



# The design, syntheses and characterizations of a series of compounds based on polyoxometalates and silver complexes



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## ABSTRACT

Seven new hybrid compounds based on polyoxometalates (POMs) and silver complexes, namely  $[\text{Ag}(2,2'\text{-bpy})_3]\{[\text{H}_{2.5}\text{BW}_{12}\text{O}_{40}][\text{Ag}(2,2'\text{-bpy})_2(\text{H}_2\text{O})]\}_2$  (**1**),  $[\text{Ag}(2,2'\text{-bpy})_3][\text{Ag}(2,2'\text{-bpy})_2][\text{H}_2\text{P}_2\text{W}_{18}\text{O}_{62}]\cdot 6\text{H}_2\text{O}$  (**2**),  $[\text{Ag}(2,2'\text{-bpy})_3]_2[\text{Ag}(2,2'\text{-bpy})_2][\text{H}_3\text{PW}_{11}\text{AgO}_{39}(\text{H}_2\text{O})]\cdot 4.75\text{H}_2\text{O}$  (**3**),  $[\text{Ag}(1,10\text{-phen})_2]_2\{[\text{Mo}_8\text{O}_{26}][\text{Ag}(1,10\text{-phen})_2]\}_2$  (**4**),  $[\text{Ag}(2,2'\text{-bpy})_3]_3[\text{Ag}(2,2'\text{-bpy})_2][\text{H}_{2.5}\text{BW}_{12}\text{O}_{40}]\cdot (4,4'\text{-bpy})_3$  (**5**),  $[\text{Ag}(1,10\text{-phen})_2]_3[\text{PMo}_{12}\text{O}_{40}]$  (**6**) and  $[\text{Ag}(2,2'\text{-bpy})_3]_2[\text{H}_4\text{P}_2\text{W}_{18}\text{O}_{62}]\cdot (2,2'\text{-bpy})_2\cdot 2\text{H}_2\text{O}$  (**7**) have been synthesized and characterized. The seven compounds can be classified into four groups based on transition metal complexes and/or dissociated organic moieties in them: (I) compounds based on POMs and two types of silver complexes, compounds **1–4** belong to this group; (II) compounds based on POMs, two types of silver complexes and organic moieties, compound **5** belongs to this group; (III) compounds based on POMs and silver complexes, compound **6** belongs to this group; (IV) compounds based on POMs, silver complexes and organic moieties, compound **7** belongs to this group.

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## 1. Introduction

The design and synthesis of organic–inorganic hybrid materials based on polyoxometalates (POMs) have become a significant research area over recent years, because of their intriguing architectures and properties as well as potential applications in catalysis, magnetism, electrochemistry, photochemistry and sensitive devices [1]. One of the most successful assembly methods for organic–inorganic hybrid materials based on POMs involves secondary transition metal species, giving rise to a number of hybrid materials with diverse structures and properties [2].

POMs can act as unusual effective ligands to coordinate to various secondary transition metal ions because of their high electronic density [3]. Many complexes constructed from different POMs and secondary transition metal species have been synthesized [4]. On the other hand, Ag(I), as a  $d^{10}$  transition metal, possesses high affinity for N and O donors, flexible coordination number of two to seven in covalent complexes, and versatile geometries, such as “linear”, “seesaw”, “square pyramidal”, and “trigonal bipyramidal” coordination geometries, and so forth [5].

These features make Ag(I) often to be used as metallic linkers and good candidates in constructing metal organic frameworks. And recently, several research groups devote to the area of hybrids based on POMs and Ag(I) species and a large number of organic–inorganic materials based on Ag species and different POMs have been reported [2,4,6–10].

Up to now, many different preparation methods have been used to prepare organic–inorganic materials based on Ag species and different POMs, of which, the hydrothermal method has been known as a method to grow highly crystalline and large-size crystals under a relatively low temperature. The synthesis under hydrothermal conditions is a powerful way to prepare hybrids based on polyoxometalates and transition metal complexes (TMCs). Using this preparation method, a large number of hybrids based on Ag species and different POMs have been reported [9a–r].

