

## Supporting Information

### **Cu(II) Coordination Polymer with Nitrogen Catenation Ligands for Efficient Photocatalytic Water Oxidation**

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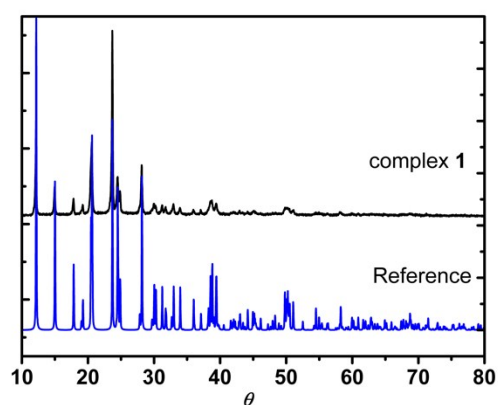
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## Experimental Procedures

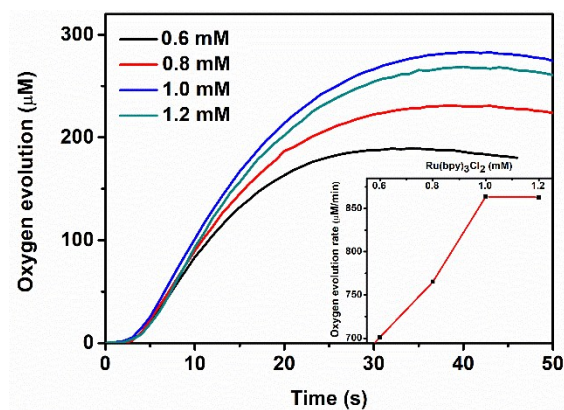
All reagents and solvents used in the present work were obtained commercially from Inno-chem without further purification if there was no special notification. The PXRD pattern of the ground powder was performed at room temperature on a Bruker D8 Focus diffractometer with Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. Elemental analysis were performed using FlashEA 1112. Linear Scan Voltammetry (LSV) and Cyclic Voltammetry (CV) experiments were performed on a Potentiostat/Galvanostat Model 283. All potentials were reported versus normal hydrogen electrode (vs. NHE). Platinum wire was used as counter electrode in the three-electrode system. The reference electrode was saturated calomel electrode (SCE) as reference electrode (+0.242 V vs. NHE), and the working electrode was 0.07 cm<sup>2</sup> glassy carbon (GC) electrode. Oxygen evolution were recorded with a Hansatech Clark Oxygen Electrode. EPR spectra at 90 K were obtained using X Band Bruker E500 Electron Spin Resonance Spectrometer. The XAS data were collected at the Beijing Synchrotron Radiation Facility (BSRF) on beamline 1W1B. <sup>1</sup>H NMR spectra were recorded with a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. UV-vis spectra were determined on a Shimadzu UV-1601PC UV-Visible spectrophotometer.



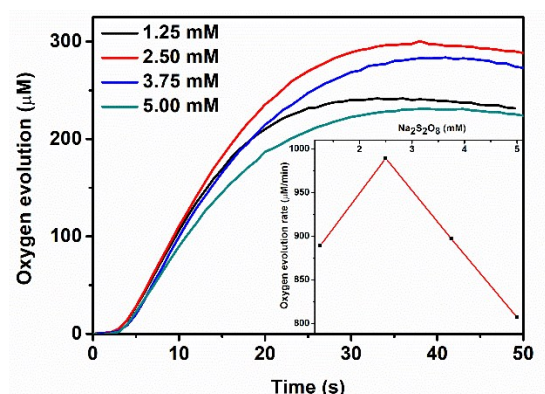
**Figure S1.** Experimental (black) and simulated (blue) powder X-ray diffraction data of **1**.

