## Supporting Information

# Synthesis of Conjugated Porous Co(II) Porphyrinylene-Ethynylene Framework Through Alkyne Metathesis and Its Catalytic Activity Study

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#### 1. Materials and measurements

All reagents and solvents were used as received from commercial suppliers unless otherwise noted.

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. Solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on an Inova 400 NMR spectrometer.

The XPS data are collected using a PHI 5600 X-ray photoelectron spectrometer with a standard dual Mg-K $\alpha$ /Al-K $\alpha$  anode X-ray excitation source; the data reported here were acquired using Mg anode (*hv* =1253.6 eV).

The FT-IR spectra of starting materials and as synthesized CoPEF were obtained from Thermo Nicolet Avatar-370 spectrometer using KBr pellets.

Scanning Electron Microscopy (SEM) images were recorded using a JSM-6480LV (LVSEM) at 5.0 kV. The samples were sputter coated with gold prior to the analysis.

Electrochemical measurements of cyclic voltammetry (CV) were performed using a computer-controlled electrochemical workstation (CHI 850D, Shanghai CH Instrument, China). Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) experiments were performed using a computer-controlled potentiostat (Pine Instrument Company, USA) with a three-electrode cell system. A glassy carbon RDE (Autolab), an Ag/AgCl (NaCl, 3 M) electrode, and a Pt wire were used as the working electrode, the reference electrode, and the counter electrode, respectively.

The onset potentials were determined from the intersection of the tangents between the baseline and the signal current, as shown in Figure S1.

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### 2. Synthetic procedures



Monomer 1: Monomer 1 (M1) was prepared following the coupling procedure reported in the literature. <sup>1</sup> A 25 mL Schlenk tube was charged with 5,10,15,20-tetrakis(4'bromophenyl)porphyrin Cobalt(II) (1.0 g, 1.1 mmol) and degassed three times. Then, Pd(PPh<sub>3</sub>)<sub>4</sub> (340 mg, 0.30 mmol) and anhydrous THF (3 mL) were added in a glovebox. A solution of ZnBr<sub>2</sub> (1.56 g, 6.9 mmol) and 1-propynyllithium (350 mg, 7.4 mmol) in anhydrous THF (3 mL) was added dropwise. An additional THF (2 mL) was added to the mixture. The resulting mixture was sealed and heated at 85 °C overnight under nitrogen atmosphere. It was then cooled to room temperature. Distilled water (30 mL) was added to the mixture and the product was extracted with  $CH_2Cl_2$  (4 × 60 mL). The combined organic layer was washed with water (100 mL) and brine (100 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by using a Rotavap, and the crude product was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub> as the eluent) to yield the pure compound M1 as a dark purple solid (0.72 g, 81%): UV-

<sup>&</sup>lt;sup>1</sup> Y. Zhu, H. Yang, Y. Jin, W. Zhang, Chem. Mater. 2013, 25, 3718.

Vis (λ: nm; DMF solution):434, 548, and 590 (Fig. S1); FT-IR (v: cm<sup>-1</sup>) (Fig. S2): 1002 (δ Co–N), 1587 (C=N), 2217, and 2252 (C=C).

**5, 10, 15, 20-tetrakis(4'-propynylphenyl)porphyrin (TPPP)**: The compound was prepared following the procedure for **M1** described above.

**Co(II) Porphyrinylene-Ethynylene Framework (CoPEF):** The triphenolsilane (4.9 mg, 0.012 mmol) and molybdenum(VI) trisamide precursor (8.0 mg, 0.012 mmol) were premixed in dry CCl<sub>4</sub> (2 mL) for 15 minutes at room temperature to generate the catalyst **2** *in situ*. Subsequently, a solution of **M1** (165 mg, 0.20 mmol) in CHCl<sub>3</sub> (10 mL) was added, followed by 5 Å molecular sieves (1.0 g, pellet, 8 – 12 mesh). The reaction was heated at 55 °C for 24 h. The suspension was separated from the molecular sieves by careful decantation. The solid was collected by filtration, washed with CHCl<sub>3</sub> until the color of the solution became colorless, and dried under high vacuum to give the product (75 mg, 52%): UV-Vis ( $\lambda$ : nm; DMF solution):440, 555, and 598 (Fig. S1). FT-IR (v: cm<sup>-1</sup>) (Fig. S2): 1004 ( $\delta$  Co-N), 1579 (C=N), 2217, and 2252 (C=C); *S*<sub>BET</sub> = 310 m<sup>2</sup>/g (Fig. S5). X-ray photoelectron spectroscopy (XPS) analysis: carbon (76.18%), cobalt (3.21%), nitrogen (5.07%), oxygen (10.65%), and chloride (4.89%). The chloride element is likely from the solvent residue (CCl<sub>4</sub>/CHCl<sub>3</sub>) remained inside of the porous structure.