Using the hydrothermal method, organic ligands play a more key role in the formation of complexes owing to their different steric effect, soft-rigid degree, and structure [11]. 2,2'-Bipyridine and 1,10'-phenanthroline are among the most popular ligands used in organic–inorganic hybrid materials. However, organic–inorganic materials based on POMs, silver and organic ligands (2,2'-bipyridine and 1,10'-phenanthroline) are relatively unexplored [9a,12]. This inspired us to use these ligands to synthesize hybrids and to study the effect on the structural dimension.

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Herein, we report the syntheses and characterizations of seven new compounds:  $[\text{Ag}(2,2'\text{-bpy})_3][\text{H}_{2.5}\text{BW}_{12}\text{O}_{40}][\text{Ag}(2,2'\text{-bpy})_2(\text{H}_2\text{O})]_2$  (**1**),  $[\text{Ag}(2,2'\text{-bpy})_3][\text{Ag}(2,2'\text{-bpy})_2][\text{H}_2\text{P}_2\text{W}_{18}\text{O}_{62}]\cdot 6\text{H}_2\text{O}$  (**2**),  $[\text{Ag}(2,2'\text{-bpy})_3]_2[\text{Ag}(2,2'\text{-bpy})_2][\text{H}_3\text{PW}_{11}\text{AgO}_{39}(\text{H}_2\text{O})]\cdot 4.75\text{H}_2\text{O}$  (**3**),  $[\text{Ag}(1,10\text{-phen})_2]_2[\text{Mo}_8\text{O}_{26}][\text{Ag}(1,10\text{-phen})_2]_2$  (**4**),  $[\text{Ag}(2,2'\text{-bpy})_3]_3[\text{Ag}(2,2'\text{-bpy})_2]_2[\text{H}_{2.5}\text{BW}_{12}\text{O}_{40}]_2\cdot(4,4'\text{-bpy})_3$  (**5**),  $[\text{Ag}(1,10\text{-phen})_2]_3[\text{PMo}_{12}\text{O}_{40}]$  (**6**) and  $[\text{Ag}(2,2'\text{-bpy})_3]_2[\text{H}_4\text{P}_2\text{W}_{18}\text{O}_{62}]\cdot(2,2'\text{-bpy})_2\cdot 2\text{H}_2\text{O}$  (**7**). The seven compounds can be grouped into four groups: compounds **1–4** belong to the first one, which is based on POMs and two types of silver complexes; compound **5** belongs to the second one, which is based on POMs, two types of silver complexes and organic moieties; compound **6** belongs to the third one, which is based on POMs and silver complexes, and compound **7** belongs to the fourth one, which is based on POMs, silver complexes and organic moieties.

## 2. Experimental

All reagents were purchased commercially and were used without further purification. The hydrothermal reaction was performed in a 25 mL Teflon-lined stainless steel autoclave under autogenous pressure. The reaction mixture each was stirred with a magnetic stirrer before being transferred into a Teflon-lined stainless steel autoclave. The crystallization was made under autogenous pressure at 160 °C for 5 days and left to cool to room temperature. The resulting crystals were collected and washed with distilled water. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 Series II CHNS/O elemental analyzer. Infrared spectra were obtained on a Perkin-Elmer spectrophotometer in the 200–4000  $\text{cm}^{-1}$  region with pressed KBr pellets. XPS measurements were performed on single crystals with an ESCALAB. MARK II apparatus, using the Mg  $K\alpha$  X-ray radiation as the excitation source (EMg  $K\alpha = 1253.6$  eV). Elemental analyses of B, Si, P, W, Mo and Ag were determined by inductively coupled plasma (ICP) analyses on a Perkin-Elmer Optima 3300DV ICP spectrometer. UV–Vis spectra of *N,N*-dimethylformamide saturated solutions of compounds **1–7** were recorded on a Shimadzu UV-3100 spectrophotometer. Small-angle X-ray diffraction (XRD) patterns were obtained on a Siemens D5005 diffractometer using the Cu  $K\alpha$  radiation.

