Supplementary Information

for

Electrocatalytic Hydrogen Evolution Reaction by an Organometallic Cobalt Complex and its Hybrid Material with MWCNT

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Materials and Methods

All the chemicals and reagents have been purchased from commercially available sources (TCI Chemicals, Sigma Aldrich, Spectrochem, BLD Pharm, SRL Chemicals) and used as received without further purification. The solvents were purchased from Finer Chemicals, SRL Chemicals and Qualigens and distilled and dried by standard protocols. ^{1}H NMR and ^{13}C NMR spectra were recorded by using a Bruker Avance 400 MHz spectrometer (Bruker, Massachusetts, USA). All ^{1}H NMR spectra are reported in the unit parts per million (ppm) and referenced in the solvent relative to the signals for residual chloroform (7.26 ppm) in $CDCl_3$ and DMSO (2.50 ppm) in d_6-DMSO. The optical absorption spectra were recorded using Shimadzu UV-3600 Plus UV-vis spectrophotometer with 1 cm path length. The elemental (C, H, and N) analysis was performed using the Perkin Elmer 2400 series H CHN analyzer. The High-Resolution mass spectrometry of the complexes was recorded on a Q-Tof Micro YA263 high-resolution (Waters Corporation) mass spectrometer in a positive ion mode. The EPR spectroscopy was performed on a Bruker (X-Band) spectrometer with 9.155 GHz microwave frequency, 100 kHz modulation frequency, 5 mW power, and 4 min of sweep time. The cyclic voltammetry (CV) and linear sweep voltammetry experiments were recorded at room temperature using Metrohm Autolab PGSTAT 204 potentiostat and CH1760E electrochemical Workstation (CH instruments). The headspace gas after bulk electrolysis was analyzed using TCD detector in High-performance gas chromatography (Agilent 8860). GC was calibrated with known volumes of standard H_2. Surface analysis studies of the graphite plate working electrode (for homogeneous catalysis) and modified carbon paper electrode (for heterogenous catalysis) using Field Emission Scanning Electron Microscopy (FE-SEM) were done with JEOL JEM 2100 (Tokyo, Japan) scanning electron microscope and ZEISS SUPRA 55-VP JSM equipped with EDAX of GEMINI column technology. Morphology analysis of heterogenous hybrid material (2/MWCNT) was done with JEOL, JEM-2100PLUS (LaB6). The surface chemistry of the modified electrodes (before and after bulk electrolysis) was examined using X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe II, ULVAC-PHI Inc., USA) with micro-focused (100 µm, 15 kV) monochromatic Al-Kα X-Ray source (hν = 1486.6 eV). A X-ray pass energy of 225 eV was used to examine the survey images. 55 eV pass energy was used to record the key elements high -resolution XPS spectra.

1. **Electrochemical Study**:

All cyclic voltammetry (CV) studies for proton reduction were studied in dry *N,N*-dimethylformamide (DMF) with 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) as supporting electrolyte. The linear sweep voltammetry (LSV) and CVs for heterogeneous hydrogen evolution reaction were performed in 1.0 M aqueous KOH solution. A standard three-electrode system under Ar atmosphere was used with a 3 mm glassy carbon disc as a working electrode, Ag/AgCl as a reference electrode connected by Vycor tip, and platinum wire for the proton reduction studies in DMF. Whereas, a carbon paper working electrode, a Hg/HgO reference electrode and graphite plate as counter electrode has been used for the heterogeneous HER in 1.0 M aqueous solution of KOH. For the heterogeneous HER studies, 1 cm x 1 cm of carbon paper was immersed in the electrolyte solution during the electrochemical measurements. The LSVs for aqueous HER were recorded at a scan rate of 5mV/s. EIS was performed in a frequency range from 1 to 10^5 Hz. All samples were measured twice to ensure reproducibility. All potentials are reported versus NHE (Normal Hydrogen Electrode) for proton reduction and versus RHE (Reversible Hydrogen Electrode) for the aqueous HER. The potentials for aqueous HER were converted to RHE using the Nernst equation, $E_{RHE} = E^0_{Hg/HgO} + E_{Hg/HgO} + 0.059*pH$. CV. All the electrochemical data furnished are without iR corrections.

Considering theoretical Nernst equation at 25 ^{0}C

$E_{RHE} = E_{Hg/HgO} + 2.303\,(RT/F)*pH + E^{\Theta}_{Hg/HgO}$

$E_{RHE} = E_{Hg/HgO} + 0.059\ pH + E^{\Theta}_{Hg/HgO}$

$E_{RHE} = E_{Hg/HgO} + 0.059 * 14 + 0.098$

$E_{RHE} = E_{Hg/HgO} + 0.925$

Here, $E^{\Theta}_{Hg/HgO} = 0.098$V (V vs. NHE, 25 ^{0}C) and pH = 14 (1.0 M KOH)

Conversion of $E_{Hg/HgO}$ to E_{RHE} considering the practical pH of 1.0 M KOH (13.89 for 1.0 M KOH)

$E_{RHE} = E_{Hg/HgO} + 2.303\,(RT/F)*pH + E^{\Theta}_{Hg/HgO}$

$E_{RHE} = E_{Hg/HgO} + 0.059\ pH + E^{\Theta}_{Hg/HgO}$

$E_{RHE} = E_{Hg/HgO} + 0.059 * 13.89 + 0.098$

$E_{RHE} = E_{Hg/HgO} + 0.9175$

2. Rinse Test

During rinse test, 25 repetitive CV cycles were recorded within the potential range of catalysis in DMF with 36 mM of acetic acid followed by rinsing the working electrode with DMF and then the rinsed working electrode was used for recording CV in a blank DMF solution. Thereafter, another CV was recorded in DMF with 36 mM of acetic acid.

No redox events were observed in the blank DMF solution by using the rinsed electrode and the slight current increase in presence of acetic acid is negligible with respect to the catalytic current with the complex **1**.

3. Experiments for homogeneity test

Homogeneity of the complex **1** during proton reduction was investigated through rinse test (as described above), UV-vis spectra of complex **1** before and after bulk electrolysis and surface analysis of the graphite plate working electrode before and after bulk electrolysis using SEM-EDS analysis. The rinse test verified that no deposition of heterogeneous materials occurred on the working electrode in during the reaction (Fig S12). Further, the UV-vis spectrum of the complex was found to remain same before and after bulk electrolysis supporting the homogenous nature of the catalyst (Fig. S13). In addition to this, the homogeneity of the catalyst was also checked through scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis of the graphite plate working electrode before and after bulk electrolysis (Fig. S14). The SEM-EDS studies showed no deposition of heterogenous materials on the working electrode during the bulk electrolysis.

4. Electrode preparation for heterogenous HER

In a glass vial, 2 mg of Complex **1** and 4 mg of MWCNT was weighed and 100 µL of DMF, 900 µL of ethanol and 25 µL of Nafion binder was added. Then the mixture was sonicated for 30 min to form a homogeneous ink. 400 µL of the ink was drop casted on cleaned carbon paper such that 1 cm x 1 cm surface area was covered by the electrocatalyst and left overnight in oven at 60 ^{o}C for drying (mass loading = 2.34 mg/cm^2). This gives the modified electrode **1/MWCNT@CP**. Further, for the modified electrode, **MWCNT@CP** was prepared in similar way only by excluding the complex from the mixture.

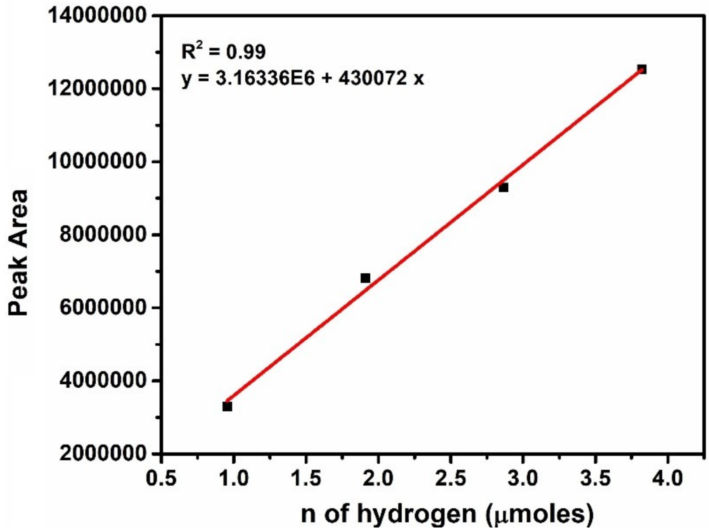
5. Characterization of 1/MWCNT@CP using SEM and XPS

The SEM image of **1/MWCNT@CP** shows the presence of porous MWCNT on the carbon paper and the SEM-elemental mapping displayed the presence of Co, N, and O on the electrode surface, thus confirming the uniform heterogenization of the Co complex **1** (Fig S23a-e). Further, the high resolution XPS spectrum of Co $2p_{3/2}$ in **1/MWCNT@CP** shows the deconvoluted peaks at binding energies of 781.1 eV and 785.8 eV characteristic for Co^{3+} along with peak at 783.8 eV and 798.3 eV for Co^{2+} in addition to satellite peaks reveals the presence of cobalt on MWCNT [1] (Fig. S23h-i).

6. Constant Potential Electrolysis (CPE) for homogeneous HER (proton reduction in DMF) and heterogeneous HER (1.0 M KOH)

The bulk electrolysis experiments for proton reduction with the complexes were done in a four-neck glass vessel (77 mL with headspace) where three of the necks were occupied with a graphite plate as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (in 3M KCl) as the reference electrode. Then the fourth neck was sealed with a rubber septum and was used for purging the solution with Ar before the bulk electrolysis and for the collection of gas from the headspace (using a gas-tight leur-lock Hamilton syringe) post-bulk electrolysis. During the experiments, 12 mL of solution of Complex **1** in DMF (0.5 mM) was added to the vessel, all electrodes along with a magnetic stirbar were inserted with a B-14/20 rubber septum cap (gas tight) and the solution was purged with Ar for 15 minutes. After purging, a chronocoulometric experiment was started at the catalytic potential along with constant stirring throughout the experiment. After the completion of the reaction the headspace gas was collected and analysed using Gas Chromatography instrument containing a TCD detector. The GC was calibrated with standard gas mixtures containing 10% H_2 , CO and N_2 .

The CPE for heterogeneous HER with hybrid material in 1.0M KOH was carried out using a sealed two-chambered H-cell setup. One chamber accommodates the working and reference electrodes in 10 mL electrolyte solution, while the other chamber contains the counter electrode in 10 mL electrolyte solution. The chambers were separated by a Nafion membrane. The headspace in the working electrode portion was 28 mL. Before bulk electrolysis the electrolyte solutions in both the chambers were purged thoroughly with Ar for 10 min. The CPE was carried out at potential corresponding to -10 mA/cm^2 for the HER. Thereafter, after 1hr, the headspace gas of the working electrode was introduced in GC instrument (using a gas-tight leur-lock Hamilton syringe) for detection and quantification of hydrogen.



Calibration curve of the standard gas mixture for the determination of hydrogen

7. Post electrolysis characterization of 1/MWCNT@CP using XPS.

The XPS survey scan of the post electrolysis electrode showed the presence of Co 2p, C 1s and O 1s (Figure S30a). The Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks in the high resolution XPS spectrum of Co 2p were deconvulated into Co^{3+} and Co^{2+} peaks along with the satellite peaks. The peaks at 779.6 eV and 795.2 eV binding energies corresponding to Co^{3+} indicates the formation of CoOOH [1]. On the other hand the Co^{2+} peaks at the binding energies 781.4 eV and 796.7 eV can be assigned to $Co(OH)_2$ [2] formed during the bulk electrolysis. (Figure S30b).

8. Computational methods

The Gaussian 16 software[4] was used for geometry optimizations of all stationary states and transition states employing the exchange and correlation functional of Perdew, Burke and Ernzerhof, (PBE) called PBE0 which includes Hartree-Fock (HF) exchange in a 3:1 ratio of PBE to HF, in addition with including the Grimme empirical dispersion correction D3 (PBE0-D3).[5]-[6] To simulate the effect of the solvent, the universal solvation model that is based on the full solute electron density (SMD) implicit solvation model was used.[7] For basis sets, we employed the split-valence plus single polarization def2-SVP for lighter atoms (H, C, N, and O), triple-ζ def2-TZVP for Co.[8] For further validation of energies, single point calculations using the SMD solvation model were performed with the hybrid-meta-GGA M06 functional[9] with the def2-TZVPP[5] for all the atoms. Unless specified otherwise, free energy values, ΔG, combining single point energy (ΔE) at M06(SMD-DMF)/def2-TZVPP with the thermal correction (ΔG-corr) at PBE0-D3(SMD-DMF)/def2-TZVP(Co)/def2-SVP(non-metals) are reported throughout the manuscript and supporting information.

9. <u>Calculations</u>

9.1. Calculation of rate of catalysis (k_{obs})

The rates (k_{obs}) of proton reduction by complex **1** and **2** were determined at saturated acid concentration of acetic acid (36 mM for **1** and 12 mM for **2**) using equation 1

$$\frac{ic}{ip} = \frac{n}{0.4463}\frac{\sqrt{RTkobs}}{Fv} \qquad \text{............(1)}$$

Where, i_c is the catalytic peak current at saturation point of acid, and i_p is the stoichiometric current without the acetic acid, n is the number of electrons transferred during catalysis, F is 1 Faraday, R is the universal gas constant, T is the temperature, v is the scan rate in V/s.[10]

9.2. Calculation of Faradaic efficiency for complex 1 in DMF with AcOH

The overall charge passed during the catalysis = 6.001 C

Amount of H_2 expected = 6.001/(96485 x 2) = 0.0311 mmol

Amount of H_2 detected in GC after the bulk electrolysis = 0.0297 mmol

Faradaic efficiency of **2** in DMF with AcOH = (0.0297/0.0311) x 100 % = 95.4 %

9.3. Mass loading for the 1/MWCNT@CP

1025 μL of homogeneous mixture ink contains = 6 mg of electrocatalyst mixture

1 μL homogeneous mixture ink contains = (6/1025) mg of electrocatalyst mixture

400 μL homogenous mixture ink contains = (6/1025) x 400 mg of electrocatalyst mixture

= 2.34 mg of electrocatalyst mixture

Mass loading = (mass of electrocatalyst mixture taken)/(Surface area of the working electrode)

= 2.34 mg/ 1 cm^2

= 2.34 mg/cm^2

Here, the surface area of the working electrode is 1 cm^2.

9.4. Calculation of Overpotential for heterogenous catalysis in 1.0 M aqueous KOH

The potential corresponding to 10 mA/cm^2 current density in the LSV curves denotes the overpotential for the heterogenous material. Notably, this current density is the key benchmark of solar driven electrolyzer, reflecting the performance of water splitting devices attaining 10% solar-to-fuel efficiency at "1 Sun" illumination (AM 1.5, 100 mW cm^2.[11] The calculations are performed by using the thermodynamic HER potential ($E^0_{H2O/H2}$ = 0 V) as the reference.

9.5. Tafel Slope

The Tafel slope was determined from the LSV curve using the Tafel equation (equation 2) where the Tafel slope was calculated by fitting the overpotential (η) vs log (j) using the equation:

$\eta = b \log j + a$……………………………….Equation 2

where, b and j represent the Tafel slope and current density, respectively.

9.6. Electrochemical double-layer capacitance (C_{dl})

The electrochemical double-layer capacitance was calculated by recording the CV at different scan rates in the non-faradaic region within the potential window 0.78 V to 0.96 V (vs RHE) in Ar saturated 1.0 M aqueous KOH, followed by plotting the graph between scan rate and current at the mid-point of the potential window. Thereafter, the linear fitting of the curve was done to obtain the slope that gives the double layer capacitance. This non-faradaic region is typically 0.18 V window about the open circuit potential, and all the measured current values are due to double layer charging.

The double-layer capacitance (C_{dl}) was calculated using the equation given below

$$i_c = \nu\, C_{dl},$$

where, i_c = Double-layer charging current, ν = Scan rate

9.7. Electrochemical active surface area (ESCA)

Electrochemically active surface area (ECSA) was calculated from the double layer capacitance (C_{dl}).[12] It is calculated using the following equation given below

$$\text{ECSA} = C_{dl}/C_s$$

Where, C_{dl} = Double Layer capacitance, C_s = specific capacitance of the system (constant factor). Generally, the C_s value is 0.02-0.06 mF/cm^2 for a flat electrode surface of 1 cm^2. Here we have considered 0.04 mF/cm^2 as the specific capacitance (C_s).[13]

The ECSA values for the **1/MWCNT@CP** and **MWCNT@CP** have been presented below in **Table 1**.

9.8. Roughness Factor (R_f)

The roughness factor for the **1/MWCNT@CP** and **MWCNT@CP** is calculated by the following equation:

$$R_f = (\text{ECSA/ Electrode geometric area})$$

The geometric area taken for the work is 1cm^2.

