

An ultra-sensitive selective fluorescence sensor based on a 3D zinc-tetracarboxylic framework for the detection and enrichment of trace Cu²⁺ in aqueous media

Mei-Rong Han^{a†}, Wen-Xia Dong^{c†}, Si-Si Feng^{a,b*}, Li-Ping Lu^{a,b*}, Zhong-Ping Li^{c*}

^a*Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi, 030006, P. R. China.*

^b*Key Laboratory of Materials for Energy Conversion and Storage of Shanxi Province, Shanxi University, Taiyuan, Shanxi, 030006, P. R. China.*

^c*Institute of Environmental Science, School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, Shanxi, 030006, P. R. China.*

*Corresponding author. E-mail: ssfeng@sxu.edu.cn & luliping@sxu.edu.cn

Experimental Section

Material and measurement

All reagents and solvents were purchased from commercial sources and used without further purification. The IR spectra were recorded from KBr pellets in the range of 4000-400 cm⁻¹ on a Bruker TENSOR27 Spectrometer. Elemental analysis (EA) was carried out using a CHNO-Rapid instrument. Powder X-ray diffractions (PXRD) were recorded on a Rigaku Smartlab X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of 5–50° in 2θ at a rate of 5°/min. The thermogravimetric (TG) study was carried out on a Dupont thermal analyzer with a temperature range of 25-800 °C under N₂ flow with a heating rate of 10 °C min⁻¹. The luminescence spectra were recorded on a PTI Quanta Master-400 Spectrofluorometer with a xenon arc lamp as the light source. The pass width of 5 nm was used in the measurement of emission and 5 nm for excitation spectra, and all the measurements were performed under the same experimental conditions. UV-vis diffuse reflectance spectroscopy (DRS) was performed by using a TU-1950 UV-vis spectrophotometer, during which BaSO₄ was adopted as the internal reflectivity standard. The UV-visible spectra were recorded with a JASCO V-570 spectrophotometer. Luminescence lifetime measurements were carried out on an Edinburgh Instruments Fluorescence Lifetime spectrometer 980 (FLS 980), and the quantum yields were measured on a Hamamatsu Absolute PL Quantum Yield spectrometer C9920-02G. The accurate elemental ratio of Zn/Cu was determined using an Agilent inductively coupled plasma atomic emission spectrometer 730 (ICP-OES 730). The X-ray photoelectron spectroscopy (XPS) data were obtained from electronic spectrometer (Shimadzu Japan).

X-ray crystal structure determination

Single-crystal X-ray diffraction data for **1** were collected on the Beijing Synchrotron Radiation Facility (BSRF) beamline 1W2B, which was equipped with a MAR CCD-165 detector ($\lambda = 0.7200$

Å) with the storage ring working at 2.5 GeV at 100(2) K. Data were collected using the MARCCD equipment and processed using the HKL2000 program^[38]. The structure was solved *via* direct methods employed in the *SHELXS-2014* program and refined by full-matrix least squares methods against F^2 with *SHELXL-2014*^[39]. After all non-H atoms were refined anisotropically, hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, with C-H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Hydrogen atoms in hydroxyl and water molecules were located from difference Fourier maps and refined using their global U_{iso} value with O-H = 0.82 Å. The residual density map showed an over-assignment at the Zn2 site, so it was checked by experiments. Firstly, there was no copper source in the synthesis of complex **1**; Secondly, ICP and XPS results of the complex showed that there was no copper in it. Therefore, radiation damage in the synchrotron beam is the likely cause, especially since it occurs at the Zn2 ion located on a centre of symmetry, which has two water molecules bound to it and is therefore more susceptible to radiation damage. Crystallographic data in CIF format are deposited with the Cambridge Crystallographic Data Center as CCDC 2031935 for **1**. Crystal data and structure refinement details were summarized in Table 1.

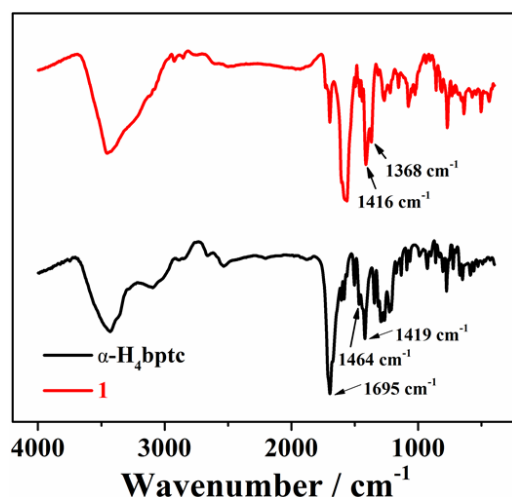


Fig. S1 FT-IR spectra of MOF **1** and H₄bptc ligand.

