Supplementary Information

Two multifunctional Cu(II) coordination complexes with mixed ligands as efficient catalysts for oxygen evolution reaction and photocatalytic degradation of methyl orange azo dyes

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The corresponding formula and calculation method

The Tafel plot can be calculated by the linear Tafel equation:

$$\eta = a \times \log(j) + b$$

where a is the Tafel slope, j and η are the catalytic current density and overpotential, respectively.

The electrochemically active surface area (ECSA) of the complexes has the following relationship to the electric double layer capacitance:

$$EASA = C_{dl}/C_s$$

The electrochemical double layer capacitance (C_{dl}) is calculated by measuring the relevant CV curves at different scan rates (10 to 50 mV/s) in a non-Faraday region. The value of C_{dl} is the slope of the plot of capacitive current as a function of scan rate. The C_s is the specific capacitance of an atomically smooth surface of the material.

The turnover frequency (TOF) value has been measured via equation:

$$TOF = j \times A/(4 \times F \times m/M)$$

where j is the current density (A cm^{-2}) at a given overpotential, A is the loading area of the electrode (cm^2), F is Faraday constant = 96485 (C mol^{-1}) , m is the mass per square centimeter of the catalyst, and M is the molecular weight of the catalyst, respectively.

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According to the Kubelka-Munk function (F), the band gap can be calculated by the following equations:

$$F = (1- R)^2 /2R$$

$$(Fhv)^n = B(hv - Eg)$$

where R is the reflectance of an infinitely thick layer at a given wavelength, h is the Plank's constant, v is the frequency of light, Eg is the optical bandgap energy of the material, and factor B depends on the transition probability assumed to be as constant within the optical frequency range, n = 2 or1/2 represent the direct and indirect transition, respectively.

The degradation efficiency of MO is defined as follows:

$$\text{Degradation efficiency} = (1-(C_t/C_0)) \times 100\%$$

Where C_0 and C_t are the concentrations of MO solution when photocatalytic reaction at time 0 min and t min, respectively.

The graphs associated with the text

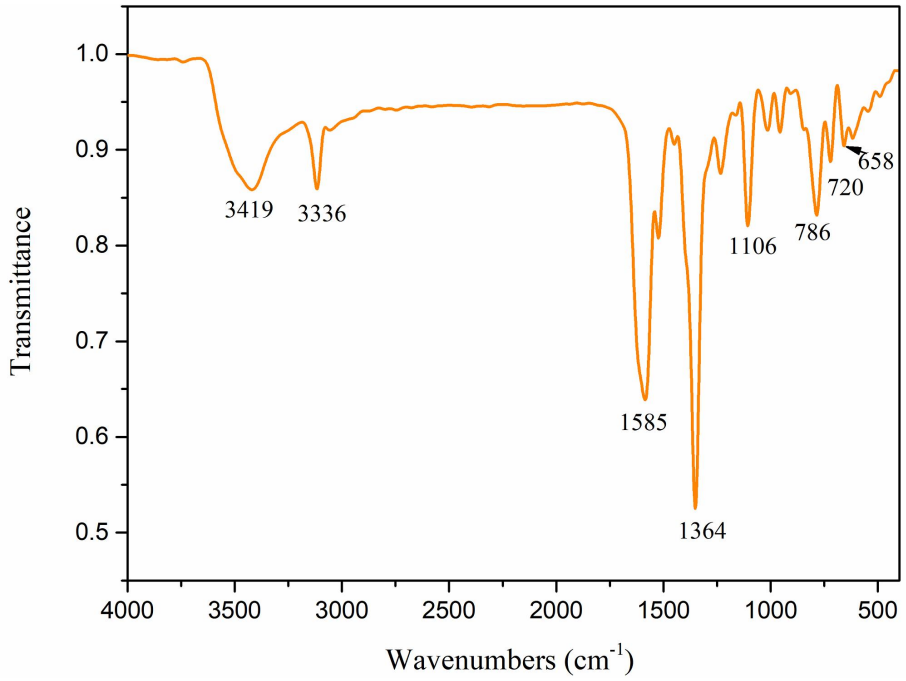

Fig. S1 The IR spectra for **1**.

