

# **An Unprecedented 3D Architecture Based on Nb/W Mixed-Addendum Polyoxometalate and Lanthanide-Organic Complex: Synthesis, Crystal Structure and Properties**

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## **CONTENTS**

### **Section 1 A Detailed Survey of Ln-Containing PONs**

#### **Section 2 Synthesis**

##### **2.1 Synthesis of 1**

##### **2.2 Synthesis Discussion**

##### **2.3 Crystal Data**

#### **Section 3 Structures**

##### **3.1 Structures of 1**

##### **3.2 The Bond Lengths, Angels and BVS Calculations of the La Cations in 1**

#### **Section 4 Experimental Section**

##### **4.1 Materials and Physical Measurements**

##### **4.2 Preparation of Compound 1-Modified Paste Electrode (1-CPE)**

##### **4.3 Electrochemical and Electrocatalytic Properties**

#### **Section 5 Supplementary Physical Characterizations**

## Section 1 A Detailed Survey of Ln-Containing PONs

**Table S1.** A detailed survey of Ln-containing PONs

Year	Polyanion Formula	Characteristics	Ref.
1994	$(\{[\text{Eu}_3\text{O}(\text{OH})_3(\text{OH}_2)_3]_2\text{Al}_2(\text{Nb}_6\text{O}_{19})_5\})^{26-}$	the first examples of Ln-containing PONs	1
2012	$[(\text{Ge}_2\text{W}_{18}\text{Nb}_6\text{O}_{78})\text{Eu}(\text{H}_2\text{O})_4]^{7-}$ $[(\text{Ge}_4\text{W}_{36}\text{Nb}_{12}\text{O}_{156})\text{Eu}(\text{H}_2\text{O})_3]^{17-}$ $[\text{Cs}(\text{GeW}_9\text{Nb}_3\text{O}_{40})_4(\text{SO}_4)\text{Eu}_5(\text{H}_2\text{O})_{36}]^{14-}$ .....	all the Eu atoms are selectively bonded to $\text{O}_i(\text{Nb})$ of $\{\text{GeW}_9\text{Nb}_3\text{O}_{40}\}$ fragments	2
2012	$[\text{Eu}_6(\text{H}_2\text{O})_{38}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4]^{18-}$ $[\text{Ce}_6(\text{H}_2\text{O})_{38}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4]^{18-}$	the first examples of Ln derivatives based on saturated Dawson-type Nb/W mixed-addendum POMs	3
2017	$\{\text{Eu}_3(\text{H}_2\text{O})_9[\text{Nb}_{48}\text{O}_{138}(\text{H}_2\text{O})_6]\}^{27-}$	the first example of an iso-PONb constructed with fragment $\{\text{Nb}_{24}\text{O}_{72}\}$ and $\text{Ln}^{3+}$ ions	4
2017	$[\text{La}_8(\text{H}_2\text{O})_{32}(\text{C}_6\text{H}_5\text{NO}_2)_6(\text{SiW}_9\text{Nb}_3\text{O}_{40})_3]^{3-}$	the first 3D framework based on lanthanide-containing Nb/W mixed-addendum POM	This work

### References:

- [1] T. Ozeki, T. Yamase, H. Naruke and Y. Sasaki, *Inorg. Chem.*, 1994, **33**, 409-410.
- [2] S.-J. Li, S.-X. Liu, N.-N. Ma, Y.-Q. Qiu, J. Miao, C.-C. Li, Q. Tang and L. Xu, *CrystEngComm*, 2012, **14**, 1397-1404.
- [3] C.-C. Li, S.-X. Liu, S.-J. Li, Y. Yang, H.-Y. Jin and F.-J. Ma, *Eur. J. Inorg. Chem.*, 2012, **2012**, 3229-3234.
- [4] S. Chen, P. Ma, H. Luo, Y. Wang, J. Niu and J. Wang, *Chem. Commun.*, 2017, **53**, 3709-371.

## Section 2 Synthesis

### 2.1 Synthesis of 1

A mixture of  $\text{Cs}_6\text{H}[\text{Si}(\text{NbO}_2)_3\text{W}_9\text{O}_{37}]\cdot 8\text{H}_2\text{O}$  (1.8 mg),  $\text{La}(\text{NO}_3)_3$  (39.0 mg) and pyridine-3-carboxylic acid (9 mg) were continual construction of three layers in a 3 mL test tube, the pH of the distilled water (1 mL) was adjusted to 2.3 with HCl (1 M) solution. Then they were sealed in Teflon-lined autoclave and heated at 130 °C for 24 hours. After cooling to ambient temperature with a cooling rate of 5 °C h<sup>-1</sup>. Finally, colorless block single crystals were obtained, washed with water several times and air-dried to give 2.6 mg of **1** (48.1% yield based on W). Anal. calcd for  $\text{C}_{36}\text{H}_{27}\text{La}_8\text{N}_6\text{Nb}_9\text{O}_{172}\text{Si}_3\text{W}_{27}$ : C 4.20, N 0.82, La 10.82, Nb 8.13, Si 0.82, W 48.23%; found: C 4.30, N 0.78, La 12.82, Nb 7.93, Si 0.73, W 49.03%.

### 2.2 Synthesis Discussion

Compound **1** was synthesized by utilizing steam-assisted conversion method of a mixture containing  $\text{Cs}_6\text{H}[\text{Si}(\text{NbO}_2)_3\text{W}_9\text{O}_{37}]\cdot 8\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3$  and pyridine-3-carboxylic acid in a stoichiometric ratio, and the pH of the solution was adjusted to 2.3 with 1 M HCl solution. In the experiment, there are some points are worthy mention here during the synthesis: (1) steam-assisted conversion method.<sup>1</sup> Developed on the foundation of the dry gel conversion way, and it is mostly applied to the preparation of the zeolites at early stage. Moreover, compared with the conventional hydrothermal synthesis approaches, the solid and liquid phase are separated to exhibit a concentration gradient with the transmission of water vapor. By this way, it couldn't improve the yield of the targeted compound in a relatively friendly environment, but decrease the solvent consumption and make the procedure more convenient. It is also widely employed in creating more tanglesome metastable or intermediate phases, and provides a wonderful chance for the formation of characteristic architectures. Noteworthy, it is the first time to take advantage of the steam-assisted conversion method for synthesizing the novel Ln-containing Nb/W mixed-addendum POMs. (2) the choice of Nb/W mixed-addendum polyoxometalates. Utilizing the higher nucleophilicity of the niobium than tungsten's, we select the Nb/W mixed-addendum  $\{\text{SiNb}_3\text{W}_9\text{O}_{40}\}$  cluster as the reaction precursor: it's not only more stable in neutral and basic media, but also relatively easy to connect to lanthanide metals or transition metals,<sup>2</sup> which may result in products with excellent catalytic properties. (3) the choice of lanthanide metals and organic ligands. The construction of 3D framework materials based on polyoxometalates building blocks and lanthanide cations or lanthanide-organic complexes, not only form a structural point of view but also facilitate the potential applications of these materials which range from gas adsorption, ion exchange, magnetism, and luminescence.<sup>3</sup> Considering that lanthanide ions preferentially precipitate rather than crystallize when they encounter polyoxoanions,<sup>4</sup> as well as the steric hindrance of polyoxoanions, herein, we choose pyridine-3-carboxylic acid as the bridging agent, its high affinity for lanthanide ions effectively inhibits them precipitation and improve the stability of the

