

Synthesis, Structure, and Heterogeneous Fenton Reaction of New Cu(II) Based Discrete Cu_2L_x Coordination Complexes

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Experiment section

Materials and Methods

All chemicals and reagents were used as received unless otherwise stated. 4-methyl-2,6-bis(pyridinyl-3-ethynyl) aniline (**L**) was synthesized following the reported process^{1,2}.

Synthesis of complex 1

In a typical solvent-diffusion synthesis, a methanol solution (5 mL) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (74.1 mg, 0.20 mmol) was carefully layered on a dichloromethane solution (5 mL) containing **L** (15.5 mg, 0.05 mmol). The green block crystal **1** was formed at room temperature in two weeks. The product was collected by filtration and dried under the vacuum condition (5.1 mg, yield: 23% based on ligand **L**). Anal. Calcd for $\text{C}_{87}\text{H}_{68}\text{Cl}_8\text{Cu}_2\text{N}_{12}\text{O}_{17}$: C 53.20, H 3.49, N 8.56%. Found: C 52.45, H 3.75, N 8.06%. IR data (KBr, cm^{-1}): 3407(br), 3108(w), 3046(w), 1637(s), 1597(s), 1530(s), 1456(s), 1388(s), 1288(m), 1207(s), 1003 (m), 851(m), 808(s), 780(s), 652(s).

Synthesis of complex 2

Blue crystal **2** was synthesized in a similar manner as for **1**. To be specific, a methanol solution (5 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (48.3 mg, 0.20 mmol) was carefully layered on a dichloromethane solution (5 mL) containing **L** (15.5 mg, 0.05mmol). The blue bar crystal **2** was formed at room temperature in two weeks. The product was collected by filtration and dried under the vacuum condition (5.0 mg, yield: 23% based on ligand **L**). Anal. Calcd for $\text{C}_{44}\text{H}_{38}\text{Cu}_2\text{N}_{10}\text{O}_{14}$: C 49.95, H 3.62, N 13.24%. Found: C 51.12, H

4.04, N 12.86%. IR data (KBr, cm^{-1}): 3401(br), 3046(w), 1625(s), 1595(s), 1375(vs), 1245(m), 1189(m), 983 (m), 851(m), 834(m), 753(m).

Synthesis of complex 3

After complex **2** is obtained, the red bar crystal **3** was formed in the filtrate in several days as a little amount. The product was collected by filtration and dried under the vacuum condition (2.6 mg, yield: 13% based on ligand **L**). Anal. Calcd for $\text{C}_{42}\text{H}_{30}\text{CuN}_8\text{O}_6$: C 62.57, H 3.75, N 13.90%. Found: C 61.98, H 3.56, N 12.91%. IR data (KBr, cm^{-1}): 3407(br), 3046(w), 1625(s), 1595(s), 1375(vs), 1245(m), 1189(m), 983 (m), 851(m), 834(m), 753(m).

Photocatalytic degradation of methylene blue experiment

There were hydrogen peroxide (30%) with a volume of 0.3 mL and the prepared solid catalyst with a mass of 3 mg adding to 30 mL of methylene blue solution (MB, 20 mg/L). The container containing the mixed solution was shaken with an ultrasonic shaker for 30 minutes to make the solid sufficient dispersed in the solution. The solution was placed in a dark place for 30 minutes to make the surface of the solid catalyst reach an adsorption-desorption equilibrium. The ultraviolet absorption spectrum of the sample was measured every 30 minutes.

Free radical inhibitor dosage experiment

Different proportions of free radical inhibitors were added to the reaction system, then the ultraviolet absorption was measured every 30 minutes through ultraviolet lamp irradiation to obtain the optimal amount of free radical inhibitors.

Photodegradation experiment in the presence of free radical scavenger

Prepare two parts of methylene blue solutions containing hydrogen peroxide with a volume of 0.3 mL and catalyst with a mass of 3 mg respectively. Free radical scavenger with a volume of 0.9 mL was added to the one portion of the MB solution we prepared before, and the other part of the MB solution was not added free radical scavenger. The container containing the mixed solution was shaken with an ultrasonic shaker for 30

minutes to make the solid sufficient dispersed in the solution. The solution was placed in a dark place for 30 minutes to make the surface of the solid catalyst reach an adsorption-desorption equilibrium. The ultraviolet absorption spectrum of the sample was measured every 30 minutes.

Element Analysis (EA)

Elemental analysis for C/H/N was performed in a Perkin- Elemental 2400 element analyzer.

Powder X-ray Diffraction (PXRD)

PXRD analysis was performed using a Rigaku Ultima IV X-ray diffractometer equipped with a Cu sealed tube ($\lambda = 0.154184$ nm) at 30 kV and 10 mA. The diffraction patterns were scanned at room temperature, with a scan speed of 1 sec/step, a step size of 0.02° in 2θ , and a 2θ range of $5\sim 50^\circ$. Simulated powder patterns were calculated by Mercury software using the crystallographic information file from the single-crystal X-ray experiment.

