

## Supporting Information for:

### Changing the selectivity of O<sub>2</sub> reduction catalysis with one ligand heteroatom

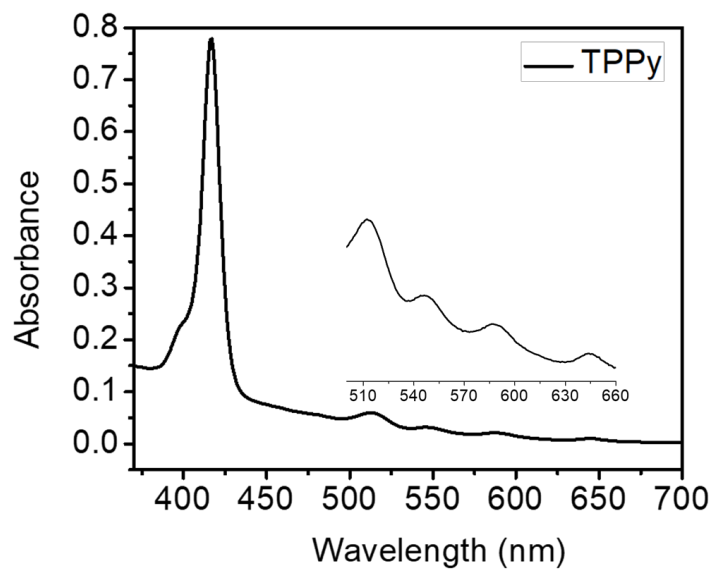
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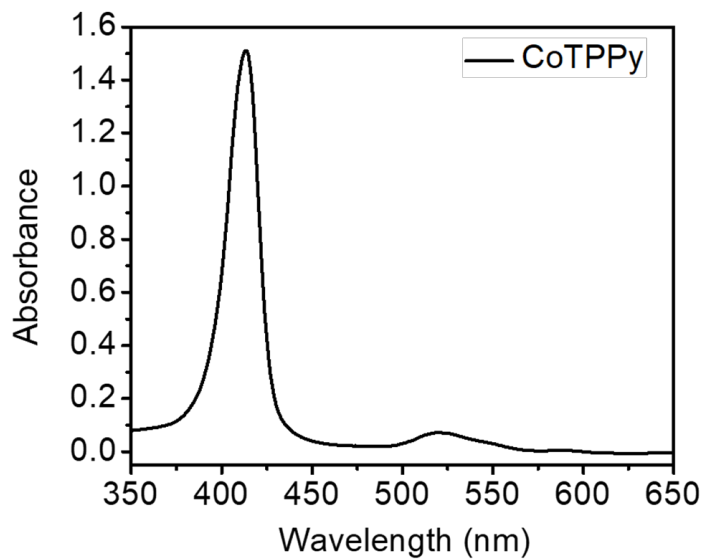
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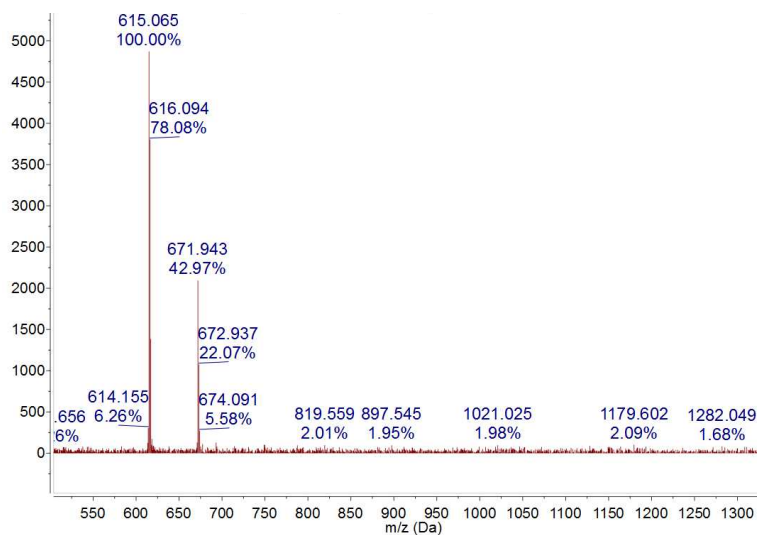
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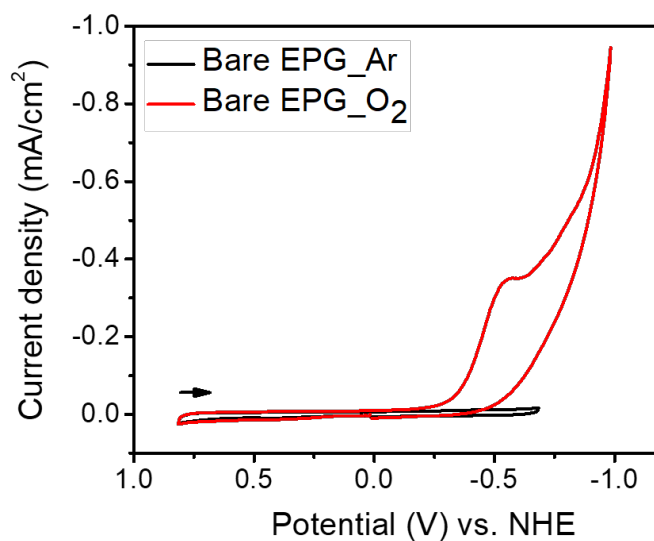
**Figure S1.** Absorption spectrum for TPPy ligand ( $\lambda_{\text{max}}$ ; 416 nm (Soret), 512 nm, 546 nm, 587 nm, and 644 nm) in dichloromethane.



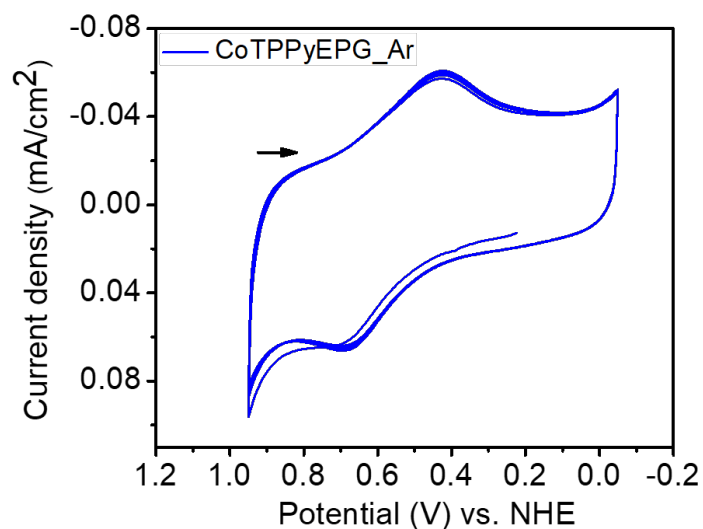
**Figure S2.** Absorption spectrum for CoTPPy ( $\lambda_{\text{max}}$ ; 412 nm, 521 nm) in dichloromethane.



