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Assembly of a novel Ag(I) supramolecular architecture constructed from flexible ligand containing asymmetrical tricarboxylate

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Abstract

A novel Ag(I) compound $[Ag(H_2cpop)(bpy)]_n$ (**1**) (H_3cpop = 4-(4-carboxyphenoxy) phthalic acid, bpy = 4,4′-bipyridine), has been hydrothermally synthesized and structurally characterized. H_3cpop came from the *in situ* decarboxylation of H_4odp (H_4odp = 4,4′-oxydiphthalic acid) in the hydrothermal reactions. Compound **1** was obtained from the self-assembly of Ag(I) salt with bpy and H_4odp ligands to form a 1D chain bearing hooks with carboxyl groups. The two chains are recognized each other to generate molecular zipper structure by hydrogen bonding interaction between the bearing carboxyl groups. Compound **1** is stable in air, and show intense photoluminescence at room temperature.

Keywords: Supramolecular architecture; Crystal structure; Luminescence

In the construction of metal–organic frameworks (MOFs), Ag(I) is often used as a metallic synthon due to its high affinity to N and O donors, its flexible coordination number and geometry, as well as Ag···Ag weak interaction. By now, many Ag(I) complexes with different frameworks and topologies have been synthesized [1–8]; some of these show useful conductivity and photoluminescent properties [9–15]. On the other hand, a lot of supramolecular assemblies have been achieved by carefully selecting building blocks and organic ligands containing appropriate functional groups through supramolecular interactions (hydrogen bonding, π···π interactions etc.) [16–19]. In order to construct novel metal–organic complexes, careful selection of a suitable multifunction organic ligand containing the ability to form hydrogen bonds is an efficient route. So we introduce a flexible V-shaped polycarboxylate ligand, 4,4′-oxydiphthalic acid (H_4odp, Chart 1) for construction of novel MOFs.

H_4odp is a quite versatile ligand for construction of novel MOFs. It has nine potential donor atoms, which can induce rich coordination modes and many interesting structure with higher dimensions. Furthermore, they have four carboxyl groups that may be completely or partially deprotonated, and can provide hydrogen bond donors and acceptors. Meanwhile, it possesses both rigidity and flexibility, since phenyl rings can freely rotate around the C–O bonds according to the small change in the coordination environment in order to minimize steric hindrance. However, the coordination chemistry and structural properties of metal polymers based on $(odp)^{4-}$ ligand have been little documented [20]. With the aim of understanding the coordination chemistry of $(odp)^{4-}$ ligand and studying the influence on the framework structures of their complexes, we have recently engaged in the research of this kind of polymer complexes.

In this paper, we report a novel Ag(I) supramolecular architecture, namely $[Ag(H_2cpop)(bpy)]_n$ (**1**), H_3cpop is

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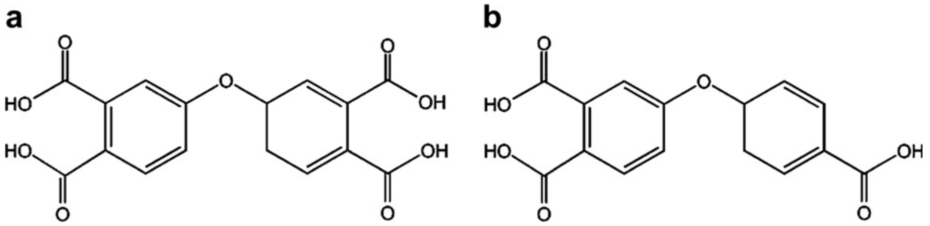

Chart 1. Molecular structures of H_4odp (a) and H_3cpop (b).

4-(4-carboxyphenoxy)phthalic acid (Chart 1), constructed by combination of coordination bonds, hydrogen bonds, and C–H···π and Ag···O weak coordinative interactions. It is noteworthy that H_3cpop ligand comes from the *in situ* decarboxylation of H_4odpa ligand during the hydrothermal synthesis reaction. H_3cpop is a flexible ligand containing asymmetrical tricarboxylic acid, the coordination chemistry of which has never been reported.