<sup>1</sup>H NMR (D<sub>2</sub>O, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) of Htza:  $\delta$  [ppm] = 9.26 (H-1, s, 1 H), 5.47 (H-2, s, 2 H). <sup>1</sup>H NMR (D<sub>2</sub>O, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) of **1**:  $\delta$  [ppm] = 9.20 (H-1, s, 1 H), 5.20 (H-2, s, 2 H). All the NMR assignments are keyed in the Figure S7 shown below.

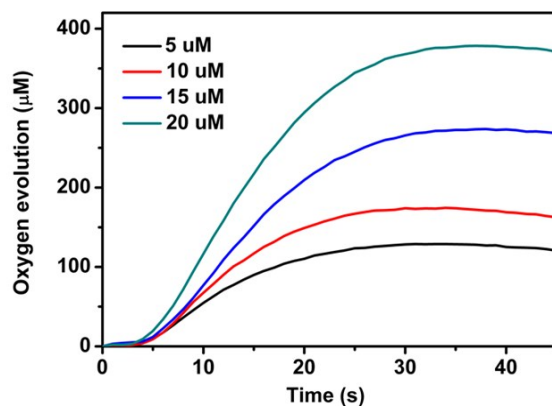
Anal. Calc. for **1**, [Cu(tza)<sub>2</sub>]<sub>n</sub>: C, 22.68; H, 1.90; N, 35.27. Found C, 22.56; H, 1.94; N, 35.41.



**Figure S2.** Photocatalytic oxygen evolution by 50  $\mu\text{M}$  complex **1** with different concentration of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ . Conditions: 1.0 mL aqueous solution, 5 mM  $\text{Na}_2\text{S}_2\text{O}_8$ , 80 mM borate buffer solution, pH 9.0, 450 nm blue LED. Inset: Plot of the initial oxygen evolution rate as a function of the concentration of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ .

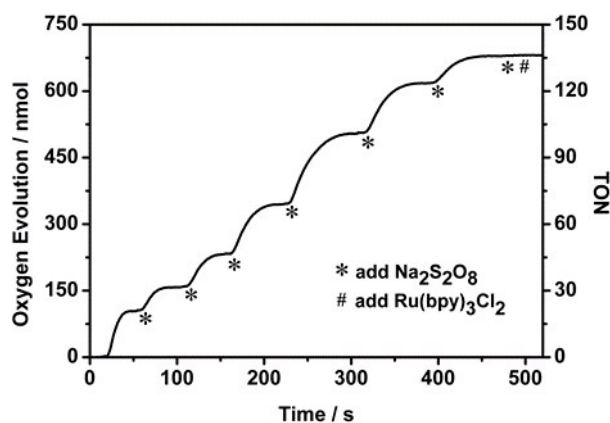


**Figure S3.** Photocatalytic oxygen evolution by 50  $\mu\text{M}$  catalyst **1** with different concentration of  $\text{Na}_2\text{S}_2\text{O}_8$ . Conditions: 1.0 mL aqueous solution, 1.0 mM  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ , 80 mM borate buffer solution, pH 9.0, 450 nm blue LED. Inset: Plot of the initial oxygen evolution rate as a function of the concentration of  $\text{Na}_2\text{S}_2\text{O}_8$ .



**Figure S4.** Photocatalytic oxygen evolution with different concentration of catalyst **1**. Conditions: a 1.0 mL aqueous solution, 1.0 mM Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, 2.5 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 80 mM borate buffer, pH 9.0, 450 nm blue LED.

Oxygen evolution was found to be appended with the addition of sacrificial electron acceptor Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The whole catalytic time could be 520 s, and the total TON could reach 136. On the other hand, addition of either photosensitizer or catalyst did not affect the oxygen evolution, indicating that the end of the first run was ascribed to the loss of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, not to the deactivation of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> or catalyst.



**Figure S5.** Oxygen evolution recorded using the Clark oxygen electrode. Initial conditions: a 1.0 mL aqueous solution containing 5 μM catalyst **1**. 1.0 mM Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, 2.5 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 80 mM borate buffer, pH 9.0, 450 nm blue LED.

