Supporting Information

A high-nuclear Cu^{I}/Cu^{II} nanocluster catalyst for phenol degradation

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Materials and reagents.

All chemicals and solvents were purchased from commercial were used without further purification.

Instrumentation.

PXRD data were collected at room temperature in the air using X'Pert PRO diffractometer (Cu Kα, λ = 1.54178 Å). In situ PXRD patterns for the samples were collected in mother liquor on a Rigaku XtaLAB Pro diffractometer with Cu-Kα radiation. UV-vis absorption spectra were recorded with a U-2000 spectrophotometer. HRESI-TOF-MS spectra were recorded on an AB Sciex X500R Q-TOF spectrometer. TEM images were acquired with a Tecnai G2 F20 S-TWIN transmission electron microscope (operated at an acceleration voltage of 200 kV). X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG Scientific ESCALAB 250 instrument. EDS measurements were carried out using Zeiss Sigma 500. Phenol degradation was carried by high Performance Liquid Chromatography (HPLC) using Agilent 300Extend C18 column (5 μm particles, 4.6 mm ID, 250 mm length). The mobile phase required for separation is CH_3OH: H_2O = 1:1.

Single-Crystal X-ray Diffraction Analysis (SCXRD).

SCXRD measurements were performed on a Rigaku XtaLAB Pro diffractometer with Cu-Kα radiation (λ = 1.54178 Å) at 293 K for **Cu_{54}**. Data collection and reduction were performed using the program CrysAlisPro[1]. The intensities were corrected for absorption using the empirical method implemented in SCALE3 ABSPACK scaling algorithm. The structures were solved with intrinsic phasing methods (*SHELXT-2015*)[2], and refined by full-matrix least-squares on F^2 using *OLEX$_2$*,[3] which utilizes the *SHELXL-2015* module.[3] The crystal structures are visualized by DIAMOND 3.2.[4]

XAFS measurements:

The X-ray absorption finds structure spectra Cu K-edge were collected at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). The data were collected in fluorescence mode using a Lytle detector while the corresponding reference samples were collected in transmission mode. The sample was finely grounded and uniformly spread on special adhesive tape.

XAFS Analysis and Results: The acquired EXAFS data were processed according to the standard procedures using the ATHENA module of Demeter software packages.

Synthesis of Cu_{54}.

(^tBuSCu)$_n$ (15 mg, 0.098 mmol) was ultrasonic dissolved in 6 mL chloroform, to which $^tBuPO_3H_2$ (5 mg, 0.037 mmol) was added. After stirring for 5 mins, $S(SiMe_3)_2$ (4 μL) was added. The resulting solution was evaporated at room temperature for about 3 days to afford red polyhedral crystals of **Cu_{54}** (yield 34%, based on Cu). Anal. Calcd for $Cu_{54}S_{13}O_6(^tBuS)_{20}(^tBuSO_3)_{12}$: C: 20.84%; H: 3.77%; S: 19.56%. Found: C: 20.963%; H: 3.78%; S: 18.98%.

Preparation of Cu_{54}/TiO_2 catalysts.

200 mg TiO_2 (Rutile-typed, 99.99% (metals basis), 5-10 nm.) was added into an acetonitrile solution of 0.2 mg, 1 mg, 2 mg, 4 mg **Cu_{54}** respectively. The resulting suspension was stirred at room temperature for 6 hours. The catalysts were collected by concentration and vacuum drying at room temperature and named as n**Cu_{54}**/TiO_2 (n= 0.1 wt.%, 0.5 wt.%, 1.0 wt.% and 2.0 wt.%). Note that the weight percentage refers to the ligand-protected form of the clusters.

Photocatalytic reaction.

The photocatalytic degradation reaction of phenol was carried out in a Pyrex reaction cell. **Cu_{54}**/TiO_2 was dispersed in an aqueous solution containing given amounts of the pollutants (C_0 = 5 ppm). The concentration of phenol was monitored by HPLC. (Retention value: 7.26 = Phenol, 3.089 = Catechol, 2.89 = Hydroquinone, 2.688 = Benzoquinone).

