



Coordination site induced controllable assembly of metal–organic units in polyoxometalate-based hybrids



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ABSTRACT

Two hybrid materials based on Keggin-type polyoxometalate, $[\text{Ag}_4(\text{mtrz})_4(\text{H}_2\text{O})_2(\text{SiW}_{12}\text{O}_{40})]$ (**1**), $[\text{Ag}_4(\text{mtez})_5(\text{SiW}_{12}\text{O}_{40})] \cdot \text{H}_2\text{O}$ (**2**), (mtrz = 1-methyl-1,2,4-triazole, mtez = 1-methyl-1,2,3,4-tetrazole), have been hydrothermally synthesized and structurally characterized. Through the use of the azole ligands mtrz and mtez, compounds **1** and **2** with totally different metal–organic units are obtained. In **1**, the mtrz ligands with N atoms in meta-positions induced the formation of chain-like metal–organic units, while in **2**, the mtez ligands with adjacent N atoms induced the assembly of tetranuclear units. The SiW_{12} anions act as bridging linkers to evolve the structural dimensionality of the two title compounds into 2D network and 3D framework, respectively.

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Polyoxometalate (POM) based hybrid materials have attracted considerable attention in recent years, owing to their potential applications in catalysis, medicine, photochemistry [1–3], as well as their intriguing architectures and topologies [4,5]. Up to now, a variety of strategies have been developed and used to assemble POM-based hybrid materials by controlling reaction factors, such as metal ions, organic ligands, POM species, pH, molar ratio of raw materials and reaction environment [6–9]. To the best of our knowledge, there are some progresses that have been made on manipulating metal–organic units to construct expectant and controllable architectures [10–13]. Indeed, it is crucial to realize the rational synthesis of POM-based hybrid materials by controlling unique metal–organic units in coordination chemistry. Previously, our efforts have been devoted to the goal-directed synthesis of metal–organic units [14,15]. As an extension of our ongoing efforts, in this work, a couple of structural related azole derivatives, 1-methyl-1,2,4-triazole (mtrz) and 1-methyl-1,2,3,4-tetrazole (mtez), were selected to induce different unique metal–organic units which would facilitate the construction of new POM-based hybrid materials. The two N-donor ligands were selected based on the two following aspects: (I) Difference. The mtrz ligand possesses coordination sites in meta-positions and mtez owns adjacent N atoms, the features of different coordination sites and angles are conducive to construct different characteristics of metal–organic units. (II) Similarity. The azole rings of mtrz and mtez have more than one

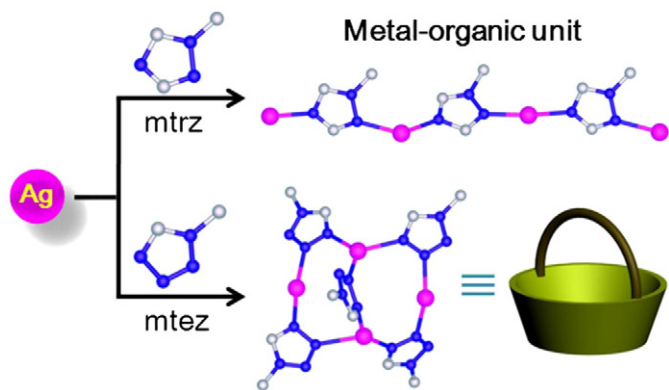
potential coordination site to coordinate with metal ions, and the configurations of two molecules are extremely close.

Herein, under the similar hydrothermal conditions, two hybrid compounds $[\text{Ag}_4(\text{mtrz})_4(\text{H}_2\text{O})_2(\text{SiW}_{12}\text{O}_{40})]$ (**1**) and $[\text{Ag}_4(\text{mtez})_5(\text{SiW}_{12}\text{O}_{40})] \cdot \text{H}_2\text{O}$ (**2**), based on Ag^I and the two selected ligands mtrz and mtez, have been obtained. Structural analyses [16] reveal that the metal–organic segments in **1** exhibit the linear chain structure, while in **2** they feature a torsional bitrack-like chain that is assembled by tetranuclear $[\text{Ag}_4(\text{mtez})_5]$ units. The POMs act as inorganic ligands to evolve the structural dimensionality of the two title compounds. These results are consistent well with the strategy of our rational design (Scheme 1).

