

Rapid communication

# Hydrothermal synthesis, crystal structure and properties of a 3D-framework polyoxometalate assembly: [Ag(4,4'-bipy)](OH){[Ag(4,4'-bipy)]<sub>2</sub>[PAgW<sub>12</sub>O<sub>40</sub>]} · 3.5H<sub>2</sub>O

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Received 22 November 2005; received in revised form 2 February 2006; accepted 16 March 2006  
Available online 22 March 2006

## Abstract

A 3D framework assembly based on the Keggin tungstophosphate POM with silver (I) transition metal and N-ligand organic moiety and of formula [Ag(4,4'-bipy)](OH){[Ag(4,4'-bipy)]<sub>2</sub>[PAgW<sub>12</sub>O<sub>40</sub>]} · 3.5H<sub>2</sub>O (**1**) (bipy = bipyridine) has been synthesized by hydrothermal method and structurally characterized. The crystal of **1** belongs to triclinic, space group *P*-1, *M*<sub>r</sub> = 3857.27, *a* = 10.2741(3) Å, *b* = 11.3723(4) Å, *c* = 14.0161(5) Å, *α* = 85.7249(5)°, *β* = 72.8795(5)°, *γ* = 79.9543(5)°, *V* = 1540.61(9) Å<sup>3</sup>, *Z* = 1, *D*<sub>calc</sub> = 4.158 Mg m<sup>-3</sup>. The final statistics based on *F*<sup>2</sup> are *GOF* = 1.045, *R*<sub>1</sub> = 0.0326 and *wR*<sub>2</sub> = 0.0843 for *I* > 2σ(*I*). X-ray diffraction analysis revealed that the molecular structure of **1** consists of a neutral fragment {[Ag<sup>I</sup>(4,4'-bipy)]<sub>2</sub>[PAg<sup>I</sup>W<sub>12</sub>O<sub>40</sub>]}<sup>+</sup>, [Ag<sup>I</sup>(4,4'-bipy)]<sup>+</sup> cation, hydroxide anion and lattice water molecules. The {[Ag<sup>I</sup>(4,4'-bipy)]<sub>2</sub>[PAg<sup>I</sup>W<sub>12</sub>O<sub>40</sub>]} subunits are interconnected through Ag(I) with bipyridine ligands, both surface bridging and terminal oxygen atoms of polyoxoanions (POMs) to represent a novel three-dimensional (3D) polymer with 1D elliptic channels. Meanwhile, the [Ag<sup>I</sup>(4,4'-bipy)]<sup>+</sup> cations are also linked each other to form 1D chains, and embedded in 1D elliptic channels.

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**Keywords:** Polyoxometalate; N ligand; Silver; Organic–inorganic hybrids; Supramolecular chemistry

## 1. Introduction

The widespread contemporary interest in the design and syntheses of inorganic–organic hybrid materials reflects their intriguing structural features as well as their extensive theoretical and practical application in the fields of molecular absorption, catalysis and electron-conductive, optical and magnetic materials [1–14]. The use of polyoxometalates (POMs) as discrete building blocks for the syntheses of extensive inorganic–organic hybrid materials has attracted considerable interest in recent years [15–28]. The most common observed geometries of POM anionic clusters are the Keggin and Dawson heteropolyanions. Furthermore, a significant amount of efforts have

been given to the decoration of POMs with transition metals and/or organic species. To date, many zero-dimensional (0D) discrete clusters [2–5] and 1D chains [4–16] have been reported. Recently, a few 2D layers [4,5,13–22] and 3D frameworks [17–19,23–25] have also been synthesized. Exploring high-dimensional open frameworks based on POMs with metal-organic moieties still remains a challenge.

POMs based on Keggin, Dawson or Anderson frameworks transition metals and/or organic moieties have received great attention. It is specially noticeable that the transition metal silver(I) can exist in several possible coordination environments: linear, T-shaped and tetrahedral, etc. For example, C.L. Hill group reported a novel compound Ag<sub>5</sub>PV<sub>2</sub>Mo<sub>12</sub>O<sub>40</sub>, which involves two PV<sub>2</sub>Mo<sub>12</sub>O<sub>40</sub><sup>5-</sup> units bridged by two Ag(I) ions bonded to both bridging and terminal oxygen atoms of the POM units