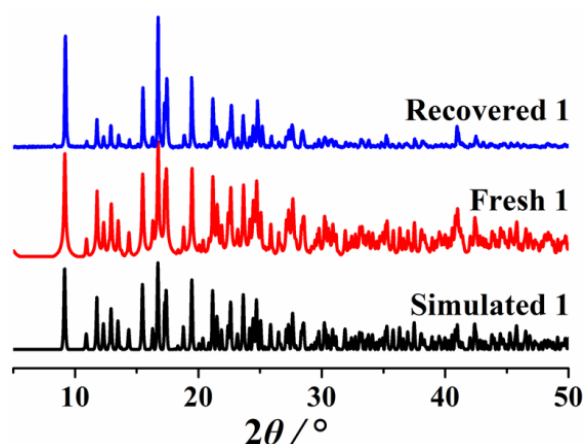


Fig. S2 The PXRD patterns of MOF **1** (simulated, fresh and recovered) at room temperature.

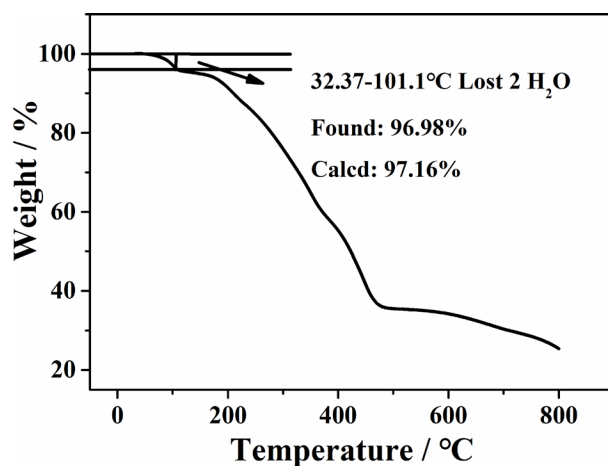


Fig. S3 TG traces of MOF 1 ranging from room temperature to 800 °C.

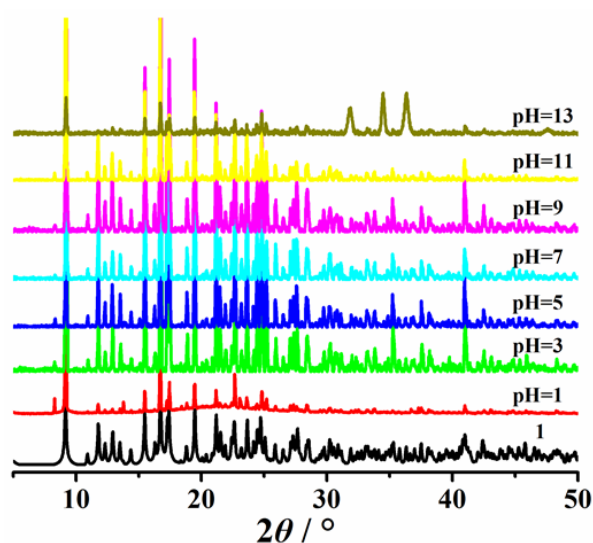


Fig. S4 The PXRD patterns of MOF 1 after being immersed in aqueous solutions at pH = 1, 3, 5, 7, 9, 11, 13 (24 h).

