Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Photocatalytic Hydrogen Evolution from Neutral Aqueous Solution by a Water-Soluble Cobalt(II) Porphyrin

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Table of Content

Materials and methods.

The chemical reagents used in this experiment ($[Ru(bpy)_3]^{2+}$ and Ascorbic acid) were purchased from commercial sources and used as received. The synthesis, purification and characterization of the ligand and catalyst (CoTPPS) was reported previously.[1] An aqueous solution of potassium phosphate buffer was uas reaction media.

Instrumentation

UV-Visible absorption spectra were recorded on Agilent 8453 spectrophotometer and fluorescence spectra by using a Varian Cary Eclipse fluorescence spectrophotometer. The cyclic voltammetry measurements were carried out on CHI 621B electrochemical analyzer (CH Instruments, Austin, TX, USA) in degassed DMSO containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte as well as in neutral aqueous solution and we reported it.[1] The UV-LED at light at 420 nm and 0.6 W/cm² was used as a light source and a 4 mL fluorescent quartz glass was used as photo reactor. GC experiment was conducted using Agilent 7890A with thermal conductivity detector and N_2 carrier gas.

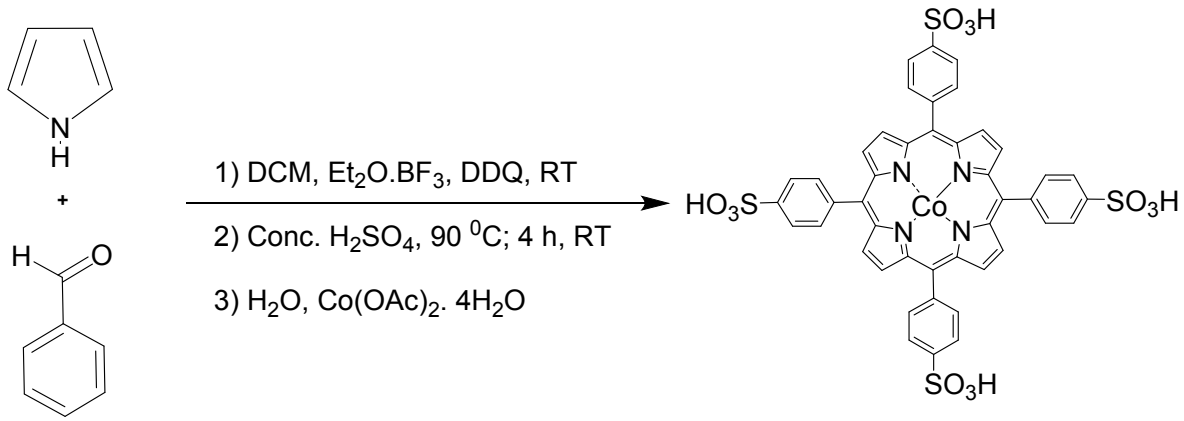
Photolysis Experiment for H_2 Evolution

Photocatalytic H_2 evolution experiments were performed in airtight 4 mL quartz glass, continuously stirring and irradiating with UV-LED light source. Before photolysis experiment, the reaction sample was purged with pure N_2 for about 20 min. Samples in 1 M phosphate buffer containing CoTPPS as catalyst, $[Ru(bpy)_3]^{2+}$ as photosensitizer, and ascorbic acid as electron donor were prepared according to required photocatalytic conditions for H_2 evolution as noted in the text. A control experiment in the dark as well as in the absence of one of the components (catalyst, electron donor or photosensitizer) was carried out up on irradiating with light under the same experimental condition. Before and after irradiation, the headspace of the cuvette was sampled by gas chromatography (with TCD detector and N_2 carrier gas) and the amount of H_2 evolved was quantified by a calibration curve plot of standard pure H_2.

