

## ***Supporting Information***

### **A water-soluble mixed-valent {Mn<sub>11</sub>} cluster embedded heteropolyoxoniobate with magnetic property**

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## Section S1 Materials and Methods

$\text{K}_7\text{H}[\text{Nb}_6\text{O}_{19}] \cdot 13\text{H}_2\text{O}$  precursor was synthesized according to the literature method and verified by IR spectroscopy<sup>1</sup>. Other reactants and solvents were purchased from commercial sources and used for the reactions without further purification. PXRD patterns were obtained by using an Ultima IV diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the range of 5-45°. UV-vis adsorption spectra were collected by using a PerkinElmer Lambda 35 spectrophotometer to monitor the release process. IR spectra were recorded on an Opus Vertex 70 FT-IR infrared spectrophotometer in the range of 400-4000  $\text{cm}^{-1}$ . Thermogravimetric analysis was conducted on a Mettler Toledo TGA/SDTA 851<sup>e</sup> analyzer in an argon atmosphere with a heating rate of 10 °C/min at 30-800 °C. ICP analysis was conducted on an Ultima2 spectrometer. Simulated XRD data was simulated by the Mercury Software with the step of 0.02° from 5° to 50° ( $\lambda = 1.54056 \text{ \AA}$ ). Energy dispersive spectroscopy (EDS) analyses were performed using a Quanta 250 FEI type desktop scanning electron microscope (SEM; Japan, Haoshi). Variable temperature susceptibility measurements were carried out in the temperature range of 2-300 K at a magnetic field of 0.1 T on polycrystalline samples with a Quantum Design PPMS-9T magnetometer. The experimental susceptibilities were corrected for the Pascal's constants. ICP analyses were conducted on an Ultima2 spectrometer. The crystal samples were vacuum dried at 80 °C for 24 h before ICP analysis. According to the TG curve, the loss of 1.80% between 30 and 80 °C corresponds to the loss of about 15 water molecules per formula (calc. 1.84%). Therefore, the formula for ICP analysis is  $\text{K}_{25}\text{H}_{43}\{(\text{Te}_4\text{Nb}_9\text{O}_{33})_3(\text{Nb}_6\text{O}_{19})_5(\text{Te}^{\text{VI}}\text{Nb}_5\text{O}_{14})[(\text{Te}^{\text{IV}}\text{O}_3)_2(\text{Mn}^{\text{II}}_7\text{Mn}^{\text{III}}_4\text{O}_{19})]\}\cdot 82\text{H}_2\text{O}$  ( $\text{H}_{207}\text{K}_{25}\text{Mn}_{11}\text{Nb}_{62}\text{Te}_{15}\text{O}_{315}$ ).

### Preparations of $\text{K}_{25}\text{H}_{43}\{(\text{Te}_4\text{Nb}_9\text{O}_{33})_3(\text{Nb}_6\text{O}_{19})_5(\text{Te}^{\text{VI}}\text{Nb}_5\text{O}_{14})[(\text{Te}^{\text{IV}}\text{O}_3)_2(\text{Mn}^{\text{II}}_7\text{Mn}^{\text{III}}_4\text{O}_{19})]\}\cdot 97\text{H}_2\text{O}$ (1)

A mixture of  $\text{K}_7\text{H}\text{Nb}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$  (0.305 g, 0.22 mmol),  $\text{Mn}(\text{acac})_3$  (0.055 g, 0.16 mmol),  $\text{K}_2\text{CO}_3$  (0.105 g, 0.76 mmol),  $\text{K}_2\text{B}_4\text{O}_7$  (0.053 g, 0.23 mmol),  $\text{KCl}$  (0.104 g, 1.78 mmol),  $\text{TeO}_2$  (0.054 g, 0.34 mmol) and 1,10-phenanthroline (0.02 g, 0.11 mmol) was added to 8 mL deionized water. After stirring for 1 hour, the resulting mixture was heated at 90 °C for 3 days. After the resulting mixture slowly cooled down to room temperature, brown block crystals were obtained. The pH values before and after the reaction are 9.8 and 9.3, respectively. Yield: about 20 mg (6.6% based on  $\text{K}_7\text{H}\text{Nb}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$ ). The calculation of chemical stoichiometry is based on the entire reaction

material molecule rather than a single atom. For example, 0.22 mmol  $\text{K}_7\text{HNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$  represents the stoichiometry of  $\text{K}_7\text{HNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$  rather than Nb atoms. ICP and elemental analyses (based on a dried sample) calcd (found %) for  $\text{H}_{197}\text{K}_{25}\text{Mn}_{11}\text{Nb}_{62}\text{Te}_{15}\text{O}_{310}$ : K, 6.74 (6.96); Mn, 4.17 (4.04); Te, 13.20 (13.68); Nb, 39.71 (41.20) (Table S5). IR (KBr,  $\text{cm}^{-1}$ ): 3226(m), 1633(s), 847(s), 647(s), 513(w) (Fig. S14).

