Supporting Materials

Construction of three coordination polymers based on tetranuclear copper(II) clusters: Syntheses, structures and photocatalytic properties

Lu Liu[a], Yan-Fen Peng[a,b], Xiu-Xiu Lv,[a] Ke Li[a], Bao-Long Li*,[a], Bing Wu[a]
[a]*State and Local Joint Engineering Laboratory for Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P.R. China. E-mail: libaolong@suda.edu.cn*
[b]*Department of Material and Chemical Engineering, Chizhou University, Chizhou, Anhui, 247000, P.R. China.*

Photocatalytic reactions in the absence of H_2O_2

The experiment was carried out in the same condition in the manuscript except the absence of H_2O_2. **1** (0.064 g), **2** (0.064 g) or **3** (0.064 g) were added into 200 mL of a methyl orange (MO) solution (10 mg/L), or methylene blue (MB) solution (10 mg/L), or rhodamine B (RhB) solution (10 mg/L). The suspension solution was stirred in the dark for about 30 min. Then, the mixture was stirred continuously under UV irradiation from a 175 W high pressure mercury vapour lamp (main output 365 nm). At a given interval, aliquots of the reaction mixture were periodically taken and analyzed with a UV-vis spectrophotometer at an absorption wavelength of 465 nm for MO, 664 nm for MB and 552 nm for RhB. This procedure was repeated in the absence of catalyst as a blank comparison experiment and $CuCl_2.2H_2O$ (0.064 g) as the reference substance.

1, **2** and **3** show the very low photocatalytic activity for the photocatalysts degradation of the organic dyes MO, MB and RhB in the same experiment condition in the manuscript except the absence of H_2O_2 (Fig. S13, Fig. S14, Fig. S15). No photocatalytic activity of the blank comparison experiment and $CuCl_2.2H_2O$ as the reference substance is observed.

Table S1 Seleted bond lengths and angles for **1**, **2** and **3** (Å and °).

	1		
Cu(1)-O(1)	1.9067(18)	Cu(1)-O(13)	1.9642(18)
Cu(1)-O(13A)	1.9536(19)	Cu(1)-N(1)	1.991(2)
Cu(1)-O(14)	2.245(3)	Cu(2)-O(2A)	1.996(2)
Cu(2)-O(3B)	1.9370(17)	Cu(2)-O(13)	1.9304(18)
Cu(2)-N(2)	2.032(2)	Cu(2)-O(15)	2.280(2)
Cu(3)-O(7)	1.9661(17)	Cu(3)-O(10C)	1.9518(18)
Cu(3)-O(16)	1.954(2)	Cu(3)-N(4)	1.951(2)
Cu(3)-O(18)	2.530(3)		
O(1)-Cu(1)-O(13)	178.80(9)	O(1)-Cu(1)-O(13A)	96.76(8)
O(1)-Cu(1)-N(1)	93.39(9)	O(13A)-Cu(1)-O(13)	82.30(8)
O(13)-Cu(1)-N(1)	87.26(8)	O(13A)-Cu(1)-N(1)	158.53(9)
O(1)-Cu(1)-O(14)	88.61(10)	O(13)-Cu(1)-O(14)	92.43(10)
O(13A)-Cu(1)-O(14)	111.67(10)	N(1)-Cu(1)-O(14)	87.38(10)
O(3B)-Cu(2)-O(2A)	93.07(8)	O(13)-Cu(2)-O(2A)	91.33(8)
O(2A)-Cu(2)-N(2)	176.91(9)	O(13)-Cu(2)-O(3B)	162.80(9)
O(3B)-Cu(2)-N(2)	88.25(8)	O(13)-Cu(2)-N(2)	86.60(8)
O(2A)-Cu(2)-O(15)	90.85(9)	O(3B)-Cu(2)-O(15)	97.61(8)
O(13)-Cu(2)-O(15)	98.94(8)	N(2)-Cu(2)-O(15)	91.75(9)
O(10C)-Cu(3)-O(7)	157.21(9)	O(16)-Cu(3)-O(7)	88.11(8)
N(4)-Cu(3)-O(7)	91.02(9)	O(10C)-Cu(3)-O(16)	87.79(8)
N(4)-Cu(3)-O(10C)	90.99(9)	N(4)-Cu(3)-O(16)	174.65(9)
O(7)-Cu(3)-O(18)	92.70(8)	O(10C)-Cu(3)-O(18)	110.02(8)
O(16)-Cu(3)-O(18)	95.89(9)	N(4)-Cu(3)-O(18)	89.43(10)
Cu(2)-O(13)-Cu(1)	119.60(10)	Cu(1A)-O(13)-Cu(1)	97.70(8)
Cu(2)-O(13)-Cu(1A)	122.31(10)		
	2		
Cu(1)-O(1)	1.9756(18)	Cu(1)-O(7A)	1.9387(19)
Cu(1)-N(1)	2.056(2)	Cu(1)-N(5B)	2.001(2)
Cu(1)-O(7)	2.434(2)	Cu(2)-O(3C)	1.9556(17)
Cu(2)-O(5D)	1.9620(19)	Cu(2)-O(7)	1.9318(18)
Cu(2)-N(2A)	2.022(2)	Cu(2)-O(2)	2.245(2)
O(7A)-Cu(1)-O(1)	91.75(8)	O(1)-Cu(1)-N(1)	169.16(9)
O(1)-Cu(1)-N(5B)	89.18(9)	O(7A)-Cu(1)-N(1)	83.95(8)
O(7A)-Cu(1)-N(5B)	164.10(10)	N(5B)-Cu(1)-N(1)	92.26(9)
O(1)-Cu(1)-O(7)	98.21(7)	O(7A)-Cu(1)-O(7)	82.44(8)
N(1)-Cu(1)-O(7)	91.11(8)	N(5B)-Cu(1)-O(7)	113.13(9)
O(3C)-Cu(2)-O(5D)	88.50(8)	O(7)-Cu(2)-O(3C)	171.96(9)
O(3C)-Cu(2)-N(2A)	89.08(8)	O(7)-Cu(2)-O(5D)	97.36(8)
O(5D)-Cu(2)-N(2A)	177.39(9)	O(7)-Cu(2)-N(2A)	84.96(8)
O(3C)-Cu(2)-O(2)	87.94(8)	O(5D)-Cu(2)-O(2)	92.43(9)
O(7)-Cu(2)-O(2)	97.27(8)	N(2A)-Cu(2)-O(2)	88.46(9)