Photochemical Quenching:

To observe florescence quenching of photosensitizer by sacrificial electron donor (reductive quenching), different concentrations of aliquots of ascorbic acid (from 0 to 76.3 mM) were added to 1.2 mM stock solution of $Ru(Bpy)_3]^{2+}$ and fluorescence intensity was monitored by exciting the sample at 420 nm. A Stern-Volmer plots was used to calculate the fluorescence quenching constant. Moreover, fluoresce quenching experiment of photosensitizer using catalyst (oxidative quenching) was conducted using similar procedure as outlined above. Different concentrations of catalyst (0 to 8.6 μM) was added to 2 mL of 1.2 mM $Ru(Bpy)_3]^{2+}$ solution and the fluorescence intensity was recorded by exciting the sampel at wavelength 420 nm, and a Stern-Volmer plots was used to calculate the fluorescence quenching constant.

Synthesis and Characterization



Scheme S1 Synthesis of Catalyst.

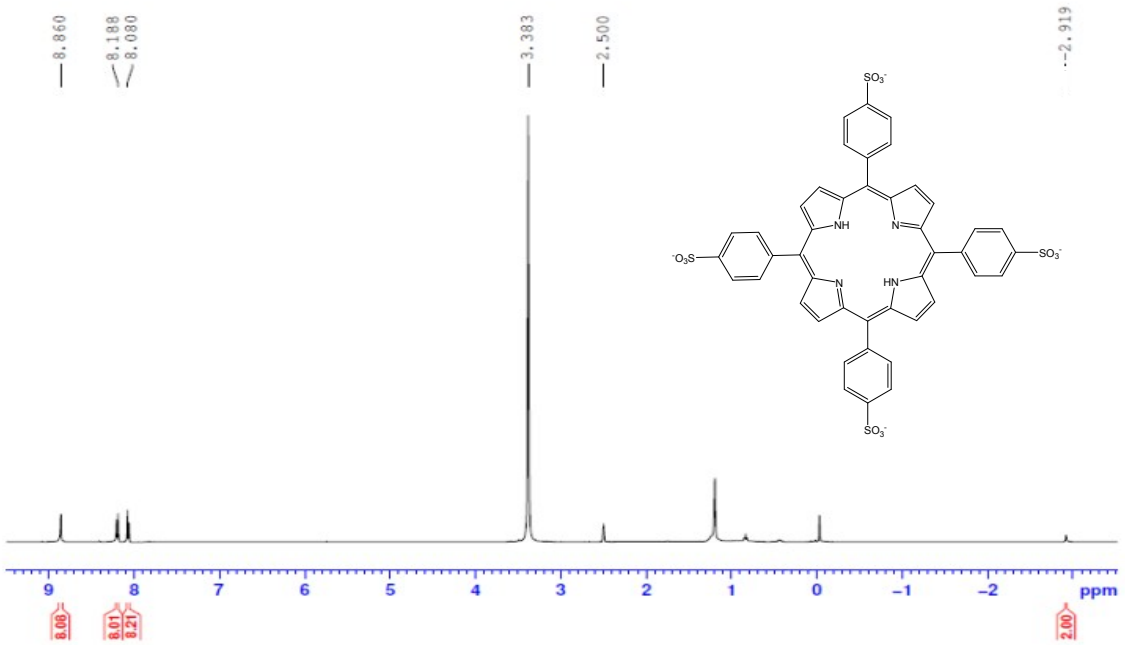


Figure S1. ^{1}H NMR spectrum of 5,10,15,20-Tetrakis-(p-SO_3HPhenyl)porphyrin in DMSO-d^{6}

