Supporting Information

for

Probing the Peripheral Role of Amines in photo- & electrocatalytic H_2 Production by Molecular Cobalt Complexes

Dependu Dolui[a], Ab Qayoom Mir[a], and Arnab Dutta[a,b]*

[a] Chemistry Discipline, Indian Institute of Technology Gandhinagar, Palaj, 382355

[b] Chemistry Department, Indian Institute of Technology Bombay, Powai, 400076

***E-mail: arnabdutta@chem.iitb.ac.in**

1. Experimental Section:

1.1. Materials and Methods:

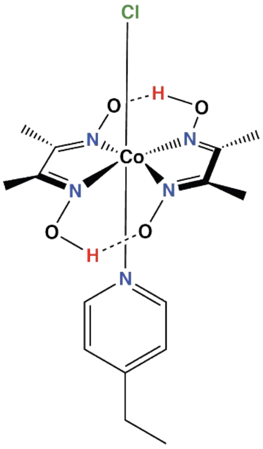
Dimethyl glyoxime (ACS reagent grade, ≥ 99.0%), MES hydrate (Titration, ≥ 99.5%) and 4-(Aminomethyl)pyridine (≥ 98%), 4-Ethyl Pyridine (≥ 98%), 4-(Ethylaminoethyl)pyridine (≥ 97%), was purchased from Sigma-Aldrich India, Cobalt Chloride, Hexahydrate Purified were purchased from Merck India Pvt. Ltd., tetrabutylammonium tetrafluoroborate (TBAF) and EOSIN-Y (≥ 95.0%) were purchased from TCI India Pvt. Ltd. Acetone (HPLC and Spectroscopy) were purchased from SD Fine chemicals Ltd. India. Triethylamine (Synthesis Grade, AR), Methanol (HPLC and gradient), Chloroform (AR/ACS), Triethanolamine (AR), Diethyl ether (AR), Hydrochloric acid (AR/ACS), Sodium Hydroxide (AR), Sodium sulfate, Anhydrous (AR/ACS), Potassium Chloride (AR), Acetonitrile (HPLC and Gradient), Acetonitrile (GC Grade) and Sodium Chloride (AR) were purchased from Finar Chemicals Pvt. Ltd. India. All reagents are used as such without any further purification. HPLC grade organic solvents and Millipore water (18.2 MΩ cm resistivity at 298K) were used in all synthesis and chemical analysis. Glassware was oven dried before use. Reactions were performed under N_2 using standard Schlenk-Line technique unless otherwise stated. Nuclear Magnetic Resonance Spectra (NMR) were recorded at ambient (~ 300K) temperature using a Bruker Avance III 500 MHz Ascent FT spectrometer with working frequencies of 500 MHz for ^{1}H and 125 MHz for ^{13}C NMR. NMR signals are reported in ppm with solutions in $(CD_3)_2SO$ (δ= 2.50 ppm) solvent. Phase-sensitive 2D EXSY NMR has been performed for all complexes at room temperature (~300K) in $(CD_3)_2SO$ solvent with 350 msec mixing time. UV-Vis spectra were recorded on a JASCO V-750 spectrophotometers using 1 cm path length in 1 mL Kozima make quartz cuvette. ATR-FTIR spectra of pure solid sample were recorded on PerkinElmer (Spectrum-Two) spectrometer. ESI Mass of the complexes was recorded with a synapt G2S ESI-QToF LCMS (Waters) in positive mode. Cyclic voltammetry (CV) experiments were carried out at room temperature using Metrohm Autolab PGSTAT 101 potentiostat. All measurement was carried out either in dry CH_3CN or in aqueous buffer medium, using 0.1M 2-(N-Morpholino)ethanesulfonic acid, hydrate (MES) in Millipore water with a solute concentration of 1 mM in presence of anhydrous sodium sulphate or TBAF (0.1 M) as supporting electrolyte. A standard three electrode system under N_2 atmosphere was used with a 1 mm glassy carbon disc as a working electrode, Ag/AgCl (saturated KCl) as a reference electrode connected by vycor tip and a platinum wire as counter electrode. All potentials are reported versus Hydroxyferrocene couple (E_{FcOH}= +0.385 V vs. SHE), added in electrolyte at the end of each measurement. Bulk electrolysis setup includes a customized H-type glass vessel separated by glass frit, coiled 23 cm Pt wire was used as counter electrode in one side of H-cell chamber separated by frit, along with Ag/AgCl (saturated KCl) as a reference electrode, and graphite plastic chip (1.5 cm x 1 cm) as working electrode. 10 mL of 0.25 mM complexes in aqueous buffer solutions were used, respectively, during their chrono-coulometric experiments. pH of the aqueous solution were measured in a bench top EUTECH INSTRUMENTS pH 700 pH Meter. The DLS studies were performed using malvern zetasizer nano zs equipment.

1.2. Synthetic Procedures:

The complexes Co(dmg)$_2$Cl$_2$[1] was a reported starting material, from this starting material (4-ethyl pyridine)Co(DH)$_2$Cl (**C1**), (4-ethylamine pyridine)Co(DH)$_2$Cl (**C2**) and (4-methyl amino ethyl pyridine)Co(DH)$_2$Cl (**C3**) were synthesized according to previously reported literature with some modifications.[2] Complexes were synthesized under a standard Schlenk-Line unless otherwise stated and stored under N_2 atmosphere.

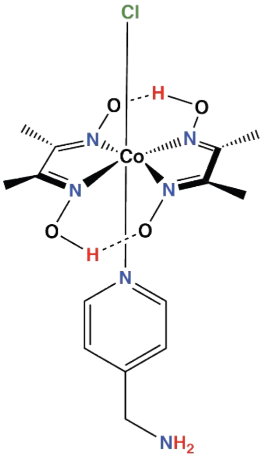
*1.2.1. Synthesis of **C1**.*

Synthesis of **C1** was executed according various other reported literature with further modification.[3] 363 mg (1 mM) of Co(dmg)$_2$Cl$_2$ was taken in a single neck round bottom flask containing 50 mL of chloroform. In this suspension 400 μL (3.5 mM) 4-Ethyl Pyridine was added with stirring and solution becomes wine red. After 7 min of stirring 20 mL of de-ionized water was added and continue stirred vigorously. Mixture was further stirred for another 2h at room temperature. Organic layer was collected by aqueous and brine solution workup. Further dried and washed with diethyl ether to remove excess ligand. (Yield= 311 mg, 72.1%). ^{1}H NMR (CDCl$_3$), 500 MHz, 300K) (**Figure S17**): δ= 18.25 (s, 2H, ***H-bonded oxime***); 8.08 (d, 2H, *J*= 5 Hz, Pyr***H***); 7.03 (d, 2H, *J*= 5 Hz, Pyr***H***); 2.61 (q, 2H, *J*= 7.5 Hz, C$\boldsymbol{H_2}$); 2.39 (s, 12H, 4C$\boldsymbol{H}_3$); 1.18 (t, 3H, *J*= 7.5 Hz, -C***H3***). ^{13}C NMR (CDCl$_3$), 125 MHz, 300K) (**Figure S18**): δ (ppm)= 156.9; 152.4; 150.3; 125.3; 27.79; 13.43; 13.05. ATR-FTIR (Neat Solid, *v* in cm^{-1}): 486 (m, **Co-N$_{\text{axial}}$**); 417 (m, **Co-Cl**). UV-Vis in CH$_3$CN (λ_{max} in nm, ε in parentheses M^{-1}cm^{-1}): λ_{max}= 305.5 (1416); 367 (501); 497 (22); 594 (4.8). HRMS (G2S-ESI-QToF) m/z calculated for (M+H$^+$) [$C_{15}H_{24}N_5O_4Cl_1Co_1$]: 432.09, found 432.13.



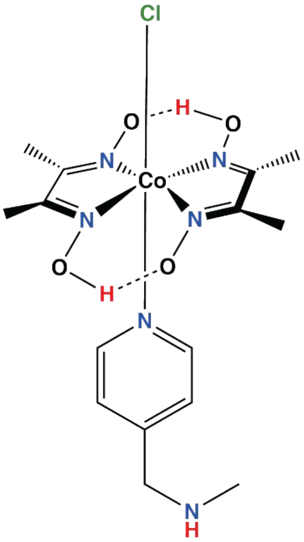
*1.2.2. Synthesis of **C2**.*

Synthesis of **C2** was executed according various other reported literature with further modification.[2] 181 mg (0.5 mM) of Co(dmg)$_2$Cl$_2$ was taken in a 100 mL two neck round bottom flask containing 35 mL of dry methanol. 69 μL (0.5 mM) trimethylamine (TEA) was added with stirring. Further 51 μL (0.5 mM) 4-(Aminomethyl)pyridine was added. After 5h of stirring under N_2 it produces yellow solid suspension. Mixture was further stirred for another 5h at room temperature. Solid precipitate was collected and washed with chloroform and dried under reduced pressure to get desired product. (Yield= 138 mg, 64%). ^{1}H NMR ((CD$_3$)$_2$SO, 500 MHz, 299K) (**Figure S19**): δ= 18.40 (s, 2H, ***H-bonded oxime***); 7.85 (d, 2H, *J*= 5 Hz, Pyr***H***); 7.22 (d, 2H, *J*= 5 Hz, Pyr***H***); 4.09 (m, 2H, -N$\boldsymbol{H}_2$); 3.16 (d, 2H, -C$\boldsymbol{H}_2$); 2.30 (s, 12H, 4C$\boldsymbol{H}_3$). ^{13}C NMR ((CD$_3$)$_2$SO, 125 MHz, 300K) (**Figure S20**): δ= 152.8;



150.6; 149.4; 125.3; 49.1; 13.0. ATR-FTIR (Neat Solid, *v* in cm^{-1}): 491 (m, **Co-N$_{axial}$**); 411 (m, **Co-Cl**). UV-Vis in CH_3CN (λ_{max} in nm, ε in parentheses $M^{-1}cm^{-1}$): λ_{max}= 309.5 (1496); 365.5 (512); 494 (29.4); 587 (7.7). HRMS (G2S-ESI-QToF) m/z calculated for $[M(OCH_3)-H]^+$ $[C_{15}H_{24}N_6O_5Cl_1Co_1]$: 462.08, found 462.70.