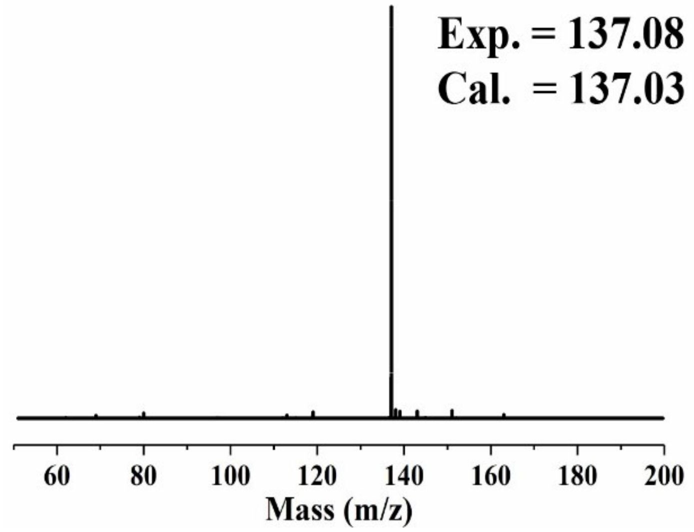

Figure S1. The mass spectrometry of **Cu_{54}** in negative ion mode.

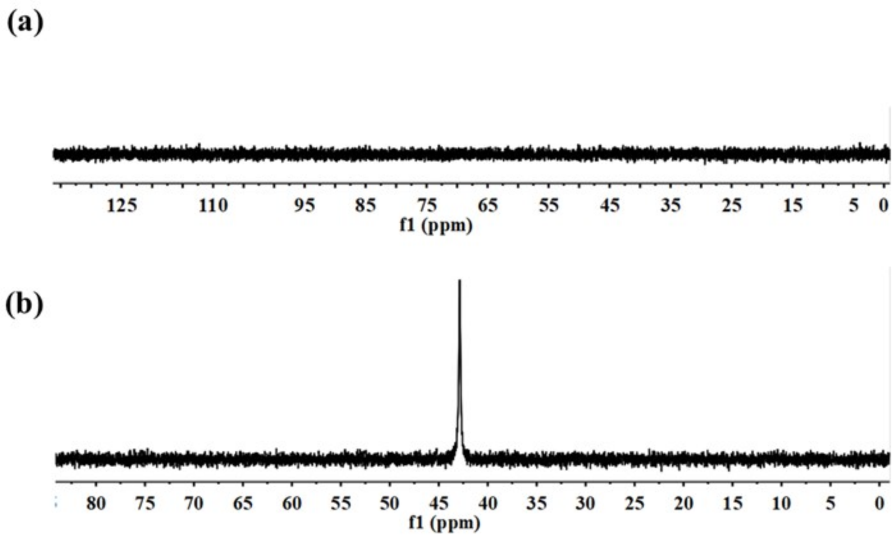

Figure S2. The ^{31}P NMR spectra of (a) **Cu_{54}**; (b)$^tBuPO_3H_2$.

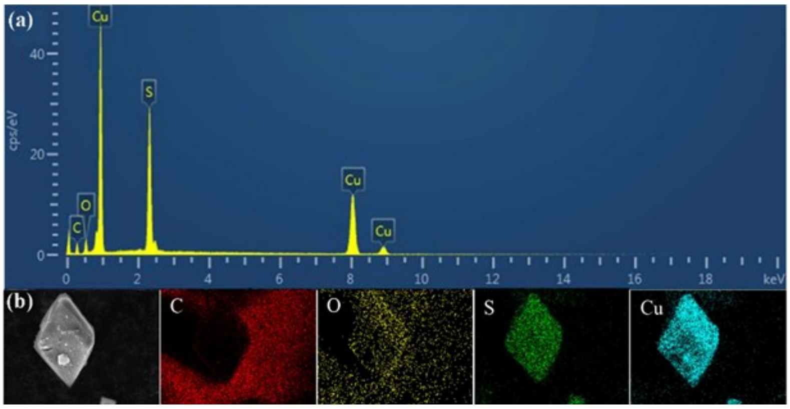

Figure S3. (a) The X-ray energy spectrum of **Cu_{54}**; (b) Elemental distribution of **Cu_{54}**.

