

Supporting materials

Copper-organic cationic ring with inserted arsenic–vanadium polyanionic cluster for efficient catalytic chromium(VI) reduction using formic acid

Experimental

Materials and methods

All reagents for syntheses were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaur FT/IR Spectrophotometer using KBr pellets. Thermogravimetric analysis (TG) was carried out using a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 $^{\circ}\text{C min}^{-1}$. Powder X-ray diffraction (PXRD) was determined by a Bruker AXS D8 Advance diffractometer.

Synthesis of **1**

NH_4VO_3 (100 mg, 0.8 mmol), NaAsO_2 (100 mg, 0.77 mmol), $\text{Cu}(\text{AC})_2$ (100 mg, 0.5 mmol), bpp (30 mg, 0.2 mmol) were stirred in distilled water (10 mL), and stirred for 30 min. The resulting solution was sealed in a 20 mL stainless steel reactor with a Teflon liner and heated at 160 $^{\circ}\text{C}$ for 5 days. And then cooled to room temperature resulting in black block crystals of **1** were obtained (Yield *ca.* 45% based on V). Anal. Calc. for $\text{C}_{52}\text{H}_{58}\text{As}_8\text{Cu}_4\text{N}_8\text{O}_{43}\text{V}_{14}$ (%): C, 20.46; H, 1.90; N, 3.67; Found: C, 20.52; H, 1.96; N, 3.60.

X-ray crystallography

Single crystal data of **1** were collected on a Smart Apex CCD diffractometer at 296(2) K with Mo K α monochromated radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELXTL crystallographic software package.[G. M. Sheldrick, *SHELXTL-97, Programs for Crystal Structure Refinement*, University of Göttingen, Germany.,1997, **30**, 5401-5407.a) C. L. Hill, *Chem. Rev.* **1998**, *98*, 1-387; b) D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105-121; c) T. Yamase, M. T. Pope, *Kluwer Academic/Plenum Publishers*, New York, NY, **2002**, pp.17-26.] Anisotropic thermal parameters were used to refine all non hydrogen atoms. All hydrogen atoms attached to carbon atoms were added to their geometrically ideal positions and refined isotropically. Hydrogen atoms of water molecules were not located. All the crystal data and structure refinement details for **1** were given in Table S1. Selected bond lengths [Å] were listed in Table S2. CCDC-1029008 can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk)

Catalytic experiment

The typical process is described as follows: Catalysis experiments were performed in the mode of sealing. Powder of compound **1** (0.020g) were dispersed into in a 500 mL aqueous solution containing $\text{K}_2\text{Cr}_2\text{O}_7$ (3.57×10^{-4} mg L^{-1}) and HCOOH (7 mL). The system was magnetically stirred at a stable temperature of either 25 or 50 $^{\circ}\text{C}$. At some time interval, 3 mL aliquot was sampled and then centrifuged to remove the particles of catalyst. The UV/Vis absorbance of dichromate ions was measured with respect to time.

Supplemental Captions of Tables and Figures:

Table S1 Crystal data for structure refinement for compound **1**.

Table S2 Selected bond lengths [\AA] for compound **1**.

Figure S1. The experimental a) and calculated b) XRD patterns of compound **1**.

Figure S2. TG curve of compound **1**.

Figure S3. Views showing α -configuration (left) and β -configuration (right) $\{[\text{As}_8\text{V}_{14}\text{O}_{42}]^{4-}\}$.

Figure S4. (a) $[\text{As}_8\text{V}_{14}\text{O}_{42}]^{4-}$ anion acts as a quadridentate ligand coordinated to four copper in compound **1**; (b) cationic metal-organic macrocycles of $\{\text{Cu}_4(\text{bpp})_4\}$ units; (c) 2-D structure of compound **1**, green polyhedra representatives $\{\text{VO}_5\}$.

Figure S5. UV/Vis spectroscopy of the reduction of Cr(VI) ions upon reaction with formic acid in the presence of a) V_2O_5 ; b) CuO ; c) $\text{V}_2\text{O}_5+\text{CuO}$; d) free bpp ligand at elevated temperature of 25 $^\circ\text{C}$ and 50 $^\circ\text{C}$, respectively.

Figure S6 . The chain-like structure of crystal $\text{Cd}_4(5,5'\text{-mbpy})_{10}[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$ (**2**) (mbpy = 5,5'-dimethyl-2,2'-dipyridyl). Polyhedra: $\{\text{VO}_5\}$. Color codes: yellow, Cd; dark yellow, As; red, O; blue, N; gray, C.

