Supporting Information

Efficacious Electrochemical Oxygen Evolution from Novel Co (II) Porphyrin-Pyrene based Conjugated Microporous Polymer

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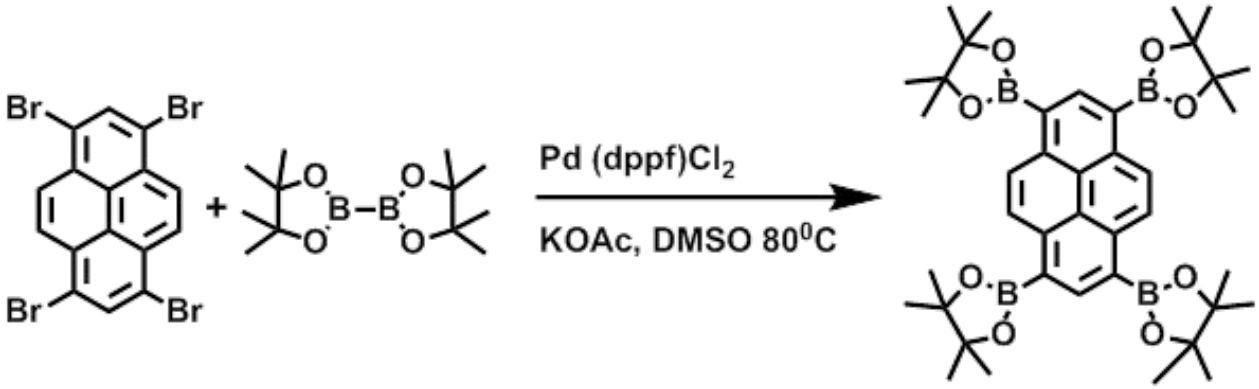
Section S1

1.Synthesis

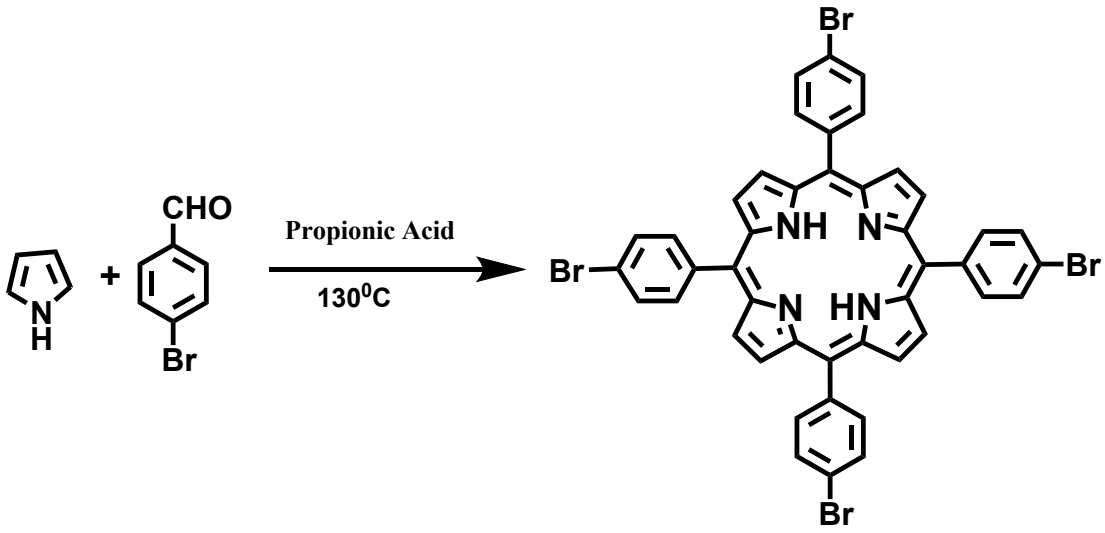
1.1. Synthesis of 1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene

1,3,6,8-tetrabromopyrene (1.0 g, 1.9 mmol) and bis(pinacolato)diboron (2.9 g, 11.4 mmol) and potassium acetate (1.2 g, 11.9 mmol) was taken in a predried scelnk flask. Pd(dppf)Cl_2 (0.12 g, 0.16 mmol) was added in anhydrous DMSO (20 mL) and transfer this slurry to the sclenk flask via cannula. The mixture was degassed properly via three freeze pump thaw cycles prior to heating. Then the reaction mixture was stirred at 80 °C for 72 h under inert atmosphere. The reaction mixture was allowed to cool down and extracted with dichloromethane. The organic layer was passed through a short column to remove the catalyst and solvent was completely removed by the evaporation to affort the greenish white solid. Then the solid was washed extensively with hot toluene to obtain the product as pale white solid (980 mg, 72%).