*1.2.3. Synthesis of **C3**.*



181 mg (0.5 mM) of $Co(dmg)_2Cl_2$ was taken in a 100 mL two neck round bottom flask containing 50 mL of dry methanol. 69 μL (0.5 mM) dry TEA was added with stirring. Further 69 μL (0.5 mM) 4-(ethylaminomethyl)pyridine was added. After 14 h of stirring under N_2 it produces yellow solid suspension. Solid precipitate was collected and washed with cold ethanol-diethyl ether and dried in high vacuum to get desired product. (Yield= 145 mg, 63%). ^{1}H NMR ($(CD_3)_2SO$, 500 MHz, 300K) (**Figure S21**): δ= 18.47 (s, 2H, ***H-bonded oxime***); 7.91 (d, 2H, *J*= 5 H$_z$; -Pyr***H***); 7.39 (d, 2H, *J*= 5 H$_z$; -Pyr***H***); 3.65 (s, 2H, -PyrC***H$_2$***); 2.42-2.39 (m, 3H, -NH- & -C***H***$_2$); 2.31 (s, 12H, -C***H$_3$***). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz, 300K) (**Figure S22**): δ= 155.7; 152.8; 149.8; 125.6; 51.2; 43.6; 15.3; 13.1. ATR-FTIR (Neat Solid, *v* in cm^{-1}): 489 (m, **Co-N$_{axial}$**); 414 (m, **Co-Cl**). UV-Vis in CH_3CN (λ_{max} in nm, ε in parentheses $M^{-1}cm^{-1}$): λ_{max}= 305 (1140); 365.5 (364); 495 (14.4); 591(3.2). HRMS (G2S-ESI-QToF) m/z$^+$ calculated for $(M+H^+)$ $[C_{16}H_{26}N_6O_4Cl_1Co_1]$: 461.1114, found 461.7045.

1.3. Cyclic Voltammetry Study in organic solvent and in aqueous pH buffer: Electrochemical behaviour on aqueous 0.1 M MES Buffer medium (pH 8.0-5.0) was observed via Cyclic Voltammetry. Due to partial solubility of **1**, CV in an organic medium (dry CH_3CN) also performed. Complex concentration (1 mM) was kept same in all case unless mentioned. In organic medium, 0.1 M TBAF has been used as supporting electrolyte. CVs were done using 1 mm diameter glassy carbon disc working electrode, Pt-wire as counter electrode, Ag/AgCl (1M KCl) reference for aqueous; Ag/Ag^+ (Ag^+ in CH_3CN) reference during organic medium study. Potential values are reported either against ferrocene couple ($FeCp_2^{+/0}$) (in organic medium) or against SHE (externally by using Fc-OH in aqueous medium).

1.4. Bulk or Control Potential Experiment in aqueous buffer: Bulk Electrolysis (BE) or control potential experiment (CPE) has been carried out in an air-tight 55 mL four neck H-type glass vessel. Three of its neck is fitted with various electrodes; 1 cm x 1.5 cm graphite plastic chip as working electrode; 23 cm coiled platinum wire as counter electrode (separated by glass frit chamber), Ag/AgCl in 1M KCl as reference electrode. Last neck was closed by a

14/20 suba seal rubber septum, which was used for N_2 purging before experiment and for headspace gas collection. During experiment, 10 mL of 0.25 mM complexes were added in the vessel, all electrodes (along with a magnetic bead) were inserted along with 14/20 rubber septum cap (in gas tight manner) and solution was purged with N_2 for 30 minutes. Then, purging was stopped and chrono-coulometric experiment was started at corresponding catalytic potentials. Solution was continuously stirred (600 rpm) with a magnetic stirrer during the experiment. Headspace gas was collected by a VICI made Leur-lock gastight syringe after 30 min interval, and it was analyzed via a gas chromatography (GC) instrument on TCD mode. Rinse bulk run was done by rinsing working electrode with 3 mL water under similar condition in absence of any catalyst.

1.5. Field Emission Scanning Electron Microscopy (FE-SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) analysis: Field emission scanning electron microscopy images of plastic chip electrode before and after bulk electrolysis were obtained using JEOL JSM7600F instrument, operated at accelerating voltage of 5 kV. Energy dispersive X-ray spectroscopy (EDS) was performed under FE-SEM to analyze the elemental composition.

1.6. Photo-catalytic study in aqueous buffer: The photocatalytic H_2 production studies were carried out in Schlenk tube, which has a total volume of 53 mL. Initially, the stock solutions of photosensitizer Eosin-Y (5 mM) and complex **C1** or **C2** or **C3** (1 mM each) were prepared in aqueous buffer solution (0.1 M MES, pH 7.0). For all the experiments, 20 mL of reactant solution were prepared from those stock solutions (with appropriate serial dilution steps), which finally contained Eosin-Y (final concentration 0.05 mM), complex **C1** or **C2** or **C3** (final concentration 0.25 mM), and triethanolamine (TEOA) (5% v/v). The photocatalytic experiment was carried out using (SLS301) Thor Lab with wavelength range of 350-2700 nm Instrument with 335-610 nm band pass filter, the power of the laser beam was fixed at 40 mW/cm^2, and the size of the beam in all the experiments was kept constant at 3.79 cm^2. Each sample was purged with nitrogen for 30 minutes before the photocatalytic experiment via LASER irradiation. During the experiment, 0.5ml of head space volume was taken using VICI made Leur-lock gastight syringe periodically after every hour. The collected gas sample was injected in the TCD of the Gas Chromatograph instrument. The Gas chromatographic instrument was calibrated using commercially available 1% and 2% of standard H_2.

1.7. Gas chromatography analysis: Amount of H_2 evolved were quantified by using Dhruva CIC gas chromatography (GC) instrument with TCD detector and 3 mL/min UHP Argon

(99.99%) as carrier gas equipped with a 5 A° molecular sieve at room temperature. Instrument calibration build up curve was manually created by externally different known amount of direct control 1% H_2 and 2% Hydrogen gas mixture injection.

1.8. Dynamic Light Scattering (DLS) study: For the DLS experiment, the sample C2 (conc. 0.25 mM) was irradiated for 6hrs in the presence of PS Eosin-Y (conc. 0.05mM), and 5% TEOA as sacrificial electron donor at pH 7 while monitoring the photocatalytic H2 production. Then 3mL of the reaction mixture was taken into the cuvette to record the DLS spectra. This data was compared to the data recorded from the reaction mixture before photo-irradiation.

1.9. Single-crystal X-ray diffraction: Crystals of C2 hetero dimer complex was grown from acetonitrile-diethyl ether mixture by slow diffusion method. A suitable crystal of dimension 0.12 mm x 0.10 mm x 0.08 mm was selected by microscope and mounted on a cryo-loop using cryoprotectant paratone oil. Single crystal diffraction data for both the complexes were collected at 298K on a Bruker Kappa APEX-II diffractometer with CCD PHOTON 2.0 detector equipped with IμS 3.0 Mo Kα (λ = 0.71073 Å) source. X-ray diffraction intensities were collected integrated and scaled with the APEX3 suite. The empirical absorption correction was applied to the data by employing the multi-scan method in SADABS programming.[4] The structure was solved by direct methods with SHELXS-97, Olex 2[5] and refined by the full matrix least square methods on F2 using the SHELXL-2014.[6] The details of the crystal data collections and data refinement parameters are given in Table S2. The complete crystallographic information file (CIF) for C2 hetero dimer complex was deposited in Cambridge crystallographic data centre (CCDC No: 2040107).[7]

Calculation of catalytic rate:

Catalytic rate of the complexes was measured from this equation S1:

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463}\left(\frac{RTk_{obs}}{Fv}\right)^{1/2}$$ (**Equation S1**)

where, i_{cat} = catalytic current, i_p = stoichiometric current, n = number of electrons involved in this process, R = universal gas constant, T = temperature in K, F = 1 Faraday, and v = scan rate.

