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Electrochemical water oxidation using a stable water-soluble mononuclear manganese clathrochelate

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Table S1 Crystal data and structure refinement for **1**.

Identification code	$[Na_2(H_2O)_3Mn^{IV}(L\text{-}6H)]\cdot 4H_2O$	
Empirical formula	$C_{12}H_{26}MnN_{12}Na_2O_{13}$	
Formula weight	647.37	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9851(11) Å	α = 105.913(4)°
	b = 11.2937(13) Å	β = 93.377(4)°
	c = 11.7998(13) Å	γ = 105.795(4)°
Volume	1218.5(2) $Å^3$	
Z	2	
Density (calculated)	1.765 Mg/m^3	
Absorption coefficient	0.667 mm^{-1}	
F(000)	666	
Crystal size	0.230 × 0.220 × 0.180 mm^3	
Theta range for data collection	1.966 to 25.065°.	
Index ranges	-11<=h<=11, -13<=k<=13, -14<=l<=14	
Reflections collected	44844	
Independent reflections	4303 [R(int) = 0.0681]	
Completeness to theta = 25.065°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6448	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4303 / 0 / 379	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R_1 = 0.0301, wR_2 = 0.0799	
R indices (all data)	R_1 = 0.0339, wR_2 = 0.0823	
Largest diff. peak and hole	0.375 and -0.267 $e.Å^{-3}$	

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_{o2})]^{1/2}$

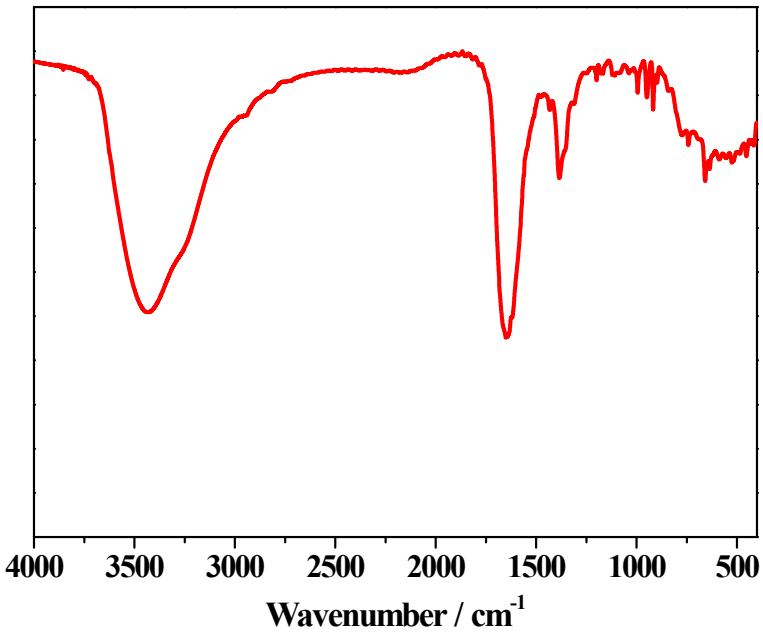

Fig. S1 Infrared spectrum of complex **1**.

