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Fullerene-like Niobovanadate Cage Built from $\{(Nb)V_5\}$ Pentagon

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Abstract: The striking aesthetic appeal of fullerene-like clusters has captured the interest of researchers. Nevertheless, the assembly of fullerene-like polyoxovanadate (POV) cages remains a significant challenge due to the scarcity of suitable pentagonal motif. Herein, we have successfully synthesized the first fullerene-like all-inorganic POV cage, $\{(V_2O)_V_{30}Nb_{12}O_{102}(H_2O)_{12}\}$ ($V_{30}Nb_{12}$), by introducing Nb into the POVs. $V_{30}Nb_{12}$ is assembled by 12 heterometallic $\{(Nb)V_5\}$ pentagons through sharing V centers with I_h symmetry, reminiscent of C_{60} . To our knowledge, the fullerene-like $V_{30}Nb_{12}$ not only represents the highest-nuclearity POV cage but also stands as the first niobovanadate cluster. Notably, $V_{30}Nb_{12}$ exhibits excellent solution stability, as confirmed by ESI-MS, FT-IR and UV-vis spectra. As there is no protection organic ligand on its outer surface, $V_{30}Nb_{12}$ can be further modified with Cu-complexes to form a fullerene-like cluster based zigzag chain ($Cu-V_{30}Nb_{12}$).

Polyoxometalates (POMs), composed of Mo, W, V, Nb and oxo ligands, are a large family of nano-sized metal oxide clusters with rich physicochemical properties and extensive range of applications.^[1] Polyoxovanadates (POVs) as a unique branch of POMs, have gained extensive attention due to their structure diversity and impressive redox activities.^[2] Unlike the dominant $\{MO_6\}$ octahedra in Mo/W/Nb-POMs, the vanadium centers exhibit versatile coordination geometries, including $\{VO_4\}$ tetrahedra, $\{VO_5\}$ square pyramids, and $\{VO_6\}$ octahedra.^[3] The characteristic condensation of $\{VO_5\}$ square pyramids lead to the

formation of various POV cages usually with encapsulated guest molecules.^[4] Since the report of the first POV cage, $\{V_{18}O_{42}\}$,^[5] in 1978, Müller and Ishaque, et. al, have successfully isolated several high-nuclearity POV cages, such as $\{V_{15}O_{36}\}$,^[6] $\{V_{16}O_{42}\}$,^[7] $\{V_{18}O_{44}\}$,^[8] $\{V_{22}O_{54}\}$,^[8] and $\{V_{34}O_{82}\}$,^[9] during the 1990s (Figure 1a). Thereafter, POVs, especially all-inorganic POVs, experienced a stagnation with limited reports on high-nuclearity cages until the recent identification of a 38-nuclearity $\{V_{30}Sb_8O_{78}\}$ by Bensch's group (Figure 1a).^[10] It is worth noting that the nuclearity of POV cages still remains significantly smaller in comparison to Mo/W/Nb-POM clusters. The lack of suitable structural motif is one of the possible reasons for this. Therefore, the formation of new structural motif is expected to significantly advance the development of POV chemistry.

Pentagonal $\{(M)M_5\}$ ($M = Mo, W, \text{ or } Nb$) are well-known structural motifs in POMs, which play a key role in constructing high-nuclearity clusters, such as $\{Mo_{368}\}$,^[11] $\{Nb_{288}\}$,^[12] $\{W_{119}Se_8Fe_2\}$,^[13] et al. These $\{(M)M_5\}$ pentagons are formed by assembling a central $\{MO_7\}$ with five surrounding $\{MO_6\}$ octahedra. In this unit, the 7-coordinated pentagonal bipyramid $\{MO_7\}$ is considered as a template to induce the formation of $\{(M)M_5\}$ pentagons. Furthermore, regular pentagonal units are essential for constructing fullerene-like clusters, since they meet the topological and symmetry requirements for curved systems.^[14] In general, fullerene-like clusters contain exactly 12 pentagons and exhibit icosahedral symmetry (I_h , the highest symmetry possible

