Supporting Information for

pH-Modulated Activation of Pendant Amine Leading to Rapid Electrocatalytic H_2 Production by a Molecular Copper Complex in Acidic Water

Naseer Ahmad Shah[1], Thinles Dolkar[1†], Suhana Karim[1†], Jumana Ishrat[2], Chandan Das[1], Srewashi Das[1], Aritro Sinha Roy[3,4], Kalishankar Bhattacharyya[2], Arnab Dutta[1,5]*

[1]Chemistry Department, Indian Institute of Technology Bombay, Powai, Maharashtra 400076, India

[2]Department of Chemistry, Indian Institute of Technology Guwahati, Assam 781039, India

[3]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

[4]National Biomedical Resource for Advanced ESR Spectroscopy, Cornell University, Ithaca, NY 14853, USA

[5]Centre for Climate Studies, Indian Institute of Technology Bombay, Powai, Maharashtra 400076, India

[†]These two authors have contributed equally

*Corresponding author: arnab.dutta@iitb.ac.in

Table of contents

General Methods and Synthetic Procedures

Materials and Methods: All the chemicals and solvents were purchased from Avra Chemicals, Sigma Aldrich, and Finar Chemicals and deployed with no further purification. Properly cleaned and oven-dried glassware was used for all the experiments. All the anaerobic experiments were performed under an N_2 atmosphere using the Schlenk lines. The NMR spectra were recorded in Bruker Avance II Ascent FT spectrometer (400 MHz) and Bruker Avance II Ascent FT spectrometer (500 MHz). All the NMR data were reported in δ (ppm) with the solvent peak of d^6-DMSO (δ 2.5 ppm). The optical spectra were recorded in a 2.0 mL quartz cuvette (Sterna) with a 1.0 cm path length in PerkinElmer Lambda 1050 spectrometer. FTIR spectra were recorded as solid samples by preparing KBr pellets in a PerkinElmer (Spectrum-I) spectrometer. The mass spectrometry (MS) of the samples was recorded on a Bruker Maxis impact instrument while operating in the positive ion mode. The pH of the aqueous solutions was measured with the help of a bench top Labman LMPH-10 pH Meter. The elemental analyses were performed using an Elementar Vario Micro cube CHNS analyzer, which is equipped with dual thermal conductivity detectors (TCDs) featuring a high-resistance filament optimized for differential measurement in a dynamic gas environment. These detectors operate with a sensitivity threshold suitable for trace-level detection of carbon, hydrogen, nitrogen, and sulfur. Calibration is performed via a reference standard system, ensuring reproducibility across extended analytical runs.

All the cyclic voltammetry (CV) experiments were recorded using a Metrohm Autolab PGSTAT 204 potentiostat at room temperature. The electrochemical studies were performed in dry N,N′-dimethyl formamide (DMF) or in an aqueous buffer medium prepared in Millipore water (resistivity 18.2 MΩ·cm @ 25 °C). The buffer of the aqueous solution is maintained employing 2-(N-morpholino)-ethanesulfonic acid (MES) (for pH 3.0-7.0) Appropriately diluted sulfuric acid solutions in distilled water was utilized for preparing pH 1.0 and pH 2.0 aqueous solutions. A standard three-electrode assembly containing 1 mm diameter glassy carbon disc working electrode, Ag/AgCl reference electrode (in 3.0 M KCl connected by Vycor tip), and platinum wire counter electrode was used for all the regular electrochemical experiments. All potentials are reported versus Ferrocenium/Ferrocene ($FeCp_2^{+/0}$) couple for data recorded in organic medium. All the potential values in aqueous solution are reported against standard hydrogen electrode (SHE), where $[Fe(CN)_6]^{3-/4-}$ couple was deployed as an internal standard after each experiment [E^0 $[Fe(CN)_6]^{3-/4-}$ = +0.360 V vs. SHE.

A customized four-neck glass vessel (volume 77.0 mL) was used for the bulk electrolysis setup. Here, a coiled 23 cm Pt wire counter electrode, Ag rod reference electrode, and plastic carbon chip (0.75 cm x 2 cm) working electrode were utilized, which occupied an entry neck of the vessel.[1] The final entry neck was closed with a B-14/20 size Suba Seal rubber septum and used for N_2 purging before the experiment and for headspace gas collection for gas chromatography (GC) measurements. During the experiment, 14.0 mL 0.1-0.5 mM complexes were added in the vessel, all electrodes (along with a magnetic bead) were inserted along with a B-14/20 rubber septum cap (gas tight), and the solution was purged with N_2 for 30 minutes. Next, the purging was stopped, and corresponding chronocoulometric experiment was started at respective catalytic potentials. The reaction solution was stirred continuously with a magnetic stirrer during the experiment. A gastight PTFE leur-lock 1000 series (1001TLL) 1.0 mL Hamiltonian syringe was used for collecting headspace gas after 1.0 hour of experiment. It was analysed via gas chromatography (GC) instrument running on a TCD mode. Here, a Dhruva CIC gas chromatography (GC) instrument with a TCD detector and a 5 Å molecular sieve/Porapak column operating at room temperature was utilized. The instrument was calibrated manually by using different samples of variable control gas samples containing 0.1-10% H_2. The SEM-EDS study was done with the help of the JEOL JSM7600F instrument operating at an accelerating voltage of 5 kV. Energy-dispersive X-ray spectroscopy (EDS) was done with FE-SEM to trace the elemental composition.

EPR Study

The ESR spectrum was collected using the Bruker cw ESR EMX spectrometer at the National Biomedical Resource for Advanced ESR Spectroscopy (ACERT). The sample solution was prepared by dissolving about 100 mg of the copper complex in 1 mL DMF, transferred to a 4 mm ESR tube and kept frozen in a liquid nitrogen Dewar. The spectrum was recorded at a microwave frequency of 9.308 GHz and an attenuation of 30 dB at 100 K.

Single Crystal X-ray Diffraction study:

Crystals of the complex were grown from the diffusion of diethyl ether into a concentrated solution of acetonitrile. A suitable green crystal of the complex was selected and mounted on a loop using cryo-protectant paratone oil. The single-crystal diffraction data were collected at 107(5) K in a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source (Mo-

Kα, λ = 0.71073 Å) and a PHOTON II detector. X-ray diffraction intensities were collected, integrated, and scaled with APEX4 software. Empirical absorption correction was applied to the data by employing the multi-scan method with program SADABS[1]. The structure was solved by intrinsic phasing with SHELXT[2] and, refined by full- matrix least-square methods on F^2 using SHELXL implemented in Olex2 interface [3,4].

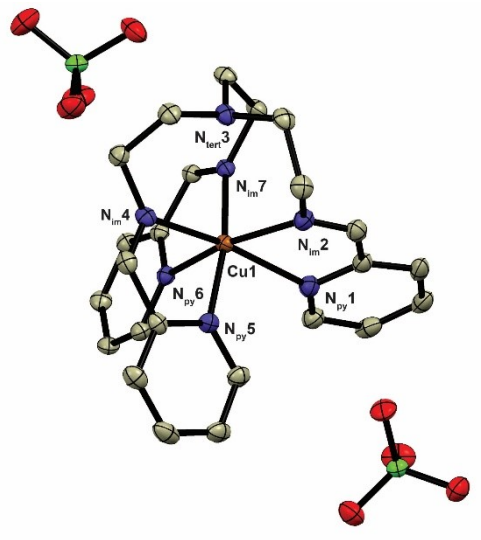


Figure S1: ORTEP view (ellipsoid probability at 50%) of complex **C1**.

All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and treated as riding atoms with Uiso(H) = 1.5Ueq for methyl groups, Uiso(H) = 1.2Ueq for other atoms. Program Mercury was used for molecular graphics, validation and preparation of publication material. Details of crystal data collection and refinement are given in Table S1.

Crystallographic data have been deposited with the Cambridge Crystallographic Data center as supplementary publication no. CCDC-2235825.

Table S1: Crystal data and refinement details for complex C1

Chemical formula	$C_{24}H_{27}Cl_2CuN_7O_8$
M_r	675.96
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	107(5)
a, b, c (Å)	28.0735(5), 10.4170(2), 19.1868(4)
β (°)	101.623(2)

V (Å^3)	5495.96(19)
Z	8
μ (mm^{-1})	1.052
Crystal size (mm)	0.20 × 0.12 × 0.10
No. of measured, independent and [$I > 2\sigma(I)$] reflections	68841, 9810, 7229
R_{int}, R_{sigma}	0.0645, 0.0537
(sin θ/λ)max (Å−1)	0.632
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0493, 0.1264
$R1$, $wR2$ [all data]	0.0750, 0.1467
No. of parameters	379
Δρ max, Δρ min (e Å^{-3})	0.43, -0.69
Goodness-of-fit on F^2 (GOF)	0.963

Table S2: Selected bond lengths (Å) and angles (°) of copper complex **C1**.

Bond lengths

Cu-$N_{Py}{}^{1}$	2.4075(16)	Cu-$N_{im}{}^{2}$	2.0623(15)
Cu-$N_{Py}{}^{5}$	2.0386(16)	Cu-$N_{im}{}^{4}$	2.2524(16)
Cu-$N_{Py}{}^{6}$	2.1177(15)	Cu-$N_{im}{}^{7}$	2.0315(16)

Bond angles

$N_{im}{}^{7}$-Cu-$N_{py}{}^{6}$	79.92(6)	$N_{py}{}^{5}$-Cu-$N_{Py}{}^{1}$	94.63(6)
$N_{im}{}^{7}$-Cu-$N_{Py}{}^{1}$	88.83(6)	$N_{py}{}^{5}$-Cu-$N_{im}{}^{4}$	77.02(6)
$N_{im}{}^{7}$-Cu-$N_{py}{}^{5}$	169.38(6)	$N_{py}{}^{5}$-Cu-$N_{im}{}^{2}$	95.00(6)
$N_{im}{}^{7}$-Cu-$N_{im}{}^{4}$	99.57(6)	$N_{im}{}^{4}$-Cu-$N_{Py}{}^{1}$	171.59(6)
$N_{im}{}^{7}$-Cu-$N_{im}{}^{2}$	95.60(6)	$N_{im}{}^{2}$-Cu-$N_{py}{}^{6}$	161.01(6)
$N_{py}{}^{6}$-Cu-$N_{Py}{}^{1}$-	86.51(6)	$N_{im}{}^{2}$-Cu-$N_{Py}{}^{1}$	74.90(6)
$N_{py}{}^{6}$-Cu-$N_{im}{}^{4}$	94.45(6)	$N_{im}{}^{2}$-Cu-$N_{im}{}^{4}$	104.51(6)
$N_{py}{}^{5}$-Cu-$N_{py}{}^{6}$	90.26(6)		
$N_{py}{}^{5}$-Cu-$N_{py}{}^{6}$	90.26(6)		

Calculation of TON:

$$TON = \frac{No.\ of\ moles\ of\ H_2\ produced}{No.\ of\ moles\ of\ Catalyst\ used}$$

(A) Calculation of current efficiency of complex C1 at pH 1.0:

The overall charge passed during the catalytic HER= 177.8 C

The theoretical amount of H_2 expected = $\frac{177.8C}{96485 \times 2C} mol$ = 921.38 μmoles.

Experimentally H_2 detected in headspace by GC= 760.45 μmoles.

Faradaic efficiency of C1 = $\frac{760.45}{921.38} \times 100$ = 82.56 %

Amount of C1 in the solution= 0.75 μmoles

TON = $\frac{760.47}{0.75}$ = 1014±10

(B) Calculation of current efficiency of the catalyst C1 at pH 2.0:

The overall charge passed during the catalytic HER= 42.63 C

The theoretical amount of H_2 expected = $\frac{98.63C}{96485 \times 2C} mol$ = 507.85 μmoles.

Experimentally H_2 detected in headspace by GC= 460.32 μmoles

Faradaic efficiency of C1 = $\frac{460.32}{507.85} \times 100$ = 90.72 %

Amount of C1 in the solution= 1.0 μmoles

TON = $\frac{460.32}{0.75}$ = 613.0±10

(C) Calculation of current efficiency of the catalyst C1 at pH 3.0:

The overall charge passed during the catalytic HER= 70.89 C

The theoretical amount of H_2 expected = $\frac{70.89C}{96485 \times 2C} mol$ = 367.36 μmoles.

Experimentally H_2 detected in headspace by GC= 327.45 μmoles.

Faradaic efficiency of C1 = $\frac{327.45}{367.36} \times 100$ = 89.13%

Amount of C1 in the solution= 0.75 μmoles

TON = $\frac{327.45}{0.75}$ = 436.0±5

(D) Calculation of current efficiency of the catalyst C1 at pH 4.0:

The overall charge passed during the catalytic HER= 60.218 C

The theoretical amount of H_2 expected = $\frac{60.22C}{96485 \times 2C} mol$ = 312.0 μmoles

Experimentally H_2 detected in headspace by GC= 249.0 μmoles

Faradaic efficiency of C1 = $\frac{249.0}{312.0} \times 100$ = 79.84 %

Amount of C1 in the solution= 0.75 μmoles

TON = $\frac{249.0}{0.75}$ = 332.0±5

(E) Calculation of current efficiency of the catalyst C1 at pH 5.0:

The overall charge passed during the catalytic HER= 56.90 C

The theoretical amount of H_2 expected = $\frac{56.90C}{96485 \times 2C} mol$ = 294.88 μmoles

Experimentally H_2 detected in headspace by GC= 242.97 μmoles

Faradaic efficiency of C1 = $\frac{242.97}{294.88} \times 100$ = 79.84 %

Amount of C1 in the solution= 0.75 μmoles

$$TON = \frac{242.97}{0.75} = 324\pm5$$

(F) Calculation of current efficiency of the catalyst C1 at pH 6.0:

The overall charge passed during the catalytic HER= 52.27 C

The theoretical amount of H_2 expected = $\frac{52.27C}{96485 \times 2C}mol$ = 270.91 μmoles

Experimentally H_2 detected in headspace by GC= 232.0 μmoles

Faradaic efficiency of C1 = $\frac{232.0}{270.88} \times 100 = 85.64\%$

Amount of C1 in the solution= 0.75 μmoles

TON = $\frac{232.0}{0.80} =$ 290.0±5

(G) Calculation of current efficiency of the catalyst C1 at pH 7.0:

The overall charge passed during the catalytic HER= 32.78 C

The theoretical amount of H_2 expected = $\frac{32.78C}{96485 \times 2C}mol$ = 169.90 μmoles

Experimentally H_2 detected in headspace by GC= 136.36 μmoles

Faradaic efficiency of C1 = $\frac{136.36}{169.90} \times 100 =$ 80.26 %

Amount of C1 in the solution= 0.50 μmoles

TON = $\frac{136.36}{0.50} =$ 273.0±5

Calculation of overpotential in organic solvent

Here, we have utilized the following equation suggested by Artero *et al.*[1]

$$E^{0}_{H^+/H_2} = -\frac{2.303\,RT}{F}pK_a + \varepsilon_D - \frac{RT}{2F}ln\frac{C_0}{C^{0}_{H_2}}$$

Here, $E^{0}_{H^+/H_2}$ is the equilibrium potential for H_2 production from the specific acid source at experimental conditions, pK_a is the logarithmic value of the dissociation constant for the acid source deployed in the experiment, ε_D is the difference in diffusion coefficients of the acid and H_2, C_0 is the acid concentration during the experiment, and $C^{0}_{H_2}$ is the concentration of dissolved hydrogen. In the H_2 production experiment by **C1** in the presence of 0.625 mM acetic acid, we have used the following values:

pK_a = 13.5 (acetic acid in DMF)

ε_D = 40 mV (in DMF)

$C^{0}_{H_2}$= 1.9 mM (H_2 in DMF)[2]

$\frac{2.303\,RT}{F}$ = 58 mV

$\frac{RT}{2F}$ = 12.6 mV

Computational details:

All geometry optimizations, frequency calculation were carried out using the B3LYP[3] functional in Gaussian 16[4]. We used the SDD pseudopotential and basis set of Preuss and co-workers for Cu[5], the 6-31G**[6,7] basis set for all the other atoms. We used the water solvent in polarizable continuum model (IEF-PCM)[8–10] to correct the final energies of the studied systems. The reduction potentials and computed ΔG are reported in eV and are referred to standard hydrogen electrode (SHE)[11] reference scale (4.28eV). The free energy and pKa is calculated using the following expressions

$\Delta G = \{E_2 - (E_1 + E_{H^+})\} \times 27.2$

$pKa = \Delta G/0.059$

where E_2, E_1 corresponds to DFT computed energy of the protonated catalyst and the pristine catalyst and E_{H^+} corresponds to computed energy of proton.

