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ARTICLE

Design and Synthesis of the Purely Inorganic 3D Frameworks Composed of Reduced Vanadium Clusters and Manganese Linkers

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Two purely inorganic three-dimensional (3D) frameworks $[\text{Mn}_4(\text{H}_2\text{O})_{11}\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{7-}$ (1) and $[\text{Mn}_2(\text{H}_2\text{O})_7\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{11-}$ (2) were synthesized under hydrothermal conditions and fully characterized by single-crystal X-ray structural analysis, IR spectroscopy, thermogravimetric analysis and PXRD. Structural analysis revealed that these two compounds contained a similar all reduced polyoxoanion $[\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{15-}$ linked by different amount of manganese centers into the 3D framework materials. The V centers in these two compounds were all reduced into the +IV oxidation state, resulting in an all reduced heteroblu, which was firstly used as building block for constructing the 3D framework materials. The all reduced typical polyoxoanion $[\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{15-}$ with 15 negative charges supplied enough charge amount to accept TM cations. In these two structures, the anions were surrounded by 12 and 5 Mn^{2+} ions, respectively, adjusted by varying the feeding amount of the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Electrocatalytic study revealed that compound 1 exhibited electrocatalytic activity for reduction of H_2O_2 .

Introduction

Metal-organic frameworks (MOFs), composed of the inorganic metal-connecting node and organic linking ligand, have attracted much more attention as they could provide a major opportunity for designing functional materials. In the past decades, various methods have been explored to realize the design and synthesis of a large number of MOFs with versatility by judicious choices of bridging ligands and metal/metal cluster connecting points.¹⁻³ Polyoxometalates (POMs), a kind of pure inorganic metal-oxo clusters covering an enormous range in size and structure, have been proven as one kind of ideal inorganic ligands usually with high thermal stability to construct the POM-based framework materials.⁴ This has been regarded as one novel and efficient method for constructing pure inorganic framework materials, although the studies on their design and synthesis are quite scarce.⁵

Polyoxovanadates (POVs), as a subfamily of the POMs, with distinct structure and chemical property, have led to numerous applications in catalysis, magnetism, biology, luminescence, and electrochemistry.⁶⁻⁸ The diversity of coordination geometry (VO_4 tetrahedra, VO_5 square pyramids and VO_6 octahedra) and

the multiple oxidation states (V^{5+} , V^{4+} and V^{3+}) of the vanadium ions make them tend to form various cage-type POVs in the self-assembly process.^{9,10} Up to date, two types of POVs, isopolyoxovanadates and heteropolyoxovanadates were usually synthesized and reported. The isopolyoxovanadate clusters, only composed of the vanadium centers and oxygen atoms, such as the common POV clusters: $[\text{V}_6\text{O}_{19}]^{8-}$, $[\text{V}_{10}\text{O}_{28}]^{6-}$, $[\text{V}_{12}\text{O}_{32}]^{4-}$, $[\text{V}_{13}\text{O}_{34}]^{3-}$, $[\text{V}_{15}\text{O}_{36}]^{5-}$, $[\text{V}_{15}\text{O}_{42}]^{9-}$, $[\text{V}_{17}\text{O}_{42}]^{4-}$, $[\text{V}_{18}\text{O}_{42}]^{12-}$, $[\text{V}_{19}\text{O}_{49}]^{9-}$ and $[\text{V}_{34}\text{O}_{82}]^{10-}$,^{11,12} have been widely studied in the past decades. Also, the incorporation of heteroatoms into the vanadate cages can produce novel polyoxoanions with excellent properties in a domain. One important progress in vanadate chemistry is that the arsenic atom was introduced into the polyoxovanadate, which attracts great attention in this field.¹³ Afterwards, more and more heteroatoms were introduced into POVs including main group elements, transition metals (TMs) or even rare earth metal, which had greatly enriched the structural variety and properties of the POVs.¹⁴ So, the POV clusters could be regarded as enormous candidates for constructing the 3D framework materials. As well known, most of the TM cations were introduced into the POV chemistry with the assistance of the organic ligands, resulting in inorganic-organic hybrid compounds.¹⁵ However, all-inorganic molecular metal-oxo networks composed of the POV clusters are rare.¹⁶ For the manganese center, it has emerged in the POV chemistry for a many years, such as the well-known $[\text{MnV}_{13}]$ unit, where the Mn^{4+} ion resided in the center of the V cage, acting as the heteroatom. The $[\text{MnV}_{13}]$ anion could also coordinate with the rare earth or TM cations as the bridging units forming extended

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structural materials, which exhibited unique catalytic properties.¹⁶ However, the Mn^{2+} ions were rarely observed in the POV chemistry.¹⁷ Herein, reactions of vanadate, manganese ion, phosphoric acid with the reducing agent 1,2-diaminopropane under hydrothermal condition afforded two purely inorganic 3D frameworks, $[\text{Mn}_4(\text{H}_2\text{O})_{11}\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{7-}$ (**1**) and $[\text{Mn}_2(\text{H}_2\text{O})_7\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{11-}$ (**2**), where the manganese cations acted as the inorganic linkers to connect the all reduced POV clusters. Electrochemistry and the electrocatalytic reduction of H_2O_2 of **1** were investigated.