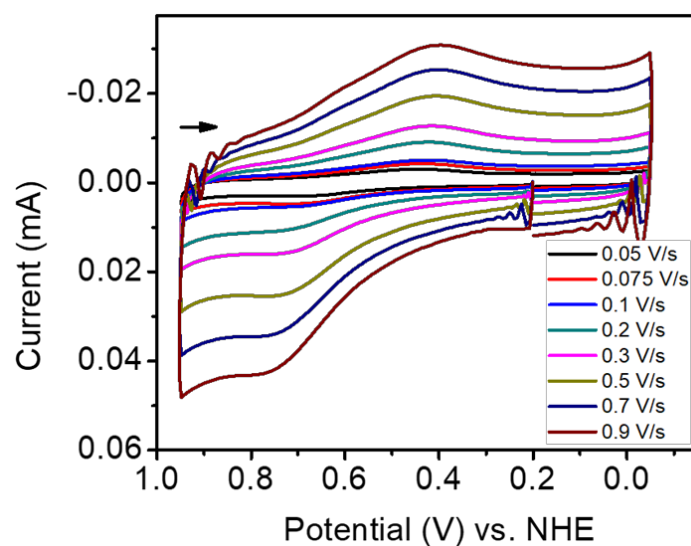
**Figure S3.** MALDI-MS spectrum for CoTPPy showed peaks at 615.06 m/z and 671.94 m/z that correspond to TPy (calcd. 615.24 m/z) and CoTPPy (calcd. 672.16 m/z), respectively.



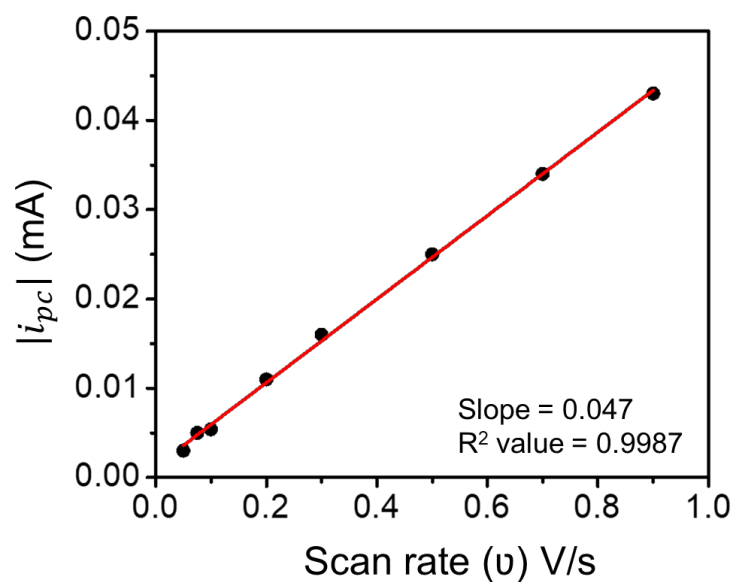
**Figure S4.** Cyclic voltammogram (CV) for bare EPG electrode under Ar- (black) and 1 atm O<sub>2</sub> (red) in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0. The scan rate was 100 mV s<sup>-1</sup> and the arrow shown in the plot indicates the scan direction.



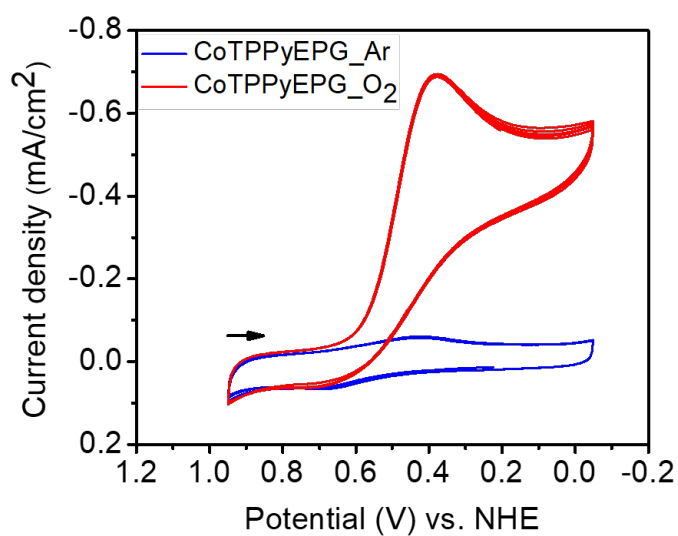
**Figure S5.** Cyclic voltammogram (CV) for CoTPPy immobilized on EPG electrode upon four repeated CV sweeps in Ar-saturated 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0. The scan rate was 100 mV s<sup>-1</sup> and the arrow shown in the plot indicates the scan direction.



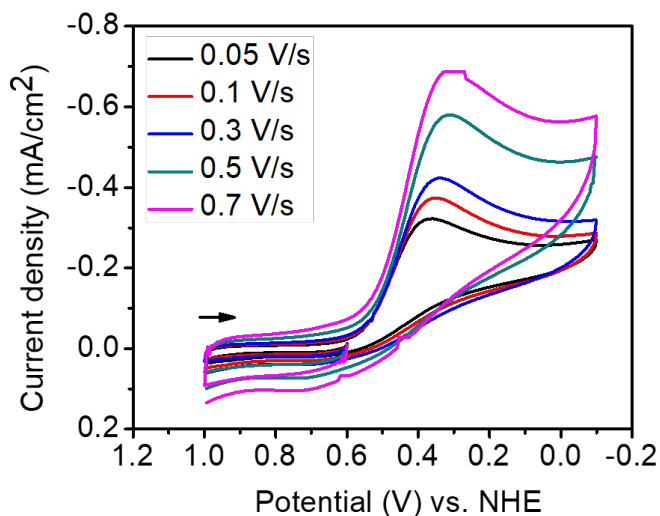
**Figure S6.** Cyclic voltammogram (CV) for CoTPPy immobilized on EPG in Ar-saturated 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0 at different scan rates (50 mV/s – 900 mV/s).