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for molecules).^[15] A handful of giant fullerene-like POM spheres have been synthesized by cross-linking homometallic $\{(M)M_5\}$ with a general formula of $[(M)(M)_5]_{12}(\text{linker})_{30}$ ($M = \text{Mo}^{\text{VI}}/\text{W}^{\text{VI}}$, linker = Mo_2^{V} , Mo^{V} , V^{IV} , Fe^{III} , or Cr^{III}) and the representative examples include $\{\text{Mo}_{102}\}$,^[16] $\{\text{Mo}_{132}\}$,^[17] $\{\text{W}_{72}\text{V}_{30}\}$,^[18] et al. The reported fullerene-like POMs have been predominantly focused on Mo-POMs and W-POMs. To our knowledge, the fullerene-like POVs are rarely documented. Due to its relatively smaller ionic radius, vanadium cannot adopt a pentagonal bipyramidal coordination mode, rendering the formation of $\{\text{V}(\text{V}_5)\}$ pentagon less possible. We believe that introducing an element with a larger ionic radius and a pentagonal bipyramidal coordination geometry into POVs could facilitate the formation of $\{\text{M}(\text{V}_5)\}$, thereby promoting the assembly of fullerene-like POV cages.

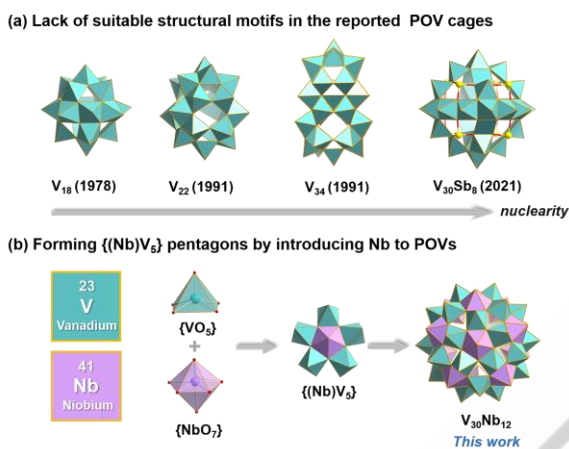


Figure 1. (a) Polyhedral structures and publication year of representative high-nuclearity POV cages: V_{18} , V_{22} , V_{34} and $\text{V}_{30}\text{Nb}_{12}$. (b) The formation of $\{(\text{Nb})\text{V}_5\}$ pentagons by introducing Nb to POVs and polyhedral presentation of fullerene-like $\text{V}_{30}\text{Nb}_{12}$.

Niobium and vanadium, two neighboring elements in Group V of the periodic table, share similar ionic radii and electronegativities. They can undergo hydrolysis and condensation reactions under alkaline conditions. Inspired by these similarities, vanadium was first introduced into polyoxoniobates (PONbs) by our group, synthesizing Keggin-type $\{\text{VNb}_{12}\text{O}_{40}(\text{VO})_2\}$.^[19] Subsequently, a series of vanadoniobates have been reported.^[20] In our recent study, we observed a rare heterometallic $\{\text{Nb}(\text{Nb}_3\text{V}_2)\}$ pentagon in $\{\text{V}_5\text{Nb}_{23}\text{O}_{80}\}$ and $\{\text{V}_6\text{Nb}_{23}\text{O}_{81}\}$, which consists of a central $\{\text{NbO}_7\}$ pentagonal bipyramid surrounded by three $\{\text{NbO}_6\}$ octahedra and two $\{\text{VO}_5\}$ square pyramids.^[21] This finding implies that incorporating niobium into POVs might induce the formation of magic $\{(\text{Nb})\text{V}_5\}$ unit, contributing to the fabrication of novel POV cages (Figure 1b).