Photocatalytic Activity Measurements

The photocatalytic activity of as-prepared complexes **1** and **2** and Cu-MOFs was evaluated by the degradation of MB as a model dye pollutant. In a typical process, the visible light source was an 80W UV lamp. In the photo-degradation experiments of MB, 3 mg of powder complex **1** was added to 30 mL of a 20 mg/L solution of MB. The distance between the light source and the reaction cell containing the reaction mixture was fixed at 15.0 cm. Before irradiation, the suspensions were magnetically stirred in the dark for 30 minutes to achieve the adsorption-desorption equilibrium of the organic contaminants on the catalyst surfaces. During the photodegradation reaction, stirring was continued to keep the mixture in suspension. Every 30 minutes, 3 mL of the suspensions were continually taken from the reaction cell and the catalyst was separated from the suspension by centrifugation. The residual concentrations of MB in solution were analyzed by recording variations of the organics at the absorption band maximum

in the UV-Vis spectra using a UV-Vis spectrophotometer. For collecting an adequate sample in the recycling experiment, two or even more of the photocatalytic processes were carried out under the same conditions, and then the samples were separated through centrifugation. All of the precipitates from the different processes were collected, combined, and dried in an oven at 60 °C for 12 h. After that, 3 mg of dried sample was used to perform the second photocatalytic experiment according to the same method as that of the first study. The third recycling experiment was also carried out with the same method. The percentage of degradation is reported as C/C_0 . Here, C is the absorption of MB at each irradiated time interval of the main peak of the absorption spectrum at 664 nm. C_0 is the absorption of the starting concentration when adsorption-desorption equilibrium is achieved.

Crystallographic data collection and refinement

Suitable single crystals of **1-3** were selected and mounted in the air onto thin glass fibers. The collected data were reduced using the SAINT program, and multi-scan absorption corrections were performed using the SADABS program. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All H atoms attached to C atoms were added at calculated positions and refined using a riding model, with C-H = 0.093 (aromatic) or 0.097 nm (methylene). The oxygen-bonded hydrogen atoms were located from electron-density difference Fourier maps and refined isotropically with O-H distances restrained to O-H = 0.082 (hydroxyl). All H atoms were refined with $U_{iso}(H) = 1.2 U_{eq}(C)$ or $1.5 U_{eq}(O)$ (parent atom).

Fourier-transform infrared (FT-IR) spectrum

FT-IR spectra were recorded using a Nicolet iS50 spectrophotometer with a wavenumber range of 4000~400 cm^{-1} with a resolution of 2 cm^{-1} .

Ultraviolet-Visible (UV-Vis) Diffuser Reflectance Spectrum

UV-visible diffuse reflectance spectroscopy was performed on an Agilent CARY 60 spectrophotometer equipped with an integrating sphere, using 100% BaSO₄ as reflectance standard for all measurements.

Photodegradation MB tests

The MB photodegradation study of complexes **1** and **2** was measured by employing an 80W, 365nm UV lamp as the continuous irradiation source at room temperature.

Supporting Tables and Figures

Table 1 Crystallographic data for coordination complexes 1 - 3

	1	2	3
Empirical formula	C ₈₇ H ₆₈ Cl ₈ Cu ₂ N ₁₂ O ₁₇	C ₄₄ H ₃₈ Cu ₂ N ₁₀ O ₁₄	C ₄₂ H ₃₀ CuN ₈ O ₆
Formula weight	1964.23	1057.94	806.28
Temperature	298(2) K	173(2) K	293(2) K
Wavelength	0.071073 nm	0.071073 nm	0.071073 nm
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P-1</i>	<i>P-1</i>	<i>P2(1)/c</i>
a / nm	1.2279(4)	0.8184(4)	0.8779(3)
b / nm	1.3059(5)	1.2719(7)	0.9042(3)
c / nm	1.6422(6)	1.2938(7)	2.3964(7)
β / (°)	86.725(5)	105.632(9)	97.906(4)
Volume / (nm ³)	2.3781(15)	1.1761(11)	1.8842(9)
Z	1	1	2
Dc / (Mg/m ³)	1.372	1.494	1.421
Absorption coefficient / (mm ⁻¹)	0.741	0.981	0.640
<i>F</i> (000)	1004	542	830
Crystal size / (mm)	0.6 x 0.38 x 0.15	0.21 x 0.12 x 0.1	0.2 x 0.12 x 0.11
θ range for data collection / (°)	1.72 to 25.50	1.77 to 26.00	1.72 to 27.52
Limiting indices	-14 ≤ h ≤ 14, -14 ≤ k ≤ 15, -19 ≤ l ≤ 18	-9 ≤ h ≤ 10, -15 ≤ k ≤ 11, -13 ≤ l ≤ 15	-11 ≤ h ≤ 7, -10 ≤ k ≤ 11, -31 ≤ l ≤ 31