architecture. In particular, due to the saturated Keggin-type  $\{\text{SiNb}_3\text{W}_9\text{O}_{40}\}$  precursor is not only active but also stable in a broad pH range, we controlled the pH values in the range of 2.0-4.0, the targeted compound was obtained with the highest yield when the pH value is 2.3. Meanwhile, in the process of synthesizing **1**, we try to substitute  $\text{La}^{\text{III}}$  with other lanthanide ions, such as  $\text{Eu}^{\text{III}}$ ,  $\text{Sm}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$ , and  $\text{Ce}^{\text{III}}$ , but no crystal samples were obtained. In addition, when pyridine-4-carboxylic acid was utilized in place of pyridine-3-carboxylic acid under the same conditions, no compounds were produced as well.

## References:

- [1] E.-L. Zhou, C. Qin, X.-L. Wang, K.-Z. Shao and Z.-M. Su, *Chem. Eur. J.*, 2015, **21**, 13058-13064.
- [2] (a) M. K. Harrup, G.-S. Kim, H. Zeng, R. P. Johnson, D. VanDerveer and C. L. Hill, *Inorg. Chem.*, 1998, **37**, 5550-5556; (b) S.-J. Li, S.-X. Liu, N.-N. Ma, Y.-Q. Qiu, J. Miao, C.-C. Li, Q. Tang and L. Xu, *CrystEngComm*, 2012, **14**, 1397-1404.
- [3] (a) W.-C. Chen, C. Qin, X.-L. Wang, C.-X. Wu, Y.-G. Li, H.-Y. Zang, K.-Z. Shao, Z.-M. Su and E.-B. Wang, *CrystEngComm*, 2016, **18**, 2820-2824; (b) W.-C. Chen, C. Qin, Y.-G. Li, H.-Y. Zang, K.-Z. Shao, Z.-M. Su and E.-B. Wang, *Chem. Asian. J.*, 2015, **10**, 1184-1191; (c) F. Hussain and U. Kortz, *Chem. Commun.*, 2005, 1191-1193; (d) U. Kortz, F. Hussain and M. Reicke, *Angew. Chem., Int. Ed.*, 2005, **44**, 3773-3777.
- [4] (a) Y. Wang, X. Sun, S. Li, P. Ma, J. Niu and J. Wang, *Cryst. Growth. Des.*, 2015, **15**, 2057-2063; (b) H. An, D. Xiao, E. Wang, Y. Li, X. Wang and L. Xu, *Eur. J. Inorg. Chem.*, 2005, **2005**, 854-859.

## 2.3 Crystal Data

**Table S2.** Crystal Data and Structure Refinements for **1**.

<b>1</b>	
Empirical formula	$C_{36}H_{27}La_8Nb_9N_6O_{172}Si_3W_{27}$
$M$	10291.32
$\lambda/\text{\AA}$	0.71073
$T/\text{K}$	296.0
Crystal system	Trigonal
Space group	$P\bar{3}$
$a/\text{\AA}$	23.4764(7)
$b/\text{\AA}$	23.4764(7)
$c/\text{\AA}$	12.1560(6)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	120
$V/\text{\AA}^3$	5802.1(4)
$Z$	1.00
$D_c/\text{Mg m}^{-3}$	2.945
$\mu/\text{mm}^{-1}$	15.288
$F(000)$	4526
$2\theta$ Range/ $^\circ$	3.904–56.62
Measured reflections	43287
Independent reflections	9601
$R_{int}$ after SQUEEZE	0.0593
Goodness-of-fit on $F^2$	1.080
$R_1(I > 2\sigma(I))^a$	0.0615
$wR_2$ (all data) <sup>b</sup>	0.1497

<sup>a</sup> $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup> $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ .

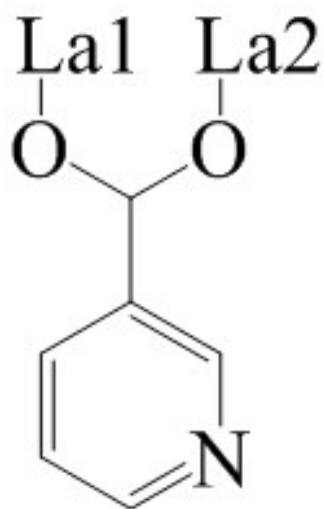
**Single-crystal X-ray diffraction:** In order to avoid weathering, we selected high-quality crystals from their mother liquors and airproofed into a capillary tube for X-ray crystal structure determination. Single-crystal X-ray diffraction data for **1** was carried out using a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromator using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by using the  $\Phi/\omega$  scan technique at ambient temperature and there was no evidence of crystal decay during data collection. Its structure was solved by direct methods of SHELXS-2014 and further refined by full-matrix least-squares refinement on  $F^2$  using the SHELXTL package,<sup>1</sup> and an absorption correction was applied using multiscan techniques. The hydrogen atoms of all the pyridine-3-carboxylic acid ligands were generated theoretically and refined with isotropic thermal parameters. We used the SQUEEZE routine of PLATON to remove the guest molecules because of the disorders in **1**.<sup>2</sup> The numbers of lattice water molecules and counter cations of **1** were estimated by the results of elemental analyses, and TG curves. In addition, CCDC 1544073 for **1** contains the supplementary crystallographic data for this article. These data can be gained free of charge from The Cambridge Crystallographic Data Centre.

