A Rare Three-Dimensional Polyniobotungstate-Based Framework and Its Structural Transformation in A Single-Crystal-to-Single-Crystal Process Induced by Iodide Ion

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Section S1 Synthesis and Methods

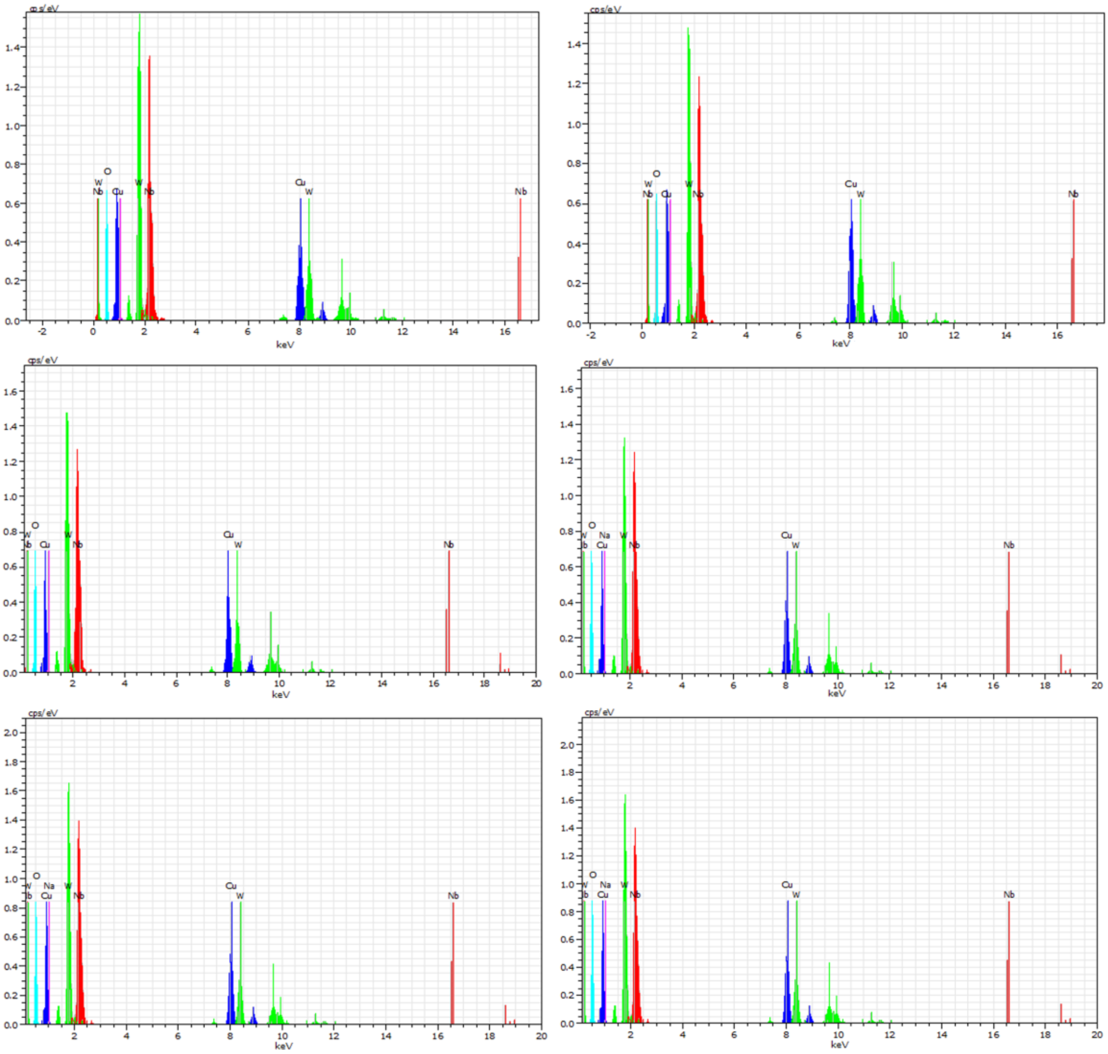
Synthesis of 1: $K_7HNb_6O_{19}\cdot 13H_2O$ (0.206 g, 0.15 mmol), $Na_2WO_4\cdot 2H_2O$ (0.203 g, 0. 617 mmol) and $Cu(Ac)_2\cdot 3H_2O$ (0.400 g, 2 mmol) were stirred in 4 mL distilled water, and then 0.25 ml en was added to the solution drop by drop under continuous stirring for 5 minutes, followed by adding 0.5 ml 2M NaOH aqueous solution. After stirred about 30 min, the mixture was sealed in a Teflon-lined autoclave (23 mL) and heated at 160 ℃ for 4 days, and then cooled to room temperature. Purple blue block-like crystals of **1** were obtained in a yield of 47.9% (based on Nb).

