

<Supporting Information>

Crystal structure and electrochemistry properties of one two-dimensional heteropolyoxoniobate based on four- and five-vanadium-capped Keggin anions

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1. Experimental Section.

1.1 Materials and methods

All the chemicals were obtained from commercial sources, and were used without further purification. Elemental analyses (C, H, N) were measured on a Perkin-Elmer 240C elemental analyzer. IR spectrum was performed in the range 4000-400 cm^{-1} using KBr pellets on a VERTEX 70 spectrophotometer. Powder X-ray diffraction measurement was recorded at room temperature on a Bruker D8 Advance with Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$). Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer-7 thermal analyzer heated from room temperature to 1050 $^{\circ}\text{C}$ under nitrogen at the heating rate of 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$. The electrochemical measurement was carried out on an electrochemical workstation (Chenhua CHI660, Shanghai, China) at ambient temperature using a conventional three-electrode system with a modified carbon paste electrode (CPE-1) as the working electrode, a Pt wire as the counter electrode and Ag/AgCl electrode as a reference electrode, respectively.

1.2 Synthesis

In a clean and dry Teflon-lined stainless steel autoclave (23 mL), $\text{KHNb}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$ (0.045 g, 0.04 mmol) and NaVO_3 (0.049 g, 0.40 mmol) and H_2SO_4 (0.15 mmol) were dissolved in 4 mL distilled water, and a 2 mL solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.040 g, 0.2 mmol) was added into the former yellow solution under stirring. 1 mol·L⁻¹ NaOH was employed to set the pH to 9.5 carefully. Subsequently, 1, 2-diaminopropane was added into the reaction system dropwise until the pH reached 10.5. After stirring for about five minutes, the magnet was removed, the Teflon-lined stainless steel autoclave was heated at 160 $^{\circ}\text{C}$ for 72 h, and black crystals of **1** were collected by manual. Yield: *ca.* 56% for **1** (based on Nb). The general chemical formula sum is $\text{V}_{21}\text{Nb}_{48}\text{O}_{233}\text{Cu}_{16}\text{K}_2\text{C}_{96}\text{N}_{64}\text{H}_{414}$. Anal. Calcd (%): C, 9.00; H, 3.34; N, 6.99, V, 8.34; Cu, 7.92; Nb, 34.76. Found: C, 8.25; H, 3.09; N, 6.51 (detected by element analysis, Vario EL cube); V, 8.42; Cu, 7.89; Nb, 34.2 (detected by ICP-AES, Optima 2100DV). IR (cm^{-1} , KBr pellet): 3120(s), 2960(s), 2878(s), 1637(m), 1584(s), 1458(m), 1384(m), 1339(w), 1302(w), 1198(w), 1057(s), 1020(s), 982(s), 938(s), 879(s), 819(vs), 752(s), 685(vs), 618(s), 566(m), 492(m).

1.3 X-ray crystal structure determination

The crystallographic data of **1** were performed on a Bruker Apex-II CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Suitable crystal of **1** were affixed to the end of a glass fiber using vaseline and transferred to the goniostat. The diffraction intensity is corrected by Lp factor and empirical absorption. The structure was solved by direct methods of SHELXS-97 [1] and refined by full-matrix least-squares method using the SHELXL-97 program package [2]. All of the non-hydrogen atoms were modified by least square anisotropic correction and secondary extinction correction. The crystal data and structure refinements of compound **1** are summarized in **Table 1**.

References

- [1] Sheldrick GM, SHELXS-97, Programs for X-ray Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1997.
- [2] Sheldrick GM, SHELXL-97, Programs for X-ray Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.

