

# Enhanced Organic Dye Adsorption and Photocatalytic Activity Through Metal-Organic Framework Featuring Heptanuclear / Binuclear Clusters and Cage-Cavities

Xi Chen,<sup>\*a</sup> Zi-tong Chen,<sup>b</sup> Feng Zhu,<sup>a</sup> Yuan Chen,<sup>b</sup> Ao-gang Liu,<sup>b</sup> Xue Yin,<sup>c</sup> Zi-ke Chen,<sup>c</sup> and Bao Li<sup>\*b</sup>

<sup>a</sup> School of Chemistry and Environmental Science, Shangrao Normal University, Shangrao, Jiangxi, 334001, People's Republic of China. Email: chenxihaoyang@163.com

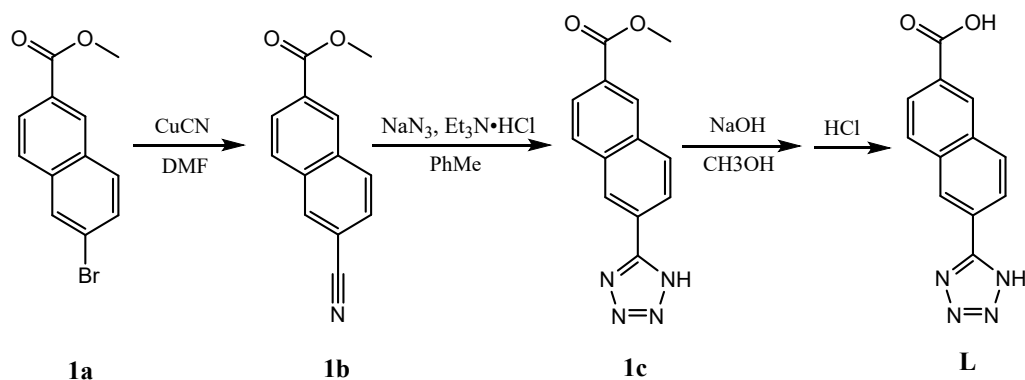
<sup>b</sup> Key Laboratory of Material Chemistry for Energy Conversion and Storage, Semiconductor chemistry center, School of Chemistry and Chemical Engineering, Hubei Key Laboratory of Bioinorganic Chemistry&Materia Medica, Huazhong University of Science and Technology, Wuhan, Hubei, 430074, People's Republic of China. Email: [libao@hust.edu.cn](mailto:libao@hust.edu.cn)

<sup>c</sup> Hubei Changjiang New Material Research and Design Institute Co., Ltd., Wuhan, Hubei, 430074, People's Republic of China

## Experimental sections

**Materials and General Methods.** All reagents were purchased from commercial sources and were used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 analyzer. FT-IR spectra were recorded as KBr pellets with an Equinox 55 FT-IR spectrophotometer (4000-400 cm<sup>-1</sup>). Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 °C, using a heating rate of 10 °C min<sup>-1</sup> under air. Powder X-ray diffraction (PXRD) patterns for the as-synthesized samples were recorded on a X-ray diffraction meter (D/max 2500 PC, Rigaku) with Cu-K $\alpha$  radiation (1.5406 Å), PXRD data were collected over the 2 $\theta$  range 5~50° at room temperature, with a step size of 0.02° in 2 $\theta$  angle. Ultraviolet-visible (UV-vis) adsorption spectra were recorded at room temperature on UV-2550 spectrophotometer.

## Synthesis of 6-(1H-tetrazol-5-yl)-2-naphthoic acid (**L**)



Scheme S1 Synthetic route for the ligand **L**

### *Synthesis of 1b*

6-bromo-2-naphthalenecarboxylic acid methyl ester (**1a**) (2.65 g, 10 mmol) and 1.08 g CuCN (12 mmol) were added into anhydrous DMF (40 mL), which was stirred to 150 °C overnight and then cooled to room temperature. The reaction solution was poured into about 200 mL of saturated ammonium chloride solution for dilution, then extracted with ethyl acetate (3 × 50 mL), washed with concentrated brine, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the organic layer was collected and spun-dried to ethyl acetate to obtain methyl 6-cyano-2-naphthalenecarboxylate (**1b**) 1.52 g (72% yield).

