

Electronic supplementary information (ESI)

Two pure MOF-photocatalysts readily prepared for the degradation of methylene blue dye under visible light

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Physical Measurements

Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) using the SMART and SAINT programs. The structure was solved by direct methods and refined on F2 by full-matrix least-squares methods with SHELXTL version 5.1. Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms. The C, H, N microanalyses were performed with a Vario EL elemental analyzer. Fourier-transform infrared spectra (FT-IR) were obtained using a Bio-Rad FTS6000 spectrophotometer in the wavelength range of 4000 - 400 cm^{-1} (KBr pellets). Thermogravimetric analysis (TGA) was measured on a STA 409 PC analyzer in the temperature range of 25 - 800 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen flow. The powder X-ray diffraction (PXRD) experiments were carried out on Rigaku D-MAX2550 ($\lambda = 0.15417 \text{ nm}$) with 2θ ranging from 5° to 80° under ambient conditions. The UV-Vis spectra for the solid state sample were obtained on a HITACHI U-4100 spectrophotometer. The X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250 spectrometer (Thermo-VG Scientific) using Mg K α radiation (1253.6 eV) and the binding energy values were calibrated with respect to the C (1 s) peak (284.6 eV). Fluorescence spectra were recorded on an F-7000 FL Spectrophotometer with a quartz cuvette (path length = 1 cm). ICP-OES results were obtained on Optima 5300DV from Perkin Elmer. BET data was obtained from ASAP2020HD88.

Materials and Methods

All reagents and solvents were used as received from commercial suppliers without further purification. 4, 4'-Bipyridine (99.00%), cobalt chloride hexahydrate (99.00%), cupric chloride dihydrate (99.00%), and hydrogen peroxide (30.00%) were purchased from Aladdin Chemical Reagent Co. Ltd, China. Ultrapure water from a Millipore Milli-Q system was used to prepare aqueous solutions for the two complexes synthesis and for the degradation experiments.

Experiment of Photoluminescence Spectra (PL)

•OH radical reactions were performed as follows. 4.00 mg of the photocatalyst was suspended in 40.0 mL aqueous solution containing 2.00×10^{-3} M NaOH and 5.00×10^{-4} M terephthalic acid. Before exposure to light, the suspension was stirred in the dark for 1 h. And then 400 μ L H₂O₂(4.20%) was added to the system before 1.00 mL sample was removed every 10 min and centrifuged for fluorescence spectroscopy measurements. A fluorescence spectrophotometer was used to measure the fluorescence signal of the 2-hydroxy terephthalic acid generated. The excitation light wavelength used in recording fluorescence spectra was 320 nm and the emission wavelength appeared to be ~426 nm.

Radical Trapping Experiments

The radical trapping experiments just have one more additional procedure than the MB photocatalytic process: 10 mM radical scavenger need to be added to the system of photogradation before 500 W Xe lamp turned on at room temperature. The specific

dosage of t-BuOH and TEOA are 38.0 μL and 53.0 μL , respectively. The MB concentration changes were monitored by measuring the absorption intensity at its maximum absorbance wavelength of $\lambda = 664 \text{ nm}$ using a UV-visible spectrophotometer. To measure the photocatalytic activity under visible light, a 420 nm cutoff filter was used to provide the visible light.

Table S1. Crystallographic data for complexes **1** and **2**

<i>Empirical fomula (Formula weight)</i>	<i>C₁₀H₈ClCuN₂ (255.18)</i>	<i>C₁₂H₁₀CoN₂O₄ (305.15)</i>
CCDC deposit no.	1542274	1572221
Crystal system , Space group	Tetragonal, I41/acd	Tetragonal, P 43 21 2
<i>a, b, c</i> (Å)	14.2202(5) 14.2202(5)	7.9778(4) 7.9778(4)
α, β, γ (°)	38.543(4)	17.3831(15)
Volume (Å ³)	90 90 90	90 90 90
Z, D (calc) (g/cm ³)	7793.9(10)	1106.35(15)
Mu (Mo-Ka) [/mm], F(000)	32, 1.740	4, 1.832
Crystal size [mm]	2.471, 4095	1.563, 620
Temp., K	0.21 \times 0.19 \times 0.04	0.21 \times 0.17 \times 0.14
Mo K α radiation (Å)	293	173
θ range (deg)	0.71073	0.71073
Dataset	2.86 - 24.99	2.809 - 26.318
Tot., uniq. data R(int)	- 11: 16 ; - 16: 16 ; - 30: 45	- 8: 9 ; - 8: 9 ; - 19: 21
Observed data [I>2.0 sigma(I)]	10278, 1696, 0.0996	4695, 1117, 0.0492
Nref, Npar	871	951
R, wR ₂ , S	1696, 127	1117, 90
Max. and Av. shift/error	0.0707, 0.2404, 1.196	0.0351, 0.0674, 1.047
Min. and Max. Resd. Dens. [e/ Å ³]	0.00, 0.00	0.00, 0.00
	- 0.308, 0.526	- 0.373, 0.367

Table S2. Selected bond distances (Å°) and angles (°) for complex **1** and **2**

