

## **Homogeneous electrochemical water oxidation catalyzed by cobalt complexes with amine-pyridine ligand**

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**Table S1** Crystallographic data and processing parameters of complex **1**

Complex parameters	Complex <b>1</b>
Empirical formula	C <sub>21</sub> H <sub>25</sub> N <sub>5</sub> Cl <sub>2</sub> O <sub>8</sub> Co
Formula weight	605.29
Temperature / K	280.0
Wavelength / Å	0.71073
Crystal system	Monoclinic
Space group	Cc
<i>a</i> / Å	13.9770(12)
<i>b</i> / Å	10.8038(10)
<i>c</i> / Å	16.1388(16)
$\alpha$ / deg	90
$\beta$ / deg	93.597(3)
$\gamma$ / deg	90
Volume / Å <sup>3</sup>	2529.94(40)
<i>Z</i>	4
Calculated density / Mg m <sup>3</sup>	1.58905
Absorption coefficient / mm <sup>-1</sup>	0.946
<i>F</i> (000)	1244
Crystal size / mm <sup>3</sup>	0.320 × 0.260 × 0.310
$\theta$ range / deg	2.60 to 25.01
	-18 ≤ <i>h</i> ≤ 18
Index ranges	-14 ≤ <i>h</i> ≤ 14
	-20 ≤ <i>h</i> ≤ 20
Reflections collected	27821
Independent reflections	5777 [ <i>R</i> (int) = 0.0607]
Completeness to theta	99.5% (25.01°)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	5777 / 2 / 336
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.028
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0669, <i>wR</i> <sub>2</sub> = 0.0951
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0406, <i>wR</i> <sub>2</sub> = 0.1072
Largest diff. peak and hole	0.354 and -0.384 e.Å <sup>-3</sup>

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|, wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o2)]^{1/2}$$

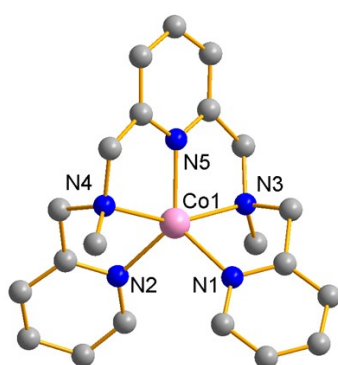
**Table S2** Crystallographic data and processing parameters of complex **2** and  $[\text{Zn}(\text{N3Py2})(\text{OH}_2)](\text{ClO}_4)_2$ 

Complex parameters	Complex <b>2</b>	$[\text{Zn}(\text{N3Py2})(\text{OH}_2)](\text{ClO}_4)_2$
Empirical formula	$\text{C}_{19}\text{H}_{31}\text{N}_5\text{Cl}_2\text{O}_9\text{Co}$	$\text{C}_{19}\text{H}_{31}\text{N}_5\text{Cl}_2\text{O}_9\text{Zn}$
Formula weight	603.32	609.76
Temperature / K	273.2	273.0
Wavelength / Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
$a$ / Å	9.0629 (18)	9.0470(13)
$b$ / Å	33.221 (8)	33.224(4)
$c$ / Å	8.842 (2)	8.7975(14)
$\alpha$ / deg	90	90
$\beta$ / deg	104.732 (9)	104.960(5)
$\gamma$ / deg	90	90
Volume / Å <sup>3</sup>	2574.6 (11)	2554.7(6)
$Z$	4	4
Calculated density / Mg m <sup>3</sup>	1.557	1.585
Absorption coefficient / mm <sup>-1</sup>	0.931	1.228
$F(000)$	1252	1264
Crystal size / mm <sup>3</sup>	$0.220 \times 0.210 \times 0.170$	$0.270 \times 0.290 \times 0.260$
$\theta$ range / deg	2.60 to 25.01	2.33 to 26.38
	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$
Index ranges	$-43 \leq h \leq 43$	$-41 \leq h \leq 41$
	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$
Reflections collected	29858	61767
Independent reflections	5876 [ $R(\text{int}) = 0.0638$ ]	5215 [ $R(\text{int}) = 0.0607$ ]
Completeness to theta	99.5% (25.01°)	99.7% (25.01°)
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	5876 / 0 / 329	5215 / 0 / 329
Goodness-of-fit on $F^2$	1.028	1.036
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0949$ , $wR_2 = 0.1778$	$R_1 = 0.0827$ , $wR_2 = 0.1574$
R indices (all data)	$R_1 = 0.0638$ , $wR_2 = 0.2034$	$R_1 = 0.0586$ , $wR_2 = 0.1777$
Largest diff. peak and hole	1.347 and -0.640 e.Å <sup>-3</sup>	1.628 and -0.771 e.Å <sup>-3</sup>

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left[ \frac{\sum (|F_o|^2 - |F_c|^2)^2}{\sum (F_o^2)} \right]^{1/2}$$

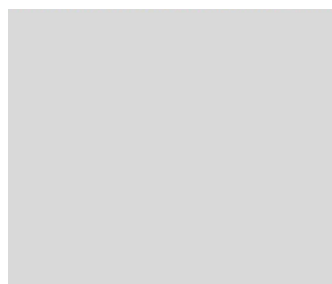
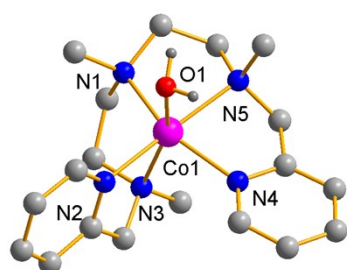
**Table S3** Selected bond lengths (Å) and angles (deg) of **1**

Complex	<b>1</b>
Bond length (Å)	
Co1–N1	2.046(10)
Co1–N2	2.051(9)
Co1–N3	2.174(8)
Co1–N4	2.184(8)
Co1–N5	2.024(3)
Bond angles (deg)	
N1–Co1–N2	101.60(13)
N1–Co1–N3	79.34(34)
N1–Co1–N4	115.95(34)
N1–Co1–N5	128.73(28)
N2–Co1–N3	115.44(34)
N2–Co1–N4	80.20(34)
N2–Co1–N5	129.64(25)
N3–Co1–N4	156.63(32)
N3–Co1–N5	77.31(32)
N4–Co1–N5	79.32(32)

**Fig. S1** The atom label of cations of complex **1**.

**Table S4** Selected bond lengths (Å) and angles (deg) of **2** and [Zn(N3Py2)(OH<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub>

Complex	<b>2</b>	Complex	[Zn(N3Py2)(OH <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>
Bond length (Å)		Bond length (Å)	
Co1–N1	2.157(3)	Zn1–N1	2.188(4)
Co1–N2	2.165(4)	Zn1–N2	2.132(4)
Co1–N3	2.245(5)	Zn1–N3	2.256(4)
Co1–N4	2.142(3)	Zn1–N4	2.262(3)
Co1–N5	2.233(4)	Zn1–N5	2.155(4)
Co1–O1	2.146(3)	Zn1–O1	2.175(3)
Bond angles (deg)		Bond angles (deg)	
N1–Co1–N2	103.90(14)	N1–Zn1–N2	99.39(14)
N1–Co1–N3	81.71(15)	N1–Zn1–N3	76.03(14)
N1–Co1–N4	153.98(15)	N1–Zn1–N4	127.44(13)
N1–Co1–N5	80.92(14)	N1–Zn1–N5	104.10(15)
N1–Co1–O1	96.34(15)	N1–Zn1–O1	84.13(13)
N2–Co1–N3	75.86(13)	N2–Zn1–N3	94.40(16)
N2–Co1–N4	99.38(13)	N2–Zn1–N4	76.64(14)
N2–Co1–N5	173.43(14)	N2–Zn1–N5	154.61(15)
N2–Co1–O1	85.44(13)	N2–Zn1–O1	95.96(14)
N3–Co1–N4	92.99(14)	N3–Zn1–N4	110.48(14)
N3–Co1–N5	109.54(13)	N3–Zn1–N5	82.19(16)
N3–Co1–O1	160.04(13)	N3–Zn1–O1	158.87(14)
N4–Co1–N5	76.91(13)	N4–Zn1–N5	81.02(14)
N4–Co1–O1	96.94(13)	N4–Zn1–O1	89.84(13)
N5–Co1–O1	89.61(13)	N5–Zn1–O1	95.88(16)

**Fig. S2** The atom label of cations of complex **2** (left) and [Zn(N3Py2)(OH<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub> (right).

