Syntheses of copper-iodine cluster-based frameworks for photocatalytic degradation of methylene blue

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Table S1 Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
Formula	$C_{12}H_{16}N_{20}I_4Cu_6$	$C_6N_{10}H_8I_4Cu_5$
*M*r	1329.35	1042.55
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	9.0012(6)	6.9852(2)
b (Å)	14.3269(10)	17.8187(6)
c (Å)	12.5315(7)	8.5879(2)
β (deg)	94.300(6)	102.313(2)
V(Å^3)	1611.50(18)	1044.32(5)
Z	2	2
Dc (g·m^{-3})	2.740	3.316
μ (mm^{-1})	7.762	10.933
F(000)	1228	936
Flack	0.04(5)	0.06(6)
R_{int}	0.0289	0.0356
GOF(F^2)	1.054	1.109
$R1$ (I>2σ (I))	0.0529,	0.0372,
wR_2 (I>2σ (I))	0.1304	0.0961
$R1$ (all data)	0.0612	0.0395
wR_2 (all data)	0.1364	0.0982

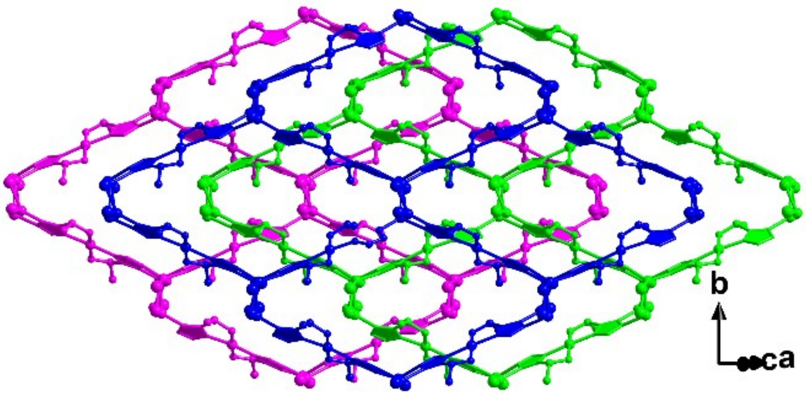

Fig. S1 The A-B-C packing mode of compound **1**.

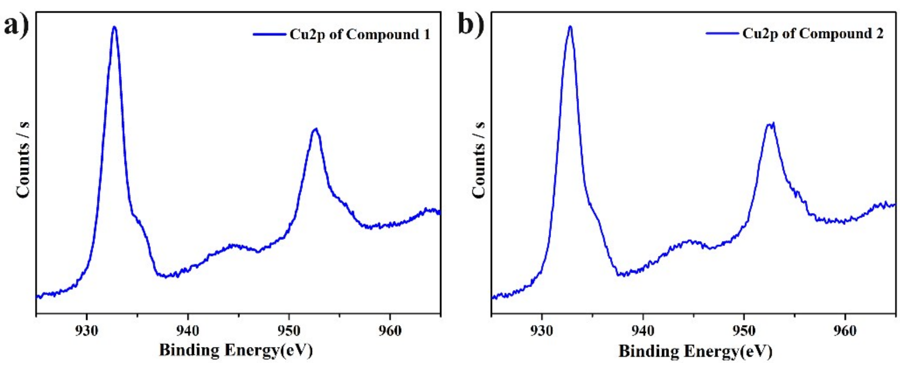

Fig. S2 XPS patterns of compound **1** and **2**.

Thermal Stability.

Thermogravimetric analyses (TGA) of compounds **1** and **2** were performed to investigate their thermal behavior in a N_2 atmosphere from 25 to 800 ˚C at a heating rate of 10 ˚C/min (Fig S5). Before the TGA test, the phase purity of all compounds was characterized by powder X-ray diffraction (Fig S3). The TGA curve demonstrated that compound **1** was stable up to 250 ˚C and then decomposed upon being heated further. TGA curve of compound **2** showed it can be stable under 230 ˚C and decomposed at higher temperature.