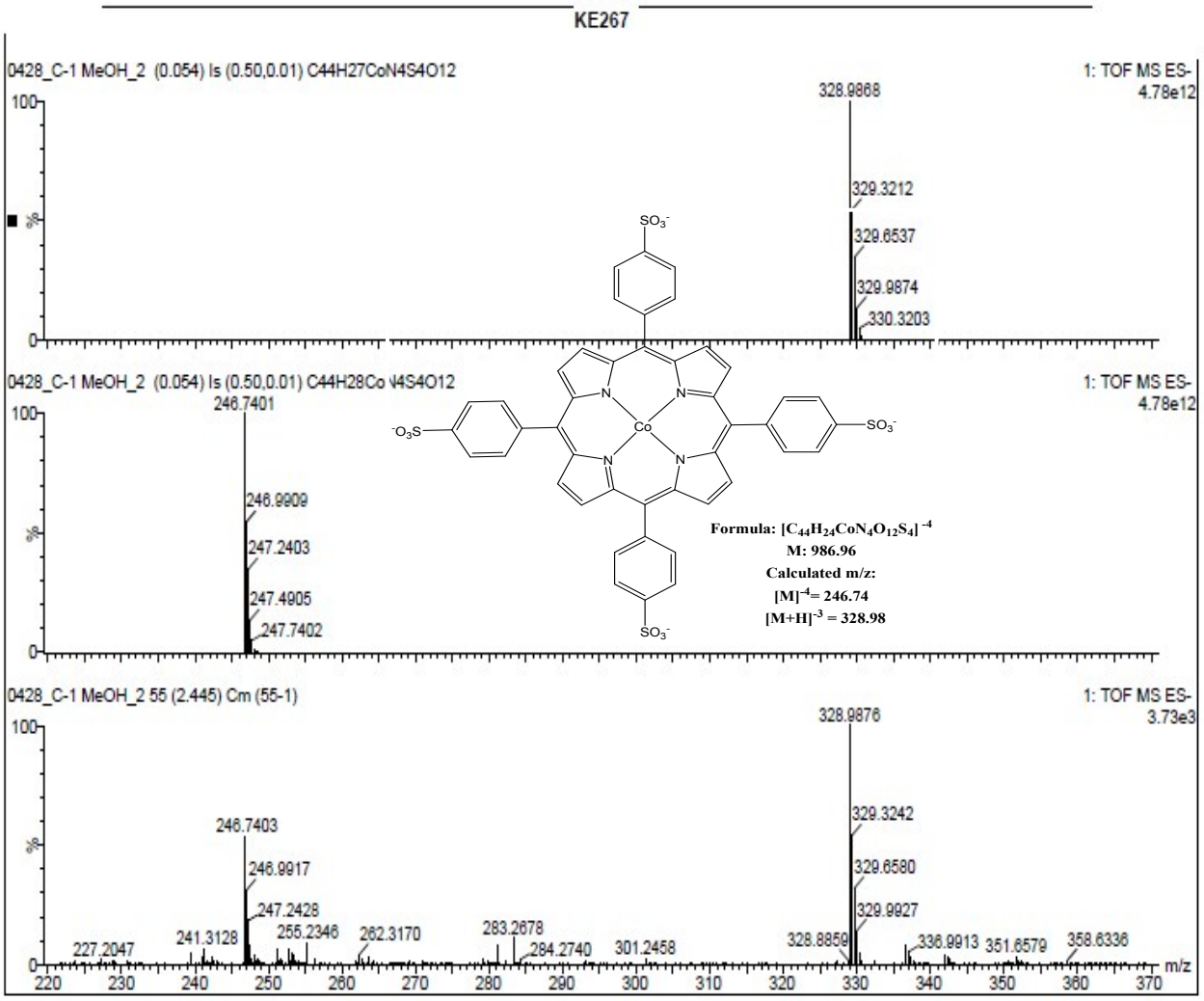


Figure S2. HR-ESI mass spectrum of 5,10,15,20-Tetrakis-(p-SO_3HPhenyl)porphyrinato cobalt(II)

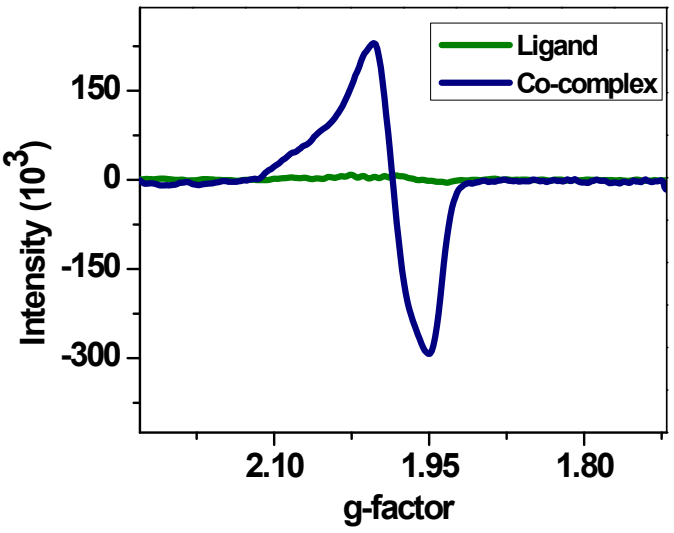


Figure S3. EPR spectra of CoTPPS (blue) and TPPS (green) in DMSO at 77 K.