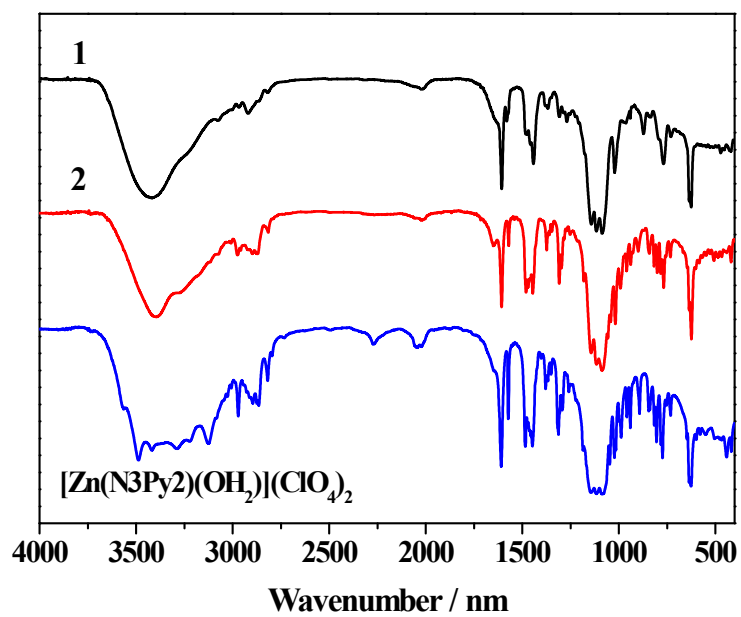


Fig. S3 Infrared spectra of complex 1, 2, and  $[\text{Zn}(\text{N3Py2})(\text{OH}_2)](\text{ClO}_4)_2$ .

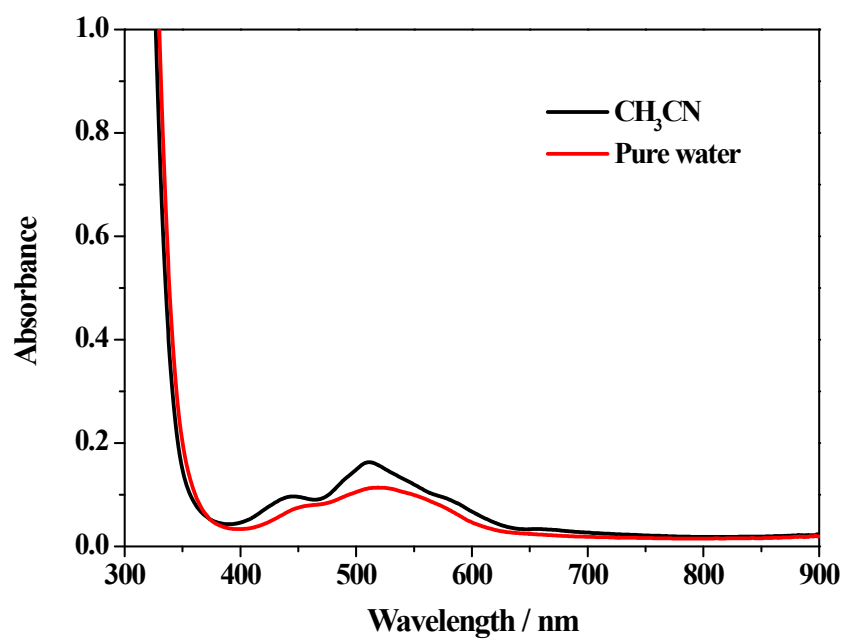
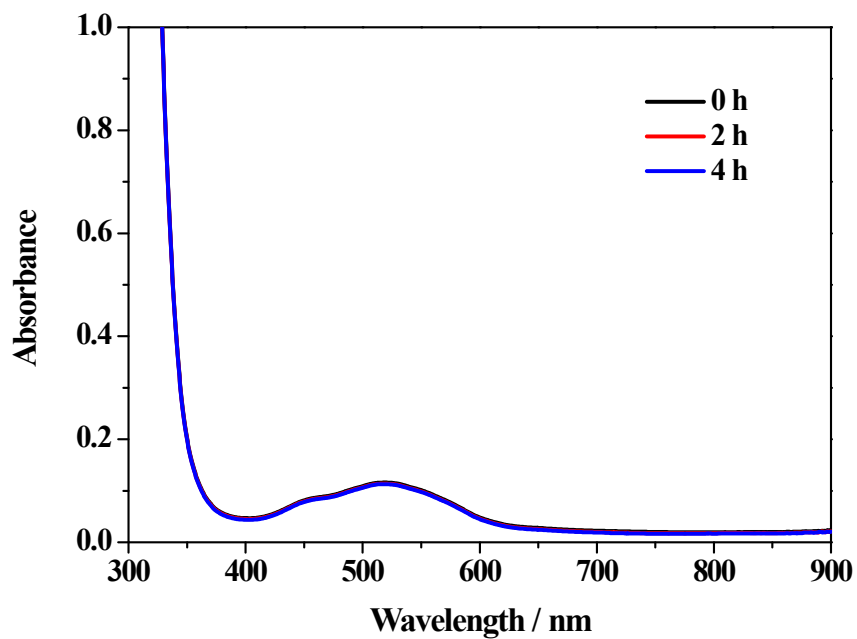
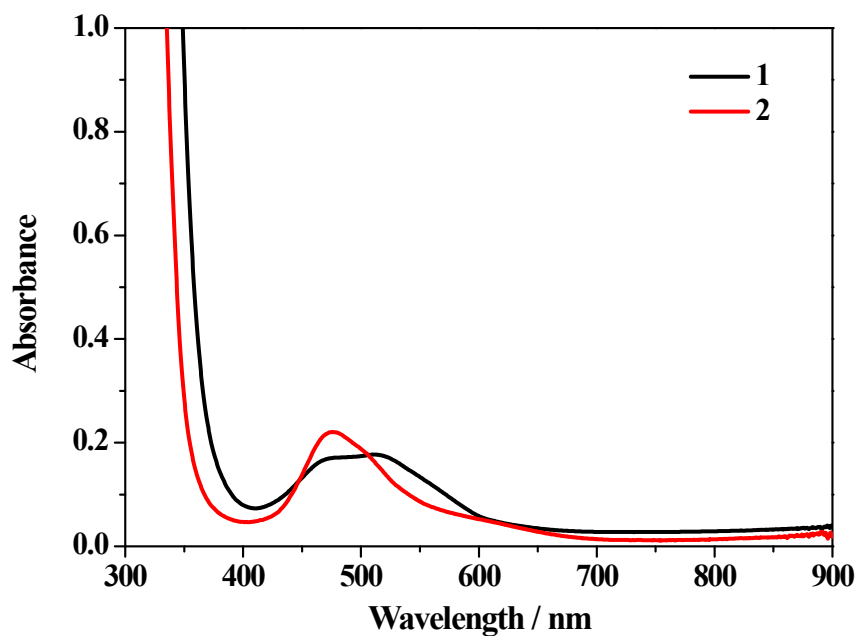


Fig. S4 UV-vis absorption spectra of 5 mM of complex 1 in  $\text{CH}_3\text{CN}$  and pure water.



