3D pure inorganic framework based on polymolybdovanadate possessing photoelectric property

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1. Materials and measurements

All the chemicals were obtained from commercial sources, and were used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Na, V, and Mo were determined by a Leaman inductively coupled plasma (ICP) spectrometer. The IR spectra were obtained in the range 400-4000cm^{-1} on the Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Powder X-ray diffraction measurement was recorded radiation ranging from 5 to 50° at room temperature on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å). The X-ray photoelectron spectra (XPS) were recorded on a USWHA150 photoelectron spectroscope using monochromatic Al Kα (1486.6 eV) radiation. Thermogravimetric analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 5ºC min^{-1}. The Ultraviolet-visible diffuse reflectance spectra were obtained using a CARY 500 scan UV-vis-NIR spectrophotometer. Morphology and composition analyses were carried out on a FEI quanta 250 field emission scanning electron microscopy (FESEM) equipped with an energy dispersive X-ray (EDX) analysis accessory. The photoluminescent (PL) properties were measured on an FLSP920 Edinburgh Fluorescence Spectrometer at room temperature. Surface photovoltage spectroscopy (SPS) and electric field induced SPS (EFISPS) were carried out on a Lock-in based surface photovoltage measurement system which was constituted of a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a sample cell and a computer.

2. Synthesis

$Na_2MoO_4 \cdot 2H_2O$ (0.80g, 3.3 mmol) and $NaVO_3 \cdot 2H_2O$ (0.07g, 0.42 mmol) were dissolved in 25 ml degassed water. Then 0.5ml 1M $CuCl_2$ was added to the above solution, followed by dropping 1.6 ml morpholine solution (1M). The pH of the mixture was adjusted to 3.5 by addition of 1 M HCl and stirred at 65–70 °C for 2 h. Light cyan crystals of **1** precipitated from the solution within 3 weeks in 30% yield (based on Mo), after achromatous octamolybdate crystals formed and were removed. Elemental analysis calcd (%): C 4.36, N 1.27, H 1.74, Na 3.48, Cu 1.90, V 3.08, Mo

47.39; Found: C 4.44, N 1.26, H 1.75, Na 3.60, Cu 1.79, V 3.06, Mo 47.65. IR (KBr): 3423 (m), 3011 (w), 2464 (w), 1609 (m), 1452 (w), 1400 (w), 1377 (w), 1309 (w), 1233 (w), 1100 (m), 1042 (w), 962 (m), 916 (s), 862 (s), 819 (m), 790 (m), 745 (m), 636 (m), 522 (w) cm^{-1}.

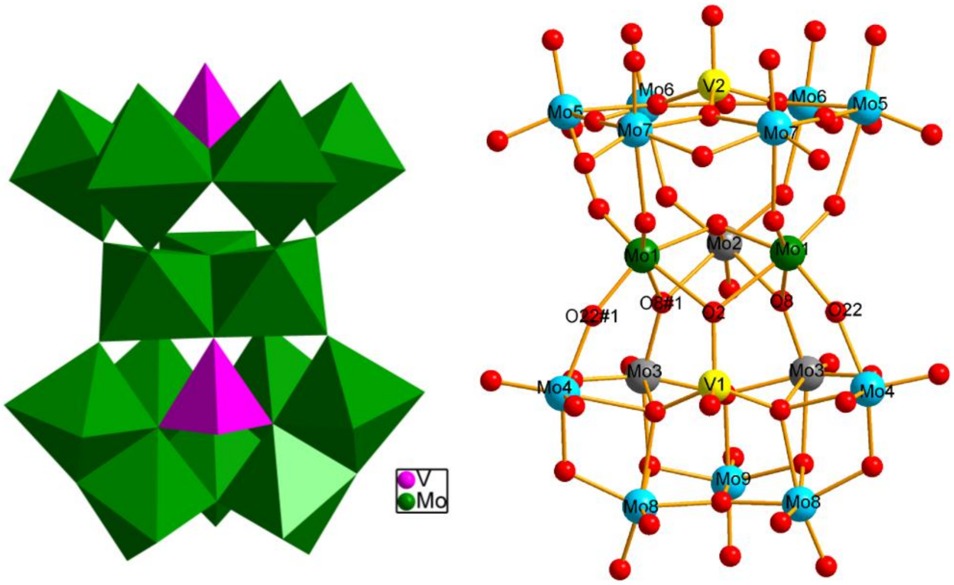


Fig. S1 Polyhedral and ball-and-stick representation of the polyanion $[V_2Mo_{16}O_{58}]^{10-}$ with main atoms labeled (#1: –y+1, -x+1, z). Color code for ball-and-stick representation: Mo atoms with no terminal oxygens, green; Mo atoms with one terminal oxygen, grey; Mo atoms with two terminal oxygens, sky blue; V, yellow; O, red.