Herein, we report the synthesis of the first fullerene-like all-inorganic POV cage, $\text{K}_{11}\text{Na}_4\text{H}_3\{(\text{V}_2\text{O})\text{V}_{30}\text{Nb}_{12}\text{O}_{102}(\text{H}_2\text{O})_{12}\} \cdot 37\text{H}_2\text{O}$ (**1**), which is assembled by 12 heterometallic $\{(\text{Nb})\text{V}_5\}$ pentagons through sharing V centers with I_h symmetry, similar to fullerene C_{60} . To our knowledge, the spherical POV cluster (denoted as $\text{V}_{30}\text{Nb}_{12}$) represents not only the highest-nuclearity POV cage

reported by far, but also the first niobovanadate cluster. By using the fullerene-like $\text{V}_{30}\text{Nb}_{12}$ as precursor, the surface oxygen atoms of $\text{V}_{30}\text{Nb}_{12}$ can be further modified with Cu-complexes to form a 1D chain, $[\text{Cu}(\text{en})_2]_{0.8}[\text{Cu}(\text{en})(\text{H}_2\text{O})_2]_{0.7}(\text{V}_2\text{O})\text{V}_{30}\text{Nb}_{12}\text{O}_{102}(\text{H}_2\text{O})_{12} \cdot 21\text{H}_2\text{O} \cdot 4.5\text{en}$ (**2**), (en = ethylenediamine).

Fullerene-like **1** crystallizes in the trigonal crystal system with space group $R\bar{3}c$ (Table S1)^[22]. The polyanion skeleton of **1** contains 30 vanadium and 12 niobium atoms bridged by 60 $\mu_3\text{-O}^{2-}$ ions (Figure 2a, left). Remarkably, the spherical cluster can be viewed as the assembly of 12 heterometallic $\{(\text{Nb})\text{V}_5\}$ units by sharing V centers with five adjacent pentagons. The pentagonal unit is formed by five edge-shared $\{\text{VO}_5\}$ around a $\{\text{NbO}_7\}$ core with C_5 symmetry (Figure 2a, middle). Interestingly, connecting the V centers of $\{(\text{Nb})\text{V}_5\}$ results in the formation of a rather regular pentagon, where five V atoms are almost coplanar (Figure 2a and S4). In $\text{V}_{30}\text{Nb}_{12}$, all the V centers are five-coordinated with square pyramidal geometries (Figure 1b) and the V-O distances range from 1.62–1.95 Å. Meanwhile, each seven-coordinated Nb center adopts a pentagonal bipyramidal geometry (Figure 1b): the equatorial plane is defined by five bridging oxygen atoms ($\mu_3\text{-O}$) and the axial positions are occupied by one terminal oxygen atom (O_t) and one water molecule (O_w) with the bond valence sum (BVS) value of 0.213 and 0.234 (Table S5). The coordinated water molecules are directed towards the center of the sphere. The spherical $\text{V}_{30}\text{Nb}_{12}$ cage has an inside diameter of ~ 1.1 nm and the outside diameter of ~ 1.5 nm (Figure 2a, left and S6). The size of $\text{V}_{30}\text{Nb}_{12}$ sphere exactly falls between the small-sized spherical Keggin-type cluster and $\{\text{V}_{18}\}$ ^[23] (diameter: ~ 1.1 nm), and the large-sized $\{\text{Mo}_{102}\}$ (~ 2.4 nm) and $\{\text{Mo}_{132}\}$ (~ 2.9 nm) (Figure S7), representing a brand-new member to POM family.

