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# Development of non-closed silver clusters by transition-metal-coordination-cluster substituted polyoxometalate templates†

Rui Ge, Ping-Wei Cai, Cai Sun, Yan-Qiong Sun, Xin-Xiong Li \* and Shou-Tian Zheng \*

Nature seems to favor the formation of closed anion-templated silver clusters. How precisely to create non-closed silver clusters remains an interesting challenge. In this work, we propose that the use of transition-metal-coordination-cluster substituted polyoxometalates (TMCC-substituted POMs) as templates is an effective synthetic strategy for creating the non-closed silver clusters, as demonstrated by the obtainment of four types of rare non-closed silver cluster species of  $\text{Ag}_{38}\text{-TM}$  (TM = Co, Ni or Zn),  $\text{Ag}_{37}\text{-Zn}$ ,  $\{\text{Ag}_{37}\text{-Zn}\}_\infty$  and  $\text{Ag}_{36}\text{-TM}$  (TM = Co, Ni). The idea of the strategy is to employ the TMCC-substituted POMs containing cluster modules with different bond interactions with  $\text{Ag}^+$  ions as templates to guide the formation of the non-closed silver clusters. For example, TMCC-substituted POM clusters are used as templates in this work, which contain POM modules that can coordinate with the  $\text{Ag}^+$  ions and TMCC moieties that are difficult to coordinate with the  $\text{Ag}^+$  ions, leading to the  $\text{Ag}^+$  ions being unable to form closed clusters around TMCC-substituted POM templates. The work demonstrates a promising approach to developing intriguing and unexplored non-closed silver clusters.

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## Introduction

The pursuit of crystalline silver clusters has progressed rapidly in the past two decades because such materials not only have fascinating structures but also exhibit promising properties in sensing, energy storage, optoelectronics, and catalysis.<sup>1–7</sup> In this area, anions have been widely used as structure-directing agents to induce the formation of new high-nuclearity silver clusters,<sup>8–10</sup> and they perform multiple roles in determining the structures and properties of the silver clusters. They can serve as anionic templates to organize the  $\text{Ag}^+$  ions together in an ordered way, control the nuclearity, size, and shape of the silver clusters, stabilize the silver clusters by balancing positive charges and electronic communications, and transfer functions into final silver clusters.<sup>11,12</sup> Given these advantages, various inorganic anions have been introduced to template the organization of the  $\text{Ag}^+$  ions, leading to the rapid development of the anion-templated silver clusters in recent years.<sup>13–15</sup>

Nevertheless, the vast majority of known anion-templated silver clusters possess closed structures, while the non-closed

silver clusters have rarely been reported.<sup>16–19</sup> Compared with closed silver clusters, non-closed ones are more appealing and favorable, as they may provide atomic-level information on the formation of the closed silver clusters and possess exposed active sites that may endow them with unique physicochemical properties.<sup>18</sup> However, the efficient fabrication of the non-closed silver clusters still remains a challenging task, and a controllable synthetic method has yet to be developed.

Due to the uniform distribution of negative charges and coordination sites of commonly used inorganic anions or anion clusters, the  $\text{Ag}^+$  ions tend to spontaneously form closed cluster structures around these anion templates.<sup>20,21</sup> As shown in Fig. 1, will it be possible to prevent the  $\text{Ag}^+$  ions from forming closed structures? Are there any feasible strategies capable of effectively creating the non-closed silver clusters? Given that the synthetic chemistry of the silver clusters has been of wide

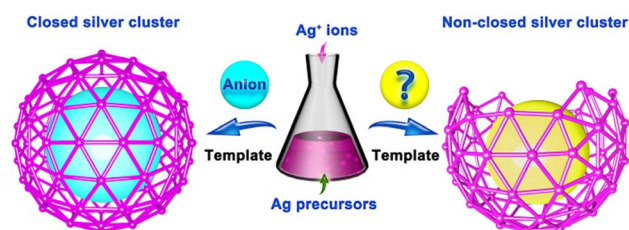


Fig. 1 Structure and synthesis of the closed and non-closed silver clusters.

Fujian Provincial Key Laboratory of Advanced Inorganic Oxygenated Materials, College of Chemistry, Fuzhou University, Fuzhou 350108, Fujian, China. E-mail: lxx@fzu.edu.cn; stzheng@fzu.edu.cn

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interest,<sup>22–25</sup> it is of significant scientific interest to investigate the possibility of the construction of the non-closed silver clusters.

