

## **Electronic Supplementary Information**

### **A Pyrene-Modified Cobalt Salophen Complex Immobilized on Multiwalled Carbon Nanotubes Acting as Precursor for Efficient Electrocatalytic Water Oxidation**

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## **Materials and Characterizations:**

4-bromobenzene-1,2-diamine, 1-pyreneboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, MgSO<sub>4</sub>, salicylaldehyde, CoCl<sub>2</sub>·6H<sub>2</sub>O and other chemicals were commercially available and all solvents were analytical grade without further purification. Carbon cloth (CC) was purchased from Taiwan CeTech Co., Ltd. MWCNTs were obtained from Wuhan Boyu Co., Ltd (Purity: > 98 %, OD: 20-30nm). The dried solvent DMF was purified by passage through activated alumina. Phosphate buffer solutions (0.1 M, pH 7.0) were prepared from mixing the sodium phosphate monobasic (NaH<sub>2</sub>PO<sub>4</sub>) and dibasic (Na<sub>2</sub>HPO<sub>4</sub>) salts, the pH value of the buffer was identified by a pH meter.

NMR spectra were obtained on a Bruker Avance II NMR spectrometer (400 MHz) at 298 K. The mass spectrometry (MS) was performed on an APEX II Model FT-ICR mass spectrometer. Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrum was recorded on a Bruker BIFLEX III mass spectrometer. Elemental analysis was performed on a PerkinElmer 2400II elemental analyzer. The morphologies of the samples were characterized using a scanning electron microscopy (SEM, Hitachi S-4800) with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images were obtained by a JEOL JEM-2100 instrument with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were acquired using an ESCALab 250 Xi electron spectrometer from VG Scientific with 300 W Al K $\alpha$  radiation. UV/Vis absorption spectra were obtained on a Shimadzu UV-2501PC spectrophotometer. Fluorescence quenching experiment were performed on a Shimadzu RF-5301PC spectrofluorophotometer. Electrochemical measurements were performed on a Shanghai Chenhua CHI760E electrochemical workstation. Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements were performed by digesting the cobalt complex modified MWCNTs composite in a mixture of concentrated HCl (6 mL) and concentrated HNO<sub>3</sub> (2.0 mL). After dilution, the ICP-OES data were recorded using a Thermo Scientific spectrometer (iCAP 7000 series). Raman spectra were recorded on a Nanofinder 30 (TII Tokyo Instrument, Inc) in ambient air at room temperature. Raman spectra were calibrated using the Raman

shift of single-crystal silicon at  $520.4\text{ cm}^{-1}$ .

#### **Synthesis of 4-(pyren-1-yl)benzene-1,2-diamine:**

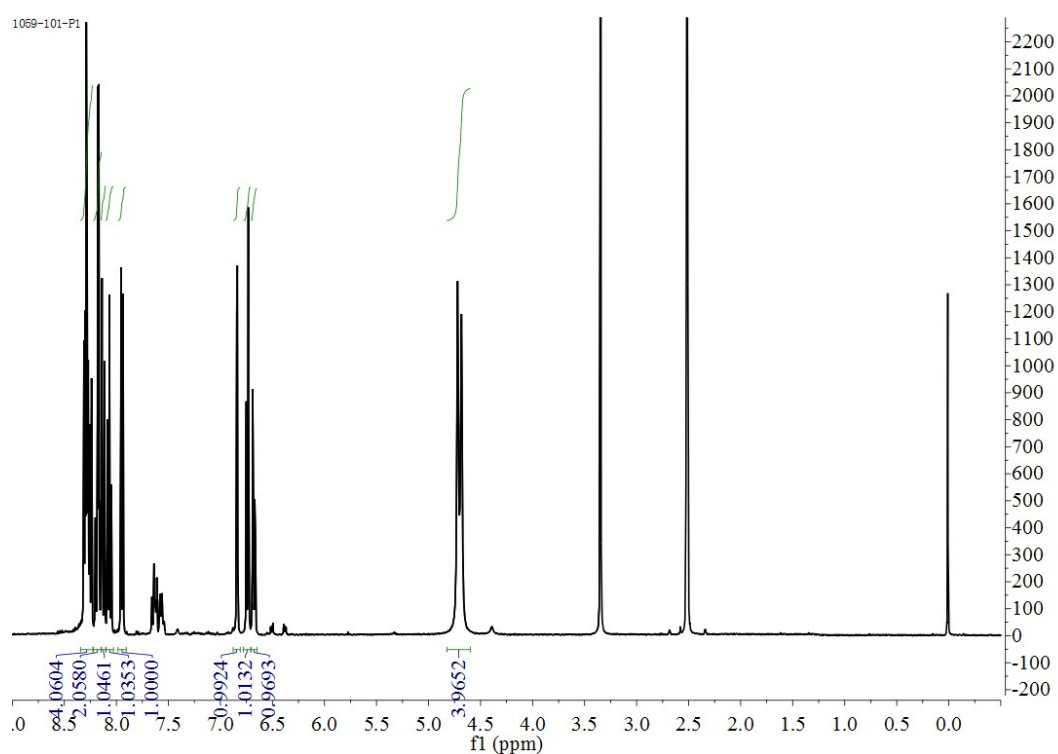
A mixture of 4-bromobenzene-1,2-diamine (12.00 g, 64.16 mmol), 1-pyreneboronic acid (31.57 g, 128.31 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (7.41 g, 6.42 mmol) in 1,4-dioxane (300 mL) was degassed with  $\text{N}_2$  for 30 min, a solution of  $\text{K}_2\text{CO}_3$  (26.56 g, 192.47 mmol) in  $\text{H}_2\text{O}$  (90 mL) was added and the resulting mixture was further degassed with  $\text{N}_2$  for another 30 min. After that, the mixture was stirred and heated to  $90\text{ }^\circ\text{C}$  for 16 h, and the mixture was then cooled to room temperature, 2000 mL dichloromethane was added, the organic phase was separated and dried with anhydrous  $\text{MgSO}_4$ . The solution was evaporated to dryness with a rotatory evaporator and purified using column chromatography with a mixture of  $\text{CH}_2\text{Cl}_2/\text{n-Hexane}$  (1:3, v/v) to give a gray solid (14.00 g, 70 % yield).  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 8.28$  (m, 4H), 8.17 (d, 2H,  $J = 4.2$  Hz), 8.13 (d, 1H,  $J = 9.4$  Hz), 8.07 (t, 1H,  $J = 7.2$  Hz), 7.94 (d, 1H,  $J = 7.9$  Hz), 6.84 (d, 1H,  $J = 1.9$  Hz), 6.74 (d, 1H,  $J = 7.8$  Hz), 6.68 (dd, 1H,  $J = 5.0, 1.9$  Hz), 4.70 (d, 4H,  $J = 16.1$  Hz).

