound **1** is a monovalent copper compound with ribbonlike chain built by two kinds of Cu_3I_3 units in chair and boat configuration, respectively. Compounds **2**, **3**, **4** and **5**, in which Cu(I) was partially auto-oxidated by O_2 under hydrothermal condition, are mixed-valent Cu(I)-Cu(II)

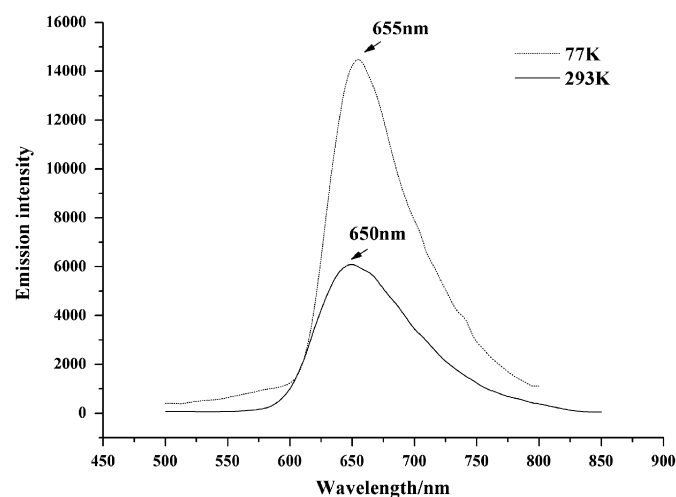


Fig. 6. Solid-state fluorescent emission spectra of compound **1** at 293 and 77 K.

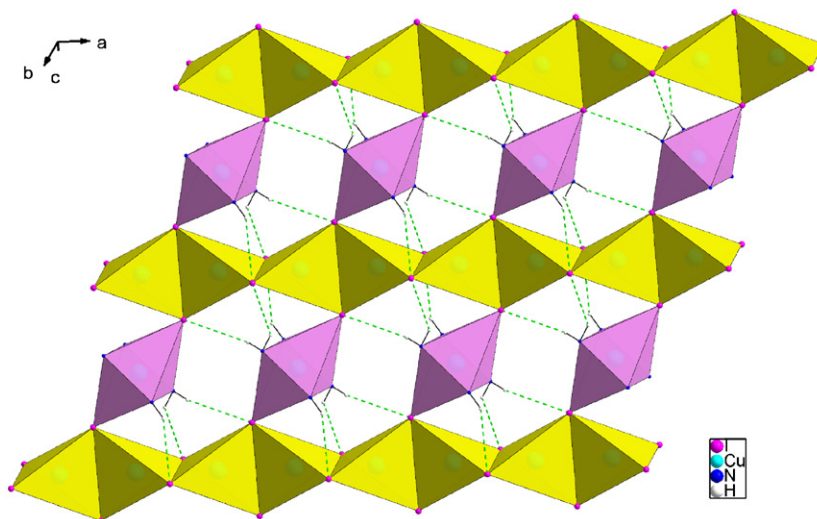


Fig. 5. Polyhedron drawing of two dimensional structure of **5**. Color codes: green dashed lines stand for N-H...I hydrogen bonds; yellow and purple polyhedrons stand for CuI_4 tetrahedron and CuN_4L_4 octahedron, respectively. Carbon atoms and hydrogen atoms absent in forming the hydrogen bonds are omitted for clarity.

compounds with the ratio of Cu(I)/Cu(II) 1:1, 3:1, 4:1, 2:1, respectively. Compound **2** is an isolated molecule and compound **3** comprises Cu₄I₆ cores bridged by Cu₂I₂ rhombus. Taking the semicoordination of Cu–I into account, N-shape chain of compound **4** and layer structure of compound **5** are constructed as well. With the help of C/N–H...I hydrogen bonds, Cu(I)–Cu(I) interaction, weak Cu–I semicoordinate interaction, C–H... π and π – π stacking interactions, supramolecular frameworks of these five compounds are assembled. Then from the synthesis aspect, it seems that pH value, synthesis temperature and reaction time have important effect on the final compounds' structure. With the same pressure and concentration, the higher synthesis temperature and the longer reaction time are propitious to obtain higher ratio of Cu(I)/Cu(II) copper complexes, which can be deduced not only from compounds **1**(1:0) and **2**(1:1) but from compounds **4**(4:1) and **5**(2:1). However, taking compound **3**(3:1) for example, it seems that sometimes the pH value plays more important role. The single crystals of **3** can be obtained under lower temperature and shorter time when pH value reached 7.4. It's no doubt that all of above tentative deduction can redound to our further hydrothermal synthesis with design more or less. Thirdly, the location of ligands' position in constructing mixed-valent copper-iodine compounds also arouses our attention. When synthesizing mixed-valent copper-iodine compounds, phen is usually bonded to divalent copper to form the cation unit which can be seen from **2** and **3**. However, from compound **4**, it can be obviously seen that once en takes part in the system, it substitutes for phen to make up of the cation unit and phen changes to locate at the anion unit. This may have something to do with the lower steric hinderance of en to phen. To the best of our knowledge, compound **4** is the first example for en and phen coexistence in the mixed-valent Cu(I)–Cu(II) copper iodides. To achieve more similar compounds, we have substituted 1, 3-propanediamine for en, it's regrettable that we just got compound **5** in which only 1, 3-propanediamine was contained in the final compound. Larger hinderance of 1, 3-propanediamine may result in this failure to some extent. Last but not the list, the un conspicuous of *d*–*d* transition of **4** and **5** may do something to do with divalent Cu(II) atoms of both two compounds locating at symmetry centre position, which shows the relation between structure and property.

4. Conclusions

In a word, with the similar synthesis resource, we have not only hydrothermally synthesized five low dimensional monovalent (for **1**) or mixed-valent Cu(I)–Cu(II) (for **2**–**5**) copper-iodide compounds by auto-oxidation, all of which can assemble to supramolecular frameworks by various supramolecular interactions, but probed how do the synthesis factors, such as pH value, synthesis temperature and reaction time, influence the final ratio of Cu(I)/Cu(II) in this copper-iodine system in the rough. And we find that the higher synthesis temperature and the longer reaction time are propitious to obtain higher ratio of Cu(I)/Cu(II) copper complexes under the same pressure and concentration. Meanwhile, it's note worthy that we also discuss the rivalrousness of phen and diamine while constructing mixed-valent Cu(I)–Cu(II) copper iodides and found that it's easier for diamine which is with lower steric hinderance to compose the cation unit with divalent copper atoms. Being enlightened by the synthesis of compounds **4** and **5**, we'll introduce two or more chelated nitrogen-containing ligands (such as en, 1, 2-propanediamine, 1, 3-propanediamine, phen, 2, 2'-bipyridine etc.) together to probe the rivalrousness of their chelation ability and synthesis more mixed-valent Cu(I)–Cu(II) inorganic-organic hybrid copper halides with mixed-chelated ligands as templates showing attractive structure.

Supplementary data

Crystallographic details and complete listings of the compounds have been deposited at the Cambridge Crystallographic Date Center (CCDC) as supplementary publications reference number: CCDC-689141 to 689145 contain the supplementary crystallographic data for the five compounds in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [of from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +441223 336-033; e-mail: deposit@ccdc.cam.ac.uk].

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Appendix A. Supplementary materials

The online version of this article contains additional supplementary data. Please visit [doi:10.1016/j.jssc.2008.09.011](https://doi.org/10.1016/j.jssc.2008.09.011).

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