Polyoxometalates (POMs) are a class of early-transition-metal–oxygen clusters assembled from corner-, edge-, or face-sharing  $MO_n$  ( $M$  generally refers to V, Mo, W, Nb, or Ta) polyhedra with  $M$  in high oxidation states. Due to their attractive structural characteristics (nanosize, high negative charge, and redox) and wide potential applications in catalysis, electronics, and biomedicine,<sup>26–32</sup> POMs have been explored as the anionic templates for the construction of high nuclear silver clusters. However, as with commonly used anionic templates, POMs have uniformly distributed negative charges and coordination sites that usually induce the  $Ag^+$  ions to form the closed clusters.

One area of particular interest is that POMs can lose one or more  $MO_n$  polyhedra *via* hydrolytic degradation to generate various lacunary POMs, which allows the introduction of transition-metal-coordination-clusters (TMCCs) into their vacancies to form intriguing and diverse TMCC-substituted POMs. The use of the TMCC-substituted POM clusters with different cluster modules (TMCCs and POMs) within same molecules as the templates would be highly desirable for the development of intriguing and rare non-closed silver clusters because the POM modules can template the formation of the silver clusters by the formation of coordination bonds between terminal oxygen and the  $Ag^+$  ions, while terminal ligands on the TMCC module can prevent TMCC from bonding to the  $Ag^+$  ions. Thus, the combination of POM and TMCC endows the TMCC-substituted POM templates with regions that show distinct bonding interactions with the  $Ag^+$  ions, which can make the  $Ag^+$  ions form the non-closed silver clusters around the whole TMCC-substituted POM cluster template.

Here, for the first time, we report the introduction of the TMCC-substituted POMs into the silver clusters and successful obtainment of a family of the rare non-closed silver cluster species of  $\{[TM_4(\mu_3-OH)_3(Ac)_3SiW_9O_{34}]@Ag_{38}({}^tBuC\equiv C)_{21}(NO_3)_4CH_3CN\}(Ac)_5$  (**Ag<sub>38</sub>-TM**) (TM = Zn/Ni/Co;  ${}^tBu$  = tertiary butyl;  $Ac^- = CH_3COO^-$ ),  $\{[Zn_5(\mu_3-OH)_3(Ac)_2(SiW_9O_{34})(SiW_{11}O_{39})]@Ag_{37}({}^tBuC\equiv C)_{22}(NO_3)(CH_3CN)_2(NO_3)\cdot(CH_3CN)_2$  (**Ag<sub>37</sub>-Zn**),  $Ag_{0.65}\{[Zn_5(\mu_3-OH)_3(Ac)_2(SiW_9O_{34})(SiW_{11}O_{39})]@Ag_{37}({}^tBuC\equiv C)_{19}(NO_3)_2\}_2(Ac)_{6.65}$  (**Ag<sub>37</sub>-Zn**) $_{\infty}$  and  $\{[TM_5(\mu_3-OH)_3(Ac)_2(SiW_9O_{34})(SiW_{11}O_{39})]@Ag_{36}({}^tBuC\equiv C)_x(Ac)_{23-x}2CH_3CN$  (**Ag<sub>36</sub>-TM**) (TM = Co/Ni;  $x = 18/17$  for Co/Ni), which demonstrate that the use of the TMCC-substituted POMs as the templates is an effective synthetic strategy for the creation of the non-closed silver clusters.

## Results and discussion

The crystals of the four types of compounds were obtained by solvothermal reactions of  $AgNO_3/CF_3SO_3Ag$ ,  ${}^tBuC\equiv CAg$ ,  $({}^tBu_4N)_6H_4[SiW_9O_{34}]$  and  $TM(Ac)_2 \cdot xH_2O$  in  $CH_3CN$  (see the experimental details in ESI, Fig. S1†). Given the isomorphism, only **Ag<sub>38</sub>-Zn** is chosen as a representative of **Ag<sub>38</sub>-TM** for single-crystal X-ray diffraction (SCXRD) analysis description. **Ag<sub>38</sub>-Zn** crystallizes in the triclinic  $P\bar{1}$  space group and comprises a zinc-cluster-substituted POM core of  $\{[Zn_4(\mu_3-OH)_3(Ac)_3SiW_9O_{34}]\}$

