

Reversible photoluminescence switch: A stair-step Cu₄L₄ coordination polymer based on a dithioether ligand



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ABSTRACT

A two-dimensional network stair-step Cu₄L₄ coordination polymer (**1**) based on 1,4-bis((methylthio)propanoyl)piperazine was prepared. No emission was observed from **1** (off state), while a heated sample (**2**) of **1** emitted a strong green light (on state). Conversion between **1** and **2** was reversible upon removal of acetonitrile or exposure of **2** to acetonitrile.

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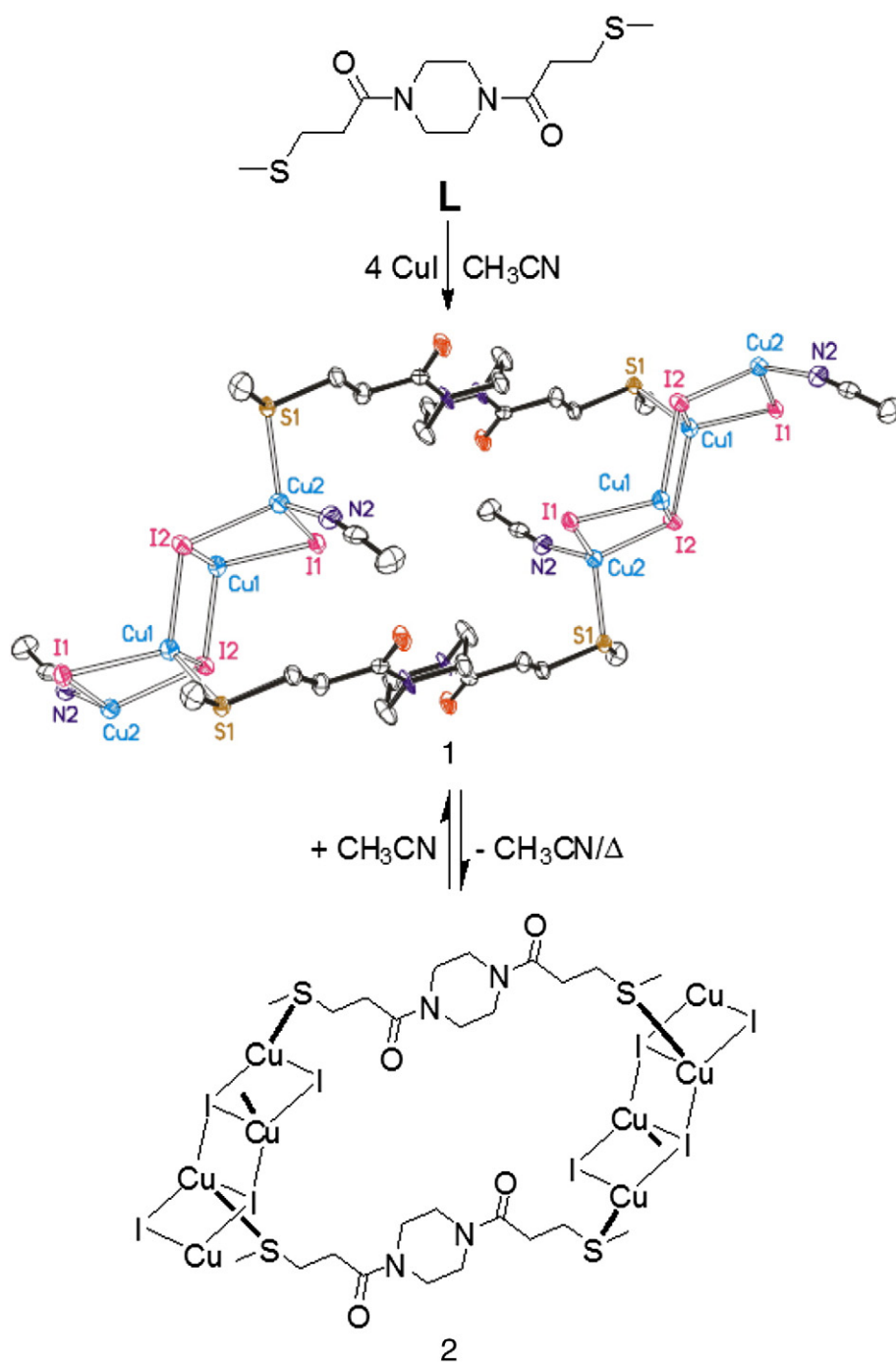
Copper(I) complexes have received continuous attention for their potential application in catalysts [1] and electroluminescent devices [2], due to their high efficiency and low cost. Specifically, copper(I) halides are capable of adopting a variety of coordination modes ranging from low-dimensional, discrete complexes to 3-D polymeric networks containing various structural motifs such as rhomboid dimers [3], cubanes [3,4] or stair-step tetramers [5], 1-D chains [6], and double-stranded stairs [5b,7]. The structures of coordination polymers self-assembled depend on a delicate balance between alternative conformations of the organic ligands and the nature of the metals and anions [8], as well as the solvent molecules [9] employed. In addition, the roles of solvents in the assemblies, structural transformations and properties of coordination polymers have been major subjects of research in this field [10]. Recently, we have been interested in the development of copper(I) coordination polymers using CuI and dithioethers. We reported the synthesis and structures of a family of fascinating copper(I) iodide coordination polymers [3,4,7b]. Some of these complexes have displayed strong luminescence. The efficient monitoring of volatile organic compounds (VOCs) has gained prominence in the area of environmental and public safety control due to the potential health hazards posed by exposure to these substances. The use of vapoluminescent metal complexes as optical sensors for VOC detection has not been exploited until fairly recently [11]. These studies have focused mainly on expensive metals such as Pd(II), Pt(II), and Au(I)