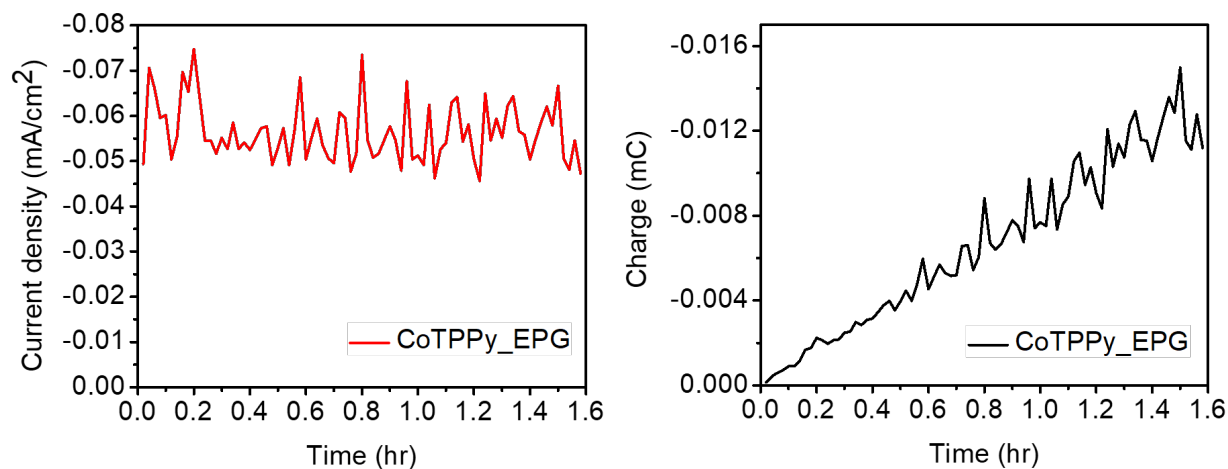
**Figure S7.** Linear fit of the cathodic peak current ( $i_{pc}$ ) vs. scan rate for CoTPPy immobilized on EPG in Ar-saturated 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0 at different scan rates (50 mV/s – 900 mV/s).



**Figure S8.** Cyclic voltammograms (CVs) for the CoTPPy immobilized on EPG electrode under Ar- (blue) and 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0. The scan rate was 100 mV s<sup>-1</sup> and the arrow shown in the plot indicates the scan direction.



**Figure S9.** Cyclic voltammograms (CVs) for CoTPPy immobilized on EPG under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0 at different scan rates (50 mV/s – 700 mV/s).



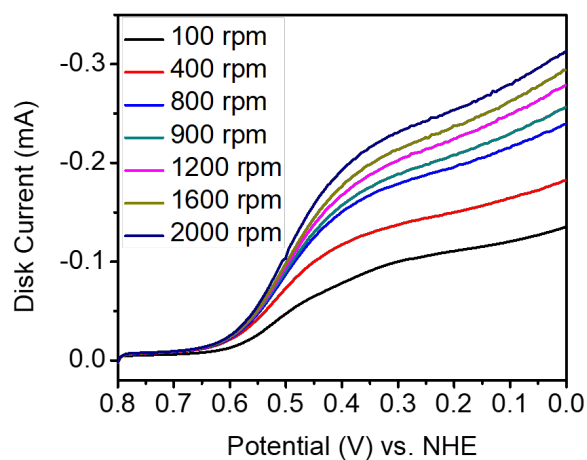
**Figure S10.** Left: Controlled potential electrolysis at 0.38 V vs. NHE for the CoTPPy immobilized on EPG under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0. The solution was continuously stirred during the experiment. Right: The charge passed over time during the electrolysis shown in the left.

### Calculations for RDE experiment:

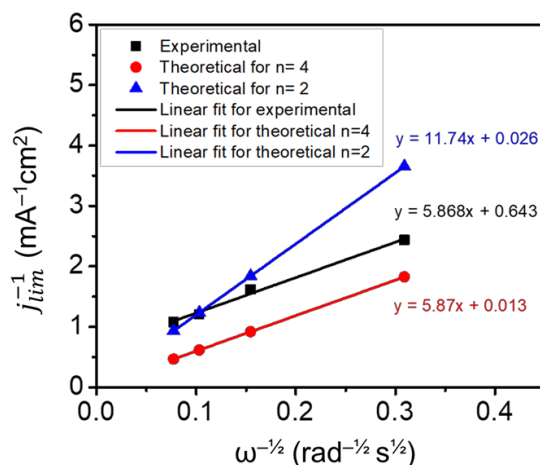
Koutecky-Levich equation<sup>1</sup> was used to calculate the number of electrons ( $n$ ) involved in the catalysis:

$$j_{lim}^{-1} = j_{Lev}^{-1} - j_k^{-1} \quad (S1)$$

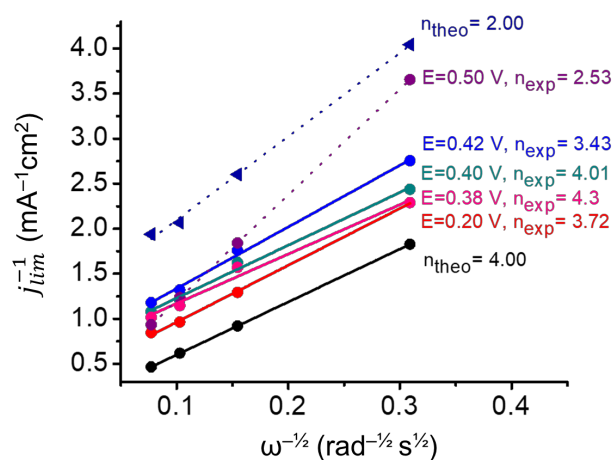
where  $j_{lim}$  is the limiting current density that is the limiting current obtained from the RDE plots for the O<sub>2</sub> reduction at the EPG disk per unit area,  $j_{Lev}$  is the Levich current density =  $0.62 n F C D^{2/3} \nu^{-1/6} \omega^{1/2}$ ;  $F$  is the Faraday constant,  $C$  is the concentration of the O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> at pH 0 (= 0.56 mM),  $\nu$  is the kinematic viscosity of the solution at 22°C = 0.01 cm<sup>2</sup>/s,<sup>2</sup>  $\omega$  = angular velocity of the disk =  $2\pi N/60$  (in sec), where  $N$  is the linear rotation speed, and  $D$  is the diffusion constant obtained from the slop of the scan rate dependence study in the Ar-saturated solution as shown in Figure S7 ( $0.446 F S C \sqrt{f} \sqrt{D} \sqrt{\nu}$  = Slope = 0.047),  $S$  is the electrode area (= 0.15 cm<sup>2</sup>),  $f = F/RT = 38.94$  V<sup>-1</sup>,  $\nu$  is the scan rate (V/s).  $j_k$  = rate of kinetically limited reaction =  $n F C k_{cat} \Gamma_{cat}$ ;  $\Gamma_{cat} = 2.52 \times 10^{-10}$  mol/cm<sup>2</sup>,  $k_{cat}$  is the overall reaction rate constant (M<sup>-1</sup>s<sup>-1</sup>)



