Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Post-Functionalization of Co(III)PPh$_3$triarylcorroles through Suzuki-Miyarura Couplings and Their Tunable Electrochemically Catalyzed Hydrogen Evolutions and Oxygen Reductions

Xu Liang*, Yuanyuan Qiu, Xifeng Zhang and Weihua Zhu*

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P. R. China

Corresponding to: E-mail: liangxu@ujs.edu.cn, Tel: +86-511-8879-1928 (to X. L.); Email: sayman@ujs.edu.cn, Tel: +86-511-8879-1928 (to W. Z.)

Contents

1. Experimental section
2. ^{1}HNMR spectrum
3. IR spectrum
4. DPV measurements
5. Electrochemical catalysis of Co(III)PPh$_3$triphenylcorrole
6. i-t curve of rGO supported **3a-d** and **3a**-**5a**.

1. Experimental Section

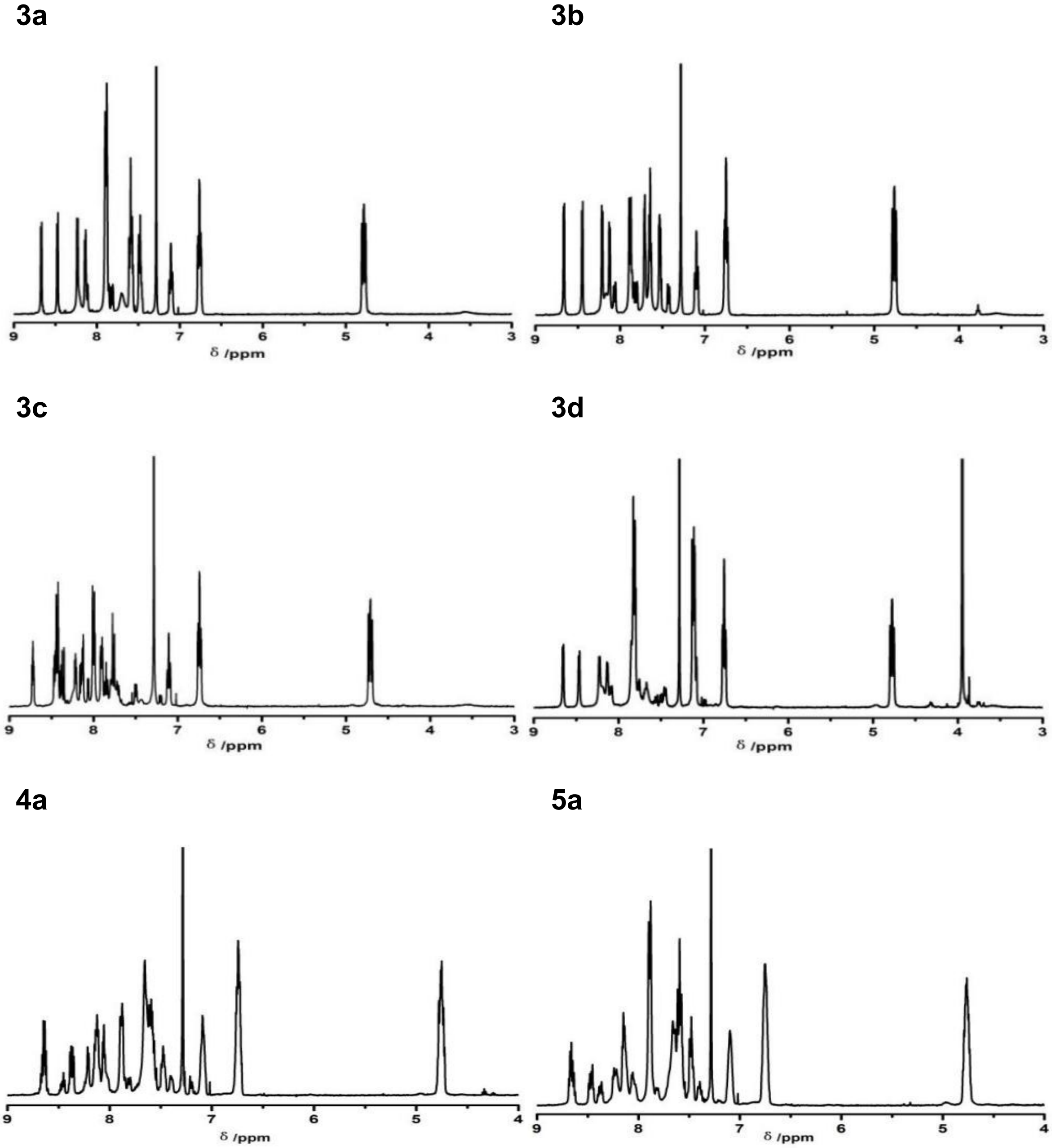
1.1 General Considerations.

