

Supporting Information for
Understanding of the low temperature auto-oxidation scheme of sec-
alcohols based on a Cu(II)-MOF with open metal sites

Jian-Ping Ma,* Chao-Wei Zhao, Shen-Qing Wang, Jin-Ping Zhang, Xue Niu and Yu-Bin Dong*

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Normal University, Jinan 250014, P. R. China. Email: yubindong@sdu.edu.cn

- I. Instruments and materials
- II. ^1H NMR spectra of 1-phenylethanol sample, 2-butanol sample and t-butyl hydroperoxide reference
- III. Thermogravimetric analysis of **1'**
- IV. MS spectra of 1-phenylethanol and 2-butanol samples before and after oxygen release
- V. XPS spectra of **1'** before and after oxygen release
- VI. XRPD spectra of **1'** after oxygen release
- VII. Typical oxygen release experiment
- VIII. ESR spectra of 2-butanol sample before and after oxygen release
- IX. X-ray structure determination
- X. Iodometry

I. Instruments and materials

All the chemicals (Acros) were used as obtained without further purification. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400–4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed

on a Perkin-Elmer model 2400 analyzer. ^1H NMR data were collected using an AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS. XRD patterns were obtained on a D8 ADVANCE X-ray powder diffractometer (XRD) with Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). XPS spectra were obtained from TH15300 (PE). EPR spectra were obtained from Bruker A300-10/12/S-LC. GC-MS analysis data were performed on a J&K S011525-300 gas chromatographic (Agilent 6890GC-5973MS). Thermogravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of $10^\circ\text{C}/\text{min}$. All crystal data were obtained by Agilent SuperNova X-Ray single crystal diffractometer.

II. ^1H NMR spectra of 1-phenylethanol sample, 2-butanol sample and t-butyl hydroperoxide reference

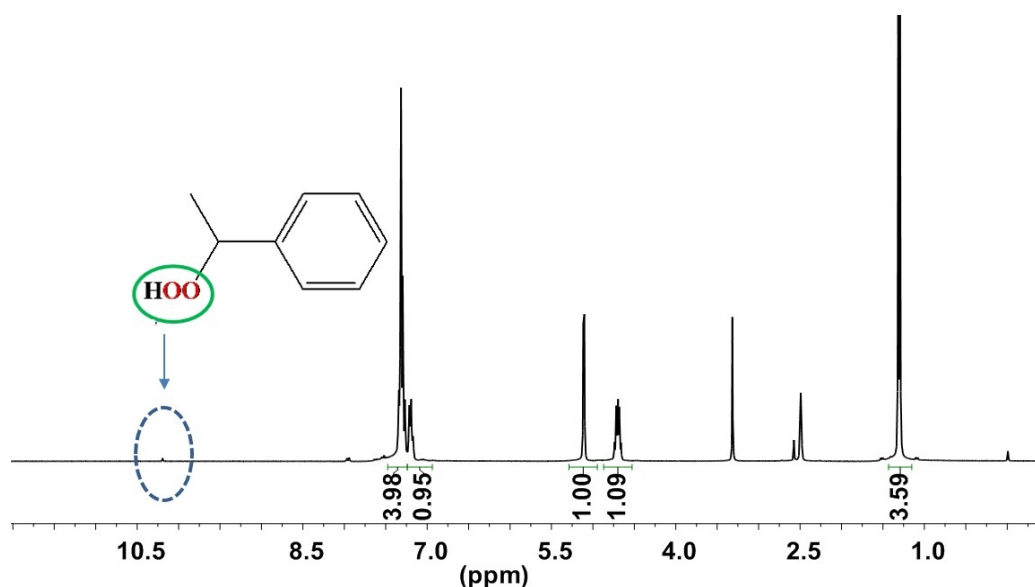


Figure S1. ^1H NMR spectrum of 1-phenylethanol sample allowed to stand at room temperature in air for a month. ^1H NMR (ppm, $\text{DMSO}-d_6$): 7.34-7.17 (m, 5H, $-\text{C}_6\text{H}_5$), 5.12 (s, 1H, $-\text{OH}$), 4.72-4.66 (m, 1H, $-\text{CH}-$), 1.32-1.29 (s, 3H, $-\text{CH}_3$).