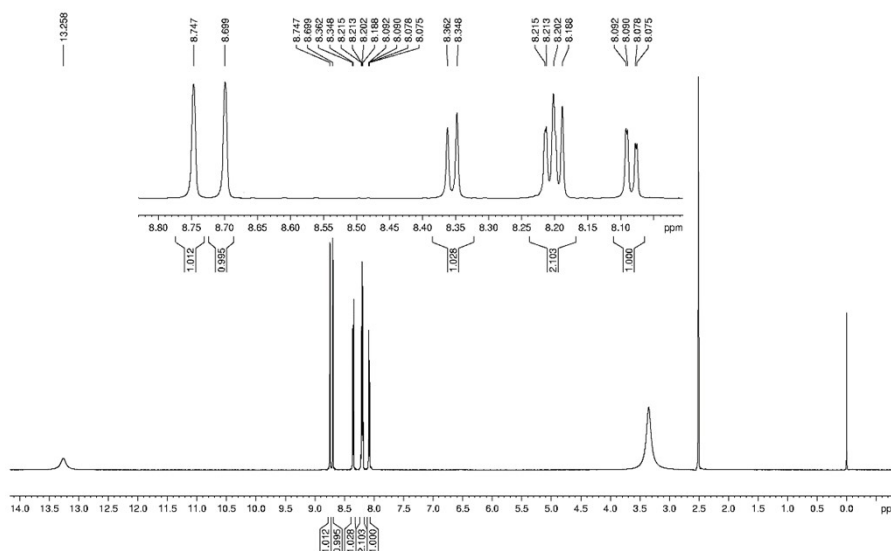
### *Synthesis of 1c*

To a solution of methyl 6-cyano-2-naphthoate (844 mg, 4.0 mmol) in toluene (30 mL), NaN<sub>3</sub> (520 mg, 8.0 mmol) was added, followed by triethylammonium chloride (1.1 g, 8.0 mmol). The resulting mixture was stirred at 110 °C for 24 h before cooling to room temperature. Then, 20 mL water was added to the reaction and the mixture was stirred for 10 min. The reaction solution was added 20 mL of water with stirring for 10 min and then extracted with water (3 × 50 mL), finally the obtained aqueous phase reaction solution was acidified with 3 M HCl, filtered, dried to give 0.85 g of 6-(1H-tetrazol-5-yl)-2-naphthoic acid methyl ester (**1c**, 96% yield).

### *Synthesis of L*

A quantity of sodium hydroxide (1.5 g) was dissolved in 50 mL methanol, and then 6-(1H-tetrazol-5-yl)-2-naphthoic acid methyl ester (**1c**, 0.85 g) was added. The mixture was stirred overnight at 75 °C. The volatiles were removed and the residue was

dissolved in water, filtered and acidified to pH~2 using dilute hydrochloric acid. The product as a precipitate was obtained after stirring. The precipitate was collected by filtration, washing with water and drying (0.72g, 90% yield). IR (KBr):  $\nu/\text{cm}^{-1}$  3494 (s), 2641 (m), 1680 (s), 1610 (m), 1573 (m), 1504 (w), 1437 (m), 1310 (s), 1190 (m), 1151 (w), 1085 (m), 902 (s), and 765 (s).



**Figure S1**  $^1\text{H}$ NMR spectra of ligand

### Synthesis of Cu-MOF

A mixture of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (45 mg, 0.2 mmol), 6-(1H-tetrazol-5-yl)-2-naphthoic acid (22.8 mg, 0.1 mmol) was dissolved in 3 mL of DMF and 3mL of ethanol. The mixture was put into a 20 ml glass vial and sonicated for 5 min at room temperature, when it was completely dissolved, the glass vial was placed in an oven at 80°C for 48 hours, and then cooled to room temperature, then green crystals were obtained. The crystals were collected by filtration, washing and drying under ambient conditions. Yield of the reaction was ca.56% based on Cu. Anal. Element analysis for fresh sample: H, 2.32%; C, 38.52%; N, 17.20%; IR (KBr,  $\text{cm}^{-1}$ ): 3437 (s), 1659 (s), 1446(s), 1392 (s), 1256 (m), 1187 (m), 1100 (m), 909 (m), 819 (s), 776 (s).