Reflections collected / unique	12510 / 8687	6394 / 4499	10892 / 4220
Completeness / %	98.10	97.50	97.20
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	8687 / 12 / 581	4499 / 1 / 322	4220 / 0 / 260
Goodness-of-fit on F ²	0.920	0.876	0.956
Final R indices [I>2σ(I)]	R ₁ = 0.0775, wR ₂ = 0.2004	R ₁ = 0.0773, wR ₂ = 0.1284	R ₁ = 0.0571, wR ₂ = 0.1050
R indices (all data)	R ₁ = 0.1362, wR ₂ = 0.2266	R ₁ = 0.1637, wR ₂ = 0.1512	R ₁ = 0.1000, wR ₂ = 0.1175
Largest diff. peak and hole (e ⁻ ·nm ⁻³)	1073 and -678	548 and -446	453 and -412

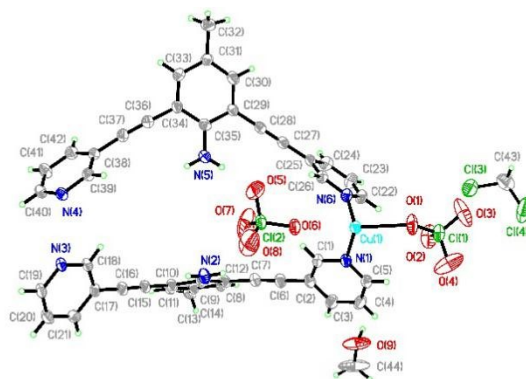
Table 2 Selected bond lengths (nm) and bond angles (°) for complexes 1 - 3

1					
Cu1-N3 ⁱ	0.2026(5)	Cu1-N4 ⁱ	0.2025(5)	Cu1-N1	0.2028(5)
Cu1-N6	0.2032(5)	Cu1-O1	0.2386(4)		
N4 ⁱ -Cu1-N3 ⁱ	91.75(19)	N4 ⁱ -Cu1-N1	90.73(19)	N3 ⁱ -Cu1-N1	172.58(18)
N4 ⁱ -Cu1-N6	173.85(18)	N3 ⁱ -Cu1-N6	89.66(19)	N1-Cu1-N6	87.2(2)
N4 ⁱ -Cu1-O1	92.57(19)	N3 ⁱ -Cu1-O1	88.56(18)	N1-Cu1-O1	98.31(18)
N6-Cu1-O1	93.45(19)				
2					
Cu1-O1	0.2000(4)	Cu1-O6	0.2003(5)	Cu1-N1	0.2005(5)
Cu1-N3 ⁱ	0.2027(5)	Cu1-O7	0.2242(5)		
O1-Cu1-O6	173.9(2)	O1-Cu1-N1	90.4(2)	O6-Cu1-N1	93.8(2)
O1-Cu1-N3 ⁱ	90.59(19)	O6-Cu1-N3 ⁱ	84.2(2)	N1-Cu1-N3 ⁱ	164.5(2)
O1-Cu1-O7	85.74(19)	O6-Cu1-O7	97.9(2)	N1-Cu1-O7	99.4(2)
N3 ⁱ -Cu1-O7	96.1(2)				
3					
Cu1-N3 ⁱ	0.2008(2)	Cu1-N3	0.2008(2)	Cu1-N1	0.2060(2)
Cu1-N1 ⁱ	0.2060(2)				
N3 ⁱ -Cu1-N3	180.00(12)	N3 ⁱ -Cu1-N1	91.34(10)	N3-Cu1-N1	88.66(10)
N3 ⁱ -Cu1-N1 ⁱ	88.66(10)	N3-Cu1-N1 ⁱ	91.34(10)	N1-Cu1-N1 ⁱ	180.000(1)

Symmetry code: ⁱ -x+1,-y+2,-z+2 for **1**; ⁱ -x,-y+1,-z+1 for **2**; ⁱ -x+2,-y+1,-z+1 for **3**.

Crystal structure of $[\text{Cu}_2\text{L}_4(\text{ClO}_4)_4] \cdot 2\text{CH}_2\text{Cl}_2 \cdot \text{CH}_3\text{OH}$ (1):

In the crystalline solid-state, one asymmetric structural unit contained two **L** molecules, one Cu(II) ion, two perchlorates as counter anions, one uncoordinated methylene chloride molecules, and a half of the uncoordinated methanol molecule. Four identical ligands coordinated with two copper ions forming a cuboid M_2L_4 cage with a macromolecular structure. Adjacent macrocyclic molecules formed a two-dimensional planar structure by parallel deposition, and three-dimensional structures were generated by the π - π interaction between the two-dimensional planar structures. There had classical hydrogen bonds connecting perchlorates and methanol molecules in complex **1**. ClO_4^- anions in the cuboid cage were further stabilized by two sets of hydrogen bonds ($\text{N5-H5A} \dots \text{O8}^{\text{ii}}$ and $\text{N2-H2A} \dots \text{O5}^{\text{ii}}$) and the perchlorates out of the cage connected the methanol molecule using $\text{O9-H9} \dots \text{O2}^{\text{ii}}$ hydrogen bond. They were connected only by a π - π stack into a three-dimensional structure, as shown in Fig. 1c. Since the two rings arranged to cross each other, there were no large holes in the crystal.



