

Electronic Supplementary Information

Electrocatalytic Water Oxidation by a Chair-like Tetranuclear Copper(II) Complex in a Neutral Aqueous Solution

Ting-Ting Li, Yue-Qing Zheng*

*Institute for Solid State Chemistry, Ningbo University, 818 Fenghua Road, Ningbo,
Zhejiang Province, 315211, PR China*

Corresponding author: Yue-Qing Zheng

Tel./fax: +86 574 87600792.

E-mail address: zhengyueqing@nbu.edu.cn

Synthesis of $[\text{Cu}_4(\text{bpy})_4(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2] \cdot (\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$:

0.17 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.0 mmol) was dissolved in 5.0 mL of H_2O , followed by addition of 2.0 mL 1.0 M of NaOH solution. The resulting solution was stirred vigorously and gave a fine blue suspension. After that, the precipitate was collected by centrifugation and washed with 10 mL ultrapure water three times, and then dried in vacuum drying chamber. The precipitate was dissolved to a 20 mL of CH_3OH solution containing 0.16 g 2,2'-bipyridine (1.00 mmol), to which an aqueous solution of sodium terephthalate (0.21 g, 1.26 mmol) in 20 mL of H_2O was added. The resulting solution was refluxed for 2 h and the residue was filtrated and the blue filtrate was maintained at room temperature and greenish blue crystals were grown in three days (43 % yield). HR-ESI-MS: m/z 574.04123 ($[\text{Cu}_4(\text{bpy})_4(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2]^{4+} + \text{C}_8\text{H}_4\text{O}_4^{2-}$, $z = 2$, calculated: 574.04091) and m/z 1312.09345 ($[\text{Cu}_4(\text{bpy})_4(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2]^{4+} + 2\text{C}_8\text{H}_4\text{O}_4^{2-} + \text{H}^+$, $z = 1$, calculated: 1312.09329). Anal. Calcd for $\text{C}_{56}\text{H}_{60}\text{Cu}_4\text{N}_8\text{O}_{20}$ (%): C, 47.35; H, 4.23; N, 7.89. Found: C, 47.28; H, 4.15; N, 7.83. FT-IR (KBr, cm^{-1}): 3385 (broad), 3109, 3057, 3034, 1653, 1601 (sharp), 1447 (sharp), 1354, 1254, 1161, 1030, 1018, 853 (sharp), 770 (sharp), 731 (sharp).

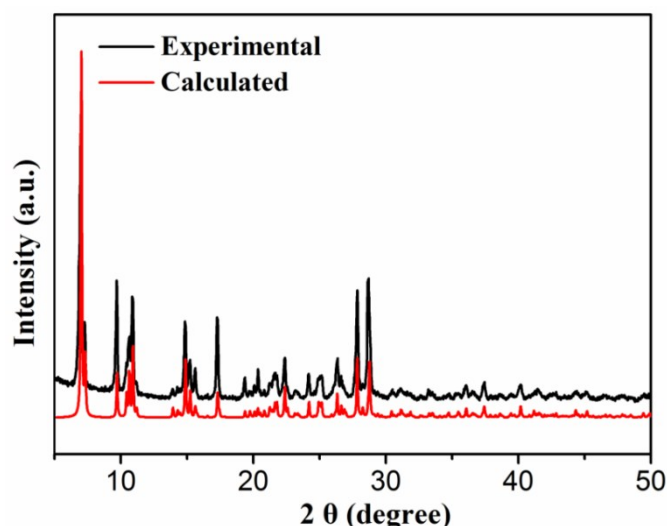


Fig. S1 The experimental PXRD pattern (black line) and simulated one (red line) based on the single crystal sample of complex 1.

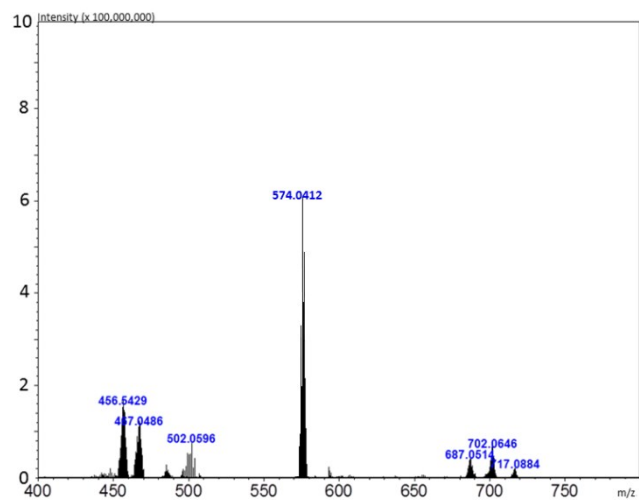


Fig .S2 MS spectrum of complex 1 in deionized water from $m/z = 400-800$.