#### **Synthesis of ligand 1:**

4-(pyren-1-yl)benzene-1,2-diamine (14.00 g, 45.40 mmol) was dissolved into 600 mL EtOH, and then salicylaldehyde (33.26 g, 27.24 mmol) was added to the solution, the solution was heated to reflux under stirring for 16 h, cooled to room temperature, the precipitate was filtered and recrystallized with EtOH (500 mL) at  $80\text{ }^\circ\text{C}$  for 0.5 h to give a yellow solid (18.00g, 76 % yield).  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 13.05$  (d, 2H,  $J = 13.6$  Hz), 9.11 (d, 2H,  $J = 3.2$  Hz), 8.43 (d, 1H,  $J = 7.9$  Hz), 8.36 (d, 1H,  $J = 7.6$  Hz), 8.32 (d, 1H,  $J = 7.4$  Hz), 8.26 (m, 4H), 8.17 (d, 1H,  $J = 7.9$  Hz), 8.13 (t, 1H,  $J = 7.6$  Hz), 7.72 (m, 5H), 7.45 (m, 2H), 7.01 (m, 4H).  $^{13}\text{C NMR}$  (101 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 165.0, 164.6, 161.0, 160.7, 142.9, 142.0, 140.4, 136.5, 134.1, 134.0, 133.0, 132.9, 131.4, 130.9, 130.8, 130.1, 128.4, 128.2, 128.1, 128.0, 127.8, 129.9, 125.5, 125.4, 125.0, 124.6, 124.5, 124.4, 122.0, 120.3, 120.1, 120.0, 119.6, 119.5, 117.2, 117.1$ . ESI-MS: Calcd for  $\text{C}_{36}\text{H}_{24}\text{N}_2\text{O}_2 + \text{H}^+$ , 517.19. Found, 517.34.

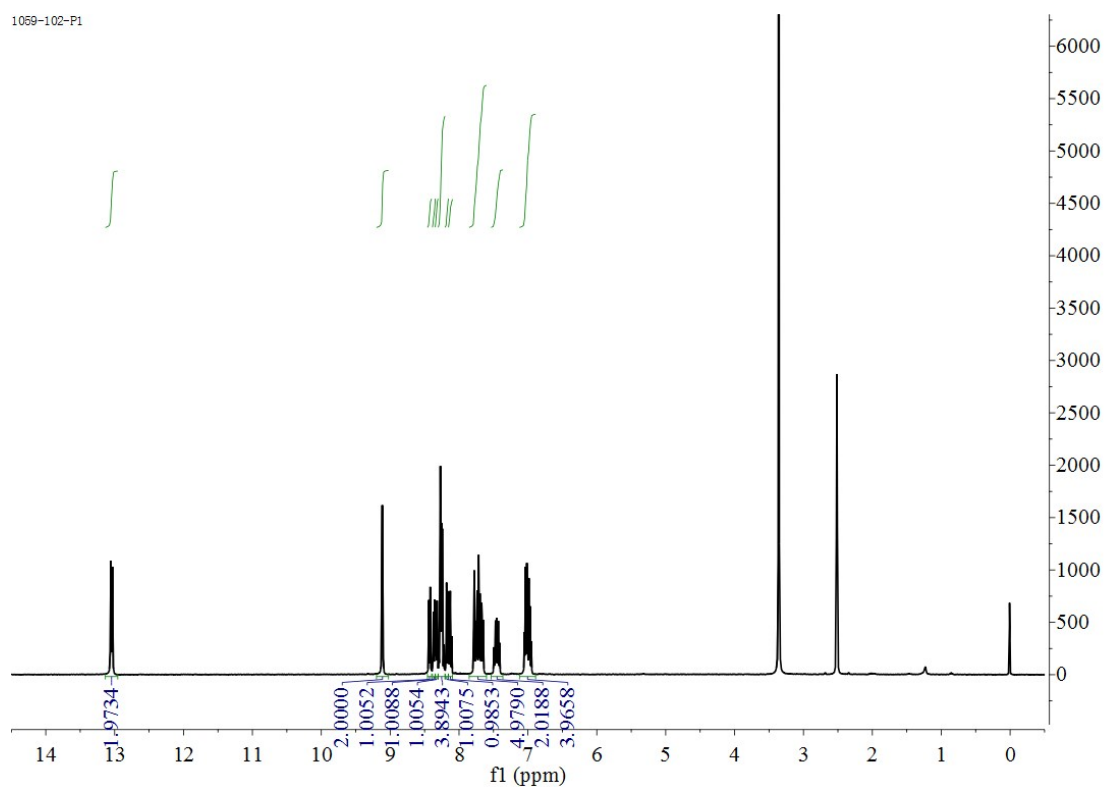
### Synthesis of complex 2:

To a 50 mL solution of EtOH were added  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (500 mg, 2.10 mmol) and ligand **1** (1.09 g, 2.10 mmol), the mixture was heated to 80 °C for 3 h. The solvent was then evaporated and the brown residue was recrystallized with EtOH to afford a brown solid. Yield: 46.3 %. HR-MS: Calcd for  $\text{C}_{36}\text{H}_{22}\text{CoN}_2\text{O}_2 + \text{H}^+$ , 574.1092. Found, 574.1072. Anal. Calcd for  $\text{C}_{36}\text{H}_{22}\text{CoN}_2\text{O}_2$ : C, 75.39; H, 3.87; N, 4.88. Found, C, 75.26; H, 4.04, N, 4.88.

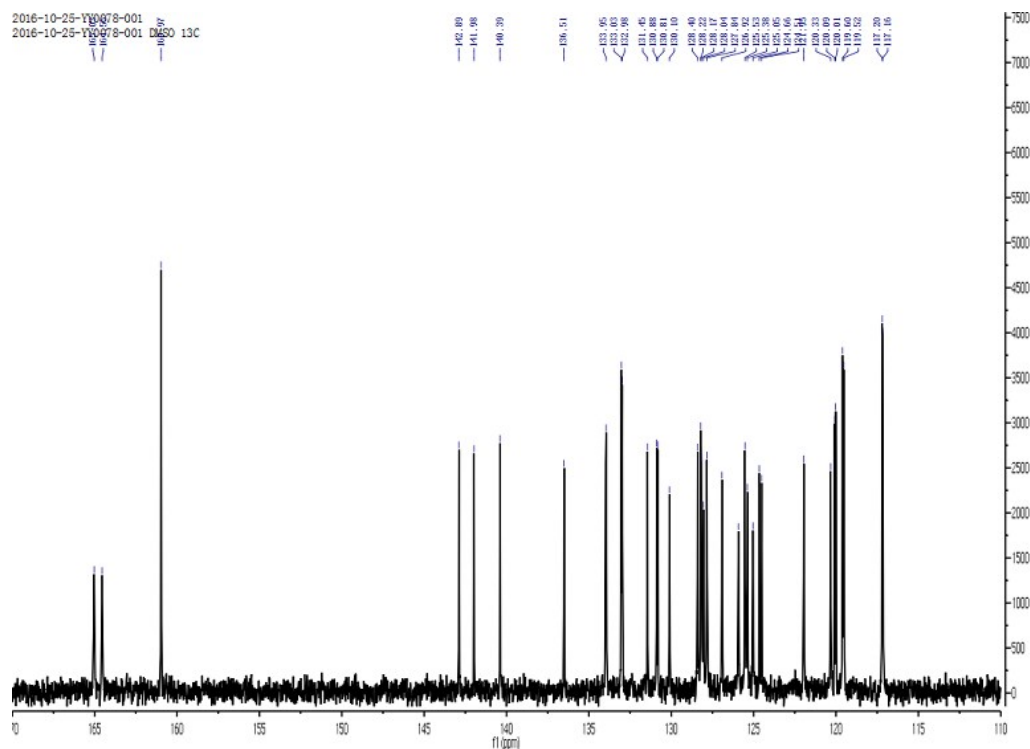


**Fig. S1**  $^1\text{H}$  NMR spectrum (400 MHz,  $[\text{D}_6]\text{DMSO}$ ) for 4-(pyren-1-yl)benzene-1,2-diamine.

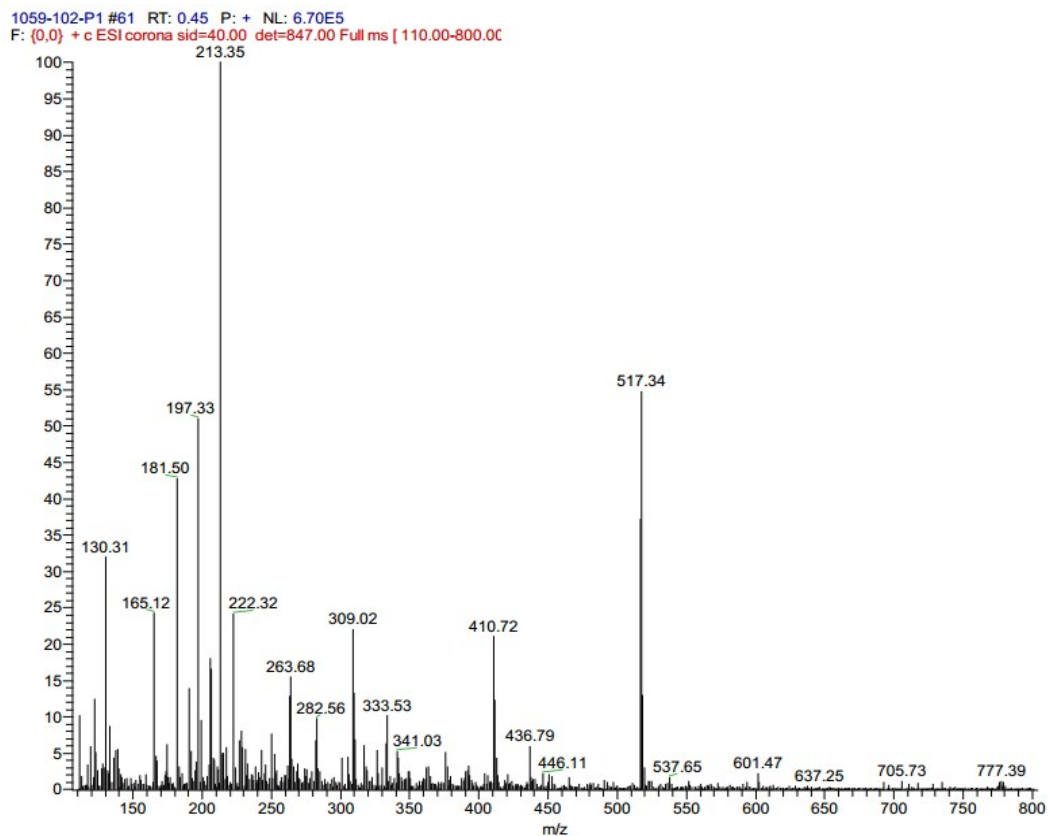
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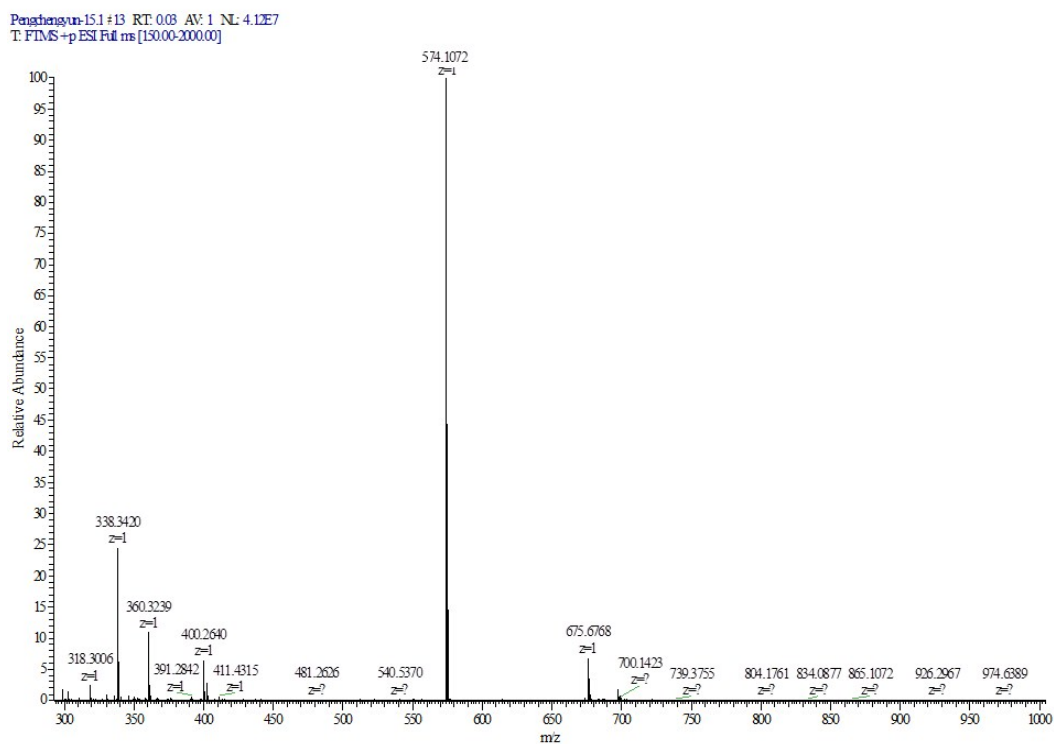
**Fig. S2**  $^1\text{H}$  NMR spectrum (400 MHz,  $[\text{D}_6]\text{DMSO}$ ) for ligand **1**.



