Electronic Supplementary Information (ESI) for Chemical Communications
 This journal is (c) The Royal Society of Chemistry 2016

3 Metal-organic framework nanosheets with flower-like structure as

4 5

probe for H₂S detection and in situ singlet-oxygen production Pinghua Ling,* Caihua Qian, Jinjin Yu and Feng Gao*

6 Laboratory of Functionalized Molecular Solids, Ministry of Education, Anhui Key Laboratory of

7 Chemo/Biosensing, College of Chemistry and Materials Science, Anhui Normal University, Wuhu

8 241002, P. R. China.

9 Experimental

Materials and reagents. Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99%), polyvinylpyrrolidone 10 (PVP, average mol wt 40,000), trifluoroacetic acid (CF₃COOH, 99%), N,N-Dimethylformamide 11 (DMF, 99.8%), ethanol glutathione (GSH), cysteine (Cys), homocysteine (Hcy), hydrogen 12 peroxide (H₂O₂; 30% aqueous solution), Na₂SO₄, Na₂SO₃, Na₂S₂O₃, Na₂HPO₄, NaClO, NaHSO₃, 13 KSCN, NaH₂PO₄, NaHCO₃, and 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA) 14 from Sigma-Aldrich Inc. (Shanghai, were purchased China). Zn(II)meso-Tetra(4-15 carboxyphenyl)Porphine (ZnTCPP) was obtained from J&K Scientific Ltd. Phosphate buffer 16 saline (PBS, 0.01 M, pH 7.4) was used for the experiments throughout. All aqueous solutions were 17 prepared using ultrapure water ($\geq 18 \text{ M}\Omega$, Milli-Q, Millipore). 18

Apparatus. The UV-vis absorption spectra were obtained with a lambda-35 UV-vis spectrophotometer (PerkinElmer, USA). Fluorescence was taken on a LS-55 (PerkinElmer, USA). The powder X-ray diffraction (pXRD) was performed on a Bruker D8 advance X-ray powder diffractometer operating at 40 kV and 40 mA (CuK α radiation, $\lambda = 1.5418$ Å). The scanning electron microscope (SEM) images and energy dispersive spectrometer (EDS) with the substrate of silicon were measured on an S-4800 scanning electron microscope (Hi-tachi, Japan). Transmission electron micrographs (TEM) were obtained on a JEOL JEM-2010 transmission electron microscope operating at an accelerating voltage of 200 kV. The electron paramagnetic
 resonance (EPR) was recorded on an EMX-10/12 EPR spectrometer (Bruker, Germany).

³ **Preparation of Cu-ZnMOF nanosheets.** The Cu-ZnMOF was synthesized according to previous ⁴ work ^{S1} with minor modifications. Typically, 3.6 mg Cu(NO₃)₂·3H₂O, 10 mg PVP and 10 μ L ⁵ CF₃COOH were dissolved in 12 mL DMF/ethanol (V:V = 3:1) and added in a 20 mL capped vial. ⁶ After sonicating for 10 min, 4.5 mg ZnTCPP dissolved in 4 mL DMF/ethanol (V:V = 3:1) was ⁷ added into the capped vial and sonicated for another 15 min. After the capped vial was heated at ⁸ 80 °C for 4 h, the solid Cu-ZnMOF were washed by centrifugation with fresh ethanol and re-⁹ dispersed in ethanol.

10 Synthesis of bulk Cu-ZnMOF. The synthesis of bulk Cu-ZnMOF was similar to that for Cu-11 ZnMOF nanosheets, as mentioned above. $Cu(NO_3)_2 \cdot 3H_2O$ (7.2 mg), ZnTCPP (9 mg) 12 trifluoroacetic acid (10 µL) and PVP (10 mg) were dissolved in 2 mL DMF/ ethanol (V:V = 3:1) 13 in a small vial. After sonicating for 10 min, the capped vial was heated at 80 °C for 4 h. After 14 centrifuging, the bulk Cu-ZnMOF was obtained.