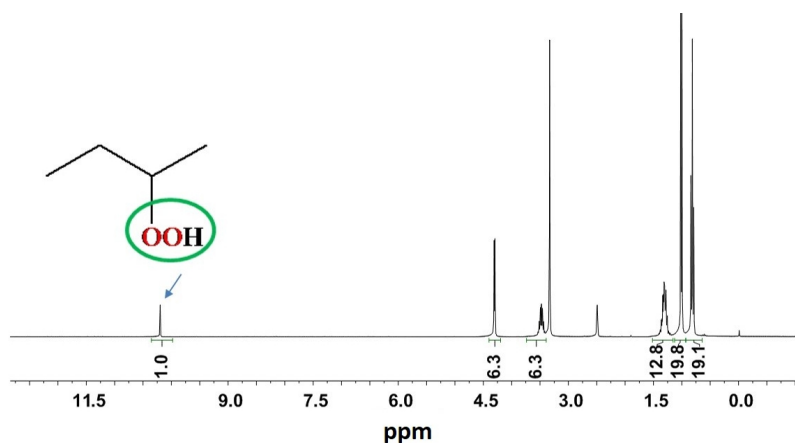


Figure S2. ^1H NMR spectrum of 2-butanol sample allowed to stand at room temperature in air for a month (for clear detection of $-\text{OOH}$, the sample was effectively concentrated due to its relative low b.p. by nitrogen blowing at room temperature). ^1H NMR (ppm, $\text{DMSO-}d^6$): 4.30 (s, 1H, $-\text{OH}$), 3.33-3.47 (m, 1H, $-\text{CH}-$), 1.26-1.29 (m, 2H, $-\text{CH}_2-$), 1.00-1.02 (m, 3H, $-\text{CH}_3$), 0.79-0.84 (m, 3H, $-\text{CH}_3$).

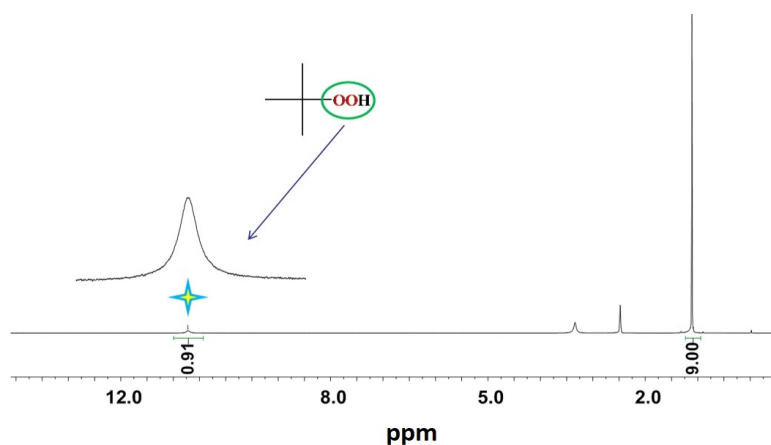


Figure S3. ^1H NMR spectrum of t-butyl hydroperoxide reference. ^1H NMR (ppm, $\text{DMSO-}d^6$): 10.72 (s, $-\text{OOH}$), 1.11 (s, $-\text{CH}_3$).

III. Thermogravimetric analysis of $\mathbf{1'}$

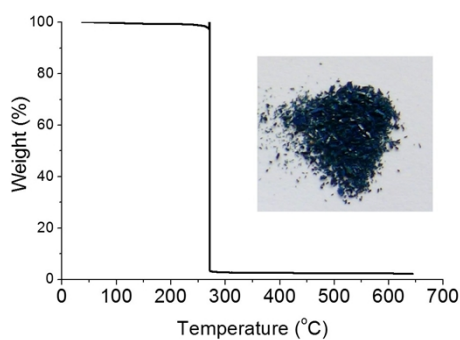


Figure S4. The TGA trace of $\mathbf{1'}$. The photograph of $\mathbf{1'}$ was inserted. No mass loss was observed before 120°C, indicating the coordinating and guest water molecules are

removed.