### Synthesis Discussion

During the synthesis process, there are some factors that affect the synthesis of compound **1**: (1) The  $\text{MnCl}_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2$  salts were used to synthesize compound **1** instead of acetylacetonate Mn salts. Unfortunately, the introduction of these acidic salts into the system caused their immediate hydrolysis, resulting in the formation of a large number of flocculating materials or gels. This could be due to the slow release of  $\text{Mn}^{2+}$  cations by the acetylacetonate salt itself, which synergistically inhibits the hydrolysis of  $\text{Mn}^{2+}$  cations. (2) We have attempted to synthesize isostructural compounds of **1** using other transition metal acetylacetonate salts  $\{\text{Ti}(\text{acac})_3, \text{Fe}(\text{acac})_3, \text{Co}(\text{acac})_3, \text{Ni}(\text{acac})_2, \text{Cu}(\text{acac})_2\}$ , but no analogous products were obtained. (3) 1,10-phenanthroline can act as an organic sustained release agent, which is favorable for inhibiting the hydrolysis of highly charged ions ( $\text{Mn}^{3+}$ ), and  $\text{K}_2\text{B}_4\text{O}_7$  can act as mineralizer, which is in favor for the crystallization of compound **1**. (4) The temperature of the initial hydrothermal reactions also plays an important role in the formation of **1**. If the reaction temperature is higher than or lower than 90 °C, the yield would decrease dramatically and only amorphous phases would be obtained. (5) The reason for the lower yield may be due to Mn ions form amorphous precipitates (Mn-oxyhydroxide) under alkaline conditions or the stoichiometric ratio of the raw materials may not be the most suitable.

### Single-crystal structure analysis

Single crystal X-ray diffraction data for **1** was collected on a Bruker APEX II diffractometer at 175 K, equipped with a fine focus, and a 2.0 kW sealed tube X-ray source (MoK radiation,  $\lambda = 0.71073 \text{ \AA}$ ) operating at 50 kV and 30 mA. The SADABS programme was used for absorption correction. The structure of **1** was solved through direct methods and refined by full-matrix least-squares refinements based on  $F^2$  using the SHELX-2014 program package. All non-H atoms were located by successive difference Fourier syntheses and refined anisotropically. The contribution of disordered solvent molecules to the overall intensity data of structures was treated using the

SQUEEZE method in PLATON, the number of electrons in the Void about 520 e<sup>-</sup>, approximately 52 solvent water molecules. The final formula of **1** was determined by combining single crystal X-ray diffraction with the element analysis, thermogravimetric analysis, ESI-MS and charge balance, where elemental analysis verifies the number of metal atoms determined by single crystal diffraction, thermogravimetric analysis calculates the amount of crystal water (the weight loss before 450°C can be attributed to the removal of crystal water, with 97 H<sub>2</sub>O for **1**) (Fig. S11), and the charge balance calculates the number of H atoms to be 43, that cannot be identified by single crystal diffraction data. Through single-crystal X-ray diffraction analysis, we can only determine that each molecular formula of **1** contains 72 lattice water molecules. However, thermogravimetric analysis indicates that each molecular formula actually contains approximately 97 lattice water molecules. This suggests that there are undetermined disordered water molecules in the structure of **1**, which is common in giant polyoxometalates containing dozens or hundreds of heavy metal ions. [2-4] Therefore, the existence of the small fraction of undetermined disordered water molecules results in relatively high residual electron densities. Crystallographic data and structure refinements for **1** are summarized in Table S1. CCDC 2344496 contains supplementary crystallographic data for **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### **Electrospray-ionisation mass spectrometry (ESI-MS)**

All MS data were collected using a Qtrap, time-of-flight MS (Maxis Impact) instrument supplied by Bruker Daltonics Ltd. A Bruker Ltd cryospray source was used to collect data under the conditions described below. The detector was a time-of-flight, micro-channel plate detector and all data was processed using the BrukerDaltonics Data Analysis 4.1 software, while simulated isotope patterns were investigated using Bruker Isotope Pattern software and Molecular Weight Calculator 6.45. All peak assignments were made by comparing of the experimentally determined isotopic patterns for each peak with the simulated isotopic patterns. The sample solutions were prepared by dissolving the compounds in pure water to a concentration of 3 mg/mL.

### **Magnetic Property**

$\chi_m T$  is given by the following equation:

$$\chi_m^T = \sum_i \frac{1}{8} g^2 J(J+1) n_i = \frac{1}{8} \times 2^2 \times \frac{5}{2} \times \left(\frac{5}{2} + 1\right) \times 7 + \frac{1}{8} \times 2^2 \times 2 \times (2+1) \times 4 = 30.63 + 12 = 42.625 \text{ cm}^3 \text{ K mol}^{-1}$$

$M$  is given by the following equation:

$$M = \sum_i n_i g J N \beta = 7 \times 2 \times \frac{5}{2} + 4 \times 2 \times 2 = 51 N \beta$$

$g$ : Landé-factor;  $J$ : angular-momentum quantum number;  $n$ : number of ions.

The derivation of the above formulae can be found in O. Kahn's "Molecular Magnetism".<sup>5</sup>

## Section S2 Additional Tables

**Table S1** X-ray crystallographic data for **1**

<b>1</b>	
Empirical formula	H <sub>237</sub> K <sub>25</sub> Mn <sub>11</sub> Nb <sub>62</sub> Te <sub>15</sub> O <sub>330</sub>
Formula weight	14775.14
Crystal system	Triclinic
Space group	$P\bar{1}$
$a$ (Å)	22.620(3)
$b$ (Å)	24.412(3)
$c$ (Å)	38.496(5)
$\alpha$ (°)	98.666(2)
$\beta$ (°)	100.990(2)
$\gamma$ (°)	112.911(2)
$V$ (Å <sup>3</sup> )	18617(4)
$Z$	2
$F(000)$	13898
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	2.636
Temperature (K)	175(2)
Refl. Collected	174520
Independent refl.	65362
Data / restraints / parameters	65362 / 222 / 3598
Completeness to theta = 25.045	99.2%
GOF on F <sup>2</sup>	1.033
Final R indices (I= 2 $\sigma$ (I))	$R_1 = 0.0894$ , $wR_2 = 0.2195$
R indices (all data)	$R_1 = 0.1461$ , $wR_2 = 0.2696$

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ ,  $P = (F_o^2 + 2F_c^2)/3$ ,