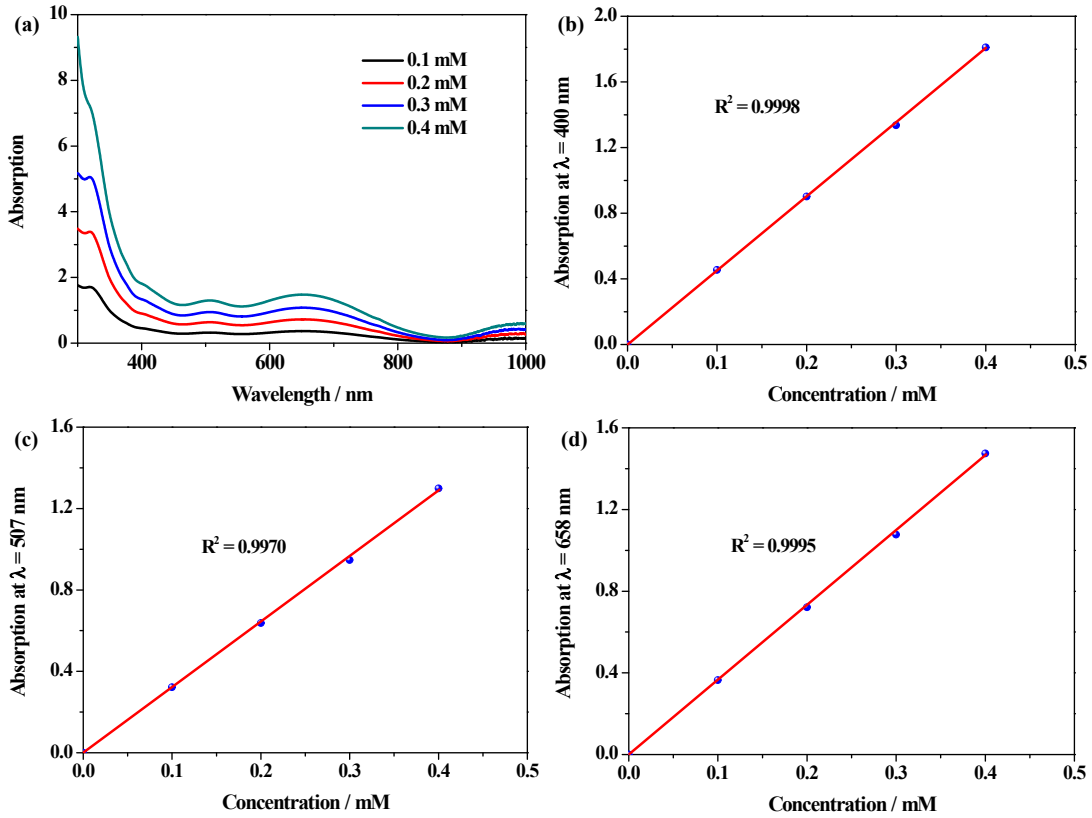

Fig. S2 The UV-vis absorption of complex **1** in phosphate buffer solution (PBS) at pH 8.0 (a), the linear relationship between absorption at 400 nm (b), 507 nm (c), and 658 nm (d) and the concentration of complex **1**.

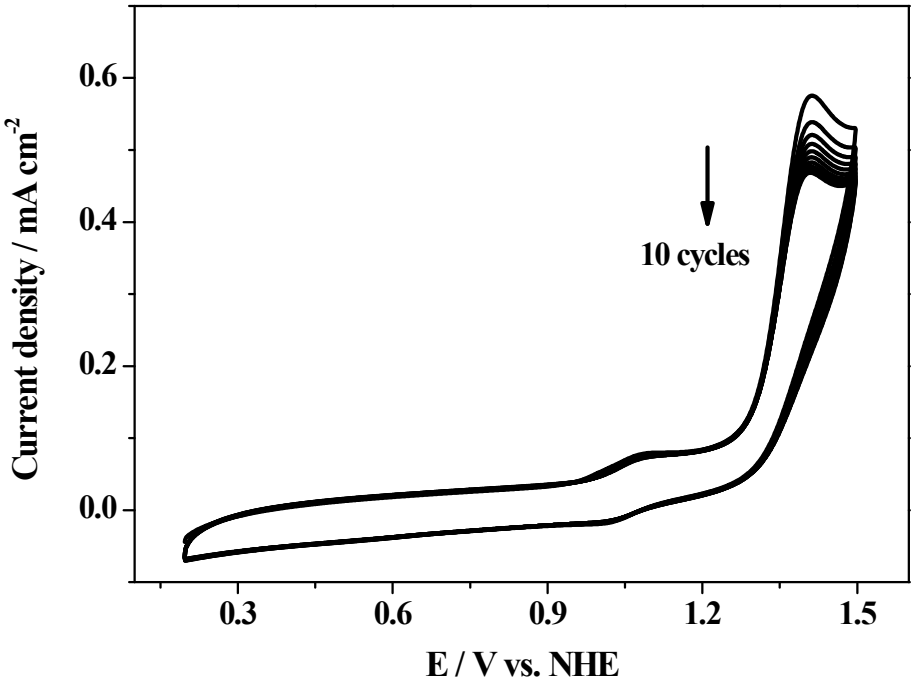

Fig. S3 Consecutive CV scan of 0.2 mM of complex **1** in 0.1 M PBS at pH 8.0.

