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One-Pot versus Sequential Reactions in the Self-Assembly of Gigantic Nanoscale Polyoxotungstates

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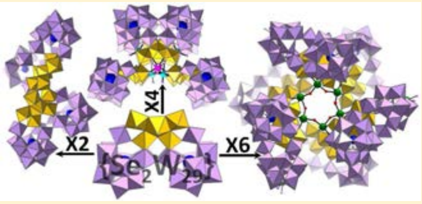
S Supporting Information

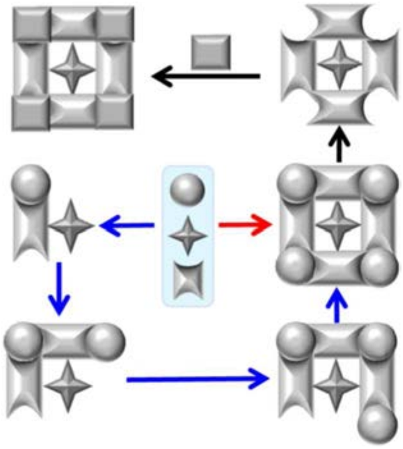
ABSTRACT: By using a new type of lacunary tungstoselenite $\{Se_2W_{29}O_{103}\}$ (**1**), which contains a "defect" pentagonal $\{W(W)_4\}$ unit, we explored the assembly of clusters using this building block and demonstrate how this unit can give rise to gigantic nanomolecular species, using both a "one-pot" and "stepwise" synthetic assembly approach. Specifically, exploration of the one-pot synthetic parameter space lead to the discovery of $\{Co_{2.5}(W_{3.5}O_{14})(SeW_9O_{33})(Se_2W_{30}O_{107})\}$ (**2**), $\{CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2\}$ (**3**), and $\{Ni_2W_2O_2Cl(H_2O)_3(Se_2W_{29}O_{103})(Se_3W_{30}O_{107})_2\}$ (**4**), effectively demonstrating the potential of the $\{Se_2W_{29}\}$ based building blocks, which was further extended by the isolation of a range of 3d transition metal doped tetramer family derivatives: $\{M_2W_nO_m(H_2O)_m(Se_2W_{29}O_{102})_4\}$ (M = Mn, Co, Ni or Zn, $n = 2$, $m = 4$; M = Cu, $n = 3$, $m = 5$) (**5** - **9**). To contrast the 'one-pot' approach, an optimized stepwise self-assembly investigation utilizing **1** as a precursor was performed showing that the high nuclearity clusters can condense in a more controllable way allowing the tetrameric clusters (**5** - **8**) to be synthesized with higher yield, but it was also shown that **1** can be used to construct a gigantic $\{W_{174}\}$ hexameric-cluster $\{Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6\}$ (**10**). Further, **1** can also dimerize to $\{(Se_2W_{30}O_{105})_2\}$ (**11**) by addition of extra tungstate under similar conditions. All the clusters were characterized by single-crystal X-ray crystallography, chemical analysis, infrared spectroscopy, thermogravimetric analysis, and electrospray ionization mass spectrometry, which remarkably showed that all the clusters, even the largest cluster, **10** (~50 kD), could be observed as the intact cluster demonstrating the extraordinary potential of this approach to construct robust gigantic nanoscale polyoxotungstates.



INTRODUCTION

The controlled assembly of large nanomolecular clusters is a great challenge since the reliable assembly of new architectures is not only important for exploring the fundamentals of structure and bonding but also to extend the range of new materials, properties, and devices ultimately perhaps suggesting that the reliable inorganic synthesis of gigantic molecules may define a new age in nanoscience.[1] There is a problem however, while inorganic materials chemists have utilized many synthetic approaches to quantum dots and nanoparticles,[2] the use of molecular precursors to generate well-defined, molecular inorganic nanostructures is much less developed.[3] Polyoxometalate (POM) clusters define a class of molecules, which are polymers of metal−oxygen units $\{MO_x\}_n^{y-}$ (where M = Mo, W, V, Nb) spanning a great range of structural types, which show great promise to bridge this gap.[4−7] This is because there has been a well-established building block strategy, which utilizes the preformed lacunary clusters to build giant POM assemblies.[8,9] Indeed, some compounds could only be obtained by using such precursors or building blocks as starting materials, for example, the well explored $\{H_7P_8W_{48}O_{184}\}$ can only be built from a "preformed" $\{P_2W_{18}O_{62}\}$ Dawson precursor.[10,11] Also, a "top−down" synthetic strategy, by the controlled decomposition of a preformed large cluster into new smaller cluster types, has recently been reported, see Scheme 1.[12] However, it is hard to control the assembly to obtain the desired precursor or building block to access a well-defined library of POM-based materials. For example, pentagonal $\{M(M)_5\}$ (M = Mo or W) based units play a key role in

Scheme 1. Representation of the Assembly of a Cluster System[a]



[a]The red route shows the direct one-pot synthesis. The blue route gives the stepwise method, and the black route gives a post-synthetic transformation.

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forming gigantic "fullerene-like" clusters from an architectural point of view as the pentagonal units are crucial for geometrical closure of the cluster structure.[13]

Such units have been widely observed in polyoxomolybdates, for example in the family of mixed valence Mo wheel-shaped and spherical Keplerate clusters first reported by Müller and co-workers.[14−19] Despite the importance of such architectures, few POM building blocks containing pentagonal units have been isolated as individual clusters and the minimum nuclearity of the pentagonal $\{M(M)_5\}$ containing cluster is $\{Mo_{36}\}$ at present.[20] This is interesting since the trigger for forming the bipyramidal core $\{MO_7\}$ unit has so far eluded detection, not to mention the elucidation of the mechanism of assembly of high nuclearity clusters based on the $\{M(M)_5\}$ units. In contrast, tungsten-based building blocks with pentagonal geometries have only very recently been observed in mixed molybdenum/tungsten or vanadium/tungsten-based POM keplerates, etc., because the reduced polyoxotungstate species are harder to access synthetically.[21−24] All the largest clusters reported so far, including $\{H_{64}Ce_{20}Ge_{10}W_{100}O_{410}\}$,[25] $\{\{Sn(CH_3)_2(H_2O)\}_{24}\{Sn(CH_3)_2\}_{12}(X_{12}W_{108}O_{408})\}$ (X = P, As),[26] $\{H_{140}Ce_{24}Ge_{12}W_{120}O_{532}\}$,[27] $\{H_{44}Gd_8As_{12}W_{124}O_{454}\}$,[28] $\{As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}\}$,[29] $\{Mn_{40}P_{32}W_{224}O_{888}\}$,[11c] etc., are built by intramolecular linkers such as lanthanide or transition metal ions and small lacunary POM precursors and high nuclearity clusters which assemble from simple condensed tungsto-oxo frameworks are still rare.

Herein, a combinatorial strategy has been used to explore the assembly process of heteropolyoxotungstates (HPOW) using selenium as the heteroatom, which has been far less explored[4b] and only recently has some progress been achieved, mainly by Cronin et al.[24,30] In this context, we show how we rationally isolated the basic building block $\{Se_2W_{29}\}$ (in the form of $[H_{10}Se_2W_{29}O_{103}]^{14-}$ (**1a**) from the study of $\{Fe_2W_3O_9(H_2O)_3(Se_2W_{29}O_{102})_4\}$, a compound simply built from four $\{Se_2W_{29}\}$ branches around two iron atom "seeds" with three extra tungstates completing the structure,[30a] by using a one-pot reaction. The family of tungstoselenite clusters described here presents several new interesting and unusual features. First, this family contains clusters with a very wide range of size (1.7−3.8 nm), nuclearity ($\{W_{29}\}$ to $\{W_{174}\}$) and we are able to demonstrate, using high resolution electrospray mass spectrometry, that the entire family of clusters (∼17−50 kDa) are stable in solution which itself is extraordinary (see electrospray section). Second, the tungstoselenite system displays a tendency to incorporate a pentagonal bipyramidal core $\{WO_7\}$ unit, as well as assembling novel building blocks and constructing a new type of HPOW family. Third, the synthetic conditions of this cluster family are extremely simple and quite mild, and the nuclearity of the isolated products could be controlled by pH and ionic strength. In addition, the surface of this family of clusters is not fully shielded by terminal oxo ligands and contains many exchangeable water ligands and thus keeps the opportunity for further condensation to higher nuclearity frameworks. Furthermore, these unusual tungstoselenites, like the classic lacunary POMs, could be modified by doping transition metal ions and further self-assemble into transition metal ion containing clusters, which has been thoroughly demonstrated by the work presented herein.