Figure S7. Control experiments showing UV/Vis spectroscopy of the reduction of Cr(VI) ion catalytic by crystal **1** in absence of HCOOH at 25 $^\circ\text{C}$.

Figure S8 . IR spectra of crystal **1** before and after catalytic experiments. The vibration modes for $\nu(\text{V}=\text{O})$, $\nu(\text{V}-\text{O}-\text{M})$ and $\nu(\text{As}-\text{O})$ ($\text{M} = \text{V}$ or As) are observed at 1000, 820, 764, 719, 555 cm^{-1} . Peaks in 1300-1750 cm^{-1} can be assigned to characteristic vibration of organic ligand bpp.

Table S1 Crystal data for structure refinement for compound **1**(CCDC-1029008).

Empirical formula	C52 H58 As8 Cu4 N8 O43 V14
Formula weight	3049.78
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
<i>a</i> , α(Å, °)	12.0877(18); 106.261(2)
<i>b</i> , β(Å, °)	12.4169(18); 109.509(2)
<i>c</i> , γ(Å, °)	16.3010(18); 93.014(2)
Volume	2184.9(5) Å ³
<i>Z</i>	1
Density (calculated)	2.318 Mg/m ³
Absorption coefficient	5.468 mm ⁻¹
<i>F</i> ₍₀₀₀₎	1472
Crystal size	0.17 x 0.15 x 0.15 mm ³
Theta range for data collection	1.81 to 25.01°.
Index ranges	-14 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 9, -16 ≤ <i>l</i> ≤ 19
Reflections collected	10967
Independent reflections	7610 [R(int) = 0.0185]
Completeness to theta = 25.01	98.9 %
Absorption correction	Empirical
Max. and min. transmission	0.440 and 0.411
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	7610 / 0 / 676
Goodness-of-fit on <i>F</i> ²	1.032
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0625, <i>wR</i> ₂ = 0.1620
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0809, <i>wR</i> ₂ = 0.1728
Largest diff. peak and hole	1.874 and -2.244 e. ⁻³

Table S2 Selected bond lengths [\AA] for compound **1**.

Cu(1)-N(2)	1.906(7)	Cu(1)-N(1)	1.913(7)
Cu(1)-O(18)	2.139(6)	Cu(2)-N(4)	1.900(7)
Cu(2)-N(3)#1	1.910(7)	Cu(2)-O(14)	2.335(6)
V(1)-O(9)	1.601(5)	V(1)-O(10)	1.943(6)
V(2)-O(18)	1.617(5)	V(2)-O(5)	1.943(6)
V(3)-O(17)	1.578(6)	V(3)-O(21)	1.946(7)
V(4)-O(6)	1.956(5)	V(4)-O(13)	1.956(6)
V(5)-O(20)	1.584(6)	V(5)-O(11)	1.945(7)
V(6)-O(15)	1.803(7)	V(6)-O(11)	1.829(6)
V(7)-As(4)	1.782(3)	V(7)-O(13)	1.836(7)
As(2)-O(12)	1.855(6)	As(2)-V(9)#2	1.857(4)
As(2)-O(24)	1.927(9)	As(3)-O(8)	1.701(6)
As(3)-O(24)#2	1.795(9)	As(3)-O(7)	1.852(5)
As(3)-As(4)	2.105(3)	As(5)-O(16)	1.663(7)
As(5)-O(27)#2	1.757(10)	As(5)-O(6)	1.835(6)
As(8)-O(22)	1.684(6)	As(8)-V(8)#2	1.844(4)
As(8)-O(5)	1.847(6)	As(8)-O(27)	1.938(10)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+1, -z+2$ #2 $-x+1, -y+1, -z$ #3 $-x+1, -y+2, -z+1$