Alternatively, the fullerene-like $\text{V}_{30}\text{Nb}_{12}$ cluster can be viewed as a combination of a sandwich wheel cluster $\{\text{V}_{20}\text{Nb}_{10}\}$ and two $\{(\text{Nb})\text{V}_5\}$ pentagons. As shown in Figure 2b, a $\{\text{V}_{10}\}$ ring formed by ten corner-shared $\{\text{VO}_5\}$ square pyramids is situated in the equatorial position of POV sphere. The $\{\text{V}_{10}\}$ ring is then sandwiched between two novel $\{\text{V}_5\text{Nb}_5\}$ rings, which are made up of five $\{\text{VO}_5\}$ and five $\{\text{NbO}_7\}$ by sharing edges, and the two $\{\text{V}_5\text{Nb}_5\}$ rings are arranged around $\{\text{V}_{10}\}$ ring in staggered fashion, affording an intriguing sandwich wheel cluster $\{\text{V}_{20}\text{Nb}_{10}\}$. Finally, the wheel is capped by two $\{(\text{Nb})\text{V}_5\}$ to form the fullerene-like sphere.

Interestingly, the 30 V atoms in $\text{V}_{30}\text{Nb}_{12}$ are situated on the vertexes of an icosidodecahedron, one of Archimedean solids composed of 12 pentagonal faces and 20 triangular faces (Figure 2a, right). The presence of exactly 12 pentagonal faces in $\text{V}_{30}\text{Nb}_{12}$ reminds us of fullerene C_{60} , which consists of 12 pentagonal faces and 20 hexagonal faces and can be classified as a truncated icosahedron, another Archimedean solid. From the geometric perspective, the icosidodecahedron, like $\text{V}_{30}\text{Nb}_{12}$, can be regarded as a “cousin” of the truncated icosahedron, such as C_{60} , since both of them are derived from the icosahedron by truncating half edges or corners, respectively (Figure 2c).

Additionally, the 12 Nb centers of $\text{V}_{30}\text{Nb}_{12}$ form an icosahedron $\{\text{Nb}_{12}\}$, which is nested within the framework of icosidodecahedron $\{\text{V}_{30}\}$ with 12 Nb vertices located at the center of each pentagonal face (Figure 3a). This arrangement imparts I_h symmetry to the fullerene-like POV cage. A similar topological

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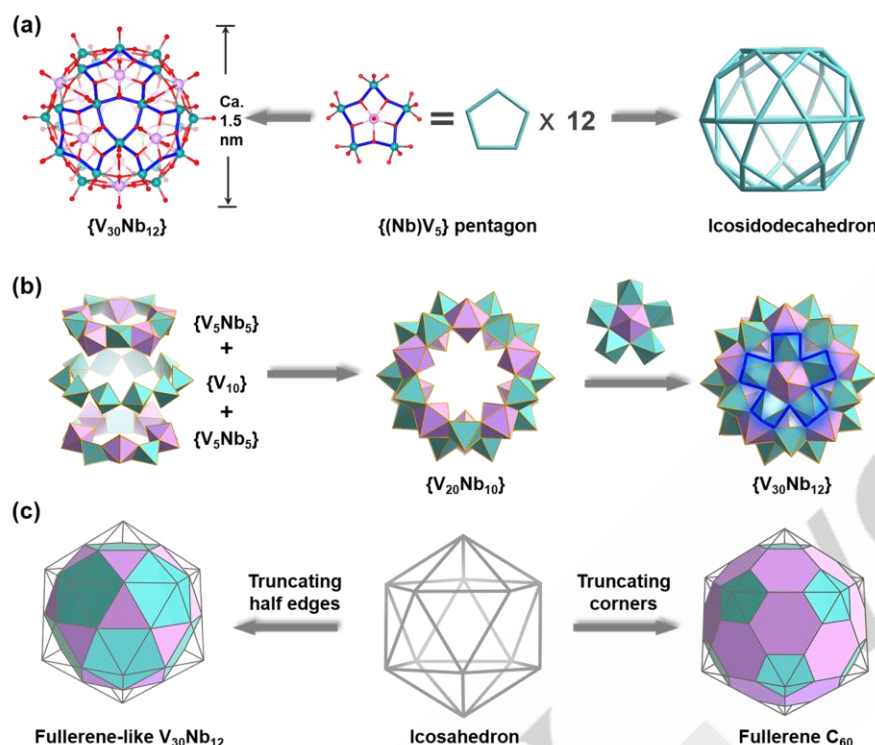