<u>1</u>		<u>2</u>	
Bond lengths (Å°)		Bond lengths (Å°)	
Cu1-N1	1.966(7)	Co1-O1	2.150(3)
Cu1-N2	1.981(7)	Co1-O2	2.144(4)
Cu1-Cl1	2.446(2)	Co1-N1	2.113(4)
Cu1-Cl1	2.493(2)	Co1-N2	2.121(4)
Cu1-Cu1	2.756(2)		
Bond angles (°)		Bond angles (°)	
N1-Cu1-N2	126.5(3)	N1-Co1-N2	180.00(3)
N1-Cu1-Cl1	107.92(18)	N1-Co1-O2	92.70(8)
N2-Cu1-Cl1	104.4(2)	N2-Co1-O2	87.30(8)
N1-Cu1-Cl1	110.45(19)	N1-Co1-O2	92.70(8)
N2-Cu1-Cl1	99.8(2)	N2-Co1-O2	87.30(8)
Cl1-Cu1-Cl1	106.09(8)	O2-Co1-O2	174.60(15)
N1-Cu1-Cu1	101.27(16)	N1-Co1-O1	90.15(8)
N2-Cu1-Cu1	132.2(2)	N2-Co1-O1	89.85(8)
Cl1-Cu1-Cu1	56.90(6)	O2-Co1-O1	84.72(10)
Cl1-Cu1-Cu1	55.29(6)	N1-Co1-O1	90.15(8)
Cu1-Cl1-Cu1	67.81(6)	N2-Co1-O1	89.85(8)
C5-N1-Cu1	123.0(6)	O2-Co1-O1	95.27(10)
C1-N1-Cu1	121.8(6)	O1-Co1-O1	179.70(17)
C10-N2-Cu1	120.7(5)	C1-N1-Co1	121.0(2)
C6-N2-Cu1	122.4(6)	C6-N2-Co1	121.4(2)
		C7-O1-Co1	125.7(3)
		C7-O2-Co1	119.0(3)

Table S3. The pore size and BET surface area of two complexes before and after photocatalysis

<i>Sample</i>	<i>BET surface area</i>	<i>Pore size (BJH)</i>	<i>Pore size (D-H)</i>
1 before photocatalysis	7.1124 m ² /g	2.8391 nm	4.5196 nm
1 after photocatalysis	2.3968 m ² /g	2.1700 nm	4.3456 nm
2 before photocatalysis	4.2314 m ² /g	2.1273 nm	0.3164 nm(BET)
2 after photocatalysis	14.2915 m ² /g	47.6506 nm	2.0728 nm

Table S4. The ICP result of centre metal ions concentration in MB aqueous solution after photocatalysis

<i>System</i>	<i>ICP result</i>
with photocatalyst 1	5.52 mg/L
with photocatalyst 2	9.44 mg/L

Figure S1. Three-dimensional network structure of complex 1 from one direction

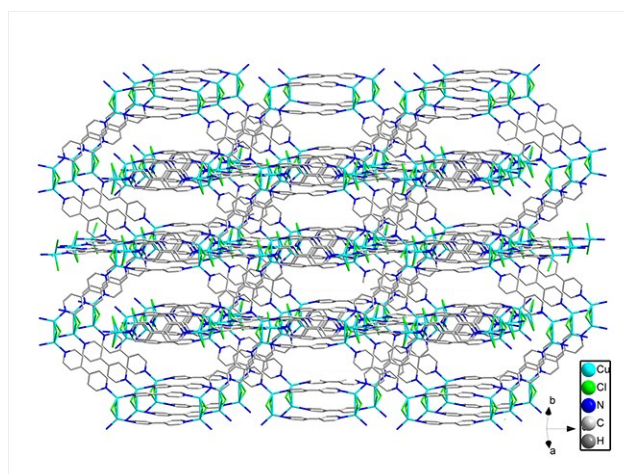


Figure S2. Views of the framework structure of complex **1** along c axis direction

