Synthesis, Structure, and Luminescent Property of a 3D Polymer Containing Silver Ions

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The hydrothermal reaction of Ag_2SO_4, pyridine-3,4-dicarboxylic acid (H_2PDC), LiF, and H_2O led to the formation of a novel complex, $[Ag_2(PDC)]_n$ (**1**). X-ray crystal structural analysis indicates that **1** has a 3D coordinated framework, which contains a mono- and dinuclear mixed 1D polymeric chain. Fluorescent analyses of **1** show intense photoluminescence at 510 nm in the solid state, suggesting potential candidates for photoactive material.

The design and synthesis of organic–inorganic hybrid compounds have received extensive interest owing to their intriguing structural topology as well as potential applications as functional materials.[1] As known, ligands containing carboxylate groups are good building blocks for the constructions of polymeric structures because of their various coordination modes.[2] Pyridine-3,4-dicarboxylate ligand, as a member of them, has also drawn more and more attention because of its unique structure features. On the other hand, Ag^I ion is a favorable building block for coordination polymers because of its various coordination modes, such as linear,[3] trigonal,[4] and tetrahedral,[5] and its high affinity for hard donor atoms, such as nitrogen or oxygen atoms. All kinds of novel structures of Ag^I, such as interpenetrating diamond, and helical, and lamellar[6] structure like graphite, have been reported in the literature. Thus, $AgSO_4$ was employed to react with H_2PDC. In this letter, we report a 3D polymer constructed from Ag^I and H_2PDC, namely $[Ag_2(PDC)]_n$.

The hydrothermal reaction of $AgSO_4$ (0.3 mmol), H_2PDC, and NaOH at 170 °C in a molar ratio 1:1:2 leads to the formation of **1**.[7] X-ray diffraction analysis[8] reveals that **1** possesses a 3D architecture containing a 1D polymeric chain. As shown in Figure 1. there are two crystallographically unique Ag centers in the compound **1**, both displaying distorted tetrahedral coordination geometry. The Ag1 center is coordinated by three carboxylate oxygen and one nitrogen atoms from three different PDC ligands, while the Ag2 center is defined by four carboxylate oxygen atoms from four different PDC ligands. The Ag–N bond length is 2.217(3) Å, and the Ag–O bond length ranges from 2.213(3) to 2.708(3) Å, which is similar to those observed previously.[9] The distances of Ag1···Ag1A and Ag1···Ag2 are 3.844 and 3.650 Å, respectively, which are significantly longer than the van der Waals contact whose distance is 3.44 Å, illustrating the lack of direct metal–metal contact between Ag ions.[10] The Ag1 and Ag1A atoms are first connected together via μ_3-oxygen atoms of PDC carboxylate in an edge-sharing mode to form a dinuclear Ag cluster, and then the dinuclear cluster is further connected by a [AgO4] tetrahedron to generate a distinctive mono- and dinuclear mixed 1D chain along the *b* axis;[12] the adjacent chains are linked by carboxyl groups of PDC ligands to form a 2D layer. The layers are cross-linked by PDC ligands via their N and carboxyl groups, leading to the formation of a novel 3D extended network (Figure 2).

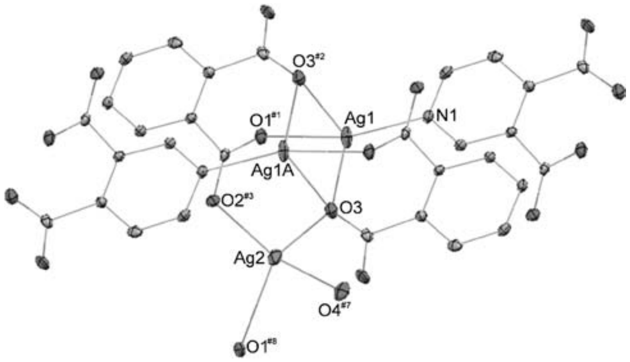


Figure 1. ORTEP representations of the coordination environment around the Ag centers for compound **1**, thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ag1–O1$^{\#1}$, 2.305(3); Ag1–N1, 2.217(3); Ag1–O3, 2.708(3); Ag1–O3$^{\#2}$, 2.542(3); Ag2–O3, 2.579(3); Ag2–O1$^{\#8}$, 2.594(3); Ag2–O2$^{\#3}$, 2.216(3); Ag2–O4$^{\#7}$, 2.213(3). Symmetry codes: #1: $x+1$, y, z; #2: $-x$, $-y$, $-z$; #7: x, $-y-1/2$, $z-1/2$; #8: $-x-1$, $y-1/2$, $-z+1/2$.