**Table S2** BVS calculations of the Nb atoms.

<i>Atoms</i>	<i>Calcd</i>	<i>Oxidation state</i>	<i>Atoms</i>	<i>Calcd</i>	<i>Oxidation state</i>
Nb1	4.71	$Nb^{5+}$	Nb2	4.75	$Nb^{5+}$
Nb3	4.70	$Nb^{5+}$	Nb4	4.99	$Nb^{5+}$
Nb5	5.12	$Nb^{5+}$	Nb6	4.77	$Nb^{5+}$
Nb7	4.75	$Nb^{5+}$	Nb8	5.05	$Nb^{5+}$
Nb9	4.80	$Nb^{5+}$	Nb10	5.01	$Nb^{5+}$
Nb11	4.96	$Nb^{5+}$	Nb12	5.03	$Nb^{5+}$
Nb13	4.81	$Nb^{5+}$	Nb14	5.06	$Nb^{5+}$
Nb15	4.73	$Nb^{5+}$	Nb16	5.03	$Nb^{5+}$
Nb17	5.07	$Nb^{5+}$	Nb18	5.13	$Nb^{5+}$
Nb19	4.94	$Nb^{5+}$	Nb20	5.11	$Nb^{5+}$
Nb21	4.98	$Nb^{5+}$	Nb22	4.79	$Nb^{5+}$
Nb23	4.99	$Nb^{5+}$	Nb24	5.25	$Nb^{5+}$
Nb25	4.66	$Nb^{5+}$	Nb26	5.09	$Nb^{5+}$
Nb27	4.87	$Nb^{5+}$	Nb28	4.87	$Nb^{5+}$
Nb29	4.98	$Nb^{5+}$	Nb30	4.69	$Nb^{5+}$
Nb31	5.09	$Nb^{5+}$	Nb32	5.27	$Nb^{5+}$
Nb33	5.11	$Nb^{5+}$	Nb34	4.80	$Nb^{5+}$
Nb35	4.82	$Nb^{5+}$	Nb36	5.30	$Nb^{5+}$
Nb37	5.18	$Nb^{5+}$	Nb38	4.66	$Nb^{5+}$
Nb39	4.86	$Nb^{5+}$	Nb40	4.92	$Nb^{5+}$
Nb41	4.73	$Nb^{5+}$	Nb42	5.25	$Nb^{5+}$

Nb43	4.92	$Nb^{5+}$	Nb44	5.16	$Nb^{5+}$
Nb45	4.91	$Nb^{5+}$	Nb46	5.36	$Nb^{5+}$
Nb47	4.94	$Nb^{5+}$	Nb48	4.84	$Nb^{5+}$
Nb49	5.31	$Nb^{5+}$	Nb50	4.58	$Nb^{5+}$
Nb51	5.00	$Nb^{5+}$	Nb52	5.10	$Nb^{5+}$
Nb53	4.75	$Nb^{5+}$	Nb54	4.88	$Nb^{5+}$
Nb55	5.02	$Nb^{5+}$	Nb56	5.04	$Nb^{5+}$
Nb57	5.08	$Nb^{5+}$	Nb58	4.99	$Nb^{5+}$
Nb59	4.91	$Nb^{5+}$	Nb60	4.76	$Nb^{5+}$
Nb61	5.16	$Nb^{5+}$	Nb62	4.82	$Nb^{5+}$

**Table S3** BVS calculations of the Te atoms.

<i>Atoms</i>	<i>Calcd</i>	<i>Oxidation state</i>	<i>Atoms</i>	<i>Calcd</i>	<i>Oxidation state</i>
Te1	3.72	$Te^{4+}$	Te2	3.84	$Te^{4+}$
Te3	3.60	$Te^{4+}$	Te4	3.87	$Te^{4+}$
Te5	4.03	$Te^{4+}$	Te6	3.74	$Te^{4+}$
Te7	3.91	$Te^{4+}$	Te8	3.56	$Te^{4+}$
Te9	3.62	$Te^{4+}$	Te10	4.02	$Te^{4+}$
Te11	3.80	$Te^{4+}$	Te12	3.71	$Te^{4+}$
Te13	6.38	$Te^{6+}$	Te14	4.59	$Te^{4+}$
Te15	4.04	$Te^{4+}$			



**Table S4** BVS calculations of the Mn atoms.

<i>Atoms</i>	<i>Calcd</i>	<i>Oxidation state</i>	<i>Atoms</i>	<i>Calcd</i>	<i>Oxidation state</i>
Mn1	3.32	$Mn^{3+}$	Mn2	3.48	$Mn^{3+}$
Mn3	2.20	$Mn^{2+}$	Mn4	3.34	$Mn^{3+}$
Mn5	1.98	$Mn^{2+}$	Mn6	1.80	$Mn^{2+}$
Mn7	2.04	$Mn^{2+}$	Mn8	2.36	$Mn^{2+}$
Mn9	1.92	$Mn^{2+}$	Mn10	2.45	$Mn^{2+}$
Mn11	3.34	$Mn^{3+}$			

**Table S5** Elemental analysis data for **1**

<i>Sample</i>		<i>K</i>	<i>Mn</i>	<i>Nb</i>	<i>Te</i>
1	Calcd. (%)	6.74	4.17	39.71	13.20
	Found. (%)	6.96	4.04	41.20	13.68