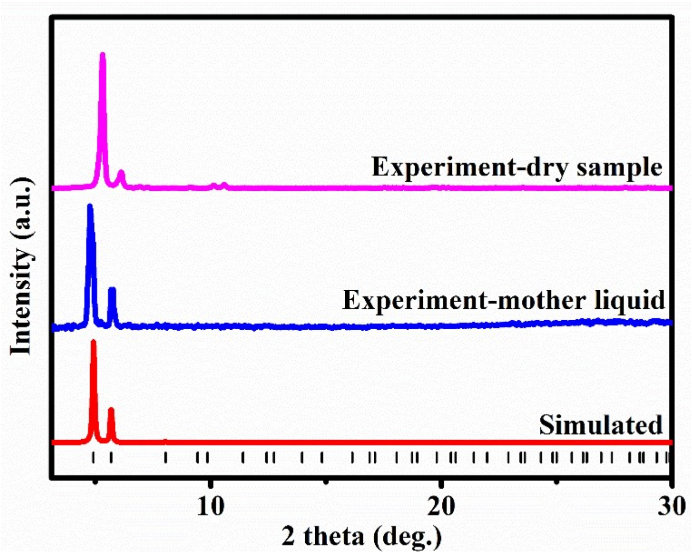

Figure S4. Powder X-ray diffraction pattern (PXRD) of **Cu_{54}**.

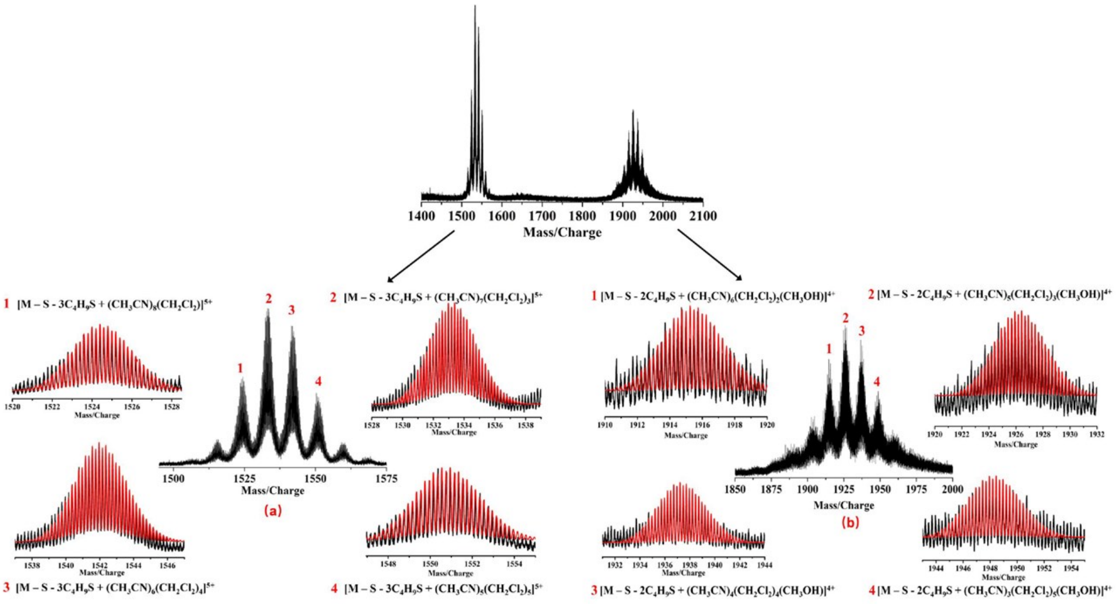

Figure S5. Positive mode ESI-TOF-MS spectra of **Cu_{54}**. Inset: Enlarged portion of the spectrum showing the measured (black) and simulated (red) isotopic distribution patterns (M = $Cu_{54}S_{13}O_8(^tBuS)_{20}(^tBuSO_3)_{12}(CH_3OH)(H_2O)$).