The reduction potential for the electrochemical and ΔG for PCET step is calculated using the following expression

$E = -\{(E_1 - E_2) \times 27.2 - 4.28\}$

$\Delta G = \{E_2 - (E_1 + E_{H^+})\} \times 27.2 + 4.28$

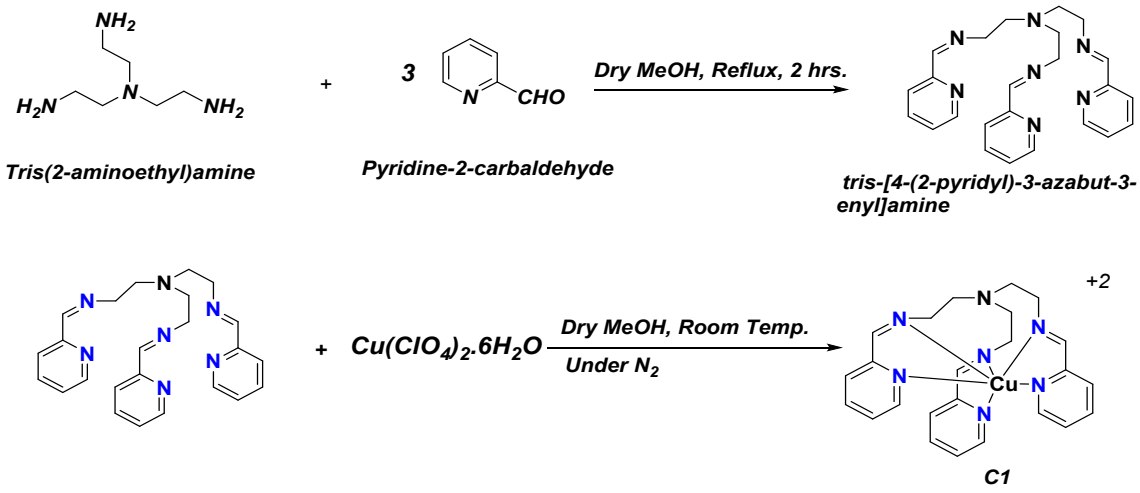
That led us to $E^0_{H^+/H_2}$= -0.73 V (vs. $FeCp_2^{+/0}$) in DMF media for acetic acid concentration we have used. The difference of $E^0_{H^+/H_2}$ and the potential at which the half maxima of the catalytic current was observed is deployed for calculating the overpotential parameter.

Synthetic Procedures

Preparation of Ligand (L1)

The synthesis of the Schiff base ligand **L1** was accomplished by the condensation reaction of 1 mmol (0.1496 mL) of tris-(2-aminoethyl)amine and 3 mmol (0.321 g) of pyridine-2-carbaldehyde in dry methanol with constant stirring. Then 10 uL of hydrochloric acid was added to the reaction mixture and allowed to stir under reflux for about 2 hours at 75 °C (Scheme S1). Brown coloured liquid was collected as the final product after removal of the solvent under reduced pressure. (Yield:85%).

^{1}H NMR (500 MHz, CD_3CN): δ 8.51 (d, *J* = 5.0 Hz, 3H), 8.25 (s, 3H), 7.86 (d, *J* = 8.0 Hz, 3H), 7.70 (td, *J* = 7.5, 1.0 Hz, 3H), 7.30 (ddd, *J* = 7.0, 4.5, 0.5 Hz, 3H), 3.68 (t, *J* = 6.5 Hz, 6H), 2.89 (t, *J* = 6.5 Hz, 6H) (***Figure S1)***. **^{13}C-NMR (125 MHz, CD_3CN) (δ/ppm)**: δ 162.7 (C), 154.6 (CH), 149.3 (CH), 136.7 (CH), 124.8 (CH), 120.6 (CH), 59.4 (CH_2), 54.9 (CH_2). (***Figure S2)*** UV-vis (in DMF) (λ_{max} in nm, ε in parentheses $M^{-1}cm^{-1}$): 284(20,000) (***Figure S3-S4)***. LRMS (G2S-ESI-QToF) m/z calculated for ($M+Na^+$) [436.22], experimentally observed 436.22.



Scheme S1. Synthetic scheme of ligand (**L1**) and complex (**C1**).

Preparation of Schiff base copper complex (C1): One equivalent of (0.370 g, 1 mmol) of blue coloured solution of $Cu(ClO_4)_2.6H_2O$ in dry methanol was added dropwise to a methanolic solution of one equivalent (0.413 mL, 1 mmol) of brown-coloured L1 ligand. The solution gradually turned into green colour and was stirred at room temperature for 1 hour. The green-coloured solid product was obtained as the final product following the removal of the solvent under reduced pressure followed by washing with diethyl ether (3 × 5 mL). The remaining powdered sample was dried under high vacuum overnight to obtain the final product. (Yield 75%) UV-vis (in DMF) (λ_{max} in nm, ε in parentheses $M^{-1}cm^{-1}$): 298(13,800), 362(3545), 720(410) (***Figure S1)***. HRMS (G2S-ESI-QToF) m/z calculated for $(M+ClO_4^-)^+$ calculated: 575.1123, Experimentally observed 575.1104. Elemental analysis: calculated: C, 42.64; H, 4.03, N, 14.5; experimental: C: 42.65.40, H: 4.01.76; N: 14.4

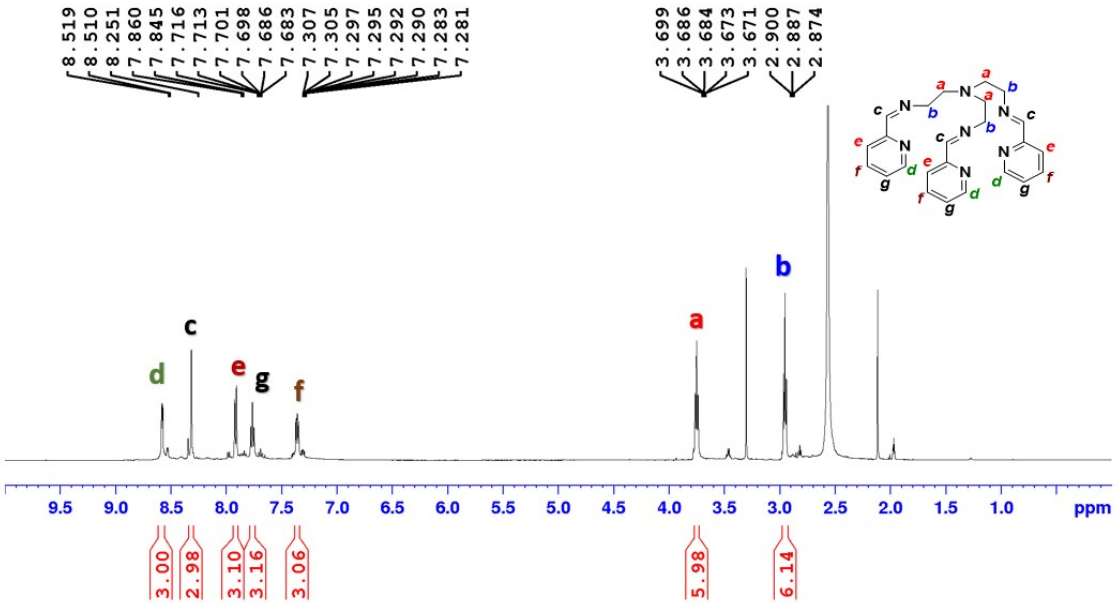


Figure S2. The **^{1}H-NMR** spectra for ligand **L1** recorded in CD_3CN solvent at room temperature.

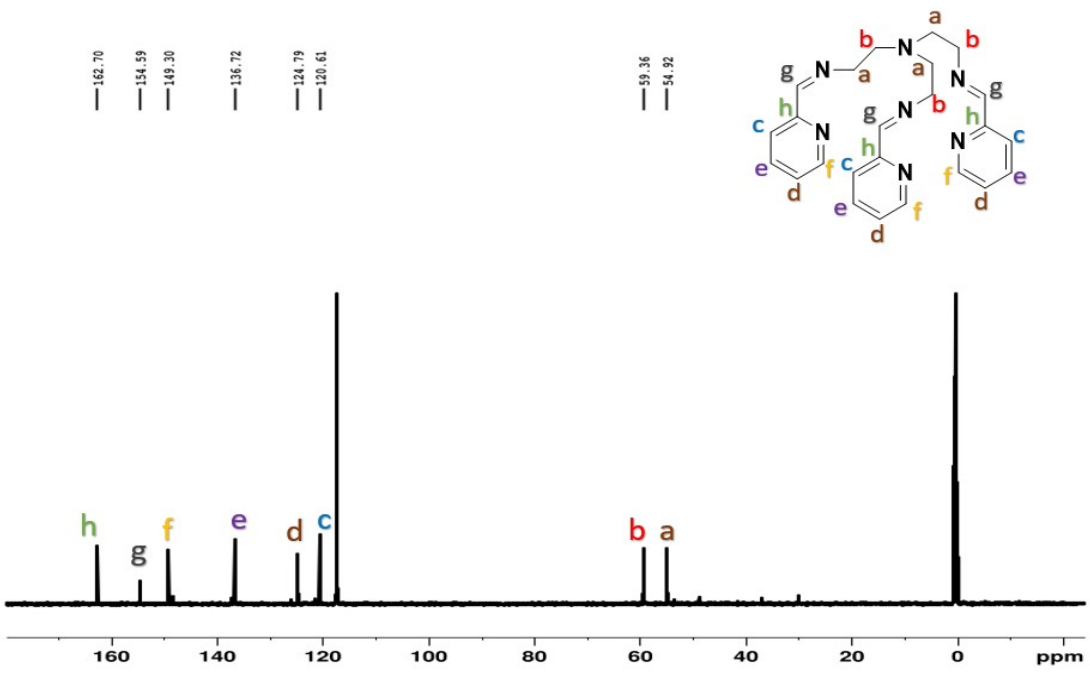


Figure S3. The **^{13}C-NMR** spectra for ligand **L1** recorded in CD_3CN solvent at room temperature.

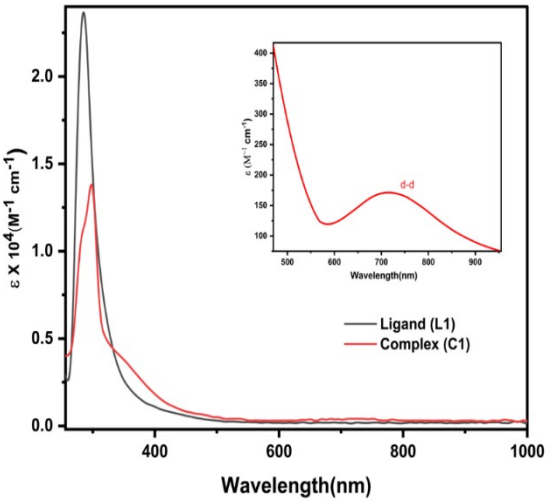


Figure S4. Comparative optical spectra recorded for ligand **L1** (black trace) and complex **C1** (red trace) in DMF exhibiting π–π* and LMCT transitions at room temperature. The inset exhibits *d–d* transition recorded for **C1** under the same conditions.

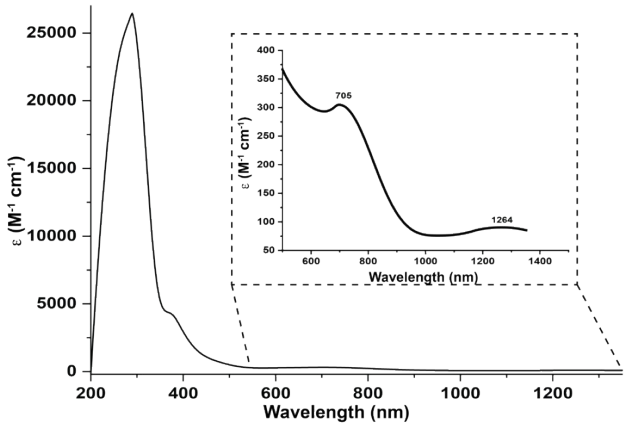


Figure S5: The optical spectra recorded for complex **C1** (black trace) in DMF expanding till 1350 nm at room temperature. The inset highlights the different bands originating from the *d–d* transition.

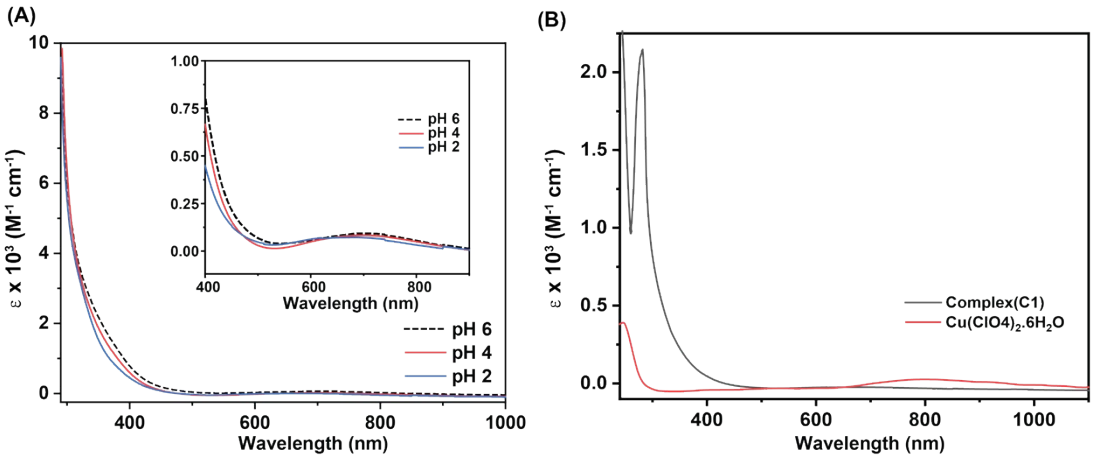


Figure S6: (A) The optical spectra recorded for complex **C1** at pH 2.0 (blue trace), pH 4.0 (red trace), and pH 6.0 (black trace) at room temperature. **(B)** The optical spectra recorded for complex **C1** (black trace) and $Cu(ClO_4)_2.6H_2O$ (red trace) at pH 6 at room temperature.

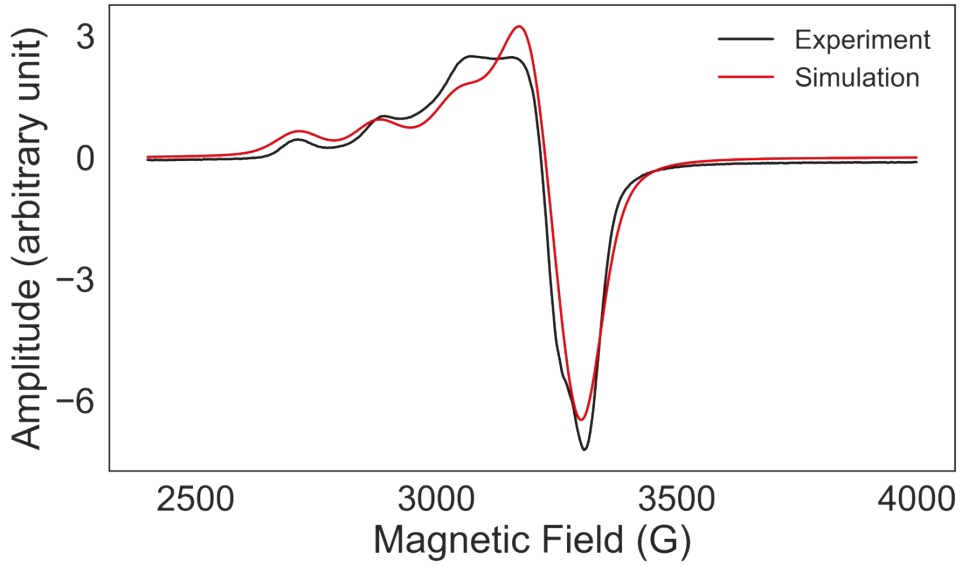


Figure S7: The experimentally observed (black trace) and simulated (red trace) EPR spectra for complex **C1** recorded at 100 K in DMF media.

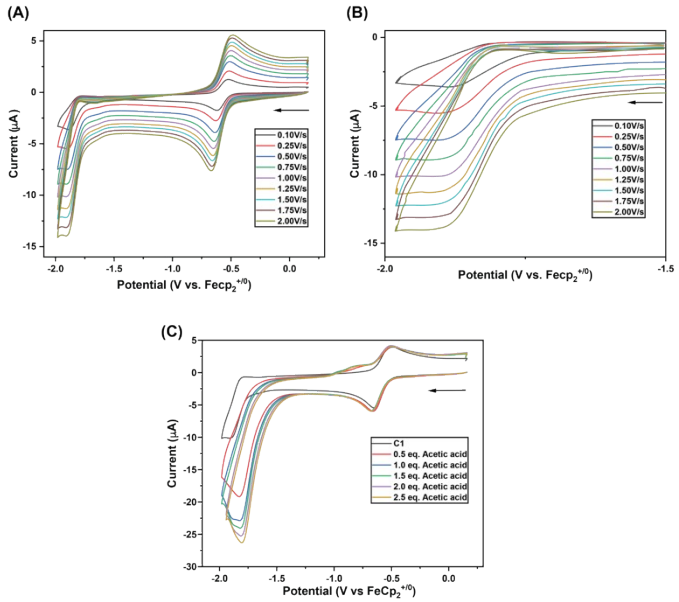


Figure S8: (A) The cyclic voltammograms (CV) of **C1** (0.25 mM) in DMF medium under Ar at various scan rates without any acid addition at variable scan rates. **(B)** The CV data of *C1* (0.25 mM) in analogous conditions representing $Cu^{+1/0}$ signal at various scan rates. **(C)** The CV data of **C1** (0.25 mM) in analogous conditions with the serial addition of acetic acid (all data recorded at the scan rate of 1 V/s). A 1 mm glassy carbon disc working electrode, Ag/AgCl reference electrode, and Pt-wire counter electrode were used along with 0.1 M TBAF as supporting electrolyte. The initial scan direction is displayed by black arrows.