IV. MS spectra of 1-phenylethanol and 2-butanol samples before and after oxygen release

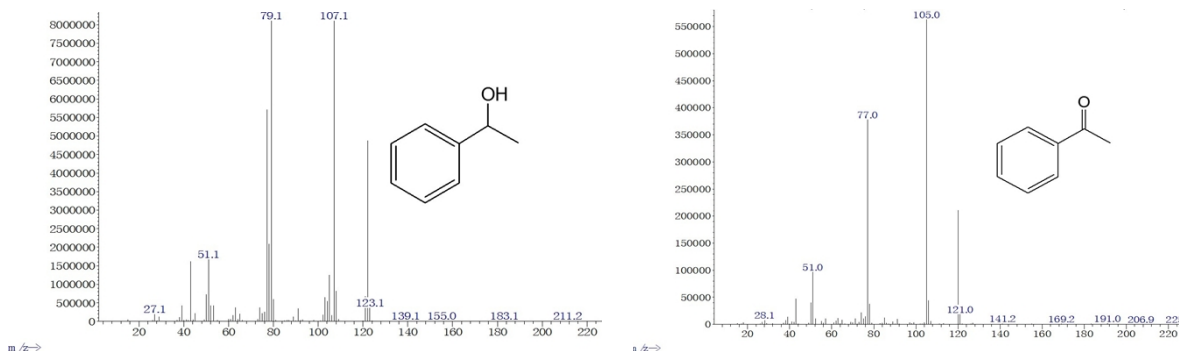


Figure S5. The MS spectra of 1-phenylethanol sample before oxygen release, including 1-phenylethanol ($m/z = 122.07$) and 1-phenylethanone ($m/z = 120.06$) components.

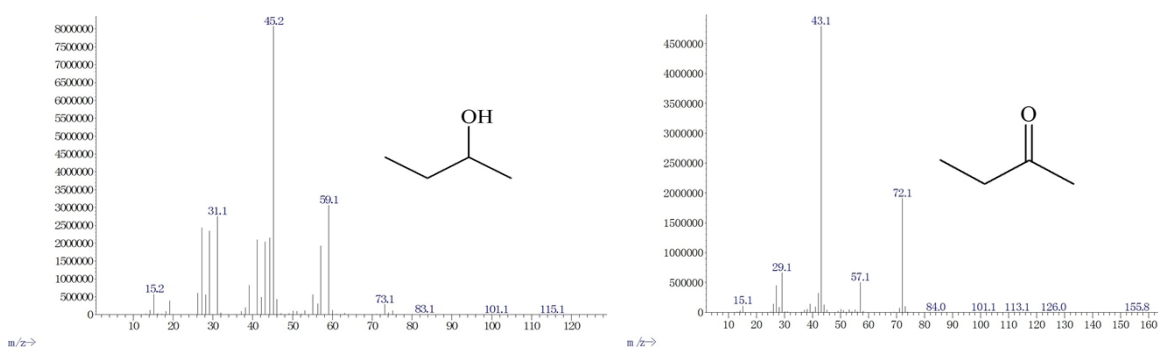


Figure S6. The MS spectra of 2-butanol sample before oxygen release, including 2-butanol ($m/z = 74.07$) and 2-butanone ($m/z = 72.06$) components.

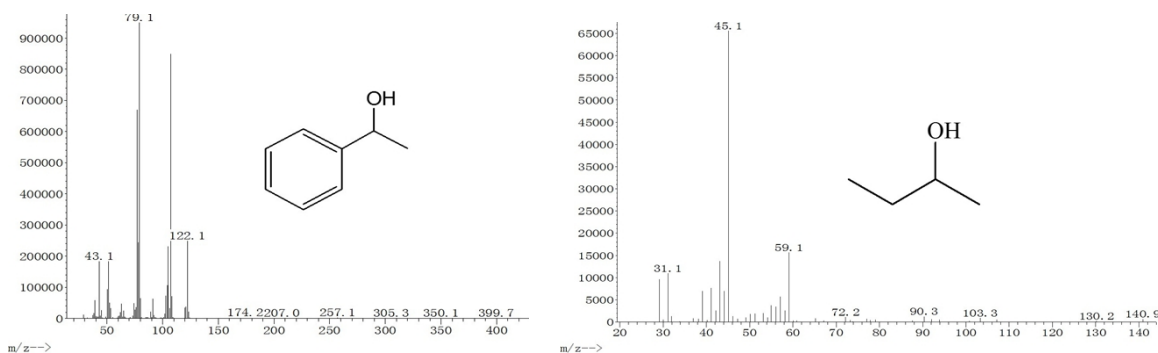


Figure S7. The MS spectra of 1-phenylethanol ($m/z = 122.07$) (left) and 2-butanol ($m/z = 74.07$) (right) sample after oxygen release.