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[3]. Guoyou Luan et al. have synthesized a  $\alpha$ -Keggin-type POM coordinated to four silver complex moieties via the surface bridging oxygen atoms:  $\{\text{PW}_9\text{V}_3\text{O}_{40} [\text{Ag}(2,2'\text{-bipy})]_2 [\text{Ag}_2(2,2'\text{-bipy})_3]_2\}$  [2]. Zhangang Han and his co-workers reported a 1D double-chain POM with pendant ligands and of formula  $\{[\text{Ag}_2(\text{bppy})_3][\text{Ag}(\text{bppy})_2][\text{Ag}(\text{bppy})]_2\text{PW}_{11}\text{Co}(\text{bppy})\text{O}_{39}\} \cdot 2\text{H}_2\text{O}$  [1]. In addition,  $\text{Ag}_2[\text{Mo}_{12}\text{O}_{16}(\text{AsC}_6\text{H}_4\text{-4NH}_2)_2(\text{AsC}_6\text{H}_4\text{-4NH}_3)_2] \cdot 2\text{H}_2\text{O} \cdot 8\text{CH}_3\text{CN}$ , organically modified POM clusters connected with silver by terminal oxygen atoms into 1D chains, was reported [26]. Also,  $[\text{Ag}_6(\text{PMo}_{10}\text{V}_2\text{O}_{40})](\text{CH}_3\text{COO}) \cdot 8\text{H}_2\text{O}$  is a 3D macro-cationic polyoxometallic Keggin complex. All the Keggin units are interlinked by Ag(I) through O–Ag–O bridging bonds [29]. Additionally, Haiyan An and coworkers reported three extended architectures based on Anderson-type POMs and silver coordination complexes [13].

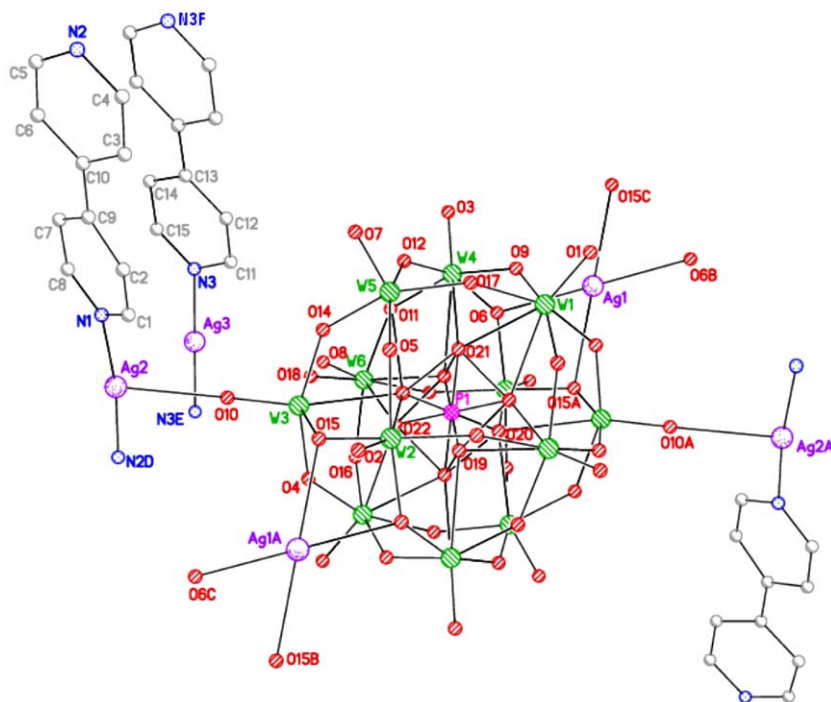
In recent years, our research group has been devoting to synthesize inorganic–organic hybrid POMs. On the one hand, in view of the ability of silver(I) to coordinate readily to both hard and soft donor centers [1], we choose Ag(I) as the transition metal to fabricate high-dimensional structure POMs. On the other hand, the introducing of organic template reagent may result in some interesting structures. 4,4'-bipyridine (bipy) was selected as the organic moiety in our research: (a) it is a potential linear bifunctional “spacer” or “rod” ligand; (b) it can provide hydrogen bond donors and acceptors; (c) its aromatic rings may form  $\pi \cdots \pi$  interactions. Based on the above two aspects, we attempted to synthesize some new solid hybrid compounds based on Ag/bipy/POMs system. Herein, we report the hydrothermal synthesis and single crystal structure analysis

of the novel compound  $[\text{Ag}(4,4'\text{-bipy})](\text{OH})\{[\text{Ag}(4,4'\text{-bipy})]_2[\text{PAgW}_{12}\text{O}_{40}]\} \cdot 3.5\text{H}_2\text{O}$  (**1**), where the  $\{[\text{Ag}^{\text{I}}(4,4'\text{-bipy})]_2[\text{PAg}^{\text{VI}}\text{W}_{12}\text{O}_{40}]\}$  subunits are interconnected through Ag(I) with bipyridine ligands, surface bridging and terminal oxygen atoms of polyoxoanions (POMs) to represent a novel 3D polymer with 1D elliptic channels. Meanwhile, the  $[\text{Ag}^{\text{I}}(4,4'\text{-bipy})]^+$  cations are also linked each other to form a 1D chains, and embedded in the 1D elliptic channels. To our knowledge, the compound represents the first characterized compound containing a 3D structure based on Ag/POMs/bipy linked through Ag(I) with both surface bridging and terminal oxygen atoms of POMs.

