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In-situ hydrothermal preparation of a novel 3D CuI-based tetrazole coordination polymer with pseudo-porphyrin secondary building units

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ABSTRACT

A novel 3D CuI-based tetrazole coordination polymer through the employment of in-situ hydrothermal techniques by using 4-cyanopyridine, NaN_3 and CuI, $[Cu_5(L)_3I_2]$ (**1**) (HL = 5-(4-Pyridyl)-1H-tetrazole) has been synthesized and structurally characterized by X-ray single-crystal diffraction as well as by powder X-ray diffraction, elemental analysis and thermogravimetric analysis. In compound **1**, each CuN_3I tetrahedron, CuN_2I_2 tetrahedron and CuN_3 triangle are linked to each other by L ligand to form a 3D framework structure. It is interesting to note that the interconnection of Cu1 and Cu2 ions by bridging L ligand form pseudo-porphyrin secondary building units. Surface photovoltage, field-induced surface photovoltage and luminescent properties of compound **1** have also been studied.

Light-emitting diodes (LEDs) technology has experienced rapid development since the 1970s, which makes use of inorganic semiconductors to convert electricity to light [1]. Recently, white-light-emitting systems are composed of components that emit either the two complementary (e.g., blue and yellow) or three primary colors (blue, green, and red) have been attracting much attention for their high luminous efficiency, good durability, low energy consumption, and safety [2–5]. Current commercial w-LEDs are based on the blue LED (InGaN/GaN diode) combined with yellow phosphor (Ce^{3+}-doped yttrium aluminum garnet) approach. Similarly to YAG:Ce^{3+}, almost all commercial phosphors used in today's LED market are rare-earth (RE) metal-doped inorganic materials, including oxides, nitrides, sulfides and so on. Advantages of these phosphors are high quantum efficiency and stability [6–8]. However, their dependence on rare-earth elements can become critical due to potential supply risk and cost issues. Several RE-free white phosphors have been developed in recent years, including ultrasmall nanocrystals of CdSe and QDs with different colors [9–12]. However, low efficiency is usually unavoidable due to particle size variation, self-absorption, and quenching.

Copper halide based hybrid materials have attracted considerable interest because of their rich structural and photophysical properties, and potential applications as low-cost, abundant materials in optoelectronics, catalysis, and biological systems [13–15]. Among them, the copper(I) iodide is a p-type semiconductor having a bandgap of about 3.1 eV, can interact with various donors such as anilines, pyridyl type ligands, thioethers and phosphines to form coordination polymers, which exhibit various structural motifs, such as rhomboid dimers, cubanes or stair-step tetramers, 1-D chains, and double-stranded stairs [16–21]. The structures of coordination polymers self-assembled depend on a delicate balance between alternative conformations of the organic ligands and the nature of the inorganic metals and anions, as well as the solvent molecules employed [22–24]. Recently, li et al. report the rational design and synthesis of a CuI-based hybrid semiconductor family 1D-CuI(L) as alternative phosphors free of rare-earth elements. That approach allows a systematic fine tuning of their band gaps and optical emissions to cover the entire visible range, including yellow and white colors [25]. In order to better understand the role played by both the coordination sphere and the topology of CuI-based hybrid materials, we have also devoted some efforts to the preparation of other CuI-based coordination polymers with excellent semiconductor properties. Herein, we synthesized a novel 3D CuI-based tetrazole coordination polymer with pseudo-porphyrin secondary building units through the employment of in-situ hydrothermal techniques (Scheme 1) [26]. Surface photovoltage, field-induced surface photovoltage and luminescent properties of compound **1** have also been studied.

Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the monoclinic space group *C*2/*c* [27]. Each fundamentally structural unit contains five unique Cu(I) cations, three unique L univalent anions and two iodide anions (Fig. 1). The L ligands as a quadridentate or pentadentate ligand show two kinds of coordination modes, which were comprised of copper(I) cation coordination with nitrogen atoms of pyridine and tetrazole, respectively. Notably, each iodide works as a μ_3-type bridge linking to three copper atoms, and the Cu1 and Cu2 atoms have the tetrahedral environment, while Cu3 atom has a triangular conformation. Two of the four coordination sites for Cu1 are filled with two tetrazole nitrogen atoms (N2A, N6) from

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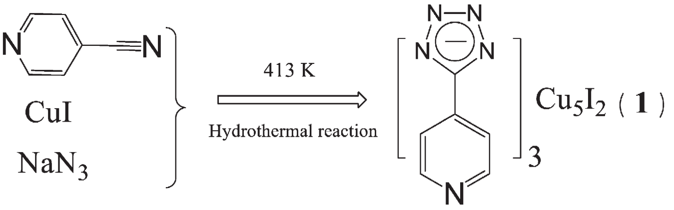

Scheme 1. In situ hydrothermal syntheses of compound **1**.

two separate L ligands. The remaining sites are occupied by the pyridine nitrogen atom (N5A) from another L ligand and the iodide anion (I1). Two of the four coordination sites for Cu2 are filled with two tetrazole nitrogen atoms (N1, N7) from two separate L ligands. The remaining sites are occupied by two iodide anions (I1, I1A). Two of the three coordination sites for Cu3 are filled with two tetrazole nitrogen atoms (N_3, N_3A) from two separate L ligands. The remaining sites are occupied by the pyridine nitrogen atom (N8A) from another L ligand. The values of the Cu–N bond lengths and N–Cu–N angles are in the ranges of 1.9578(15)–2.0711(15) Å, and 101.94(6)–134.54(9)°, respectively. The values of the Cu–I bond lengths and N–Cu–I angles are in the ranges of 2.6835(3)–2.7355(3) Å and 56.877(9)–114.55(5)°, respectively. The values of the I–Cu–I angles are 115.498(10)°. The shortest Cu…Cu distance is 2.8920(5) Å as a diagonal of the Cu_2I_2 rhombus repeating motif, suggesting the presence of a d^{10}–d^{10} metallophilic interaction. These values are close to those reported for other copper coordination polymers [28–33].

The overall structure of compound **1** can be described as a 3D framework type. The Cu(1)N_3I and Cu(2)N_2I_2 tetrahedra are interconnected into a tetramer *via* corner and edge sharing. Such tetramers are linked to each other by tetrazole moiety of L ligand to form infinite 2D layers, which is further connected to adjacent layers through L ligands to form a 3D open-framework structure (Fig. 2). It is interesting to note that the interconnection of 2Cu1 and 2Cu2 ions by bridging four tetrazole moiety of L ligand leads to pseudo-porphyrin secondary building units, which were further connected by the nitrogen atoms of tetrazole to form dimers of pseudo-porphyrin (Fig. 3). Such a structural connection may play an important role in enhancing the electron transport of the 3D space, and improving the semiconductor properties of the coordination polymer.

The powder XRD patterns of the as-synthesized compound **1** with that simulated on the basis of the single-crystal structure are presented in Fig. S1. The diffraction peaks on the patterns correspond well in position, confirming that the product is a pure phase. The differences in reflection intensity are probably due to preferred orientation in the powder samples. Thermogravimetric analysis of compound **1** revealed that it is thermally stable up to 330 °C (Fig. S2). Above this temperature, it gradually loses weight until 530 °C. The total weight loss (59.9%) is consistent with theoretical value calculated (60.4%).

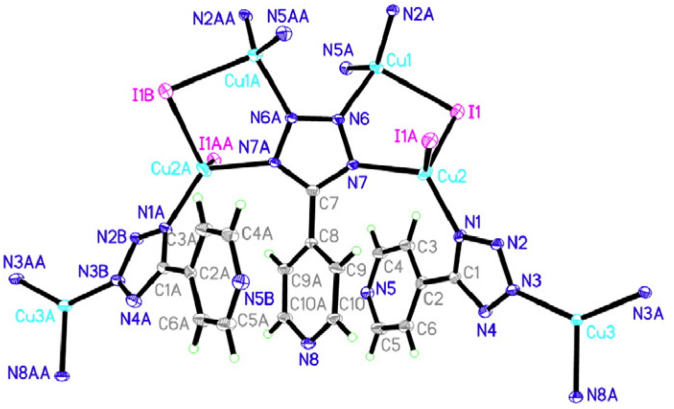

Fig. 1. The fundamentally structural unit of compound **1** showing the atom labeling. Thermal ellipsoids are shown at the 30% probability level.

