Supporting Information

Synthesis, Structure, Photocatalytic and Magnetic Properties of an Oxo-bridged Copper Dimer

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Table S1.Crystal data and structure refinement parameters of compound **1**.[a]

Empirical formula	$C_8H_{14}N_6O_8Cu$
Formula weight	385.77
Crystal system	Orthorhombic
Space group	*Pbca* (No. 61)
Crystal size	0.20 x 0.15 x 0.15
a	11.6890 (3) Å
b	14.7288(4) Å
c	17.9191(5) Å
α	90.000
β	90.000
γ	90.000
Volume	3085.04(2) $Å^3$
Z	8
$\rho_{calcd}(gcm^{-3})$	1.661
μ (mm^{-1})	1.467
θ range (deg)	2.86 to 30.50
reflection collected	19348
unique reflections	4657
number of parameters	211
Goodness of fit	1.053
R index [I > 2σ(I)]	$R_1 = 0.0370$, $wR_2 = 0.1157$
R indices (all data)	$R_1 = 0.0538$, $wR_2 = 0.1290$
largest diff. peak and hole e $Å^{-3}$	0.843 and -0.350

[a] $R_1 = \Sigma||F_0| - |F_c||/ \Sigma|F_0|$; $wR_2 = \{[w(F_0^2 - F_c^2)^2]/ [w(F_0^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$; $P = [\max(F_0^2,0) + 2(F_c)^2]/3$,
where $a = 0.0798$ and $b = 0.7863$ for **1**, respectively.

Table S2. Characteristic IR bands of compound **1**.

IR BANDS	**Compound 1**
ν_S (H_2O)	3415 cm^{-1}
ν_S (N – H)	3139 cm^{-1}
ν_S (C – H)asym	2990 cm^{-1}
ν_S (C – H)sym	2813 cm^{-1}
δ_S(H_2O)	1645 cm^{-1}
ν_S (C =O)	1685 cm^{-1}
δ_S(N-H)	1566 cm^{-1}
δ_S(C-H)	1431 cm^{-1}
ν_S (C – N)	1288 cm^{-1}
ν_S (C-O)	1245 cm^{-1}

Table S3: Selected bond distances and angles in compound **1**[a].

Bond	**Distance (Å)**
Cu(1)-O(2)	1.9101(14) [0.535]
Cu(1)-O(1)#1	1.9195(13) [0.522]
Cu(1)-O(1)	1.9296(13) [0.508]
Cu(1)-O(3)	1.9310(15) [0.506]
Cu(1) - O(7)	2.6262(13) [0.077]
Σ (Cu – O)	**[2.12]**
O(1)-C(1)	1.416(2)
O(6)-C(4)	1.254(2)
O(5)-C(3)	1.233(2)
C(1)-C(2)	1.534(3)
C(1)-C(6)#1	1.535(3)
C(1)-C(4)	1.547(3)
O(4)-C(5)	1.234(3)
O(3)-C(5)	1.289(2)
O(2)-C(3)	1.284(2)
C(6)-C(5)	1.515(3)
C(6)-C(1)#1	1.535(3)
C(4)-O(7)	1.252(2)
C(4)-O(7)	1.252(2)
C(4)-O(7)	1.252(2)
C(2)-C(3)	1.542(3)
Moiety	**Angle ( )**
Cu(1)#1-O(1)-Cu(1)	95.36(6)

[a] Values in brackets are the bond valences. Their sum SVB appears in bold type at the end of the list of the distances around copper atom. Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z+1