a

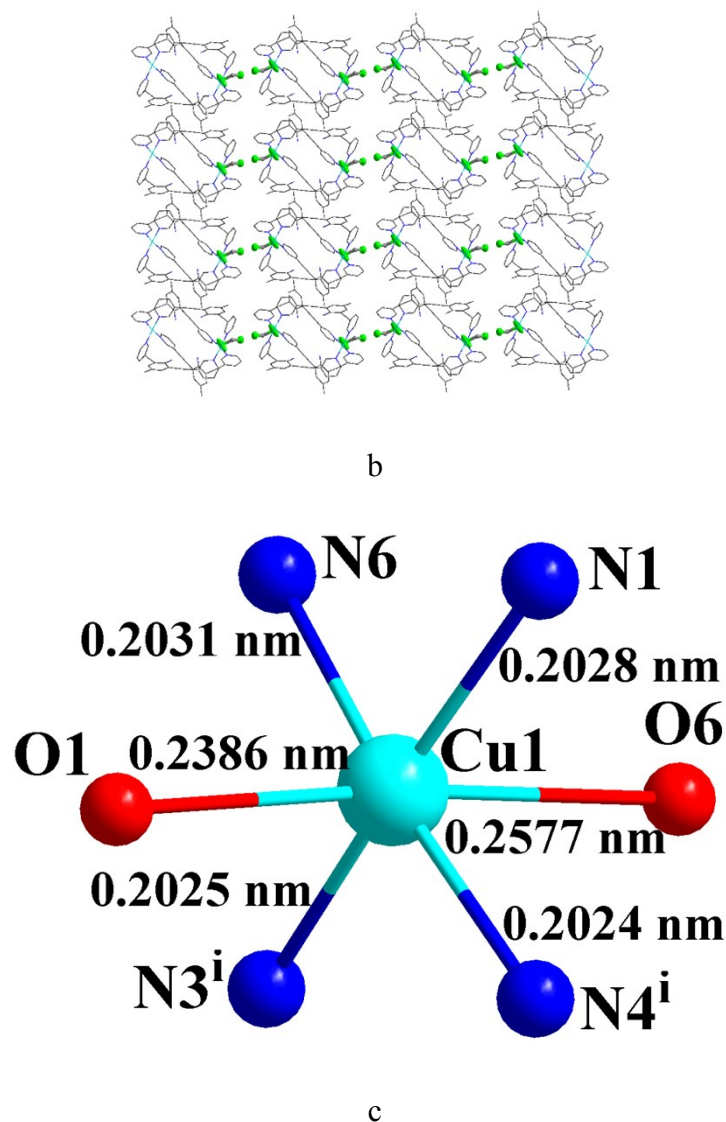


Fig. S1. Structure of complex 1 (a) and solvent CH₂Cl₂ molecules in complex 1(b)

Crystal structure of [Cu₂L₂(NO₃)₄(CH₃OH)₂] (2):

There was an angle between the benzene ring and the pyridine ring in the ligand of 8.119 (189) and 19.993 (197) degrees. The face angles were approximately parallel. The Cu ions in the neighbor macrocycle were connected by two hydrogen bonds (O7-H7A ... O4ⁱⁱ and O7-H7A ... O5ⁱⁱ) to form a 1-D macrocycle chain in which another hydrogen bonds (O7-H7A ... N5ⁱⁱ) frozen the ligand and anions, as shown in Fig. S2 (b).

Two-dimensional curved surfaces formed by parallel stacking between adjacent macrocyclic molecules, in the same way, a three-dimensional structure was generated by the adjacent surfaces. Due to the interdigitated arrangement, large holes have not

appeared in the crystal.

