



Short communication

A highly electrical conducting, 3D supermolecular Ag(I) coordination polymer material with luminescent properties

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ARTICLE INFO

Article history:

Received 11 March 2016

Received in revised form 12 April 2016

Accepted 13 April 2016

Available online 27 April 2016

Keywords:

Metal-organic frameworks

3D supermolecular

Electrical conducting

Photoluminescent

ABSTRACT

A stable, 3D supermolecular material, $[\text{Ag}(\text{H}_2\text{O})(2,6\text{-ndc})_{0.5}(\text{L})_{0.5}]_n$ (2,6-H₂ndc = 2,6-naphthalenedicarboxylic acid; L = *N,N'*-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (dpndi)) with high electrical conducting ability was successfully synthesized under a solvothermal condition and characterized by single-crystal X-ray diffraction, IR spectroscopy and thermogravimetric analysis (TGA). The electrical conducting and photoluminescence properties were investigated.

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Coordination polymers (CPs) are crystalline materials with various sizes and structures, which are composed of metal ions connected by multitopic organic ligands to form the different topologies [1–2]. These materials are normally used in many fields, such as gas storage and separation, drug delivery, catalysis and luminescence [3–6]. However, in conducting fields, these materials are poor electrical conductors due to the insulating character of the organic ligands and the poor overlap between their π orbitals and the d orbitals of the metal ions. There are two venues to use the coordination polymers materials as conducting materials. The first method is to infiltrate MOFs which have open metal sites with molecules capable of charge transfer such as TTF (tetrathiafulvalene) or TCNQ (7,7,8,8-tetracyanoquinodimethane) molecules. In 2004, Allendorf and co-workers reported a strategy for realizing tunable electrical conductivity in HKUST-1 in which the nanopores were infiltrated with TCNQ molecules [7]. The electrical conductivity over six orders of magnitude is achieved and with values as high as 7 S per meter. The second type is a series of Ag(I) coordination polymers, but they perform not well with the above-mentioned materials, just compared with the same kind of Ag(I) coordination polymers materials [8].

In Ag(I) coordination polymers materials, two factors can be observed for electrical conducting. On one hand, electron donor-acceptor compounds featuring condensed aromatic hydrocarbons may be needed which were found around 1950 [9]. On the other hand, the aromatic π - π stacking interactions or significant interactions between the Ag(I) ion and aromatic group lead to these electrical conducting

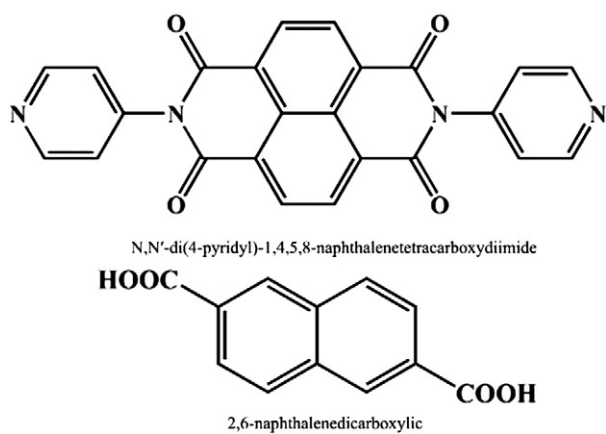
behaviour [10]. At present, the development of the conducting character of Ag(I) coordination polymers materials is still on the way. In 2003, Chen and co-workers synthesized a single-component molecular material which was used to perform electrical conducting and it is regarded as the first highly electrical conducting, molecule material with non-TTF-dithiolate type ligand [11].