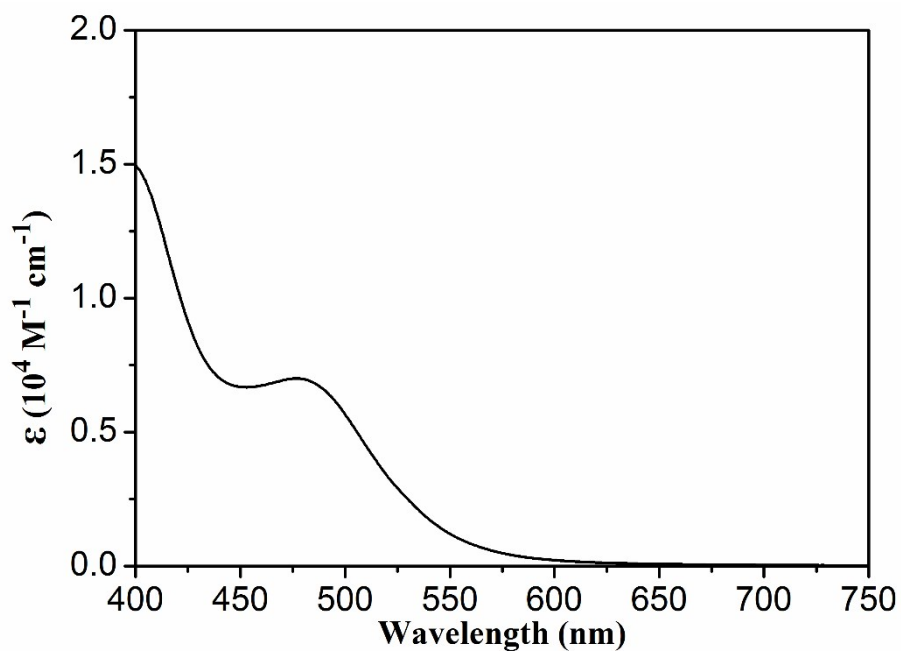
**Fig. S3**  $^{13}\text{C}$  NMR spectrum (101 MHz,  $[\text{D}_6]\text{DMSO}$ ) for ligand **1**.



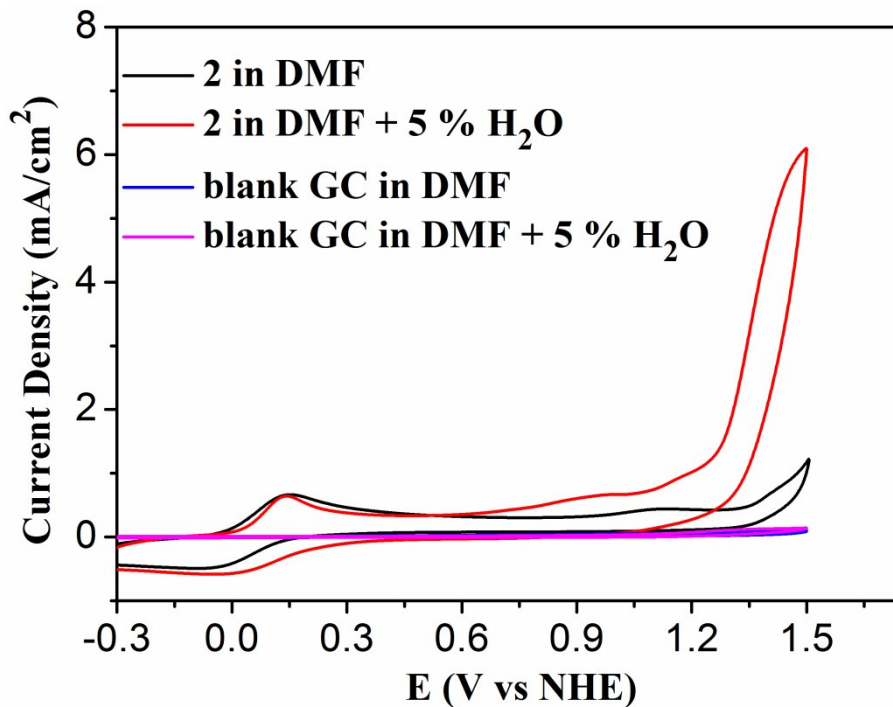
**Fig. S4** ESI-MS for ligand **1**, the signal centered at 517.34 is assigned to  $[1 + H]^+$ .



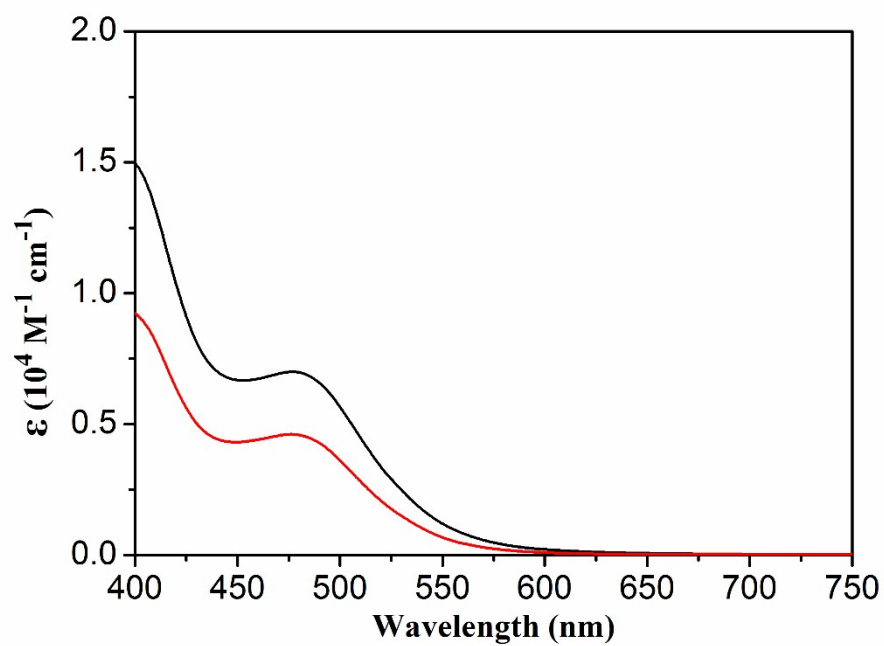
**Fig. S5** HR-MS for complex **2**, the signal centered at 574.1072 is assigned to  $[2 + H]^+$ .