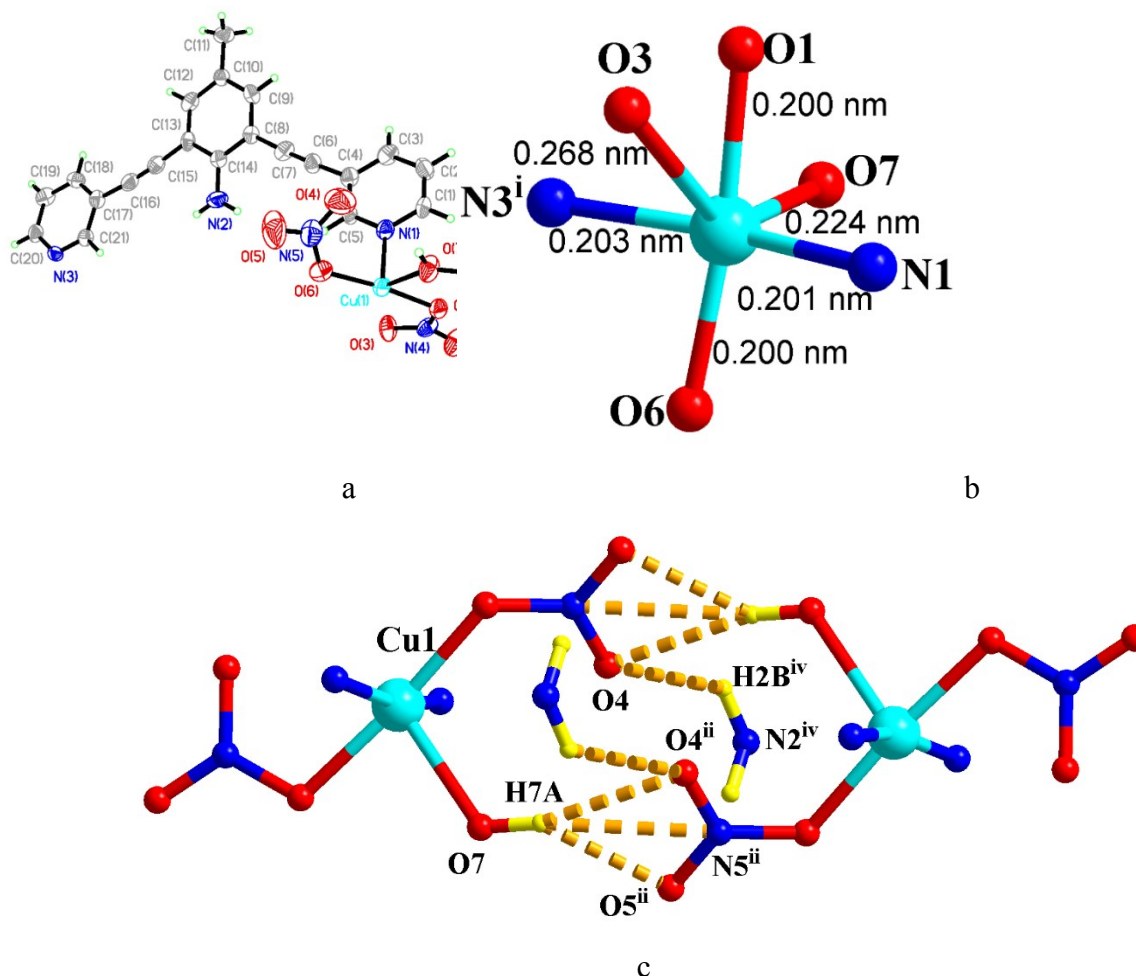


Fig. S2. Structure of complex 2 (a) Cu-N and Cu-O bond lengths (b) and H-bonds (c)
 symmetry code: ⁱⁱ 2-x, 1-y, 1-z ^{iv} 1+x, y, z

Table 3 Hydrogen bonds for complexes 2 (nm and deg.)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O7-H7A...N5 ⁱⁱ	0.091(4)	0.259(5)	0.3471(9)	163(7)
O7-H7A...O4 ⁱⁱ	0.091(4)	0.237(5)	0.3267(8)	165(7)
O7-H7A...O5 ⁱⁱ	0.091(4)	0.215(6)	0.2890(8)	137(7)
N2-H2B...O4 ⁱⁱⁱ	0.088	0.250	0.3104(8)	126.3

Symmetry transformations used to generate equivalent atoms: ⁱ-x, 1-y, 1-z, ⁱⁱ 2-x, 1-y, 1-z; ⁱⁱⁱ -1+x,y,z.

Crystal structure of {[Cu₂L₄(NO₃)₄]}_n (3):

Compared to complex **2**, complex **3** had a set of N2-H2B...O2ⁱⁱ classical hydrogen bonds in the interior of the macrocycle. The corresponding aromatic ring of the adjacent coordination macrocycle had only a dihedral angle of 1.198-2.062 (254) degrees, which was nearly parallel, and there was π - π stacking between adjacent macrocyclic molecules (double ring spacing 0.405 nm). The chains were connected only by a π - π stack into a two-dimensional structure and further stacked as AB fashion to form the 3-D structure viewed down the a-axis. Since the two rings arranged to cross each other, there were no large holes in the crystal.