^{1}H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400.03 MHz). Residual solvent peaks were used to provide internal references (δ = 7.26 ppm for $CDCl_3$). All reagents and solvents used were of reagent grade and were used as received unless noted otherwise. Cyclic voltammetry was carried out on a Chi-730D electrochemistry station with a three-electrode cell. A glassy carbon disk, a platinum wire and an Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. An inert nitrogen atmosphere was introduced during all of the electrochemical measurements, which were carried out at room temperature. The UV and visible regions of the electronic absorption spectra were recorded with an HP 8453A diode array spectrophotometer.

Preparation of modified electrodes

1.0 mg of rGO was mixed with 1 mL of isopropyl alcohol containing 0.2% nafion and the mixture sonicated in an ultrasonic bath for 30 min to produce a homogeneous mixture of concentration 1 mg/mL. The surface of the glassy carbon electrode (GCE) was polished with 0.05 µm alumina and rinsed with doubly distilled water in the ultrasonic bath to remove any adhered Al_2O_3 particles. The electrodes were rinsed with ethanol and dried under room temperature for ca. 5 min. Three 3 µL of the rGO/isopropyl alcohol/nafion suspensions were drop cast on the surface of the GC electrode and allowed to dry at room temperature. 10 µL aliquots of 0.2 mM dichloromethane solutions of **2a-c** and **4a-c** were added dropwise to the rGO/nafion-coated electrodes and dried at room temperature for 1 h. The electrodes were stored in MilliQ water in the dark.

2. ¹HNMR spectra



3a

3b

3c

3d

4a

5a

Figure S1. ¹HNMR spectra of **3a**-**d**, **4a** and **5a** in $CDCl_3$.