**Figure S11.** Limiting currents ( $i_{lim}$ ) obtained from RDE experiments under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0 for the CoTPPy immobilized onto rotating EPG disk electrode at different rotations (100 rpm – 2000 rpm)

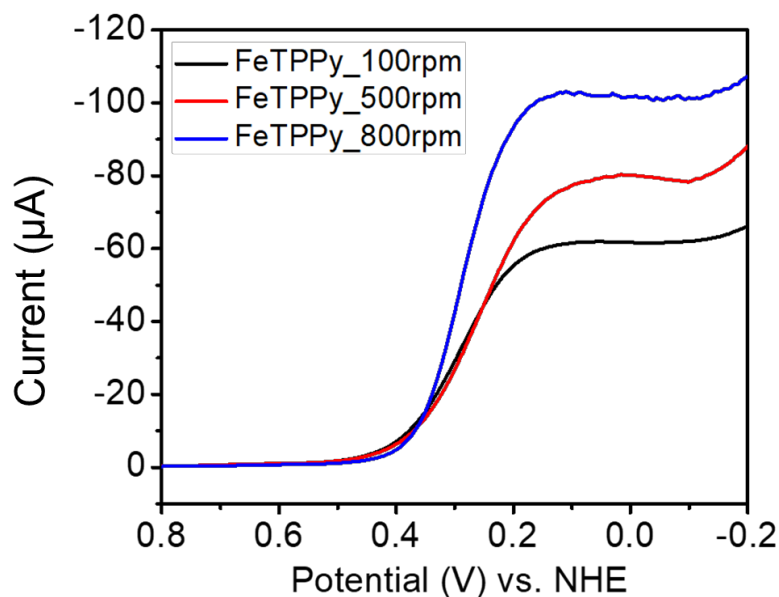


**Figure S12.** Koutecky-Levich (K-L) plots for the CoTPPy at 0.4 V vs. NHE under the identical conditions as Figure S11, and the theoretical (K-L) plots for  $2e^-$  (blue) and  $4e^-$  (red) processes are shown for comparison. The slope obtained from the linear fit of experimental data (black) is 5.868 that corresponds to 4.0 electrons involved in catalysis.

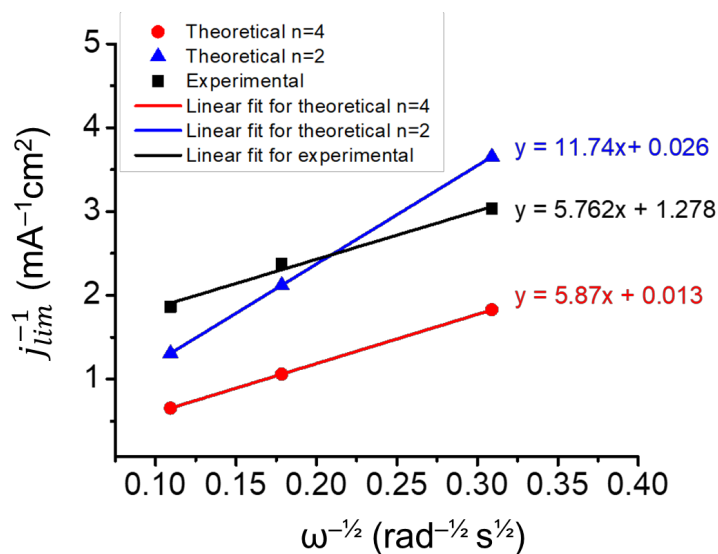


**Figure S13.** Koutecky-Levich (K-L) plots for the CoTPPy at different potentials (as mentioned in the figure) vs. NHE under the identical conditions as Figure S11, and the theoretical (K-L) plots for  $2e^-$  and  $4e^-$  processes are shown for comparison. The number of electrons involved in the catalysis were calculated from the individual slope value and mentioned in the figure as ( $n_{exp}$ ).





**Figure S14.** Limiting currents ( $i_{lim}$ ) obtained from RDE experiments under 1 atm  $O_2$  in 1 M  $H_2SO_4$  solution at pH 0 for the ClFeTPPy immobilized onto rotating EPG disk electrode at three different rotations (100, 500, and 800 rpm).



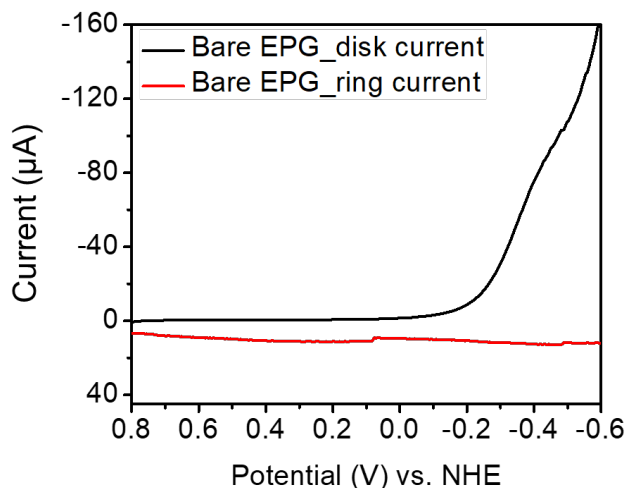
**Figure S15.** Koutecky-Levich (K-L) plots for the ClFeTPPy at -0.11 V vs. NHE under the identical conditions as Figure S14, and the theoretical (K-L) plots for  $2e^-$  (blue) and  $4e^-$  (red) processes are shown for comparison. The slope obtained from the linear fit of experimental data (black) is 5.76 that corresponds to 4.07 electrons involved in catalysis.

