Electronic Supporting Informations

An unprecedented arsenic-substituted Lindqvist-type peroxopolyoxoniobate moieties based on the cluster of $\{As_2Nb_4(O_2)_4O_{14}\}^{6-}$

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Synthesis

$K_7H[Nb_6O_{19}]\cdot 13H_2O$ was prepared according to the literature method and identified by IR spectra. The reaction of potassium hexaniobate (2.00 g, 1.46 mmol $K_7H[Nb_6O_{19}]\cdot 13H_2O$) was dissolved in 200 mL of 0.1 M aqueous H_2O_2 (20 mL of a 30-35% aqueous solution dissolved in 180 mL of deionized water) with moderate stirring. HCl solution (1.0 M) was added dropwise to give a yellow, effervescent solution of pH 2.0. Then, $Na_3AsO_4\cdot 12H_2O$ (2.6 g, 6.19 mmol) was added in a single step while the mixture was rapidly stirred to give a clear solution of pH 5.0. Finally, the resulting mixture was stirred at 80℃ for 3 h. The resulting mixture was cooled to room temperature, filtered and then solid CsCl (1.20 g, 7.13 mmol) was added. The resulting clear solution was stirred for twenty minutes, filtered and finally the filtrate was transferred to a straight glass tube, then a mixed solvent of CH_3CH_2OH/H_2O (1:2, volume ratio) was carefully layered onto the solution of filtrate. Last but not least, pure CH_3CH_2OH was carefully layered on. The test tube was sealed with film and left at room temperature. Block colorless crystals appeared at the interface after three weeks 0.5 g (Yield: 24.6%, based on the hexaniobate precursor). Elemental analysis calcd (%) for $H_{23.5}Cs_{2.5}Na_2As_2Nb_4O_{33}$: Cs, 29.16; As, 13.15; Nb, 32.62. found: Cs, 29.13; As, 13.10; Nb, 32.60.

Materials

All chemical reagents were purchased and used without further purification. Elemental analyses were conducted on a Perkin-Elmer 2400-II CHNS/O analyzer. Inductively coupled plasma (ICP) analyses were performed on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. The Infrared spectra (using KBr in pellets) were recorded on a Bruker VERTEX 70 IR spectrometer (4000–400 cm^{-1}). The following abbreviations were used to assign the peak intensities: w= weak，m= medium, and s= strong. UV absorption spectra were obtained with a U-4100 spectrometer at room temperature. Thermogravimetric analyses (TGA) were performed under N_2 atmosphere on a Mettler–Toledo TGA/SDTA851^e instrument with the heating rate of 10 $^oC\ min^{-1}$ from 25 to 800 ^oC. XRPD was performed on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation in the range $2\theta = 10–40°$ at 293 K. Photocatalytic reactions were carried out in a LabSolar-□AG reaction vessel with a magnetic stirrer at room temperature. The reactant solution was evacuated using N_2 several times to ensure complete air removal and then irradiated by using a 300 W Xe lamp. The produced H_2 was analyzed by a GC7900 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (4 mm× 3 m) using N_2 as carrier gas.

X-Ray Crystallography

Intensity data were collected at 293 or 296 K on a Bruker APEX-II CCD diffractometer for **1** using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the

SADABS program. Direct methods were used to solve the structure and refined by full-matrix least-squares on F^2 using the SHELXTL-97 program package. Non-hydrogen atoms were refined anisotropically. Moreover, Cs^+ and lattice H_2O could not be distinguished based on electron densities, and we thus determine the lattice water molecules and Cs^+ ions by elemental analysis. For overall consistency we show in the CIF files the same formula units as in the text with the exact numbers of counter cations and crystal waters (based on elemental analysis and TGA), as this reflects the true bulk composition of **1**.

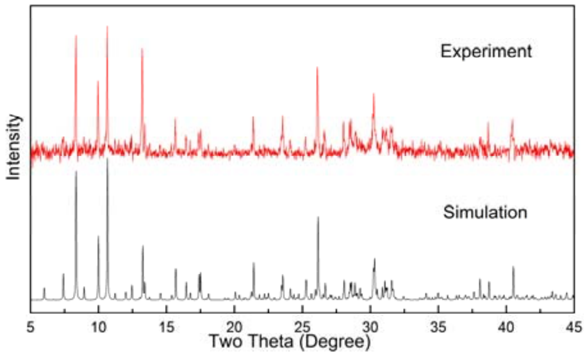

Fig. S1 The PXRD pattern of **1** and its calculated pattern based on the single-crystal solution.

