# **Electronic Supplementary**

# Information

## Water oxidation by copper(II) complex: New findings, questions, challenges and a hypothesis

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#### Experimental

#### Materials

All reagents and solvents were purchased from commercial sources and were used without further purification. The fluorine-doped tin oxide (FTO, surface resistivity of ~7  $\Omega$ /sq) coated glass plate, copper(II) phthalocyanine-3,4',4",4"'-tetrasulfonic acid tetrasodium salt, phthalocyanine tetrasulfonate hydrate and copper(II) sulfate pentahydrate were purchased from Sigma-Aldrich. Ethylene diamine tetraacetic acid disodium salt dehydrate (≥ 99.0%) was purchased from Fluka.

#### Characterization

SEM and EDX were carried out with VEGA\TESCAN-XMU. The high-resolution visible spectra were recorded by a mini spectrophotometer (Pooyesh Tadbir Karaneh (Phystec)). Electrochemical experiments were performed using an EmStat<sup>3+</sup> from PalmSens (Netherlands). Cyclic voltammetry studies were carried out with a conventional three-electrode setup, in which FTO, Ag/AgCl/KCl<sub>sat</sub> (or Hg/HgO for KOH solution) and a platinum foil served as working, reference and auxiliary electrodes, respectively. All potentials in this project were reported vs. Ag/AgCl/KCl<sub>sat</sub>. The distance between two opposite sides of the FTO electrode was measured by a digital caliper MarCal 16ER model (Mahr, Germany). The temperature was measured by Laserliner 082 (Germany).

### Table S1 Selected X-ray data for **2**.

	2		
Formula	$C_{14}H_{11}CuN_3O_6$		
Formula weight	380.80		
Temperature [K]	100(2)		
λ [Å]	0.71073		
Crystal system	Triclinic		
Space group	Pī		
a [Å]	7.344(3)		
b [Å]	8.507(3)		
c [Å]	12.926(4)		
α [°]	73.95(3)		
β [°]	83.60(3)		
γ [°]	80.66(3)		
V [ų]	763.9(5)		
Z, $\rho_{calc}$ [g cm <sup>-3</sup> ]	2, 1.656		
μ [mm <sup>-1</sup> ]	1.47		
F(000)	386		
Crystal size [mm]	0.28x0.18x0.10		
θ range[º]	1.64-25.00		
rflns: total/unique	5636/2686		
R(int)	0.1141		
Abs. corr.	numerical		
Min., max.	0.787, 0.919		
transmission factors			
Data/restraints/params	2686/0/217		
GOF on F <sup>2</sup>	1.01		
R1 [I > 2σ(I)]	0.0624		
wR <sub>2</sub> (all data)	0.1483		
Max., min. Δρ <sub>elect</sub> [e Å <sup>-3</sup> ]	0.65, -0.86		

1.940 (4)	Cu1—N3	2.000 (4)
1.943 (4)	Cu1—O1W	2.315 (4)
1.978 (4)		
171.87 (18)	N1-Cu1-N3	162.49 (17)
81.97 (17)	N2—Cu1—O1W	96.07 (16)
96.85 (17)	O3—Cu1—O1W	92.06 (15)
82.59 (17)	N1-Cu1-O1W	98.32 (16)
97.26 (16)	N3-Cu1-01W	91.47 (16)
	1.940 (4) 1.943 (4) 1.978 (4) 171.87 (18) 81.97 (17) 96.85 (17) 82.59 (17) 97.26 (16)	1.940 (4)Cu1-N31.943 (4)Cu1-O1W1.978 (4)1000000000000000000000000000000000000

Table S2 Selected geometric parameters [Å, °] for **2**.



Fig. S1 Atomic structure of 2.



Fig. S2 LSV (scan rate 50.0 mV/s (a) and SWV (b); amplitude: 25 mV; frequency: 10 Hz) for **1** (red), **2** (blue), **3** (olive), **4** (gray), copper(II) salt (pink), and bare FTO electrode (black as a reference) in the buffer solution. The conditions: in the phosphate buffer solution (0.25 M, pH = 11.0) at room temperature. The electrochemical studies were carried out with a conventional three-electrode setup, in which FTO, Ag/AgCI/KClsat and a platinum foil served as working, reference and auxiliary electrodes, respectively. The concentrations of copper(II) compounds were 0.25 mM.