Single crystal structure analysis: The crystallography data of **1** was collected on a Bruker APEX II diffractometer at room temperature equipped with a fine focus, 2.0 kW sealed tube X-ray source (MoK radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. The empirical absorption correction was based on equivalent reflections. Structures were solved by direct methods followed by successive difference Fourier methods. Computations were performed using SHELXTL and final full-matrix refinements were against F2. All non-hydrogen atoms were refined anisotropically. CCDC-1433428 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Others: All raw materials were commercially purchased and directly used without further purification. $K_7H[Nb_6O_{19}]\cdot 13H_2O$ complex was prepared as described in the literature (M. Filowitz, R. K. C. Ho, W. G. Klemperer, W. Shum, *Inorg. Chem*, 1979, **18**, 93). PXRD patterns were obtained by using a RIGAKU-Miniflex II diffractometer with Mo-$K\alpha$ radiation (λ = 0.71069 Å). EDS analyses were performed on a Hirox SH4000-M type desktop scanning electron microscopy (SEM) of Japan Haoshi. IR spectrum was determined in the range 400 - 4000 cm^{-1} on a Nicolet iS50 Fourier transform infrared (FT/IR) spectrometer. TG analysis was recorded on a NETZSCH STA 449C thermal analyzer instrument in flowing air atmosphere with a heating rate of 10℃ min^{-1}.

Section S2 Additional Tables

Table S1. EDS analyses of **1**, showing the Nb/W ratio in **1** is 1:1. The total amount of Nb and W is normalized to 100%.



Tests	Experimental values from EDS			Calculated values from formula		
	Nb (wt%)	W (wt%)	Mole Ratio of Nb/W	Nb (wt%)	W (wt%)	Mole Ratio of Nb/W
1	35.07	64.93	1.07	33.57	66.42	1.00
2	31.64	68.36	0.92			
3	34.05	65.95	1.02			
4	33.55	66.45	0.99			
5	34.16	65.84	1.03			
6	33.42	66.58	0.99			
Average	33.65	66.35	1.01			

Table S2. Hydrogen bonds for 1 [Å and Degree].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1B)...O(1)	0.90	2.16	3.042(18)	165.9
N(2)-H(2A)...O(5)	0.90	2.28	3.051(17)	144.2
N(2)-H(2B)...O(6)#7	0.90	2.07	2.964(17)	169.4
N(2)-H(2B)...O(5)#7	0.90	3.48	4.203(18)	139.4

Symmetry transformations used to generate equivalent atoms: #1: -x+1, -y, z; #2: x, y, -z; #3: x, y, -z+1; #4: x+1/2, -y+1/2, z+1/2; #5: x-1/2, -y+1/2, z-1/2; #6: -x+1, -y, -z; #7: x+1/2, -y+1/2, -z+1/2.

Section S3 Additional Structural Figures

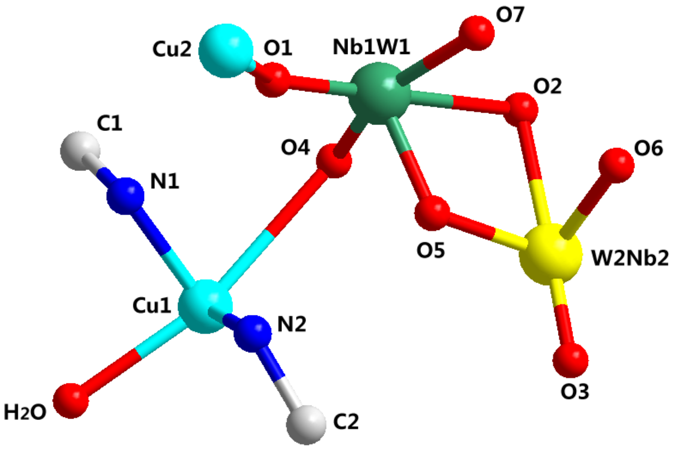


Figure S1. View of the asymmetric unit of **1**, in which the crystallographically independent atoms consist of two metal sites (Nb1W1 and W2Nb2) simultaneously occupied by Nb and W elements, seven oxygen atoms, two half en ligands, and one water ligand. In the asymmetric unit, the special positions include 1) the W2/Nb2 and Cu1 sites are on a mirror plane at z = 0; 2) the Cu2 is on a mirror plane at z - 0.5; 3) the O2 is at a site with 2/m symmetry; 4) the O7 is at a site with twofold symmetry; 5) the O3, O4 and O1W are at sites with m-symmetry; 6) the two half en ligands lay across a mirror planar.