**Table S6** The m/z assignment of **1**

	<i>m/z(obs.)</i>	<i>Assignment</i>
5-	2566.54	$H_xK_y(Te_4Nb_9O_{33})_3(TeO_3)_2(TeO_6)(Nb_6O_{19})_5(Nb_5O_8)(Mn^{II}_7Mn^{III}_4O_{19})(H_2O)_z$
6-	2134.45	$H_xK_y(Te_4Nb_9O_{33})_3(TeO_3)_2(TeO_6)(Nb_6O_{19})_5(Nb_5O_8)(Mn^{II}_7Mn^{III}_4O_{19})(H_2O)_z$
7-	1821.54	$H_xK_y(Te_4Nb_9O_{33})_3(TeO_3)_2(TeO_6)(Nb_6O_{19})_5(Nb_5O_8)(Mn^{II}_7Mn^{III}_4O_{19})(H_2O)_z$
8-	1589.96	$H_xK_y(Te_4Nb_9O_{33})_3(TeO_3)_2(TeO_6)(Nb_6O_{19})_5(Nb_5O_8)(Mn^{II}_7Mn^{III}_4O_{19})(H_2O)_z$

As a multitude of charged states resulting from the variable number of protons, potassium ions and water molecules, the m/z assignment of compound **1** should contain an 'x, y, z' somewhere

in the formula. Based on the molecular formula and m/z value of compound **1**, the combinations of x, y, and z can be listed. {[Mr(H<sub>2</sub>O)=18, Mr(K)=39, Mr(H)=1], ensure that the error of m/z value is less than 1 }

5-			6-			7-			8-		
(H <sub>2</sub> O) <sub>z</sub>	K <sub>y</sub>	H <sub>x</sub>	(H <sub>2</sub> O) <sub>z</sub>	K <sub>y</sub>	H <sub>x</sub>	(H <sub>2</sub> O) <sub>z</sub>	K <sub>y</sub>	H <sub>x</sub>	(H <sub>2</sub> O) <sub>z</sub>	K <sub>y</sub>	H <sub>x</sub>
z=3	y=19	x=28	z=4	y=18	x=28	z=3	y=17	x=28	z=3	y=16	x=28
z=4	y=19	x=10	z=5	y=18	x=10	z=4	y=17	x=10	z=4	y=16	x=10
z=5	y=18	x=31	z=6	y=17	x=31	z=5	y=16	x=31	z=5	y=15	x=31
z=6	y=18	x=13	z=7	y=17	x=13	z=6	y=16	x=13	z=6	y=15	x=13
z=7	y=17	x=34	z=8	y=16	x=34	z=7	y=15	x=34	z=7	y=14	x=34
z=8	y=17	x=16	z=9	y=16	x=16	z=8	y=15	x=16	z=8	y=14	x=16
z=9	y=16	x=37	z=10	y=15	x=37	z=9	y=14	x=37	z=9	y=13	x=37
z=10	y=16	x=19	z=11	y=15	x=19	z=10	y=14	x=19	z=10	y=13	x=19
z=11	y=15	x=40	z=12	y=14	x=40	z=11	y=13	x=40	z=11	y=12	x=40
z=12	y=15	x=22	z=13	y=14	x=22	z=12	y=13	x=22	z=12	y=12	x=22
z=13	y=14	x=43	z=14	y=13	x=43	z=13	y=12	x=43	z=13	y=11	x=43
z=14	y=14	x=25	z=15	y=13	x=25	z=14	y=12	x=25	z=14	y=11	x=25
z=15	y=14	x=7	z=16	y=13	x=7	z=15	y=12	x=7	z=15	y=11	x=7
z=16	y=13	x=28	z=17	y=12	x=28	z=16	y=11	x=28	z=16	y=10	x=28
z=17	y=13	x=10	z=18	y=12	x=10	z=17	y=11	x=10	z=17	y=10	x=10
z=18	y=12	x=31	z=19	y=11	x=31	z=18	y=10	x=31	z=18	y=9	x=31
z=19	y=12	x=13	z=20	y=11	x=13	z=19	y=10	x=13	z=19	y=9	x=13
z=20	y=11	x=34	z=21	y=10	x=34	z=20	y=9	x=34	z=20	y=8	x=34
z=21	y=11	x=16	z=22	y=10	x=16	z=21	y=9	x=16	z=21	y=8	x=16
z=22	y=10	x=37	z=23	y=9	x=37	z=22	y=8	x=37	z=22	y=7	x=37

z=23	y=10	x=19	z=24	y=9	x=19	z=23	y=8	x=19	z=23	y=7	x=19
z=24	y=9	x=40	z=25	y=8	x=40	z=24	y=7	x=40	z=24	y=6	x=40
z=25	y=9	x=22	z=26	y=8	x=22	z=25	y=7	x=22	z=25	y=6	x=22
z=26	y=8	x=43	z=27	y=7	x=43	z=26	y=6	x=43	z=26	y=5	x=43
z=27	y=8	x=25	z=28	y=7	x=25	z=27	y=6	x=25	z=27	y=5	x=25

### Section S3 Additional Figures



Fig. S1 The crystal morphology of compound **1** under an optical microscope.

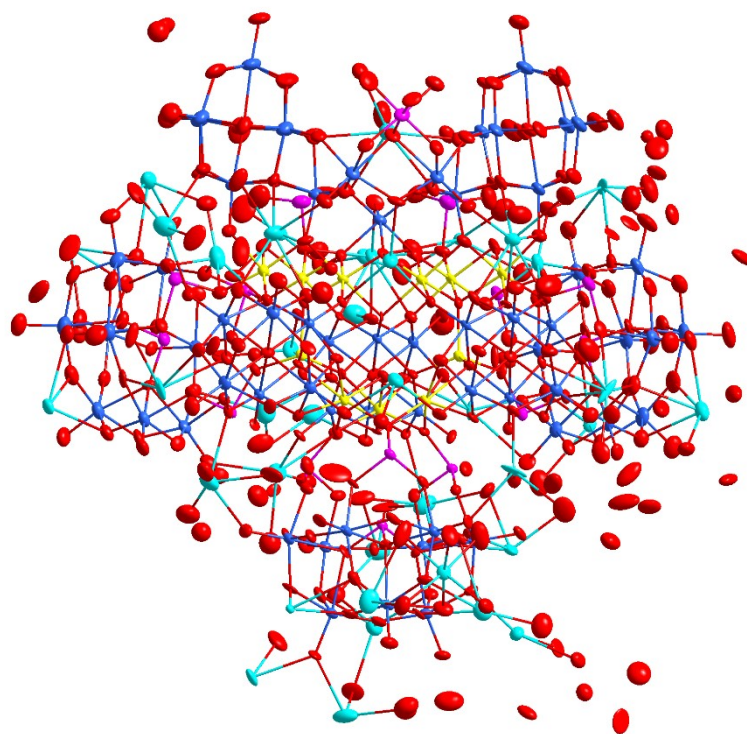


Fig. S2 The ellipsoid diagram of compound **1**.