**Fig. S5** UV-vis absorption spectra of 5 mM of complex 1 with different aging time in PBS at pH 3.0.



**Fig. S6** UV-visible absorption spectra of complex 1 and 2 in 0.1 M phosphate buffer solution (PBS) at pH 11.0.

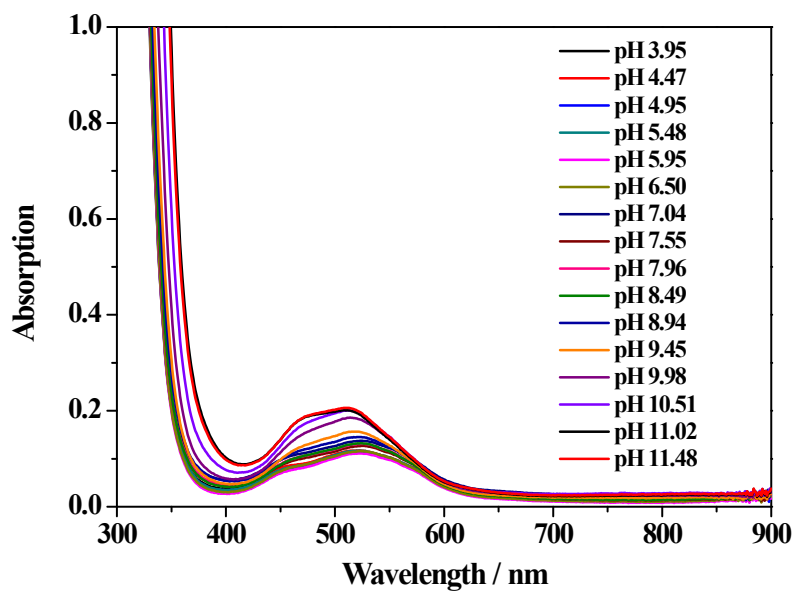


Fig. S7 pH dependent UV-vis spectra of 5 mM of complex 1 in 0.1 M PBS.

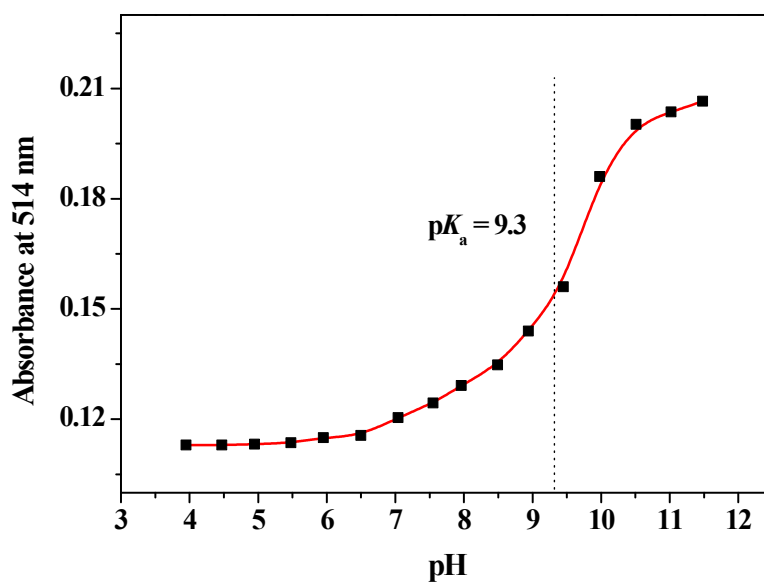


Fig. S8 Representative plot of the absorbance at 514 nm of complex 1 vs. pH value of 0.1 M PBS.

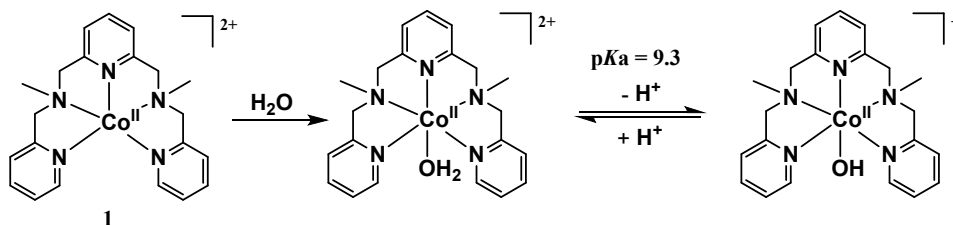


Fig. S9 Protonation-deprotonation equilibrium of complex 1 in 0.1 M PBS.



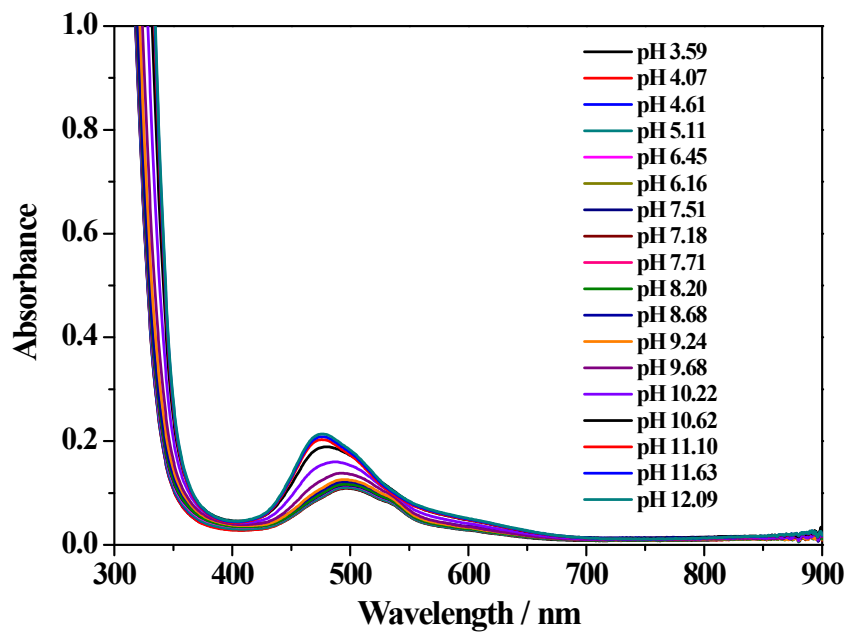


Fig. S10 pH dependent UV-vis spectra of 5 mM of complex **2** in 0.1 M PBS.

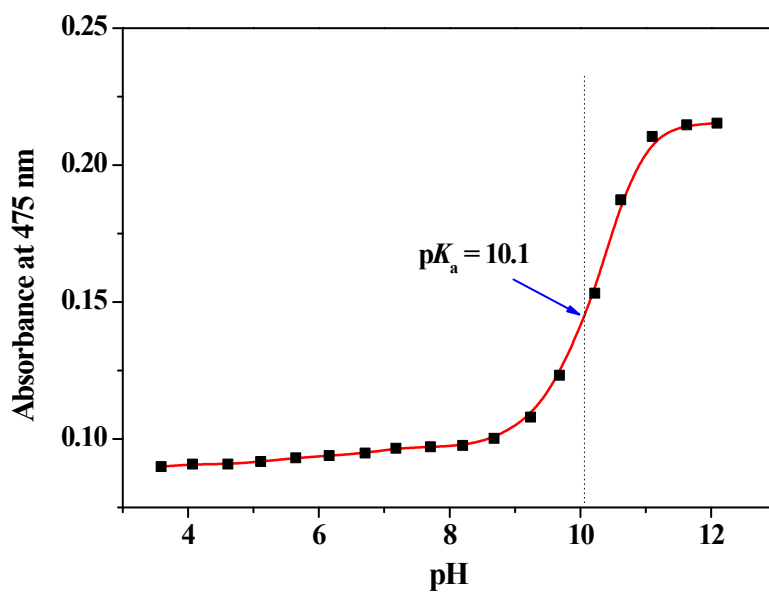


Fig. S11 Representative plot of the absorbance at 475 nm of complex **2** vs. pH value of 0.1 M PBS.