#### References:

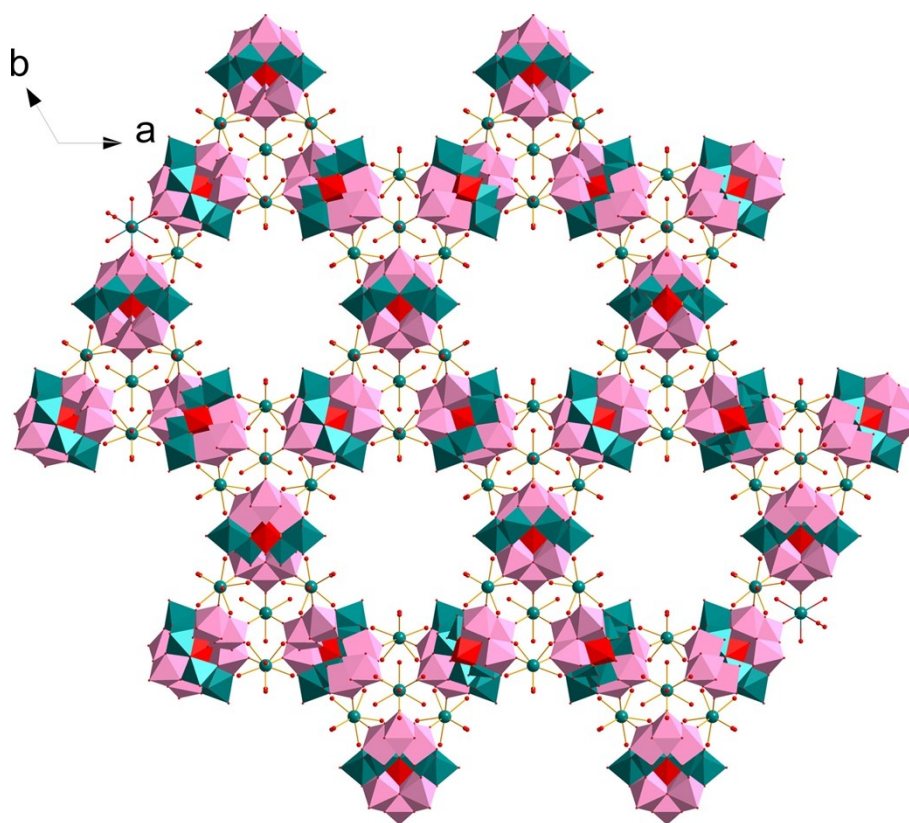
- [1] A.L. Spek, *Acta Cryst.* (2015). C71, 9–18.
- [2] Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University, Utrecht, The Netherlands, 2003.

### 3 Structures

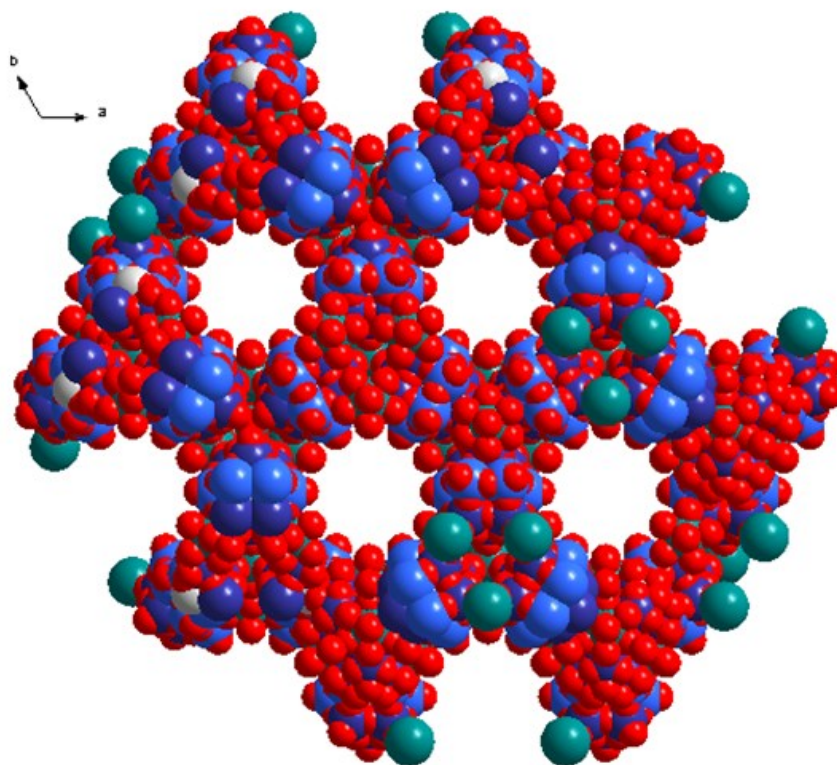
#### 3.1 Structures of 1



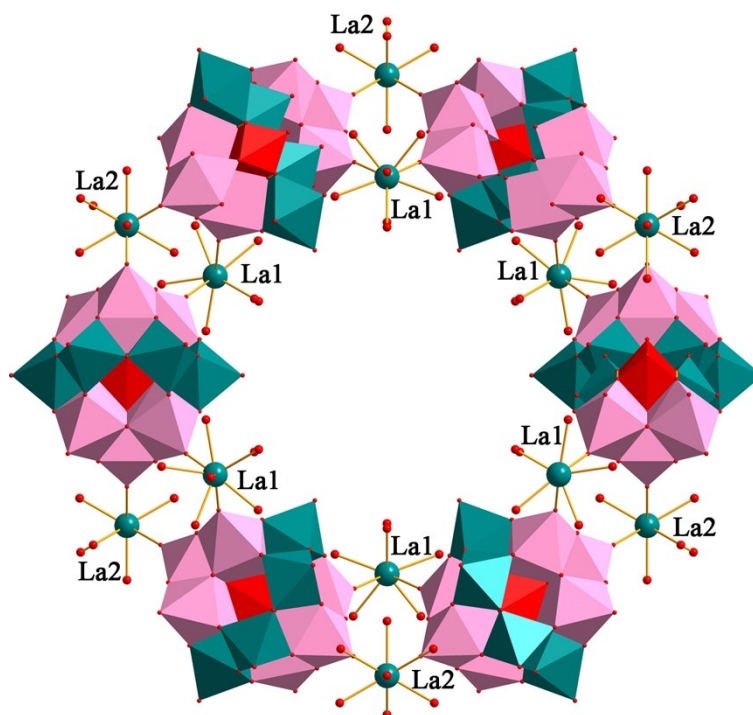
**Fig. S1.** The bridging mode of pyridine-3-carboxylic acid in **1**.



