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Two photoluminescent crystal architectures with wire frameworks directly assembled by Ag (I) ions

Ya Hong Wu[1], Gui-Ping Tan[2], Sheng Hu[1], Shan-Ling Tong[1], Yan Yan*[1]

[1]College of Light Industry & Chemical Engineering, Guangdong University of Technology, Guangzhou 510006, (CHINA)

[2]College of Chemistry & Environmental Engineering, Dongguan University of Technology, Dongguan 523808, (CHINA)

E-mail : yanyan-gdut@hotmail.com

ABSTRACT

Two novel crystal architectures with wire frameworks, $[Ag_2(btc)(im)]_n$ (1) and $[Ag_3(btc)(im)\cdot H_2O]_n$ (2) (btc = 1, 3, 5-benzene tricarboxylic acid, im = imidazole), have been assembled by hydrothermal method and characterized by X-ray diffractions, elemental analysis, fluorescence spectra and thermal gravimetric analyses (TGA), respectively. Using silver sulfate, complex 1 was arranged as “zigzag” chains of silver ions, while using silver nitrate, complex 2 was presented as straight Ag wires. In addition, both complexes exhibit photoluminescence and conductivity at room temperature.

KEYWORDS

Silver;
Wire;
Luminescence;
Conductivity;
Crystal;
Architecture.

INTRODUCTION

Many of the crystal motifs are based on the interaction of anions, including both counter ions and electronegative ligands in crystal self-assembly[1,2]. In the crystal architectures, the counter ions, such as Cl^-, Br^-, I^-, ClO_4^-, BF_4^-, and NO_3^-, sustain the polymeric structures mainly by their size effect[3,4]. Meanwhile, the cation-cation interactions are also believed as the driving forces to sustain their wire-like structures. Recently research works focused on the coordination polymers with weak metal-metal interactions. For example, the redox-active molecular wires based on extended Rh-Rh bonded coordination chains are prepared and examined[5]. Some transition metal chalco-halide polymers also exhibit well conductivity[6]. Therefore inorganic coordination polymers with weak cation-cation interactions can be developed as molecular wires. Herein two wire-like crystal architectures of silver atoms are obtained by hydrothermal method. By reaction of 1, 3, 5-benzene tricarboxylic acid (bta) and imidazole (im) with silver sulfate and silver nitrate respectively, two colorless column crystal architectures for complex 1 $[Ag_2(btc)(im)]_n$ and complex 2 $[Ag_3(btc)(im)\cdot H_2O]_n$ are obtained.

RESULTS AND DISCUSSION

For complex 1 (Figure 1-A), two crystallographically independent silver (I) ions are labeled as Ag1 and Ag2. The bridging coordination from two carboxyl groups makes the distances between Ag1-Ag1A (2.9570 Å) and Ag1-Ag2 (2.9878 Å) shorter than that between Ag2-Ag2A (3.3376 Å), all Ag ions are linked together with weak metal-metal interaction[7]. The dihedral angle between Ag2-O6-Ag2A-O6A and

Ag1-Ag2-Ag1A-Ag2B is 101.48°. As a result the silver parallelograms are arranged as “zigzag” chain with interaction between Ag2-Ag2A in its 3D framework (Figure 2).

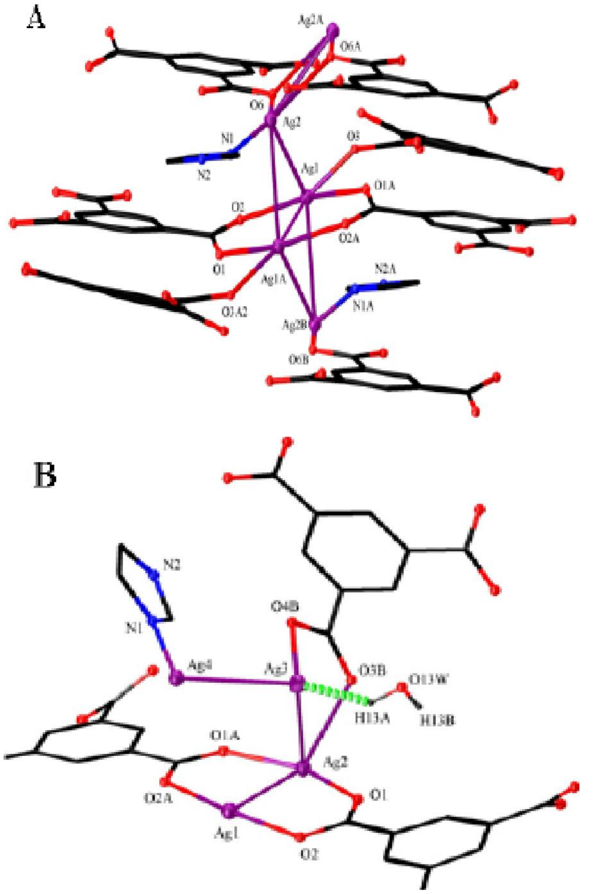

Figure 1 : Coordination circumstance around silver atoms in complexes 1 (A) and 2 (B) Some H atoms are omitted for clarity.