The obtained R_f factor are below in the **Table 1.**

9.9. Calculation of Faradaic efficiency for complex 1/MWCNT@CP in 1.0 M aqueous KOH

The overall charge passed during the catalysis = 35.34 C

Amount of H_2 expected = 35.34/(96485 x 2) = 0.183 mmol

Amount of H_2 detected in GC after the bulk electrolysis = 0.1095 mmol

Faradaic efficiency of **1/MWCNT@CP** = (0.1095/0.183) x 100 % = 60 %

Table 1. Performance parameters of **1/MWCNT@CP** and **MWCNT@CP** for HER

Parameters \ Material	1/MWCNT@CP	MWCNT@CP
Overpotential (mV) at 10mA/cm^2 current density	401 mV	654 mv
Tafel slope	175 mV dec^{-1}	190 mV dec^{-1}
Double layer capacitance (c_{dl})	5.21 mF	4.69 mF
Electrochemical surface area (ECSA)	130 cm^2	117 cm^2
Roughness factor (R_f)	130	117

Table 2. Comparison of the Electrocatalytic HER Activities of Different molecular catalysts heterogenized on different carbon surfaces

Sl. No.	Catalyst	Conditions	HER Overpotential (mV)	Tafel slope (mV dec^{-1})	Ref
1	CoTBImPc-CNT/GCE	0.5 M H_2SO_4 (pH = 0.3)	63	43.2	14
2	GDL/MWCNT/Co-material	Acetate buffer solution	590	160	15
3	CuL/GO	0.5 M NaCl	167	-	16
4	Pyrene substituted CoTMPA /SWCNH	1M phosphate buffer (pH 7.4)	540	160	17
5	rGO/2-Cox	0.5 M H_2SO_4	340	111	18
6	CNT-f-FeP^F	0.1 M H_2SO_4	457	68	19
7	1/MWCNT@CP	0.1 M KOH	401	175	**This Work**

10. Synthetic procedure

The ligand 2-methyl-*N*-(quinolin-8-yl)benzamide (BQN), the organometallic cobalt complex [Co(BQNN)(BQN)(H_2O)](**1**), and the cobalt complex [Co($BQN)_2$](**2**) were synthesized following the previously reported methods. [20], [21]

10.1. Synthesis of [Co^{III}(BQNN)(BQN)(H_2O)] (1)

The ligand BQN (1000 mg, 3.81 mmol), sodium pivalate (946 mg, 7.62 mmol), potassium persulfate ($K_2S_2O_8$) (2060 mg, 7.62 mmol) and $Co(OAc)_2{\cdot}4H_2O$ (946 mg, 3.80 mmol) were taken in a round bottom flask and then trifluoroethanol (TFE) (15 mL) was added to the mixture. The resulting deep pink solution was heated at 70 ^{o}C for 24 hours to give a deep brown solution. Thereafter, the solvent was removed under vacuum and to the resulting mixture DCM was added and then it was passed through small silica plug. Further, the silica plug was washed with ethyl acetate. Then the resulting solution was purified through column chromatography with silica gel (60-100 mesh size) as the stationary phase using hexane-ethyl acetate mixture as eluent. The complex was isolated as yellowish brown solid that was recrystallized as dark brown crystals by layering hexane over a concentrated solution of complex in DCM.

Yield: 15%; ^{1}HNMR (400 MHz, $CDCl_3$): 9.54 (2H), 9.30 (1H),8.35 (1H), 8.23 (1H), 8.01 (1H), 7.80 (1H), 7.68-7.61 (4H), 7.48-7.43 (5H), 7.08-7.06 (3H). 2.85 (3H), 2,66 (3H); UV-vis (DMF; λ_{max} (ε/M^{-1} cm^{-1})): 412 nm (ε~ 8063 M^{-1} cm^{-1})

HRESI-MS (MeCN): Calculated (m/z) for [$C_{34}H_{25}CoN_4O_2$ + H^+] = 581.1388 , Found: 581.1381 ([Co(BQNN)(BQN)] + H^+)

10.2. Synthesis of [$Co^{II}(BQN)_2$] (2)

The ligand BQN (267.3 mg, 1.02 mmol), sodium hydride (49 mg, 1.10 mmol) and stir-bar were taken in a 50 mL Schlenk RB under inert atmosphere and to this mixture 10 mL of dry dimethylformamide was added with a syringe. The resulting mixture was stirred for 1 hour under inert atmosphere resulting in a deep yellow solution. Thereafter, to this solution, solid $CoBr_2$ (111.5 mg, 0.51 mmol) was added resulting an immediate colour change to deep burgundy colour. Then the homogeneous solution was dried under reduced pressure to give a dark maroon coloured solid. Thereafter, the solid was extracted in DCM and was passed through a Celite ® plug. This obtained solution was layered with petroleum ether to yield dark red coloured crystals of the complex.

Yield: 85%; ^{1}H NMR ($CDCl_3$, 400 MHz): -20.89, -19.70, -9.36, -8.03, 26.22, 39.74, 42.48, 45.66, 65.59; UV-vis (DMF; λ_{max} (ε/M^{-1} cm^{-1})): 387 nm (2801 M^{-1} cm^{-1}); HRESI-MS (MeCN): Calculated (m/z) for $C_{34}H_{26}CoN_4O_2$: 581.1388 [Co(BQN)(BQN)], Found: 581.1387.

Supporting Figures:

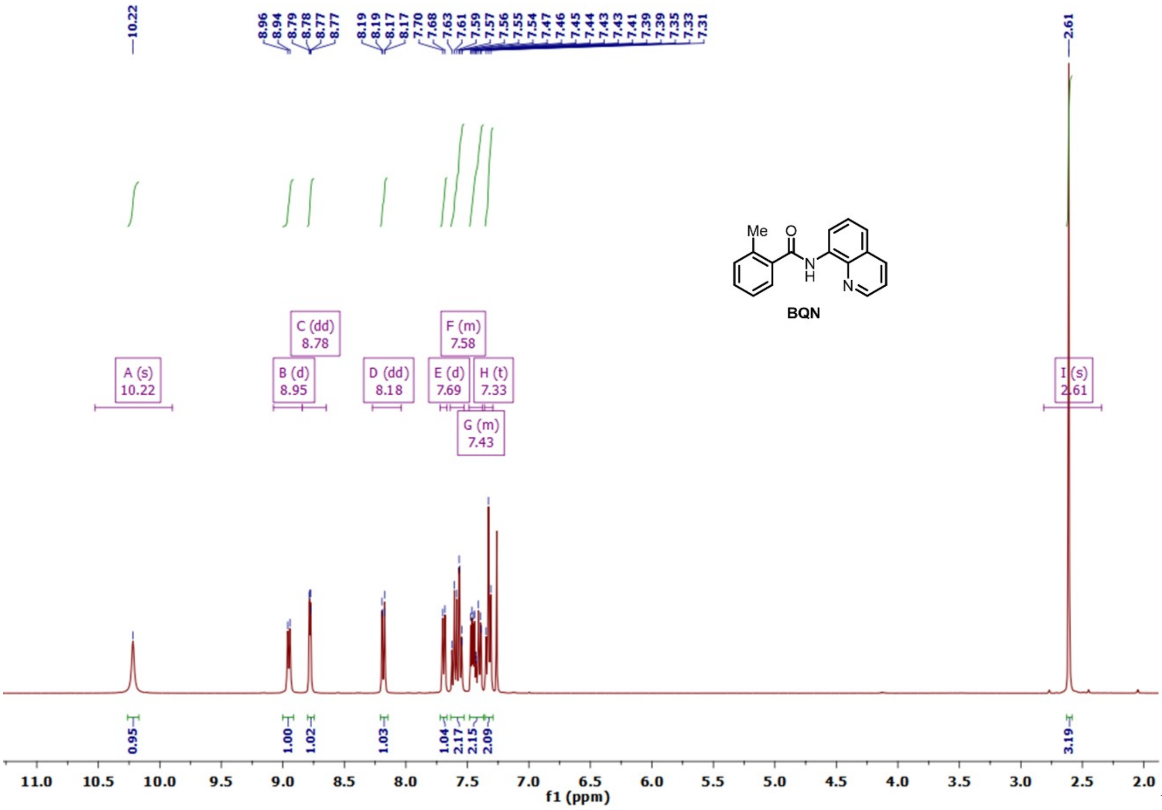


Fig. S1. ^{1}H NMR spectrum of BQN ligand in $CDCl_3$

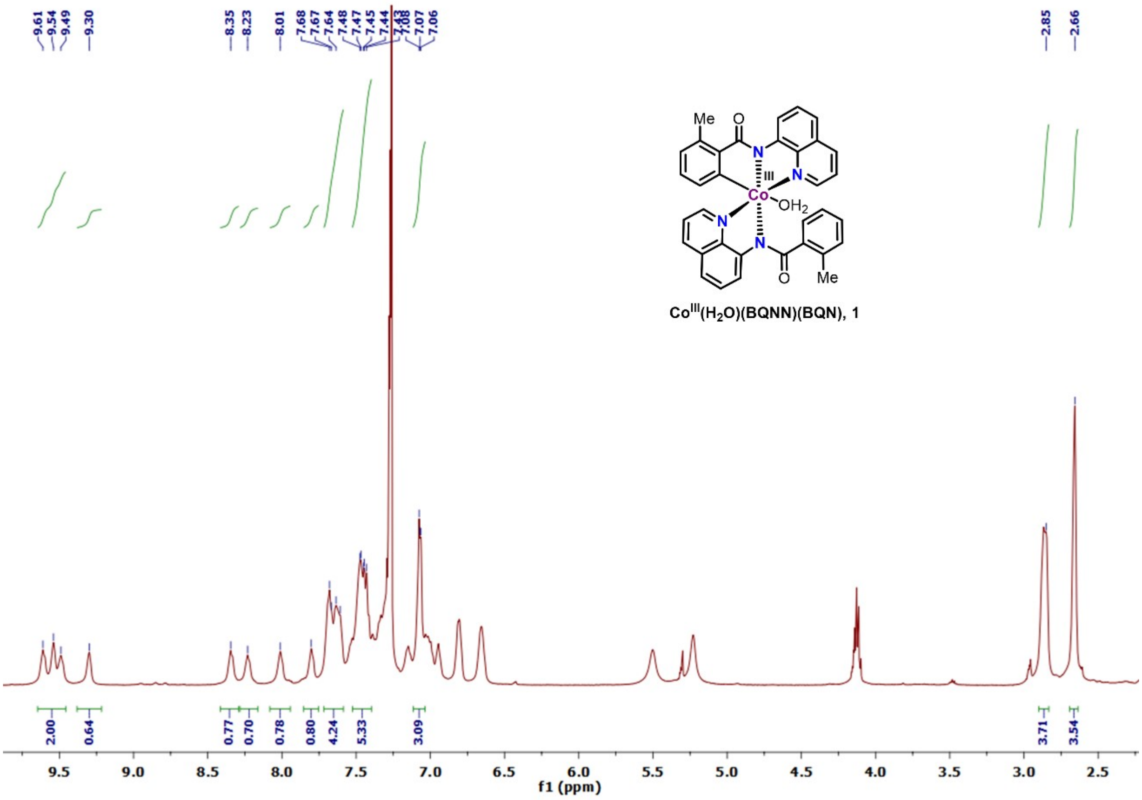
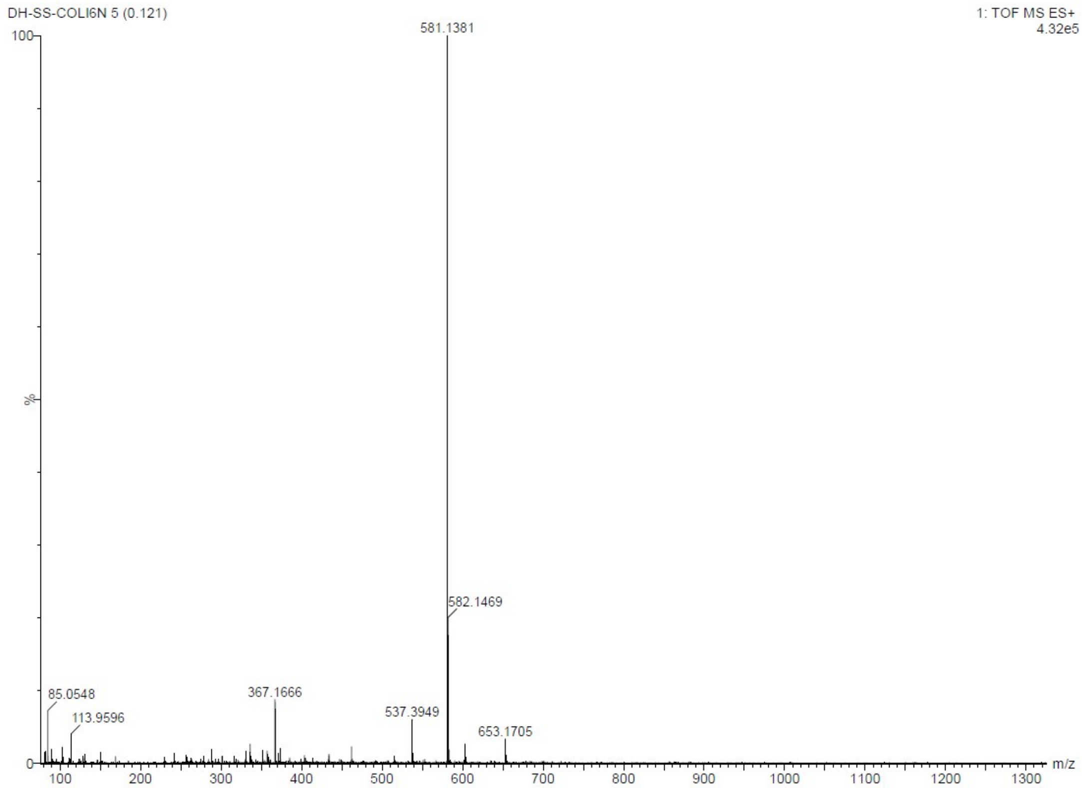


Fig. S2. ^{1}H NMR spectrum of Complex **1** in $CDCl_3$



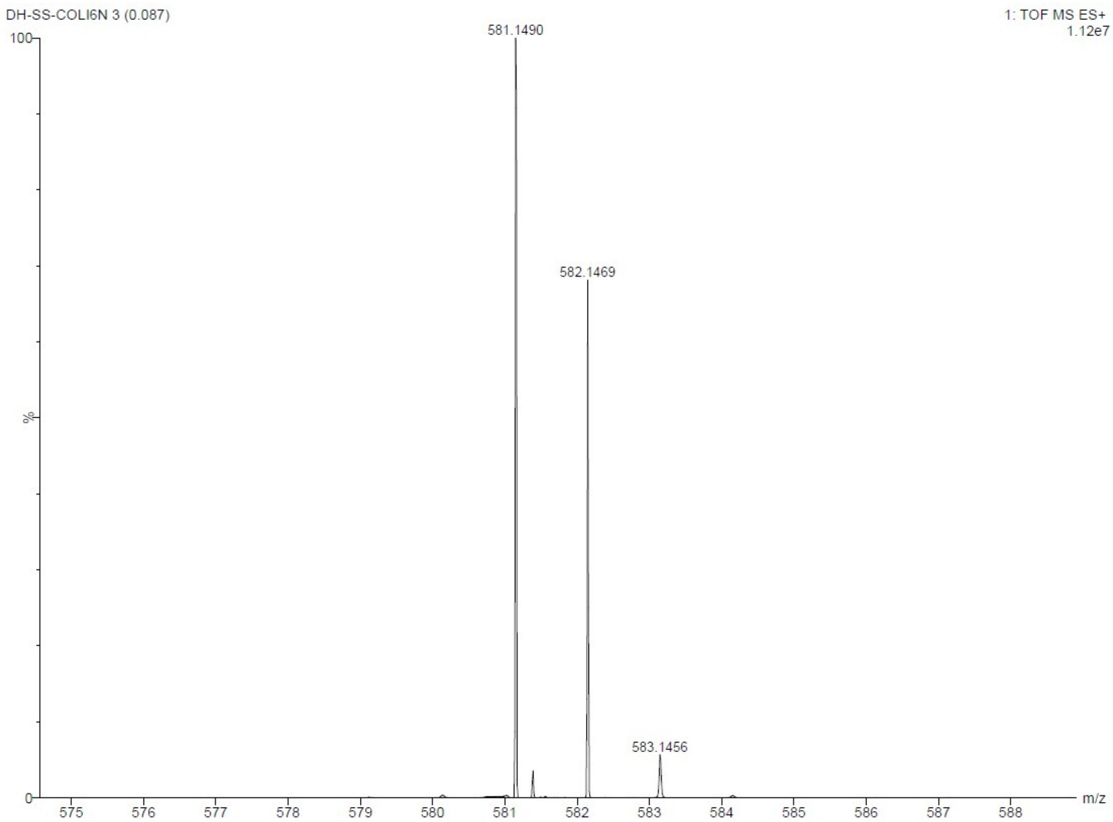


Fig. S3. HRESI-MS of Complex **1** in MeCN (Top). Calculated (m/z) for [$C_{34}H_{25}CoN_4O_2$ + H^+] = 581.1388 , Found: 581.1381 ([Co(BQNN)(BQN)] + H+). Isotopic distribution of m/z value of ([Co(BQNN)(BQN)] + H^+) (Bottom)