**Table S1.** Electrochemical Data of related Cu-WOC in the literatures and this work.

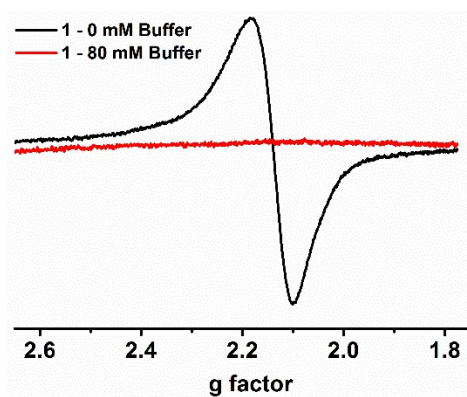
catalyst	$\eta$ ,mV	pH	Ref
[(bpy)Cu(OH)] <sub>2</sub>	750 <sup>a</sup>	12.5	1
[(TGG <sup>4-</sup> )Cu(H <sub>2</sub> O)] <sup>2-</sup>	520 <sup>b</sup>	11	2
[(6,6'-dhbp) <sub>2</sub> Cu(CH <sub>3</sub> OH)] <sup>2+</sup>	410 <sup>b</sup>	12.6	3
Na <sub>2</sub> [Cu(opba)]	626 <sup>a</sup>	10.8	4
[(dhbp)Cu(μ-OH)] <sub>n</sub>	540 <sup>a</sup>	12.4	5
[(Py <sub>3</sub> P)Cu]	400 <sup>b</sup>	8	6
[Cu(Me <sub>2</sub> oxpn)Cu(OH) <sub>2</sub> ]	636 <sup>b</sup>	10.4	7
[L <sub>1</sub> Cu] <sup>2-</sup>	700 <sup>a</sup>	11.5	8
[L <sub>2</sub> Cu] <sup>2-</sup>	400 <sup>a</sup>	11.5	8
[L <sub>3</sub> Cu] <sup>2-</sup>	270 <sup>a</sup>	11.5	8
[L <sub>4</sub> Cu] <sup>2-</sup>	170 <sup>a</sup>	11.5	8
[Cu <sub>2</sub> (BPMAN)(μ-OH)] <sup>3+</sup>	1050 <sup>a</sup>	7	9
[Cu(en) <sub>2</sub> ] <sup>2+</sup>	440 <sup>b</sup>	8	10
[Cu <sub>4</sub> (H <sub>2</sub> L) <sub>4</sub> ] <sup>4+</sup>	388 <sup>b</sup>	12.5	11
[Cu(F <sub>3</sub> TPA)(ClO <sub>4</sub> )(CH <sub>3</sub> CN)] <sup>+</sup>	610 <sup>b</sup>	8.5	12
CuPcTS	570 <sup>b</sup>	9.5	13
[L <sub>1</sub> Cu(OH <sub>2</sub> )] <sup>2+</sup>	900 <sup>b</sup>	9	14
[L <sub>2</sub> Cu(OH <sub>2</sub> )] <sup>2+</sup>	460 <sup>b</sup>	9	14
[Cu(pimH)(H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	328 <sup>b</sup>	12	15
[(bztpen)Cu] <sup>2+</sup>	440 <sup>c</sup>	11.5	16
[Cu(tza) <sub>2</sub> ] <sub>n</sub>	501 <sup>b</sup>	9.0	this work

<sup>a</sup> Based on the half-peak potential for CVs. <sup>b</sup> Estimated by the extrapolation method. <sup>c</sup> defined as  $j = 0.2 \text{ mA/cm}^2$ .