### X-Ray Structural Determination.

Diffraction data for Cu-MOF ( $0.1 \times 0.05 \times 0.05$  mm) was collected via Bruker APEX-II CCD using Mo-K $\alpha$  ( $\lambda = 0.71 \text{ \AA}$ ) radiation at 293 K. The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial

structure and then refined anisotropically with SHELXTL using a full-matrix leastsquares procedure based on  $F^2$  values. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. Attempts to define the highly disordered solvent molecules were unsuccessful, so the structure was refined with the PLATON “SQUEEZE” procedure. The disordered process for the structural solution had been carried out, which must be responsible for the corresponding alert A. CCDC-2340774 for the data under different temperature contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/datarequest/cif>.

**Table S1** Crystal data and structure refinements for Cu-MOF

Compound	Cu-MOF
Formula	$C_{60}H_{30}Cu_{4.5}N_{20}O_{11}$
$M_r$	1493.96
Crystal system	Orthorhombic
$a/\text{\AA}$	29.618(2)
$b/\text{\AA}$	15.2128(13)
$c/\text{\AA}$	24.2347(11)
$\alpha/^\circ$	90.00
$\beta/^\circ$	90.00
$\gamma/^\circ$	90.00
$V/\text{\AA}^3$	10919.6(13)
T/K	293(2)
Space group	$Pnmm$
$Z$	8
$R_{int}$	0.0791
$R_I [I > 2\sigma(I)]$	0.0868
$wR(F^2) [I > 2\sigma(I)]$	0.2177

$R_I$ (all data)	0.1167
$wR(F^2)$ (all data)	0.2410

**Table S2** Selected Bond Distances (Å) and Angles (°) for Cu-MOF

Cu1-N2B	2.051(4)	Cu1-N1C	2.343(2)
Cu2-O2A	1.925(9)	Cu2-N3B	2.010(8)
Cu3-O1A	1.882(3)	Cu3-N2A	2.011(2)
Cu4-O1C	1.950(1)	Cu4-N3A	1.974(2)
Cu4-O2C	2.070(6)	Cu4-N4C	2.218(1)
N2B-Cu1-N1C	88.59(5)	O2A-Cu2-N3B	86.87(6)
O2A-Cu2-N2C	102.65(3)	N2C-Cu2-N3B	92.91(5)
O1A-Cu3-N2A	86.82(8)	O1A-Cu3-N3C	100.32(3)
N2A-Cu3-N3C	93.87(5)	O1C-Cu4-N3A	154.20(9)
O1C-Cu4-O2C	61.60(7)	O1C-Cu4-N4C	99.41(2)
O2C-Cu4-N3A	163.17(7)	N4C-Cu4-N3A	92.55(3)

Asymmetric code: (A) -x+2, -y+2, z; (B) -x+3/2, y-1/2, -z+3/2; (C) -x+2, -y, z.

### Dyes adsorption experiments

Dye-uptake analyses were executed by soaking the fresh samples of Cu-MOF (10 mg) in DMF solutions containing different kinds of dyes (5 mL,  $2.5 \times 10^{-5}$  mmol·L<sup>-1</sup>), respectively, and the progress was monitored by UV-vis spectroscopy at various time intervals. The adsorption degree had been calculated based on UV/vis spectroscopy testing results. The amounts of absorbed dyes at time  $q_t$  and adsorption kinetics constant were calculated as follows:

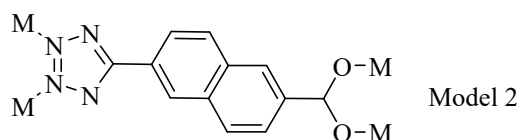
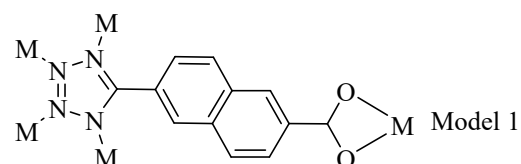
$$q_t = (C_0 - C) \frac{V}{m} \quad (1)$$