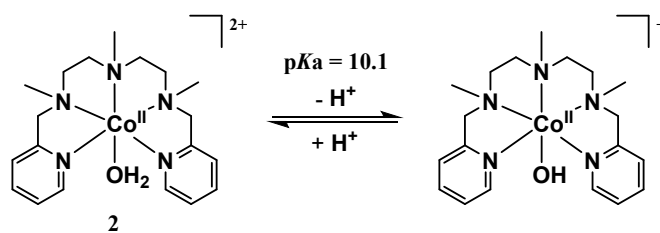
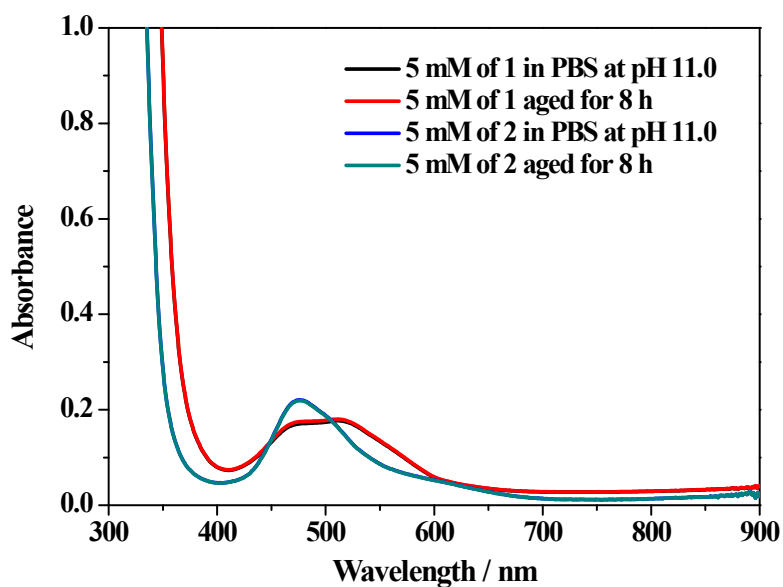
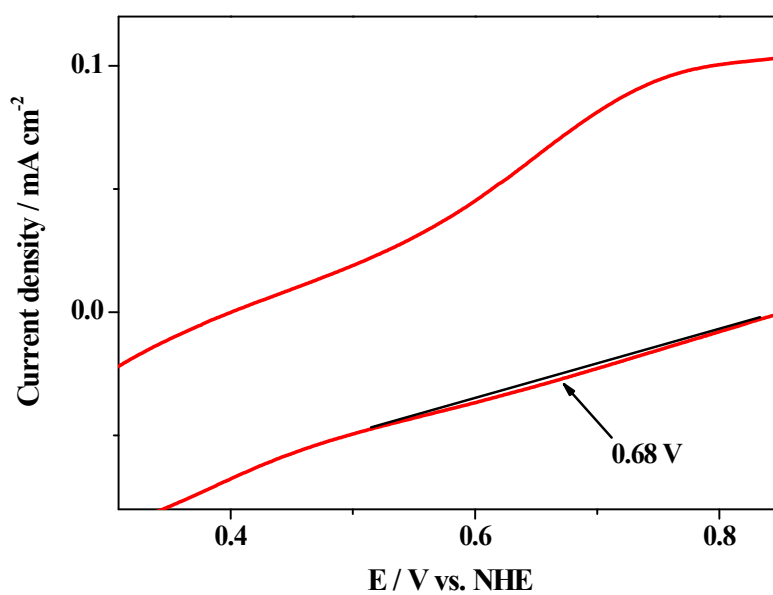


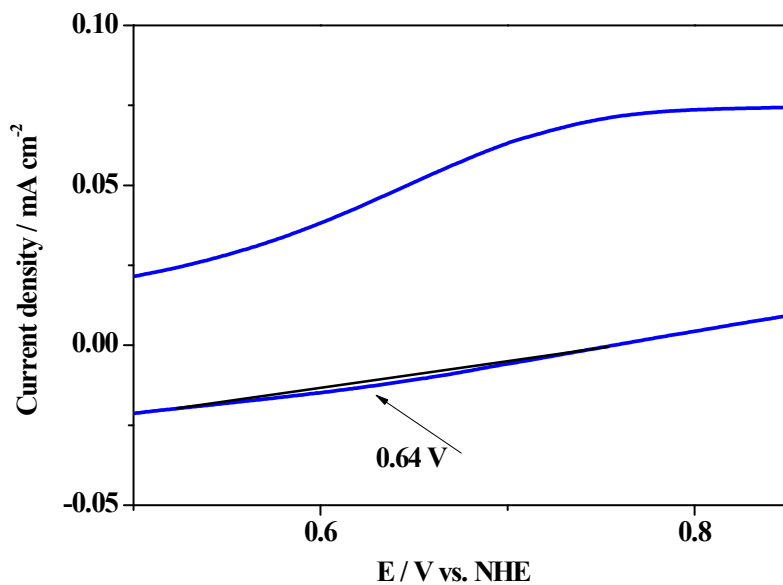
Fig. S12 Protonation–deprotonation equilibrium of complex **2** in 0.1 M PBS.



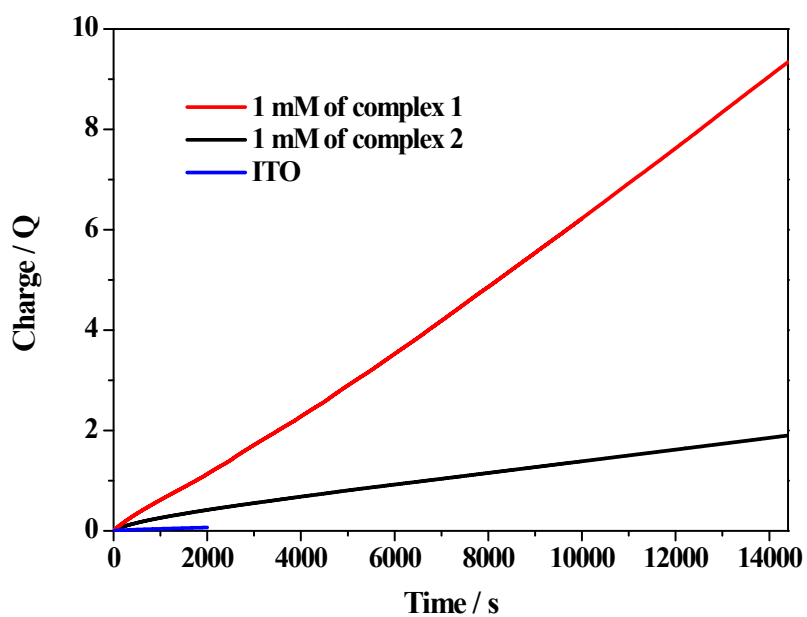
**Fig. S13** UV-vis absorption spectra of 5 mM of complex **1** and **2** in 0.1 M PBS at pH 11.0 before and after 8 hours aging time.



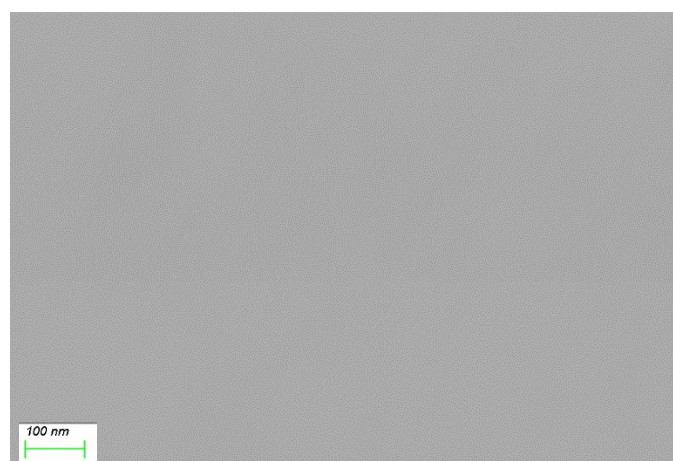
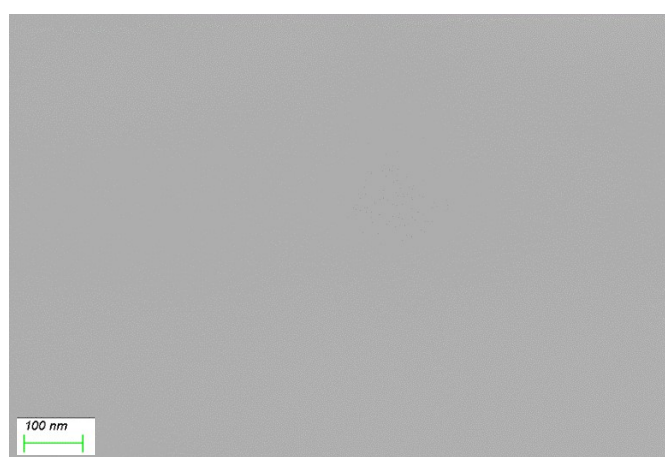
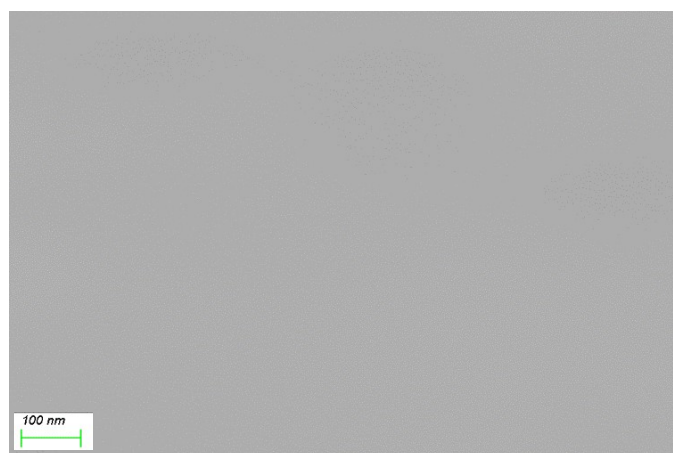
**Fig. S14** CV curves of 1 mM of complexes **1** in 0.1 M PBS at pH 11.0, GC electrode as working electrode, scan rate = 100 mV/s.