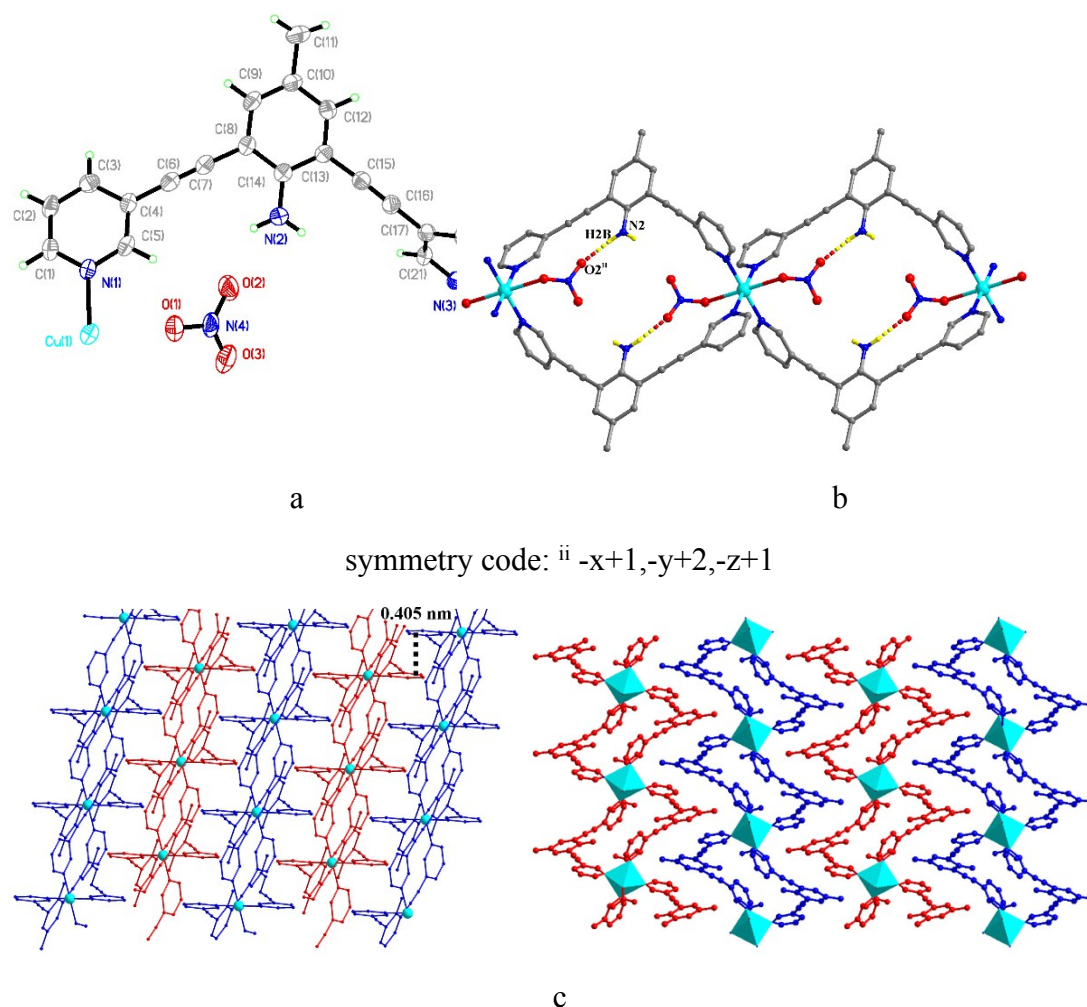


Fig. S3. Structure of complex **3** (a), H-bonds (b) and AB pattern(c)

Table 4 Hydrogen bonds for complexes **3** (nm and deg.)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2B)...O(2) ^{iv}	0.086	0.229	0.2916(4)	129.4

Symmetry transformations used to generate equivalent atoms: ⁱ -x+2,-y+1,-z+1, ⁱⁱ x+1,y-1,z, ⁱⁱⁱ x-1,y+1,z, ^{iv} -x+1,-y+2,-z+1.

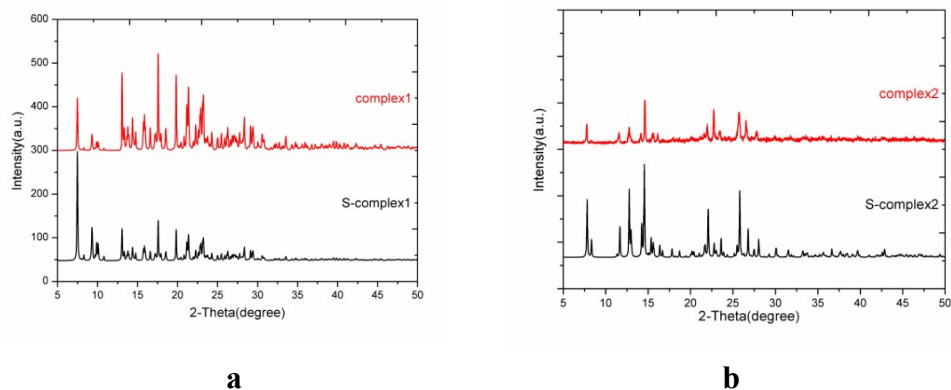


Fig. S4. Simulated XRD patterns from the single-crystal data and PXR patterns of complex1 (a) and 2 (b).