Structural analysis reveals that compound **1** contains one Keggin type $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anion (abbreviated as SiW_{12}), four Ag ions, four mtrz ligands and two coordinated water molecules (Fig. S1a). Bond valence sum calculations show that all the W sites exhibit +6 oxidation state in SiW_{12} cluster, and all the Ag atoms are in the +1 oxidation state [17]. Two crystallographically independent Ag^I ions are four-coordinated by two N and two O atoms in a seesaw-shaped $[\text{AgN}_2\text{O}_2]$ geometry (Fig. 1a). Note that the two O-donors around Ag atoms ($\text{Ag}1$ and $\text{Ag}2$) are different. The O atoms coordinated to $\text{Ag}1$ are from two SiW_{12} clusters, while the O atoms around $\text{Ag}2$ are from one SiW_{12} anion and one coordinated water molecule. Bond lengths around the Ag ions are in the normal range [18]. The two independent mtrz ligands exhibit the same coordination mode (Fig. S2a). The mtrz adopts a $\mu_2\text{-}\eta^1\text{:}\eta^1$ coordination mode with two N atoms in meta-positions to coordinate with two Ag ions ($\text{Ag}1$, $\text{Ag}2$). Herein, the two independent Ag atoms and two mtrz ligands aggregate into an infinite one-dimensional (1D) linear chain structure. The SiW_{12} anion acts as a hexa-

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Scheme 1. Coordination site induced different unique metal-organic units.

dentate inorganic ligand to coordinate with six Ag ions (Fig. 1b). Combination of these structural features induces a two-dimensional (2D) network, as shown in Fig. 1c.

Compound **2** exists as an infinite three-dimensional (3D) network, which is constructed by one SiW_{12} anion, four Ag ions, five mtez ligands and one free water molecule (Fig. S1b). Bond valence sum calculations show that all W atoms are present in +6 oxidation state, and all the Ag atoms are in the +1 oxidation state. Four crystallographically independent Ag^I ions exhibit different kinds of coordination geometries (Fig. 2a). The Ag1 ion adopts distorted trigonal bipyramidal geometry of

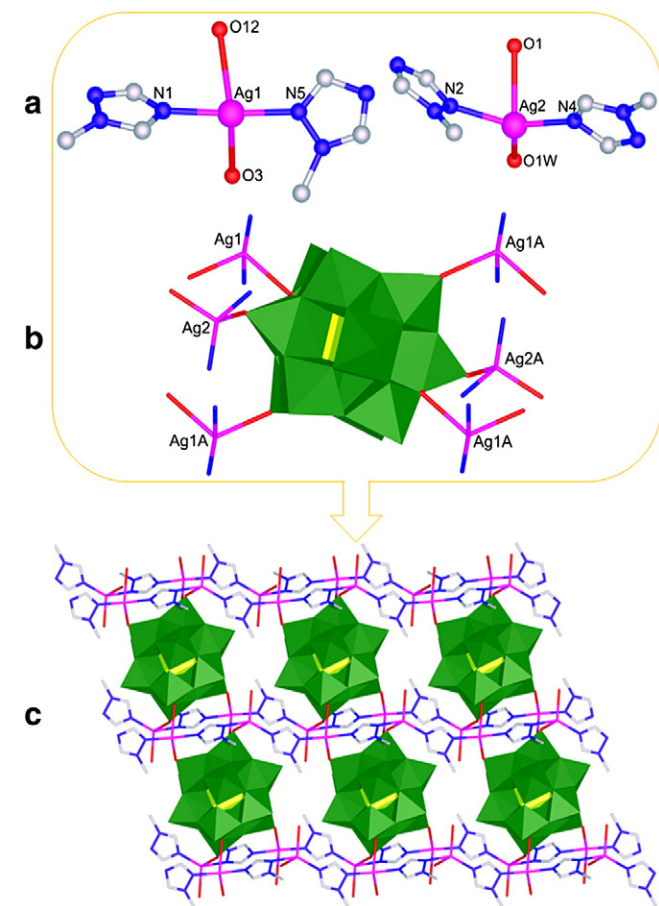


Fig. 1. Coordination environments of Ag ions (a) and SiW_{12} cluster (b) in **1**. Perspective view of 2D sheet (c).