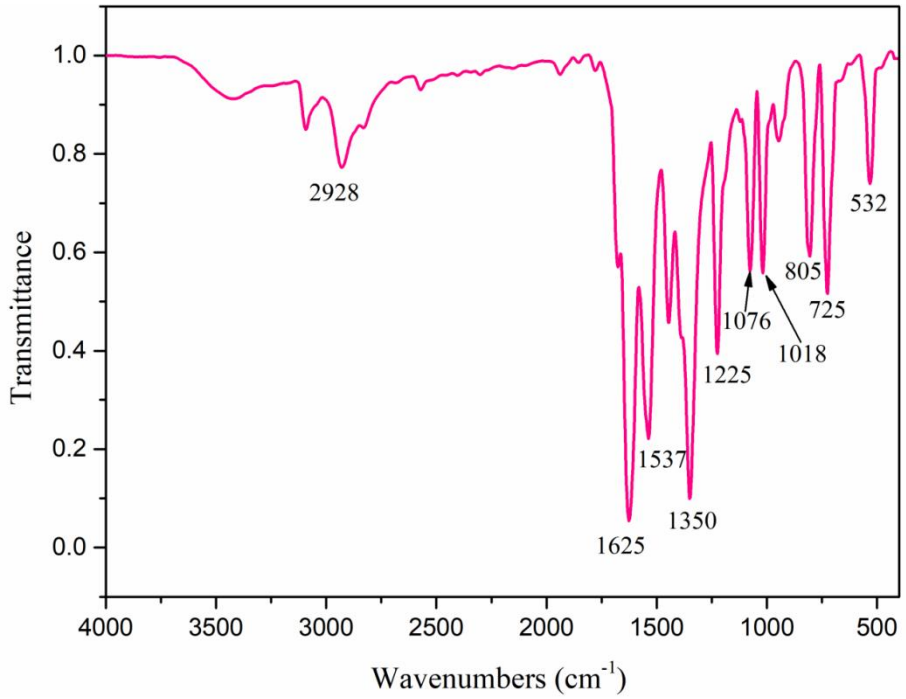

Fig. S2 The IR spectra for **2**.

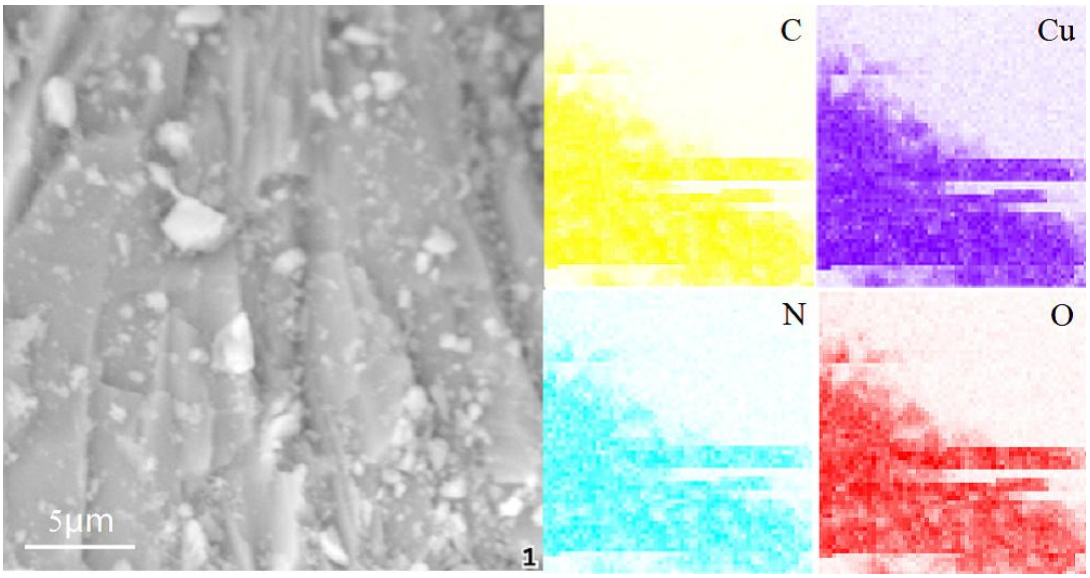

Fig. S3 EDS mapping images of **1**.