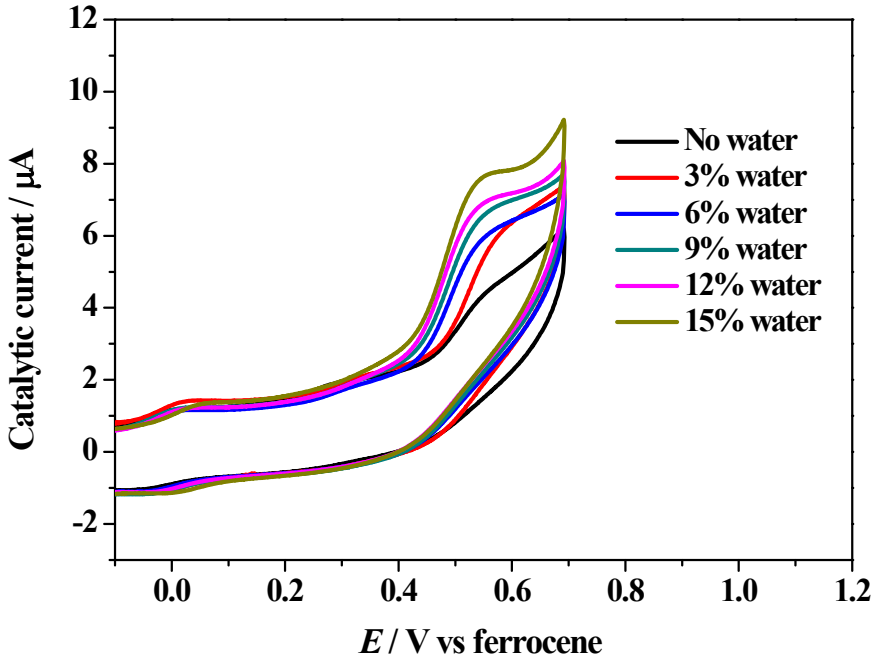

Fig. S4 The Cyclic voltammograms of the manganese clathrochelate (0.05 mM) in anhydrous dimethylformamide (0.1 M tetrabutylammonium hexafluorophosphate as electrolyte) at 100 mV/s with increasing amounts of H_2O (GC working electrode, 0.071 cm^2).

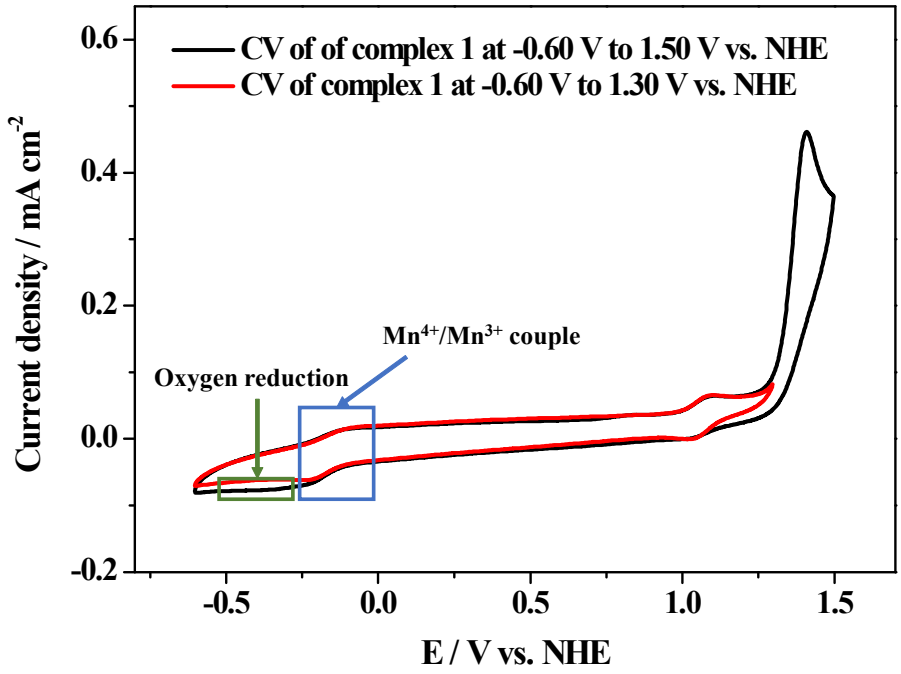

Fig. S5 Controlled CV experiment that indicating the oxygen generation at the catalytic current. 0.2 mM of complex **1** in 0.1 M phosphate buffer solution at pH 8.0, scan rate = 100 mV/s.