3

Cu(1)-O(4A)	1.970(2)	Cu(1)-O(8)	1.897(2)
Cu(1)-N(1)	2.024(3)	Cu(1)-N(4B)	1.974(3)
Cu(1)-O(1)	2.347(2)	Cu(2)-O(2C)	1.965(2)
Cu(2)-O(8)	1.901(2)	Cu(2)-O(9)	1.970(2)
Cu(2)-N(2)	2.012(3)	Cu(2)-O(8C)	2.564(2)
Cu(2)-O(10)	2.564(3)		
O(8)-Cu(1)-O(4A)	93.36(9)	O(4A)-Cu(1)-N(1)	174.17(10)
O(4A)-Cu(1)-N(4B)	85.54(10)	O(8)-Cu(1)-N(1)	86.40(9)
O(8)-Cu(1)-N(4B)	174.67(10)	N(4B)-Cu(1)-N(1)	94.16(10)
O(4A)-Cu(1)-O(1)	93.34(8)	O(8)-Cu(1)-O(1)	95.89(8)
N(1)-Cu(1)-O(1)	92.48(9)	N(4B)-Cu(1)-O(1)	89.39(9)
O(8)-Cu(2)-O(2C)	91.16(9)	O(2C)-Cu(2)-O(9)	90.75(9)
O(2C)-Cu(2)-N(2)	166.73(10)	O(8)-Cu(2)-O(9)	171.13(10)
O(8)-Cu(2)-N(2)	86.84(9)	O(9)-Cu(2)-N(2)	93.24(10)
O(2C)-Cu(2)-O(8C)	92.65(8)	O(8)-Cu(2)-O(8C)	82.24(8)
O(9)-Cu(2)-O(8C)	89.02(8)	N(2)-Cu(2)-O(8C)	100.07(9)
O(2C)-Cu(2)-O(10)	84.86(9)	O(8)-Cu(2)-O(10)	96.25(11)
O(9)-Cu(2)-O(10)	92.55(11)	N(2)-Cu(2)-O(10)	82.32(10)
O(8C)-Cu(2)-O(10)	177.07(9)		

Symmetry transformations used to generate equivalent atoms: A -x+1, -y+1, -z+1; B x-1, y-1, z; C x-1, y, z for **1**; A -x, -y+1, -z+1; B -x, y-1/2, -z+3/2; C -x+1, -y+1, -z+1; D x, -y+1/2, z+1/2 for **2**; A x+1, y, z; B -x, -y+1, -z+1; C -x, -y, -z for **3**.

Table S2 Hydrogen bonds for **1**, **2** and **3** (Å and º).