Results and discussion

Crystal structure. X-ray single-crystal diffraction analysis revealed that compound **1** crystallizes in the tetragonal crystal system, space group I_{41}/acd , and exhibits a unique 3D framework structure, composed of $[\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{15-}$ clusters (abbreviated as $\{\text{PV}_{18}\}$) and Mn^{2+} linkers. As shown in Fig. 1a and S1, the $\{\text{PV}_{18}\}$ was composed of one $[\text{PV}_8]$ “cycle” and two $[\text{V}_5]$ “cap” units. In the $[\text{PV}_8]$ unit, four square pyramids VO_5 and four octahedra VO_6 connected each other alternatively through edge-sharing pattern into a ring, and a $[\text{PO}_4]$ tetrahedron located in the center of the ring through ligating to four oxygen atoms on the inner side of V-O octahedra (Fig. S1), with the P-O bond length of 1.544(6)-1.557(7) Å. Further, two $[\text{V}_5]$ clusters composed of three distorted square pyramids and two octahedra, capped on the $[\text{PV}_8]$ “cycle” through edge-sharing to build up the $\{\text{PV}_{18}\}$ anion. The bond length of V-O is in the range of 1.604(7)-2.445(6) Å. Bond valence calculations revealed that the V centers in the $\{\text{PV}_{18}\}$ anion are all in the oxidation state of +4 (Table S1). Previously, the similar isolated $\{\text{PV}_{18}\}$ and $\{\text{VV}_{18}\}$ anions were reported in the literatures, where the vanadium

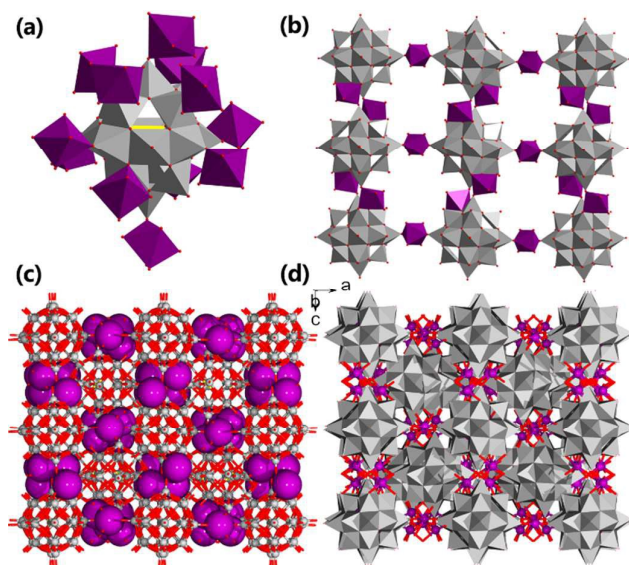


Fig. 1 (a) Polyhedral representation of polyoxoanion **1**; (b) The 2D layer structure on b,c -plane in **1**; (c) Ball and stick representation of the 3D structure in **1** with the space-filling Mn centers on a,c -plane; (d) Mixed polyhedral and ball-stick representation of the 3D structure in **1**. Color code: V (gray), Mn (amethyst), P (yellow), O (red).

centers are in the mixed oxidation states of +4 and +5.¹⁸ In compound **1**, there are three six-coordinated Mn^{2+} cations: Mn(1) coordinated with one $\{\text{PV}_{18}\}$ cluster through a μ_2 -O atom and a μ_4 -O atom, and offered another two μ_2 -O atoms to connect another two $\{\text{PV}_{18}\}$ clusters; Mn(2) O_6 octahedron acting as a bridge between two $\{\text{PV}_{18}\}$ clusters through two corner-sharing modes with the VO_x octahedra; Mn(3) center disordered into two sites and coordinated with the $\{\text{PV}_{18}\}$ cluster through a μ_2 -O atom. And, two $\{\text{PV}_{18}\}$ clusters coordinated with the Mn(3) center through a μ_2 -O atom and a Mn-O-V bridge. The average bond distance is 2.183 Å for Mn(1)-O, 2.165 Å for Mn(2)-O and 2.208 Å for Mn(3)-O.