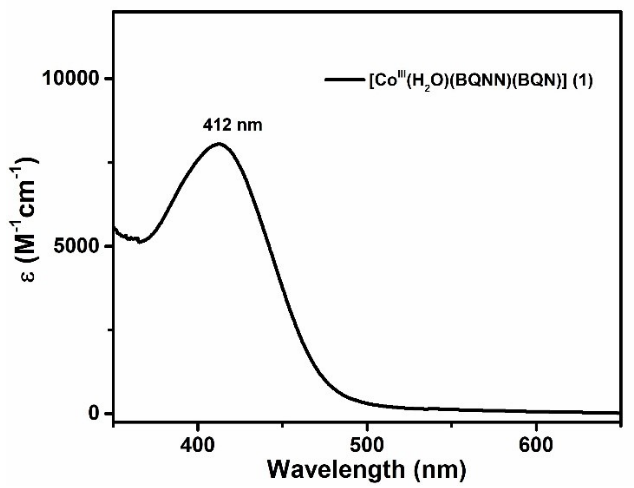


Fig. S4 UV-vis spectra of Complex **1** in DMF

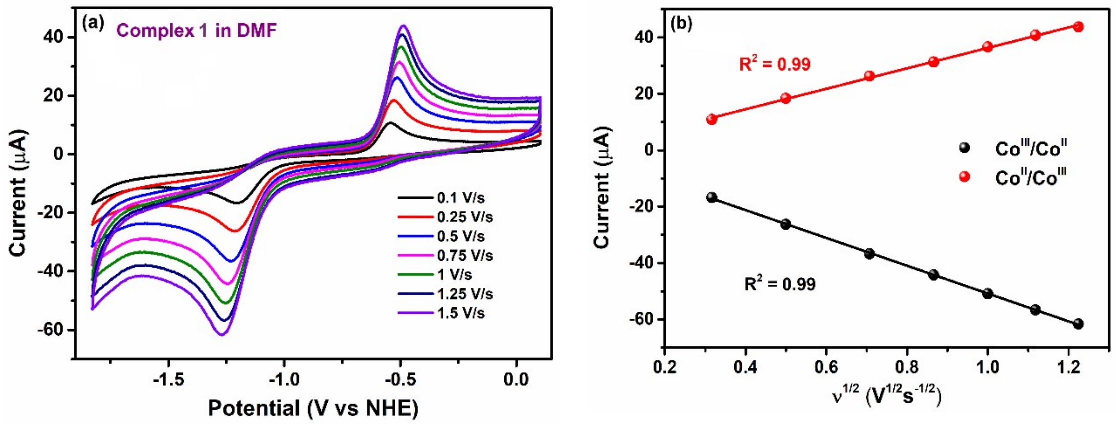


Fig. S5. (a) Cyclic Voltammogram (CV) of Complex **1** (1 mM) under Ar atmosphere in DMF at various scan rates. (b) Plots of peak current *vs*. square root of scan rate for the Co^{II}/Co^{I} reduction peak (black) and Co^{I}/Co^{II} oxidation event. Linear variation of the peak currents (anodic and cathodic peak) of Co^{II}/Co^{I} redox event with the square root of scan rate validate the diffusion controlled redox events showing a diffusion coefficient of D = 9.011 x 10^{-7} cm^2/s in DMF.

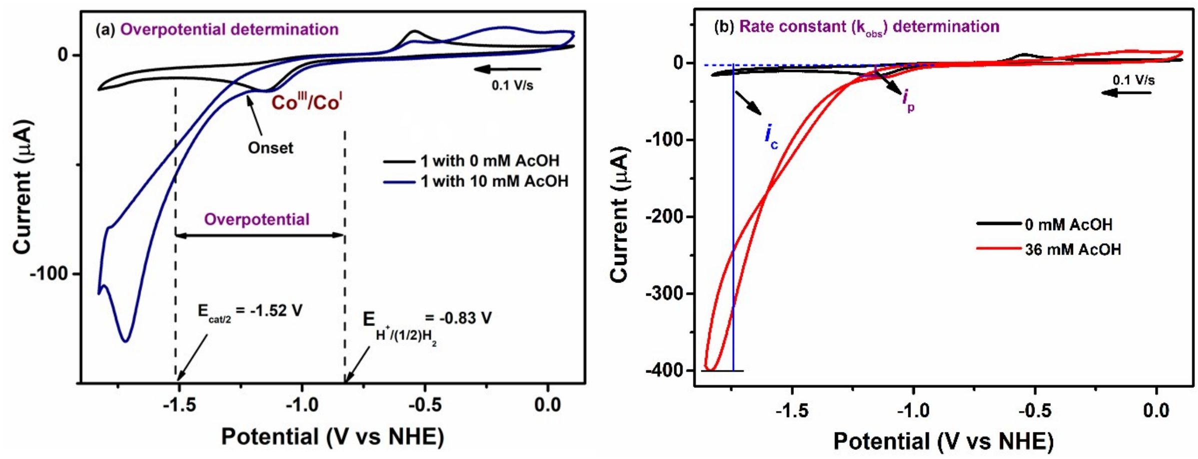


Fig. S6 (a) Representation for the calculation of overpotential of HER by complex **1** in DMF. (b) representation of i_c and i_p for complex **1** at saturated acid condition for the calculation of the rate constant (k_{obs}) of proton reduction

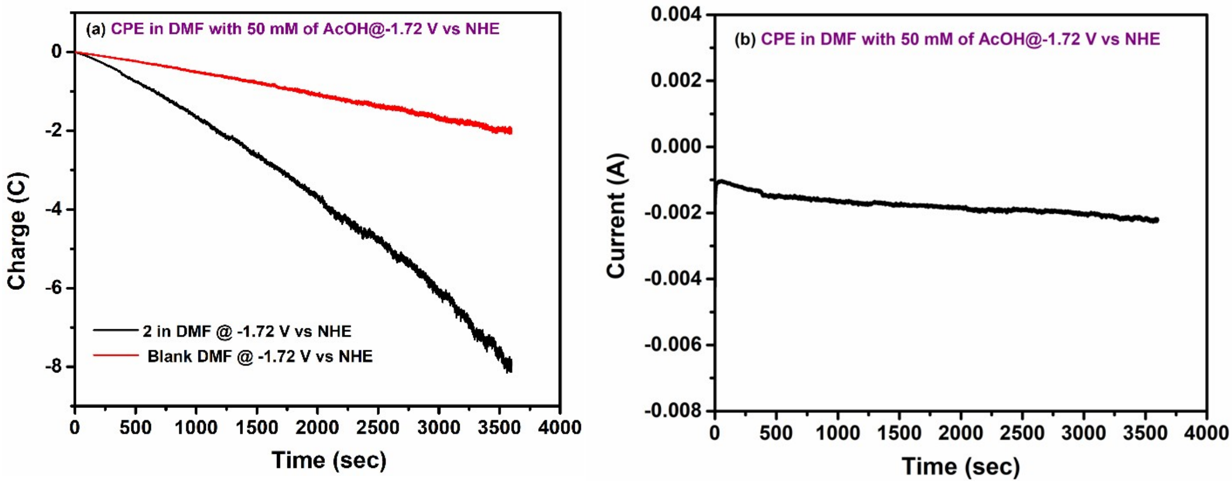


Fig. S7 (a) Charge vs Time plot and (b) Current vs Time plot during bulk electrolysis using complex **1** (0.5 mM) in dimethylformamide with 50 mM of AcOH and 0.1 M $TBABF_4$ as the supporting electrolyte at an applied potential of -1.7 V vs NHE using Graphite plate as working electrode, Ag/AgCl (3.0 M KCl) as reference electrode and platinum mesh as counter electrode.

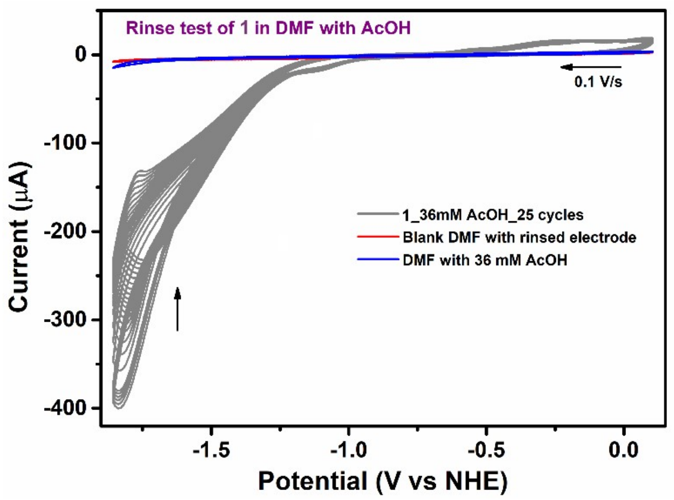


Fig. S8 Rinse Test for complex 1 (1 mM) in DMF at 0.1 V/s: Initially, 25 continuous CV cycles was recorded in DMF in presence of 36 mM AcOH with cathodic scan from 0.1 V to -1.85 V then a returning anodic scan to 0.1 V/s (0.1 M $TBABF_4$ as supporting electrolyte). Then the working electrode was washed with deionised water followed by DMF without polishing. Thereafter, the washed electrode was used for recording the CV within the same potential window in fresh DMF solution (containing only 0.1M $TBABF_4$ as the supporting electrolyte) which showed no catalytic current. Further, another CV was recorded after adding 36 mM AcOH in the same blank DMF solution which shows no current increment. This reveals that no active film is generated during the 25 cycles, suggesting the homogeneous nature of the catalyst **1** in DMF.

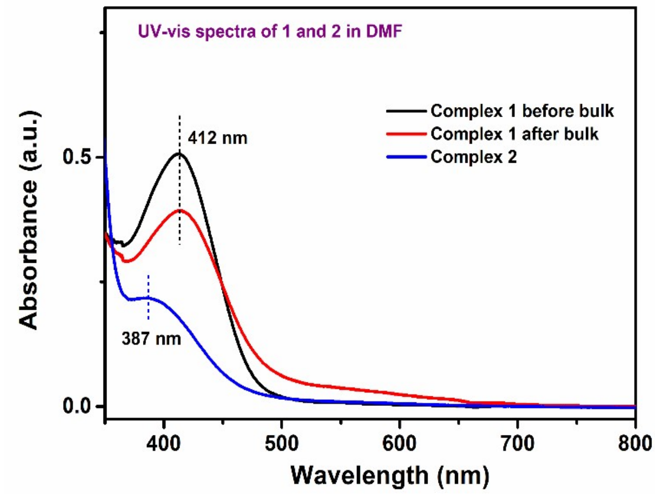


Fig. S9 UV-vis spectra of Complex **1**, before and after bulk electrolysis in DMF with 50 mM AcOH at -1.7 V vs NHE along with the UV-vis spectra of Co(II) complex **2** for comparison.

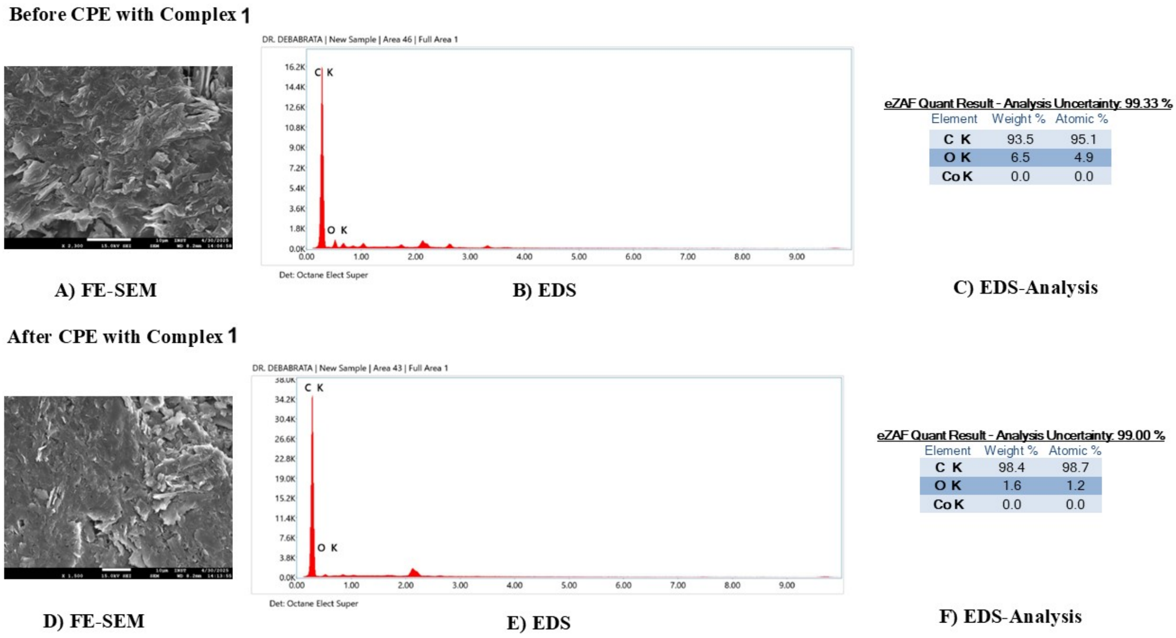


Fig. S10 (a) SEM image, EDS spectra of graphite plate working electrode before and after electrolysis of complex **1** in DMF. The working electrode was rinsed with DMF only after bulk electrolysis and analysed by SEM and EDS experiment. No cobalt deposit was found on working electrode.

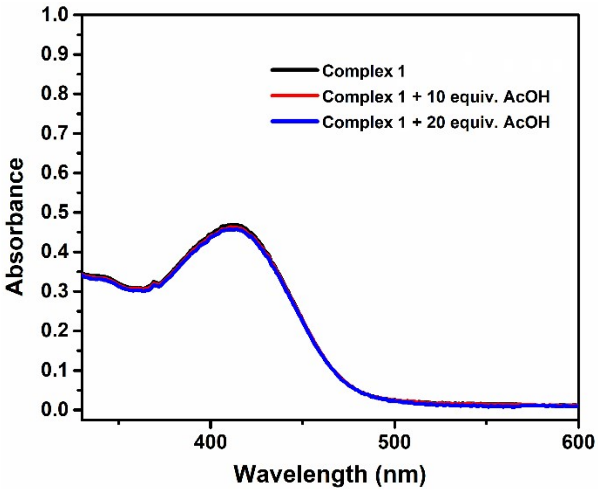
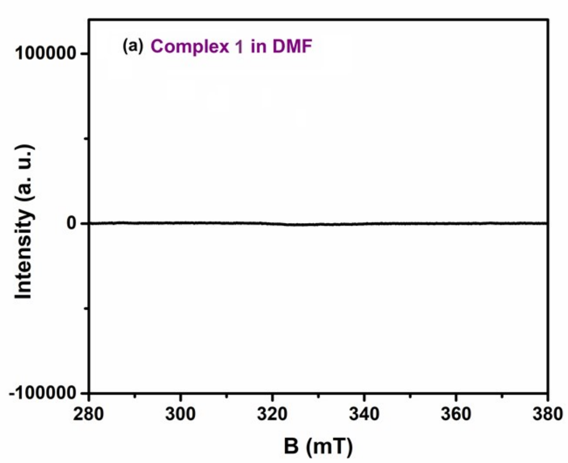


Fig. S11. UV-vis spectra of complex **1** in DMF in presence of different amount of acetic acid (AcOH).



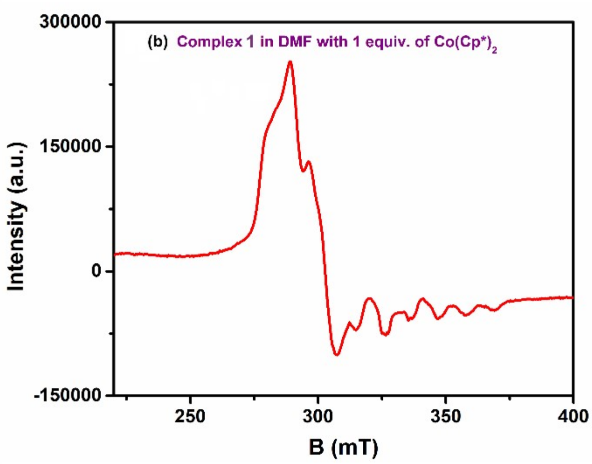
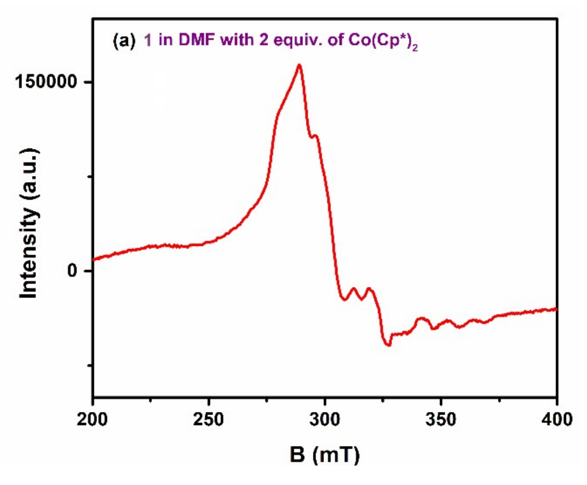


Fig. S12 EPR spectra of (a) Complex **1** in DMF at 77K (b) 1e^{-} reduced species of **1** using $Co(Cp^*)_2$ in DMF at 77K.