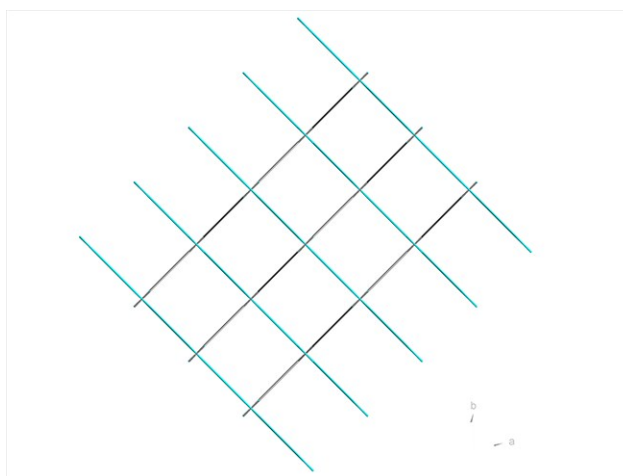


Figure S3. TG, DSC and DTG curves of complex **1**

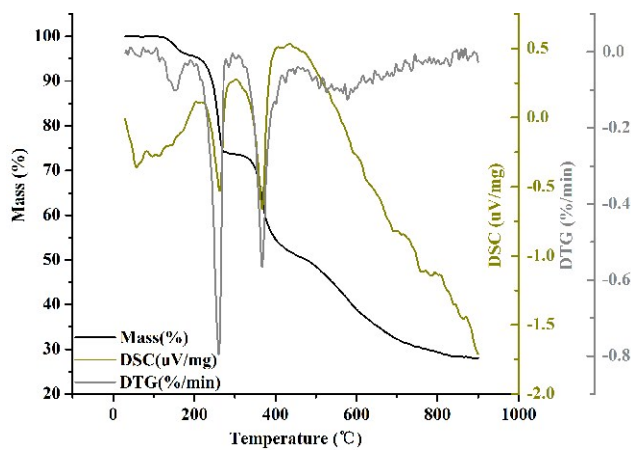


Figure S4. TG, DSC and DTG curves of complex **2**

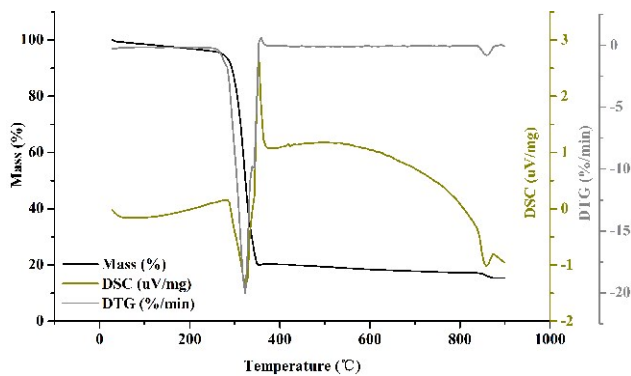


Figure S5. The N₂ adsorption–desorption isotherms (a. **1** before photocatalysis, b. **1** after photocatalysis, c. **2** before photocatalysis, d. **2** After photocatalysis)

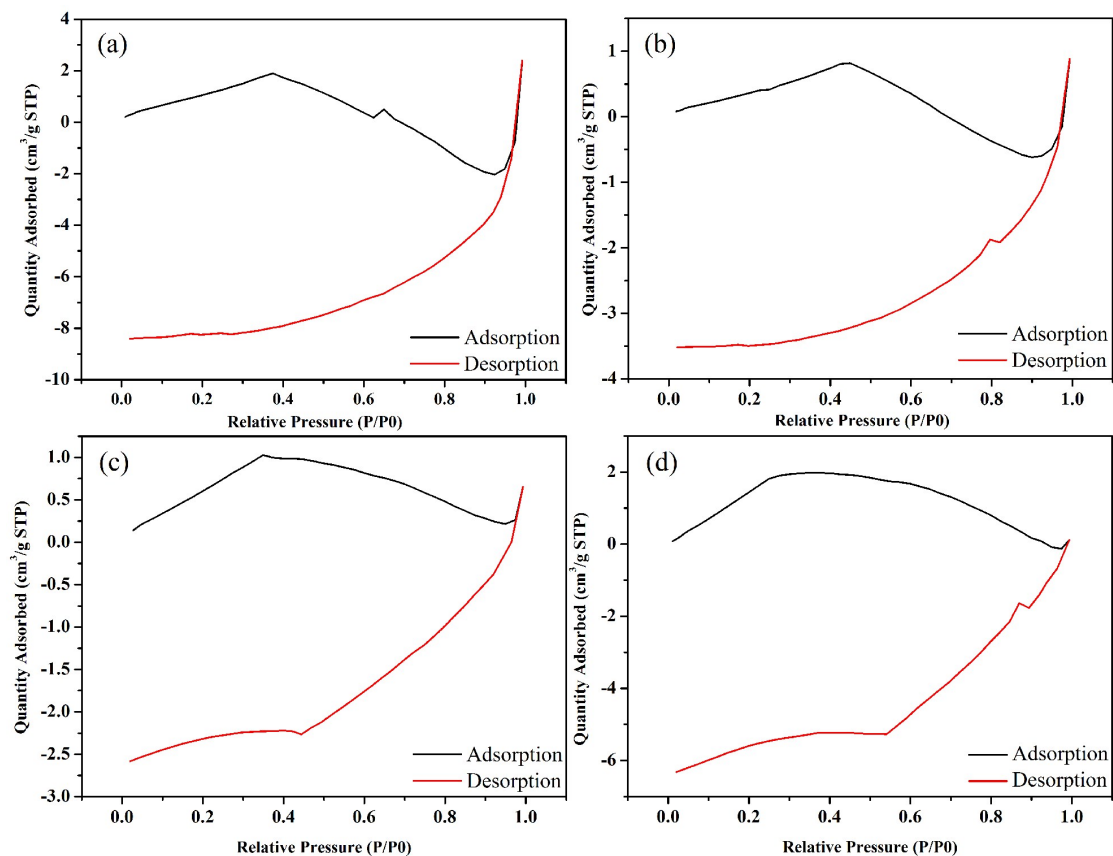


Figure S6. The degradation of MB with different concentration H₂O₂ under UV light