The yellow rod crystalline compound **1** was synthesized by treating $AgNO_3$ with 4,4′-oxydiphthalic anhydride, 4,4′-bipyridine and NaOH in the molar ratio of 2:1:1:1 in a solution of H_2O and ethanol under 160 °C for 96 h [21]. X-ray single-crystal diffraction analysis reveals that **1** crystallizes in monoclinic system, $P2_1/n$ space group [22]. Compound **1** consists of a neutral 1D chain polymer bearing hooks with carboxyl groups, $[Ag(H_2cpop)(bpy)]_n$, which is stable in air and insoluble in common organic solvents.

As shown in Fig. 1, Ag(I) center adopts three-coordinated mode with a T-shaped coordination geometry *via* binding with two nitrogen atoms (N1,N2A) from two different bpy ligands and one oxygen atom of a carboxylate group from $(H_2cpop)^-$ ligand in monodentate mode. The Ag–N bond lengths are 2.171(3) Å and 2.166(3) Å and Ag–O bond length is 2.584(3) Å, which is similar to those observed previously [23]. The N1–Ag1–N2A bond angle is 170.12° and the three atoms almost in a line. The pyridyl rings of the bpy ligand are noncoplanar with a dihedral angle of 35.31° and the Ag···Ag separation based on bpy is 11.409 Å. Each pair of parallel chains is nearly completely overlapping with the separation of Ag···Ag being 4.093 Å, which is significantly longer than the van der Waals contact whose distance is 3.40 Å, illustrating the lack of direct metal–metal contact between Ag(I) ions. Additionally, the distance between the centroids of the pyridyl rings (4.124 Å) exceeds the maximum contact for the π···π stacking interaction (3.8 Å for centroid–centroid distance), indicating no obvious π···π stacking interaction. In **1**, the phenyl rings of $(H_2cpop)^-$ are almost perpendicular to each other (the dihedral angle is 87.85°).

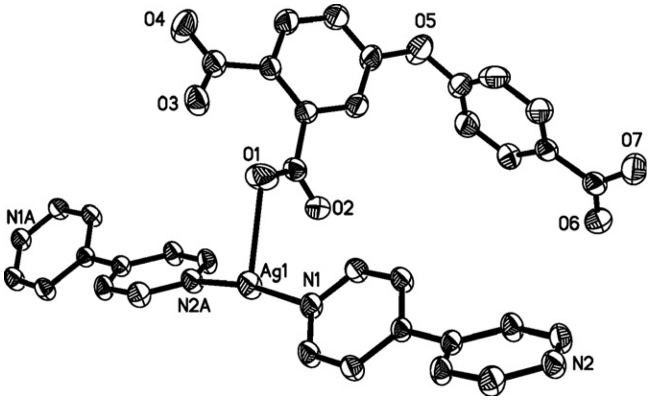

Fig. 1. The coordination environment of Ag(I) atom in **1**. All H atoms are omitted for clarity.

The first feature of **1** is its unusual three-coordinate structure (AgN_2O), the coordination polyhedron can be described as a T-shaped coordination geometry. Although Ag(I) atom with three-coordinate is not rare in the complexes containing bpy [24–27], and structure of **1** is different from the reported Ag complexes containing bpy and carboxylate ligands [28], in which the carboxylate ligands are not coordinated with Ag atom and Ag–bpy chains are linked into a 1D molecular ladder by ligand-unsupported Ag···Ag interaction, only exist Ag···O weak interaction. But in **1**, oxygen atom of carboxylate from $(H_2cpop)^-$ coordinated with Ag(I) atom directly. Hence, the bpy ligands bridge Ag centres to form 1D chain bearing hooks with carboxyl groups (Fig. 2). More interestingly, two 1D chains are recognized each other to generate the molecular zipper-like structure by intermolecular hydrogen bonding interaction between 4′-carboxyl oxygen atom (O7) of one $(H_2cpop)^-$ and 3-carboxylate oxygen atom (O2) of another opposite $(H_2cpop)^-$ ligand [O7–H7···O2^i, 2.608(5) Å, 163.4°, symmetry code i: $(-x+2, -y, -z+1)$] and intramolecular hydrogen bonding interaction [O3–H3···O1, 2.410(5) Å, 168.5°] (Fig. 2).