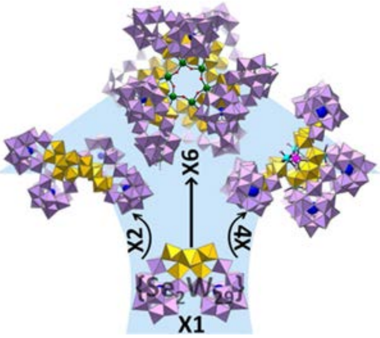
The lacunary $\{Se_2W_{29}\}$ cluster represents the smallest polyoxotungstate that contains pentagonal unit so far isolated, and electrospray ionization, cyclic voltammetry and powder-XRD were used to investigate the stability and purity of **1**, demonstrating the outstanding potential of $\{Se_2W_{29}O_{103}\}$ as a precursor for the assembly of new POM clusters. Inspired by the isolation of compound **1**, we have further extended this work to the synthesis of a family of derivatives by tuning reaction parameters, see Table 1 from **1a** to **9a**, in which the "degree of polymerization" of $\{Se_2W_{29}\}$ type building blocks can vary from 1 to 4. Furthermore, the architectural parameter space defined by the $\{Se_2W_{29}O_{103}\}$ has been explored.

Table 1. Representation of the Cluster Anions 1a−11a Found in Corresponding Compounds 1−11, of Which the Full Compositions Are Shown in Experimental Section

no.	anion {building block} formula
1a	$[H_{10}Se_2W_{29}O_{103}]^{14-}$
2a	$[H_{19}Co_{2.5}(W_{3.5}O_{14})(SeW_9O_{33})(Se_2W_{30}O_{107})]^{17-}$
3a	$[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2]^{40-}$
4a	$[H_{14}Ni_2W_2O_2Cl(H_2O)_3(Se_2W_{29}O_{103})(Se_3W_{30}O_{107})_2]^{43-}$
5a	$[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]^{44-}$
6a	$[H_{22}Co_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]^{58-}$
7a	$[H_{25}Ni_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]^{55-}$
8a	$[H_{25}Zn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]^{55-}$
9a	$[H_{24}Cu_2W_3O_5(H_2O)_5(Se_2W_{29}O_{102})_4]^{52-}$
10a	$[H_{18}Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6]^{99-}$
11a	$[H_{18}(Se_2W_{30}O_{105})_2]^{26-}$

By directly using compound **1** as precursor in multistep reactions, not only can the tetramer clusters (**5** - **8**) be synthesized with higher yield, but also **1** can dimerize to $K_{26}[H_{18}(Se_2W_{30}O_{105})_2]\cdot 104H_2O$ **11** by addition of extra tungstate under similar reaction conditions, see Table 1. Further, by using this approach, the gigantic HPOM compound, $K_{90}(C_2H_8N)_9[H_{18}Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6]\cdot 246H_2O$ **10** has been obtained which could be viewed as a hexamer of $\{Se_2W_{29}\}$ moieties, giving a gigantic $\{W_{174}\}$ polyoxotungstate cluster comprising building blocks with pentagonal geometries, see Scheme 2. Importantly, all the cluster anions shown in Table 1 were observed using electrospray ionisation mass spectrometry without any decomposition including the largest ever POM cluster observed in solution,

Scheme 2. General Building Block Principle, Based upon $\{Se_2W_{29}\}$-Based Building Blocks Aggregating ×2, ×4, and ×6[a]



[a]Light purple polyhedra, $\{WO_6\}$; yellow polyhedra, pentagonal unit $\{(WO_7)W_4\}$; cyan spheres, W; blue spheres, Se; light purple spheres, O; red spheres, disordered O and Cl; pink and dark green spheres, heterometal ions.

$[H_{18}Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6]^{99-}$, which has a molecular weight of around 50 kDa.

■ RESULTS AND DISCUSSION

Isolation of the $\{Se_2W_{29}\}$ Building Block. To develop a synthetic framework to understand and control the self-assembly of tungstoselenite building blocks, a combinational strategy taking advantage of inorganic "cation-directing" and organic "shrink-wrapping" effects has been explored.[31] This is because our preliminary experimental exploration showed that the formation of large building blocks such as $\{Se_2W_{29}\}$ in solution is strongly affected by the presence of potassium cations and WO_4^{2-}/SeO_3^{2-} ionic strength. An excess amount of organic cation dimethylammonium (DMA) has also been introduced to the chosen system to probe the assembly process. Thus the $\{Se_2W_{29}\}$ building block in the form of polyanion $[H_{10}Se_2W_{29}O_{103}]^{14-}$ (**1a**) has been isolated as compound **1** $K_9(C_2H_8N)_5[H_{10}Se_2W_{29}O_{103}]\cdot 30H_2O$ (see Figure 1) from a simple one-pot reaction of K_2WO_4, K_2SeO_3 (W/Se molar ratio 12.8: 1) and dimethylamine hydrochloride at an approximate pH of 3.0 in aqueous solution. Subsequent crystallization over a one-week period yielded a colorless hydrated salt with the yield of 48% (based on W).

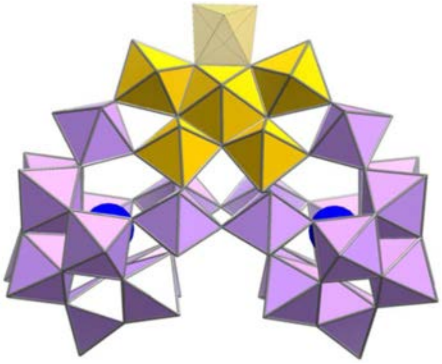


Figure 1. Polyhedral representation of anion **1a**. All cations and solvent water molecules are omitted for clarity. Light purple polyhedra, $\{WO_6\}$; yellow polyhedra, pentagonal unit $\{(WO_7)W_4\}$ with the lacunary position shown with semitransparent polyhedron; blue spheres, Se.

Single crystal X-ray structural analysis showed that compound **1** crystallizes in triclinic system (space group $P\bar{1}$). The overall anion $[H_{10}Se_2W_{29}O_{103}]^{14-}$ **1a** contains three main parts: one lacunary pentagonal unit $\{(WO_7)W_4\}$, two B-β-$\{SeW_9O_{33}\}$ units and six $\{WO_6\}$ octahedra linking the first two parts together in a corner-shared coordination mode (see Figure 1). This cluster could be viewed as a "monomer" member of the $\{Se_2W_{29}\}$ polyanion family. In the lacunary pentagonal unit $\{(WO_7)W_4\}$, each W atom has one water ligand with the W−OH$_2$ bond length varying between 2.22(6) and 2.41(5) Å. The defect position of the $\{(WO_7)W_4\}$ unit is occupied by two off-plane K^+ cations and the whole clusters are well separated by K^+ and DMA cations (see Supporting Information Figure S1).

The structural novelty of compound **1a**, which is a "pure" polyoxotungstate cluster containing a lacunary pentagonal unit $\{(WO_7)W_4\}$, is very intriguing so we also set out to explore the basic physical properties. First, cyclic voltammetry experiments were performed to examine the redox properties and solution stabilities of compound **1** in 0.1 M CH_3COOK/CH_3COOH buffer solution containing 0.2 M K_2SO_4 with pH value varying from 1.7 to 6.6 (see Figure 2, for CV spectrum at pH = 6.6 see Supporting Information Figure S7). At a scan rate of 100 mV s^{-1} with the pH value of the media at 3, a merged broad reduction wave of tungsten appeared with its location at −0.674 V and the relevant oxidation wave is located at −0.548 V ($E_{1/2}$ = −0.611 V vs Ag/AgCl, see Supporting Information for more details). Further, cyclic voltammetry experiments were also performed under different pH values of the media.