**Fig. S2.** (a) Combined polyhedral/ball-and-stick representation of the 3D framework of **1**. The H atoms are omitted for clarity. SiO<sub>4</sub> tetrahedron (red), WO<sub>6</sub> octahedra (teal), Nb/WO<sub>6</sub> octahedra (rose), in which W and Nb are disordered. O (red), and La (teal).

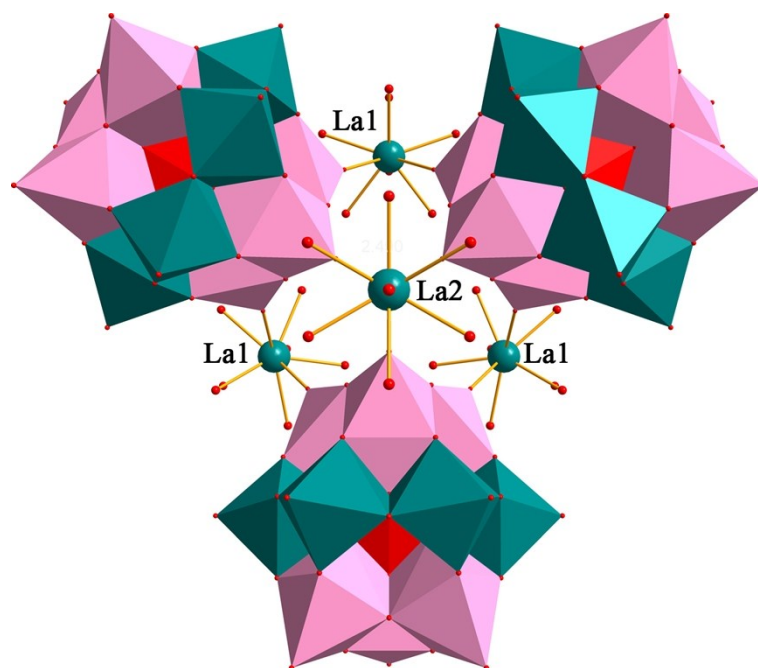


**Fig. S3.** The space-filling representation of **1**. The balls represent Nb/W (indigo), W (light blue), La (teal), Si (gray), N (blue), and O (red).

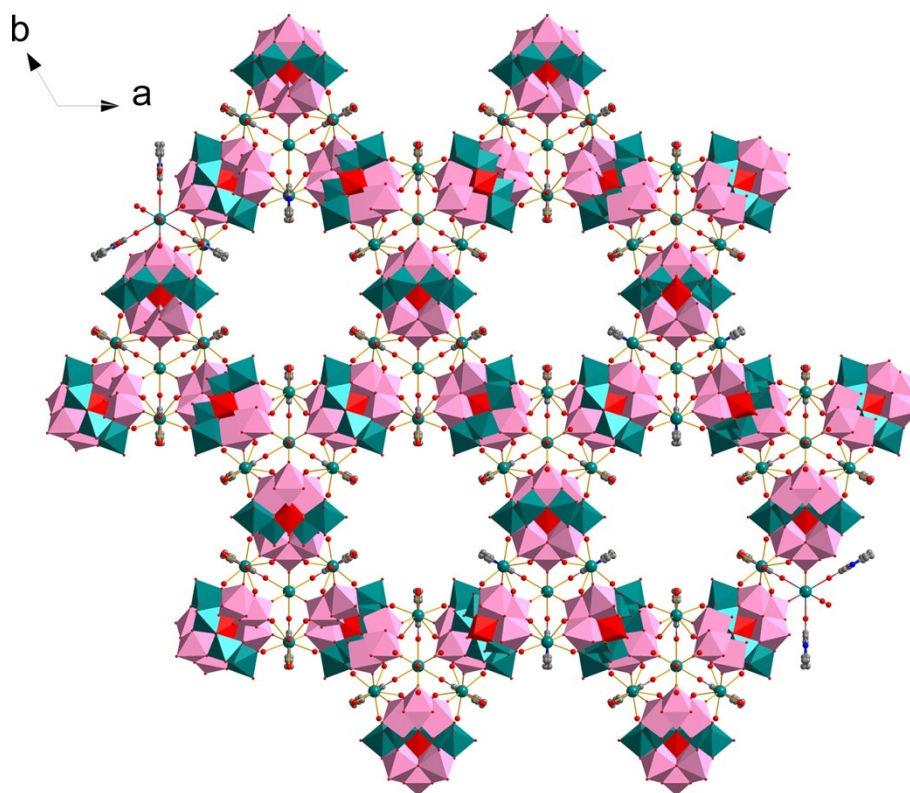


**Fig. S4.** View of 1D hexagonal channel of **1**. The H atoms are omitted for clarity. SiO<sub>4</sub> tetrahedron (red), WO<sub>6</sub> octahedra (teal), Nb/WO<sub>6</sub> octahedra (rose), in which W and Nb are disordered. O (red), and La (teal).





**Fig. S5.** View of the La2 cations, which fill in the central gap of the three adjacent  $\{\text{SiNb}_3\text{W}_9\text{O}_{40}\}$  units. The H atoms are omitted for clarity.  $\text{SiO}_4$  tetrahedron (red),  $\text{WO}_6$  octahedra (teal), Nb/ $\text{WO}_6$  octahedra (rose), in which W and Nb are disordered. O (red), and La (teal).



**Fig. S6.** Combined polyhedral/ball-and-stick representation of the 3D framework of **1** in the presence of pyridine-3-carboxylic acid. The H atoms are omitted for clarity.  $\text{SiO}_4$  tetrahedron (red),  $\text{WO}_6$  octahedra (teal), Nb/ $\text{WO}_6$  octahedra (rose), in which W and Nb are disordered. O (red), C (gray-50%), N (blue), and La (teal).