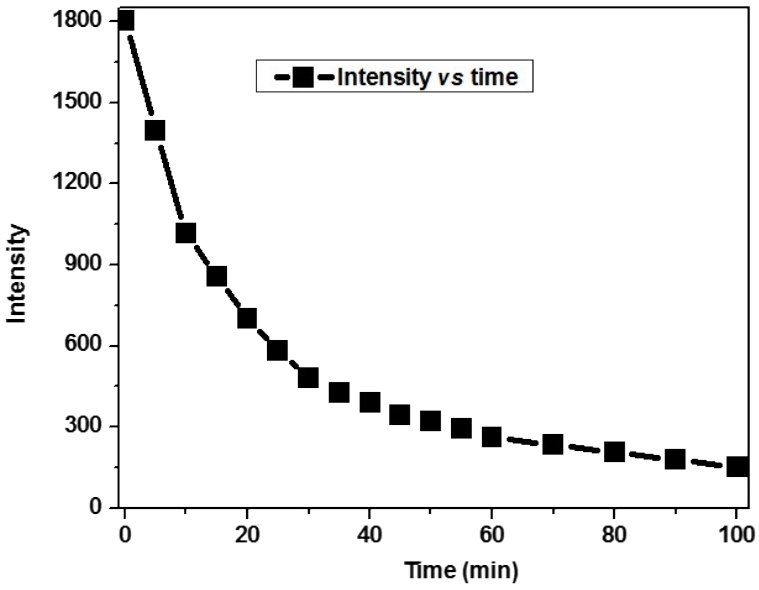


Figure S4. The decay of fluorescence emission intensity of a three-component system as a function of irradiation time

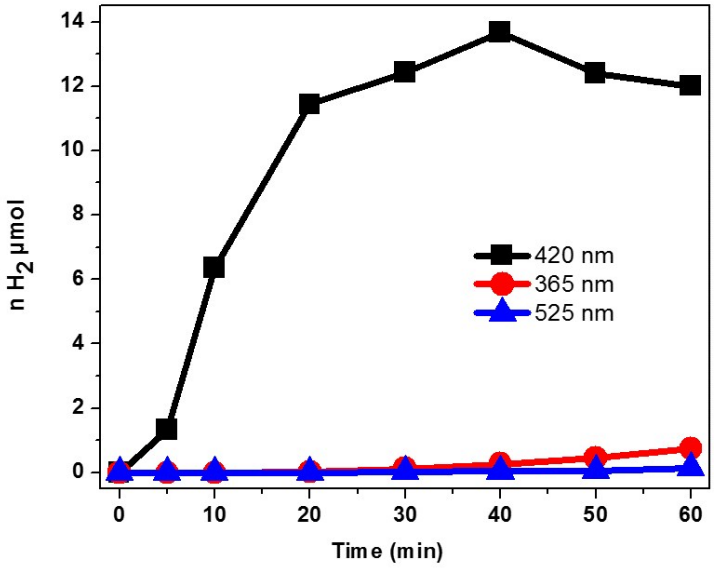


Figure S5. Amount of H_2 evolved with time as a function of wavelength of light source. Condition: 1M KPi pH 6.8, [AscH]= 0.08 M, [Ru^{2+}] = 0.3 mM; [CoTPPS] = 2.0 µM