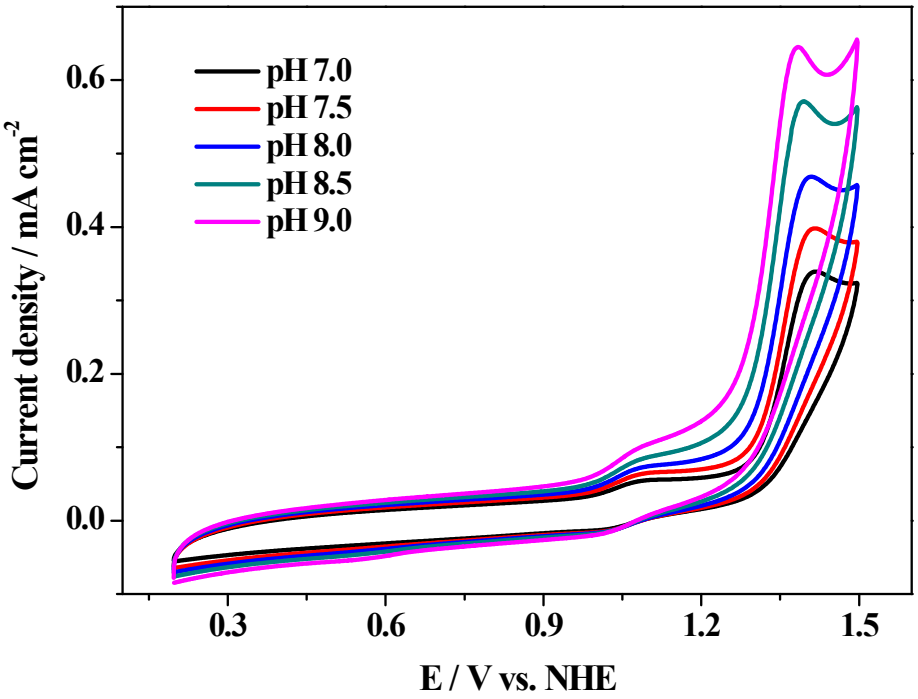

Fig. S6 CV scan of 0.2 mM of complex **1** in 0.1 M PBS at various pH.

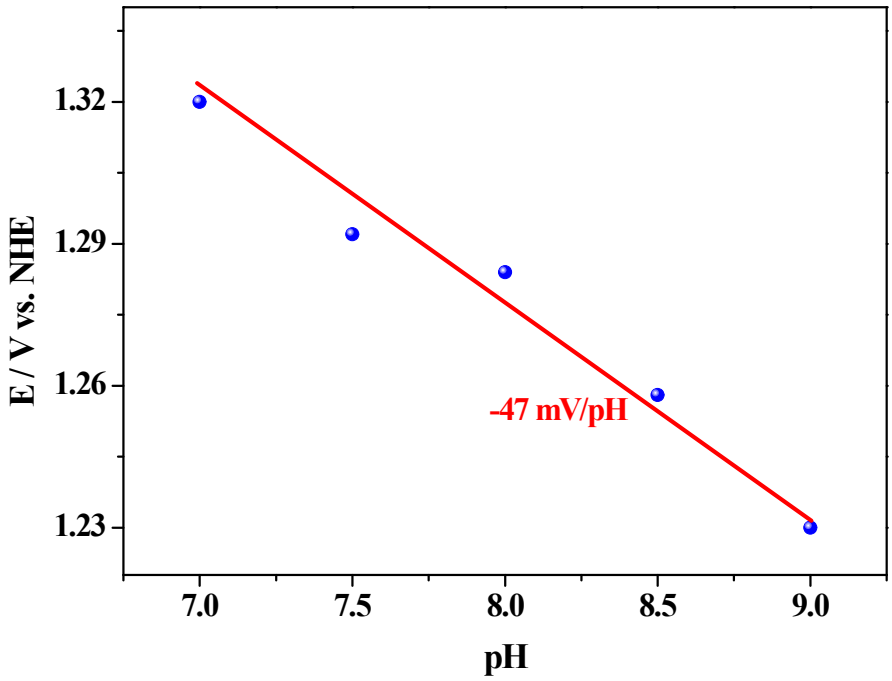

Fig. S7 The relationship between the onset potential for water oxidation mediated by complex **1** and the pH value of PBS electrolyte.