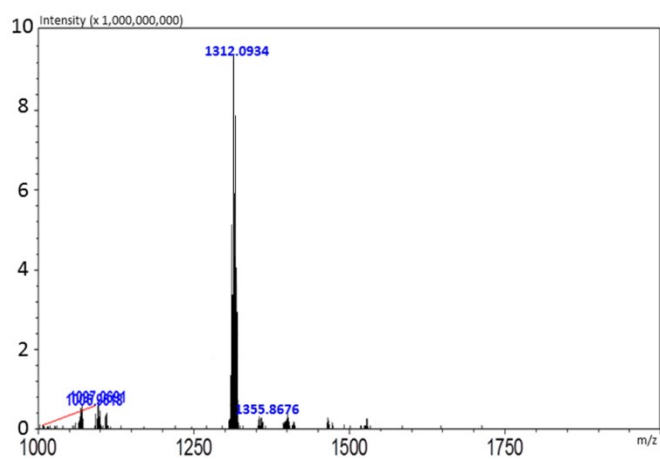


Fig .S3 MS spectrum of complex 1 in deionized water from $m/z = 1000-2000$.

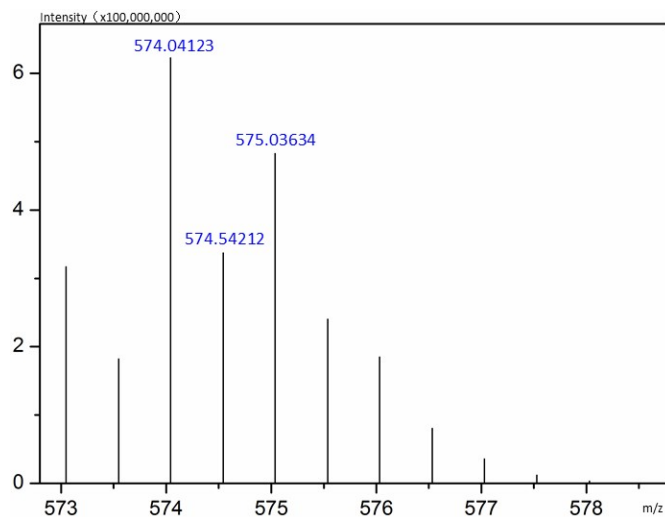


Fig .S4 Isotopic peaks of signals at 574.04123 ascribed to $\{[\text{Cu}_4(\text{bpy})_4(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2]^{4+} + \text{C}_8\text{H}_4\text{O}_4^{2-}\}^{2+}$.

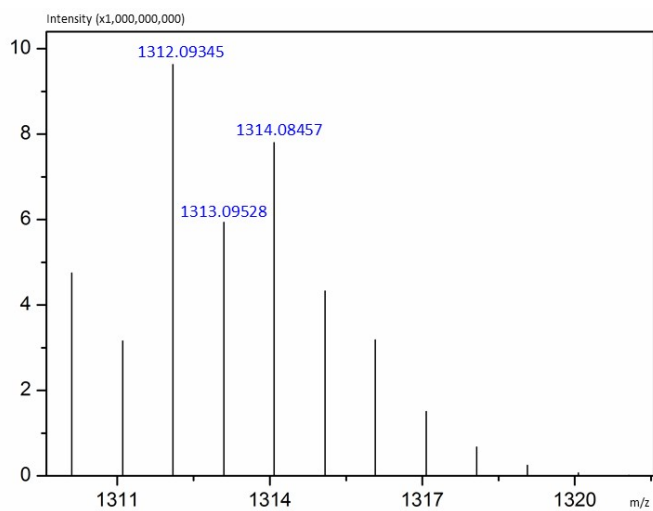


Fig. S5 Isotopic peaks of signals at 1312.09345 ascribed to $\{[\text{Cu}_4(\text{bpy})_4(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2]^{4+} + 2\text{C}_8\text{H}_4\text{O}_4^{2-} + \text{H}^+\}^+$.