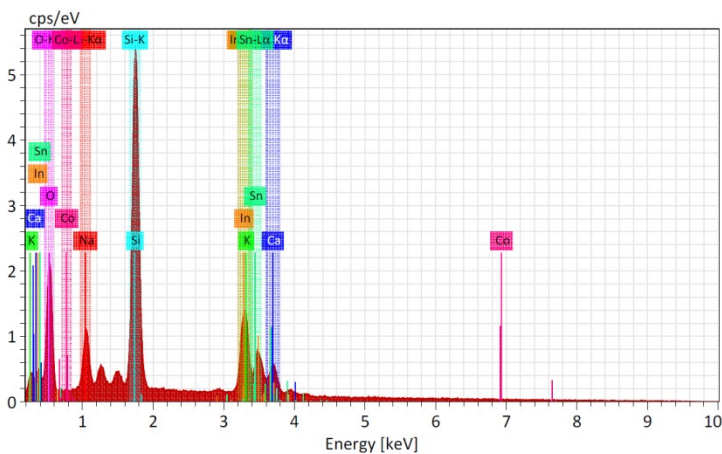
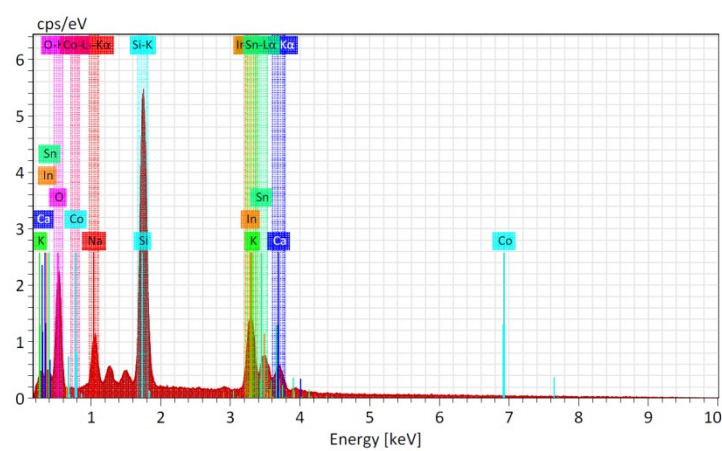
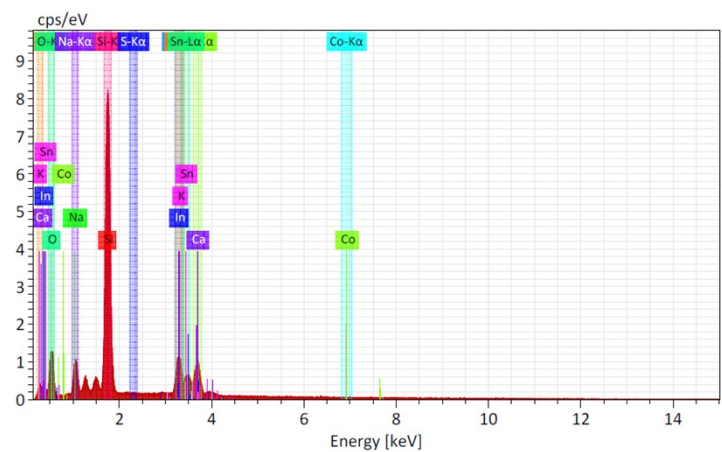
**Fig. S15** CV curves of 1 mM of complexes **2** in 0.1 M PBS at pH 11.0, GC electrode as working electrode, scan rate = 100 mV/s.



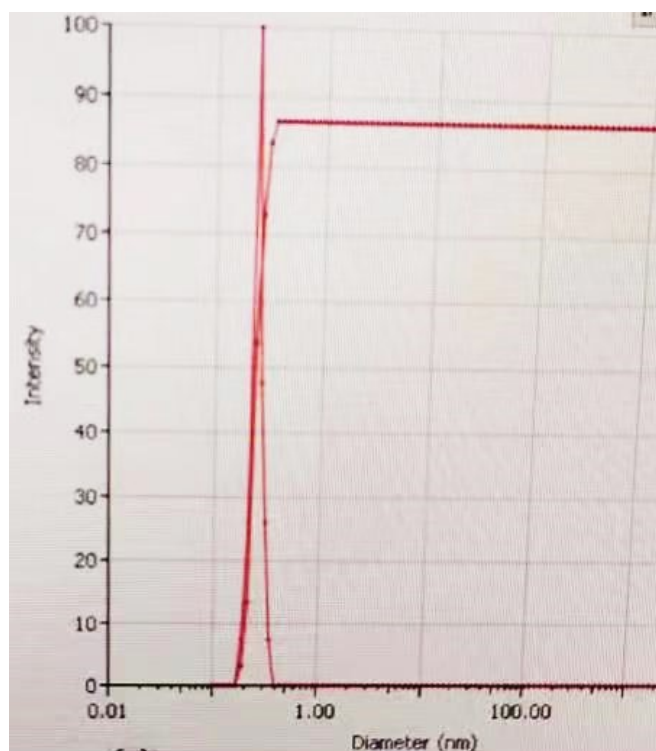
**Fig. S16** Chronocoulometric ( $Q = \text{charge vs. time}$ ) plot from controlled potential electrolysis with 1 mM of **1** or 1 mM of **2** at ITO working electrode and pH 11.0 (0.1 M PBS) at an applied potential of 1.55 V vs. NHE. A charge-versus-time trace for the background ITO electrode is also shown.



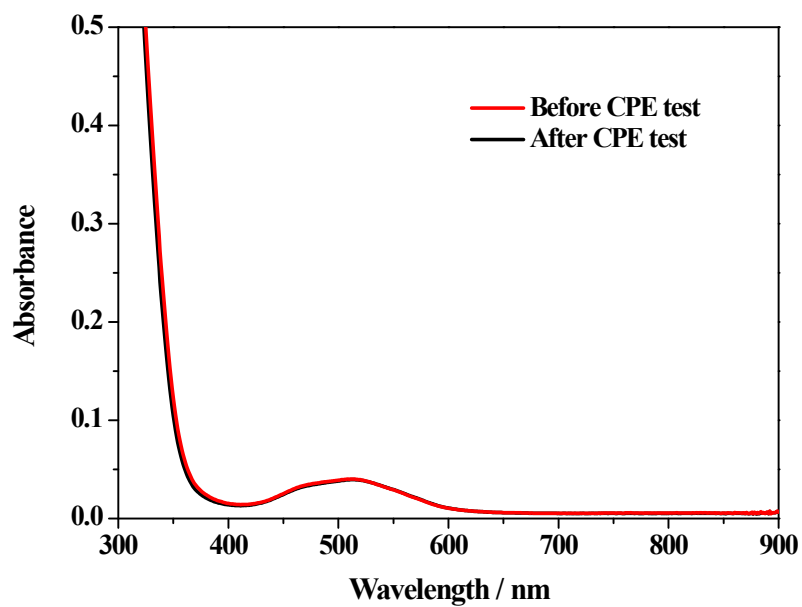
**Fig. S17** SEM images of the surface of ITO electrode before (top) and after 4 h CPE experiments of 1 mM of **1** (middle) and 1 mM of **2** (bottom) in 0.1 M PBS at pH 11.0.