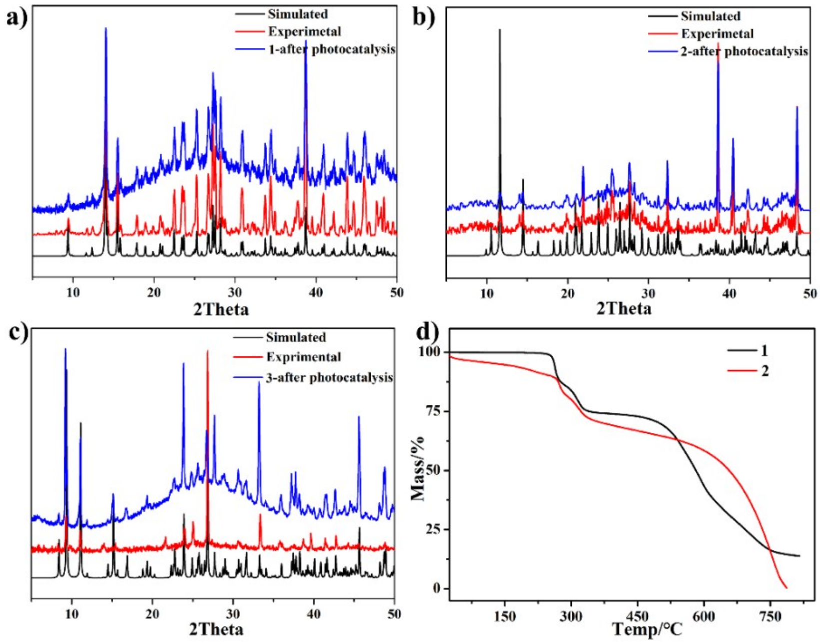

Fig. S3 (a), (b) and (c)The PXRD patterns of compounds **1-3**, (d) The TG plots of compounds **1** and **2**.

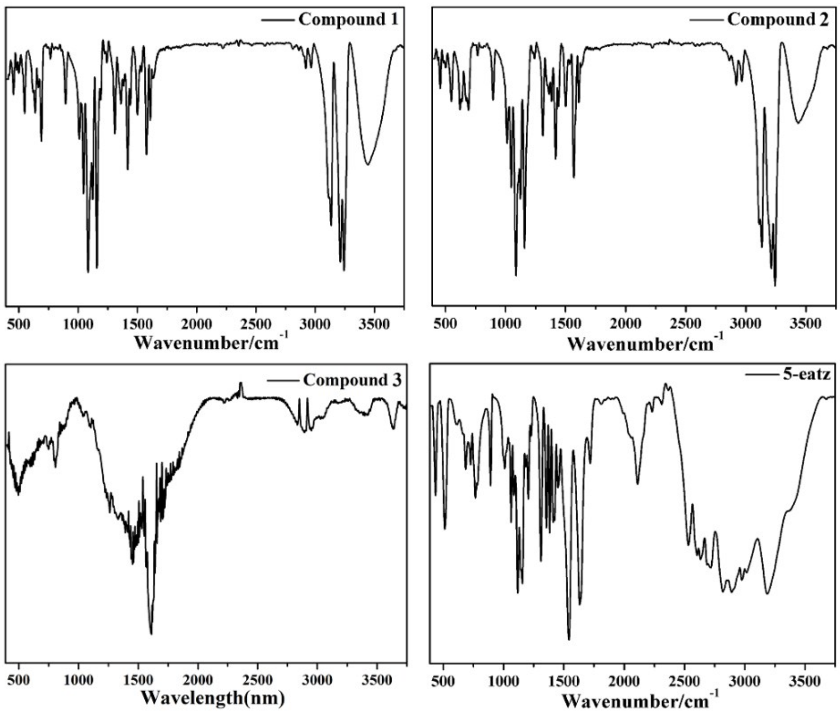

Fig. S4 The IR spectra of and compounds **1-3** and 5-eatzH ligand.