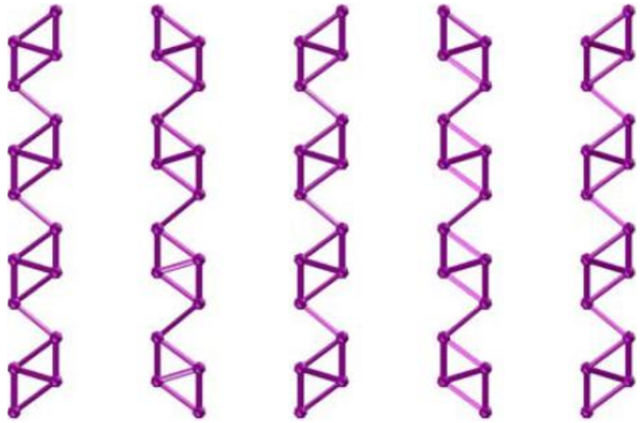

Figure 2 : The ‘zigzag’ silver chains in complex 1 viewed down the *c*-axis (all other atoms are omitted for clarity).

Figure 1-B and Figure 3-B indicate that in complex 2, the ratio of Ag1 and Ag2 over all of the four independent silver atoms is 25%. The bond lengths between silver atoms are list as below: 2.8168Å (Ag1-Ag2), 3.0499Å (Ag2-Ag3), and 2.9766Å (Ag3-Ag4). Water molecules fill the interlayer voids with hydrogen bonding (HB) interaction of Ag3···H13A (1.929Å). The bridging chelations from carboxylic ligands construct the silver wires of (Ag2-Ag3-Ag3)$_n$ stretching along the *a*-axis (Figure 3). Both complexes can be simplified as Ag wires, and an electric experiment is designed to detect their conductivity (no crystal anisotropy was examined). The semiconductive properties for both complexes 1 and 2 indicate that the electrons of silver atoms are capable of free flow in both crystal architectures.

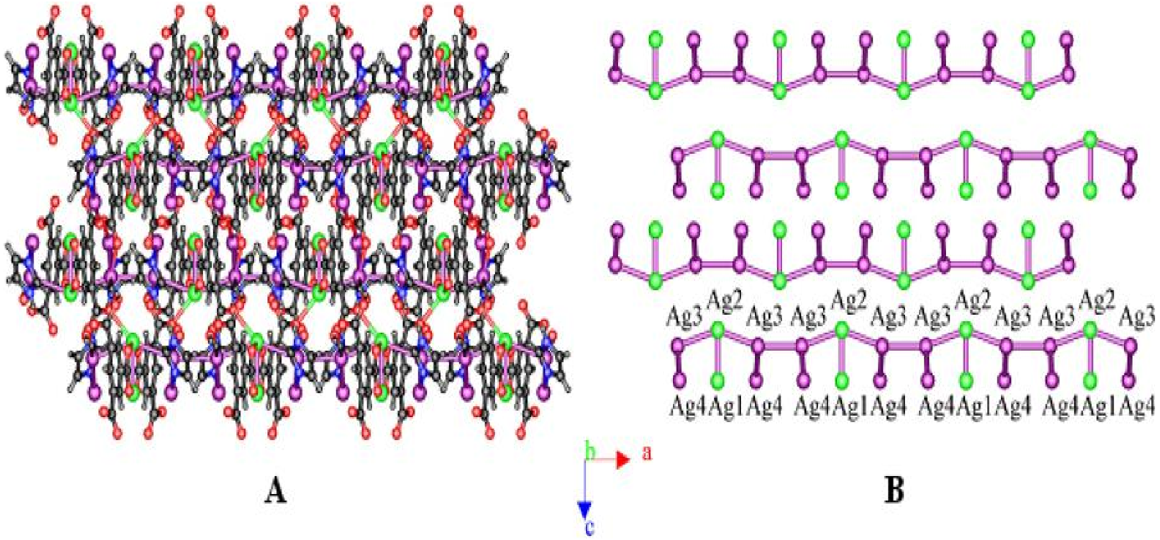

Figure 3 : (A)Silver ions packed in the crystal structure of complex 2 viewed down the *b*-axis. (B)The silver wires of (Ag2-Ag3-Ag3)$_n$ in the crystal architecture of complex 2, other atoms are omitted for clarity