Figure 2. (a) Left: ball-and-stick view of $\text{V}_{30}\text{Nb}_{12}$; Middle: ball-and-stick view and simplified presentation of $\{(\text{Nb})\text{V}_5\}$ in $\text{V}_{30}\text{Nb}_{12}$; Right: $\text{V}_{30}\text{Nb}_{12}$ as an icosidodecahedron by considering the $\{(\text{Nb})\text{V}_5\}$ as a pentagon. (b) Left: polyhedral presentation of $\{\text{V}_5\text{Nb}_5\}$ and $\{\text{V}_{10}\}$ rings; Middle: polyhedral presentation of the sandwich wheel cluster $\{\text{V}_{20}\text{Nb}_{10}\}$; Right: polyhedral presentation of $\text{V}_{30}\text{Nb}_{12}$. (c) The geometric relationship between truncated icosahedron, like fullerene C_{60} , and icosidodecahedron, such as fullerene-like $\text{V}_{30}\text{Nb}_{12}$.

structure has been identified in $\{\text{Ti}_{42}\text{O}_{60}(\text{O}i\text{Pr})_{42}(\text{OH})_{12}\}$ ($i\text{Pr}$ = isopropyl, denoted as Ti_{42}).^[24] As illustrated in Figure 3a, a comparative analysis highlights the distinctions between the Group V fullerene-like metal-oxo cluster, $\text{V}_{30}\text{Nb}_{12}$, and the Group VI counterpart, Ti_{42} . Firstly, $\text{V}_{30}\text{Nb}_{12}$ is constructed by heterometallic $\{(\text{Nb})\text{V}_5\}$ pentagons, whereas Ti_{42} is based on homometallic $\{(\text{Ti})\text{Ti}_5\}$ pentagons. Secondly, $\text{V}_{30}\text{Nb}_{12}$ is an all-inorganic fullerene-like cluster with 42 terminal O atoms on its outer surface, while Ti_{42} is an organic-functionalized metal-oxo cluster surrounded by 42 isopropanol ligands. Thirdly, the all-inorganic $\text{V}_{30}\text{Nb}_{12}$ synthesized in an aqueous solution shows solubility and stability in water, as confirmed by following analyses, while the organic-functionalized Ti_{42} , obtained in an organic system, is soluble and stable in toluene. Finally, $\text{V}_{30}\text{Nb}_{12}$ exhibits potential redox activity attributed to the electron transfer behaviour of V center, while Ti_{42} can be considered as a molecular model of TiO_2 with potential semiconductor properties. In summary, all-inorganic $\text{V}_{30}\text{Nb}_{12}$ represents a unique addition to the family of fullerene-like clusters, exhibiting distinctive characteristics owing to the incorporation of Nb with V elements.

Pentagons, due to their inability to tessellate a plane, are important in constructing curved structures, especially fullerene-like molecules. Compared to the frequently encountered homometallic pentagonal $\{(\text{M})\text{M}_5\}$ ($\text{M} = \text{Mo}, \text{W}, \text{Nb}$), the presence of heterometallic $\{(\text{M}')\text{M}_5\}$ pentagons is still limited in POMs (Table S4),^[16, 21, 24–25] although such units have been found in the mixed metal oxides.^[26] The heterometallic $\{(\text{M})\text{V}_5\}$ ($\text{M} = \text{W}$ or Nb) units

