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Temperature effect-driven assembly of $[Cu_nX_n]$-based coordination polymers from CuX and 1,4-bis(imidazol-1-yl)butane

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ABSTRACT

Three $[Cu_nX_n]$-based (X = Br, I) coordination polymers, $\{[Cu_2(\mu\text{-}I)_2(bimb)_2]\cdot iodobenzene\}_n$ (**1**), $\{[Cu_4(\mu_3\text{-}I)_4(bimb)_2][Cu_2(\mu\text{-}I)_2(bimb)]\}_n$ (**2**) and $\{[Cu_2Br(bimb)_2]Br\}_n$ (**3**) were prepared from solvothermal reactions of CuX (X = I, Br) with 1,4-bis(imidazol-1-yl)butane (bimb) at different temperatures. These compounds were characterized by elemental analysis, IR, and single crystal X-ray diffraction. Compound **1** contains a rhombic $[Cu_2(\mu\text{-}I)_2]$ dimer that acts as a planar four-connected node to link four equivalent ones via bimb bridges to form a 2D (4,4) network. Each layer is further stacked by π–π interactions to form a 3D structure with 1D rhombic channels occupied by the guest iodobenzene molecules. Compound **2** consists of $[Cu_2(\mu\text{-}I)_2]$ dimers and $[Cu_4(\mu_3\text{-}I)_4]$ tetramers which are interconnected by bimb bridges to generate another 2D network. Compound **3** contains $[Cu_2Br(bimb)_2]^+$ cations that are linked by bimb ligands to form a 1D cationic chain. We also investigated the solid state photoluminescent properties of **1**–**3** at ambient temperature. The results provide an interesting insight into how reaction temperatures exert a great effect on the assembly of $[Cu_nX_n]$-based coordination polymers.

Over the past decades, the self-assembly of functional metal-organic coordination polymers has attracted considerable attention due to not only their fascinating architectures and topologies, but also their potential applications in photoluminescence, magnetism, catalysis and adsorption [1–4]. The formation of these compounds depends on many subtle synthetic factors, such as metal/ligand ratios, the solvent systems, structures of the metal precursors, flexibility and rigidity of the ligands, and so on [5]. On the other hand, multitopic nitrogen-donor ligands with flexible spacers like those imidazolyl-based linkers are always used to assemble various coordination polymers with interesting topological networks and physical properties [6–9]. There are many examples in which people investigated the role of the aforementioned factors in the changes of the configuration of the linkers, coordination geometry of the metal ions, the topological structures of the coordination polymers and their physical and/or chemical properties. However, temperature effects on the formation of cluster-based coordination polymers seem less explored [10].

We have been interested in the construction and properties of $[Cu_nX_n]$-based coordination polymers [11]. We explored the influence of many factors on the formation of a series of $[Cu_nX_n]$-based coordination polymers through solvothermal reactions of CuX with pyridyl, imidazolyl-, and triazolyl-based ditopic ligands. As an extension of this project, we employed 1,4-bis(imidazol-1-yl)butane (bimb) [9] to react with CuX and PhX (X = Br, I) in MeCN at different temperatures. In the case of CuI, its reactions with bimb at two different temperatures did afford two different coordination polymers, one 2D $[Cu_2(\mu\text{-}I)_2]$-based coordination polymer $\{[Cu_2(\mu\text{-}I)_2(bimb)_2]\cdot iodobenzene\}_n$ (**1**) and one 2D $[Cu_2(\mu\text{-}I)_2]$ and $[Cu_4(\mu_3\text{-}I)_4]$-supported polymer $\{[Cu_4(\mu_3\text{-}I)_4(bimb)_2][Cu_2(\mu\text{-}I)_2(bimb)]\}_n$ (**2**). While in the case of CuBr, the temperature effects did not work and only one 2D [CuBr]-based coordination polymer $\{[Cu_2Br(bimb)_2]Br\}_n$ (**3**) was isolated. Herein we report their syntheses and structures along with their solid state photoluminescent properties.

Solvothermal reactions of CuI with equimolar bimb and excess iodobenzene in MeCN at 150 °C for 70 h followed by a standard workup produced brown blocks of **1** in 31% yield while the same components at 170 °C under the similar conditions gave rise to red blocks of **2** in 23% yield [12]. Analogous reactions of the same components with different molar ratios at 150 °C or 170 °C did not afford the same products. The reactions of the same components with the same CuI/bimb molar ratio at lower than 150 °C or higher than 170 °C could form the corresponding product in very low yields. Treatment of a suspension of **1** and excess iodobenzene in MeCN at 170 °C did not yield complex **2**, which may be ascribed to the very low solubility of **1** in iodobenzene and MeCN. These results indicated that the CuI-to-bimb ratio did not work in the two cases. The different outcomes of the above two reactions should be attributed to the temperature effects. Intriguingly, similar solvothermal reactions of CuBr with equimolar bimb and excess

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bromobenzene in MeCN at either 150 °C or 170 °C for 70 h only gave rise to the same product **3** in various yields. The yield (15%) of **3** obtained at 170 °C was relatively higher than that (ca. 5%) at 150 °C. As described later in this article, the structures along with the luminescent properties of these complexes are quite different. To our knowledge, reactions of CuX with the same ligands in the same molar ratios under the same solvothermal conditions usually generated the products with similar structures. Therefore compounds **1**–**3** represent rare examples in which they hold different structures caused by distinct temperature effects. For **1**–**3**, the powder X-ray diffraction (PXRD) showed that the observed patterns for each compound correlated well with the simulated ones generated from single-crystal X-ray diffraction data (Fig. S1). The identities of **1**–**3** were further confirmed by single-crystal diffraction analysis [13].