## 2. Results and discussion

### 2.1. Structure description

Single crystal X-ray diffraction analysis revealed that **1** contains one  $[\text{Ag}(4,4'\text{-bipy})]^+$  complex cation, one  $\{[\text{Ag}(4,4'\text{-bipy})]_2[\text{PAgW}_{12}\text{O}_{40}]\}$  inorganic–organic hybrid POM, one oxyhydrogen anion, and three and a half lattice water molecules. As shown in Fig. 1, a significant aspect of **1** is that, there exist three crystallographic independent silver(I) centers, which have different coordination environments with four-coordinate Ag1 center, three-coordinate Ag2 center and two-coordinate Ag3 center. The Ag1 atom is defined by four surface bridging oxygen atoms (O6, O6B, O15A and O15C) of two adjacent Keggin anions to show a planar parallelogram coordination geometry. The bond distances of Ag1–O6 and Ag1–O15A are 2.446(8) and



2.532(9) Å, respectively. The bond angle for O6B–Ag1–O6 is 180.0°. The Ag1 atom is exactly on the plan of the four surface bridging oxygen atoms (O6, O6B, O15A and O15C). Additionally, the proximity of the third oxygen atom (O9) from the polyoxoanion with Ag1 atom (Ag1⋯O9 = 2.805 Å), which is shorter than the sum of the Van der Waals radii of Ag and O (3.20 Å) [30], implies weak binding between Ag1 and additional two oxygen atoms (O9) from two adjacent POMs, and leads to the formation of distorted octahedral coordination geometry around Ag1 center. The three coordinated Ag2 center is ligated by two nitrogen atoms (N1 and N2D) from two 4,4'-bipy ligands and one terminal oxygen atom (O10) of the Keggin anion to give distorted “T-shape” geometry environment with the bond lengths of 2.161(7), 2.143(7) and 2.638 Å for Ag2–N1, Ag2–N2D and Ag2–O10, respectively. The bond angle for N2D–Ag2–N1 is 172.7(3)°. Additionally, the weak interaction distance of Ag2⋯O8 (equivalent oxygen atom of adjacent polyoxoanion) is 2.760 Å, which implies the other coordination fashion with “wing-shape” around Ag2 center. The third kind of silver center Ag3, possesses two coordination sites occupied by two nitrogen atoms from two 4,4'-bipy with the distance Ag3–N3 of 2.131(7) Å. The bond angle for N3E–Ag3–N3 is 180.00°. Therefore, Ag3 exhibits a linear coordination environment.

The heteropolyanion  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  unit exhibits the well-known Keggin-type structure, which is formed from 12  $\text{WO}_6$  octahedron and one  $\text{PO}_4$  tetrahedron. The central P atom is surrounded by a cube of eight oxygen atoms with site half occupied. The P–O distances are in the range of 1.495–1.582 Å. While the angles vary from 106.2(6) to 114.6(7)°. The W–O distances can be divided into three groups:  $\text{W–O}_t$  1.626(10)–1.691(8) Å,  $\text{W–O}_{b/c}$  1.859(10)–1.988(9) Å, and  $\text{W–O}_a$  2.419(11)–2.491(12) Å. Additionally, in the Keggin unit  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ , both W1 and W2 atoms exist positional disorder with site occupancy of one half for W1A and W1B, 0.15 and 0.85 for W2A and W2B, respectively. It is interesting that the Keggin units are interlinked by Ag1 atom to form 1D linear polymer chain

$\{\text{PAgW}_{12}\text{O}_{40}\}_n^{2n-}$  along *a*-axis through {AgO4} spacer (Fig. 2). In addition, the Ag2 atoms are bound with 4,4'-bipy to form 1D polymer chain  $\{\text{Ag}(4,4' - \text{bipy})\}_n^{n+}$  along the *b*-axis (Fig. 3). These 1D  $\{\text{Ag}(4,4' - \text{bipy})\}_n^{n+}$  polymer chains interact with the above-mentioned  $\{\text{PAgW}_{12}\text{O}_{40}\}_n^{2n-}$  chains (see Fig. 2) into a 3D framework  $\{[\text{Ag}(4,4' - \text{bipy})]_2[\text{PAgW}_{12}\text{O}_{40}]\}_n$  with 1D elliptic channels of size about  $6.6308 \times 11.3722$  Å (based on nuclei separation) through coordinated bonds (Ag2–O10) and weak binding interactions (Ag2⋯O8) (Fig. 3), while chains  $\{\text{Ag}(4,4' - \text{bipy})\}_n^{n+}$  of Ag3 are embedded in the 1D elliptic channels formed by chains of Ag2 and chains of Ag1–POMs along the *b*-axis (Fig. 4).