1.2. 5,10,15,20-(tetra-4-bromophenyl)porphyrin Cobalt (II)

A mixture of p-bromobenzaldehyde (1.86 g, 10 mmol) in propionic acid (40 mL) was heated up to 120 °C and then freshly distilled pyrrole (0.7 mL, 10 mmol) was added to the mixture. The mixture was stirred at 120 °C for 3h and cooled to room temperature for 3 days. The blackish violet precipitate was collected through filtration and washed with methanol extensively. The crude mixture was recrystallized from chloroform/methanol mixture to get the pure product as an needle like violet crystal (540 mg, 23%). The metalation step had been done by the mixing of methanolic solution (20 ml) of 5,10,15,20-(tetra-4-bromophenyl)porphyrin (0.54 g, 0.575 mmol) with $Co(OAc)_2$, $4H_2O$ (143.21 mg, 0.575 mmol) and reflux for 4 h. purple solid was obtained through filtration (453 mg, 81%).



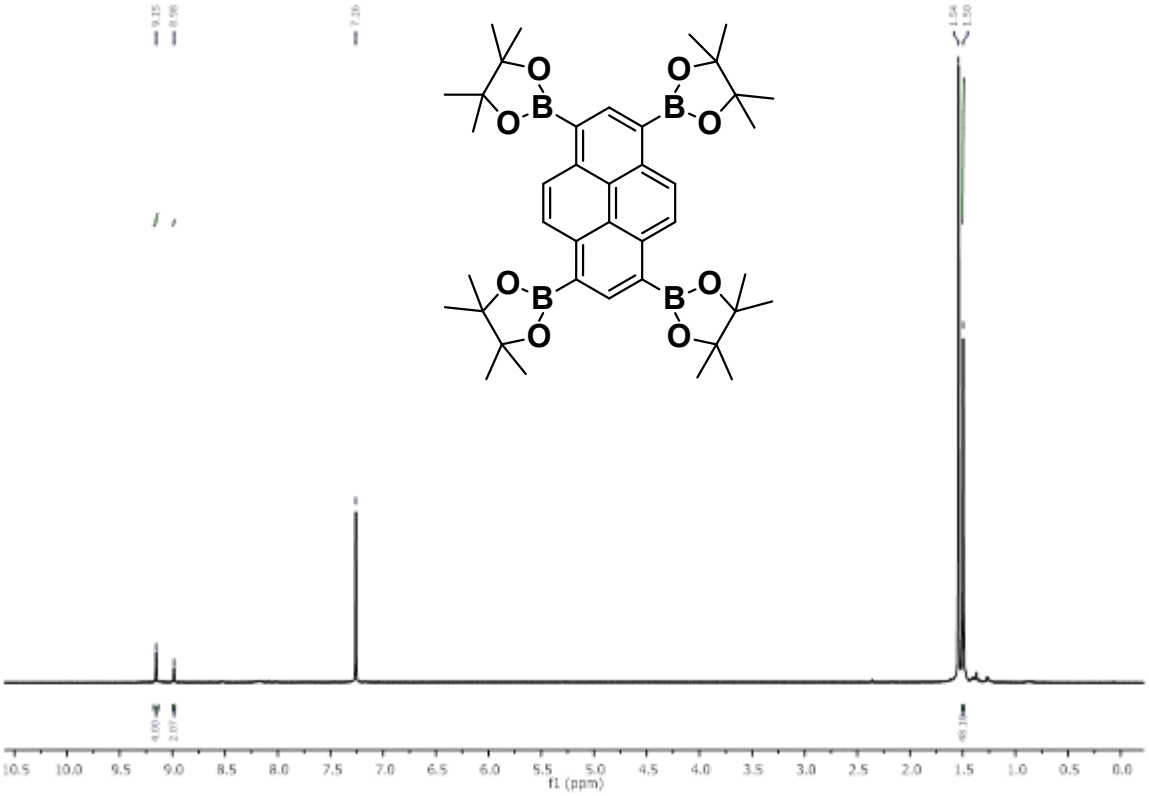


Figure S1a. ^{1}H NMR of 1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene

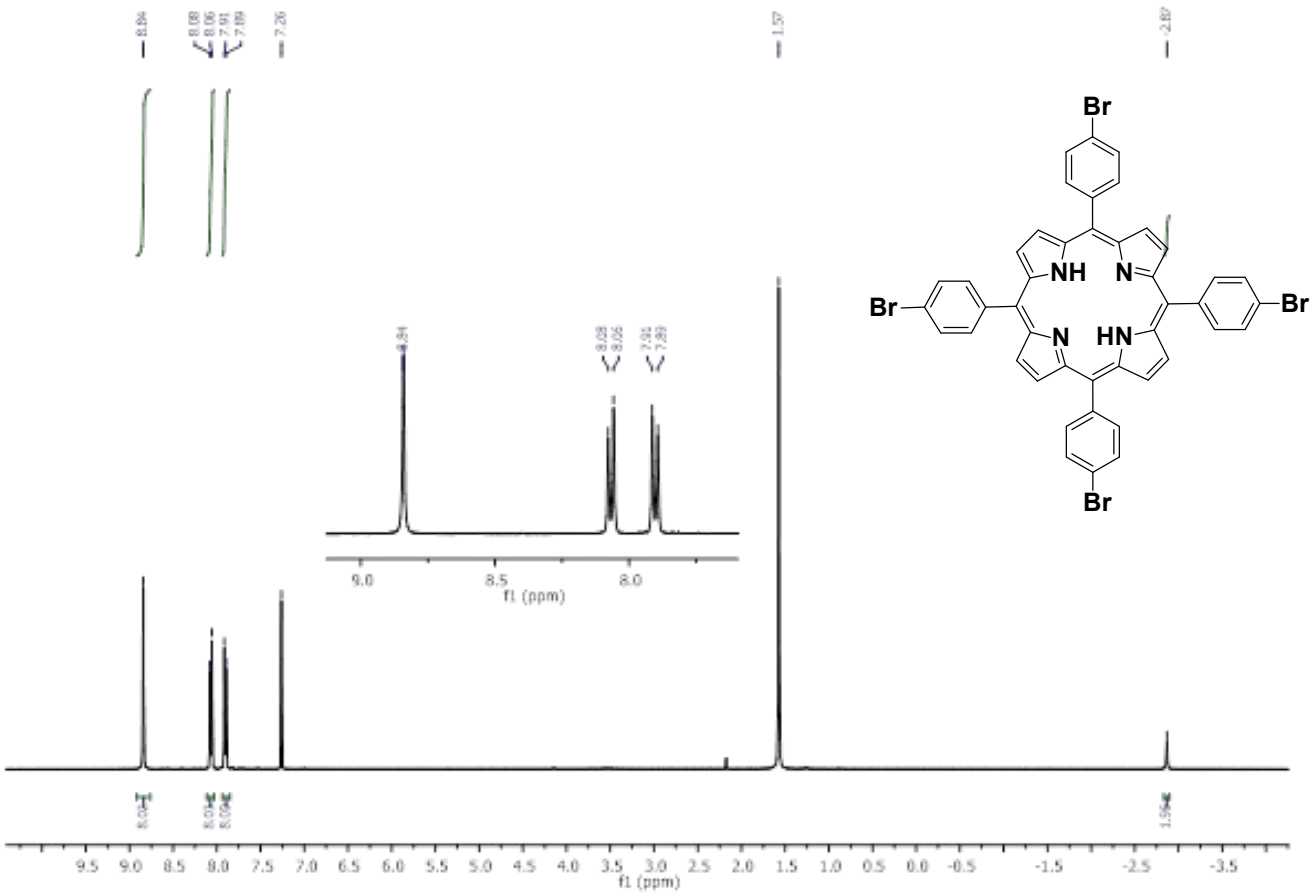


Figure S1b. ^{1}H NMR of 5,10,15,20-(tetra-4-bromophenyl)porphyrin

Figure S2

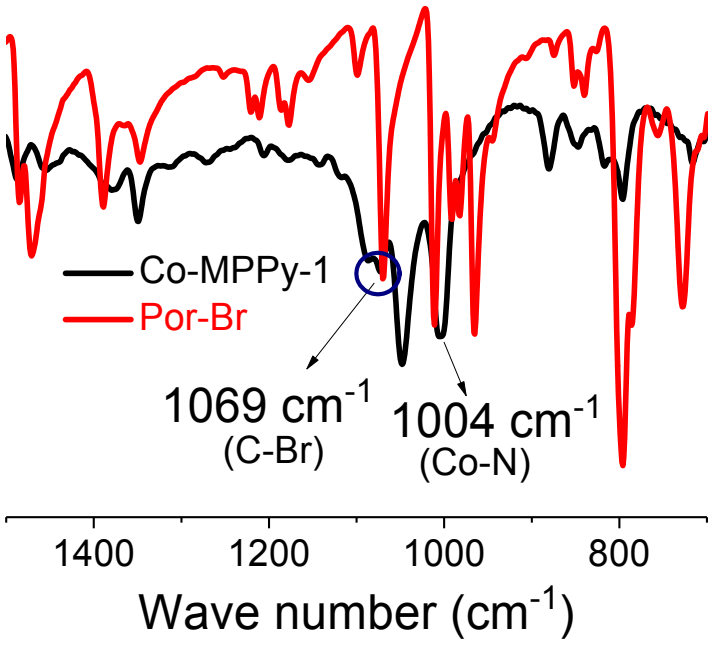


Figure S2. Absence of C-Br bond in Co-MPPy-1 (blue