### 3.2 The Bond Lengths, Angels and BVS Calculations of the La Cations in 1

**Table S3.** The bond lengths of the La cations in 1.

Bonds	Bond Lengths(Å)
La2-O1	2.548(7)
La2-O1 <sup>2</sup>	2.548(7)
La2-O1 <sup>3</sup>	2.548(7)
La2-O1W	2.597(14)
La2-O2W	2.611(1)
La2-O2W <sup>2</sup>	2.611(1)
La2-O2W <sup>3</sup>	2.611(1)
La2-O24	2.5064(11)
La2-O24 <sup>2</sup>	2.5064(11)
La2-O24 <sup>3</sup>	2.5064(11)
La1-O3W	2.602(16)
La1-O4W	2.56(2)
La1-O5W	2.589(16)
La1-O6W	2.54(2)
La1-O7W	2.64(2)
La1 <sup>4</sup> -O2	2.518(9)
La1 <sup>5</sup> -O3	2.520(9)
La1-O23	2.4880(13)
La1-O25	2.617(1)

Noteworthy, there are some symmetry transformations used to generate equivalent atoms: <sup>2</sup>:+Y-X, 2-X, +Z; <sup>3</sup>: 2-Y, 2+X-Y, +Z; <sup>4</sup>: 2-Y, 2+X-Y, -1+Z; <sup>5</sup>: 2-X, 3-Y, 1-Z.

**Table S4.** The bond angles of the La cations in **1**.

Bonds	Angels(°)	Bonds	Angels(°)
O1 <sup>2</sup> -La2-O1 <sup>3</sup>	73.6(2)	O2 <sup>6</sup> -La1-O3W	143.7(4)
O1-La2-O1 <sup>3</sup>	73.6(2)	O2 <sup>6</sup> -La1-O4W	70.2(6)
O1-La2-O1 <sup>2</sup>	73.6(2)	O2 <sup>6</sup> -La1-O5W	74.6(4)
O1 <sup>3</sup> -La2-O1W	136.23(15)	O2 <sup>6</sup> -La1-O6W	112.1(6)
O1-La2-O1W	136.23(15)	O3 <sup>5</sup> -La1-O3W	74.7(4)
O1 <sup>2</sup> -La2-O1W	136.23(15)	O3 <sup>5</sup> -La1-O5W	143.7(4)
O24-La2-O1 <sup>3</sup>	140.82(16)	O3 <sup>5</sup> -La1-O6W	69.9(6)
O24-La2-O1 <sup>2</sup>	75.24(19)	O4W-La1-O3W	136.7(6)
O24 <sup>2</sup> -La2-O1	140.82(16)	O3 <sup>5</sup> -La1-O4W	112.2(6)
O24 <sup>3</sup> -La2-O1 <sup>3</sup>	75.2(2)	O4W-La1-O5W	66.5(7)
O24 <sup>2</sup> -La2-O1 <sup>3</sup>	75.24(19)	O5W-La1-O3W	133.0(6)
O24 <sup>3</sup> -La2-O1	75.24(19)	O6W-La1-O3W	66.5(7)
O24 <sup>2</sup> -La2-O1 <sup>2</sup>	75.2(2)	O6W-La1-O4W	75.8(7)
O24-La2-O1	75.2(2)	O6W-La1-O5W	136.9(6)
O24 <sup>3</sup> -La2-O1 <sup>2</sup>	140.82(16)	O23-La1-O2 <sup>6</sup>	137.8(2)
O24-La2-O1W	82.95(6)	O23-La1-O3 <sup>5</sup>	137.0(2)
O24 <sup>2</sup> -La2-O1W	82.95(6)	O23-La1-O3W	77.5(4)
O24 <sup>3</sup> -La2-O1W	82.95(6)	O23-La1-O4W	69.6(5)
O24-La2-O24 <sup>2</sup>	118.52(2)	O23-La1-O5W	78.3(4)
O24-La2-O24 <sup>3</sup>	118.52(3)	O23-La1-O6W	69.2(5)

Noteworthy, there are some symmetry transformations used to generate equivalent atoms: <sup>2</sup>: +Y-X, 2-X, +Z; <sup>3</sup>: 2-Y, 2+X-Y,+Z; <sup>5</sup>: 2-X, 3-Y, 1-Z; <sup>6</sup>: +Y-X, 2-X, 1+Z.

**Table S5.** The BVS calculation result of all La atoms in **1**.

Compound <b>1</b>			
Code	Bond Valence	Code	Bond Valence
La1	2.999	La2	3.312

## Section 4 Experimental Section

### 4.1 Materials and Physical Measurements

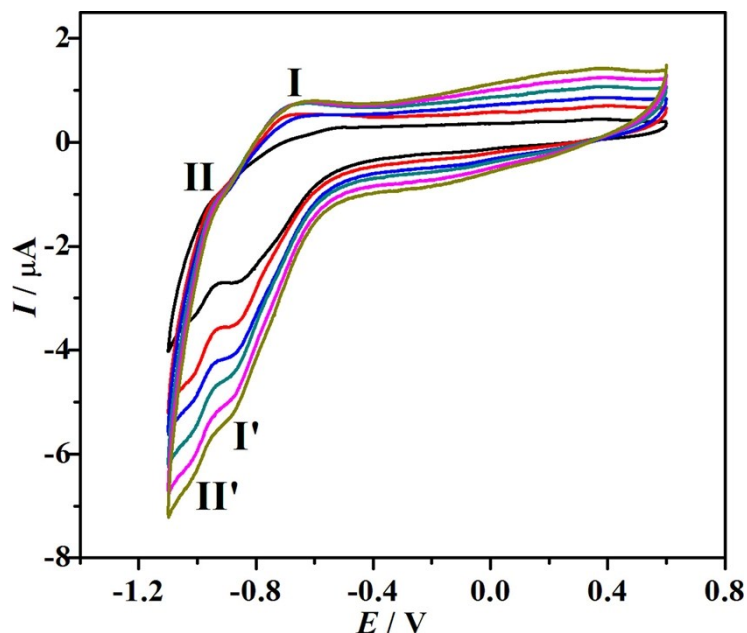
**Materials:**  $\text{Cs}_6\text{H}[\text{Si}(\text{NbO}_2)_3\text{W}_9\text{O}_{37}] \cdot 8\text{H}_2\text{O}$  was synthesized following the procedure described in the literature (*Inorg.Chem.*, 1998, **37**, 5550-5556), it has been characterized by IR spectra and elemental analyses. And the powder was used without further purification. All other reagents and solvents for the synthesis were purchased from commercial sources and used as received without further purification.