¹O₂ generation. Disodium 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA) which 15 could react with ¹O₂ to produce endoperoxide and decrease the absorption intensity of itself is as 16 probe to evaluate the ability of ¹O₂ generation of Cu-ZnMOF. 70 µM NaHS was reacted with the 17 solution of Cu-ZnMOF in PBS (7.4) for 20 min, then ABDA was added. Laser device with 635 18 nm was used to irradiate the above solution, and then measured the UV-vis spectra on lambda-35 19 UV-vis spectrophotometer with 2 min interval. For the control experiment, ABDA was added into 20 the solution of Cu-ZnMOF without NaHS in PBS (7.4), and measured the UV-vis spectra as the 21 similar condition with NaHS. 22

The quantum yield of ${}^{1}O_{2}$ production. The quantum yield of ${}^{1}O_{2}$ generation was measured via the chemical method^{S2}. In this method, 1,3-diphenylisobenzofuran (DPBF) and rose bengal (RB) were used as the ${}^{1}O_{2}$ -trapping agent and standard photosensitizer, respectively. Typically, DPBF was mixed with Cu-ZnMOF, the mixture of Cu-ZnMOF and NaHS, or RB in the dark and irradiated with 635 nm laser for different periods of time. The ${}^{1}O_{2}$ quantum yield (Φ) was calculated with the following formula:

$$\Phi_x = \Phi_{RB} \times \frac{K_x}{K_{RB}} \times \frac{F_{RB}}{F_x}$$

1

where K_x and K_{RB} are the decomposition rate constants of DPBF (at 410 nm) by the sample and RB, respectively. F represent the absorption correction factor, which is determined by F =1-10^{-OD} (OD represents the optical density of sample and RB at 635 nm). Φ_{RB} is the ¹O₂ quantum yield of RB, which is 0.75.

1 Supporting figures

2 EDS of Co-FeMOF.



3

4 Fig. S1 The EDS of Cu-ZnMOF.

5 XPS spectrum Cu-ZnMOF.



7 Fig. S2 XPS spectrum of Cu-ZnMOF.

8

2 Fig. S3 Fluorescence spectra of Cu-ZnMOF with different concentration of NaHS of 0 μM (a),

3 0.20 μ M (b), and 10 μ M (c) in pH 7.4 PBS. Ex=420 nm.

4 The quantum yield of ¹O₂ production

Fig. S4. Chemical trapping measurements of the ¹O₂ quantum yield of Cu-ZnMOF before and after
treating with NaHS. (A) Photodegradation of DPBF with Cu-ZnMOF. (B) photodegradation of
DPBF with RB. (C) Photodegradation of DPBF with Cu-ZnMOF after treating with NaHS.

9

1 FL of Cu-ZnMOF with different concentration.

2

- 3 Fig. S5 Fluorescence spectrum and intensity at 610 nm of Cu-ZnMOF with different concentration,
- 4 2.50 mg/mL, 7.50 mg/mL, 15 mg/mL, 22.5 mg/mL, 30 mg/mL, 37.5 mg/mL, 40 mg/mL and 50
- 5 mg/mL in the absence (A) and (B) and presence (C) and (D) of NaHS (70 µM) in 0.01 PBS
- 6 (pH=7.4). Ex=420 nm.
- 7 Kinetic curves.

8

9 Fig. S6 Kinetic curves plotting the time-dependent fluorescence emission intensity at 610 nm of
10 Cu-ZnMOF in the presence (a) and absence (b) of 70 μM NaHS in 0.01 M pH=7.4 PBS. Ex=420
11 nm.

1 SEM and TEM images of Cu-ZnMOF after treating with NaHS.

- 3 Fig. S7 (A) SEM and (B) TEM images of Cu-ZnMOF after treating with NaHS (70 μ M) in 0.01
- 4 M PBS (pH=7.4)

2

5 XRD of Cu-ZnMOF after incubating with NaHS.

7 Fig. S8 XRD of Cu-ZnMOF nanosheets (a) and bulk Cu-ZnMOF (b) after incubating with NaHS

8 (70 μM) in 0.01 M PBS (pH=7.4).

