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Supporting Information

Polyoxoniobate-Based 3D Framework Materials with Photocatalytic Hydrogen Evolution Activity

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CONTENTS

Section 1 Experimental Section

Materials and general methods. All chemicals were commercially purchased and used without further purification. $K_7HNb_6O_{19}\cdot 13H_2O$ was prepared according to the literature and identified by IR spectra.[4c] Elemental analysis for Nb, V, P and Cu were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range 400-4000 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. Solid state UV-vis absorption spectra were recorded from 200 to 900 nm using barium sulfate ($BaSO_4$) as a standard with 100% reflectance on a Varian Cary 500 UV-Vis spectrophotometer. Emission/excitation spectra were recorded on a HITACHI F-7000 fluorescence spectrophotometer. Powder X-ray diffraction measurement was recorded at room temperature on a Siemens D5005 diffractometer with Cu–Kα (λ = 1.5418 Å). Thermogravimetric analysis (TGA) of the samples were performed using a Perkin-Elmer TG-7 analyzer heated from 55 ºC to 900 ºC under nitrogen at the heating rate of 10 $°C\cdot min^{-1}$.

Synthesis of 1. $Cu(Ac)_2\cdot 2H_2O$ (0.044 g, 0.200 mmol) was added to 2 mL distilled water with stirring. Then the resulting blue solution was added dropwise to a 4 mL aqueous solution containing $K_7HNb_6O_{19}\cdot 13H_2O$ (0.045 g, 0.033 mmol), $NaVO_3$ (0.049 g, 0.400 mmol) and H_3PO_4 (5 M, 0.030 mL, 0.150 mmol). The mixture was adjusted to pH 9.50 using 1 M NaOH solution. Subsequently, en was used to adjust the pH value of mixture to 10.50, and the mixture was transferred to a Teflon-lined stainless steel autoclave (23 mL). The Teflon-lined stainless steel autoclave was heated at 160 ºC for 72 h, and was then cooled to room temperature at a rate of 10 ºC/h. Brown block-like crystals of **1** were obtained from the solid product in a yield of 39.8% (based on Nb). Anal. For **1**: Calcd (%): P 0.98, Cu 8.08, V 9.71, Nb 35.43. Found (%): P 1.05, Cu 8.22, V 9.46, Nb 35.27. **Synthesis of 2**. **2** was prepared according to the similar method of **1**, except enMe was used instead of en. After cooling to room temperature, brown block-like crystals were collected. Yield: ca. 58.3% (based on Nb). Anal. For **2**: Calcd (%): P 0.96, Cu 7.87, V 9.47, Nb 34.54. Found (%): P 1.02, Cu 8.06, V 9.21, Nb 34.69.

X-ray Crystallography

The crystal data of **1** and **2** were collected on a Rigaku R-AXIS RAPID IP diffractometer ($\mathrm{Mo}_{K\alpha}$, graphite monochromator, λ = 0.71073 Å). The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 crystallographic software package.[S1] During the refinement, all H atoms on water molecules were directly included in the molecular formula. Hydrogen atoms of organic ligands were fixed in the calculated positions. The crystal data and structure refinements of compounds **1** and **2** are summarized in Table S1. CCDC reference numbers are 973046 and 973047 for **1** and **2**, respectively. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

S1. G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen: Göttingen, Germany, 1997; G. M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, University of Göttingen: Göttingen, Germany, 1997.

Photocatalytic Experiments

The UV photocatalytic experiments with irradiation of 125 W Hg lamp. The photocatalytic reactions were carried out in a Pyrex inner-irradiation-type reaction vessel with magnetic stirring at room temperature. The photocatalytic reactions were performed in 100 mL 20% CH_3OH aqueous solution, containing 100 mg photocatalyst and loading 0.75% Pt. Before the photocatalytic reaction, nitrogen gas was bubbled through the reaction mixture for 0.5 h to remove air. The mixture was then irradiated using a 125 W Hg lamp, and the produced H_2 was analyzed using a GC 7890T instrument.

The photocatalytic experiments with irradiation of 300 W Xe lamp. This photocatalytic experiments were performed similar to the UV process, except a 300 W Xe lamp (without filter) was used instead of 125 W Hg lamp. Before the photocatalytic reaction, vacuum pump was bubbled through the reaction mixture for 0.5 h to remove air.