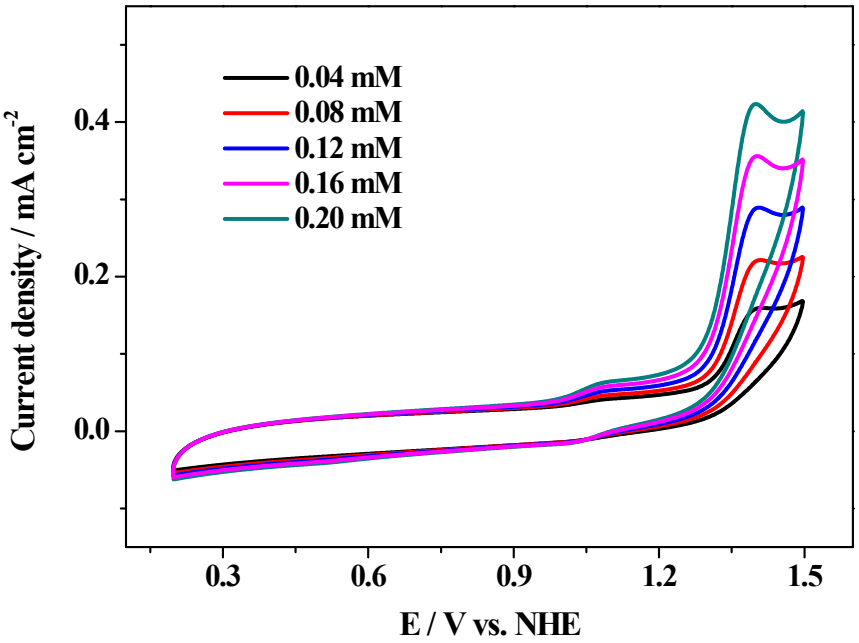

Fig. S8 CV curves of complex **1** at various concentration in 0.1 M PBS at pH 8.0.

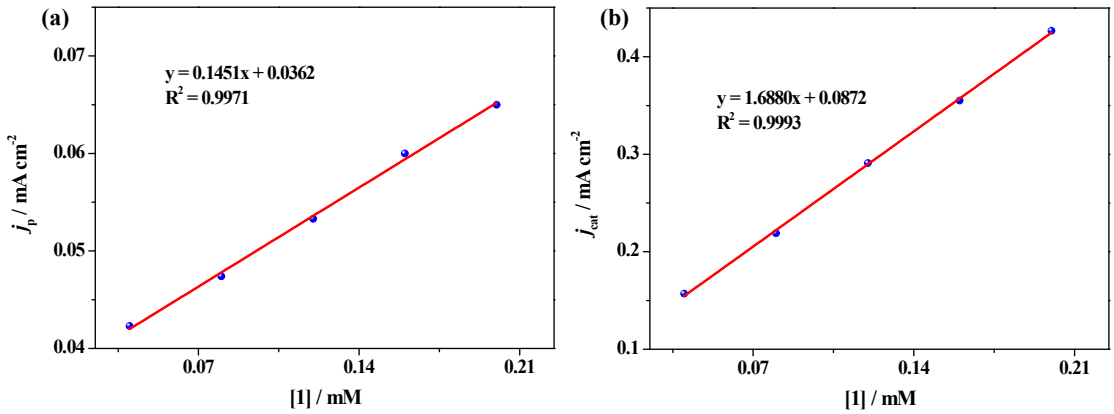

Fig. S9 The dependence of anodic peak current density j_p (a) and catalytic wave current density j_{cat} (b) on the concentration of complex **1** ([**1**]) in PBS at pH 8.0.

