

Self-assembly of a giant heterometallic polyoxovanadate with catalytic activity for epoxidation of alkenes

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ABSTRACT: The self-assembly of giant polyoxovanadates (POVs) is highly attractive yet extremely challenging, hampered by protonation complexity and structural instability. Here, we obtain the largest POV cluster **1** via self-assembly in aqueous solution, in which tartaric acid serves as a structure-directing agent via synergistic coordination interactions between the metal linkers and the POV motifs. This aesthetically appealing giant compound **1** contains 128 vanadium ions and represents the highest-nuclear V cluster known in POV chemistry to date. Compound **1** is a tetramer of manganese-bridged $[V_{20}^{IV}V_{12}^{IV}(C_4H_2O_6)_8(OH)_{10}O_{66}(Cl)]^{27-}$ units that are unique configurations and potential building blocks. Meanwhile, **1** exhibits excellent catalytic performance in the epoxidation reaction of cyclooctene, achieving 98% conversion and 99% selectivity under oxygen atmosphere. This work not only provides a new topology structure to POM chemistry but also establishes a synthesis strategy for constructing high-nuclear POVs.

KEYWORDS: polyoxometalates, giant polyoxovanadate, high-nuclear, catalysis

1 Introduction

The design and construction of giant polyoxometalates (POMs) constitutes a fascinating and venerable area of POM chemistry, in which highly symmetrical MO_x units ($M = V, Mo, W$) self-assemble into clusters under the direction of structure-directing agents, exhibiting unique aesthetic beauty and captivating properties at the nanoscale [1-8]. Polyoxovanadates (POVs), an important subclass of POMs, have various coordination geometries, flexible oxidation states, rich redox behaviors. By virtue of their unique properties, POVs are of both fundamental and applied interest, encompassing diverse fields such as catalysis, energy storage, magnetism, and medicine. Consequently, research on POVs have flourished and continues to surge [9-16]. According to the varied oxidation states of vanadium, POVs can be divided into four general families: fully-oxidized (V^V), mixed-valent (V^V/V^{IV} or V^{IV}/V^{III}), fully-reduced (V^{IV}) and highly-reduced (V^{III}) species [17]. At the same time, the structural stability of POVs confines by the variable oxidation states of vanadium. The coordination geometries at the vanadium centers are diversiform, including $\{VO_4\}$ tetrahedron, $\{VO_5\}$ square pyramid, and $\{VO_6\}$ octahedron that can exist independently or be co-assembled in one compound leading to unprecedented structures [9, 10, 18-21]. While, in stark contrast to the giant polyoxomolybdates (POMos) and polyoxotungstates (POTs), the development of high-nuclear POVs encounter

obstacles owing to the complex protonation chemistry, poor stability and relatively smaller ionic radius, et al [13, 22-24].

Based on the presence or absence of organic components, the reported high-nuclear POVs are classified as either pure-inorganic or organic-inorganic hybrid POVs. Since 1991, the best-known $K_{10}[V_{16}^{IV}V_{18}^{V}O_{82}] \cdot 20H_2O$ was discovered by Muller's group [25]. Pure-inorganic high-nuclear POVs experienced a stagnation, until 2021 Bensch's group reported the largest antimonato-POV $\{V_{30}Sb_8O_{78}\}$ [24]. Whereafter, Chi discovered a novel $\{(Nb)V_5\}$ structural motif to fabricate the first fullerene-like all-inorganic POV cage $\{(V_2O)V_{30}Nb_{12}O_{102}(H_2O)_{12}\}$ promoting the development of high-nuclear POVs [24]. Nowadays, the high-nuclear POVs have been predominantly focused on organic-inorganic hybrid POVs. The O atoms on the surface of POV anion clusters have strong coordination ability and are apt to connect with metal-organic complex via a metal-oxygen covalent bond into POV-based inorganic-organic hybrid materials. The modification of organic ligands expands the framework, improves stability, and optimizes performance [27-29]. In addition, POV building blocks preferentially coordinate with O-/N-donor ligands due to the hard Lewis acidic nature of V ions [30]. Therefore, coordination-driven self-assembly is regarded as a feasible strategy to synthesize giant POV clusters by introducing organic ligands into POV systems [22]. In 2008, Schmitt has selected different rigid dual-connected organic ligands to lengthen the distance between the "bowl" building blocks $\{V_5O_9\}$