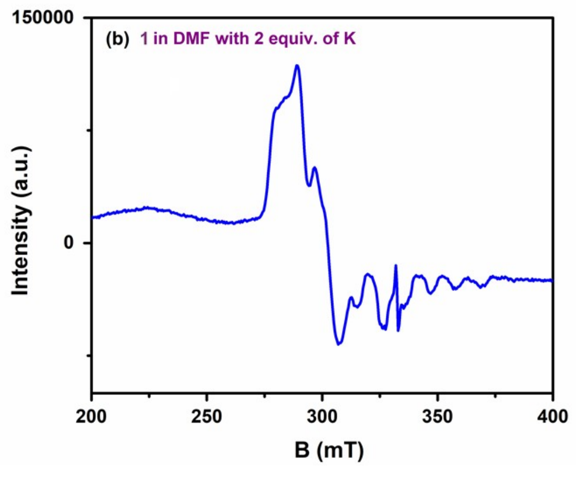


Fig. S13 EPR of Complex **1** in DMF (a) with 2 equivalent of $Co(Cp^*)_2$; (b) with 2 equivalent of K at 77 K.

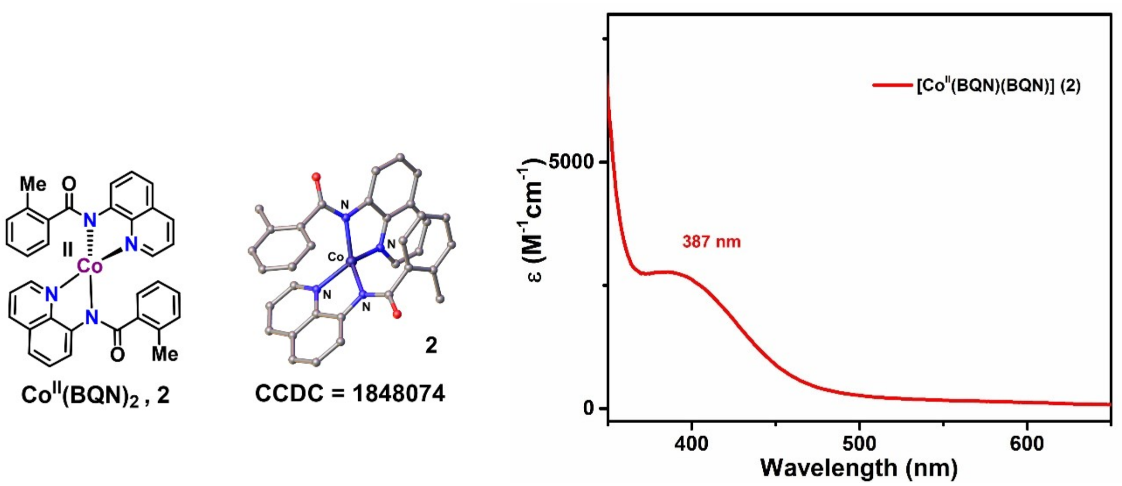


Fig. S14. Structures of complex **2** with the ORTEP diagrams at 50% probability level, solvent and H omitted for clarity; UV-vis spectrum of complex **2** in DMF.

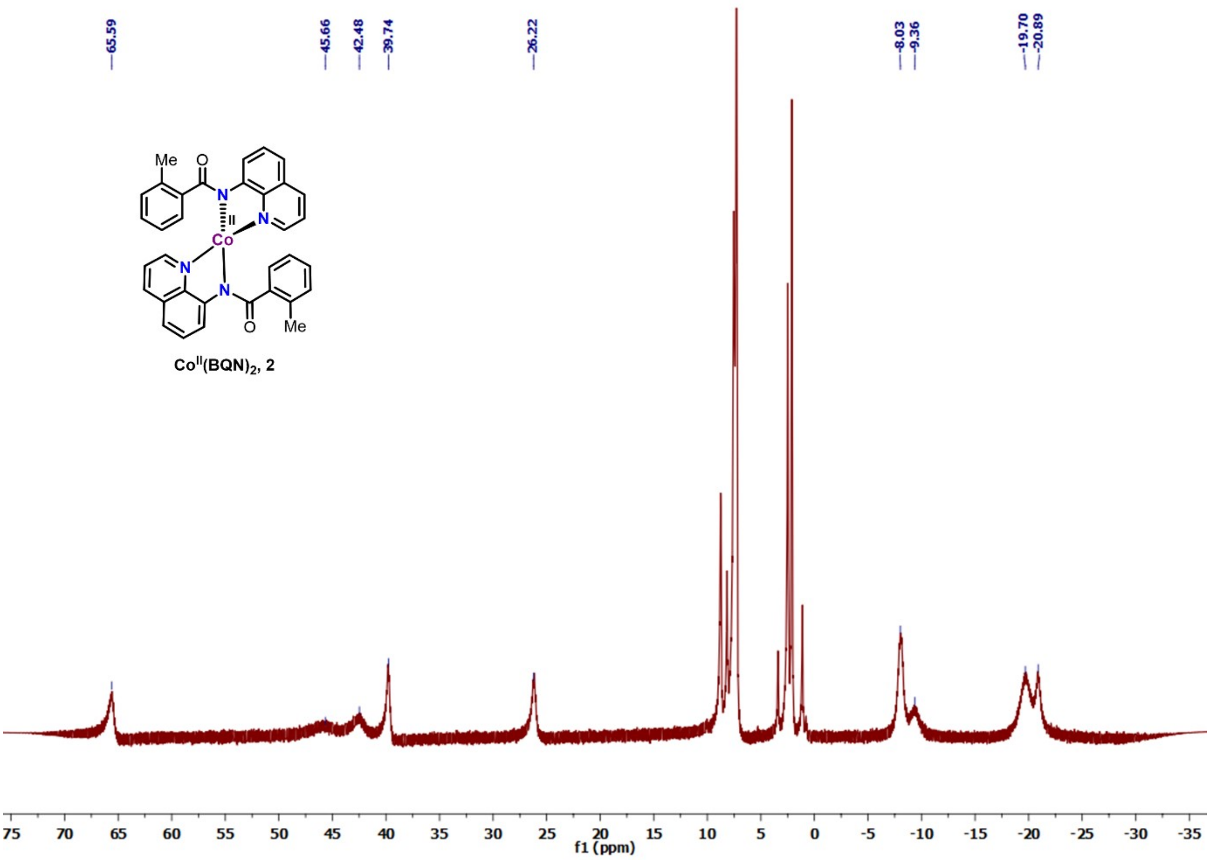


Fig. S15. ^{1}H NMR spectrum of Complex **2** in $CDCl_3$

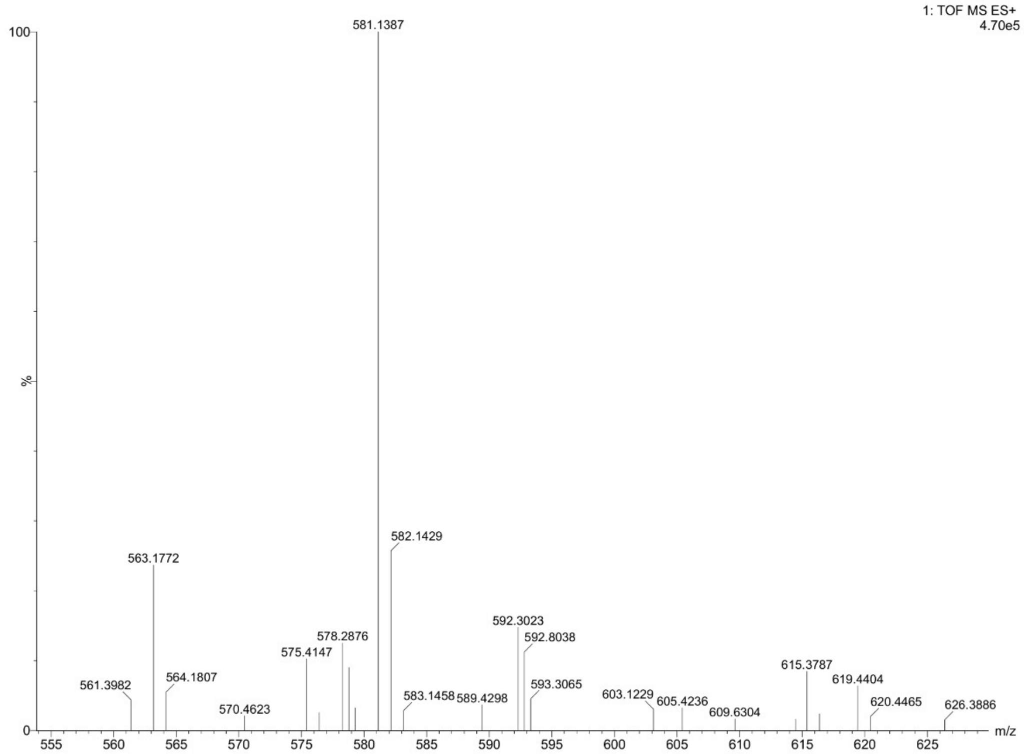


Fig. S16. HRESI-MS of Complex **2** in MeCN. m/z = 581.1387 for $[Co(BQN)_2]^+$

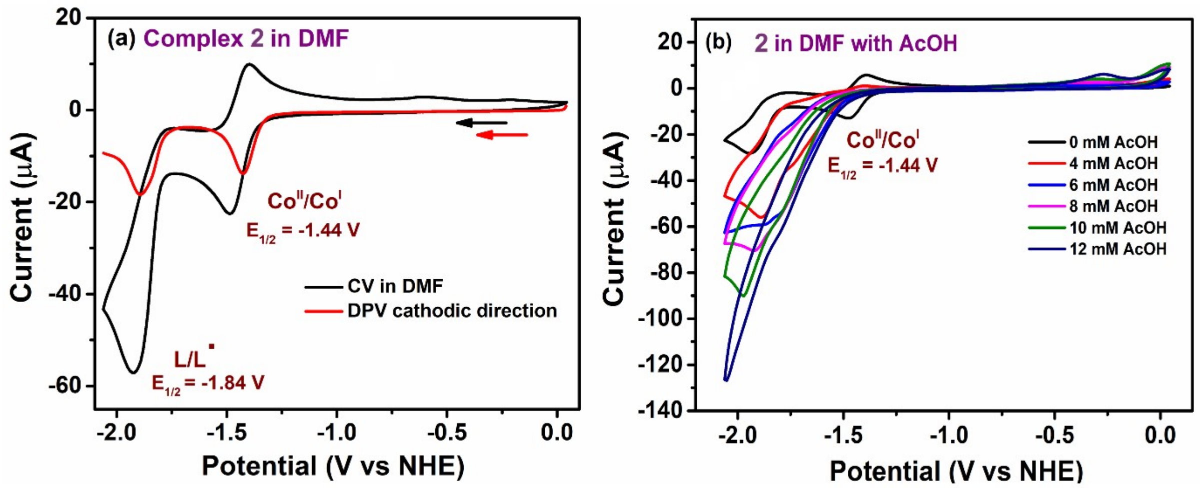


Fig. S17 (a) Cyclic voltammogram (CV) and Differential Pulse Voltammetry (DPV) of Complex **2** in DMF and (b) CV of Complex **2** in DMF with the sequential addition of AcOH at 0.1 V/s.

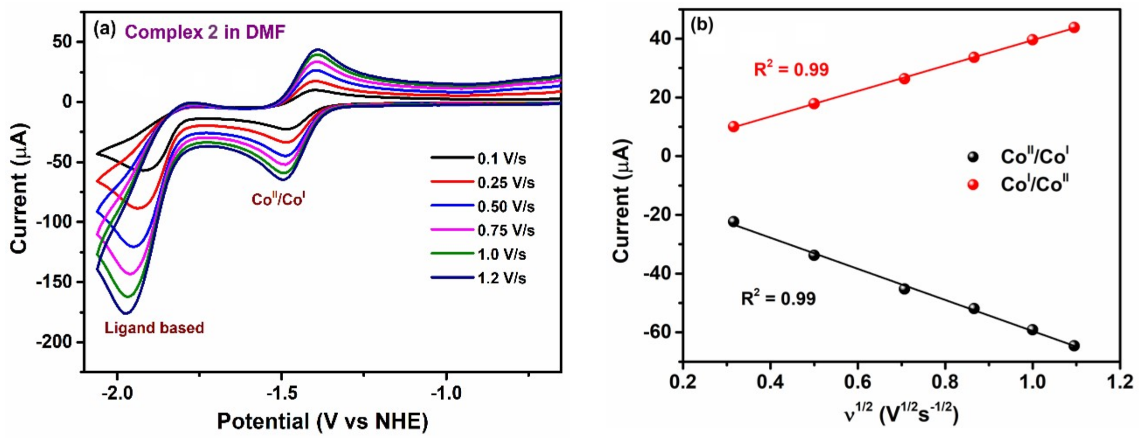


Fig. S18. (a) CV of Complex **2** (1 mM) under Ar atmosphere in DMF at various scan rates. (b) Plots of peak current *vs*. square root of scan rate for the Co^{II}/Co^{I} reduction peak (black) and Co^{I}/Co^{II} oxidation event. The linear variation of the cathodic and anodic peak currents with the square root of scan rate during the scan rate variation CVs of the complex confirms the diffusion-controlled behaviour of the redox processes.

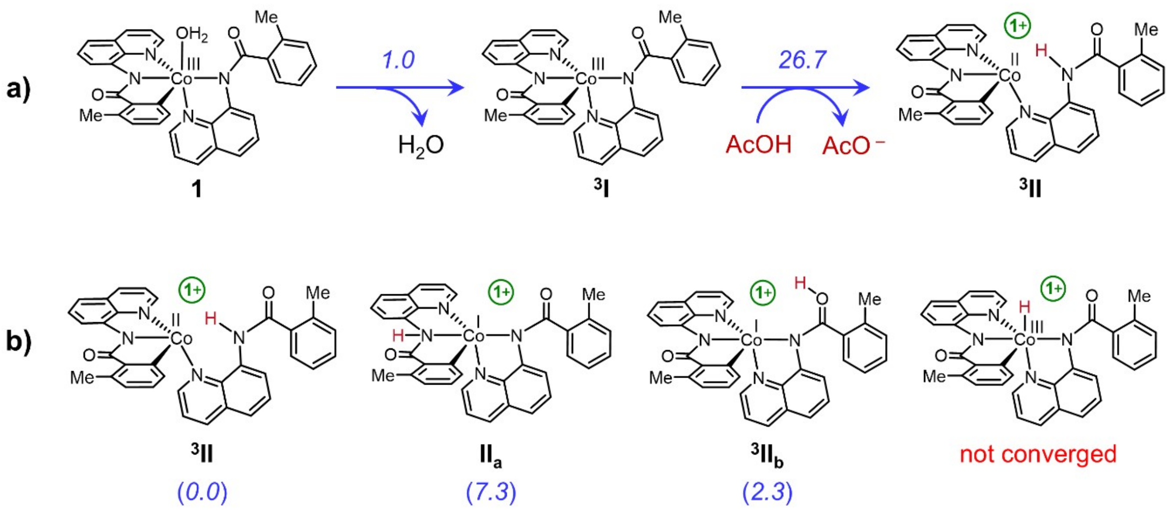


Fig. S19 a) DFT calculated free energy (in kcal/mol) of protonation step on complex **1**. b) Relative energies of different regioisomer of **^{3}II**. Free energy values are at the M06(SMD-DMF)/def2-TZVPP//PBE0-D3(SMD-DMF)/def2-TZVP(Co)/def2-SVP(non-metals) level of theory.