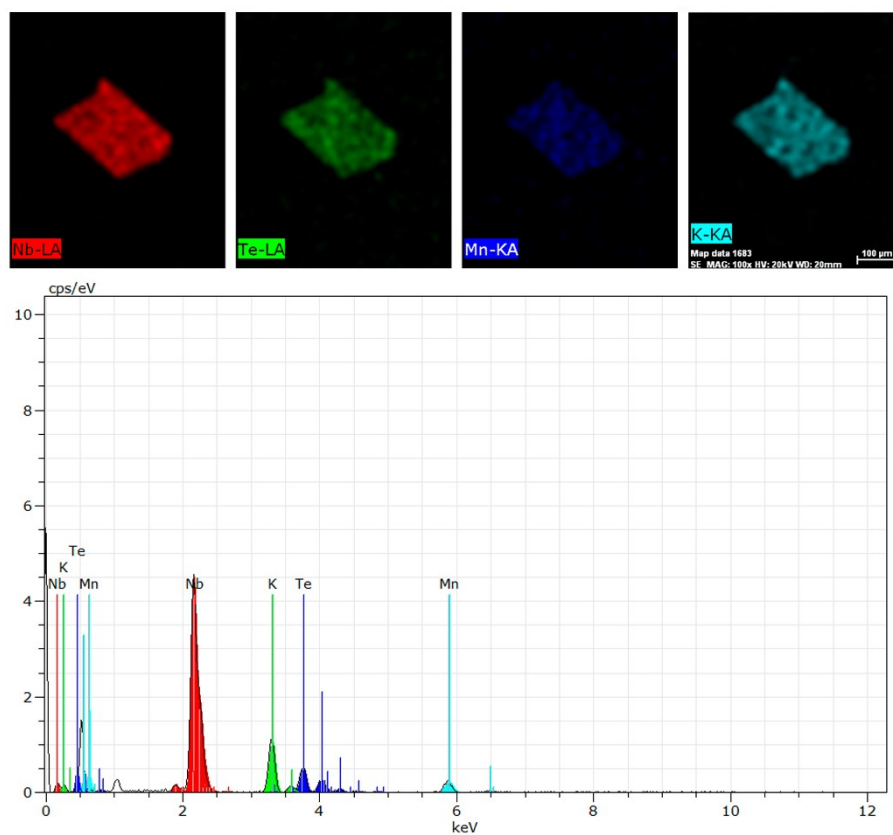


Fig. S3 The EDS spectra of **1**.

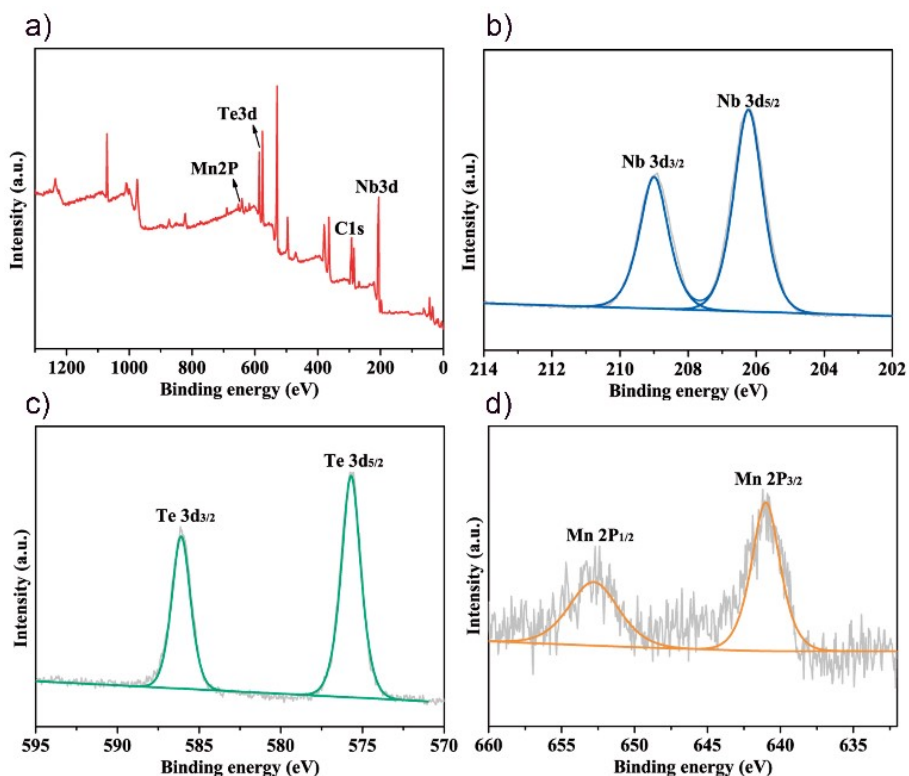


Fig. S4 The XPS spectra of **1**

The XPS measurement was performed to verify the valence state of Nb, Te and Mn ions in Fig S3. As shown in the Fig S4 b-d, the main peaks at the binding energy about at  $\sim 206.2$  eV and  $\sim 208.9$  eV were the two characteristic peaks of Nb  $3d_{5/2}$  and Nb  $3d_{3/2}$  signals, respectively, which corresponded to the surface Nb<sup>5+</sup> species. The main peaks at the binding energy about at  $\sim 575.7$  eV and  $\sim 586.1$  eV were the two characteristic peaks of Te  $3d_{5/2}$  and Te  $3d_{3/2}$  signals, respectively, which corresponded to the surface Te<sup>6+</sup> and Te<sup>4+</sup> species. The main peaks at the binding energy about at  $\sim 641.2$  eV and  $\sim 652.8$  eV were the two characteristic peaks of Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$  signals, respectively, which corresponded to the surface Mn<sup>3+</sup> and Mn<sup>2+</sup> species.