### Calculations for RRDE experiments:

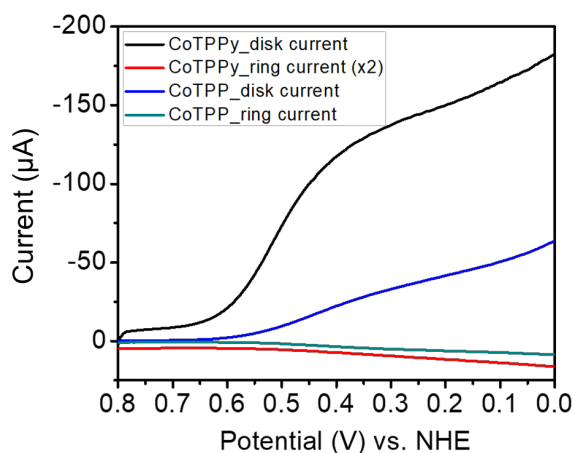
The number of electrons ( $n$ ) involved in the catalysis are calculated considering the equation,

$$n = 4 I_d / (I_d + I_r / N) \quad (\text{S2})$$

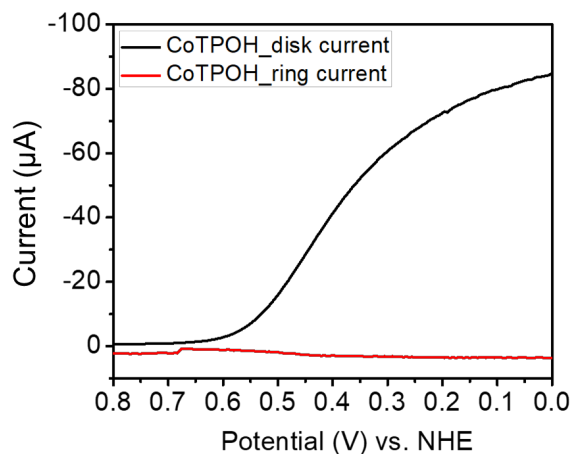
where  $I_d$  and  $I_r$  are the limiting currents obtained for the EPG disk and Pt-ring electrodes, respectively, and  $N$  is the collection efficiency ( $I_r/I_d$ ) of the electrode measured to be 24% using potassium ferricyanide in 1 M  $\text{H}_2\text{SO}_4$  solution.



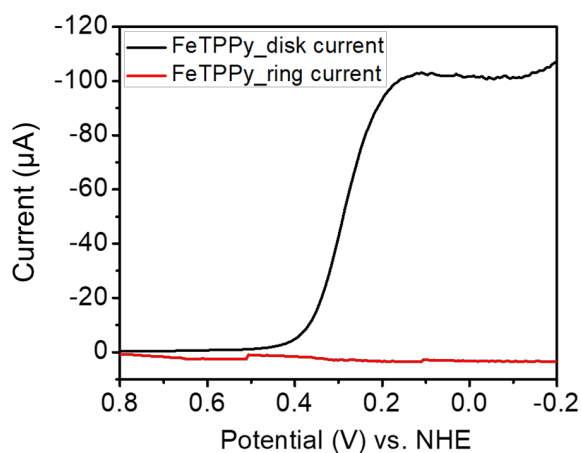
**Figure S16.** RRDE results for the bare rotating EPG disk under 1 atm  $\text{O}_2$  in 1 M  $\text{H}_2\text{SO}_4$  solution (pH 0) at 500 rpm rotation rate. The scan rate was 20 mV/s. Ag/AgCl and Pt-wire were used as the reference and counter electrode, respectively. The potential at the Pt-ring was held at 1.2 V vs. reference electrode.



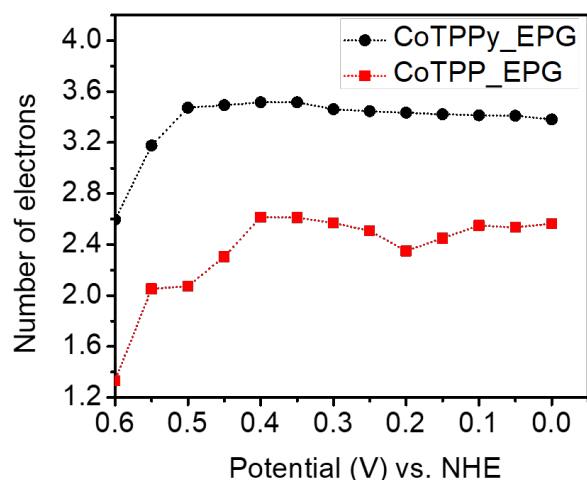
**Figure S17.** RRDE results for the CoTPP and CoTPPy immobilized on the rotating EPG disk under 1 atm  $\text{O}_2$  in 1 M  $\text{H}_2\text{SO}_4$  solution (pH 0) at 500 rpm rotation rate. The scan rate was 20 mV/s. Ag/AgCl and Pt-wire were used as the reference and counter electrode, respectively. The potential at the Pt-ring was held at 1.2 V vs. reference electrode. The ring current for the CoTPPy was magnified by 2 times for clarity.



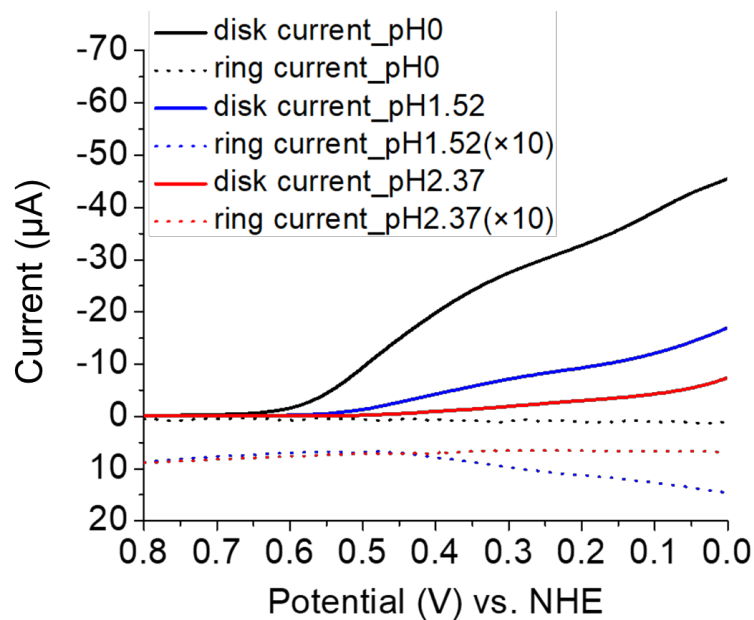
**Figure S18.** RRDE results for the CoTPPOH immobilized on the rotating EPG disk under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution (pH 0) at 500 rpm rotation rate. The scan rate was 20 mV/s. Ag/AgCl and Pt-wire were used as the reference and counter electrode, respectively. The potential at the Pt-ring was held at 1.2 V vs. reference electrode.