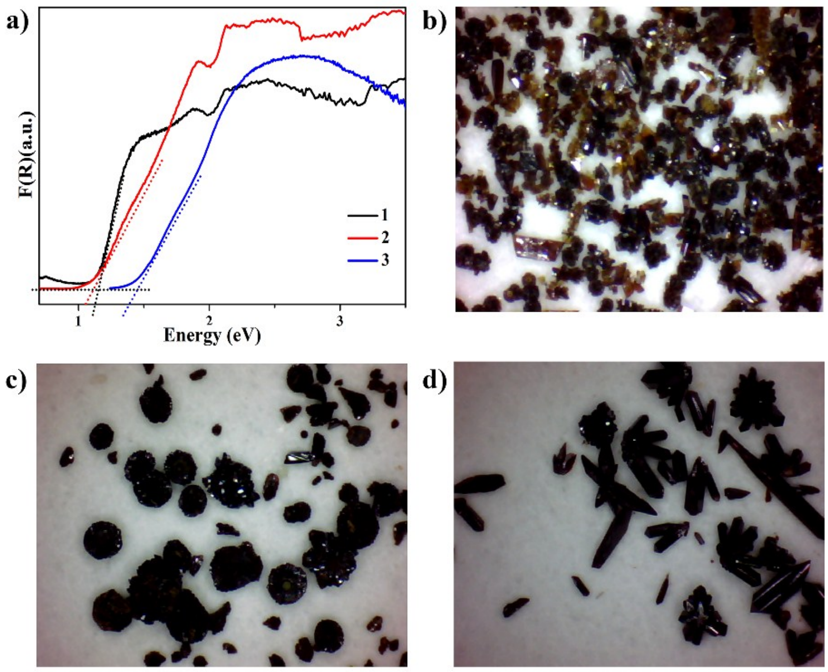

Fig. S5 a) The solid state UV-Vis reflectance spectrum of crystal **1** (black), **2** (red) and **3** (blue); b), c) and d) the crystal images of compound **1**, **2** and **3**.

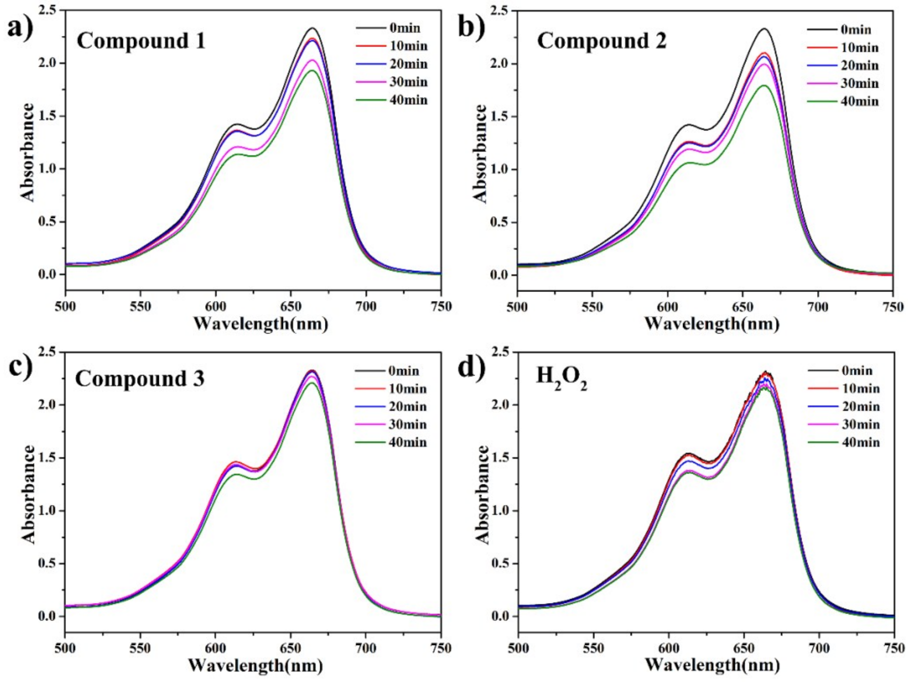

Fig. S6 (a), (b), (c) and (d) The temporal UV-Vis absorption spectrum changes of MB aqueous solutions with the photo-degradation catalyzed by compounds **1**-**3** and H_2O_2.

