Supporting Information

A novel organic-inorganic hybrid constructed from the Nyman-type dititanoniobate $[Ti_2Nb_8O_{28}]^{8-}$ and copper-organic cations†

Yu-Teng Zhang, Peng Huang, Chao Qin*, Li-Kai Yan, Bai-Qiao Song, Zhao-Xia Yang, Kui-Zhan Shao and Zhong-Min Su*

Institute of Functional Material Chemistry, Key Lab of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, People's Republic of China

*Corresponding author. Tel.: (+86)-431-85099108.

E-mail address: zmsu@nenu.edu.cn.

1. Materials and Methods

All the reagents except $K_7HNb_6O_{19}\cdot 13H_2O$[1] were obtained from commercial sources and used without further purification. 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 (PXRD) measurement was recorded radiation ranging from 5 to 50º at room temperature on a Siemens D5005 diffractometer with Cu-*Kα* (λ = 1.5418 Å). Elemental analyses (Nb, Ti, Cu) were performed on a Plasma-SPEC(I) inductively coupled plasma atomic emission spectrometer. X-ray photoelectron spectroscopy analyses were performed on a VG ESCALABMKII spectrometer with an Al-Kα (1486.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis. Field-emission scanning electron microscopy (FE-SEM) images were obtained with a XL30 ESEM FEG micro-scope. Solid-state luminescent spectrum was measured on a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 ºC under nitrogen at the heating rate of 10 °C·min^{-1}. The UV-Visible diffuse reflectance spectrum was recorded at ambient temperature on a Cary-500 UV-Vis Spectrophotometer.

2. Synthesis

$K_7HNb_6O_{19}\cdot 13H_2O$ (0.10 g), $Cu(NO_3)_2\cdot 3H_2O$ (0.10 g), titanium isopropoxide (0.3 ml) were mixed in water (8 ml). Then five drops of en were added to adjust the pH value of mixture to 11.5-12.2. The mixture was transferred into a 23ml capacity PTFE-lined autoclave and heated at 140 °C for 3 days. After slow cooling to room temperature, purple block-like crystals for X-ray crystallography were obtained, washed with distilled water and then air-dried to give **1** in 56% yield (based on $K_7HNb_6O_{19}\cdot 13H_2O$). Elemental analysis calcd (%) for **1**: Nb 32.68, Ti 4.21, Cu 44.71; found: Nb 32.57, Ti 4.17, Cu 44.82.

	Ti1	Nb1	Nb2	Nb3	Nb4
Compound 1	4.00	4.91	4.95	4.91	4.94

Table S1. BVS results for compound **1.**

Empirical formula	$C_{16}H_{92}N_{16}Cu_4Ti_2Nb_8O_{42}$
Formula weight	2274.15
Crystal system	Triclinic
Space group	P-1
Temperature	293(2) K
Wavelength	0.71069 Å
Unit-cell dimensions	a = 11.059(5) Å, α = 102.834(5)°
	b = 12.347(5) Å, β = 109.562(5)°
	c = 15.178(5) Å, γ = 105.878(5)°
Volume	1762.2(1) $Å^3$
Z	1
Density (calculated)	2.118 g/cm^3
Absorption coefficient	2.739 mm^{-1}
F(000)	1066
Crystal size	0.30 x 0.22 x 0.17 mm^3
Limiting indices	$-13 \leqq h \leqq 13$, $-14 \leqq k \leqq 14$, $-18 \leqq l \leqq 13$
Theta range for data collection	2.01-25.00°
Reflections collected	9094
Independent reflections	6132 [R(int) = 0.0250]
Completeness to theta = 25.00°	98.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6132 / 4 / 411
Goodness-of-fit on F^2	1.003
Final R indices [I > 2sigma(I)]	R_1 = 0.0422, wR_2 = 0.1358
R indices (all data)	R_1 = 0.0473, wR_2 = 0.1422
Largest diff. peak and hole	2.101 and -0.809 eA^{-3}