**Porphyrinylene-ethynylene framework (PEF):** The analogous framework without cobalt (II) ions was prepared following the procedure for CoPEF described above.

#### **3. Electrochemical characterization of ORR**

The electrochemical experiments were conducted in  $O_2$  saturated aqueous 0.1 M KOH or 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte for the oxygen reduction reaction (ORR). The potential range was cyclically scanned between -0.8 and 0.2 V in aqueous 0.1 M KOH or between -0.2 and 0.8 V in aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 100 mV s<sup>-1</sup> at room temperature after purging  $O_2$  or  $N_2$  for 25 minutes. RDE measurements were conducted at different rotating speeds from 225 to 2500

rpm, using an Autolab Model. RRDE measurements were carried out at 1600 rpm with an Autolab Model.

The temporarily stable suspension of the composite **CoPEF/C** (3 wt% Co content) was prepared by dispersing **CoPEF** (5.8 mg) and carbon black (10.2 mg) in DMF (0.6 mL) and nafion (0.2 mL, 5 wt%) and subsequent sonication for around 30 min. Similarly, the suspension of **M1/C** was prepared from **M1** (6.9 mg), carbon black (9.1 mg), DMF (0.6 mL), and nafion (0.2 mL). Pt/C (1.6 mg, 20 wt%) was used to prepare Pt/C suspension in DMF (0.6 mL) and nafion (0.2 mL). The above suspensions of 5  $\mu$ L and 13.8  $\mu$ L were then drop-cast on the surfaces of the pre-polished glassy carbon electrode (3 mm in diameter) and RDE electrode (5 mm in diameter), respectively. The electrodes were then dried overnight at room temperature before the measurement.

Table S1. Loading amount of CoPEF/C catalyst materials on glassy carbon electrode

| Molar loading of         | Areal loading of         | Areal loading of            | Areal loading of              |
|--------------------------|--------------------------|-----------------------------|-------------------------------|
| Co (mM/cm <sup>2</sup> ) | Co (mg/cm <sup>2</sup> ) | CoPEF (mg/cm <sup>2</sup> ) | CoPEF/C (mg/cm <sup>2</sup> ) |
| $7.07 \times 10^{-4}$    | 4.2×10 <sup>-2</sup>     | 0.506                       | 1.4                           |

Table S2. Loading amount of 20 wt% Pt/C catalyst materials on glassy carbon electrode

| Molar concentration of   | Areal loading of Pt   | Areal loading of 20 wt%    |
|--------------------------|-----------------------|----------------------------|
| Pt (mM/cm <sup>2</sup> ) | (mg/cm <sup>2</sup> ) | Pt/C (mg/cm <sup>2</sup> ) |
| 1.52×10 <sup>-4</sup>    | 3×10 <sup>-2</sup>    | 0.15                       |

Koutecky–Levich (K-L) equations were used to analyze the data from RDE measurements:

$$\frac{1}{j_{Lim}} = \frac{1}{j_{Lev}} + \frac{1}{j_k}$$
(1)

$$j_{Lev} = 0.62nFCD^{2/3}v^{-1/6}\omega^{1/2}$$
<sup>(2)</sup>

$$j_k = nFkC\Gamma \tag{3}$$

Where, *j* is the measured current density,  $\omega$  is the electrode rotation rate, *F* is the Faraday constant  $C_0$  is the bulk concentration of  $O_2$ ,  $D_0$  is the diffusion coefficient of  $O_2$ , *v* is the kinetic viscosity of the electrolyte, and *k* is the electron-transfer rate constant.