Calculation of overpotential (OP):

$$\eta\,(OP) = E_{cat/2} - 0.059 \times pH \ \ (in\,V\,units)$$ (**Equation S2**)

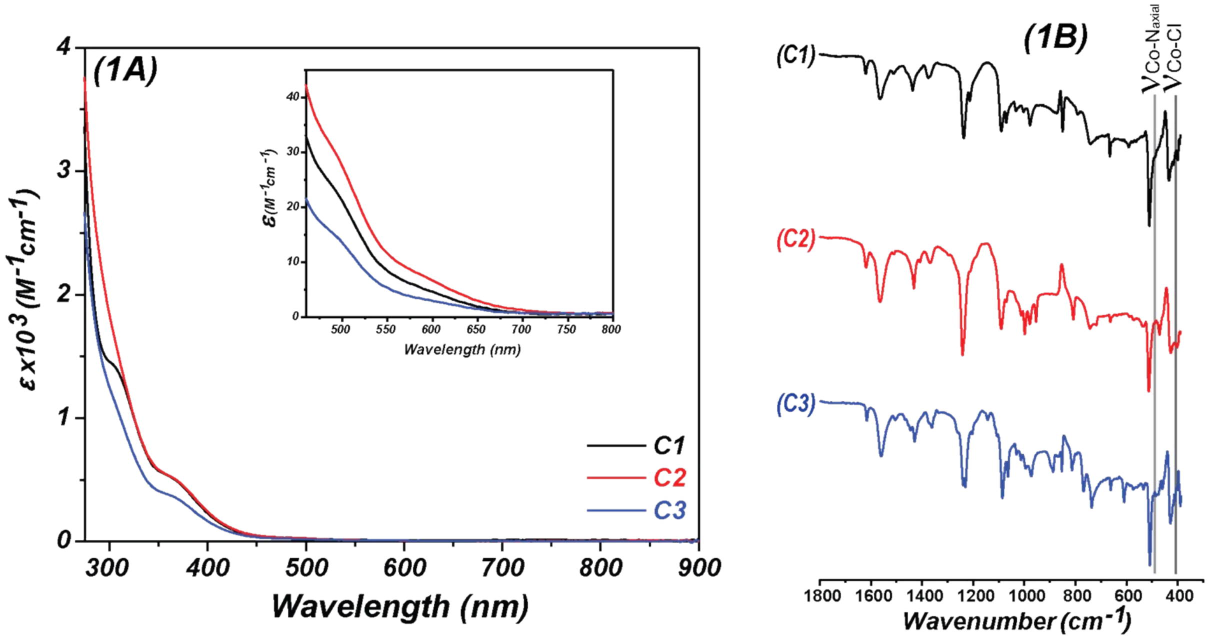
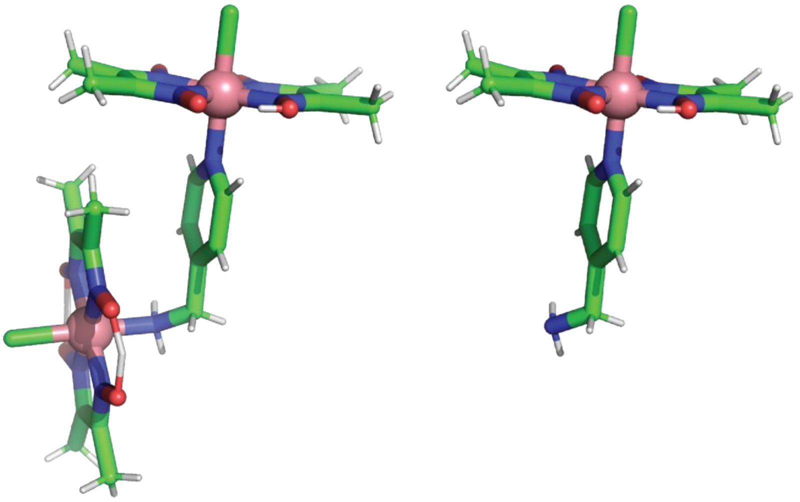


Figure S1. Comparative optical absorbance (**1A**) and ATR-IR spectrum (**1B**) for complexes **C1** (black trace), **C2** (red trace) and C**3** (blue trace). Onset figure in 1A depicts d-d transition in the visible region.



C2 heterodimer **C2 monomer**

Figure S2. (Left) The heterodimeric crystal structure of C2 grown in acetonitrile-ether media (diffracted at 298 K). (Right) The possible monomeric C2 structure following the cleavage of cobaloxime-amine bond.

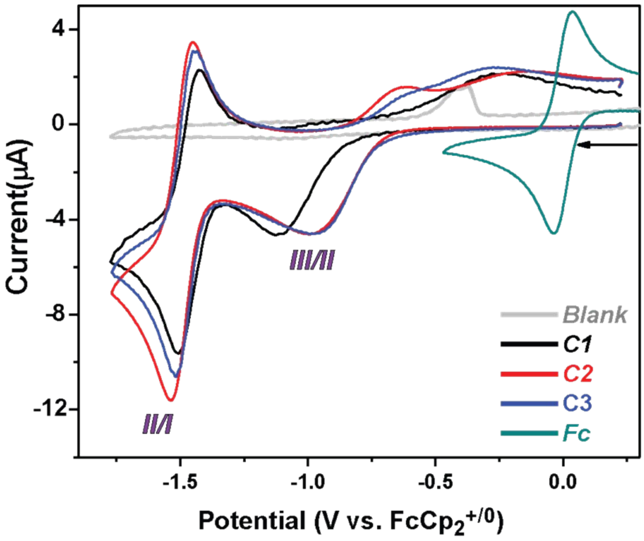


Figure S3. Comparative cyclic voltammograms (CVs) for 1mM of **C1** (black trace), **C2** (red trace), **C3** (blue trace) and Ferrocene (cyan trace) recorded in CH_3CN solvent. For all experiments, 1 mm diameter glassy carbon disc, Pt wire, and $Ag/AgNO_3$ (in CH_3CN) was employed as working, counter, and reference electrode, respectively during this experiment (scan rate 1 V/s). 0.1 M TBAF (tetrabutylammonium tetrafluoroborate) was used as supporting electrolyte. CVs were recorded at room temperature.

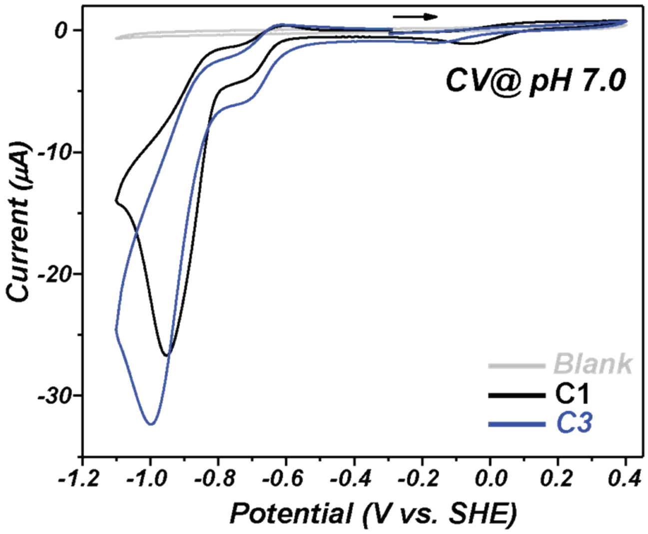


Figure S4. Cyclic voltammograms recorded for 1 mM complex **C1** (black trace), **C3** (blue trace), along with their corresponding blank (grey trace) at aqueous solutions pH 7.0. For all experiments, 1 mm diameter glassy carbon disc, Pt wire, and Ag/AgCl (in 1M KCl) was employed as working, counter, and reference electrode, respectively during this CV experiment (scan rate 1 V/s). All data were recorded at room temperature.