As shown in Fig. 5, there are significant  $\pi \cdots \pi$  stacking interactions of pyridine rings linked to Ag2 and Ag3 with the interplane separations of 3.455–3.825 Å. The adjacent chains exhibit less-favorable head-to-head aromatic ring  $\pi \cdots \pi$  interactions (see Fig. 5 top section) [27]. The strong  $\pi \cdots \pi$  interactions between two types of  $\{\text{Ag}(4,4' - \text{bipy})\}_n^{n+}$  chains enable the Ag3–bipy chains firmly embedded in the 1D elliptic channels (see Fig. 4). The two adjacent silver–silver distance of Ag2⋯Ag3 (3.534 Å) is longer than the Van der Waals contact distances (3.44 Å) of silver [31]. Meanwhile, adjacent Ag2–bipy chains also exhibit strong  $\pi \cdots \pi$  interactions (see Fig. 5 bottom section), where the distances are of 3.696–3.872 Å. Unlike the interactions between Ag2 and Ag3 chains, they are involved in face-to-face interactions in a favorable “head-to-tail” fashion [27]. As aforementioned, 4,4'-bipy is employed in our studies for its versatile coordination ability and ability for providing supramolecular interactions [28]. Compound **1** shows that we have successfully utilized the reaction of Ag(I) salt and 4,4'-bipy to form 1D linear Ag–bipy chains; then, these chains are further self-assembled to 3D supramolecular frameworks via coordination bonds or supramolecular interactions with tungstophosphate units.

Besides  $\pi \cdots \pi$  interactions of pyridine rings, the crystal structure of **1** is further strengthened by hydrogen bonding. The crystallographic water molecules and oxyhydrogen

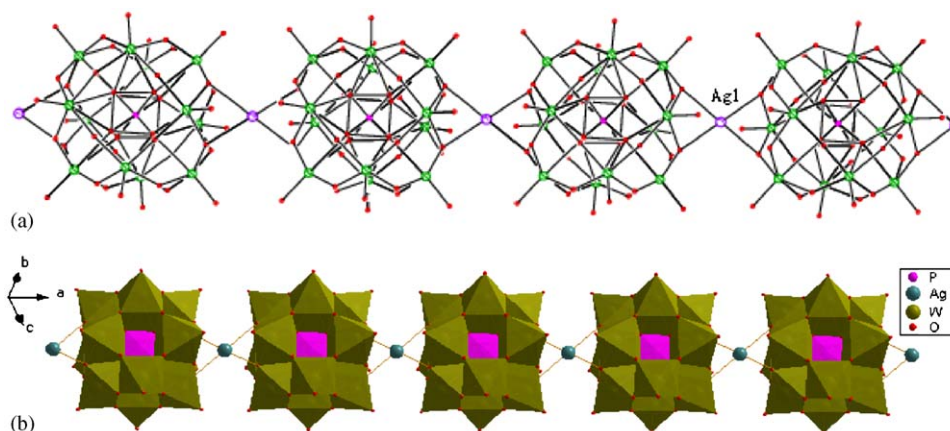


Fig. 2. (a) View of 1D Ag1–POMs polymer chain along the *a*-axis based on the bonding of Ag atoms with surface oxygen atoms of POMs; (b) polyhedral and ball-and-stick representation of 1D polymer chain Ag1–POMs.

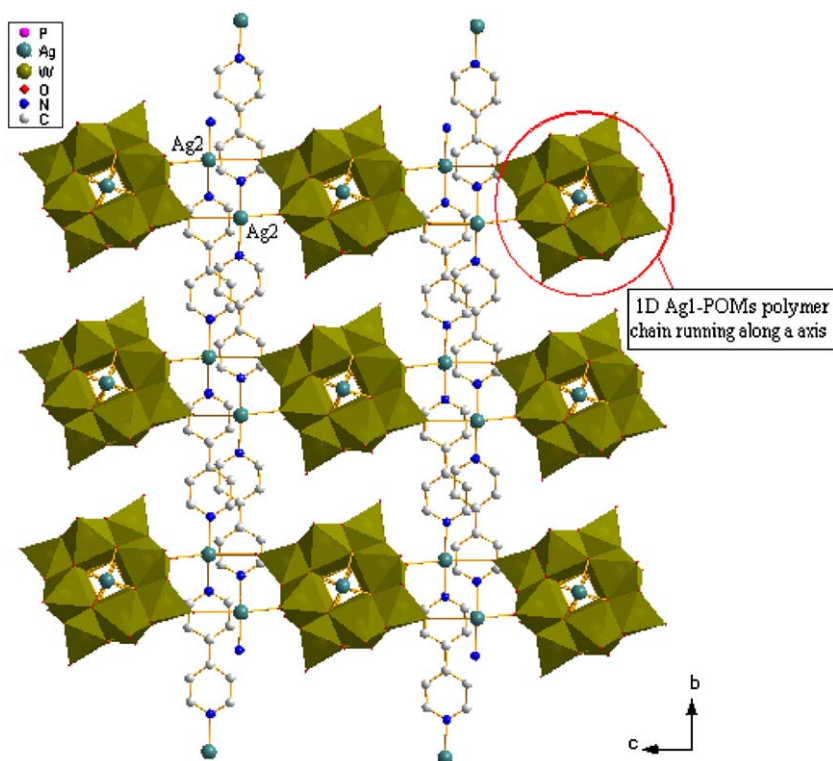


Fig. 3. Three-dimensional framework architecture of compound **1** projected down the *a*-axis. Water molecules, oxyhydrogen anion and H atoms have been omitted for clarity.