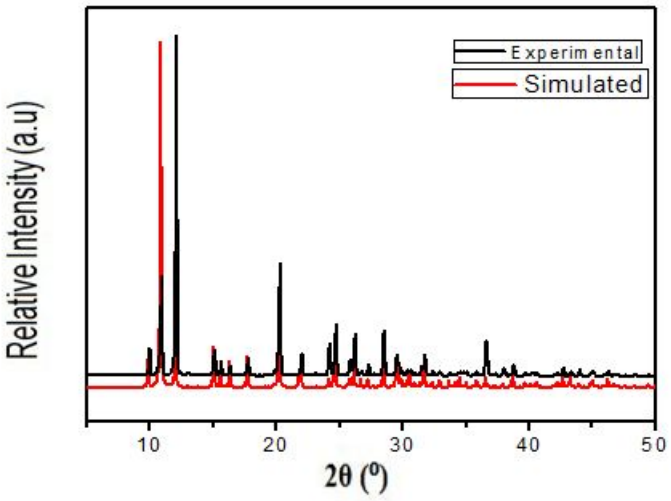


Figure S1. The experimental and simulated XRD pattern of **1**.

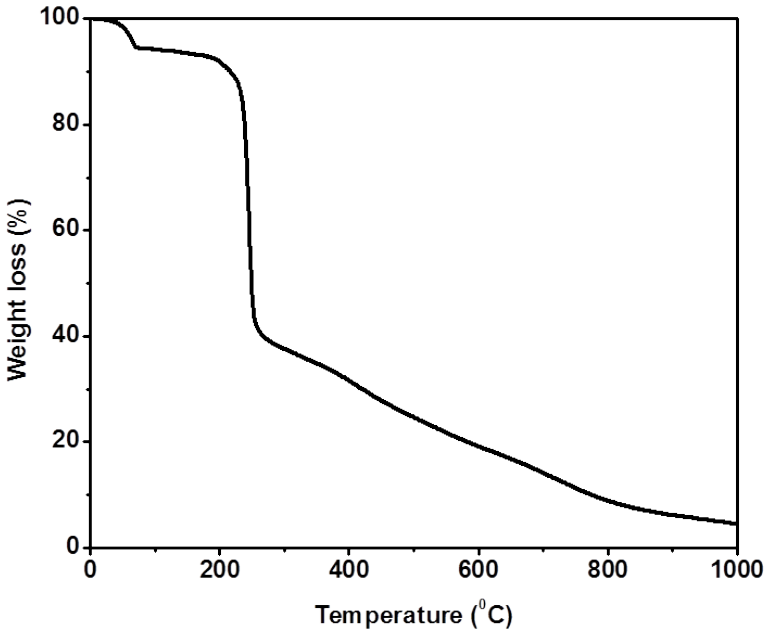


Figure S2. Thermogravimetric Analysis (TGA) plot of **1**.

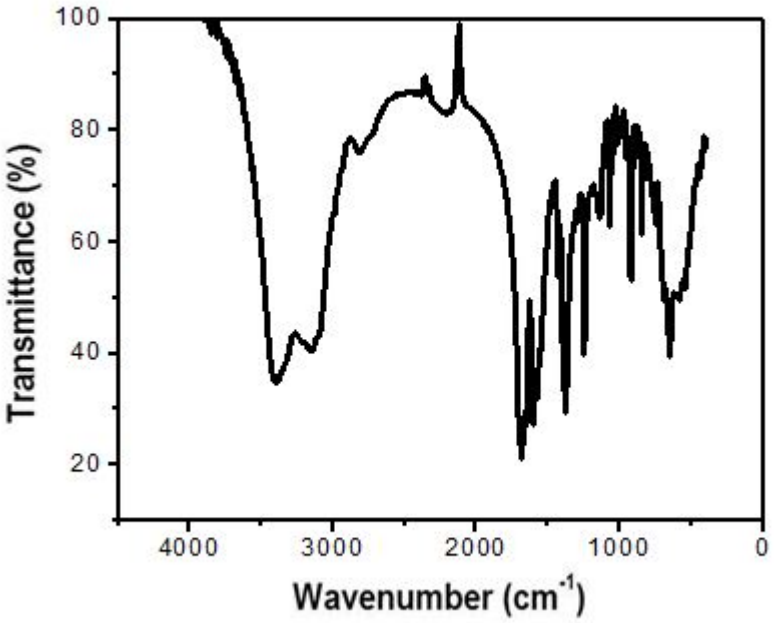


Figure S3. Characteristic IR peaks of compound **1**.

