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$\{Nb_{288}O_{768}(OH)_{48}(CO_3)_{12}\}$: A Macromolecular Polyoxometalate with Niobium Atoms Close to 300

Yan-Lan Wu, Xin-Xiong Li, Yan-Jie Qi, Hao Yu, Lu Jin, and Shou-Tian Zheng*

Dedicated to Professor Xintao Wu on the occasion of his 80th birthday

Abstract: A protein-sized (ca. 4.2 x 4.2 x 3.6 nm^3) non-biologically derived molecule $\{Nb_{288}O_{768}(OH)_{48}(CO_3)_{12}\}$ (**Nb_{288}**) containing up to 288 niobium atoms has been obtained, which is by far the largest and the highest nuclearity polyoxoniobate (PONb). Particularly, in terms of metal nuclearity number, **Nb_{288}** is the second largest cluster so far reported in classic polyoxometalate chemistry (V, Mo, W, Nb, and Ta). **Nb_{288}** can be described as a giant windmill-like cluster aggregate of six brand-new, nanoscale high-nuclearity PONb units $\{Nb_{47}O_{128}(OH)_6(CO_3)_2\}$ (**Nb_{47}**) joined together by six additional Nb ions. Interestingly, the *in situ* generated 47-nuclearity **Nb_{47}** units can be isolated and bridged by copper complexes to form an inorganic-organic hybrid three-dimensional PONb framework, which exhibits effective catalytic activity for hydrolyzing nerve agent simulant of dimethyl methylphosphonate. The unique **Nb_{47}** cluster also provides a new type of topology to very limited family of Nb-O clusters.

The most common macromolecules in nature are biomolecules composed of thousands of atoms or more, such as proteins, DNA, and nucleic acids. Compared with biomacromolecules, the majority of known inorganic molecules are much smaller in size, nuclearity number, and molecular mass. The creation of giant inorganic molecules at biomacromolecule size has continuously been one of the most interesting subjects in synthetic chemistry as it is challenging to achieve on the one hand.[1-11] Especially, how large an inorganic molecule that can be synthesized artificially is a scientific interest. And on the other hand, giant inorganic molecules have appealing structural features (e.g., nanometer dimensions, multiple configurations, and high-nuclearity metal centers) associated with unusual physical properties that do not occur for smaller molecules.[1-11]

Giant polyoxometalates (POMs) are of special attention, as they represent the largest inorganic molecules ever made combined with fascinating structures and manifold applications in catalysis, medicine, and material sciences.[3-8] Typically, Müller's group has achieved great success in creating giant polyoxomolybdates (POMos) during the past two decades, establishing a series of incredibly large POMos with hundreds of Mo centers, such as $\{Mo_{132}\}$,[4a] $\{Mo_{154}\}$,[4b] $\{Mo_{176}\}$,[4c] $\{Mo_{248}\}$,[4d] and $\{Mo_{368}\}$.[4e] Especially, $\{Mo_{368}\}$ with more than 360 Mo atoms still is the largest POM to date despite many new huge POMos reported in recent years.[5] In POM chemistry, another significant progress on the synthesis of giant clusters has been made in the field of polyoxotungstates (POTs).[6-8] A handful of giant hetero-metallic POTs with more than 100 metal centers have also been made, including $\{Ce_{16}W_{148}\}$,[8a] $\{Sn_{12}W_{108}\}$,[8b] $\{Ce_{20}Ge_{10}W_{100}\}$,[8c] $\{Ce_9Mn_6W_{90}\}$,[8d] $\{Gd_8W_{124}\}$,[8e] $\{Ce_{24}Ge_{12}W_{120}\}$,[8f] $\{Mn_{40}W_{224}\}$,[8g] $\{Co_8W_{200}\}$,[8h] and $\{Dy_{30}Co_8Ge_{12}W_{108}\}$.[8i]

Polyoxoniobates (PONbs), as an important subclass of POMs, often have unique stoichiometry and structure with promising applications in the domains of photocatalysis, nuclear-waste treatment, and base-catalyzed reactions.[9-11] However, due to synthetic challenges caused by the narrow working pH region, the slight solubility, and the low reaction activity of niobate species, the development of PONb chemistry falls far behind that of POMo or POT chemistry. Especially, even after decades of research, almost all reported PONbs are in the small-to-medium nuclearity range (< 100). The development of much larger PONb materials parallel to the POMos and POTs has long been an attractive but challenging target in POM chemistry. Recently, the first PONb $\{Nb_{114}\}$ with more than 100 Nb atoms has been identified by us,[11d] however it is still considerably smaller than many reported giant POMo and POT species.