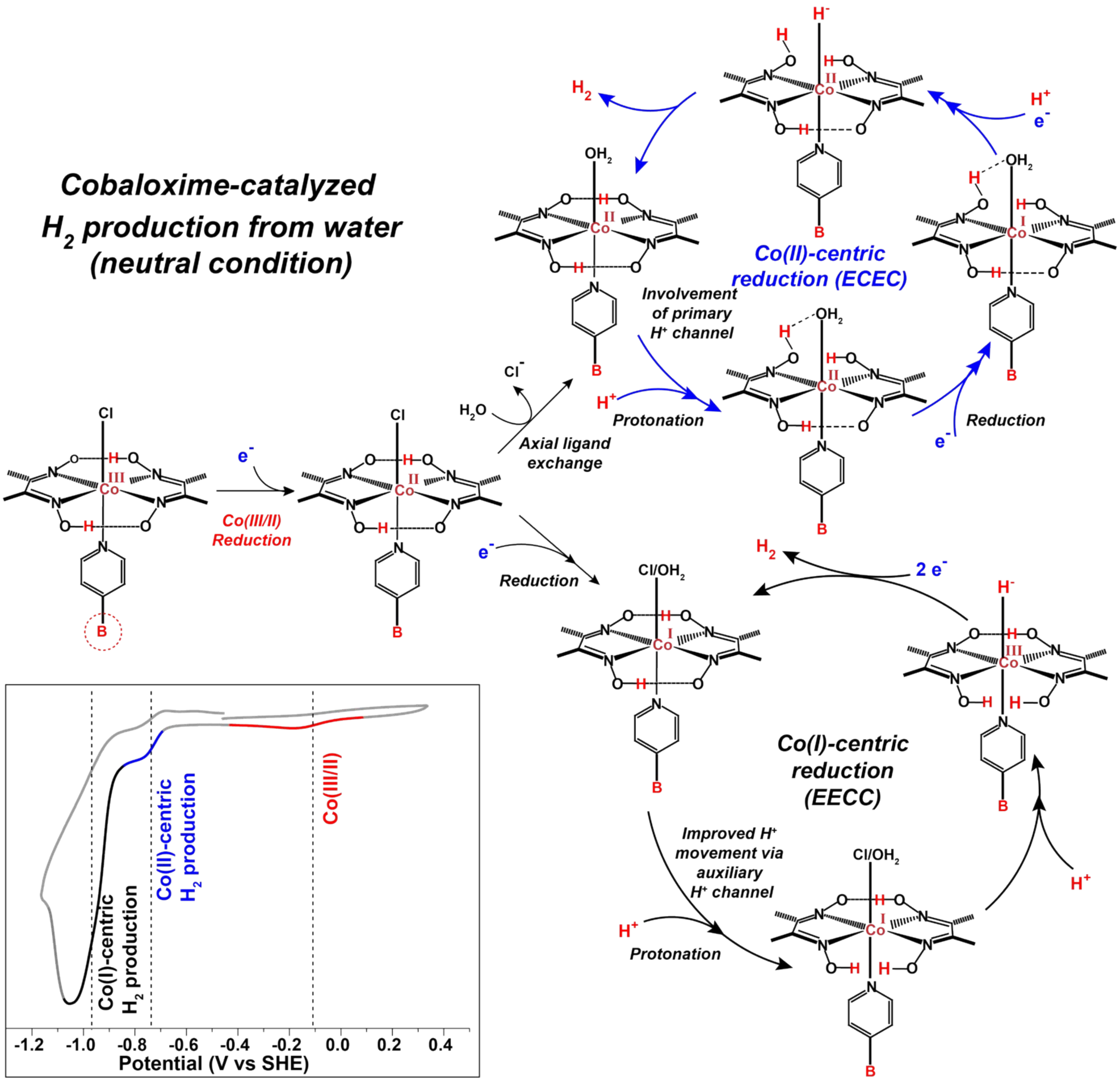


Figure S5. The probable catalytic mechanism for catalytic H_2 production from water by synthetic outer coordination sphere containing cobaloxime derivative complexes in neutral aqueous media. (Adapted from Reference [2]).

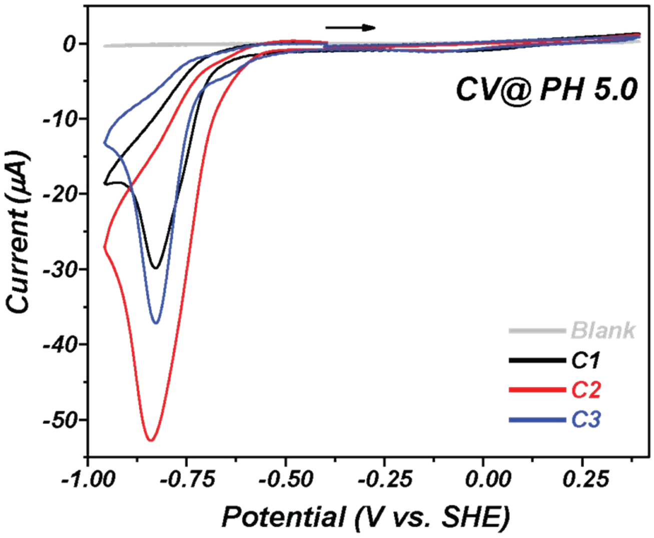


Figure S6. Cyclic voltammograms recorded for 1 mM complex **C1** (black trace), **C2** (red trace), and **C3** (blue trace) along with their corresponding blank (grey trace) at aqueous solutions pH 5.0. For all experiments, 1 mm diameter glassy carbon disc, Pt wire, and Ag/AgCl (in 1M KCl) was employed as working, counter, and reference electrode, respectively during this CV experiment (scan rate 1 V/s). All data were recorded at room temperature.

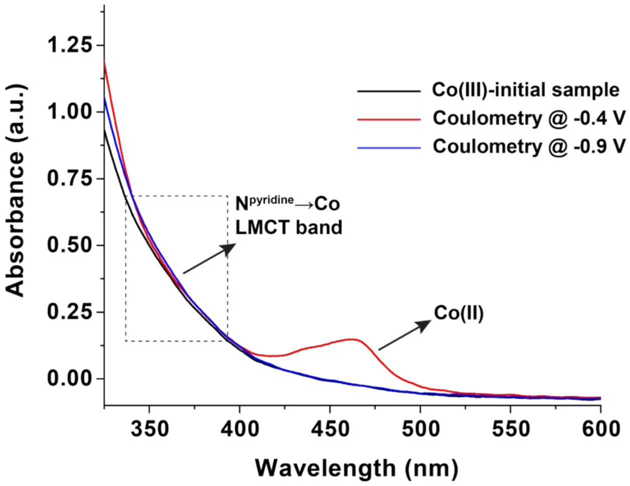


Figure S7. The spectroelectrochemical response of C2 at variable conditions, recorded at pH 7.0 solution.

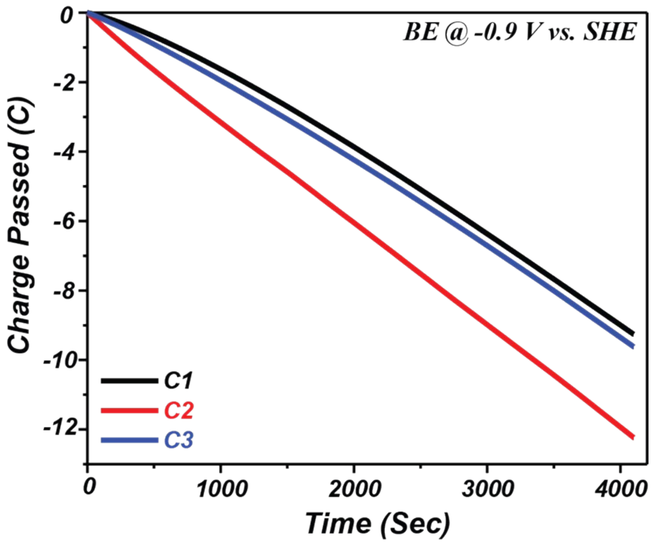


Figure S8. The chrono-coulometric (bulk electrolysis: BE) data recorded for 0.25 mM complexes C1 (black trace); C2 (red trace); C3 (blue trace) in aqueous buffer (pH 6.0) solution. The data was recorded at -0.9 V vs. SHE.

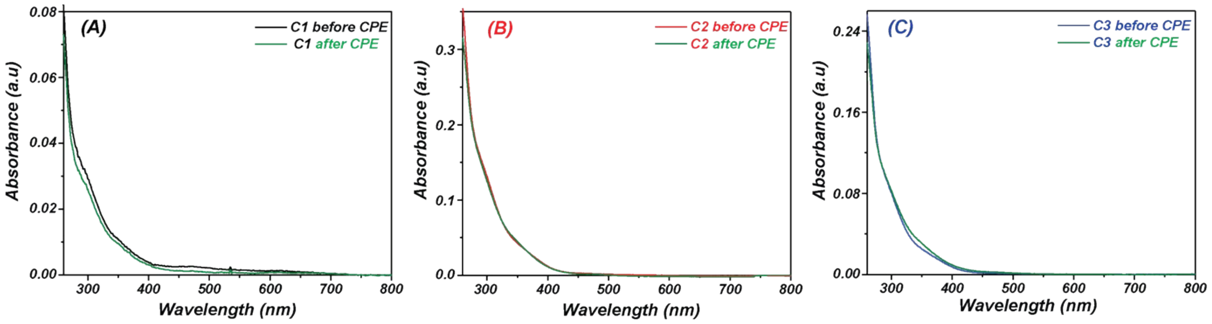


Figure S9. Comparative optical spectrum for complex (A) **C1** (black trace), (B) **C2** (red trace) and (C) 3 (blue trace) respectively before and after (olive trace) the bulk electrolysis experiment at pH 6.0 solution. The bulk electrolysis (CPE) of 0.25 mM corresponding complex was done at -0.9 V (vs. SHE) for 1800 s using a plastic chip working electrode (active area 1 cm x 1.5 cm), coiled Pt wire as counter and Ag/AgCl as reference electrode.