Inspired by the above point of view, we considered that the condensed aromatic ligands may be a good candidate for the syntheses of Ag(I)-CPs to be used for electrical conducting. So, we chose 2,6-naphthalenedicarboxylic acid and L (Scheme 1) as raw materials to synthesize a new compound, named $[\text{Ag}(\text{H}_2\text{O})(2,6\text{-ndc})_{0.5}(\text{L})_{0.5}]_n$ (**1**). The orange needle crystals of **1** was synthesized by the reaction of AgNO_3 (0.034 g, 0.20 mmol), L (0.042 g, 0.10 mmol) and 2,6-naphthalenedicarboxylic acid (0.022 g, 0.10 mmol) in 8 mL of DMA-MeOH-H₂O (1:1:2, v/v/v) and stirred for 30 min at ambient temperature and then placed in a 23 mL Teflon-lined autoclave under autogenous pressure and heated at 100 °C for 3 days. The purity of the as-synthesized **1** was confirmed by similarities between simulated and experimental powder X-ray diffraction (PXRD) patterns (Fig. S1). Thermal analysis indicates that **1** can be thermally stable up to ca. 380 °C in N₂ atmosphere where the framework begins to collapse. The remaining residue corresponds to the formation of Ag₂O (obsd 26.80%, calcd 26.14%). (Fig. S2).

Single crystal X-ray diffraction analysis exhibits that **1** crystallizes in the triclinic space group *P*-1. As shown in Fig. 1a, the asymmetric unit of **1** is composed of one Ag(I) ion, one 2,6-naphthalenedicarboxylic acid ligand, one L ligand and one coordinated H₂O molecule. Each Ag(I) atom is three-coordinated forming a plane-trigonal coordination geometry which is surrounded by one oxygen atom from one 2,6-ndc

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Scheme 1. The ligands used in the work.

anion (Ag—O1 2.177(3) Å), one nitrogen atom from one L ligand (Ag—N1 2.164(3) Å) and one coordinated H₂O molecule (Ag—O1W 2.612(3) Å). As shown in Fig. 1b, every two ligands, L ligand and 2,6-ndc anion, one coordinated H₂O molecule are connected by one Ag(I) ion to form a 1D chain. Furthermore, each 1D chain is likely to interact through hydrogen bonds from the coordinated H₂O molecules and extend to a 2D layer. As illustrated in Fig. 1c, these 2D layers are interacted by face-to-face $\pi \cdots \pi$ each other as well to form a 3D supermolecular structure and from a certain angle, these 1D chains are arranged in order. The nearest distance of Ag(I)⋯Ag(I) is 4.1217(18) Å (Fig. S3). It is noteworthy that, in the crystal structure of

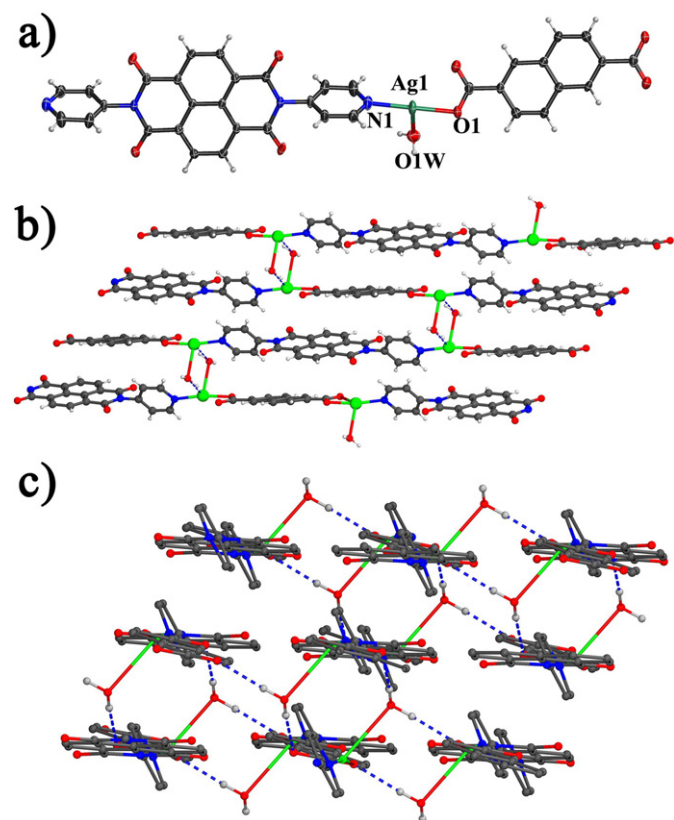


Fig. 1. (a) The coordination environment of one Ag(I) ion in **1**. All hydrogen atoms are omitted for clarity. (b) The structure of 1D chains of **1**. (c) The 3D supermolecular structure arranged in order from a certain angle. The green, gray, red and blue represent silver, carbon, oxygen and nitrogen atoms, respectively.

