Electronic Supplementary Information for

Highly Efficient Electrocatalytic Hydrogen Evolution from Neutral Aqueous Solution by Water-Soluble Anionic Cobalt(II) Porphyrin

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Materials

Both the ligand and cobalt complex were synthesized as previously reported.[1, 2] All the chemicals and solvents were purchased commercially and used without further purification. Reverse phase column chromatography was carried out using C18 silica gel (Carbon 17%, 60A) powder and TLC analysis by using analytical Merck PR-18F aluminum sheets. NMR spectra were recorded on a Bruker Avance 400 FT spectrometer. UV-Visible absorption spectra were recorded on Agilent 8453 spectrophotometer.

Synthesis and characterization

5, 10, 15, 20-Tetrakis (4-sulfonatophenyl)porphyrin (TPPS): H_2TPP (1 g) and 25 mL of H_2SO_4 (98%) were stirred for 8 h at 100 ^oC. The solution was then left overnight at room temperature, filtered, and washed with a small quantity of water, after which 150 mL of hot water was added. Neutralization of pH 9 was achieved by slow addition of 0.1 M sodium hydroxide solution at 0 ^oC. The formed sodium sulfate salt was filtered and washed 5 times with methanol to extract the compound. The solution was evaporated to dryness and purified by reverse phase column chromatography using water:methanol (80:20) solvent system to afford highly water soluble purple crystal, with 91% yield. ^1H NMR (400 MHz, DMSO-d_6) δ: 8.85 (s, 8H, H-pyrrolic), 8.18 (d, 8H, *m*-phenyl), 8.06 (d, 8H, *o*-phenyl), -2.93 (s, 2H, NH) ppm; UV-vis (λ_{max} in H_2O): 414, 516, 553, 580, 634 nm.

Cobalt-5, 10, 15, 20-Tetrakis (4-sulfonatophenyl)porphyrin (CoTPPS): 250 mg of TPPS was dissolved in 100 ml of distilled water. To the solution, an aqueous solution of 6 eq. of $Co(OAc)_2$. $4H_2O$ was added slowly and the reaction mixture was heated at 60 ^oC for 3 hrs. Metalation was confirmed by UV-visible spectroscopy. The solvent was then removed and the mixture was purified by reverse phase column chromatography on C18 gel using 100% water and then water/methanol (90:10, v/v). The chromatographed solution was evaporated to dryness using rotary evaporator and then kept in a vacuum oven at 70 ^oC for 2 days to get the desired cobalt porphyrin in 62% yield. UV-vis (λ_{max} in H_2O): 427, 548 nm.

Electrochemical Studies

All electrochemical measurements were carried out using a CHI 621B electrochemical analyzer, with a three-electrode cell in which Ag/AgCl (3 M NaCl) as reference electrode, glassy carbon (with surface area of 0.07cm^2) as working electrode, and platinum wire as the counter electrode. All the potentials were measured *vs.* Ag/AgCl, at room temperature with the scan rate of 0.1 V/s and converted to SHE scale by adding 0.210 V. Cyclic voltammograms in dry DMSO were obtained using 0.1 M [Bu_4NPF_6] as the supporting electrolyte. The CVs were also measured in potassium phosphate buffer pH 7 and distilled neutral water using 0.1M $LiClO_4$ as supporting electrolyte. Controlled potential electrolysis (CPE) experiments were conducted at different potentials *vs.* Ag/AgCl (3 M NaCl) in 10-mL of 0.1 M and 2.0 M phosphate buffer with pH 7 and 0.1 M $LiClO_4$ aqueous solution stirred constantly.

Determination of Faradaic efficiency, TOF and TON

In order to determine Faradaic efficiency and TOF, CPE experiments were conducted in 10 mL of 2.0 M KPi, pH 7 and 0.1 M $LiClO_4$ neutral aqueous solutions at an applied potential of -1.39 V *vs.* SHE for 1 hr. The charge build up versus time was plotted in Figure 2A and Figure S9. Quantification of H_2 produced during 1 hr CPE was performed by Agilent 7890A Gas Chromatography (GC), with thermal conductivity detector and N_2 carrier gas.

Faradaic efficiency was, therefore, calculated by the following equation:

$$\textit{Faradaic efficiency}\ (\%) = [96485 * 2 * \text{mol } H_2\ (\text{GC}) * 100] / [Q(\text{CPE})]^3$$

The moles of hydrogen detected by GC were calibrated using injected volume of pure H_2. The volume of hydrogen injected is linearly dependent on GC peak area. Turn over frequency (TOF, moles of H_2 produced per moles of catalyst per time unit) was then calculated at the end of 1 h CPE experiment. For determination of TON values, extended CPE experiments were done by measuring charge passed at applied potential of -1.29 V *vs.* SHE in 2.0 M KPi, pH 7 solution (with 0.1 mM catalyst) and in 0.1 M $LiClO_4$ neutral aqueous solution (with 20 μM catalyst) assuming 100 % Faradaic efficiency.

Table S1. Comparison of some of H_2 evolution electrocatalysts working in phosphate buffer pH 7, as measured by CPE experiments.