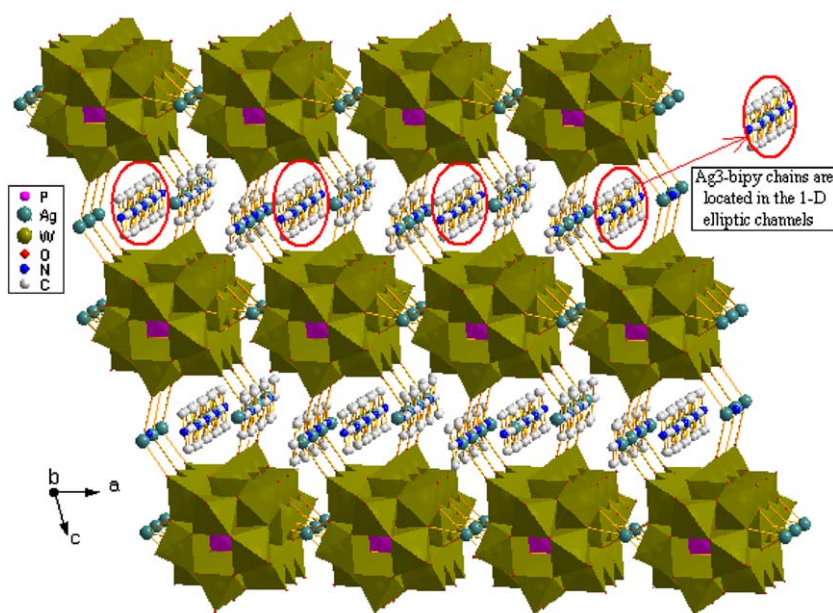


Fig. 4. Three-dimensional framework architecture of compound **1** viewed slightly off the *b*-axis showing that 1D Ag<sub>3</sub>-bipy chains are arranged in the 1D elliptic channels of the framework structure. Water molecules, oxyhydrogen anion and H atoms have been omitted for clarity.

anions are located between  $\{P\text{AgW}_{12}\text{O}_{40}\}_n^{2n-}$  chains. They have multipoint hydrogen bonding interactions with the surface oxygen atoms of the Keggin units and between themselves. The representing short distances [Å] are: O5...O1W 2.823, O7...O1W 2.644, O16...O1W 2.507, O17...O1W 2.356, O2...O2W 2.709, O1...O2A

2.554, O17...O3W 2.842, O5...O3W 2.800, O1W...O3W 2.174, O2W...O3W 2.606, O3W...O4W 2.319. Also, there are weak supramolecular interactions between the surface oxygen atoms of the POM units and the organic ligands with the C–H...O distances ranging from 2.384 to 2.563 Å.

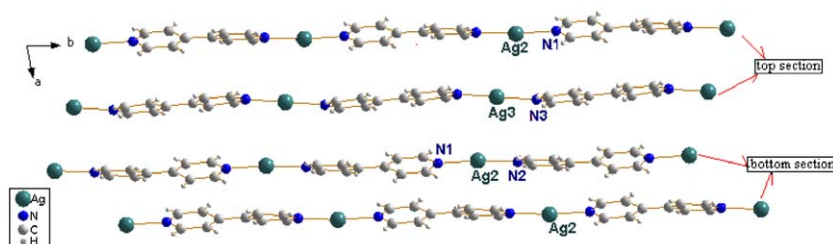


Fig. 5. Packing diagram of Ag-bipy chains projected down  $c$ -axis, which shows the arrangement and  $\pi \cdots \pi$  interactions of two types of Ag-bipy infinite chains.

To be noted, the reaction stoichiometry was 1:1:1 for Ag:POM:bipy, yet the product is 4:3:1. We have tried to produce a pure product by altering the starting ratio, but failed. Additionally,  $\text{CH}_3\text{CN}$  was added to the reaction mixture as a mineralizer. We also have experimented with the Cu(II), Ni(II), Mn(II) transition metal salts under similar reaction conditions. However, no crystal compounds were obtained. This confirmed that the transition metals perform a very important role in constructing 3D open frameworks due to their different natures.