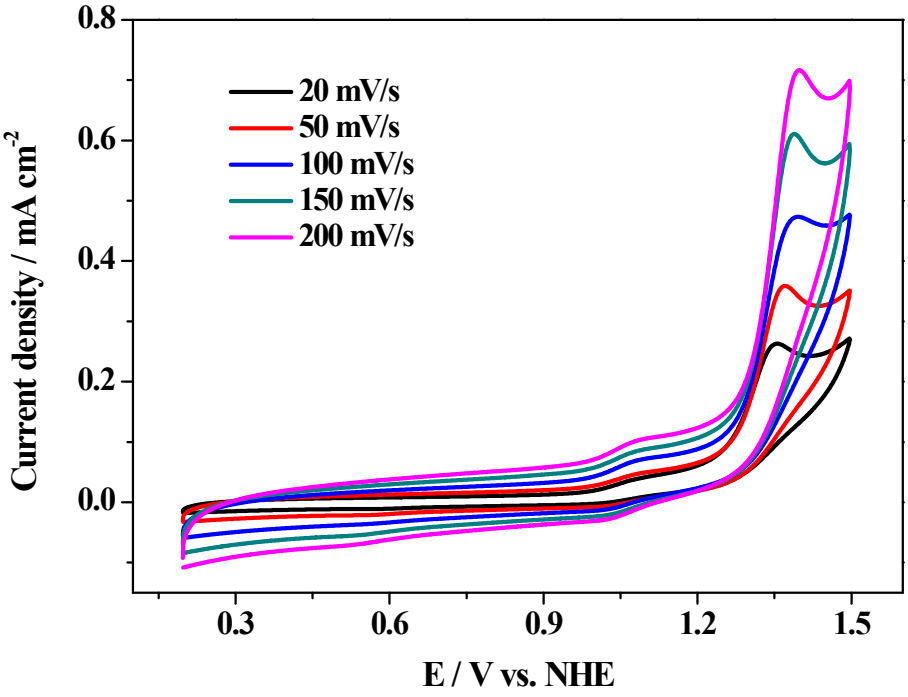

Fig. S10 CV curves of 0.2 mM of complex **1** at various scan rate, 0.1 M PBS at pH 8.0 is used as electrolyte.

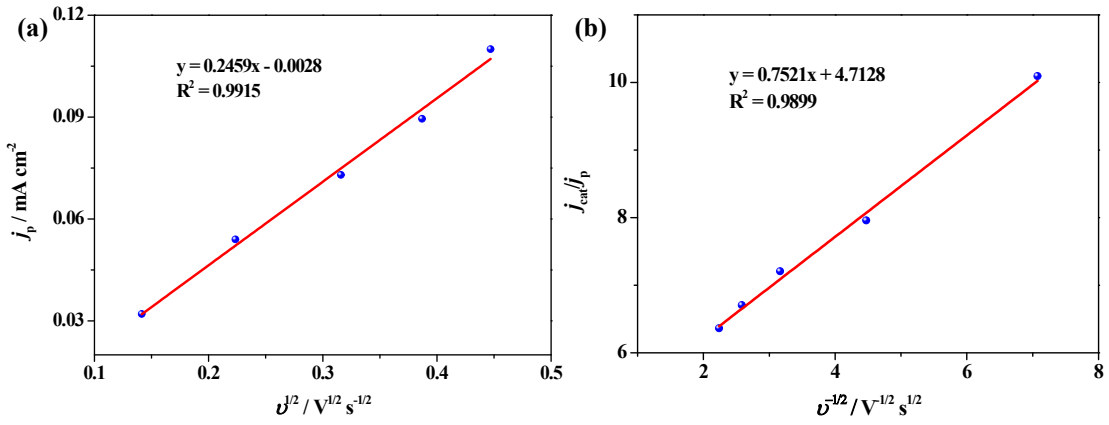

Fig. S11 The dependence of anodic peak current density j_p (a) and j_{cat}/j_p (b) on the value of $\upsilon^{-1/2}$ (υ is the scan rate), 0.1 M PBS at pH 8.0 is used as electrolyte.

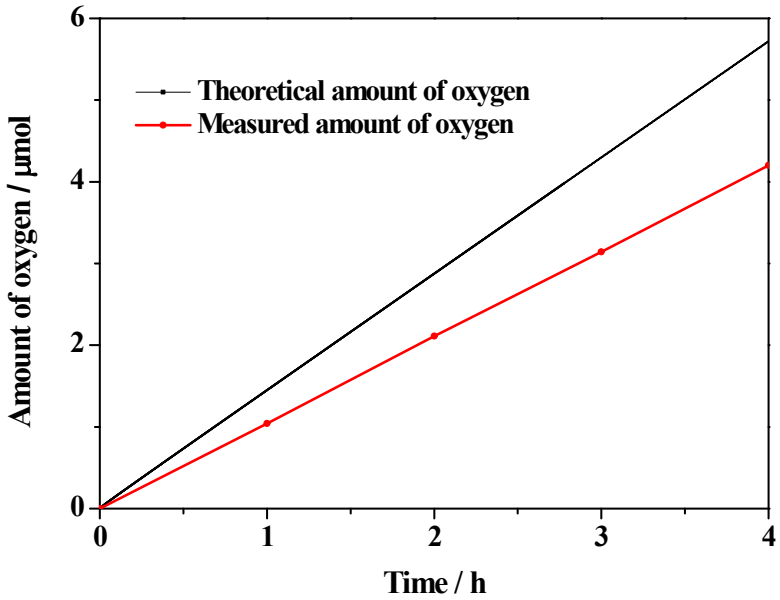

Fig. S12 Faradaic efficiency of O_2 evolution for complex **1** under electrolysis of 14400 s at 1.42 V (vs. NHE) in 0.1 M PBS at pH 8.0.