In this structure, two neighbouring $\{\text{PV}_{18}\}$ clusters are linked together by two Mn(1) atoms to form a one-dimensional (1D) polymer chain along c -axis (Fig. S2). Then, each chain connected to another two parallel chains through Mn(2) atoms to form a two-dimensional (2D) sheet (Fig. 1b). Finally, the adjacent 2D sheets polymerized to form a 3D framework by the Mn(3) linkers (Fig. 1c and 1d). In this network, each POM anion is linked by twelve Mn^{2+} cations into a 3D framework. Each POM anion $\{\text{PV}_{18}\}$ could be regarded as a polydentate ligand to coordinate with 12 Mn^{2+} cations through V-O-Mn bonds (Fig. 1a), forming the POV-based 3D framework (Fig. 1c and 1d).

As well known, the polyoxoanions were usually decorated by the TM or Ln cations *via* the terminal or μ_2 -oxo atoms, which usually coordinated by the 1 to 9 TM^{2+} cations,¹⁹ as the limited charge amount and volume of the typical polyoxoanions. Recently, the sandwich polyoxoanions and other TM-substituted polyoxoanions were reported to coordinate with more TM^{2+} cations as the increase of their charge amount and volume.²⁰ Here, one polyoxoanion coordinated by 12 TM^{2+} cations was achieved by using an all reduced typical polyoxoanion $[\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{15-}$, which was rarely observed in the POM chemistry.

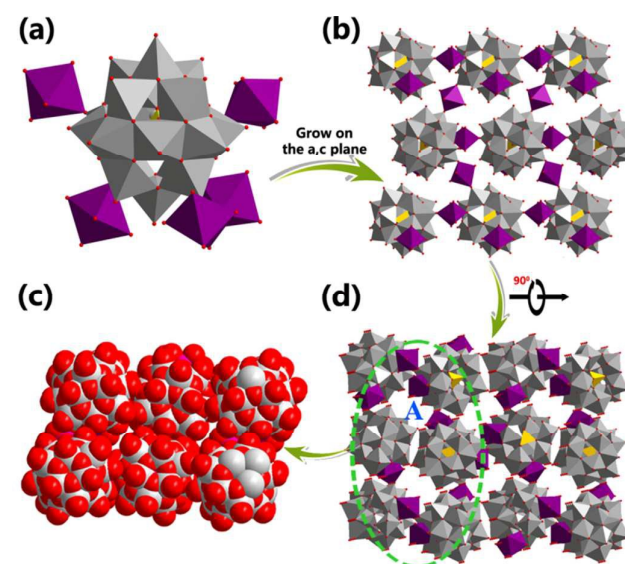


Fig. 2 (a) Polyhedral representation of polyoxoanion **2**; (b) The 2D layer structure in **2**; (c) Space-filling of the 3D framework of **2**; (d) Mixed polyhedral and ball-stick representation of the 3D structure in **2**.

Polyhedral representation of the 3D porous framework of **2**. Color code: V (gray), Mn (amethyst), P (yellow), O (red).

Structure analysis revealed that compound **2** crystallizes in the orthorhombic crystal system, space group $P2_12_12_1$, and consists of a $[V^{IV}_{18}O_{42}(PO_4)]^{15-}$ cluster, two Mn^{2+} linkers, and a protonated 1,2-diaminopropane ligand. The POV anion $[V^{IV}_{18}O_{42}(PO_4)]^{15-}$ here is a little different from that of **1**, which drives from the coordination diversity of the vanadium ion. As shown in Fig. 2a and S3, the $\{PV_{18}\}$ in **2** consisting of one $[PV_8]$ “cycle” and two different $[V_5]$ “cap” units. The $[PV_8]$ “cycle” here, is composed of six distort square pyramids and only two VO_6 octahedra. And, one of the $[V_5]$ “cap” is same as that in **1** and the other one constructed from one distorted square pyramid on the top, one square pyramid and three octahedra at the bottom. The bond length alteration and structure distortion resulted in the chiral skeleton, which was constructed by removing the symmetry center or mirror in POM. The flack parameter of 0.02(3) confirmed compound **2** with an absolute chiral configuration. It crystallized into the chiral crystalline materials *via* the chiral symmetry breaking. This is the first chiral materials constructed from the reduced POVs, obtained from achiral precursors. Besides the $\{PV_{18}\}$ cluster, there are two crystallographically independent Mn^{2+} ions in the asymmetric unit of **2**, which both adopt a distorted octahedral coordinated geometry by two oxygen atoms from the $\{PV_{18}\}$ cluster and four water molecules. The band length located in the range of 2.140(7)-2.224(8) Å for Mn(1) and 2.099(7)-2.270(11) Å for Mn(2). It is interesting that each $\{PV_{18}\}$ acts as a 5-dentate ligand coordinating with five $Mn(H_2O)_4^{2+}$ cations, forming an inorganic 3D porous framework with the pore size of $3.8 \text{ \AA} \times 6.4 \text{ \AA}$ (Fig. 2c and 2d). As shown in Fig. S4, the neighboring $\{PV_{18}\}$ clusters are firstly linked by the Mn(2) ions to form a 1D wavy chain along *c*-axis, and then each chain is connected to another two parallel chains through Mn(1) ions alone *a*-axis to yield a 2D layer on *a,c*-plane (Fig. 2b and S5). Further, such a 2D layer was linked to a 3D purely inorganic framework through additional Mn(1) cations (Fig. 2d).