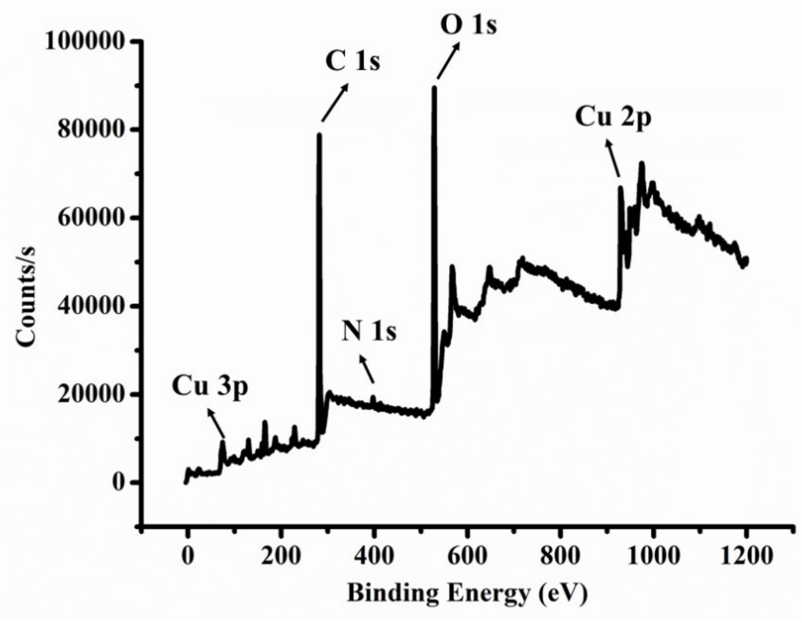

Figure S6. XPS spectrum of **Cu_{54}**.

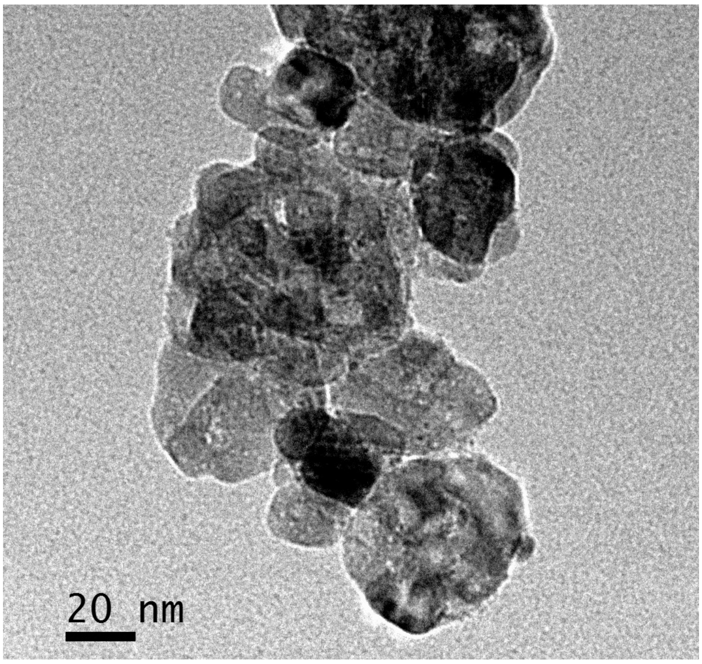

Figure S7. TEM image of 1.0 wt.% **Cu_{54}**/TiO_2.