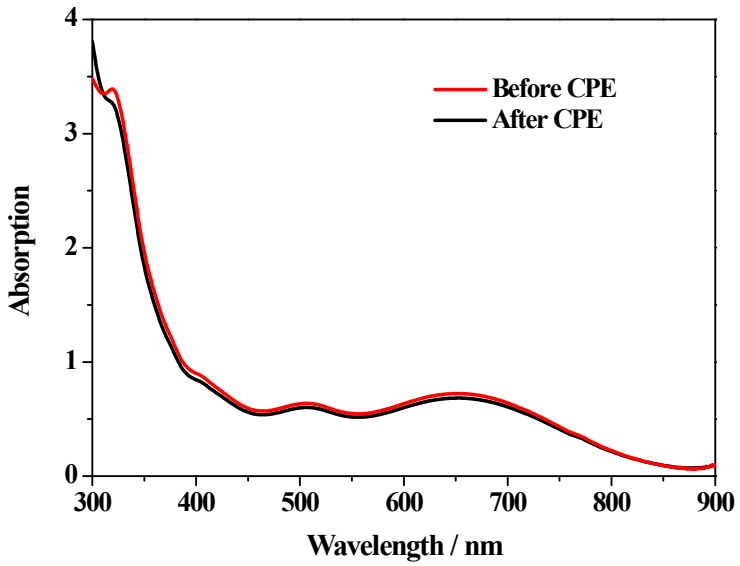

Fig. S13 The absorption spectra of complex **1** before and after controlled potential electrolysis at 1.42 V vs. NHE for 4 h, 0.1 M PBS at pH 8.0 is used as electrolyte.

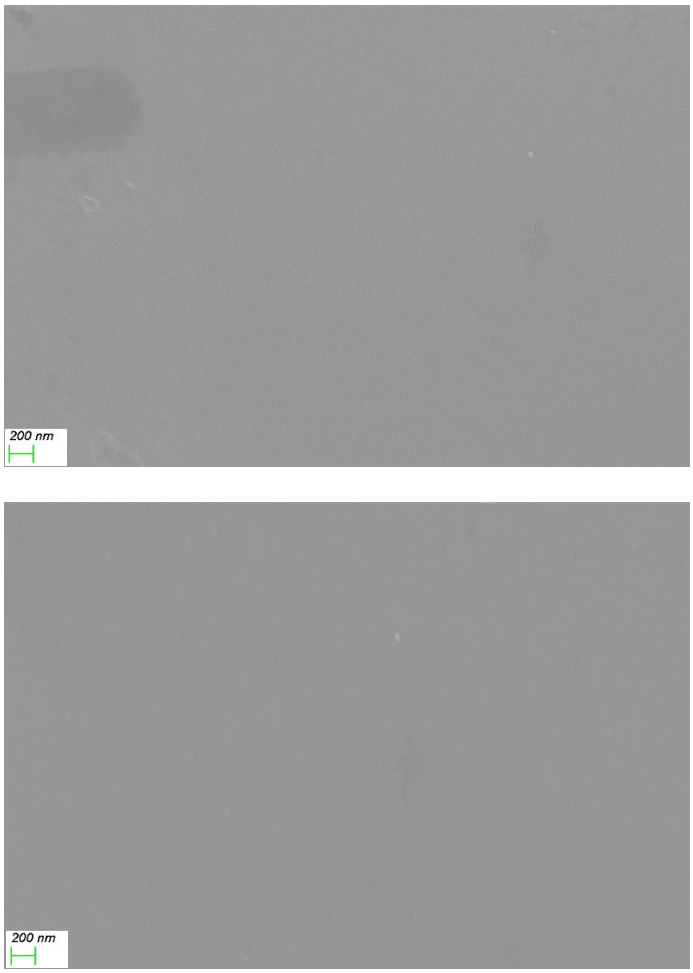

Fig. S14 SEM images of the surface of ITO electrode before (top) and after (bottom) 4 h CPE experiments (1.42 V vs. NHE) of 0.2 mM of **1** in 0.1 M PBS at pH 8.0.