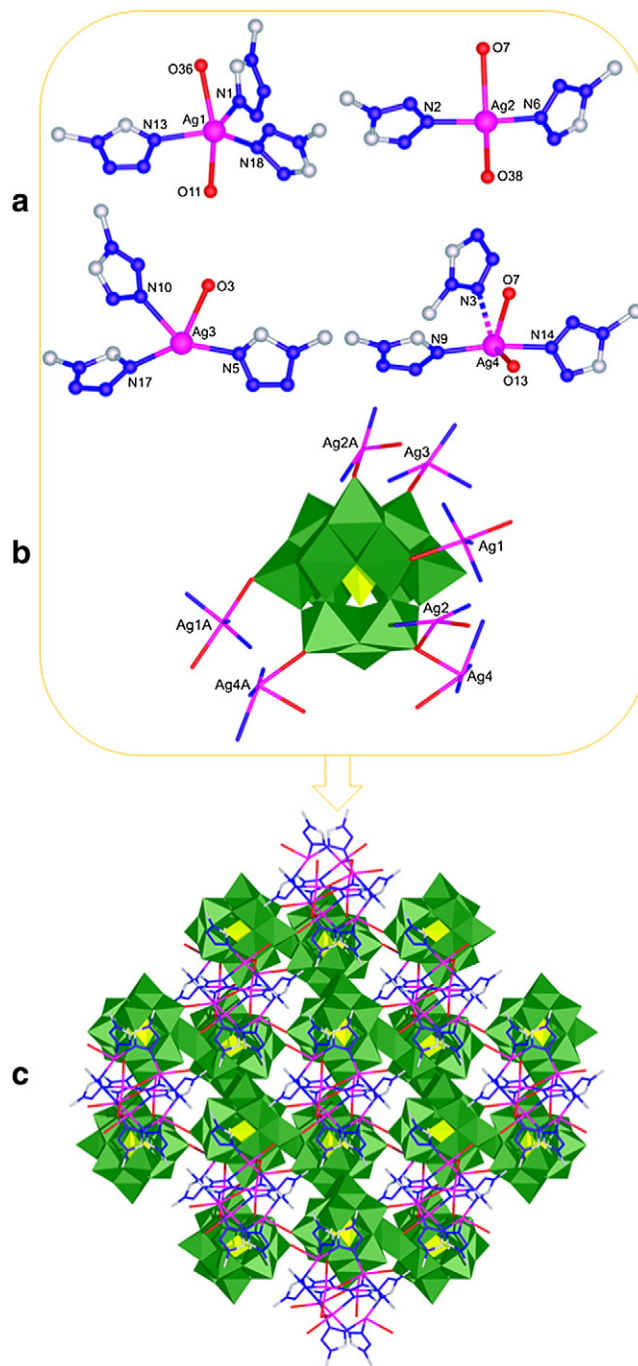


Fig. 2. Coordination environments of Ag ions (a) and SiW_{12} cluster (b) in **2**. Perspective view of 3D framework (c). Dotted line represents the weak coordination interaction.

$[\text{AgN}_3\text{O}_2]$ by three N atoms of three mtez ligands and two terminal O atoms (O_t) of two SiW_{12} clusters. The Ag2 ion is four-coordinated by two N and two O_t atoms in a seesaw-shaped $[\text{AgN}_2\text{O}_2]$ geometry. While the four-coordinated Ag3 ion possesses a distorted tetrahedral geometry of $[\text{AgN}_3\text{O}]$ taken by three N atoms and one O_t atom. The Ag4 ion is five-coordinated adopting distorted tetragonal pyramid geometry of $[\text{AgN}_3\text{O}_2]$ by three N and two O_t atoms. Bond distances around the Ag centers are normal, except a weak coordination interaction ($\text{Ag4}-\text{N3}$, 2.872 Å) within the $[\text{AgN}_3\text{O}_2]$ moiety [19]. In **2**, the mtez ligands exhibit two different coordination modes (Fig. S2b). The mtez1 adopts a $\mu_3:\eta^1:\eta^1:\eta^1$ coordination mode with its three adjacent N atoms, bridging three Ag ions (Ag1, Ag2 and Ag4) in an asymmetrical

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