D-H···A	d(D-H)	d(H···A)	D(D···A)	<(DHA)
		1		
O(11)-H(1W)···O(17)^{i}	0.886(19)	1.85(2)	2.705(4)	162(4)
O(13)-H(2W)···O(16)^{ii}	0.844(18)	2.26(2)	2.949(3)	139(3)
O(14)-H(3W)···O(9)^{iii}	0.875(19)	1.96(3)	2.723(4)	145(4)
O(14)-H(4W)···O(18)^{ii}	0.880(18)	1.87(2)	2.729(4)	166(4)
O(15)-H(5W)···O(5)^{iv}	0.752(16)	1.970(17)	2.706(3)	166(4)
O(15)-H(6W)···O(3)^{v}	0.817(14)	2.640(14)	3.181(3)	125.2(14)
O(16)-H(7W)···O(4)^{i}	0.861(17)	1.844(18)	2.696(3)	171(3)
O(16)-H(8W)···O(6)^{vi}	0.866(17)	1.703(19)	2.558(3)	169(3)
O(17)-H(9W)···O(8)	0.882(18)	1.960(18)	2.835(4)	171(3)
O(17)-H(10W)···O(19)^{vii}	0.882(18)	1.96(2)	2.786(4)	156(3)
O(18)-H(12W)···O(8)^{i}	0.932(18)	1.77(2)	2.696(3)	172(4)
O(19)-H(13W)···O(9)^{viii}	0.874(18)	1.862(19)	2.727(3)	170(4)
O(19)-H(14W)···O(12)	0.892(19)	1.97(2)	2.838(4)	164(4)
		2		
O(7)-H(1W)···O(6)^{i}	0.845(18)	1.91(2)	2.703(3)	155(3)

O(8)-H(2W)···O(1)^{ii}	0.869(18)	2.02(2)	2.874(3)	167(4)
O(8)-H(3W)···O(3)	0.865(18)	1.90(2)	2.732(3)	162(3)
O(9)-H(9A)···O(3)^{iii}	0.82	2.23	2.984(4)	153.0
		3		
O(8)-H(1W)···O(3)^{i}	0.844(18)	1.95(2)	2.712(3)	150(3)
O(9)-H(2W)···O(5)^{ii}	0.857(17)	1.818(18)	2.675(3)	178(3)
O(9)-H(3W)···O(1)^{iii}	0.861(17)	1.864(19)	2.662(3)	153(3)
O(10)-H(4W)...O(11)	0.877(18)	1.98(2)	2.830(4)	164(4)
O(10)-H(5W)...O(11)^{iv}	0.887(18)	2.00(2)	2.876(4)	167(4)
O(11)-H(6W)...O(6)^{v}	0.877(18)	1.92(2)	2.774(3)	166(4)
O(11)-H(7W)...O(12)^{i}	0.886(18)	1.849(19)	2.728(4)	171(4)
O(12)-H(8W)...O(3)^{vi}	0.889(18)	1.892(19)	2.778(3)	174(3)
O(12)-H(9W)...O(3)	0.874(17)	1.966(19)	2.835(3)	173(3)

Symmetry transformations used to generate equivalent atoms: i -x+1, -y+2, -z; ii -x, -y+1, -z; iii -x+1, -y+1, -z; iv -x+1, -y+2, -z+1; v x-1, y-1, z; vi -x, -y+2, -z; vii x, y-1, z; viii x, y+1, z for **1**; i i x, -y+1/2, z+1/2; ii -x, y-1/2, -z+1/2; iii -x+1, y-1/2, -z+1/2 for **2**; i x+1, y, z; ii x, y-1, z; iii -x, -y, -z; iv -x+1, -y, -z+1; v x+1, y-1, z; vi -x-1, -y, -z for **3**.