complexes, whereas studies on much less expensive copper(I) complexes have been comparatively less reported [12]. Our interest in sensing VOCs led us to consider the possibility of exploiting our copper(I) coordination polymers. Herein, we report the reversible interaction of a tetrameric copper(I) coordination polymer, [Cu₄L₄(CH₃CN)₂]_n (**1**), which results in a dramatic luminescence change by “switching on” the luminescence upon removal of acetonitrile by heating (Scheme 1).

The ligand, 1,4-bis((methylthio)propanoyl)piperazine (**L**) was synthesized using a method similar to that in the literature (Supporting Information Scheme S1) and the crystal structure of **L** was determined by single crystal X-ray diffraction (Fig. S1 and Table S1) [3a]. The complex (**1**) was obtained by diethyl ether vapor diffusion into an acetonitrile solution of CuI (0.076 g, 0.40 mmol) and **L** (0.029 g, 0.10 mmol) in 72% yield (Scheme S2), and characterized by IR spectroscopy, single-crystal and powder X-ray diffraction studies [13]. The coordination polymer (**1**) was nearly insoluble in most organic solvents.

The crystal structure of **1** consists of 2-D networks formed with the stair-step tetramer Cu₄L₄ and **L** as building blocks (Scheme 1, Fig. S2, and Table S2). Four Cu₄L₄ tetramers occupy each grid point (lattice point) of the network. The sulfur atoms bound to Cu1 and Cu2 coordinate to a symmetry equivalent Cu2 and Cu1 of the neighboring Cu₄L₄ cluster, respectively. Therefore, the four S atoms of two ligands link these tetranuclear cores into a 2-D network along the *ac* plane. This 2-D network is packed along the crystallographic *b* direction. Each [Cu₄L₄(CH₃CN)₂] unit shows a crystallographically imposed inversion symmetry and contains two crystallographically independent CuI centers. The half ligand has a unique structure with its inversion center located at the center of the ligand molecule. Both of the two crystallographically independent CuI centers display a tetrahedral geometry. Although both Cu1 and Cu2 are in a tetrahedral coordination arrangement,

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Scheme 1. Synthesis of **1** and conversion between [Cu₄I₄L(CH₃CN)₂]_n (**1**) and [Cu₄I₄L]_n (**2**).

Cu1 is coordinated to three iodide ions and one sulfur atom of a ligand molecule, whereas Cu2 is bonded to two iodide ions, one nitrogen atom of an acetonitrile molecule, and one sulfur atom of another ligand molecule.