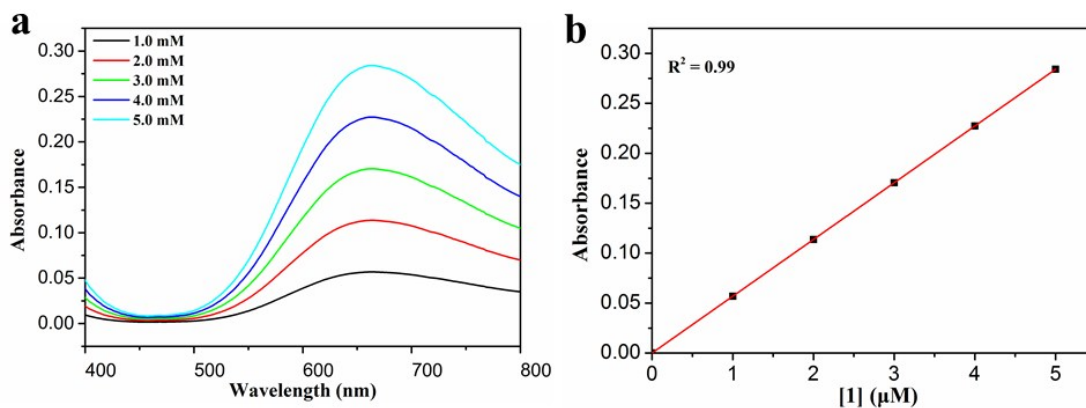


Fig. S6 (a) The UV/Vis spectra for different concentration of complex 1 in 0.1 M phosphate buffer at pH 7.0; (b) Plot of the absorbance at $\lambda_{\text{max}} = 655 \text{ nm}$ as a function of the complex concentration.

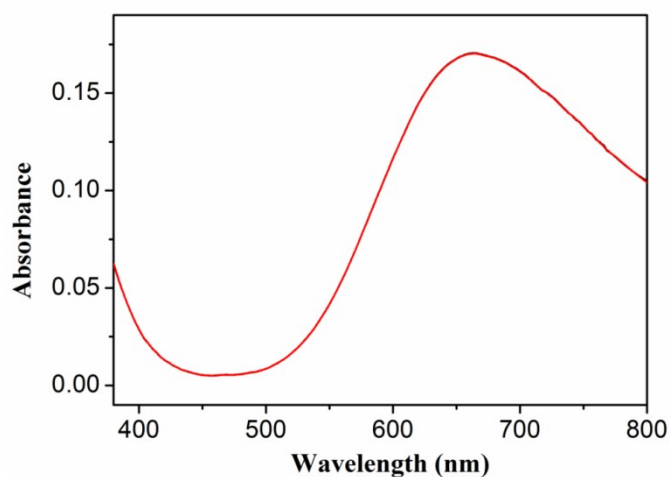


Fig. S7 The UV/vis spectra of complex 1 in 0.1 M phosphate buffer (pH 7.0) when recorded after 0 (black line) and 5 days (red line).

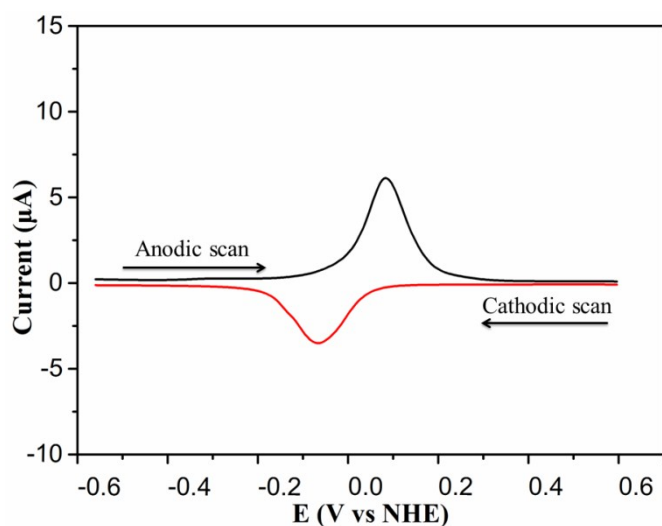


Fig. S8 DPV curves of complex 1 recorded in 0.1 M phosphate buffer (pH 7.0) in a range from -0.6 to 0.6 V (anodic scan, black line) and from 0.6 to -0.6 V (cathodic scan, red line) with a scan rate of 10 mV s^{-1} .