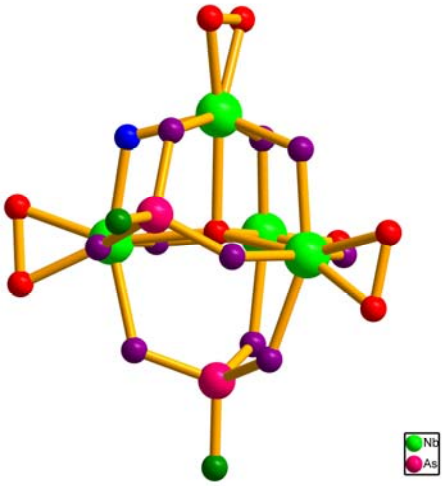

Fig. S2 Charge distribution of O atoms in **1**. Oxygen atoms with different bond valence sums are represented by different colours.

Scheme. S1 The bond valence sum calculations of all the Nb and As atoms on polyanion **1**

Atom lable	Calc. For Nb(VI)
Nb (1)	5.37
Nb (2)	5.40
Nb (3)	5.41
Atom lable	Calc. For As(VI)
As (1)	5.04
As (2)	5.08

Scheme. S2 The bond valence sum calculations of all the oxygen atoms on polyanion **1**

Atom	Bond valence	Atom	Bond valence
O3	1.74	O9	1.67

O4	1.72	O13	1.71
O5	1.78	O14	1.35
O6	1.87	O15	1.36
O7	2.05	O10	1.82

Scheme. S3 The bond valence sum range of all the oxygen atoms on polyanion **1**

Oxygen	Bond valence sum range	Number	Oxygen	Bond valence sum range	Number
🟡	−2.1 ~ −1.9	1	🔵	−1.7~ −1.5	1
🟣	−1.9 ~ −1.7	10	🟢	−1.5 ~ − 1.2	2