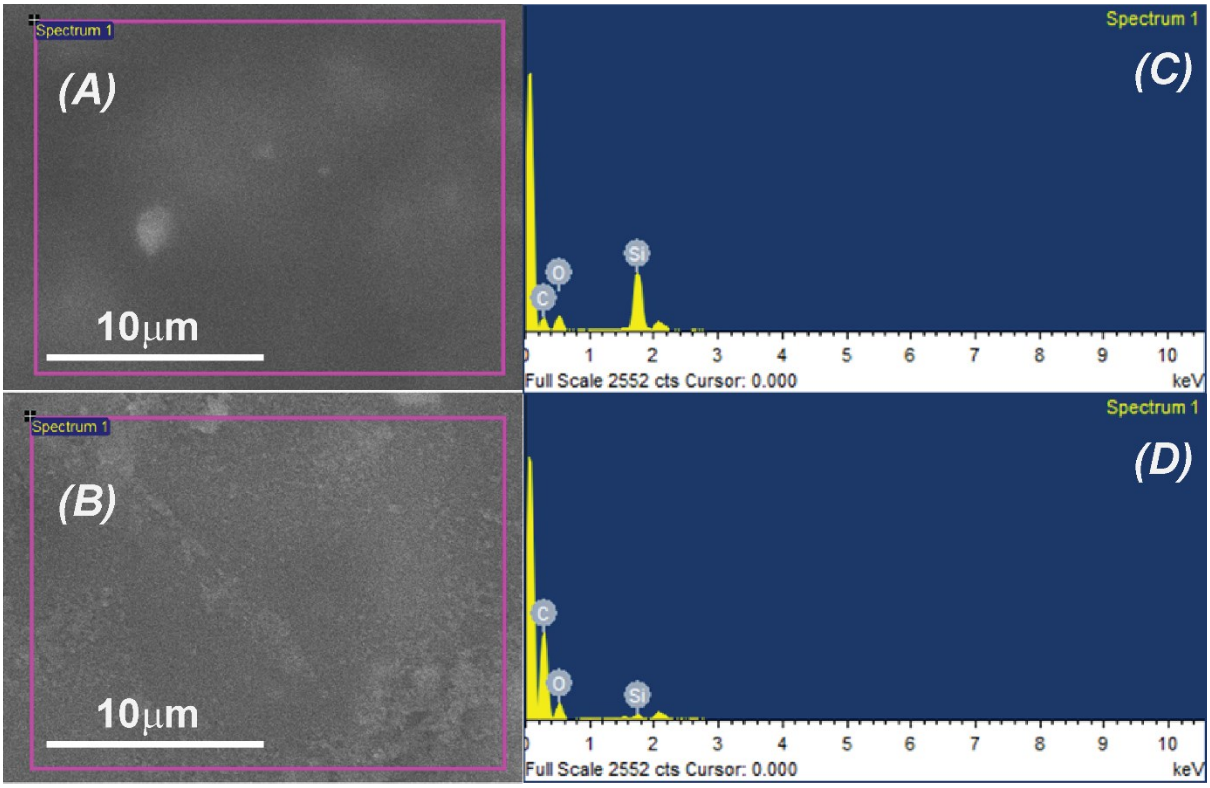


Figure S10. The SEM image, of the plastic chip working electrode [generated from graphite powder and poly(methyl methacrylate)][8] (A) before and, (B) after the chrono-coulometric experiment with **C2** at pH 6.0 solution. EDS spectra of the plastic chip working electrode (C) before and (D) after the chrono-coulometric experiment with C2 at pH 6.0 solution. The bulk electrolysis data was recorded at -0.9 V (vs. SHE) for 1800 s using a plastic chip working electrode (active area 1 cm x 1.5 cm), coiled Pt wire (23 cm) as counter and Ag/AgCl as reference electrode.

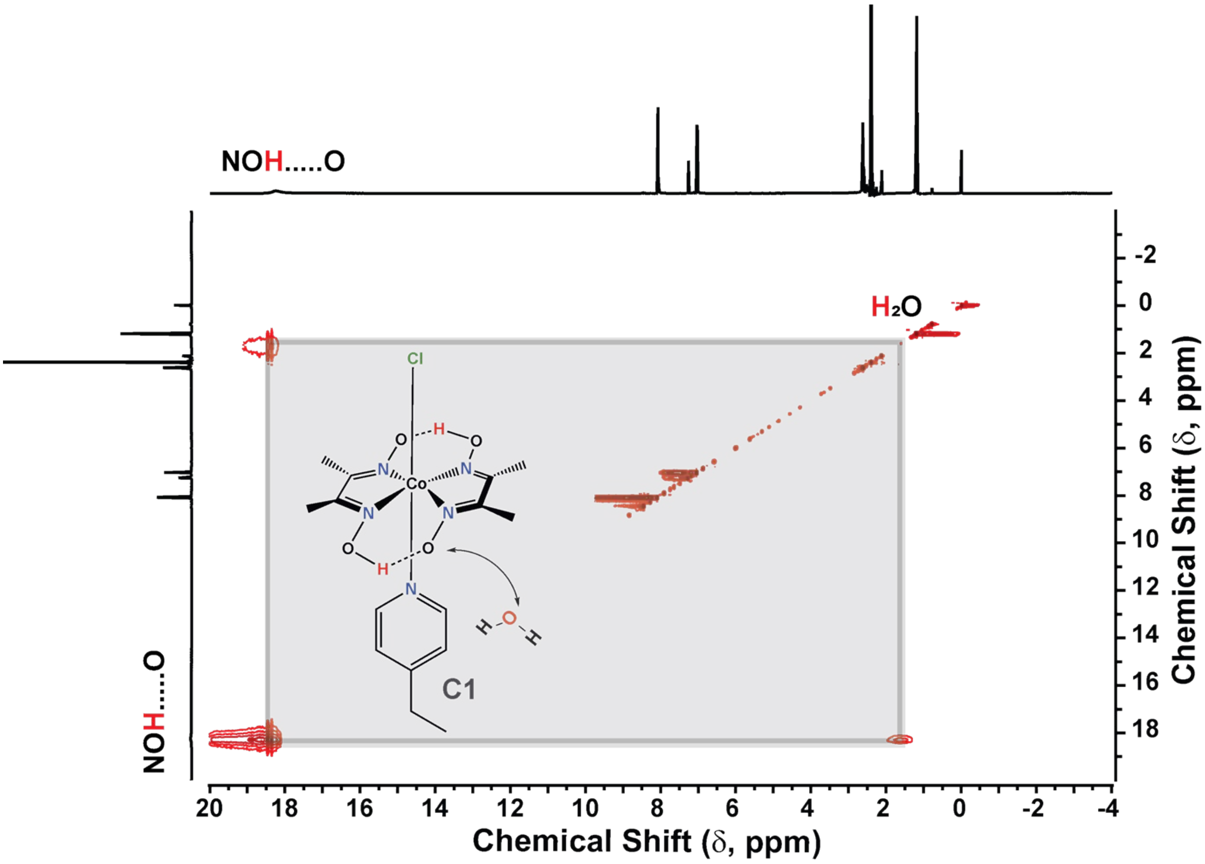


Figure S11. Two-dimensional EXSY NMR of complex **C1** in $CDCl_3$ at ~300K temperature with 350 milliseconds mixing time. The water-mediated proton transport (between oxime and solvent water) is demonstrated by the solid black trace. The inset picture depicts the molecular picture of the proton relay pathway.

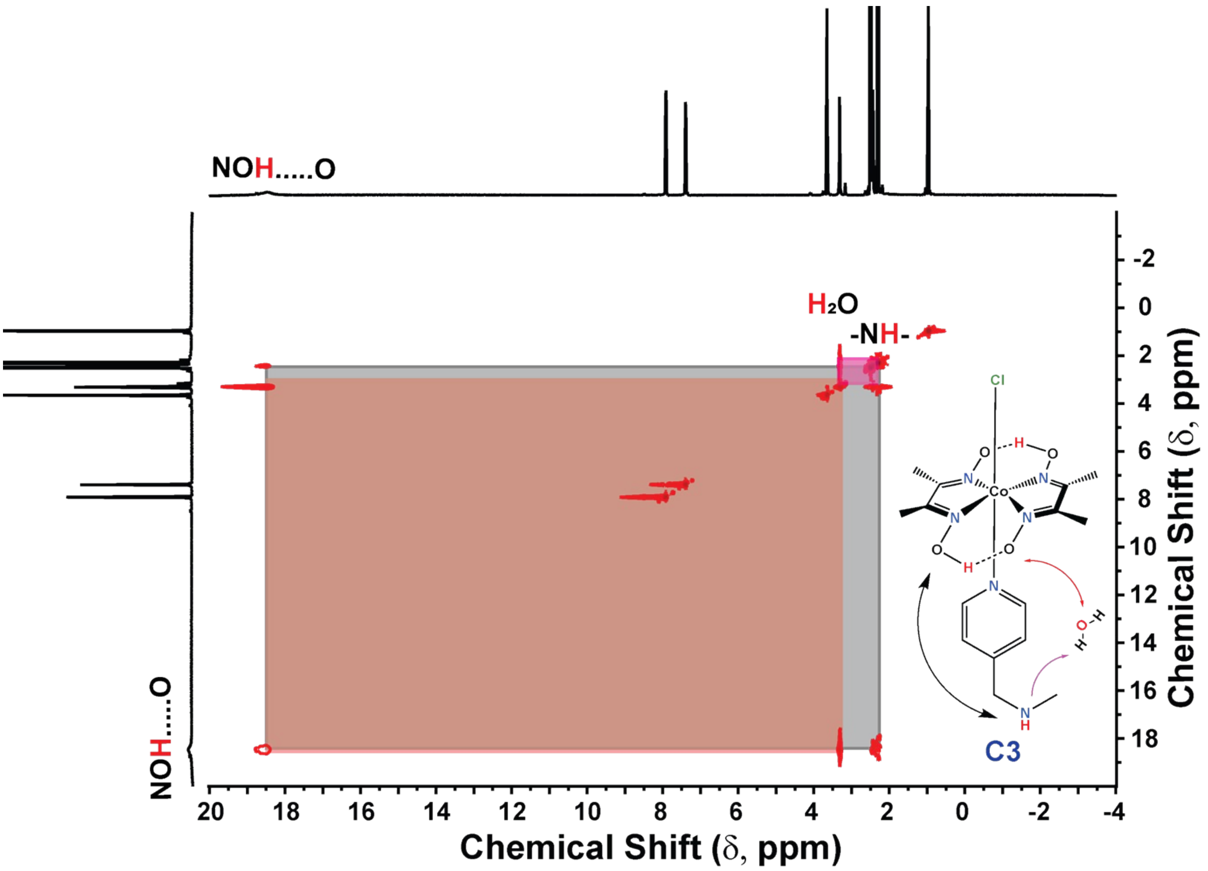


Figure S12. Two-dimensional EXSY NMR of complex **C3** in d^6-DMSO at 300K temperature with 350 milliseconds mixing time. The cross peaks appeared due to oxime- secondary amine proton exchange is displayed by black traces. The water-mediated proton transport between oxime is demonstrated by the red (oxime) and pink trace (secondary amine). The inset picture depicts the molecular picture of the various proton relay pathways.