V. XPS spectra of 1' before and after oxygen release

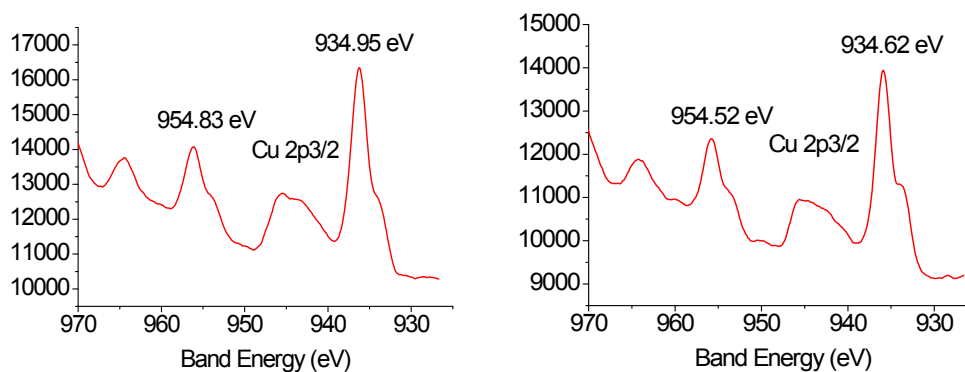


Figure S8. The XPS spectra of **1'** after oxygen release in 1-phenylethanol (left) and 2-butanol (right) sample. No valence change for Cu(II) node was observed ion after the reactions.

VI. XRPD spectra of **1'** after oxygen release

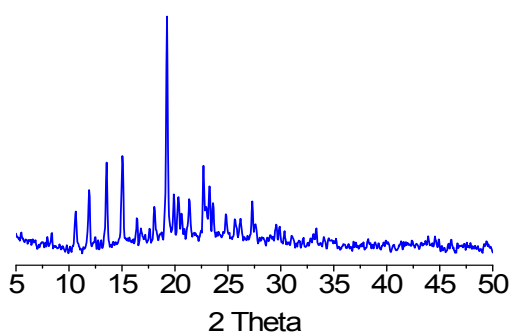


Figure S9. The XRPD pattern of **1'** after the oxygen release, indicating the framework is stable during the reaction.

VII. Typical oxygen release experiment

A mixture of **1'** (40 mg, 0.056 mmol) and sec-alcohol sample (2 mL, allowed to stand at room temperature in air for a month) was sealed in Labsolar-IIIAG system. After removal of air, the sec-alcohol sample was dropped on **1'**. The generated oxygen was online detected on Shimadzu GC-2014C (TCD detector). The sample was taken online every 10 min. The oxygen and alkyl hydroperoxide amounts were obtained by external standard method ($PV = nRT$, by means of standard curve $y = 102857x + 59530$). The contents of 1-phenylethyl

hydroperoxide and 2-butyl hydroperoxide in 1-phenylethanol and 2-butanol samples are up to 0.86 % and 0.71 %, respectively.

Table S1. GC analysis of 1-phenylethanol and 2-butanol samples before and after oxygen release.

Entry	Retention time (min)	Content (%)
Before the reaction	(a) 30.911	0.946
Before the reaction	(b) 30.911	99.054
Entry	Retention time (min)	Content (%)
After the reaction	(b) 30.911	100.00

a = 1-phenylethanone, b = 1-phenylethanol.

Entry	Retention time (min)	Content (%)
Before the reaction	(c) 5.992	0.753
Before the reaction	(d) 8.337	99.247
Entry	Retention time (min)	Content (%)
After the reaction	(d) 8.258	100

c = 2-butanone, d = 2-butanol

VIII. ESR spectra of 2-butanol sample before and after oxygen release

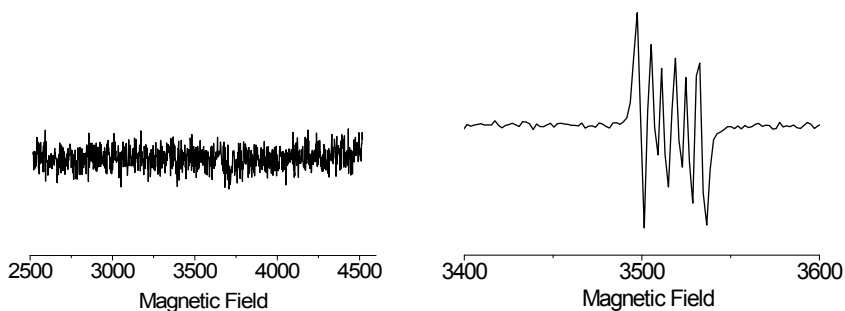


Figure S10. The ESR spectra of 2-butanol sample before (left) and after (right) the oxygen release. No the four characteristic peaks of the DMPO-·OH were observed, indicating the no H₂O₂ species formed in the 2-butanol system.