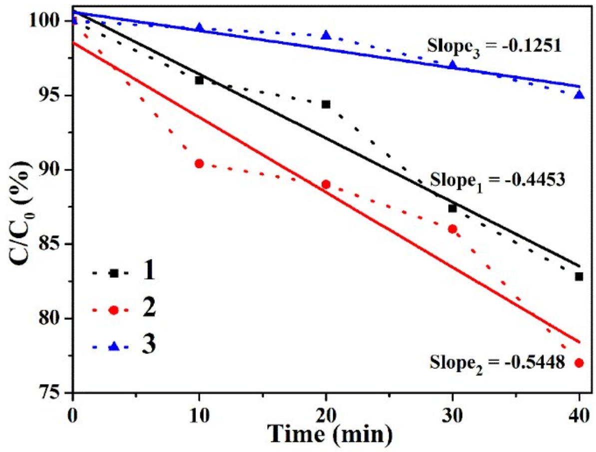

Fig. S7 The reaction kinetics of compound **1**, **2** and **3** fitted by liner-fitting model.

The MB photo-degradation of **1** and **2** in 360 min are detected. As can be seen in Fig S8 and Fig S9, compound **1** can almost completely photo-degrade MB solution in 300 minutes, with a photo-degradation amount of 90% (Fig S8, S9). Meanwhile, compound **2** shows a MB photo-degrade amount of 50% at 300 minutes. At 360 minutes, the degradation amounts of MB solution by photo-degradation of **1** and **2** almost stay the same as 300 minutes.

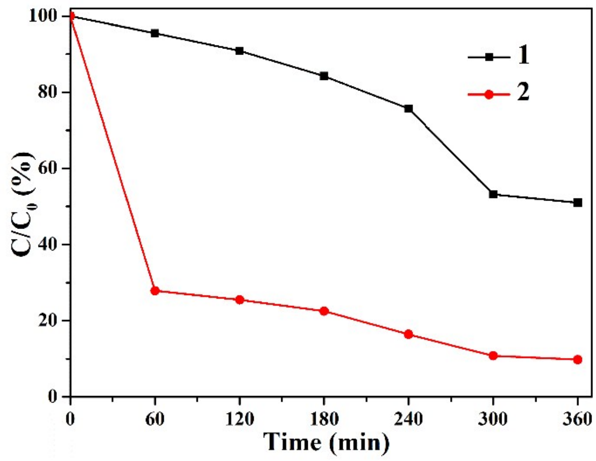

Fig. S8 The MB photo-degradation of **1** and **2** without H_2O_2.

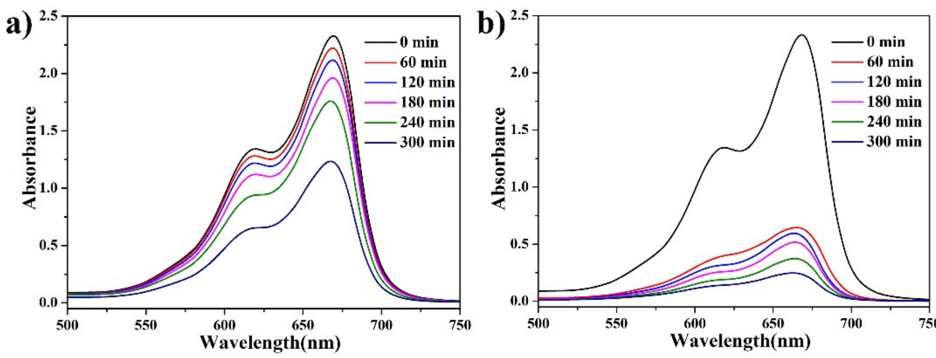

Fig. S9 The temporal UV-Vis absorption spectrum changes of MB aqueous solutions with the photo-degradation catalyzed by compounds **1** and **2**