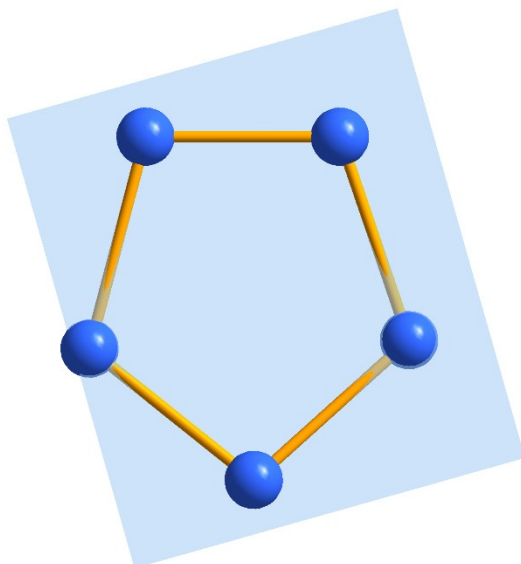


Fig. S5 The five Nb atoms in the  $\{Nb_5\}$  cluster in one plane

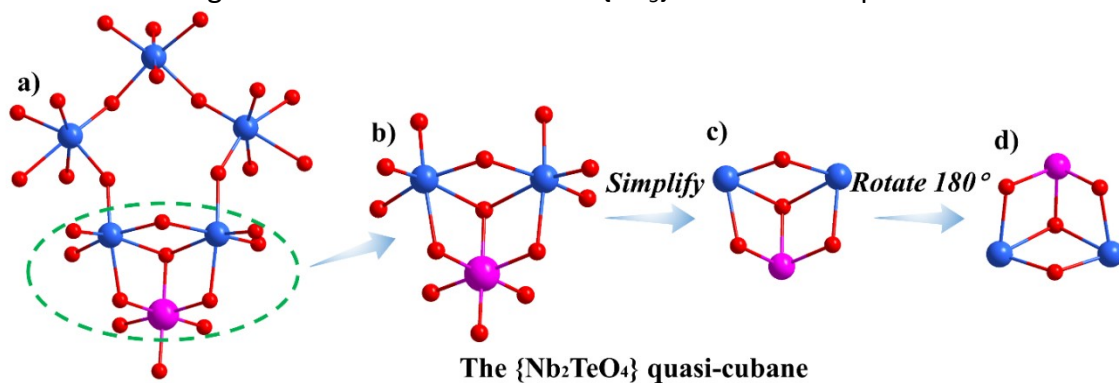


Fig. S6 (a) Ball-stick representation of the  $\{Te^VI Nb_5\}$ ; (b, c, d) The structural illustration of the quasi-cubane  $\{Nb_2TeO_4\}$  cluster.

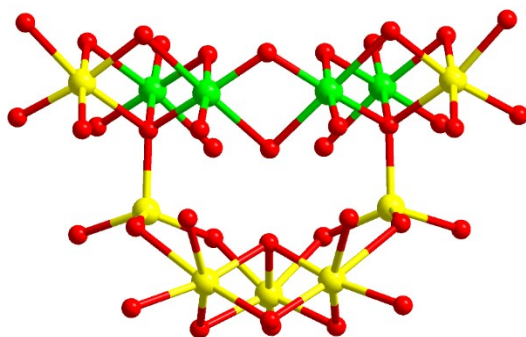


Fig. S7 The positions of  $Mn^{3+}$  ions in  $\{Mn_{11}\}$  cluster; color code:  $Mn^{3+}$ , green;  $Mn^{2+}$ , yellow

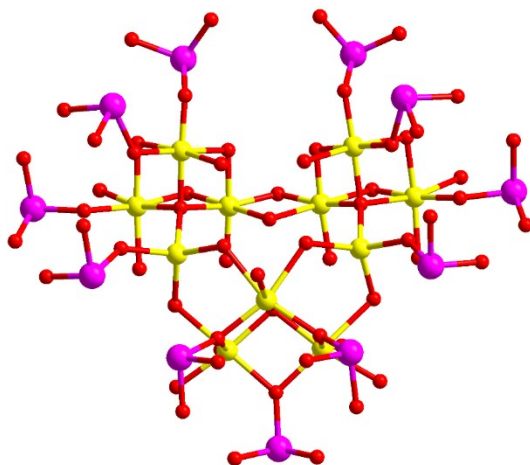


Fig. S8 Ball-stick representation of 22-nuclearity 3d-5p  $\{Mn_{11}Te_{11}O_{61}\}$  cluster.