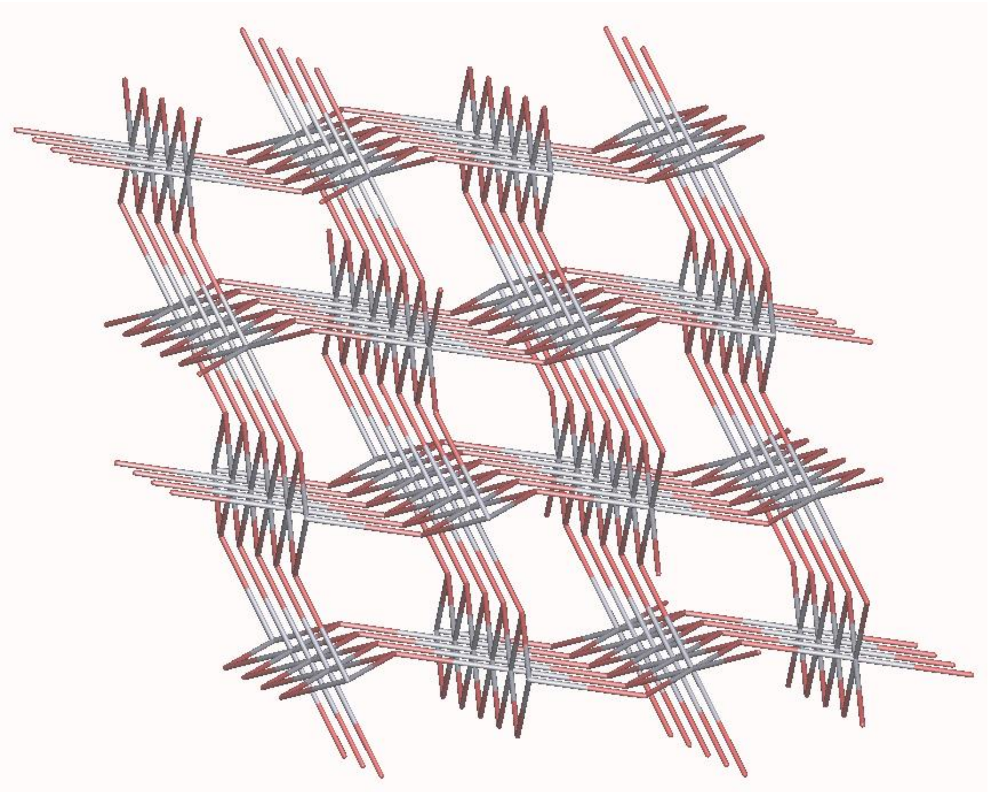


Figure S2. View of rtl-type structural topology of compound **1** based on simplifying polyoxoanions $[Nb_3W_3O_{19}]^{5-}$ as 6-connected nodes and Cu^+ ions as 3-connected linkers.

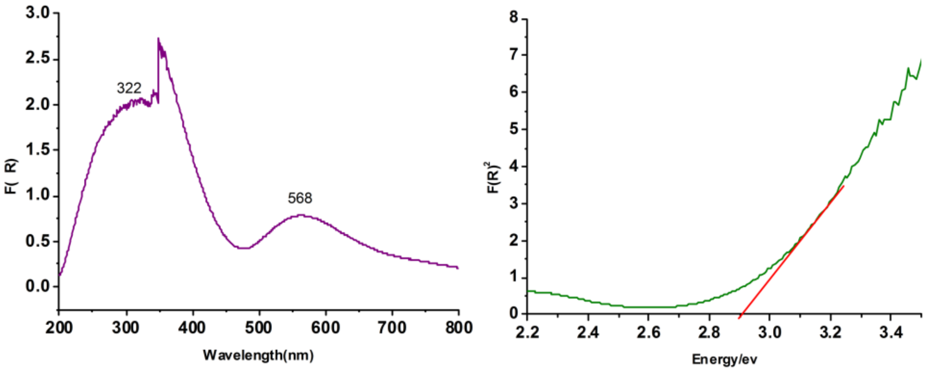


Figure S3. Solid-state diffuse reflectance UV−vis spectrum of **1**.