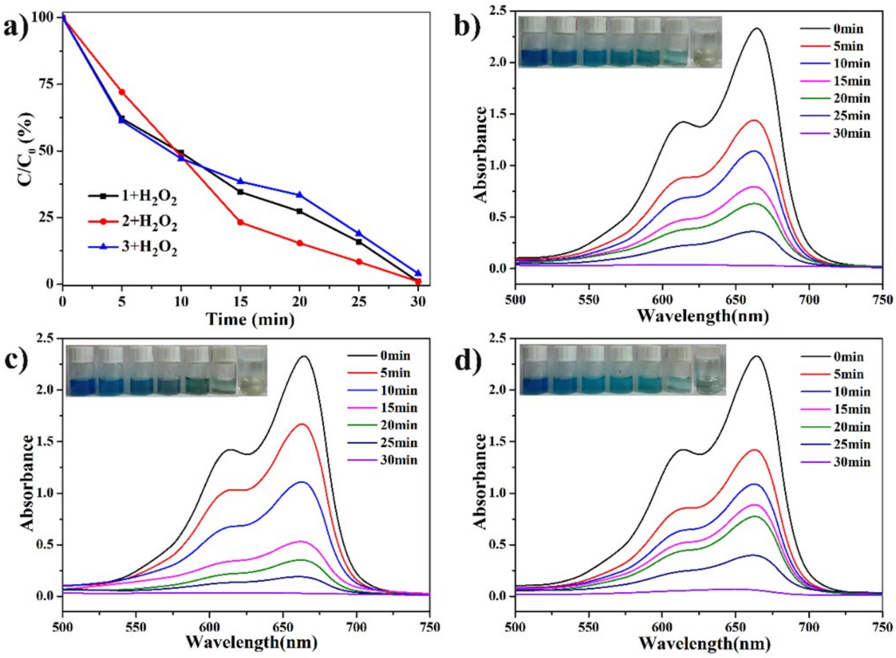

Fig. S10 (a) The MB photo-degradation rate of **1** (black**)**, **2** (red), **3** (blue) in the presence of H_2O_2 additive (b), (c) and (d) the images and temporal UV-Vis absorption spectrum changes of MB aqueous solutions with the photo-degradation catalyzed by **1**, **2** and **3** in the presence of H_2O_2 additive.

In comparison, we did the blank experiments without light. As shown in Fig. S10 and S11, there is a small decreasing amounts by physical adsorption in dark, 16% for **1** and 20% for **2** in 300 min. While the decreasing amounts of photodegradation are 50% for **1** and 90% for **2**. Thus, it can be inferred that the decreasing amounts of photodegradation are not caused by the physical adsorption. You can find these data in the support information of Fig S11.

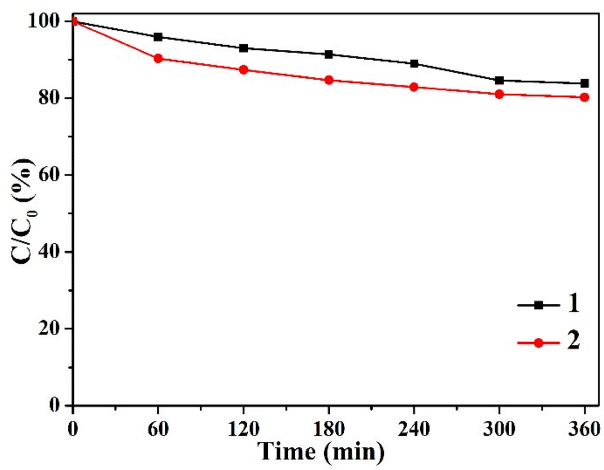

Fig. S11 The decreasing amounts by physical adsorption of **1** and **2** in dark.

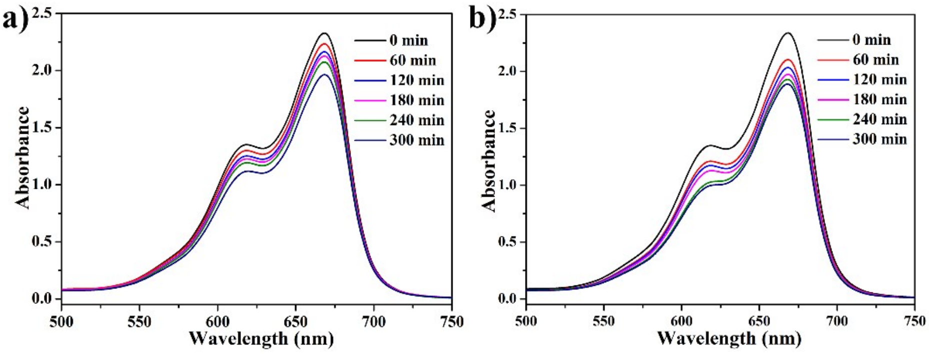

Fig. S12 The temporal UV-Vis absorption spectrum changes of MB solutions by physical adsorption of **1** and **2** in dark