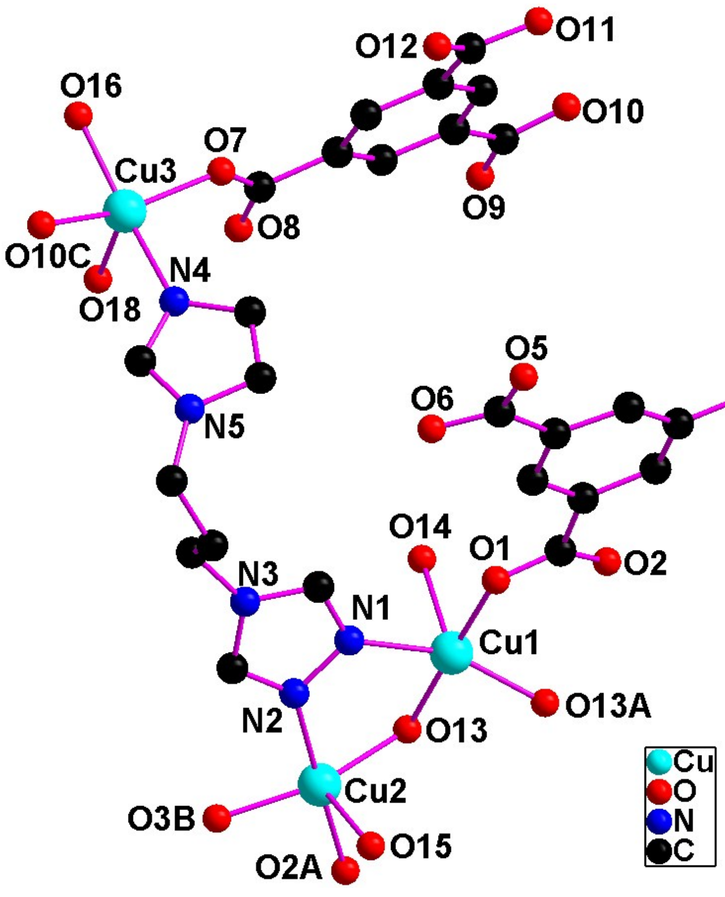


Fig. S1 The coordination environment of Cu(II) atoms in **1**.

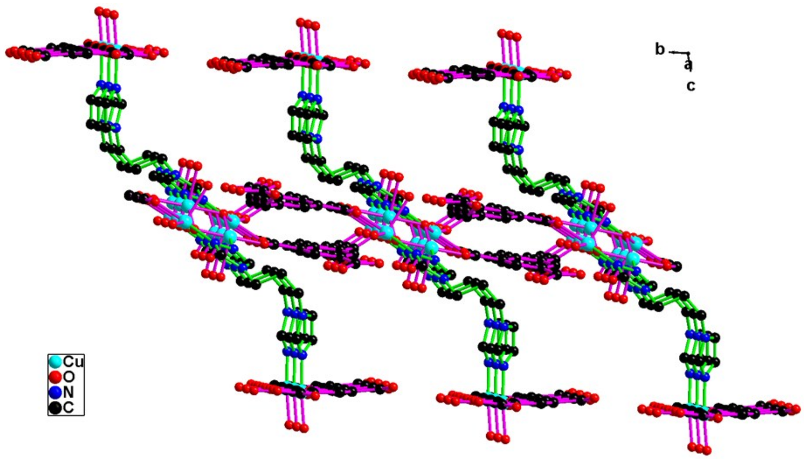


Fig. S2 Viewing an unusual 2D network along the *a*-direction in **1**.

