A New heteropolyniobate based on bicapped Keggin-type {VNb_{14}} cluster with selective adsorption and photocatalytic properties

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1. Materials and methods.

All reagents and solvents for the syntheses were purchased from commercial sources and used as received, except for $K_7HNb_6O_{19}\cdot 13H_2O$, which were synthesized according to the literature[1] and characterized by IR spectra and elemental analysis. Elemental analyses (C, H and N) were measured on a Perkin–Elmer 2400 CHN elemental analyzer; Nb, V, Na and K were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. IR spectrum was performed in the range 4000–400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer. Powder X–ray diffraction measurement was recorded radiation ranging from 5 to 50º at room temperature on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å). Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG–7 analyzer heated from room temperature to 900 ºC under nitrogen at the heating rate of 5 °C·min^{-1}. UV−vis absorption spectroscopy was obtained on a U-3010 spectrophotometer (Hitachi, Japan).

2. Synthesis.

Syntheses of **1a**: V_2O_5 (0.182 g, 1.00 mmol) was added to the solution of NaOH (0.04 g, 1.00 mmol) in water (20 mL) under stirring. Then the resulting yellow solution was added dropwise to the solution of $K_7HNb_6O_{19}\cdot 13H_2O$ (1.370 g, 1.00 mmol) in water (80 mL) under stirring. Subsequently, $Co(NO_3)_2\cdot 6H_2O$ (0.29 g, 1.00 mmol) was added to the solution and the mixture was adjusted to pH 11 using ethanediamine, condensed to 50 mL at 50 °C for 10 h, filtered and then transferred to a 100 mL beaker. One weeks later, the pink precipitate that formed was filtered off.

The filtrate was transferred to a 50 mL open beaker and was allowed to evaporate slowly under ambient temperature (room temperature about 20 °C). Over a period of 6 weeks, colourless block single crystals for X-ray crystallography were obtained, washed with distilled water and then air-dried to give **1a** in 51% yield (based on $K_7HNb_6O_{19}\cdot 13H_2O$). Elemental analysis: Anal. Calcd: C, 4.45; H, 2.76; N, 6.23; Na, 0.85; V, 1.88; Nb, 48.22 %; Found: C, 4.41; H, 2.79; N, 6.19; Na, 0.86; V, 1.85; Nb, 48.24 %.

Synthesis of **1b**: Compound **1b** was prepared by following the procedure described for **1a**, but using a larger quantity of V_2O_5 (0.364 g, 2.00 mmol) and the mixture was adjusted to pH 11 using NaOH (1 mol L^{-1}) solution. The resulting products were colourless block crystals (yield: 58%). Elemental analysis: Anal. Calcd: H, 1.81; K, 9.12; Na, 3.07; V, 1.70; Nb, 43.36; N, 0.93 %; Found: H, 1.84; K, 9.11; Na, 3.10; V, 1.68; Nb, 43.37; N, 0.95 %.

3. Photocatalytic Measurements.

Photocatalytic reactions were carried out in a Pyrex inner-irradiation-type 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 150 W mercury lamp for **1b**. The produced H_2 was analyzed by a GC9800 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm× 2 m) using N_2 as carrier gas.

4. Sorption experiments.

The sorption isotherms were measured at 298 K with an increase in the pressure using an automatic volumetric adsorption equipment (Belsorp mini II). The sample was dried under a dynamic vacuum at 303 K overnight. Before the measurement, the sample was dried again by using the 'outgas' function of the surface area analyzer for 12 h at 303 K. For the measurement of water, methanol and ethanol adsorption, 50 mg sample **1a** were used, respectively.

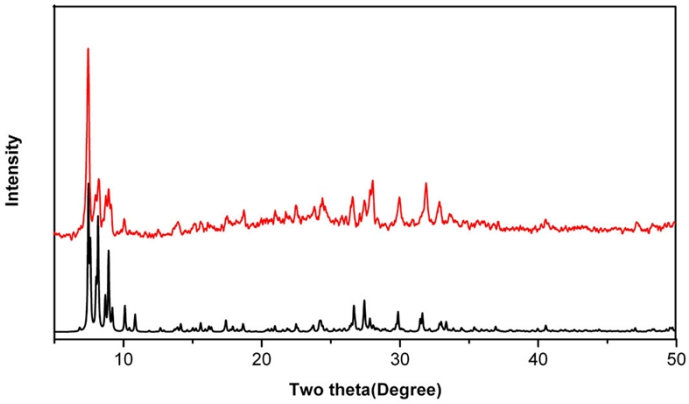

Fig. S1 The XRPD pattern (top) and simulated pattern (bottom) of **1a**.

