

**Electrocatalytic water oxidation studies of a tetranuclear Cu(II) complex with
cubane-like core $\text{Cu}_4(\mu_3\text{-O})_4$**

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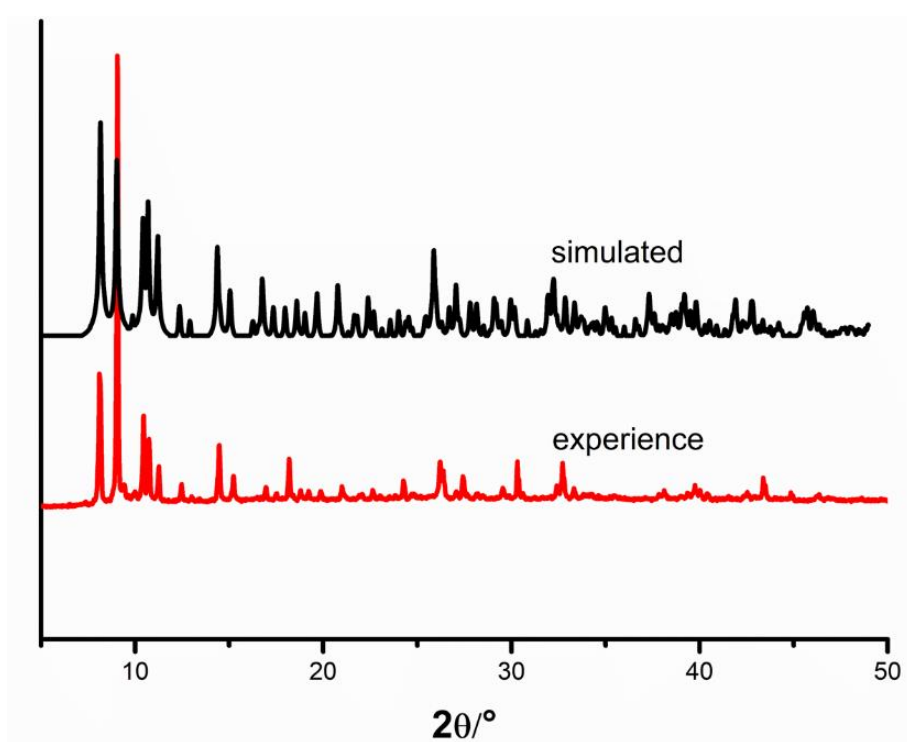


Fig. S1. Experimental (red) and theoretical (black) powder X-ray diffraction (PXRD) patterns of complex **1**.

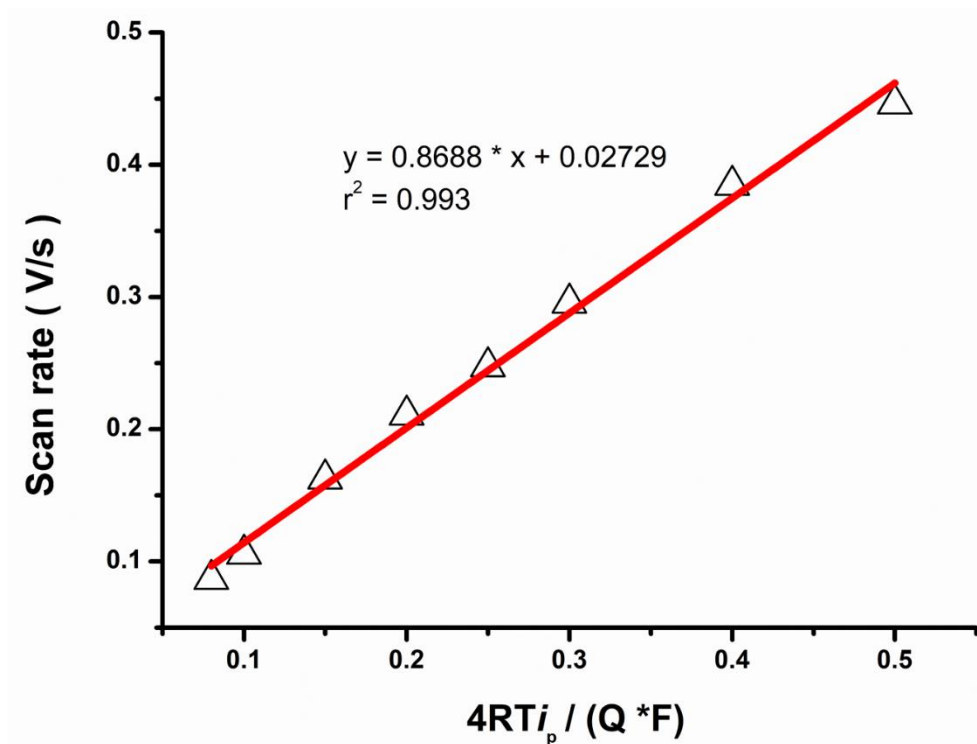


Fig. S2. The linear plot of scan rate versus $\frac{4RTi_p}{FQ}$ for irreversible peak at $E_p = 0.38$ V process for complex 1.