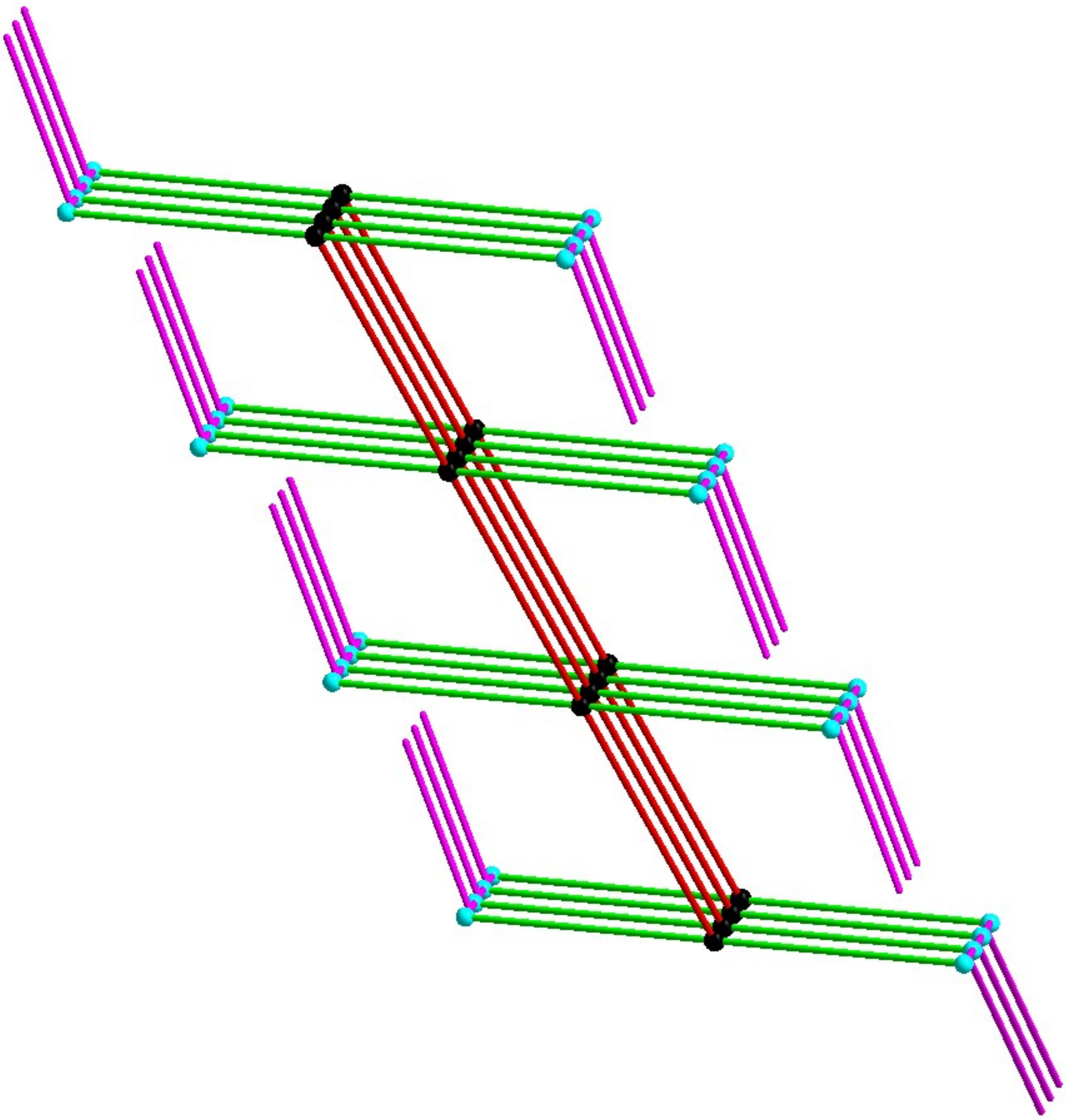


Fig. S3 Schematic depiction of the (3,4)-connected 2D network in **1**. The black and turquiose balls show the 4-connected [$Cu_4(\mu_3\text{-}OH)_2$] tetranuclear copper(II) clusters and the 3-connected Cu_1 core (Cu3 atom), respectively. The red and bright green sticks represent the 2-connected double btc and itp ligands, respectively. The pink "T-shape" sticks represent the 2-connected Hbtc.

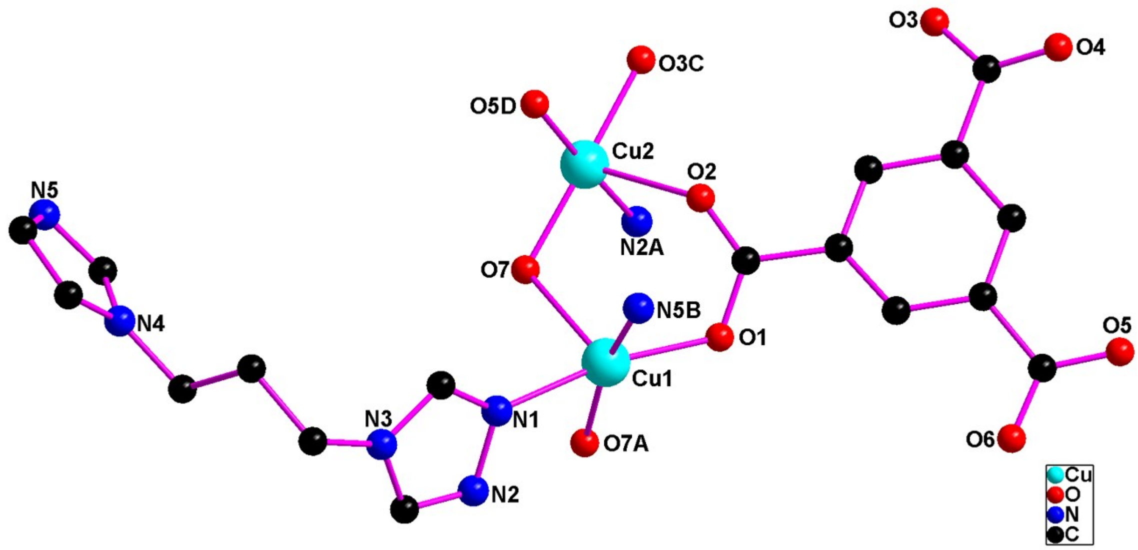


Fig. S4 The coordination environment of Cu(II) atoms in **2**.