Table 1 Crystal Data and Structure Refinement for **1 - 2**.

	1	**2**
Empirical formula	$C_{16}H_{80}Cu_4N_{16}PV_6$ $Nb_{12}O_{59}$	$C_{24}H_{97}Cu_4N_{16}PV_6$ $Nb_{12}O_{57}$
M	3146.65	3227.87
λ/Å	0.71073	0.71073
T/K	293(2)	293(2)
Crystal dimensions/mm	0.25× 0.17×0.15	0.24×0.18×0.16
Crystal system	Tetragonal	Tetragonal
Space group	*I4/m*	*I4/m*
a/Å	15.141(2)	15.229(2)
b/Å	15.141(2)	15.229(2)
c/Å	19.257(4)	19.207(4)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	4414.7(12)	4454.5(12)
Z	2	2
D_c/Mg m^{-3}	2.367	2.407
μ/mm^{-1}	3.151	3.125
F(000)	3042	3140
θ Range/°	3.19– 25.00	3.17 – 25.00
Data/restraints/parameters	2014 / 0 / 137	2029 / 13 / 154
$R_1(I > 2\sigma(I))$ ^{a}	0.0649	0.0645
wR_2 (all data)^a	0.2145	0.2226
Goodness-of-fit on F^2	1.002	1.038

$^aR_1 = \sum||F_0|-|F_C||/\sum|F_0|$; $wR_2 = \sum[w(F_0^2-F_C^2)^2]/\sum[w(F_0^2)^2]^{1/2}$

Section 2 Supplementary Structural Section

Bond valence sum calculations of compounds 1 and 2

Table S1. Bond valence sum calculations of compound **1**.[S2,S3]

Bonds	Bond length (Å)	BVS	Bonds	Bond length (Å)	BVS
V(1) - O(7)	1.628(14)	1.526328	V(2) - O(6)	1.653(10)	1.426759
V(1) - O(1) #2	1.981(6)	0.587175	V(2) - O(2)	1.968(7)	0.608008
V(1) - O(1)	1.981(6)	0.587175	V(2) - O(2)#1	1.968(7)	0.608008
V(1) - O(1) #1	1.981(6)	0.587175	V(2) - O(3)	1.995(6)	0.565373
V(1) - O(1)#6	1.981(6)	0.587175	V(2) - O(3) #1	1.9956)	0.565373
$V_{V(1)}$ = 3.875			**$V_{V(2)}$ = 3.774**		

Table S2. Bond valence sum calculations of compound **2**.[S2,S3]

Bonds	Bond length (Å)	BVS	Bonds	Bond length (Å)	BVS
V(1) - O(1)	1.604(13)	1.628659	V(2) - O(2)	1.632(11)	1.510038
V(1) - O(3) #1	1.978(6)	0.591955	V(2) - O(4) #2	1.969(7)	0.606367
V(1) - O(3)#4	1.978(6)	0.591955	V(2) - O(4)	1.969(7)	0.606367
V(1) - O(3) #5	1.978(6)	0.591955	V(2) - O(5) #2	1.993(6)	0.568437
V(1) - O(3)	1.978(6)	0.591955	V(2) - O(5)	1.993(6)	0.568437
$V_{V(3)}$ =3.996			**$V_{V(4)}$ = 3.860**		

S2. The valence sum calculations are performed on a program of bond valence calculator, version 2.00 February **1993**, written by C. Hormillosa, with assistance from S. Healy, distributed by I. D. Brown.

S3 I. D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, *B41*, 244-247.