Electrochemical and Electrocatalytic properties

POMs, a class of metal-oxo clusters that can undergo fast reversible and stepwise multi-electron-transfer reactions without changing their structures, can be used for the assembly of chemically bulk-modified carbon paste electrodes (abbreviated as CPEs). These CPEs have been widely used for the electrochemical study due to their low cost and high sensitivity. The electrochemical and electrocatalytic property of compound **1** was measured through cyclic voltammetry (CV) in pH = 6.5 0.20 M Na_2HPO_4 - NaH_2PO_4 buffer solution. And, the reproducibility of CV proved that 1-CPE was stable in such solution. Fig. 3a shows the unique CV curve of 1-CPE in the potential region of -0.9 to 1.1 V with a scan rate of 40 mV s^{-1} . Four pairs of redox peaks are detected with the peak potentials $E_{1/2} = 602.5, 256, -31, \text{ and } -265 \text{ mV}$, ($E_{1/2} = (E_{pc} + E_{pa})/2$), which can be ascribed to the redox process of the V centers in the anion cluster. The effect of the scan rates (ν) on the peak currents (i_{pa}

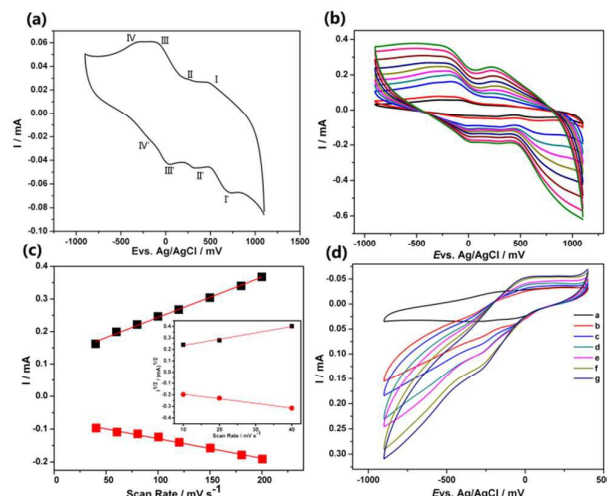


Fig. 3 (a) CV of 1-CPE in 0.20 M pH = 6.5 Na_2HPO_4 - NaH_2PO_4 buffer solution. Scan rate: 40 mV s^{-1} ; (b) CV of 1-CPE in 0.20 M Na_2HPO_4 - NaH_2PO_4 buffer solution with different scan rates from 10 to 200 mV s^{-1} ; (c) The corresponding plots of peak II and II' current versus scan rates from 40 to 200 mV s^{-1} ; insert: the corresponding plots of the square root of peak current versus scan rates from 10 to 40 mV s^{-1} ; (d) The evolution of CV of 1-CPE in 0.2 M Na_2HPO_4 - NaH_2PO_4 and 0.3 M KCl buffer solution containing various H_2O_2 concentrations (a: 0 mM, b: 5 mM, c: 10 mM, d: 15 mM, e: 20 mM, f: 25 mM, g: 30 mM). Scan rate: 75 mV s^{-1} .

and i_{pc}) has been investigated in the range of 10 – 200 mV s^{-1} . As is shown in the Fig 3b, the peak potentials changed gradually accompanying with the scan rate shift from 10 to 200 mV s^{-1} . As illustrated in Fig. 3c, when the scan rates are higher than 40 mV s^{-1} , the relationship between the peak currents and scan rates is liner, indicating that the electrochemical process is surface controlled; however, the redox processes is a diffusion-controlled process, when scan rates are lower than 40 mV s^{-1} .

The hydrogen peroxide was widely used as processing aid in food industry, thereby widely existed in our daily life. Also, the discharge of hydrogen peroxide can cause toxicosis of the aquatic organism. Therefore, the design and synthesis of the electrocatalysts for decomposition of the H_2O_2 was a significant project. The electrocatalytic reduction of H_2O_2 for **1** was studied in 0.2 M pH = 6.5 Na_2HPO_4 - NaH_2PO_4 and 0.3 M KCl buffer solution. Fig. 3d showed the CV curves of 1-CPE accompanying with different concentrations of the H_2O_2 . When the hydrogen peroxide were added to the buffer solution, the reduction peak currents increased, meanwhile the opposite oxidation peak currents decreased. The experimental data proved that compound **1** had the electrocatalytic activity for the reduction of the hydrogen peroxide.