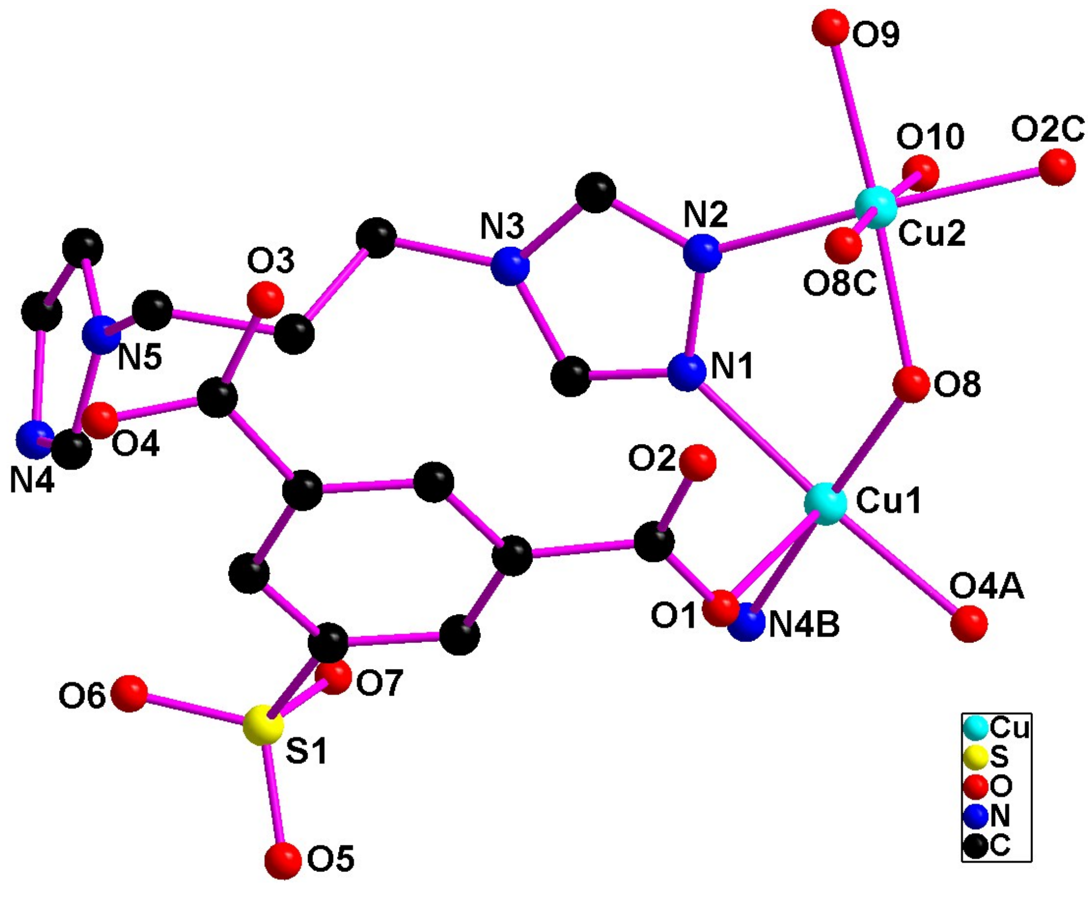


Fig. S5 The coordination environment of Cu(II) atoms in **3**.

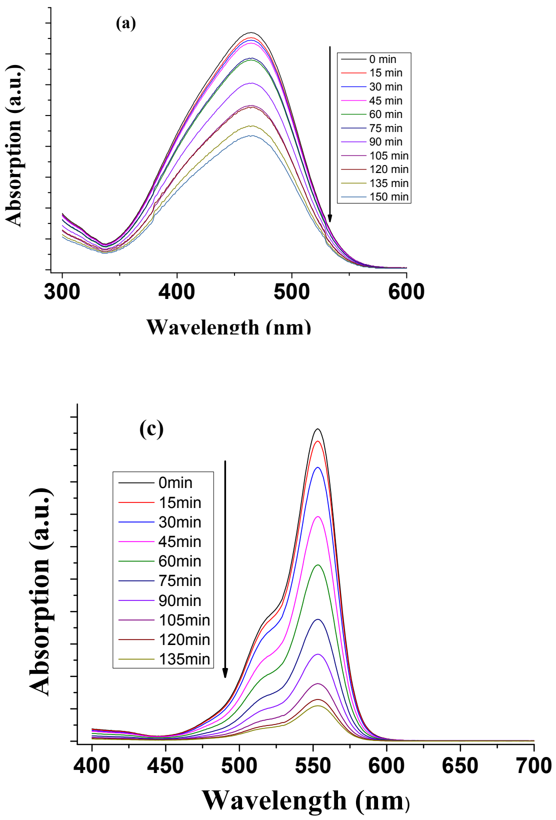
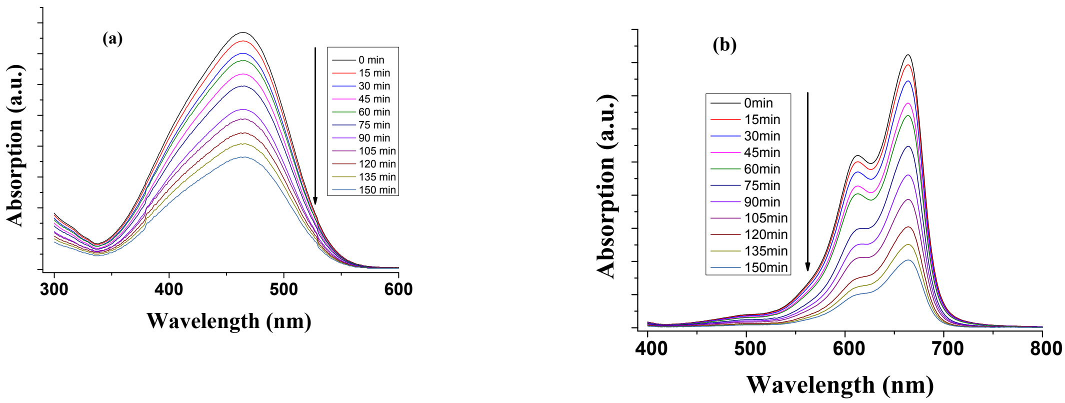