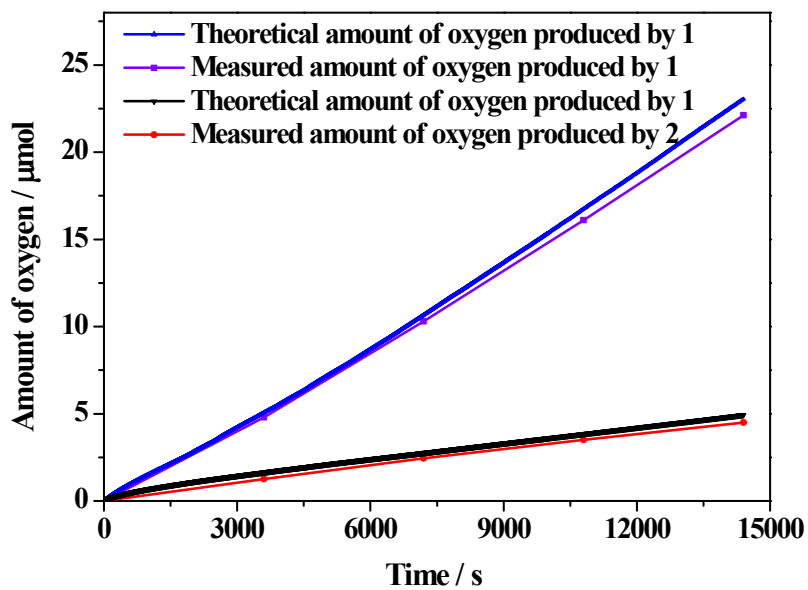
**Fig. S18** EDX analysis of the surface of ITO electrode before (top) and after 4 h CPE experiments of 1 mM of **1** (middle) and 1 mM of **2** (bottom) in 0.1 M PBS at pH 11.0.



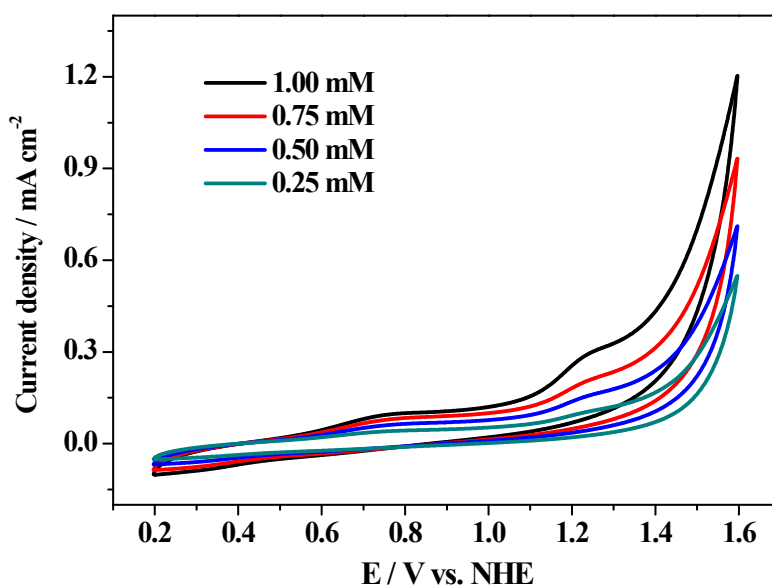
**Fig. S19** Dynamic light scattering (DLS) measurement of the electrolyte solutions after 4 h CPE experiment of complex **1**. The signal at diameter below 1 nm is ascribed to the background signal of true solution.<sup>1</sup>



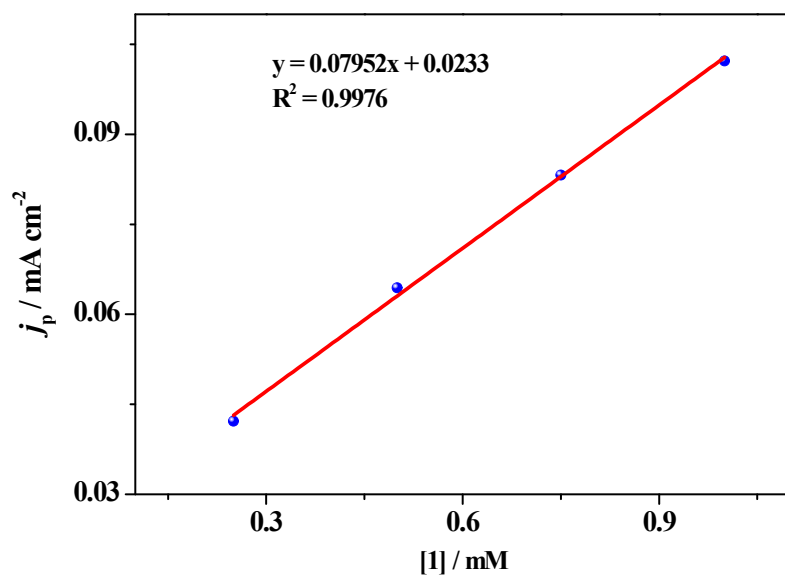
**Fig. S20** UV-vis absorbance spectra of 1 mM of complex **1** before and after 4 h CPE test at 1.55 V vs. NHE, 0.1 M PBS at pH 11.0 was used as electrolyte.



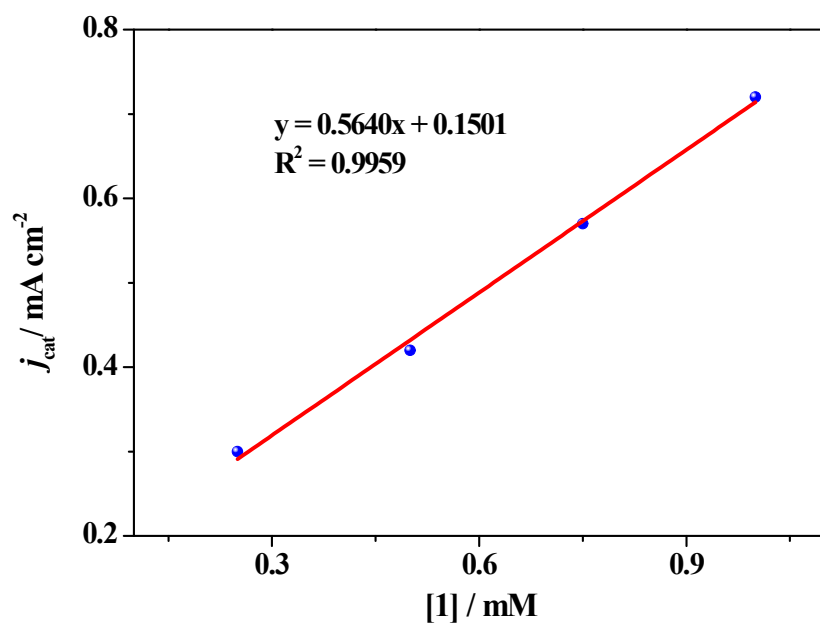
**Fig. S21** Faradaic efficiency of  $\text{O}_2$  evolution for complex **1** and complex **2** under electrolysis of 14400 s at 1.55 V (vs. NHE) in 0.1 M PBS at pH 11.0.



**Fig. S22** CV of complex **1** with various concentrations in 0.1 M PBS at pH 11.0.



**Fig. S23** Relationship between current of anodic wave and concentration of complex **1**, scan rate = 100 mV/s, 0.1 M PBS at pH 11.0 as electrolyte.



**Fig. S24** Relationship between current density at 1.55 V vs. NHE and concentration of complex **1**, scan rate = 100 mV/s, 0.1 M PBS at pH 11.0 as electrolyte.