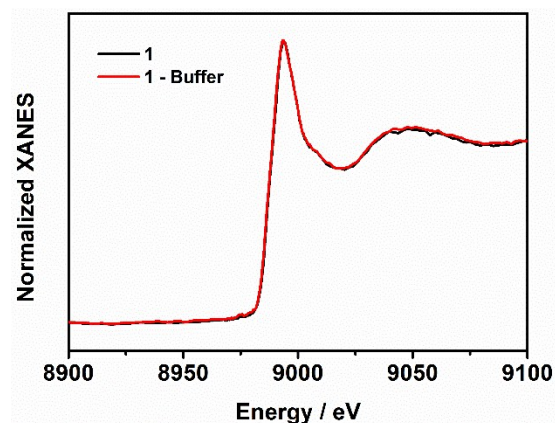
**Table S2.** Photocatalytic oxygen evolution by different copper-based catalysts.

Catalyst	Ru(bpy) <sub>3</sub> <sup>2+</sup>	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	pH	[cat]	TOF/s <sup>-1</sup>	Ref
1	1 mM <sup>b</sup>	2.5 mM	9.0	5 μM	1.68	this work
[Cu(F <sub>3</sub> TPA)(ClO <sub>4</sub> ) <sub>2</sub> ]	0.4 mM <sup>c</sup>	5 mM	8.5	30 μM	0.16	12
CuPcTS	0.2 mM <sup>d</sup>	7 mM	9.5	20 μM	0.063	13
Cu-POM <sup>a</sup>	1 mM <sup>b</sup>	5 mM	9.0	5 μM	0.22	17

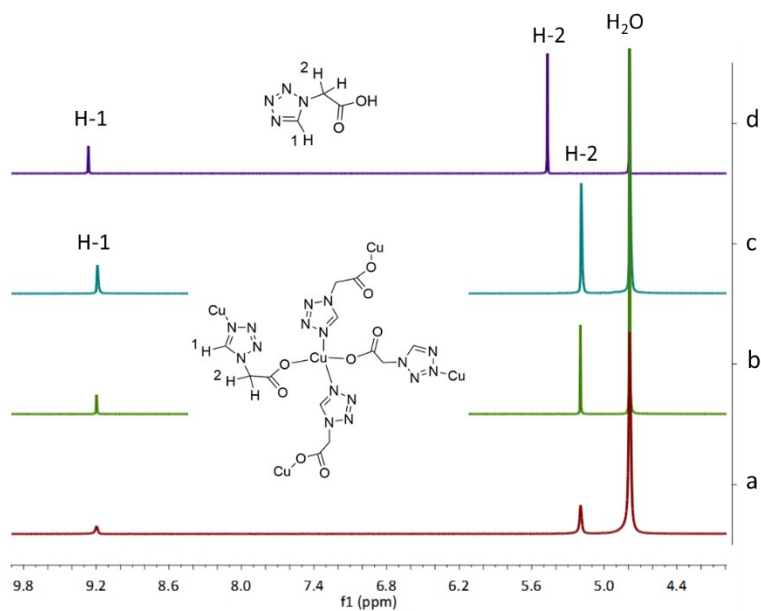
<sup>a</sup> {[Cu<sub>5</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(A- $\alpha$ -SiW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]}<sup>10-</sup>, <sup>b</sup> Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, <sup>c</sup> Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>, <sup>d</sup> Ru(bpy)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>.



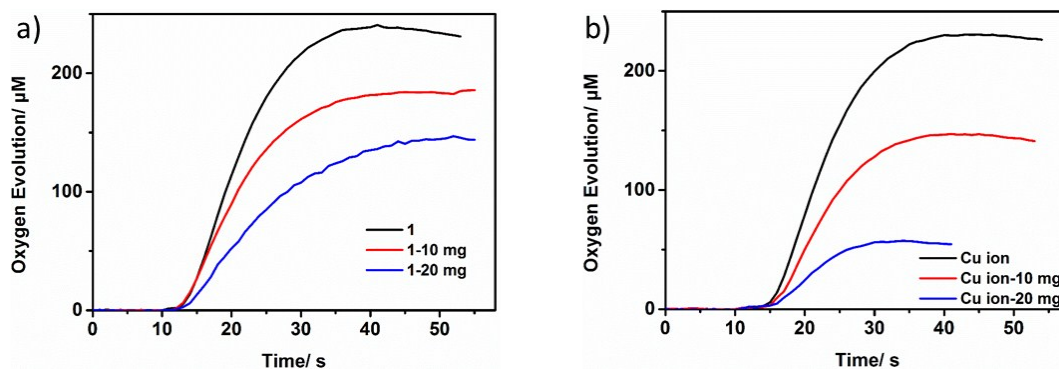
**Figure S6.** EPR spectra at 90 K of 1 in H<sub>2</sub>O (black) and 80 mM borate buffer solution (pH 9.0, red).