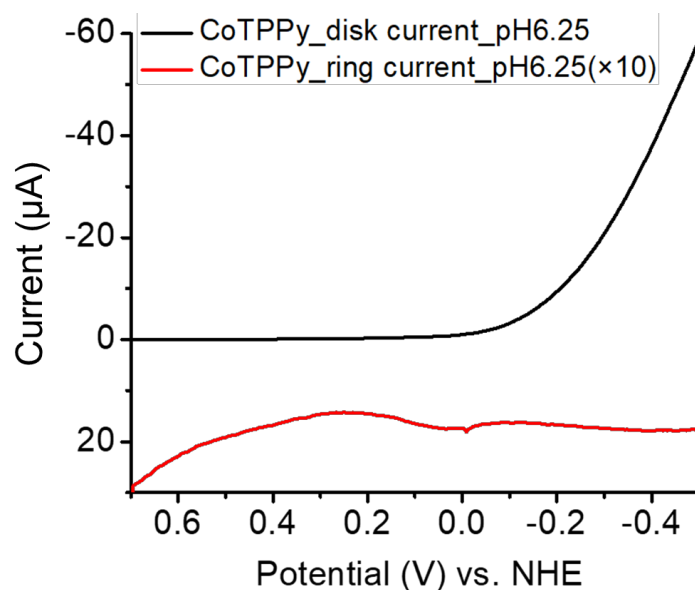
**Figure S19.** RRDE results for the ClFeTPPy immobilized on the rotating EPG disk under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution (pH 0) at 500 rpm rotation rate. The scan rate was 20 mV/s. Ag/AgCl and Pt-wire were used as the reference and counter electrode, respectively. The potential at the Pt-ring was held at 1.2 V vs. reference electrode.



**Figure S20.** The number of electrons involved in the ORR in a single step were calculated at different potentials by using the equation S2 for the CoTPPy (black) and CoTPP (red) immobilized on the EPG disk. Electrochemical conditions were identical as RRDE experiments.



**Figure S21.** Comparative RRDE results for the CoTPPy immobilized on the rotating EPG disk under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0 (black), 1.52 (blue), 2.37 (red) at 100 rpm rotation rate. The scan rate was 20 mV/s. Ag/AgCl and Pt-wire were used as the reference and counter electrode, respectively. The potential at the Pt-ring was held at 1.2 V vs. reference electrode. The ring currents for the pH 1.52 and pH 2.37 were magnified by 10 times for clarity.

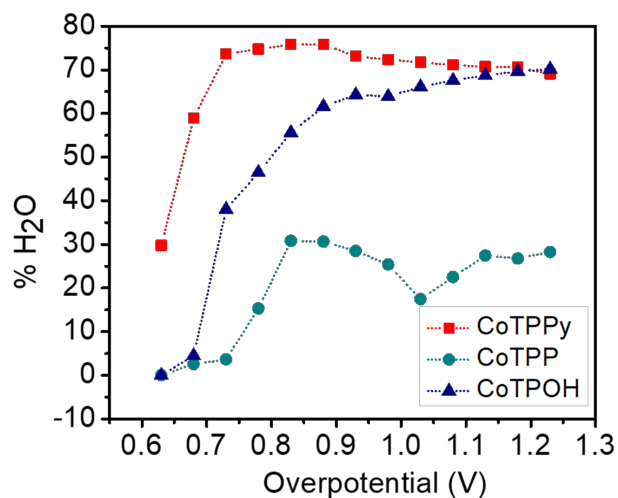


**Figure S22.** RRDE results for the CoTPPy immobilized on the rotating EPG disk under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 6.25 at 100 rpm rotation rate. The scan rate was 20 mV/s. Ag/AgCl and Pt-wire were used as the reference and counter electrode, respectively. The potential at the Pt-ring was held at 1.2 V vs. reference electrode. The ring current was magnified by 10 times for clarity.

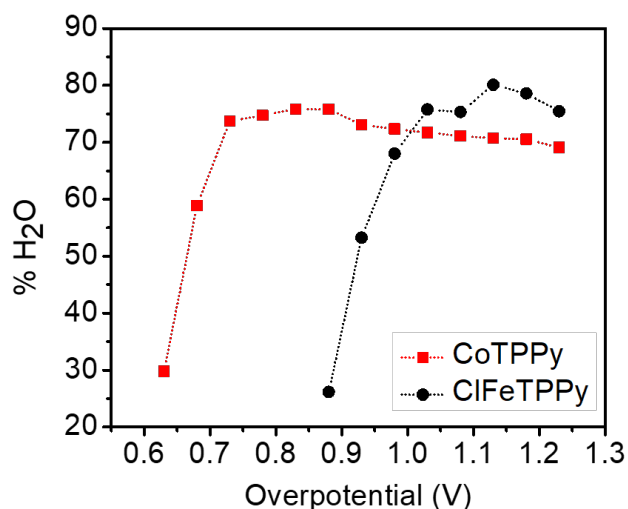
### Calculation of %H<sub>2</sub>O from RRDE<sup>3</sup>:

$$100 - \%H_2O_2 = 100 - \frac{2 \times \frac{I_r}{N}}{I_d + \frac{I_r}{N}} \times 100 \quad (S3)$$