In the $\{VMo_6\}$ ring, each Mo atom possesses two cis positioned terminal oxygens with Mo=O bond lengths vary from 1.686(7) to 1.739(7) Å. The central V2 atom is coordinated by three triply-bridging oxygen atoms with V–O bond lengths of 1.722(10) and 1.730(7) Å and one terminal oxygen atom with V=O of 1.644(11) Å. In the $[VMo_7O_{28}]^{9-}$ unit, five Mo atoms possess two cis positioned terminal O atoms while the other two Mo atoms have one terminal oxygen. The central V1 atom is also coordinated by three triply-bridging oxygen atoms with V–O bond lengths of 1.749(10) and 1.762(7) Å and one terminal oxygen atom with V=O of 1.573(12) Å.

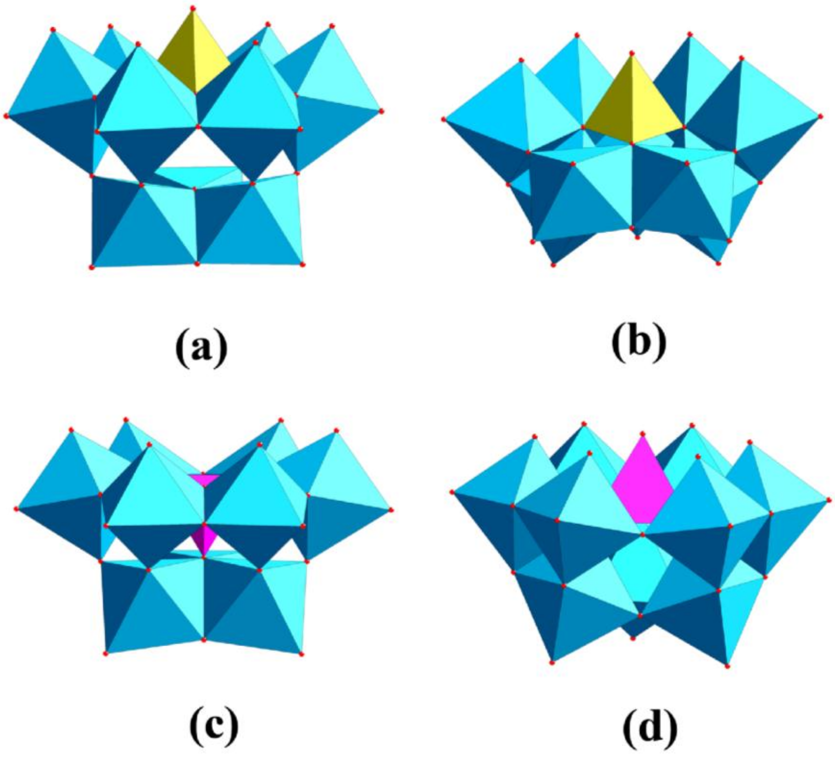
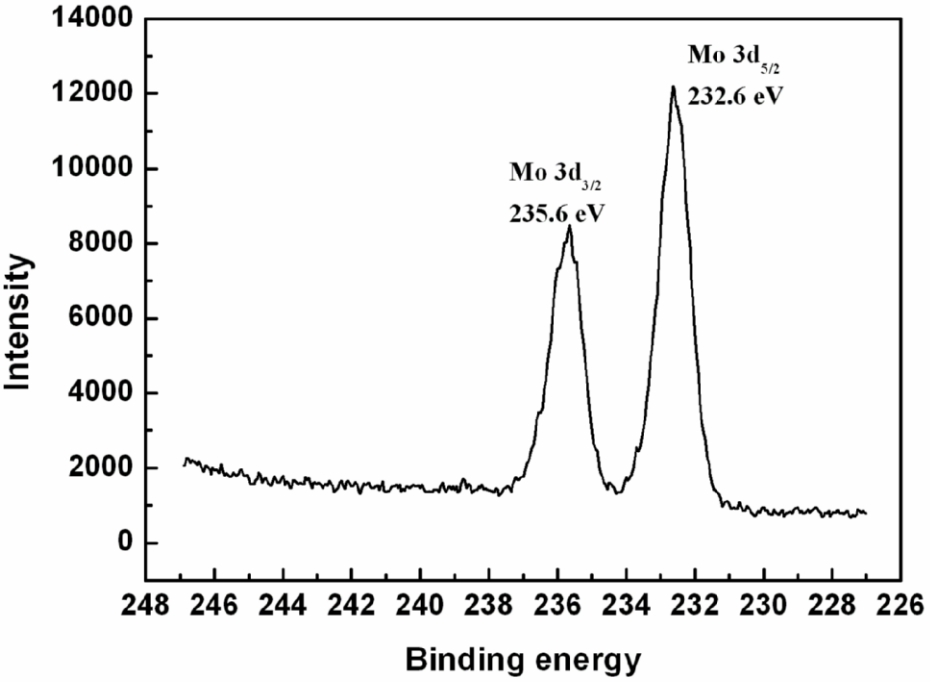
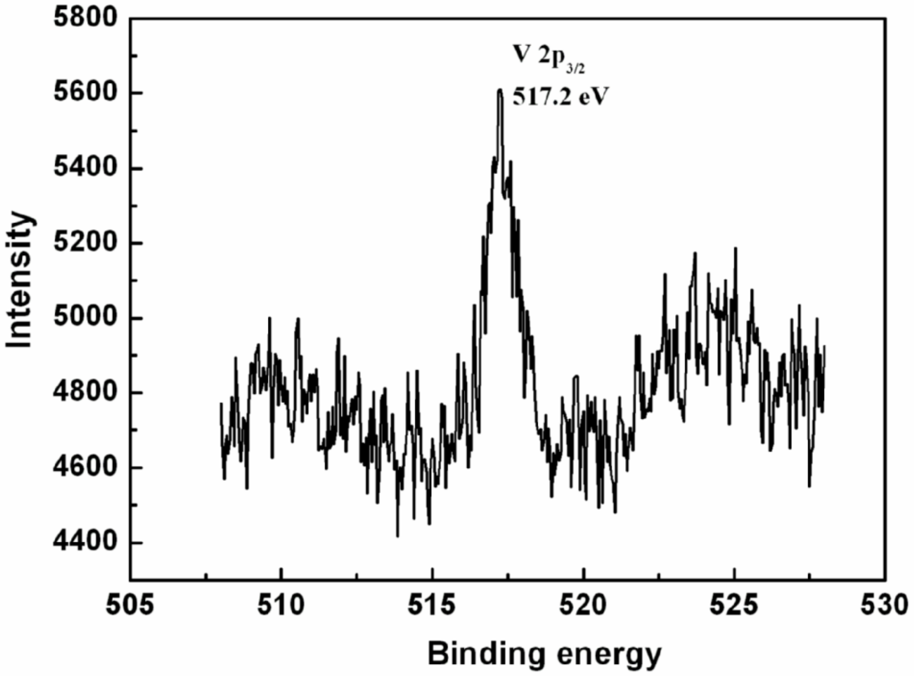