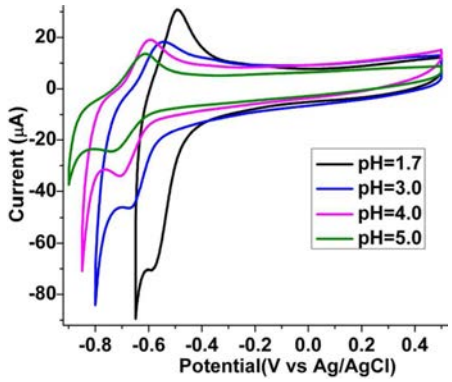


Figure 2. Cyclic voltammograms of compound **1** in 0.1 M CH_3COOK/CH_3COOH buffer solution with pH varying from 1.7 to 5.0 using 0.2 M K_2SO_4 as electrolyte. The scan rate was 100 mV s^{-1}. The working electrode was glassy carbon (3 mm) and the reference electrode was Ag/AgCl.

From Figure 2 it can be seen that as the media becomes less acidic (pH value increasing from 1.7 to 5.0), the redox waves shift toward more negative values in the investigated region at a scan rate of 100 mV s^{-1}, with their corresponding current intensities gradually decreasing. The shifts and the current intensity decrease of reduction waves are more obvious (155 mV, 46.1 μA from pH 1.7 to 5.0) than those of the oxidation ones (119 mV, 17.2 μA from pH 1.7 to 5.0). When the pH value was increased to 6.6, although the reversible tungsten redox couple was still observed, its current intensity decreased greatly due to the precipitation of compound **1** as a result of its markedly reduced solubility in the nearly neutral media (see Supporting Information Figure S7). The reproducible voltammetric pattern of compound **1** in media with different pH values shows that it is quite stable in solution, which is also the prerequisite for its use as precursor in later multistep synthesis work.

Exploring the One-Pot Self-Assembly with the First Row Transitional Metal Ions. The first row transition metal ions can stabilize the tungstoselenite clusters and their coordination modes allow them to easily assemble around many building blocks. We decided to explore how they could interact with the defect position on the $\{(WO_7)W_4\}$ unit as we imagined this could change the whole assembly process yielding new clusters. To do this we screened a range of parameters, for example the W/Se ratio. When the ionic strength of $[SeO_3]^{2-}$ was increased (thus the W/Se molar ratio was decreased to 8.1:1) at pH around 4.0, the introduction of Co^{2+} ions into the solution yielded: $[H_{19}Co_{2.5}(W_{3.5}O_{14})(SeW_9O_{33})(Se_2W_{30}O_{107})]^{17-}$ (**2a**), see Figure 3.

Structural analysis of **2a** shows that it has very close nuclearity to that of the anion $[H_2(SeO_3)_3W_{43}O_{139}]^{24-}$ isolated under similar conditions but without Co^{2+} and DMA.[24] Both structures have two main parts, that is, one $\{Se_2W_{29}\}$ type

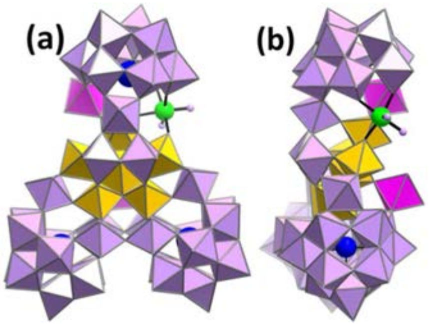


Figure 3. Polyhedral representation of the structure of anion **2a** $[H_{19}Co_{2.5}(W_{3.5}O_{14})(SeW_9O_{33})(Se_2W_{30}O_{107})]^{17-}$: (a) front-view and (b) side-view. All cations and solvent water molecules are omitted for clarity. Light purple polyhedra, $\{WO_6\}$; yellow polyhedra, $\{(WO_7)W_5\}$ pentagonal unit; pink polyhedra, $\{CoO_6\}$; blue spheres, Se; green spheres, metal position half occupied by Co and W; light purple spheres, O.

subunit (for **2a** it is $\{Se_2W_{30}\}$) and one B-β-$\{SeW_9\}$ unit. In **2a**, these two parts are connected by three kinds of linkers: one $\{W_3O_{13}\}$ unit, which consists of three corner-sharing $\{WO_6\}$ octahedra, one $\{CoO_6\}$ octahedron, and an additional $\{MO_6\}$ octahedron, where M is equally occupied by W and Co (which could be viewed as a "Monomer+" based on $\{Se_2W_{29}\}$). In addition, it should be noted that there is one more $\{CoO_6\}$ octahedron hanging from the $\{Se_2W_{30}\}$ subunit (see Figure 3). However, in the anion $[H_2(SeO_3)_3W_{43}O_{139}]^{24-}$ the linkers are one $\{W_3O_{13}\}$ unit constructed by three edge-shared $\{WO_6\}$ octahedra and two $\{WO_6\}$ octahedra. The $\{Se_2W_{30}\}$ subunit has the same structure as in anion **1a** with the lacunary pentagonal unit $\{(WO_7)W_4\}$ being fully complete $\{(WO_7)W_5\}$. The average W−O bond length within the pentagon-shaped $\{WO_7\}$ unit is 1.987(3) Å and it is slightly shorter than that found in anion **1a**, which is 2.001(9) Å. Also, it should be noted that because the $\{(WO_7)W_5\}$ pentagonal unit in anion **2a** is "sandwiched" by the $\{W_3O_{13}\}$ linker and the pendant $\{CoO_6\}$ unit (see Figure 3 right) none of its oxygen atoms are protonated.

By adjusting the pH value from 4.0 to around 3.5 and 3.3 in similar reaction systems, another two polyanions were produced as $[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_2W_{30}O_{107})_2]^{40-}$ (**3a**) and $[H_{14}Ni_2W_2O_2Cl(H_2O)_3(Se_2W_{29}O_{103})(Se_3W_{30}O_{107})_2]^{43-}$ (**4a**), respectively. X-ray structure analysis shows that in anion **3a** there is one $\{Se_2W_{26}\}$ unit "bridged above" two $\{Se_3W_{30}\}$ subunits (which could be viewed as a "Dimer+" based on $\{Se_2W_{29}\}$). The $\{Se_3W_{30}\}$ subunit in **3a**, compared to the $\{Se_2W_{30}\}$ subunit in **2a**, has one more Se^{IV} closely capped on one side of its pentagonal unit $\{(WO_7)W_5\}$ via three μ_2 oxygen ligands. In addition, a $\{(W/Co)O_6\}$ octahedron attached to the other side of the $\{(WO_7)W_5\}$ unit through one bridging oxygen atom (see Figure 4a). The structure of the $\{Se_2W_{26}\}$ subunit is a derivative of $\{Se_2W_{29}\}$ with the $\{WO_7\}$ unit and two outmost $\{WO_6\}$ units in the lacunary $\{(WO_7)W_4\}$ pentagon missing. Although the two $\{Se_3W_{30}\}$ units have the same connecting mode to the $\{Se_2W_{26}\}$ unit, they are rotated with respect to each other, which might decrease the steric hindrance and hence it is good for the stabilization of the whole structure with C_2 symmetry (see Supporting Information Figure S2a).

The structure of anion **4a** is very similar to that of anion **3a**. However, the bridged unit between the two $\{Se_3W_{30}\}$ units becomes $\{Se_2W_{29}\}$ plus two isolated $\{WO_6\}$ octahedra instead of $\{Se_2W_{26}\}$ in anion **3a**. As a result, **4a** could be viewed as a "Trimer" based on the $\{Se_2W_{29}\}$ building block. Additionally, each $\{(WO_7)W_5\}$ pentagonal unit in the two $\{Se_2W_{30}\}$ units is capped by one $\{SeO_3\}$ unit outside while their inner faces are connected together by two isolated $\{NiO_6\}$ octahedra, in which one of the Ni^{II} ion coordinates with a Cl^- instead of a water ligand with a Ni−Cl bond length of 2.323(5)Å. The two $\{Se_3W_{30}\}$ subunits are attached to the bridged unit in parallel mode, giving the whole cluster a *Cs* symmetry (see Figure 4b and Supporting Information Figure S2b).