2. Supplementary Structural Tables.

Table S1 Selected bond distances (Å) for compound **1**

Bond	length	Bond	length
Nb(1)-O(1)	1.733(11)	Cu(1)-N(1)	1.97(3)
Nb(1)-O(7)	2.007(8)	Cu(1)-N(1')	2.22(3)
Nb(1)-O(8)	1.997(8)	Cu(1)-N(2)	1.82(3)
Nb(1)-O(14)	2.440(8)	Cu(1)-N(2')	2.11(3)
Nb(2)-O(2)	1.757(8)	Cu(1)-O(5W)_w	2.53(7)
Nb(2)-O(8)	2.026(7)	Cu(2)-N(3)	2.031(11)
Nb(2)-O(9)	1.933(8)	Cu(2)-N(4)	2.009(11)
Nb(2)-O(12)	1.966(5)	Cu(2)-O(3)_v	2.484(8)
Nb(2)-O(15)	2.450(6)	Cu(2)-N(3)_y	2.031(11)
Nb(2)-O(11)_y	2.050(8)	Cu(2)-N(4)_y	2.009(11)
Nb(3)-O(3)	1.747(8)	V(1)-O(14)	1.686(7)
Nb(3)-O(11)	1.985(7)	V(1)-O(15)	1.698(8)
Nb(3)-O(13)	2.002(7)	V(1)-O(14)_y	1.686(7)
Nb(3)-O(15)	2.468(8)	V(2)-O(5)	1.596(11)
Nb(3)-O(11)_y	1.985(7)	V(2)-O(7)	2.109(8)
Nb(3)-O(13)_y	2.002(7)	V(2)-O(8)	1.930(6)
Nb(4)-O(4)	1.747(8)	V(2)-O(11)_y	2.078(7)
Nb(4)-O(6)	1.967(8)	V(2)-O(13)_y	1.963(6)
Nb(4)-O(7)	2.006(8)	V(3)-O(6)	2.306(14)
Nb(4)-O(10)	1.954(3)	V(3)-O(10)	1.939(17)
Nb(4)-O(14)	2.464(6)	V(3)-O(16)	1.66(4)
Nb(4)-O(13)_y	2.047(8)	V(3)-O(6)_y	2.306(14)
Cu(1)-O(1)	2.532(10)	K(1)-N(4)	3.399(10)

Symmetry codes are $y = x, y, -z+1$; $w = 1-x, 1-y, z$; $v = 1-y, x, z$.

Table S2 Selected bond angles (°) for compound **1**

Bond	Angle	Bond	Angle
O(1)-Nb(1)-O(8)	102.0(3)	O(13)-Nb(3)-O(15)	86.3(2)
O(1)-Nb(1)-O(14)	168.3(3)	O(13)-Nb(3)-O(13)_y	85.7(3)
O(7)-Nb(1)-O(8)	83.5(3)	O(11)_y-Nb(3)-O(13)	156.0(3)
O(7)-Nb(1)-O(14)	71.5(3)	O(11)_y-Nb(3)-O(15)	71.5(3)
O(8)-Nb(1)-O(14)	86.4(2)	O(11)_y-Nb(3)- O(13)_y	84.2(3)
O(2)-Nb(2)-O(8)	99.5(3)	O(13)_y-Nb(3)-O(15)	86.3(2)
O(2)-Nb(2)-O(9)	103.0(4)	O(4)-Nb(4)-O(6)	100.6(4)
O(2)-Nb(2)-O(12)	100.9(4)	O(4)-Nb(4)-O(7)	101.8(4)
O(2)-Nb(2)-O(15)	171.7(3)	O(4)-Nb(4)-O(10)	103.4(5)
O(2)-Nb(2)-O(11)_y	102.4(3)	O(4)-Nb(4)-O(14)	170.0(4)
O(8)-Nb(2)-O(9)	87.0(3)	O(4)-Nb(4)-O(13)_y	100.3(3)
O(8)-Nb(2)-O(12)	158.7(3)	O(6)-Nb(4)-O(7)	92.1(4)
O(8)-Nb(2)-O(15)	84.3(2)	O(6)-Nb(4)-O(10)	90.7(5)
O(8)-Nb(2)-O(11)_y	80.7(3)	O(6)-Nb(4)-O(14)	73.3(3)
O(9)-Nb(2)-O(12)	94.5(4)	O(6)-Nb(4)-O(13)_y	159.0(3)
O(9)-Nb(2)-O(15)	84.5(3)	O(7)-Nb(4)-O(10)	153.7(4)
O(9)-Nb(2)-O(11)_y	153.3(3)	O(7)-Nb(4)-O(14)	71.0(3)
O(11)_y-Nb(2)-O(12)	88.8(4)	O(7)-Nb(4)-O(13)_y	81.5(3)
O(11)_y-Nb(2)-O(15)	70.9(3)	O(10)-Nb(4)-O(14)	84.8(4)
O(12)-Nb(2)-O(15)	74.7(3)	O(10)-Nb(4)-O(13)_y	86.6(3)
O(3)-Nb(3)-O(11)	101.6(3)	O(14)-V(1)-O(15)	109.7(2)
O(3)-Nb(3)-O(13)	101.7(3)	O(14)-V(1)-O(14)_y	108.7(3)
O(3)-Nb(3)-O(15)	169.0(3)	O(14)_y-V(1)-O(15)	109.7(2)
O(3)-Nb(3)-O(11)_y	101.6(3)	O(5)-V(2)-O(11)_y	104.6(5)
O(3)-Nb(3)-O(13)_y	101.7(3)	O(5)-V(2)-O(13)_y	119.7(4)
O(11)-Nb(3)-O(13)	84.2(3)	O(7)-V(2)-O(8)	82.5(3)
O(11)-Nb(3)-O(15)	71.5(3)	O(7)-V(2)-O(11)_y	148.3(3)