Fig. S2 Illustrations of some representative lacunary heteropolymolybdate anions previously reported. (a) $[VMo_9O_{35}]^{11-}$ in **1**; (b) $[VMo_9O_{33}]^{7-}$ (c) $[A\text{-}\alpha\text{-}XMo_9O_{34}]^{n-}$ (no related compounds are reported, and the structure was drawn according to $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$; (d) $[B\text{-}\alpha\text{-}GeMo_9O_{34}]^{10-}$.

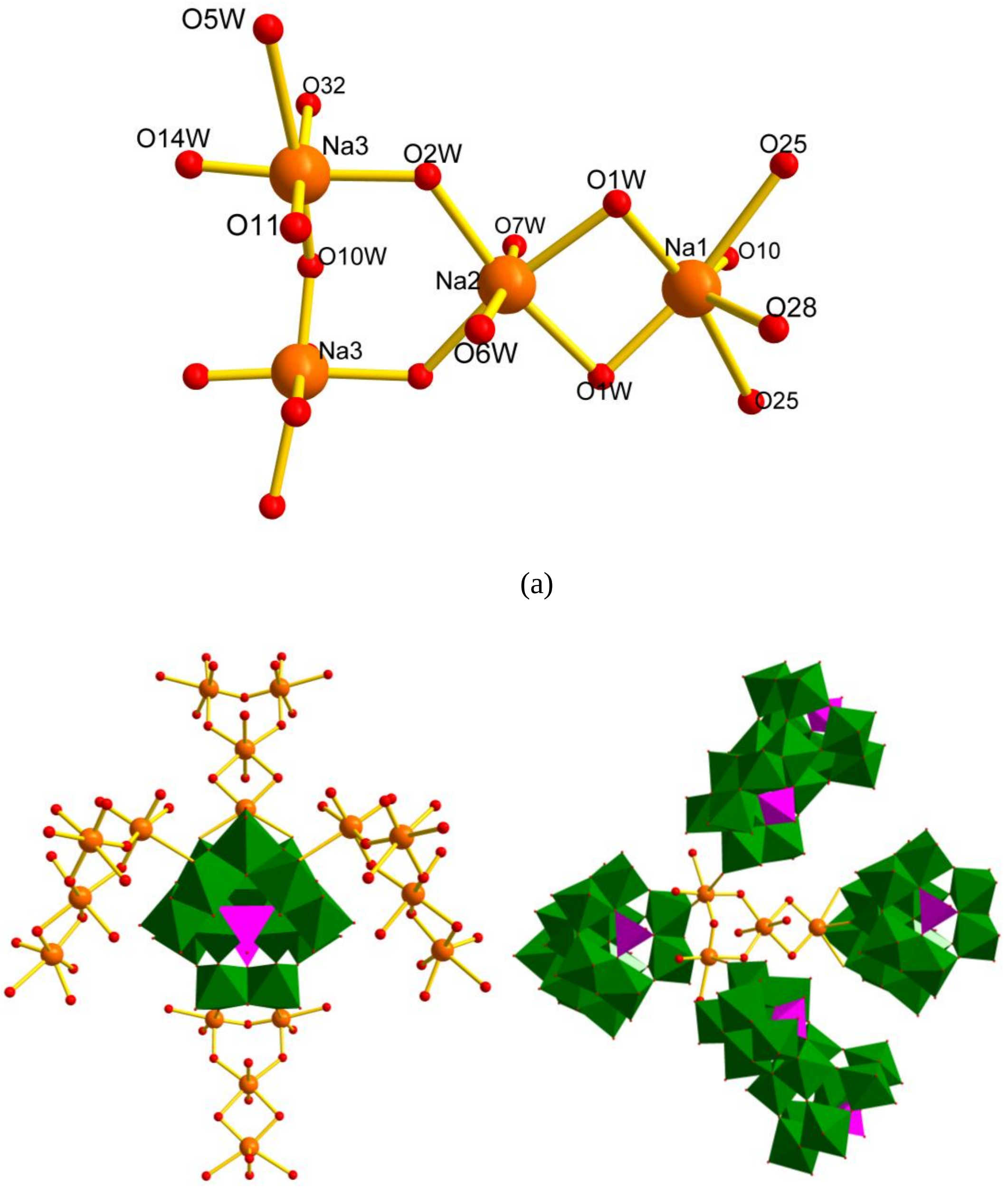


(a)



(b)

Fig. S3 The XPS spectra of compound **1**, (a) Mo and (b) V.



(a)

(b)

(c)

Fig. S4 (a) Ball-and-stick representation of the $\{Na_4O_8(H_2O)_{11}\}$ fragment in **1**. Each Na^+ ion from the Na4 fragment