Experimental Section

Synthesis of 1. A mixture of NH_4VO_3 (0.20 g, 1.71 mmol), $MnCl_2 \cdot 4H_2O$ (0.15 g, 0.76 mmol), L-proline (0.058 g, 0.51 mmol), and 10 mL distilled water was stirred for 30 min. Then 1,2-diaminopropane (0.10 ml) and H_3PO_4 (0.10 ml, 7.50 mol·L⁻¹

¹) were added to the mixture. The mixture was transferred to a Teflon-lined autoclave (25 mL) and kept at 150 °C for 4 days. After slowly cooled to room temperature at a rate of 10 °C·h⁻¹, the black crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of ca. 22% (based on vanadium). Anal.Calcd (%) for **1**: Mn, 10.08; V, 42.04; P, 1.42; Found: Mn, 9.98; V, 42.26; P, 1.34. IR (KBr pellet) for **1**: $\tilde{\nu}$ = 1612 (s), 1411 (s), 1044 (s), 883 (m), 674 (w), 607 (w), 566 (w).

Synthesis of 2. A similar procedure for compound **1** was used for the isolation of **2**, only the quality of the MnCl₂·4H₂O changed to (0.10 g, 0.51 mmol). The black crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of ca. 5% (based on vanadium). Anal.Calcd (%) for **2**: C, 1.69; N, 4.61; Mn, 5.17; V, 43.12; P, 1.46; Found: C, 1.54; N, 4.72; Mn, 5.08; V, 43.36; P, 1.39. IR (KBr pellet) for **2**: $\tilde{\nu}$ = 1616 (s), 1403 (s), 1044 (s), 902 (m), 676 (w), 617 (w), 566 (m).

X-ray Crystallography

The measurement for compounds **1** and **2** was performed on a Bruker SMART CCD diffractometer. In all cases, the data was collected at 293 K, and graphite monochromated Mo-K α radiation (λ = 0.71073 Å) was used. These structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 software. In the refinement, the restraint command 'isor' was employed to restrain several O and Mn atoms so as to avoid the ADP and

Table 1 Crystal data and structure refinements for **1** – **2**.

Compound	1	2
Empirical formula	H ₃₇ Mn ₄ O ₆₁ PV ₁₈	C ₃ H ₅₄ Mn ₂ N ₇ O ₅₅ PV ₁₈
λ / Å	0.71073	0.71073
Mr	2180.95	2126.30
T / K	293(2)	293(2)
Crystal dimensions	0.26×0.12	0.26×0.10
/ mm	×0.08	×0.06
Crystal system	Tetragonal	Orthorhombic
Space group	<i>I</i> ₄₁ /acd	<i>P</i> 2 ₁ 2 ₁
<i>A</i> / Å	29.0398(13)	12.1286(19)
<i>B</i> / Å	29.0398(13)	20.336(3)
<i>C</i> / Å	24.4712(19)	21.324(3)
<i>V</i> / Å ³	20637(2)	5259.5(14)
<i>Z</i>	16	4
<i>D</i> _c / Mg m ⁻³	2.808	2.685
μ / mm ⁻¹	4.194	3.654
<i>F</i> (000)	16864	4160
θ range / °	1.40–25.08	1.38–25.99
Data / restraints	4594 / 36	10260 / 72
/ parameters	/ 403	/ 761
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0626	0.0544
<i>wR</i> ₂ (all data) ^a	0.2562	0.1564
Goodness-of-fit on <i>F</i> ²	0.983	1.058

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$$

NPD problems in the crystal data. Such refinement led to the restraint value of 36 for **1** and 72 for **2**. All H atoms on solvent water molecules were directly included into the final molecular formula. The hydrogen atoms attached to organic ligands in **2** were fixed in calculated positions. The crystal data and structure refinements of compounds **1** and **2** were summarized in Table 1. CCDC-1428572 for **1**, and CCDC-1421262 for **2** will supply further details of the crystal structure.

Conclusions

In conclusion, two purely inorganic 3D frameworks based on POV clusters were designed and synthesized, which enriched the class of the 3D POM chemistry. In these 3D frameworks, the V centers were all in the +IV oxidation state, resulting in an all reduced polyoxoanion, which was firstly used as the building block for constructing the 3D framework materials. The all reduced typical polyoxoanion in **1** with 15 negative charges was surrounded by 12 Mn²⁺ ions, which was rarely observed in the POM chemistry. The bond length alteration and structure distortion in **2** resulted in the chiral skeleton. The absolute chiral configuration was confirmed by the flack parameter of 0.02(3). Electrocatalytic study revealed that the anion cluster exhibited electrocatalytic activity for reduction of H₂O₂.