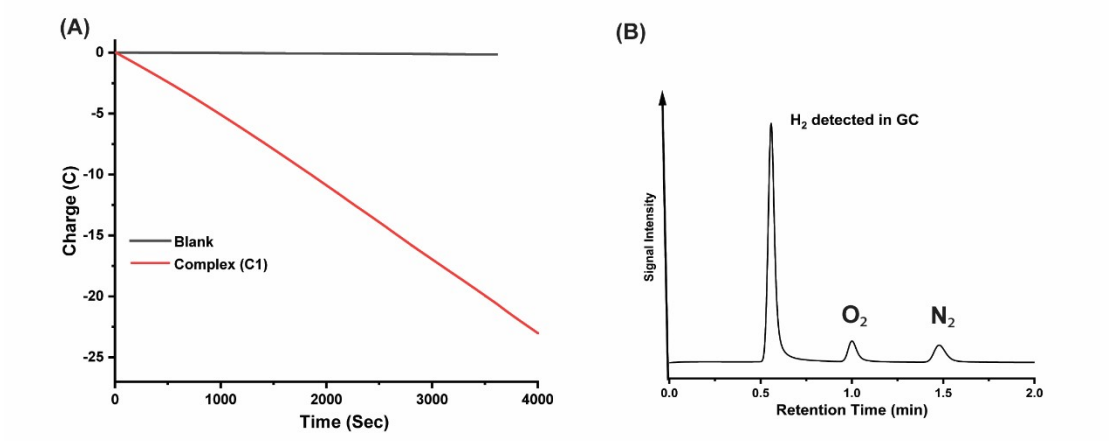


Figure S9. (A) Bulk electrolysis data recorded in DMF for 0.25 mM of **C1** (red trace) and blank DMF (Black Trace). Reticulated Vitreous Carbon was used as working electrode, Ag/AgCl as reference electrode and Coiled Pt-wire as counter electrode. (B) The Gas Chromatography data recorded after injecting 0.6 mL of head space gas using leur-lock gas-tight syringe after 4000 sec.

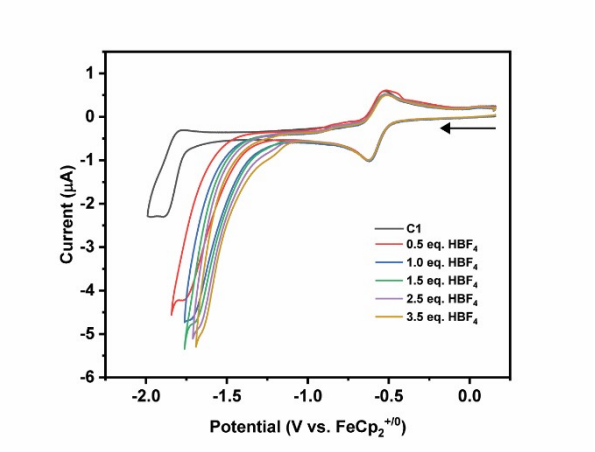


Figure S10. The CV data of **C1** (0.25mM) in analogous conditions with the serial addition of HBF_4 where all the data were recorded at the scan rate of 1 V/s. Here 1mm glassy carbon disc working electrode, Ag/AgCl reference electrode, and Pt-wire counter electrode was used along with 0.1 M TBAF as a supporting electrolyte. The initial scan direction is displayed by the black arrows.

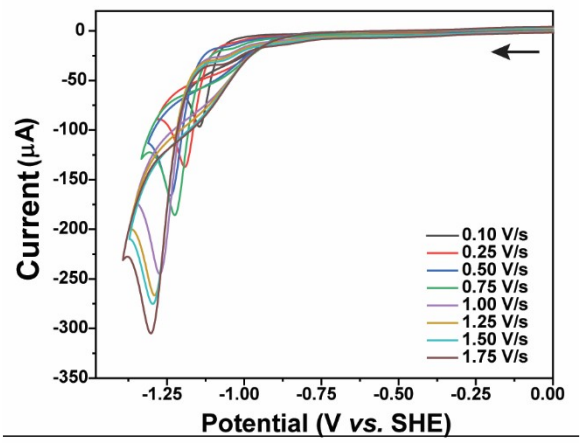


Figure S11: The cyclic voltammograms (CV) of complex **C1** (0.25 mM) at pH 6.0 under N_2 at various scan rates. A 1 mm glassy carbon disc working electrode, Ag/AgCl reference electrode, and Pt-wire counter electrode were used along with Na_2SO_4 as supporting electrolyte. The initial scan direction is displayed by the black arrows.

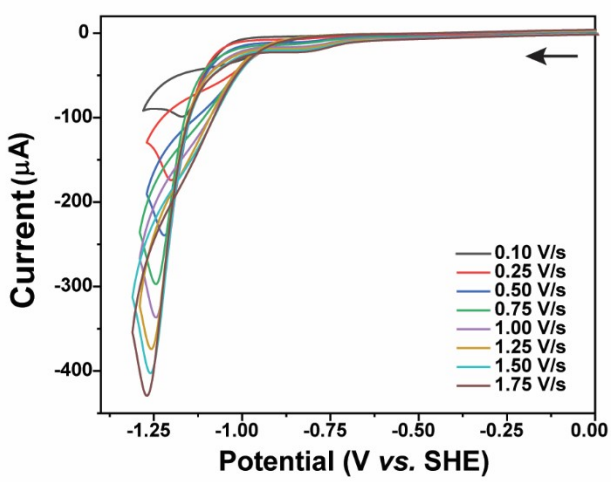


Figure S12: The cyclic voltammograms (CV) of complex C1 (0.25mM) at pH 5.0 under N_2 at various scan rates. A 1 mm glassy carbon disc working electrode, Ag/AgCl reference electrode, and Pt-wire counter electrode were used along with Na_2SO_4 as supporting electrolyte. The initial scan direction is displayed by the black arrows.

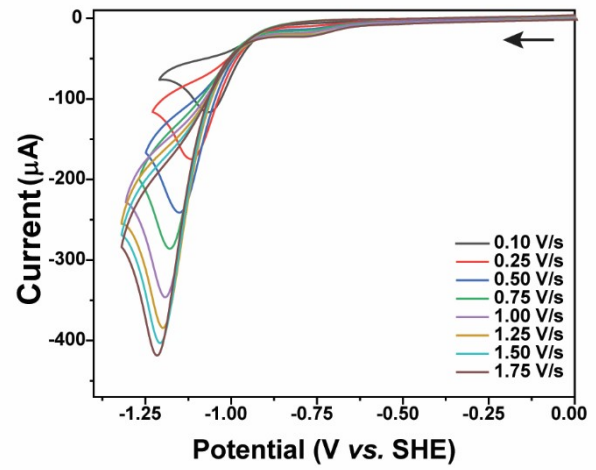


Figure S13: The cyclic voltammograms (CV) of complex C1 (0.25mM) at pH 4.0 under N_2 at various scan rates. A 1 mm glassy carbon disc working electrode, Ag/AgCl reference electrode, and Pt-wire counter electrode were used along with Na_2SO_4 as a supporting electrolyte. The initial scan direction is displayed by the black arrows.

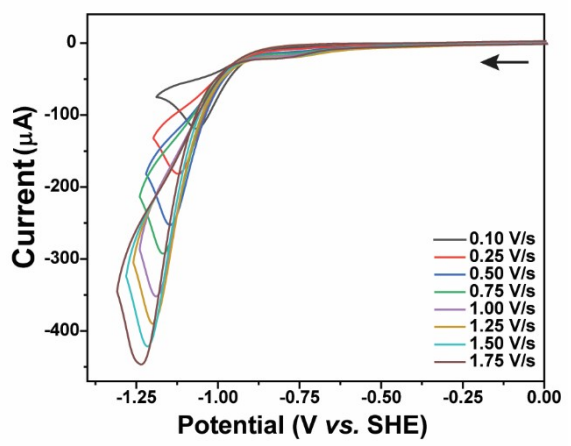


Figure S14: The cyclic voltammograms (CV) of complex C1 (0.25 mM) at pH 3.0 under N_2 at various scan rates. A 1 mm glassy carbon disc working electrode, Ag/AgCl reference electrode, and Pt-wire counter electrode were used along with Na_2SO_4 as a supporting electrolyte. The initial scan direction is displayed by the black arrows.

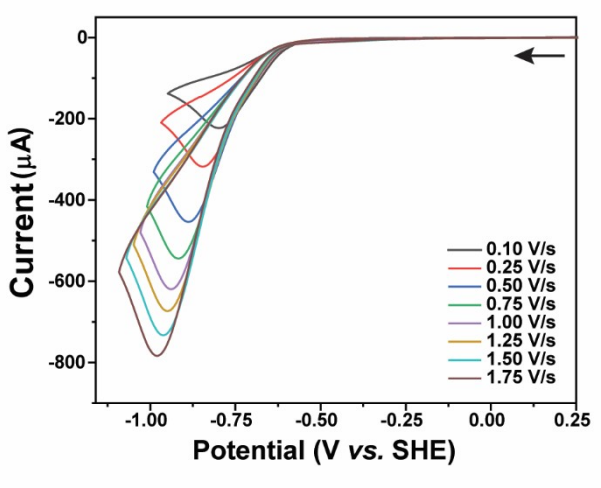


Figure S15: The cyclic voltammograms (CV) of complex **C1** (0.25 mM) at pH 2.0 under N_2 at various scan rates. A 1 mm glassy carbon disc working electrode, Ag/AgCl reference electrode, and Pt-wire counter electrode were used along with Na_2SO_4 as a supporting electrolyte. The initial scan direction is displayed by the black arrows.

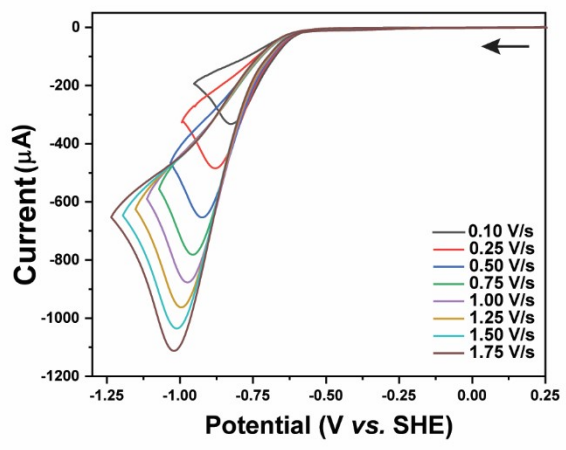


Figure S16: The cyclic voltammograms (CV) of complex **C1** (0.25mM) at pH 1.0 under N_2 at various scan rates. (A), Here 1 mm glassy carbon disc working electrode, Ag/AgCl reference electrode, and Pt-wire counter electrode was used along with Na_2SO_4 as a supporting electrolyte. The initial scan direction is displayed by the black arrows.

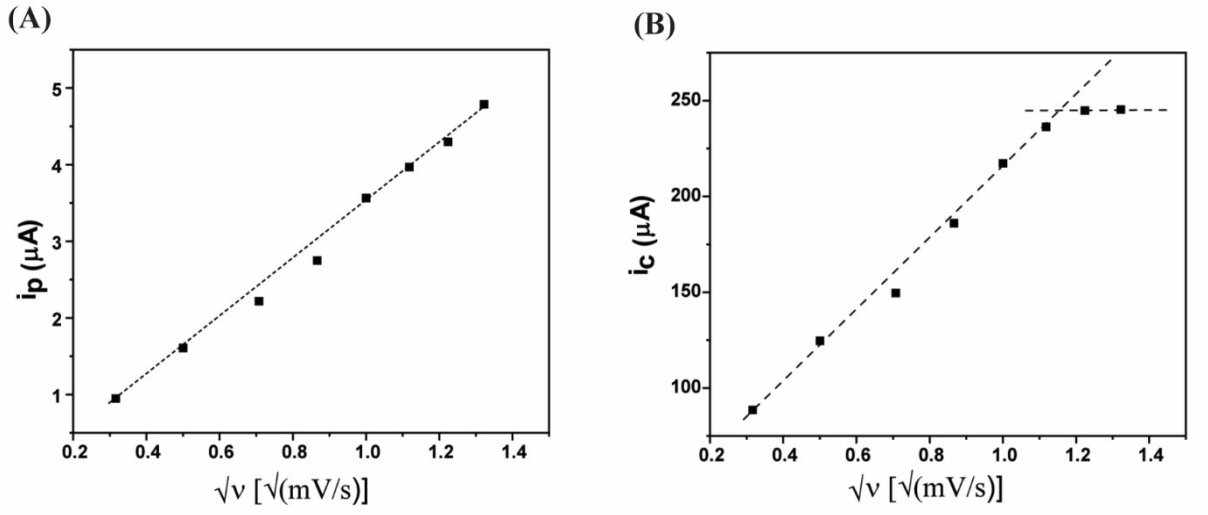


Figure S17: (A) Plot of current at -0.5 V vs. square root of scan rate recorded for **C1** at pH 6.0. The linear increase in the current with scan rate shows the stoichiometric nature of the signal. **(B)** Plot of current at -1.25 V vs. square root of scan rate recorded for **C1**. The non-linear variation at higher scan rate indicates the involvement of catalysis.

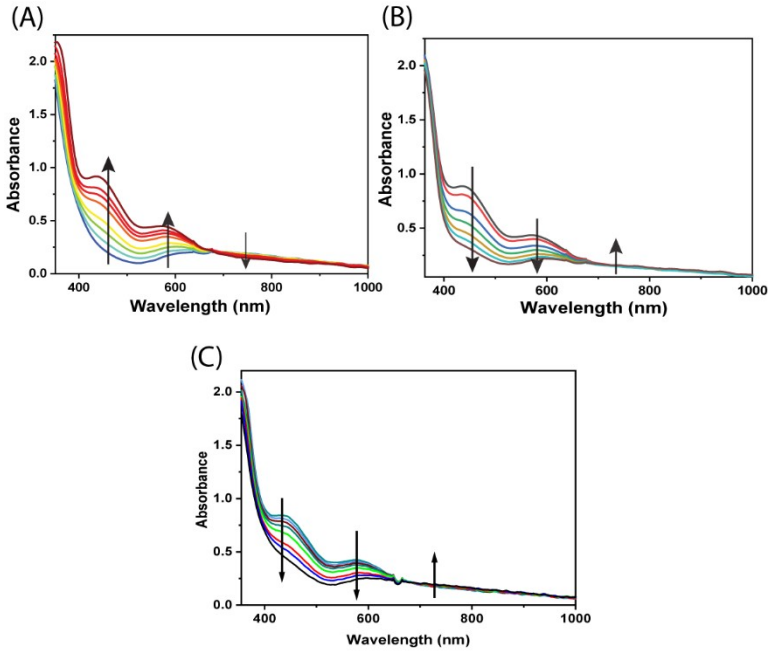


Figure S18: The gradual changes in the optical spectra of complex **C1** (0.2 mM) at pH 6.0 at room temperature: (A), potential of the solution held at -0.63 V vs. SHE; (B) potential held at -1.25 V vs. SHE; (C) potential held at -0.05V vs. SHE. A 3 mm glassy carbon rod, a Pt wire, and Ag/AgCl (in saturated KCl) were used as working electrode, counter electrode, and reference electrode, respectively, during the chronocoulometric experiment.

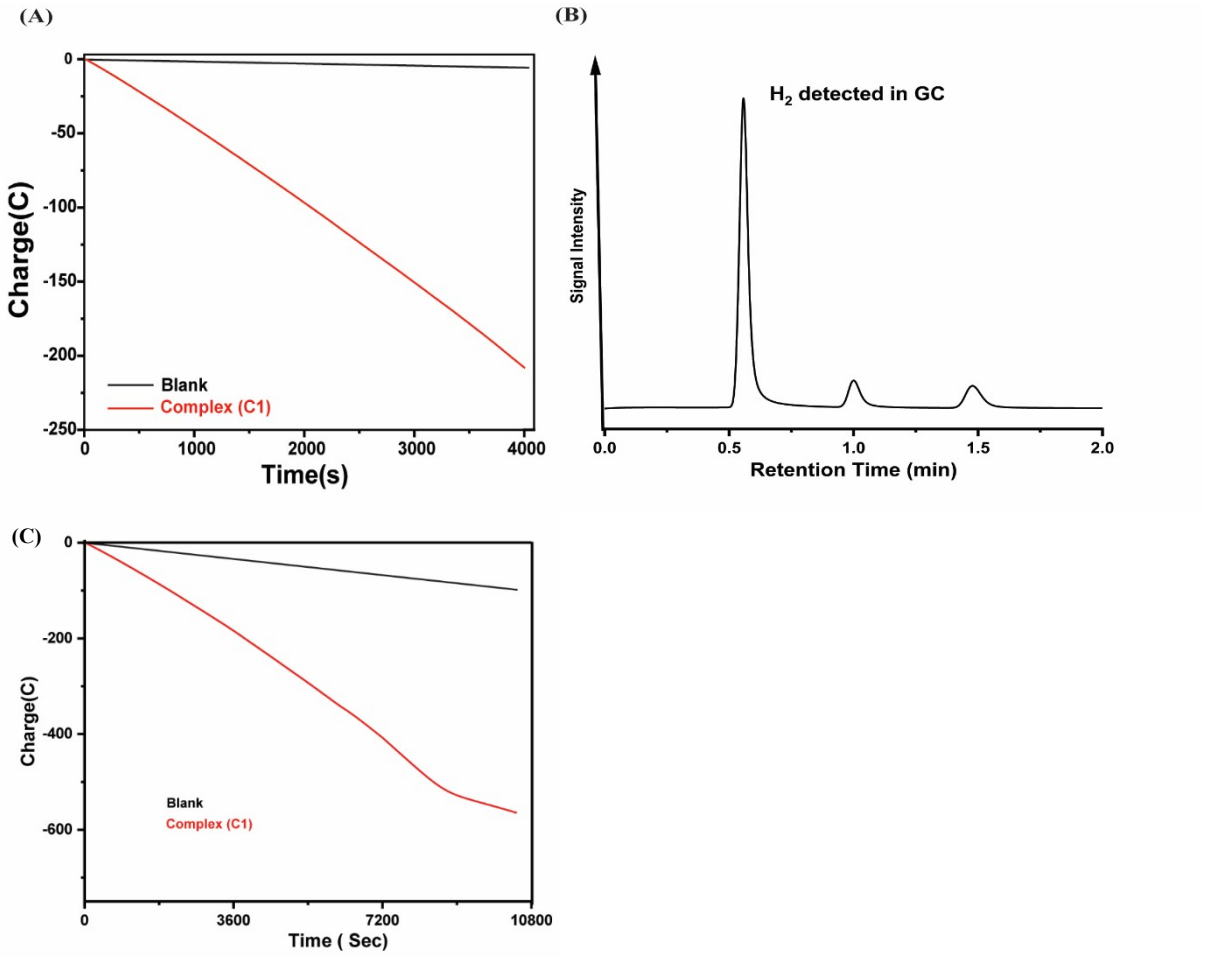


Figure S19: (A) The chronocoulometric data recorded for 0.5 mM C1 complex (red trace) at pH 1.0 for 1 hour along with a blank (black trace) recorded at analogous conditions. The data were recorded using a reticulated vitreous carbon working electrode, coiled Pt wire counter electrode (separated by an auxiliary electrode chamber), and Ag/AgCl reference electrode. The data were recorded at -1.13 V for pH 1 (Vs. SHE). (B) The gas chromatography (GC) data recorded after injecting the headspace gas using a leur-lock gas tight syringe. (C) The chronocoulometric data recorded for 0.5 mM **C1** complex (red trace) at pH 1.0 for 3 hours along with a blank (black trace) recorded at analogous conditions.