is six-coordinated in a distorted octahedral environment; (b,c) Coordination modes of the $[V_2Mo_{16}O_{58}]^{10-}$ polyanions with the Na4 fragments. Each $[V_2Mo_{16}O_{58}]^{10-}$ polyanion connects with four different Na4 fragments and each Na4 unit bridges four different $[V_2Mo_{16}O_{58}]^{10-}$ polyanions, which results in a 3D pure inorganic framework.

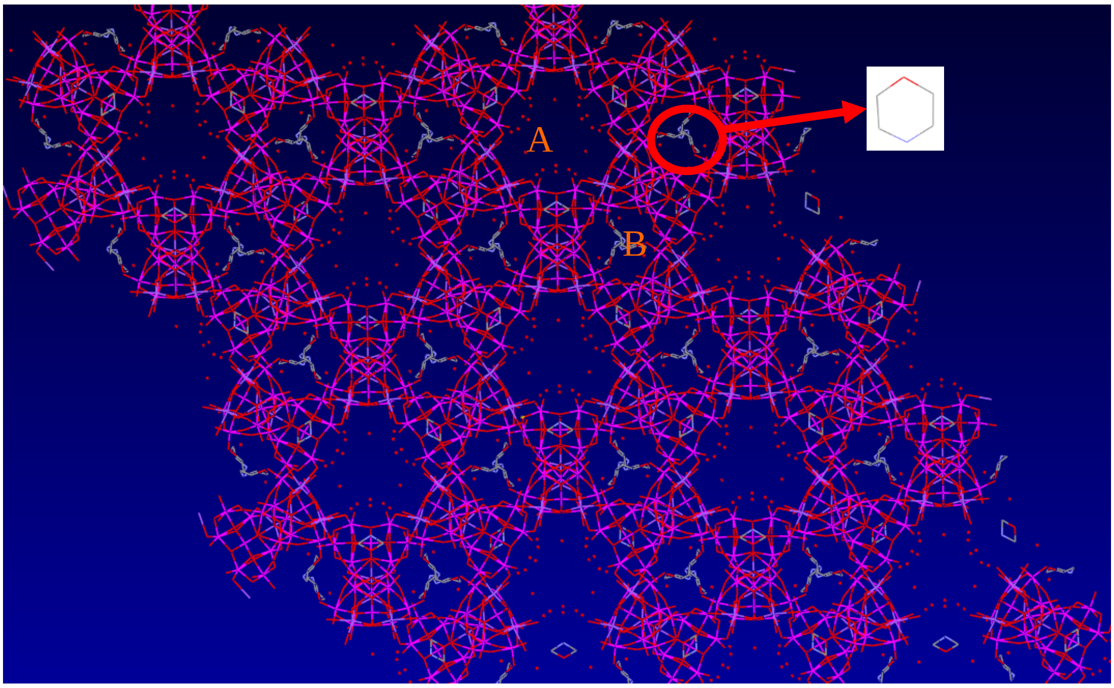


Fig. S5 3D packing arrangement of compound **1**. Channel B is filled with both the protonated morpholine cations and water molecules, while in channel A only water molecules are filled. Color code: water molecules, red ball; C, grey; N, blue.