Here, we report an unprecedented inorganic macromolecular PONb $[Nb_{288}O_{768}(OH)_{48}(CO_3)_{12}]^{180-}$ (**Nb_{288}**) with more than 1000 non-hydrogen atoms per molecular cluster, which was isolated as alkali salt $H_7Li_{24}Na_{50}K_{87}$**[Nb_{288}]**$\cdot 132H_2O$ (**1**). With 288 niobium metal ceners, **Nb_{288}** is by far the largest PONb and contains the largest number of niobium centers so far reported in a POM. In particular, in terms of metal nuclearity number, **Nb_{288}** already surpasses any known giant POTs and represents the second largest molecular POM to date (second only to $\{Mo_{368}\}$). Another fascinating feature of **Nb_{288}** is the existance of fundamentally new, high-nuclearity PONb building unit $\{Nb_{47}O_{128}(OH)_6(CO_3)_2\}$ (**Nb_{47}**). What's more, the novel building unit **Nb_{47}** can be isolated by introduction of copper complexes, giving an inorganic-roganic hybrid 3D PONb framework $H_2Li_5Na_5K_5[Cu(en)_2]_7$**[$Nb_{47}$]**$\cdot 20H_2O$ (**2**) (en = ethylenediamine). Both **Nb_{288}** and **Nb_{47}** enrich the very limited structural types of Nb-O cluster family. Additionally, **2** shows effective catalytic activity in the hydrolyzation of nerve agent simulant of dimethyl methylphosphonate (DMMP) under mild conditions.

Macromolecular **Nb_{288}** crystallizes in trigonal space group *R*-3 with a very large unit cell (ca. 116000 $Å^3$), which consists of six nanosized PONb building units **Nb_{47}** and six additional Nb atoms. As shown in Figure 1, the building unit **Nb_{47}** has a unique W-shaped configuration formed by three kinds of unusual PONb fragments $\{Nb_{17}(OH)_2O_{53}\}$ (Nb_{17}), $\{Nb_{10}(OH)_2O_{31}\}$ (Nb_{10}), and $\{Nb_3O_{14}\}$ (Nb_3). Protonated oxgen atoms are identified by bond valence sum calculations (Figure S1).[12] The C_s-symmetric Nb_{17} fragment can be described as a new-type superlacunary POM. In 2010, Cronin's group reported a 27-nuclearity PONb $[HNb_{27}O_{76}]^{16-}$ that can be seen as a combination of a *α*-Keggin $\{Nb_{12}O_{40}\}$ unit with a bowl-like $\{Nb_{15}O_{51}\}$ unit.[10a] The Nb_{17} fragment can be derived from $[HNb_{27}O_{76}]^{16-}$ by the removel of its

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[a] Y.L. Wu, Dr. X.X. Li, L. Jin, Y.J. Qi, H. Yu, Prof. Dr. S.T. Zheng
State Key Laboratory of Photocatalysis on Energy and Environment
College of Chemistry
Fuzhou University
Fuzhou, Fujian 350108, China
E-mail: stzheng@fzu.edu.cn

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author three Nb atoms from the *α*-Keggin unit and seven Nb atoms from the bowl-like unit (Figure S2). Note that **Nb_{47}** has two inequivalent Nb_{17} fragments as one of them bonds to two additional bidentate CO_3^{2-} ligands. The coordination of CO_3^{2-} ion to PONb has been observed before in $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$.[10a]