O(11)-Nb(3)-O(13)_y	156.0(3)	O(5)-V(2)-O(7)	107.1(5)
O(5)-V(2)-O(8)	120.5(4)	O(6)_y-V(3)-O(10)	81.6(4)
O(5)-V(2)-O(11)_y	104.6(5)	N(1)-Cu(1)-N(2)	89.4(11)
O(5)-V(2)-O(13)_y	119.7(4)	O(1)-Cu(1)-N(1)	93.8(9)
O(7)-V(2)-O(8)	82.5(3)	O(1)-Cu(1)-N(2)	89.5(8)
O(7)-V(2)-O(13)_y	81.0(3)	O(1)-Cu(1)-O(5W)_w	176.8(16)
O(8)-V(2)-O(11)_y	82.3(3)	O(5W)_w-Cu(1)-N(1)	83.7(17)
O(8)-V(2)-O(13)_y	119.8(3)	O(5W)_w-Cu(1)-N(2)	92.6(16)
O(11)_y-V(2)- O(13)_y	82.8(3)	N(3)-Cu(2)-N(4)	83.2(4)
O(6)-V(3)-O(6_y)	148.7(7)	N(3)-Cu(2)-N(3)_y	98.8(4)
O(6)-V(3)-O(10)	81.6(4)	N(3)-Cu(2)-N(4)_y	175.1(4)
O(6)-V(3)-O(16)	105.7(4)	N(3)_y-Cu(2)-N(4)	175.1(4)
O(6)_y-V(3)-O(16)	105.7(4)	O(3)_v-Cu(2)-N(3)	90.0(3)
O(10)-V(3)-O(16)	122.6(15)	O(3)_v-Cu(2)-N(4)	94.5(3)

Symmetry codes are $y = x, y, -z+1$; $w = 1-x, 1-y, z$; $v = 1-y, x, z$.

Table S3 The bond valance sum calculation for compound **1**

	V1	V2	V3	
BVS	5.36	3.80	2.76	
	Nb1	Nb2	Nb3	Nb4
BVS	5.00	4.98	4.94	5.01

3. Supplementary Structural Figures.

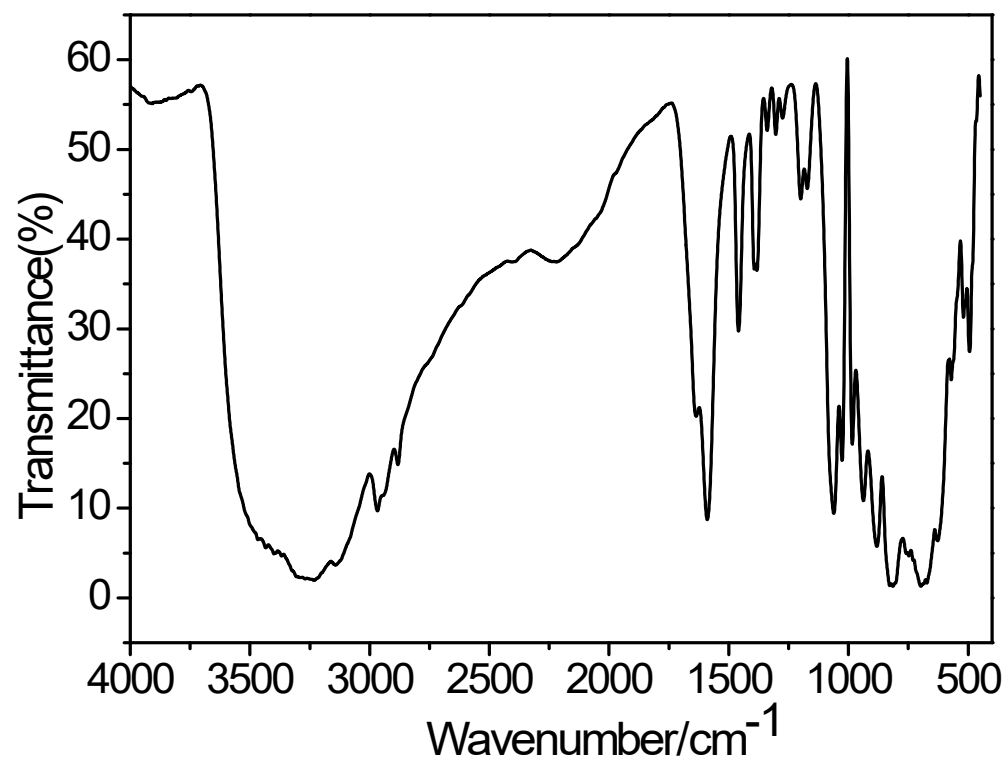


Fig. S1 IR spectrum of compound 1.