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to synthesize a series of molecular capsules [31-34]. Since then, chemists have been fascinated by the design of high-nuclear POVs by adopting rigid multi-connected ligands that embody tunable electrostatic repulsion and $\pi\cdots\pi$ stacking interactions [35]. Zaworotk, Fang, and Su's group directionally construct numerous POV-based metal-organic polyhedra (VMOPs) by selecting POV as polyatomic secondary building units (SBUs) and linking with complicated rigid organic ligands, advancing in the structural engineering of modules via coordination interactions [22, 36-41]. Our group has been focusing on the flexible multidentate carboxylate functionalized POVs: $[V^{IV}_{17}V^{IV}_{12}(OH)_4O_{60}(OOC(CH_2)_4COO)_8]^{7-}$, $[P_8V^{IV}_{24}(C_4H_2O_6)_{15}(H_2O)_{15}(OH)O_{51}]^{27-}$, and et al [9, 10, 42-43]. While these achievements mark a significant breakthrough in POV chemistry, the synthesis of giant organic-inorganic hybrid POVs still faces a series of challenges, primarily due to the difficulty in selecting appropriate organic ligands and the high susceptibility of POVs to oxidation, making it difficult to link POV structural motif to organic ligands in a controlled manner [44]. Furthermore, a comprehensive understanding of the self-assembly pathways of giant POVs and the functions of various structure-directing agents is essential for the rational design and assembly of complex high-nuclear POV species.

The epoxidation of alkenes is an important and commercially valuable organic transformation [45]. Owing to their manifold redox chemistry, POVs have been regarded as promising candidates for catalyzing selective olefin epoxidation via both heterogeneous and homogeneous. In the last decade, modifying POVs to develop highly active, readily recoverable heterogeneous catalysts represents a current research priority in POMs catalysis (Table S1). Compared with traditional oxidants (H_2O_2 , PhIO, TBHP, and et al.), molecular oxygen is more attractive and challenging owing to its low cost and environmentally friendly nature. Moreover, Liu proposed that the catalytic performance of mixed-valence vanadium oxo-clusters is superior to that of single valent vanadium oxo-cluster [46].

In this work, we make a breakthrough in the development of giant POV-clusters through building of 128-nuclearity heterometallic POV $Cs_{16}K_{40}H_{36}\{[(V^{IV}_4V^{IV}_4(OH)_2(tart)_4O_{11})_2V^{IV}_4V^{IV}_{12}(OH)_6O_{44}(Cl)][Mn(H_2O)_2]_2\}_4\cdot 109H_2O$ (**1**, $tart=C_4H_2O_6$) by employing DL-tartaric acid as ligands and $\{MnO_4(H_2O)_2\}$ as bridging groups. Featuring 128 vanadium centers, **1** represents the largest POV reported to date. In addition, **1** exhibits outstanding catalytic efficiency for olefin epoxidation reactions with 98% conversion and 99% selectivity under aerobic conditions. More importantly, this work suggests a coordination-driven self-assembly pathway to synthesize giant POV.

2 Experimental

Synthesis of **1**

Solution A: A solution of KVO_3 (1.15 g, 8.33 mmol) in H_2O (15 mL) was treated at 90 °C together with hydrazine hydrate ($N_2H_4\cdot H_2O$, 80%, 100 μ L, 1.65 mmol) stirring for 1 h. Thereafter, DL-tartaric acid (1.25 g, 8.33 mmol) was added to the black solution at this temperature, and the mixture was stirred until the

solid was completely dissolved.

Solution B: $MnCl_2\cdot 4H_2O$ (1.00 g, 5.05 mmol) and CsCl (0.33 g, 1.98 mmol) were dissolved in 5 mL water, stirring at room temperature until all solid materials were completely dissolved.

Solution B was added to solution A and mixed for 30 min at 90 °C. After cooling to room temperature, the resultant solution was adjusted to pH = 4.00 with 2 M KOH then heated at 90 °C for 4 h. The above mixture was filtered to remove the precipitate and allowed to evaporate slowly until blackish-green crystals were suitable for X-ray study form (usually 1 week). Yield: 0.05 g (3.38% based on KVO_3). Elemental analysis calcd (%) for **1**: C, 7.36; H, 1.72; V, 31.22; Mn, 2.11; Cl, 0.68; Cs, 10.18; K, 7.49. Found (%): C, 7.41; H, 1.42; V, 32.02; Mn, 1.97; Cl, 0.56; Cs, 10.60; K, 7.56. Selected IR (KBr, cm^{-1}): 1618 (s), 1398 (w), 977 (s), 824 (w), 763 (w), 689 (w), 608 (m).