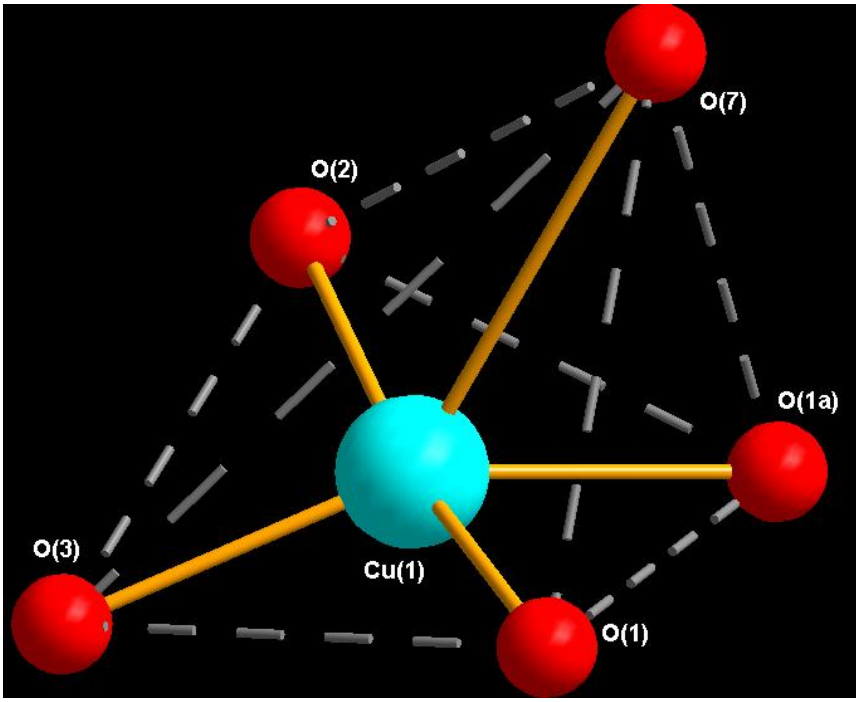
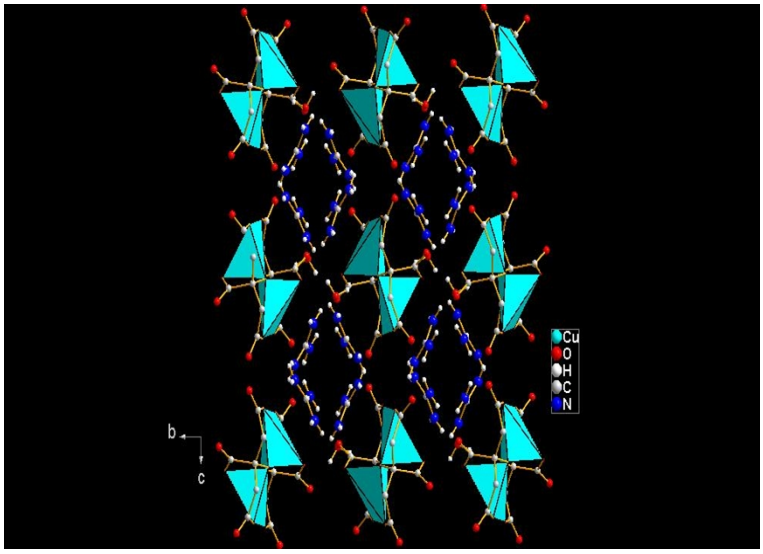
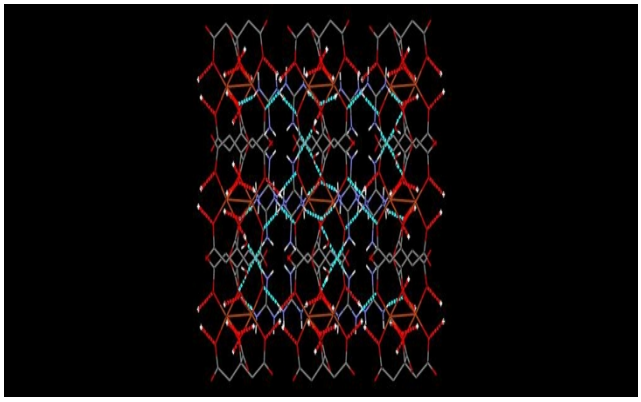


Figure S4. Distorted-square-pyramidal geometry of copper atom in **1**.