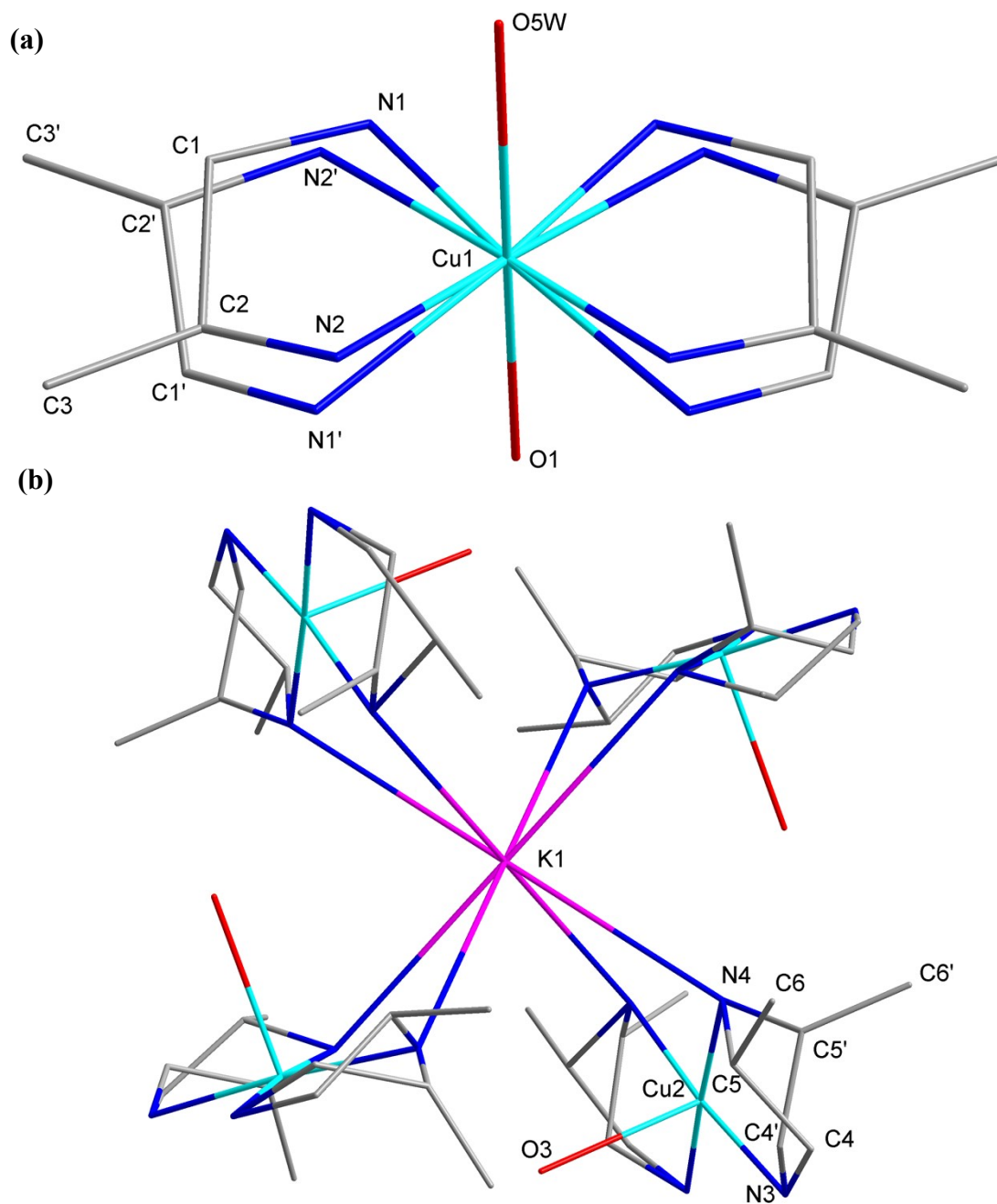


Fig. S2 Schematic diagram of coordination of Cu1 (a) and Cu2 (b). Occupancy of C1, C2, C3, N1, N2 is 0.5; and occupancy of C1', C2', C3', N1', N2' is 0.5. Occupancy of C4, C5, C6 is 0.7; and occupancy of C4', C5', C6' is 0.3. Cu, K, C, and N atoms are shown in cyan, light yellow, gray, and blue, respectively. Hydrogen atoms are omitted.