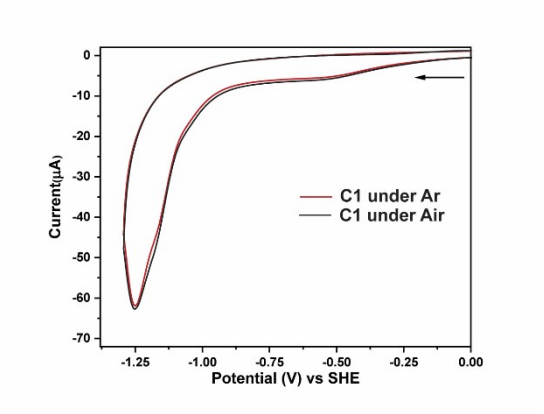


Figure S20: The comparative CV data recorded for complex **C1** at 1.25 V/s under Ar (red trace), and air (black trace).

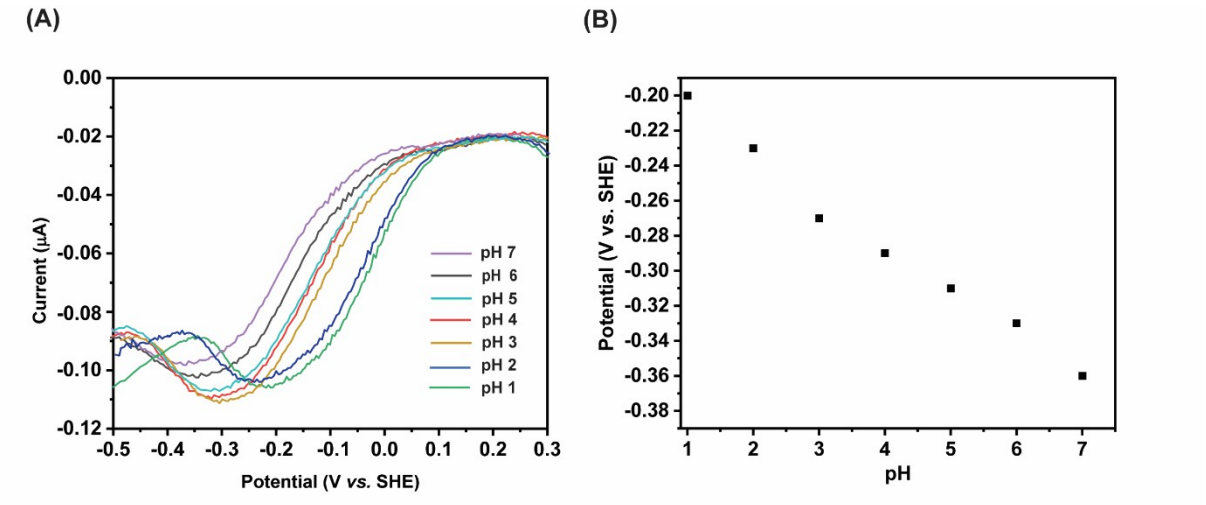


Figure S21: (**A**) The differential pulse voltammetry (DPV) data for **C1** (0.5mM) recorded at pH 1.0-7.0 (**B**) pH-dependency of the stoichiometric Cu(II/I) reduction potential for **C1** at different pH conditions ranging from pH 1.0 to pH 7.0.

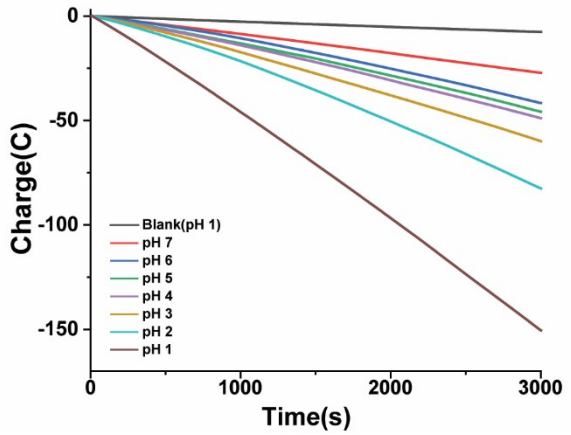


Figure S22: The chrono-coulometric data recorded for 0.25 mM **C1** complex in aqueous solution at pH 1 (orange solid trace), pH 2 (green solid trace), pH 3 (violet solid trace), pH 4 (blue solid trace), pH 5 (green solid trace), pH 6 (yellow solid trace) and pH 7 (red solid trace) along with a blank (black solid trace) recorded at pH 1.0. The data were recorded at -1.2 V for pH 7.0 (vs. SHE), -1.27 V (vs. SHE) for pH 6.0 (vs. SHE), -1.24 V (vs. SHE) for pH 5.0 (vs. SHE), -1.20 V (vs. SHE) for pH 4.0, -1.19 V (vs. SHE) for pH 3.0, -0.98V (vs. SHE) for pH 2.0 and -1.12 V (vs. SHE) for pH 1.0 for about 3000 s. All data were recorded using a plastic chip working electrode [generated from graphite powder and poly(methyl methacrylate)], coiled Pt wire reference electrode (separated by an auxiliary electrode chamber), and Ag/AgCl reference electrode.

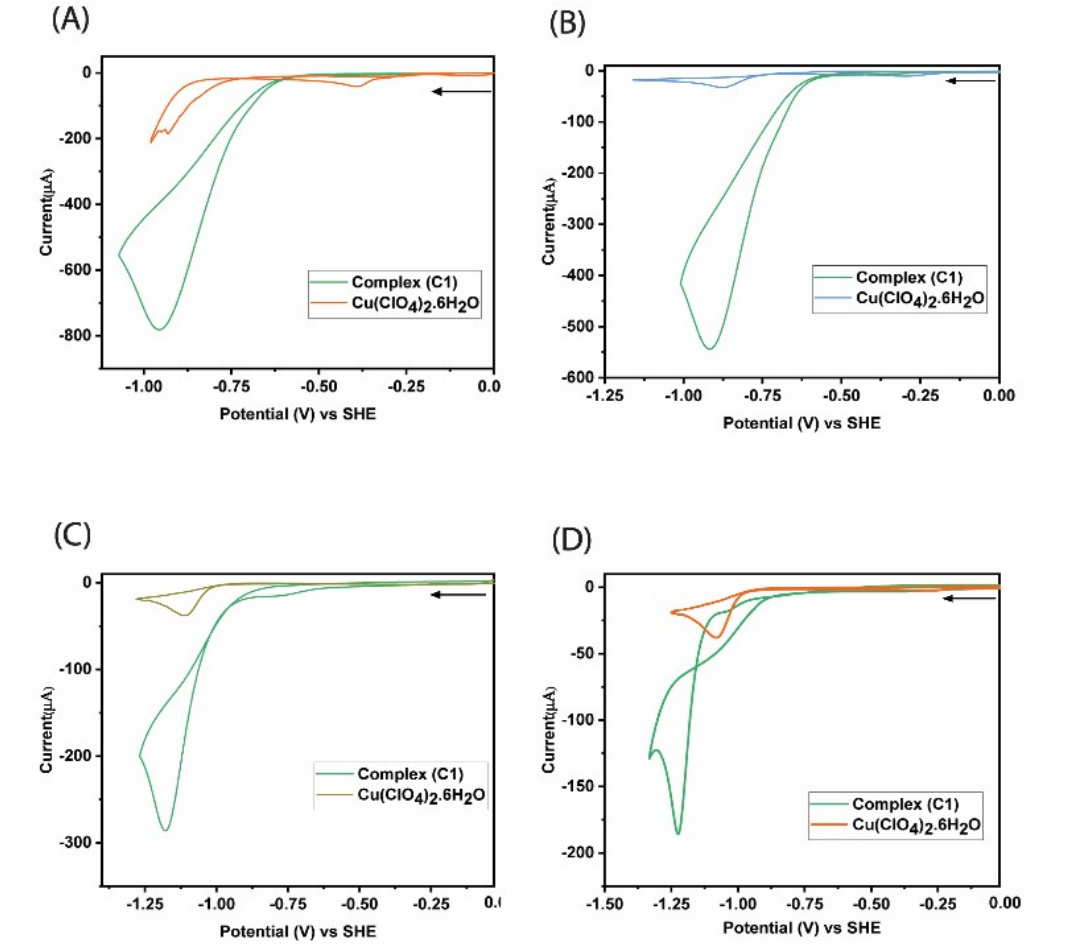


Figure S23: The comparative Cyclic Voltammetry data recorded for the complex (0.25 mM) and $Cu(ClO_4)_2.6H_2O$ (0.25mM) at various pH: (A) pH 1 (B) pH 2 (C) pH 4 (D) pH 6.

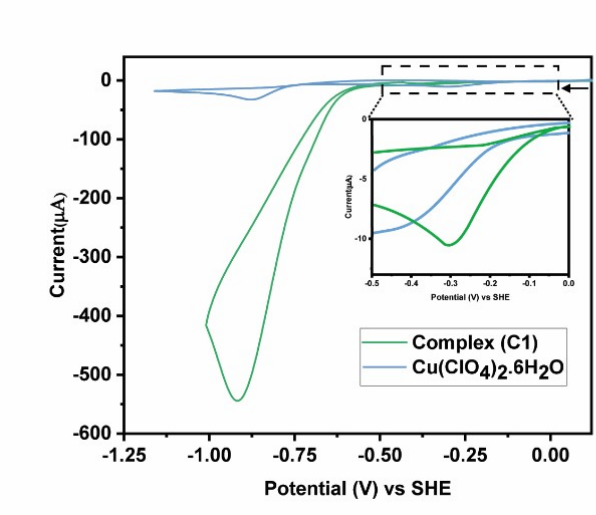


Figure S24: The comparative cyclic voltammetry data recorded for complex (0.5 mM) and $Cu(ClO_4)_2.6H_2O$ (0.5mM) at pH 2. The scan rate of 0.75 V/s were used during this experiment.

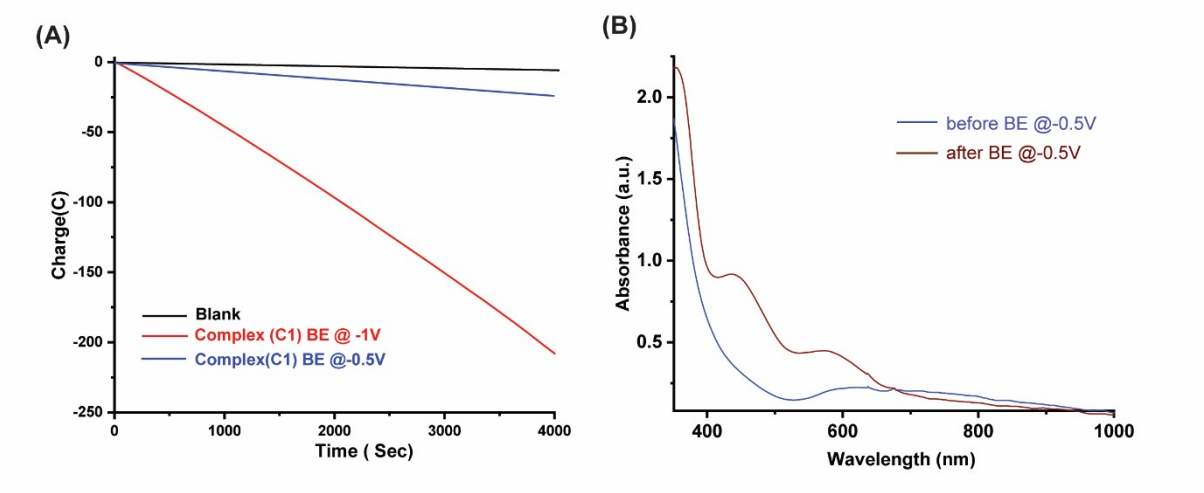


Figure S25: (A) The comparative Bulk electrolysis data recorded for **C1** at pH 1 at -0.5 V (vs. SHE) and -1 V (vs. SHE). (B). The comparative UV spectra before and after bulk electrolysis.

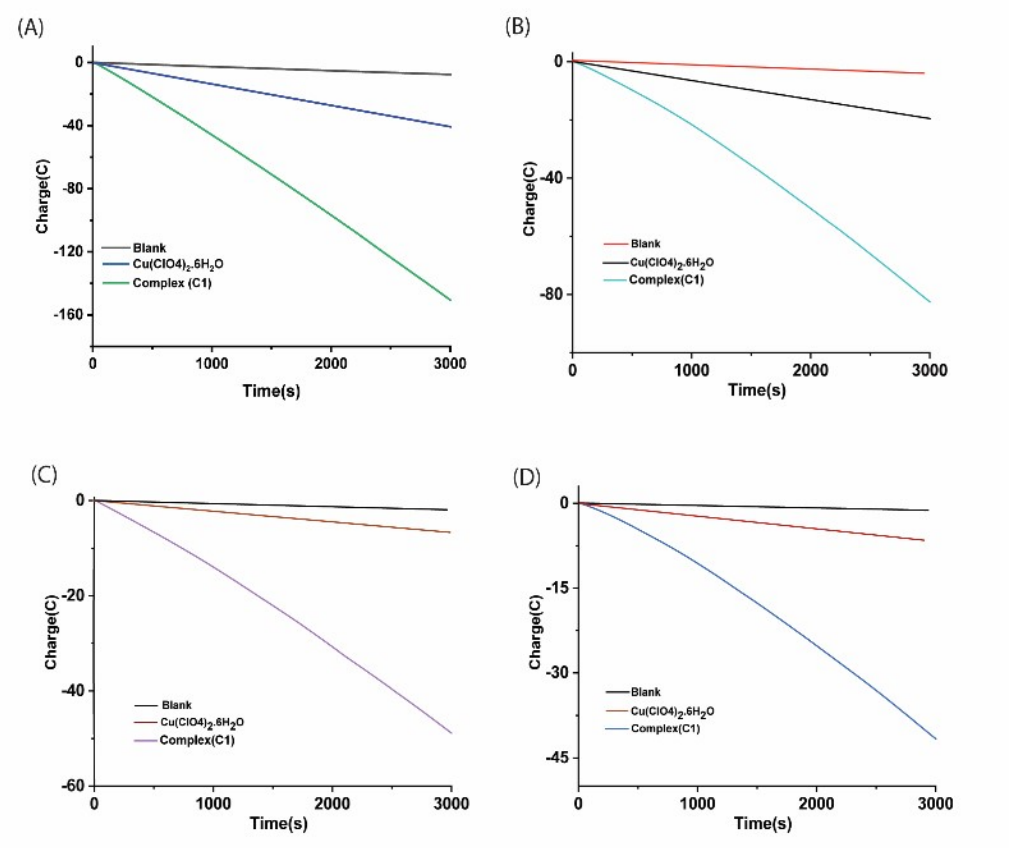
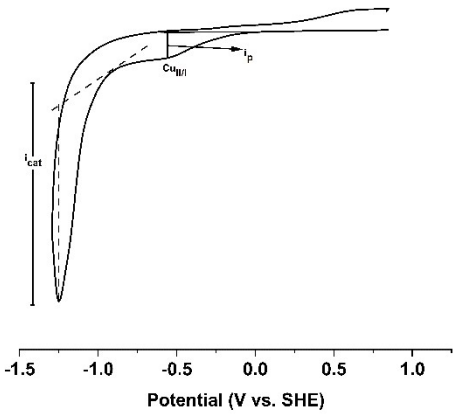
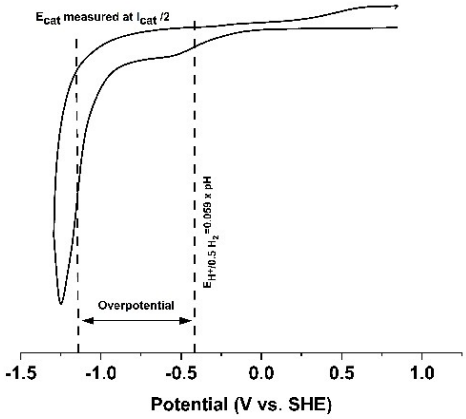


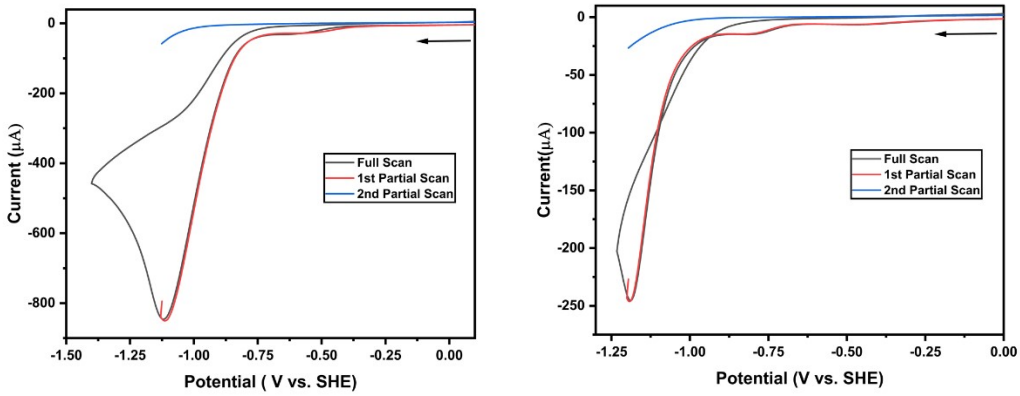
Figure S26: The comparative Chronocoulometry data recorded for the complex (0.25 mM) and $Cu(ClO_4)_2.6H_2O$ (0.25 mM) at various pH conditions (A) pH 1.0, (B) pH 2.0, (C) pH 4.0, and (D) pH 6.0


i_{cat}
$Cu_{II/I}$
i_p
-1.5
-1.0
-0.5
0.0
0.5
1.0
Potential (V vs. SHE)


E_{cat} measured at i_{cat} /2
$E_{H^+/0.5\,H_2}$ at pH = 0.059 pH
Overpotential
-1.5
-1.0
-0.5
0.0
0.5
1.0
Potential (V vs. SHE)

(A) **(B)**

Figure S27: Simplified cyclic voltammograms showcasing the measurement of (A) Turn Over Frequency (TOF) and (B) overpotential requirement (OP) for **C1** under homogeneous reaction conditions.



