Supplementary Information

Synthesis, structure, and photocatalytic hydrogen evolution of a trimeric Nb/W addendum cluster

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CONTENTS

1. Table S1. BVS calculation results of all the atoms on polyanion 1a

Atom Code	Bond Valence	Atom Code	Bond Valence	Atom Code	Bond Valence
W1	6.13	O4	1.61	O16	2.02
W2	6.15	O5	2.34	O17	1.55
W3	6.19	O6	2.07	O18	1.89
W4	6.07	O7	1.96	O19	1.59
W5	6.14	O8	1.91	O20	1.61
W6	5.89	O9	2.00	O21	1.88
Nb1	5.22	O10	1.63	O22	1.79
Nb2	4.75	O11	2.05	O23	1.82
Si1	3.99	O12	1.99	O24	2.04
O1	1.98	O13	1.99	O25	1.27
O2	2.06	O14	1.75		
O3	1.87	O15	2.01		

2. Figure S1. The site of three terminal oxygen atoms (O25) on the W6 site

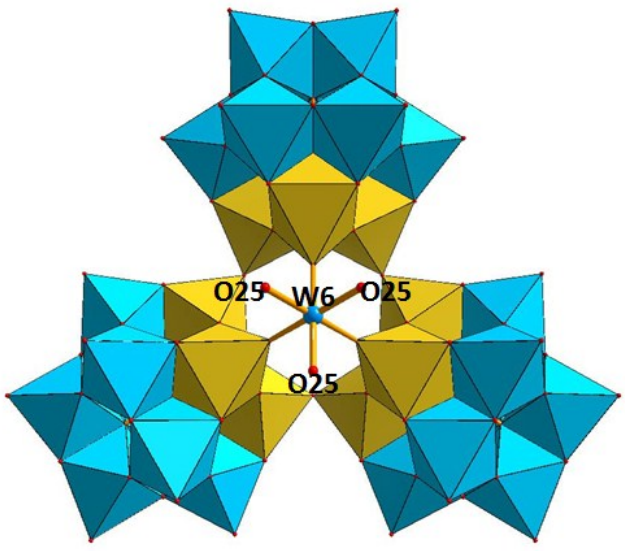

Figure S1. Combined polyhedral/ball-and-stick representation of polyanion **1a**, highlighting the three O25 atoms on the W6 center.

3. Figure S2. IR spectra of 1, SiW_9 and $\{SiW_9(NbO_2)_3\}$

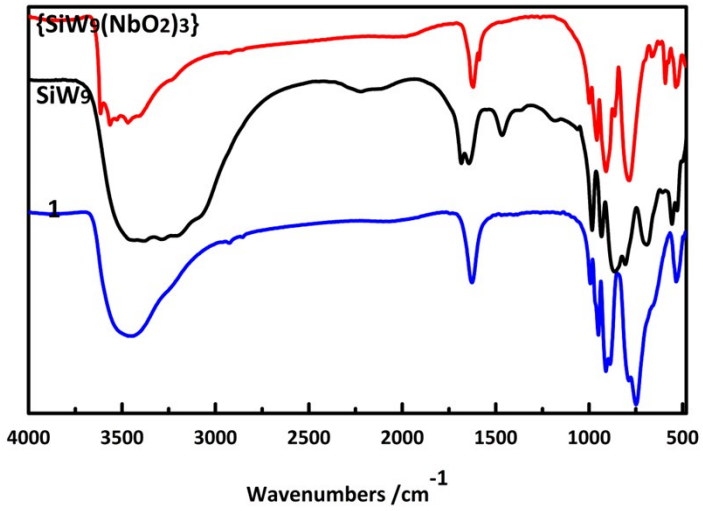

Figure S2. IR spectra of **1**, **SiW_9** and **$\{SiW_9(NbO_2)_3\}$** in the region between 4000 to 500 cm^{-1}.

4. Figure S3. Plots of Kunelka-Munk function versus energy *E* (eV) for $K_7HNb_6O_{19}\cdot 13H_2O$ and compound 1

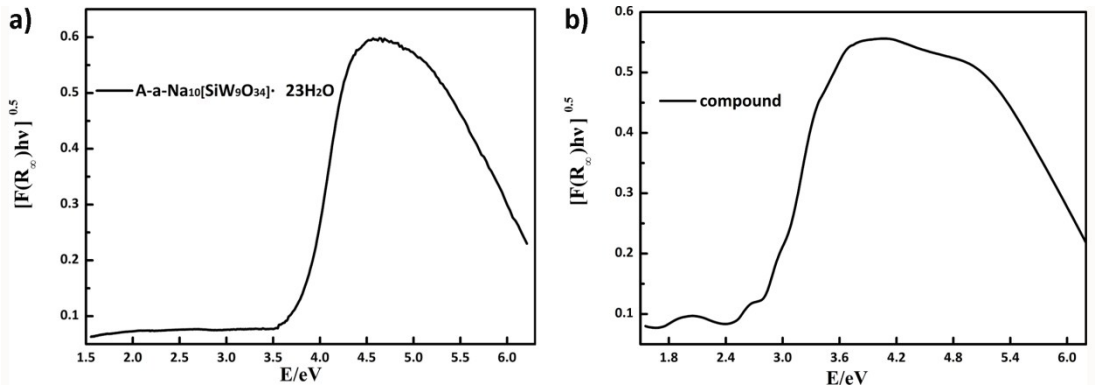

Figure S3. Plots of Kunelka-Munk function versus energy *E* (eV) for compound **1** and **SiW_9**.