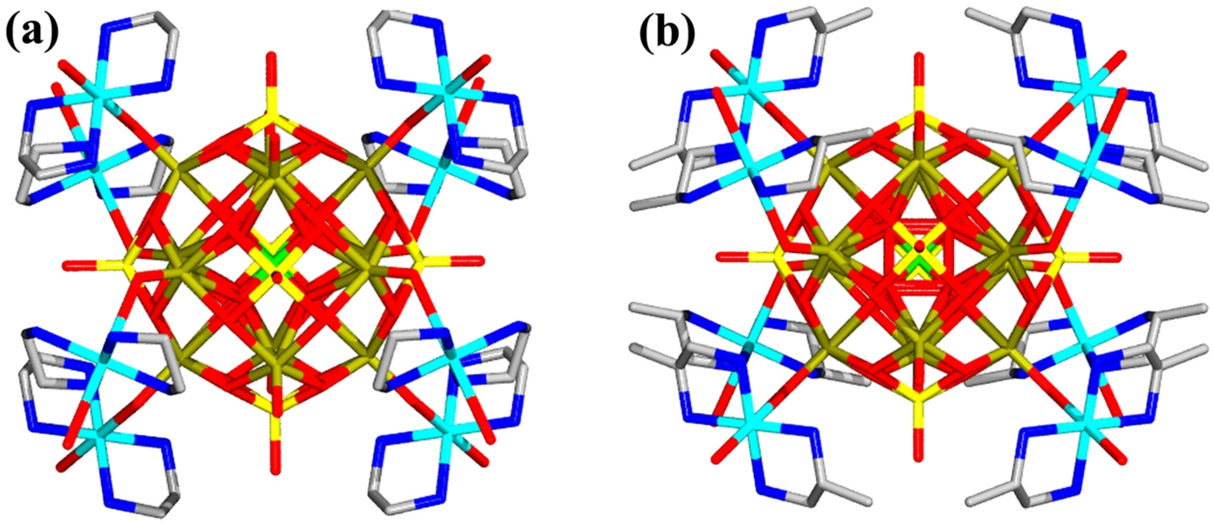

Fig. S1. The stick representation of compounds **1** (a) and **2** (b) decorated by the Cu-organic amine fragments; color codes: red spheres: O; yellow spheres: V; green spheres: P.

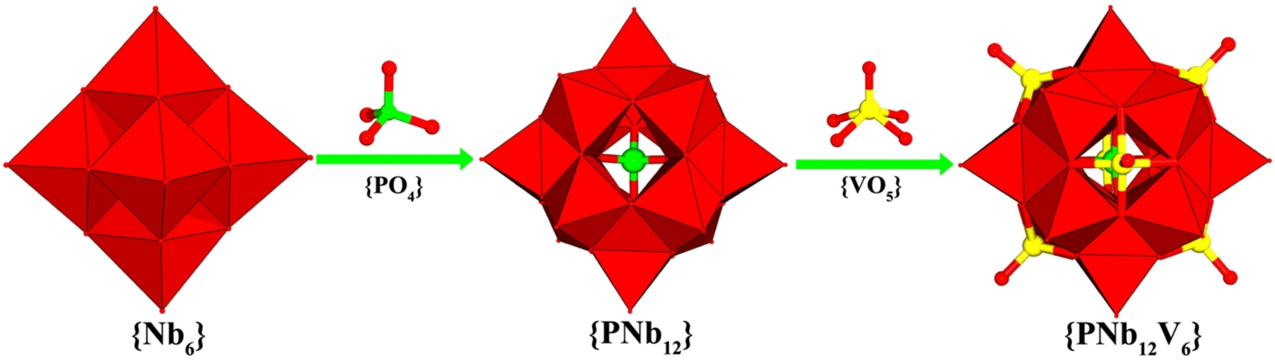

Fig. S2. Schematic presentations of possible mechanisms of the formation of $\{PNb_{12}O_{40}(VO)_6\}$ cluster.