3. IR spectra

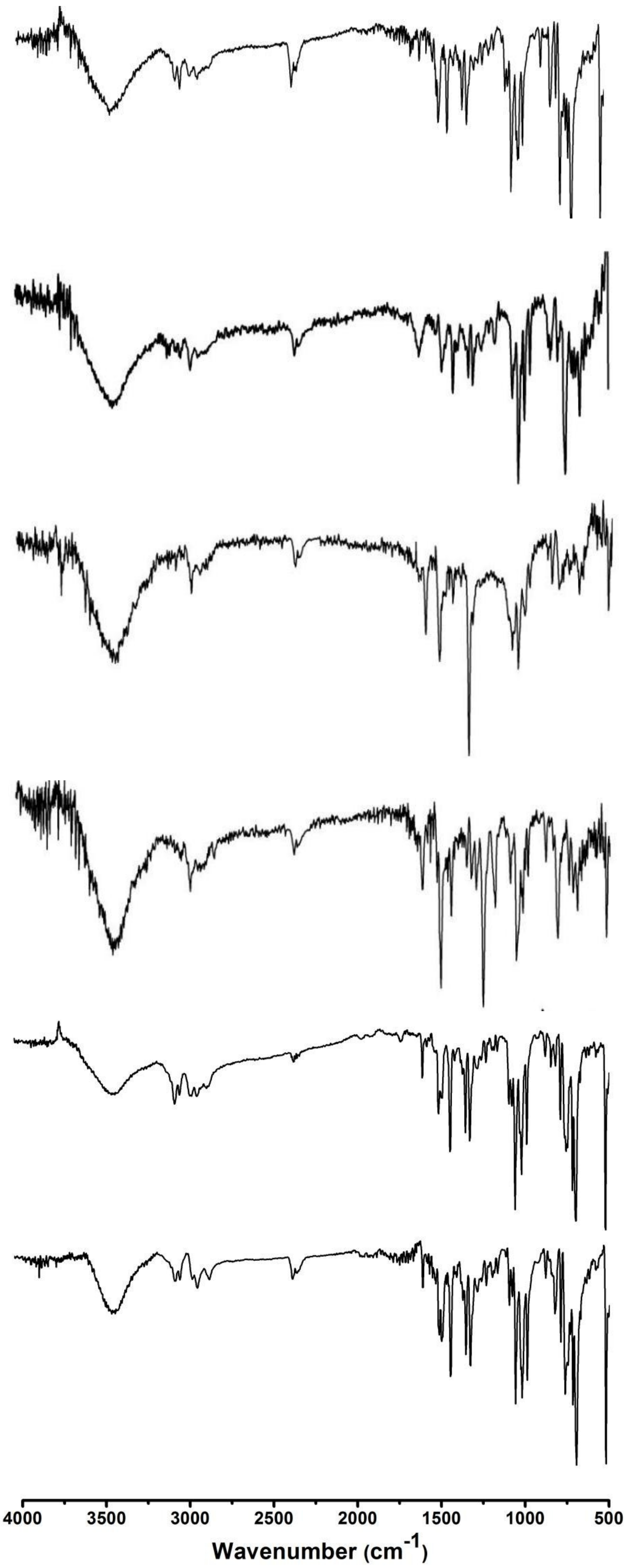


Figure S2. IR spectra of **3a**-**d**, **4a** and **5a** (from top to bottom).