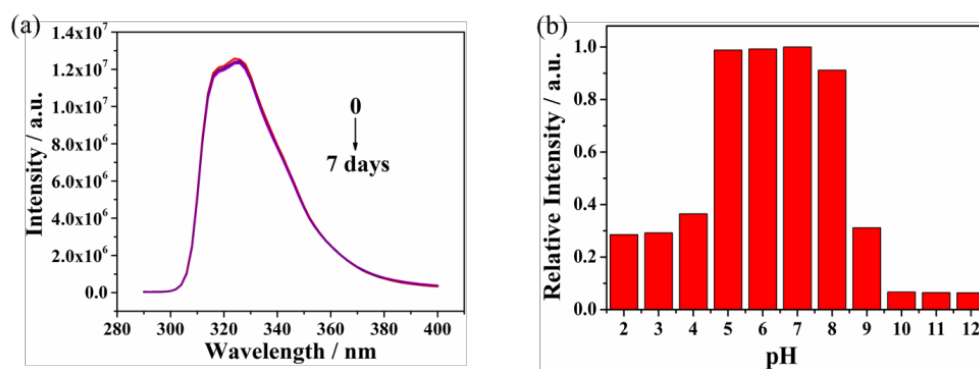


Fig. S5 Emission spectra of MOF 1 (a) in aqueous solution for 7 days; (b) in a series of aqueous solutions with pH values ranging from 2.0 to 12.0 for 24 hours.

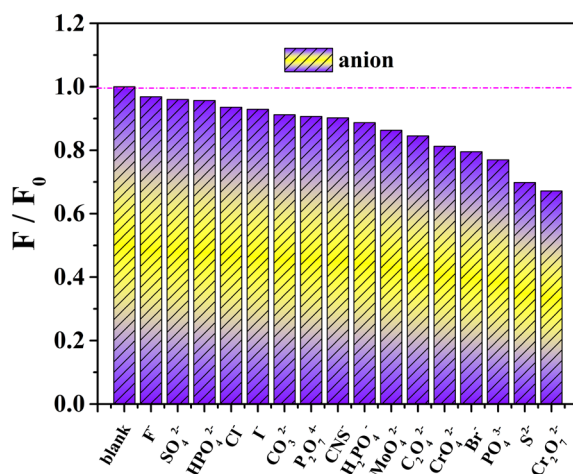


Fig. S6 Luminescence intensities of **1** in the presence of different anions with the concentration of 80 μM .

Table S1. Comparison of Various MOFs Sensors for the Detection of Cu^{2+} .

Sensor	Linear range(μM)	Type (M^{-1})	K (M^{-1})	LOD (nM)	Media	Refs
UiO-66(OH) ₂ @PCN-224	0–10	off	4.03×10^5	0.068	CH ₃ OH: H ₂ O (v:v= 1:1)	S1
BPEI-CQDs/ZIF-8	0.002–1	off	3.688×10^5	0.08	pH=8 PBS	S2
MOF-525	0.01–0.25	off	2.56×10^7	0.22	pH=7.4 HEPES	S3
SiO ₂ @ZIF-8	0.01–0.5	off	1.83×10^6	3.8	HEPES	S4
[Zn₃(μ_3-Hbptc)₂(μ_2-4,4'-bpy)₂(H₂O)₄]_n·2nH₂O	0–0.7	off	1.641×10^5	32.4	pH=7.4 HEPES	This Work
PCN-222-Pd(II)	0.05–2	on	–	50	H ₂ O	S5
MOF-525	3.4×10^6 – 4×10^7	off	4.5×10^5	67	H ₂ O	S6
[Ca(H ₂ tcbpe-F)(H ₂ O) ₂]	0.5–4	off	4.39×10^5	130	H ₂ O	S7
Eu ³⁺ @Bio-MOF-1	0–250	ratio metri c	6.167×10^5	Cu ²⁺ /S ²⁻ 140/ 1.3×10^3	H ₂ O	S8
[Tb ₂ (DCSAL) ₃ (H ₂ O) ₁₁] 3DCSAL·4H ₂ O	3–50	off	4.8×10^4	170	acetonitr ile	S9
Tb ³⁺ @UiO-66-(COOH) ₂	0–200	off	4.12×10^4	230	H ₂ O	S10
UiO-66-NH-BT	0–80	off	1.1×10^5	Cu ²⁺ /Cr ₂ O ₇ ⁻ / CrO ₄ ²⁻	H ₂ O	S11