To get the plots of Kunelka-Munk function versus energy, we first need to obtain the UV-vis diffuse reflectance spectrum, which can be recorded on a U-4100 spectrometer by using the powder sample. The powder sample was prepared by grinding the single crystals directly. Then, the band gap (E) was determined as the

intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of Kubelka-Munk function versus energy E.

5. Figure S4. UV-vis spectra of 1, SiW_9 and $\{SiW_9(NbO_2)_3\}$

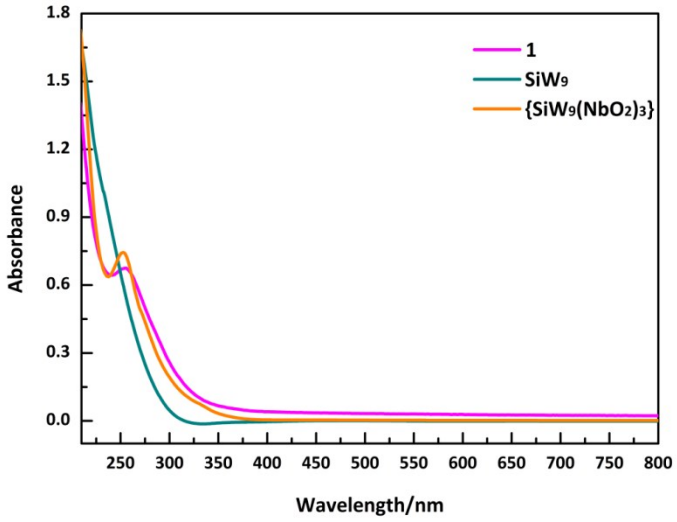

Figure S4. The UV spectra of **1**, SiW_9 and $\{SiW_9(NbO_2)_3\}$ in the region of 800–200 nm.

6. Figure S5. TG curves of 1

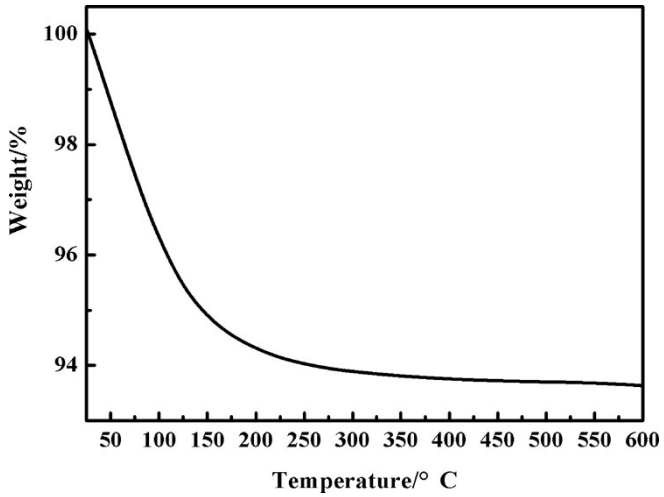

Figure S5. TG curves of **1.**

As shown in Figure S5, the TG curve of compound **1** indicates that the weight

loss of **1** can be regarded as a one-step weightlessness, corresponding to the release of 33 lattice water molecules and three protons in the form of aqua ligands. It should be noted that the number of lattice water molecule from X-ray crystallography is ten, however, the final lattice water molecules in compound 1 were determined by TG results.

7. Figure S6. The comparison of experimental XRPD patterns (blue) and simulated (black) of 1

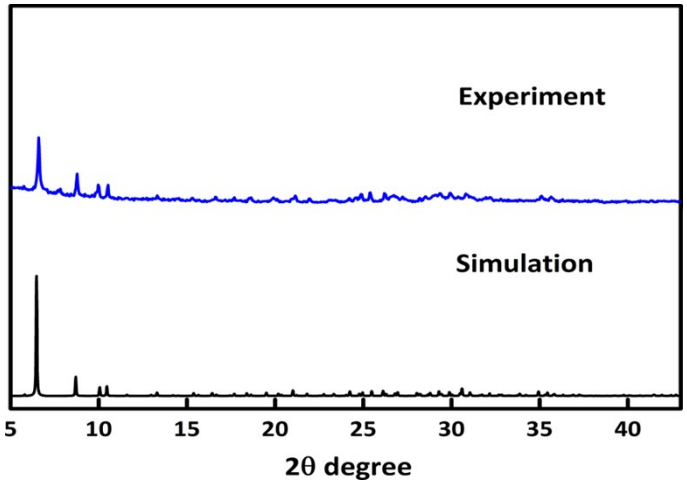

Figure S6. The comparison of experimental XRPD patterns (blue) and simulated (black) of **1.**