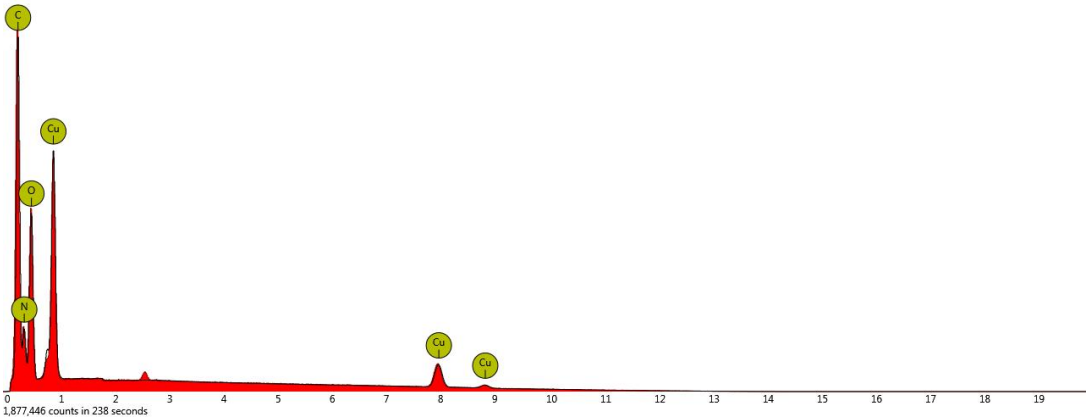

Fig. S4 EDX spectrum of **1**.

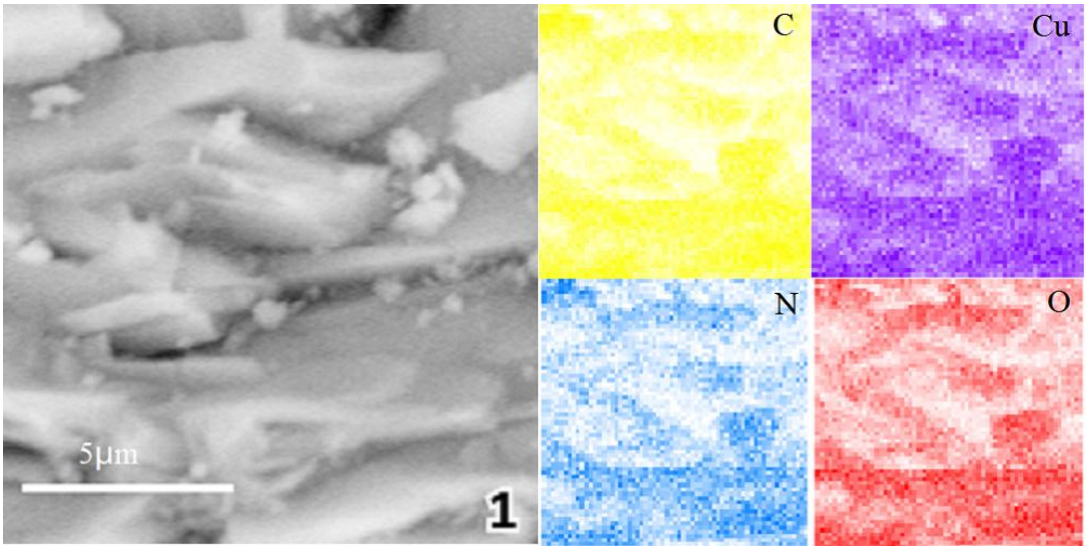

Fig. S5 EDS mapping images for **2**.