To study the stability of **1**, thermogravimetric analysis was carried out (Fig. 1a). First weight loss of 7.6% (calculated 7.2%, 'heated sample') began at ~80 °C; this corresponds to the acetonitrile content in **1**. Second weight loss of 24.5% (calculated 25.6%) started at ~200 °C; this loss corresponds to the ligand content. In order to investigate the reversibility of the acetonitrile removal process, a desorption experiment and a sorption experiment of the acetonitrile molecules were carried out (Fig. 1b). The weight of the sample (**1**) decreased when it was heated to 100 °C under atmospheric pressure for 1 h. The weight increased to the original weight when a few drops of acetonitrile were introduced

into the heated sample, [Cu₄I₄L]_n (**2**) and excess acetonitrile evaporated at room temperature in air. There was no substantial change after the 5th cycle, which indicates that the process is completely reversible (Fig. 1b).

This was also verified by the powder X-ray diffraction (PXRD) patterns and IR spectra shown in Fig. 2 and Fig. S4, respectively. When acetonitrile was removed by heating, the C–N stretching vibration peaks at 2299 and 2270 cm⁻¹ disappeared (Fig. S3b). These peaks reappeared upon exposure of the heated sample to acetonitrile.

The experimental PXRD pattern of **1** (Fig. 2b) agreed with the calculated pattern (Fig. 2a), with the parameters obtained from single crystal X-ray diffraction analysis. The powder pattern obtained from the heated sample (Fig. 2c) did not coincide with the pattern of the original sample. Interestingly, the first low-angle peak disappeared,

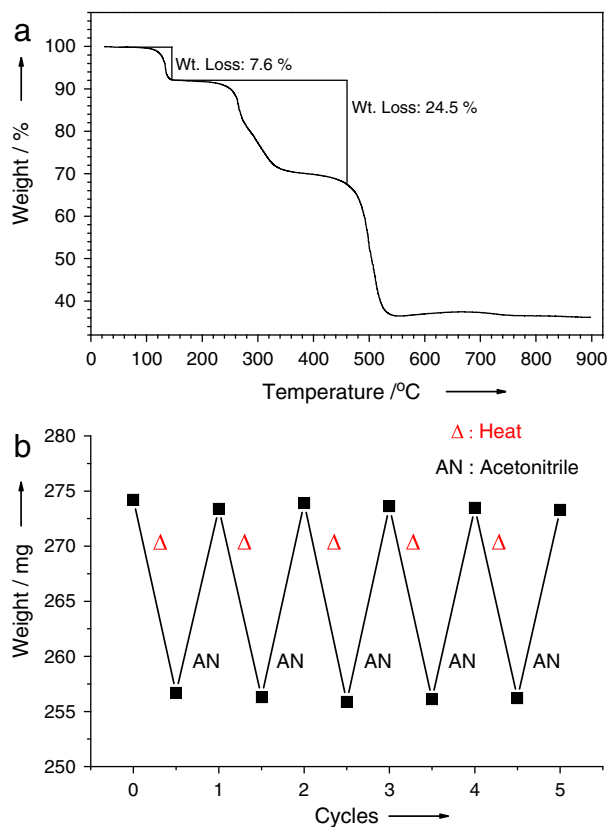


Fig. 1. Thermogravimetric analysis curve (a) and desorption–sorption data (b) of **1**.

which indicates a smaller lattice constant b upon removal of acetonitrile. Some peaks remain at the same angles, indicating very little change in the crystallographic a or c direction. After exposure to