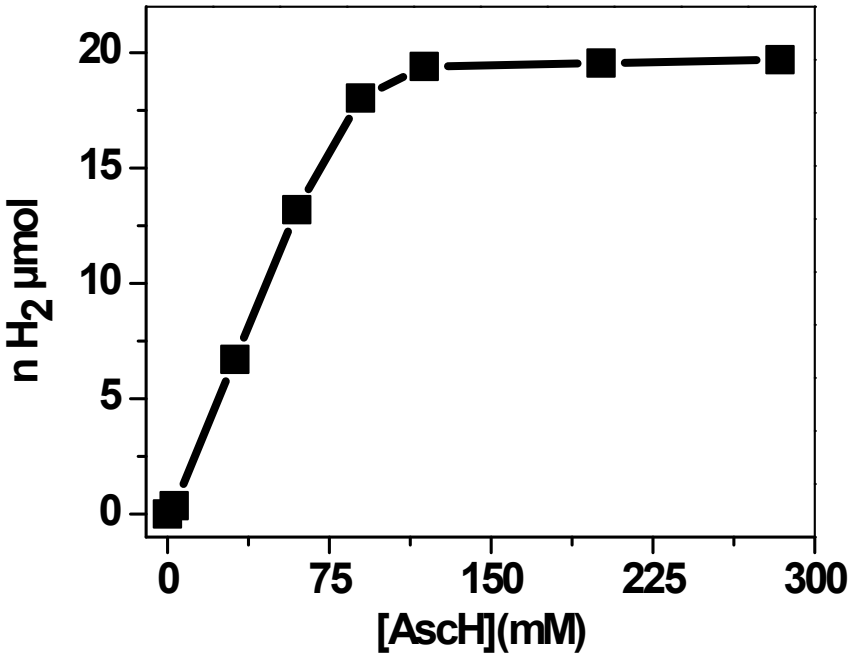


Figure S6. Amount of H_2 evolved as a function of [AscH]; Condition: 1M KPi pH 6.8, [Ru^{2+}] = 0.3 mM; [CoTPPS] = 2.9 µM, light source 420 nm.

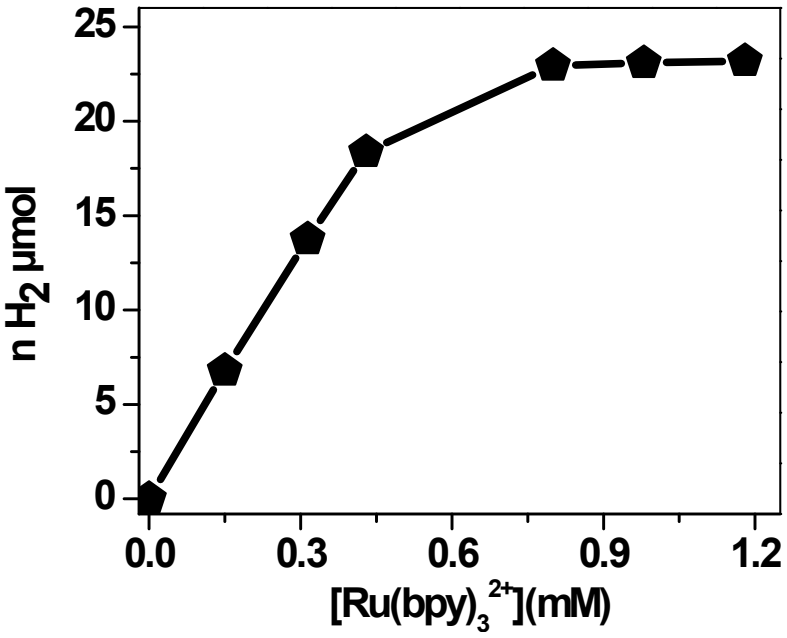


Figure S7. Amount of H_2 evolved with time as a function of [Ru^{2+}]; Condition: 1M KPi pH 6.8, [AscH] = 0.3 M; [CoTPPS] = 6 µM, light source 420 nm.