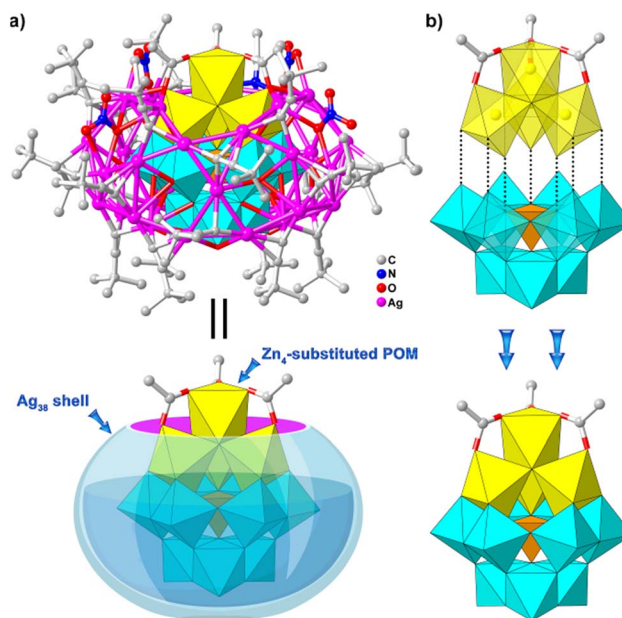


Fig. 2 (a) and (b) View of the structures of **Ag<sub>38</sub>-Zn** and the **Zn<sub>4</sub>SiW<sub>9</sub>** template, respectively. Polyhedral code:  $WO_6$ , cyan;  $SiO_4$ , orange; and  $ZnO_6$ , yellow (the same thereafter).

(**Zn<sub>4</sub>SiW<sub>9</sub>**) surrounded by a unique 38-nuclearity non-closed silver shell of  $\{Ag_{38}({}^tBuC\equiv C)_{21}(NO_3)_4CH_3CN\}$  (**Ag<sub>38</sub>**) (Fig. 2a). The inner **Zn<sub>4</sub>SiW<sub>9</sub>** template can be described as a tetra-nuclear  $\{Zn_4(\mu_3-OH)_3(Ac)_3\}$  (**Zn<sub>4</sub>**) zinc coordination cluster trapped into vacant sites by a trilacunary Keggin-type  $\{SiW_9O_{34}\}$  POM through the sharing of nine oxygen atoms (Fig. 2b). **Zn<sub>4</sub>** consists of four edge-sharing octahedral-coordinated  $Zn^{2+}$  ions integrated by three  $\mu_3-OH$  groups, three of which are exactly located on the vacant sites of trilacunary POM to give a triangular  $\{Zn_3(\mu_3-OH)_3\}$  trimer, and the fourth  $Zn^{2+}$  ion is capped onto the planar trimer by sharing three  $\mu_3-OH$  groups and three terminal acetate ligands.

Interestingly, the presence of the terminal acetate ligands prevents the possibility of coordination between zinc clusters and the  $Ag^+$  ions. As a result, the **Zn<sub>4</sub>SiW<sub>9</sub>** template allows the formation of a non-closed nest-shaped **Ag<sub>38</sub>** shell through  $Ag-O$  bonds ranging from 2.381 to 2.597 Å (Fig. 2a). As shown in Fig. S2,†  $Ag^+$  atoms are arranged into a sandwich-type three-layer structure protected by 21  ${}^tBuC\equiv C^-$  ligands, 4  $NO_3^-$  and 1 terminal  $CH_3CN$  molecule. Upper and basal layers can be described as a larger  $Ag_{11}$  ring and small  $Ag_9$  ring, and upper and lower rings are interlinked by three silver ions and three  $Ag_5$  tetragonal pyramids in an alternating arrangement, leading to the overall **Ag<sub>38</sub>** shell with  $Ag-Ag$  distances in the range of 2.849 to 3.965 Å.  ${}^tBuC\equiv C^-$  and  $CH_3CN$  ligands adopt a  $\mu_3$ -bridging mode to cap the **Ag<sub>38</sub>** shell (Fig. S2†), each of which is ligated to three  $Ag^+$  ions ( $Ag-C$ : 1.919–2.409 Å;  $Ag-N$ : 2.104–2.269 Å). Half of the 4  $NO_3^-$  anions are situated on the top of the  $Ag_{11}$  ring *via* a  $\mu_3-\eta_2-\eta_1$  coordination mode, and the remaining two  $NO_3^-$  anions connect the  $Ag_{11}$  ring with two  $Ag_5$  tetragonal pyramids, respectively, by two kinds of modes,  $\mu_2-\eta_2$  and  $\mu_3-\eta_3-\eta_1$  modes with  $Ag-O$  distances of 2.399–2.874 Å (Fig. S2†).



Note that the  $\{\text{SiW}_9\text{O}_{34}\}$  cluster has been used as a template to form the closed silver clusters because of its abundant terminal oxo atoms that can coordinate with the  $\text{Ag}^+$  ions.<sup>33</sup> When the TMCC-substituted POMs formed by  $\{\text{SiW}_9\text{O}_{34}\}$  and TM-coordination clusters are used as the templates, non-closed  $\text{Ag}_{38}$  clusters are formed, as found in **Ag<sub>38</sub>-TM**. Obviously, the introduction of relatively large TM-coordination clusters (compared to metal ions) without epitaxial coordination sites can prevent the  $\text{Ag}^+$  ions from wrapping around the entire  $\text{TM}_4\text{SiW}_9$  template to form the closed silver clusters. It is also noteworthy that  $\text{TM}_4\text{SiW}_9$  clusters have been reported for more than a decade,<sup>34</sup> but this is the first time that they have been recognized and introduced into the silver clusters as the templates for building the non-closed silver clusters.