$$\ln(C_0/C) = k_1 t \quad (2)$$

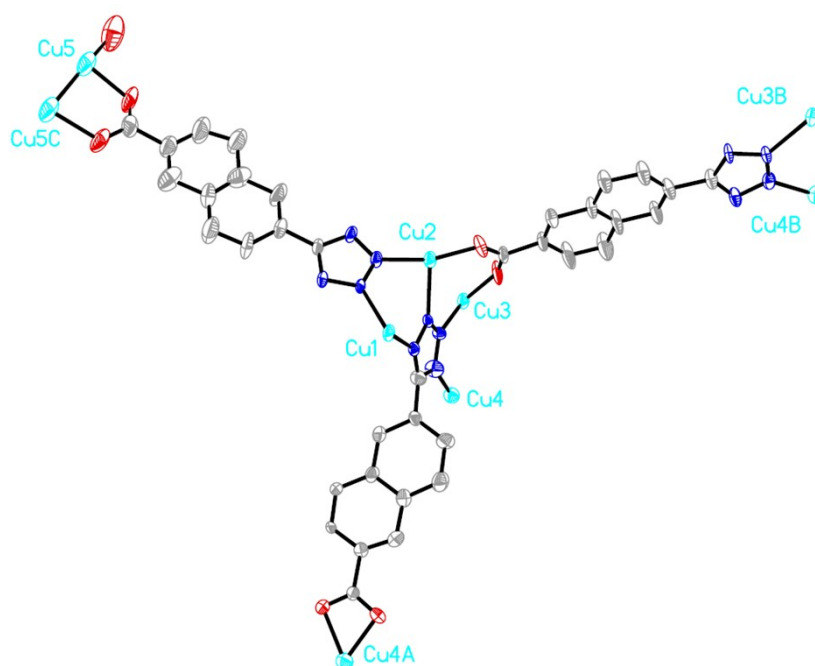
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

in which  $C_0$  and  $C$  are the concentrations of dyes at initial and time, respectively (in

mg L<sup>-1</sup>).  $V$  is the volume of the dye solutions (in L) and  $m$  is the mass of MOF adsorbents (in g).  $k_1$  and  $k_2$  are the pseudo-first-order rate constant (in min<sup>-1</sup>) and pseudo-second-order rate constant (in g mg<sup>-1</sup> min<sup>-1</sup>), respectively.  $k_1$  and  $k_2$  can be obtained from the fitted plots of  $\ln(C_0/C)$  vs.  $t$  and  $t/q_t$  vs.  $t$ , respectively.



**Scheme S2** The presented coordination modes of L ligand existed in Cu-MOF.



**Figure S2** Perspective view of the asymmetric unit of Cu-MOF at the 30% probability level (hydrogen atoms were omitted for the sake of clarity). Asymmetric code: A,  $-x+2, -y+2, z$ ; B,  $-x+3/2, y-1/2, -z+3/2$ ; C,  $-x+2, -y, z$ .

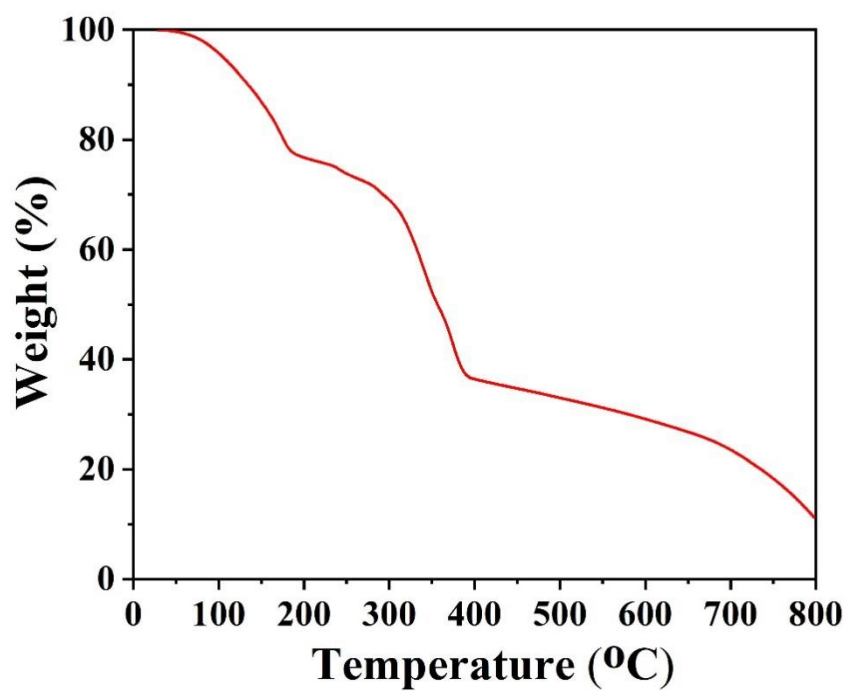


Figure S3 TGA curves of Cu-MOF under air atmosphere.