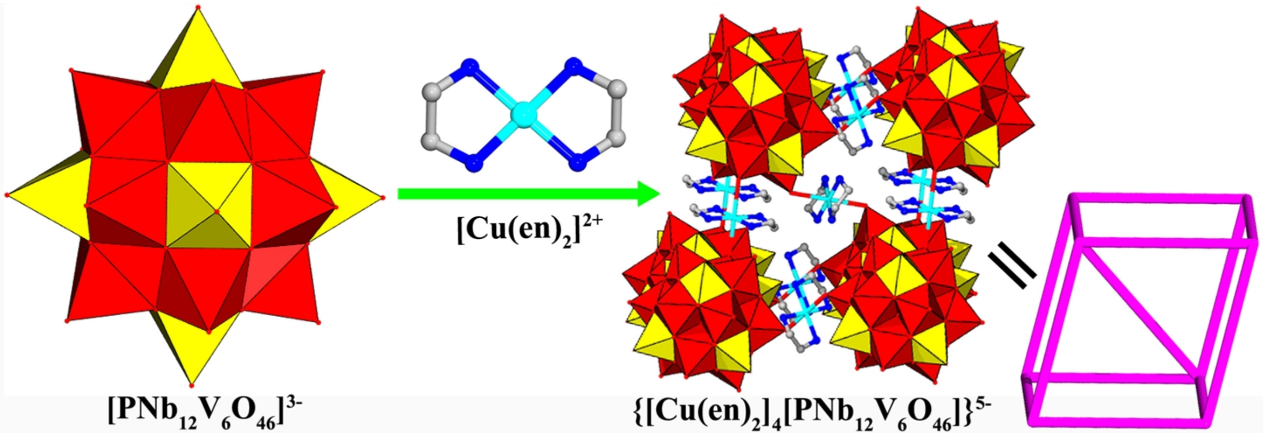

Fig. S3. Structural view and schematic view of a parallelepiped cage composed of eight polyoxoanions.

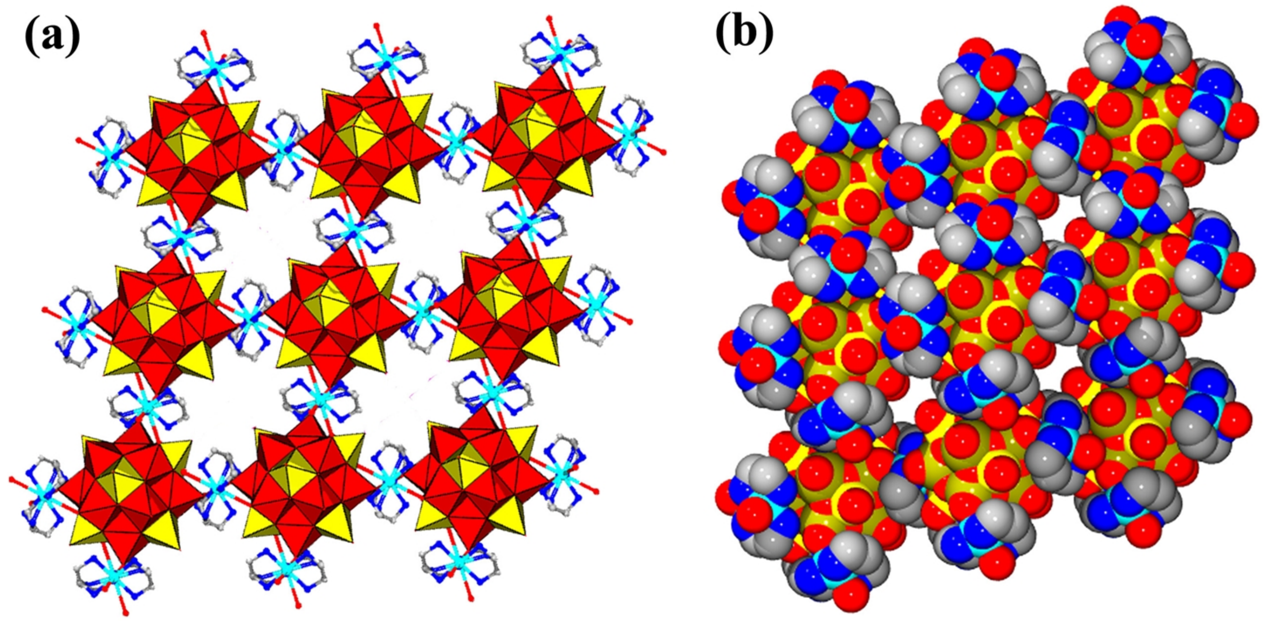

Fig. S4. View of the 3D porous framework of **1** along *a* and *b* directions.