 Table S3. Parameters for Koutecky–Levich equations.

| Solution                             | F (C mol <sup>-1</sup> ) | C <sub>0</sub> (mol cm <sup>-3</sup> ) | $D_0 (cm^2 s^{-1})$  | $\nu (\mathrm{cm}^2 \mathrm{s}^{-1})$ |
|--------------------------------------|--------------------------|--|----------------------|---------------------------------------|
| 0.5 M H <sub>2</sub> SO <sub>4</sub> | 96485                    | 1.1×10 <sup>-6</sup>                   | 1.4×10 <sup>-5</sup> | 0.01                                  |
| 0.1 M KOH                            | 96485                    | 1.2×10 <sup>-6</sup>                   | 1.9×10 <sup>-5</sup> | 0.01                                  |

The electron transfer numbers (*n*) were calculated from RRDE measurements based on the disk current (I  $_{disk}$ ) and ring current (I  $_{ring}$ ) via the following equation:

$$n = 4I_{disk} / (I_{disk} + I_{ring} / N)$$
(4)

where N is current collection efficiency of the Pt ring and equal to 25.6%.



**Fig. S1.** UV-vis spectra of **M1** and **CoPEF**. The concentration of **M1** solution in DMF was 0.016 mg/mL. The sample of **CoPEF** was prepared by dispersing **CoPEF** (1 mg) in DMF (25 mL) and then sonicating the suspension overnight.



**Fig. S2.** FT-IR spectra of **TPPP** (red), **M1** (green), **PEF** (black) and **CoPEF** (blue) (a); enlarged 2030-2470 cm<sup>-1</sup> range (b), enlarged 850–1350 cm<sup>-1</sup> range (c), and enlarged 3100–3810 cm<sup>-1</sup> range (c). Two C=C stretch bands around 2190-2270 cm<sup>-1</sup> diminished compared to those observed for **M1**, indicating the formation of symmetrical alkyne bonds in the framework from the asymmetrical propynyl groups in the **M1**. In the IR spectra of **CoPEF**, the N-H stretch band around 3317 cm<sup>-1</sup> is absent and strong N–Co vibration band<sup>2</sup> around 1002 cm<sup>-1</sup> was observed, indicating the presence of Co(II) in the framework.

<sup>&</sup>lt;sup>2</sup> Z. S. Wu, L. Chen, J. Z. Liu, K. Parvez, H. W. Liang, J. Shu, H. Sachdev, R. Graf, X. Feng, K. Müllen, *Adv. Mater.* 2014, **26**, 1450.



Fig. S3. The solid state <sup>13</sup>C NMR spectrum of CoPEF.



Fig. S4. Powder X-ray diffraction pattern of CoPEF.



Fig. S5. Thermogravimetric analysis (TGA) curve of CoPEF.



**Fig. S6.** SEM images of **CoPEF** (a), carbon black (b), **CoPEF/C** (c), and the mixture of **CoPEF/C** and Nafion (d). The solid samples of **CoPEF** and carbon black were used directly for images a and b. The samples for images c and d were prepared by drop-casting the suspension of the sample mixture in DMF.



Fig. S7. The determination of onset potential.



Fig. S8. Cyclic voltammetry (CV) curves of CoPEF/C and PEF/C in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>.



Fig. S9. Open circuit potential (OCP) of CoPEF/C and M1/C in 0.5 M  $H_2SO_4$  (a); and 0.1 M KOH (b).



**Fig. S10**. Linear sweep voltammetry (LSV) curves for 20 wt% Pt/C at different rotation rates in RDE measurements in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 10 mV s<sup>-1</sup> (a) and the corresponding Koutecky–Levich (K-L) plots (b). The inset shows the average *n* values of 20 wt% Pt/C calculated from RDE against the electrode potential.



**Fig. S11**. Linear sweep voltammetry (LSV) curves for 20 wt% Pt/C at different rotation rates in RDE measurements in O<sub>2</sub>-saturated 0.1 M KOH at 10 mV s<sup>-1</sup> (a) and the corresponding Koutecky–Levich (K-L) plots (b). The inset shows the average *n* values of 20 wt% Pt/C calculated from RDE against the electrode potential.



Fig. S12. CV curves of 20 wt% Pt/C in  $O_2$ - and  $N_2$ -saturated in 0.5 M H<sub>2</sub>SO<sub>4</sub> at the scanning rate of 0.1 V s<sup>-1</sup>.



Fig. S13. Durability evaluation of CoPEF/C, M1/C and 10 wt% Pt/C in  $O_2$ -saturated 0.1 M KOH.