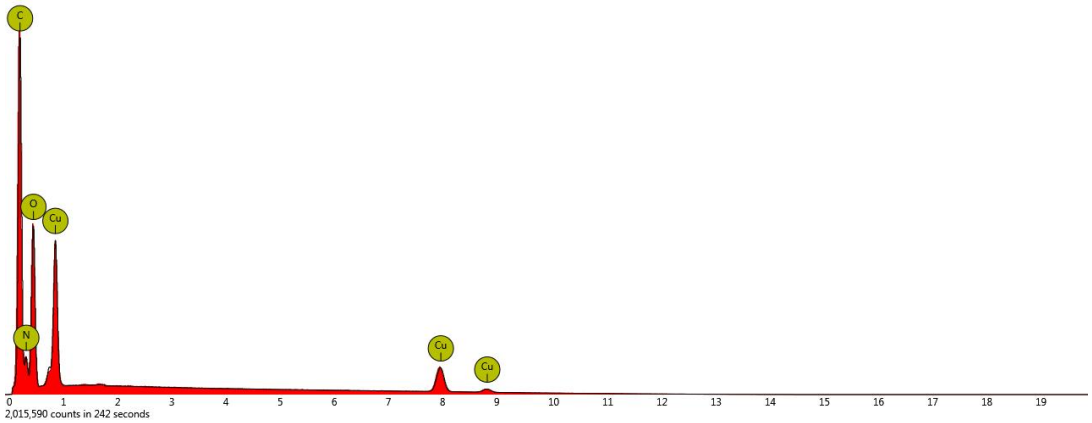

Fig. S6 EDX spectrum of **2**.

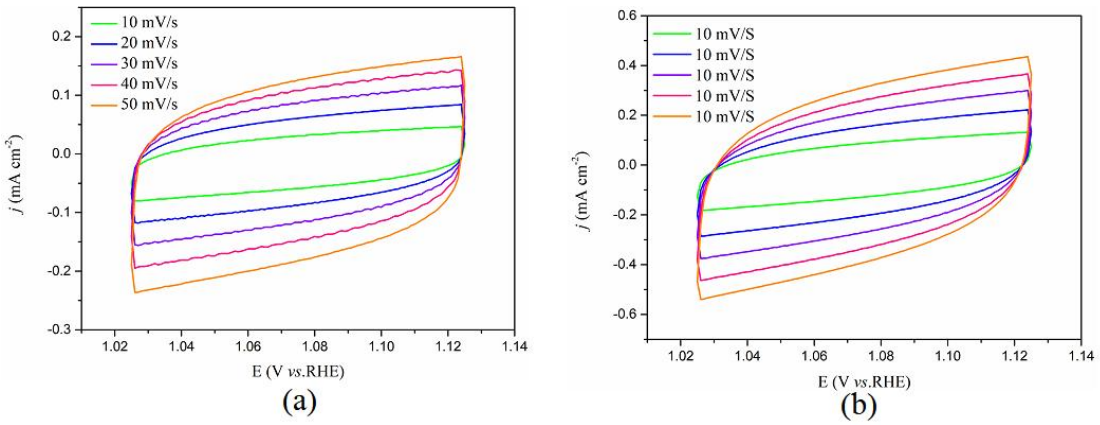

Fig. S7 Cyclic voltammetry (CV) curve in a non-Faraday region. (a) Corresponds to **1**. (b)

Corresponds to **2** .

The corresponding parameters of crystallographic data, selected bonds, angles and hydrogen bonds

Table S1 Crystallographic Data and Structural Refinements for **1-2**

Identification code	**1**	**2**
Empirical formula	$C_{20}H_{20}CuN_4O_7$	$C_{47}H_{53}Cu_2N_{11}O_{13}$
Formula weight	491.94	1107.08
Temperature/K	296.15	296.15
Wavelength	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P21/n	C2/c
Unit cell dimensions	a = 0.85793(10) nm, α = 90 º B = 1.00590(11) nm, β = 92.552(2) º C = 2.4193(3) nm, γ = 90 º	a = 2.68482(18) nm, α = 90 º b = 1.03399(7) nm, β = 125.809(10) º c = 2.2165(2) nm, γ = 90 º
Volume/nm^3	2.0857(4)	4.9900(7)
Z	4	4
Calculate density/g/cm^3	1.567	1.474
Absorption coefficient/mm^{-1}	1.099	0.928
F(000)	1012.0	2296.0
Crystal size/mm^3	0.11 × 0.1 × 0.08	0.16 × 0.15 × 0.12
Theta range for data collection	3.37 º to 50.028 º	3.37 º to 50.028 º
Index range	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -21 ≤ l ≤ 28	-29 ≤ h ≤ 31, -12 ≤ k ≤ 12, -26 ≤ l ≤ 26
Reflections collected	10336	12419
Independent reflection	3667 [R(int)= 0.0269, R(sigma) = 0.0327]	4395 [R(int) = 0.0336, R(sigma) = 0.0404]
Completeness to theta	99.7% (25.014 º)	99.8% (25.009 º)
Max. and min. transmission	0.631 and 0.741	0.682 and 0.746
Goodness-of-fit on F^2	1.077	1.058
Final R indices[I>2σ(I)]	R_1= 0.0434, wR_2= 0.1191	R_1 = 0.0480, wR_2 = 0.1269
R indexes (all data)	R_1= 0.0576, wR_2= 0.1334	R_1 = 0.0704, wR_2 = 0.1467
Largest diff. peak and hole/$e \cdot nm^{-3}$	330 and -710	1010 and -400
CCDC number	2166017	2166018