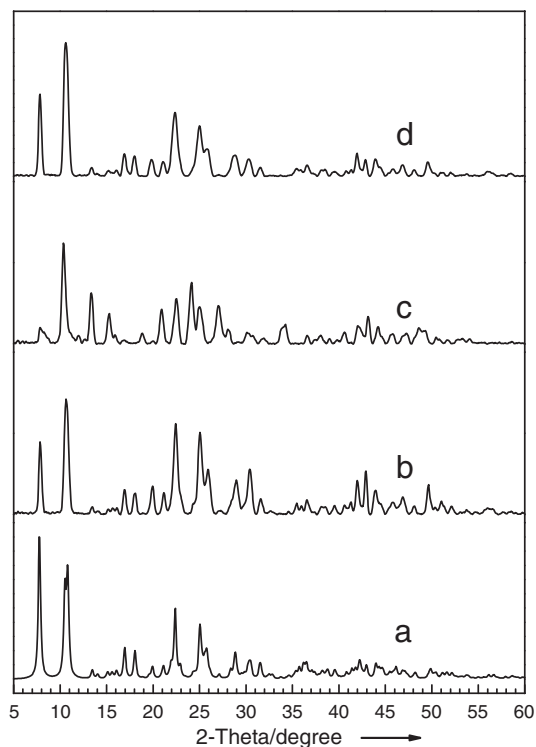


Fig. 2. PXRD patterns for $[\text{Cu}_4\text{I}_4\text{L}(\text{CH}_3\text{CN})_2]_n$ (**1**) (a, b, d) and $[\text{Cu}_4\text{I}_4\text{L}]_n$ (**2**) (c): calculated (a), observed (b), heated (c), and exposed to acetonitrile (d).

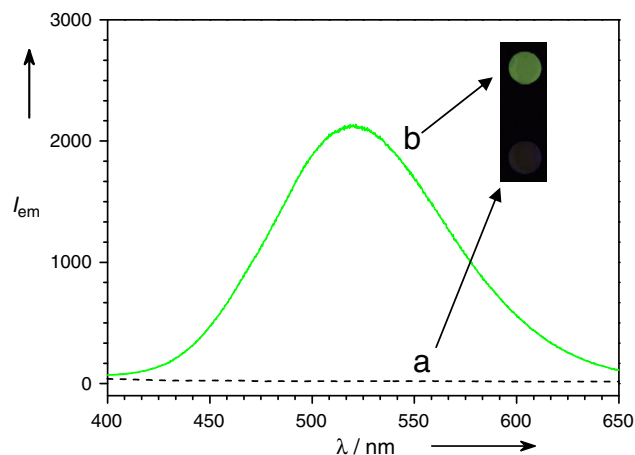


Fig. 3. Solid state emission spectra and photograph image with UV irradiation: $[\text{Cu}_4\text{I}_4\text{L}(\text{CH}_3\text{CN})_2]_n$ (**1**) (a) and heated sample $[\text{Cu}_4\text{I}_4\text{L}]_n$ (**2**) (b).

acetonitrile, the PXRD pattern was fully recovered, as shown in Fig. 2d. Photoluminescence spectra (Fig. 3) for **1** and **2** were measured to demonstrate luminescence switching by acetonitrile. No emission was observed from the original sample (**1**) (off state), while the heated sample (**2**) emitted a strong green light (on state) [14]. This is reversible upon removal of acetonitrile and exposure to acetonitrile. The photoluminescence spectrum of the heated sample shows a broad band at 520 nm ($\lambda_{\text{ex}} = 350$ nm). The emission might be designated a metal-centered $d-s$ state or metal-to-ligand charge-transfer state [15]. Che et al. reported a new emission band of $[\text{Cu}_2(\text{dcpm})_2(\text{PF}_6)_2]$ at 475 nm upon removal of acetonitrile from $[\text{Cu}_2(\text{dcpm})_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ [16]. Lee et al. also reported a new emission band of $\{[(\text{Cu}_3\text{I}_3)\text{L}](0.5\text{H}_2\text{O})\}_n$ at 420 nm upon removal of acetonitrile from $\{[(\text{Cu}_3\text{I}_3)\text{L}(\text{CH}_3\text{CN})](\text{CH}_2\text{Cl}_2)(2\text{H}_2\text{O})\}_n$, where **L** is a Calix[4]-bis-dithiacrown [14].

In summary, photoluminescence switching induced by the removal/binding of acetonitrile was demonstrated. The reversible vapoluminescent behavior was attributed to the 2-D network structure, thermal stability, and covalent bonding between **2** and acetonitrile. Further luminescence and theoretical studies are necessary to understand the luminescent properties and molecular orbitals of **1** and **2**. The heated sample (**2**) can also be used as a catalyst or a gas separating material, specifically, for separating acetonitrile from mixtures containing acetonitrile.

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Appendix A. Supplementary material

Supplementary crystallographic data associated to **1** have been deposited at the Cambridge Crystallographic Data Centre [CCDC 661132 and 661133]. This data can be obtained free of charge on application to the CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or electronically via www.ccdc.ac.uk/data_request/cif. Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2013.04.018>.

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