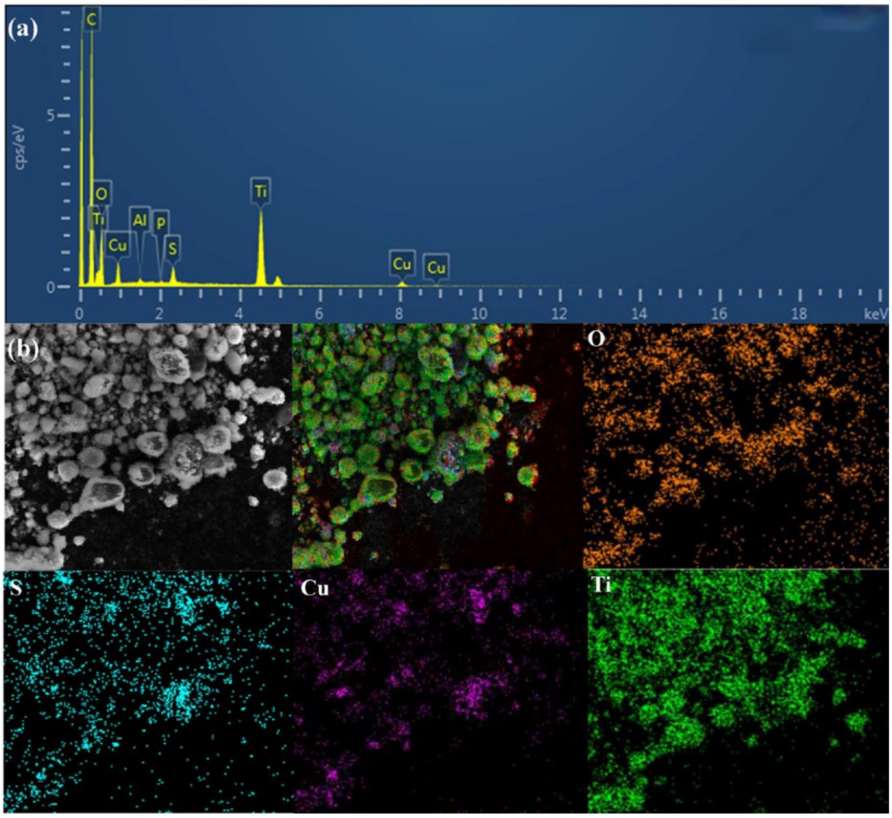

Figure S8. (a) The X-ray energy spectrum of 1.0 wt.% **Cu_{54}**/TiO_2; (b) Elemental distribution of 1.0 wt.% **Cu_{54}**/TiO_2.