Structures based on tungstophosphate units linked with silver atoms by bridging oxygen atoms and decorated with bipyridine moieties are rare, though the decoration of POMs with transition metals and organic moieties has been one of the thematic issues in POM.  $\{\text{PW}_9\text{V}_3\text{O}_{40}[\text{Ag}(2,2'\text{-bipy})_2[\text{Ag}_2(2,2'\text{-bipy})_3]_2]\}$  (**2**) [2] and  $\{[\text{Ag}_2(\text{bppy})_3][\text{Ag}(\text{bppy})_2][\text{Ag}(\text{bppy})_2]\text{PW}_{11}\text{Co}(\text{bppy})\text{O}_{39}\} \cdot 2\text{H}_2\text{O}$  (**3**) [1] are characterized recently. Compared to **2** and **3**, the striking differences among them lie in, (i) the building units, (ii) the types of silver coordination environments and (iii) the dimension of their structure. The POM units for **1**, **2** and **3** are normal, V-trisubstituted and Co-monosubstituted Keggin tungstophosphate units, respectively. Besides, their organic moieties are based on different ligands 4,4'-bipy, 2,2'-bipy and bppy (bppy = 5-(4-bromophenyl)-2-(4-pyridinyl) pyridine), which can provide different linkages. As a consequence, the silver atoms exist various coordination environments. There are three types of silver coordination sites in **1** as earlier described. Compound **2** exhibits three kinds of Ag atoms in dissimilar coordination fashions [2]. In **3**, five silver atoms have different environments: four-coordinate Ag(1) and Ag(2) and three-coordinate Ag(3), Ag(4) and Ag(5) [1]. It is notable that all of them confirm the multi-coordination ability of silver(I) atom. Besides, the difference in dimension (3D, 0D and 1D for compounds **1–3**, respectively) may be ascribed to multifactors of synthesis conditions such as reaction time, reaction temperature, organic templates, mineralizers and so on.

The bond valence sum (BVS) calculations [32] indicated that all Ag sites are in the +1 oxidation state, and all W sites are in the +6 oxidation state in compound **1**.

#### 2.1.1. FT-IR spectrum and fluorescence spectrum

The IR spectrum of **1** exhibits characteristic peaks of the Keggin anion at 939, 888 and  $807\text{ cm}^{-1}$ , attributable to

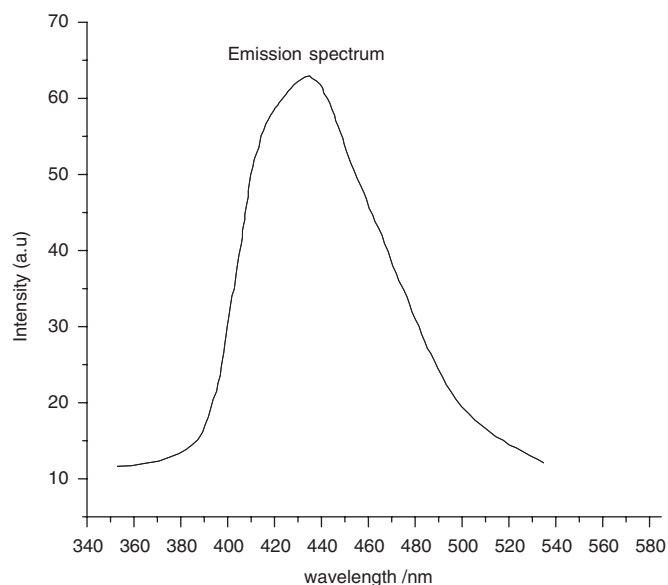


Fig. 6. Solid-state emission spectrum of compound **1** at room temperature.

$\nu(\text{W}=\text{O}_t)$ ,  $\nu(\text{W}-\text{O}_b-\text{W})$  and  $\nu(\text{W}-\text{O}_c-\text{W})$  ( $\text{O}_t$  = terminal oxygen,  $\text{O}_b$  = bridged oxygen of two octahedral sharing a corner,  $\text{O}_c$  = bridged oxygen of two octahedral sharing an edge), respectively. The informative bands at 1076 and  $1047\text{ cm}^{-1}$  can ascribe to the P–O stretching vibrations in **1**. Comparing with a typical value of about  $1067\text{ cm}^{-1}$  for the Keggin anion [33,34], the P–O stretch in **1** splits into two bands because of the lower symmetry than that in the  $T_d$  parent Keggin anion. The bands in the  $1620\text{--}1200\text{ cm}^{-1}$  region are due to characteristic vibration of 4,4'-bipy groups.

The emission spectrum of compound **1** in solid state at room temperature is depicted in Fig. 6. Compound **1** exhibits intense photoluminescence with an emission maximum at ca. 435 nm upon excitation at ca. 272 nm. Whereas the 4,4'-bipy ligand shows a fluorescent emission band at  $\lambda_{\text{max}} = 437\text{ nm}$  ( $\lambda_{\text{excitation}} = 272\text{ nm}$ ) [35]. The emission spectrum of compound **1** may be attributed to an intra-ligand emission state instead of ligand-to-metal charge transfer (LMCT) in nature. The result suggests that compound **1** may be a potential photoactive material.