1, it exits relatively strong intermolecular forces including aromatic rings. Further analysis of the crystal packing reveals that adjacent 1D chains are further connected interactions between pyridine aromatic rings of L ligands with a distance of ca 3.70 Å (Fig. S4). This phenomenon plays an important role in stabilizing the network structure which is consistent with the TG curve mentioned above. Meanwhile, due to the existing of L ligand in **1**, we can see the part of planarity characteristic in the structure of **1**. Planarity is often consumed to be the significant geometric characteristic and it can also stabilize the framework.

Many examples of silver(I) complexes with condensed aromatics such as benzene, cyclophane, acenaphthene, naphthalene, and anthracene are synthesized and studied [12]. But the conductivity of them were often neglected. In order to investigate the electrical conducting ability of **1**, the room-temperature conductivities of **1** and the ligand of 2,6-naphthalenedicarboxylic acid and L in compacted pellets were measured by the conventional two-probe technique. As a result, **1** shows a conductivity of $\sigma = 2 \times 10^{-1} \text{ S cm}^{-1}$ at ambient temperature, but the two ligands exhibit no conductivity. Based on the result, we discover that maybe the conductivities of Ag(I) compounds concluding condensed aromatic rings are strongly dependent on inter- and/or intramolecular aromatic stacking which are agreement with our original opinions of choosing the ligands used for synthesizing materials [13]. Materials which have too weak or no aromatic stacking, usually have very low conductivity. The values usually range from 0 to $1 \times 10^{-5} \text{ S cm}^{-1}$ [14]. The stacking interaction generally originates from the interaction between the π -orbitals of condensed aromatic rings, especially between the highest occupied molecular orbital (HOMO) of the donor ring and the lowest unoccupied orbital (LUMO) of the acceptor ring, which is crucial to decrease the HOMO-LUMO gaps, providing the π -to- π^* and π -to-metal/metal-to- π^* electron-transfer pathways [11].

As luminescent materials, silver(I) coordination polymers can be used in areas such as light emitting diodes, luminescent probe and so on [15]. So, it is necessary for us to investigate the solid-state luminescent properties of **1**, 2,6-naphthalenedicarboxylic acid ligand and L ligand at ambient temperature. The main emission peaks of 2,6-naphthalenedicarboxylic acid ligand and L ligand are at 468 and 375 nm. As depicted in Fig. 2a, the emission peak of **1** is at 370 nm ($\lambda_{\text{ex}} = 320 \text{ nm}$). Obviously, 2,6-naphthalenedicarboxylic acid ligand is nearly nonfluorescent at room temperature. Compared with the L ligand, these main emission peaks are nearly the same. Due to the presence of empty π^* orbitals of condensed aromatic rings from L ligand, the emission is associated with metal-to-ligand charge transfer (MLCT). There are also Ag(I)⋯Ag(I) interactions within the compound [16]. At the same time, we observed the luminescent properties of **1** in various organic solvents, such as *N,N*'-dimethylacetamide (DMA), *N,N*'-dimethylformamide (DMF), acetone, dichloromethane (CH₂Cl₂), methanol, chloroform (CHCl₃), ethanol, acetonitrile and ethyl acetate. In Fig. 2b and c, except for CH₂Cl₂, the luminescence signals quench in the other organic solvents. The main emission peak of **1** in CH₂Cl₂ occurs a certain degree of red shifts and the intensity becomes stronger. It indicates that, maybe, **1** is a good candidate luminescent probe for selectively detecting CH₂Cl₂ molecule.

In summary, we synthesized a stable, 3D supermolecular material, [Ag(H₂O)(2,6-ndc)_{0.5}(L)_{0.5}]_n (**1**) and structurally characterized. It has a good electrical conducting ability and it shows important luminescent properties which can also be used as a luminescent probe for selectively detecting CH₂Cl₂ molecule. Relative works of Ag(I) coordination polymers materials are still underway.

Acknowledgements

This work was financially supported by the NSFC of China (No. 21471027, 21171033, 21131001, 21222105), National Key Basic Research Program of China (No. 2013CB834802), Changbai

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