				266/1.3×10 ³ / 411		
[Eu ₂ (MTBC)(OH) ₂ (DMF) ₃ (H ₂ O) ₄]·2DMF·7H ₂ O	0– 7.87×10 ³	off	2.2514×10 ³	Cu ²⁺ /UO ₂ ²⁺ 270.7/ 1.1451×10 ³	DMF: H ₂ O (v:v= 1:1)	S12
(Ln-CPN)AMP-Tb	1.5–24	off	2.4×10 ⁴	300	pH=7.4 HEPES	S13
[Cd(H ₂ ttac)bpp] _n	–	off	–	630	DMF	S14
{[Zn ₂ Na(L)(HL) ₂ (H ₂ O) ₂] [OAc]·2H ₂ O} _n	0.5– 1.2×10 ³	off	7.75×10 ⁴	650	H ₂ O	S15
Eu ³⁺ @MOF-253	0–100	off	1.0975×10 ⁴	660	H ₂ O	S16
[Ca(H ₂ tcupe)(H ₂ O) ₂]	2.5–25	off	1.56×10 ⁵	790	H ₂ O	S7
ZnMGO	1–70	off	3.07×10 ⁴	1×10 ³	H ₂ O	S17
[Tb ₃ (L) ₂ (HCOO)(H ₂ O) ₅] ·DMF·4H ₂ O	1–10 ⁴	off	2.0218×10 ³	1×10 ³	pH=7 HEPES	S18
{[Eu ₂ K ₂ (dcppa) ₂ (H ₂ O) ₆] 5H ₂ O} _n	0–10 ⁴	off	5.2 × 10 ⁴	Cu ²⁺ /Fe ³⁺ 1×10 ³ /5×10 ³	EtOH	S19
{[Cd(μ ₃ -HL) ₂ (H ₂ O)]·2.3 H ₂ O} _n	0–1.8×10 ³	off	5.6×10 ⁶	1.07×10 ³	H ₂ O	S20
MIL-101-NH ₂	10–10 ⁴	off	1.555×10 ⁴	Cu ²⁺ /Fe ³⁺ / Pb ²⁺ 1.6×10 ³ /1.8× 10 ³ / 5.2×10 ³	pH=5 H ₂ O	S21
[Ce(1,5-NDS) _{1.5} (H ₂ O) ₅] _n	5–100	off	7.668×10 ³	3×10 ³	H ₂ O	S22
Cd(INA)(pytpy)(OH)·2H ₂ O	0–12	off	1.3 × 10 ⁵	3.98×10 ³	H ₂ O	S23
Tb(BTC)(H ₂ O) _{1.5} ·(DMF) @silk fiber	10–10 ³	off	1.192×10 ³	7.87×10 ³	H ₂ O	S24
Eu(FBPT)(H ₂ O)(DMF)	–	off	–	1×10 ⁴	DMF	S25
[H ₂ N(CH ₃) ₂][Eu ₃ (L ₁) ₂ (H COO) ₂ (DMF) ₂ (H ₂ O)]	–	off	2.35×10 ³ ±40	1×10 ⁴	DMF	S26
[Eu(pdc) _{1.5} (DMF)]·(DM F)·0.5(H ₂ O) _{0.5}	10 ³ –6×10 ³	off	2.146×10 ³ ±65	1×10 ⁴	DMF	S27
{[Mg ₃ (ndc) _{2.5} (HCO ₂) ₂ (H 2O)][NH ₂ Me ₂ ·2H ₂ O·DM F]}	0–10 ⁴	off	1.986×10 ³	1×10 ⁴	EtOH	S28
InPCF-1	100– 2.8×10 ³	off	1.84×10 ³ ± 45.9	1×10 ⁴	DMF	S29