A more interesting feature of **1** that hydrothermal synthesis in the presence of Ag(I) ions unexpectedly caused the *in situ* decarboxylation of H_4odp ligand that resulted in formation of a coordination polymer of H_3cpop. In this reaction, H_4odp ligand was converted into H_3cpop by the loss of one carboxyl group. Several cases of hydro(solvo)thermal decarboxylation of a single carboxyl group from aryl carboxylic acids have been reported in reactions involving Cu(II), but which is very rare in Ag(I) complexes. To our knowledge, this reaction is the first example in which elimination of one carboxyl group in the presence of transition metal and H_4odp ligand under hydrothermal conditions. Notably, the decarboxylation did not occur in the reactions when transition metal ions other than Ag(I) were used, such as Cd(II) and Zn(II). We also found that the decarboxylation can take place

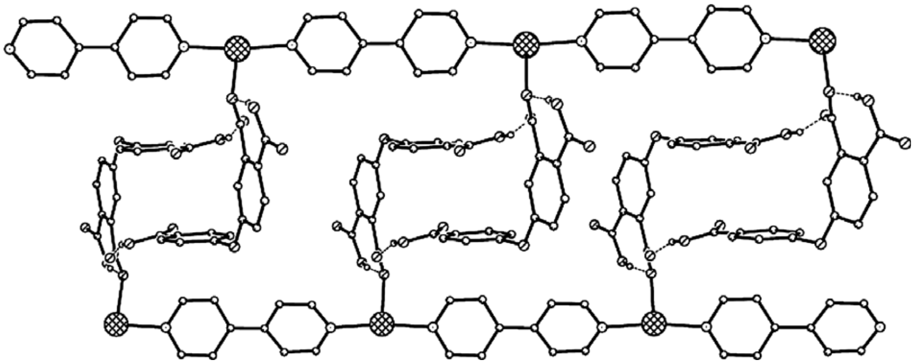

Fig. 2. Perspective view of the 1D chain bearing hooks with carboxyl groups and the molecular zipper-like structure in **1**. All H atoms are omitted for clarity.

when Ag(I) exists in different hydrothermal reaction conditions. These results indicate that Ag(I) atom plays an important role in the decarboxylation under hydrothermal conditions. Although the decarboxylation of carboxylic acids can happen both by homolytic and heterolytic cleavage of the C–C bond by a variety of mechanisms (with a heterolytic pathway occurring most frequently under hydro(solvo)thermal conditions) [29], we have not yet determined the mechanism by which the decarboxylation takes place on H_4odp ligand, which is necessary to further study in this field.

Additionally, H_3cpop ligand is partially deprotonated, so each pair of $(H_2cpop)^-$ ligands from adjacent chains forms a novel head-to-tail 26-membered hydrogen bonding ring, containing a type of pore with size of ca. 11.55 × 9.89 Å based on the C1···C1 and O5···O5 distances (Fig. 2). To our knowledge, supramolecular synthons involved in head-to-head carboxylic acid hydrogen bonds have well been documented in previous works, [30,31] but the carboxylic synthons of Ag(I) have seldom been reported owing to its strong coordination ability and flexible coordination geometry [17].

Furthermore, as shown in Fig. 3, 1D chain bearing hooks with carboxyl groups form 2-D double layer structure by week hydrogen bonding interactions (C14–H14···O6^{ii}, 3.286 Å, 167.4°; C22–H22···O4^{iii}, 3.481 Å, 142.7°; symmetry code ii: (x, $y+1$, z), iii: ($x+1$, $y-1$, z)) along a-axis. The adjacent 2-D double layers are further form a 3D supramolecular framework through weak hydrogen bonds (C21–H21···O3^{iv}, 3.330 Å, 136.2°; C26–H26···O3^{v}, 3.400 Å, 133.5°; symmetry code iv: ($1.5-x$, $-0.5+y$, $1.5-z$), v: ($2.5-x$, $-0.5+y$, $1.5-z$)), C═O···π interaction (3.183 Å) and Ag···O weak coordinative interaction (Ag···O, 2.949 Å) (Fig. 4 and S1).