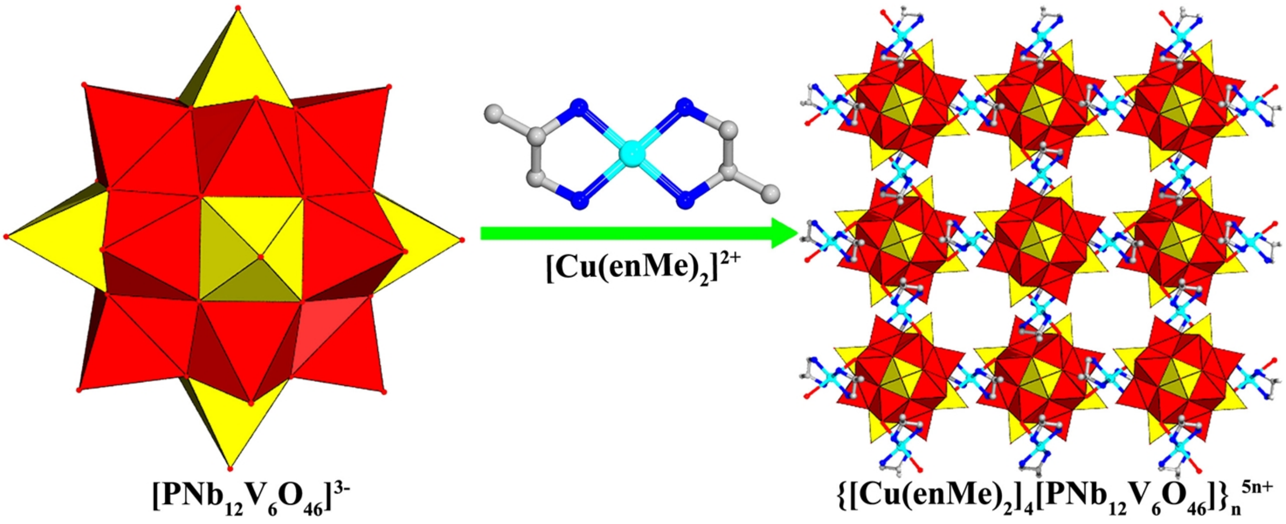

Fig. S5. Structural view of compound **2**.

Section 3 Supplementary Physical Characterizations

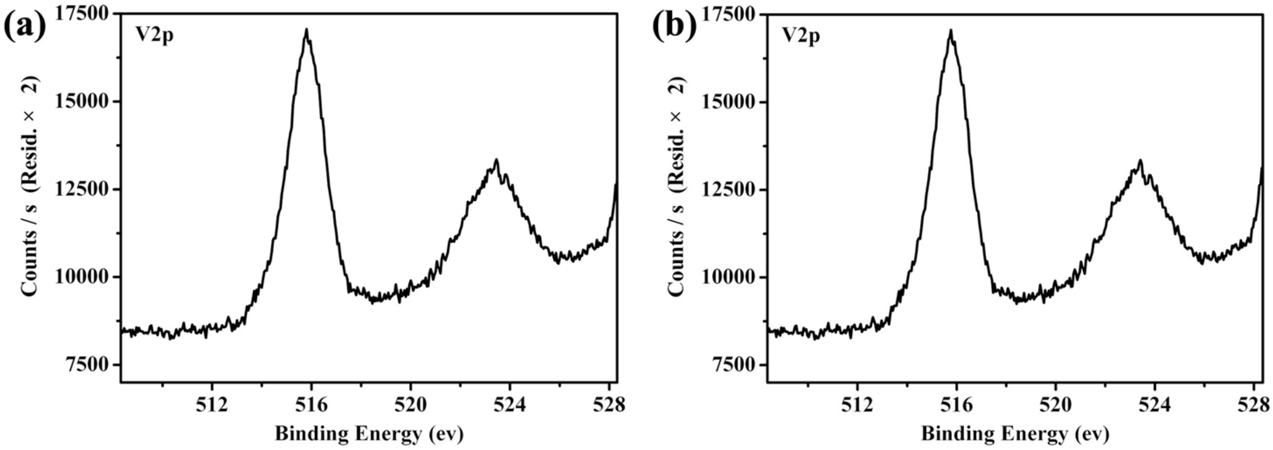

Fig. S6. The XPS spectra of **1** and **2** each give one peak at 515.76 eV for **1**, and 515.79 eV for **2**, which can be ascribed to V^{4+} $2p_{3/2}$, respectively.[11a]

