

A Simultaneous Redox, Alkylation, Self-Assembly Reaction under Solvothermal Conditions Afforded a Luminescent Copper(I) Chain Polymer Constructed of Cu_3I_4^- and $\text{EtS-4-C}_5\text{H}_4\text{N}^+\text{Et}$ Components (Et = CH_3CH_2)

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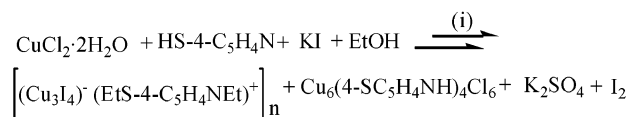
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The design and synthesis of novel coordination architectures with ligands generated in situ (especially those that are inaccessible by direct preparation) is of great interest in coordination chemistry and organic chemistry for discovering new organic reactions and understanding their mechanisms.^{1–3} Although various preparation methods have been proposed to obtain such coordination architectures, a predictable synthetic result is still one of the major challenges in coordination chemistry.

In particular, the reactions of copper salts with thio-pyridine ligands are liable to result in uncharacterized precipitate that is insoluble in conventional solutions or by a hydrothermal method. As a result of this tendency, it is difficult to control the reaction of thio-pyridine with metal ions to obtain single crystals of polymeric metal thiolates suitable for X-diffraction analysis. Although the reactions of pyridine-2-thiol with Cu or Ag ions have led to soluble species,⁴ analogues containing pyridine-4-thiol have not been reported. In addition, open-framework cuprous halides are obtained mainly by using Cu^+ as the precursor,^{4–7} while few efforts have been directed toward investigating the reduction of Cu^{2+} to Cu^+ . To our knowledge, open-framework cuprous halides, prepared by the redox reaction of cupric halides with thio-pyridine ligands, have not been reported to date.

In this Communication, we report the first example of the simultaneous redox, alkylation, and self-assembly reaction under solvothermal conditions affording a luminescent copper(I) chain polymer, $[(\text{Cu}_3\text{I}_4)^-(\text{EtS-4-C}_5\text{H}_4\text{NEt})^+]_n$ (**1**, Scheme 1). In addition, the synthesis and structure of the byproduct, $\text{Cu}_6(4\text{-SC}_5\text{H}_4\text{NH})_4\text{Cl}_6$ (**2**), are also discussed.

Scheme 1^a



^a Conditions: (i) 160 °C, 60 h.

The solvothermal reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, KI, HS-4-C₅H₄N, and EtOH in a molar ratio of 1:1:1:500 at 160 °C for 60 h afforded a large amount of yellow prismatic crystals of **1**. Single-crystal X-ray analysis⁸ of compound **1** showed that it was a novel one-dimensional inorganic–organic hybrid coordination polymer (Figure 1a). The present structure of **1** is the first example of a linear chain formed by trinuclear Cu_3I_4 units (Figure 1b). Its unit structure feature is similar to those of the incomplete cubane-like M_3S_4 (M = Mo, Fe) clusters, whose structure and reactivity regulation have long been an important and attractive subject in biochemical research.⁹

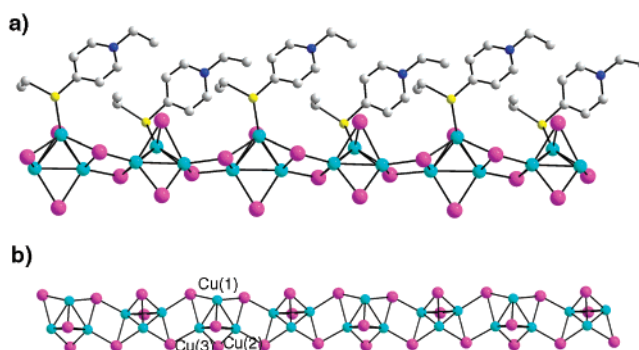


Figure 1. (a) Linear chain structure of **1**. (b) Linear chain of **1** without heterocyclic ligands. Sky-blue balls, Cu; pink balls, I; yellow balls, S; blue balls, N; gray balls, C.

As shown in Figure 1b, Cu(1), Cu(2), and Cu(3) atoms form a slightly distorted equilateral triangle (Cu(1)–Cu(2) 2.7057(17) Å, Cu(1)–Cu(3) 2.6736(18) Å, Cu(2)–Cu(3) 2.7681(17) Å; Cu(1)–Cu(2)–Cu(3) 58.46(4)°, Cu(1)–Cu(3)–Cu(2) 59.60(4)°, Cu(2)–Cu(1)–Cu(3) 61.93(5)°). A very significant structure feature of **1** is the relatively short Cu–Cu distances, which are less than twice the van der Waals radius (1.4 Å) of Cu(I), implying strong Cu–Cu interaction. The phenomenon of Cu–Cu interaction has been observed for Cu_4I_4 clusters and other multinuclear copper(I) complexes.^{10,11} Similar to the complexes,^{10,11} compound **1** exhibits remarkably rich photoluminescent properties. The emission spectrum of compound **1** is shown in Figure S1. It can be observed that the intense emission occurred at 558 nm ($\lambda_{\text{ex}} = 371$ nm) in the solid state at room temperature. According to the photoluminescent properties of Cu_4I_4 clusters,^{10,11} the emission band might be assigned to a combination of iodide-to-copper charge transfer (LMCT) and d–s transitions by Cu–Cu interaction within Cu_3 clusters.