Catalyst	**Applied overpotential (mV)**	**TON**[a]	**Faradaic efficiency (%)**	**TOF**[a] **(s^{-1})**	**Reference**
Ni_2(biscyclam)$^{4+}$	847	Up to100	3	0.04	4
Mo-OxoPY5Me_2	987	$6.1x10^5$(71 h)	>99	2.4(71 h)	5
CoPY5Me_2	887	$5.5x10^4$(60 h)	>99	0.3(12 h)	6
CoDPA-Bpy	987	300 (1 h)	99	0.08(1 h)	7
(bztpen)Co	837	$1.6x10^5$(60 h)	>99	0.14(60 h)	8
Co(P_4N_2)	576	$9.24x10^4$(20 h)	100	1.28(20 h)	9
CoMP11-Ac(N_2)	852	$2.5x10^4$(4 h)	98	6.7(10 m)	10
CoTPPS (in 2 M KPi)	876	1.9 $x10^4$ (73 h)	100	1.83 (1 h)	This work
CoTPPS(in 0.1 M LiCLO4)	976	4.9 $x10^3$ (44 h)	100	0.38 (1h)	

[a] In parenthesis is the length of electrolysis experiment used to determine the corresponding value.

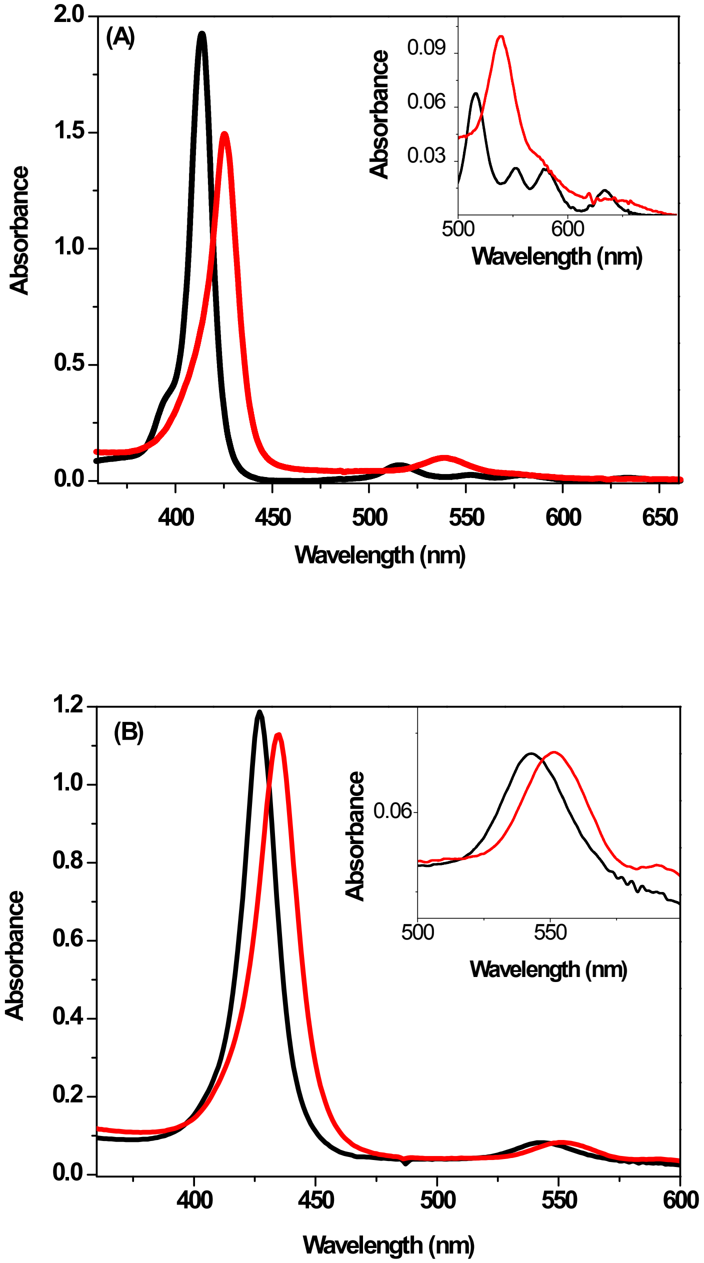

Figure S1. Absorption spectra of; A) TPPS (black) and CoTPPS (red) in water; B) CoTPPS in DMSO (red) compared with in water (black)