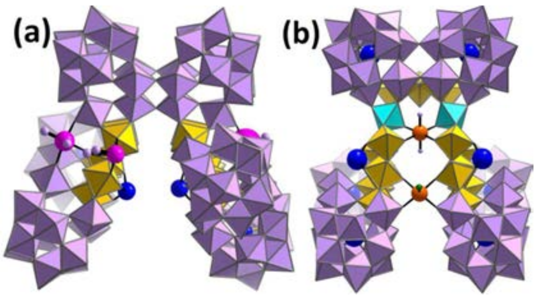


Figure 4. Polyhedral representations of the structures of (a) anion **3a** $[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_2W_{30}O_{107})_2]^{40-}$ and (b) anion **4a** $[H_{14}Ni_2W_2O_2Cl(H_2O)_3(Se_2W_{29}O_{103})(Se_3W_{30}O_{107})_2]^{43-}$. All cations and solvent water molecules are omitted for clarity. Light purple polyhedra: $\{WO_6\}$; yellow polyhedra, $\{(WO_7)W_5\}$ or $\{(WO_7)W_4\}$ pentagonal unit; cyan polyhedra, $\{WO_6\}$ linker; blue spheres, Se; pink spheres, disorder position occupied by Co and W; orange spheres, Ni; dark green spheres, Cl; light purple spheres, O.

Furthermore, decreasing the pH of solutions containing different transition metal ions in the range from 2.7 to 3.0 in similar systems, more members of the saddle-shaped cluster family $\{M_2W_nO_m(H_2O)_m(Se_2W_{29}O_{102})_4\}$ (M = Mn, Co, Ni, or Zn, n = 2, m = 4; M = Cu, n = 3, m = 5), which are referred to compounds **5**−**9** with their corresponding anions **5a**−**9a**, respectively, have been successfully synthesized. Structural analysis revealed that the structure of $[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]^{54-}$ **5a** is very similar to that of the polyanion $\{Fe_2W_3O_9(H_2O)_3(Se_2W_{29}O_{102})_4\}$[30a] but with subtle differences. For instance, both anions are saddle-shaped clusters containing four $\{Se_2W_{29}\}$ branches linked together by a middle core (which could be viewed as a "Tetramer" based on $\{Se_2W_{29}\}$). In $\{Fe_2W_3O_9(H_2O)_3(Se_2W_{29}O_{102})_4\}$ this middle core is $\{Fe_2W_3\}$ in which three W atoms are disordered in six positions in a parallel direction to the two iron ions (see Figure 5a). However; in **5a** the central core comprises a $\{Mn_2W_2\}$ moiety in which the two W atoms are equally disordered in four positions distributed in a direction perpendicular to that of the two manganese ions (see Figure 5b). Furthermore, except the disordered W atom in the very center of the whole cluster, the other two disordered W atoms in the $\{Fe_2W_3\}$ core cap the outside face of the two opposite $\{(WO_7)W_4\}$ pentagonal units respectively (see Figure 5a), while in $\{Mn_2W_2\}$ core the rest of the disordered W atom falls in the gap between these two pentagonal units, bridging them together (see Figure 5b). The structures of polyanions $[H_{22}Co_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]^{58-}$ **6a**, $[H_{25}Ni_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]^{55-}$ **7a**, $[H_{25}Zn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]^{55-}$ **8a**, and $[H_{24}Cu_2W_3O_5(H_2O)_5(Se_2W_{29}O_{102})_4]^{52-}$ **9a**, are almost the same to that of anion **5a** except that the two Mn^{2+} ions have been replaced by two Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} ions,

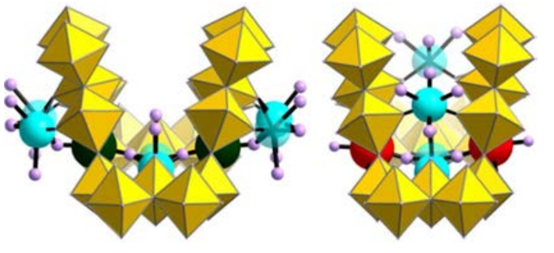


Figure 5. Comparisons of the core (a) $\{Fe_2W_3\}$ in $\{Fe_2W_3O_9(H_2O)_3(Se_2W_{29}O_{102})_4\}$ and (b) $\{Mn_2W_2\}$ in $\{Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4\}$ (**5**) from a side-view. All cations and solvent water molecules are omitted for clarity. Yellow polyhedra, $\{(WO_7)W_4\}$ pentagonal unit; cyan spheres, W; dark green spheres, Fe; red spheres, Mn; light purple spheres, O. Each pair of disordered positions is highlighted with one position occupied by a half transparent W atom.

respectively. However it should be pointed out that the W atom in the center $\{M_2W_2\}$ core which falls in the gap between two opposite $\{(WO_7)W_4\}$ pentagonal units, is disordered in two positions with each having a 50% occupancy in clusters **5a**−**8a**, while in anion **9a**, these two positions are fully occupied by W atoms, which is exactly the reason why anion **9a** has one more W atom compared to anions **5a**−**8a** (see Supporting Information Figure S3).

When we take into account the synthetic conditions required for the formation of these compounds, it is clear that influence of pH is vital. Generally, all these compounds are formed in a pH range from 2.8 to 4.0, implying that in this pH range the $\{Se_2W_{29}\}$ type building blocks are the main species and quite stable in solution. This observation is in line with our experience regarding the optimal conditions for the synthesis and isolation of compound **1**, which could be obtained over a wide pH range from 2.8 to around 3.7 but with higher purity and yield at pH value around 3.0. When transition metal ions are introduced into this reaction system, in the pH range from 2.8 to 3.0, the final product always contains four main $\{Se_2W_{29}\}$ building blocks linked together in a saddle form, irrespective of the transition metal ion species ("Tetramer", nuclearity is 118 or 119). If the pH value goes a little higher, i.e., at around 3.3, compound **4** would be obtained ("Trimer", nuclearity is 91), which is mainly built from one $\{Se_2W_{29}\}$ and two $\{Se_3W_{30}\}$ subunits. While continuing to increase the pH value to around 3.5, compound **3** would be produced ("Dimer+", nuclearity is 87). However, the building blocks of compound **3** are changed somewhat based on the fact that except the two $\{Se_3W_{30}\}$ subunits, another fragment $\{Se_2W_{26}\}$ which could be viewed as a derivative of $\{Se_2W_{29}\}$ appeared, indicating that the $\{Se_2W_{29}\}$ species at this pH value in solution is no longer so stable. Finally when the pH value was increased to around 4.0, compound **2** ("Monomer+", nuclearity is 43) with more kinds of building blocks, for example, $\{W_3O_{14}\}$, $\{SeW_9\}$, and $\{Se_2W_{30}\}$, has been isolated, which is consistent with our hypothesis that the $\{Se_2W_{29}\}$ might not be the main species at higher pH values (around 4) in one-pot reaction solution. Thus it could be concluded that the nuclearity of compounds **2**−**9** increases from 43 to 118/119, with the corresponding "degree of polymerization" of $\{Se_2W_{29}\}$ family building blocks increasing from one to two, three, and finally, four, as the pH value of the reaction solution decreased from 4.0, 3.5, 3.3, and 3.0 accordingly. This is not only consistent with the current understanding of how POMs form, that is, a strong acidic environment is favored for higher nuclearity metal−oxide clusters, while in weakly acidic environments, they are prone to decomposition by hydrolysis but also offers a more controllable method to synthesize polyoxotungstates with different nuclearities.