During the reaction, red crystals of complex **2** and colorless crystals of K_2SO_4 were synchronously obtained as the byproducts. They enable us to speculate that the desulfurization process is followed by oxidation and reduction of S^{2-} to S^{6+} and of Cu^{2+} to Cu^+ in the reaction. According to the yield of K_2SO_4 , it is obvious that only a small amount of pyridine-4-thiol undergoes the desulfurization reaction. This case is different from the desulfurization reaction of heterocyclic ligands, which was reported by Dong et al.¹² Furthermore, dropwise addition of the reaction filtrate into a solution of amylum resulted in a color change from orange to dark blue. This indicated that iodine was obtained and KI also participated in the redox reaction. X-ray crystallography¹³ of complex **2** has shown that it exists as a hexanuclear $\text{Cu}_6\text{S}_4\text{Cl}_6$ cluster with a $\mu_3\text{-S}$ mode of neutral pyridine-4-thione (Figure 2). Compared

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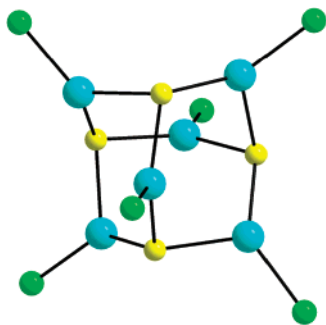
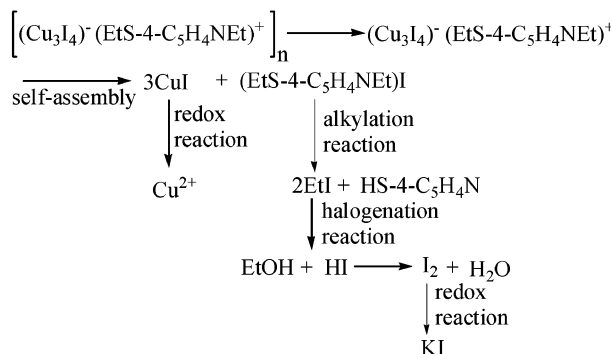


Figure 2. Molecular structure of compound **2** (pyridine rings in pyridine-4-thione were omitted for clarity). Sky-blue balls, Cu; yellow balls, S; green balls, Cl.

Scheme 2. Converse Deduction of the Synthesis of Compound **1**



to complex **1**, the Cu...Cu distances (3.186(2)–3.889(2) Å) found in complex **2** are much longer. This may be why complex **2** does not display a remarkable photoluminescent property.

It is notable that the reaction chemistry is rather interesting. The presence of Cu⁺ ions in the products indicates that Cu²⁺ ions may act as oxidants, similar to the in situ hydro(solvo)thermal reactions previously reported.^{1,2} In comparison with the previous examples,^{1,2} the oxidation process in the present reaction is more distinct because K₂SO₄ and I₂ as oxidation products have been obtained and proved, respectively. To clarify the complexity of the present reaction, reasonable converse deduction of the synthesis of complex **1** is shown in Scheme 2. We think that CuI and (EtS-4-C₅H₄NEt)I are two important intermediates, as they directly resulted in complex **1**. This point of view has been proved by an ESI-MS spectrum showing EtS-4-C₅H₄NEt⁺ at *m/z* = 168.0954, CuI₂⁻ at *m/z* = 316.7404, and Cu₃I₄⁻ at *m/z* = 696.4015. All the assignments are confirmed by good agreement between the observed and calculated isotopic distributions (see Figure S2). In addition, the ¹H NMR spectrum (see Figure S3), showing two ethyl signals of S-Et and N-Et groups, also confirms the existence of heterocyclic EtS-4-C₅H₄N⁺Et. It is well-known that alkyl halides are a class of alkylation reagents in organic synthesis. As shown in Scheme 2, we assumed that, in the present reaction, ethanol acted indirectly as a sort of alkylation reagent. It potentially resulted in EtI when it was activated by HI, which is generated by the reaction of I₂ with H₂O. The interaction of EtI and pyridine-4-thiol gave rise to

(EtS-4-C₅H₄NEt)I. Although the mechanism of each step has yet to be investigated in detail, the present result is the first example of a clear transformation from HS-4-C₅H₄N to EtS-4-C₅H₄N⁺Et.

In summary, a luminescent polymer **1** was synthesized via a series of complicated processes under solvothermal condition. These results are significant not only for developing a new alkylation method using inexpensive alcohols and haloids instead of alkyl halides but also for developing a new method to prepare a new luminescent Cu₃I₄ cluster. Further studies will be carried out, and we expect that more progress will be procured on the basis of the present reaction, for example, by using other alcohols, such as methanol, propanol, and butanol.

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Supporting Information Available: X-ray crystallographic data (CIF); elemental analysis for compounds **1** and **2** and spectral data for compound **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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