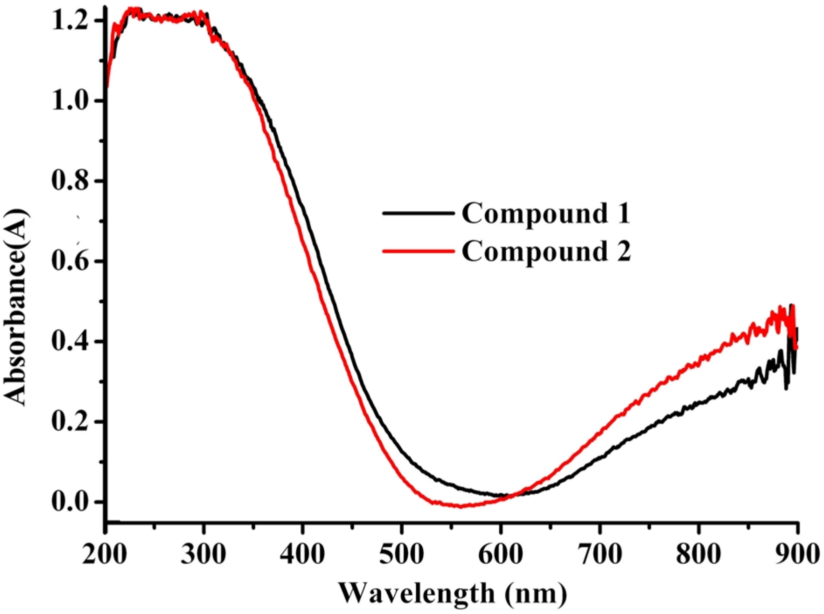

Fig. S7. The solid state UV/Vis absorption spectra of compound **1**(black) and **2** (red).

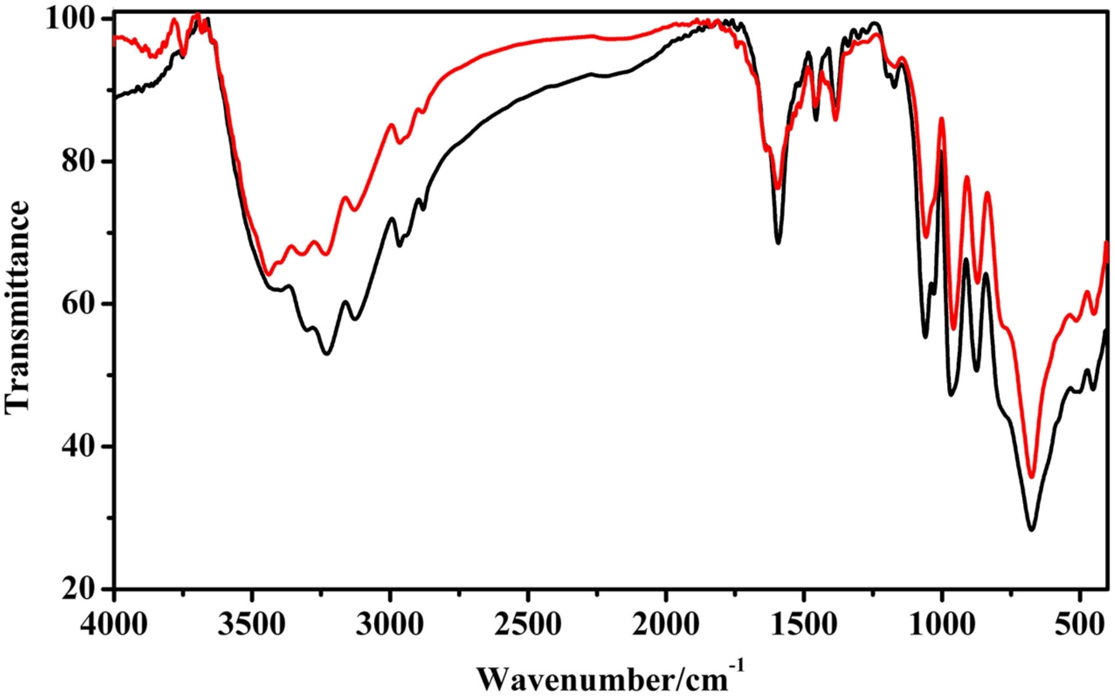

Fig. S8. The IR spectra of **1** (black) and **2**(red).