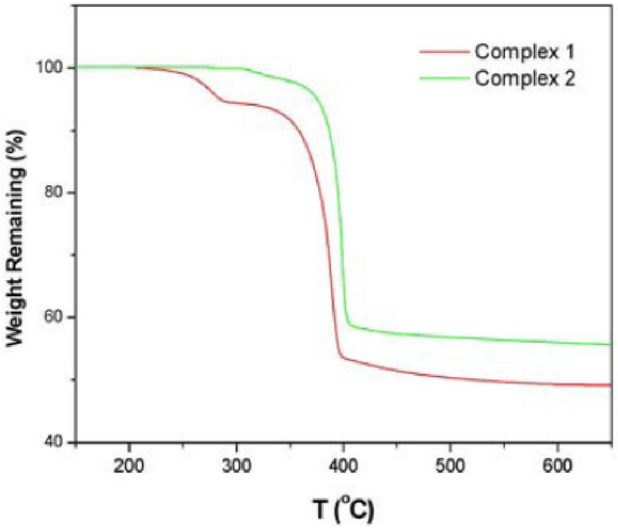

Figure 4 : The TGA curves of complexes 1 and 2

Even though using the same amount of btc ligands in self-assembly, the crystal architecture of complex 1 (Ag_2SO_4 as silver source) is much different from that of complex 2 ($AgNO_3$ as silver source). The intriguing structural features of 1, 3, 5-benzene tricarboxylic acid and the steric effects form the different anions may be the explanations[8]. In the crystal architecture of complex 2, the carboxylic groups combine with silver atoms by μ_2-η^1:η^1-bridging and μ_2-η^2:η^1-coordination modes to construct the silver ions almost as straight silver wires. On the contrast, the coordination situation becomes more complicated in complex 1, the μ_2-η^1:η^1-bridging coordination mode makes the silver ions exhibit the “zigzag” chains in its crystal architecture. Indeed, the contribution from the co-crystallized water molecules can not be neglected. The TGA determinations indicate that, just after the evaporation of the crystallized water molecules at 275 °C, the crystal architecture of complex 2 begins to collapse (Figure 4). Meanwhile, the crystallized water molecules can also weaken its photoluminesce (Figure 5). When temperature is higher than 400°C, both complexes are collapsed completely. The quenching effect of hydrogen-bond vibrations in complex 2 makes its fluorescence much weaker than that of complex 1, although the fluorescence for both complexes is only generated by the same charge migration from metal to ligand[9]. For both crystal architectures, after excitation at 280 nm, their emission peaks appear around 520 nm, but owing to the influence from waters of crystallization, the emission peak of complex 2 is much weaker than that of complex 1 (Figure 5).

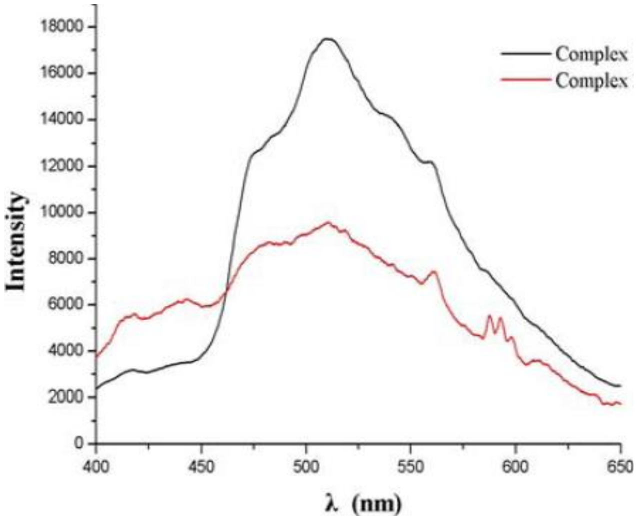

Figure 5 : Fluorescence spectra of complexes 1 and 2 (λ_{Ex} = 280nm)

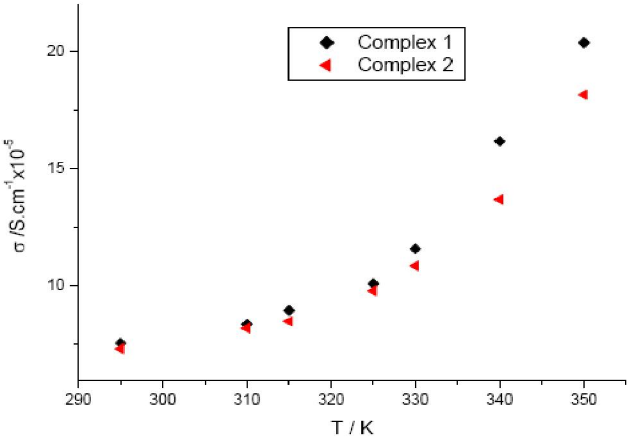

Figure 6 : Conductivity determinations for complexes 1 and 2

The electrical conductivity determinations for complexes 1 and 2 (powder samples of the crystals) reveal their conductivities of 7.58 × 10^{-6} and 7.32 × 10^{-6} S cm^{-1} at room temperature, and the conductivities increase with temperature (Figure 6). Because of the presence of silver chains in both crystals 1 and 2, the electrical experimental results demonstrate that both complexes 1 and 2 possess semiconducting properties, and their conductivities is little strong compared to the reported value[10].

CONCLUSIONS

In conclusion, two fluorescent complexes have been prepared with distinct silver-wire structures. The coordination modes of 1, 3, 5-benzene tricarboxylic acids with silver ions decided the differences in their crystal architectures. For complex 2, the co-crystallized water molecules can weaken both the thermal stability and the fluorescence. These silver wire architectures should be developed as nano-semiconductor.

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