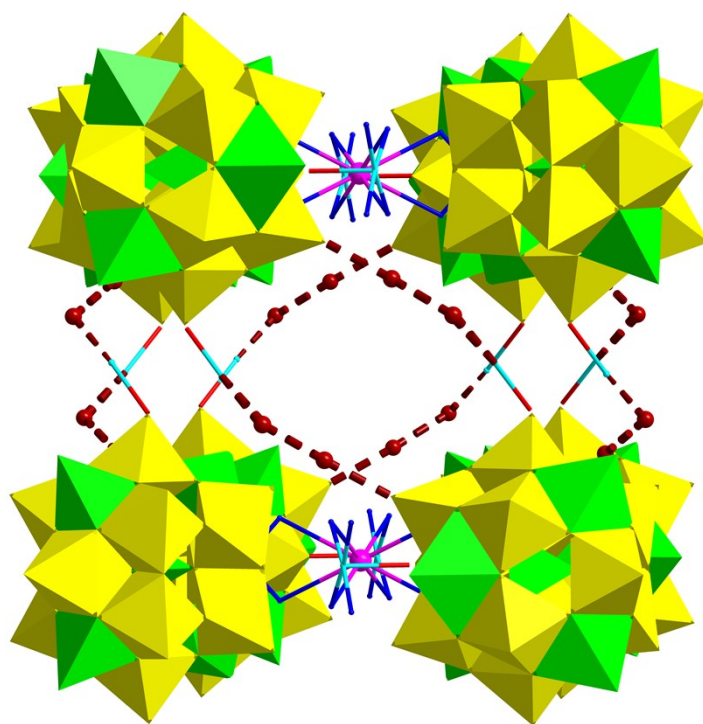


Fig. S3 Observe the arrangement of compound **1** along b axis. Green polyhedron: NbO_6 ; yellow polyhedron: VO_4 . O, Cu, K, and N atoms are shown in red, cyan, fuchsia, and blue, respectively. The free water molecules in the structure are not shown. Hydrogen and carbon atoms are omitted.

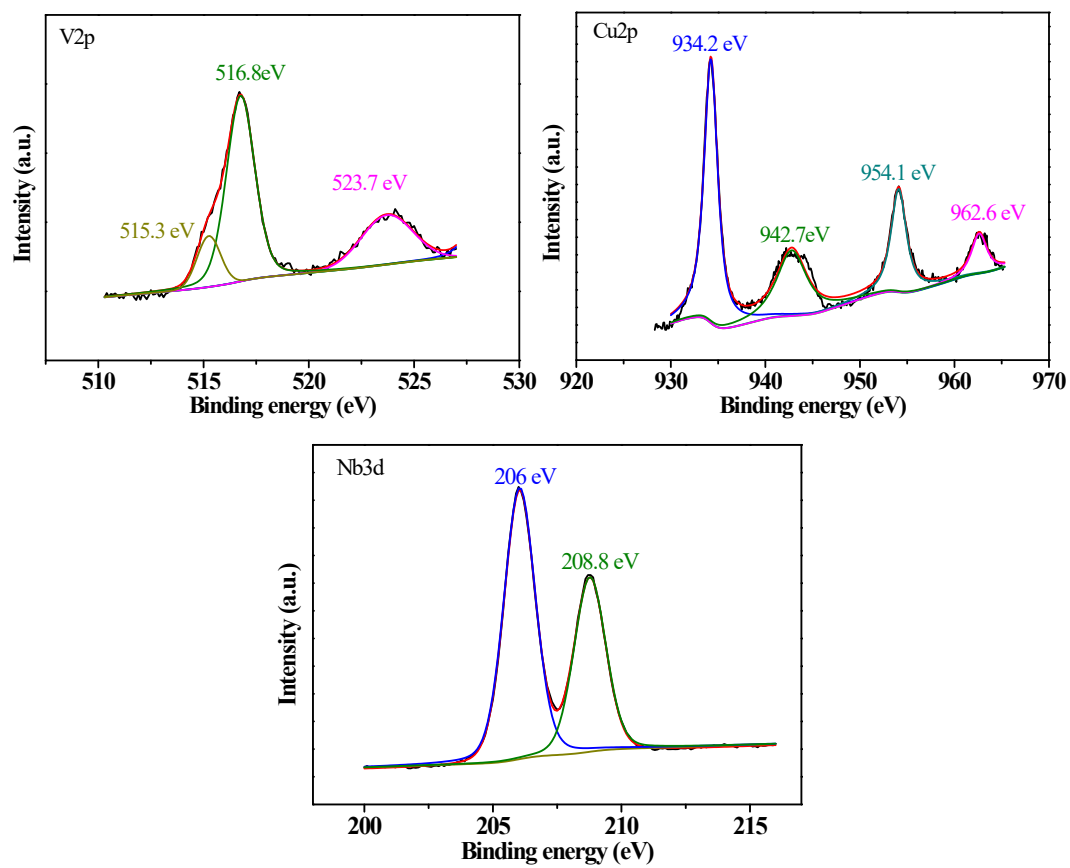


Fig. S4 The XPS spectrum for compound 1.