Complex **1** crystallizes in the monoclinic space group $P\bar{1}$, and its asymmetric unit of **1** contains one $[Cu_2(\mu\text{-}I)_2(bimb)_2]$ dimeric unit and one iodobenzene molecule. In each dimeric unit (Fig. 1a), each Cu(I) center is tetrahedrally coordinated by two μ-I and two N atoms from two different bimb ligands. The mean Cu-μ-I bond length (2.7024(14) Å) is longer than that of $\{[Cu_2(\mu\text{-}I)_2(bpp)_2]{\cdot}2aniline\}_n$ (2.650(2) Å,

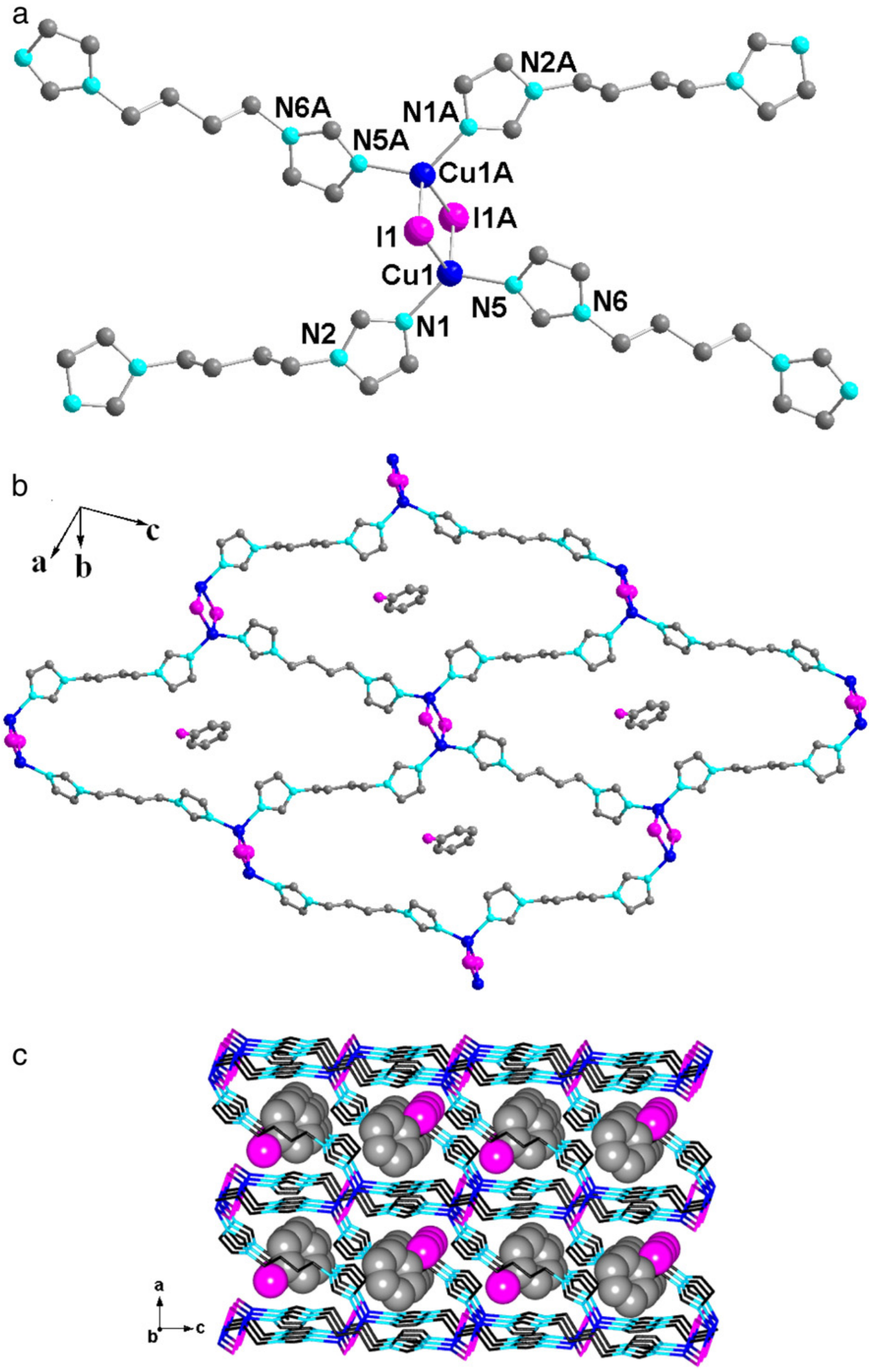

Fig. 1. (a) View of the structure of the $[Cu_2(\mu\text{-}I)_2(bimb)_2]$ dimeric unit of **1**. Symmetry code: A: $-x, -y, 1 - z$. (b) View of the 2D (4,4) network of **1**. (c) View of the encapsulation of the iodobenzene molecules into 1D channels formed by layer-to-layer stacking through the π–π interactions between the imidazolyl groups. Atom color codes: Cu, blue; I, pink; N, cyan; C, gray (the same hereinafter). All H atoms are omitted for clarity.