2.2 Synthesis

The synthesis of compound **1** involves the hydrolysis and polymerization of the simple precursor KVO_3 in aqueous solution, and during this process the reductant, heteroatoms, counterions, and other factors influence the generation and assembly of building blocks [47]. $N_2H_4\cdot H_2O$ is a common reducing agent in synthesis of POVs. By carefully adjusting the $KVO_3/N_2H_4\cdot H_2O$ molar ratio such that only a portion of the V centers undergoes reduction, a coexistence of V^{IV} and V^{V} in an approximately ratio of 1:2 is achieved. The aggregation of $\{VO_3\}$ fragments tends to the formation of various host-guest cage-shaped POVs [27]. Using organic ligands rationally as functionalities and modulators has emerged as an efficient strategy to achieve improved stability and richer architectures [29]. DL-tartaric acid, an aliphatic dicarboxylic acid, possesses outstanding flexibility, conformational freedom, two inorganic groups $\{COOH\}$ and two hydroxyl groups supplying sufficient coordination sites, chelating ability, which is regarded as an ideal ligand for the modification of POV clusters. The incorporation of transition-metal (TM) cations not only increases the active-site density and structural stability but also extends the application of material in photoelectric, catalytic, and magnetic domains [28, 48-50]. In conclusion the incorporation of additional functional components (TM ions, counter cations, and metal-organic moieties) into synthesis system can significantly enrich both the structural diversity and application potential of the POV family [51]. In the absence of CsCl or replacement with other counter cations, only powders are obtained, indicating that CsCl is necessary for the synthesis of compound **1**. The Cl^- ions, encapsulated within the core, serve as a template to maintain the sphere structure [52] and the Cs^+ ions are employed to occupy the cavity and extend the architectural dimensionality. Given the excellent solubility of the precursors (KVO_3), neither high pressure nor elevated temperature is required to facilitate dissolution, thereby allowing the use of a conventional aqueous solution synthesis method that is environmentally friendly.

3 Results and discussion

3.1 Structure

The **1** crystallizes in the tetragonal crystal system with space group $I4/mmm$, consisting of one tetramer polyoxoanion $[\text{Mn}_8(\text{H}_2\text{O})_{16}\text{V}_{80}\text{V}_{48}^{\text{IV}}(\text{tart})_{32}(\text{OH})_{40}\text{O}_{264}(\text{Cl})_4]^{92-}$ ($\{\text{Mn}_8\text{V}_{128}\}$, Fig. 1a), 40 K^+ ions, 16 Cs^+ ions, 109 water molecules and 36 protons for charge balance. An interesting feature is that $\{\text{Mn}_8\text{V}_{128}\}$ exhibits the highest-nuclear POV observed so far. In $\{\text{Mn}_8\text{V}_{128}\}$, the V centers adopt three kinds of coordination geometries: 8 $\{\text{VO}_6\}$ octahedron, 108 $\{\text{VO}_5\}$ square pyramids and 16 $\{\text{VO}_4\}$ distorted tetrahedra. This diversity confirms the Khan's view that the coexistence of multiple V coordination configurations is

essential for constructing larger and more novel POVs [50]. The result of the BVS shows that the eighty atoms (V1, V3, V4, V5, V9) are in +5 oxidation states and the forty-eight atoms (V2, V6, V7, V8, V10, V11) are in the reduced +4 states (Table S2). Further, the X-ray photoelectron spectra confirms the mixed $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ oxidation states in **1**. As shown in Fig. 2a, the V 2p peaks of **1** at 516.4 eV and 523.5 eV corresponding to the binding energies of V^{IV} 2p_{3/2} and V^{IV} 2p_{1/2}, and peaks at 517.5 eV and 524.8 eV corresponding to the binding energies of V^{V} 2p_{3/2} and V^{V} 2p_{1/2}, respectively.