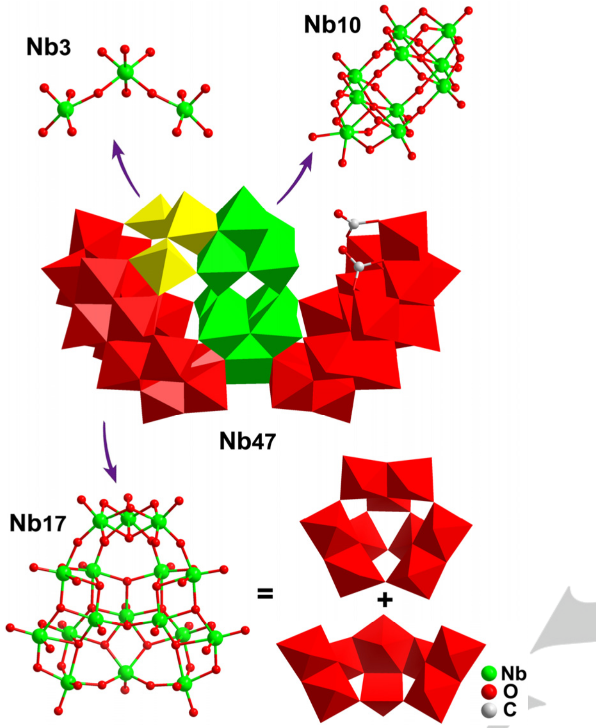

Figure 1. Structure of **Nb_{47}**. Polyhedra key: Nb_{17}, red; Nb_{10}, green; Nb_3, yellow.

Different from the Nb_{17}, the Nb_{10} fragment is derived from Lindqvist PONb $[Nb_6O_{19}]^{8-}$. As shown in Figure 1, Nb_{10} exhibits a special dimeric entity composed of two distinct monolacunary Lindqvist units $\{Nb_5O_{18}\}$ and $\{Nb_5O_{19}\}$ condensed together via four corner-sharing O atoms in an eclipsed face-to-face fashion, forming a C_{2v}-symmetric structure with a cavity in the center. The $\{Nb_5O_{18}\}$ is a typical monolacunary Lindqvist-type structure constructed from five edge-sharing NbO_6 octahedra. Comparing $\{Nb_5O_{19}\}$ with $\{Nb_5O_{18}\}$, the difference is that the Nb atom located at the cap site in $\{Nb_5O_{19}\}$ doesn't bond to a terminal O atom as usual but two addtional bridging O atoms from two Nb_{17} fragments (Figure S3), resulting in a 7-coordinate center and capped trigonal-prismatic coordination geometry. As thus, the overall configuration of Nb_{10} is unique thought it is similar to known decatungstate ion $[W_{10}O_{32}]^{4-}$ formed by two equivalent $\{W_5O_{18}\}$ units.[13] The third fragment Nb_3 is a rare Nb-O trimer comprising two NbO_5 square pyramids corner-sharingly bridged by a NbO_6 octahedron.

The combination of one Nb_3, one Nb_{10}, and two Nb_{17} fragments produces a particular W-like building unit **Nb_{47}** wth 47 Nb centers. Specifically, two co-planar Nb_{17} fragments represent a horn-like arrangement with C_{2v} symmetry and lie at an angle of ca. 81° with respect to each other (Figure 1, S3). Further, the Nb_{10} stands between these two Nb_{17} fragments and acts as a linker via corner- and edge-sharing O atoms with eight Nb atoms from Nb_{17} fragments, forming a W-shaped aggregation $\{W_{44}\}$ bearing two bilaterally symmetrical V-type holes. Interestingly, the symmetrical holes encapsulate different components. One hole traps a Nb_3 via two corner-sharing and three edge-sharing O atoms from the middle Nb_{10} and four corner-sharing O atoms from one side Nb_{17} (Figure 1). While, another hole captures two CO_3^{2-} ligands coordinating to the lacunary sites on the other side Nb_{17}. As a result, a total of 47 Nb atoms are involved to form a nanoscale W-shaped high-nuclearity PONb building unit **Nb_{47}** with dimensions of 2.3 × 1.4 ×1.3 nm^3.