(a)



(b)

Figure S5. (a) Arrangement of the cluster units, protonated guanidine molecules and water molecules in *bc* plane in compound **1**. (b) H-bonded network in **1**.

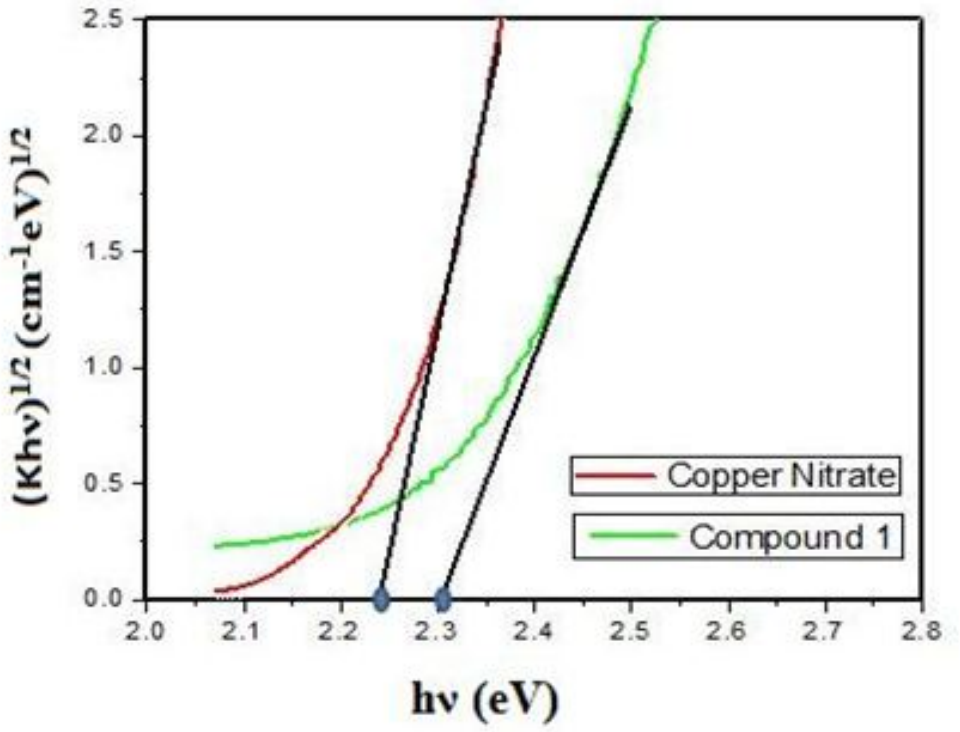
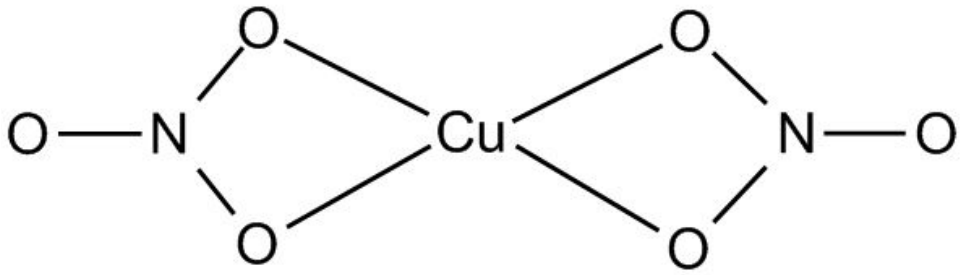


Figure S6. Diffuse reflectance UV-vis-NIR spectra of K–M functions *vs*. energy (eV) of **1** and metal precursor, $Cu(NO_3)_2$. $2.5H_2O$.