**Instruments:** Infrared spectroscopy (IR) data was obtained on a Matton Alpha-Centauri spectrophotometer using KBr pellets in the rang 400-4000  $\text{cm}^{-1}$ . TG analyses were recorded on a Perkin-Elmer TGA7 instrument in flowing  $\text{N}_2$  with a heating rate of 10  $^\circ\text{C min}^{-1}$  from room temperature to 600  $^\circ\text{C}$ . Power X-ray diffraction (PXRD) data was obtained by using a Siemens D5005 diffractometer with  $\text{Cu-K}_\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation in the range 3-50 $^\circ$ . Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer, and elemental analyses for Si, La, W, and Nb were determined with a PLASMASPEC (I) ICP atomic emissionspectrometer. Electrochemical measurements were performed on a BAS Epsilon Analyzer in a three-electrode cell: glassy carbon electrode (GCE, diameter 2 mm) as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode. Photoluminescence properties were measured on fluorescence spectrophotometer (Cary Eclipse) at room temperature.

### 4.2 Preparation of compound 1-modified paste electrode (1-CPE)

1-CPE was fabricated as follows: graphite powder (90 mg) and **1** (15 mg) were mixed and grounded 0.5 h in an agate mortar to obtain a uniform phase. The 0.04 mL of nujol was added to the mixture. The homogenized mixture was used to pack into a glass tube with a 2 mm diameter, and the tube surface was wiped with the weighting paper. Electrical contact was established with a copper rod through the back of the electrode.

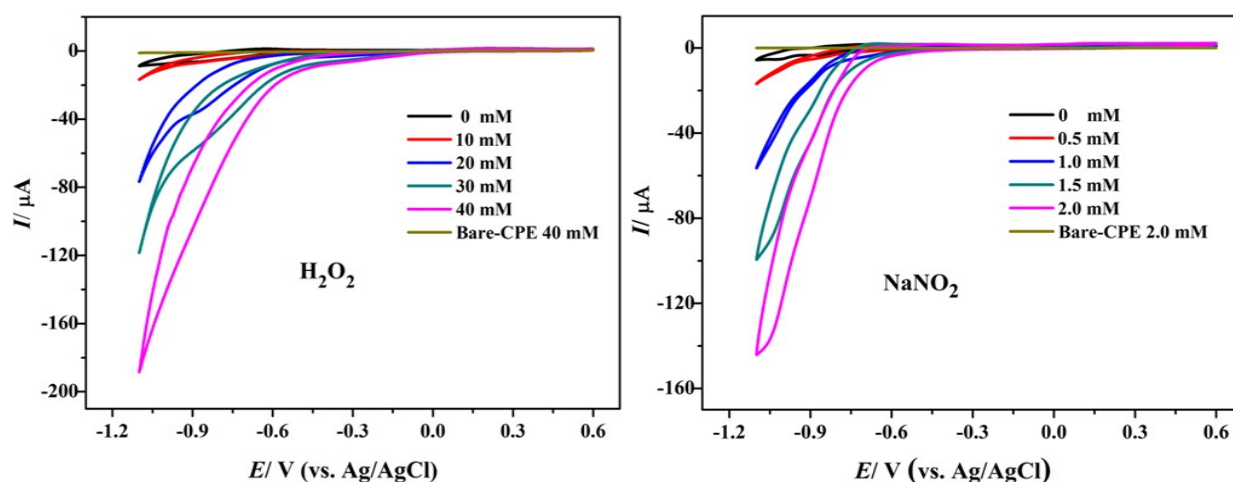
### 4.3 Electrochemical and Electrocatalytic Properties



**Fig. S7** The cyclic voltammogram of **1-CPE** in the potential region of -1.1V to 0.6 V at scan rates (from inner to outer) of 50, 100, 150, 200, 250, and 300  $\text{mV s}^{-1}$ .

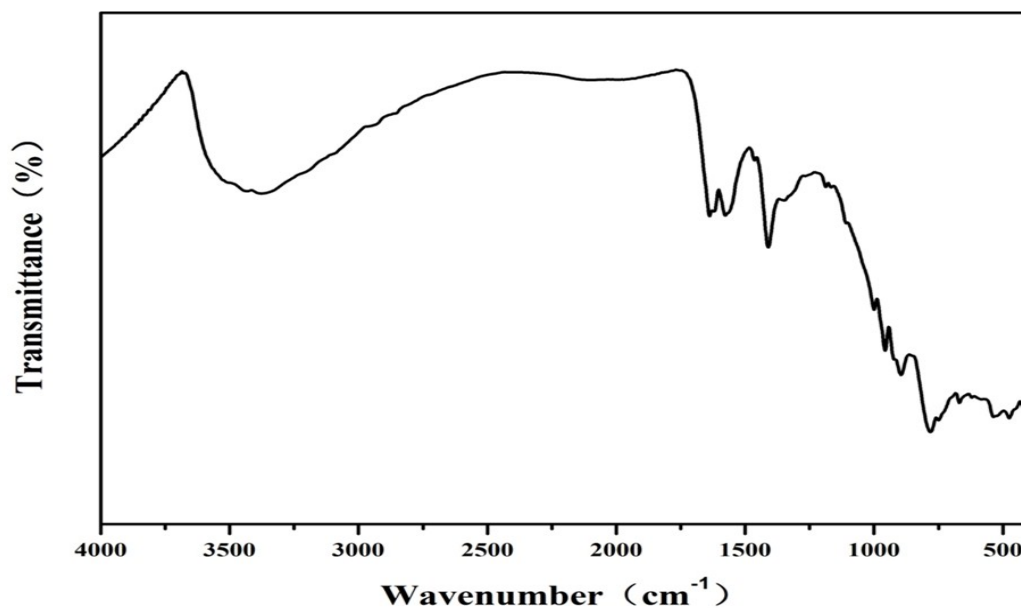
**Table S6.** The detailed values of two pairs of quasi-reversible redox peaks

Peaks	$E_{1/2} / \text{V}$	$E_{\text{pa}} / \text{V}$	$E_{\text{pc}} / \text{V}$	$\Delta E_{\text{p}} / \text{mV}$
I/I'	-0.784	-0.738	-0.830	92
II/II'	-0.985	-0.956	-1.014	58