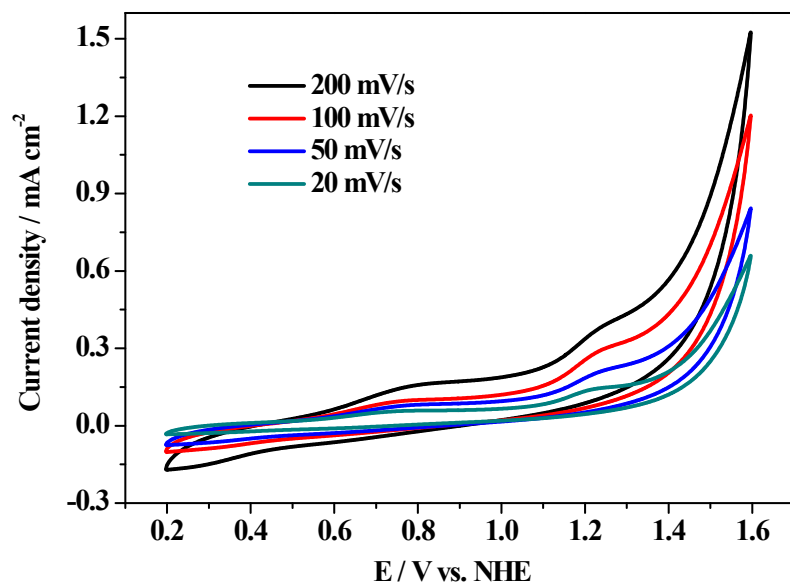


Fig. S25 CV of 1.0 mM of **1** with various scan rates, 0.1 M PBS at pH 11.0 as electrolyte.

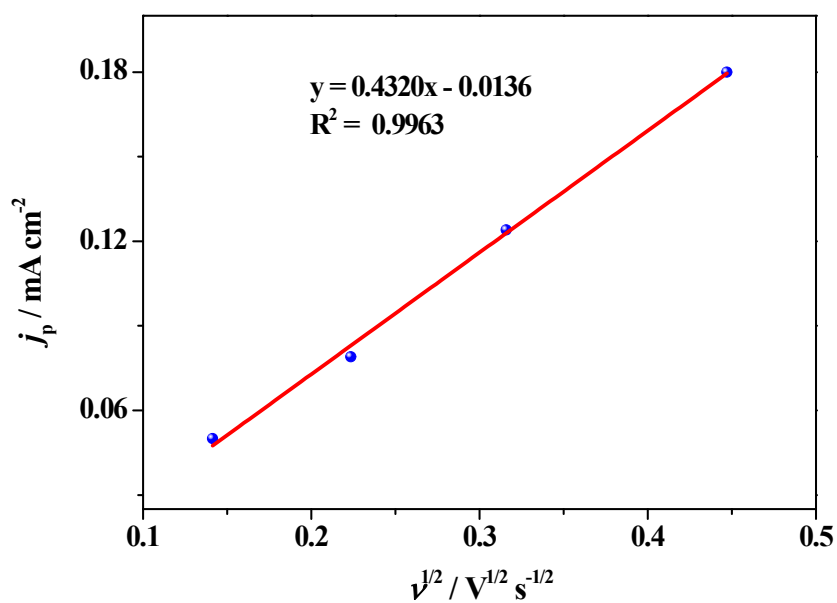
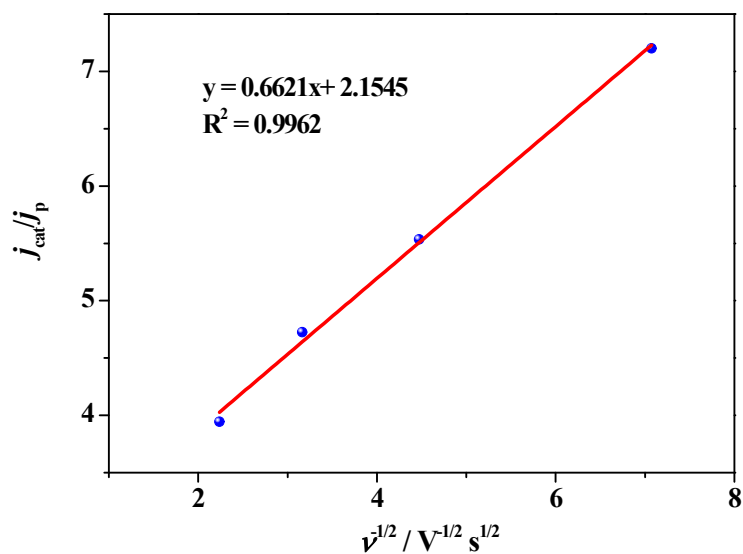
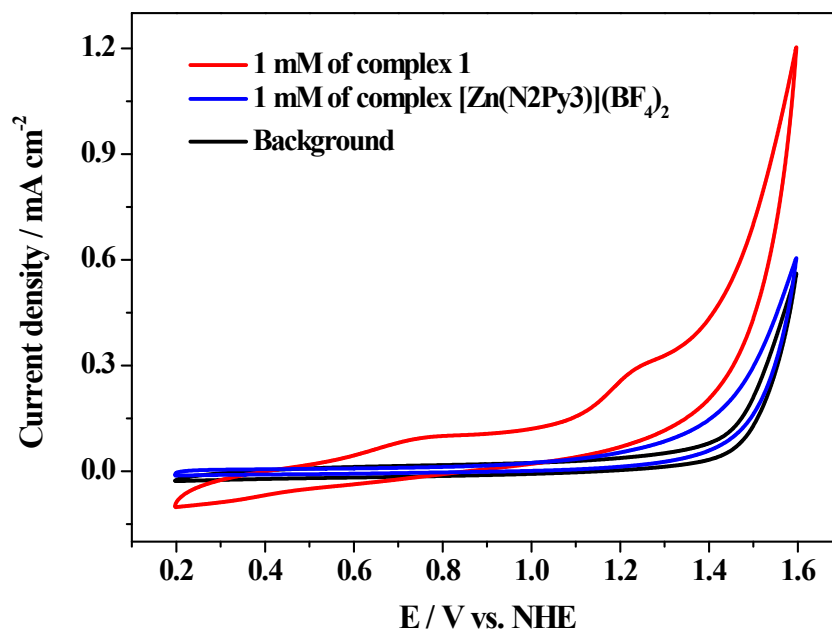


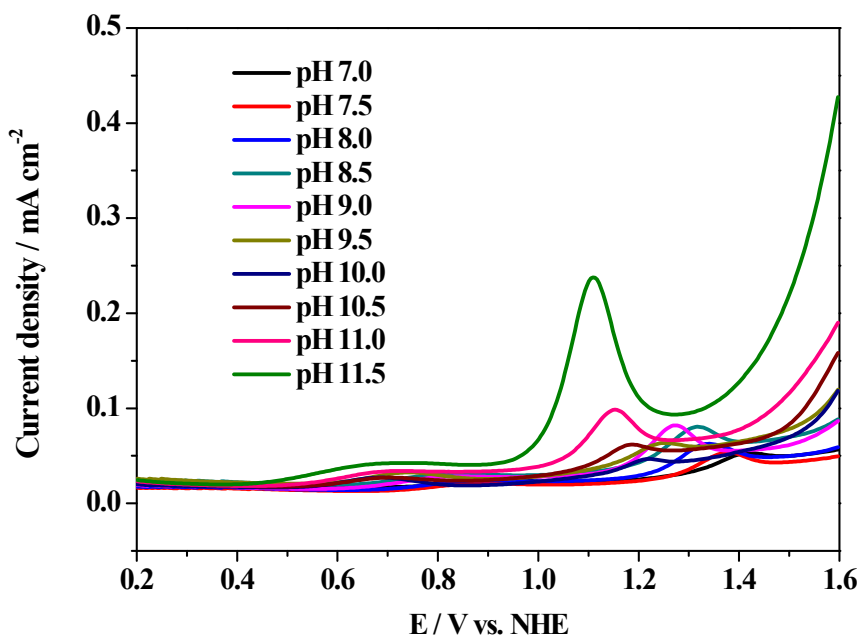
Fig. S26 Dependence of oxidation wave current density of the non-catalytic process of 1 mM of **1** on the square root of scan rates, 0.1 M PBS at pH 11.0 as electrolyte.