### 2.1. Preparation of compound 1

The reaction mixture for compound **1** was  $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$  (0.5 g, 1.5 mmol),  $\text{H}_3\text{BO}_3$  (0.1 g, 1.6 mmol),  $\text{AgNO}_3$  (0.2 g, 1.2 mmol), 2,2'-bpy (0.3 g, 1.9 mmol) and distilled water (20 ml). The pH was necessarily adjusted to 5 with 37% HCl solution. Green crystals could be isolated in about 55% yield (based on W). *Anal. Calc.* for  $\text{C}_{130}\text{H}_{113}\text{Ag}_5\text{B}_2\text{N}_{26}\text{O}_{82}\text{W}_{24}$ : W, 53.00; Ag, 6.48; B, 0.26; C, 18.76; H, 1.37; N, 4.37. Found: W, 53.28; Ag, 6.54; B, 0.31; C, 18.55; H, 1.12; N, 4.33%. IR ( $\text{cm}^{-1}$ ): 3441, 1598, 1400, 1159, 953, 909, 825, 769, 535, 386.

### 2.2. Preparation of compound 2

A mixture of  $\text{AgNO}_3$  (0.12 g, 0.7 mmol),  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  (0.2 g, 1.6 mmol), 2,2'-bpy (0.23 g, 1.5 mmol) and distilled water (20 ml) was stirred for about 10 min, then  $\text{Na}_9[\alpha\text{-A-PW}_9\text{O}_{34}]$  (0.5 g) was added [13]. The suspension was then stirred for an hour, the pH was necessarily adjusted to 4 with  $\text{NH}_3\cdot\text{H}_2\text{O}$ . Red crystals could be isolated in about 20% yield (based on W). *Anal. Calc.* for  $\text{C}_{110}\text{H}_{102}\text{Ag}_4\text{N}_{22}\text{O}_{68}\text{P}_2\text{W}_{18}$ : W, 49.97; Ag, 6.51; P, 0.94; C, 19.95; H, 1.55; N, 4.65. Found: W, 49.17; Ag, 6.23; P, 0.54; C, 19.90; H, 1.24; N, 4.29%. IR ( $\text{cm}^{-1}$ ): 3427, 1595, 1470, 1440, 1316, 1244, 1167, 1103, 1021, 947, 914, 877, 841, 794, 757, 384.

### 2.3. Preparation of compound 3

The reaction mixture was  $\text{Na}_2\text{HPW}_{12}\text{O}_{40}\cdot 2\text{H}_2\text{O}$  (0.5 g, 1.7 mmol),  $\text{AgNO}_3$  (0.12 g, 0.7 mmol), 2,2'-bpy (0.23 g, 1.5 mmol) and distilled water (20 ml). The pH was necessarily adjusted to 6 with 37% HCl solution. Grey white crystals could be isolated in about 26% yield (based on W). *Anal. Calc.* for  $\text{C}_{80}\text{H}_{78.5}\text{Ag}_4\text{N}_{16}\text{O}_{44.75}\text{PW}_{11}$ : W, 45.29; Ag, 9.66; P, 0.69; C, 21.52; H, 1.77; N, 5.02. Found: W, 45.72; Ag, 9.29; P, 0.41; C, 21.35; H, 1.46; N, 4.54%. IR ( $\text{cm}^{-1}$ ): 3431, 2873, 1629, 1599, 1467, 1441, 1325, 1314, 1248, 1105, 1054, 1020, 947, 878, 820, 763, 729, 512.

### 2.4. Preparation of compound 4

The reaction mixture was  $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$  (0.5 g, 2.1 mmol),  $\text{H}_3\text{PO}_4$  (0.26 ml),  $\text{AgNO}_3$  (0.12 g, 0.7 mmol), 1,10-phen (0.15 g, 0.8 mmol) and distilled water (20 ml). The pH was necessarily adjusted to 5 with  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution. Glassy yellow crystals could be isolated in about 62% yield (based on Mo). *Anal. Calc.* for  $\text{C}_{72}\text{H}_{48}\text{Ag}_4\text{Mo}_8\text{N}_{12}\text{O}_{26}$ : Mo, 28.47; Ag, 16.00; C, 32.07; H, 1.79; N, 6.23. Found: Mo, 28.44; Ag, 15.77; C, 31.82; H, 1.24; N, 6.20%. IR ( $\text{cm}^{-1}$ ): 3432, 1619, 1507, 1421, 1136, 1093, 937, 906, 833, 690, 523, 359.