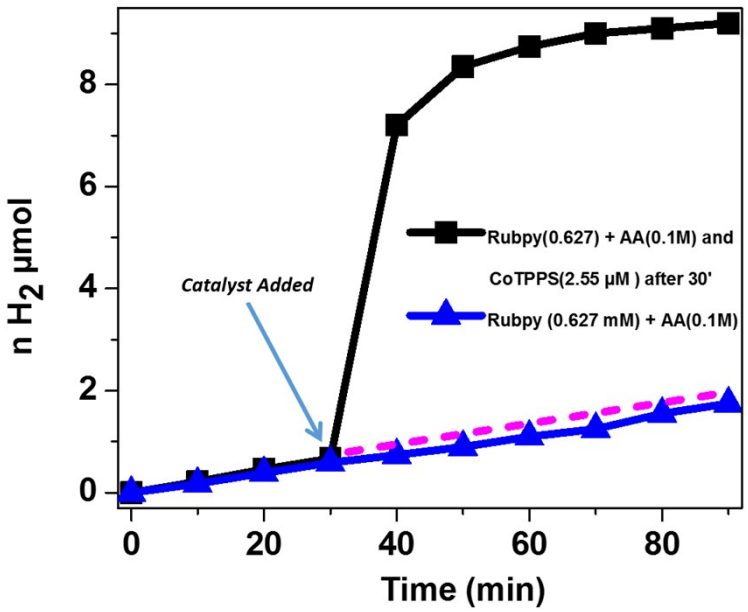


Figure S8. Significant amount of H_2 evolved up on addition of CoTPPS to a control photo-reaction system initially containing Ru^{2+}, and AscH.

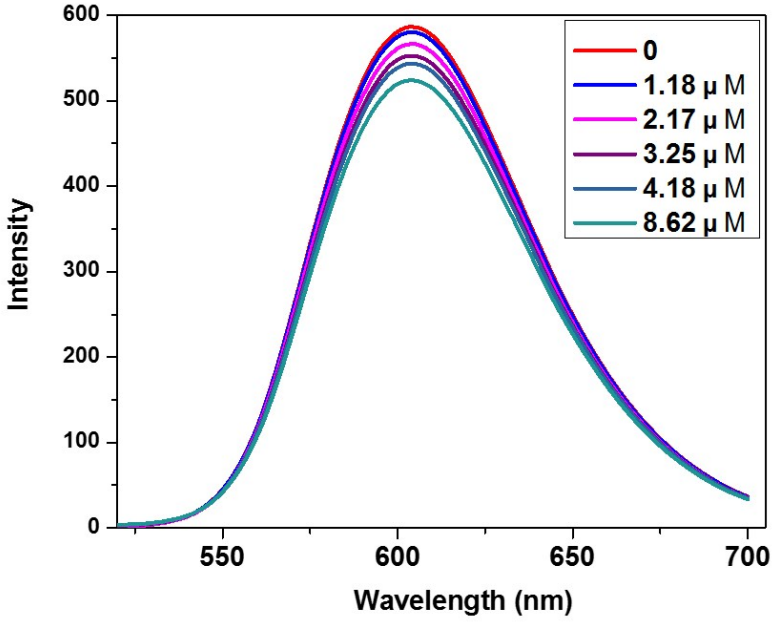


Figure S9. Fluorescence quenching of $(Ru(bpy)_3)^{2+})$* by successive addition of CoTPPS. Condition: pH 6.8, $[Ru^{2+}]$ = 1.1 mM; [CoTPPS]= 0 to 8.6 µM at 420 nm.