encircled) and the C-Br bond in Por-Br (monomer)

Figure S3

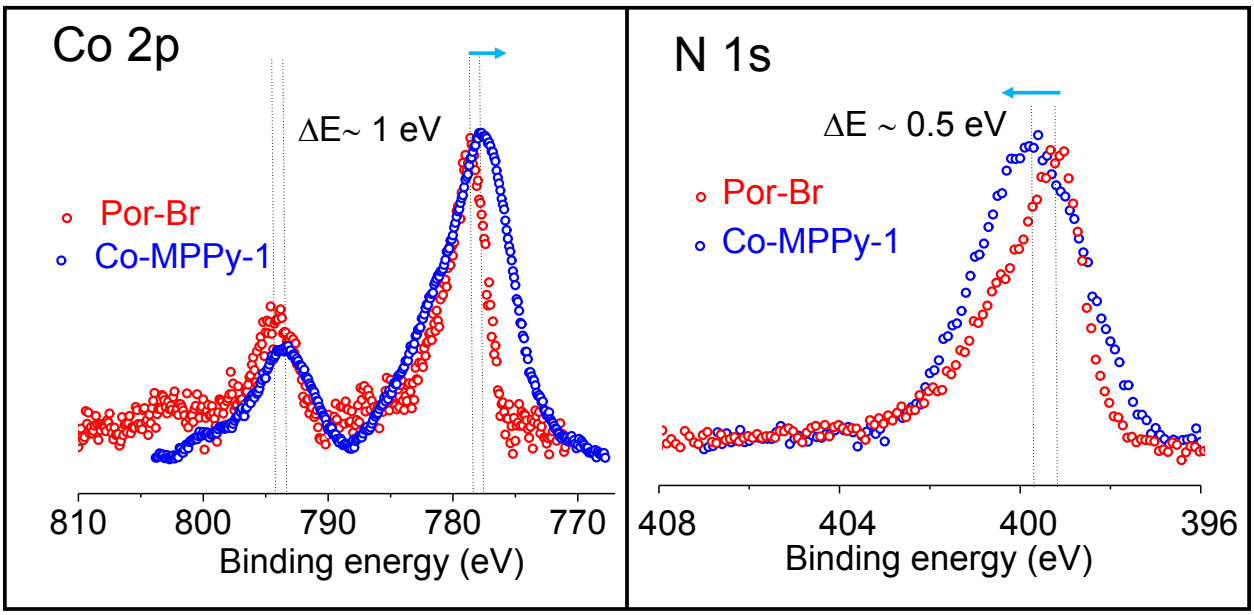


Figure S3. XPS analysis of Co-MPPy-1 (blue solid line) and Por-Br monomer (red solid line) for Co 2p (left) and N 1s (right)