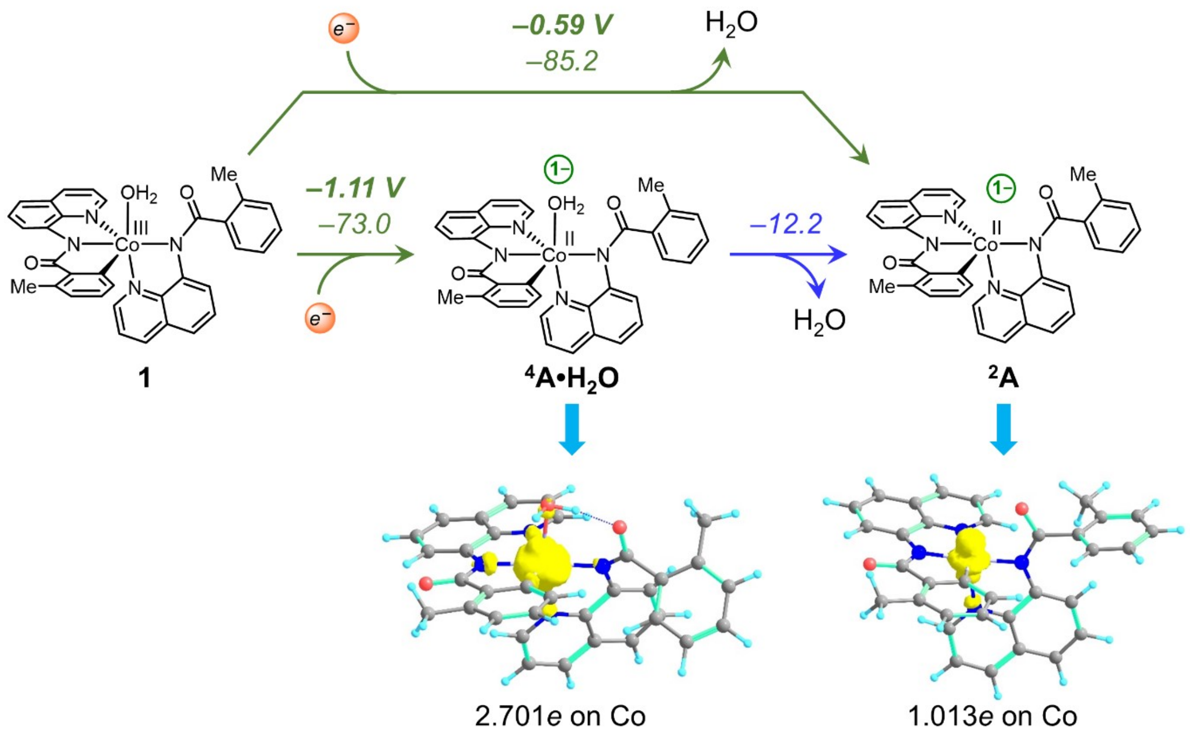


Fig. S20 DFT calculated free energy change (in kcal/mol) and reduction potential (in V vs. NHE) of **1**. Mulliken spin density plots (isosurface = 0.01 au) of open-shell molecules.

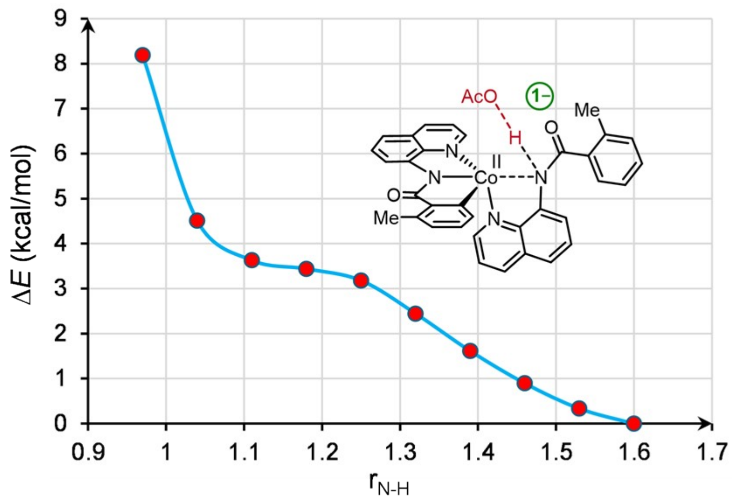
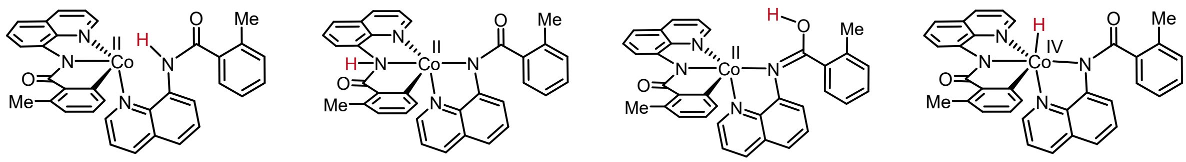


Fig. S21 Potential energy surface (PES) calculated at the PBE0-D3(SMD-DMF)/def2-TZVP(Co)/def2-SVP(nonmetals) level of theory for the protonation step in the active catalyst **^{2}A**.



^{2}**B**	^{2}**B**$_{a}$	^{2}**B**$_{b}$	not converged
(*0.0*)	(*13.8*)	(*8.7*)	

Fig. S22 Relative energies of different regioisomer of ^{2}**B**.

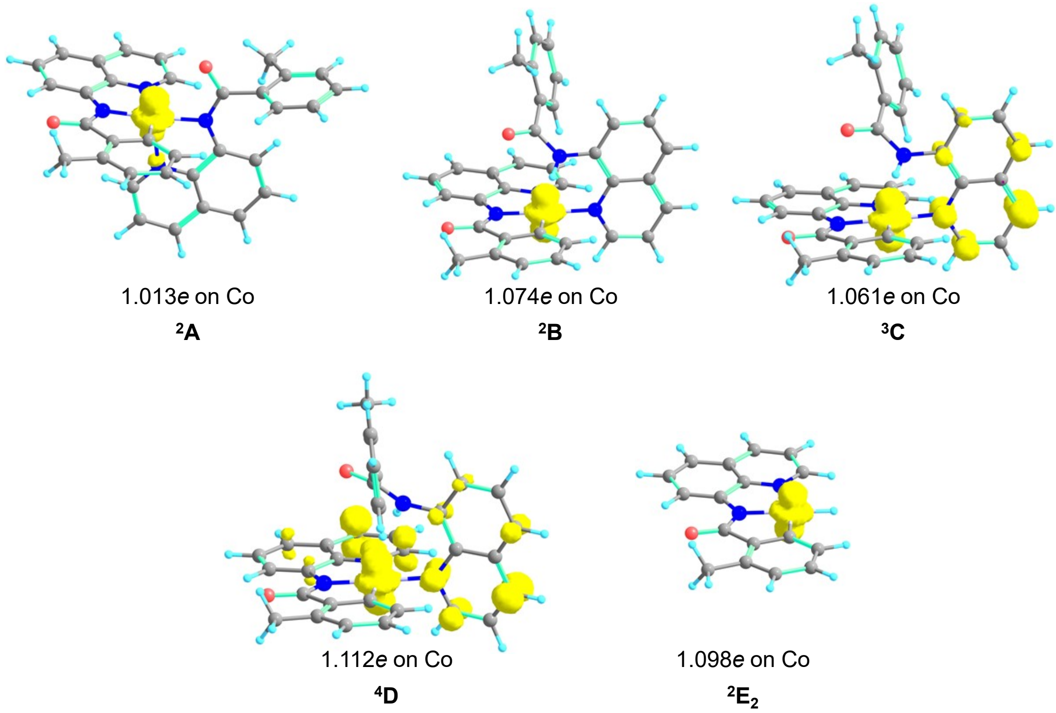


Fig. S23 Mulliken spin density plots (isosurface = 0.01 au) of open-shell intermediates involved in catalytic cycle.

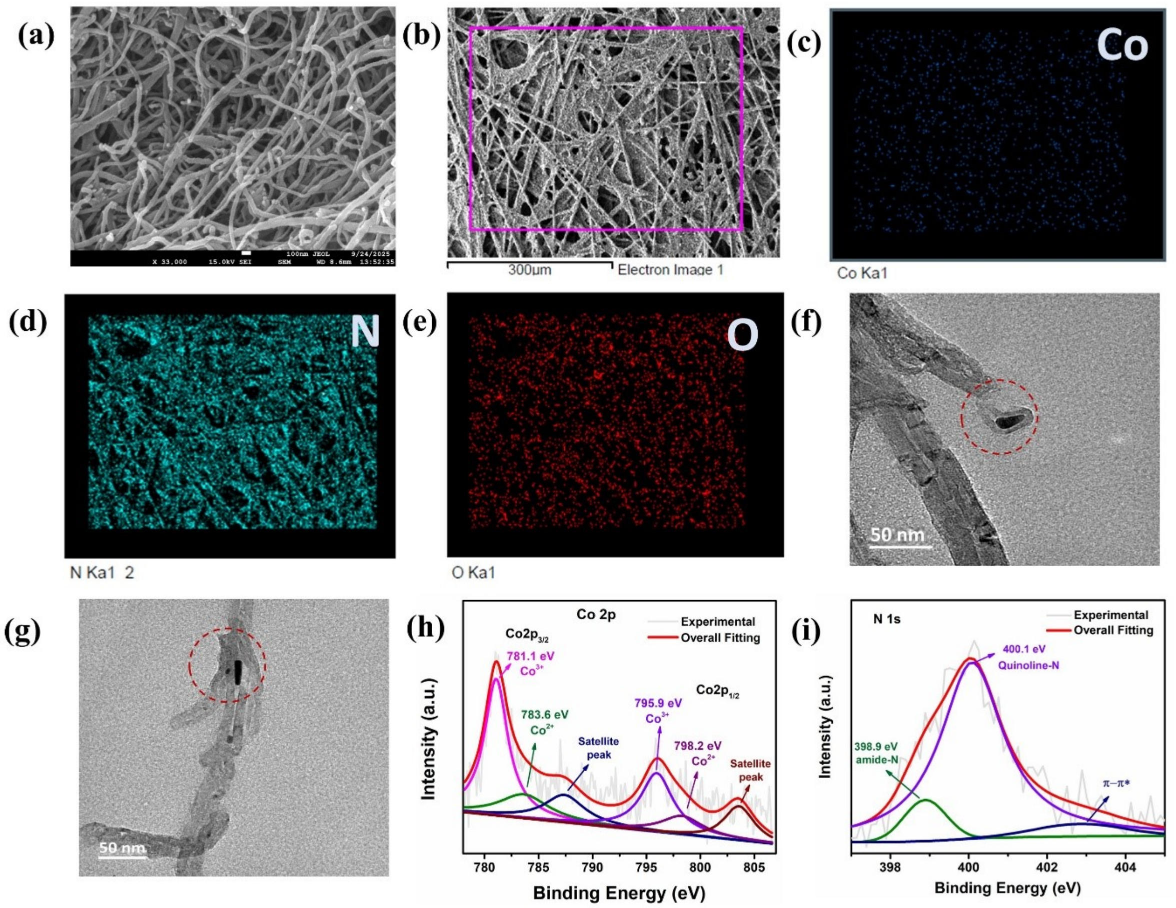


Fig. S24 (a)-(b) FE-SEM images of **1/MWCNT@CP** illustrating the deposition of **1/MWCNT** on carbon paper; (c)-(e) elemental mapping of the elements through EDX in **1/MWCNT@CP** : (c) Co, (d) N, (e) O; (f)-(g)TEM images of **1/MWCNT** showing that the complex is embedded within the nanotubes; (h) high resolution XPS spectrum of Co 2p and (i) high resolution XPS of N1s.

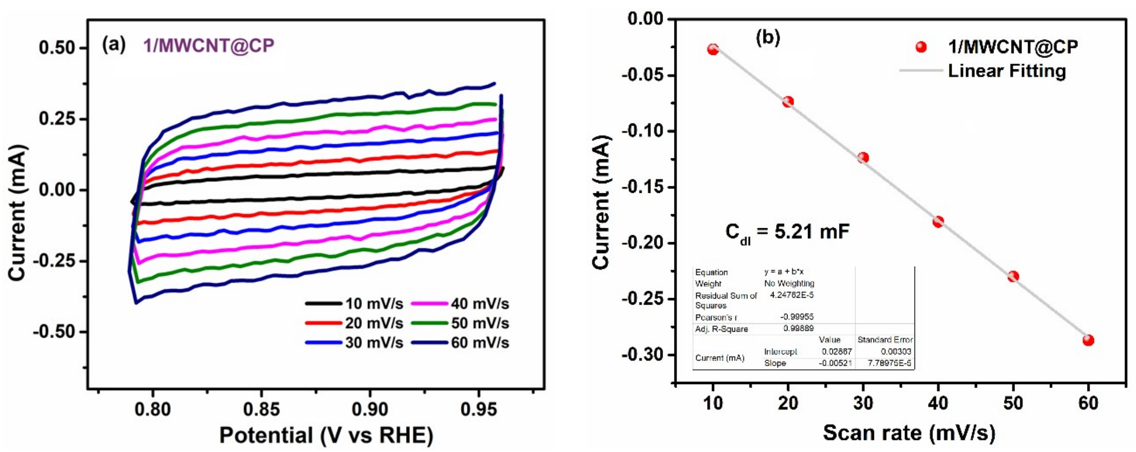


Fig. S25 (a) CV of **1/MWCNT@CP** in the non-faradaic region at various scan rates (10 mV/s to 60 mV/s) in the potential window of 0.79V to 0.96V in Ar-saturated 1M aqueous KOH solution; (b) Plot of scan rate vs current from (a) for the calculation of double layer capacitance (C_{dl}).

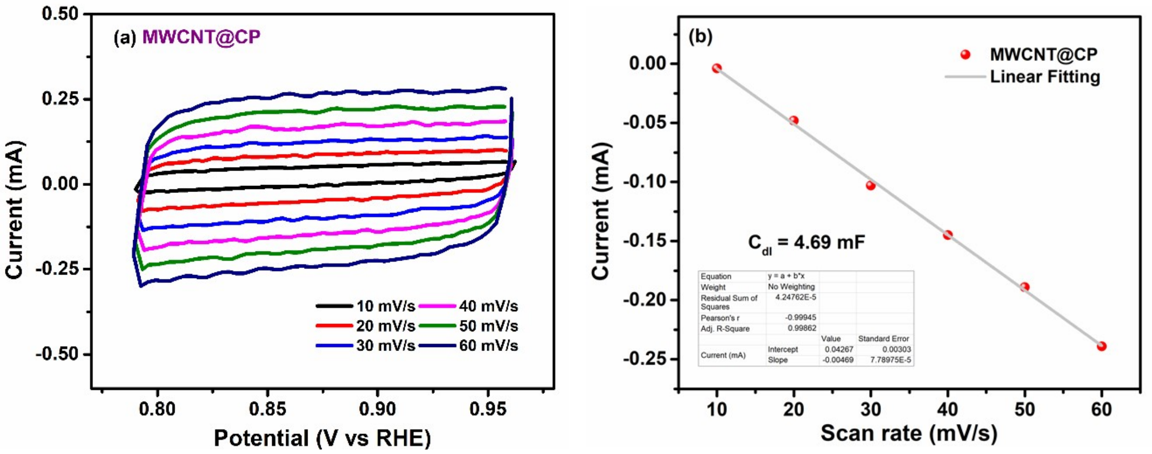


Fig. S26 (a) CV of **MWCNT@CP** in the non-faradaic region at various scan rates (10 mV/s to 60 mV/s) in the potential window of 0.79V to 0.96V in Ar-saturated 1M aqueous KOH solution (b) Plot of scan rate vs current from (a) for the calculation of double layer capacitance (C_{dl}).

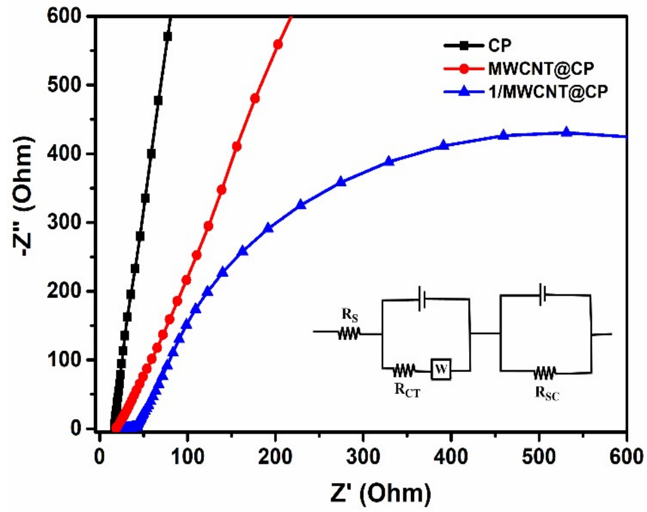


Fig. S27 EIS Nyquist plot of **1/MWCNT@CP** (red) and **MWCNT@CP** (blue) in 1.0 M aqueous KOH solution. (Inset: Equivalent Circuit used to fit the Nyquist plot)

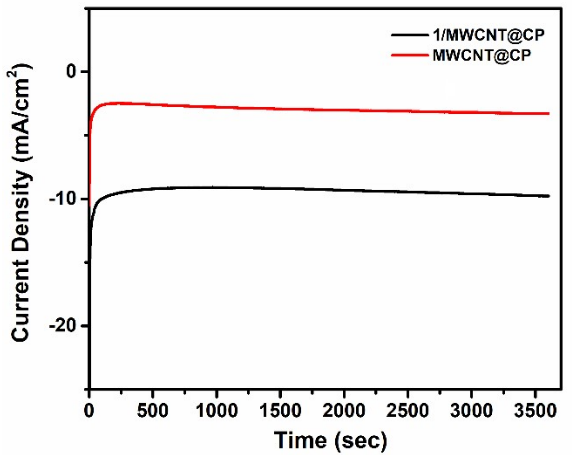


Fig. S28 Constant Potential Electrolysis (CPE) recorded at -0.40 V in 1.0 M KOH for 1 hour using **1/MWCNT@CP** (black) and **MWCNT@CP** (red)

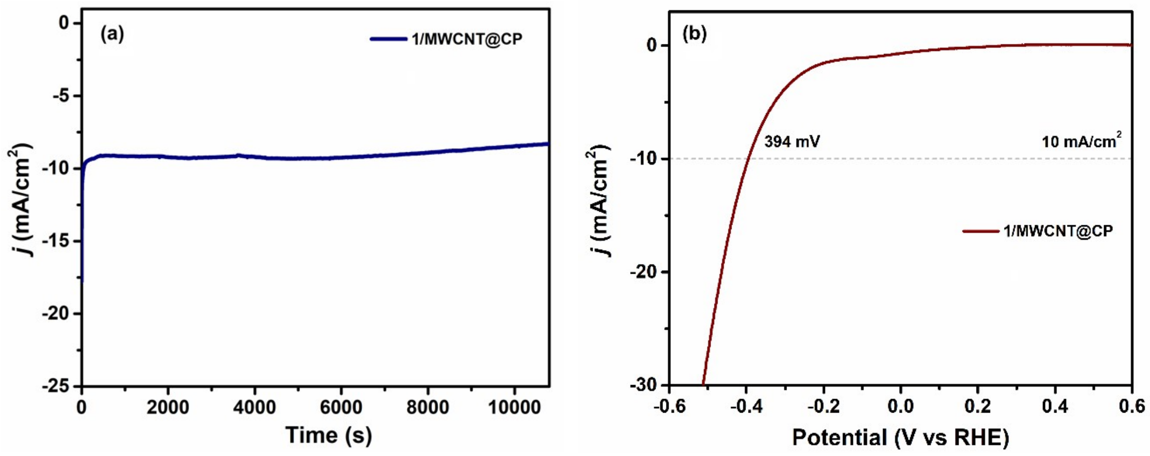


Fig. S29 (a) CPE recorded at -0.40 V in 1.0 M KOH for 3 hrs with **1/MWCNT@CP**; (b) LSV recorded at 5 mV/s in Ar saturated 1.0 M KOH using **1/MWCNT@CP** after bulk electrolysis for 3 hrs.