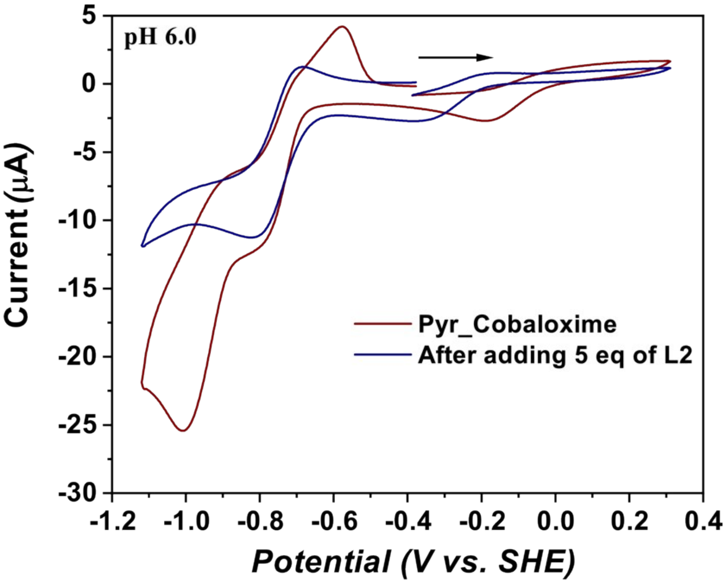


Figure S13. The comparative CV data of unsubstituted pyridine-linked cobaloxime in the absence (brown trace) and in the presence of 5 equivalent of L2 ligand (blue trace) in pH 6.0 with 0.5 V/s scan rate.

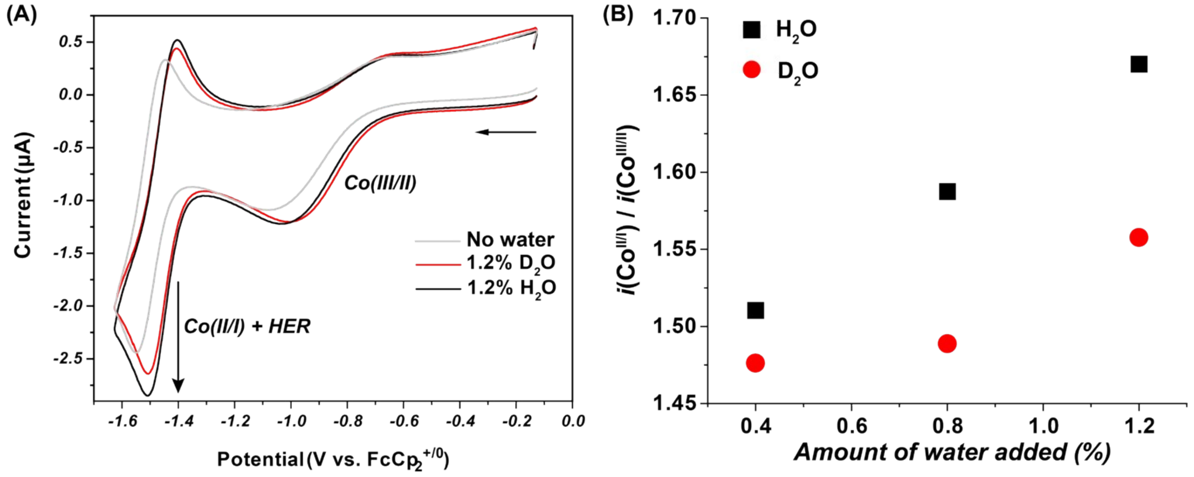


Figure S14. (A) Comparative CV of C2 in acetonitrile in the presence of no water (grey trace), 1.2% H_2O (black trace), and 1.2% D_2O (red trace). **(B)** the ratio of Co(II/I) and Co(III/II) reduction signals in the presence of varying amounts of H_2O (black squares) and D_2O (red circles).

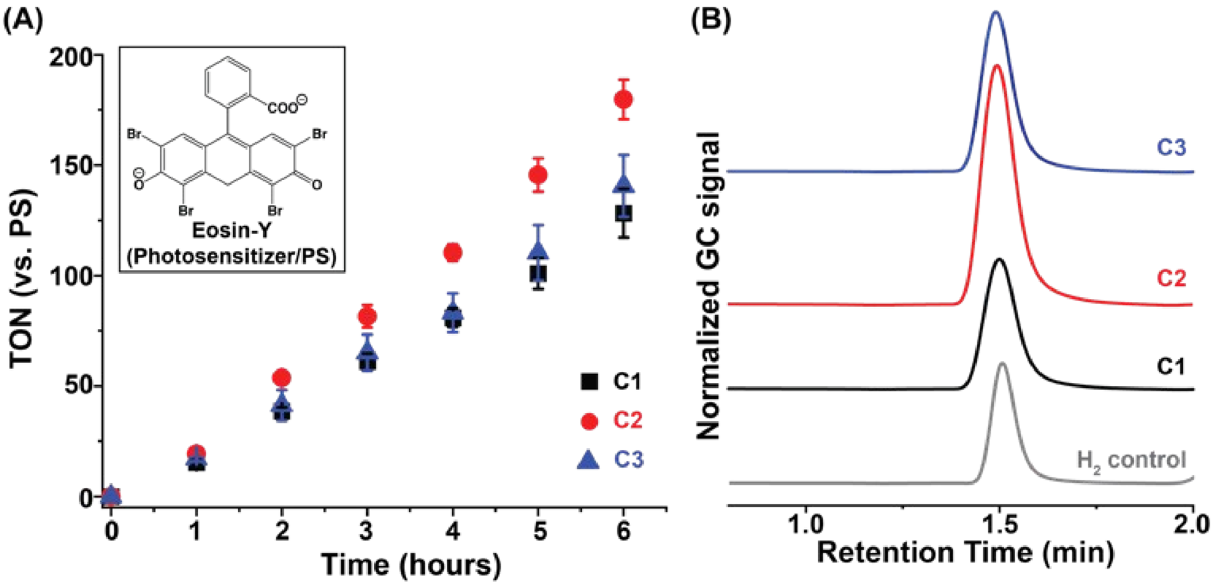


Figure S15. (A) The photocatalytic H_2 production activity, represented by TON (vs. PS), recorded for 0.25 mM of C1 (black square), C2 (red circle), and C3 (blue triangle) over 6 hours of photo-irradiation (λ_{ex} 335-610 nm) in buffered pH 7.0 solution at 298 K in the presence of 0.05 mM of PS Eosin-Y(inset), and 5% (v/v) TEOA as sacrificial electron-donor. **(B)** The normalized GC response for C1 (black trace), C2 (red trace), and C3 (blue trace) recorded during the photocatalytic HER experiment along with control 1% H_2 (grey trace).

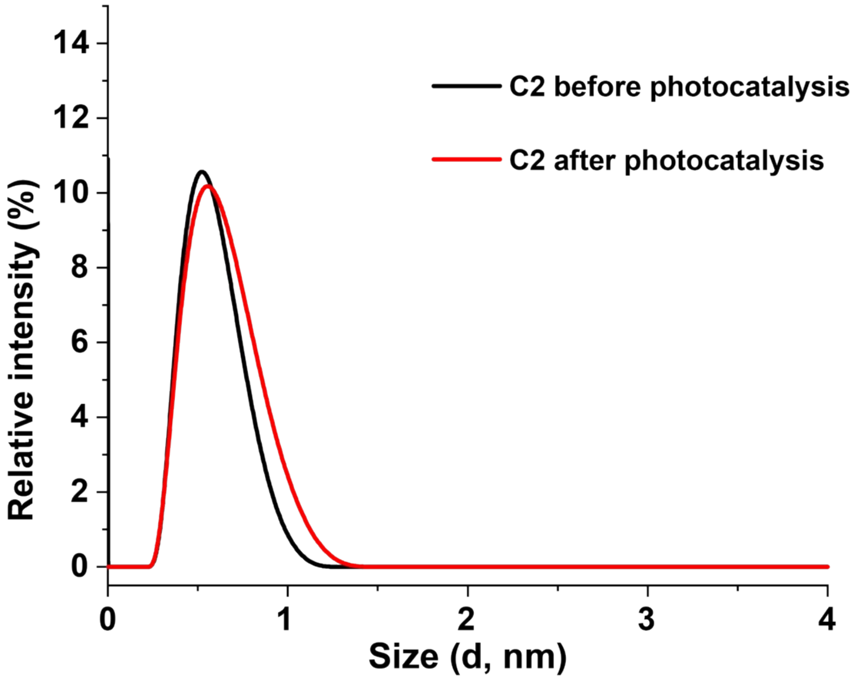


Figure S16. The comparative DLS spectra of C2 recorded before and after photocatalytic study (6 hours) in aqueous solution (pH 7.0).