To characterize the thermal stability of the supramolecular framework constructed from H_3cpop and bpy, compound **1** was investigated by the TGA technique. There is only one step mass loss in the TG curve of **1**, which is stable until 190 °C. The weight loss of 79.8% (calc. 80.9%) observed from 200 to 480 °C corresponds to the release of ligands. The remaining weight of 20.4% corresponds to the final product Ag_2O (calc. 19.8%).

The emission spectra of **1** and H_4odp in the solid state at room temperature are shown in Fig. S2. H_4odp exhibits

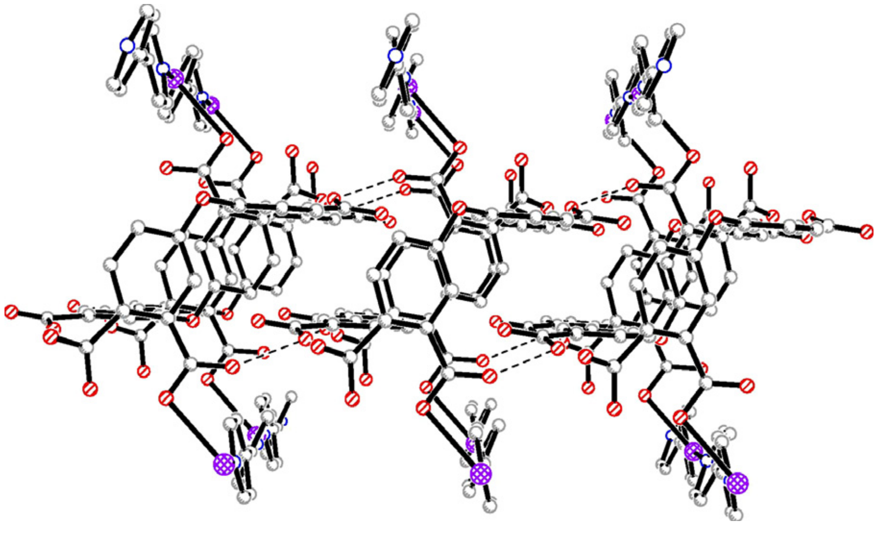

Fig. 3. The 2-D double layer structure formed by weak hydrogen bonding interactions along a-axis.

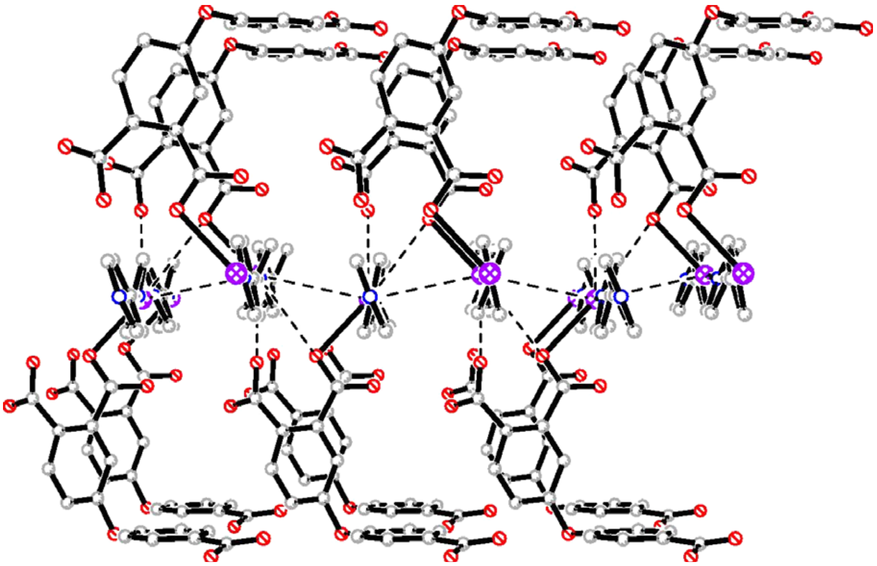

Fig. 4. View of supramolecular interactions between adjacent 2-D double layers along *a*-axis.