Table S2. Crystallographic data for compound **1**

Length [Å]			
Ti1-O3#1	1.811(4)	Nb4-O14#1	1.983(4)
Ti1-O12#1	1.833(4)	Nb4-O10	1.982(4)
Ti1-O5#1	1.990(4)	Nb4-O9	1.993(4)
Ti1-O8	2.011(4)	Nb4-O12	2.026(4)
Ti1-O4#1	2.134(4)	Nb4-O4#1	2.501(4)
Ti1-O4	2.153(4)	Cu1-N5#2	1.997(6)
Nb1-O6	1.755(4)	Cu1-N5	1.997(6)
Nb1-O2	1.922(4)	Cu1-N6#2	2.008(6)
Nb1-O14	1.919(4)	Cu1-N6	2.008(6)
Nb1-O8	2.096(4)	Cu2-N7#3	2.015(6)
Nb1-O5	2.098(4)	Cu2-N7	2.015(6)
Nb1-O4	2.415(4)	Cu2-N8#3	2.025(6)
Nb2-O7	1.750(4)	Cu2-N8	2.025(6)
Nb2-O9	1.919(4)	Cu2-O2W	2.5784(9)
Nb2-O1#1	1.924(4)	Cu3-N2	2.000(6)
Nb2-O5	2.091(4)	Cu3-N2#4	2.000(6)
Nb2-O8	2.092(4)	Cu3-N1	2.025(6)
Nb2-O4#1	2.403(4)	Cu3-N1#4	2.025(6)
Nb3-O13	1.764(4)	Cu3-O1W	2.5790(9)
Nb3-O10#1	1.975(4)	Cu4-N4	2.009(7)
Nb3-O2	1.983(4)	Cu4-N4#5	2.009(7)
Nb3-O1	1.991(4)	Cu4-N3	2.018(8)
Nb3-O3	2.026(4)	Cu4-N3#5	2.018(8)
Nb3-O4	2.462(4)	Cu4-O3W	2.5891(8)
Nb4-O11	1.758(4)		
Angle [°]			
O3#1-Ti1-O12#1	105.37(19)	O1#1-Nb2-O8	90.27(17)
O3#1-Ti1-O5#1	97.14(18)	O5-Nb2-O8	74.57(16)
O12#1-Ti1-O5#1	95.87(18)	O7-Nb2-O4#1	175.61(19)
O3#1-Ti1-O8	95.80(18)	O9-Nb2-O4#1	79.57(15)
O12#1-Ti1-O8	96.43(18)	O1#1-Nb2-O4#1	79.38(15)
O5#1-Ti1-O8	159.11(17)	O5-Nb2-O4#1	73.65(14)
O3#1-Ti1-O4#1	86.76(17)	O8-Nb2-O4#1	74.19(14)
O12#1-Ti1-O4#1	167.88(17)	O13-Nb3-O10#1	103.4(2)
O5#1-Ti1-O4#1	82.38(16)	O13-Nb3-O2	101.8(2)
O8-Ti1-O4#1	82.05(16)	O10#1-Nb3-O2	87.76(18)
O3#1-Ti1-O4	167.79(17)	O13-Nb3-O1	104.4(2)
O12#1-Ti1-O4	86.84(17)	O10#1-Nb3-O1	88.14(18)
O5#1-Ti1-O4	81.42(15)	O2-Nb3-O1	153.78(16)
O8-Ti1-O4	82.46(15)	O13-Nb3-O3	105.2(2)
O4#1-Ti1-O4	81.03(16)	O10#1-Nb3-O3	151.40(16)
O6-Nb1-O2	102.7(2)	O2-Nb3-O3	85.89(17)