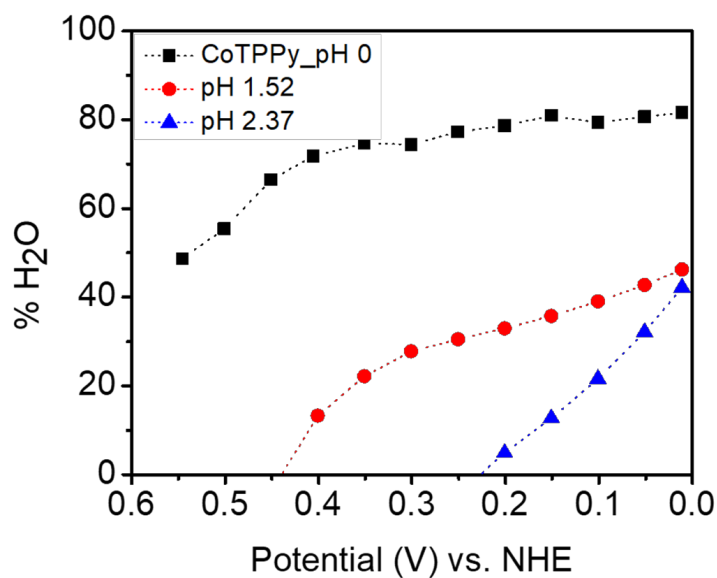
The notations are mentioned above.



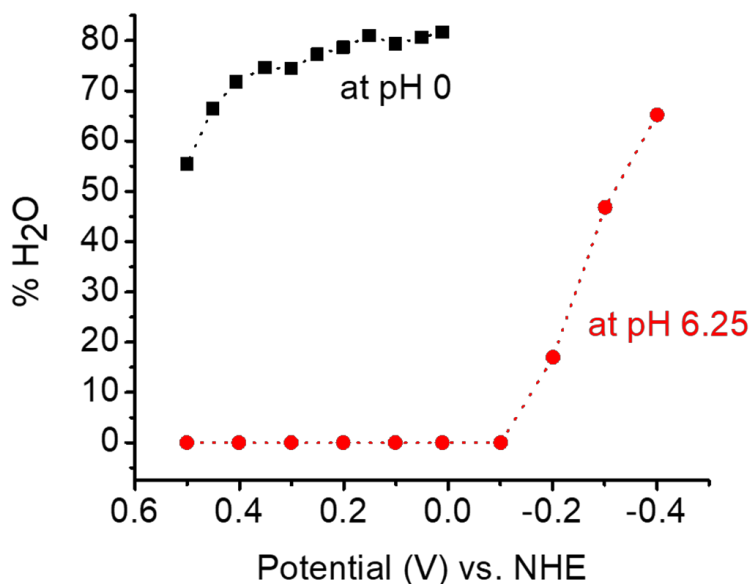
**Figure S23.** Comparison in percentage of H<sub>2</sub>O calculated using eq. S3 at the different overpotentials for the CoTPPy (red), CoTPP (cyan), and CoTPOH (navy blue) immobilized on the EPG disk. Electrochemical conditions were identical as RRDE experiments.



**Figure S24.** Comparison in percentage of H<sub>2</sub>O calculated using eq. S3 at the different overpotentials for the CoTPPy (red) and ClFeTPPy (black) immobilized on the EPG disk. Electrochemical conditions were identical as RRDE experiments.



**Figure S25.** Comparison in percentage of H<sub>2</sub>O calculated using eq. S3 at the pH 0, 1.52, and 2.37 for the CoTPPy immobilized on the EPG disk. Electrochemical conditions were identical as RRDE experiments.



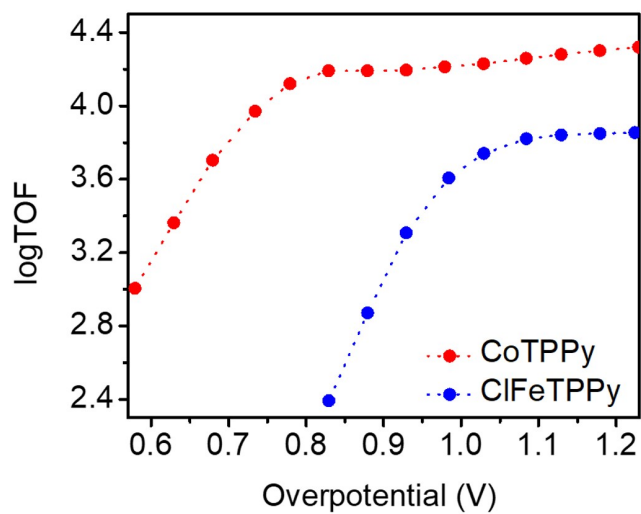
**Figure S26.** Comparison in percentage of H<sub>2</sub>O calculated using eq. S3 between pH 0 and 6.25 for the CoTPPy immobilized on the EPG disk. Electrochemical conditions were identical as RRDE experiments.

**Table S1.** Comparative data obtained from the RDE and RRDE results for the CoTPP, CoTPPy, and ClFeTPPy

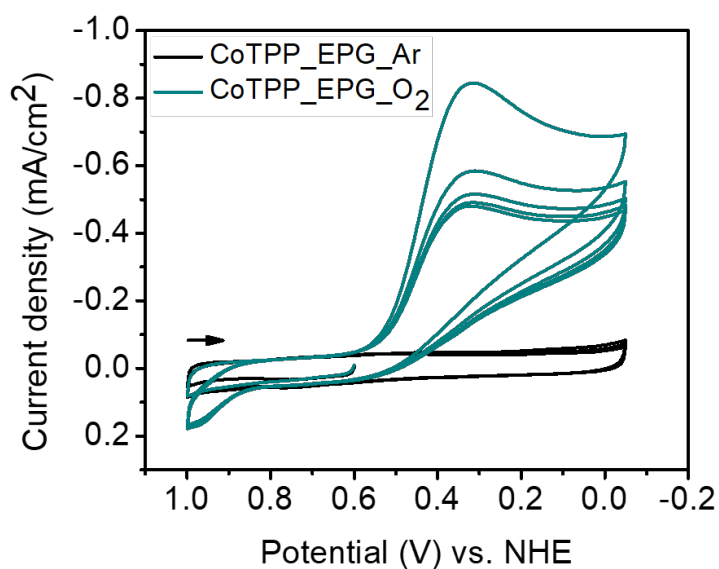
	No. of electrons from RDE	No. of electrons from RRDE	%H <sub>2</sub> O <sub>2</sub> measured at the ring	%Faradaic efficiency for H <sub>2</sub> O (from RRDE)
CoTPP	–	2.6±0.1	73±3	27±3
CoTPPy	4.01±0.3	3.51±0.02	30±3	70±3
ClFeTPPy	3.9±0.3	3.6±0.02	22±2	80±2

#### Calculations of $k_{cat}$ from K-L plots:

$k_{cat}$  was calculated from the intercept of the K-L equation (eq. S1),  $1/j_k$ , where  $j_k = nFCk_{cat}\Gamma_{cat}$ . The intercept obtained for CoTPPy and FeTPPy was 0.643 and 1.278, respectively and that corresponds to  $k_{cat} = 2.85 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  and  $1.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ , respectively. The values of  $n$  ( $= 4$ ),  $F$ ,  $C$ , and  $\Gamma_{cat}$  are identical for both cases as used in the K-L equation above.