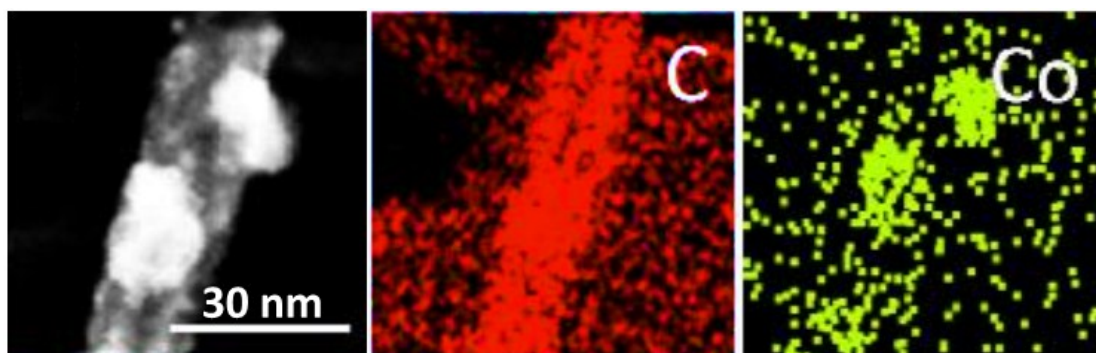
**Fig. S6** UV-Vis spectrum of complex **2** (0.2 mM) in DMF solution.



**Fig. S7** The CV curves of complex **2** in dry DMF (black line) and in DMF + 5 % H<sub>2</sub>O (red line), 0.1 M (Bu)<sub>4</sub>NPF<sub>6</sub> was used as the supporting electrolyte.

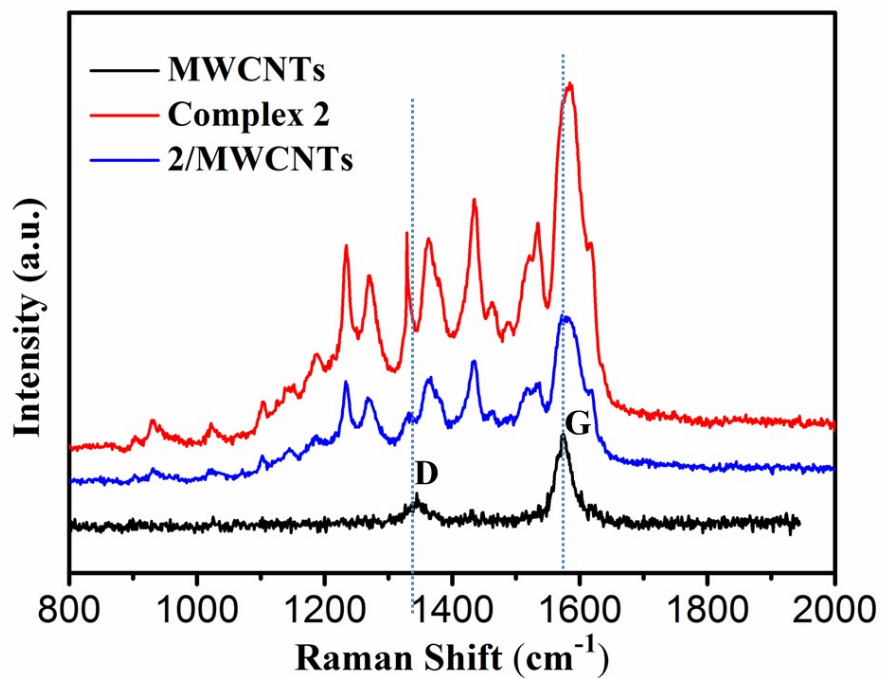


**Fig. S8** UV-Vis spectra of complex **2** in DMF (0.2 mM) with (red line) and without (black line) the addition of 5 mg MWCNTs.