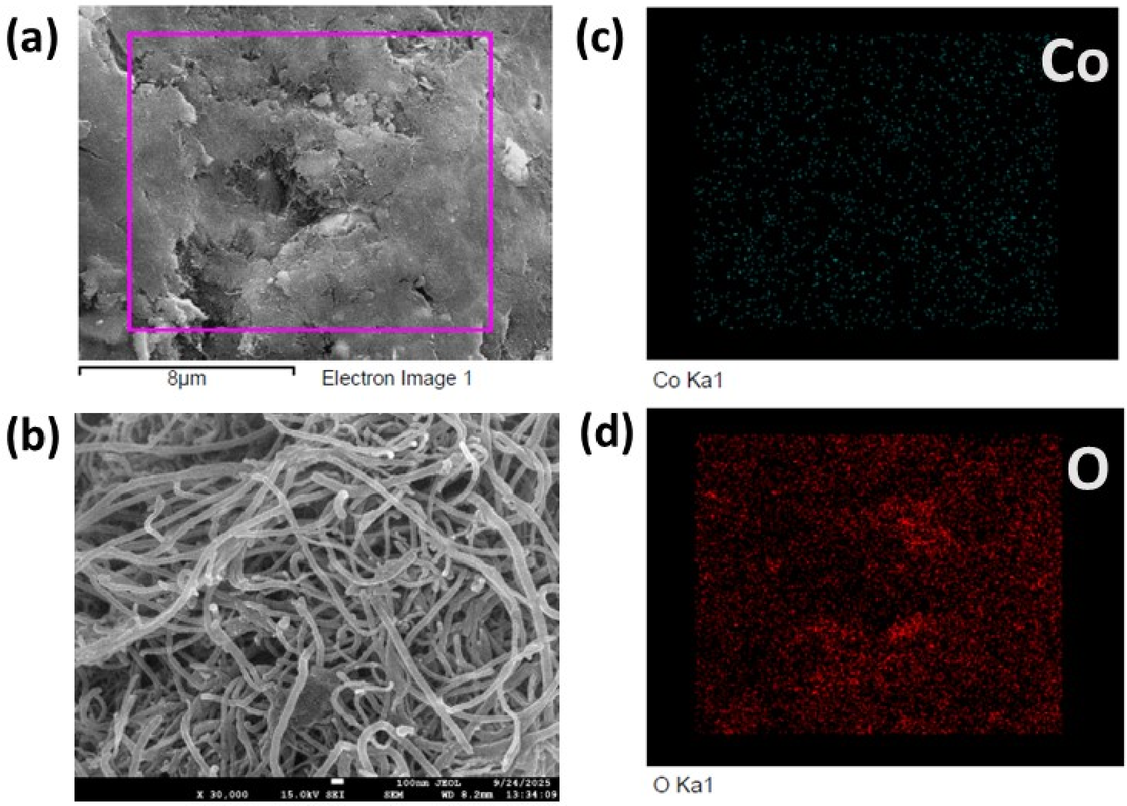


Fig. S30 (a)-(b) FE-SEM images of **1/MWCNT@CP** after CPE at -0.40 V vs RHE for 3 hrs in 1.0 M KOH; (c)-(d) elemental mapping of the elements through EDX in **1/MWCNT@CP** : (c) Co, (e) O indicating the presence of Co after bulk electrolysis.

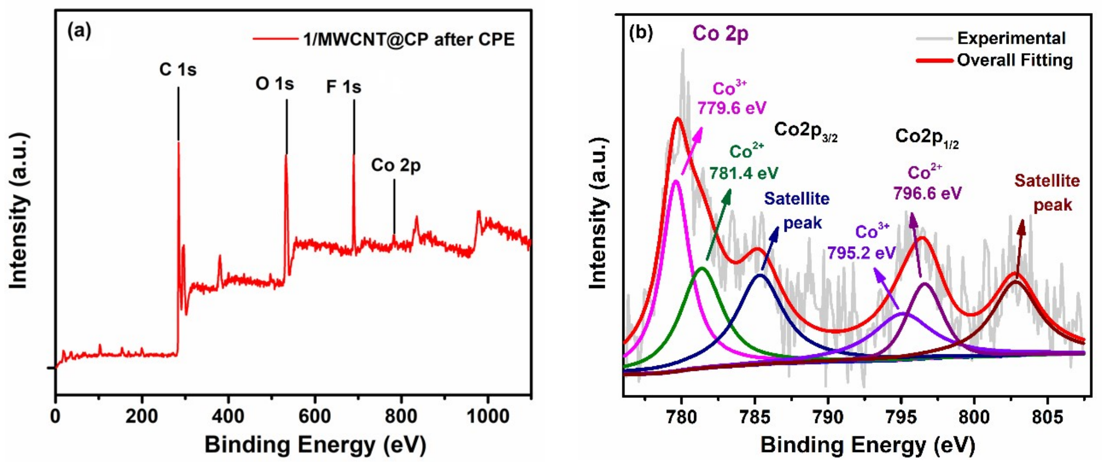


Fig. S31. (a) XPS survey spectrum of **1/MWCNT@CP** after bulk electrolysis for 3 hrs indicating the presence of C, O and Co along F coming from nafion used as binder; (b) High resolution XPS spectrum of Co 2p after bulk electrolysis.

References

[1] S.-L. Meng, C. Zhang, C. Ye, J.-H. Li, S. Zhou, L. Zhu, X.-B. Li, C.-H. Tung, L.-Z. Wu, *Energy Environ. Sci.* **2023**, *16*, 1590-1596.

[2] N. Li, Y. Li, Y. Han, W. Pan, T. Zhang, B. Tang, *Anal. Chem.* **2014**, *86*, 3924-3930.

[3] J. Y. Park, H. Y. Kim, Y.-I. , Kim, S. Y. Jo, S. A. Abbas, D. Seo, A. Ma, K. M. Nam, *J. Mat. Chem. A* **2022**, *10*, 12047-1205.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. E., Jr. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas;; J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 16, revision B.01* **2016,** *Gaussian Inc., Wallingford, CT,* .

[5] C. Adamo and V. Barone, *J. Chem. Phy.*, 1999, **110**, 6158-6170.

[6] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phy.*, 2010, **132**, 154104.

[7] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.

[8] F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.

[9] Y. Zhao and D. G. Truhlar, *Theor. Chem, Acc.*, 2008, **120**, 215-241.

[10] A. Z. Haddad, S. P. Cronin, M. S. Mashuta, R. M. Buchanan and C. A. Grapperhaus, *Inorg. Chem.*, 2017, **56**, 11254-11265

[11] C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2015, **137**, 4347-4357.

[12] S. Anantharaj, P. E. Karthik and S. Noda, *Angew. Chem. Int. Ed.*, 2021, **60**, 23051-23067.

[13] K. Banerjee, A. Roy, S. Ghosh, H. R. Inta, A. Mondal, S. Ghosh, A. Mitra, A. K. Mahato and V. Mahalingam, *ACS Appl. Energy Mater.*, 2024, **7**, 7745-7758.

[14] S. Hadimane, S. Aralekallu, K. Prabhu CP, M. Hojamberdiev, and L. K. Sannegowda, *ACS Appl. Energy Mater*. **2021**, *4*, 10826−10834.

[15] E. S. Andreiadis, P.-A. Jacques, P. D. Tran, A. Leyris, M. Chavarot-Kerlidou, B. Jousselme, M. Matheron, J. Pécaut, S. Palacin, M. Fontecave and V. Artero, *Nature Chem*, 2013, **5**, 48-53.

[16] C. Taechaworaphong, M. Juthathan, P. Thamyongkit, T. Tuntulani and P. Leeladee, *ChemPlusChem*, 2024, **89**, e202300679.

[17] E. Benazzi, F. Begato, A. Niorettini, L. Destro, K. Wurst, G. Licini, S. Agnoli, C. Zonta and M. Natali, *J. Mater. Chem. A*, 2021, **9**, 20032-20039.

[18] S. Gümrükçü, E. Kaplan, T. Karazehir, M. Özçeşmeci, İ. Özçeşmeci and E. Hamuryudan, *Int. J. Hydrog. Energy*, 2024, **89**, 462-473.

[19] B. Jin, X. Tan, X.-X. Zhang, Z.-Y. Wang, Y.-P. Qu, Y.-B. He, T.-P. Hu and P.-H. Zhao, *Electrochim. Acta*, 2022, **434**, 141325.

[20] S. Maity, R. Kancherla, U. Dhawa, E. Hoque, S. Pimparkar and D. Maiti, *ACS Catal.*, 2016, **6**, 5493-5499.

[21] L.-P. Xu, E. E. L. N. Liu, J. Bacsa, C. E. MacBeth and D. G. Musaev, *Chem. Sci.*, 2020, **11**, 6085-6096.

Cartesian coordinates (Å) of the optimized structures of all intermediates and transition states at PBE0-D3(SMD-DMF)/def2-TZVP(Co)/def2-SVP(non-metals) level of theory. *E* represents the absolute electronic energy in Hartree at M06(SMD-DMF)/def2-TZVPP level of theory.

2
69
E: -3138.88719460

Co	4.872745	12.311022	2.890450
O	2.701500	14.457285	1.964061
O	4.475524	12.975162	1.093959
H	3.700075	13.617934	1.318018
H	4.083906	12.246848	0.591270
N	3.823786	13.730268	3.790456
N	5.261852	11.751813	4.679310
O	5.914491	8.870132	1.153703
N	6.580475	13.385739	2.847003
N	5.944225	10.976872	2.089924
C	1.856484	15.247410	3.991738
C	2.859658	14.452904	3.205492
C	3.948367	14.844328	6.037359
H	3.468732	15.765383	5.711212

C	2.163771	11.100536	3.193368
H	1.807541	12.001960	3.693814
C	8.902777	13.166806	2.164296
C	4.164675	13.805342	5.137225
C	5.911972	10.665335	5.049357
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C	1.713812	8.871016	2.355532
H	1.011953	8.045720	2.202800
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C	7.256754	11.318958	1.878993
C	3.912218	9.816775	2.123771
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C	5.279015	12.548566	6.972830
C	5.971604	11.370285	7.345307
H	6.265535	11.229359	8.388723
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C	5.351315	9.803603	1.721648
C	3.034188	8.730905	1.908615
C	4.341302	14.727992	7.387033
H	4.134214	15.563747	8.060385
C	3.455701	7.457370	1.235321
H	2.611461	6.754604	1.176555
H	4.285098	6.974011	1.772589
H	3.833868	7.645365	0.219538
C	6.806921	14.622566	3.238093
H	5.957855	15.173153	3.650468
C	8.078528	15.221975	3.134501
H	8.214871	16.249784	3.475818
C	9.120825	14.496517	2.605000
H	10.119497	14.932404	2.513689
C	9.578187	11.067723	1.186953
H	10.348559	10.429995	0.743929
C	8.273967	10.545264	1.318806
H	8.040409	9.536795	0.984137
C	9.906081	12.344512	1.593016
H	10.919964	12.735658	1.481112
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H	2.497195	17.044587	1.806769
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C	-0.108952	16.667426	5.371178
H	-0.873965	17.233870	5.909052
C	0.010555	15.291860	5.563099
H	-0.658161	14.766501	6.249598

^{3}I

66

E: -3062.42464817

Co	4.953272	12.190887	3.201945
O	3.276674	13.796154	2.067002
N	3.892690	13.518604	4.166927
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O	5.633433	9.076724	0.794397
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N	5.786500	11.078553	1.935119
C	2.115485	15.175678	3.609718
C	3.132161	14.135825	3.251871
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C	1.914057	8.602070	3.055963
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H	0.497488	13.763990	3.408224
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C	3.622842	10.794787	3.229903
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C	6.612056	10.667080	7.009493
H	7.321562	9.898439	7.321384
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H	6.136172	11.334460	8.999906
C	2.495968	16.503616	3.879763
C	5.188720	9.882539	1.599905
C	3.069516	8.604021	2.263921
C	3.439180	14.214642	7.825524
H	2.872124	14.870542	8.491653
C	3.354811	7.444862	1.355369
H	2.563218	6.685919	1.438028
H	4.321952	6.976902	1.592157
H	3.429683	7.766678	0.305911
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C	7.969937	15.282811	3.005346
H	8.171044	16.246641	3.476218
C	8.820408	14.752914	2.059328
H	9.722975	15.289447	1.754212
C	8.963093	11.633194	0.005097
H	9.585232	11.138434	-0.745797
C	7.787692	10.975658	0.436262

H	7.517530	10.003491	0.029800
C	9.343235	12.861769	0.499000
H	10.255873	13.356037	0.158300
C	1.615330	9.661262	3.913985
H	0.703818	9.625943	4.518425
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H	4.459001	16.483587	4.763477
H	4.050755	17.997809	3.926212
H	4.467078	16.539209	2.990251
C	1.487293	17.427706	4.176228
H	1.765455	18.464987	4.384777
C	0.144145	17.051845	4.211287
H	-0.621693	17.794732	4.449962
C	-0.218956	15.733789	3.937472
H	-1.269373	15.432312	3.959147

^{3}II

67

E: -3062.87063739

Co	6.540080	10.728895	4.736742
O	4.919417	14.012230	5.439534
N	5.684700	12.145202	6.434257
N	7.041825	9.750807	6.385606
O	4.287399	12.346091	1.880830
N	8.366653	11.525372	4.386108
N	6.035335	11.765643	3.271165
C	6.972770	14.287550	6.613834
C	5.788345	13.527242	6.130795
C	5.834613	12.126109	8.893488
H	5.310970	13.083725	8.938037
C	4.181972	9.037587	5.380604
H	4.745394	8.555356	6.181986
C	9.387822	13.284904	3.057671
C	6.093617	11.553577	7.667333
C	7.653823	8.581257	6.308655
H	7.843385	8.193719	5.303862
C	2.117112	9.267764	4.125540
H	1.081661	8.958351	3.957345
C	8.163883	13.619370	6.937517
H	8.213249	12.534202	6.874908
C	6.766058	10.304290	7.600763
C	4.745787	10.029754	4.582475
C	6.881471	10.271535	10.046597
H	7.188076	9.765813	10.965168
C	8.275055	12.486163	3.424325
C	7.000170	12.644329	2.801265
C	3.999962	10.639571	3.560596
C	8.052785	7.862136	7.448913
H	8.552758	6.900452	7.326007
C	7.154973	9.649793	8.802996
C	7.807236	8.398050	8.691571
H	8.109430	7.872353	9.601025
C	6.915063	15.701153	6.698803
C	4.740571	11.677860	2.794741
C	2.662393	10.271103	3.312353

C	6.239562	11.487653	10.085711
H	6.026726	11.967231	11.043615
C	1.832181	10.902400	2.235900
H	0.826141	10.459745	2.214961
H	2.296522	10.777651	1.246349
H	1.739666	11.988062	2.388433
C	9.528449	11.286240	4.969365
H	9.550902	10.503633	5.731624
C	10.688098	12.013512	4.651900
H	11.622180	11.780178	5.165247
C	10.614248	13.018405	3.711094
H	11.495707	13.613028	3.456730
C	7.974560	14.440567	1.483159
H	7.831112	15.209778	0.719740
C	6.868722	13.631232	1.830804
H	5.907375	13.772292	1.342299
C	9.211823	14.284619	2.067626
H	10.060232	14.911276	1.783959
C	2.857948	8.659784	5.138106
H	2.396478	7.880939	5.752083
C	5.690333	16.506090	6.380950
H	5.479934	16.495157	5.301285
H	5.828464	17.548439	6.700780
H	4.792621	16.101323	6.870654
C	8.071956	16.375793	7.111079
H	8.038782	17.465698	7.192354
C	9.253442	15.703390	7.412782
H	10.136660	16.268699	7.721880
C	9.303387	14.313561	7.323262
H	10.222037	13.769433	7.554219
H	4.738028	11.850175	6.176305