### 3. Conclusion

A 3D framework assembly based on the Keggin tungstophosphate POM with silver(I) transition metal and bipyridine organic moieties has been synthesized by hydrothermal method and structurally characterized. The success in synthesizing compound **1** provided a novel example of the utilities of Keggin tungstophosphate clusters as precursors and silver ions as bridges in the presence of organic ligands for constructing extended solid-state materials. Other physical properties investigations of compound **1** are underway.

### 4. Experimental section

#### 4.1. Materials and physical measurements

All analytical grade chemicals and solvents were purchased commercially and used without further purification. Infrared spectrum was measured on a Nicolet AVATAR 360 FT-IR spectrometer using KBr pellets in the 4000–400  $\text{cm}^{-1}$  region. Emission/excitation spectrum was recorded on a RF-540 fluorescence spectrophotometer. Elemental analysis was carried out on an EA1112 CHNS elemental analyzer.

#### 4.2. Preparation of compound **1**

A mixture of  $\text{AgNO}_3$  (0.25 mmol),  $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O}$  (0.25 mmol), 4,4'-bipy (0.25 mmol),  $\text{CH}_3\text{CN}$  (0.5 mL) and  $\text{H}_2\text{O}$  was sealed in a 15 mL Teflon-lined stainless steel autoclave with about 60% filling. The pH value of the mixture was adjusted to 8.5 with 1 mol/L NaOH solution. The resulting mixture was heated at a rate of ca. 100  $^\circ\text{C}/\text{h}$  to 160  $^\circ\text{C}$  and held at this temperature for 3 days. Subsequently the autoclave was cooled at a rate of ca. 3  $^\circ\text{C}/\text{h}$  to 140  $^\circ\text{C}$  and held at this temperature for 2 days. Finally, it was cooled at a rate of ca. 3  $^\circ\text{C}/\text{h}$  to room temperature. The resulting light-brown plate crystals of compound **1** along with amorphous powders were filtered off and washed with water, then dried at ambient temperature. The crystals were collected mechanically. Anal. calc. (%) for  $\text{C}_{30}\text{H}_{32}\text{O}_{44.50}\text{N}_6\text{P}\text{Ag}_4\text{W}_{12}$ : C, 9.34; H, 0.83; N, 2.18; P, 0.80; W, 57.20; Ag, 11.19. Found (%): C, 9.42; H, 0.81; N, 2.24; P, 0.73; W, 57.30; Ag, 11.02.

#### 4.3. X-ray crystallographic study

A single crystal of **1** with the dimensions 0.27  $\times$  0.67  $\times$  0.76 mm was glued on a glass fiber. Data were collected on a Bruker's SMART-CCD area detector with graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71703 \text{ \AA}$ ) at 293 K. Data were corrected for Lorentz and polarization

Table 1  
Selected bond lengths ( $\text{\AA}$ ) and angles (deg) for compound **1**