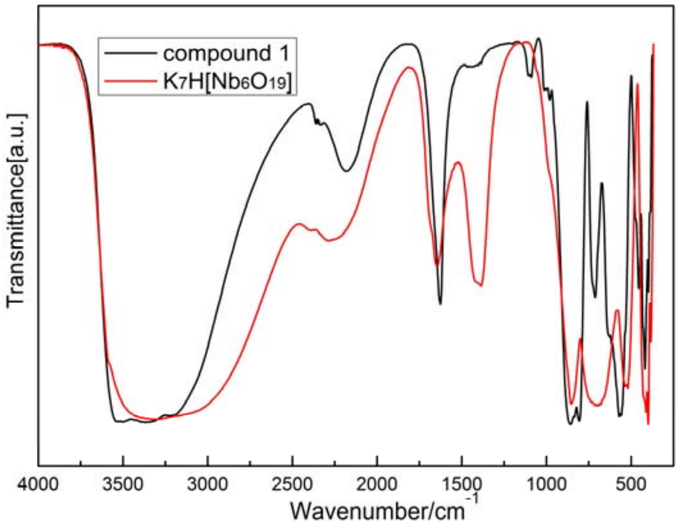

Figure. S3 IR spectra of **1**

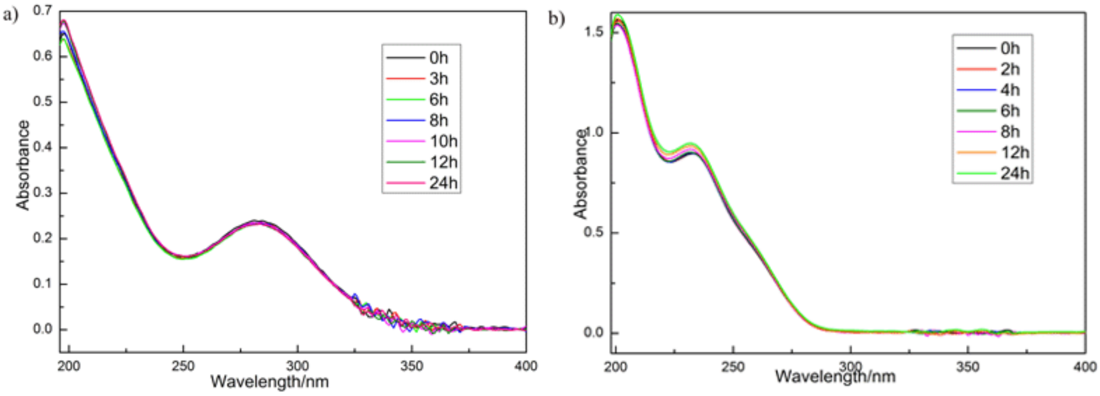

Figure. S4 The influence of time on the stability of **1** in the aqueous solution: a, compound **1**; b, $K_7H[Nb_6O_{19}]\cdot 13H_2O$.

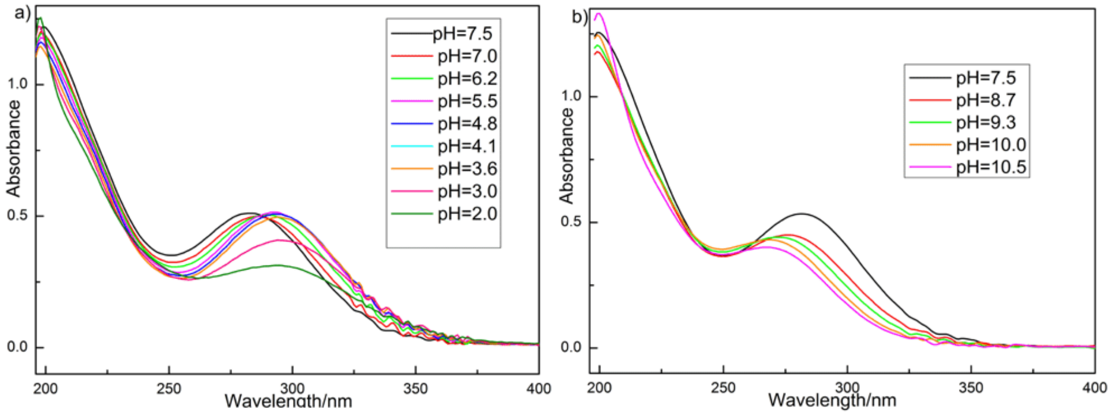

Figure. S5 (a) Influence of the pH values on the stability of compound **1** in aqueous solution: The UV spectral evolution in acidic direction; (b) The UV spectral evolution in alkaline direction.

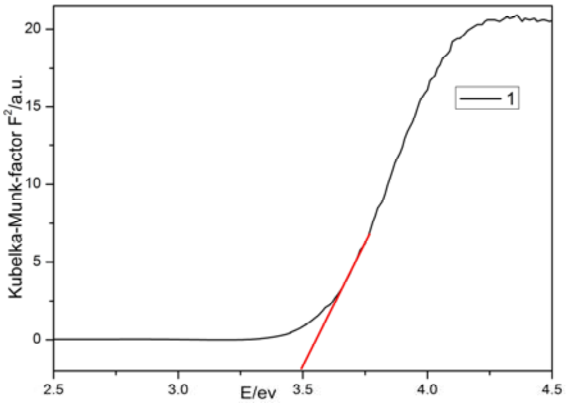

Figure. S6 The diffuse reflectance UV-vis-NIR spectra of K-M function vs energy (eV) of compound **1**.