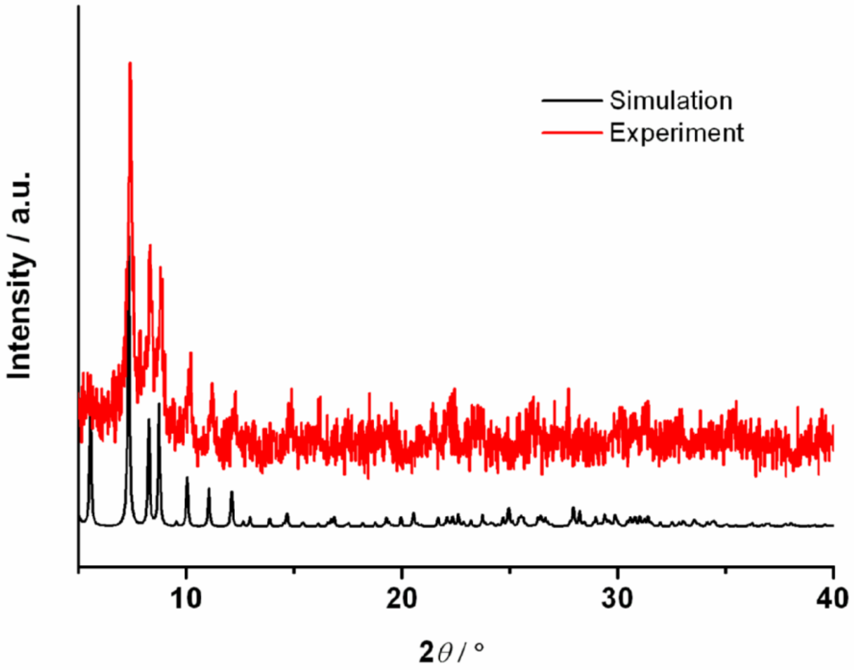


Fig. S6 The PXRD pattern and simulated pattern of **1**.

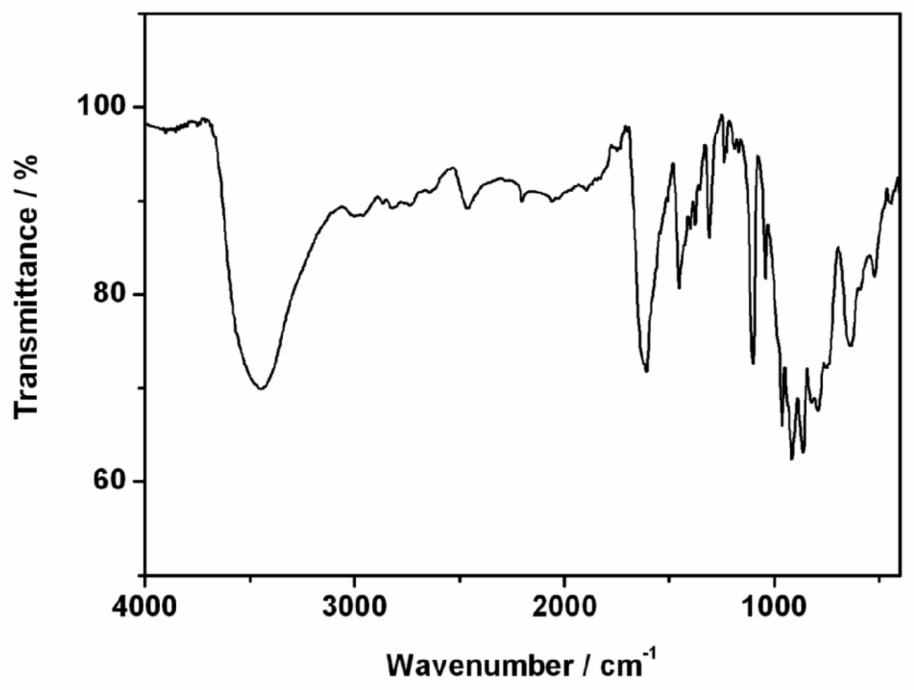


Fig. S7 The IR spectrum of **1** in KBr pellets from 4000 cm^{-1} to 400 cm^{-1}.