Laviron's Method for the calculation of the number of electrons involved in the anodic and cathodic irreversible processes:

$$i_p = \frac{nFQv}{4RT} \quad (\text{Equation 1})$$

$$v = \frac{1}{n} \times \frac{4RTi_p}{FQ} \quad (\text{Equation 2})$$

In the equation:

i_p = peak current

n = number of electrons transferred in the irreversible processes

F = Faraday constant

Q = quantity of electric charge

v = scan rate

R = ideal gas constant

T = temperature

It is found that v has linear relationship with $\frac{4RTi_p}{FQ}$. According to Equation 2, the slope (k) of the v vs $\frac{4RTi_p}{FQ}$ plot is represented as: $k = 1 / n$ (Equation 3), from which we can get n.

For complex **1**, the value of the slop $k = 0.8688$ for the irreversible peak at $E_p = 0.38$ V process can be obtained from figure S2. While, the k value for the peak at $E_p = -0.80$ V process can be got as 0.8206 from figure S3. Accordingly, the number of electrons involved in the anodic and cathodic irreversible peaks can both be calculated as approximately one.

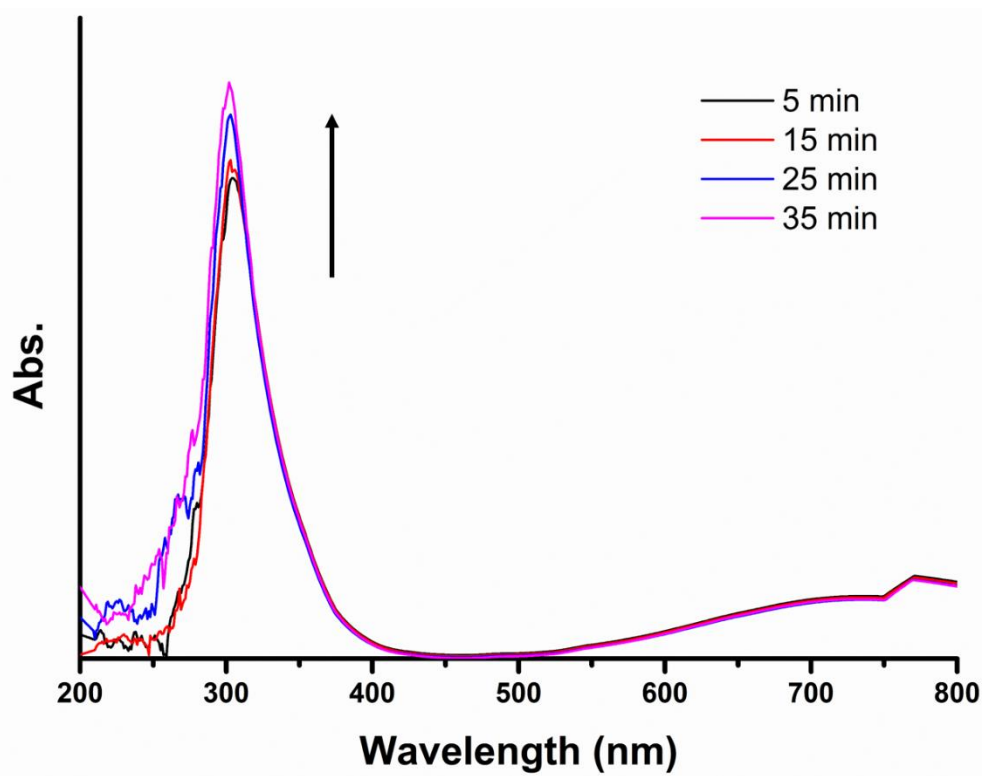


Fig. S3. The *in situ* UV-vis spectroelectrochemistry of complex **1** during the controlled potential electrolysis at 1.35 V

Table S1. Selected bond lengths (Å) and angles (°) for complex **1**.

Cu2—O1	1.9404(15)	Cu1—O1(A)	1.9845(15)
Cu2—O3(A ^a)	1.9806(14)	Cu1—O3	1.9253(14)
Cu2—O5	1.9717(15)	Cu1—O0AA	1.9627(15)
Cu2—O4	2.3113(16)	Cu1—O2	2.3117(16)
Cu2—N2	1.9835(18)	Cu1—N1	1.9655(18)
O3—Cu2(A)	1.9805(14)	O1—Cu1(A)	1.9845(15)
O1(A)—Cu1—O2	92.09(6)	O1—Cu2—O3(A)	78.22(6)
O3—Cu1—O1(A)	78.47(6)	O1—Cu2—O5	95.62(6)
O3—Cu1—O6	95.97(6)	O1—Cu2—O4	112.84(6)
O3—Cu1—O2	111.02(6)	O1—Cu2—N2	167.84(6)
O3—Cu1—N1	168.30(7)	O3(A)—Cu2—O4	92.94(6)
O0AA—Cu1—O1(A)	173.35(6)	O3(A)—Cu2—N2	94.60(6)
O0AA—Cu1—O2	93.33(6)	O5—Cu2—O3(A)	172.31(6)
O0AA—Cu1—N1	90.37(7)	O5—Cu2—O4	93.72(6)
N1—Cu1—O1(A)	94.50(6)	O5—Cu2—N2	90.66(7)
N1—Cu1—O2	78.30(7)	N2—Cu2—O4	77.02(6)

^aSymmetry transformations used to generate equivalent atoms: A: $-x + 1, y, -z + 3/2$.