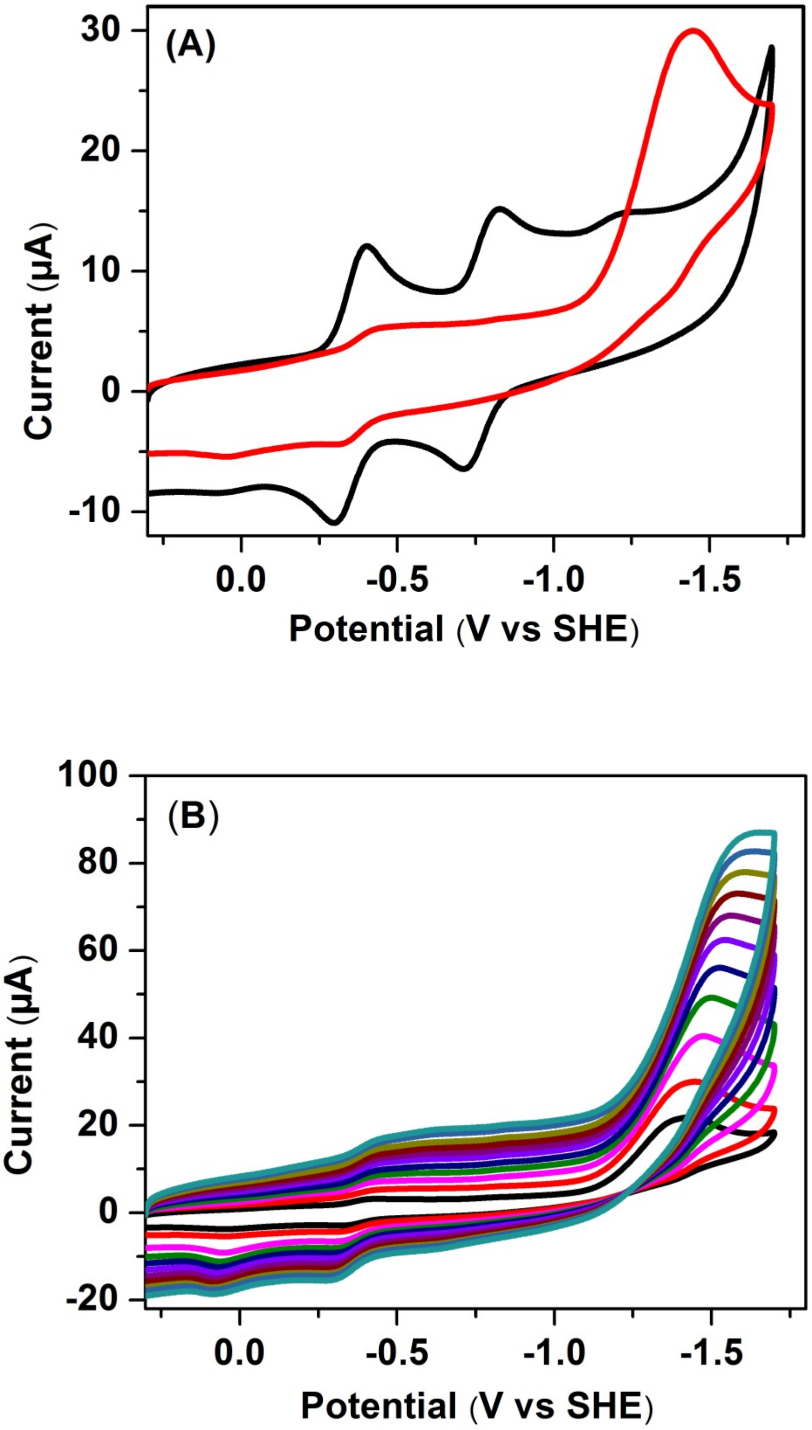

Figure S2. A) Cyclic voltammogram of 1 mM TPPS (black) and 1 mM CoTPPS (red) in DMSO at scan rate of 0.1 V/s; B) 1mM CoTPPS at scan rates of 0.05, 0.75, 0.2, 0.3, 0.4, 0.5,0.6,0.7 V/s, with glassy carbon working electrode.

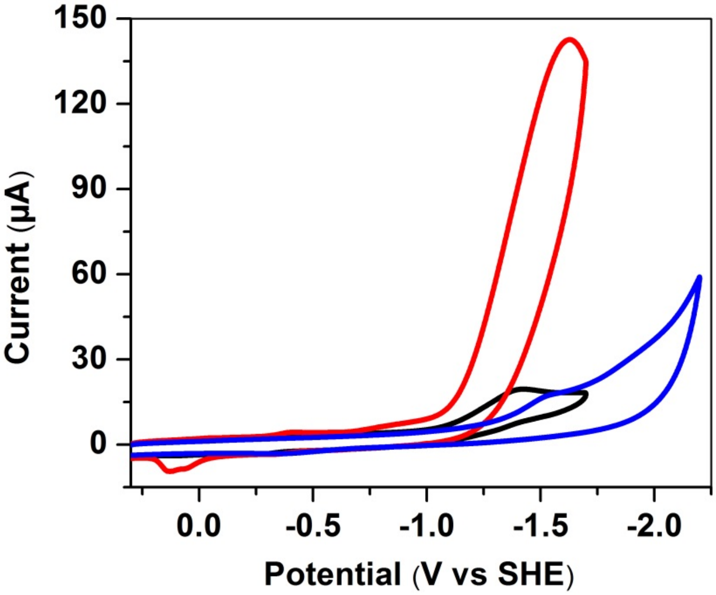

Figure S3. Cyclic Voltammogram of 1 mM CoTPPS; With no acid (black), with 10 eq. acid (red), and 10 eq AcOH alone (blue); at scan rate of 0.1 V/s with glassy carbon working electrode.

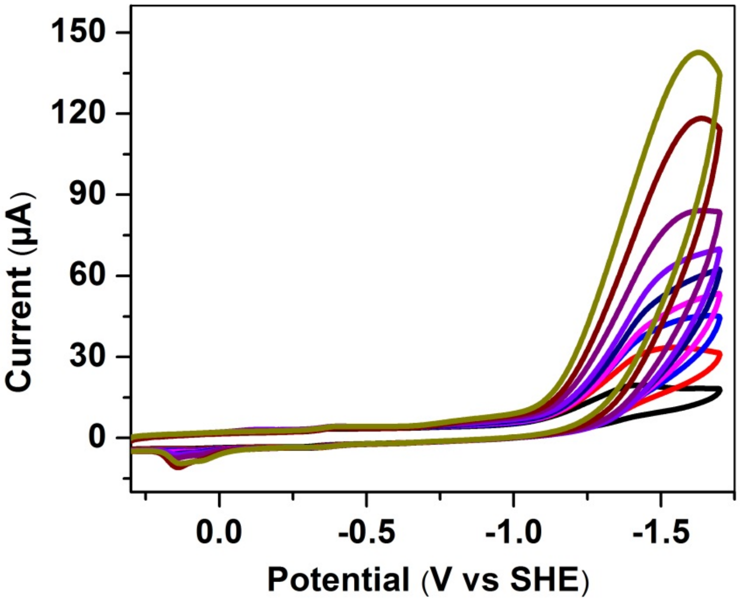

Figure S4. CV of 1 mM of CoTPPS in DMSO solution containing 0.1 M Bu_4NPF_6 in the presence of acetic acid: (bottom-top) no acid, 0.5, 1, 2, 3, 4, 5, 7.5 and 10 eq of AcOH. Scan rate 0.1 Vs-1; Glassy carbon working electrode.