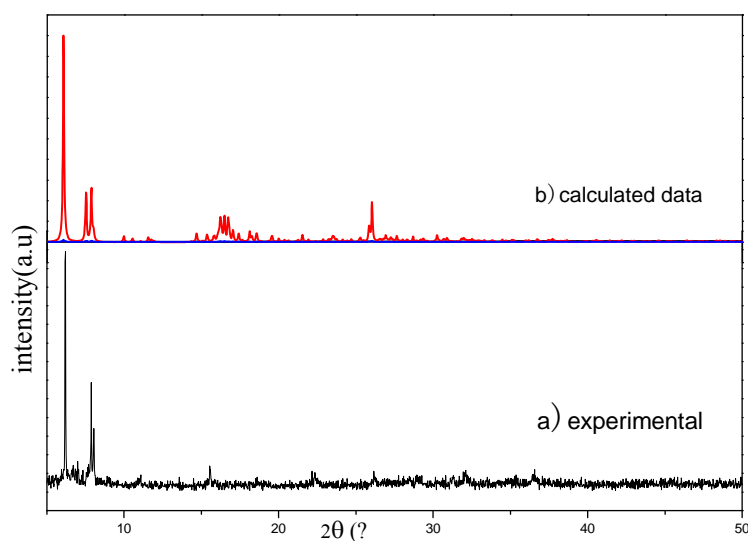


Figure S1. The experimental a) and calculated b) XRD patterns of compound **1**.

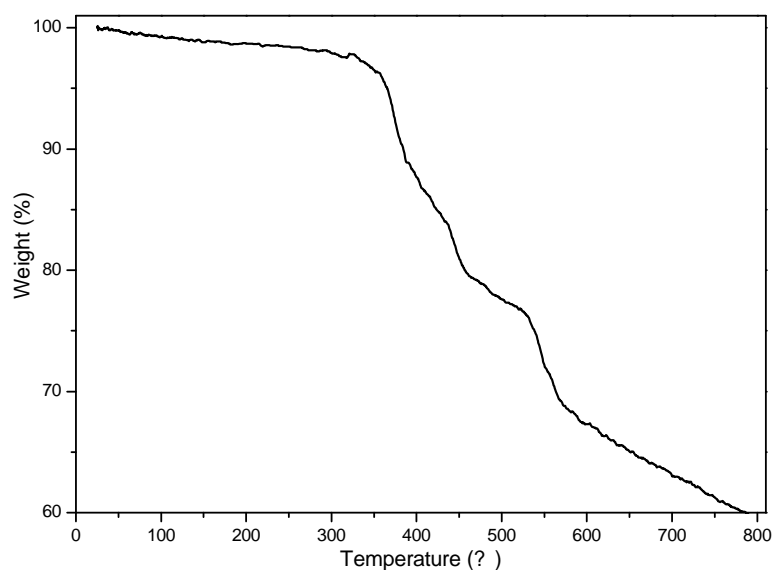


Figure S2. TG curve of compound **1**.

TG and PXRD data indicate that compound **1** is thermally robust. The good agreement of simulated and experimental PXRD patterns supports the composite of material. TG curve shows that the main structure of **1** is stable below 320 °C. As mentioned, the close packing mode and multiple interactions existing among/between the double 2D layers result in a highly stable supramolecular system. The first step of weight loss is slight, corresponding to the removal of water molecules. There is a continuous three-step weight loss process in the 320-800 °C temperature range, attributable to the decomposition and loss of bpp ligands and the sublimation of the part As_2O_3 from **1**.

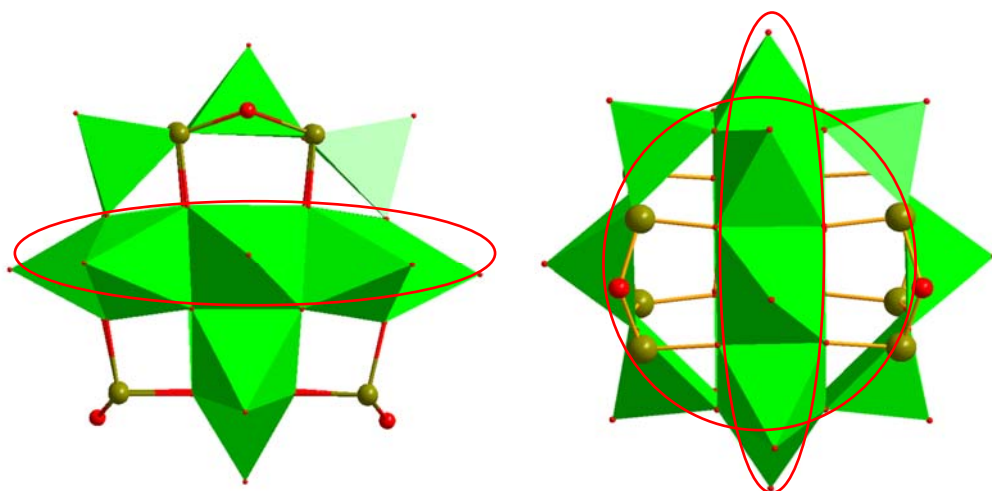


Figure S3. Views showing α -configuration (left) and β -configuration (right) $\{[\text{As}_8\text{V}_{14}\text{O}_{42}]^{4-}\}$.