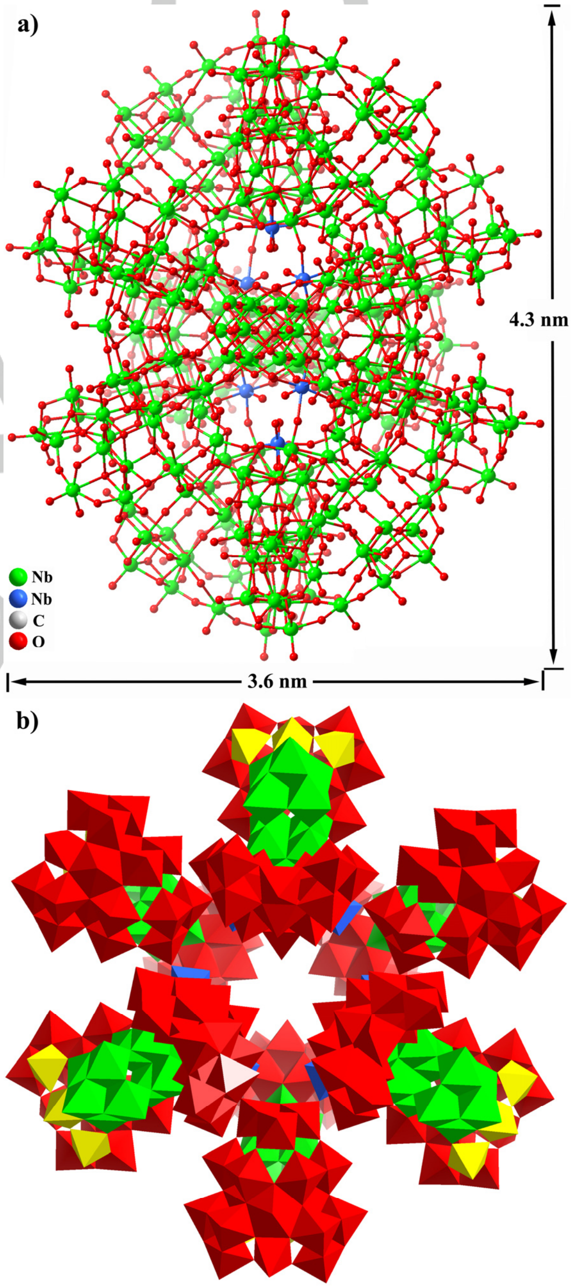

Figure 2. a) Side view of **Nb_{288}**, showing the six additional Nb linkers (blue) are in the same plane and form a C_6-symmetry hexagonal array. b) Top view of **Nb_{288}**, showing a windmill-like strcuture. Polyhedra key: Nb_{17}, red; Nb_{10}, green; Nb_3, yellow; Nb, blue.

Besides the six $\mathbf{Nb_{47}}$ units, $\mathbf{Nb_{288}}$ also contains six additional Nb atoms. The six Nb atoms lie in the same plane forming a C_6-symmetry hexagonal array with adjacent Nb···Nb distances of 6.6 Å and Nb-Nb-Nb angles of 120 °C (Figure 2a, S4a). The six $\mathbf{Nb_{47}}$ are evenly distributed on either side of the ring plane defined by the six additional Nb atoms, and entire 6-$\mathbf{Nb_{47}}$ arrangement has S_6 symmetry with the principal axis coinciding with the sixfold axis of the middle hexagonal ring (Figure S4b). Alternatively, the 6-$\mathbf{Nb_{47}}$ arrangement can be viewed as a triangular antiprism geometry with a $\mathbf{Nb_{47}}$ at each of its six vertexes (Figure S4c). In $\mathbf{Nb_{288}}$, all of the six addtional Nb atoms are 6-coordinate and act as bridges between $\mathbf{Nb_{47}}$ units. Specifically, each addtional Nb atom links two $\mathbf{Nb_{47}}$ units via four corner-sharing Nb-O-Nb bonds (Nb-O bond lengths: 1.829(12)-2.164(14) Å) whilst each $\mathbf{Nb_{47}}$ unit bonds to two addtional Nb atoms. The two remaining coordinate sites of each addtional Nb atom are occupied by two terminal OH groups (Nb-O bond lengths: 1.802(2)-1.906(13) Å) confirmed by BVS calculations (Figure S1). Thus, the assembly of six $\mathbf{Nb_{47}}$ units and six bridging Nb atoms generates a fascinating windmill-like PONb macromolecule $\mathbf{Nb_{288}}$ with a diameter of ca. 4.3 nm and a side length of ca. 3.6 nm and with a molecular mass over 45000 (Figure 2b), displaying one of the largest non-biologically derived molecules so far synthesized.

Despite classic POM chemistry has a long history of almost two centuries, known giant macromolecular POMs have generally been restricted to POMos and POTs. Molecular cluster $\mathbf{Nb_{288}}$ shows a significant breakthrough in the nuclearity number and also the size of PONbs. This is the first PONb with size and nuclearity number comparable to known the largest POMos and POTs since PONb has been known for over one and a half centuries.[14]

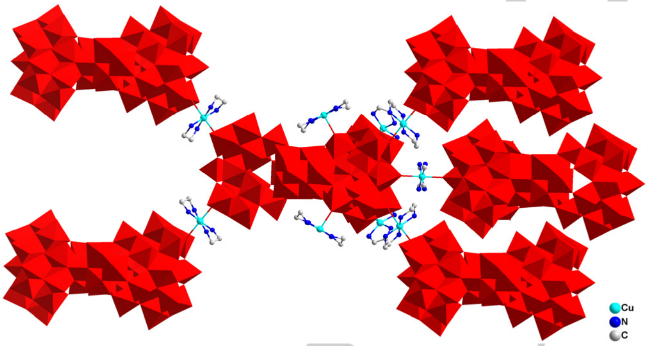

Figure 3. View of coordination mode of cluster $\mathbf{Nb_{47}}$ in **2**.