(a)



(b)

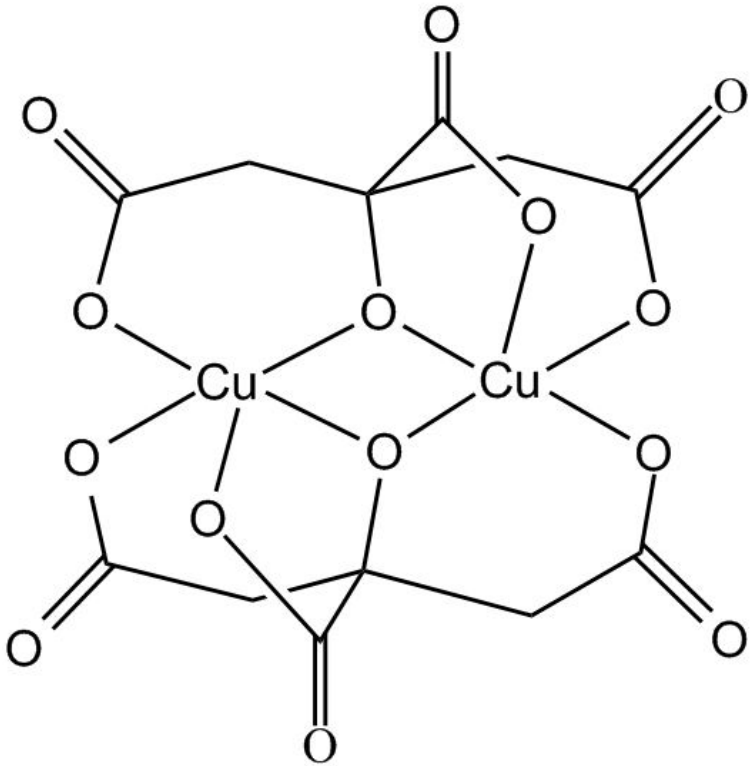


Figure S7. Binding mode of Cu atom with (a) nitrate anion in $Cu(NO_3)_2$ and (b) citrate anions in compound **1**.