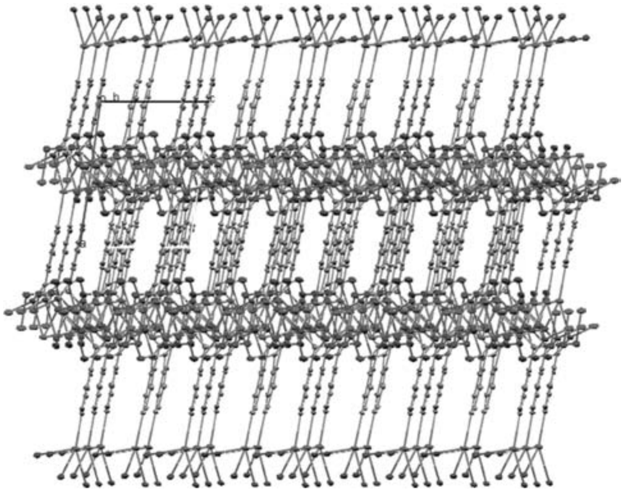
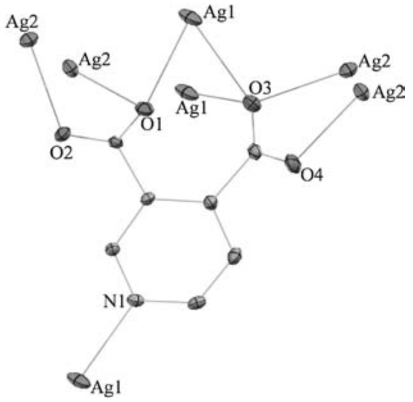


Figure 2. The 3D framework of the compound **1**.

It is worthwhile to point out that in this 3D coordination polymer, there are two kinds of noncovalent bonds interactions: Ag···Ag interactions and π–π packing interaction between pyridyl rings. The diatance of Ag2···Ag2 is 3.2667(6) Å, which is below the van der Waals diameter, indicating that there exist weak Ag···Ag interactions. Additionally, the distance between the centroids of the pyridyl rings (3.445 and 3.476 Å) are within the maximum contact for the π–π stacking interaction (3.8 Å for centroid–centroid distance), indicating there exists π–π stacking interaction. Both kinds of noncovalent interactions further



Scheme 1. The coordination mode of PDC ligand.

strengthen the 3D structure.

The most interesting characteristic of **1** is rather unusual coordination modes of PDC ligand. As shown in Scheme 1, the PDC ligand exhibits octadentate coordination modes. Two carboxyl groups are in different coordination fashions, one is one- and two-coordinated while the other is one- and three-coordinated. The coordination modes of PDC ligands play a key role in forming the present 3D structure. To the best of our knowledge, this kind of coordination mode of PDC ligand has not been observed in the known PDC complexes.[11]

To investigate the thermal stability of compound **1**, thermogravimetric analysis (TGA) was carried out between 30 and 930 °C in a static atmosphere of air with a heating rate of 7 °C min^{-1}. There is only one-step mass loss in the TG curve of **1**, which is stable until 210 °C. The weight loss of 40.1% (calcd 39.2%) observed from 210 to 330 °C corresponds to the release of PDC ligand. The remaining weight of 59.9% corresponds to the final product Ag_2O (calcd 60.8%).

The fluorescence emission spectrum of **1** was measured in the solid state at room temperature (Figure 3). **1** exhibits an intense broad emission band with a maximum at ca. 510 nm ($\lambda^{ex} = 397$ nm), which may originate from a ligand-centered n–π or π–π^* process including significant charge-transfer character induced by the Ag cation. This observation suggests that complex **1** may be an excellent candidate for potential photoactive materials.

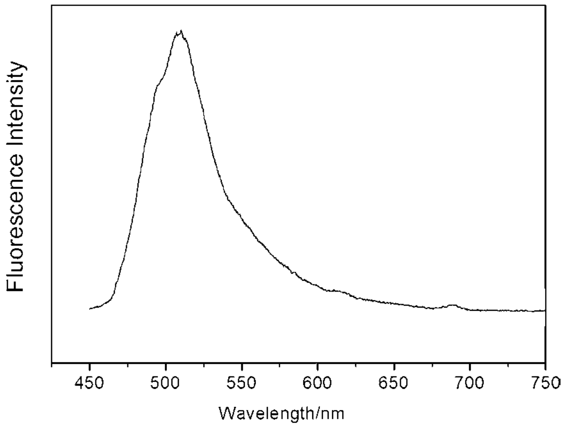


Figure 3. Emission spectra of **1** in the solid state at room temperature ($\lambda_{ex} = 397$ nm).

In summary, a novel 3D Ag$^{\text{I}}$ coordination polymer containing 1D polymeric chain has been hydrothermally synthesized and structurally characterized. It shows strong luminescence in the solid state, which makes it a possible candidate for new types of luminescent materials.

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7 A mixture of H_2PDC (0.2 mmol, 0.0334 g), Ag_2SO_4 (0.2 mmol, 0.0624 g), and H_2O (8 mL) was added into a Teflon-lined stainless-steel Parr acid digestion vessel (15 mL) and heated at 170 °C for three days under autogenous pressure. After slow cooling to room temperature, colorless crystals were obtained as a pure phase. Yield: 46%. Found: C, 21.89; H, 0.83; N, 3.56%. Calcd for $C_7H_3Ag_2NO_4$: C, 22.08; H, 0.79; N, 3.68%.

8 Crystal data for **1**: $C_7H_3Ag_2NO_4$, $M_r = 380.84$, monoclinic, space group $P2(1)/c$, $a = 8.6580(17)$ Å, $b = 13.735(3)$ Å, $c = 6.5009(13)$ Å, $\beta = 98.09(3)°$, $V = 765.4(3)$ Å^3, $Z = 4$, $D_{calcd} = 3.305$ g cm^{-3}, $T = 293(2)$ K, $R_1 = 0.0322$, $wR_2 = 0.0644$ based on 1752 reflections [$I > 2\sigma(I)$]. The crystal data for **1** have been deposited with the Cambridge Crystallographic Data Center as a supplementary publication no. CCDC-669078.

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