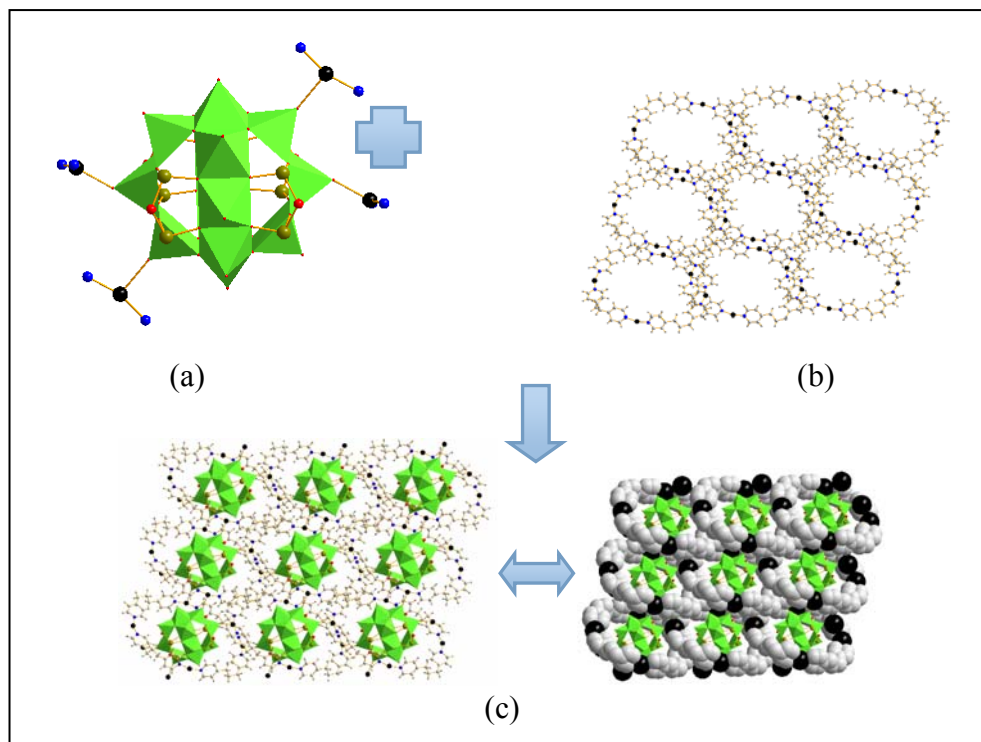


Figure S4. (a) $[\text{As}_8\text{V}_{14}\text{O}_{42}]^{4-}$ anion acts as a quadridentate ligand coordinated to four copper in compound **1**; (b) cationic metal-organic macrocycles of $\{\text{Cu}_4(\text{bpp})_4\}$ units; (c) 2-D structure of compound **1**, green polyhedra representatives $\{\text{VO}_5\}$. T-shaped Cu(I) center is defined by two nitrogen donors from two bpp ligands ($\text{Cu}(1)\text{--N}(1) = 1.913(7) \text{ \AA}$, $\text{Cu}(1)\text{--N}(2) = 1.906(7) \text{ \AA}$, and $\text{Cu}(2)\text{--N}(3) = 1.916(7) \text{ \AA}$, $\text{Cu}(2)\text{--N}(4) = 1.900(7) \text{ \AA}$), and one terminal oxo atom of $[\text{As}_8\text{V}_{14}\text{O}_{42}]^{4-}$ anion ($\text{Cu}(1)\text{--O}(18) = 2.139(6) \text{ \AA}$, $\text{Cu}(2)\text{--O}(14) = 2.335(6) \text{ \AA}$). The $\text{N}(2)\text{--Cu}(1)\text{--N}(1)$ and $\text{N}(4)\text{--Cu}(2)\text{--N}(3)\#1$ ($\#1 -x+1, -y+1, -z+2$) angles are $153.2(3)^\circ$ and $162.4(3)^\circ$, and $\text{N}(1)\text{--Cu}(1)\text{--O}(18)$ and $\text{N}(2)\text{--Cu}(1)\text{--O}(18)$ angles are $103.7(3)^\circ$ and $102.8(3)^\circ$.