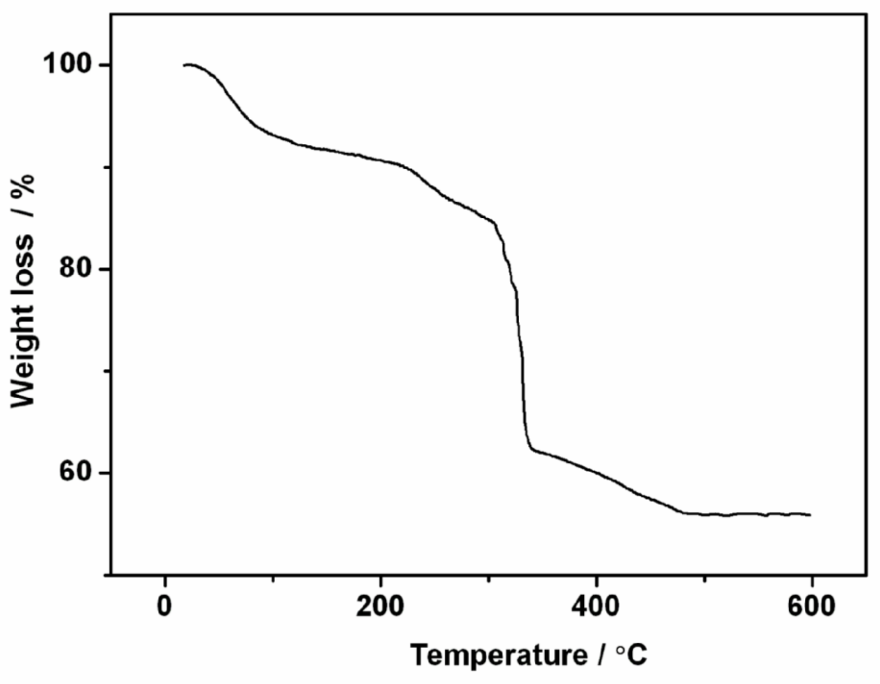


Fig. S8 The TGA curve of **1** measured under N_2 atmosphere from room temperature to 600 ºC with a heating rate of 5ºC min^{-1}.

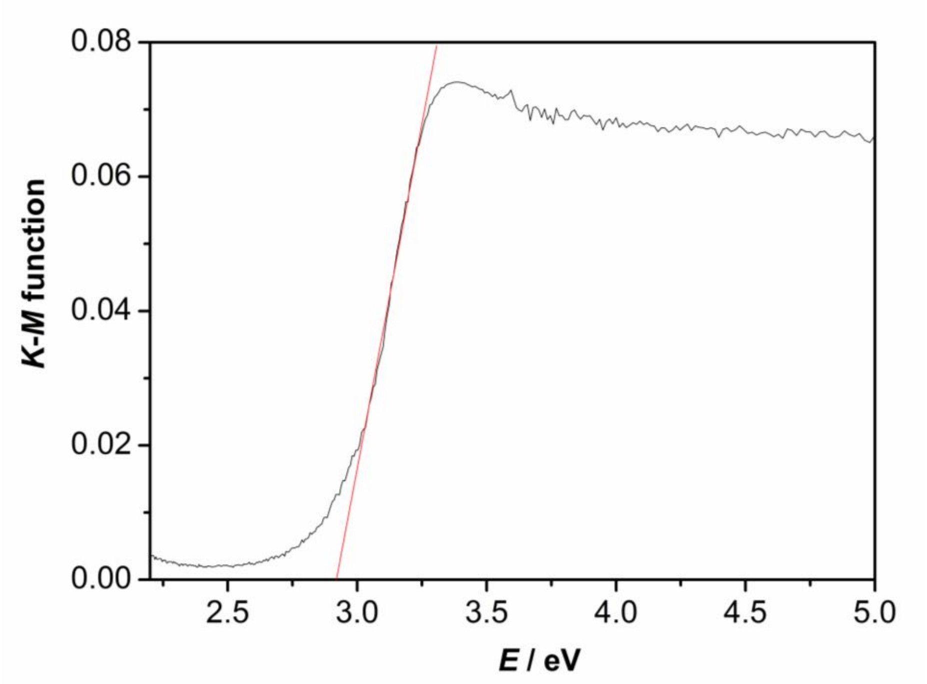


Fig. S9 Diffuse reflectance UV-vis spectrum of *K*-*M* function versus *E* (eV) of compound **1**.