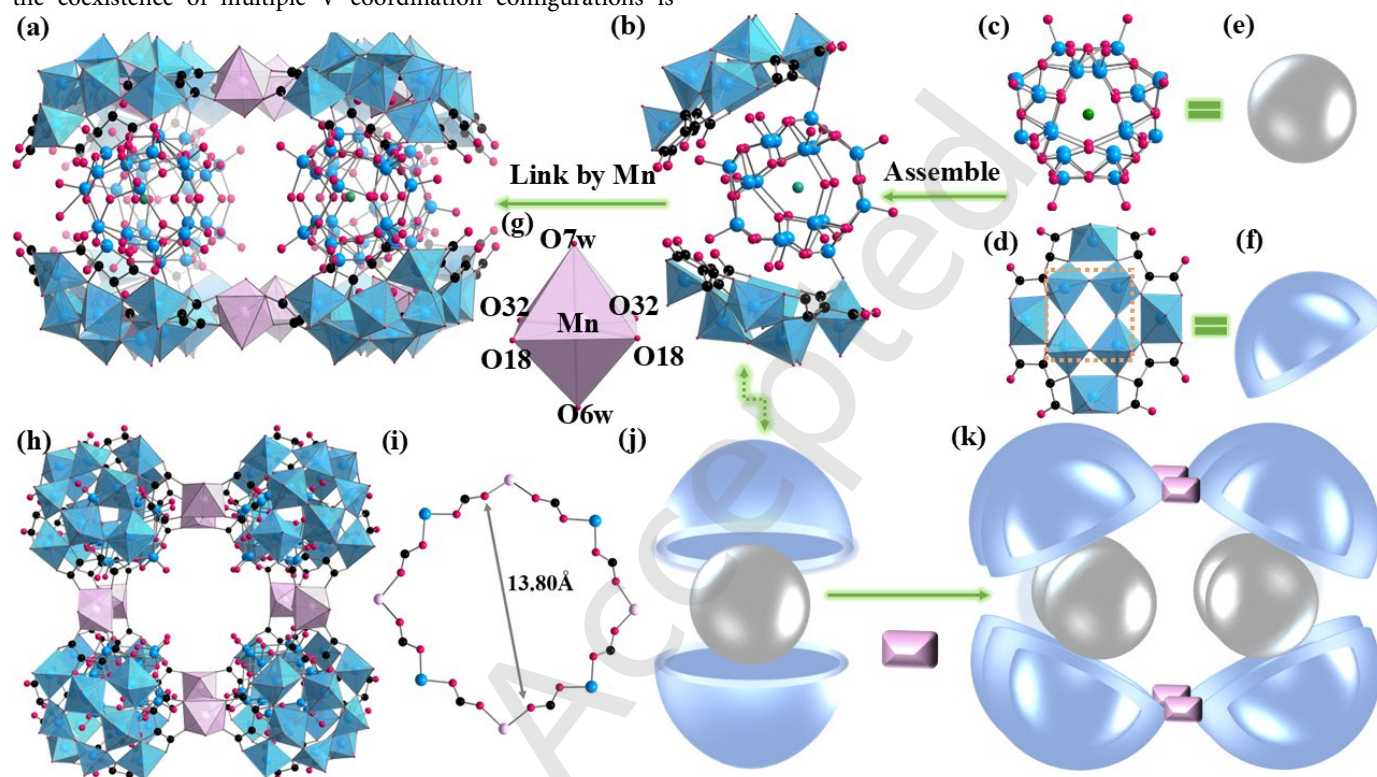


Figure 1 Polyhedral/ball-and-stick representation of (a) the polyoxoanion of **1** in front view; (b) $\{\text{V}_{32}\}$; (c) $\{\text{V}_{16}\}$; (d) $\{\text{V}_8\}$; (e) the coordination environment around the $\{\text{MnO}_6\}$; (h) the polyoxoanion of **1** in top view; (i) the 32-crown-6 window. Simplified view of (e) $\{\text{V}_{16}\}$; (f) $\{\text{V}_8\}$; (j) $\{\text{V}_{32}\}$; (k) the polyoxoanion of **1** in front view. Color code: V blue, Mn pink, Cl green, C black, O red.