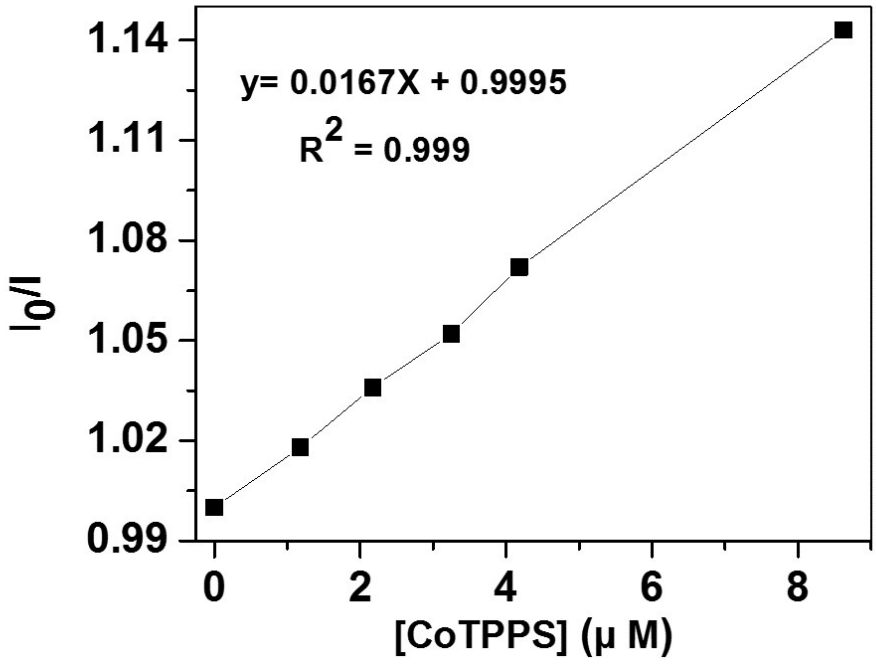


Figure S10. Stern-Volmer plot obtained from fluorescence quenching of (Ru(bpy)32+)* by

successive addition of CoTPPS (Figure S8).

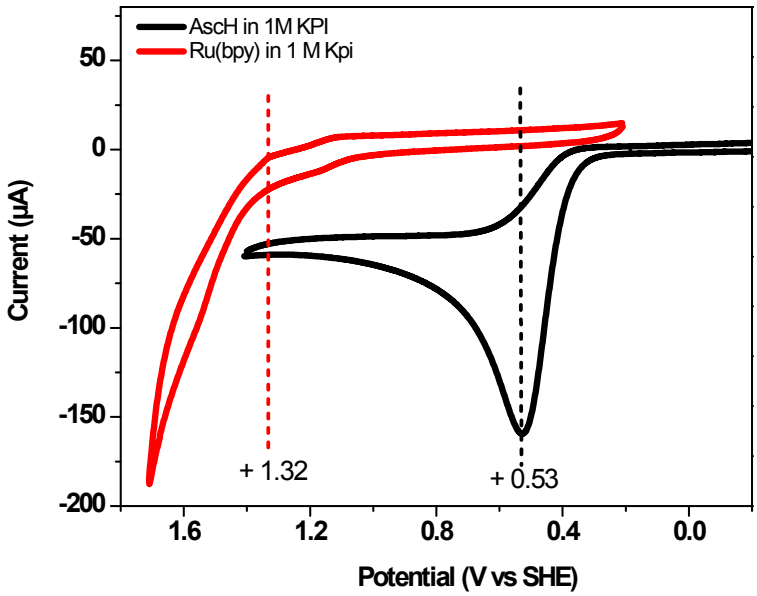


Figure S11. CV of 1 mM of $Ru(bpy)_3^{2+}$ (red) and Ascorbic acid(black) in 1 M aqueous phosphate buffer solution using glassy carbon as working electrode, Pt wire counter and Ag wire reference electrode.

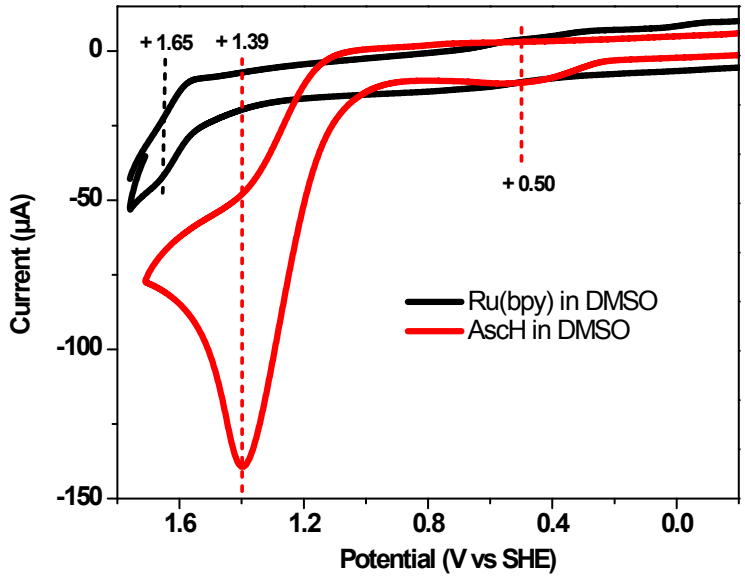


Figure S12. CV of 1 mM of $Ru(bpy)_3^{2+}$ (red) and ascorbic acid (red) in 0.1 M $[Bu_4N]PF_6$/DMSO solution using glassy carbon as working electrode, Pt wire counter and Ag

wire reference electrode.