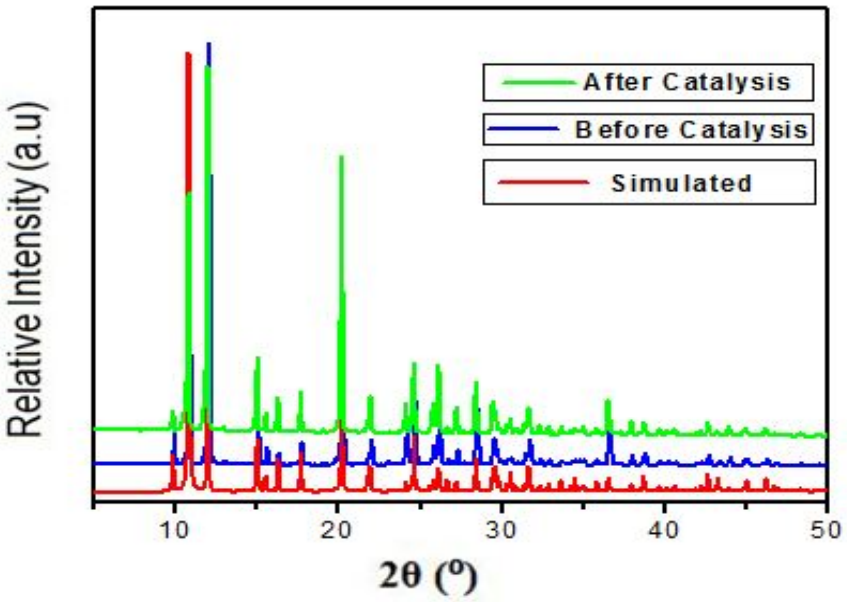
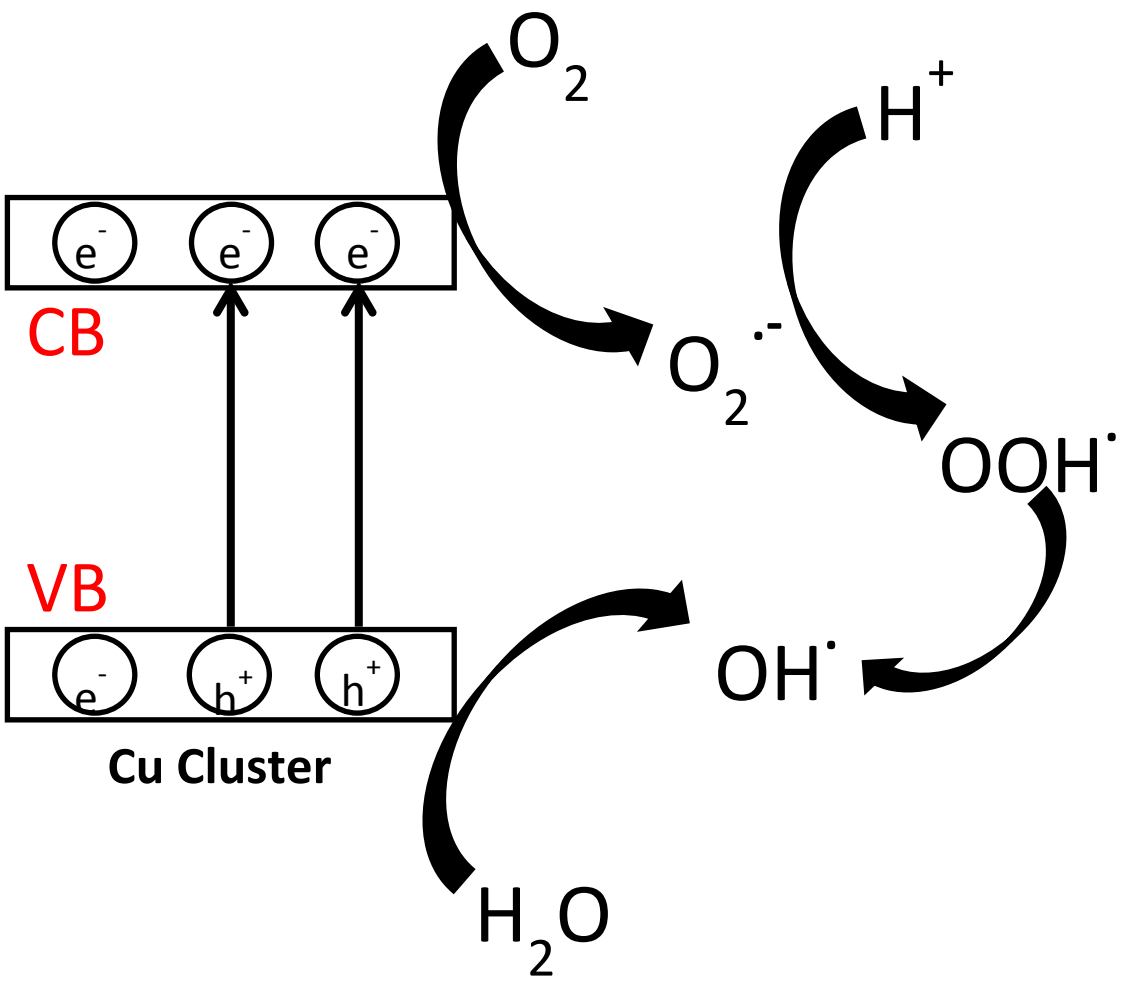


Figure S8. The PXRD patterns of compound **1** before and after photocatalysis.


O2
H+
e-
e-
e-
CB
O2.-
OOH.
VB
OH.
e-
h+
h+
Cu Cluster
H2O

Scheme 1. Schematic diagram of the photocatalytic mechanism of **1**.