Optical absorption spectrum of **1** shows two broad peaks centring at 322 and 568 nm, which are attributed to the charge transfer of O → M (M = Nb/W or W/Nb) and the d–d transfer of copper ions, respectively. The energy gap is calculated roughly as 2.90 eV by using the Kubelka–Munk function.

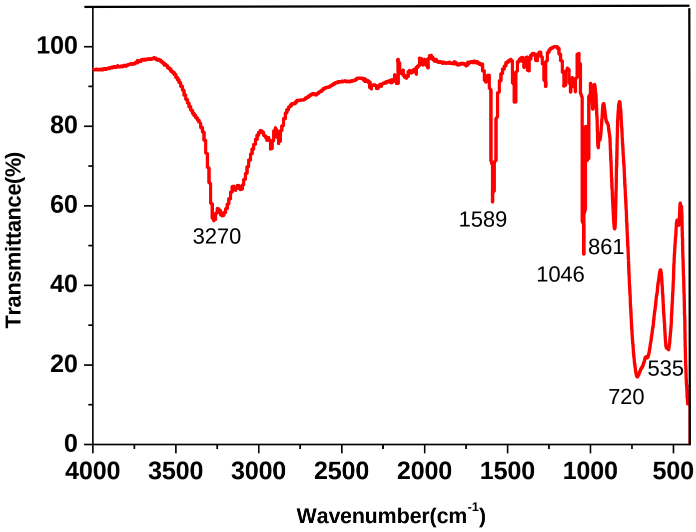


Figure S4. The IR spectrum of compound **1**.

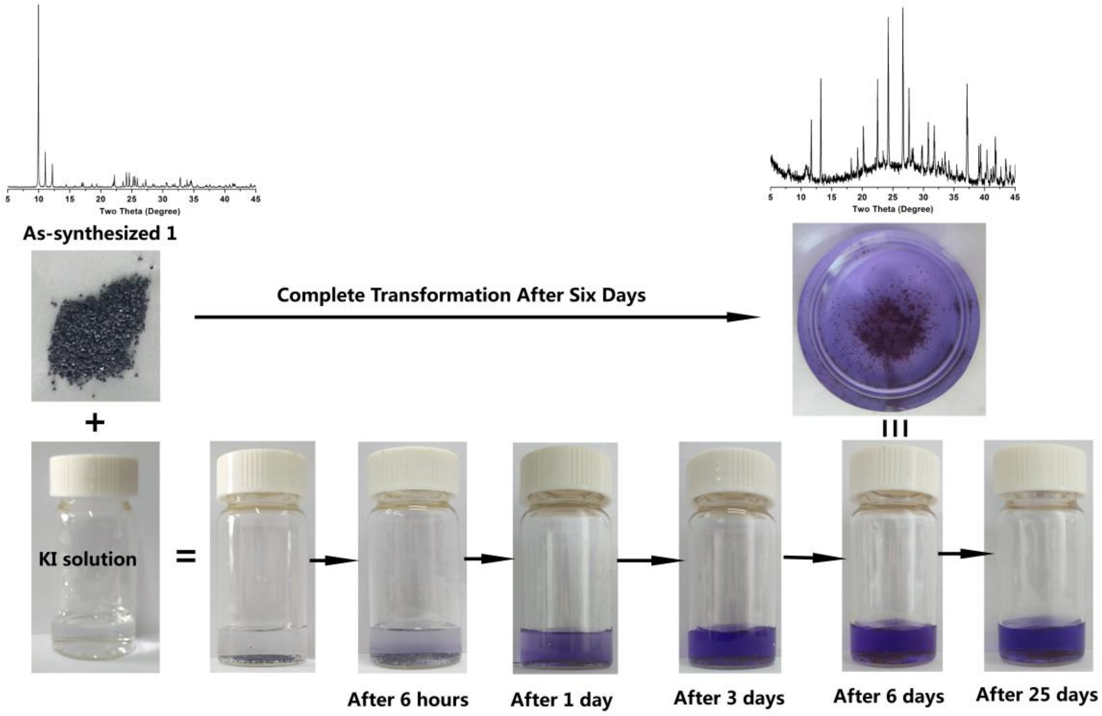


Figure S5. View of the phase transformation process from crystal **1** to copper halide **2**. The color change from initial colorless to final violet should be attributed to the solid-liquid reaction of crystal **1** with I$^-$ ions to yield crystal **2** and I_2.