Figure S4

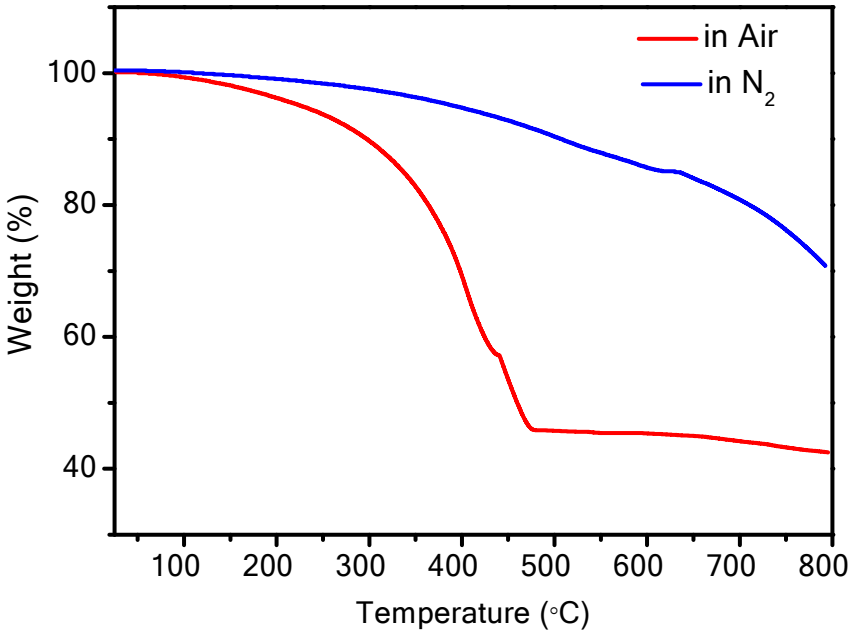


Figure S4. Thermo-gravietric analysis (TGA) of Co-MPPy-1 in presence of air (red solid line) and N_2 (blue solid line)

Figure S5

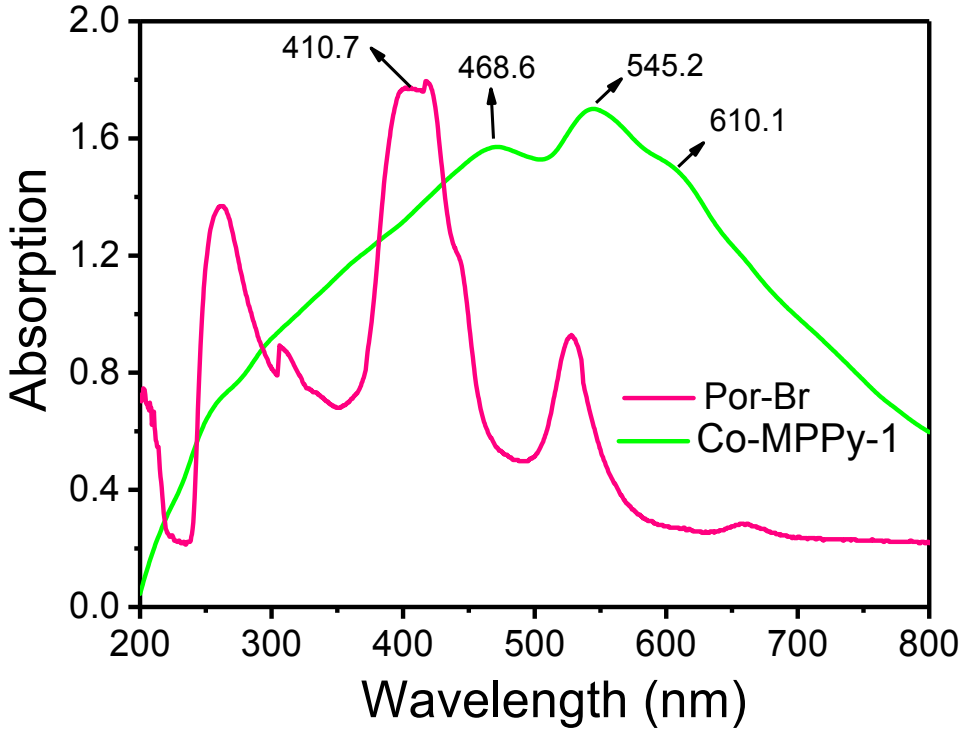


Figure S5. a) Solid state UV-vis spectra of Co-MPPy-1 electrocatalyst (green solid line) and the UV-vis spectra of Por-Br monomer (pink solid line) in $CHCl_3$.