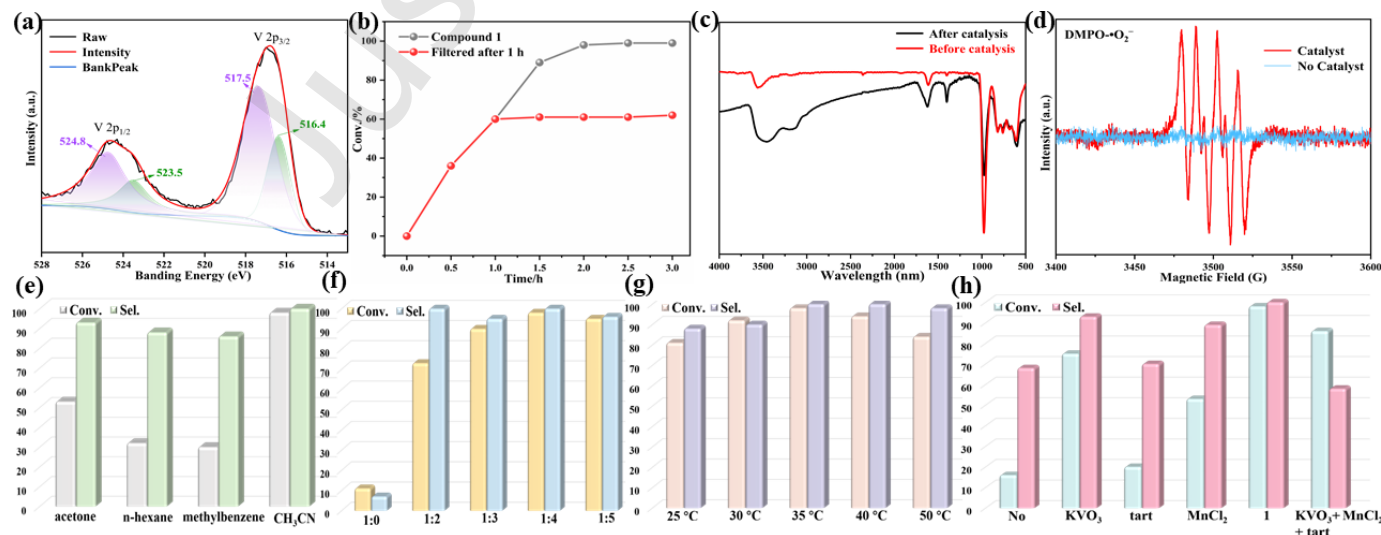


Figure 2 (a) Fitting curves for XPS spectra of V 2p; (b) time-dependent curve of cyclooctene epoxidation reaction over **1** (gray) and the hot filtration test for **1** catalyst (red); (c) FT-IR spectra; (d) DMPO spin-trapping EPR spectra for $\text{DMPO} \cdot \text{O}_2^-$ radical species. The conversions and selectivity of different reaction conditions on the epoxidation reaction of cyclooctene to 1,2-epoxycyclooctane catalyzed by **1** with O_2 as the oxidant: (e) reaction solvent; (f) the mole ratio of cyclooctene to IBA; (g) reaction temperature; (h) different catalysts.

As is well known, the reported structural types of giant POVs are limited owing to synthetic challenges caused by a small ionic radius, low valence and the tendency to form decavanadates in acidic solution of V centers [53]. The $\{Mn_8V_{128}\}$ exhibits an unprecedented giant structure with external dimension of ca. $27.69 \times 27.69 \times 18.27$ Å (Fig. S1a, 1b), which comprises of four novel POV building units $[V_{20}^{IV}V_{12}^{IV}(tart)_8(OH)_{10}O_{66}(Cl)]^{27-}$ ($\{V_{32}\}$) bridged by eight μ_4 -Mn(H₂O)₂, resulting D_{4h} symmetry for the whole assembly. When viewed from the top, two 32-crown-6 windows are evident (Fig. 1i), in which the farthest O...O distance measures 13.80 Å.

The C_{2v} -symmetric building unit $\{V_{32}\}$ possesses a chloride-templated, 32-nuclear cluster consisting of one spherical $[V_{12}^{IV}V_4^{IV}(OH)_6O_{44}(Cl)]^{18-}$ ($\{V_{16}\}$) cluster (Fig. 1c) and two bowl-type $[V_4^{IV}V_4^{IV}(OH)_2(tart)_4O_{11}]^{4-}$ ($\{V_8\}$) fragment (Fig. 1d). It is worth noting that the sixteen V atoms of $\{V_{16}\}$ cluster take up twenty atomic positions with six intact V atoms (V1–V8) and twenty disorder V atoms (4V9, 4V9B, 4V10, 4V10B, 4V11) with 50% occupancy (Fig. 1c). The spherical $\{V_{16}\}$ fragment is similar to the structure of $[V_9^{IV}V_7^{IV}O_{38}(Cl)]^{4-}$ in the compound (n-Bu₄N)₄[V₁₆O₃₈(Cl)] reported by Hayashi in 2013 [51]. In 2002, the $[V_{16}O_{38}(H_2O)]^{7-}$ was first observed as a novel structural motif within the three-dimensional framework $[[Cu(1,2-pn)_2]_7\{V_{16}O_{38}(H_2O)\}_2] \cdot 109H_2O$, a hexadecavanadate cluster [52]. Since then, a series of inorganic–organic hybrid materials based on $[V_{16}O_{38}(H_2O)]^{7-}$ shell is prepared by introducing transition metal as inorganic bridging ligands to link hexadecavanadate clusters into one-, two- and three-dimensional networks [56–59]. What is different from the structure of $\{V_{16}\}$ cluster is that these reported hexadecavanadate cluster is composed of sixteen twisted $\{VO_5\}$ tetrahedrons without $\{VO_4\}$ tetrahedra. $\{V_{16}\}$ is composed of six $\{VO_4\}$ tetrahedra (V9, V11) and ten $\{VO_5\}$ square pyramids. As Khan predicted, the coexistence of $\{VO_4\}$ tetrahedra and $\{VO_5\}$ square pyramids facilitate the construction of high-nuclear POVs [50]. The bowl-typed $\{V_8\}$ fragment is a novel struct type composed of seven $\{VO_5\}$ tetragonal pyramids, one $\{VO_6\}$ octahedron, two L-tart ligands, and two D-tart ligands (Fig. S2). The four $\{VO_5\}$ of $\{V_8\}$ are fused with each other through common angles forming a square-shaped $\{V_4\}$ core framework, and every of them is defined by one $\{V=O\}$ oxo-group (O14, O17) (O14–V3 = 1.592(6) Å, O17–V5 = 1.599(6) Å), four μ_2 -oxygens of the neighbouring $\{VO_5\}$ tetragonal pyramid, and two μ_4 -oxygens from the hydroxyl of a tartrate ligand (Fig. 1d). Then three $\{VO_5\}$ tetragonal pyramids and one $\{VO_6\}$ octahedron connected to $\{V_4\}$ section through corner-sharing modes, generating bowl-type $\{V_8\}$ fragment (Fig. S2). The $\{VO_5\}$ tetragonal pyramids, which form the edge of $\{V_8\}$, are connected to the L- and D-tartaric ligands in an alternating pattern. This connection is facilitated by two μ_3 -oxygens and two μ_2 -oxygens, which originate from the hydroxyl and carboxyl groups, respectively. The edge $\{VO_6\}$ octahedron is protected by two tartaric ligands through two μ_2 -O and two μ_3 -O bonds forming a square plane, that subsequently connects to the V_{16} spherical fragment via a μ_2 -O bond (V2–O15–V4 = 147.3(5)°) adding a terminal oxygen to form octahedron (Fig. S2). The carbonyl oxygens of tartaric acid, which are attached to the $\{VO_6\}$