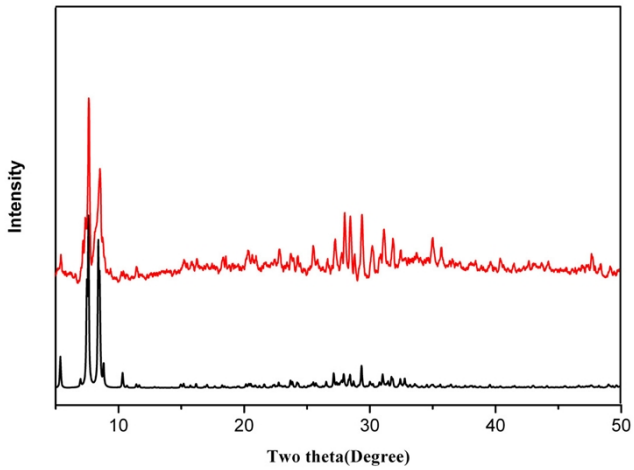

Fig. S2 The XRPD pattern (top) and simulated pattern (bottom) of **1b**.

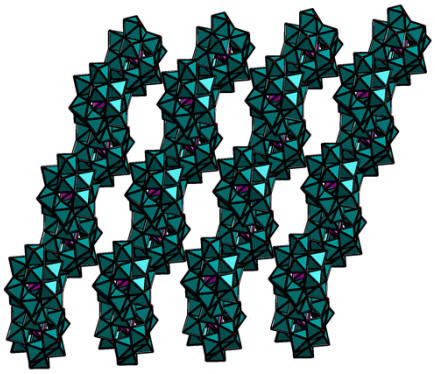

Fig. S3 The 3D architecture with 1D tetragonum channels built by {VNb_{14}} units and Na cations for **1a** (H atom, Na atom, water, and en molecules are omitted for clarity).

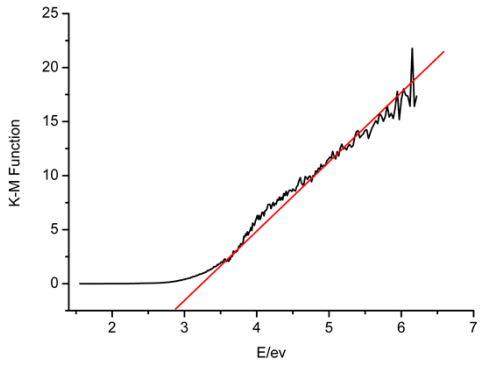

Fig. S4 The diffuse reflectance UV–vis-NIR spectra of K–M function vs. energy (eV) of compound **1a**.

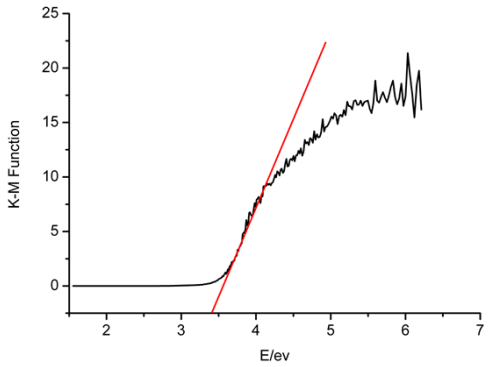

Fig. S5 The diffuse reflectance UV–vis-NIR spectra of K–M function vs. energy (eV) of compound **1b**.