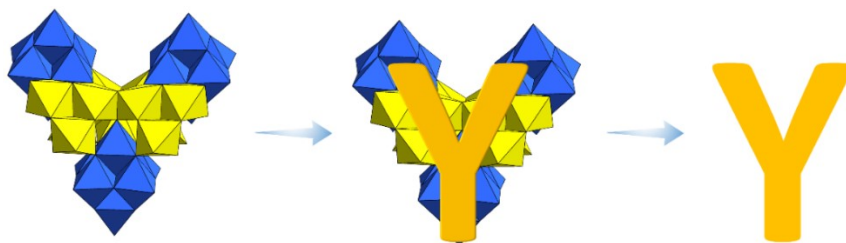


Fig. S9 The "Y"-shaped  $\{Mn_{11}(Nb_6)_3\}$  cluster. Color code: Nb, light blue; Mn, yellow.

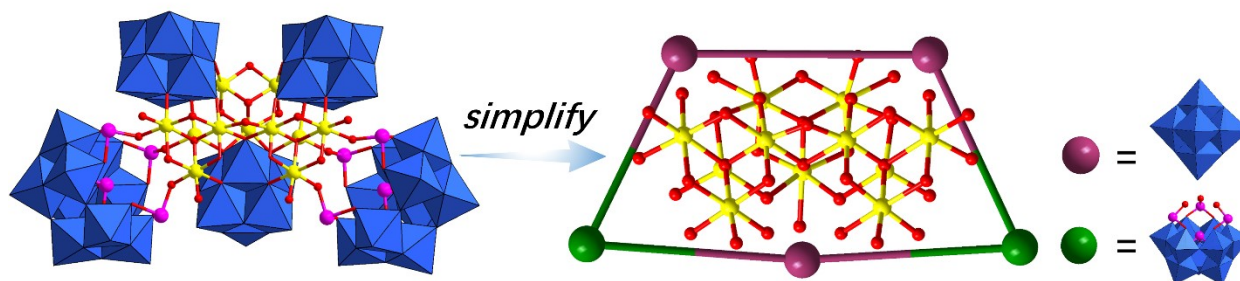


Fig. S10 The slightly twisted pentagon wrapped around the  $\{Mn_{11}\}$  cluster. Color code: Nb, light blue; Mn, yellow.



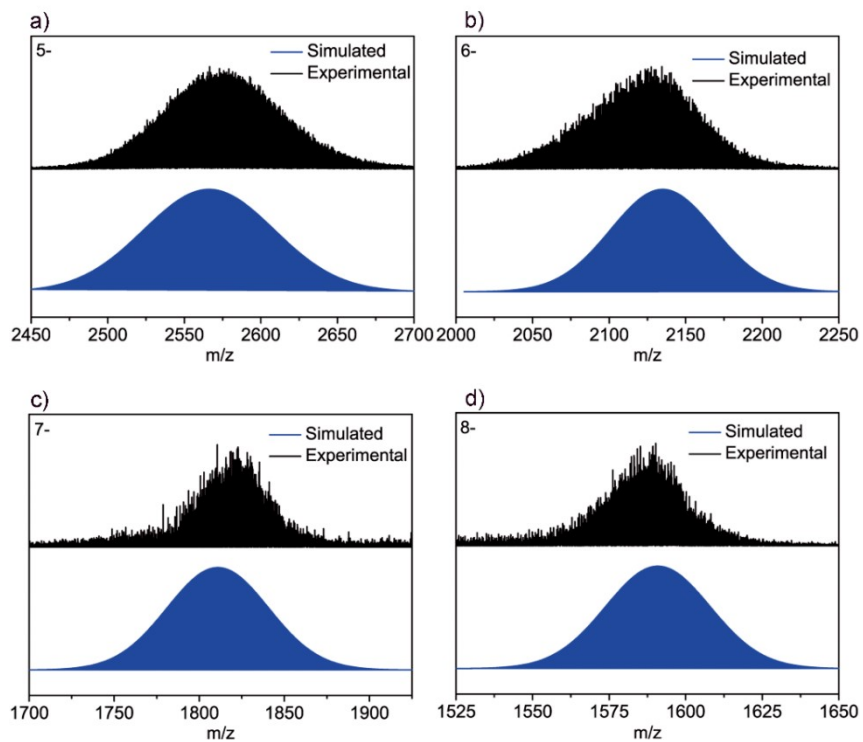


Fig. S11 Experimental (upper, black) and simulative (under, blue) peaks of the ESI-MS spectra for **1**.

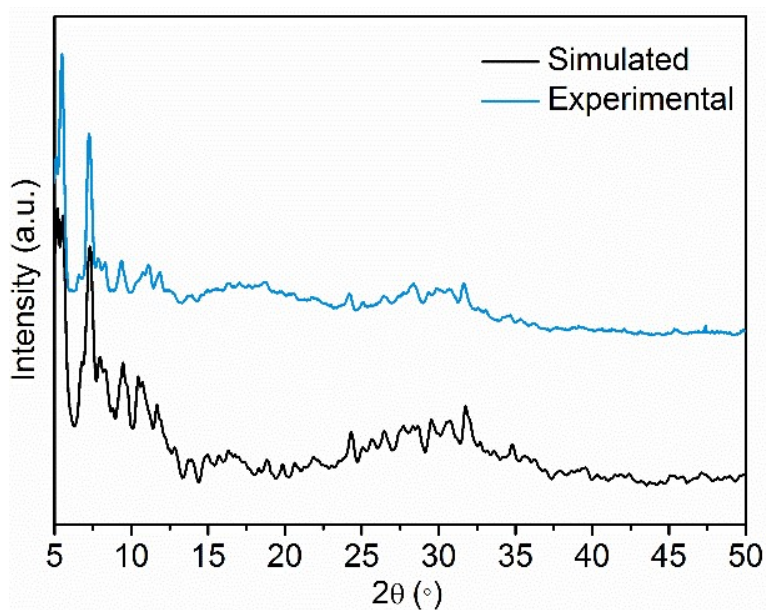


Fig. S12 Simulated and experimental PXR D patterns of **1**.