II_a
67
E: -3062.86310247

Co	5.267884	11.837953	3.924257
O	4.032814	13.444828	3.799887
N	4.695343	12.439139	5.557263
N	6.181717	10.479406	4.949620
O	5.920697	9.275691	1.145851
N	6.961192	12.898891	3.813522
N	5.664239	11.422849	2.028249
C	3.029608	14.296410	5.823596
C	3.936363	13.405164	5.072964
C	4.580444	11.787388	7.966491
H	3.900622	12.589142	8.258580
C	2.679017	10.422649	4.451563
H	2.486356	11.045557	5.328849
C	8.905825	13.215491	2.385302
C	4.986919	11.665196	6.648744
C	7.006078	9.526195	4.561595
H	7.258325	9.478546	3.500117
C	1.991867	8.582921	3.015137
H	1.268035	7.799053	2.776163
C	1.676265	14.273776	5.461099

H	1.352272	13.619218	4.648182
C	5.852718	10.589352	6.276448
C	3.815255	10.615192	3.666937
C	5.915394	9.842103	8.591701
H	6.280163	9.143579	9.348004
C	7.618635	12.674109	2.640118
C	6.979149	11.875034	1.659806
C	4.019164	9.770430	2.554894
C	7.551349	8.592883	5.465280
H	8.228095	7.825621	5.086037
C	6.337097	9.679740	7.246507
C	7.213542	8.660350	6.796967
H	7.611857	7.939262	7.515307
C	3.492961	15.144199	6.851150
C	5.257949	10.030278	1.805941
C	3.126997	8.727523	2.213909
C	5.052958	10.864777	8.926513
H	4.724078	10.976224	9.962650
C	3.364588	7.813568	1.051033
H	2.490270	7.171381	0.875575
H	4.239632	7.169695	1.229049
H	3.577978	8.375504	0.128727
C	7.529242	13.637976	4.743877
H	6.966006	13.777445	5.669454
C	8.800108	14.224126	4.574643
H	9.217995	14.830362	5.379913
C	9.487964	14.011819	3.402478
H	10.478102	14.446259	3.242162
C	8.885708	12.150255	0.208488
H	9.367675	11.936200	-0.748120
C	7.597461	11.621305	0.457419
H	7.096758	11.017711	-0.299302
C	9.527934	12.930103	1.143778
H	10.520194	13.341814	0.944245
C	1.771063	9.417320	4.113662
H	0.873134	9.273826	4.722194
C	4.949840	15.257416	7.189364
H	5.358886	14.317260	7.590785
H	5.115694	16.040383	7.941893
H	5.541110	15.513176	6.296155
C	2.544274	15.929563	7.516502
H	2.881347	16.600091	8.311964
C	1.191918	15.885142	7.178927
H	0.477900	16.509198	7.722935
C	0.753094	15.059593	6.144313
H	-0.303785	15.027805	5.868816
H	4.949753	12.011874	1.578972

$^{3}II_{b}$

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E: -3062.86546363

Co	5.045373	12.148570	3.140887
O	2.780174	14.103300	2.032631
N	3.911395	13.656808	3.945767
N	5.190208	11.664342	5.133732

O	5.800305	9.174947	0.590470
N	6.766806	13.211592	3.110508
N	5.979966	10.998291	1.993737
C	1.899726	15.114832	3.937789
C	2.945225	14.259916	3.328475
C	3.984790	14.954429	6.080349
H	3.570456	15.854052	5.626611
C	2.329025	10.970115	3.402910
H	2.082684	11.716293	4.160354
C	9.052361	13.012597	2.303453
C	4.199054	13.819328	5.317800
C	5.762473	10.593531	5.644215
H	6.029970	9.797695	4.942976
C	1.672999	9.057656	2.062461
H	0.905710	8.334942	1.770831
C	1.047309	14.547758	4.892015
H	1.179158	13.503721	5.185234
C	4.839768	12.703471	5.930591
C	3.586742	10.920726	2.809560
C	4.834862	13.859320	8.080403
H	5.057374	13.865754	9.149871
C	7.721850	12.532629	2.412110
C	7.313126	11.316522	1.783423
C	3.899549	9.926315	1.869918
C	6.037044	10.479533	7.021355
H	6.503180	9.569428	7.402251
C	5.133203	12.703131	7.319500
C	5.735935	11.535429	7.851300
H	5.963122	11.492788	8.919704
C	1.770712	16.461437	3.546139
C	5.307142	9.956407	1.387717
C	2.940175	8.974189	1.468924
C	4.298861	14.963890	7.456625
H	4.101194	15.872783	8.029440
C	3.228811	7.906354	0.457133
H	2.334621	7.292276	0.278181
H	4.048646	7.251966	0.789021
H	3.559621	8.339200	-0.498674
C	7.071588	14.358607	3.691994
H	6.273794	14.873823	4.231445
C	8.364511	14.908067	3.635830
H	8.562850	15.856156	4.138337
C	9.351673	14.236032	2.949029
H	10.367043	14.637076	2.890363
C	9.589843	11.084017	0.959604
H	10.309366	10.496263	0.383384
C	8.263279	10.606243	1.058010
H	7.973387	9.681303	0.564700
C	9.993431	12.255490	1.560402
H	11.021039	12.615745	1.475288
C	1.371854	10.028271	3.017609
H	0.375936	10.052637	3.469247
C	2.693623	17.085887	2.542111
H	3.745542	16.821297	2.735089
H	2.608384	18.180958	2.562769

H	2.457072	16.747064	1.521367
C	0.758509	17.213454	4.153920
H	0.648105	18.266089	3.879329
C	-0.099686	16.651793	5.097682
H	-0.881274	17.266672	5.551592
C	0.039379	15.313966	5.467208
H	-0.630547	14.868646	6.206306
H	3.487203	13.553290	1.644381

$^4A \bullet H_2O$
69
E: -3138.99098004

Co	4.806034	12.452418	2.747576
O	2.639968	14.889562	2.048894
O	4.337141	13.420358	0.663747
H	3.706834	14.053430	1.102137
H	3.776097	12.649716	0.500081
N	3.975173	14.150511	3.727533
N	5.274951	12.067934	4.840746
O	5.807940	8.648867	1.340844
N	6.842995	13.264935	2.632457
N	5.943291	10.845290	2.041067
C	1.768281	15.156999	4.215772
C	2.866764	14.748761	3.265404
C	4.313710	15.446228	5.797694
H	3.851699	16.335192	5.364263
C	1.897863	11.263245	2.364471
H	1.476886	12.218899	2.702773
C	9.167665	12.616529	2.392565
C	4.412578	14.288064	5.028134
C	5.880811	11.009259	5.332015
H	5.999499	10.158568	4.653493
C	1.527873	9.013882	1.573619
H	0.840567	8.205639	1.302644
C	1.265073	14.195895	5.099740
H	1.719731	13.201492	5.117148
C	5.101092	13.168692	5.613846
C	3.292247	11.108276	2.283258
C	5.418882	14.415275	7.705750
H	5.792664	14.457759	8.731622
C	7.774257	12.317550	2.359263
C	7.297726	10.987963	2.028085
C	3.779230	9.858422	1.815238
C	6.373520	10.959537	6.653285
H	6.866222	10.054257	7.013755
C	5.588694	13.227417	6.951496
C	6.233874	12.068992	7.454586
H	6.617312	12.075282	8.478812
C	1.202614	16.446607	4.173660
C	5.280712	9.707867	1.704621
C	2.909279	8.795276	1.458643
C	4.801860	15.499603	7.119127
H	4.686786	16.429964	7.682357
C	3.367702	7.450473	0.962763
H	2.501078	6.805382	0.748656

H	4.014832	6.946522	1.695308
H	3.979095	7.539303	0.052941
C	7.213444	14.491740	2.931206
H	6.409196	15.205394	3.137547
C	8.566715	14.883075	2.991406
H	8.823535	15.913239	3.247067
C	9.537384	13.944837	2.724696
H	10.598497	14.207949	2.762615
C	9.648343	10.335626	1.783598
H	10.367885	9.543033	1.555177
C	8.274593	10.022730	1.743273
H	7.939104	9.019811	1.487427
C	10.108727	11.597299	2.099109
H	11.176745	11.827292	2.126479
C	1.019657	10.233990	2.018197
H	-0.064525	10.375527	2.090644
C	1.732587	17.501268	3.247255
H	2.816447	17.647082	3.387290
H	1.232036	18.465451	3.414927
H	1.593839	17.203139	2.197983
C	0.142674	16.730172	5.043905
H	-0.295280	17.732887	5.032959
C	-0.362878	15.767474	5.918397
H	-1.195681	16.018379	6.581115
C	0.196923	14.490929	5.944692
H	-0.191820	13.727662	6.623925

^{2}A
66
E: -3062.55934610

Co	4.889903	12.240081	3.059913
O	3.160249	14.269836	2.009729
N	3.835934	13.575294	4.034885
N	5.526605	11.820406	5.031424
O	5.807613	8.879984	1.040504
N	6.466536	13.395729	2.691951
N	5.855886	10.993357	1.975962
C	2.020848	15.286158	3.778129
C	3.061870	14.339759	3.239854
C	3.293847	14.382786	6.347961
H	2.587544	15.144328	6.025952
C	2.259982	10.856002	3.628505
H	1.917342	11.732021	4.190487
C	8.646064	13.355634	1.602350
C	3.938426	13.572714	5.404891
C	6.385098	10.912484	5.442709
H	6.876197	10.316861	4.665894
C	1.837711	8.610654	2.823597
H	1.176157	7.741366	2.751838
C	0.731405	14.805871	4.024097
H	0.517870	13.743104	3.876281
C	4.872369	12.597699	5.929841
C	3.527016	10.872858	3.022595
C	4.406925	13.304603	8.234557
H	4.579585	13.201755	9.308603

C	7.411679	12.745972	1.954464
C	7.086652	11.404788	1.544505
C	3.920564	9.706684	2.312275
C	6.670135	10.698978	6.807694
H	7.390080	9.930854	7.098375
C	5.099589	12.462751	7.330636
C	6.028945	11.473797	7.745798
H	6.223866	11.342278	8.813927
C	2.318331	16.650827	3.954677
C	5.285051	9.782931	1.698328
C	3.093061	8.565544	2.200570
C	3.530514	14.241109	7.729609
H	2.991912	14.902859	8.414277
C	3.492657	7.323054	1.454732
H	2.692553	6.568538	1.502782
H	4.417068	6.886916	1.861785
H	3.714707	7.538922	0.399023
C	6.693260	14.632682	3.093835
H	5.898652	15.104758	3.676548
C	7.887241	15.317709	2.792778
H	8.022300	16.340429	3.151013
C	8.859889	14.683846	2.052525
H	9.796826	15.189909	1.803295
C	9.259790	11.329808	0.441571
H	9.977821	10.758075	-0.154407
C	8.036759	10.716001	0.781936
H	7.809873	9.701532	0.460281
C	9.578617	12.616160	0.830958
H	10.531512	13.075083	0.556321
C	1.424742	9.741787	3.531208
H	0.439123	9.747129	4.009676
C	3.709886	17.160635	3.722308
H	4.397048	16.787268	4.500991
H	3.746232	18.259062	3.742856
H	4.102924	16.815069	2.754244
C	1.297125	17.499763	4.396149
H	1.517013	18.561669	4.542840
C	0.012048	17.018537	4.652534
H	-0.767047	17.703588	4.997948
C	-0.274060	15.667015	4.463426
H	-1.278906	15.281799	4.656558

^{2}B

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E: -3063.03552984

Co	6.533353	10.662317	4.676548
O	4.865960	14.045343	5.486743
N	5.779185	12.279626	6.542839
N	6.948155	9.751158	6.344627
O	4.466176	12.101215	1.563101
N	8.365643	11.386738	4.365858
N	6.135477	11.587029	3.073311
C	6.815243	14.507182	6.769590
C	5.731574	13.625917	6.231787
C	6.304013	12.286680	8.925041

H	5.854241	13.276490	9.020207
C	3.942875	9.289684	5.436267
H	4.415302	8.867160	6.329516
C	9.557394	12.919990	2.895020
C	6.327111	11.672472	7.686623
C	7.415146	8.516395	6.257153
H	7.438628	8.078456	5.255185
C	1.974344	9.522372	4.046486
H	0.923735	9.286679	3.850278
C	8.140825	14.059325	6.735401
H	8.354548	13.055224	6.367439
C	6.883031	10.361023	7.566211
C	4.678995	10.110992	4.570996
C	7.344711	10.377645	9.983018
H	7.732554	9.864104	10.865907
C	8.385300	12.217451	3.283292
C	7.154260	12.342628	2.553262
C	4.014969	10.638114	3.434329
C	7.879362	7.786659	7.366378
H	8.250362	6.770589	7.222710
C	7.367914	9.704122	8.736973
C	7.868242	8.385947	8.602367
H	8.237446	7.863801	9.488844
C	6.512009	15.802412	7.239725
C	4.864228	11.521764	2.572091
C	2.661966	10.355461	3.150492
C	6.832121	11.650695	10.066509
H	6.804147	12.173216	11.025468
C	1.936922	10.899536	1.952893
H	0.899959	10.532323	1.928969
H	2.436797	10.615894	1.014926
H	1.924493	11.999585	1.956285
C	9.473956	11.198664	5.061400
H	9.413266	10.521936	5.917217
C	10.683885	11.845502	4.744419
H	11.567106	11.657443	5.357536
C	10.723184	12.709121	3.673080
H	11.645051	13.234393	3.408546
C	8.312178	13.894559	1.073777
H	8.263856	14.553575	0.201891
C	7.146323	13.191628	1.444063
H	6.225194	13.299478	0.875186
C	9.499881	13.776141	1.766720
H	10.394758	14.324687	1.463872
C	2.601433	8.996795	5.175334
H	2.035440	8.352968	5.856464
C	5.107676	16.326571	7.303461
H	4.713460	16.515220	6.294084
H	5.068901	17.263692	7.876375
H	4.423436	15.603012	7.772766
C	7.576712	16.603999	7.670855
H	7.358845	17.605476	8.052901
C	8.897533	16.159559	7.622250
H	9.703777	16.816506	7.959655
C	9.185303	14.880952	7.147414

H	10.215958	14.520666	7.099684
H	5.044257	11.741334	6.068053

$^{2}B_{a}$
67
E: -3063.01352746

Co	5.241360	11.865205	3.616920
O	3.679760	14.171644	3.973046
N	4.539256	12.568060	5.277510
N	6.162375	10.503065	4.962656
O	6.159809	9.045301	1.273636
N	6.925385	12.928295	3.537730
N	5.804999	11.285964	1.779602
C	2.988637	14.302605	6.208777
C	3.774974	13.662674	5.096374
C	4.303269	12.025665	7.710257
H	3.605976	12.833621	7.919545
C	2.521830	10.534760	3.936143
H	2.239332	11.232653	4.730845
C	9.005356	13.113511	2.276389
C	4.791591	11.836654	6.413868
C	7.001029	9.515011	4.733678
H	7.343792	9.385050	3.702345
C	1.986746	8.579267	2.592495
H	1.286420	7.779907	2.332843
C	1.631190	13.989763	6.326654
H	1.188253	13.259996	5.642658
C	5.696505	10.723229	6.219371
C	3.759864	10.676797	3.289994
C	5.564615	10.137890	8.601303
H	5.861467	9.495678	9.433847
C	7.695367	12.596091	2.459364
C	7.148216	11.700014	1.504279
C	4.068782	9.721135	2.288456
C	7.448279	8.642965	5.747973
H	8.144375	7.838366	5.502359
C	6.083700	9.888202	7.307805
C	6.985800	8.829376	7.028751
H	7.301710	8.172012	7.843616
C	3.578934	15.248275	7.068185
C	5.411844	9.890913	1.700369
C	3.215071	8.652167	1.931090
C	4.689495	11.187713	8.775062
H	4.273837	11.389053	9.766512
C	3.583527	7.635620	0.891176
H	2.727269	6.987016	0.656318
H	4.415641	7.002088	1.234800
H	3.926211	8.111867	-0.040685
C	7.408105	13.766829	4.431999
H	6.756458	13.993515	5.278744
C	8.691766	14.342555	4.326489
H	9.031293	15.032524	5.101097
C	9.491173	14.015590	3.256213
H	10.494037	14.436922	3.148045
C	9.196486	11.822169	0.233144