Figure S6

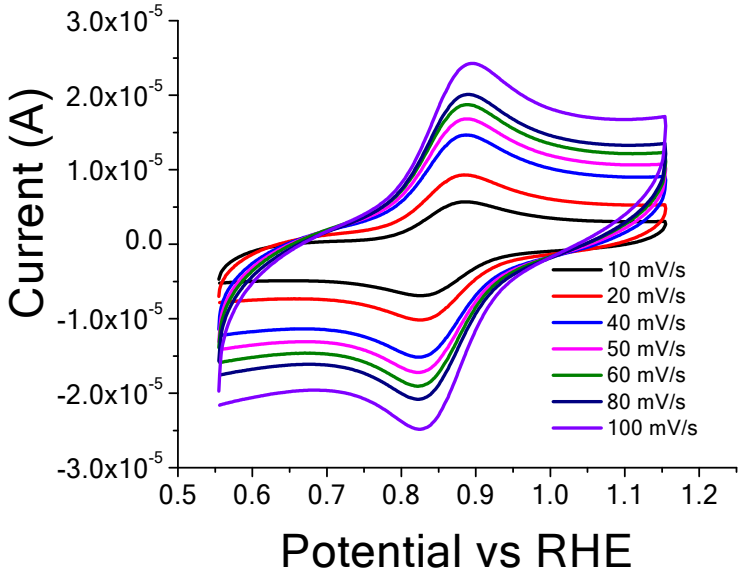


Figure S6. CV in different scan rate in 1mM solution of potassium ferricyanideK_3[Fe(CN)6] in 0.1 M pH 7 phosphate buffer solution.

Section S2

a) Areal catalyst loading on rotating disc electrode (RDE)

Area loading of Co-MPPy-1 (mg/cm²)	Area loading of Co (mg/cm²)	Area loading of Co (mM/cm²)
0.571	2.8×10^{-2}	4.7×10^{-4}

b) Calculation of Surface Coverage (τ_o) and number of active cobalt mol/m² in Co-MPPy-1

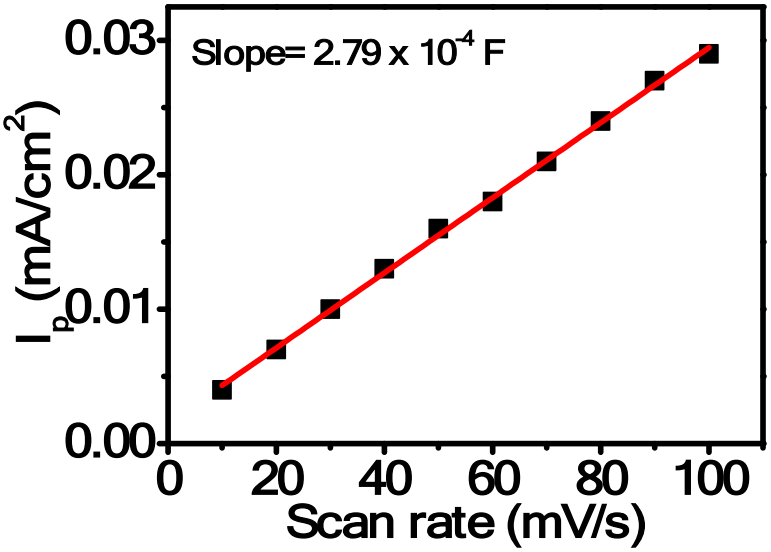


Figure S7. Linear fit of the plot of i_p vs scan rate.

CV of Co-MPPy-1 coated GC electrode had been taken at different scan rate to determine the active Co atom (mol/cm^2) at the surface. The surface coverage of active cobalt atom was determined by the slope of anodic current corresponding to Co^{2+}/Co^{3+} redox system vs scan rate (mV/s) using the following equation.

$$\textbf{Slope} = n^2 F^2 A\tau_o/4RT$$

n = number of electrons involved; F = Faraday Constant in C/mol; A = geometrical surface area of the electrode (0.07 cm^2); τ_o = surface coverage, R = gas constant; T = temperature (K).

The surface coverage of the cobalt atom was 4.23 x 10^{-9} mol/ cm^2.

Turn over frequency calculation (TOF)

$$TOF = \frac{(J \times A)}{(4 \times F \times m)} = 0.43/\text{ sec.}$$

J= Current density (A/cm^2) at overpotential 420 mV.

A= Geometrical surface area of the RDE.

F= 96500 C/mol.

m= moles of the active cobalt atom present on electrode.