[Eu(HL)(L)(H ₂ O) ₂] ₂ ·2H ₂ O	10 ³ –5×10 ³	off	1.163×10 ³ ±52	1×10 ⁴	EtOH	S30
MIL-53-L	0–500	off	6.15×10 ³	1×10 ⁴	H ₂ O	S31
H ₂ [Dy ₂ (PABA) ₄ (bpy) ₂ (NO ₃) ₂](bpy) ₂ (EtOH) ₂ (NO ₃) ₂	–	off	–	1×10 ⁴	H ₂ O	S32
[Cd ₂ (L)(OH)(H ₂ O) ₂]	0–50	off	3.09×10 ⁴	Cu ²⁺ /Cr ₂ O ₇ ²⁻ 1.048×10 ⁴ / 3.917×10 ³	H ₂ O	S33
{[Nd ₂ (NH ₂ -BDC) ₃ (DMF) ₄] _n }	0–10 ³	off	359.855	2.495×10 ⁴	DMF	S34
[Cd ₃ (Htcs) ₂ (btap)(H ₂ O) ₆]	0–8×10 ⁴	off	1.03×10 ⁴	Cu ²⁺ /Fe ³⁺ 3.25×10 ⁴ /8.7 ×10 ³	H ₂ O	S35
[Zn(btca)(py) ₂]	0–550	off	2.92×10 ⁴	Cu ²⁺ /PO ₄ ³⁻ 4.7210×10 ⁴ / 4.738×10 ⁵	H ₂ O	S36
[Cd (Ligand)] ₂ ·2DMF	0–9441.98	off	4.1 × 10 ³	4.7210×10 ⁴	DMF	S37
[Cd(L) ₂](DMF) _{0.92}	0–500	off	4.4×10 ³	6.1373×10 ⁴	DMF	S38
Eu ₂ (TBrTA) ₃ (H ₂ O) ₈ ·2H ₂ O	–	off	4.612×10 ³	Cu ²⁺ /Fe ³⁺ 7.52×10 ⁴ / 6.79×10 ⁴	EtOH	S39
Cd-MOF-74	78.68– 1.2589×10 ⁴	off	1.806×10 ³	7.87×10 ⁴	pH=6.7 HEPES	S40
{NH ₂ (CH ₃) ₂ ·Cd _{2.5} (L) ₂ (H ₂ O)·(H ₂ O)} _n	–	off	–	1×10 ⁵	DMSO	S41
FITC Eu Fe ₃ O ₄ @ZIF-8	10 ² –10 ³	ratio metri c	–	1×10 ⁵	H ₂ O	S42
C ₃ N ₄ @ZIF-8	78.68– 173.1	off	–	Cu ²⁺ /Ag ⁺ / Fe ²⁺ 1.7625×10 ⁵ /1. 2237×10 ⁵ / 1.1711×10 ⁶	DMF	S43
[Zn ₂₁ (BTC) ₁₁ (μ ₃ -OH) ₃ (μ ₄ -O) ₃ (H ₂ O) ₁₈] ₂ ·21EtOH	10 ³ –10 ⁵	off	286.1	Cu ²⁺ /Al ³⁺ 1.34×10 ⁶	CH ₃ OH	S44
[Cd(2-aip)(bpy)] ₂ ·2DMF	–	off	–	1×10 ⁷	DMF	S45
Eu ₂ (FMA)(OX)(H ₂ O) ₄ ·4H ₂ O	–	off	528.7	–	H ₂ O	S46
{[Tb ₄ (μ ₃ -OH) ₄ (BPDC) ₃ (–	off	344.9±10.	Cu ²⁺ /CrO ₄ ²⁻	pH=7	S47

BPDCA) _{0.5} (H ₂ O) ₆]ClO ₄ · 5H ₂ O _n			2	—	HEPES	
[Cd ₃ (L) ₂ (H ₂ O) ₅]·(H ₂ O) ₄	0–100	off	3.65×10 ⁴	—	H ₂ O	S48
CPP-16	—	off	7.8467×10 ³	—	MeCN	S49
{[Eu ₂ (L ₂) ₂]·(H ₂ O) ₃ ·(Me ₂ NH ₂) ₂ } _n	—	off	—	Cu ²⁺ /Fe ²⁺	H ₂ O	S50
{[Eu ₂ (abtc) _{1.5} (H ₂ O) ₃ ·(D MA)]·H ₂ O·DMA} _n	5×10 ² – 5×10 ⁴	off	529	—	H ₂ O	S51

Table S2. Determination of Cu²⁺ in Real Samples.

Sample	initial Cu ²⁺ (nM)	Spiked Cu ²⁺ (nM)	proposed method Cu ²⁺ (nM)	recovery (%)
Tap water 1	66.08	0	65.85	99.65
Tap water 2	66.08	24.94	93.17	102.36
Tap water 3	66.08	49.75	115.39	99.62
River 1	83.89	0	82.02	97.77
River 2	83.89	24.94	106.33	97.70
River 3	83.89	49.75	134.13	100.37

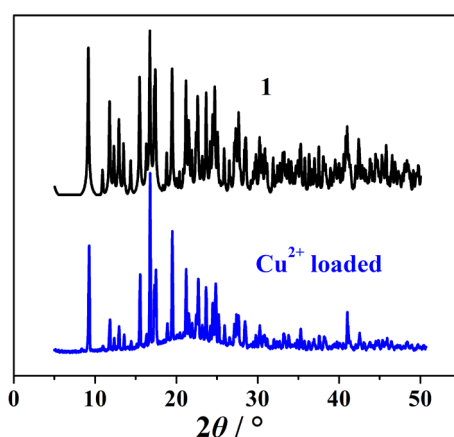


Fig. S7 PXRD patterns of complex **1** before and after soaking in Cu²⁺ solution.