Table S2 Selected Bond lengths (nm) and Angles (°) for **1-2**

Parameter	Value	Parameter	Value
Cu(1)−O(1)	0.1967(3)	Cu(1)−O(1W)	0.2295(3)
Cu(1)−O(4)#1	0.2013(2)	Cu(1)−N(1)#2	0.1991(3)
Cu(1)−N(4)	0.1985(3)	O(4)−Cu(1)#3	0.2013(2)
N(1)−Cu(1)#4	0.1991(3)		
O(1)−Cu(1)−O1W	98.55(12)	O(1)−Cu(1)−O(4)#1	159.42(11)
O(1)−Cu(1)−N(1)#2	90.61(13)	O(1)−Cu(1)−N(4)	89.08(13)
O(4)#1−Cu(1)−O1(W)	101.95(11)	N(1)#2−Cu(1)−O1(W)	94.94(12)
N(1)#12−Cu(1)−O(4)#1	89.42(12)	N(4)−Cu(1)−O(1W)	90.77(12)
N(4)−Cu(1)−O(4)#1	88.86(11)	N(4)−Cu(1)−N(1)#2	174.26(13)
Cu(1)−O(2)	0.1982(3)	Cu(1)−O(3)#1	0.2040(2)
Cu(1)−O(1)#2	0.2335(3)	Cu(1)−N(1)	0.2004(3)
Cu(1)−N(3)	0.1990(3)	O3−Cu(1)#3	0.2040(2)
O1−Cu(1)#2	0.2335(3)		
O(2)−Cu(1)−O(3)#1	162.64(11)	O(2)−Cu(1)−O(1)#2	109.56(11)
O(2)−Cu(1)−N(1)	88.43(12)	O(2)−Cu(1)−N(3)	89.28(12)
O(3)#1−Cu(1)−O(1)#2	87.68(10)	N(1)−Cu(1)−O(3)#1	89.67(12)
N(1)−Cu(1)−O(1)#2	89.71(12)	N(3)−Cu(1)−O(3)#1	91.44(12)
N(3)−Cu(1)−O(1)#2	94.44(12)	N(3)−Cu(1)−N(1)	175.74(13)

1 Symmetry code: #1 = +x, 1+y, +z; #2 = 3/2-x, -1/2+y, 3/2-z; #3 = +x, -1+y, +z; #4 = 3/2-x, 1/2+y, 3/2-z. **2** Symmetry code: #1 = +x, -1+y, +z; #2 = 3/2-x, 1/2-y, 1-z; #3= +x, 1+y, +z.

Table S3 Hydrogen-bonding Geometry of **1** (nm and °)

D-H···A	D-H	H···A	[D···A]	∠D-H···A
C1-H1···O2W#1	0.0929(5)	0.2589(5)	0.3300(7)	133.7(3)
C3-H3···O2#2	0.0930(5)	0.2637(3)	0.3515(6)	157.6(3)
C11-H11A···O2W#2	0.0972(7)	0.2394(6)	0.3233(9)	144.3(4)
C11-H11B···O5#2	0.0930(5)	0.2634(3)	0.3487(6)	152.8(3)
C13-H13···O5#3	0.0970(6)	0.2548(3)	0.3295(6)	133.9(4)
C17-H17···O2W#4	0.0930(4)	0.2863(7)	0.3642(8)	142.1(3)
C18-H18···O2W	0.0931(4)	0.2447(7)	0.3254(8)	154.0(3)
O2W-H2WA···O5	0.1026(7)	0.1864(2)	0.2882(7)	170.8(4)
O2W-H2WB···O5#5	0.1002(5)	0.1956(3)	0.2843(6)	146.1(4)
O1W-H1WB···O2#6	0.847(3)	0.2055(4)	0.2832(4)	152.5(2)
O1W-H1WA···O2	0.844(3)	0.2390(3)	0.2952(4)	124.6(2)