4. DPV measurements

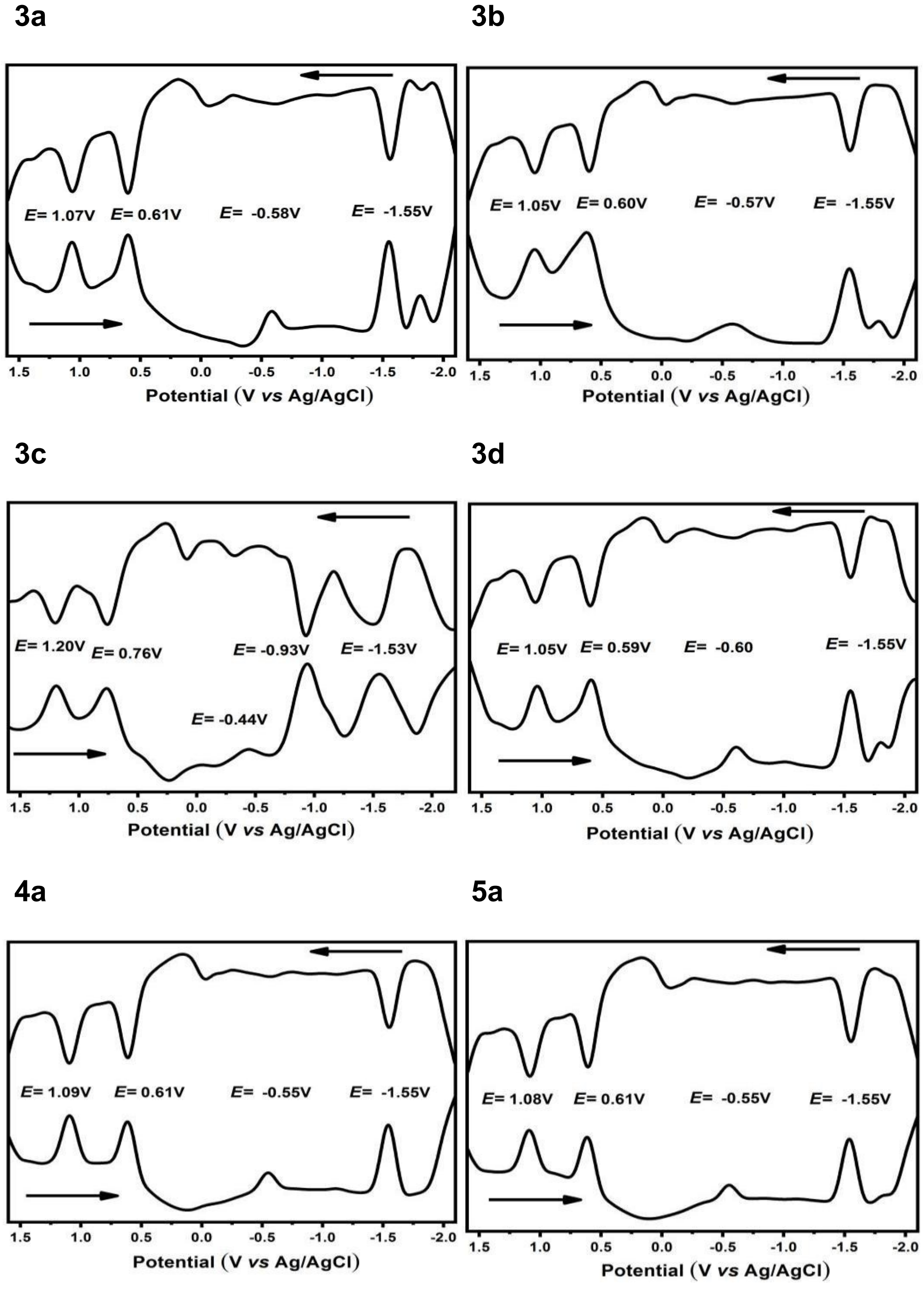


Figure S3. DPV measurements of **3a**-**d**, **4a** and **5a** in o-dichlorobenzene (*o*-DCB) containing 0.1M TBAP.