To verify the validity of the synthesis concept and diversity of products, we carried out further exploration and successfully obtained two kinds of new non-closed silver clusters, **Ag<sub>37</sub>-Zn** and **Ag<sub>36</sub>-TM**. SCXRD analysis revealed that these compounds have the same TMCC-substituted POM template,  $\{\text{TM}_5(\mu_3\text{-OH})_3(\text{Ac})_2(\text{SiW}_9\text{O}_{34})(\text{SiW}_{11}\text{O}_{39})\}$  (Fig. 3a), but slightly different non-closed silver shell structures. **Ag<sub>37</sub>-Zn** also crystallizes in the  $P\bar{1}$  space group and consists of a  $\text{Zn}_5$ -substituted POM core of  $\{\text{Zn}_5(\mu_3\text{-OH})_3(\text{Ac})_2(\text{SiW}_9\text{O}_{34})(\text{SiW}_{11}\text{O}_{39})\}$  ( $\text{Zn}_5\text{Si}_2\text{W}_{20}$ ) and a 37-nuclearity non-closed silver shell of  $\{\text{Ag}_{37}(\text{BuC}\equiv\text{C})_{22}(\text{NO}_3)\}$  ( $\text{Ag}_{37}$ ). V-shaped  $\text{Zn}_5\text{Si}_2\text{W}_{20}$  exhibits an unknown TMCC-substituted POM composed of a 5-nuclearity  $\{\text{Zn}_5(\mu_3\text{-OH})_3(\text{Ac})_2\}$  zinc coordination cluster sandwiched by monolacunary  $\{\text{SiW}_{11}\text{O}_{39}\}$  POM and trilacunary  $\{\text{SiW}_9\text{O}_{34}\}$  POM (Fig. 3a). Alternatively,  $\text{Zn}_5\text{Si}_2\text{W}_{20}$  can be viewed as a dimer consisting of  $\text{Zn}_4$ -substituted  $\text{Zn}_4\text{SiW}_9$  and a Keggin-type mono-Zn-substituted  $\{\text{ZnSiW}_{11}\text{O}_{40}\}$  joined together by one edge-sharing

bioctahedral  $\text{Zn}_2\text{O}_{10}$  group and one corner-sharing bioctahedral  $\text{ZnWO}_{11}$  group, accompanied by the removal of one  $\text{Ac}^-$  ligand.

The skeleton of  $\text{Ag}_{37}$  in **Ag<sub>37</sub>-Zn** can be derived from that of nest-like  $\text{Ag}_{38}$  in **Ag<sub>38</sub>-Zn** by removing one  $\text{Ag}^+$  ion from its upper  $\text{Ag}_{11}$  ring, wherein the vacancy after the removal of the  $\text{Ag}^+$  ion is occupied by the fifth zinc ion from the  $\text{Zn}_5\text{Si}_2\text{W}_{20}$  template (Fig. 3b and S3†). In addition, there is a difference between the peripheral ligands of  $\text{Ag}_{37}$  and  $\text{Ag}_{38}$ : that is, the  $\text{CH}_3\text{CN}$  ligand in  $\text{Ag}_{38}$  is replaced by a  $\text{BuC}\equiv\text{C}^-$  ligand in  $\text{Ag}_{37}$  (Fig. S4†). Such a structural transformation suggests that silver cluster shells can respond simultaneously to changes in TMCC-substituted POM cores. The formation of **Ag<sub>37</sub>-Zn** shows the tunability and flexibility of inner TMCC-substituted POM templates and further demonstrates the effectiveness of our synthetic strategy.