O6-Nb1-O14	103.7(2)	O1-Nb3-O3	85.41(17)
O2-Nb1-O14	94.65(18)	O13-Nb3-O4	178.56(19)
O6-Nb1-O8	102.9(2)	O10#1-Nb3-O4	77.53(15)
O2-Nb1-O8	152.48(16)	O2-Nb3-O4	77.11(15)
O14-Nb1-O8	89.14(17)	O1-Nb3-O4	76.72(14)
O6-Nb1-O5	103.2(2)	O3-Nb3-O4	73.87(15)
O2-Nb1-O5	89.96(17)	O11-Nb4-O14#1	103.9(2)
O14-Nb1-O5	150.94(16)	O11-Nb4-O10	104.7(2)
O8-Nb1-O5	74.35(15)	O14#1-Nb4-O10	87.41(18)
O6-Nb1-O4	176.35(19)	O11-Nb4-O9	104.4(2)
O2-Nb1-O4	79.36(15)	O14#1-Nb4-O9	151.55(17)
O14-Nb1-O4	79.01(15)	O10-Nb4-O9	87.90(18)
O8-Nb1-O4	74.64(14)	O11-Nb4-O12	104.9(2)
O5-Nb1-O4	73.68(14)	O14#1-Nb4-O12	84.82(17)
O7-Nb2-O1#1	103.2(2)	O10-Nb4-O12	150.41(17)
O9-Nb2-O1#1	93.46(18)	O9-Nb4-O12	85.54(18)
O7-Nb2-O5	103.22(19)	O11-Nb4-O4#1	178.85(19)
O9-Nb2-O5	89.86(17)	O14#1-Nb4-O4#1	75.77(15)
O1#1-Nb2-O5	151.75(16)	O10-Nb4-O4#1	76.45(15)
O7-Nb2-O8	102.1(2)	O9-Nb4-O4#1	75.85(15)
O9-Nb2-O8	152.32(16)	O12-Nb4-O4#1	73.97(15)

[a] Symmetry codes for compound **1**: #1 -x,-y+1,-z; #2 -x+1,-y+1,-z; #3 -x,-y+1,-z-1; #4 -x,-y+2,-z; #5 -x+1,-y+2,-z+1.

Table S3. Selected bond lengths and angles of compound **1**.

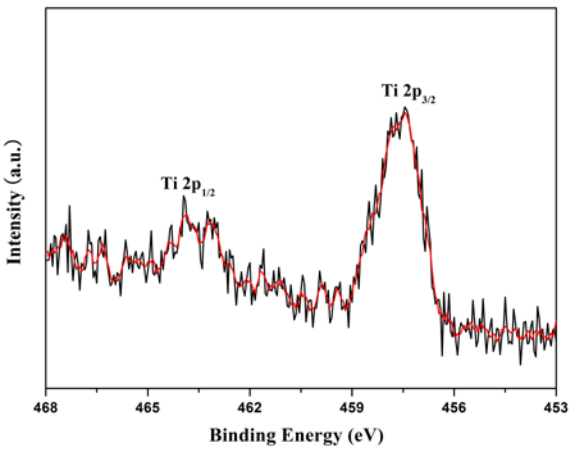

Fig. S1. The XPS spectrum of compound **1** for Ti $2p_{1/2}$ and Ti $2p_{3/2}$.

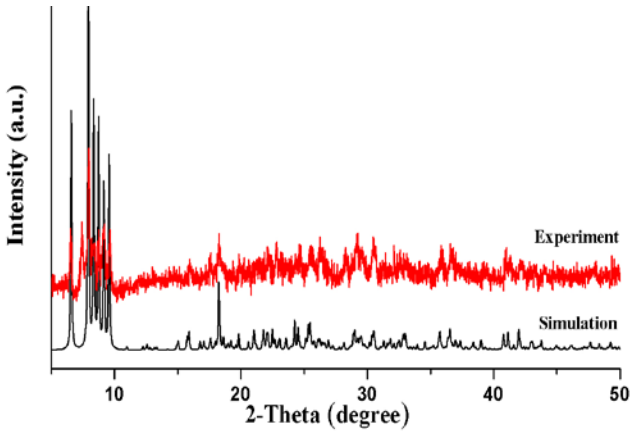

Fig. S2. The experimental (red) and simulated (black) powder X-Ray diffraction patterns for **1**.