were observed in the V-based metal-organic polyhedra.^[27] However, the reported $\{(\text{M})\text{V}_5\}$ were stabilized by O-donor organic ligands and the participation of SO_4^{2-} partially decreases the C_5 symmetry of $\{(\text{M})\text{V}_5\}$ (Figure S10). To our knowledge, the synthesized $\text{V}_{30}\text{Nb}_{12}$ represents the first fullerene-like cluster based on heterometallic pentagonal units. Additionally, in the fullerene-like $\text{V}_{30}\text{Nb}_{12}$, the heterometallic $\{(\text{Nb})\text{V}_5\}$ fragments are assembled through sharing V centers, while the $\{(\text{M})\text{M}_5\}$ units in the reported fullerene-like $\{\text{Mo}_{102}\}$,^[16] $\{\text{Mo}_{132}\}$,^[17] $\{\text{Mo}_{72}\text{V}_{30}\}$,^[28] $\{\text{Mo}_{72}\text{Fe}_{30}\}$,^[29] and $\{\text{W}_{72}\text{V}_{30}\}$,^[18] are connected by $\{\text{Mo}_6\}/\{\text{M}_2\text{O}_{10}\}$ linkers.

Considering the presence of exposed terminal oxygen atoms on its outer surface, $\text{V}_{30}\text{Nb}_{12}$ was used as a precursor to further modify with Cu-complex, resulting in the isolation of compound **2** (denoted as $\text{Cu-V}_{30}\text{Nb}_{12}$).^[22] $\text{Cu-V}_{30}\text{Nb}_{12}$ consists of one $\text{V}_{30}\text{Nb}_{12}$, 0.8 $[\text{Cu}(\text{en})_2]^{2+}$ and 0.7 $[\text{Cu}(\text{en})(\text{H}_2\text{O})_2]^{2+}$. As shown in Figure 3b, the fullerene-like $\text{V}_{30}\text{Nb}_{12}$ are linked by $[\text{Cu}(\text{en})_2]^{2+}$ to form a 1D chain with $[\text{Cu}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ as counter cations anchoring on the cluster. To reduce the electrostatic repulsion between the fullerene-like clusters, the Cu-complexes are arranged in a zigzag way along the chain.

$\text{V}_{30}\text{Nb}_{12}$ can dissolve in water but is almost insoluble in common organic solvents. The stability of $\text{V}_{30}\text{Nb}_{12}$ in the aqueous solution is confirmed by electrospray ionization mass spectrometry (ESI-MS) and cation exchange experiment. As shown in Figure 4a, the negative mode ESI-MS of **1** aqueous solution shows a prominent signal centered at $m/z = 921.65$, which can be assigned to

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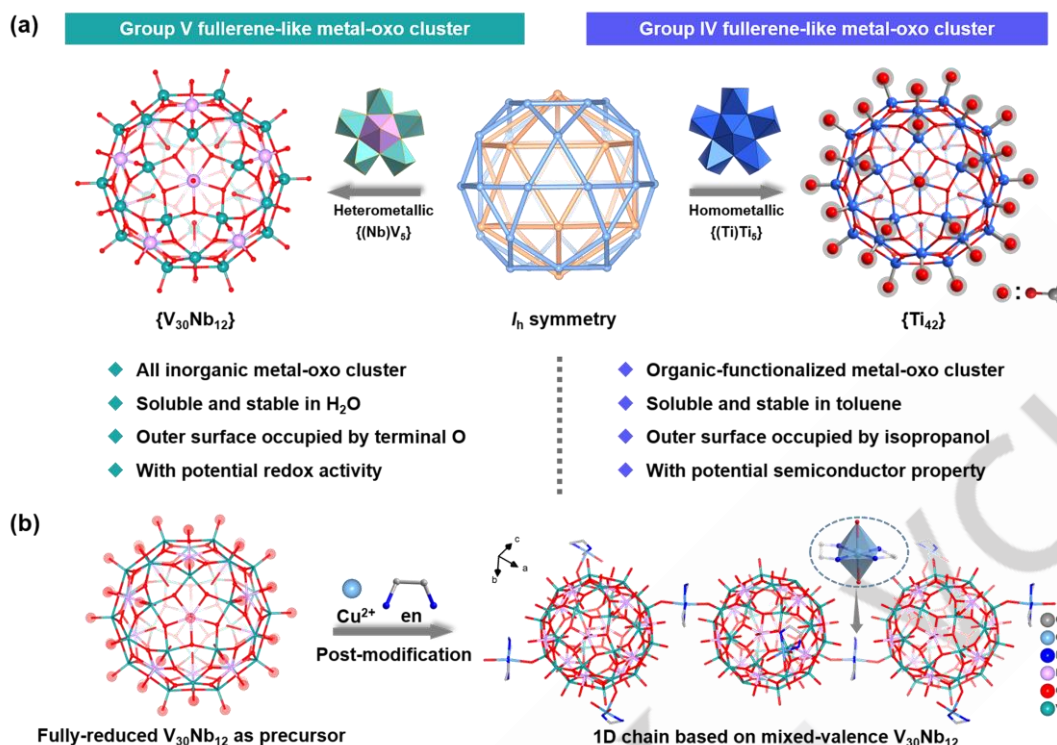