Beside the pivotal effect of pH on the self-assembly process, another key factor to the synthesis of these compounds is the use of potassium cations. In many of our experimental studies it was found that none of these compounds could be obtained in a crystalline form without the presence of potassium cations in this reaction system, which is in line with single crystal X-ray diffraction structure analysis. Moreover, compared to the influence of pH value and the use of potassium cations, it seems that the impact of the W/Se ratio is not so important yet could not be ignored. Specifically, for the synthesis of $\{M_2W_nO_m(H_2O)_m(Se_2W_{29}O_{102})_4\}$ (M = Mn, Co, Ni, or Zn, $n = 2$, $m = 4$; M = Cu, $n = 3$, $m = 5$) compounds, different W/Se ratios have been tried in numerous experiments, which are in a range from 2.6 to 10.6. It turned out that these crystals could be obtained when the W: Se ratio falls into the range of 6.6 to 10.6, however with the ratio lower than 6.6, the common "sandwiched" compounds[32−34] $\{M_mW_n(SeW_9)_2\}$ (M = transition metal ions; $m = 2$, $n = 1$; $m = 3$, $n = 0$) would be more easily produced and are always obtained when W/Se ratio is lower than 3.5.

Stepwise Assembly Based on the Cluster $\{Se_2W_{29}O_{103}\}$. Although the one-pot assembly method is very promising in discovering new clusters with high nuclearity,[24,35,36] it is still a big challenge to experimentally control the synthetic process. To better understand the assembly process in this system, a stepwise approach based on compound **1** $\{Se_2W_{29}O_{103}\}$ has been utilized in our studies also. Here, the cluster $\{Se_2W_{29}O_{103}\}$ **1** was chosen for the following reasons: (i) it is the smallest $\{(WO_7)W_4\}$ containing cluster, and it has a defect position occupied by potassium cations which could be easily substituted and also the water ligand position on $\{(WO_7)W_4\}$ could be further condensed; (ii) solution behavior studies have shown that cluster **1** is stable over a wide pH range, and it was observed that the main basic building blocks of a few clusters are the $\{Se_2W_{29}\}$ derivatives, for example, compounds **3**−**9**. Additionally, the powder XRD data shows that the product we have isolated is very pure (see Supporting Information Figure S5). All these studies together suggest that cluster **1** has excellent potential to be utilized as a precursor for the stepwise assembly of new cluster architectures.

As a result, the previously mentioned clusters **5**−**8** were successfully synthesized by a stepwise approach, and importantly it should be noted that there is an advantage in terms of increased product yield for the stepwise process vs the one-pot approach. Furthermore, a range of new unexpected clusters that were not obtained by one-pot reactions have been discovered, such as the gigantic cluster $\{H_{18}Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6\}^{99-}$, which is constructed by six $\{Se_2W_{29}\}$ units (which could be viewed as a "Hexamer"), and a "pure" HPOM polyanion $[H_{18}(Se_2W_{30}O_{105})_2]^{26-}$ (which could be viewed as a "Dimer").

The compound $K_{90}(C_2H_8N)_9[H_{18}Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6]\cdot 246H_2O$ (**10**) represents the largest polyoxotungstate framework containing pentagonal units so far. It has six $\{Se_2W_{29}\}$ subunits, six copper linkers and three aqueous copper ions hanging alternatively on the outside of the $\{Se_2W_{29}\}$ branches (see

Figure 6a). The six $\{Se_2W_{29}\}$ subunits, with their inner lacunary pentagon units connected to each other through a corner-shared oxygen atom, are arranged in a circular way directed by the six copper linkers. The average W−O bond length of the pentagon-shaped $\{WO_7\}$ is 2.004(7) Å, showing accordance with those found in other structures reported here. The six coplanar copper linkers are located in the lacunary position of each $\{(WO_7)W_4\}$ pentagonal unit (see Figure 6b). Each copper linker is five-coordinated, giving it a pyramidal geometry. Among the five atoms coordinated to it, three are oxygen atoms from two neighboring $\{Se_2W_{29}\}$ subunits and two are disordered chloride and oxygen atoms, bridging it to two adjacent linkers. The three pendant aqueous copper ions, however, are all six-coordinated with five water ligands and an oxygen atom from a $\{Se_2W_{29}\}$ subunit, thus they function as counterions instead of building up the whole cluster framework.

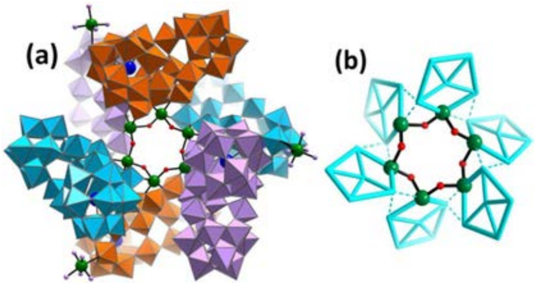


Figure 6. (a) Structural representation of polyanion **10a** and (b) a schematic figure showing the core of anion **10a**, the basic building units $\{Se_2W_{29}\}$ are simplified as pentagons and the dashed lines show how they are linked together; all the oxygen atoms have been omitted. All cations and solvent water molecules are omitted for clarity. Polyhedra, $\{WO_6\}$ (shown in different colors for clarity); blue spheres, Se; dark green spheres, Cu; red spheres, positions equally occupied by O and Cl; light purple spheres, O.

Interestingly, when the introduced transition metal ion was Mn^{2+}, Co^{2+}, Ni^{2+}, or Zn^{2+}, both "one-pot" reactions and stepwise synthesis yielded similar tetrameric clusters. While in the case of Cu^{2+}, although the synthetic conditions were similar, the "one-pot" reaction led to the formation of a tetramer cluster **9**, yet the "stepwise" reaction produced the hexametric compound **10**. The difference might be related to the very strong pseudo-Jahn−Teller effect of Cu^{2+} ions, which allows further structural diversity compared to Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} ions. Furthermore, as shown in compounds **9** and **10**, the copper ions are six-coordinated having octahedral coordination geometry and five-coordinated with square pyramidal coordination geometry, respectively.

Nevertheless, while introducing additional tungstate, further stepwise assembly on pure tungstoselenites under similar conditions generates the anion $[H_{18}(Se_2W_{30}O_{105})_2]^{26-}$ (**11a**). X-ray structure analysis shows that anion **11a** contains two $\{Se_2W_{30}\}$ subunits, binding together through four corner-shared oxygen atoms from two $\{(WO_7)W_5\}$ pentagonal units. The average W−O bond length of the pentagon-shaped $\{WO_7\}$ is 1.999(1) Å, which is in accordance with that found in other structures reported here. The anion itself has an inversion center, located in the plane built by the four corner-shared oxygen atoms. The dihedral angle of these two $\{Se_2W_{30}\}$ subunits is 66.90°. BVS calculations show that the protonated oxygen atoms are all from the two $\{(WO_7)W_5\}$ pentagonal units.

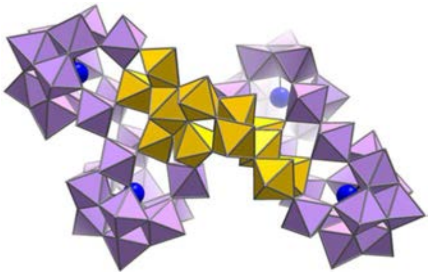


Figure 7. Structural representation of polyanion **11a** $[H_{18}(Se_2W_{30}O_{105})_2]^{26-}$. All cations and solvent water molecules are omitted for clarity. Light purple polyhedra, $\{WO_6\}$; yellow polyhedra, $\{(WO_7)W_5\}$ pentagonal unit; blue spheres, Se; light purple spheres, O.

Electrospray Ionization Mass Spectrometry. Characterization of these high nuclearity POM clusters is another challenge because of their complex and large structures and consequently high charge states and molecular weight. Of course, their solid-state structures can be determined by X-ray crystallography and their solution behaviors are primarily studied by electrospray ionization mass spectrometry.[37−39] ESI-MS has been found to be a valuable tool in the analysis of polyoxometalates since it can detect high mass molecules. However, the ESI-MS studies of these gigantic clusters and their highly charged fragments are pushing even the highest resolution instruments to the limit.