(A) **(B)**

Figure S28: (A) Rinse test for C1 at pH 1.0 solution: Run 1 (black trace) is a complete cyclic voltammograms recorded for **C1** (0.25 mM) with a cathodic scan starting from 0.1 to -1.4 V, followed by an anodic scan to 0.1 V. The electrode was polished and cleaned after this run. Run 2 (red trace) was a scan in the same solution, where only a cathodic scan from 0.1 to -1.12 V (close to the maxima of H_2 production) was recorded. The rinsed electrode with deionized water (no polishing) was then used for run 3 in a different aqueous solution (pH 1.0), not containing complex C1. Third run (blue trace) was performed with a cathodic scan from -1.12 to 0.1 V. No significant reduction current was observed in the third run in the cathodic stretch, indicating that no heterogeneous species was forming during the catalytic H_2 production. **(B) Rinse test for C1 at pH 6.0 solution:** Run 1 (black trace) is a complete cyclic voltammograms recorded for **C1** (0.25 mM) with a cathodic scan starting from 0 to -1.23 V, followed by an anodic scan at 0 V. Then the electrode was polished and cleaned. Run 2 (red trace) was a scan of the complex in the same solution, by recording only a cathodic scan from 0 to -1.23 V (close to the maxima of H_2 production). The electrode was only rinsed with deionized water (no polishing) and was used for run 3 in a different aqueous solution (pH 6.0), which did not contain complex **C1**. The third run (blue trace) was performed with the cathodic scan varying from -1.23 to 0 V. No significant reduction current was observed in the third run in the cathodic stretch, demonstrating that no heterogeneous species was forming during the catalytic H_2 production.

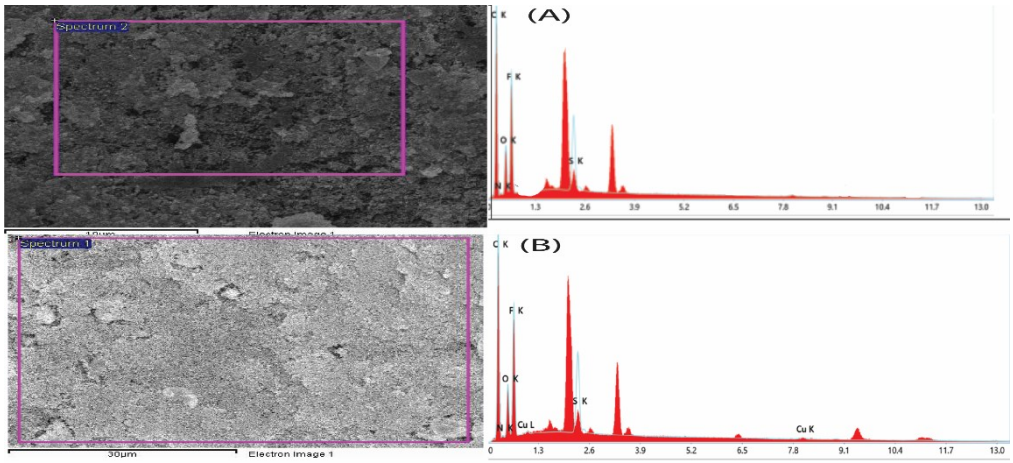


Figure S29: SEM image and EDS spectra of plastic chip working electrode (A) before and (B) after chronocoulometric experiment. The bulk electrolysis data was recorded at -1.25 V vs SHE of complex for 4000 seconds using Ag/AgCl reference electrode, Pt coil as counter electrode and plastic chip as working electrode [generated from graphite powder and poly(methyl methacrylate)]. The active size of the plastic chip electrode was 1 x 1 cm and it was rinsed with water (NOT polished) before the SEM and EDS experiments after the bulk electrolysis. No significant trace of copper was found onto the working electrode.

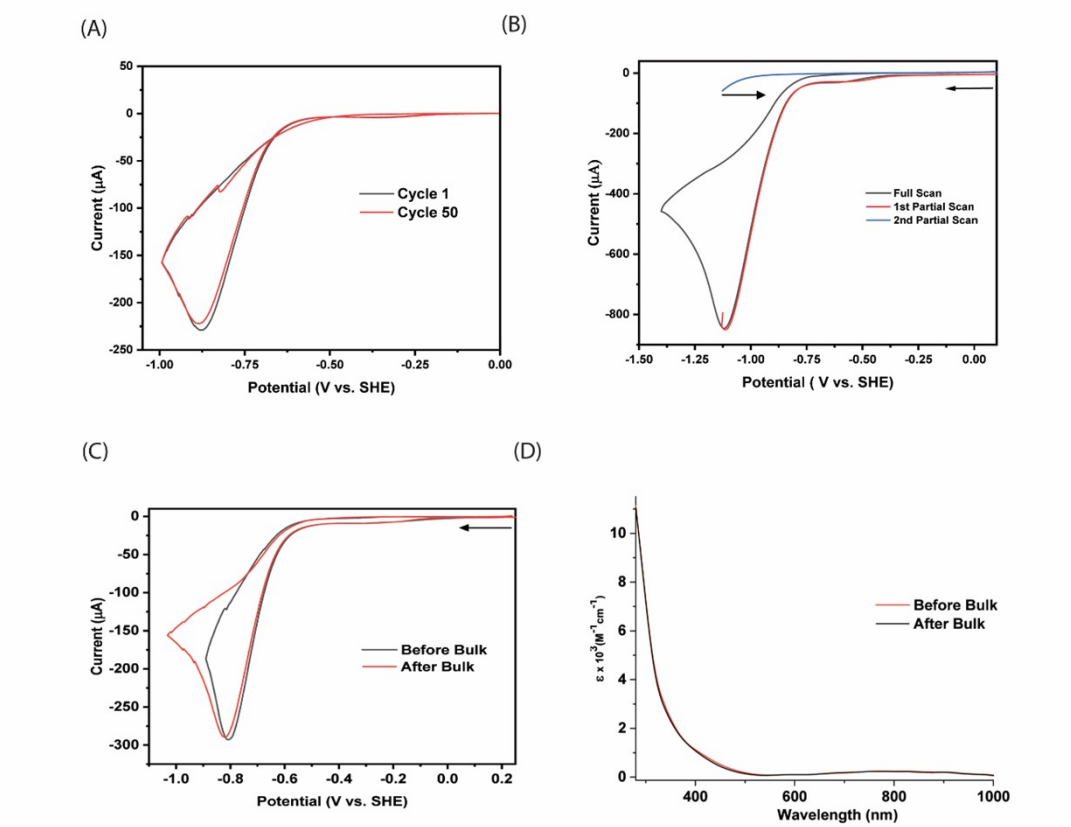


Figure S30: (A) The initial cyclic voltammogram (CV) data recorded for the copper complex (0.25 mM) (black trace, cycle 1) along with the 50th cycle data (red trace, cycle 50) recorded following consecutive fifty scans at pH 1.0 condition (scan rate: 0.25 V/s). (B) Rinse test: The CV response for the complex recorded following a full uninhibited scan (black trace) and a halted scan till -1.12 V (red trace, at the peak of the catalytic signal) recorded in a solution containing 0.25 mM copper complex. The working electrode was rinsed but not polished following the 1st partial run, and dipped into a blank solution prepared at analogous conditions (pH 1.0). Then another partial scan was recorded initiating from -1.12 V (blue trace). The lack of any significant current showcases the homogeneous nature of the HER catalysis. All the data were recorded at 1.0 V/s scan rate. (C) The CV and (D) optical spectral data recorded for the copper complex (0.25 mM) before (black trace) and after (red trace) bulk electrolysis studies at pH 1.0 aqueous solution in the presence of 0.1 M Na_2SO_4 electrolyte under 1 atm N_2 at 298 K. All the data were recorded at 0.25 V/s scan rate. The bulk electrolysis of corresponding complex was done at -1.25 V (vs. SHE) for 7200 sec.

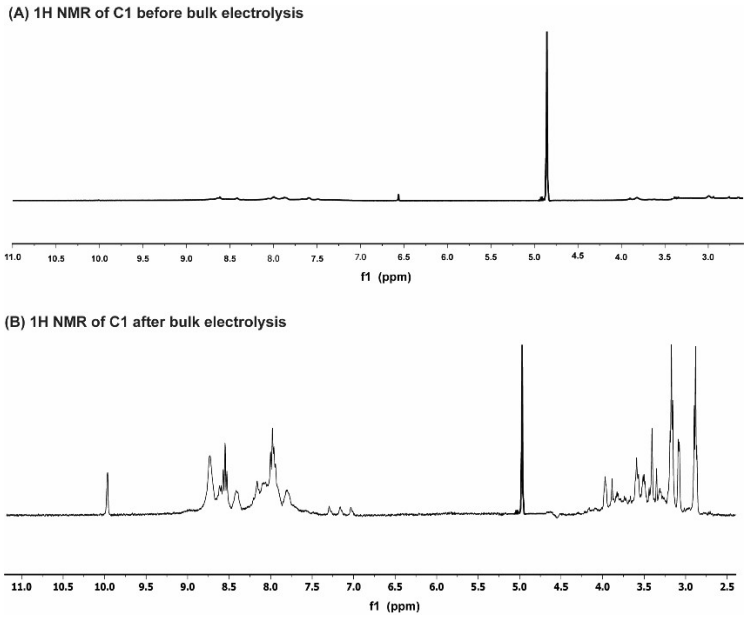


Figure S31: The ^{1}H NMR data recorded for complex **C1** in H_2O blended D_2O solution (pD~6.0) (A) before and (B) after bulk electrolysis.

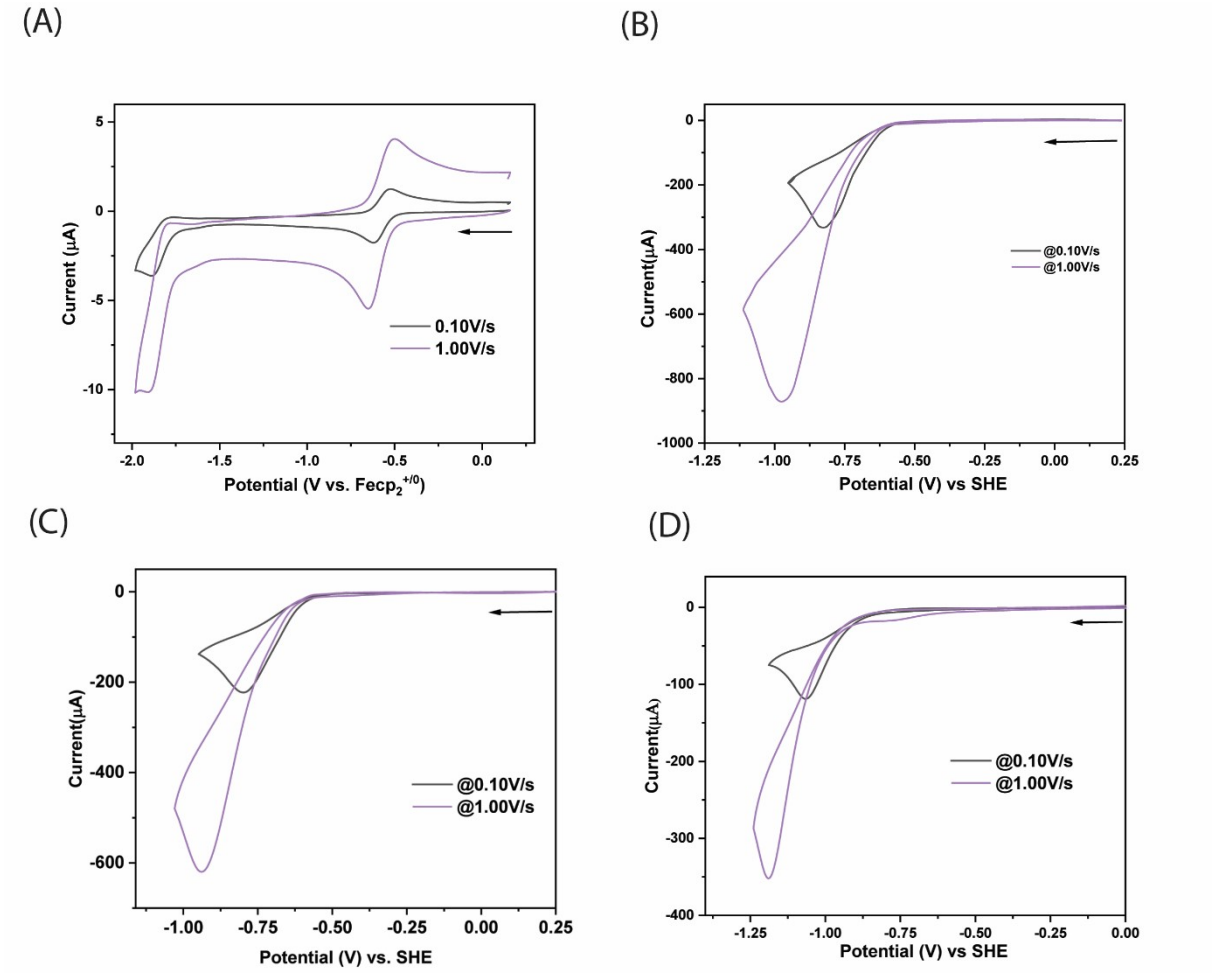


Figure S32: The comparative CV data recorded at low (0.1 V/s, black trace) and high (1.0 V/s, purple trace) recorded for **C1** in (A) DMF, (B) pH 1.0, (C) pH 2.0, and (D) pH 3.0 solution.

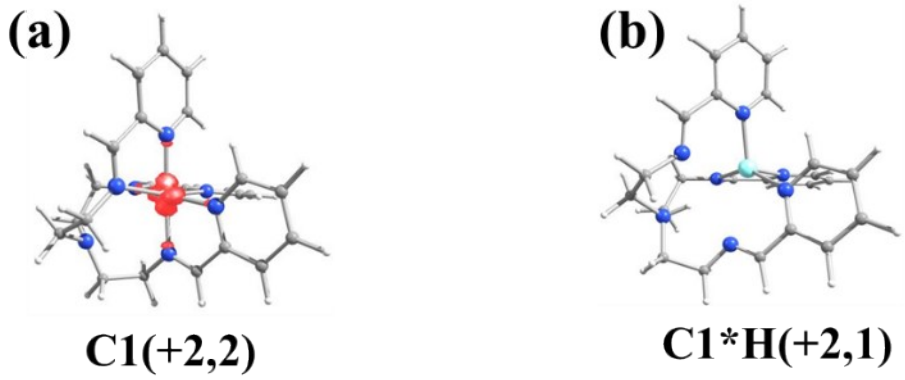


Figure S33: Spin density difference between the (a) C1 (initial catalyst) and (b) C1*H (subsequent first ET-PT step).