Figure 3. (a) The comparison between Group V fullerene-like metal-oxo cluster $V_{30}Nb_{12}$ and Group IV fullerene-like metal oxo cluster Ti_{42} . (b) The synthesis and structure of $Cu-V_{30}Nb_{12}$. Insert: The coordination geometry of Cu center.

$[NaH_{12}V_{32}Nb_{12}O_{103}(H_2O)_{10}]^{5-}$ and the other main signal centered at $m/z = 1171.56$ corresponds to $[K_3NaH_{10}V_{32}Nb_{12}O_{103}(H_2O)_8]^{4-}$. ESI-MS results indicate not only the integrity of the cluster, but also the existence of two V atoms within the cage. During the crystal data analysis of **1**, relatively high residual electron density was observed within $V_{30}Nb_{12}$ cage. Upon assigning V during the refinement, both equivalent isotropic displacement parameter (U_{eq}) and bond length fell within the normal range. The determined V centers are highly disordered with total occupancy of two and interacts with the water ligand of Nb (Figure S21). In addition, a tetrabutylammonium (TBA) salt of $V_{30}Nb_{12}$ (denoted as **TBA- $V_{30}Nb_{12}$**) was prepared by combining tetrabutylammonium bromide with an aqueous solution of **1** and FT-IR results confirm that the polyanion skeleton keeps intact during ion-exchange process (Figure S23-S24). Moreover, UV-vis absorption spectra of **1** in aqueous solution and **TBA- $V_{30}Nb_{12}$** in acetonitrile show negligible changes over a period of 72 h (Figure S25), revealing the excellent stability of **1** in both water and acetonitrile solution. The crystals of **1** can also keep stable after soaking in organic solvents for 24 h (Figure 4b and S26) or heating in DMF in the temperature range of 40–140 °C for 2 h (Figure S27), as confirmed by powder X-ray diffraction (PXRD) and FT-IR. The single crystals of **1** retain their crystallinity even after being exposed to ambient conditions for over one year (Figure S29 and S30).

BVS calculations (Table S5) and X-ray photoelectron spectrum (XPS) (Figure 4c) indicate that all V atoms in $V_{30}Nb_{12}$ are in the +4 oxidation state and the cluster is a fully-reduced POV cage. However, after modifying with Cu-complex, part of V^{IV} was oxidized to V^V in $Cu-V_{30}Nb_{12}$ with the Cu^{II} ion potentially serving