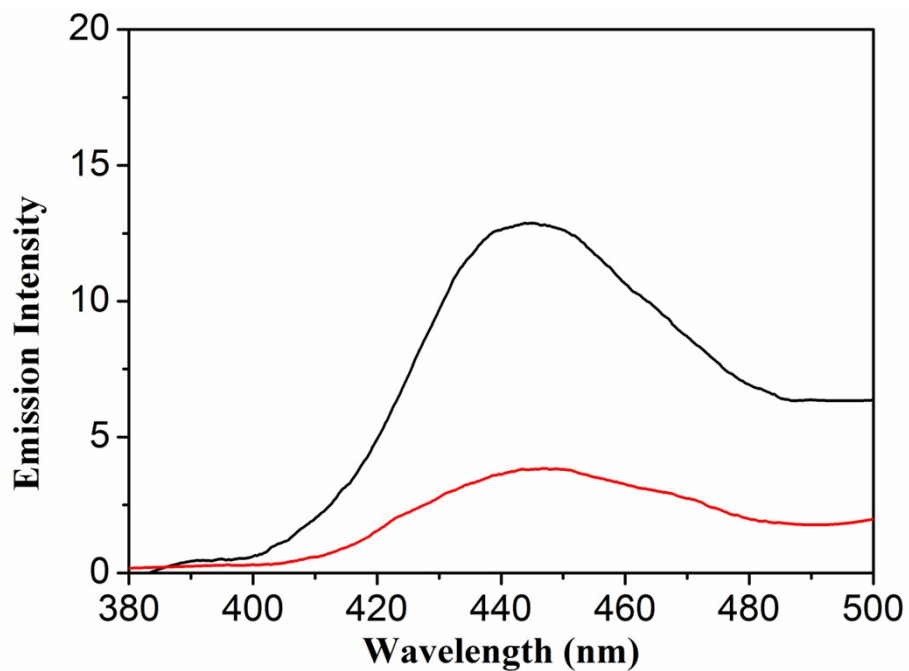


**Fig. S9** EDX elemental mapping images of the **2**/MWCNTs composite.

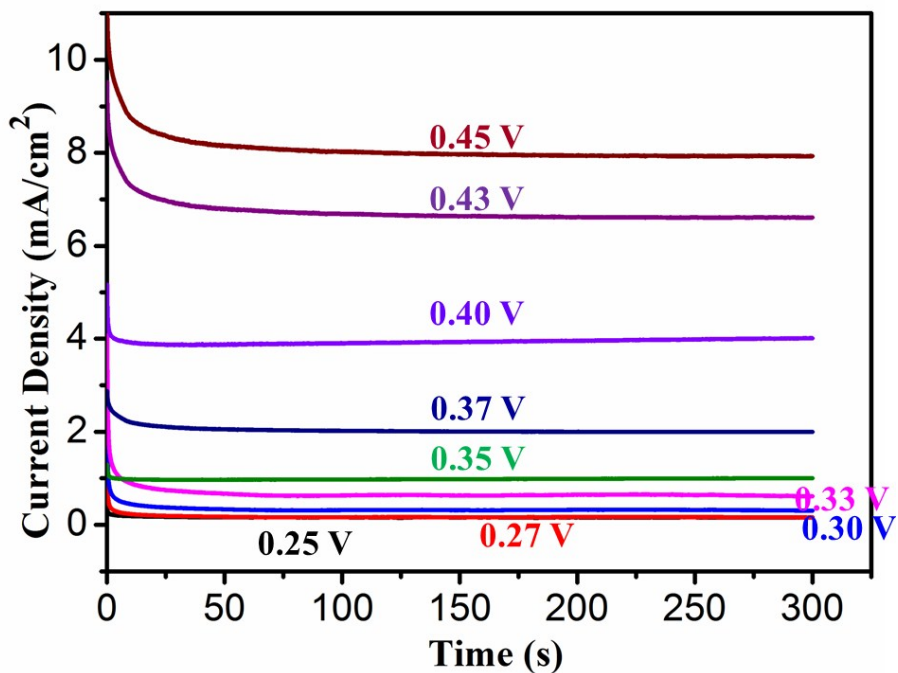




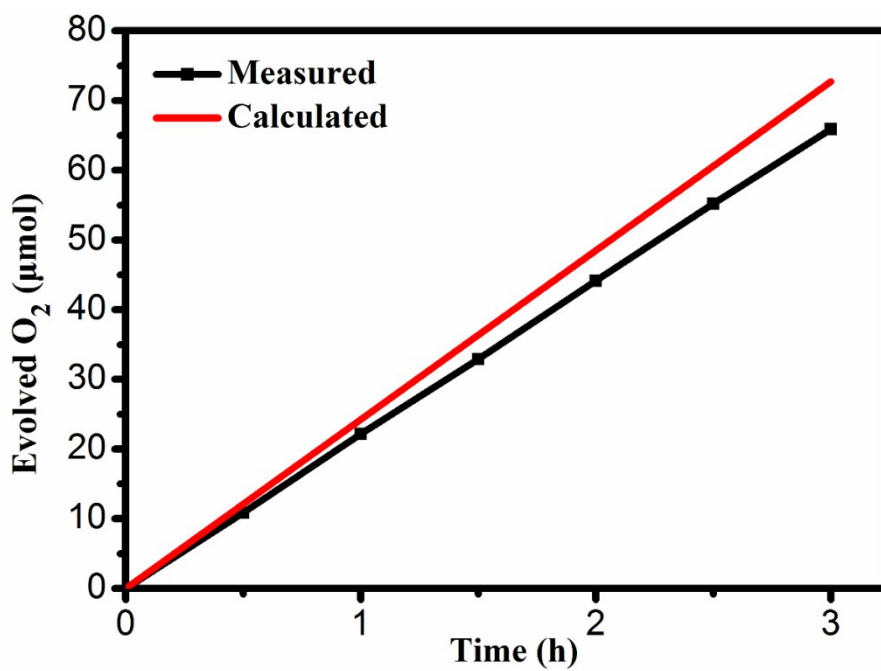
**Fig. S10** Raman spectra of MWCNTs (black line), complex 2 (red line) and 2/MWCNTs composite (blue line).