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Fig. S3 Continuous CV for FTO (a), Cu salt (b), 1 (c), 2 (d), 3 (e) and 4 (f) in the buffer solution. The magnified insert small diagram in each case shows the current at 1.5 V. The conditions: in the phosphate buffer solution (0.25 M, pH = 11.0) at room temperature. The electrochemical studies were carried out with a conventional threeelectrode setup, in which FTO, Ag/AgCl/KClsat and a platinum foil served as working, reference and auxiliary electrodes, respectively. The concentrations of copper(II) compounds were 0.25 mM. The continuous CV recorded for a fresh FTO electrode in the absence of any copper(II) complex showed a decrease from 490 to 414 ( $\mu$ A/cm<sup>2</sup>) after 4 cycles and then an increase to 1330 after 250 cycles ( $\mu$ A/cm<sup>2</sup>) (Fig. S3a). This increase was previously reported, and attributed to trace metal ions such as Fe, Ni, Mn, etc., in glass cell or electrolyte at nanomolar concentrations [R1]. The continuous CV for the salt, copper(II) sulfate pentahydrate, displayed a sharp decrease from 3250 to 2880 (µA/cm<sup>2</sup>) after 10 cycles (Fig. S3b). Then, a decrease with low slope from 2880 to 1980  $(\mu A/cm^2)$  was observed after 250 cycles for the copper(II) salt. On the other hand, continuous CV for **1** showed a decrease from 850 to 720 ( $\mu$ A/cm<sup>2</sup>) and then an increase after 150 cycles to 1350 ( $\mu$ A/cm<sup>2</sup>) (Fig. S3c). After this increase, a low decrease was observed at 1200 ( $\mu$ A/cm<sup>2</sup>) after 250 cycles. **2** showed a decrease from 970 to 810  $(\mu A/cm^2)$  and then an increase after 80 cycles to 1260  $(\mu A/cm^2)$  (Fig. S3d). After this increase, a decrease was observed to be 1020 ( $\mu$ A/cm<sup>2</sup>) after 250 cycles. The continuous CV for **3** indicated an increase after 20 cycles to 2630 (μA/cm<sup>2</sup>) (Fig. S3e). After this increase, a decrease was observed at 2000 (μA/cm<sup>2</sup>) after 250 cycles. Finally, the continuous CV for 4 showed a decrease from 535 to 444 (µA/cm<sup>2</sup>) after 15 cycles and then an increase after 115 cycles to 515 ( $\mu$ A/cm<sup>2</sup>) (Fig. S3f). After this increase, a low decrease was observed at 500 ( $\mu$ A/cm<sup>2</sup>) after 250 cycles.



Fig. S4 CV diagrams for FTO (a), Cu salt (b), **1** (c), **2** (d), **3** (e) and **4** (f) in the buffer solution after the 250 cycles of continuous CV (black) and after floating in EDTA (saturated in 5.0 mL) for one hour (red). The conditions: in the phosphate buffer solution (0.25 M, pH = 11.0) at room temperature. The electrochemical studies were carried out with a conventional three-electrode setup, in which FTO, Ag/AgCl/KClsat and a platinum foil served as working, reference and auxiliary electrodes, respectively. The scan rates are 50.0 mV/s.



Fig. S5 <sup>1</sup>HNMR for **1** (0.5 mM in D<sub>2</sub>O) (a). The results show that the complex is stable at least for a few hours under water-oxidation condition (b). The amperometric condition: 1.6 V; in the phosphate buffer (0.25 M, pH = 11.0).





Fig. S7 SEM (a,b), EDX-Mapping (scale bare 1  $\mu$ m; C: blue; N: orange; O: yellow; P: green; K: pink; Cu: red; S: brown) (c) images, EDX spectrum (d) and the composition of the surface of FTO electrode (e) in the presence of **1** under the amperometric test conditions after 10 hours. Amperometric test conditions: 1.6 V; in the phosphate buffer (0.25 M, pH = 11.0). The concentrations of copper(II) compounds were 0.5 mM.



Fig. S8 SEM images for **3** under the amperometric condition after 10 hours. The amperometric condition: 1.6 V; in the mixture of phosphate buffer (0.25 M, pH = 11.0). The concentrations of copper(II) compounds were 0.5 mM.





Fig. S9 SEM (a,b), EDX-Mapping (scale bare 1  $\mu$ m; N: green; O: yellow; Cu: red) (c) images, EDX spectrum (d) and the composition of the surface of FTO electrode (e) in the presence of copper(II) salt under the amperometric test conditions after 10 hours. Amperometric test conditions: 1.6 V; in the phosphate buffer (0.25 M, pH = 11.0). The concentrations of copper(II) compounds were 0.5 mM.

Reference

R1. I. Roger and M. D. Symes, J. Am. Chem. Soc., 2015, **137**, 13980-13988.