Symmetry code: #1 = -1/2+x, 1/2-y, 1/2+z; #2 = -1+x, 1+y, +z; #3 = 1-x, -y, 1-z; #4 = 2-x, -y, 1-z; #5 = 2-x, -1-y, 1-z; #6 = 3/2-x, 1/2+y, 3/2-z.

Table S4 Hydrogen-bonding Geometry of complex **2** (nm and °)

D-H···A	D-H	H···A	[D···A]	∠D-H···A
C14-H14A···O6#1	0.0960(5)	0.2392(5)	0.3188(7)	140.1(3)
C6-H6C···O6#2	0.0961(5)	0.2817(5)	0.3726(8)	157.8(4)
C4-H4···O5#3	0.0930(6)	0.2782(4)	0.3487(6)	133.3(3)
C12-H12···O4	0.0932(7)	0.2483(5)	0.3191(9)	132.8(3)
C8-H8···O1	0.0930(4)	0.2794(3)	0.3395(5)	123.3(3)

Symmetry code: #1 = 1-x, +y, 1/2-z; #2 = 1/2+x, 1/2-y, 1/2+z; #3 = 1-x, 1-y, 1-z.

Table S5 Comparison of the OER activities of copper complexes electrocatalysts

Catalyst	Overpotential (mV)	Electrolyte	Ref.
[L-Cu^{II}-DMF]	650	0.10 M Carbonate buffer(pH = 10)	1
CuxS-2	530	0.1 M KOH	2
CuxS-3	430	0.1 M KOH	2
$[Cu(N_2Py_3)](BF_4)_2$	831	0.10 M Phosphate buffer(pH = 11)	3
Cu_2L	630	0.1 M TBAP	4
Cu-CNTCPP	430	1 M KOH	5
1	500	1 M KOH	This work
2	360	1 M KOH	This work

Table S6 Comparison of photocatalytic degradation of dyes by copper complexes

Catalyst	Type of dye	Initial concentration of dye	light source	Degradation efficiency (%)	Time (min)	Rate constant (min^{-1})	Eg(eV)	Ref.
CP1	MB	16 mg/L	visible light	93.7	30	0.05642	1.68	6
CP1	RhB	23.95mg/L	visible light	95.8	30	0.07684	1.68	6
CuOF	MO	0.1M	UV light	100	270	-	-	7
[Cu(NPT)$_2$(NO$_2$-BDC)]$_n$	RhB	10 mg/L	UV light	95.72	160	-	-	8
[Cu(NPT)$_2$(NO$_2$-BDC)]$_n$	MB	10 mg/L	UV light	95.49	160	-	-	8
[Cu(NPT)$_2$(NO$_2$-BDC)]$_n$	MO	10 mg/L	UV light	31.93	160	-	-	8
[Cu(BMIOPE)(Br-BDC)]$_n$	MO	10 mg/L	UV light	91	70	-	3.45	9
[Cu(BMIOPE)(Br-BDC)]$_n$	MB	10 mg/L	UV light	91	70	-	3.45	9
Cu(pc)$_2$•2H$_2$O	RhB	20 mg/L	UV light	97	8	-	-	10
Cu(pc)$_2$•2H$_2$O	MO	20 mg/L	UV light	97	8	-	-	10
Cu(pc)$_2$•2H$_2$O	RhB	20 mg/L	visible light	95	90	-	-	10
Cu(pc)$_2$•2H$_2$O	MO	20 mg/L	visible light	90	55	-	-	10
1	MO	40 mg/L	visible light	96.2	150	0.02133	2.17	This work
2	MO	40 mg/L	visible light	90.8	150	0.01644	2.46	This work

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