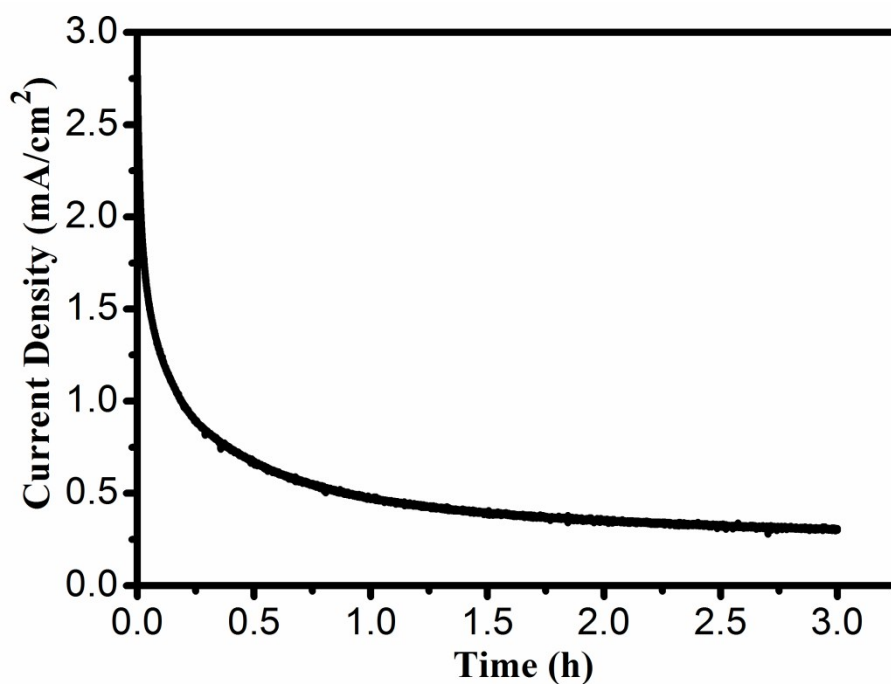
**Fig. S11** Fluorescence spectra (with an excitation at 300 nm) of complex 2 in DMF (0.2 mM) with (red line) and without (black line) the addition of 5 mg MWCNTs.



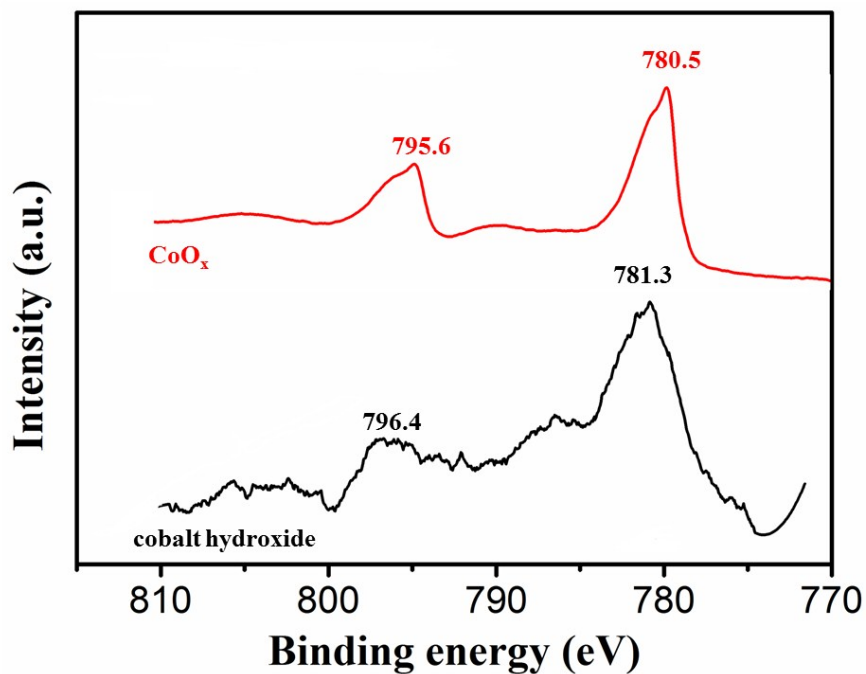
**Fig. S12** Plots of current density vs time for 2/MWCNTs@GC electrode under different overpotential.



**Fig. S13** Calculated and measured oxygen evolution results in pH 7.0 PBS by bulk electrolysis at 1.35 V vs NHE using 2/MWCNTs@CC electrode as working electrode.



**Fig. S14** Bulk electrolysis at 1.35 V vs NHE using **2**/MWCNTs@CC electrode with the presence of EDTA.



**Fig. S15** XPS pattern of Co 2p for **2**/MWCNTs (black line) after bulk electrolysis. The XPS pattern of Co(NO<sub>3</sub>)<sub>2</sub>/MWCNTs (red line) after bulk electrolysis was also shown for comparison.