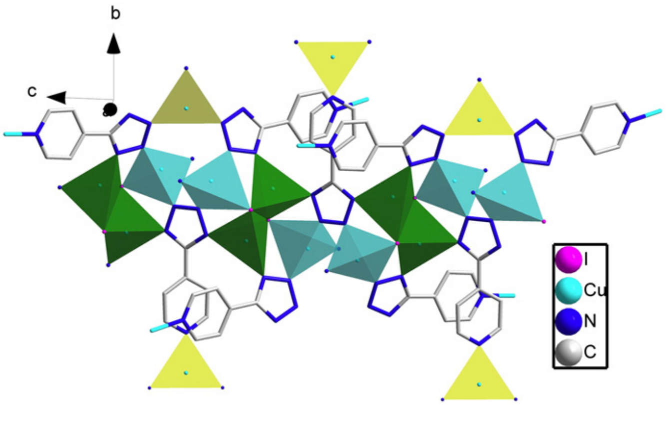

Fig. 2. A polyhedral representation of the structure of compound **1** in the *bc* plane. Aqua tetrahedra: CuN_3I, green tetrahedra: CuN_2I_2, yellow triangle: CuN_3.

The surface photovoltage technique based on lock-in amplifier, is a well-established contactless and non-destructive technique for semiconductor characterization which depends on analyzing the illumination-induced changes in the surface voltage and can be used to investigate the photophysics of the excited states and the surface charge behavior of the sample [34–36]. It is well documented that the separation of illumination-induced excess charge carriers will lead to a rise in photo-voltage [37]. Therefore, it is noted that the formation of an SPV signal is determined by the transport of excess carriers in a semiconducting material [38]. Compound **1** appears as two positive SPV responses in the range 300–600 nm, which indicates that it possesses *p*-type semiconductor characteristics (Fig. 4) [39]. The SPV response at $\lambda_{max} = 362$ nm is assigned to the $\pi \rightarrow \pi^*$ transition of the ligand and the response at $\lambda_{max} = 390$ nm is attributed to the LMCT (from ligand-to-metal charge transfer) transition, which reveals that a high separation efficiency of photoinduced charge carriers for the compound **1** [40].

Field-induced surface photovoltage spectrum (FISPS) can determine the direction of the built-in field and the mobile direction of

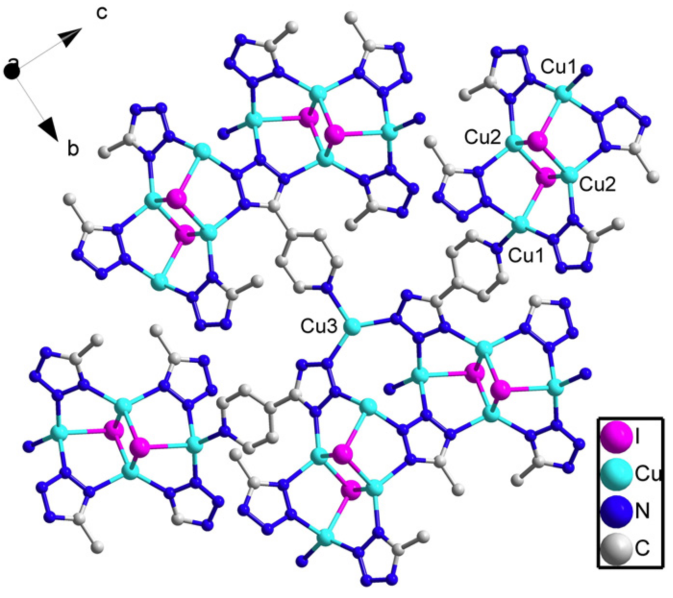

Fig. 3. Packing diagram of 3D framework for compound **1** with pseudo-porphyrin secondary building units in the *bc* plane. H atoms have been omitted for clarity.