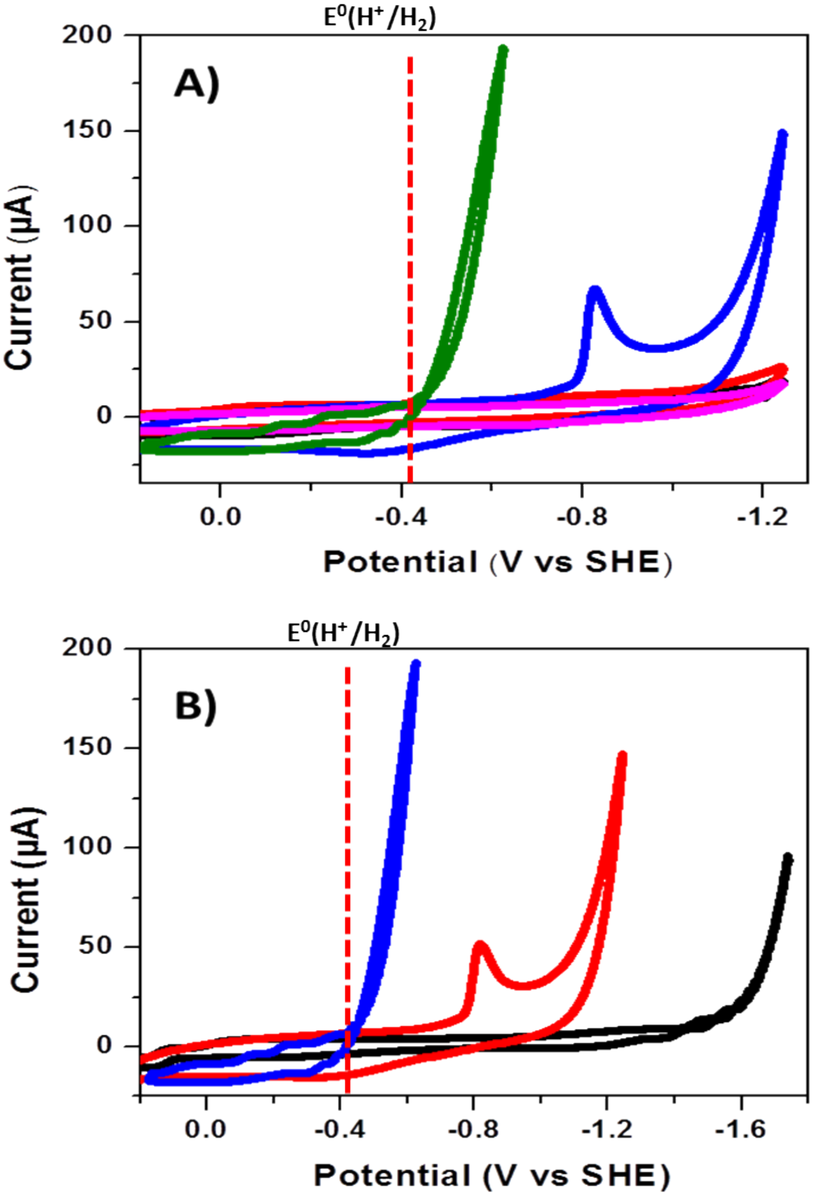

Figure S5 A CV of 0.1 mM CoTPPS in 0.1 M $LiClO_4$ aqueous solution using glassy carbon working electrode (blue), 0.1 mM free-bas (red), 0.1 mM $Co(OAc)_2$•$4H_2O$ (magenta), control glassy carbon electrode (black), and Pt (green) when scanned to -1.29 V vs SHE.; (**B**) CV of 0.1 mM CoTPPS in 0.1 M $LiClO_4$ aqueous solution using glassy carbon as working electrode (red), control glassy carbon as working electrode (black) and control Pt working electrode (blue) when scanned to more negative potential (-1.79 V vs SHE). Conditions: Scan rate 0.1 V/s, at RT.