Supplementary data of the complexes:

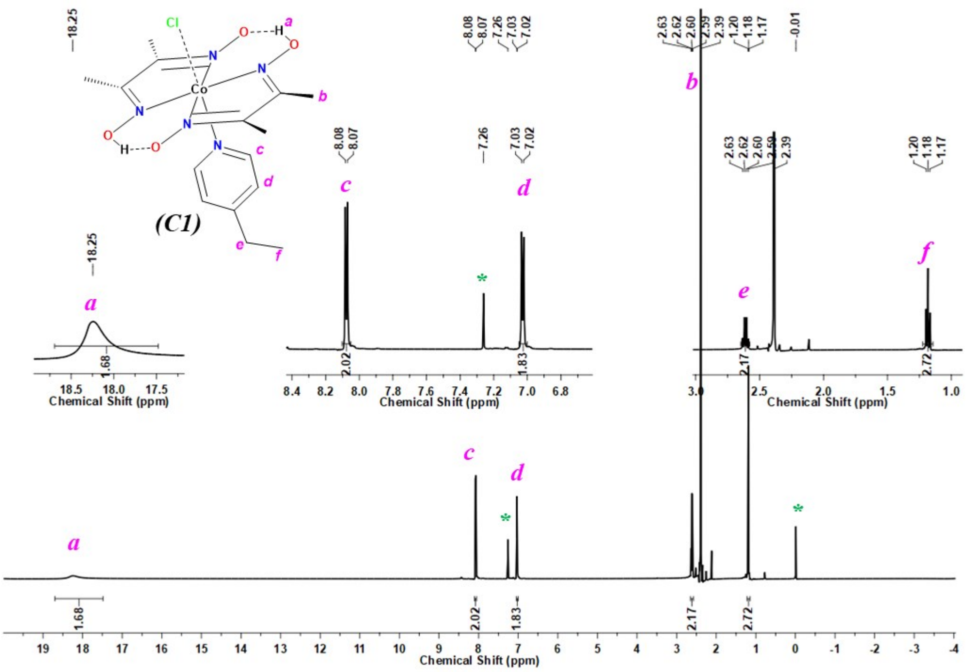


Figure S17. ^1H NMR of the complex **C1** recorded in $CDCl_3$ solvent at room temperature (300 K).

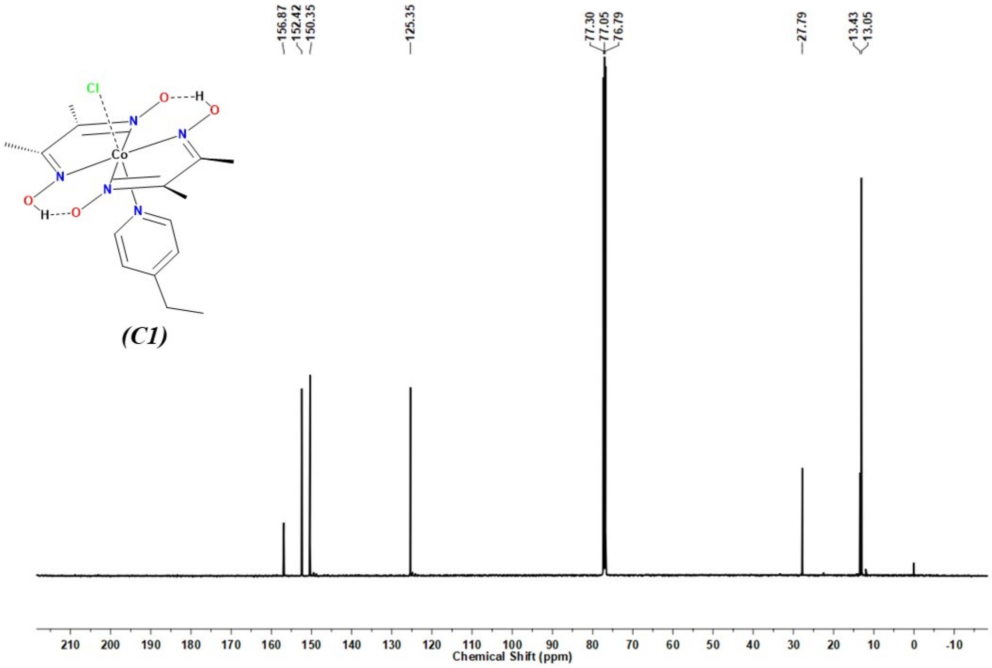


Figure S18. ^{13}C NMR of the complex **C1** recorded in $CDCl_3$ solvent at room temperature (300 K).

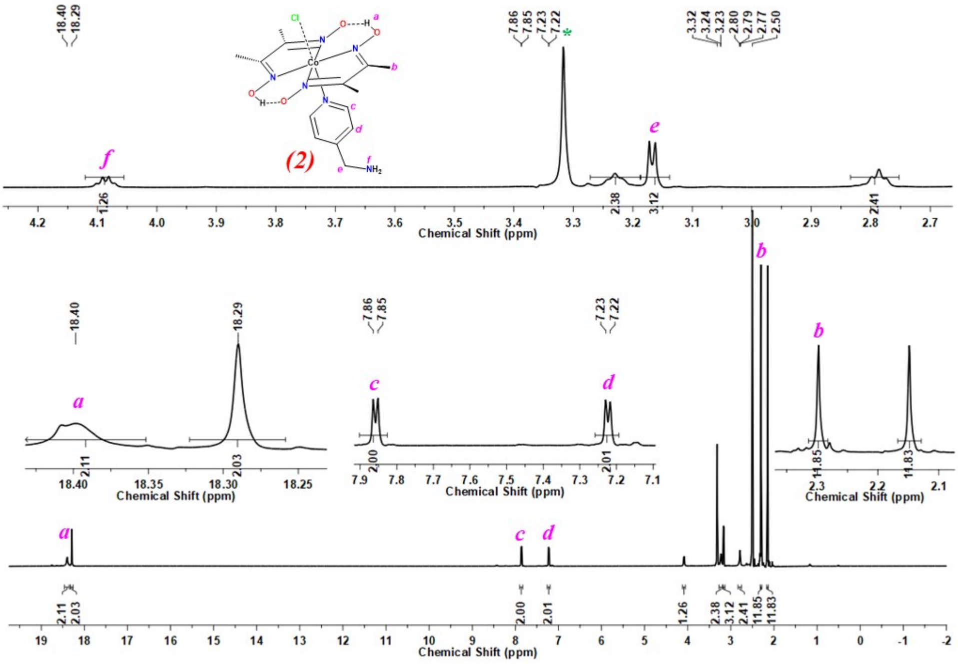


Figure S19. ^{1}H NMR of the complex **C2** recorded in d$_6$-DMSO solvent at room temperature.

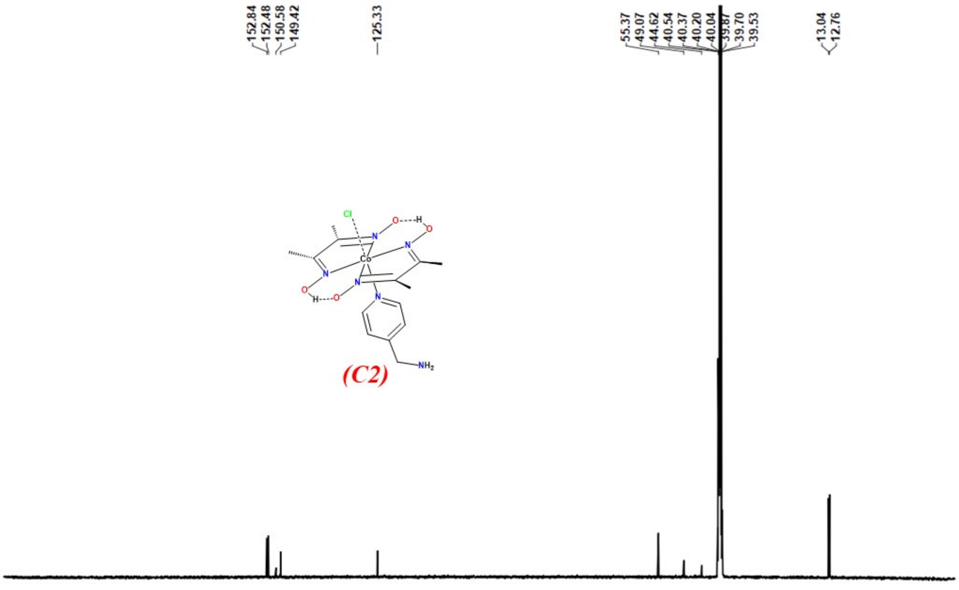


Figure S20. ^{13}C NMR of the complex **C2** recorded in d$_6$-DMSO solvent at room temperature (300 K).