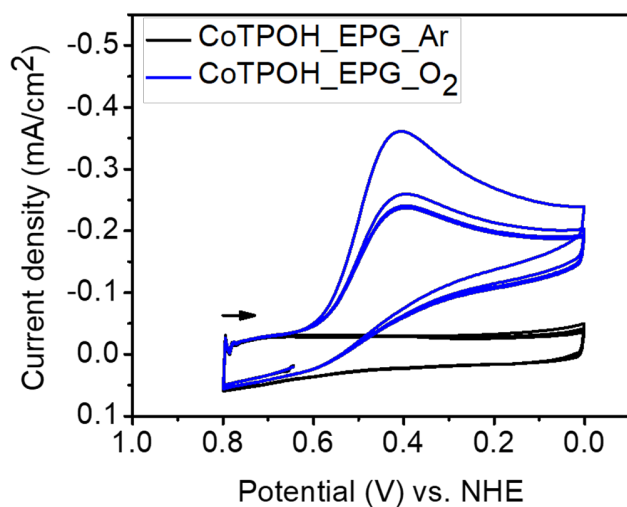


**Figure S27.** Comparative turnover-overpotential relationship for CoTPPy and ClFeTPPy under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0.

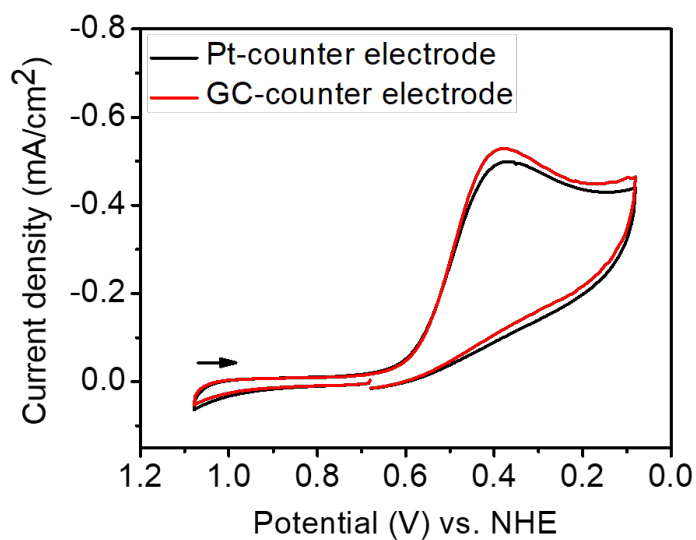


**Figure S28.** Cyclic voltammogram (CVs) for the CoTPP immobilized on EPG electrode under Ar- (black) and 1 atm O<sub>2</sub> (green) in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0. The scan rate was 100 mV s<sup>-1</sup> and the arrow shown in the plot indicates the scan direction.

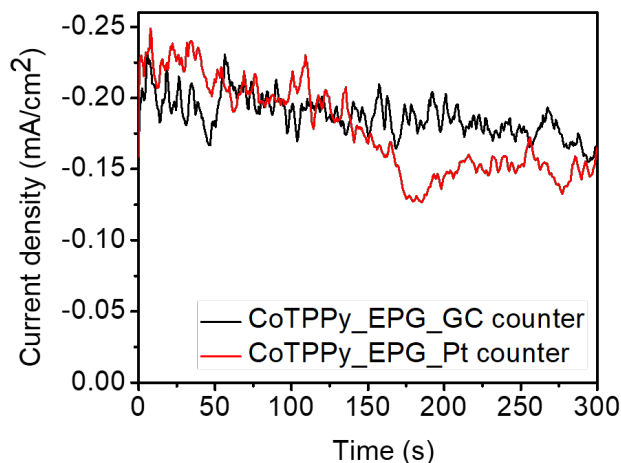




**Figure S29.** Cyclic voltammogram (CV) for the CoTPOH immobilized on EPG electrode under Ar- (black) and 1 atm O<sub>2</sub> (blue) in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0. The scan rate was 100 mV s<sup>-1</sup> and the arrow shown in the plot indicates the scan direction.



**Figure S30.** Comparative CVs for the CoTPPy adsorbed on the EPG surface using glassy carbon (GC) and Pt as the counter electrode under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0.



**Figure S31.** Comparative controlled-potential electrolysis at 0.38 V vs. NHE for the CoTPPy immobilized on EPG surface using glassy carbon (GC) and Pt as the counter electrode under 1 atm O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> solution at pH 0.

#### References:

- (1) Chatterjee, S.; Sengupta, K.; Hematian, S.; Karlin, K. D.; Dey, A. Electrocatalytic O<sub>2</sub> - Reduction by Synthetic Cytochrome *c* Oxidase Mimics: Identification of a “Bridging Peroxo” Intermediate Involved in Facile 4e<sup>-</sup>/4H<sup>+</sup> O<sub>2</sub> -Reduction. *J. Am. Chem. Soc.* **2015**, *137* (40), 12897–12905. <https://doi.org/10.1021/jacs.5b06513>.
- (2) Zhang, W.; Shaikh, A. U.; Tsui, E. Y.; Swager, T. M. Cobalt Porphyrin Functionalized Carbon Nanotubes for Oxygen Reduction. *Chem. Mater.* **2009**, *21* (14), 3234–3241. <https://doi.org/10.1021/cm900747t>.
- (3) Carver, C. T.; Matson, B. D.; Mayer, J. M. Electrocatalytic Oxygen Reduction by Iron Tetra-Arylporphyrins Bearing Pendant Proton Relays. *J. Am. Chem. Soc.* **2012**, *134* (12), 5444–5447. <https://doi.org/10.1021/ja211987f>.