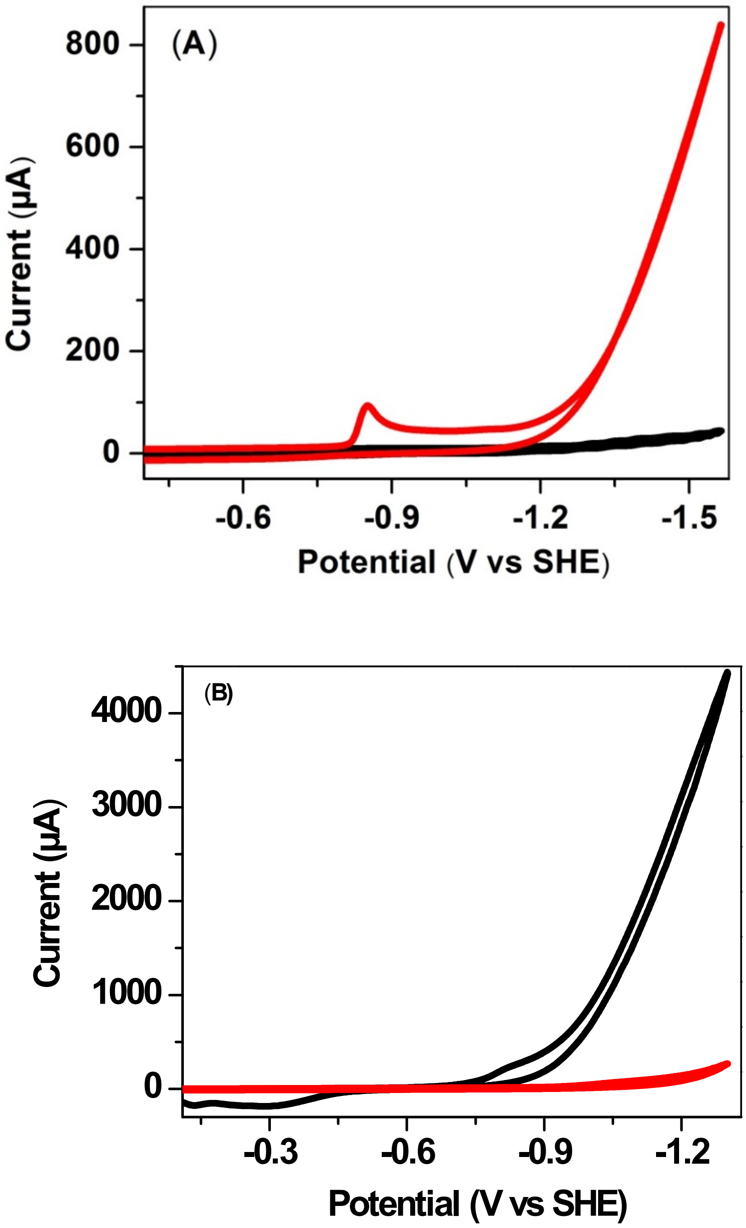

Figure S6. Cyclic Voltammogram of 0.5 mM CoTPPS; A) in 0.1 M $LiClO_4$ aqueous solution (red); blank solution (black) when scanned to -1.69 V *vs.* SHE; B) in 2.0 M KPi, pH 7 solution (black), buffered solution alone (red) when scanned to -1.29 V vs SHE. Condition: scan rate is 0.1 Vs^{-1}; Glassy carbon working electrode at room temperature.

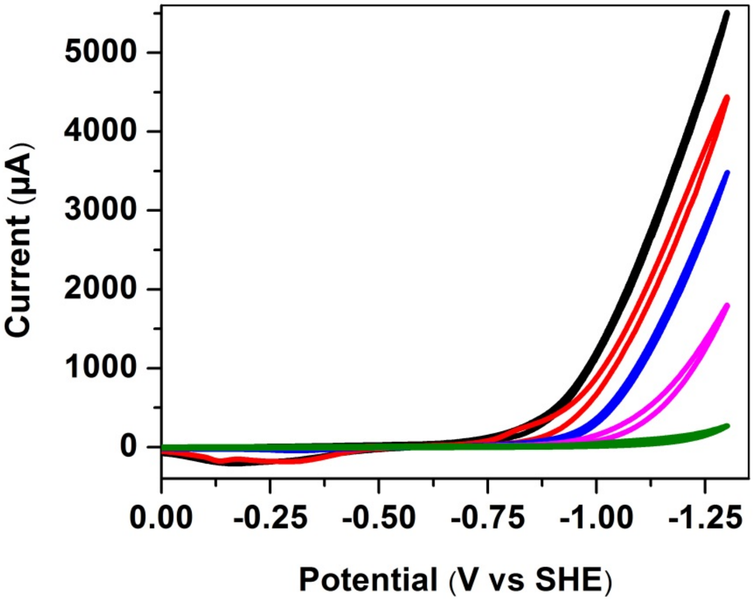

Figure S7. Cyclic voltammogram of CoTPPS in 2.0 M KPi, pH 7 at catalyst concentrations of 1 mM (black), 0.5 mM (red), 0.1 mM (blue), 0.05 mM (magenta) and buffered solution alone (green). Scan rate 0.1 Vs^{-1}; Glassy carbon working electrode.

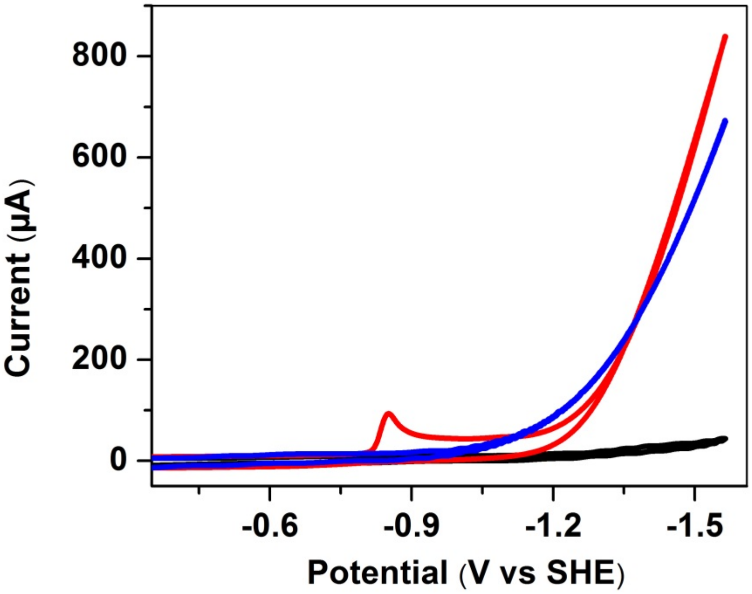

Figure S8. CV of CoTPPS in 0.1 M $LiClO_4$ bulk solution (red), when adsorbed on to glassy carbon electrode (blue) and blank solution alone (black) at scan rate 0.1 Vs^{-1}.