The manipulation of  $\text{TM}^{2+}$  ions with distinct electronic configurations presents a feasible method to fine-tune the structures and physicochemical properties of the products. In this regard, the use of cobalt and nickel salts led to the crystallization of **Ag<sub>36</sub>-Co** and **Ag<sub>36</sub>-Ni** (Fig. S5†). Energy dispersive spectroscopy elemental mapping spectra (Fig. S6–S12†) and crystal colors (Fig. S1†) confirmed the presence of different  $\text{TM}^{2+}$  ions in the clusters. **Ag<sub>36</sub>-Co** and **Ag<sub>36</sub>-Ni** have the same isomorphous TMCC-substituted POM template as **Ag<sub>37</sub>-Zn**, but their silver shells differ slightly in the number of the  $\text{Ag}^+$  ions and  $\text{BuC}\equiv\text{C}^-$  ligands (Fig. S13 and S14†). The  $\{\text{Ag}_{36}(\text{BuC}\equiv\text{C})_x\}$  ( $\text{Ag}_{36}$ ) ( $x = 18/17$  for Co/Ni) shells of **Ag<sub>36</sub>-Co** and **Ag<sub>36</sub>-Ni** can be derived from the further removal of one  $\text{Ag}^+$  ion from the upper  $\text{ZnAg}_{10}$  ring of **Ag<sub>37</sub>-Zn**, and the incorporated  $\text{TM}^{2+}$  ion is located near the fifth  $\text{Zn}^{2+}$  ion in **Ag<sub>37</sub>-Zn** (Fig. S3†). Additionally, in response to the introduction of different  $\text{TM}^{2+}$  ions, the number of  $\text{BuC}\equiv\text{C}^-$  ligands around the silver shell varied from 22 in **Ag<sub>37</sub>-Zn** to 18 in **Ag<sub>36</sub>-Co** and 17 in **Ag<sub>36</sub>-Ni** (Fig. S14 and S15†). Results reveal that the  $\text{TM}^{2+}$  differences of the TMCC-substituted POM templates can precisely regulate Ag shells at the atomic level.

Notably, the obtainment of **Ag<sub>37</sub>-Zn**, **Ag<sub>36</sub>-Co** and **Ag<sub>36</sub>-Ni** shows that the presence of TM clusters can not only cause the formation of broken silver clusters but also gather additional POM units (e.g. the monolacunary  $\{\text{SiW}_{11}\text{O}_{39}\}$  POM in this work) to form unique non-closed structures with half the molecular template in the silver cluster and half outside the silver cluster. Interestingly, outside POM units have abundant terminal oxo atoms that can coordinate with the  $\text{Ag}^+$  ions, which is expected to enable the non-closed silver clusters to undergo further assembly reactions. For example, by adjusting reaction parameters, an **Ag<sub>37</sub>-Zn**-cluster-based two-dimensional (2D) infinitely extended structure  $\{\text{Ag}_{37}\text{-Zn}\}_\infty$  was obtained. As shown in Fig. 4, the **Ag<sub>37</sub>-Zn** cluster self-assembled into one-dimensional (1D) chains through the coordination of one terminal oxo atom of the outside  $\{\text{SiW}_{11}\text{O}_{39}\}$  unit with one  $\text{Ag}^+$  ion from the adjacent **Ag<sub>37</sub>-Zn** cluster. Adjacent chains are further bridged into 2D layers by additional  $\text{Ag}^+$  ions (with a site occupancy factor of 0.65), each of which forms a linear coordination with two oxo atoms from two  $\{\text{SiW}_{11}\text{O}_{39}\}$  units (Fig. 4). Generally, closed alkynyl-protected silver clusters are difficult to assemble into extended structures due to the bulky steric hindrance of

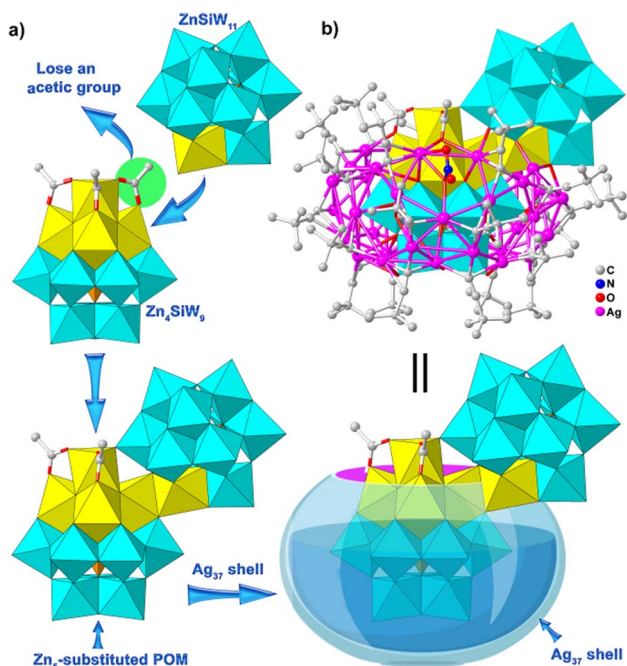


Fig. 3 (a) and (b) Views of the structures of the  $\text{Zn}_5\text{Si}_2\text{W}_{20}$  template and **Ag<sub>37</sub>-Zn**, respectively.