Fig. S6 UV-vis absorption spectra of the MO (a), MB (b), RhB (c) solutions degraded by photocatalyst **2** under UV irradiation at different time intervals.



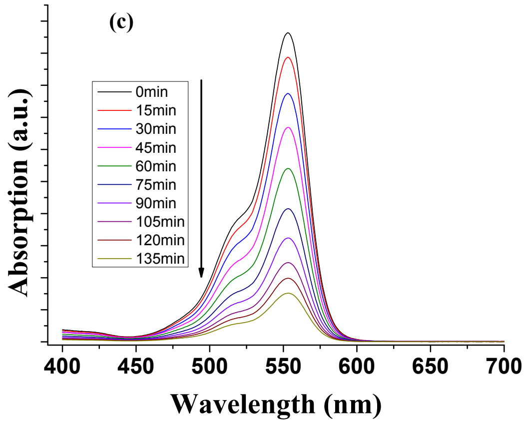


Fig. S7 UV-vis absorption spectra of the MO (a), MB (b), RhB (c) solutions degraded by photocatalyst **3** under UV irradiation at different time intervals.

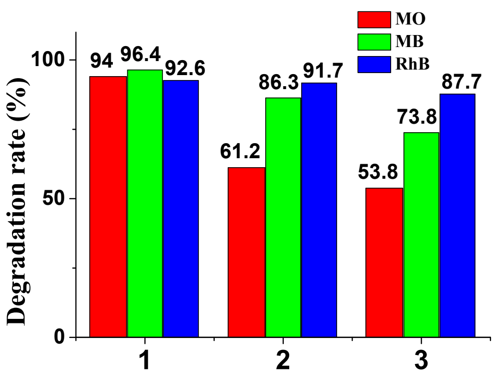


Fig. S8 Photocatalytic degradation rate of the MO, MB and RhB solutions using catalyst **1**, **2**, **3** in 150 min.

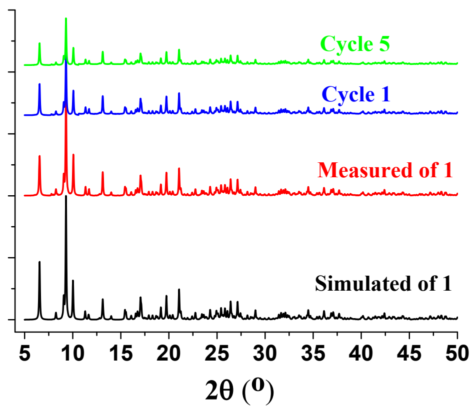


Fig. S9 PXRD patterns of the measured, simulated, cycle 1 and cycle 5 after photocatalytic degradation of the MO solution of **1**, as the example.

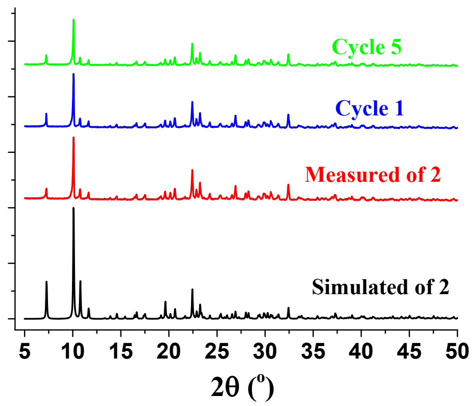


Fig. S10 PXRD patterns of the measured, simulated, cycle 1 and cycle 5 after photocatalytic degradation of the MO solution of **2**, as the example.

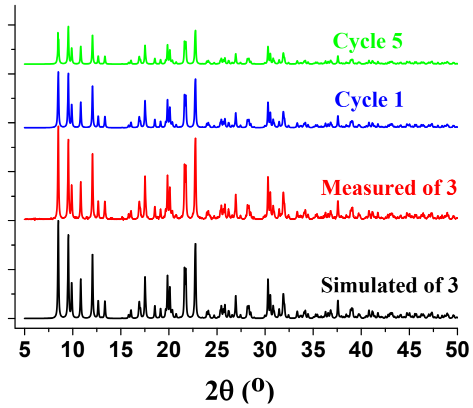


Fig. S11 PXRD patterns of the measured, simulated, cycle 1 and cycle 5 after photocatalytic degradation of the MO solution of **3**, as the example.