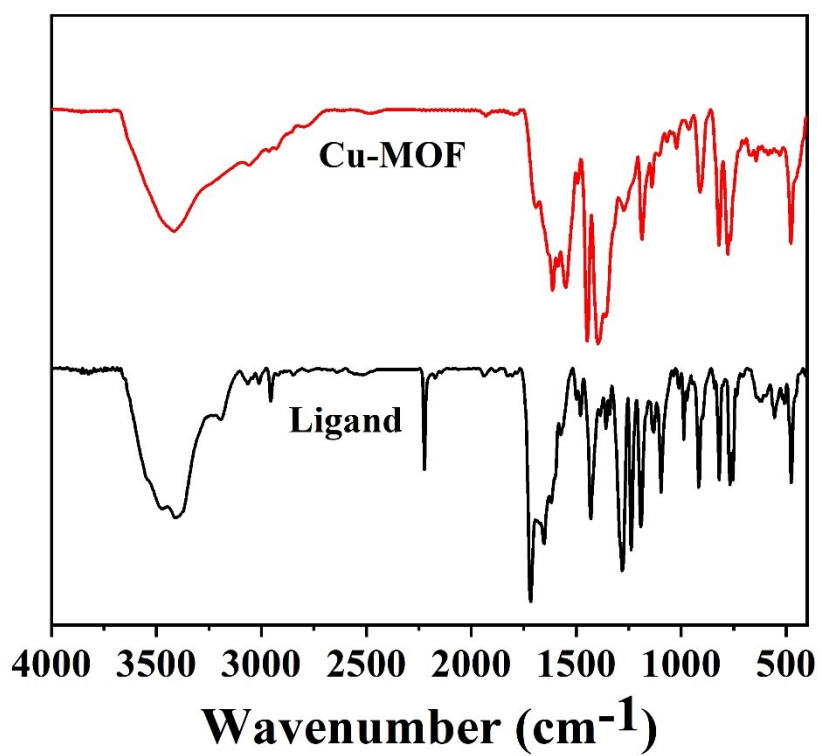


Figure S4 IR spectra of Ligand (black) and Cu-MOF (red)

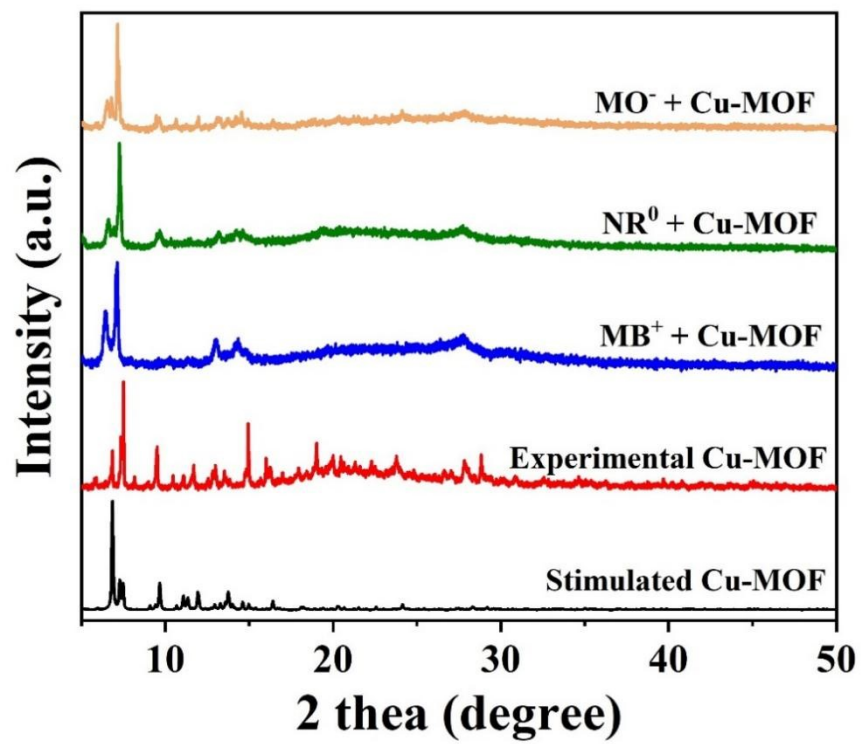


Figure S5 PXRD of Cu-MOF