# **Supporting information**

Cu Induced  $[H_6W_{12}O_{42}]^{6-}$  Polyoxometalate Based Bimetallic Cluster Formation for Renewable Biomass Inulin Hydrolysis toward Fructose Production

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# Experimental

#### General methods and materials

All syntheses and manipulations were performed in the open air, all other chemicals, including solvents, were commercially available as reagent grade and used as received without further purification from Adamas-beta®. Fourier transform infrared spectoscopy (FT-IR) was recorded on a Perkin Elmer FT-IR spectrometer. UV-Vis spectra were measured in acetonitrile by Agilent Cary 300 spectrophotometer. The mass spectra were obtained using an ion trap mass spectrometer (Thermofisher LTQ). Negative mode was chosen for the experiments (capillary voltage 33 V). Sample solution (in H<sub>2</sub>O) was infused into the ESI source at a flow rate of 300  $\mu$ L min<sup>-1</sup>. The Elemental analyses of H were performed by Elementar Analysensysteme GmbH (vario EL) while the elemental analyses of metallic elements were performed by X-ray fluorescence (XRF) element analyzer PANalytical Epsilon 5. X-ray photoelectron spectroscopy (XPS) measurements were performed under ultrahigh vacuum (UHV) with 1.0×10<sup>-7</sup> Torr, axis HS monochromatized Al K $\alpha$  cathode source at 150W, focused X-ray 100 um beam, Pass energy:

55 eV wih 0.1eV step length, detect angle (take off): 45° on X-ray microprobe (ULVAC-PHI Quantera SXM). Binding energy was calibrated With C1s = 284.8 eV. Thermal gravimetric analysis (TGA) was recorded on a Mettler Toledo TGA/SDTA851 in flowing air of 50.0 ml/min with a heating rate of 20 °C /min. Agilent 1290 Infinity High pressure liquid chromatograph (HPLC), were used for catalytic analysis. HPLC were equipped with a column packed with ion exchange resin in calcium form. The units included differential refractometers which were used as a detector. The mobile phase at a flow rate of 0.6 ml/min. The samples were centrifuged before injection into the HPLC. The powder product was measured by PANalytical X'Pert Powder X-ray powder diffractometer operated at a voltage of 60 kV and current of 55 mA with CuK $\alpha$  radiation ( $\lambda = 1.5406$  Å).

#### The synthesis of Cu<sub>3</sub>(H<sub>2</sub>O)<sub>8</sub>[H<sub>6</sub>W<sub>12</sub>O<sub>42</sub>]

2.956g  $(NH_4)_6H_2W_{12}O_{40}$  was dissolved in 30 mL H<sub>2</sub>O. And then the solution was acidized by 1M HCl to pH 4.0. Further, 0.5628 g Cu(NO<sub>3</sub>)<sub>2</sub> was added into the solution with vigorous stirring and refluxing for 1 h. Then large number precipitate of Cu<sub>3</sub>[H<sub>6</sub>W<sub>12</sub>O<sub>42</sub>] cluster was obtained as verdure powder (90% yields based on W).

 $Cu_{3}H_{22}O_{50}W_{12}$ ,  $M_{r} = 3218.86$ ,  $Cu \ 6.11 \ W \ 68.38$  while calc.  $Cu \ 5.92 \ W \ 68.54$ . IR (major absorbances, cm<sup>-1</sup>): 3166, 3033, 2830, 1607, 1411, 1343, 931, 860 and 721. UV-Vis (MeCN, nm):  $\lambda_{1} = 383$ ,  $\lambda_{1} = 691$ . ESI mass spectrometry (MeCN): calc. m/z (z = 2)=1505.58 { $Cu_{2}[H_{6}W_{12}O_{42}]$ }<sup>2-</sup>; found 1506.06.

The crystallization of Cu<sub>3</sub>(H<sub>2</sub>O)<sub>8</sub>[H<sub>6</sub>W<sub>12</sub>O<sub>42</sub>].24H<sub>2</sub>O,

 $Cu_3H_{70}O_{74}W_{12}, M_r = 3651.23.$ 

The water solubility of such polytungstate based bimetallic compound was very poor. 0.2g  $Cu_3(H_2O)_8[H_6W_{12}O_{42}]$  was redissolved in 20 mL H<sub>2</sub>O and heated to 120°C to form verdure solution. Suitable single crystals for X-ray diffraction were grown by slow evaporation in air. The crystal compound was further characterized by EA.

H 2.12 Cu 5.13 W 60.46 while calc. H 1.93 Cu 5.22 W 60.42

## X-ray crystallography

Suitable single crystals were selected. Data collections were performed by graphite-

monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data reduction, cell refinement and experimental absorption correction were performed with the software package of Agilent Gemini Ultra CrysAlisPro (Ver 1.171.35.11). The structures were solved by direct methods and refined against  $F^2$  by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. All calculations were carried out by the program package of SHELXTL *ver* 5.1 and Olex2 *ver* 1.2.9.<sup>1,2</sup>

#### Crystal data and structure refinement

§ Crystal data: Cu<sub>3</sub>(H<sub>2</sub>O)<sub>8</sub>[H<sub>6</sub>W<sub>12</sub>O<sub>42</sub>].24H<sub>2</sub>O, Cu<sub>3</sub>H<sub>70</sub>O<sub>74</sub>W<sub>12</sub>, M<sub>r</sub> = 3651.23, triclinic, space group  $P_1$ , a = 10.6753(5), b = 12.7814(5), c = 13.0976(5) Å,  $\alpha$ = 113.737(4)°,  $\beta$ = 90.433(3)°,  $\gamma$ = 112.560(4)°, V = 1482.73(12) Å<sup>3</sup>, Z = 2, T = 293(2) K, 6153 reflections measured, R<sub>1</sub>= 0.0482, wR<sub>2</sub>= 0.1062.