octahedra, undergo further activation and form connections with the Mn ion. The Mn atom is hexacoordinated in a distorted octahedral geometry. The basal plane is defined by four O atoms from two carboxylate ligands [Mn–O18 = 2.135(7) Å, Mn–O32 = 2.151(10) Å], while the axial positions are occupied by two O atoms from water molecules [Mn–O7w = 2.166(12) Å, Mn–O6w = 2.152(10) Å] (Fig. 1g). It's worth noting that the $\{VO_4\}$ tetrahedra, $\{VO_5\}$ square pyramids, and $\{VO_6\}$ octahedra coexist in compound **1**. The coexistence of multiple coordination geometries is a major feature of mixed-valence POVs [58–62]. In summary, one sphere-type $\{V_{16}\}$ fragment is sandwiched by two $\{V_8\}$ fragments via two $\{VO_6\}$ octahedrons ($\{V_{32}\}$), thereby forming the distinctive $\{V_{32}\}$ building unit (Fig. 1e). Subsequently, further combine and coordinate with $[MnO_4(H_2O)]^{2+}$ ions on upper and lower leading to the formation of the tetrameric $\{Mn_8V_{128}\}$ polyoxoanion (Fig. 1j, 1k). Finally, the neighboring $\{Mn_8V_{128}\}$ polyoxoanions extend into the three-dimensional framework through the K⁺ and Cs⁺ ions.

One fascinating structural feature of **1** is the diverse coordination mode of its 32 tartrate ligands: (i) The first coordination mode is previously reported by our group, which the tartaric acid ligand is covalently linked to three vanadium metal centers through oxygen atoms from two hydroxyl and two carboxyl groups, forming three five-membered chelating rings (Fig. S3(a)). (ii) The second coordination mode only occurs in the tartrate ligand which connected to $\{VO_6\}$, engaging in bonding with the V and Mn atoms via abundant O sites to produce heterometallic clusters. Tartrate, as a tetradentate ligand, not only coordinates with three vanadium metal centers but also connects to Mn centers through two carboxyl oxygens, forming four five-membered chelating rings, which play a significant role in the formation and stabilization of the giant framework (Fig. S3b).

3.2 Catalytic Epoxidation Reaction of Olefins

The catalytic ability of **1** is evaluated in acetonitrile solution (1 mL) containing isobutyraldehyde (IBA) (0.4 mmol) as the reductant and cyclooctene (0.1 mmol) as the substrate under 1 atm O₂ gas at 35 °C. The catalyst **1** (0.3 μmol) displays an impressive conversion rate of 98% and selectivity of 99% in the cyclooctene epoxidation reaction with a reaction time of 2 hours. A series of control experiments reveals that the reaction proceeded with difficulty in the absence of catalyst **1**, O₂, or IBA individually. (Fig. 2f, 2h, S6). At the same time, we respectively substitute CH₃CN with acetone, n-hexane, and methylbenzene, achieving cyclooctene conversions of only 53%, 32%, and 30%. (Fig. 2e). Temperature plays an important role in the catalytic epoxidation reaction of olefins. Conversion and selectivity increase with temperature, reaching 98% and 99% respectively at 35°C, then decline as the temperature continued to rise (Fig. 2f). The reason may be that the increase in temperature causes the solubility of O₂ in the liquid phase to decrease [65]. In addition, the molar ratios of cyclooctene to IBA influence on the conversion of cyclooctene. As the ratio increases from 1:2 to 1:4, the conversion rises from 73% to 98%. However, when the ratio is increased beyond 1:4, the conversion rate of cyclooctene shows little change, indicating that 1:4 is the optimal proportion (Fig. 2g).