9

1 EDS of Cu-ZnMOF after reacting with NaHS in 0.01 M PBS (pH=7.4)

3 Fig. S9. EDS of Cu-ZnMOF after reacting with NaHS (70 μM) in 0.01 M PBS (pH=7.4).

4 XPS spectra of Cu-ZnMOF reacted with NaHS.

6~ Fig. S10. XPS spectra of (A) Cu 2p and (B) S 2p.

7

1 EPR of Cu-ZnMOF after reacting with NaHS in 0.01 M PBS (pH=7.4)

2

- 3 Fig. S11. EPR spectra of Cu-ZnMOF with treating with NaHS (70 μM) in 0.01 M pH 7.4 PBS.
- 4 UV-Vis absorption spectra of Cu-ZnMOF without and with treating with NaHS in 0.01 M
 5 pH 7.4 PBS.

6

7 Fig. S12. UV-Vis absorption spectra of Cu-ZnMOF without (a) and with (b) treating with NaHS

 $8~(70~\mu M)$ in 0.01 M pH 7.4 PBS.

1 SEM image of Cu-ZnMOF in 0.01M PBS (pH=6.85).

- 2
- 3 Fig. S13. SEM image of Cu-ZnMOF in 0.01 M PBS (pH=6.85).
- 4 SEM image of Cu-ZnMOF after reacting with NaHS in 0.01M PBS (pH=6.85).

- 5
- 6~ Fig. S14. SEM image of Cu-ZnMOF in the presence of NaHS (70 μM) in 0.01 M PBS (pH=6.85).

3 Fig. S15 XRD of Cu-ZnMOF in the presence of NaHS (70 μM) in 0.01 M PBS (pH=6.85).

4

5

6 **Fig. S16**. Fluorescence intensity at 610 nm response of Cu-ZnMOF toward various reactive 7 species, NaHS (70 μM), GSH (10 mM), SO_3^{2-} (1 mM), SO_4^{2-} (1 mM), $S_2O_3^{2-}$ (1 mM), SCN^- (1 8 mM), HPO_4^{2-} (1 mM), H_2PO^{4-} (1 mM), HCO^{3-} (1 mM), ClO^- (200 μM), H_2O_2 (200 μM), HSO^{3-} (1 9 mM), Hcy (100 μM) and Cys (100 μM) in 0.01 M pH 7.4 PBS. Ex = 420 nm.

Element	Weight %	Atomic %
С	65.80	80.74
0	11.07	10.19
Si	12.71	6.67
Cu	7.30	1.69
Zn	3.13	0.71

2 Table S1. The obtained elemental ratio of Cu-ZnMOF by EDS.

3

4 Supporting references

- 5 S1. Y. Huang, M. T. Zhao, S. K. Han, Z. C. Lai, J. Yang, C. L, Tan, Q. L. Ma, Q. P. Lu, J. Z.
- 6 Chen, X. Zhang, Z. C. Zhang, B. Li, B. Chen, Y. Zong, and H. Zhang, Adv. Mater. 2017,
- 7 1700102.
- 8 S2. (a) J. C. Ge, M. H. Lan1, B. J. Zhou, W. M. Liu, L. Guo, H. Wang, Q. Y. Jia, G. L. Niu, X.
- 9 Huang, H. Y. Zhou, X. M. Meng, P. F. Wang, C. S. Lee, W. J. Zhang and X. D. Han, Nat.
- 10 Commun. DOI: 10.1038/ncomms5596. (b) J. W. Tian, L. Ding, H. J. Xu, Z. Shen, H. X. Ju, L.
- 11 Jia, L. Bao, J. S. Yu, J. Am. Chem. Soc. 2013, 135, 18850-18858.