Figure S8

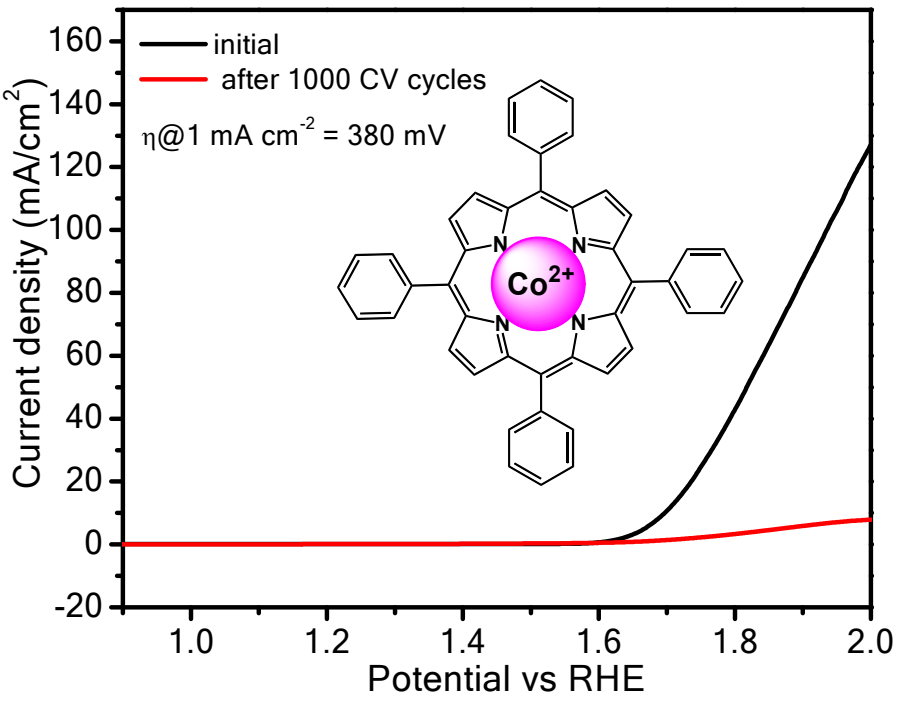


Figure S8. Initial LSV study (black solid line) and final LSV study after 1000 cycle (red solid line) of *meso*-Tetraphenylporphyrin cobalt(II) complex (Por-Br)

Table S1

Benchmarking of cobalt based OEC with Co-MPPy-1

Electrocatalyst	Overpotential (η)	references
Co_3O_4/mMWCNT	510 mV@10 mA/cm^2	2
Co_3O_4/graphene (CG–CoO)	430 mV@10 mA/cm^2	3
Co-TpBpy (COF material)	400 mV@1 mA/cm^2	4
(CoP)n-MWCNTs (carbon nanotube)	300 mV@1 mA/cm^2	5
FeTPyP-Co (Bimetallic MOF)	430 mV@1 mA/cm^2	6
Co−Fe Prussian Blue (Co-ordination polymer)	400 mV@ 1 mA/cm^2	7
Co-N-doped carbon	371 mV@10 mA/cm^2	8
Co-MPPy-1	**340 mV@1 mA/cm^2** **420 mV@ 10 mA/cm^2**	**-This work-**

References

1. Han, A.; Jia, H.; Ma, H.; Ye, S.; Wu, H. ; Lei, H.; Han, Y.; Cao, R. ; Du, P. *Phys. Chem. Chem. Phys*. **2014**, *16*, 11224-11232 .
2. Lu, X.; Zhao, C. *J. Mater. Chem. A* **2013**, *1*, 12053–12059.
3. Mao, S.; Wen, Z.; Huang, T.; Hou Y.; J. Chen, *Energy Environ. Sci.* **2014**,*7,* 609-616.
4. Aiyappa, H. B.; Thote, J.; Shinde, D. B.; Banerjee, R.; Kurungot, S. *Chem. Mater.* **2016**, *28*, 4375−4379.
5. Jia, H.; Sun, Z.; Jiang, D.; Du, P. *Chem. Mater.* **2015**, *27*, 4586−4593.
6. Wurster, B.; Grumelli, D.; Hötger, D.; Gutzler, R.; Kern, K. *J. Am. Chem. Soc.* **2016**, *138*, 3623−3626.
7. Pintado, S.; Goberna-Ferrón, S.; Escudero-Adán, E. C.; Galán-Mascarós, J. R. *J. Am. Chem. Soc.* **2013**, *135*, 13270−13273.
8. Su, Y.; Zhu, Y.; Jiang, H.; Shen, J.; Yang, X.; Zou, W.; Chen, J., Li, C. *Nanoscale* **2014**, *6*, 15080-15089.