The structure of $\mathbf{Nb_{288}}$ indicates its likely formation mechanism by initial formation of the cluster $\mathbf{Nb_{47}}$ in solution. It is known that cationic metal complexes are easily coordinated with anionic POMs, which may hinder further aggregation of *in situ* generated POM intermediates. So, to check if $\mathbf{Nb_{47}}$ is actually present in solution, we investigated the introduction of copper complex $[Cu(en)_2]^{2+}$ for the stabilization and isolation of novel cluster $\mathbf{Nb_{47}}$. The approach resulted in successful formation of a targeted compound **2** built from $\mathbf{Nb_{47}}$ clusters and $[Cu(en)_2]^{2+}$ complexes. In **2**, each $\mathbf{Nb_{47}}$ acts as a 9-dentate ligand bonding to nine $[Cu(en)_2]^{2+}$ cations via its three terminal O and six μ_2-O atoms with Cu-O bond lengths of 2.275(18) - 2.618(2) Å. Specifically, each $\mathbf{Nb_{47}}$ is decorated by four $[Cu(en)_2]^{2+}$ cations that are not further connected to other $\mathbf{Nb_{47}}$ clusters, forming a tetra-Cu-supported polyoxoanion (Figure S5). Then, every tetra-Cu-supported polyoxoanion is further bridged to five adjacent ones by remaining five $[Cu(en)_2]^{2+}$ complexes (Figure 3), forming a 3D inorganic-organic hybrid, anionic PONb framework charge-balanced by alkali metal ions and isolated Cu-complexes (Figure S6). Notably, it is important to develop POMs beyond the Mo-, W-, and V-based building units.[10a] Cluster $\mathbf{Nb_{47}}$ represents a remarkably different structure from all of known POMs.

The formulas of **1** and **2** were determined by single-crystal X-ray diffractions and ICP analyses, and their phase purity was confirmed by PXRD patterns (Figure S7,8). To balance the charges of polyoxoanions, seven and two protons should be added to **1** and **2**, respectively. These protons can not be located and are assumed to be delocalized on the overall structures, which is common in POMs.[15] Due to high negative charges and basic surface oxygens, PONbs have been shown as promising candidates for hydrolyzing chemical warfare agents in the past a few years.[16] Dimethyl methylphosphonate (DMMP), as a quite inert nerve agent simulant, was nominated by the U.S. Army as an ideal model chemical for toxicology and carcinogenesis studies.[17] The brand-new PONbs **1** and **2** triggered us to check if they could display excellent catalytic performances in the hydrolysis of DMMP.

To examine the water stability, both **1** and **2** were dissolved in water and then recrystallized from water. IR spectra of **2** before and after recrystallization proved to be identical, that is, **2** kept stable and no other PONbs were formed (Figure S9). While, the IR spectra of **1** are different (Figure S10), indicating $\mathbf{Nb_{288}}$ just can exist in solid. Note that IR spectrum of **1** after recrystallization is somewhat similar to that of **2**, indicating $\mathbf{Nb_{288}}$ probably partial degrade into $\mathbf{Nb_{47}}$. Unfortunately, the structure of the recrystallized phase of **1** could not be determined due to powder crystallinity. Thus, only **2** was employed for catalytic test.