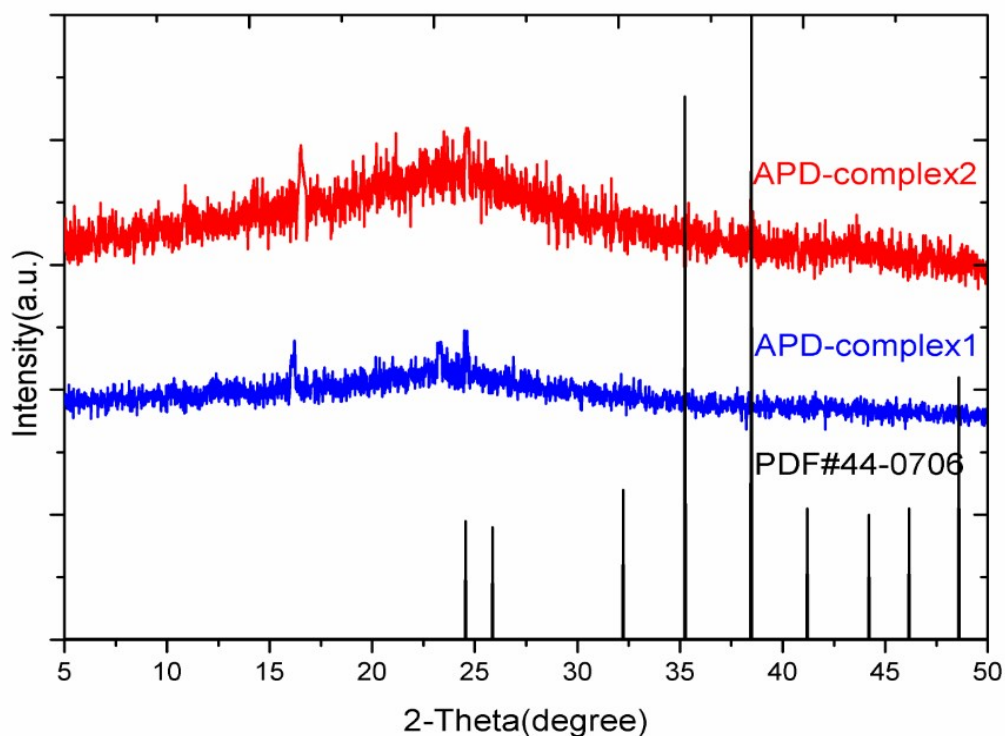


Fig. S5. PXR patterns of complexes 1 (a) and 2 (b) after MB photodegradation under the UV lamp