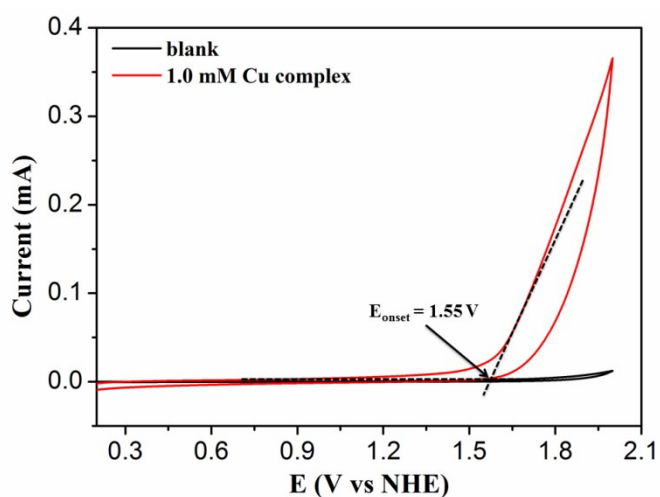


Fig. S9 The onset potential for electrocatalytic water oxidation in our system is defined by a tangent method.

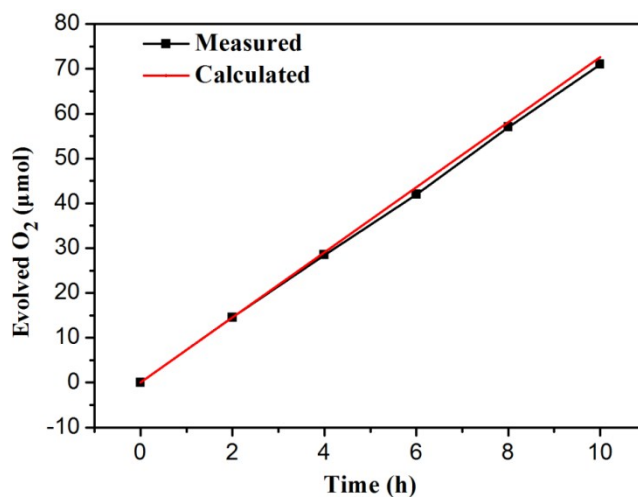


Fig. S10 O₂ evolution quantified by GC method (black line) and calculated amount of evolved O₂ according to the recorded passed charge during CPE (red line).

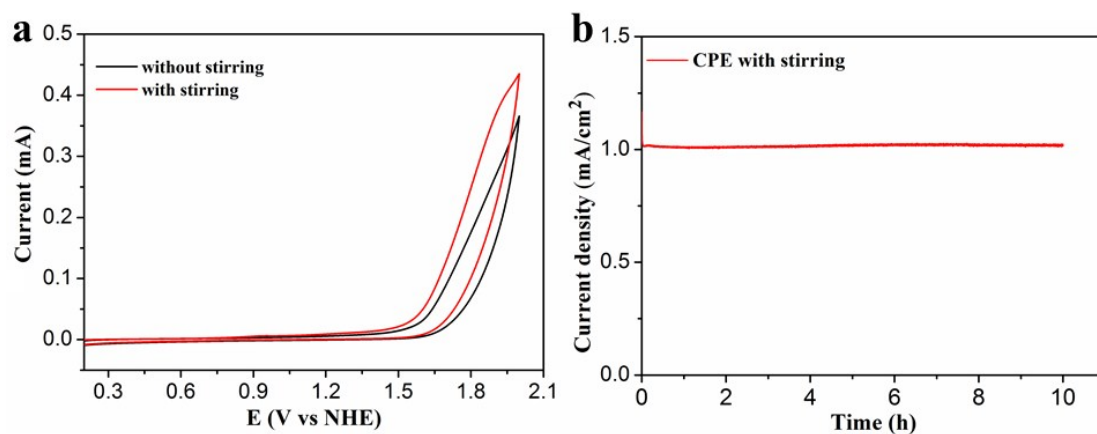


Fig. S11 (a) The CVs of complex 1 recorded in a deoxygenated phosphate buffer (0.1 M, pH 7.0) with (red line) and without stirring (black line); (b) CPE was carried out at 1.8 V vs NHE with stirring.