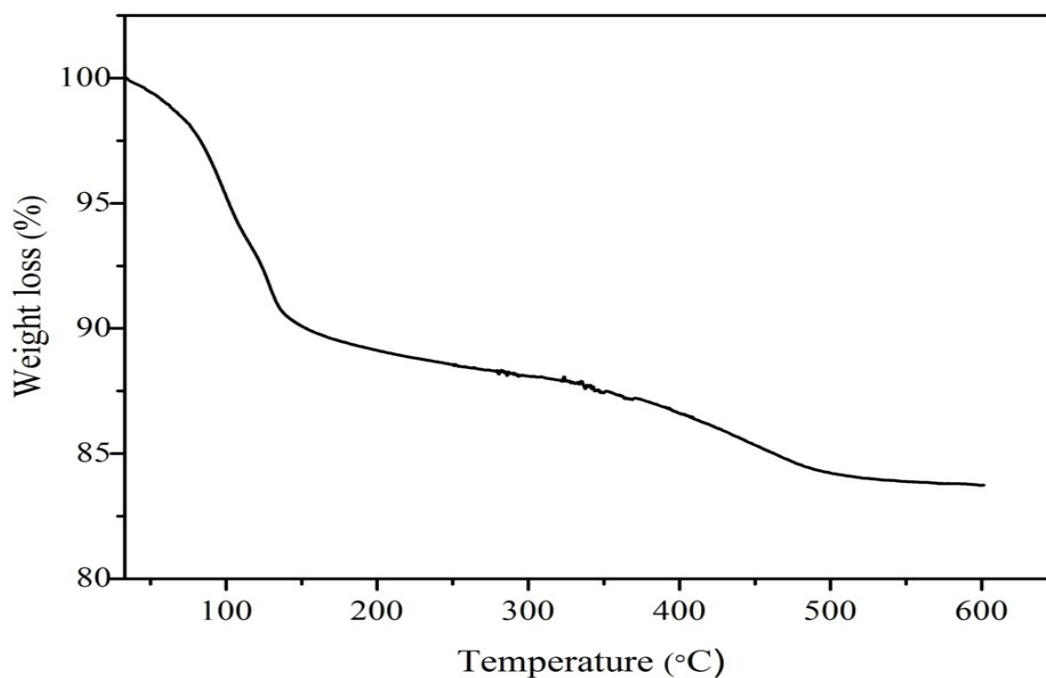


**Fig. S8** (a) Electrocatalytic reduction of  $\text{H}_2\text{O}_2$  by **1-CPE** in pH 4.7 0.5 M HAc–NaAc buffer solution. Scan rate: 100  $\text{mV s}^{-1}$ . (b) Electrocatalytic reduction of  $\text{NaNO}_2$  by **1-CPE** in pH 4.7 0.5 M HAc–NaAc buffer solution. Scan rate: 100  $\text{mV s}^{-1}$ .

## Section 5 Supplementary Physical Characterizations



**Fig. S9.** IR spectrum of **1**. In the low-wavenumber region ( $\nu < 1050 \text{ cm}^{-1}$ ), it exhibits the characteristic vibration of Keggin-type structure.<sup>1</sup> Therefore, the presence of strong peaks at 957, 894, and 781  $\text{cm}^{-1}$  are assigned to the  $\nu_{\text{as}}$  (Si-O<sub>a</sub>), corner-sharing  $\nu_{\text{as}}$  (W-O<sub>b</sub>), and edge-sharing  $\nu_{\text{as}}$  (W-O<sub>c</sub>). The terminal M = O<sub>t</sub> (M = W and Nb) vibrations appear at 1008  $\text{cm}^{-1}$ . The peaks at 1576 and 1410  $\text{cm}^{-1}$  are attributed to the characteristic band of  $\nu_{\text{as}}$  (COO) and  $\nu_{\text{s}}$  (COO) of the carboxyl group.<sup>2</sup> Broad peaks at 3376 and 1638  $\text{cm}^{-1}$  may correspond to the stretching and bending modes of lattice and coordinated water molecules.<sup>3</sup>

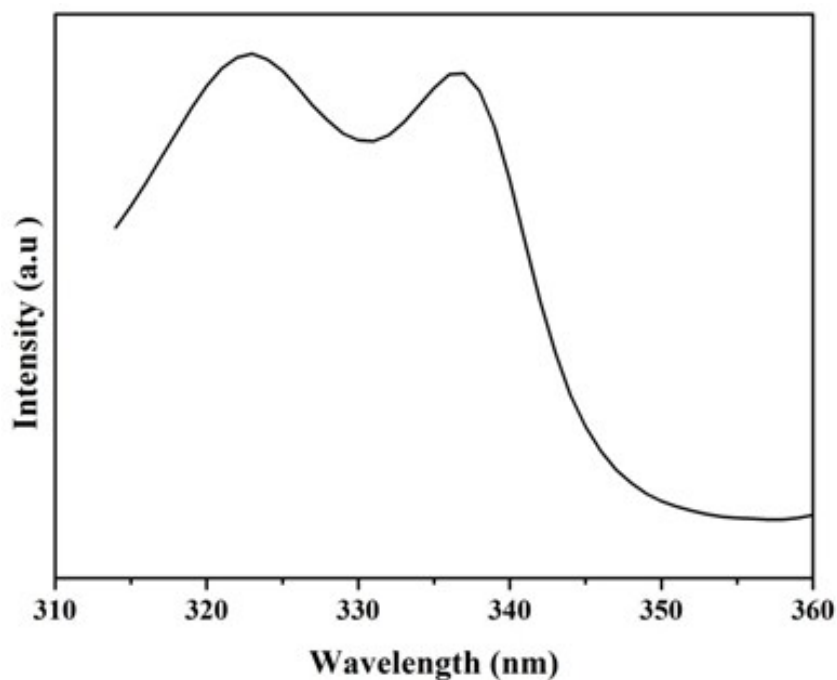


**Fig. S10.** TG curve of **1**. The shown first weight loss of **1** is 9.2% from 40-162 °C, corresponding to the loss of 8 lattice water molecules and 32 coordinated water (calcd 6.9%), followed by two-step consecutive weight loss of 6.3% from 162-543 °C assigned to the removal of 6 pyridine-3-carboxylic acid