The IR spectra of **1** and **2** are recorded between 400 and 4000 cm^{-1} with a KBr pellet, which could be used for identification of the characteristic vibration bands of PONs and organic components in products. In the IR spectra, the terminal M = O_t (M = V, Nb) vibrations appear at 961 cm^{-1} and 874 cm^{-1} for **1** and at 964 and 875 cm^{-1} for **2**, respectively.[10,11] The characteristic peaks at 678 and 453 cm^{-1} (**1**) and 675 and 452 cm^{-1} (**2**) are attributed to the bridging Nb–O_b–Nb vibrations, respectively.[4-6] Bands at 1059 cm^{-1} for **1** and 1060cm^{-1} for **2** are assigned to P-O_c vibration, respectively.[S4] Bands in the 1170–1598 cm^{-1} (**1**) and 1172–1593 cm^{-1} (**2**) region are attributed to the organic amine groups.[10-13]

S4 M. Nyman, A. J. Celestian, J. B. Parise, G. P. Holland and T. M. Alam, *Inorg. Chem.*, 2006, **45**, 1043.

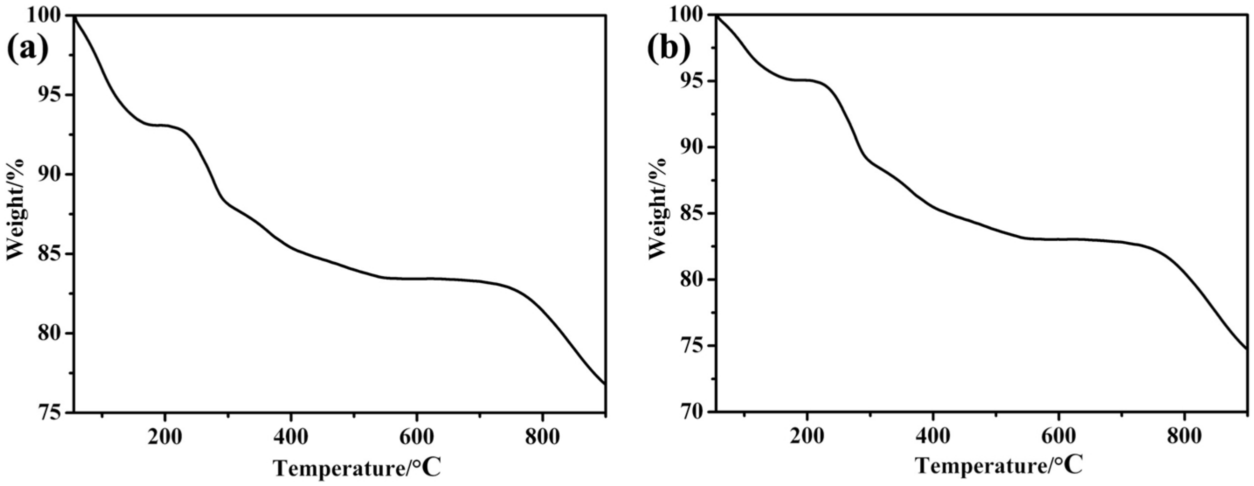

Fig. S9. The TGA curves of **1** and **2**.

To investigate the thermal stabilities of compounds **1** and **2**, thermogravimetric analyses (TGA) were carried out under a nitrogen atmosphere with a heating rate of 10 °C/min. Three continuous weight losses steps were observed on the TGA curve of **1**. The first weight loss of 7.37% (calcd. 7.28%) in the range 55–232°C is attributed to the removal of lattice water molecules and OH^- groups. And the other two weight loss of 10.13% from 232 to 767°C and 6.55% from 767 to 900°C all come from the release of eight en ligands (calcd. 15.28%). For **2**, the first weight loss of 5.86% (calcd. 5.98%) in the range 55–240°C is attributed to the removal of six lattice water molecules and five OH^- groups. And the other two weight loss of 12.27% from 225 to 767°C, and 7.17% from 767 to 900°C all come from the release of eight enMe ligands (calcd. 18.37%).