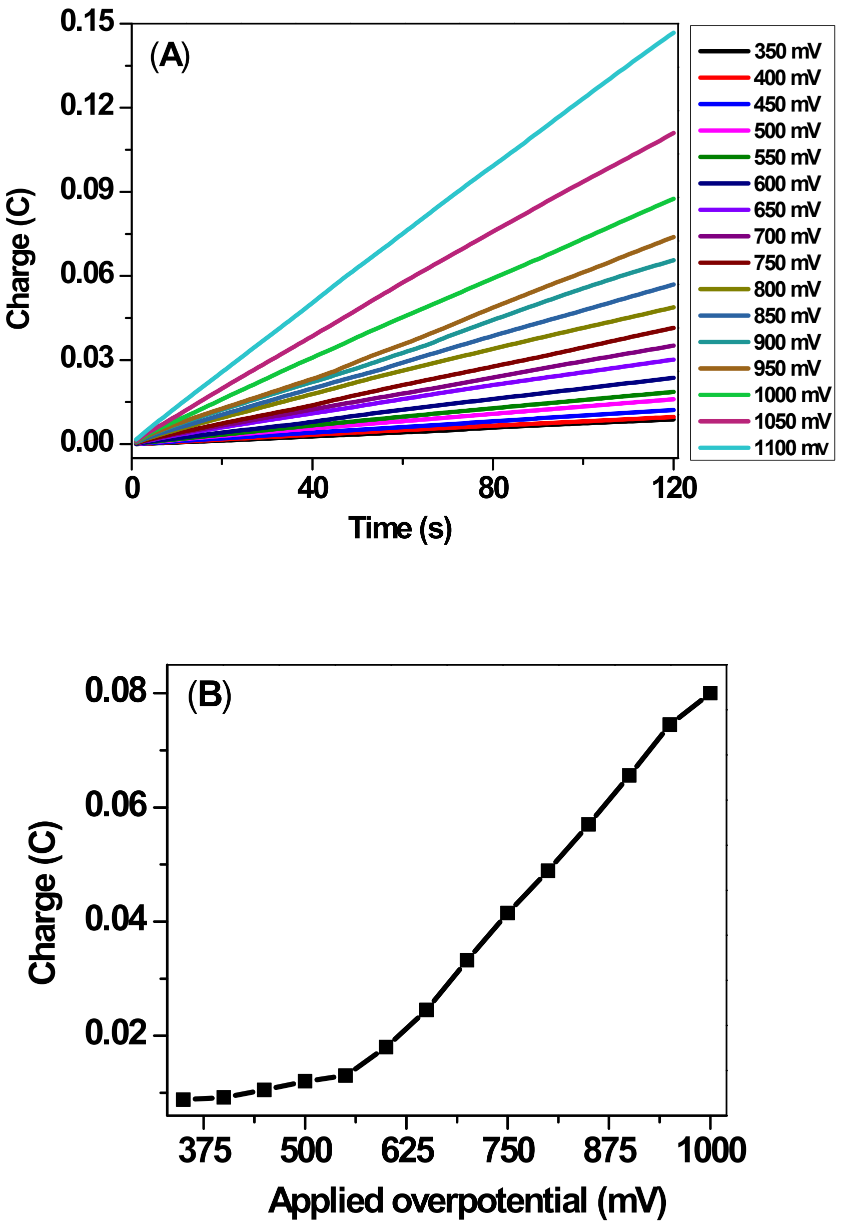

Figure S9. A) Charge build up versus times and (B) the accumulated charge at the end of 2 min for controlled potential electrolysis of 0.05 mM solution of CoTPPS in 0.1 M KPi, pH 7 buffer at various overpotentials.

Table S2: GC Experiment- for calibration of standard hydrogen

Standard H_2 (100%) injected for calibration (μ L)	Peak area
2	125.23
5	329.94
7	462.0
10	641.83
13	852.88

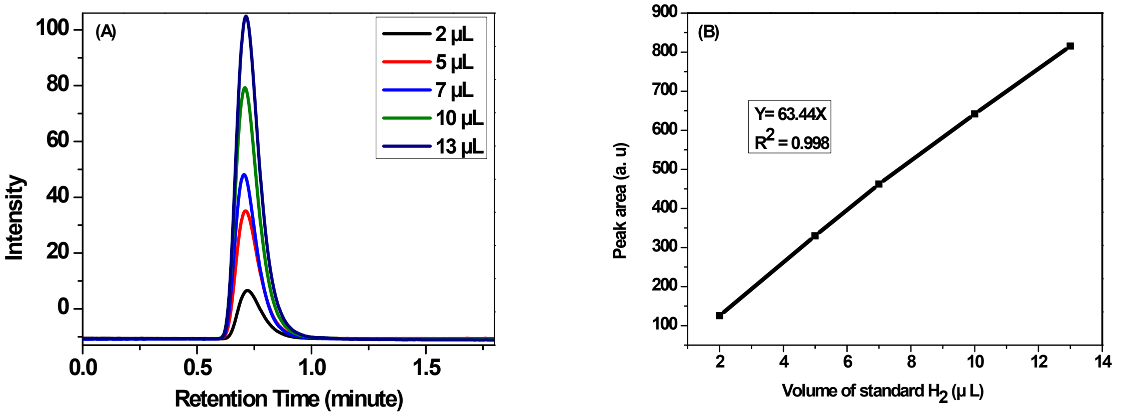

Figure S10: A) GC chromatogram of standard H_2 with different volume; B) Calibration curve used to calculate the amount of hydrogen generated from CPE experiment by using GC.