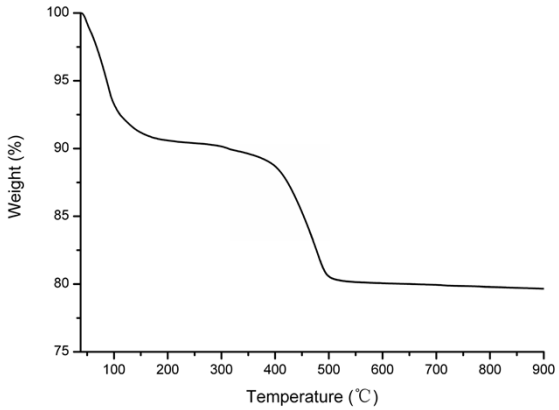

Fig. S6 The TGA curve of **1a**.

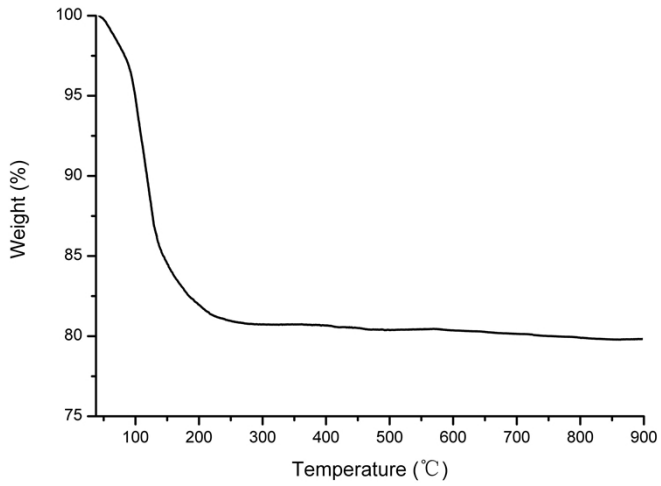

Fig. S7 The TGA curve of **1b**.

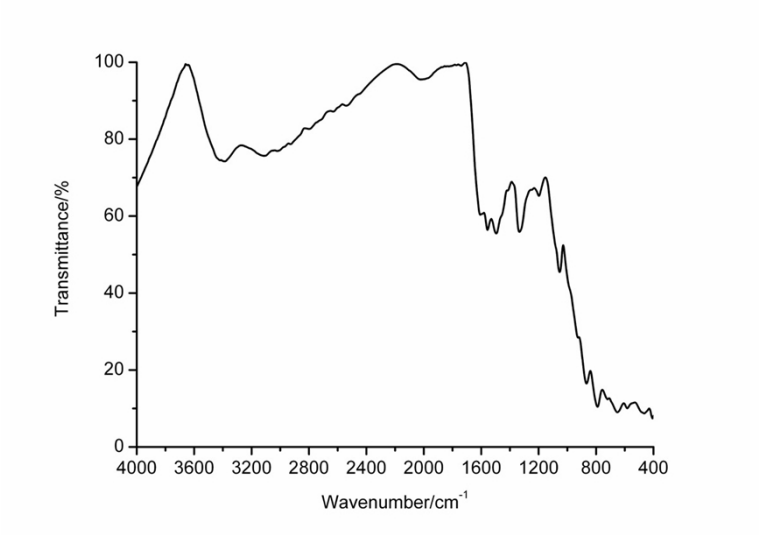

Fig. S8 The IR spectrum of compound **1a**.

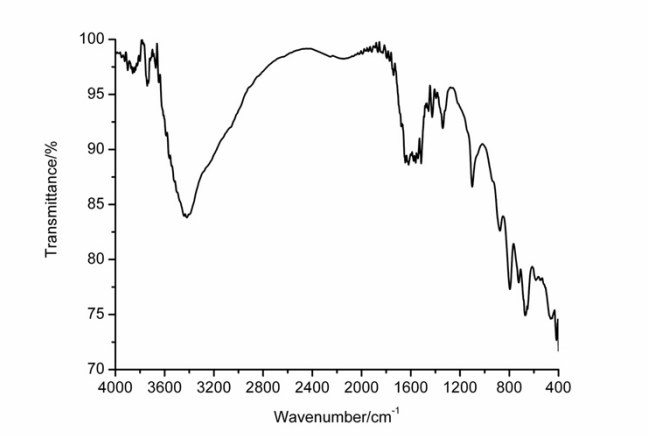

Fig. S9 The IR spectrum of compound **1b**.

References

1 M. Filowitz, R. K. C. Ho, W. G. Klemperer, W. Shum, *Inorg. Chem.,* 1979, **18**, 93.