Comparative catalysis experiments:

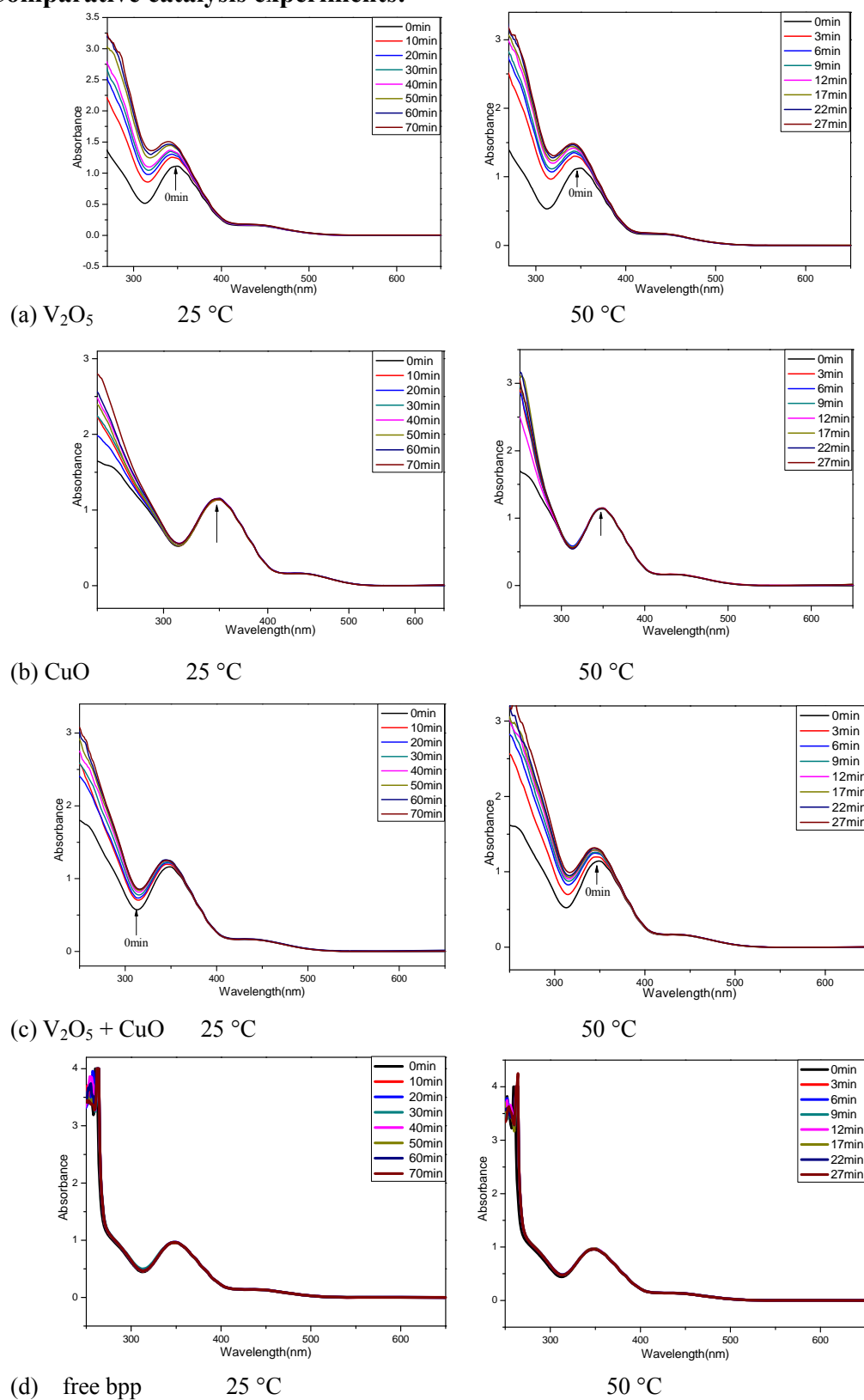


Figure S5. UV/Vis spectroscopy of the reduction of Cr(VI) ions upon reaction with formic acid in the presence of a) V_2O_5 ; b) CuO; c) $V_2O_5 + CuO$; d) free bpp ligand at elevated temperature of 25 °C and 50 °C, respectively.