Solutions of the systems investigated were prepared by making up a solution of each compound in water/acetonitrile (5%: 95%) mixture solvent (1 mg/mL). For the most basic cluster **1**, Figure 8 shows its mass spectrum, from which it could be seen there are eight peaks with the strongest ones centered at m/z 1825.9 and m/z 1904.2, whose charges are both −4. It should be especially mentioned that for the peaks whose m/z values are 2160.3 and 2268.3, although their intensities are very low, both their charge numbers could directly be observed as in the −7 charge state in the intact cluster; in fact, the mass spectrum and peak assignments show that they are dimers of the parent cluster $\{H_{10}Se_2W_{29}O_{103}\}$. Assignments of these peaks show that compound **1** is observed as an assembly of related clusters with differing numbers of cations and water molecules existing either as a $\{H_{10}Se_2W_{29}O_{103}\}$ monomer or as a $\{H_{10}Se_2W_{29}O_{103}\}_2$ dimer, showing some degree of stability in solution.

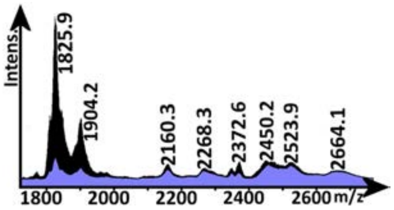


Figure 8. Negative mode ESI of compound **1** in mixed H_2O/MeCN solvent (5%: 95%). All the peaks shown relate to different charge states of the same basic parent cluster $[H_{10}Se_2W_{29}O_{103}]^{14-}$, which is observed as either a monomer or a dimer in the gas phase (see Supporting Information for a full analysis).

Figure 9 shows the mass spectrum of cluster **10**, which is the largest polyoxometalate cluster complex to be observed directly by electrospray mass spectrometry so far. The cluster **10** forms strong ionic interactions with the cations and many strong H-bonds with solvent water molecules because of its quite high

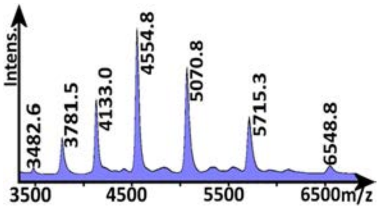


Figure 9. Negative mode ESI of compound **10** in mixed H_2O/MeCN solvent (5%: 95%). All the peaks shown relate to different charge states of the same basic parent cluster $[H_{18}Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6]^{99-}$, which is observed as a monomer in the gas phase (see Supporting Information for a full analysis).

negative charge (~99) and gigantic molecular weight (over 51400), which means that it is hard to observe the naked single cluster without any cations and solvent molecules intact. Also because the molecular weight is beyond the instrument resolution limit, it is hard to resolve the charge number associated with each peak, making the assignments for the peaks impracticable. Fortunately, it is possible to unambiguously deconvolute the mass spectra of these clusters, as they are quite similar in the way that the peaks (m/z) in the mass spectra of each cluster appear in an approximate harmonic sequence, i.e., the spacing between peaks from right to left becomes narrower and their reciprocals (z/m) roughly form an arithmetic sequence that implies the charges of the peaks change continuously and the mass are roughly the same coming from the molecule of similar compositions.

For each set of mass spectrometry data, we could determine the charges and mass of the molecule from a group of relevant peaks, i.e., assign them as gradually charged anions that are derived from the parent polyanion (see Supporting Information). Mass spectra of other compounds **2**−**9** and **11** have shown similar features and so are processed by using the same method. Peak assignments of the mass spectrum indicate that these clusters retained their structural integrity in solution, since they could be observed as an assembly of related clusters with differing numbers of cations and water molecules existing either as a monomer, a dimer or even as a trimer of the related parent polyanion (see Supporting Information).

■ CONCLUSIONS

In summary, the first example of the pentagonal unit containing lacunary polyoxotungstate building block $K_9(C_2H_8N)_5[H_{10}Se_2W_{29}O_{103}]\cdot 30H_2O$ (**1**) has been rationally isolated. Further exploration by screening pH and ionic strength over a range of one-pot reactions lead to the discovery of a family of derivatives of $\{Se_2W_{29}\}$ doped with various first row transition metal species, showing that this "dynamic building block library" has a great deal of complexity in solution (see Figure 10).

In addition, cyclic voltammetry and electrospray ionization mass spectrometry studies demonstrate that compound **1** is quite stable in solution over a wide pH range (from 1.7 to 6.6), showing its potential for use as a synthetic precursor for the assembly of a family of gigantic robust clusters. This potential was realized in the stepwise self-assembly investigations using compound **1** as precursor, showing that not only the tetrameric derivatives of **1** (doped with Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}) could be obtained in higher yield, but also **1** can dimerize into $\{(Se_2W_{30}O_{105})_2\}$ by addition of extra tungstate under similar conditions. Moreover, a gigantic hexameric cluster, $\{H_{18}Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6\}$, was isolated which is by far the largest tungsten-oxo-framework containing $\{(W)W_4\}$ pentagonal units isolated so far. Interestingly, electrospray ionization mass spectrometry studies of these clusters revealed extraordinary stability in solution, with masses approaching those of proteins, and $\{H_{18}Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6\}$ represents the heaviest polyoxotungstate detected in solution so far (molecular weight *ca.* 50,000) and this shows the fantastic potential of such clusters, based upon well-defined building blocks, to occupy the space as the largest nonbiologically derived molecules to be assembled from the bottom-up. In future work we will attempt to develop polyoxotungstate cluster building blocks with intact pentagonal units to see if polyoxotungstate fullerene wheel and ball topologies are synthetically accessible.

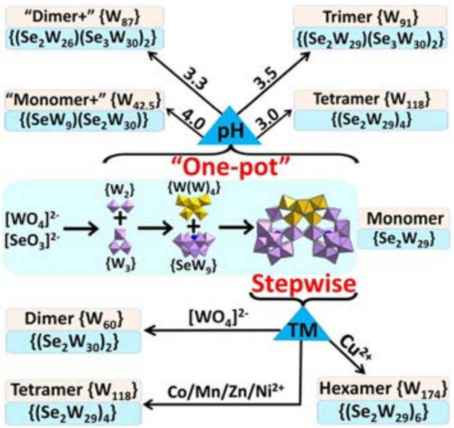


Figure 10. Representative figure showing the strategies and key factors to synthesize compounds **1**−**11**.

■ EXPERIMENTAL SECTION

Measurements. Infrared spectra were measured using samples dispersed in a KBr disk on a Jasco FTIR-410 spectrometer. Wavenumbers are given in cm^{-1}. ICP-OES carried out at Zentralabteilungfür Chemische Analysen, ForschungszentrumJülich GmbH. Thermogravimetric Analyses (TGA) were performed on a TA Q500 instrument under an atmosphere of air, with heating at a rate of 10.0 °C per minute from room temperature to 800 °C.

Electrospray Mass Spectrometric Measurements. ESI-MS measurements were carried out at 30 °C. The solution of the sample was diluted so the maximum concentration of the cluster ions was of the order of 10^{-5} M, and this was infused at a flow rate of 180 μL/h. The mass spectrometer used for the measurements was Bruker micro TOF-Q and the data were collected in both positive and negative modes. The spectrometer was previously calibrated with the standard tune mix to give a precision of ~1.5 ppm in the region of 500−7000 m/z. the standard parameters for a medium mass data acquisition were used and the end plate voltage was set to −500 V and the capillary to +4000 V. The collision cell was set to collision energy of −10 eV with a gas flow rate at 25% of maximum and the collision cell RF was set at 1800 Vpp. Transfer time was set to 60 μs.

Single-Crystal X-ray Diffraction. Suitable single crystals were selected from their respective mother liquors and mounted onto the end of a thin glass fiber using Fomblin oil. X-ray diffraction intensity data were measured at 150(2) K on an Oxford Diffraction Excalibur Gemini Ultra diffractometer with an ATLAS detector using CuKα radiation [λ = 1.54184 Å]. Structure solution and refinement were performed using SHELXS-97[40] and SHELXL-97[41] via WinGX.[42] Corrections for incident and diffracted beam absorption effects were applied using analytical methods.[43]

Vis Spectroscopy. Vis spectra were collected using a Shimadzu PharmaSpec UV-1700 UV−vis spectrophotometer in transmission mode using quartz cuvettes with 1.0 cm optical path length.