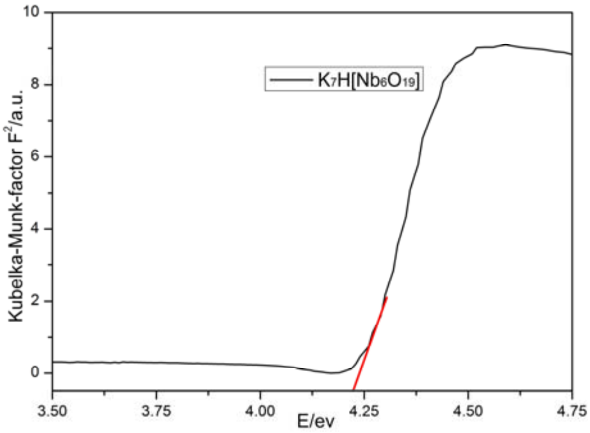

Figure. S7 The diffuse reflectance UV-vis-NIR spectra of K-M function vs energy (eV) of $K_7H[Nb_6O_{19}]\cdot 13H_2O$.

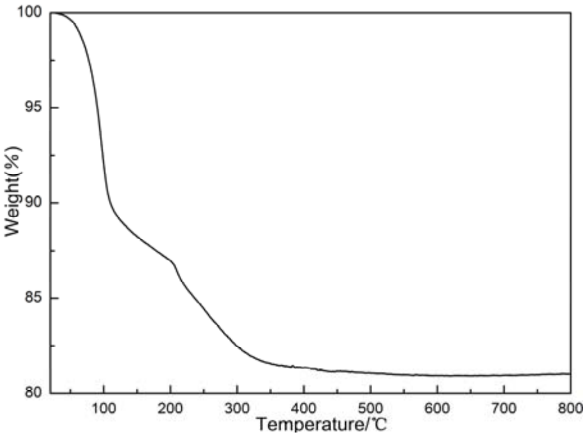

Figure. S8 The TG curves of **1** were measured in the range of 25–800 ºC under nitrogen gas atmosphere with the heating rate of 10 ºC/min.

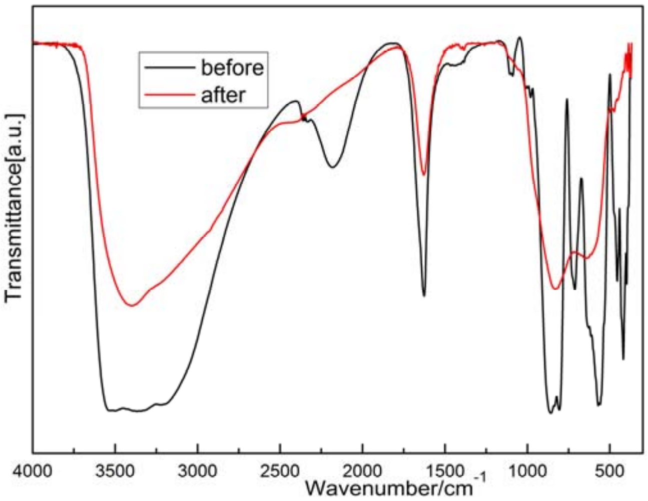

Fig. S9 FT-IR spectra of compound 1 before (black) and after (red) the photocatalytic reactions with 50mg compound **1** and 10 mL CH_3OH, 40 mL 0.5 M HCl, 1.0 mL H_2PtCl_6 solution (1.50 mg Pt).

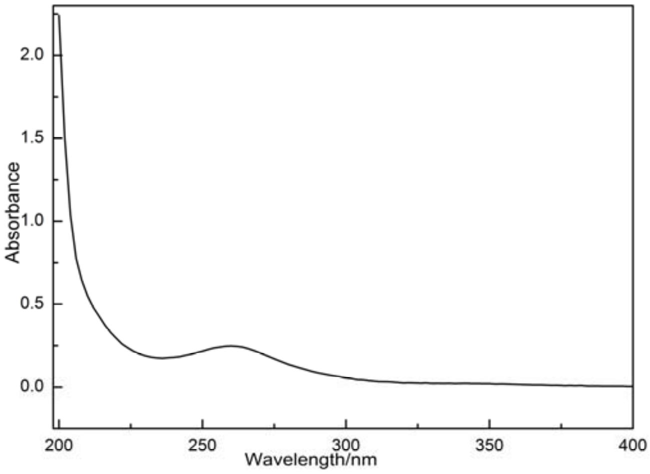

Fig. S10 UV-Vis spectra of compound **1** after the photocatalytic reaction in the solution of H_2PtCl_6.