Acknowledgements

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Notes and references

- (a) B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature.*, 2008, **453**, 207; (b) J. Zhang, H. S. Chan and Z. Xie, *Angew. Chem. Int. Ed.*, 2008, **47**, 9447; (c) Y. P. Chen, Y. Liu, D. Liu, M. Bosch and H. C. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 2919; (d) T. Grancha, J. Ferrando-Soria, H. C. Zhou, J. Gascon, B. Seoane, J. Pasan, O. Fabelo, M. Julve and E. Pardo, *Angew. Chem. Int. Ed.*, 2015, **54**, 6521; (e) K. Lu, C. He and W. Lin, *J. Am. Chem. Soc.*, 2015, **137**, 7600; (f) Z. M. Zhang, T. Zhang, C. Wang, L. S. Long and W. Lin, *J. Am. Chem. Soc.*, 2015, **137**, 3197.
- (a) W. M. Xuan, C. F. Zhu, Y. Liu and Y. Cui, *Chem. Soc. Rev.*, 2012, **41**, 1677; (b) J. P. Zhang, P. Q. Liao, H. L. Zhou, R. B. Lin and X. M. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5789; (c) Q. L. Zhu and Q. Xu, *Chem. Soc. Rev.*, 2014, **43**, 5468; (d) R. Zhang, S. Ji, N. Wang, G. Zhang and J. R. Li, *Angew. Chem. Int. Ed.*, 2014, **53**, 9775; (e) J. P. Zhao, Q. Yang, Z. Y. Liu, R. Zhao, B. W. Hu, M. Du, Z. Chang and X. H. Bu, *Chem. Commun.*, 2012, **48**, 6568.
- (a) K. Suzuki, Y. Kikukawa, S. Uchida, H. Tokoro, K. Imoto, S. Ohkoshi and N. Mizuno, *Angew. Chem. Int. Ed.*, 2012, **51**, 1597; (b) S. T. Zheng, J. Zhang and G. Y. Yang, *Angew. Chem. Int. Ed.*, 2008, **47**, 3909; (c) X. Zhao, M. Wong, C. Mao, T. X. Trieu, J. Zhang, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2014, **136**, 12572.