IX. X-ray structure determination

X-ray Structure Determination of 1. For further confirmation of our previous results, the single crystal structure of **1** was resolved in this work. A deep blue block-like crystal was epoxied onto the end of a thin glass fiber. X-ray intensity data were measured at 298.2 K on a Agilent SuperNova CCD-based diffractometer (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$).¹ After determination of crystal quality and initial tetragonal unit cell parameters, a hemi sphere of frame data was collected. The raw data frames were integrated with CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171. NET) (compiled Aug 2 2013, 16 : 46 : 58),¹ Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The final unit cell parameters are based on the least-squares refinement of 3352 reflections from the data set with $I > 5\sigma(I)$. Analysis of the data showed negligible crystal decay during data collection. Systematic absences in the intensity data were consistent with the space groups $P4(3)2(1)2$. Solution and refinement in $P4(3)2(1)2$ yielded. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against F^2 , using the SHELXTL software package.²

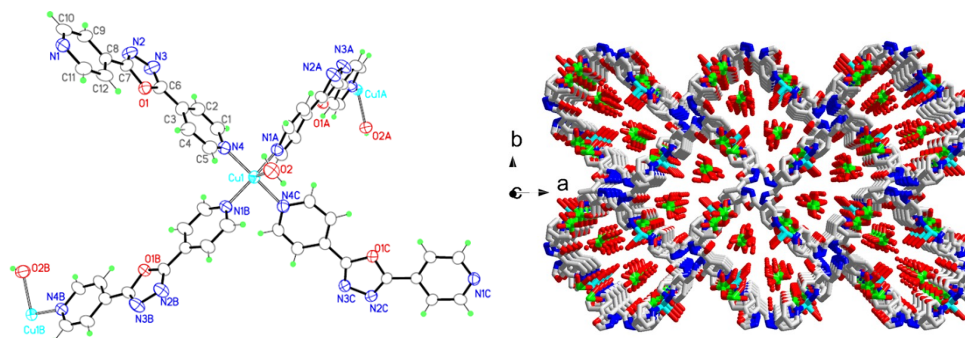


Figure S11. Left: ORTEP figure of **1** (displacement ellipsoids drawn at the 50 % probability level). Right: crystal packing of **1**. Water guest molecules and ClO_4^- anions are located in the pores of **1**.

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

Identification code	1	
Empirical formula	$\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{CuN}_8\text{O}_{15}$	
Formula weight	800.97	
Temperature	298.2(2) K	
Wavelength	1.54184 Å	
Crystal system, space group	Tetragonal, $P4(3)2(1)2$	
Unit cell dimensions	$a = 16.4013(3)$ Å	alpha = 90 deg.
	$b = 16.4013(3)$ Å	beta = 90 deg.
	$c = 13.9201(5)$ Å	gamma = 90 deg.
Volume	$3744.54(17)$ Å ³	
Z, Calculated density	4, 1.421 Mg/m ³	
Absorption coefficient	2.785 mm ⁻¹	
F(000)	1636	
Crystal size	0.2100 x 0.1200 x 0.0700 mm	
Theta range for data collection	3.81 to 67.05 deg.	
Reflections collected / unique	9665 / 3352 [R(int) = 0.0225]	
Completeness to theta = 26.36	100.0 %	
Data / restraints / parameters	3352 / 21 / 230	
Goodness-of-fit on F ²	1.063	
Final R indices [I > 2sigma(I)]	R1 = 0.0811, wR2 = 0.2280	

X. Iodometry

Pipetted out the sec-alkyl alcohol sample into a flask which contains KI (2 g), H_2SO_4 (0.5 M, 25 mL) and drops of $(\text{NH}_4)_5\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (30 g/L). The solution was the titrated with thiosulfate (0.1 M) till the solution lost its pale yellow color. Then added starch as indicator

and again titrated it till the purple color disappeared.

The consumed thiosulfate solution (mL)

	1	2	3	Average value
For 2-butanol sample	1.87	1.87	1.93	1.89
For 1-phenyethanol sample	1.75	1.65	1.73	1.71

Reference

(1) CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171.NET) (compiled Aug 2 2013, 16:46:58).

(2) Sheldrick, G. M. SHELXTL Version 5.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.