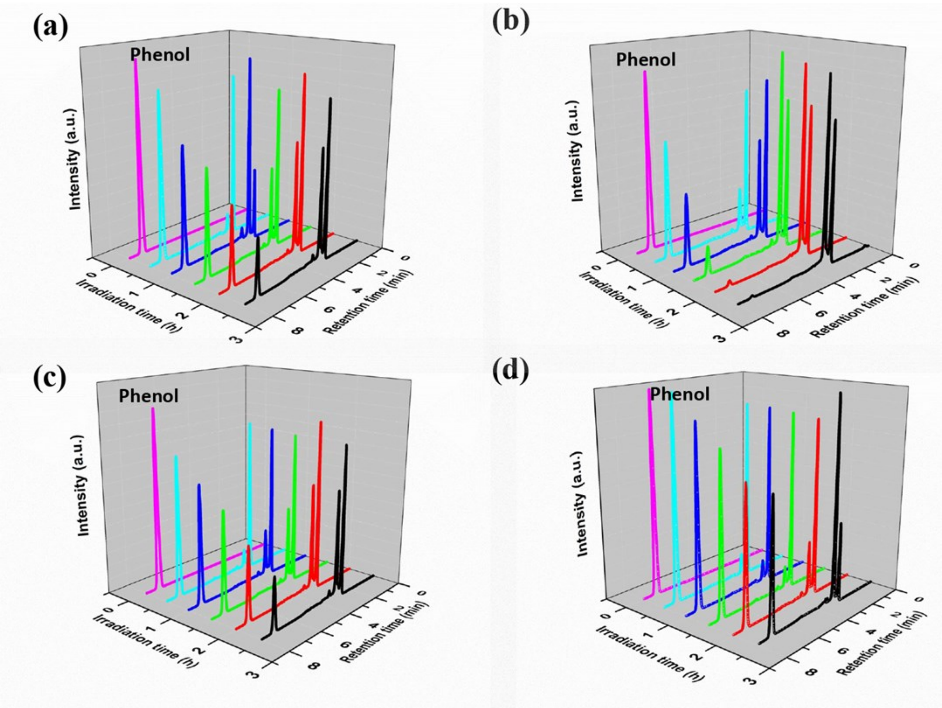

Figure S9. HPLC chromatograms of phenol degradation over (a) 0.1 wt.% **Cu_{54}**/TiO_2; (b) 0.5 wt.% **Cu_{54}**/TiO_2; (c) 2.0 wt.% **Cu_{54}**/TiO_2; (d) TiO_2.

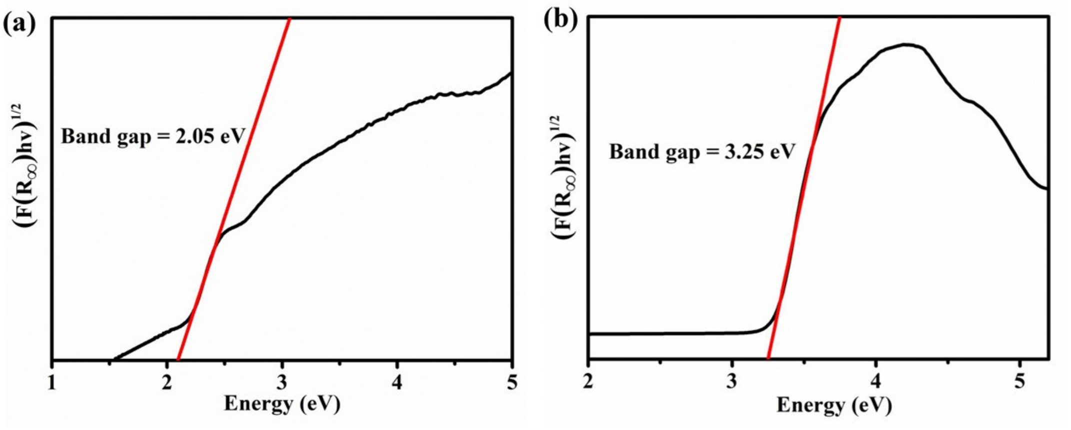

Figure S10. Band gap energy estimation using extrapolation method for (a) **Cu_{54}**; (b) TiO_2.