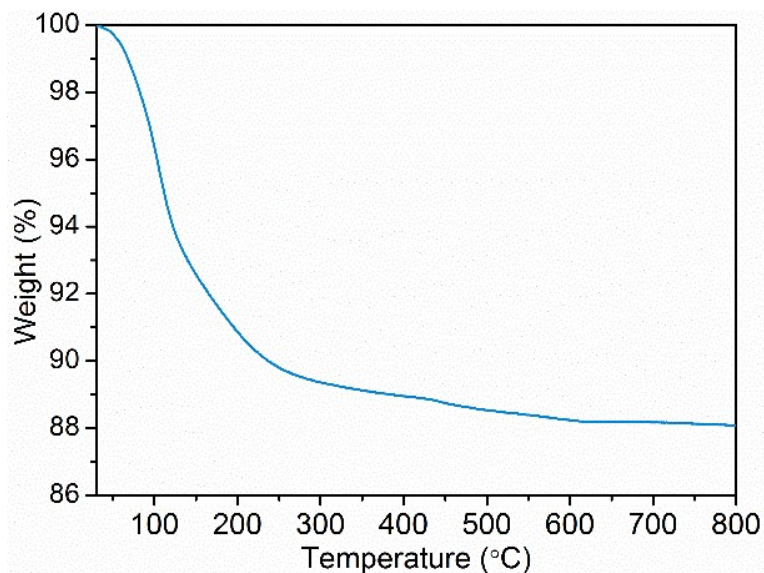


Fig. S13 TGA curve of **1**.

The thermogravimetric curve of **1** was measured at a heating rate of 10 °C/min in an argon atmosphere from 30 °C to 800 °C. As shown in Fig. S13, the TG curve of the compound **1** indicates that **1** the initial weight loss from 30 °C to 450 °C is about 11.8% , which is attributed to the loss of about 97 lattice water molecules. After 450 °C, compound **2** begins to decompose.

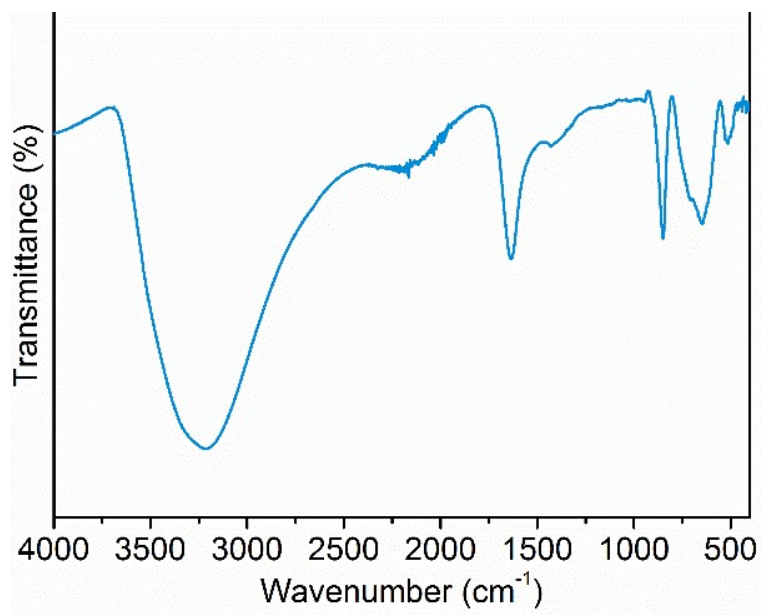


Fig. S14 IR spectrum of **1**

In the IR spectrum, the broad absorption peak at  $3226\text{ cm}^{-1}$  is attributed to the  $\nu(\text{O-H})$  stretching vibration of water, and the bending vibration of O-H appears at about  $1633\text{ cm}^{-1}$ . The peaks that appear in the range of  $400$  to  $1000\text{ cm}^{-1}$  can be attributed to the characteristic absorption peak of Nb-O, of which  $847\text{ cm}^{-1}$  is the stretching vibration peak of  $\nu(\text{Nb-O}_t)$  and  $647\text{ cm}^{-1}$  and  $513\text{ cm}^{-1}$  are the stretching vibration peaks of  $\nu(\text{Mn-O})$ .

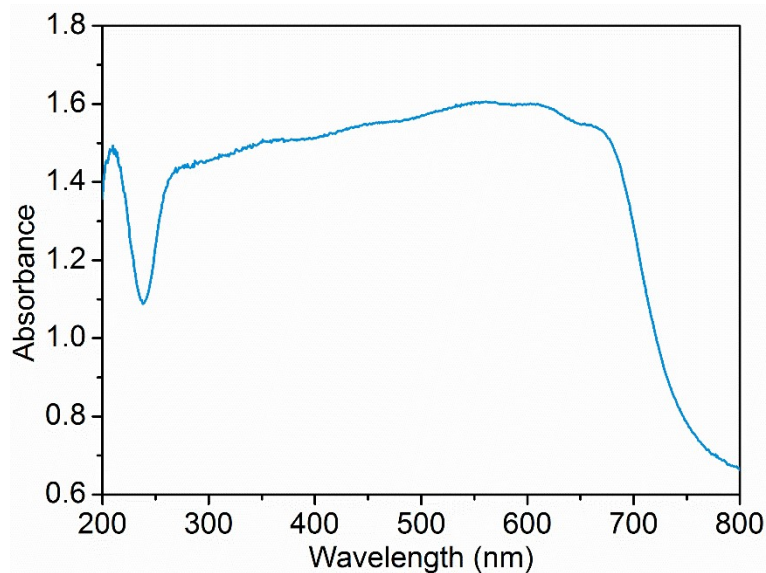


Fig. S15 UV-vis spectrum of **1**

## Section 4: References

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