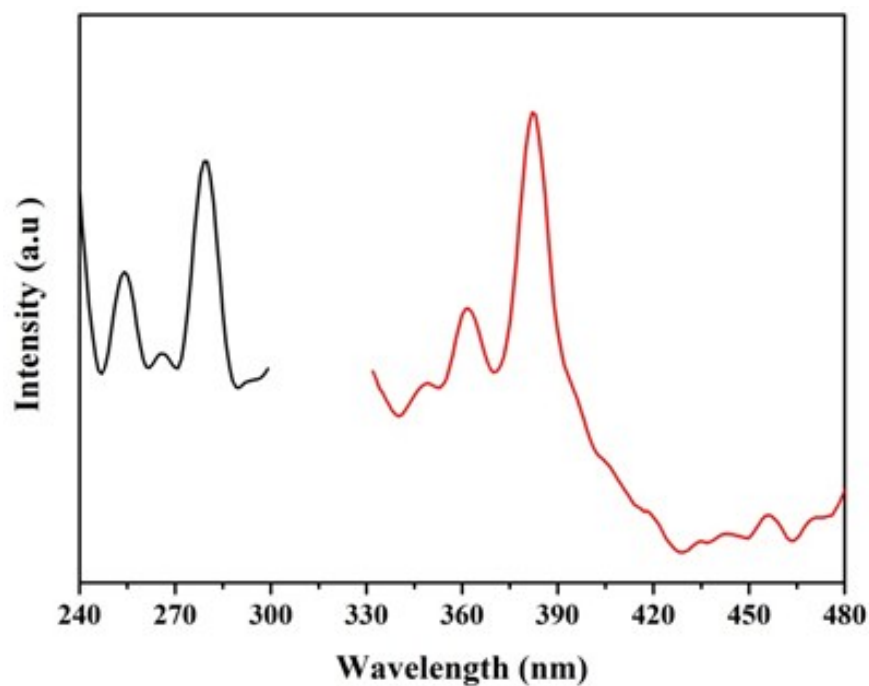
molecules (calcd 7.0%). Making a comparison, the first weight loss is more 2.3% than the calculated value, which may be attributed to the samples used for test were not dry totally.

#### References:

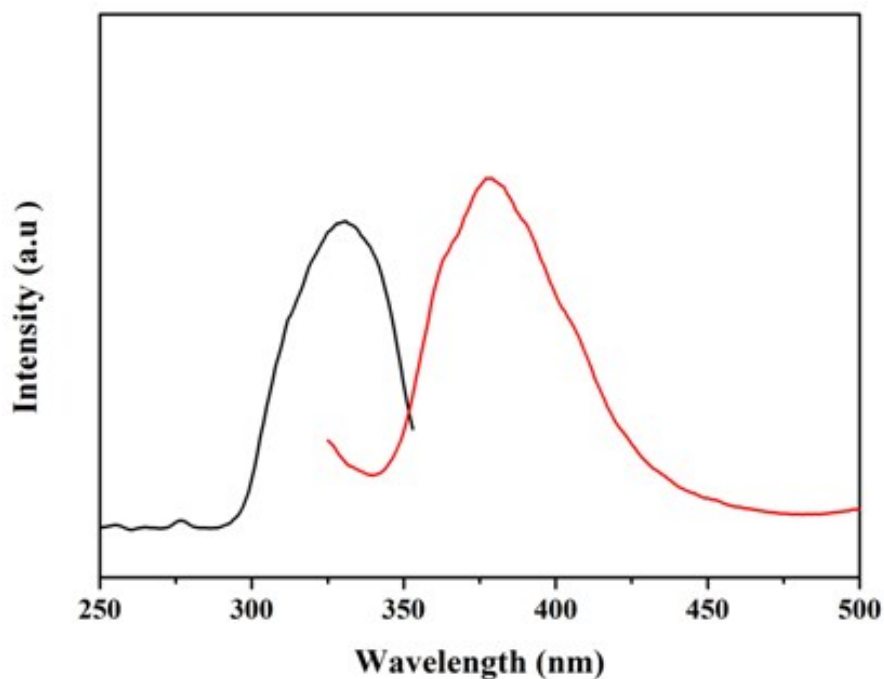
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**Fig. S11** The excitation spectrum of **1** under emission at 380 nm at ambient temperature.

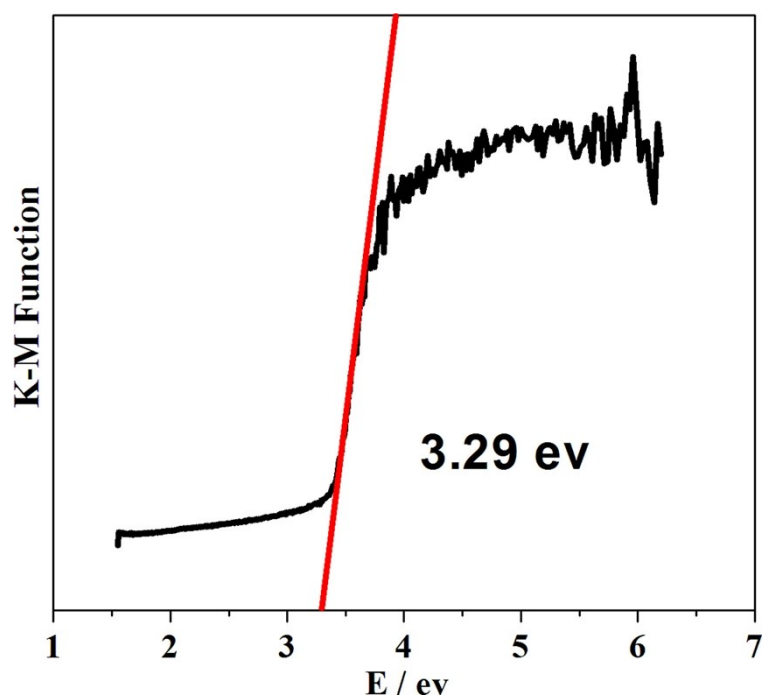


**Fig S12** The excitation spectrum (black,  $\lambda_{em} = 382$  nm) and emission spectrum (red,  $\lambda_{ex} = 280$  nm) of  $Cs_6H[Si(NbO_2)_3W_9O_{37}] \cdot 8H_2O$  in solid state at room temperature.



**Fig S13** The excitation spectrum (black,  $\lambda_{em} = 378$  nm) and emission spectrum (red,  $\lambda_{ex} = 330$  nm) of pyridine-3-carboxylic acid in solid state at room temperature.





**Fig. S14** The diffuse reflectance UV-Vis absorption spectra of compound **1**. The corresponding well-defined optical absorption associated with HOMO–LUMO ( $E$ ) can be assessed at 3.29 eV.