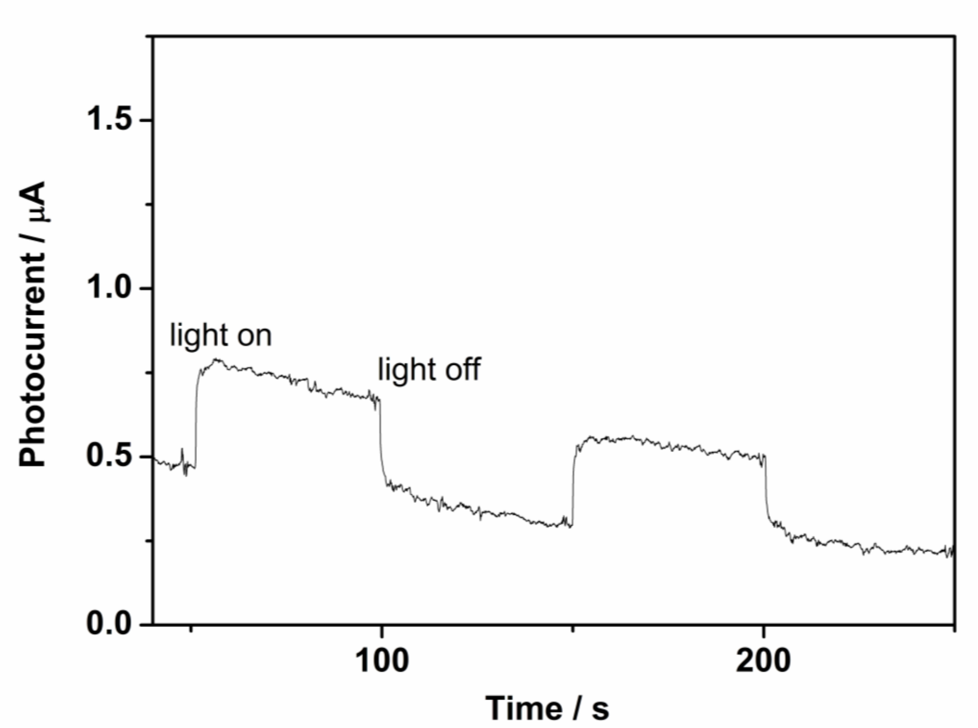


Fig. S10 Photocurrent response of the film of compound **1**. The solution of **1** was spin-coated on the ITO glass and then annealed at 200 ºC for 1h. A three-electrode system was employed in a quartz cell with a Ag/AgCl (saturated KCl) electrode as the reference electrode, a platinum foil as the counter electrode, the film assembled ITO glass as the working electrode and 0.1 M Na_2SO_4 electrolyte.

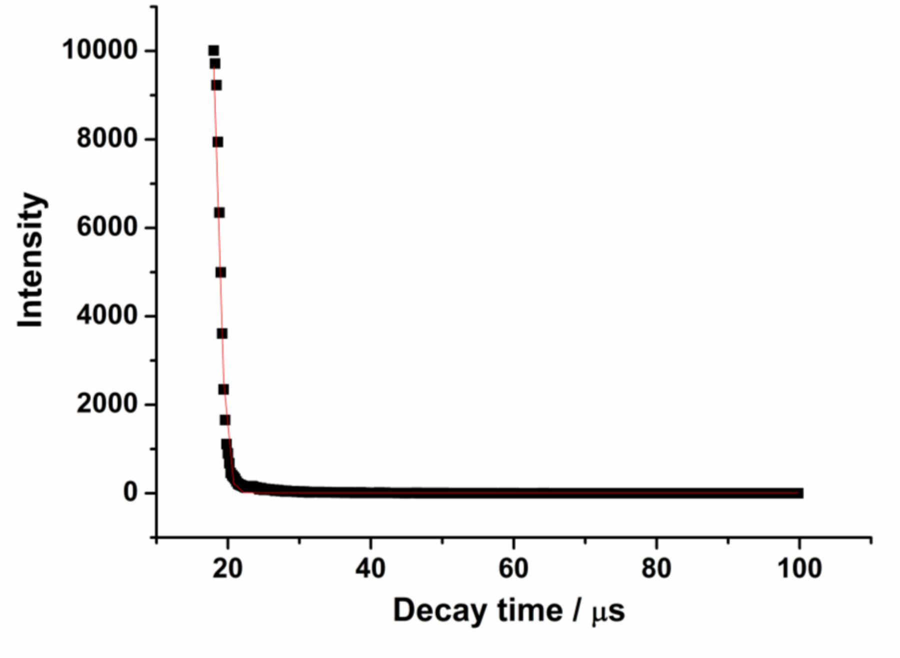


Fig. S11 Fluorescence decay curve for compound **1**. The black blocks represent experimental data and the solid red line represents the fitting result (λ_{em} = 480 nm). The emission decay lifetimes are $\tau(1)$ = 0.44 μs and $\tau(2)$ = 0.46 μs (χ^2 = 0.9965).