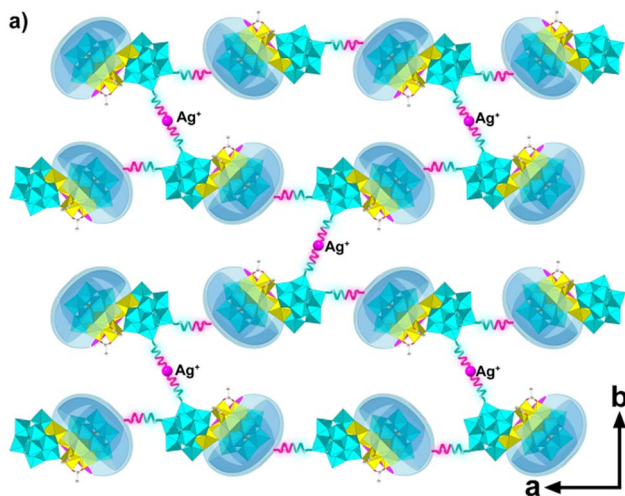


Fig. 4 Schematic diagram of the 2D structure  $\{\text{Ag}_{37}\text{-Zn}\}_{\infty}$ .

peripheral tertiary butyl groups.<sup>35–38</sup> To date, only a few high-dimensional (2D/3D) structures have been reported, constructed from the silver clusters alone.<sup>39–43</sup>  $\{\text{Ag}_{37}\text{-Zn}\}_{\infty}$  represents a new 2D layer structure constructed with POM-templated silver cluster building blocks without auxiliary connecting ligands (Fig. S16†).<sup>44–46</sup> Finally, the stacking of the 2D layers in  $\{\text{Ag}_{37}\text{-Zn}\}_{\infty}$  produces irregular 1D channels of a size of about  $4.18 \times 2.59 \text{ nm}^2$  along the *a* axis (Fig. S16b†), and the total potential solvent-accessible volume is  $11\,658 \text{ \AA}^3$ , occupying 38% of the volume of the unit cell. The acquisition of  $\{\text{Ag}_{37}\text{-Zn}\}_{\infty}$  indicates that the synthetic strategy based on the TMCC-substituted POM templates also provides the possibility of the development of high-dimensional silver cluster-based framework materials. The successful syntheses of the various series of  $\text{Ag}_{38}\text{-TM}$ ,  $\text{Ag}_{37}\text{-TM}$  or  $\text{Ag}_{36}\text{-TM}$  are attributed to the following synthetic strategy: using lacunary POMs to induce TMs and organic ligands to form TMCCs at their lacunary sites, thus forming the TMCC-substituted POMs for templating the formation of the non-closed silver clusters. Further, we find that non-closed silver cluster assembly reactions based on the above assembly strategy are sensitive to the reaction parameters; for example, different reaction times can form different products  $\text{Ag}_{38}\text{-Zn}$  (1 day) and  $\text{Ag}_{37}\text{-Zn}$  (3 days), and different starting silver reagents lead to different products  $\text{Ag}_{37}\text{-Zn}$  and  $\text{Ag}_{36}\text{-Co}$ . These results indicate that the synthetic strategy is a feasible route to diversifying the structural family of the non-closed silver clusters.

It is worth mentioning at this point that Ozeki and co-workers reported two non-closed silver alkynyl clusters,  $\text{P}_2\text{W}_{15}\text{Nb}_3\text{@Ag}_{25}$  and  $(\text{SiW}_9\text{Nb}_3)_2\text{@Ag}_{42}$ , using triniobium-oxo cluster-substituted POMs as the templates.<sup>16,17</sup> In their synthetic method, the non-closed silver cluster was achieved by changing the affinity of the  $\text{Ag}^+$  ions to the surface of the POM templates. They increased the surface negative charge of the top of the POM templates by the selective substitution of less positively charged Nb(v) for W(vi), leading to the preferential aggregation of the  $\text{Ag}^+$  ions around triniobium-oxo clusters instead of tungsten-oxo clusters. In this work, the TMCC-

substituted POM templates in the four types of compounds also feature a non-uniform distribution of negative charges, but they have additional impacts on the formation of the series of the non-closed silver clusters. First, acetic ligands on the TMCC-substituted POM templates play a key role in preventing the  $\text{Ag}^+$  ions from forming closed structures. Second, the POM templates with diverse TMCCs can enrich the structures of final non-closed silver clusters. Finally, the TMCC-substituted POM templates with unpaired electrons would introduce additional optical/electrical/magnetic properties into final composite clusters.