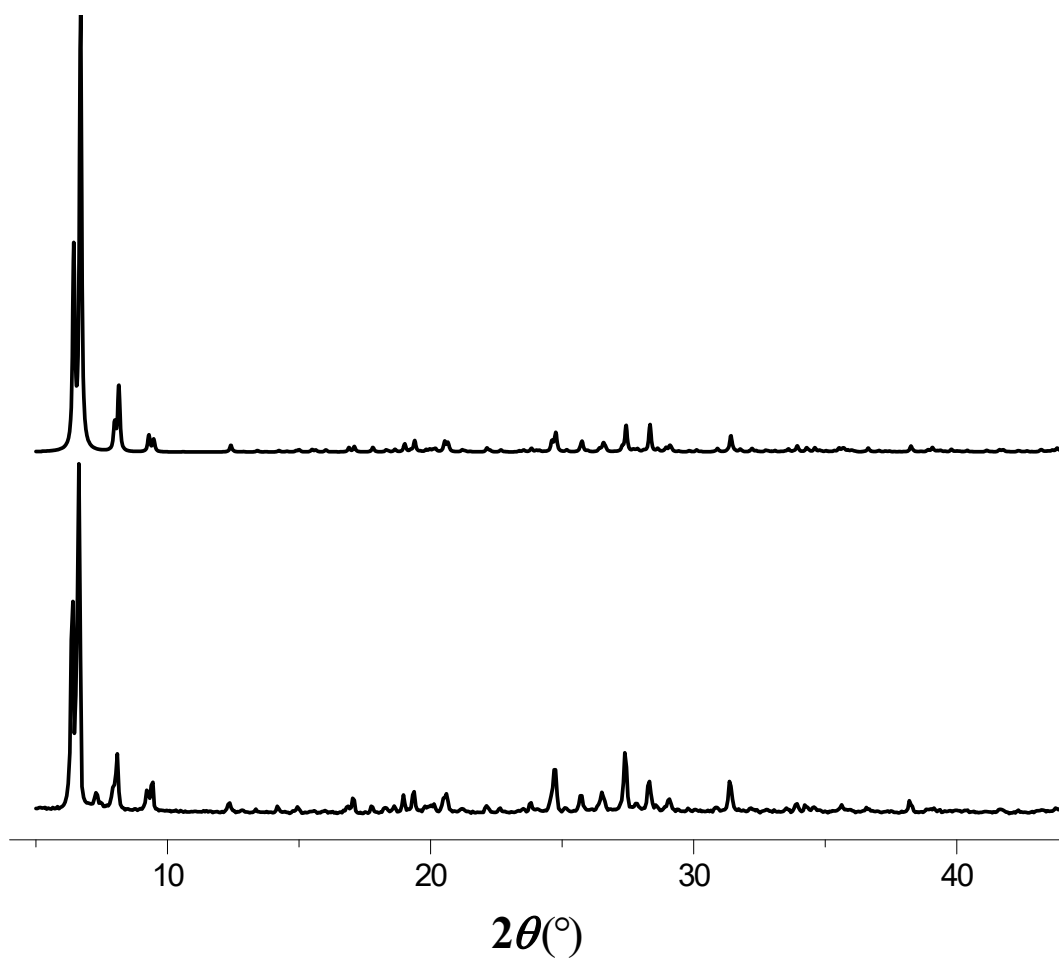


Fig. S5 The powder X-ray diffraction pattern calculated from the single-crystal data (top) and that from the experiment (bottom) for compound **1**.