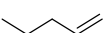
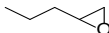
Meanwhile, 0.3 μmol of the catalyst is significantly superior to the other three dosages in both conversion and selectivity (Fig. S7). When only KVO_3 , DL-tartaric acid, or MnCl_2 is used as catalyst for the reaction (with the same total metal content), the conversions decrease significantly to 75%, 20%, and 53%, respectively (Fig. 2h). When KVO_3 , DL-tartaric acid, and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ simultaneously replace **1** as the catalyst, the conversion improved, but the selectivity is significantly reduced (Fig. 2h). These results indicate that the formation of the POV framework may have contribution to catalyze this reaction.

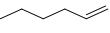
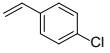
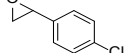
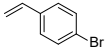
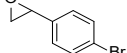
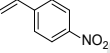
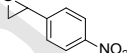
The hot filtering experiment confirms that **1** is heterogeneous catalyst in this reaction system. Filtering catalysts out after 1 h, the remaining solution continues to react under the same conditions, while the conversion rate remains unchanged basically (Fig. 2b). The catalytic activity of **1** is not obvious loss after the four rounds of catalysis (Fig. S8). The IR and XRD results manifest that the structure of recovered **1** is maintained in the cycle tests (Fig. 2c, S10). The ICP testing of the postreaction filtrate revealed V content of 0.0024 mg/L and Mn content of 0.0013 mg/L, further demonstrating the outstanding stability of catalyst. In conclusion, heterogeneous catalyst **1** possess outstanding stability in the catalytic epoxidation reaction of cyclooctene.

To evaluate the generality of the catalyst, the epoxidation of various olefins is examined under the optimized conditions. High conversions are obtained for cyclopentene and cyclohexene; however, epoxide selectivity only reach 63% and 70%, respectively (Table 1, entries 1–2). When linear terminal olefins act as substrates (1-pentene and 1-hexene), the conversion of alkenes is relatively low at 56% and 30%, respectively (Table 1, entries 3–4). Affected by the conjugative effect of benzene ring, low conversion and selectivity are observed in styrene (Table 1, entries 5). As shown in Table 1 entry 6, 4-methylstyrene bearing electron-donating groups, increases the electron density of the olefinic double bond, which achieves high conversion (94%, Table 1, entries 6). While the presence of the electron-withdrawing group at the para position, the conversion and selectivity significantly enhance (Table 1, entries 7–9). **1** exhibits high conversion and selectivity toward 4-chlorostyrene, 4-bromostyrene, and 4-nitrostyrene after 10h, with conversion of 97%, 98%, and 96%, and selectivity of 93%, 97%, and 98%, respectively. In short, catalyst **1** achieves the excellent suitability of the catalytic epoxidation reaction of olefins.

Table 1 Catalytic performance of **1** in epoxidation of several olefins^a

^aReaction conditions: Substrate (0.1 mmol), Cat. (0.3 μmol), IBA (0.4 mmol), CH_3CN (1 mL), 35 $^\circ\text{C}$, 1 atm O_2 . ^bResults determined by GC.

Entry	Substrate	Product	Time/h	Conv. ^b /%	Sel. ^b /%
1			4	98	63
2			4	99	70
3			8	56	99

4			8	30	99
5			8	80	85
6			5	94	83
7			10	97	93
8			10	98	97
9			10	96	98

For the purpose of the exploration of catalytic mechanism, a series of radical capture experiments are conducted. When the (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO), as a radical scavenger, is introduced into the catalytic system, there is little desired product [Fig. S11]. In addition, the $\bullet\text{O}_2^-$ EPR spectrum (Fig. 2b) shows typical signals (1:1:1:1) with the introduction of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO). Based on the aforementioned experimental results and relevant literature [46, 65–68], a plausible catalytic mechanism is proposed (Fig. 3). Firstly, O_2 and IBA are adsorbed onto the **1** surface simultaneously, resulting in the formation of the $\bullet\text{O}_2^-$ and isobutyryl radical. Then the isobutyryl radical and $\bullet\text{O}_2^-$ radical are combined to generate peroxyisobutyric acid anions. Finally, the cyclooctene is oxidized by these peroxyisobutyrate acid anions to the target product.