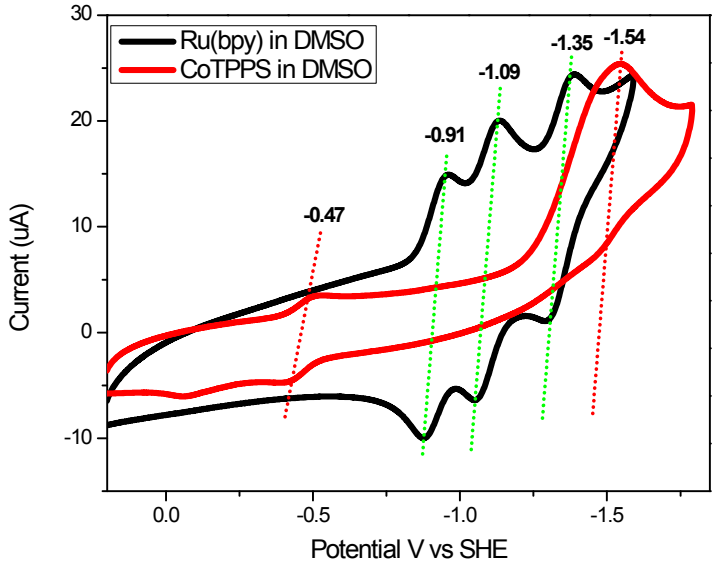


Figure S13. CV of 1 mM of $Ru(bpy)_3^{2+}$ (black) and CoTPPS (red) in 0.1 M $[Bu_4N]PF_6$/DMSO solution using glassy carbon as working electrode, Pt wire counter and Ag wire reference electrode.

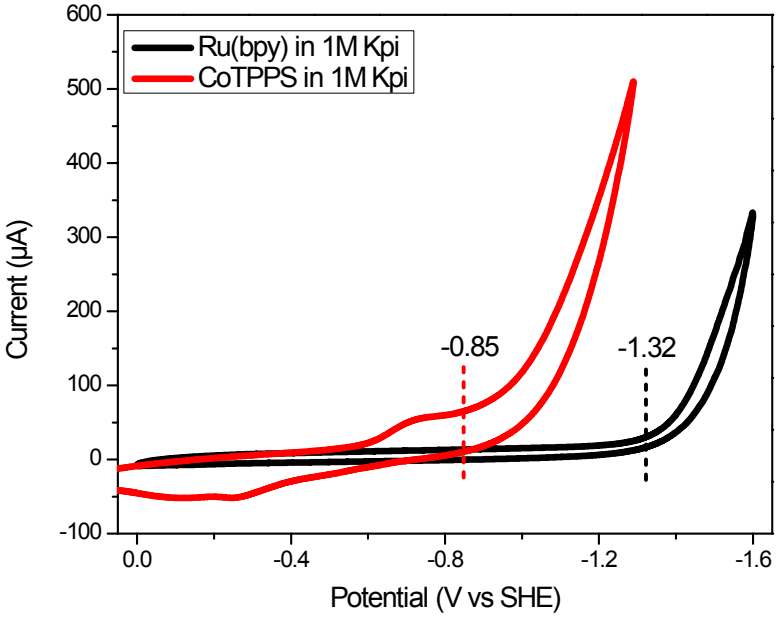


Figure S14. CV of 1 mM of $Ru(bpy)_3^{2+}$ (black) and CoTPPS (red) in 1 M aqueous phosphate

buffer solution using glassy carbon as working electrode, Pt wire counter and Ag wire reference electrode.

Reference

1. B. B. Beyene, S. B. Mane and C.-H. Hung, *Chemical Communications*, 2015, **51**, 15067-15070.

2. R. S. Khnayzer, V. S. Thoi, M. Nippe, A. E. King, J. W. Jurss, K. A. El Roz, J. R. Long, C. J. Chang and F. N. Castellano, *Energy & Environmental Science*, 2014, **7**, 1477-1488.