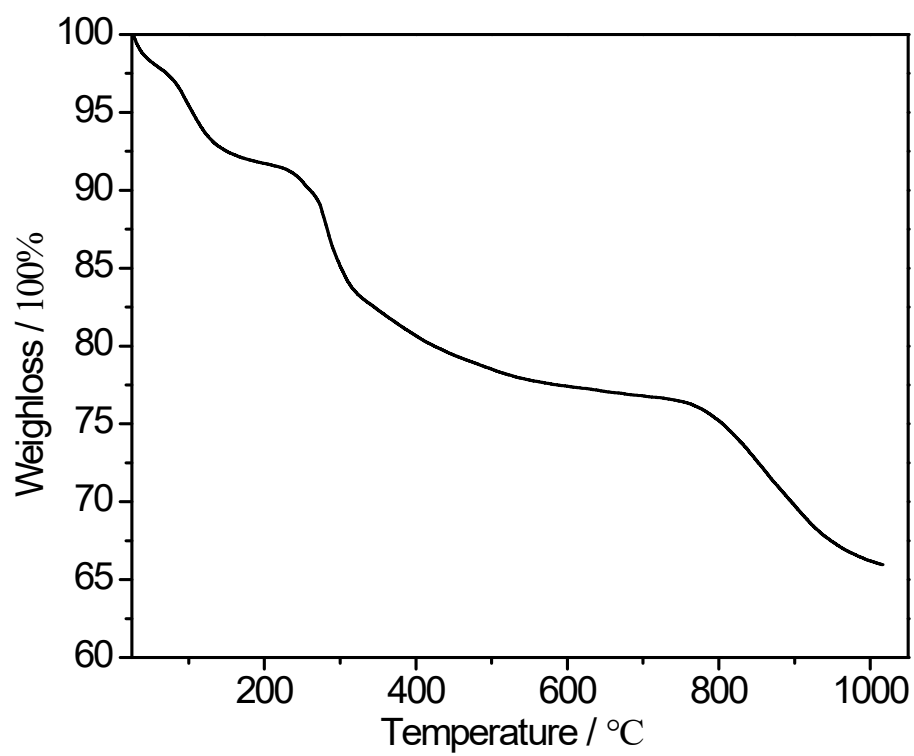


Fig. S6 TG curve of compound **1**.

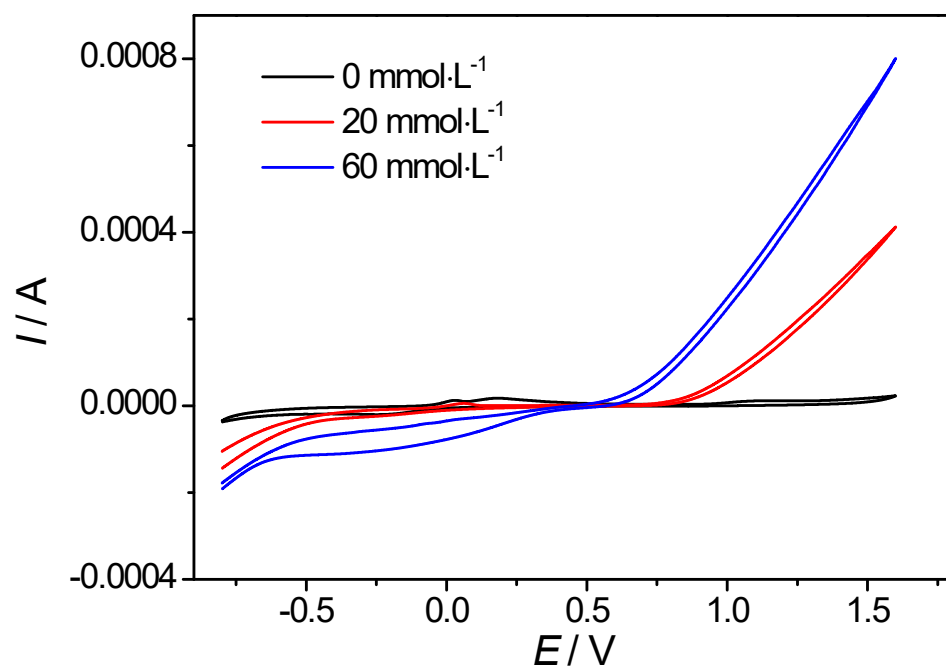


Fig. S7 Compound **1** catalyzed the electric decomposition of NaNO₂ in 0.1 mol·L⁻¹ H₂SO₄ + 0.5 mol·L⁻¹ Na₂SO₄ (vs. Ag/AgCl reference electrode).