Table S3. Reported molecular copper complexes exhibiting electrocatalytic H_2 production

Sr. No	Copper catalyst	Catalytic Conditions	Electrocatalytic HER			*Ref.*
			TOF (s^{-1})	OP (mV)	TON	
1	$[(bztpen)Cu](BF_4)_2$	Aqueous	10000	420	1400 (2h)	[12]
2	[CuL] (L=2,3-bis(2-hydroxybenzylideneimino) -2,3-butenedinitrile)	Aqueous	457	817	-	[13]
3	$Na_2[Cu(opba)]$	Aqueous (pH 7)	1332	788	-	[14]
4	$Cu_2(L)_2$ HL= 1-[(2-methoxy)benzene]-3-[2 (chloro)benzene]triazene	Aqueous (pH 7)	324	939	-	[15]
5	$[Cu^I_3(L)(L')_2]$.THF L' = 1-[(2 carboxymethyl)benzene]-3-[benzothiazole]triazene ion	Aqueous (pH 7)	355	789	-	[16]
6	$Cu_2L_4(NCCH_3)$ (L = 1,3-bis[(4-chloro) benzene]triazene)	Aqueous (pH 7)	174	628	-	[17]
7	Copper Corroles	Acetonitrile	450	450	--	[18]
8	$[Cu^{II}(L^{N2Py3})](PF_6)_2$	Aqueous (pH 7)	557	617	1670 (3h)	[19]
9	$Cu(dpp)(ClO_4)_2$	Acetonitrile	367	520	12.5 (6h)	[20]
10	$[Cu(DQPD)]_2$	DMF	110	817		[21]
11	**C1** Cu[tris-[4-(2-pyridyl)-3-azabut-3-enyl]amine]$(ClO_4)_2$	DMF, in presence of acetic acid	-	870	10 (1h)	This work
		Aqueous (pH 1)	-	770	1014 (1h) 2980 (3h)	

The calculated coordinates of optimized structures of various intermediates observed during the computational study

Coordinates of C1

Cu	-0.14680200	-0.00659200	0.05472700
N	-0.37472700	-1.12360000	1.78190800
N	0.59710900	1.35155100	1.49216600
N	2.11644200	-0.98905400	-0.30105800
N	0.00681800	1.37723000	-1.51650200
N	-2.24204300	0.97142500	-0.05126400
N	-2.84901400	-1.78476600	0.36373400
N	-0.40479200	-1.58854700	-1.29536000
C	0.04570300	-0.53530700	2.83855700
H	0.00032600	-1.01023900	3.82040700
C	0.59284400	0.82065200	2.73880900
C	1.55500700	2.81343900	3.66431800
H	1.92836600	3.38310600	4.50826400
C	-0.98217500	-2.44970400	1.88050300
H	-0.79144300	-2.88779800	2.86709200
H	-0.50922100	-3.08837500	1.12952700
C	1.06721300	2.59004500	1.32089900
H	1.05504600	2.98189300	0.31086300
C	1.96263600	-2.03968800	-1.13320900
C	-2.50402300	-2.38369700	1.63708700
H	-2.89504300	-3.40941700	1.74601700
H	-2.95322500	-1.78703200	2.43645000
C	1.06348800	1.51895300	3.84797000
H	1.04305200	1.05693200	4.82859400
C	-1.08577800	2.14186600	-1.76205300
C	1.10379200	1.55095100	-2.26468800
H	1.95196100	0.91992700	-2.02624400
C	1.55592900	3.35676800	2.38342300
H	1.92684300	4.35726500	2.19408400
C	-3.41756900	0.62751000	0.72822900

H	-4.23625800	1.34643500	0.58897600
H	-3.12905200	0.63874100	1.78534800
C	-2.64086800	-2.57963900	-0.83109100
H	-3.58772800	-2.80894700	-1.34340500
H	-2.19986500	-3.54166800	-0.54989500
C	4.27795800	-2.64409200	-0.94019300
H	5.11689500	-3.28477200	-1.19013400
C	-1.09353400	3.10668600	-2.76830900
H	-1.98556500	3.70053500	-2.93506700
C	-2.27926100	1.89166500	-0.93080800
H	-3.16608200	2.50393900	-1.12402400
C	-3.90479700	-0.78791000	0.33886700
H	-4.74377000	-1.04930000	1.00252000
H	-4.30923000	-0.74007000	-0.67699800
C	0.61255000	-2.27169900	-1.66914900
H	0.50548000	-3.07067900	-2.40735000
C	3.01567500	-2.88730400	-1.48497100
H	2.84656800	-3.71629000	-2.16402700
C	-1.71825800	-1.90067700	-1.86511400
H	-1.61281800	-2.55347200	-2.73986200
H	-2.16808400	-0.95982700	-2.19484500
C	3.32652300	-0.76400000	0.21415400
H	3.41898900	0.09062500	0.87842700
C	1.16783000	2.49429700	-3.29192100
H	2.07919200	2.59668900	-3.86926600
C	0.05116900	3.28575500	-3.54637500
H	0.06709300	4.02949100	-4.33582400
C	4.43746500	-1.56622500	-0.07390600
H	5.39918800	-1.33806700	0.37176600

Coordinates of C1Ha

Cu	0.11393500	-0.06115500	0.02325400
N	-0.45220000	-1.16009100	1.77668600

N	0.65951200	1.26987800	1.48264600
N	2.14131400	-0.99364100	-0.28025500
N	-0.00128100	1.40511300	-1.47012600
N	-2.44944500	0.89562800	-0.14250800
N	-2.82089800	-1.68817200	0.25953000
N	-0.31483400	-1.61439400	-1.31651200
C	-0.09723600	-0.54170900	2.84291700
H	-0.23254500	-0.97642500	3.83455900
C	0.50023500	0.78915600	2.74253200
C	1.42999200	2.78735800	3.69101100
H	1.72893900	3.37897100	4.54901700
C	-1.10972500	-2.46718500	1.89684700
H	-0.99801600	-2.87703800	2.90511700
H	-0.62871900	-3.15866700	1.20080100
C	1.19646400	2.48263800	1.31668300
H	1.31568600	2.83246400	0.29912300
C	2.04205400	-2.04492400	-1.12555900
C	-2.60971700	-2.33429400	1.60578800
H	-3.10500900	-3.30619100	1.60791000
H	-3.08281000	-1.69420100	2.35200200
C	0.87350800	1.51756900	3.86758800
H	0.73012300	1.09671300	4.85617900
C	-1.09214700	2.19323900	-1.64939600
C	1.08525700	1.62810900	-2.22504000
H	1.93680900	0.98097300	-2.04987100
C	1.59412100	3.27411400	2.39921200
H	2.02297500	4.25138200	2.21246700
C	-3.72295800	0.59676800	0.50717900
H	-4.53715400	1.26068400	0.19880700
H	-3.58878100	0.70043700	1.58939400
C	-2.55304100	-2.60942500	-0.91408400
H	-3.50519100	-2.86451600	-1.37924900
H	-2.10561900	-3.52647900	-0.53152300

C	4.37281900	-2.55645600	-0.89052700
H	5.24080800	-3.16134800	-1.12854600
C	-1.09299900	3.23753400	-2.57497300
H	-1.98008200	3.85143200	-2.68556900
C	-2.32670400	1.92003300	-0.88991100
H	-3.14433900	2.63122300	-1.04072200
C	-4.08692800	-0.85535200	0.14310400
H	-4.85815500	-1.27529800	0.78862200
H	-4.41956900	-0.91349900	-0.89307900
C	0.71032600	-2.30143100	-1.67900200
H	0.61379600	-3.10137500	-2.41529000
C	3.13106200	-2.84741000	-1.46198100
H	3.00822300	-3.67689700	-2.14943700
C	-1.61993600	-1.93162100	-1.92168400
H	-1.49842600	-2.60591800	-2.77408500
H	-2.05812800	-1.00084500	-2.29176700
C	3.32951200	-0.72065300	0.26112100
H	3.37560200	0.13073300	0.93238900
C	1.14822900	2.64482600	-3.17943700
H	2.05433300	2.77792800	-3.75848400
C	0.04218400	3.46951500	-3.35239500
H	0.05601700	4.27593700	-4.07732400
C	4.47378100	-1.47963800	-0.01595900
H	5.41704900	-1.21667900	0.44864100
H	-2.10602900	-0.94483100	0.19512000

Coordinates of C1*Ha

Cu	0.23344900	-0.12400400	0.10793800
N	-0.55644100	0.55700400	2.04764100
N	1.95461900	0.98114100	1.01730200
N	0.60545100	-2.21146000	0.30362000
N	0.66919400	0.34572000	-1.94155000
N	-1.41485900	2.01794500	-1.00859200

N	-3.19441300	0.79056300	0.61531100
N	-2.07251600	-1.58800600	-0.37159000
C	0.33984700	1.09972100	2.78834600
H	0.15035700	1.34027900	3.83875300
C	1.66881500	1.43106500	2.25884500
C	3.81601500	2.48986400	2.46296000
H	4.53860200	3.07271400	3.02427500
C	-1.84788100	0.26496500	2.67343200
H	-1.83570800	0.46075400	3.75253000
H	-2.06260800	-0.79887300	2.53180800
C	3.14797000	1.28416600	0.49556100
H	3.34647100	0.90873800	-0.50411900
C	-0.29346700	-3.17937600	0.00390000
C	-2.95938800	1.12512900	2.06979000
H	-3.90139700	0.97948100	2.60098700
H	-2.68741700	2.17920700	2.13021400
C	2.57288700	2.18161600	3.01527800
H	2.30046500	2.51821800	4.01014300
C	0.26113200	1.43290600	-2.63961700
C	1.59691600	-0.44233000	-2.50723700
H	1.89908100	-1.31176100	-1.93325600
C	4.10921600	2.03449700	1.17916500
H	5.06358600	2.24530500	0.70965500
C	-2.49223300	2.87511500	-0.54388300
H	-2.81910200	3.62047800	-1.28036000
H	-2.14556200	3.41639400	0.34408200
C	-4.04725000	-0.44804400	0.42529100
H	-5.07086500	-0.13259500	0.21872400
H	-4.04016000	-1.00359700	1.36343300
C	1.30764300	-4.92302600	0.46422400
H	1.57582100	-5.97255500	0.52215400
C	0.78908600	1.75658600	-3.89359200
H	0.43230000	2.64086600	-4.41113000

C	-0.80058500	2.29614200	-2.08745300
H	-1.04343700	3.18399000	-2.68415000
C	-3.68169100	1.97149900	-0.19432400
H	-4.45578900	2.49003200	0.37335500
H	-4.12081200	1.56767100	-1.10794800
C	-1.66739800	-2.79626300	-0.37360300
H	-2.33060500	-3.62996900	-0.63518100
C	0.02717300	-4.53877600	0.06925900
H	-0.72472700	-5.27944400	-0.18200600
C	-3.46549100	-1.31286600	-0.69471000
H	-4.08151000	-2.21608200	-0.79510200
H	-3.50310300	-0.77548700	-1.64997100
C	1.83311700	-2.59340500	0.68917500
H	2.52730300	-1.79427700	0.92839100
C	2.16710300	-0.19211000	-3.75728500
H	2.91376700	-0.87164200	-4.15241100
C	1.75926400	0.93475500	-4.46422900
H	2.18004000	1.16837000	-5.43641000
C	2.22799100	-3.92932500	0.78487200
H	3.23638700	-4.17037200	1.10186600
H	-2.26136100	0.57489500	0.21149300

Coordinates of C1*

Cu	-0.65404800	-0.15863100	0.02378200
N	-1.43784000	-1.87723500	1.02943100
N	0.54718100	-0.34801200	2.04407100
N	2.01538800	-1.42250900	-0.86432200
N	1.01056400	2.38960500	-0.28625700
N	-1.70660100	1.65194100	0.30473100
N	-3.20020200	-0.61543800	-0.83350300
N	-0.47405300	-0.58508900	-2.02640500
C	-0.95080000	-2.21789100	2.16038800
H	-1.30337200	-3.09403700	2.71512000

C	0.12134500	-1.40836900	2.76429100
C	1.65757200	-0.92606500	4.54902200
H	2.08853100	-1.15067500	5.51933700
C	-2.50838300	-2.65125400	0.42228400
H	-2.89268600	-3.43188400	1.09331600
H	-2.09299300	-3.14837100	-0.46290400
C	1.50951700	0.41916400	2.56412400
H	1.82088100	1.26356000	1.95656500
C	1.75317300	-1.59769100	-2.17272900
C	-3.65997400	-1.72138000	-0.00401400
H	-4.43560400	-2.33054000	-0.49792500
H	-4.11434400	-1.30519800	0.90020100
C	0.64987600	-1.73088300	4.01790400
H	0.27418100	-2.59309000	4.55976800
C	0.05079900	3.31345600	-0.08405700
C	2.23364200	2.82033400	-0.60506000
H	2.98694400	2.05117800	-0.76118700
C	2.09661800	0.17039900	3.80921600
H	2.87839700	0.82457500	4.17992900
C	-3.12535500	1.42338100	0.59577500
H	-3.65664300	2.36679800	0.78227600
H	-3.18634100	0.81657500	1.50604300
C	-2.93482900	-0.92087700	-2.23186700
H	-3.78164800	-0.65966900	-2.88938500
H	-2.78222200	-1.99974700	-2.33191300
C	3.88148800	-2.66049800	-2.54932000
H	4.60218900	-3.13949900	-3.20430900
C	0.29614800	4.69028300	-0.18782600
H	-0.50616200	5.40060000	-0.01454700
C	-1.31680900	2.87162900	0.24445800
H	-2.02795700	3.68490100	0.42946700
C	-3.81266400	0.67847300	-0.56328200
H	-4.88554100	0.59162000	-0.32677700

H	-3.74108300	1.29949100	-1.46149000
C	0.46408200	-1.12964500	-2.71098800
H	0.33731000	-1.28087300	-3.78892500
C	2.65990100	-2.21129700	-3.04914800
H	2.40742900	-2.33235700	-4.09791200
C	-1.68348500	-0.20314500	-2.76688200
H	-1.58106100	-0.42099100	-3.83861200
H	-1.80844900	0.87975400	-2.65732200
C	3.18814600	-1.85599400	-0.39845700
H	3.37059100	-1.69693300	0.66221400
C	2.57077800	4.17250200	-0.73511700
H	3.58416600	4.45924800	-0.99479800
C	1.57848600	5.12568000	-0.51920000
H	1.79512000	6.18550000	-0.60678000
C	4.15492500	-2.48057100	-1.19526700
H	5.09150300	-2.81091000	-0.75883500

Coordinates of C1*H2a

Cu	1.22842400	-0.20572800	0.21627200
N	1.18822600	-0.87755200	-1.76953300
N	2.95167900	0.75443300	-0.50142600
N	-2.64516300	1.44167500	-1.07587200
N	0.38510300	0.91792800	1.76226000
N	0.94453300	-1.71586100	1.66826300
N	-0.58575800	-3.02717400	-0.35231400
N	-2.90257900	-1.15583500	-0.25488300
C	2.18603200	-0.41963700	-2.43805900
H	2.38150400	-0.73327300	-3.46591400
C	3.11733200	0.53465700	-1.82750800
C	4.97552000	2.05072500	-1.92586000
H	5.76303200	2.55322700	-2.47701000
C	0.35976300	-1.90373800	-2.40934700
H	0.74890500	-2.17502000	-3.39692100

H	-0.64972800	-1.50353300	-2.55214000
C	3.77594800	1.61182300	0.11111700
H	3.61472700	1.76165000	1.17394500
C	-3.88165400	0.91322200	-0.90422500
C	0.32241900	-3.17688200	-1.56133100
H	-0.05075700	-4.02389000	-2.13796500
H	1.32301900	-3.41981000	-1.20561600
C	4.11920700	1.15810300	-2.57211900
H	4.21863900	0.94859700	-3.63180600
C	0.27485000	0.19798200	2.90772000
C	0.16595800	2.23715600	1.82206100
H	0.27371900	2.78782700	0.89387000
C	4.80126000	2.28126800	-0.56300800
H	5.44726400	2.96115800	-0.01929400
C	1.13694800	-3.15526900	1.51539300
H	1.28071500	-3.66151000	2.47697900
H	2.03455200	-3.31669400	0.91413700
C	-2.02590800	-3.38218800	-0.68472500
H	-2.14848800	-4.45037700	-0.50224300
H	-2.17105300	-3.19306100	-1.74830700
C	-4.79817500	3.03448000	-1.57073300
H	-5.65707100	3.66661800	-1.76620300
C	-0.07317800	0.77637500	4.12813400
H	-0.15066900	0.15884800	5.01650200
C	0.54854300	-1.23933900	2.79242600
H	0.40372000	-1.86535700	3.67643000
C	-0.09461500	-3.79612400	0.85887200
H	0.11840500	-4.81695400	0.53638200
H	-0.92261800	-3.81723800	1.56784800
C	-3.96676400	-0.49547400	-0.47986000
H	-4.97525900	-0.91053000	-0.39230800
C	-4.98833700	1.71374800	-1.15305100
H	-5.98240000	1.30393500	-1.02111800

C	-3.02137300	-2.55653500	0.12607700
H	-4.02443100	-2.96480600	-0.04838900
H	-2.81807200	-2.63658700	1.20046700
C	-2.42560700	2.70356300	-1.48057800
H	-1.39276200	3.00779300	-1.58868300
C	-0.18412500	2.89307000	3.00591900
H	-0.35589800	3.96334400	2.99457000
C	-0.30816100	2.15124700	4.17771900
H	-0.57890300	2.62996600	5.11252400
C	-3.50668300	3.53511500	-1.73856000
H	-3.33052700	4.55206700	-2.06486600
H	-0.57371900	-2.02863700	-0.09177500
H	-1.85764100	0.82096700	-0.87927300