One-Pot Synthesis of Compound 1: $K_9(C_2H_8N)_5[H_{10}Se_2W_{29}O_{103}]\cdot 30H_2O$. K_2WO_4 (1.0 g, 3.07 mmol), $K_2SeO_3\cdot H_2O$ (0.05 g, 0.24 mmol), and dimethylamine hydrochloride (0.5 g, 6.13 mmol) were dissolved in 40 mL of H_2O. The pH of the mixture was adjusted to 3.1 quickly by 37% hydrochloric acid. Then the solution was filtered and left for evaporation. Colorless block crystals were obtained within one week. Yield: 0.42 g (48% based on W). IR (KBr disk, cm^{-1}): 3429.8 (s), 3165.6 (s), 2796.3 (w), 1618.9 (m), 1463.7 (m), 1437.7 (w), 937.9 (s), 883.2 (s), 830.2 (s), 784.9 (s), 735.7 (s), 645.1 (s), 622.9 (s). Elemental analysis, calcd for $C_{10}H_{110}K_9N_5O_{133}Se_2W_{29}$: C 1.45, H 1.34, N 0.85, K 4.25, W 64.5%; found C 1.42, H 0.88, N 0.82, K 4.34, W 64.4%.

One-Pot Synthesis of Compound 2: $K_{10}(C_2H_8N)_7[H_{19}Co_{2.5}(W_{3.5}O_{14})(SeW_9O_{33})(Se_2W_{30}O_{107})]\cdot 51H_2O$. K_2WO_4 (1.0 g, 3.07 mmol), $K_2SeO_3\cdot H_2O$ (0.08 g, 0.38 mmol), and dimethylamine hydrochloride (0.8 g, 9.81 mmol) were dissolved in 40 mL of H_2O. The pH of the mixture was quickly adjusted to 4.0 by 37% hydrochloric acid. After the solution was stirred for around 20 min, $Co(NO_3)_2\cdot 6H_2O$ (0.08 g, 0.27 mmol) was then added into the solution. Then the solution was filtered and left for evaporation. Pink block crystals were obtained within two weeks. Yield: 0.13 g (14.8% based on W). IR (KBr disk, cm^{-1}): 3162.7 (w), 2773.1 (w), 2538.5 (w), 1611.2 (m), 1467.6 (m), 1411.6 (w), 973.9 (s), 890.9 (s), 826.3 (s), 727.9 (s), 637.3 (s). Elemental analysis, calcd for $C_{14}H_{177}Co_{2.5}K_{10}N_7O_{205}Se_3W_{42.5}$: C 1.37, H 1.45, N 0.80, K 3.2, Co 1.20, W 63.5%; found C 1.39, H 0.59, N 0.78, K 3.4, Co 1.18, W 63.5%.

One-Pot Synthesis of Compound 3: $H_{0.5}K_{28}(C_2H_8N)_{11}Co_{0.25}[H_4CoWO(H_2O)_3(Se_2W_{26}O_{85})(Se_3W_{30}O_{107})_2]\cdot 98H_2O$. K_2WO_4 (1.0 g, 3.07 mmol), $K_2SeO_3\cdot H_2O$ (0.12 g, 0.58 mmol), and dimethylamine hydrochloride (0.5 g, 6.13 mmol) were dissolved in 40 mL of H_2O. The pH of the mixture was quickly adjusted to 3.3 by 37% hydrochloric acid. After the solution was stirred for around 20 min, it increased to 3.7. $Co(NO_3)_2\cdot 6H_2O$ (0.08 g, 0.27 mmol) was then added into the solution, whose pH decreased to 3.5 automatically. Then the solution was filtered and left for evaporation. Purple block crystals were obtained within two weeks. Yield: 0.14 g (16% based on W). IR (KBr disk, cm^{-1}): 3399.9 (m), 3162.7 (w), 2780.8 (w), 1615.1 (m), 1460.8 (w), 973.9 (s), 890.9 (s), 826.3 (s), 788.7 (s), 731.8 (s), 682.7 (s), 633.5 (s), 566.0 (s). Elemental analysis, calcd for $C_{22}H_{294.5}Co_{1.25}K_{28}N_{11}O_{401}Se_8W_{87}$: C 1.06, H 1.19, N 0.62, K 4.4, Co 0.30, W 64.2%; found C 1.16, H 0.72, N 0.60, K 4.5, Co 0.21, W 64.4%.

One-Pot Synthesis of Compound 4: $K_{23}Na_3(C_2H_8N)_{17}[H_{14}Ni_2W_2O_2Cl(H_2O)_3(Se_2W_{29}O_{103})(Se_3W_{30}O_{107})_2]\cdot 158H_2O$. $Na_2WO_4\cdot 2H_2O$ (1.0 g, 3.03 mmol), $K_2SeO_3\cdot H_2O$ (0.05 g, 0.24 mmol), and dimethylamine hydrochloride (0.5 g, 6.13 mmol) were dissolved in 30 mL of H_2O. The pH of the mixture was adjusted to 5.5 by 37% hydrochloric acid. After the solution was stirred for around 30 min, $NiCl_2\cdot 6H_2O$ (0.07 g, 0.29 mmol) was then added into the solution, whose pH was further adjusted to 3.3 by 37% hydrochloric acid. KCl (1.0 g, 13.4 mmol) was added in to the solution, which was then filtered and left for evaporation. Green block crystals were obtained within two weeks. Yield: 0.12 g (13% based on W). IR (KBr disk, cm^{-1}): 3399.9 (m), 3158.8 (m), 3019.0 (w), 2969.8 (w), 2784.7 (m), 2362.4 (w), 1618.9 (m), 1463.7 (m), 1019.2 (w), 966.2 (s), 946.9 (s), 887.1 (s), 822.5 (s), 762.7 (s). Elemental analysis, calcd for $C_{34}H_{472}ClK_{23}N_{17}Na_3Ni_2O_{480}Se_8W_{91}$: C 1.50, H 1.74, N 0.87, K 3.3, Ni 0.43, W 61.3%; found C 1.78, H 1.13, N 0.88, K 3.4, Ni 0.48, W 61.2%.

One-Pot Synthesis of Compound 5: $K_{34}(C_2H_8N)_{20}[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]\cdot 202H_2O$. K_2WO_4 (1.0 g, 3.07 mmol), $Na_2SeO_3\cdot H_2O$ (0.05 g, 0.29 mmol), and dimethylamine hydrochloride (0.5 g, 6.13 mmol) were dissolved in 40 mL of H_2O. The pH of the mixture was adjusted to 3.3 by 37% hydrochloric acid. After the solution was stirred for around 25 min, $MnCl_2\cdot 4H_2O$ (0.06 g, 0.30 mmol) was added into the solution, whose pH decreased to 3.0 quickly. Then the solution was filtered and left for evaporation. Orange block crystals were obtained within one week. Yield: 0.26 g (28% based on W). IR (KBr disk, cm^{-1}): 3403.7 (s), 3169.4 (m), 2780.8 (w), 2423.1 (w), 1618.9 (m), 1463.7 (m), 1411.6 (w), 973.9 (s), 887.0 (s), 830.2 (s), 784.9 (s), 739.6 (s), 633.5 (s), 573.7 (s). Elemental analysis, calcd for $C_{40}H_{598}K_{34}Mn_2N_{20}O_{618}Se_8W_{118}$: C 1.37, H 1.72, N 0.80, K 3.8, Mn 0.31, W 61.9%; Found C 1.24, H 0.79, N 0.81, K 3.9, Mn 0.38, W 61.7%.

One-Pot Synthesis of Compound 6: $K_{39}(C_2H_8N)_{19}[H_{22}Co_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]\cdot 164H_2O$. The procedure is similar to that for preparing **5**, but after around 25 min of stirring the solution, $Co(NO_3)_2\cdot 6H_2O$ (0.05 g, 0.17 mmol) was then added into the solution, whose pH was adjusted back to 3.0 by 37% hydrochloric acid. Then the solution was filtered and left for evaporation. Purple block crystals were obtained within one week. Yield: 0.22 g (24% based on W). IR (KBr disk, cm^{-1}): 3396.0 (s), 3169.4 (s), 2788.6 (m), 2426.0 (w), 1618.9 (s), 1463.7 (m), 1411.6 (w), 973.9 (s), 887.1 (s), 830.2 (s), 739.6 (s), 630.6 (s). Elemental analysis, calcd for $C_{38}H_{510}Co_2K_{39}N_{19}O_{580}Se_8W_{118}$: C 1.32, H 1.49, N 0.77, K 4.4, Co 0.34, W 62.9%; found C 1.35, H 0.76, N 0.74, K 4.5, Co 0.32, W 63.1%.