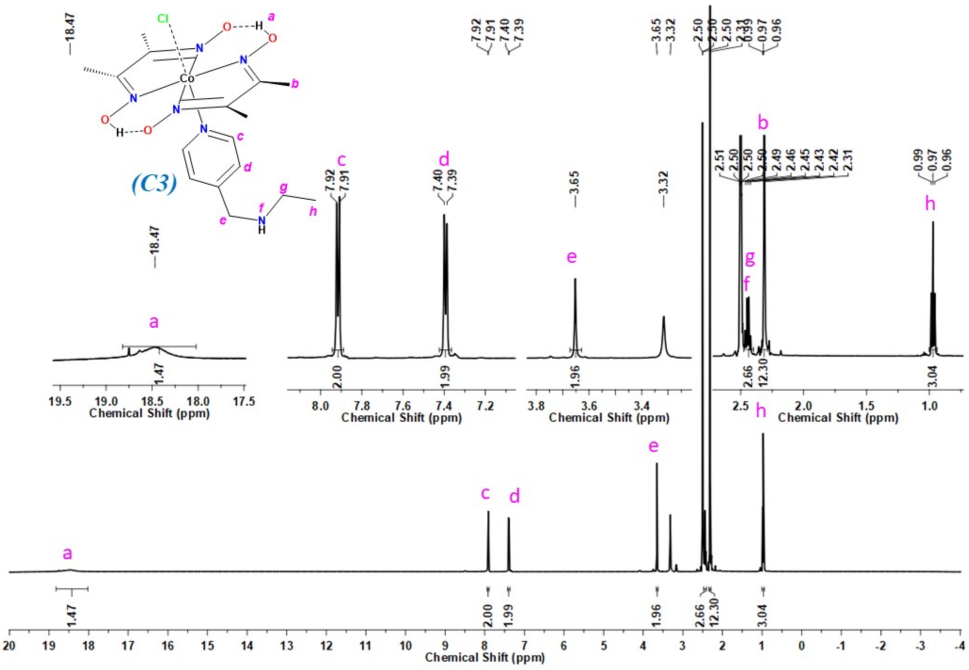


Figure S21. ^{1}H NMR of the complex **C3** recorded in d$_6$-DMSO solvent at room temperature (300 K).

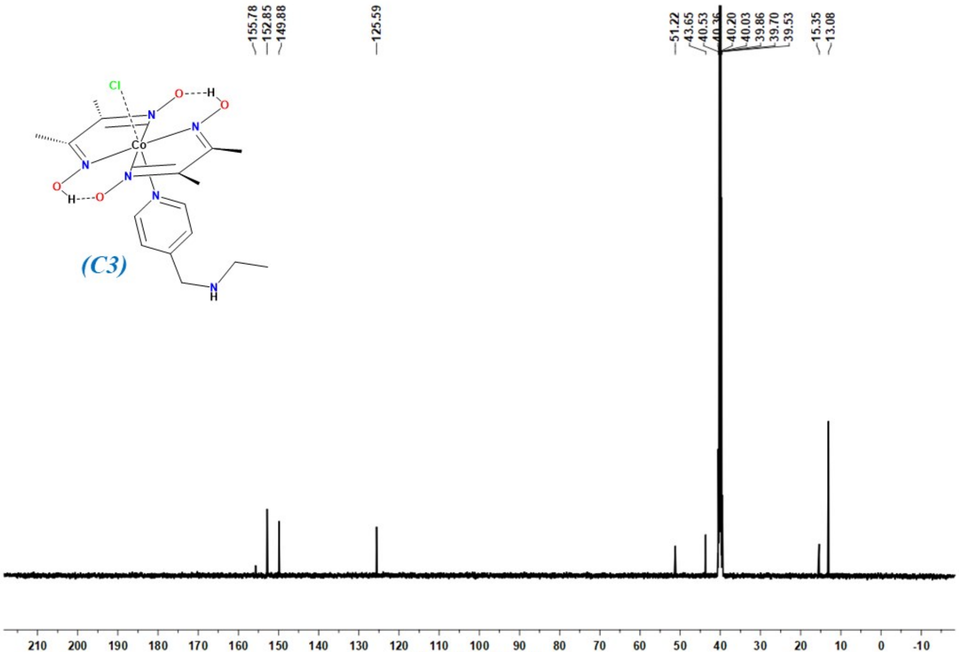


Figure S22. ^{13}C NMR of the complex **C3** recorded in d$_6$-DMSO solvent at room temperature (300 K).

Table S1. Table for selected ATR-FTIR stretching frequencies, redox parameter and optical absorbance data for all complex.

Complex	**ATR-FTIR bands** (ν/cm^{-1})		**Redox peak position in CH_3CN** (V vs. $FeCp_2^{+/0}$)		**Optical bands** [λ/nm (ε/M^{-1}cm^{-1})]	
	$\upsilon_{Co\text{-}Naxial}$	$\upsilon_{Co\text{-}Cl}$	**$E_{Co(III/II)}$**	**$E_{Co(II/I)}$**	**LMCT**	***d-d***
C1	486	417	-1.11	-1.47	305.5 (1416); 367 (501)	497 (22); 594 (4.8)
C2	491	411	-0.99	-1.49	309.5 (1496); 365.5 (512)	494 (29.4); 587 (7.7)
C3	489	414	-0.97	-1.48	305 (1140); 365.5 (364)	495 (14.4); 591 (3.2)

Table S2. Crystal data and refinement details of heterodimer C2 complex.

Crystal data	C2 hetero dimer
Crystal Color	Yellow
Empirical formula	$C_{22}H_{36}N_{10}O_8Cl_2Co_2$
Molecular weight	757.37
Crystal system, space group	Hexagonal, *P*6_5
Temperature (K)	298
a, b, c (Å)	20.3990 (12), 14.7613 (9)
V (Å^3)	5319.5 (6)
Z	6
Radiation type	MoKα
μ (mm−1)	1.14
Crystal size (mm)	0.12 x 0.10 x 0.08
Data collection	
Diffractometer	Bruker Kappa APEX-II CCD
Absorbtion Correction	Multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1000 before and 0.0613 after correction. The Ratio of minimum to maximum transmission is 0.7534. The λ/2 correction factor is Not present.
T_{min}, T_{max}	0.562, 0.746
No. of measured, independent and observed [I > 2σ(I)] reflections	49657, 8863, 8389
R_{int}	0.030
(sin θ/λ)$_{max}$ (Å^{-1})	0.670
Refinement	
R[F^2 > 2σ(F^2)], wR(F^2), S	0.030, 0.088, 0.99
No. of reflections	8863
No. of parameters	433
H-atom treatment	A combination of independent and constrained refinement were performed for treating H-atoms
Δρmax, Δρmin (e Å^{-3})	0.54, -0.25
CCDC	2040107

Acknowledgements

The authors would like to thank the experimental facility and financial support provided by the Indian Institute of Technology Gandhinagar (IITGN), and Indian Institute of Technology Bombay (IITB). D. D. would like to thank the support of the DST-Inspire fellowship provided by the Department of Science and Technology (DST), India (DST/ INSPIRE Fellowship/ 2017/ IF170385). A. D. acknowledges the Shastri Institutional Collaborative Research Grant (SICRG) for 2017-19 provide by Shastri Indo-Canadian Institute (SICI). The authors also thank Prof. Saumyakanti Khatua and Prof. Sudhanshu Sharma for their assistance with the photocatalytic experiments. We also thank Dr. D. N. Srivastava for his support with plastic chip electrode. We also acknowledge the assistance from Ms. Varsha Thambi for her aid during EDS/FE-SEM studies. We also thank Prof. Superb Mishra and Prof. Vijay Thiruvenkatam for their guidance during the DLS and SCXRD study, respectively.

References:

(1) Schrauzer, G. N.; Parshall, G. W.; Wonchoba, E. R. Bis(Dimethylglyoximato)Cobalt Complexes: (“Cobaloximes”). In *Inorganic Syntheses*; John Wiley & Sons, Ltd, 2007; pp 61–70. https://doi.org/10.1002/9780470132425.ch12.

(2) Dolui, D.; Khandelwal, S.; SHAIK, A.; Gaat, D.; Thiruvenkatam, V.; Dutta, A. Enzyme-Inspired Synthetic Proton Relays Generate Fast and Acid Stable Cobalt-Based H2 Production Electrocatalysts. *ACS Catal.* **2019**. https://doi.org/10.1021/acscatal.9b02953.

(3) Trogler, W. C.; Stewart, R. C.; Epps, L. A.; Marzilli, L. G. Cis and Trans Effects on the Proton Magnetic Resonance Spectra of Cobaloximes. *Inorganic Chemistry* **1974**, *13* (7), 1564–1570.

(4) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Gottingen, Germany, 1996.

(5) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. a. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J Appl Cryst* **2009**, *42* (2), 339–341. https://doi.org/10.1107/S0021889808042726.

(6) Gruene, T.; Hahn, H. W.; Luebben, A. V.; Meilleur, F.; Sheldrick, G. M. Refinement of Macromolecular Structures against Neutron Data with SHELXL2013. *J Appl Crystallogr* **2013**, *47* (Pt 1), 462–466. https://doi.org/10.1107/S1600576713027659.

(7) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Cryst B* **2016**, *72* (2), 171–179. https://doi.org/10.1107/S2052520616003954.

(8) Perween, M.; B. Parmar, D.; Ram Bhadu, G.; N. Srivastava, D. Polymer–Graphite Composite: A Versatile Use and Throw Plastic Chip Electrode. *Analyst* **2014**, *139* (22), 5919–5926. https://doi.org/10.1039/C4AN01405G.