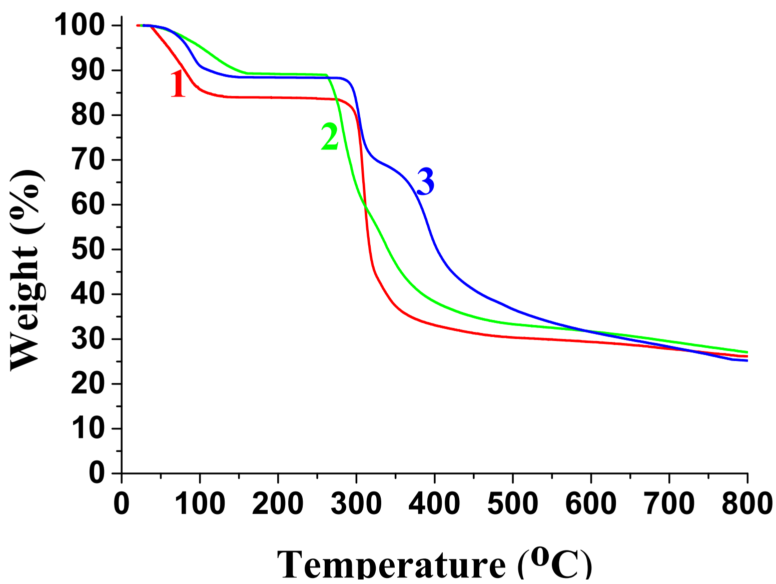


Fig. S12 The TG curves of **1**, **2** and **3**.

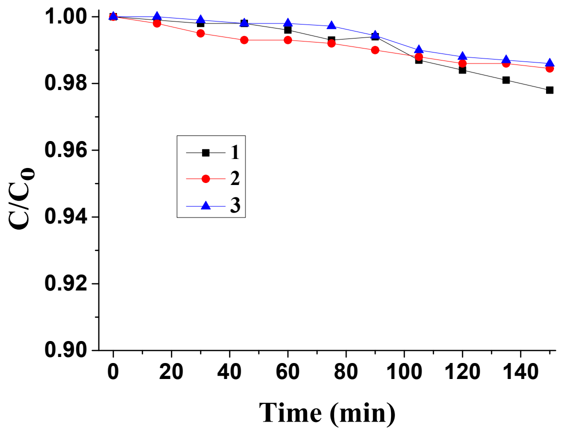


Fig. S13 Photocatalytic degradation of the MO solution under UV light using catalyst **1**, **2**, **3** in the absence of H_2O_2.

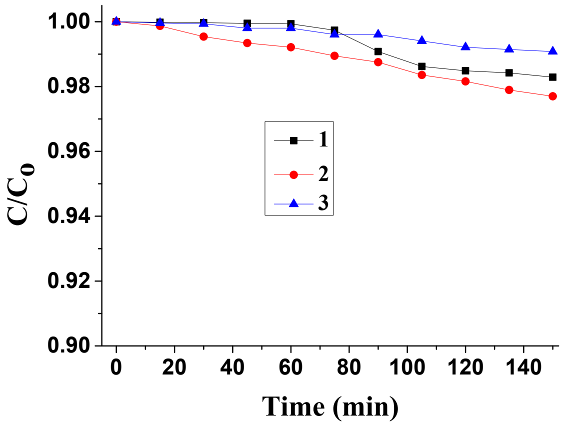


Fig. S14 Photocatalytic degradation of the MB solution under UV light using catalyst **1**, **2**, **3** in the absence of H_2O_2.

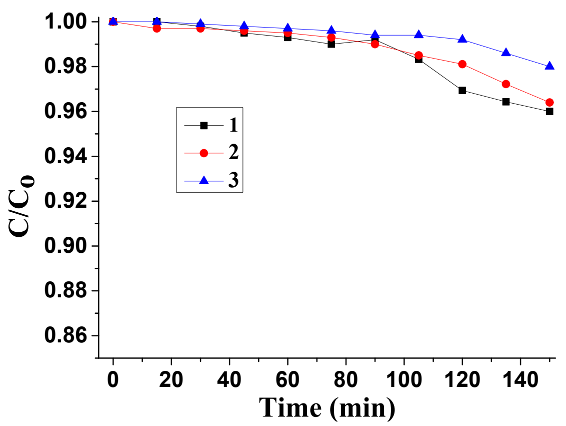


Fig. S15 Photocatalytic degradation of the RhB solution under UV light using catalyst **1**, **2**, **3** in the absence of H_2O_2.