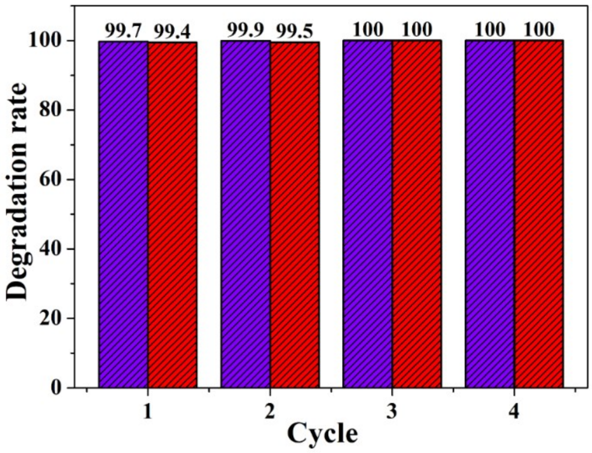

Fig. S13 Degradation rate of MB solution catalyzed by **1** (purple) and **2** (red) in the presence of H_2O_2 additive after 4 cycles

Table S2. A survey of MOF-based treatment of Methylene Blue (MB).

MOFs material	Band gap	Dye	Concertration and quantity	Irrigation	Degradation time	Degradation Efficiency (%)
[Co_2(tkcomm)(tkiymm)][1]	3.78	MB	3.51 mg.L^{-1}	Vis (500 W)	300 min	49.6
MIL-53(Fe)[2]	2.72	MB	140 mg L^{-1}	Vis (500 W)	40 min	20
Fe_3O_4@MIL-100(Fe)[3]	2.36	MB	40 mg.L^{-1}	Vis (500 W)	20 min	20
[Co_2(1,4-bdc)(ncp)$_2$][4]	---	MB	35.1 mg.L^{-1}	UV (375 W)	300 min	62.75
MIL-88A[5]	2.05	MB	32 mg.L^{-1}	Vis (300 W)	20 min	100
g-C_3N_4/NH_2-MIL-88B(Fe)[6]	1.14	MB	30mg.L^{-1}	Vis (500 W)	120 min	30
Compound 1	1.18	MB	55 mg.L^{-1}	Vis (300 W)	300 min	50
Compound 2	1.12	MB	55 mg.L^{-1}	Vis (300 W)	300 min	90
MIL-53(Fe)[2]	2.72	MB (H_2O_2)	140 mg L^{-1}	Vis (500 W)	20 min	20
Fe_3O_4@MIL-100(Fe)[3]	2.36	MB (H_2O_2)	40 mg.L^{-1}	Vis (500 W)	200 min	100
NTU-9[7]	1.74	MB (H_2O_2)	31.9 mg.L^{-1}	Vis (300 W)	20 min	100
Cu(ptz)(II)[8]	2.24	MB (H_2O_2)	18.7 mg.L^{-1}	Vis (500 W)	24 min	85
[Cu^{II}(salimcy)](Cu^{I}I)$_2$[9]	---	MB (H_2O_2)	12 mg.L^{-1}	Vis (500 W)	22 min	96
Cu(ptz)(I)[8]	1.65	MB (H_2O_2)	18.7 mg.L^{-1}	Vis (500 W)	24 min	98
Compound 3[10]	1.49	MB (H_2O_2)	55 mg.L^{-1}	Vis (300 W)	30 min	98
Compound 1	1.18	MB (H_2O_2)	55 mg.L^{-1}	Vis (300 W)	30 min	100
Compound 2	1.12	MB (H_2O_2)	55 mg.L^{-1}	Vis (300 W)	30 min	100

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