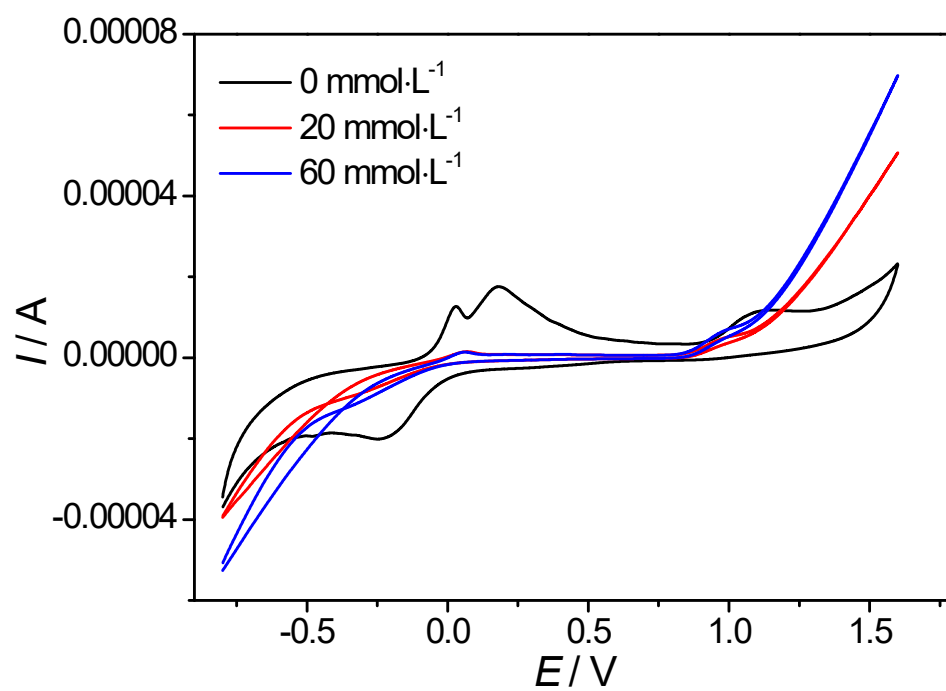


Fig. S8 Compound **1** catalyzed the electric decomposition of H_2O_2 in $0.1 \text{ mol}\cdot\text{L}^{-1} H_2SO_4 + 0.5 \text{ mol}\cdot\text{L}^{-1} Na_2SO_4$ (vs. Ag/AgCl reference electrode).

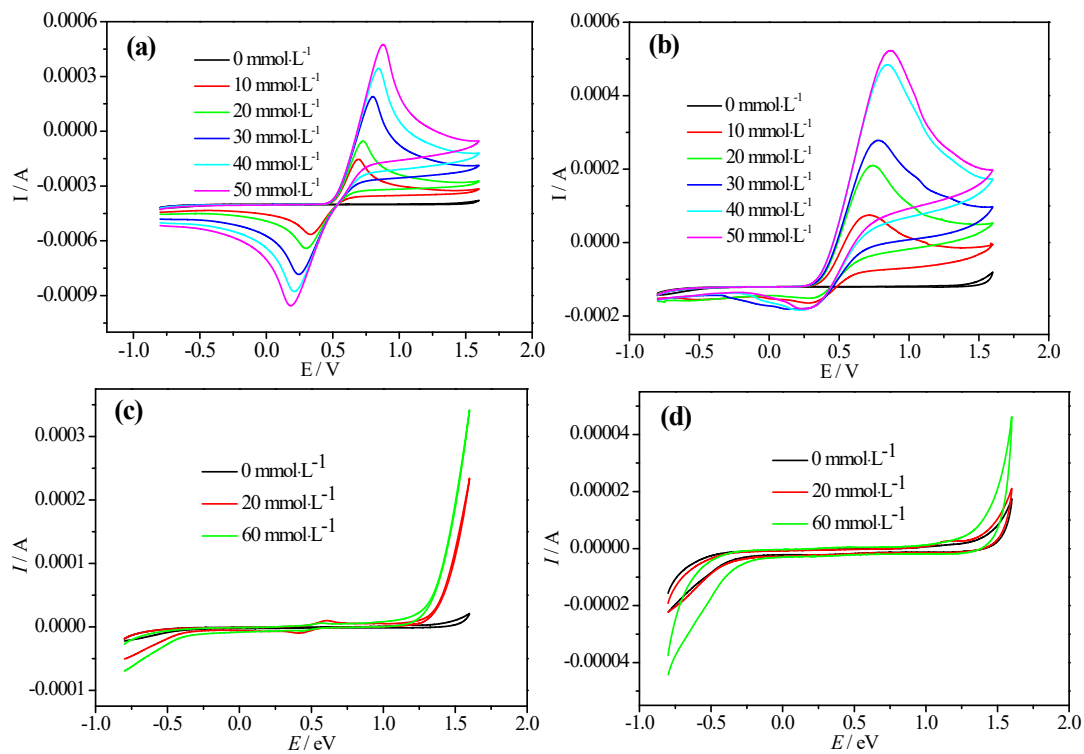


Fig. S9 Bare electrode catalyzed the electric decomposition of DA (a), AA (b), H₂O₂ (c) and NaNO₂ (d) in 0.1 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ Na₂SO₄ (vs. Ag/AgCl reference electrode).