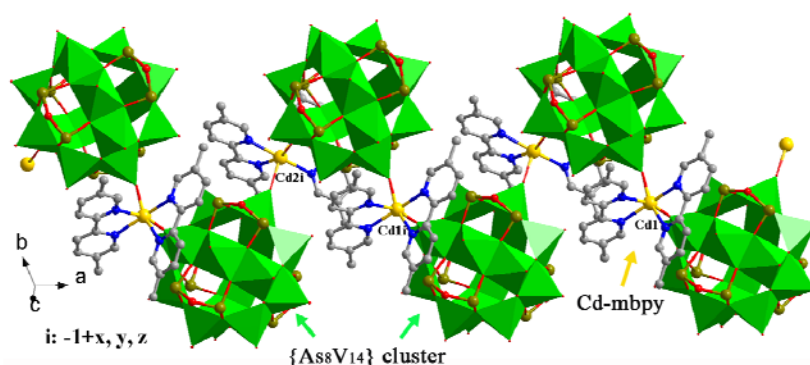


Figure S6 . The chain-like structure of crystal $\text{Cd}_4(5,5'\text{-mbpy})_{10}[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$ (**2**) (mbpy = 5,5'-dimethyl-2,2'-dipyridyl). The bond distances are $\text{Cd-O} = 2.205(5) \sim 2.276(5) \text{ \AA}$ and $\text{Cd(1)-N} = 2.270(6) \sim 2.295(6) \text{ \AA}$, respectively. Polyhedra: $\{\text{VO}_5\}$. Color codes: yellow, Cd; dark yellow, As; red, O; blue, N; gray, C.

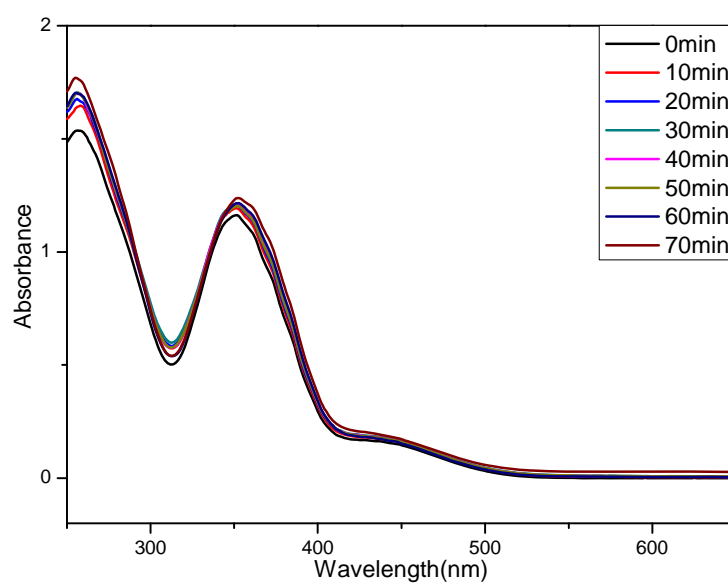


Figure S7 . Control experiments showing UV/Vis spectroscopy of the reduction of Cr(VI) ions catalytic by crystal **1** in absence of HCOOH at 25°C .

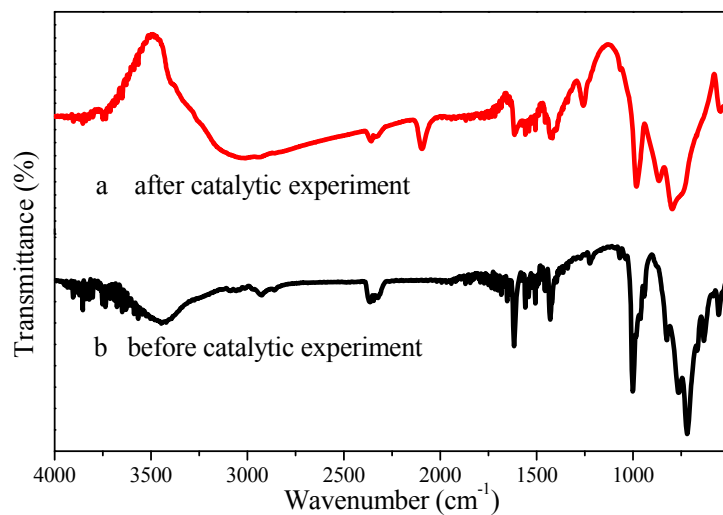


Figure S8 . IR spectra of crystal **1** before and after catalytic experiments. The vibration modes for $\nu(\text{V}=\text{O})$, $\nu(\text{V}-\text{O}-\text{M})$ and $\nu(\text{As}-\text{O})$ ($\text{M} = \text{V}$ or As) are observed at 1000, 820, 764, 719, 555 cm^{-1} . Peaks in 1300-1750 cm^{-1} can be assigned to characteristic vibration of organic ligand bpp.