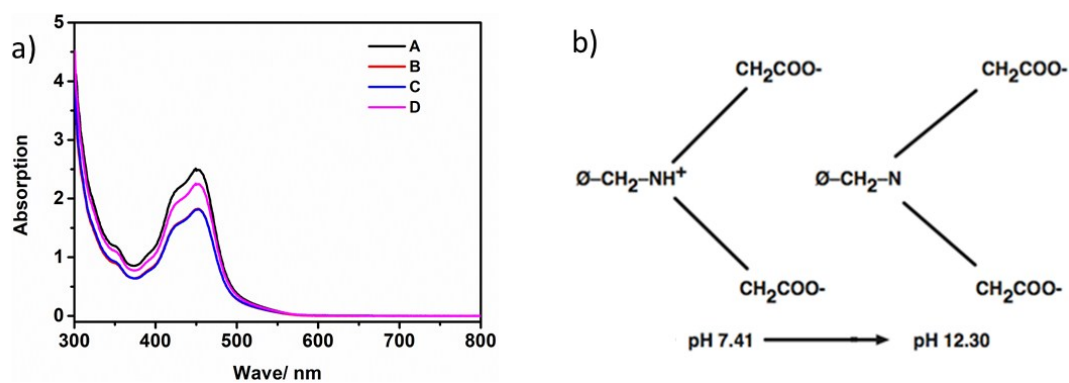
**Figure S7.** XANES spectra of **1** in H<sub>2</sub>O (black) and 80 mM borate buffer solution (pH 9.0, red).



**Figure S8.** <sup>1</sup>H NMR spectra of 0.5 mg (a), 1.0 mg (b), 2.0 mg (c) of **1** and 5 mg Htza (d) in 0.5 mL D<sub>2</sub>O containing the equal amount of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.

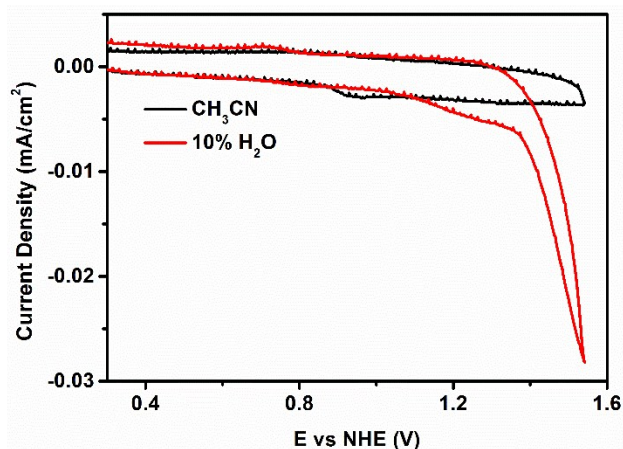


**Figure S9.** Photocatalytic oxygen evolution by 50  $\mu\text{M}$  catalyst **1** (a) and  $\text{CuCl}_2$  (b) with the addition of Chelex resin. Conditions: 1.0 mL aqueous solution, 1.0 mM  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ , 2.5 mM  $\text{Na}_2\text{S}_2\text{O}_8$ , 80 mM sodium borate buffer, pH 9.0, 450 nm blue LED.