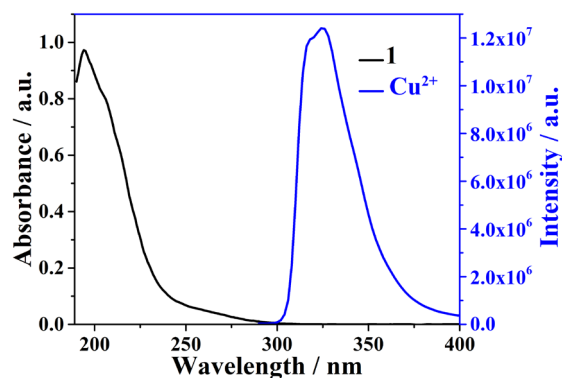


Fig. S8 Liquid UV-vis spectra of Cu²⁺ and emission spectrum of **1** in the aqueous solution.

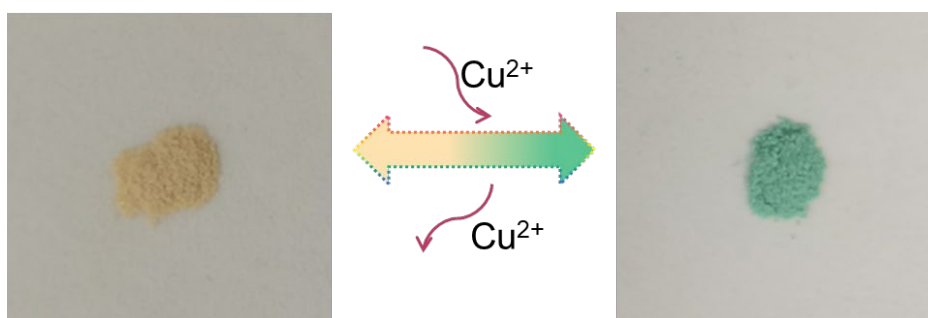


Fig. S9 Graphical representation of the powder **1** adsorption and desorption of the Cu^{2+} .

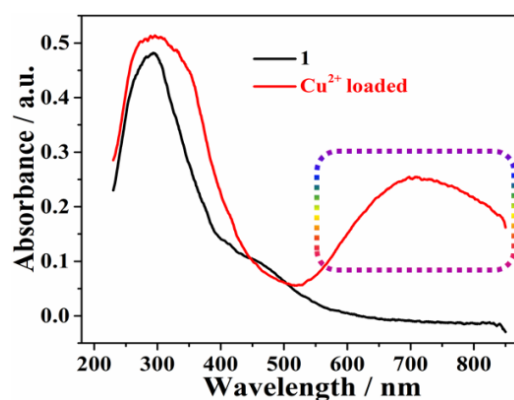


Fig. S10 UV-Vis DRS of the powder **1** before and after the adsorption of the Cu^{2+} .

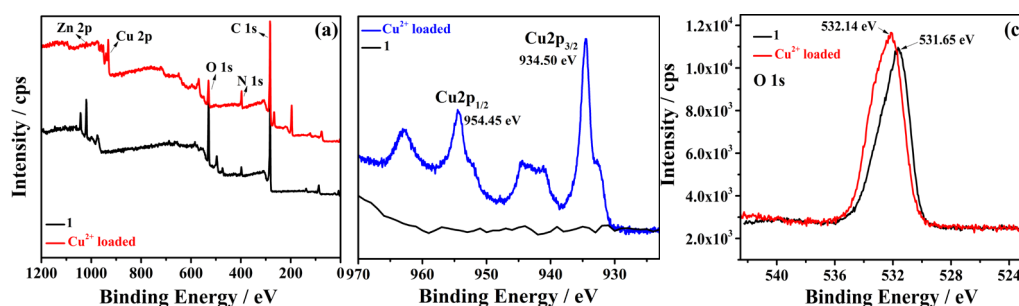


Fig. S11 (a) XPS patterns of the powder **1** before and after the adsorption of the Cu^{2+} . (b) An enlarged image of XPS spectra of Cu 2p. (c) The binding energy of O 1s in **1** before and after the adsorption of the Cu^{2+} .

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