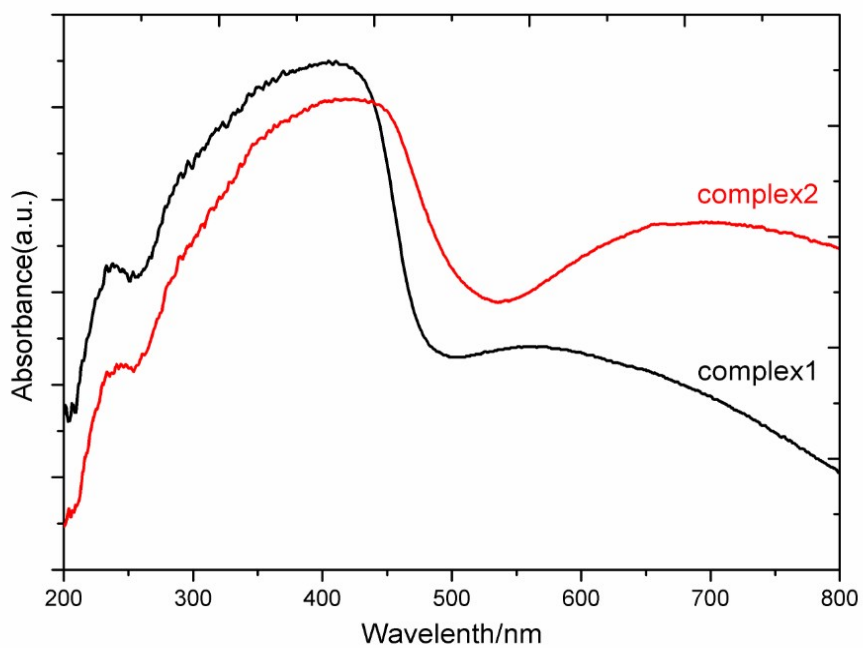


Fig. S6. The absorption spectrum of complexes 1 and 2

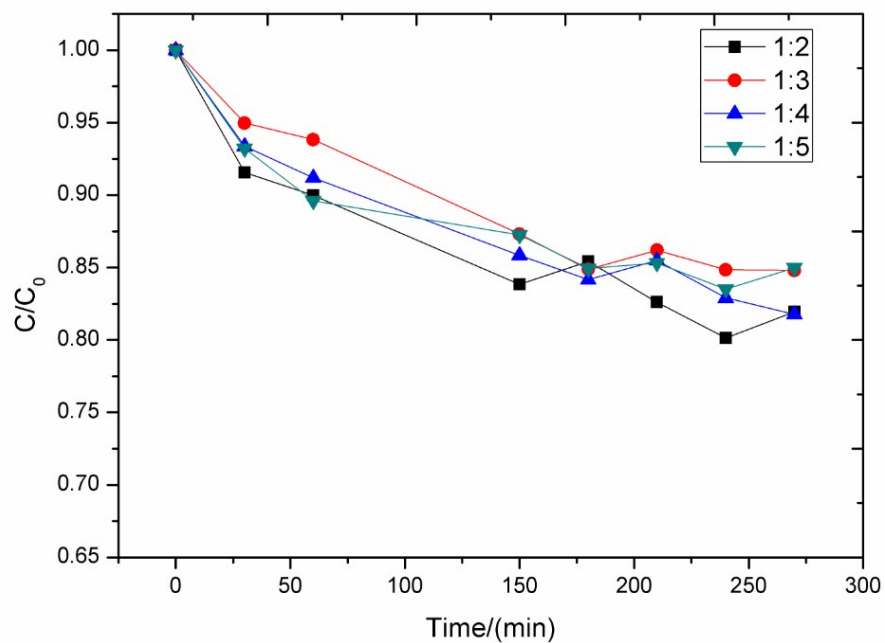


Fig. S7. Diagram of the dosage of free radical inhibitors in different proportions

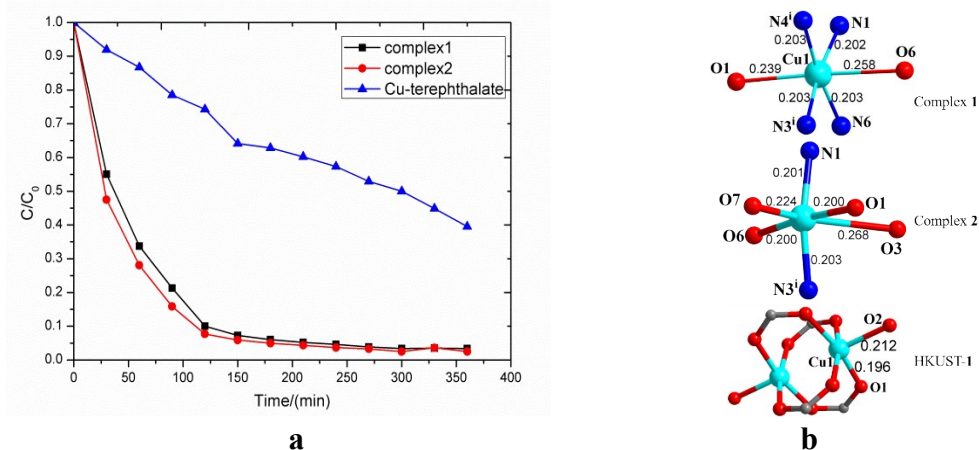


Fig. S8. (a) Photocatalytic diagram of the same metal in different coordination environments; (b) The Cu coordination environments in Complexes 1 and 2 and HKUST-1

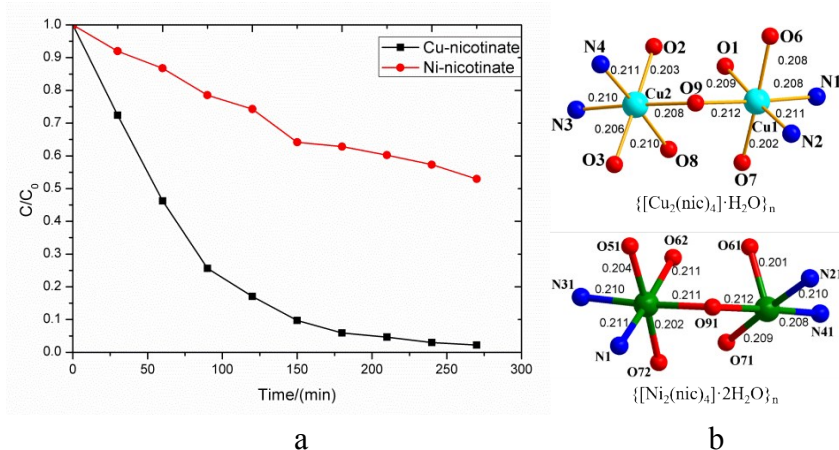


Fig. S9. (a) Photocatalytic diagram of different metals in the same coordination environment; (b) Cu-based and Ni-based complexes coordinated by nicotinic acid ligand

References

1. P. Wang, J. Zhao, Z. Wang, D. Cao and J. Xu, *Chinese Journal of Organic Chemistry*, 2011, **31**, 757-761.
2. X. Li, H.-A. Zhao, J. Su, J.-Y. Cheng and P. Wang, *Chinese Journal of Inorganic Chemistry*, 2019, **35**, 109-115.