5. Electrochemical catalysis of Co(III)PPh$_3$triphenylcorrole

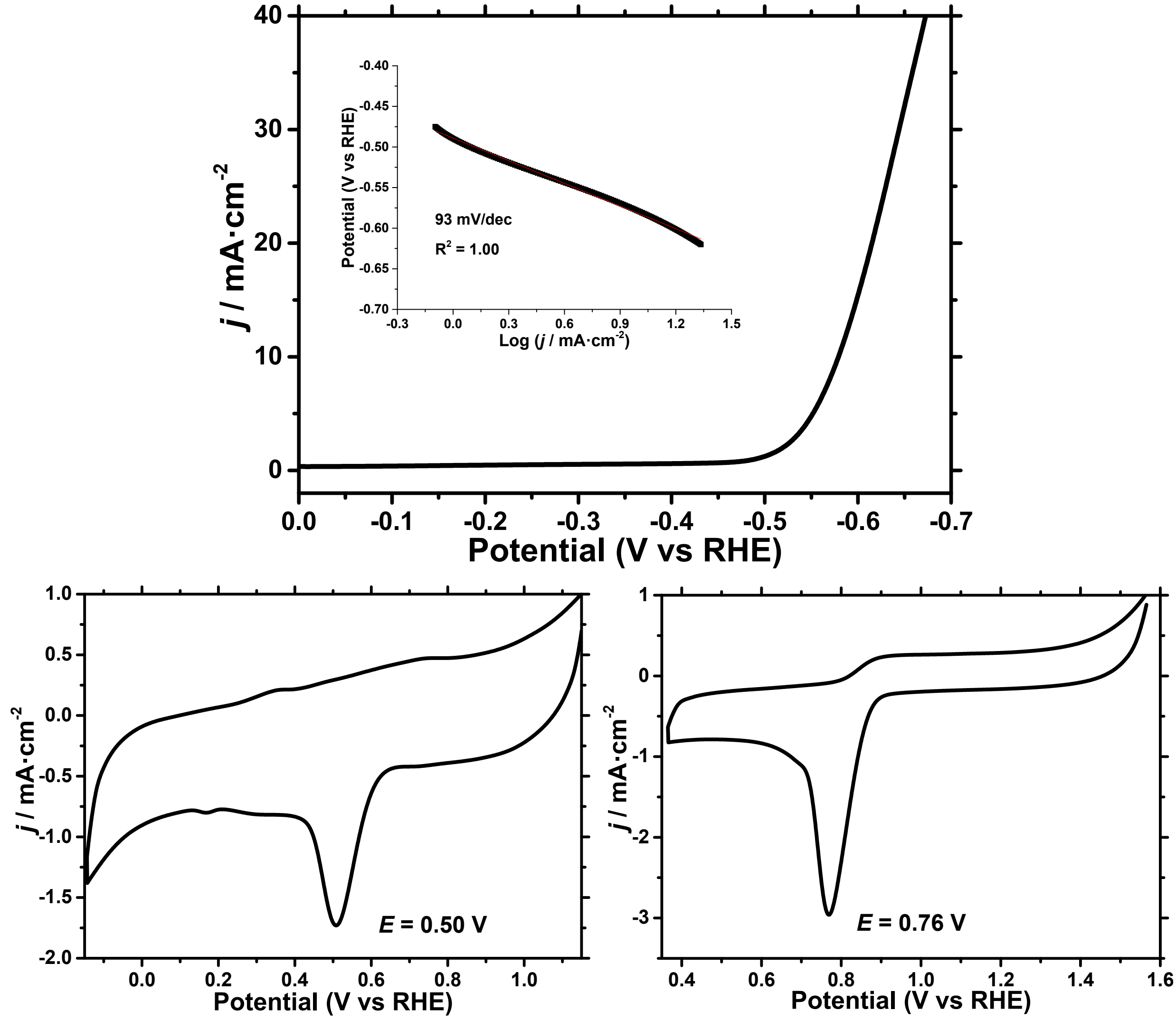


Figure S4. (a) LSV measurements of rGO supported Co(III)PPh$_3$triphenylcorrole in 0.5M H_2SO_4 under N_2; (inner: Tafel slope); (b) CV of rGO supported Co(III)PPh$_3$triphenylcorrole in 0.5M H_2SO_4 under O_2; (c) CV of rGO supported Co(III)PPh$_3$triphenylcorrole in 0.1M NaOH under O_2.

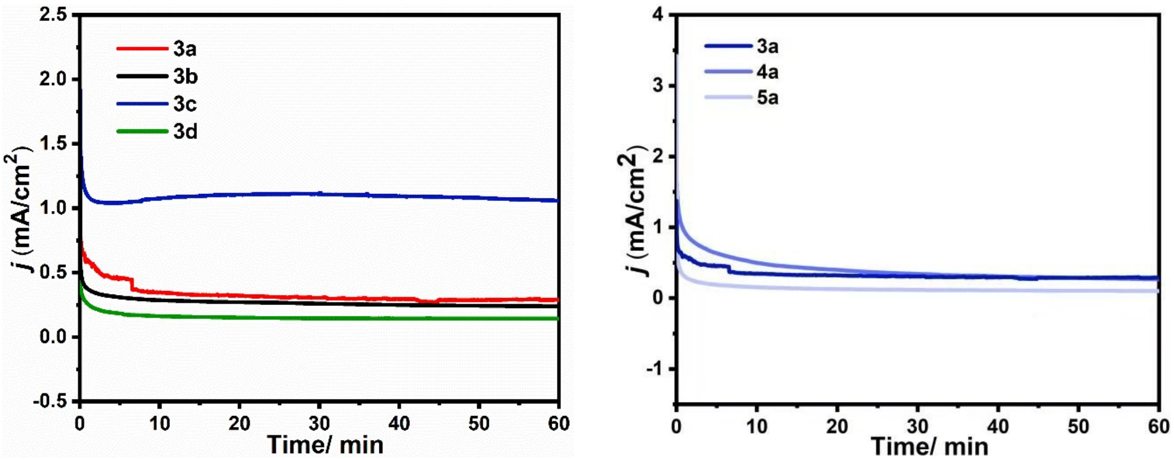


Figure S5 *i*-t curve of rGO supported **3a**-**d** and **3a**-**5a** in 0.5M H_2SO_4 under N_2.