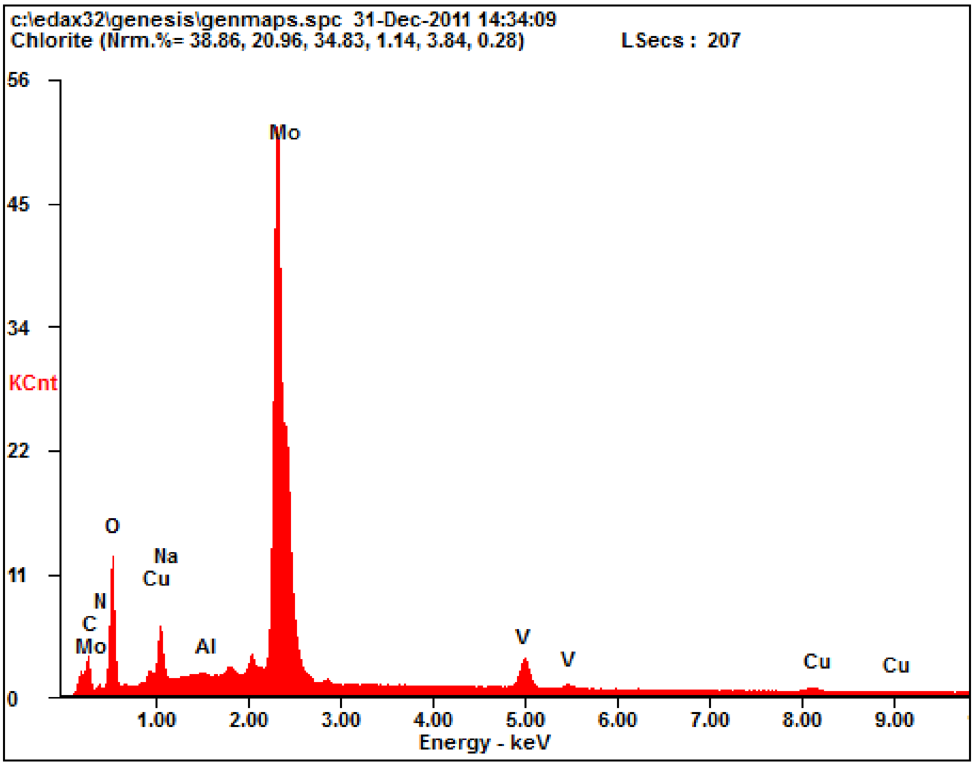


Fig. S12 EDX analyses of compound **1**.

Table S1. Selected bond lengths [Å] for the compound **1**.

V(1)-O(33)	1.586(14)	V(2)-O(34)	1.647(13)
V(1)-O(2)	1.725(12)	V(2)-O(19)	1.737(9)
V(1)-O(18)	1.772(8)	V(2)-O(19)#1	1.737(9)
V(1)-O(18)#1	1.772(8)	V(2)-O(13)	1.740(8)
Mo(1)-O(15)	1.710(8)	Mo(2)-O(10)	1.770(14)
Mo(1)-O(9)	1.752(9)	Mo(2)-O(14)#1	1.772(8)
Mo(1)-O(22)	1.877(8)	Mo(2)-O(14)	1.772(8)
Mo(1)-O(1)	2.002(6)	Mo(2)-O(1)	2.202(11)
Mo(1)-O(8)	2.208(8)	Mo(2)-O(8)	2.244(8)
Mo(1)-O(2)	2.287(7)	Mo(2)-O(8) #1	2.244(8)
Mo(3)-O(25)	1.691(9)	Mo(4)-O(20)	1.689(10)
Mo(3)-O(23)	1.769(9)	Mo(4)-O(29)	1.711(10)
Mo(3)-O(8)	1.884(8)	Mo(4)-O(16)	1.932(9)
Mo(3)-O(6)	1.976(3)	Mo(4)-O(22)	1.938(8)
Mo(3)-O(12)	2.106(10)	Mo(4)-O(23)	2.196(10)
Mo(3)-O(18)	2.533(10)	Mo(4)-O(18)	2.258(8)
Mo(5)-O(26)	1.697(9)	Mo(6)-O(31)	1.715(10)
Mo(5)-O(27)	1.717(9)	Mo(6)-O(35)	1.727(10)
Mo(5)-O(17)	1.911(8)	Mo(6)-O(7)	1.898(19)
Mo(5)-O(21)	1.950(8)	Mo(6)-O(21)#1	1.966(12)
Mo(5)-O(19)	2.202(8)	Mo(6)-O(14)	2.227(9)
Mo(5)-O(15)	2.404(8)	Mo(6)-O(19)#1	2.266(8)
Mo(7)-O(11)	1.711(9)	Mo(8)-O(30)	1.679(12)
Mo(7)-O(24)	1.722(9)	Mo(8)-O(32)	1.706(10)
Mo(7)-O(17)	1.885(8)	Mo(8)-O(16)	1.943(9)
Mo(7)-O(5)	1.946(6)	Mo(8)-O(3)	1.951(4)
Mo(7)-O(13)	2.200(8)	Mo(8)-O(18)	2.263(8)
Mo(7)-O(9)	2.359(9)	Mo(8)-O(12)	2.347(11)
Mo(9)-O(4)	1.704(16)	Na(1)-O(28)	2.190(2)
Mo(9)-O(28)	1.736(16)	Na(1)-O(1W)	2.320(2)
Mo(9)-O(12)	1.957(9)	Na(1)-O(1W)#1	2.320(2)
Mo(9)-O(12)#1	1.957(9)	Na(1)-O(10)	2.330(2)
Mo(9)-O(6)	2.167(13)	Na(1)-O(25)#1	2.763(13)
Mo(9)-O(3)	2.259(14)	Na(1)-O(25)	2.763(13)
Na(2)-O(6W)	2.410(3)	Na(3)-O(14W)	1.920(5)
Na(2)-O(2W)	2.450(2)	Na(3)-O(10W)	2.000(3)
Na(2)-O(2W)#1	2.450(2)	Na(3)-O(2W)#2	2.240(3)
Na(2)-O(1W)	2.480(2)	Na(3)-O(11)	2.400(2)
Na(2)-O(1W) #1	2.480(2)	Na(3)-O(5W)	2.650(3)
Na(2)-O(7W)	2.480(3)	Na(3)-O(32)#3	2.83(2)

Symmetry code: #1 -y+1,-x+1,z #2 x,y,z-1 #3 -x+y-1/3,-x+4/3,z-2/3