One-Pot Synthesis of Compound 7: $K_{36}(C_2H_8N)_{19}[H_{25}Ni_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]\cdot 164H_2O$. The procedure is similar to that for preparing **5**, but after around 25 min of stirring the solution, $Ni(NO_3)_2\cdot 6H_2O$ (0.05 g, 0.17 mmol) was then added, and the pH was adjusted to 2.8 by 37% hydrochloric acid finally. Then the solution was filtered and left for evaporation. Green block crystals were obtained within two weeks. Yield: 0.19 g (21% based on W). IR (KBr disk, cm^{-1}): 3433.6 (s), 3169.4 (s), 2792.4 (w), 2423.1 (w), 1618.9 (s), 1471.4 (m), 1415.5 (w), 973.9 (s), 887.1 (s), 830.2 (s), 784.9 (s), 739.6 (s), 637.4 (s), 577.6 (s). Elemental analysis, calcd for $C_{38}H_{513}K_{36}N_{19}Ni_2O_{580}Se_8W_{118}$: C 1.33, H 1.50, N 0.77, K 4.1, Ni 0.34, W 63.1%; found C 1.35, H 0.75, N 0.77, K 4.3, Ni 0.39, W 62.8%.

One-Pot Synthesis of Compound 8: $K_{36}(C_2H_8N)_{19}[H_{25}Zn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]\cdot 168H_2O$. The procedure is exactly the same as that for preparing **5**, but after around 25 min of stirring the solution, $Zn(NO_3)_2\cdot 6H_2O$ (0.05 g, 0.17 mmol) was then added, and the pH was adjusted to 2.9 by 37% hydrochloric acid finally. Then the solution was filtered and left for evaporation. Colorless block crystals were obtained within one week. Yield: 0.24 g (27% based on W). IR (KBr disk, cm^{-1}): 3423.0 (s), 3169.4 (s), 2792.4 (m), 2429.9 (w), 1618.9 (s), 1463.7 (m), 973.9 (s), 887.0 (s), 830.2 (s), 784.9 (s), 735.7 (s), 637.3 (s), 573.7 (s). Elemental analysis, calcd for $C_{38}H_{521}K_{36}N_{19}O_{584}Se_8W_{118}Zn_2$: C 1.32, H 1.52, N 0.77, K 4.1, Zn 0.38, W 63.0%; found C 1.36, H 0.68, N 0.73, K 4.2, Zn 0.41, W 62.8%.

One-Pot Synthesis of Compound 9: $K_{34}(C_2H_8N)_{18}[H_{24}Cu_2W_3O_5(H_2O)_5(Se_2W_{29}O_{102})_4]\cdot 168H_2O$. The procedure is exactly the same as that for preparing **5**, but after around 25 min of stirring the solution, $CuCl_2\cdot 2H_2O$ (0.05 g, 0.29 mmol) was then added, and the pH was adjusted to 2.9 by 37% hydrochloric acid finally. Then the solution was filtered and left for evaporation. Green block crystals were obtained within one week. Yield: 0.29 g (32% based on W). IR (KBr disk, cm^{-1}): 3437.5 (s), 3173.3 (m), 2796.3 (w), 2429.9 (w), 1618.9 (s), 1463.7 (m), 1415.5 (w), 973.9 (s), 887.1 (s), 830.2 (s), 755.0 (s), 633.5 (s), 573.7 (s). Elemental analysis, calcd for $C_{36}H_{514}Cu_2K_{34}N_{18}O_{586}Se_8W_{119}$: C 1.25, H 1.50, N 0.73, K 3.8, Cu 0.37, W 63.3%; found C 1.27, H 0.67, N 0.72, K 4.0, Cu 0.41, W 62.9%.

Stepwise Synthesis of Compound 5, $K_{34}(C_2H_8N)_{20}[H_{26}Mn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]\cdot 202H_2O$. $K_9(C_2H_8N)_5[H_{10}Se_2W_{29}O_{103}]\cdot 34H_2O$ (0.2 g, 0.025 mmol) was dissolved in 25 mL of 0.2 M KCl. After the solution was stirred for around 5 min, $MnCl_2\cdot 4H_2O$ (0.22 g, 1.29 mmol) was then added into the solution, and its pH was adjusted to 3.0 by 37% hydrochloric acid. Then the solution was stirred at 60 °C for 20 min, cooled, filtered and left for evaporation. Orange block crystals were obtained within one week. Yield: 0.15 g (72% based on W).

Stepwise Synthesis of Compound 6, $K_{39}(C_2H_8N)_{19}[H_{22}Co_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]\cdot 164H_2O$, Compound 7, $K_{36}(C_2H_8N)_{19}[H_{25}Ni_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]\cdot 164H_2O$, Compound 8, $K_{36}(C_2H_8N)_{19}[H_{25}Zn_2W_2O_4(H_2O)_4(Se_2W_{29}O_{102})_4]\cdot 168H_2O$, and compound 10, $K_{90}(C_2H_8N)_9[H_{18}Cu_9Cl_3(H_2O)_{18}(Se_2W_{29}O_{102})_6]\cdot 246H_2O$. The procedure is exactly the same as that for bottom-up synthesis of compound **5** except that $Co(NO_3)_2\cdot 6H_2O$ (0.20 g, 0.69 mmol), $Ni(NO_3)_2\cdot 6H_2O$ (0.22 g, 0.76 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.22 g, 0.74 mmol) and $CuCl_2\cdot 2H_2O$ (0.22 g, 1.29 mmol) were used for synthesizing compound **6**, **7**, **8**, and **10**, respectively. Yield for compound **6**: 0.16 g (78% based on W). Yield for compound **7**: 0.15 g (73% based on W). Yield for compound **8**: 0.16 g (78% based on W, 78% based on Se). For compound **10**, Yield: 0.20 g (95% based on W). IR (KBr disk, cm^{-1}): 3115.3 (m), 1615.1 (s), 973.9 (s), 887.1 (s), 830.2 (s), 788.7 (s), 743.4 (s), 637.4 (s). Elemental analysis, calcd for $C_{18}H_{618}Cl_3Cu_9K_{90}N_9O_{876}Se_{12}W_{174}$: C 0.41, H 1.20, N 0.24, K 6.8, Cu 1.10, W 61.4%; found C 0.35, H 0.78, N 0.22, K 6.9, Cu 1.18, W 61.3%.

Stepwise Synthesis of Compound 11: $K_{26}[H_{18}(Se_2W_{30}O_{105})_2]\cdot 104H_2O$. $K_7(C_2H_8N)_5[H_{10}Se_2W_{29}O_{102}]\cdot 30H_2O$ (0.2 g, 0.025 mmol) was dissolved in 25 mL of 0.3 M KCl. After the solution was stirred for around 5 min, $Na_2WO_4\cdot 2H_2O$ (0.10 g, 0.30 mmol) was then added into the solution. The pH of the solution was kept in the range from 3.0 to 5.0 during the addition of $Na_2WO_4\cdot 2H_2O$, and finally was adjusted to 3.0 by 37% hydrochloric acid. Then the solution was stirred at 60 °C for 40 min, cooled, filtered and left for evaporation. Colorless block crystals were obtained within one week. Yield: 0.17 g (80% based on {W_{29}} precursor). IR (KBr disk, cm^{-1}): 3381.6 (s), 1615.1 (s), 977.7 (s), 830.2 (s), 630.7 (s). Elemental analysis, calcd for $H_{226}K_{26}O_{314}Se_4W_{60}$: K 5.8, W 62.6%; found K 5.9, W 62.3%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic procedures and data (CIF), crystal structure figures, BVS calculation results, electrospray mass spectrometry studies, cyclic voltammetry, powder XRD, and thermogravimetric analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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