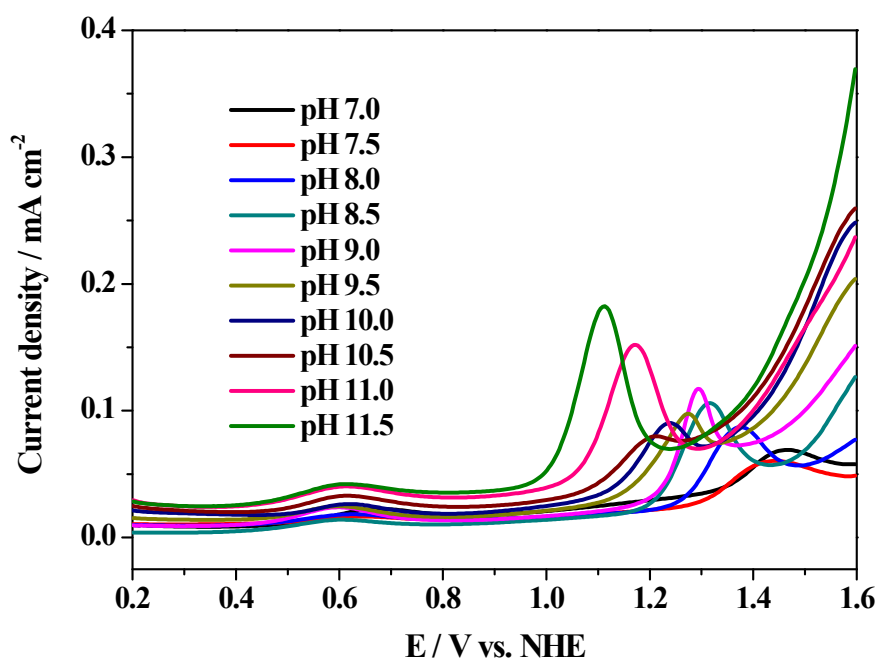
**Fig. S27** Plots of the ratio of  $j_{cat}$  to  $j_p$  of complex **1** versus the reciprocal of the square root of scan rate.



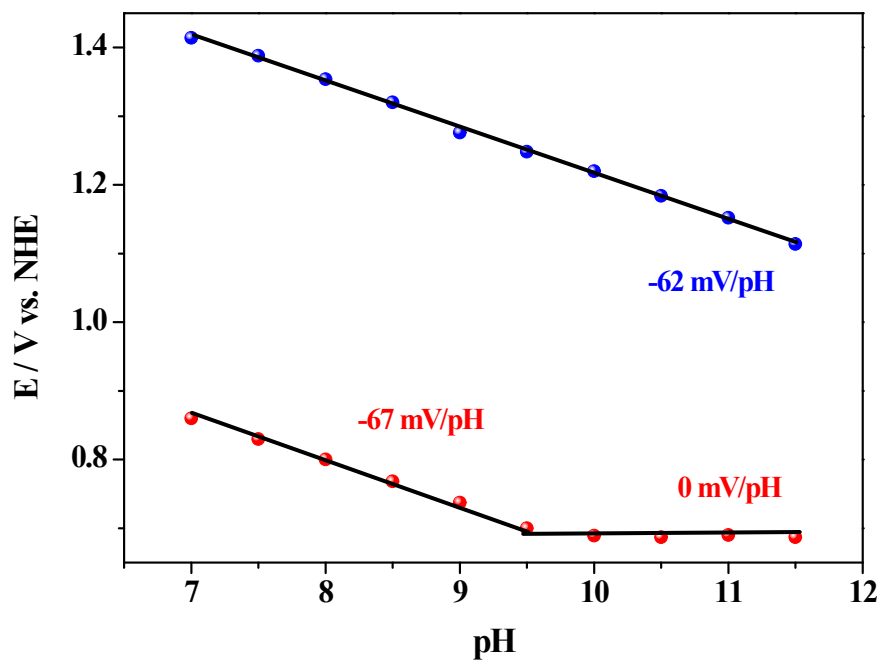
**Fig. 28** CV curves of 1 mM of complexes **1** and  $[Zn(N2Py3)](BF_4)_2$  in 0.1 M PBS at pH 11.0, GC electrode as working electrode, scan rate = 100 mV/s.



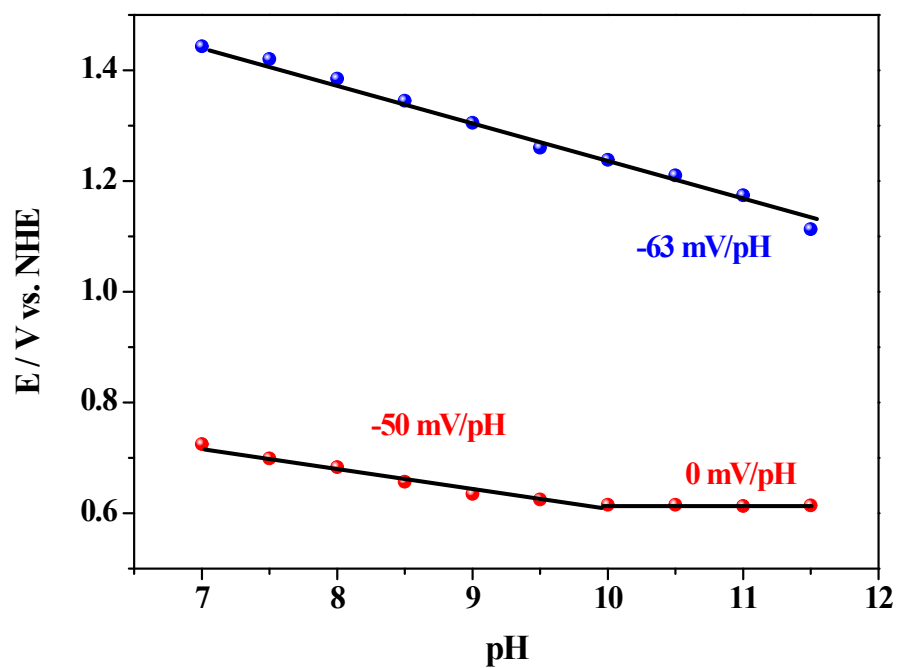
**Fig. S29** Differential pulse voltammetry (DPV) examination of 1 mM complex **1** in 0.1 M PBS at various pH values.



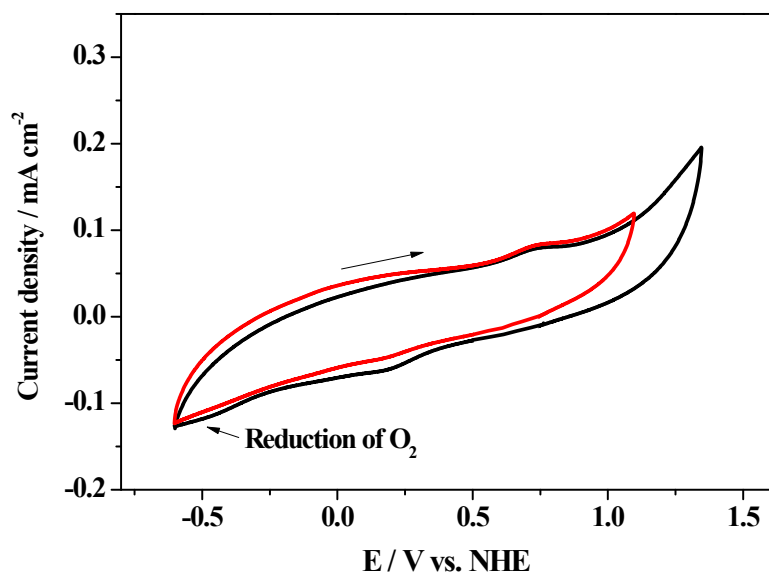
**Fig. S30** Differential pulse voltammetry (DPV) examination of 1 mM complex **2** in 0.1 M PBS at various pH values.



**Fig. S31** The relationship between the potential of each redox couple of complex 1 and the pH value of electrolyte.



**Fig. S32** The relationship between the potential of each redox couple of complex 2 and the pH value of electrolyte.



**Fig. S33** The reduction process of oxygen production by ligand-assistant water oxidation catalyzed by complex **1**.

#### Reference

- S1 L. Wang, L. Duan, R. B. Ambre, Q. Daniel, H. Chen, J. Sun. B. Das, A. Thapper, J. Uhlig, P. Dinér and L. Sun, *J. Catal.*, 2016, **335**, 72–78.