Coordinates of C1H2a**

Cu	-1.11821100	0.32605100	0.32862800
N	-1.16964300	1.07484000	-1.63799700
N	-2.94111500	-0.48843500	-0.29863900
N	2.02996000	-1.55444800	-1.29415900
N	-0.21671300	-0.95858900	1.72345100
N	-0.54648800	1.71585500	1.79153900
N	0.90301500	3.05017600	-0.32517400
N	2.80150600	1.01855600	-0.51401700
C	-2.24185000	0.71052600	-2.24539500
H	-2.49346300	1.08278300	-3.24114200
C	-3.18256100	-0.21339500	-1.60293500
C	-5.12020000	-1.63031400	-1.62333100
H	-5.96745600	-2.07317700	-2.13571800
C	-0.32294200	2.07334000	-2.29805900
H	-0.76413100	2.40753000	-3.24348100
H	0.64661700	1.61472200	-2.52257900
C	-3.76716300	-1.32541000	0.34034200
H	-3.54420200	-1.52069500	1.38446900
C	3.37479500	-1.21831600	-1.14777800

C	-0.13180600	3.30109600	-1.40295900
H	0.20861800	4.15934800	-1.98333900
H	-1.07406900	3.56675600	-0.92465100
C	-4.26339300	-0.75884100	-2.29676800
H	-4.42113800	-0.50757300	-3.34014800
C	0.09003700	-0.30417700	2.87197600
C	-0.11088900	-2.29292900	1.70933500
H	-0.36932000	-2.78953100	0.78026700
C	-4.86817900	-1.91812900	-0.28350700
H	-5.51140800	-2.58382300	0.28071200
C	-0.61523400	3.17340100	1.72119500
H	-0.62006300	3.63450600	2.71598300
H	-1.54789100	3.44727300	1.22289500
C	2.31591800	3.36192400	-0.79611200
H	2.53909800	4.39587300	-0.52789900
H	2.32021100	3.26636600	-1.88220800
C	3.91861500	-3.48798200	-1.82990800
H	4.65414000	-4.25681800	-2.03984600
C	0.52359500	-0.96568800	4.02094800
H	0.75927600	-0.39847500	4.91506200
C	-0.06146600	1.15519200	2.83946300
H	0.25011400	1.72630800	3.71766800
C	0.60095600	3.74650800	0.98064000
H	0.45386900	4.80558000	0.76115600
H	1.49385400	3.64013600	1.59833100
C	3.71134100	0.10072000	-0.76054300
H	4.78172900	0.32132700	-0.69783200
C	4.31958700	-2.23549900	-1.42660200
H	5.37208000	-1.99480000	-1.31500000
C	3.28354700	2.34810000	-0.18755100
H	4.28578300	2.56509400	-0.58361800
H	3.33979200	2.48731500	0.90296300
C	1.61522900	-2.79020300	-1.70762000

H	0.54424200	-2.92193000	-1.80393800
C	0.31325300	-3.03034000	2.81850400
H	0.38748100	-4.10954300	2.74802600
C	0.63773300	-2.35623000	3.99311500
H	0.97103800	-2.89874300	4.87116900
C	2.52217000	-3.77361900	-1.97934000
H	2.17863100	-4.74770600	-2.30457900
H	0.92935900	2.02927700	-0.14780100
H	1.35509900	-0.82695800	-1.09281300

Coordinates of C1 Ha**

Cu	0.21248900	0.14397600	-0.28511600
N	-0.70166600	-0.71216300	-1.97754800
N	1.91042000	-0.95640600	-1.07008700
N	0.53847900	2.25801100	-0.35880100
N	0.74596700	-0.24336100	1.92868700
N	-1.41055100	-1.94686700	1.28035700
N	-3.23381100	-0.85504100	-0.40953300
N	-2.12198900	1.63304000	0.41156700
C	0.19354600	-1.42731400	-2.67438000
H	-0.09587700	-1.88811100	-3.62312500
C	1.52956100	-1.59639400	-2.24142400
C	3.75858600	-2.52946600	-2.49793700
H	4.47835300	-3.13246100	-3.04484900
C	-2.01261300	-0.57244000	-2.58332000
H	-2.03626000	-0.94267900	-3.61917700
H	-2.29812100	0.48768700	-2.62809700
C	3.17157800	-1.12026300	-0.63962000
H	3.42088400	-0.60640400	0.28804500
C	-0.36769500	3.22483600	-0.07592100
C	-3.09135800	-1.35907500	-1.82837700
H	-4.07351000	-1.28425800	-2.30168800
H	-2.80704400	-2.41043400	-1.77396700

C	2.47144300	-2.38984700	-2.96314500
H	2.15123100	-2.88040400	-3.87898000
C	0.46777300	-1.34596800	2.66466200
C	1.73998500	0.54656700	2.35885700
H	1.93609800	1.43131600	1.76220700
C	4.13423100	-1.87938400	-1.29323300
H	5.13690700	-1.96313800	-0.88868900
C	-2.52222800	-2.81704400	0.94547800
H	-2.83472900	-3.48062600	1.76274000
H	-2.22702800	-3.45173600	0.10121000
C	-4.06886000	0.40314200	-0.32650700
H	-5.10004400	0.11376400	-0.11720900
H	-4.03617300	0.88370800	-1.30438900
C	1.21417900	4.97473100	-0.58545500
H	1.47198900	6.02530400	-0.66836400
C	1.19187400	-1.68607400	3.81352500
H	0.93155800	-2.58380100	4.36510400
C	-0.65856300	-2.21493800	2.27054200
H	-0.81305400	-3.10103500	2.90036500
C	-3.70159900	-1.92101500	0.55279900
H	-4.51561300	-2.47657200	0.08450100
H	-4.08642100	-1.40906100	1.43629300
C	-1.73921000	2.84389700	0.31525200
H	-2.42095200	3.68492100	0.49897700
C	-0.05995100	4.58646000	-0.17678100
H	-0.81851200	5.32528200	0.06033100
C	-3.51204400	1.35616500	0.73296100
H	-4.14767200	2.25235600	0.76041700
H	-3.55416700	0.88853300	1.72421300
C	1.75989000	2.64546000	-0.76217100
H	2.45606900	1.84398900	-0.99090300
C	2.50501700	0.28624400	3.49906700
H	3.29374100	0.97242100	3.78761700

C	2.23035100	-0.86025000	4.23928600
H	2.80309800	-1.10422800	5.12795700
C	2.14241100	3.98168200	-0.88904900
H	3.14668200	4.22528500	-1.21767400
H	-2.26938300	-0.61369100	-0.09763700

Coordinates of Py-N

Coordinates of C1

Cu	-0.14680200	-0.00659200	0.05472700
N	-0.37472700	-1.12360000	1.78190800
N	0.59710900	1.35155100	1.49216600
N	2.11644200	-0.98905400	-0.30105800
N	0.00681800	1.37723000	-1.51650200
N	-2.24204300	0.97142500	-0.05126400
N	-2.84901400	-1.78476600	0.36373400
N	-0.40479200	-1.58854700	-1.29536000
C	0.04570300	-0.53530700	2.83855700
H	0.00032600	-1.01023900	3.82040700
C	0.59284400	0.82065200	2.73880900
C	1.55500700	2.81343900	3.66431800
H	1.92836600	3.38310600	4.50826400
C	-0.98217500	-2.44970400	1.88050300
H	-0.79144300	-2.88779800	2.86709200
H	-0.50922100	-3.08837500	1.12952700
C	1.06721300	2.59004500	1.32089900
H	1.05504600	2.98189300	0.31086300
C	1.96263600	-2.03968800	-1.13320900
C	-2.50402300	-2.38369700	1.63708700
H	-2.89504300	-3.40941700	1.74601700
H	-2.95322500	-1.78703200	2.43645000
C	1.06348800	1.51895300	3.84797000
H	1.04305200	1.05693200	4.82859400

C	-1.08577800	2.14186600	-1.76205300
C	1.10379200	1.55095100	-2.26468800
H	1.95196100	0.91992700	-2.02624400
C	1.55592900	3.35676800	2.38342300
H	1.92684300	4.35726500	2.19408400
C	-3.41756900	0.62751000	0.72822900
H	-4.23625800	1.34643500	0.58897600
H	-3.12905200	0.63874100	1.78534800
C	-2.64086800	-2.57963900	-0.83109100
H	-3.58772800	-2.80894700	-1.34340500
H	-2.19986500	-3.54166800	-0.54989500
C	4.27795800	-2.64409200	-0.94019300
H	5.11689500	-3.28477200	-1.19013400
C	-1.09353400	3.10668600	-2.76830900
H	-1.98556500	3.70053500	-2.93506700
C	-2.27926100	1.89166500	-0.93080800
H	-3.16608200	2.50393900	-1.12402400
C	-3.90479700	-0.78791000	0.33886700
H	-4.74377000	-1.04930000	1.00252000
H	-4.30923000	-0.74007000	-0.67699800
C	0.61255000	-2.27169900	-1.66914900
H	0.50548000	-3.07067900	-2.40735000
C	3.01567500	-2.88730400	-1.48497100
H	2.84656800	-3.71629000	-2.16402700
C	-1.71825800	-1.90067700	-1.86511400
H	-1.61281800	-2.55347200	-2.73986200
H	-2.16808400	-0.95982700	-2.19484500
C	3.32652300	-0.76400000	0.21415400
H	3.41898900	0.09062500	0.87842700
C	1.16783000	2.49429700	-3.29192100
H	2.07919200	2.59668900	-3.86926600
C	0.05116900	3.28575500	-3.54637500
H	0.06709300	4.02949100	-4.33582400

C	4.43746500	-1.56622500	-0.07390600
H	5.39918800	-1.33806700	0.37176600

Coordinates of C1Hp

Cu	-0.47432600	-0.01530000	0.11975400
N	-0.11538300	-0.76298500	1.98783300
N	-0.07553400	1.78678800	1.19122400
N	2.90624300	-0.61698900	0.29321600
N	-0.65600700	0.98105300	-1.67371500
N	-2.62793100	-0.00939800	-0.16721900
N	-1.92091800	-2.58231100	0.67480900
N	0.46849000	-1.74176900	-0.92178700
C	0.04962400	0.13354800	2.89436900
H	0.17499500	-0.13381100	3.94413900
C	0.07441600	1.54540500	2.51709400
C	0.24705600	3.88711200	2.99875100
H	0.37291500	4.70481600	3.69963200
C	-0.16078100	-2.18184300	2.36771100
H	0.07409100	-2.29536600	3.43074900
H	0.61209000	-2.70683600	1.79964700
C	-0.06926300	3.05168700	0.76439700
H	-0.19332100	3.21396900	-0.29921000
C	2.89232700	-1.34915800	-0.85077900
C	-1.53662100	-2.78791200	2.06348100
H	-1.50882300	-3.85181400	2.34844100
H	-2.27846300	-2.30477500	2.70493400
C	0.23955300	2.56444100	3.45029200
H	0.35597000	2.32513600	4.50111800
C	-1.93521700	1.21204900	-2.06613400
C	0.35064800	1.46139100	-2.41595900
H	1.35803100	1.27490600	-2.06329600
C	0.09087900	4.13267400	1.63912900
H	0.09172300	5.14123500	1.24295800

C	-3.59357700	-0.74641000	0.63253400
H	-4.62550400	-0.51314100	0.34536400
H	-3.45331300	-0.46100700	1.68013600
C	-1.26815300	-3.42345200	-0.31688200
H	-1.97319000	-4.11711700	-0.79563700
H	-0.50650600	-4.04139100	0.16842800
C	5.23269900	-0.83062500	-1.10863800
H	6.15617400	-0.92157600	-1.66907200
C	-2.23047600	1.92669300	-3.22355900
H	-3.26449200	2.08784000	-3.50690000
C	-2.98266100	0.63261900	-1.21169000
H	-4.02526900	0.74281600	-1.51859300
C	-3.32423500	-2.25465100	0.44485400
H	-4.00133400	-2.81819000	1.10350700
H	-3.58220200	-2.52245100	-0.58369300
C	1.65982300	-2.01378200	-1.30622000
H	1.83830100	-2.80653200	-2.03562800
C	4.07817800	-1.47435200	-1.56484700
H	4.09121500	-2.06587300	-2.47228200
C	-0.60041300	-2.61139200	-1.44768800
H	-0.20082100	-3.29776600	-2.20195800
H	-1.34523300	-1.97201500	-1.92937600
C	3.99935300	0.00764800	0.76616900
H	3.88267500	0.54991100	1.69524400
C	0.12918300	2.18593700	-3.58885600
H	0.97613100	2.55249500	-4.15643100
C	-1.17977300	2.42128500	-3.99887600
H	-1.38378500	2.98084200	-4.90511400
C	5.19427000	-0.08011100	0.06575000
H	6.07262000	0.42439800	0.44741800
H	2.04703700	-0.55854100	0.83567000

Coordinates of C1*Hp

Cu	-0.94858100	-0.08991000	0.01443700
N	-1.27200600	-1.54533800	1.41954000
N	1.16625100	-0.25560900	1.82174400
N	1.79125800	-1.56717600	-0.85831900
N	0.93525700	2.06444100	-0.81345600
N	-1.69100100	1.79923700	0.25580300
N	-3.30142000	-0.51642700	-0.33409500
N	-0.84774600	-0.83967400	-1.89476100
C	-0.59542200	-1.77119700	2.48184600
H	-0.90576700	-2.53115800	3.20478200
C	0.60614300	-0.98673400	2.81009000
C	2.18055700	-0.16609000	4.43261100
H	2.57644300	-0.13805900	5.44236200
C	-2.47057000	-2.34081700	1.14595300
H	-2.75137800	-2.96143200	2.00574100
H	-2.23162900	-3.01394200	0.31416600
C	2.20194400	0.53213200	2.13627000
H	2.62452000	1.11494100	1.32315500
C	1.35820300	-1.86214600	-2.11199300
C	-3.64826000	-1.42951900	0.75932300
H	-4.51791500	-2.06017400	0.51927100
H	-3.92047800	-0.82915100	1.63166600
C	1.09512700	-0.98416800	4.12047300
H	0.62064000	-1.60015200	4.87723600
C	0.19605800	3.14562100	-0.49260900
C	2.15481800	2.27570700	-1.31468500
H	2.73122600	1.39046100	-1.57266400
C	2.73952100	0.61571000	3.42431900
H	3.58186500	1.27053700	3.61768700
C	-3.08991900	1.74310400	0.69284400
H	-3.55026100	2.73874100	0.71104900
H	-3.10469000	1.34687200	1.71456100
C	-3.30650100	-1.10841900	-1.67308700

H	-4.24764800	-0.92105700	-2.21183500
H	-3.20589900	-2.19299800	-1.57864700
C	3.45654800	-3.00188500	-2.48858700
H	4.11163900	-3.56788500	-3.14124800
C	0.65929100	4.45728600	-0.65986400
H	0.02509400	5.29604300	-0.39126700
C	-1.16872100	2.94533900	0.02523100
H	-1.74768400	3.85923000	0.19261900
C	-3.89768600	0.82082500	-0.23828800
H	-4.94024000	0.78678300	0.11157700
H	-3.91189900	1.26652500	-1.23697900
C	0.02935300	-1.46384900	-2.58877600
H	-0.17703400	-1.76966400	-3.61700800
C	2.20510700	-2.59042300	-2.94630700
H	1.87202400	-2.83277500	-3.94833300
C	-2.14747800	-0.58384300	-2.54022700
H	-2.19607000	-1.04366400	-3.53422200
H	-2.23572400	0.50082700	-2.66346500
C	2.99065100	-1.95761400	-0.38787600
H	3.21970600	-1.66670400	0.62827100
C	2.70375300	3.54841700	-1.51312400
H	3.70311800	3.65131300	-1.92176300
C	1.93861300	4.66132400	-1.17565900
H	2.32421500	5.66621900	-1.31303300
C	3.85608300	-2.68452800	-1.18988700
H	4.81835800	-2.98899600	-0.79848300
H	1.19689300	-1.02485600	-0.20701700

Coordinates of C1*

Cu	-0.65404800	-0.15863100	0.02378200
N	-1.43784000	-1.87723500	1.02943100
N	0.54718100	-0.34801200	2.04407100
N	2.01538800	-1.42250900	-0.86432200

N	1.01056400	2.38960500	-0.28625700
N	-1.70660100	1.65194100	0.30473100
N	-3.20020200	-0.61543800	-0.83350300
N	-0.47405300	-0.58508900	-2.02640500
C	-0.95080000	-2.21789100	2.16038800
H	-1.30337200	-3.09403700	2.71512000
C	0.12134500	-1.40836900	2.76429100
C	1.65757200	-0.92606500	4.54902200
H	2.08853100	-1.15067500	5.51933700
C	-2.50838300	-2.65125400	0.42228400
H	-2.89268600	-3.43188400	1.09331600
H	-2.09299300	-3.14837100	-0.46290400
C	1.50951700	0.41916400	2.56412400
H	1.82088100	1.26356000	1.95656500
C	1.75317300	-1.59769100	-2.17272900
C	-3.65997400	-1.72138000	-0.00401400
H	-4.43560400	-2.33054000	-0.49792500
H	-4.11434400	-1.30519800	0.90020100
C	0.64987600	-1.73088300	4.01790400
H	0.27418100	-2.59309000	4.55976800
C	0.05079900	3.31345600	-0.08405700
C	2.23364200	2.82033400	-0.60506000
H	2.98694400	2.05117800	-0.76118700
C	2.09661800	0.17039900	3.80921600
H	2.87839700	0.82457500	4.17992900
C	-3.12535500	1.42338100	0.59577500
H	-3.65664300	2.36679800	0.78227600
H	-3.18634100	0.81657500	1.50604300
C	-2.93482900	-0.92087700	-2.23186700
H	-3.78164800	-0.65966900	-2.88938500
H	-2.78222200	-1.99974700	-2.33191300
C	3.88148800	-2.66049800	-2.54932000
H	4.60218900	-3.13949900	-3.20430900