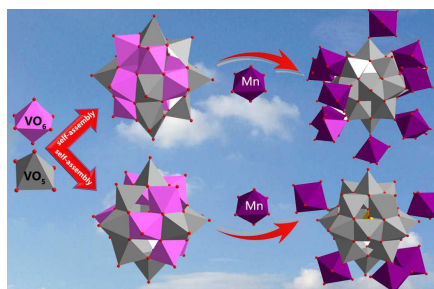
4. (a) D. Y. Du, J. S. Qin, S. L. Li, Z. M. Su and Y. Q. Lan, *Chem. Soc. Rev.*, 2014, **43**, 4615; (b) B. Nohra, H. E. Moll, L. M. R. Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O'Keefe, R. N. Biboum, J. Lemaire, B. Keita, L. Nadjo and A. Dolbecq, *J. Am. Chem. Soc.*, 2011, **133**, 13363; (c) C. Y. Sun, S. X. Liu, D. D. Liang, K. Z. Shao, Y. H. Ren and Z. M. Su, *J. Am. Chem. Soc.*, 2009, **131**, 1883; (d) J. Yu, Y. Cui, C. D. Wu, Y. Yang, B. Chen and G. Qian, *J. Am. Chem. Soc.*, 2015, **137**, 4026; (e) M. L. Wei, C. He, W. J. Hua, C. Y. Duan, S. H. Li and Q. J. Meng, *J. Am. Chem. Soc.*, 2006, **128**, 13318; (f) J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.*, 2011, **133**, 16839.
5. (a) C. C. Zhao, E. N. Glass, B. Chica, D. G. Musaev, J. M. Sumliner, R. B. Dyer, T. Q. Lian and C. L. Hill, *J. Am. Chem. Soc.*, 2014, **136**, 12085; (b) S. G. Mitchell, C. Streb, H. N. Miras, T. Boyd, D. L. Long and L. Cronin, *Nature Chem.*, 2010, **2**, 308; (c) W. B. Yang, C. Z. Lu, Q. Z. Zhang, S. M. Chen, X. P. Zhan and J. H. Liu, *Inorg. Chem.*, 2003, **42**, 7309; (d) X. B. Han, Z. M. Zhang, Z. S. Wang, H. Zhang, H. Duan and E. B. Wang, *Inorg. Chem. Commun.*, 2012, **18**, 47.
6. (a) D. L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105; (b) A. Proust, R. Thouvenot and P. Gouzerh, *Chem. Commun.*, 2008, **16**, 1837; (c) C. Streb, *Dalton Trans.*, 2012, **41**, 1651.
7. (a) P. Kögerler, B. Tsukerblat and A. Müller, *Dalton Trans.*, 2010, **39**, 21; (b) U. Kortz, A. Müller, J. V. Slageren, J. Schnack, N. S. Dalal and M. Dressel, *Coord. Chem. Rev.*, 2009, **253**, 2315; (c) B. Hasenknopf, *Front. Biosci.*, 2005, **10**, 275.
8. (a) L. Zhang and W. Schmitt, *J. Am. Chem. Soc.*, 2011, **133**, 11240; (b) J. Spandl, C. Daniel, I. Brüdgam and H. Hartl, *Angew. Chem. Int. Ed.*, 2003, **42**, 10.
9. (a) Y. Z. Gao, Y. N. Chi and C. W. Hu, *Polyhedron*, 2014, **83**, 242; (b) E. Antonova, C. Näther, P. Kögerler and W. Bensch, *Angew. Chem. Int. Ed.*, 2011, **50**, 764.
10. (a) H. X. Wan, C. L. Wang, Y. Zhang, H. Mia, S. Zhou and Y. Xu, *Inorg. Chem.*, 2014, **19**, 10498; (b) J. Zhou, J. W. Zhao, Q. Wei, J. Zhang and G. Y. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 5065; (c) G. J. Cao, S. T. Zheng, N. Zhao, J. K. Sun and G. Y. Yang, *Inorg. Chem.*, 2010, **49**, 10211.
11. (a) V. W. Day, W. G. Klemperer and O. M. Yaghi, *J. Am. Chem. Soc.*, 1989, **111**, 4518; (b) H. K. Chae, W. G. Klemperer and V. W. Day, *Inorg. Chem.*, 1989, **28**, 1423; (c) V. W. Day, W. G. Klemperer and D. J. Maltbie, *J. Am. Chem. Soc.*, 1987, **109**, 2991; (d) V. W. Day, W. G. Klemperer and O. M. Yaghi, *J. Am. Chem. Soc.*, 1989, **111**, 5959; (e) D. Hou, K. S. Hagen and C. L. Hill, *J. Am. Chem. Soc.*, 1992, **114**; (f) A. Müller, E. Krickemeyer, M. Penk, E. Rohlfing, A. Armatage and H. Bögge, *Angew. Chem. Int. Ed.*, 1991, **30**, 1674.
12. (a) Y. Hayashi, K. Fukuyama, T. Takatera and A. Uehara, *Chem. Lett.*, 2000, 770; (b) G. K. Johnson and E. O. Schlemper, *J. Am. Chem. Soc.*, 1978, 3645; (c) A. Müller, M. Penk, E. Krickemeyer, H. Bögge and H. J. Wallberg, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1719; (d) A. Müller, J. Döring, M. I. Khan and V. Wittneben, *Angew. Chem. Int. Ed.*, 1999, **38**, 103; (e) C. L. Pan, J. Q. Xu, G. H. Li, X. B. Cui, L. Ye and G. D. Yan, *Dalton Trans.*, 2003, 517.
13. (a) A. Müller and J. Döring, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1721; (b) D. Gatteschi, L. Pardi, A. L. Barra, A. Müller and J. Döring, *Nature*, 1991, **354**, 463.