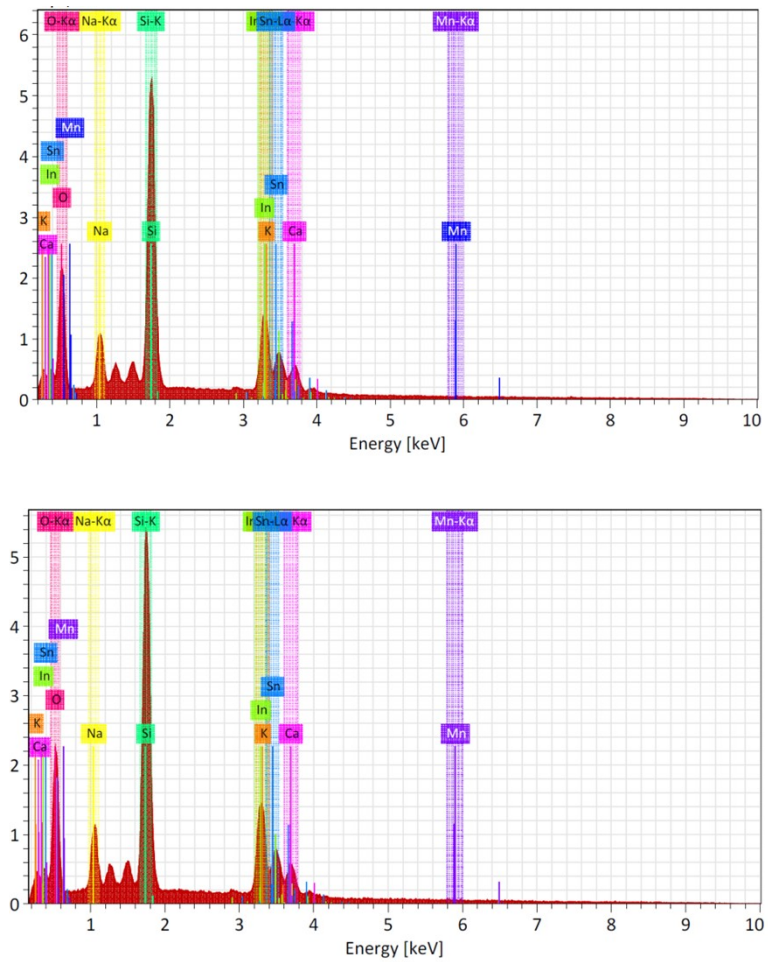

Fig. S15 EDX analysis of the surface of ITO electrode before (top) and after (bottom) 4 h CPE experiments of 0.2 mM of **1** in 0.1 M PBS at pH 8.0.

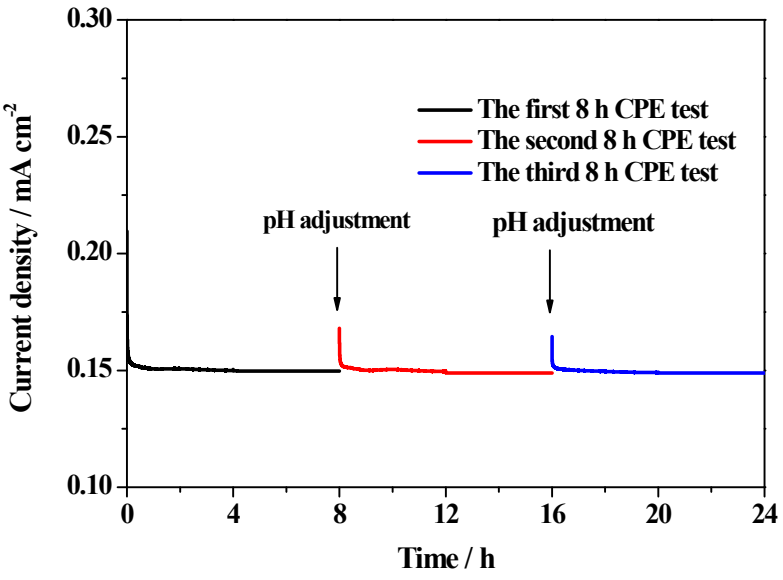

Fig. S16 Three times CPE test of 0.2 mM of complex **1** at 1.42 V vs. NHE using 0.1 M PBS at pH 8.0 as electrolyte and ITO electrode as working electrode. For each CPE test, the solution pH was adjusted back to its original pH in the initial time.