### 2.5. Preparation of compound 5

The reaction mixture for compound **5** was  $\text{Na}_2\text{WO}_4$  (0.5 g, 1.5 mmol),  $\text{H}_3\text{BO}_3$  (0.12 g, 1.8 mmol)  $\text{AgNO}_3$  (0.13 g, 0.8 mmol),  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  (0.2 g, 1.6 mmol), 2,2'-bpy (0.27 g, 1.7 mmol), 4,4'-bpy (0.26 g, 1.7 mmol) and distilled water (20 ml). The pH was necessarily adjusted to 5 with  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution. Black crystals could be isolated in about 50% yield (based on W). *Anal. Calc.* for  $\text{C}_{160}\text{H}_{131}\text{Ag}_5\text{N}_{32}\text{O}_{80}\text{B}_2\text{W}_{24}$ : W, 50.39; Ag, 6.16; B, 0.25; C, 21.94; H, 1.53; N, 5.12. Found: W, 49.81; Ag, 6.07; B, 0.45; C, 21.47; H, 1.42; N, 4.85%. IR ( $\text{cm}^{-1}$ ): 3428, 1598, 1464, 1440, 1310, 1157, 990, 950, 909, 824, 759, 732, 531, 387.

### 2.6. Preparation of compound 6

The reaction mixture was  $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$  (0.5 g, 2.1 mmol),  $\text{H}_3\text{PO}_4$  (0.26 ml),  $\text{AgNO}_3$  (0.12 g, 0.7 mmol), 1,10-phen (0.15 g, 0.8 mmol) and distilled water (20 ml). The pH was necessarily adjusted to 4. Yellow crystals could be isolated in about 43% yield (based on Mo), but with some unidentified amorphous materials present as minority phases. Unfortunately, it is not easy to mechanically select the pure crystals from the mixture. Thus, we did not obtain the satisfied results of elemental analysis and XRD analysis. *Anal. Calc.* for  $\text{C}_{72}\text{H}_{48}\text{Ag}_3\text{Mo}_{12}\text{N}_{12}\text{O}_{40}\text{P}$ : Mo, 35.68; Ag, 10.03; P, 0.96; C, 26.80; H, 1.50; N, 5.21. IR ( $\text{cm}^{-1}$ ): 3429, 1617, 1506, 1422, 1139, 1062, 955, 877, 796, 723, 501, 385.

### 2.7. Preparation of compound 7

The reaction mixture was  $\text{H}_3\text{O}_{40}\text{PW}_{12}\cdot\text{XH}_2\text{O}$  (0.5 g, 1.7 mmol), AgI (0.12 g, 0.5 mmol),  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  (0.2 g, 1.6 mmol), 2,2'-bpy (0.23 g, 1.5 mmol) and distilled water (20 ml) The pH was necessarily adjusted to 6 with  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution. Dark orange crystals could be isolated in about 31% yield (based on W). *Anal. Calc.* for  $\text{C}_{80}\text{H}_{72}\text{Ag}_2\text{N}_{16}\text{O}_{64}\text{P}_2\text{W}_{18}$ : W, 56.39; Ag, 3.68; P, 1.06; C, 16.37; H, 1.24; N, 3.82%. Found: W, 56.16; Ag, 3.51; P, 0.94; C, 16.11; H, 1.02; N, 3.56%. IR ( $\text{cm}^{-1}$ ): 3435, 1600, 1438, 1088, 1020, 954, 914, 791, 761, 386.

### 2.8. X-ray crystallography

The reflection intensity data of compounds **1–7** were measured at 293 K on a Rigaku R-Axis RAPID IP diffractometer with graphite

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