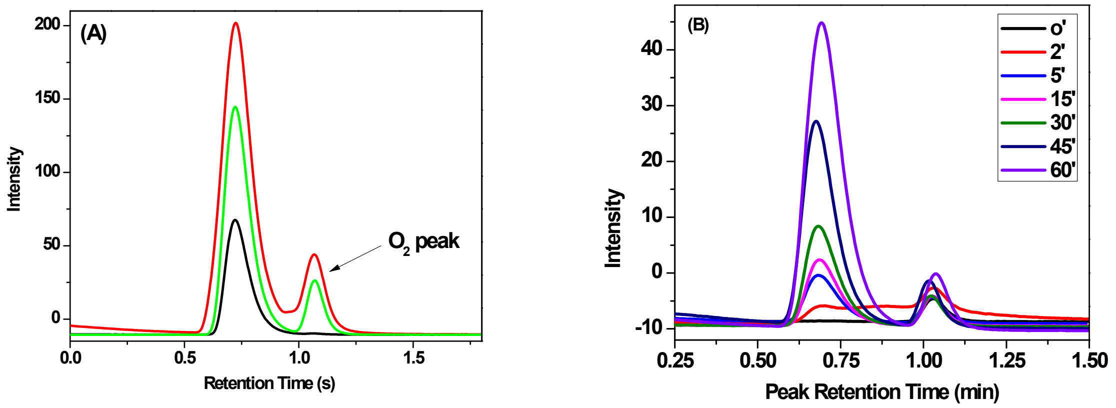

Figure S11. A) GC Chromatogram of standard H_2 (black), head scape after CPE (green) and after purging with little standard H_2 (Red); B) GC Chromatogram of 0.05 mM CoTPPS in 2 M KPi, pH 7 before CPE (Black) and after CPE at different time intervals.

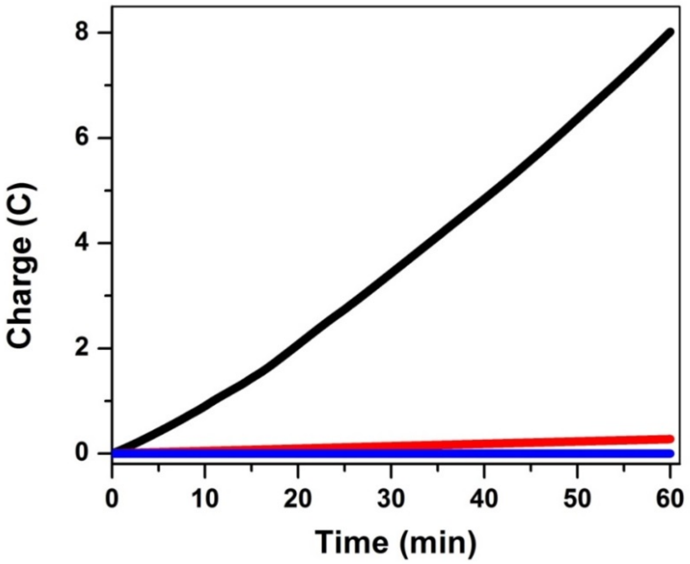

Figure S12. Charge versus time for 1 h controlled potential electrolysis at -1.39 V *vs.* SHE in 0.1 M $LiClO_4$ neutral aqueous solution. CoTPPS (black) is compared with buffer control (blue), and metal free TPPS (red).

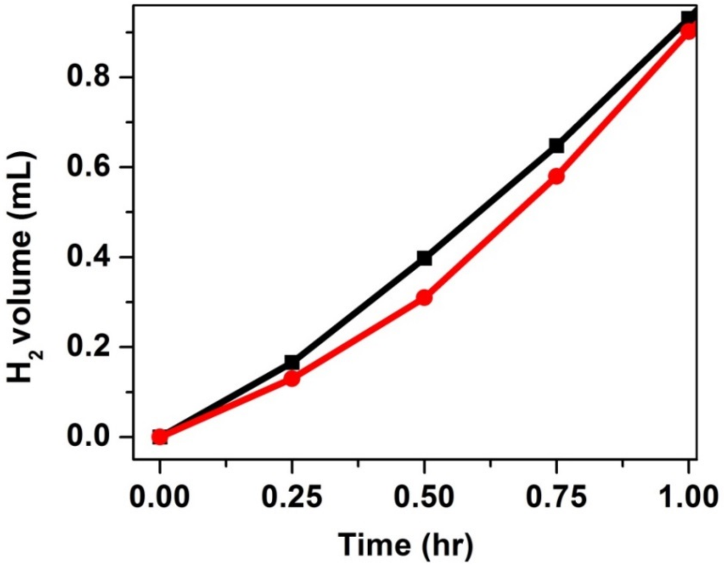

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Figure S13. Generated hydrogen volume calculated from passed charge (black) and measured from gas chromatography (red) during 1 h electrolysis of CoTPPS in 0.1 M $LiClO_4$ at -1.39 V *vs.* SHE.