14. (a) A. Wutkowski, C. Näther, P. Kögerler and W. Bensch, *Inorg. Chem.*, 2013, **52**, 3280; (b) U. Lee, H. C. Joo, K. M. Park, S. S. Mal, U. Kortz, B. Keita and L. Nadjo, *Angew. Chem., Int. Ed.*, 2008, **47**, 793; (c) D. Pitzschke, J. Wang, R. D. Hoffmann, R. Pöttgen and W. Bensch, *Angew. Chem. Int. Ed.*, 2006, **45**, 1305; (d) L. Zhang and W. Schmitt, *J. Am. Chem. Soc.*, 2011, **133**, 11240; (e) L. Krivosudský, P. Schwendt, R. Gyepes and J. Filo, *Inorg. Chem. Commun.*, 2014, **49**, 48; (f) P. Huang, C. Qin, X. L. Wang, C. Y. Sun, G. S. Yang, K. Z. Shao, Y. Q. Jiao, K. Zhou and Z. M. Su, *Chem. Commun.*, 2012, **48**, 103; (g) T. Yamase, M. Suzuki and K. Ohtaka, *J. Chem. Soc., Dalton Trans.*, 1997, **14**, 2463.
15. (a) A. Wutkowski, C. Näther, P. Kögerler and W. Bensch, *Inorg. Chem.*, 2013, **52**, 3280; (b) E. Antonova, C. Näther, P. Kögerler and W. Bensch, *Angew. Chem. Int. Ed.*, 2011, **50**, 764; (c) J. Zhou, J. Zhang, W. H. Fang and G. Y. Yang, *Chem. Eur. J.*, 2010, **16**, 13253; (d) E. Antonova, C. Näther and W. Bensch, *Dalton Trans.*, 2012, **41**, 1338; (e) Y. Qi, Y. Li, C. Qin, E. Wang, H. Jin, D. Xiao, X. Wang and S. Chang, *Inorg. Chem.*, 2007, **46**, 3217.
16. (a) D. Liu, Y. Lu, H. Q. Tan, W. L. Chen, Z. M. Zhang, Y. G. Li and E. B. Wang, *Chem. Commun.*, 2013, **49**, 3673; (b) S. G. Mitchell, T. Boyd, H. N. Miras, D. L. Long and L. Cronin, *Inorg. Chem.*, 2011, **50**, 136.
17. (a) L. Luo, Y. H. Zeng, L. Li, Z. X. Luo, T. I. Smirnova and P. A. Muggard, *Inorg. Chem.*, 2015, **54**, 7388; (b) Luo, L. and P. A. Muggard, *Cryst. Growth. Des.*, 2013, **13**, 5282; (c) Q. Wu, W. Hao, X. Feng, Y. Wang, Y. Li, E. Wang, X. Zhu and X. Pan, *Inorg. Chem. Commun.*, 2012, **22**, 137; (d) G. J. Cao, S. T. Zheng, W. H. Fang and G. Y. Yang, *Inorg. Chem. Commun.*, 2010, **13**, 834; (e) J. Wang, C. Näther, M. Speldrich, P. Kögerler and W. Bensch, *CrysEngComm*, 2013, **15**, 10238.
18. (a) W. B. Yang, C. Z. Lu, Q. Z. Zhang, S. M. Chen, X. P. Zhan and J. H. Liu, *Inorg. Chem.*, 2003, **42**, 7309; (b) C. L. Pan, J. Q. Xu, G. H. Li, X. B. Cui, L. Ye and G. D. Yan, *Dalton Trans.*, 2003, 517; (c) T. Yamase, K. Ohtaka and M. Suzuki, *J. Chem. Soc., Dalton Trans.*, 1996, 283; (d) M. I. Khan, E. Yohannes and D. Powell, *Chem. Commun.*, 1999, 23.
19. (a) A. X. Tian, J. Ying and J. Peng, *Inorg. Chem.*, 2008, **47**, 3274; (b) L. N. Xiao, L. M. Wang, X. N. Shan, H. Y. Guo, L. W. Fu, Y. Y. Hu, X. B. Cui, K. C. Li and J. Q. Xu, *CrysEngComm*, 2015, **17**, 1336; (c) M. Mirzaei, H. Eshtiagh-Hosseini, N. Lotfian, A. Salimi, A. Bauzá, R. Deun, R. Decadt, M. Barceló-Oliver and A. Frontera, *Dalton Trans.*, 2014, **43**, 1906; (d) J. Q. Sha, C. Wang, J. Peng, J. Chen, A. X. Tian and P. P. Zhang, *Inorg. Chem. Commun.*, 2007, **10**, 1321; (e) T. Soumahoro, E. Burkholder, W. Ouellette and J. Zubieta, *Inorg. Chin. Acta.*, 2005, **358**, 606; (f) H. X. Yang, J. C. Meng, X. F. Sun, L. Z. Chen and D. Yang, *Inorg. Chem. Commun.*, 2014, **39**, 43.
20. (a) Z. M. Zhang, J. Liu, E. B. Wang, C. Qin, Y. G. Li, Y. F. Qi and X. L. Wang, *Dalton Trans.*, 2008, 463; (b) Y. Y. Li, J. W. Zhao, Q. Wei, B. F. Yang and G. Y. Yang, *J. Solid. State. Chem.*, 2014, **210**, 166; (c) J. W. Zhao, B. Li, S. T. Zheng and G. Y. Yang, *Cryst. Growth. Des.*, 2007, **7**, 2659; (d) Y. Zhang, J. Q. Shen, L. H. Zheng, Z. M. Zhang, Y. X. Li and E. B. Wang, *Cryst. Growth. Des.*, 2014, **14**, 110.

Graphical abstract

**Design and Synthesis of the Purely Inorganic 3D Frameworks
Composed of Reduced Vanadium Clusters and Manganese Linkers**

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Two 3D purely inorganic frameworks $[\text{Mn}_2(\text{H}_2\text{O})_7\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{11-}$ (**1**) and $[\text{Mn}_4(\text{H}_2\text{O})_{11}\text{V}^{\text{IV}}_{18}\text{O}_{42}(\text{PO}_4)]^{7-}$ (**2**), based on the all reduced polyoxovanadates were firstly designed and synthesized.