|                   |           |                   |           |                  |           |
|-------------------|-----------|-------------------|-----------|------------------|-----------|
| P(1)–O(21)        | 1.495(11) | P(1)–O(19)        | 1.511(12) | P(1)–O(22)       | 1.510(13) |
| P(1)–O(20)        | 1.582(11) | Ag(1)–O(6)        | 2.446(8)  | Ag(1)–O(15)A     | 2.532(9)  |
| Ag(2)–N(2)D       | 2.143(7)  | Ag(2)–N(1)        | 2.161(7)  | Ag(3)–N(3)       | 2.131(7)  |
| W(1)–O(1)         | 1.650(10) | W(1)–O(4)A        | 1.913(8)  | W(1)–O(16)A      | 1.919(9)  |
| W(1)–O(17)        | 1.943(9)  | W(1)–O(9)         | 1.950(9)  | W(1)–O(21)       | 2.469(10) |
| W(2)–O(2)         | 1.626(10) | W(2)–O(6)A        | 1.988(9)  | W(2)–O(5)        | 1.946(11) |
| W(2)–O(13)A       | 1.924(11) | W(2)–O(15)        | 1.980(12) | W(3)–O(18)       | 1.927(9)  |
| W(3)–O(4)         | 1.883(8)  | W(3)–O(10)        | 1.660(8)  | W(3)–O(15)       | 1.859(10) |
| W(3)–O(14)        | 1.931(9)  | W(4)–O(3)         | 1.673(7)  | W(4)–O(21)       | 2.476(12) |
| W(4)–O(6)         | 1.874(7)  | W(4)–O(11)        | 1.906(7)  | W(4)–O(12)       | 1.908(7)  |
| W(4)–O(9)         | 1.887(8)  | W(5)–O(5)         | 1.865(9)  | W(5)–O(7)        | 1.691(8)  |
| W(5)–O(12)        | 1.913(8)  | W(5)–O(17)        | 1.870(9)  | W(5)–O(14)       | 1.886(9)  |
| W(6)–O(13)        | 1.861(8)  | W(6)–O(11)        | 1.906(9)  | W(6)–O(16)       | 1.911(9)  |
| W(6)–O(18)        | 1.918(8)  | W(6)–O(22)        | 2.486(12) | W(6)–O(8)        | 1.681(8)  |
| O(19)–W(4)A       | 2.462(13) | O(19)–W(6)A       | 2.491(12) | O(20)–W(5)A      | 2.435(12) |
| O(20)–W(2)A       | 2.458(11) | O(20)–W(3)A       | 2.476(12) | O(22)–W(1)A      | 2.419(11) |
| O(21)–P(1)–O(19)  | 114.6(7)  | O(21)–P(1)–O(22)  | 110.9(6)  | O(19)–P(1)–O(20) | 106.2(6)  |
| O(6)–Ag(1)–O(15)C | 115.2(4)  | O(6)–Ag(1)–O(15)A | 64.8(4)   | N(2)D–Ag(2)–N(1) | 172.7(3)  |
| O(1)–W(1)–O(16)A  | 98.9(6)   | O(1)–W(1)–O(4)A   | 99.9(6)   | O(9)–W(1)–O(21)  | 64.4(4)   |
| O(1)–W(1)–O(21)   | 159.4(6)  | O(1)–W(1)–O(17)   | 101.5(5)  | O(4)A–W(1)–O(17) | 158.4(5)  |
| O(2)–W(2)–O(13)A  | 102.8(5)  | O(15)–W(2)–O(6)A  | 84.6(4)   | O(2)–W(2)–O(5)   | 100.8(6)  |
| O(13)A–W(2)–O(5)  | 89.2(5)   | O(5)–W(2)–O(6)A   | 157.6(5)  | O(5)–W(2)–O(15)  | 88.3(4)   |
| O(18)–W(3)–O(14)  | 86.7(5)   | O(10)–W(3)–O(15)  | 104.9(6)  | O(15)–W(3)–O(18) | 157.6(6)  |
| O(3)–W(4)–O(21)   | 160.9(5)  | O(9)–W(4)–O(21)   | 65.0(4)   | O(6)–W(4)–O(11)  | 88.1(3)   |
| O(9)–W(4)–O(12)   | 88.6(3)   | O(5)–W(5)–O(12)   | 157.2(6)  | O(7)–W(5)–O(17)  | 105.3(5)  |
| O(5)–W(5)–O(17)   | 86.0(4)   | O(18)–W(6)–O(22)  | 65.2(4)   | O(8)–W(6)–O(22)  | 159.1(4)  |
| O(8)–W(6)–O(11)   | 99.7(5)   | O(13)–W(6)–O(16)  | 86.4(4)   |                  |           |

Symmetry transformations used to generate equivalent atoms: (A)  $-x, -y+1, -z$ ; (C)  $x-1, y, z$ ; (D)  $x, y+1, z$ .

effects. Data reduction was carried out using the SAINT suite of programs [36] and the intensities were corrected for absorption with the assistance of the program SADABS [37]. The structure was studied by direct methods and refined by full-matrix least-squares using the SHELXTL package [38]. All non-hydrogen atoms except for O4W were refined anisotropically. All hydrogen atoms were placed in idealized positions, refined as riding atoms assigned the same isotropic temperature factors and included in the structure factor calculations. Those hydrogen atoms attached to lattice water molecules and oxyhydrogen anions were not located, however. Selected bond lengths (Å) and angles (deg) for compound 1 are listed in Table 1. Crystal data:  $C_{30}H_{32}Ag_4N_6O_{44.50}PW_{12}$ , triclinic,  $P-1$ ,  $Mr = 3857.27$ ,  $a = 10.2741(3)$  Å,  $b = 11.3723(4)$  Å,  $c = 14.0161(5)$  Å,  $\alpha = 85.7249(5)^\circ$ ,  $\beta = 72.8795(5)^\circ$ ,  $\gamma = 79.9543(5)^\circ$ ,  $V = 1540.61(9)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_{\text{calc}} = 4.158$  Mg m<sup>-3</sup>,  $\mu = 23.665$  mm<sup>-1</sup>, crystal size:  $0.270 \times 0.670 \times 0.760$  mm. The final statistics based on  $F^2$  are  $GOF = 1.045$ ,  $R_1 = 0.0326$  and  $wR_2 = 0.0843$  for  $I > 2\sigma(I)$ . CCDC-284034 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; Fax: (internat.) +44 1223/336 033; <mailto:deposit@ccdc.cam.ac.uk>].

## Acknowledgments

The authors are thankful for the financial supports from the Natural Science Foundation of Fujian Province, China (E0310016) and the Education Commission Foundation of Fujian Province, China (JA02176).

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