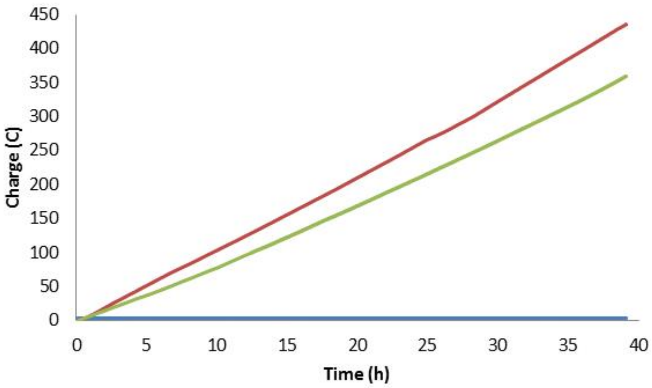
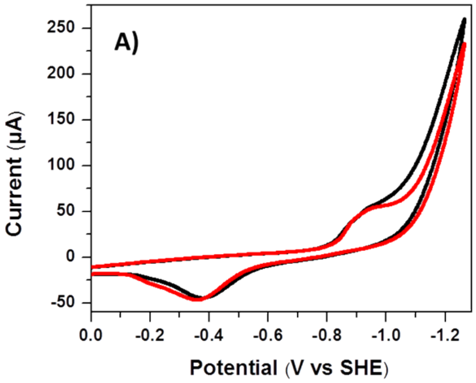


Figure S14. Extended CPE of 0.05 mM CoTPPS in 0.1 M $LiClO_4$ bulk neutral solution (green), when catalyst adsorbed on glassy carbon electrode (red) in neat 0.1 M $LiClO_4$ solution, and blank solution alone (blue), with an applied potential -1.39 V vs. SHE.



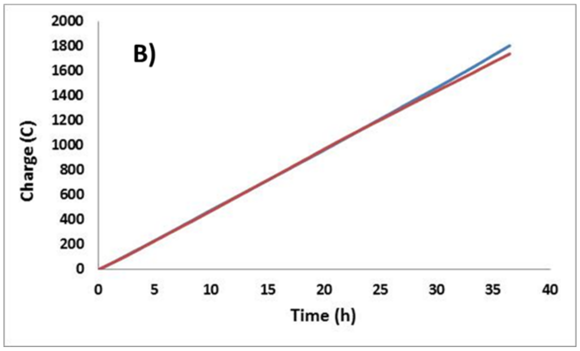


Figure S15 (A) Cyclic voltammogram of 0.1 mM CoTPPS in 0.1M KPi, pH 7 measured in closed system (black) and under open air (red) using glassy carbon electrode. Conditions: scan rate 0.1 V/s, at room temperature. **(B)** Controlled-potential electrolysis of 0.1 mM CTPPS in 2 M KPi, pH 7 measured in closed system (blue) and open air (red) at an applied potential of -1.29 V vs SHE, using glassy carbon as working electrode.

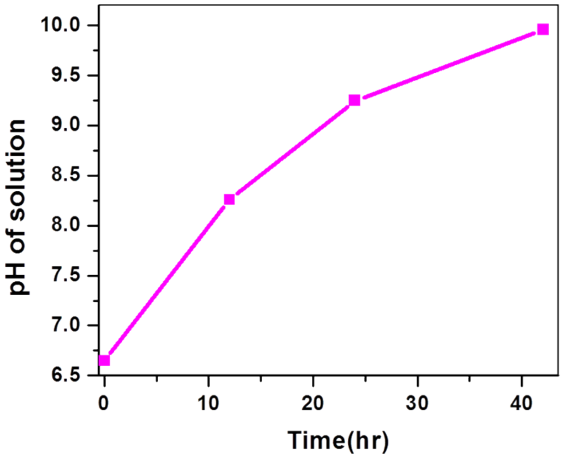


Figure S16 pH *vs* electrolysis time for CPE experiment performed in 0.1M KPi pH 7 solution using 0.1mM CoTPPS at an aplied potential of -1.29 V vs SHE on glassy carbon electrode.

References

1. G. Abellán, E. Coronado, C. J. Gómez-García, C. Martí-Gastaldo and A. Ribera, *Polyhedron*, 2013, **52**, 216-221.

2. X.-T. Zhou, G.-Q. Ren and H.-B. Ji, *J. Porphyrins Phthalocyanines*, 2013, **17**, 1104-1112.

3. J. G. Kleingardner, B. Kandemir and K. L. Bren, *J. Am. Chem. Soc.*, 2014, **136**, 4-7

4. Collin, J. P.; Jouaiti, A.; Sauvage, J. P. *Inorg. Chem.* **1988**, *27*, 1986.

5. H. I. Karunadasa, C. J. Chang and J. R. Long, *Nature*, 2010, **464**, 1329-1333

6. Y. Sun, J. P. Bigi, N. A. Piro, M. L. Tang, J. R. Long and C. J. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 9212-9215.

7. Singh, W. M.; Baine, T.; Kudo, S.; Tian, S. L.; Ma, X. A. N.; Zhou, H. Y.; DeYonker, N.J.; Pham, T. C.; Bollinger, J. C.; Baker, D. L.; Yan, B.; Webster, C. E.; Zhao, X. *Angew. Chem. Int. Ed.Engl.* **2012**, *51*, 5941.

8. Zhang, P.; Wang, M.; Gloaguen, F.; Chen, L.; Quentel, F.; Sun, L. Chem. Comm. 2013,49, 9455

9. L. Chen, M. Wang, K. Han, P. Zhang, F. Gloaguenb and L. Sun, *Energy Environ. Sci.*, 2014, **7**, 329–334

10. J. G. Kleingardner, B. Kandemir and K. L. Bren, *J. Am. Chem. Soc.*, 2014, **136**, 4-7