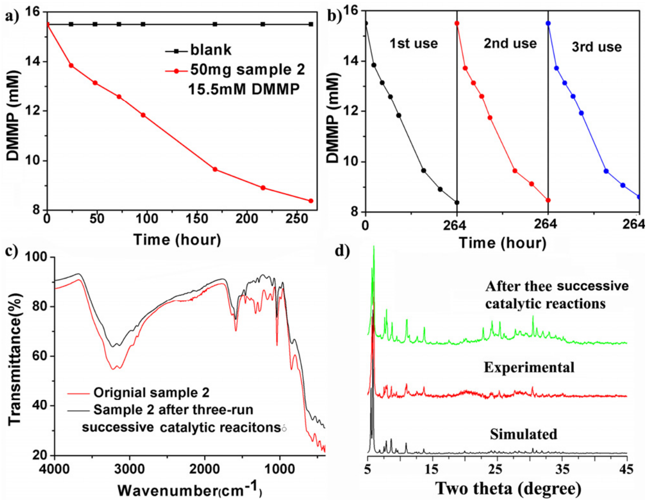

Figure 4. a) DMMP decomposition using **2**. b) Three consecutive runs of DMMP decomposition using **2**. c) and d) IR and PXRD spectra of **2** before and after 3-run catalytic reactions, respectively. Conditions: [DMMP] = 15.5 mm, 50 mg **2**, 0.6 mL D_2O and 1.0 mL H_2O at room temperature.

Experiment was performed in a homogeneous system by dissolving 15.5 mM DMMP and 50 mg **2** (5.8 umol) in a solution of 1 ml H_2O and 0.6 ml D_2O at room temperature and 1 atm. The results showed that **2** can convert about 46% of quite inert DMMP to nontoxic methyl phosphonic acid (MP) over a time course of 263 h without using additional chemicals (Figure 4a). Compared with a blank experiment without **2** under the same conditions, no obvious conversion detected, revealing that **2** is an efficient DMMP hydrolysis catalyst. Notably, **2** is more active than many MOFs towards DMMP and comparable with the effective PONb $K_{12}[Ti_2O_2][GeNb_{12}O_{40}]\cdot 19H_2O$ reported recently by Hill's group (56 % conversion under the same reaction conditions).[16a] The extent of conversion was calculated as the ratio of the integrated ^{31}P NMR peak for MP (the only hydrolysis product) to that of DMMP (Figure S11).

In order to check the stability of **2** during the catalytic process, some experiments were performed by us. On the one hand, the recyclability of **2** was investigated by directly adding additional substrate DMMP (15.5 mM) into the reaction mixture when the previous run was completed. The results show **2** has very good recyclability with almost the same DMMP conversions for three-run duplicate operations (Figure 4b). On the other hand, IR and PXRD measurements were conducted for powder crystallinity obtained by volatilizing the solution after three-run successive catalytic reactions at room temperature. Both IR spectrum and PXRD of **2** were well consistent with those of the powder crystallinity obtained from the solution after catalytic reactions (Figure 4c,d), confirming that **2** could maintain its structural integrity after catalytic reaction.

In summary, for the first time, a PONb $\mathbf{Nb_{288}}$ with hundreds of niobium centers and over 4 nm in diameter has been artificially synthesized. It is the largest molecular niobium aggregate and the second highest nuclearity POM to date. Further, in $\mathbf{Nb_{288}}$, the W-shapled high-nuclearity PONb building unit $\mathbf{Nb_{47}}$ with three types of new fragments Nb_{17}, Nb_{10}, and Nb_3 has a brand-new topology to POM chemistry, providing a new member of very limited Nb-O clluster family. Especially, the novel $\mathbf{Nb_{47}}$ formed *in situ* can be stabilized and isolated by copper complexes to form an extended framework, which is effective hydrolysis catalyst for nerve agent simulant of DMMP. The results represent a major step forward in the development of PONb system and open up new perspectives for the development of diverse and larger PONb materials parallel to the POMo and POT systems.

Acknowledgements

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Keywords: polyoxometalate • polyoxoniobate • macromolecule • high-nuclearity

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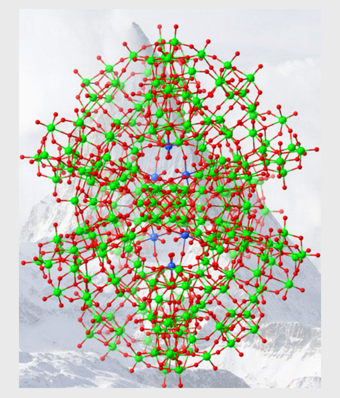
Giant Polyoxoniobate An unprecedentedly huge polyoxoniobate (PONb) with as many as 288 Nb centers has been made. This is by far the largest PONb and the second highest nuclearity polyoxometalate reported to date. It incorporates a unique 47-nuclearity PONb building unit formed *in situ*, which can be stabilized by metal complexes to form an extended PONb framework with the capability of hydrolyzing dimethyl methylphosphonate.



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