Fig. S3. SEM images of the untreated sample (a), the resulted samples after immersed in the solution at pH =3 (b), and 12 (c), respectively.

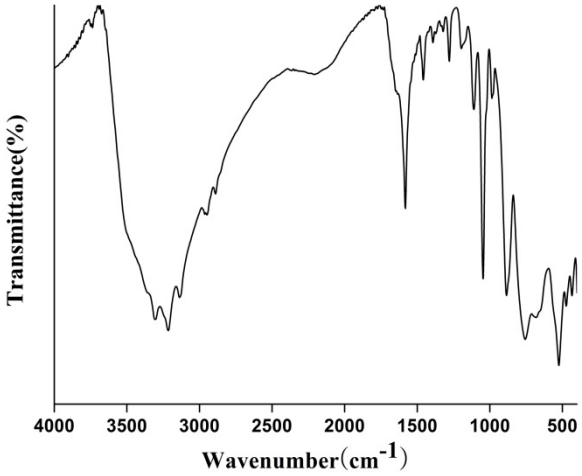

Fig. S4. The IR spectrum of compound **1**.

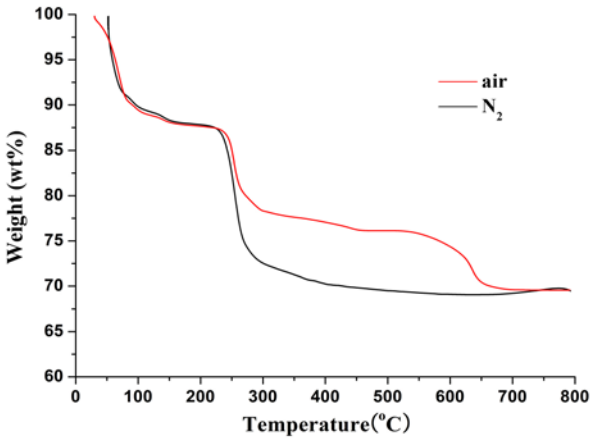

Fig. S5. The TGA curves of compound **1** under nitrogen (black) and air (red).

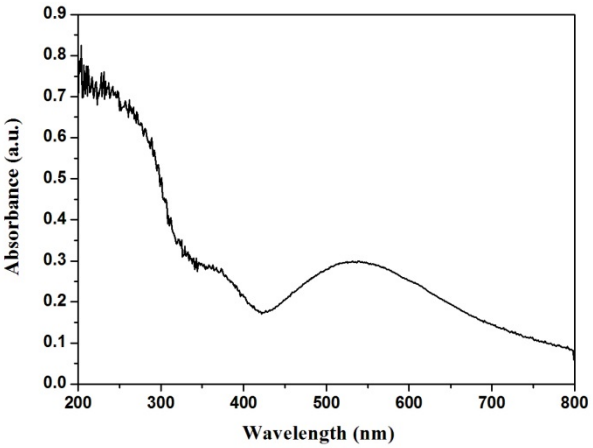

Fig. S6. The diffuse reflectance UV-Vis absorption spectrum of compound **1.**

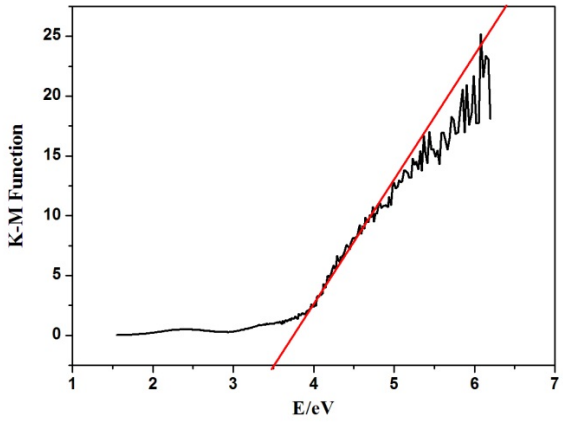

Fig. S7. The diffuse reflectance UV-Vis-NIR spectra of K-M function vs. energy (eV) of compound **1**.

References

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