**Figure S10.** a) UV-Vis spectra of 50  $\mu\text{M}$   $\text{Ru}(\text{bpy})_3\text{Cl}_2$  with the addition of Chelex resin. A:  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  only; B: addition of 10 mg Chelex resin; C: addition of 50  $\mu\text{M}$  **1** and 10 mg Chelex resin; D: addition of 50  $\mu\text{M}$   $\text{CuCl}_2$  and 10 mg Chelex resin. b) The structure of Chelex resin at pH 7.41-12.30.





**Figure S11.** CV spectra of 1 mM **1** in CH<sub>3</sub>CN (black) and in CH<sub>3</sub>CN/H<sub>2</sub>O (9:1, red) solutions. working electrode, glassy carbon; scan rate, 100 mV/s; electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate.

## References

- 1 S. M. Barnett, K. I. Goldberg and J. M. Mayer, *Nat. Chem.*, 2012, **4**, 498.
- 2 M.-T. Zhang, Z. Chen, P. Kang and T. J. Meyer, *J. Am. Chem. Soc.*, 2013, **135**, 2048.
- 3 D. L. Gerlach, S. Bhagan, A. A. Cruce, D. B. Burks, I. Nieto, H. T. Truong, S. P. Kelley, C. J. Herbst-Gervasoni, K. L. Jernigan, M. K. Bowman, S. Pan, M. Zeller and E. T. Papish, *Inorg. Chem.*, 2014, **53**, 12689.
- 4 L.-Z. Fu, T. Fang, L.-L. Zhou and S.-Z. Zhan, *RSC Adv.*, 2014, **4**, 53674.
- 5 T. Zhang, C. Wang, S. Liu, J.-L. Wang and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 273.
- 6 M. K. Coggins, M.-T. Zhang, Z. Chen, N. Song and T. J. Meyer, *Angew. Chem., Int. Ed.*, 2014, **53**, 12226.
- 7 L.-L. Zhou, T. Fang, J.-P. Cao, Z.-H. Zhu, X.-T. Su and S.-Z. Zhan, *J Power Sources*, 2015, **273**, 298.
- 8 P. Garrido-Barros, I. Funes-Ardoiz, S. Drouet, J. Benet-Buchholz, F. Maseras and A. Llobet, *J. Am. Chem. Soc.*, 2015, **137**, 6758.

- 9 X. J. Su, M. Gao, L. Jiao, R. Z. Liao, P. E. Siegbahn, J. P. Cheng and M. T. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 4909.
- 10 C. Lu, J. Du, X.-J. Su, M.-T. Zhang, X. Xu, T. J. Meyer and Z. Chen, *ACS. Catal.*, 2016, **6**, 77.
- 11 V. K. K. Praneeth, M. Kondo, P. M. Woi, M. Okamura and S. Masaoka, *Chempluschem*, 2016, **81**, 1123.
- 12 R. J. Xiang, H. Y. Wang, Z. J. Xin, C. B. Li, Y. X. Lu, X. W. Gao, H. M. Sun and R. Cao, *Chem. Eur. J.*, 2016, **22**, 1602.
- 13 R. Terao, T. Nakazono, A. R. Parent and K. Sakai, *Chempluschem*, 2016, **81**, 1064.
- 14 J. Shen, M. Wang, J. Gao, H. Han, H. Liu and L. Sun, *Chemsuschem*, 2017, **10**, 4581.
- 15 L. A. Stott, K. E. Prosser, E. K. Berdichevsky, C. J. Walsby and J. J. Warren, *Chem. Commun.*, 2017, **53**, 651.
- 16 J. Shen, M. Wang, P. Zhang, J. Jiang and L. Sun, *Chem. Commun.*, 2017, **53**, 4374.
- 17 L. Yu, X. Du, Y. Ding, H. Chen and P. Zhou, *Chem. Commun.*, 2015, **51**, 17443.