one weak emission band at 393 nm upon excitation at 245 nm. The similar emission at 395 nm was observed for **1** at the same excitation condition. It is suggested that the emission of **1** originated from the π–π^* electronic transition of ligand [32]. By comparing the emission spectra of **1** and H_4odp, we can conclude that the enhancement of luminescence in **1** may be attributed to the rigidity of **1**. This rigidity is favor of energy transfer and reduces the loss of energy through a radiationless pathway [33–36]. Compound **1** may be a good candidate for highly fluorescent materials owing to its strong luminescence.

In conclusion, we succeeded in access and structurally characterized a novel Ag(I) supramolecular framework $[Ag(H_2cpop)(bpy)]_n$(**1**) based on a flexible asymmetrical tricarboxylic acid ligand through hydrothermal method. Interestingly, H_3cpop comes from the *in situ* decarboxylation of H_4odp in the presence of Ag(I) under the hydrothermal reaction conditions. These results of the comparison with a series of hydrothermal reactions of H_4odp and transition metal ions indicate that Ag(I) possibly plays a key role in the hydrothermal decarboxylation process. In **1**, the 1D chain may be first formed through coordination bond and the supramolecular interactions allow them to extend to higher dimensional architectures. It may be believed that low-dimensional coordination polymers, such as the $[Ag(H_2cpop)(bpy)]_n$ described here, are good choices for the construction of novel porous materials through supramolecular interactions. Additionally, **1** exhibit very intense luminescence at room temperature.

Acknowledgements

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Appendix A. Supplementary material

CCDC 654624 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.10.007.

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[21] A mixture of $AgNO_3$ (0.034 g, 0.2 mmol), 4,4′-oxydiphthalic anhydride (0.0310 g, 0.1 mmol), 4,4′-bpy (0.0156 g, 0.1 mmol) and NaOH (0.04 g, 0.1 mmol), and water (8 mL) was stirred for 30 min in air, then sealed in a 25 mL Telfon-lined stainless steel container, which was heated to 160 °C for 96 h. Then cooling to 80 °C at a rate of $5\,^{\circ}C\,h^{-1}$ and kept to 80 °C for 10 h, after cooling to room temperature at a rate of $8\,^{\circ}C\,h^{-1}$. Yellow rod crystals were obtained in ca. 56% yield (based on H_4odp). Anal. Calc. for $C_{25}H_{17}AgN_2O_7$: C, 53.12; H, 3.03; N, 4.96%. Found: C, 53.14; H, 3.04; N, 4.92%. IR (KBr cm^{-1}): 3404m, 3047w, 1681w, 1565s, 1409s, 1372m, 1268m, 1228m, 1140w, 1068w, 841m, 626w.

[22] *Crystallographic data for* **1**: $C_{25}H_{17}AgN_2O_7$ (Mr = 565.28), 296(2) K, monoclinic, $P2_1/n$, $a = 11.4086(11)$ Å, $b = 7.5988(7)$ Å, $c = 25.514(2)$ Å, $\alpha = 90°$, $\beta = 99.312(1)°$, $\gamma = 90°$, $Z = 4$, $V = 2182.7(4)$, $D_{calc} = 1.720$, $\mu = 0.976\ mm^{-1}$. Reflections collected: 10,569; Unique reflections: 3852 [$R_{int} = 0.0315$]. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0443$, $wR_2 = 0.1013$ (R for all data: $R_1 = 0.0654$, $wR_2 = 0.1118$). GOF on $F^2 = 1.028$. The structure was solved by direct methods and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 program [37]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically.

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