CCDC-1568674 contain the supplementary crystallographic data for  $Cu_3[H_6W_{12}O_{42}]$  cluster in this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via <u>https://www.ccdc.cam.ac.uk/structures/</u>.

## Typical procedure for inulin hydrolysis

The inulin hydrolysis were carried out in a flask in air. In a typical reaction, 500 mg inulin and 5 mg Cu<sub>3</sub>[H<sub>6</sub>W<sub>12</sub>O<sub>42</sub>] was added into 4 ml H<sub>2</sub>O. Then the solution was heated at 80 °C for 12 h, while the centrifuged sample solution was monitored at different periods of catalytic reaction time of 0, 1, 2, 4, 6, 8, 12 h respectively. The inulin conversion and the selectivity for fructose was determined by HPLC (Shodex SH1011 column) using an external standard method.

# References

- 1. G. M. Sheldrick, Acta Crystallogr. A, 2008, 64, 112.
- 2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.



Figure S1. The single crystal of Cu<sub>3</sub>[H<sub>6</sub>W<sub>12</sub>O<sub>42</sub>].



**Figure S2a.** 3D framework of  $Cu_3[H_6W_{12}O_{42}]$  cluster packing along *a*-axis as analogous molecular sieve material possessed nanoporous (local amplification veiw).



Figure S2b. 3D framework of  $Cu_3[H_6W_{12}O_{42}]$  cluster packing along (a) *b*-axis and (b) *c*-axis.



**Figure S3.** The FT-IR spectrum of  $Cu_3[H_6W_{12}O_{42}]$  cluster.



Figure S4. ESI-MS of Cu<sub>3</sub>[H<sub>6</sub>W<sub>12</sub>O<sub>42</sub>] cluster.



**Figure S5.** (a) UV/Vis spectrum and (b) optical energy gap of  $Cu_3[H_6W_{12}O_{42}]$  cluster.



Figure S6. TGA analysis of the Cu<sub>3</sub>[H<sub>6</sub>W<sub>12</sub>O<sub>42</sub>] cluster.



Figure S7a. The full XPS spectrum survey of Cu<sub>3</sub>[H<sub>6</sub>W<sub>12</sub>O<sub>42</sub>] cluster.



Figure S7b. The narrow element XPS spectrum of Cu with raw intensity and peak fitting sum.



Figure S7c. The narrow element XPS spectrum of W with raw intensity and peak.



**Figure S8.** The simulated, original experimental and fifth catalytic run recovered powder XRD pattern of catalyst  $Cu_3[H_6W_{12}O_{42}]$ . Simulation based on the single crystal X-ray diffraction data.



Figure 9a. A sample chromatogram of inulin before the hydrolysis reaction.



**Figure S9b.** A sample chromatogram of inulin after 6h of the hydrolysis reaction catalyzed by  $Cu_3[H_6W_{12}O_{42}]$  cluster.

Table S1. Details and results of the BVS calculations.

Subroutine Calc\_BVS (JRC-LLB, version: March-2005).

Atom	Coord	D_aver Sigm	Distort(x10-4)	Valence	BVSum(Sigma)
W1	6	1.9517(36)	75.797	6	5.993(60)
W3	6	1.9550(35)	74.713	6	5.953(62)
Cu3	6	2.1117(37)	80.149	2	2.090(25)
W6	6	1.9545(36)	82.788	6	6.027(66)
W5	6	1.9725(36)	122.126	6	6.025(62)
W2	6	1.9449(36)	64.877	6	6.053(63)
W4	6	1.9613(36)	89.06	6	5.958(65)
Cu1	6	2.0937(37)	70.219	2	2.158(24)
Cu2	6	2.1226(36)	105.033	2	2.095(24)
06	2	1.9229(65)	9.472	-2	1.994(34)
O10	2	1.9351(69)	3.397	-2	1.913(37)
O15	3	1.8723(74)	42.927	-2	2.424(50)
07	2	1.9457(66)	0.312	-2	1.851(33)
O11	3	1.8653(64)	13.133	-2	2.387(40)
O24	2	2.0110(102)	0	-2	0.815(22)
O4	2	1.9864(65)	35.695	-2	1.744(35)
O9	2	1.9608(45)	54.27	-2	1.914(24)
01	3	2.2405(49)	3.401	-2	1.259(18)
05	2	1.9828(57)	21.804	-2	1.727(29)
O13	2	1.9471(63)	1.277	-2	1.847(32)
O19	3	2.0791(51)	279.447	-2	1.916(34)
08	2	1.9601(49)	64.266	-2	1.943(25)
O20	3	1.8610(58)	13.757	-2	2.417(38)
O17	1	1.7383(109)	0	-2	1.621(48)
O18	2	1.9187(60)	4.824	-2	2.004(32)
016	1	1.7392(90)	0	-2	1.617(39)
O22	2	2.3402(78)	0	-2	0.335(7)
O21	1	1.7419(109)	0	-2	1.605(47)
O2	3	2.1288(57)	52.239	-2	1.257(34)
O3	3	2.1479(55)	83.714	-2	1.271(32)
O14	1	1.7256(63)	0	-2	1.678(29)
O23	2	1.9460(88)	0	-2	0.972(23)
O25	2	2.0290(93)	0	-2	0.777(20)
O12	3	2.0629(52)	226.465	-2	1.866(31)

Title: Summary of Bond-Valence calculations for file:  $Cu_3[H_6W_{12}O_{42}].cfl$