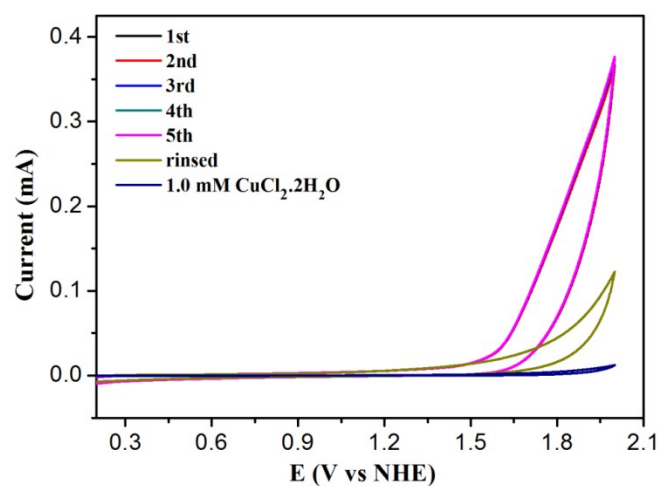


Fig. S12 Successive CV cycles with 1.0 mM complex 1 and 1.0 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at a GC electrode in 0.1 M pH 7.0 phosphate buffer.

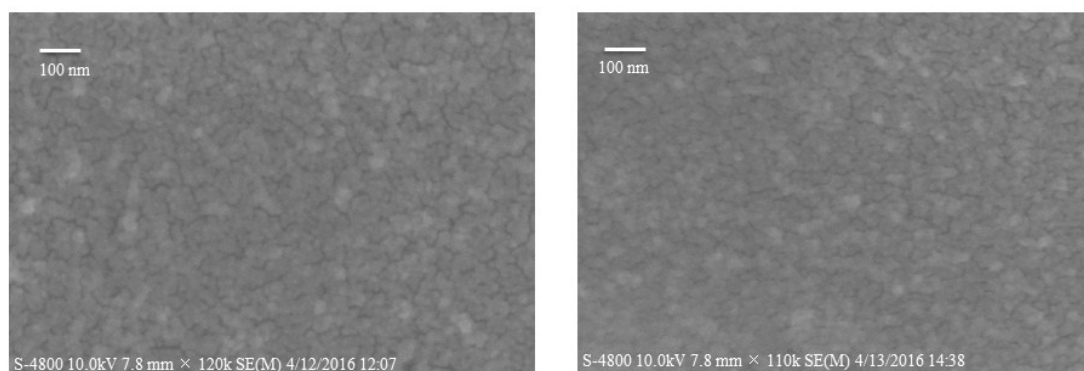


Fig. S13 SEM of blank ITO electrode (left) and the ITO surface after 10 h CPE with 1.0 mM complex 1 (right) in phosphate buffer, respectively.

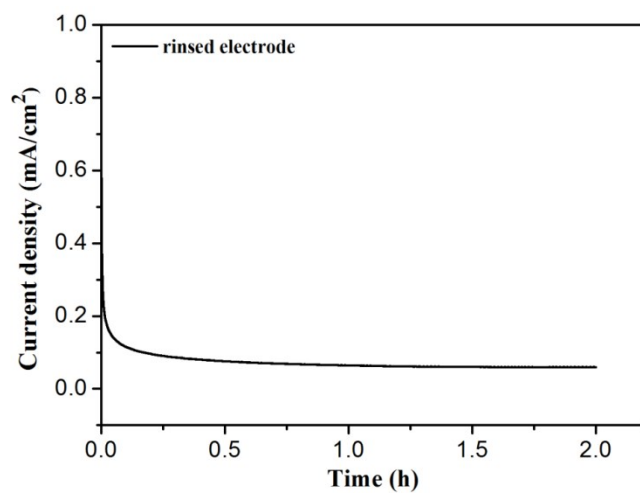


Fig. S14 The electrolysis performance of the rinsed ITO working electrode in a fresh, catalyst-free buffer.