Due to the fascinating luminescent properties of the silver clusters,<sup>47–55</sup> the luminescent characteristics of  $\text{Ag}_{38}\text{-Zn}$ ,  $\text{Ag}_{37}\text{-Zn}$  and  $\{\text{Ag}_{37}\text{-Zn}\}_{\infty}$  were studied.  $\text{Ag}_{38}\text{-Zn}$ ,  $\text{Ag}_{37}\text{-Zn}$  and  $\{\text{Ag}_{37}\text{-Zn}\}_{\infty}$  are all nearly emission-silent at room temperature. When the clusters are cooled gradually to low temperature, sharply enhanced emission can be observed in the near-infrared (NIR) region (Fig. 5a–c), which can be attributed to ligand-to-metal charge transfer (LMCT) or combination with metal-centered (MC)  $d^{10} \rightarrow d^9 s^1$  transitions.<sup>56</sup> When cooled from 283 K to 83 K,  $\text{Ag}_{38}\text{-Zn}$  exhibits wide-band emission, the maximum emission shifts from 696 to 708 nm, and the emission intensity increases by about 24 times, which can be assigned to the low-temperature-induced decrease in non-radiative decay.<sup>57,58</sup>  $\text{Ag}_{37}\text{-Zn}$  and  $\{\text{Ag}_{37}\text{-Zn}\}_{\infty}$  exhibited similar emission spectra to

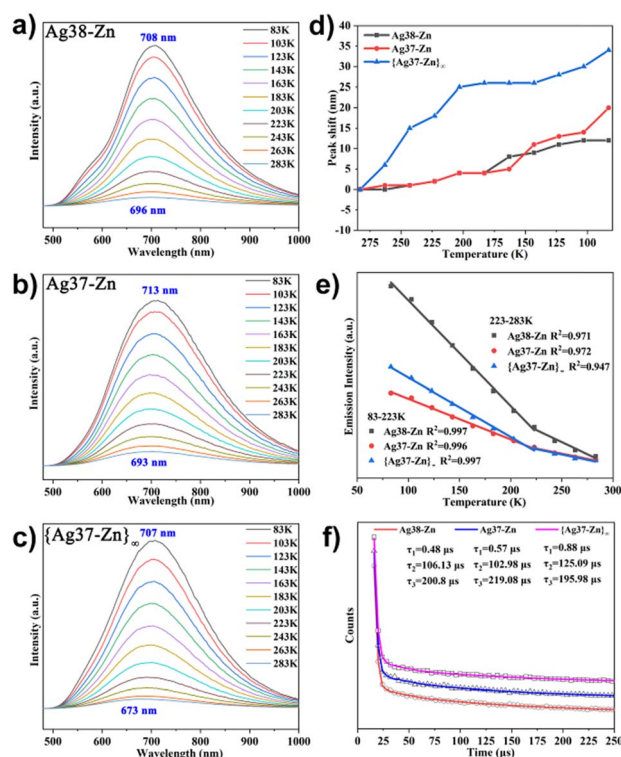


Fig. 5 (a)–(c) Temperature-dependent emission spectra of  $\text{Ag}_{38}\text{-Zn}$ ,  $\text{Ag}_{37}\text{-Zn}$  and  $\{\text{Ag}_{37}\text{-Zn}\}_{\infty}$  in the range of 83–283 K, respectively. (d) Peak shift vs. temperature in the range of 83–283 K. (e) Plot of maximum emission intensity vs. temperature of three clusters fitted in the range of 83–223 and 223–283 K. (f) Emission decay curve of three clusters measured at 83 K.



**Ag<sub>38</sub>-Zn** from 283 K to 83 K, except that the maximum emissions of **Ag<sub>37</sub>-Zn** and **{Ag<sub>37</sub>-Zn}<sub>∞</sub>** shift from 693 nm to 713 nm and from 673 nm to 707 nm, respectively. The emission intensities of **Ag<sub>37</sub>-Zn** and **{Ag<sub>37</sub>-Zn}<sub>∞</sub>** increase by about 14-fold and 22-fold as the temperature cools from 283 K to 83 K, respectively. In other words, the emission intensities of **Ag<sub>38</sub>-Zn**, **Ag<sub>37</sub>-Zn** and **{Ag<sub>37</sub>-Zn}<sub>∞</sub>** increase by 11.4%, 6.7% and 10.5% per K, respectively. The bathochromic shift may be due to reduced Ag<sup>+</sup>⋯Ag contacts at low temperature, which can decrease the energy gap of the MC transition to a certain extent. Interestingly, the degree of bathochromic shift of emission peaks is gradually enhanced from **Ag<sub>38</sub>-Zn** (12 nm) to **Ag<sub>37</sub>-Zn** (20 nm) to **{Ag<sub>37</sub>-Zn}<sub>∞</sub>** (34 nm), which may be caused by the increased bonding strength and enhanced rigidity of silver skeletons from **Ag<sub>38</sub>-Zn** to **Ag<sub>37</sub>-Zn** to **{Ag<sub>37</sub>-Zn}<sub>∞</sub>** (Fig. 5d).<sup>59,60</sup> All the clusters showed good linear functions of emission intensity to temperature in the range of 223–83 K. The linear equation can be described as  $I_{\max} = -8719T - 2240700$  with a correlation coefficient of 0.997 for **Ag<sub>38</sub>-Zn**,  $I_{\max} = -3355T - 891426$  with a correlation coefficient of 0.996 for **Ag<sub>37</sub>-Zn**, and  $I_{\max} = -4897T - 1220250$  with a correlation coefficient of 0.997 for **{Ag<sub>37</sub>-Zn}<sub>∞</sub>** (Fig. 5e). The good linearity suggests that **Ag<sub>38</sub>-Zn**, **Ag<sub>37</sub>-Zn** and **{Ag<sub>37</sub>-Zn}<sub>∞</sub>** may be potential sensors for luminescent thermometers to detect a broad range of temperature from 83 to 223 K. In fact, even in the temperature range of 283–223 K, the correlation coefficients of **Ag<sub>38</sub>-Zn**, **Ag<sub>37</sub>-Zn** and **{Ag<sub>37</sub>-Zn}<sub>∞</sub>** are 0.971, 0.972 and 0.947, respectively, also showing good linearity for the function of emission with temperature. All of their emission lifetimes fall into the microsecond scale at 83 K (Fig. 5f), indicating that their luminescences all display a triplet phosphorescence origin.<sup>61,62</sup>