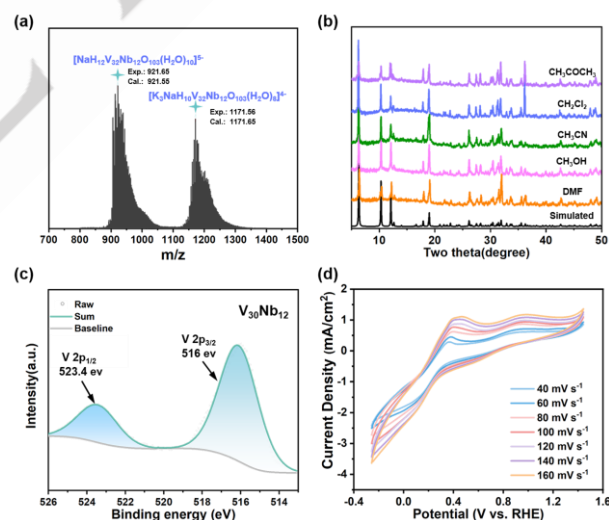


Figure 4. (a) ESI-MS spectra of **1** in water. (b) The PXRD patterns of **1** after soaking in common organic solvents for 24 h. (c) XPS of V in $V_{30}Nb_{12}$. (d) CV curves of $V_{30}Nb_{12}$ in 0.5 M pH = 9 $KHCO_3$ - K_2CO_3 buffer with different scan rates.

as the oxidant (Figure S31 and Table S6). This reveals that the oxidation state of the fullerene-like POV cage can be regulated by the reaction conditions. To assess the redox behavior of the fully-reduced $V_{30}Nb_{12}$, the scan-rate-dependent cyclic voltammogram (CV) of **1** was recorded (Figure 4d). In the positive scan, two peaks at ~ 0.4 and ~ 0.94 V_{RHE} are assigned to the oxidation of V^{IV} to V^V , while only one reduction peak is observed at ~ 0.15 V_{RHE} in

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the reverse scan, indicating that the redox process is irreversible. As the scan rate increase, the oxidation and reduction peaks shift to more positive and negative potential, respectively. The electrocatalytic activity of **Cu-V₃₀Nb₁₂** for the oxidation of toluene was also estimated (Figure S36-44). Under ambient conditions, benzaldehyde (BA) and N-benzylacetamide (NBA), a C-N bond coupling product, were yielded with the total Faradaic efficiency of 99.7%. The control experiments show that the presence of both Cu and **V₃₀Nb₁₂** contributes to the formation of NBA. Moreover, the catalytic activity of **Cu-V₃₀Nb₁₂** is basically maintained after four cycles.

In conclusion, we have successfully synthesized the first fullerene-like all-inorganic POV cage, **V₃₀Nb₁₂**, by incorporating Nb to POVs. In this fascinating cage, twelve {(Nb)V₅} pentagons are assembled by sharing V, resulting in an icosidodecahedron with *I_h* symmetry similar to that of C₆₀. Due to its water solubility and excellent stability, **V₃₀Nb₁₂** as precursor can be further modified with Cu-complex to form a 1D zigzag chain, **Cu-V₃₀Nb₁₂**. The discovered {(Nb)V₅} pentagon can serve as a structural motif to fabricate additional fascinating molecular clusters, fostering the advancement of POM chemistry.

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Keywords: polyoxovanadate cage • fullerene-like metal-oxo cluster • pentagonal structural motif • niobovanadate

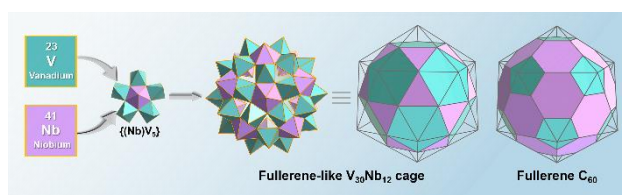
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The first fullerene-like all-inorganic polyoxovanadate cage, $\text{V}_{30}\text{Nb}_{12}$, has been successfully synthesized by introducing of Nb to polyoxovanadates and the $\text{V}_{30}\text{Nb}_{12}$ cage is assembled by 12 $\{(\text{Nb})\text{V}_5\}$ pentagons through sharing V centers with I_h symmetry, similar to fullerene C_{60} .