C	0.29614800	4.69028300	-0.18782600
H	-0.50616200	5.40060000	-0.01454700
C	-1.31680900	2.87162900	0.24445800
H	-2.02795700	3.68490100	0.42946700
C	-3.81266400	0.67847300	-0.56328200
H	-4.88554100	0.59162000	-0.32677700
H	-3.74108300	1.29949100	-1.46149000
C	0.46408200	-1.12964500	-2.71098800
H	0.33731000	-1.28087300	-3.78892500
C	2.65990100	-2.21129700	-3.04914800
H	2.40742900	-2.33235700	-4.09791200
C	-1.68348500	-0.20314500	-2.76688200
H	-1.58106100	-0.42099100	-3.83861200
H	-1.80844900	0.87975400	-2.65732200
C	3.18814600	-1.85599400	-0.39845700
H	3.37059100	-1.69693300	0.66221400
C	2.57077800	4.17250200	-0.73511700
H	3.58416600	4.45924800	-0.99479800
C	1.57848600	5.12568000	-0.51920000
H	1.79512000	6.18550000	-0.60678000
C	4.15492500	-2.48057100	-1.19526700
H	5.09150300	-2.81091000	-0.75883500

Coordinates of C1*H2p

Cu	-0.98523500	0.08147000	-0.01520500
N	-1.35411500	1.26778600	-1.64499500
N	1.16971500	0.10732200	-1.72908000
N	1.67204400	2.00124900	0.55225300
N	0.95005900	-2.20646600	1.44240700
N	-1.53911100	-1.92421900	-0.00381100
N	-3.28084500	0.39928000	0.25084000
N	-0.88023200	1.10460100	1.74958900
C	-0.66265700	1.33576000	-2.71730900

H	-0.99044600	1.92925200	-3.57518600
C	0.59492900	0.58122700	-2.85831800
C	2.27905900	-0.42911800	-4.24606900
H	2.71032200	-0.63089000	-5.22078100
C	-2.59928700	2.02442500	-1.51438100
H	-2.91576100	2.45901000	-2.46976200
H	-2.40501300	2.85095100	-0.82054900
C	2.27381500	-0.64027400	-1.85581100
H	2.72257600	-1.00121200	-0.93489400
C	1.19820800	2.41124300	1.75800700
C	-3.71243800	1.12011500	-0.95813100
H	-4.61190700	1.72561800	-0.77861600
H	-3.97157100	0.38123600	-1.72085400
C	1.12956700	0.35263800	-4.12888100
H	0.64256900	0.76936000	-5.00416500
C	0.33783600	-3.24285500	0.81706400
C	2.15495400	-2.29912400	2.03424700
H	2.53168300	-1.40302400	2.50988800
C	2.85835800	-0.94319500	-3.08897400
H	3.75292500	-1.55439000	-3.12693800
C	-2.93647600	-1.94564500	-0.48056500
H	-3.35760300	-2.95496400	-0.42421600
H	-2.92693900	-1.63882000	-1.53166700
C	-3.34974300	1.17858000	1.49453700
H	-4.28503500	1.00368100	2.04523800
H	-3.32123000	2.24152600	1.24120600
C	3.18224000	3.77226700	1.99346400
H	3.77477200	4.47243300	2.57131400
C	0.98459500	-4.47405100	0.79430700
H	0.50285200	-5.31581900	0.31154100
C	-0.99839300	-3.06049800	0.23361600
H	-1.52718700	-3.99347400	0.02848200
C	-3.79247000	-0.97430900	0.34701300

H	-4.83601100	-1.05364200	0.01112100
H	-3.76823000	-1.28915700	1.39357500
C	-0.09693700	1.96540700	2.28680100
H	-0.37454000	2.45836900	3.22053000
C	1.96351600	3.31241900	2.49519000
H	1.59745300	3.64875300	3.45784900
C	-2.17072800	0.86907000	2.43400800
H	-2.25501200	1.48263200	3.33746100
H	-2.19092100	-0.18282500	2.73612800
C	2.83870400	2.43371600	0.04105600
H	3.10797500	2.04205900	-0.93078900
C	2.83609100	-3.50711600	2.01315200
H	3.80676400	-3.57902700	2.48675400
C	2.24271100	-4.60451200	1.38719400
H	2.75283700	-5.56089300	1.36372500
C	3.62584300	3.33089700	0.74785800
H	4.56196400	3.66976300	0.32279000
H	0.44988400	-1.31632500	1.47705500
H	1.14425600	1.32789900	-0.03016900

Coordinates of C1H2p**

Cu	-0.74548100	-0.33075700	-0.00961400
N	-1.24696900	-2.32104500	0.33720200
N	0.46874400	-0.89074000	1.83631500
N	2.33873300	-0.89882100	-0.83724200
N	0.40268500	2.66457800	-0.17870200
N	-2.00267200	1.30717300	0.59955300
N	-2.97300800	-0.71822800	-1.21882200
N	-0.18866200	0.17760700	-1.91361800
C	-0.72850000	-2.91715400	1.33958700
H	-0.92330400	-3.96656000	1.57882400
C	0.16171400	-2.15200300	2.23025900
C	1.44242000	-1.92084300	4.25185100

H	1.82157300	-2.32143100	5.18605000
C	-2.14380700	-2.98811700	-0.59040300
H	-2.48041300	-3.96473800	-0.21989200
H	-1.58463600	-3.15831700	-1.51852000
C	1.24348200	-0.15086000	2.64186500
H	1.47835600	0.85216400	2.30012400
C	2.11680600	-0.62382400	-2.18237000
C	-3.36109000	-2.08545600	-0.87204200
H	-3.97950600	-2.56005000	-1.65032200
H	-3.96897000	-2.04311600	0.03657700
C	0.63562500	-2.70050300	3.42310300
H	0.36754900	-3.71661600	3.69321100
C	-0.49504200	3.19942300	0.68948000
C	1.59186700	3.23217000	-0.44921800
H	2.21957800	2.71821500	-1.16538100
C	1.74923900	-0.62066200	3.85646000
H	2.37356100	0.02351700	4.46523000
C	-3.37403300	0.80495800	0.71042900
H	-4.05916000	1.57139500	1.09335900
H	-3.36857000	-0.03918600	1.40744000
C	-2.50589900	-0.50886600	-2.59109200
H	-3.32526500	-0.20947300	-3.26597400
H	-2.11155000	-1.45664300	-2.96915500
C	4.41316300	-1.32783100	-2.59451800
H	5.23436400	-1.49999200	-3.28172500
C	-0.17783500	4.40182500	1.31417300
H	-0.89226700	4.84683200	1.99614300
C	-1.78458800	2.52754800	0.91317500
H	-2.56055000	3.16092300	1.35141900
C	-3.84359800	0.32349800	-0.68008400
H	-4.88646000	-0.01226200	-0.58939600
H	-3.84794000	1.18089400	-1.35929700
C	0.87775900	-0.13644000	-2.64968600

H	0.82236400	-0.00895000	-3.73224000
C	3.20996300	-0.85957300	-3.06135400
H	3.06400900	-0.65431700	-4.11668100
C	-1.38941900	0.54966900	-2.68111500
H	-1.14553800	0.70108900	-3.74059200
H	-1.77270600	1.50563900	-2.30398000
C	3.52859900	-1.36910100	-0.35976700
H	3.56794700	-1.54745100	0.70779600
C	1.95111200	4.41927000	0.17179800
H	2.91057600	4.86911600	-0.04915900
C	1.05296800	5.01027000	1.06158200
H	1.30558300	5.94190600	1.55535400
C	4.58310200	-1.58970500	-1.19967900
H	5.52086900	-1.95866100	-0.80403000
H	0.16089900	1.77963000	-0.66675300
H	1.56254100	-0.79142400	-0.18705200

Coordinates of C1 Hp**

Cu	-0.98605500	-0.06311300	-0.00876200
N	-1.36056100	-1.40000600	1.52253600
N	1.14184500	-0.20302500	1.91500100
N	1.74948000	-1.58392500	-0.92666300
N	1.05304300	2.02937000	-0.81579400
N	-1.62524200	1.88536400	0.16321100
N	-3.36815000	-0.38510800	-0.28598700
N	-0.96160200	-0.92437500	-1.86261500
C	-0.68101200	-1.64485900	2.58009700
H	-1.03116300	-2.36888600	3.32279700
C	0.58305100	-0.95530800	2.88527100
C	2.31013100	-0.37374900	4.45709600
H	2.76422700	-0.44612400	5.44000500
C	-2.60800500	-2.13746200	1.30662000
H	-2.91256300	-2.69302300	2.20285200

H	-2.41958300	-2.86898000	0.51187500
C	2.25566400	0.47367300	2.21250900
H	2.67497900	1.07751900	1.41226900
C	1.22308300	-1.97404400	-2.15915500
C	-3.74054900	-1.18984200	0.87764700
H	-4.65038200	-1.78672900	0.70349700
H	-3.95889300	-0.51391200	1.70955200
C	1.14295800	-1.07723200	4.16313700
H	0.66338500	-1.70348600	4.90866000
C	0.33831200	3.14245500	-0.55919900
C	2.29748000	2.18100600	-1.27477800
H	2.84868700	1.26523700	-1.47708200
C	2.87610500	0.42477300	3.46543900
H	3.78178200	0.99348400	3.64600800
C	-3.02957400	1.92017900	0.58811400
H	-3.44169300	2.93679300	0.54573900
H	-3.06781200	1.58776800	1.63199200
C	-3.42852100	-1.07871200	-1.57685700
H	-4.37899200	-0.89021100	-2.10181100
H	-3.37648000	-2.15538100	-1.39148900
C	3.33798600	-3.11120700	-2.59340400
H	3.96710400	-3.70887700	-3.24413700
C	0.85305500	4.43239200	-0.75225000
H	0.23923400	5.30110200	-0.53612500
C	-1.04721600	3.00386700	-0.07811600
H	-1.59035300	3.94535000	0.05700000
C	-3.88314600	0.98483500	-0.28636800
H	-4.92898800	1.04064900	0.05534300
H	-3.86346500	1.36080000	-1.31326700
C	-0.08667500	-1.62473600	-2.56047400
H	-0.36737700	-1.99370200	-3.55085300
C	2.07186400	-2.75551300	-2.98858700
H	1.68318600	-3.06837400	-3.95257000

C	-2.25945200	-0.68830900	-2.49811000
H	-2.35642200	-1.24846600	-3.43904100
H	-2.34087500	0.37837200	-2.75069600
C	3.00725400	-1.93747300	-0.51947500
H	3.29631300	-1.57899900	0.46047900
C	2.89738700	3.42684500	-1.49380600
H	3.91509100	3.48383700	-1.86478700
C	2.15692300	4.57541300	-1.22460500
H	2.58174300	5.56180000	-1.38042000
C	3.82332000	-2.69002800	-1.31278500
H	4.81484600	-2.95639400	-0.96838500
H	1.18584800	-1.01074500	-0.29888400

References

(1) Fourmond, V.; Jacques, P.-A.; Fontecave, M.; Artero, V. H2 Evolution and Molecular Electrocatalysts: Determination of Overpotentials and Effect of Homoconjugation. *Inorg. Chem.* **2010**, *49* (22), 10338–10347. https://doi.org/10.1021/ic101187v.

(2) Brunner, E. Solubility of Hydrogen in 10 Organic Solvents at 298.15, 323.15, and 373.15 K. *J. Chem. Eng. Data* **1985**, *30* (3), 269–273. https://doi.org/10.1021/je00041a010.

(3) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98* (45), 11623–11627. https://doi.org/10.1021/j100096a001.

(4) Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, 2016. No Title.

(5) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. Energy-Adjusted a b i n i t i o Pseudopotentials for the First Row Transition Elements. *J. Chem. Phys.* **1987**, *86* (2), 866–872. https://doi.org/10.1063/1.452288.

(6) Petersson, G. A.; Al-Laham, M. A. A Complete Basis Set Model Chemistry. II. Open-Shell Systems and the Total Energies of the First-Row Atoms. *J. Chem. Phys.* **1991**, *94* (9), 6081–6090. https://doi.org/10.1063/1.460447.

(7) Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theor. Chim. Acta* **1973**, *28* (3), 213–222. https://doi.org/10.1007/BF00533485.

(8) Miertuš, S.; Scrocco, E.; Tomasi, J. Electrostatic Interaction of a Solute with a Continuum. A Direct Utilizaion of AB Initio Molecular Potentials for the Prevision of Solvent Effects. *Chem. Phys.* **1981**, *55* (1), 117–129. https://doi.org/10.1016/0301-0104(81)85090-2.

(9) Miertuš̃, S.; Tomasi, J. Approximate Evaluations of the Electrostatic Free Energy and Internal Energy Changes in Solution Processes. *Chem. Phys.* **1982**, *65* (2), 239–245. https://doi.org/10.1016/0301-0104(82)85072-6.

(10) Pascual-ahuir, J. L.; Silla, E.; Tuñon, I. GEPOL: An Improved Description of Molecular Surfaces. III. A New Algorithm for the Computation of a Solvent-excluding Surface. *J. Comput. Chem.* **1994**, *15* (10), 1127–1138. https://doi.org/10.1002/jcc.540151009.

(11) Isse, A. A.; Gennaro, A. Absolute Potential of the Standard Hydrogen Electrode and the Problem of Interconversion of Potentials in Different Solvents. *J. Phys. Chem. B* **2010**, *114* (23), 7894–7899. https://doi.org/10.1021/jp100402x.

(12) Zhang, P.; Wang, M.; Yang, Y.; Yao, T.; Sun, L. A Molecular Copper Catalyst for Electrochemical Water Reduction with a Large Hydrogen-Generation Rate Constant in Aqueous Solution. *Angew. Chem. Int. Ed.* **2014**, *53* (50), 13803–13807. https://doi.org/10.1002/anie.201408266.

(13) Cao, J.-P.; Fang, T.; Fu, L.-Z.; Zhou, L.-L.; Zhan, S.-Z. First Mononuclear Copper(II) Electro-Catalyst for Catalyzing Hydrogen Evolution from Acetic Acid and Water. *Int. J. Hydrog. Energy* **2014**, *39* (26), 13972–13978. https://doi.org/10.1016/j.ijhydene.2014.07.030.

(14) Fu, L.-Z.; Fang, T.; Zhou, L.-L.; Zhan, S.-Z. A Mononuclear Copper Electrocatalyst for Both Water Reduction and Oxidation. *RSC Adv.* **2014**, *4* (96), 53674–53680. https://doi.org/10.1039/C4RA07211A.

(15) Fang, T.; Lu, H.-X.; Zhao, J.-X.; Zhan, S.-Z.; Lv, Q.-Y. A New Copper(I)–Triazenido Electro-Catalyst for Catalyzing Hydrogen Evolution from Acetic Acid and Water. *J. Mol. Catal. Chem.* **2015**, *396*, 304–309. https://doi.org/10.1016/j.molcata.2014.10.008.

(16) Fang, T.; Zhou, L.-L.; Fu, L.-Z.; Zhan, S.-Z.; Lv, Q.-Y. Synthesis and Studies of a Molecular Copper(I)-Triazenido Electrocatalyst for Catalyzing Hydrogen Evolution from Acetic Acid and Water. *Polyhedron* **2015**, *85*, 355–360. https://doi.org/10.1016/j.poly.2014.08.030.

(17) Cao, J.-P.; Fang, T.; Wang, Z.-Q.; Ren, Y.-W.; Zhan, S. A Dinuclear Triazenido–Copper Complex: A New Molecular Electro-Catalyst for Generating Hydrogen from Acetic Acid or Water. *J. Mol. Catal. Chem.* **2014**, *391*, 191–197. https://doi.org/10.1016/j.molcata.2014.04.034.

(18) Lei, H.; Fang, H.; Han, Y.; Lai, W.; Fu, X.; Cao, R. Reactivity and Mechanism Studies of Hydrogen Evolution Catalyzed by Copper Corroles. *ACS Catal.* **2015**, *5* (9), 5145–5153. https://doi.org/10.1021/acscatal.5b00666.

(19) Ekanayake, D. M.; Kulesa, K. M.; Singh, J.; Kpogo, K. K.; Mazumder, S.; Schlegel, H. B.; Verani, C. N. A Pentadentate Nitrogen-Rich Copper Electrocatalyst for Water Reduction with pH-Dependent Molecular Mechanisms. *Dalton Trans.* **2017**, *46* (48), 16812–16820. https://doi.org/10.1039/C7DT02711G.

(20) Xin, Z.-J.; Liu, S.; Li, C.-B.; Lei, Y.-J.; Xue, D.-X.; Gao, X.-W.; Wang, H.-Y. Hydrogen Production in a Neutral Aqueous Solution with a Water-Soluble Copper Complex. *Int. J. Hydrog. Energy* **2017**, *42* (7), 4202–4207. https://doi.org/10.1016/j.ijhydene.2016.11.103.

(21) Majee, K.; Patel, J.; Das, B.; Padhi, S. K. μ-Pyridine-Bridged Copper Complex with Robust Proton-Reducing Ability. *Dalton Trans.* **2017**, *46* (43), 14869–14879. https://doi.org/10.1039/C7DT03153J.