The introduction of the TM clusters can also endow the silver clusters with magnetic properties. The temperature-dependent magnetic susceptibilities of **Ag<sub>38</sub>-Co** and **Ag<sub>38</sub>-Ni** were measured in the temperature range of 2–300 K under an applied external field of 1 kOe (Fig. S17 and S18<sup>†</sup>). At 300 K, the  $\chi_m T$  values of **Ag<sub>38</sub>-Co** and **Ag<sub>38</sub>-Ni** are 16.78 cm<sup>3</sup> K mol<sup>-1</sup> and 9.61 cm<sup>3</sup> K mol<sup>-1</sup>, respectively, which are lower than the theoretical values of 21.9 cm<sup>3</sup> K mol<sup>-1</sup> for four Co<sup>2+</sup> ions ( $g = 2, s = 3/2$ ) and 11.31 cm<sup>3</sup> K mol<sup>-1</sup> for four Ni<sup>2+</sup> ions ( $g = 2$  and  $s = 1$ ). With cooling from 300 K to 2 K, the  $\chi_m T$  values of **Ag<sub>38</sub>-Co** and **Ag<sub>38</sub>-Ni** decrease slowly at first in the range of 300–20 K and later rapidly decrease in the range of 20–2 K. The  $\chi_m T$  values reach minimum values of 1.37 and 0.7 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K, respectively. These behaviors indicate that **Ag<sub>38</sub>-Co** and **Ag<sub>38</sub>-Ni** are antiferromagnetic. These results are consistent with those of reported TM<sub>4</sub>SiW<sub>9</sub> clusters,<sup>34</sup> suggesting that the antiferromagnetic properties of the TMCC cluster have been introduced to originally diamagnetic silver cluster materials.

## Conclusions

In summary, we have successfully developed a synthetic method for constructing the rare non-closed silver clusters based on the TMCC-substituted POMs as the templates. With the method, four series of a total of seven new non-closed silver cluster species have been successfully synthesized, showing a fusion of

three distinct research areas of POM, TM clusters, and silver clusters. These examples provide atomically precise structural information on how the TMCC-substituted POM templates could prevent the Ag<sup>+</sup> ions from forming closed clusters. Furthermore, the POM moiety and TMCC moiety of the TMCC-substituted POM templates show good tunability and flexibility, which provides the possibility for constructing diverse non-closed silver clusters. In particular, the TMCC moiety can further aggregate POMs, and it is expected to introduce giant high-nuclearity TMCC-substituted POMs into the assembly reaction of the silver clusters, which will show great potential in the construction of novel silver clusters, including high-dimensional cluster-based framework materials. Additionally, given their distinct physicochemical properties, the integration of TMCCs, POMs, and silver clusters into same molecular clusters is expected to endow the silver clusters with more abundant and unique optical, electrical, magnetic, and catalytic properties. The results demonstrate that the TMCC-substituted POM-templated synthetic strategy is a promising method for the development of unexplored non-closed multicomponent materials.

## Data availability

The datasets supporting this article have been uploaded as part of the ESI.<sup>†</sup>

## Author contributions

Rui Ge: investigation, data curation, writing – original draft; Ping-Wei Cai: characterization and methodology; Cai Sun: characterization and methodology; Yan-Qiong Sun: characterization and methodology; Xin-Xiong Li: writing – original draft, supervision, project administration, funding acquisition; Shou-Tian Zheng: supervision, project administration, funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

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