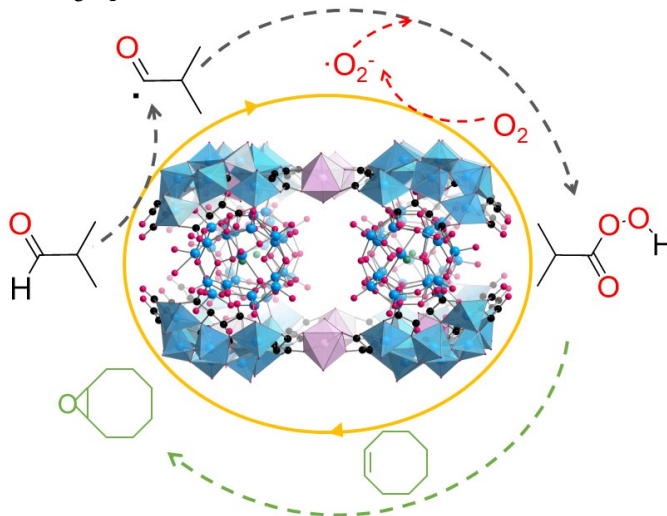


Figure 3 The possible catalytic mechanism of **1** in the epoxidation reaction of cyclooctene.

4 Conclusions

The successful synthesis of giant POV compound **1** from simple vanadium precursors, Mn cations, and organic carboxylate ligands demonstrates the remarkable potential of this combination approach for constructing giant POVs via self-assembly. Specifically, **1** exhibits an unprecedented topology

structure in POM chemistry which can be described as four novel $\{V_{32}\}$ building units bridging by Mn cations. Compound **1** contains the largest number of V centers and represents the current largest POV cluster. The success of this strategy provides an encouraging expectation that the aggregation of greater level of POV clusters may indeed be feasible. Further, compound **1** exhibits excellent catalytic activity in the epoxidation reaction of cyclooctene achieving 98% conversion and 99% selectivity with O_2 as the oxidant.

Electronic Supplementary Material: Supplementary material (TGA, XRD, BVS values, crystallographic table, experiment sections, additional catalytic test) is available in the online version of this article at <https://doi.org/10.26599/POM.2026.9140166>.

Data availability

CCDC 2575579 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Declaration of competing interest

The authors declare no competing financial interest. Author Jingyang Niu is the advisory board member of this journal, but he is not involved in the peer-review or decision of this article.

Author contribution statement

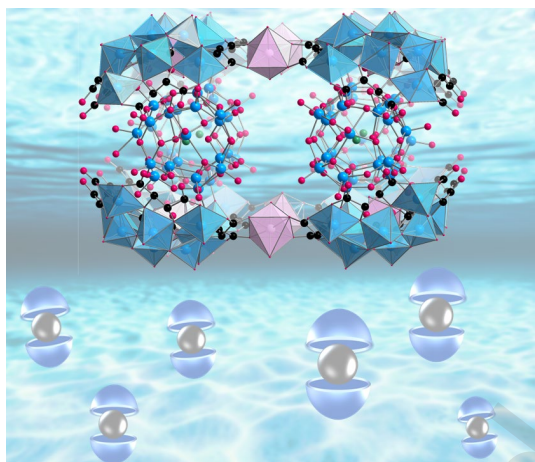
S. Y. L.: Data curation, visualization, writing – original draft. S. L.: Validation. K. H. L.: Writing – original draft. Y. Z. H.: writing – original draft. P. T. M.: Supervision, validation. J. P. W.: Funding acquisition, project administration, conceptualization, supervision, writing – reviewing & editing. J. Y. N.: Funding acquisition, project administration, supervision. All the authors have approved the final manuscript.

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A giant heterometallic polyoxovanadate anion $[\text{Mn}_8(\text{H}_2\text{O})_{16}\text{V}_{80}^{\text{V}}\text{V}_{48}^{\text{IV}}(\text{tart})_{32}(\text{OH})_{40}\text{O}_{264}(\text{Cl})_4]^{92-}$ has been obtained via self-assembly, constructed from four unique $[\text{V}_{20}^{\text{V}}\text{V}_{12}^{\text{IV}}(\text{tart})_8(\text{OH})_{10}\text{O}_{66}(\text{Cl})]^{27-}$ units and Mn^{2+} ions. This compound contains 128 V atoms, representing the highest-nuclear POV reported to date.