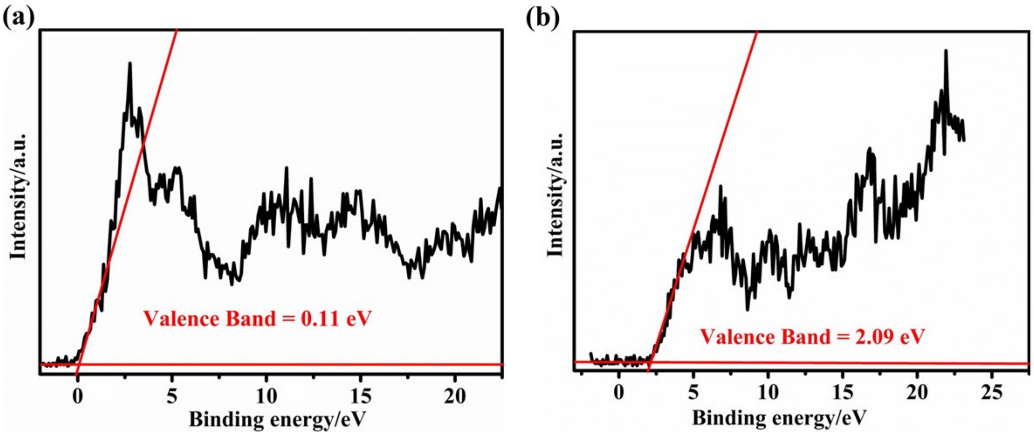

Figure S11. Valence band XPS spectrum of (a) **Cu_{54}**; (b) TiO_2.

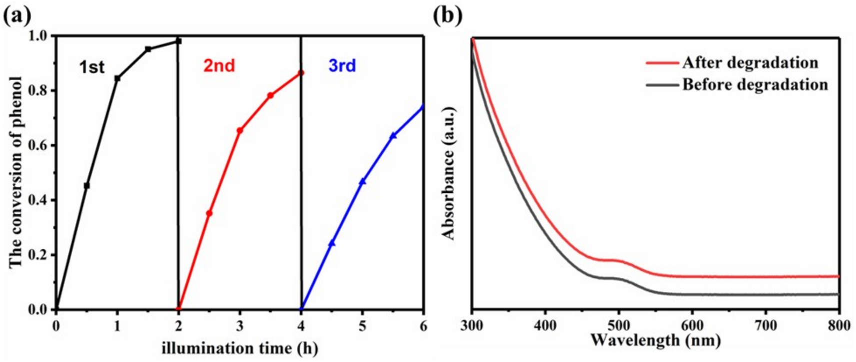

Figure S12. (a) Recycling tests of 1.0 wt.% **Cu_{54}**/TiO_2 for phenol degradation under visible light irradiation. (b) UV-visible absorption spectra of **Cu_{54}** in CH_2Cl_2/CH_3CN mixture (CH_2Cl_2: CH_3CN = 1:1).

Table S1. Crystallographic data and structure refinement for Cu_{54}.

CCDC number	2047196
Empirical formula	$C_{127.99}H_{287.98}Cu_{54}O_{44}S_{45}$
Formula weight	7404.83
Temperature/K	293(2)
Crystal system	cubic
Space group	*Fm*-3
a/Å	31.03414(18)
b/Å	31.03414(18)
c/Å	31.03414(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	29889.5(5)
Z	4
ρ_{cale} g/cm^3	1.646
μ /mm^{-1}	7.282
F(000)	14776.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54178)
2θ range for data collection /°	11.404 to 130.724
Index ranges	$-14 \le h \le 36$, $-23 \le k \le 35$, $-25 \le l \le 17$
Reflections collected	6632
Independent reflections	2224 [R_{int} = 0.0218, R_{sigma} = 0.0253]
Data/restraints/parameters	2224/63/170
Goodness-of-fit on F^2	1.059
Final *R* indexes [I>=2σ(I)]	R_1 = 0.0745, wR_2 = 0.2086
Final *R* indexes [all data]	R_1 = 0.0824, wR_2 = 0.2164
Largest diff. peak/hole / e Å^{-3}	1.08/-0.74

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2. Correlation linear fitting calibration parameters of precise oxidation state determination of Cu_{54}, and Cu foil, CuO references.

Equation	y = a + b*x
Plot	E_0
Weight	No Weighting
Intercept	Cell://[Book1]Fi
Slope	Cell://[Book1]Fi
Residual Sum of Squares	0
Pearson's r	1
R-Square (COD)	1

Reference

(1) CrysAlisPro 2012, Agilent Technologies. Version 1.171.36.31.

(2) Sheldrick, G. M. *Acta Cryst. A* **2015**, *71*, 3-8.

(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

(4) Brandenburg, K. Diamond, 2010.