H	9.771889	11.508957	-0.641211
C	7.885277	11.320367	0.405697
H	7.457451	10.635173	-0.326324
C	9.746299	12.700709	1.140033
H	10.756735	13.092337	0.998558
C	1.646707	9.508410	3.583219
H	0.679078	9.417755	4.087813
C	5.039715	15.569983	6.961917
H	5.653607	14.704877	7.265650
H	5.312694	16.417461	7.606278
H	5.320163	15.818757	5.926757
C	2.775715	15.844270	8.047201
H	3.223089	16.578940	8.723530
C	1.424881	15.518623	8.177178
H	0.822157	15.996512	8.954255
C	0.848173	14.588887	7.312832
H	-0.210416	14.331099	7.403084
H	5.126703	11.845927	1.248987

^{2}B$_{b}$

67

E: -3063.02246091

Co	4.907735	12.227137	3.054951
O	2.657388	13.976292	2.109154
N	3.810657	13.597392	4.003339
N	5.231104	11.640268	5.049326
O	5.837955	9.085365	0.741712
N	6.604525	13.286465	3.044095
N	5.918556	11.027874	1.987896
C	1.887249	15.188203	3.957172
C	2.860414	14.222792	3.388336
C	3.855315	14.802837	6.197744
H	3.361129	15.691019	5.807846
C	2.132137	11.000139	3.138667
H	1.770472	11.814890	3.774819
C	8.915554	13.137120	2.283681
C	4.123677	13.725343	5.369233
C	5.890922	10.597120	5.501649
H	6.176095	9.841038	4.763043
C	1.677699	8.900677	2.022483
H	0.980942	8.093674	1.775515
C	0.874045	14.707623	4.791755
H	0.825406	13.640036	5.022266
C	4.857687	12.621412	5.907583
C	3.453474	11.001326	2.666534
C	4.864152	13.686578	8.110070
H	5.133580	13.664176	9.168799
C	7.597638	12.617169	2.389615
C	7.234908	11.361625	1.793810
C	3.861856	9.899931	1.870829
C	6.238360	10.445827	6.861788
H	6.778906	9.553764	7.184099
C	5.206396	12.586810	7.285404
C	5.906448	11.443387	7.748044
H	6.180296	11.375843	8.804306

C	1.987707	16.554982	3.638417
C	5.298552	9.931623	1.453845
C	2.990893	8.839832	1.534647
C	4.223675	14.774169	7.560697
H	3.985460	15.640274	8.182886
C	3.404141	7.664798	0.694649
H	2.562722	6.967402	0.565917
H	4.248669	7.123155	1.146012
H	3.758117	7.982069	-0.297343
C	6.865242	14.464350	3.582391
H	6.040436	14.972856	4.086996
C	8.141016	15.058540	3.525776
H	8.297154	16.032902	3.992620
C	9.163271	14.396433	2.885177
H	10.165517	14.829825	2.827056
C	9.539072	11.178162	1.021335
H	10.291200	10.596439	0.480221
C	8.230146	10.659117	1.110163
H	7.974065	9.708806	0.646611
C	9.895024	12.385686	1.586230
H	10.912044	12.776266	1.504382
C	1.253027	9.963724	2.819281
H	0.224610	9.980375	3.194722
C	3.084535	17.060792	2.749747
H	4.071368	16.712557	3.096136
H	3.099288	18.158929	2.721977
H	2.960522	16.693848	1.718778
C	1.042320	17.421333	4.198837
H	1.106545	18.489749	3.974315
C	0.030173	16.949130	5.034261
H	-0.693655	17.650722	5.457305
C	-0.059514	15.589365	5.330291
H	-0.852242	15.214162	5.981979
H	3.212832	13.193585	1.872817

^{3}C

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E: -3063.12804343

Co	6.555906	10.711315	4.672898
O	5.025986	14.163409	5.376017
N	5.724974	12.338899	6.502669
N	7.018753	9.859913	6.350962
O	4.423031	12.027385	1.539586
N	8.373577	11.453048	4.302760
N	6.125297	11.578187	3.035882
C	6.897396	14.477081	6.811038
C	5.798193	13.670761	6.184741
C	5.988658	12.310659	8.938808
H	5.478124	13.275484	8.981889
C	4.008336	9.286186	5.477336
H	4.506798	8.887560	6.367499
C	9.534726	12.923108	2.746191
C	6.191063	11.704824	7.684622
C	7.592468	8.622552	6.284925
H	7.708682	8.209642	5.278469

C	2.012424	9.467869	4.118556
H	0.962035	9.213697	3.944547
C	8.189989	13.944396	6.864017
H	8.358193	12.928361	6.506212
C	6.820807	10.439684	7.576102
C	4.719610	10.107269	4.589594
C	7.048082	10.433941	10.026152
H	7.384816	9.931399	10.937748
C	8.371817	12.235586	3.185876
C	7.126843	12.321795	2.470875
C	4.026395	10.604210	3.454762
C	8.012392	7.927589	7.399860
H	8.467459	6.941253	7.277599
C	7.246035	9.781859	8.788598
C	7.854802	8.499980	8.674799
H	8.186018	7.979781	9.577022
C	6.650246	15.786088	7.274685
C	4.848323	11.480961	2.557668
C	2.672003	10.297775	3.199182
C	6.428549	11.685359	10.098855
H	6.275126	12.165976	11.069035
C	1.916637	10.813668	2.007168
H	0.882548	10.437077	2.011737
H	2.398997	10.517745	1.063781
H	1.894232	11.913445	1.990098
C	9.494453	11.292271	4.983834
H	9.439825	10.650303	5.866754
C	10.698171	11.924763	4.616016
H	11.594056	11.762052	5.218270
C	10.715913	12.744595	3.510078
H	11.632228	13.258450	3.206404
C	8.252630	13.815717	0.907721
H	8.186778	14.437280	0.009676
C	7.096520	13.124573	1.326892
H	6.165267	13.203622	0.769705
C	9.453483	13.730669	1.583638
H	10.340612	14.268235	1.240517
C	2.668213	8.967569	5.243698
H	2.123745	8.324204	5.943001
C	5.280186	16.398044	7.252920
H	4.950178	16.584305	6.220673
H	5.268826	17.347990	7.805861
H	4.529978	15.727056	7.699948
C	7.732876	16.514548	7.785036
H	7.554804	17.525872	8.162297
C	9.022467	15.985127	7.821295
H	9.845220	16.585401	8.219307
C	9.256209	14.692504	7.354292
H	10.261600	14.264027	7.374478
H	4.969500	11.859344	6.004539

^{4}D

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E: -3063.20723681

Co	5.892514	11.446948	3.907215

O	4.379000	14.701683	2.176673
N	4.660742	14.017454	4.306979
N	5.770858	11.933834	5.829402
O	4.866995	9.930739	0.367900
N	7.475710	12.539746	3.511265
N	5.968145	11.027833	2.080667
C	2.395295	14.200092	3.383780
C	3.883134	14.351051	3.240417
C	3.399780	14.761759	6.258203
H	2.981062	15.567881	5.652546
C	3.532249	9.902865	4.989902
H	3.752277	10.245220	6.006918
C	8.928253	13.170006	1.621523
C	4.299775	13.859746	5.659974
C	6.417281	11.023981	6.620514
H	7.131386	10.372348	6.108626
C	2.094044	8.662690	3.485356
H	1.208217	8.040291	3.322724
C	1.882049	12.962369	3.784290
H	2.573382	12.158599	4.050385
C	4.902588	12.819980	6.415962
C	4.362478	10.290896	3.925791
C	3.655845	13.639195	8.377730
H	3.413131	13.548260	9.440665
C	7.819165	12.463343	2.175076
C	6.999125	11.633233	1.364221
C	4.029484	9.811208	2.631935
C	6.186092	10.899165	7.973996
H	6.735857	10.145500	8.544033
C	4.591037	12.737128	7.823105
C	5.245916	11.737627	8.598241
H	5.025578	11.653890	9.665373
C	1.527728	15.253081	3.032726
C	4.980725	10.246356	1.554367
C	2.898168	9.005817	2.385425
C	3.064095	14.636938	7.600987
H	2.354718	15.336720	8.051564
C	2.515416	8.508760	1.019292
H	1.592200	7.911251	1.069088
H	3.312384	7.894844	0.574084
H	2.362575	9.340581	0.315797
C	8.245269	13.320878	4.328781
H	7.939739	13.347698	5.378268
C	9.333681	14.035866	3.869344
H	9.905225	14.643229	4.577408
C	9.703920	13.981948	2.508236
H	10.561490	14.542038	2.126783
C	8.373409	12.203719	-0.552216
H	8.588988	12.103608	-1.620935
C	7.287630	11.509434	-0.010074
H	6.649443	10.875946	-0.623259
C	9.184786	13.020326	0.237993
H	10.030463	13.556369	-0.204148
C	2.409812	9.098184	4.772513
H	1.767598	8.809968	5.611837

C	2.053530	16.593294	2.609942
H	2.745246	17.006798	3.362119
H	1.235094	17.312429	2.464261
H	2.626058	16.510127	1.674722
C	0.148954	15.020174	3.109560
H	-0.538178	15.832380	2.854082
C	-0.362472	13.782369	3.501303
H	-1.444604	13.630962	3.545144
C	0.506838	12.745204	3.836188
H	0.120519	11.769168	4.141673
H	5.651507	13.924437	4.074909

[2]D-TS
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E: -3292.26122545

Co	5.161444	12.017307	3.236551
O	2.759858	11.805757	0.184594
N	3.078858	13.174176	1.947143
N	4.577598	13.569405	4.308069
O	5.151610	8.467658	1.384009
N	6.738143	12.904948	2.482896
N	5.660167	10.616978	2.070945
C	2.843234	14.105203	-0.340726
C	2.894851	12.945447	0.615815
C	1.968741	15.322866	2.303479
H	1.354361	15.134820	1.423008
C	2.845473	10.926090	4.824580
H	2.768934	11.869815	5.376235
C	8.475777	12.589607	0.799836
C	2.915108	14.354761	2.698991
C	5.204100	13.743843	5.510929
H	5.860065	12.922517	5.809409
C	2.034434	8.677214	4.432396
H	1.336339	7.868863	4.672931
C	1.741510	14.143364	-1.204960
H	0.976181	13.368370	-1.113617
C	3.678313	14.522595	3.891160
C	3.831747	10.784628	3.829650
C	2.548094	16.702124	4.194027
H	2.416138	17.615166	4.782225
C	7.334088	12.147615	1.518706
C	6.736264	10.863733	1.269776
C	3.875237	9.539021	3.140369
C	5.041382	14.864145	6.298761
H	5.585759	14.935176	7.244569
C	3.461465	15.728905	4.661263
C	4.183352	15.893344	5.874591
H	4.038513	16.800742	6.466724
C	3.868678	15.064500	-0.460999
C	4.945904	9.454396	2.097311
C	2.990959	8.476429	3.425187
C	1.804203	16.493818	3.032084
H	1.074144	17.239026	2.703448
C	3.025269	7.157334	2.704812
H	2.245806	6.483171	3.092071

H	4.004102	6.665800	2.807785
H	2.878845	7.285445	1.621938
C	7.256749	14.083080	2.786059
H	6.746797	14.652791	3.566111
C	8.394970	14.598890	2.136928
H	8.776419	15.580252	2.427220
C	8.999023	13.862846	1.141695
H	9.878408	14.242507	0.613761
C	8.440756	10.513773	-0.435849
H	8.864806	9.860116	-1.204656
C	7.313835	10.060072	0.279714
H	6.877118	9.083293	0.081128
C	9.024814	11.743563	-0.198420
H	9.901476	12.075323	-0.760439
C	1.961671	9.888308	5.124421
H	1.202573	10.017582	5.903903
C	5.097485	15.021718	0.393200
H	5.506368	14.003627	0.454193
H	4.877263	15.335061	1.426733
H	5.877886	15.686147	-0.003263
C	3.721961	16.064448	-1.432706
H	4.515199	16.810167	-1.541458
C	2.604412	16.122910	-2.262983
H	2.518872	16.920836	-3.005757
C	1.607098	15.153340	-2.152902
H	0.731752	15.179963	-2.807186
H	3.196672	12.303778	2.492741
H	6.006478	11.348890	4.343152
O	6.806965	11.019300	5.459636
C	8.061486	11.249042	5.301241
C	8.761178	11.739357	6.565986
H	8.396841	11.206852	7.457145
H	9.852497	11.637627	6.482624
H	8.521573	12.807737	6.704169
O	8.700268	11.143701	4.257272

E_1
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E: -840.712983862

O	7.326035	13.585401	8.137156
N	6.953339	11.549839	7.267333
N	7.361177	10.355769	4.933757
C	5.558119	12.356734	9.133269
C	6.691399	12.544770	8.171539
C	6.049130	9.451763	8.213657
H	5.911053	9.883510	9.204303
C	6.570080	10.217622	7.184192
C	7.581924	9.813099	3.758365
H	8.043569	10.450400	2.994862
C	4.275580	12.131943	8.621721
H	4.137581	12.036972	7.540926
C	6.798154	9.600960	5.905955
C	5.878349	7.493584	6.777057
H	5.604969	6.447778	6.617028
C	7.256978	8.472015	3.448546

H	7.461639	8.080055	2.449929
C	6.444759	8.234346	5.709472
C	6.691998	7.686612	4.425270
H	6.432186	6.642063	4.231862
C	5.768581	12.481503	10.519855
C	5.698315	8.100789	7.998814
H	5.280843	7.533540	8.834698
C	7.137231	12.724147	11.084214
H	7.857382	11.970585	10.726548
H	7.123378	12.692068	12.182558
H	7.522715	13.703956	10.765409
C	4.657525	12.354486	11.362382
H	4.803461	12.432783	12.443629
C	3.377546	12.134291	10.853353
H	2.529702	12.044845	11.537917
C	3.181142	12.029328	9.476956
H	2.180843	11.861593	9.069834
H	7.544543	11.834916	6.484049

$^2E_2$

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E: -2222.98796136

Co	5.432335	12.126940	3.881679
O	5.724821	9.194787	1.130534
N	6.795234	13.428612	3.261395
N	6.016411	11.144691	2.334100
C	3.245514	10.388303	5.084671
H	3.079365	11.123876	5.879658
C	8.432484	13.776100	1.483954
C	2.658369	8.268165	4.075267
H	2.048515	7.359070	4.071850
C	4.227070	10.627672	4.107569
C	7.421883	13.006470	2.120976
C	7.002320	11.734022	1.593917
C	4.390093	9.631619	3.102680
C	5.439043	9.936636	2.072412
C	3.620510	8.446685	3.069968
C	3.780108	7.379853	2.022818
H	3.076222	6.553226	2.204119
H	4.803965	6.977902	2.007506
H	3.609508	7.776665	1.011105
C	7.137302	14.592418	3.790395
H	6.610165	14.887626	4.700477
C	8.126087	15.422100	3.225922
H	8.364703	16.372346	3.707887
C	8.771196	15.017587	2.079464
H	9.543440	15.639757	1.618468
C	8.633880	12.049365	-0.190786
H	9.101525	11.657941	-1.099354
C	7.631183	11.277213	0.430769
H	7.328303	10.316197	0.019431
C	9.039724	13.272297	0.305559
H	9.817598	13.858950	-0.188975
C	2.469447	9.226824	5.070641
H	1.709527	9.061323	5.841931

H	4.964905	12.924515	5.160715

^{2}E-TS

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E: -3063.68973990

Co	5.298502	11.633995	3.364100
O	2.902033	15.230395	2.057939
N	3.223470	13.985654	3.912307
N	5.011629	12.312806	5.271853
O	6.130936	8.670741	0.771484
N	6.557362	13.054066	2.803062
N	6.094412	10.678406	1.912401
C	2.332554	16.303642	4.074376
C	2.836577	15.113866	3.281180
C	1.779167	13.971599	5.880641
H	0.998790	14.502660	5.335031
C	3.429083	9.623973	4.640991
H	3.136334	10.358801	5.398540
C	8.195514	13.573814	1.075811
C	2.952433	13.625933	5.202309
C	5.964464	11.723454	5.979297
H	6.829990	11.356190	5.416832
C	3.194748	7.391697	3.729999
H	2.734529	6.399278	3.768466
C	1.068230	16.797059	3.729448
H	0.504816	16.291714	2.940365
C	3.921218	12.825250	5.917755
C	4.366545	9.965177	3.652770
C	2.555288	13.029650	7.970288
H	2.433189	12.830134	9.037489
C	7.263474	12.696508	1.691432
C	7.018103	11.375253	1.181347
C	4.701126	8.964172	2.702192
C	5.893515	11.514808	7.367325
H	6.715619	11.014034	7.881608
C	3.733681	12.590768	7.319194
C	4.759054	11.917880	8.027503
H	4.632799	11.737161	9.098593
C	3.096435	16.961843	5.058847
C	5.710045	9.387692	1.681201
C	4.125688	7.673141	2.720378
C	1.586022	13.682846	7.241984
H	0.656525	13.999272	7.723359
C	4.463421	6.603162	1.720499
H	5.538023	6.367676	1.727434
H	4.243719	6.927350	0.692401
H	3.896328	5.683781	1.931687
C	6.749639	14.245250	3.339637
H	6.162842	14.473518	4.231085
C	7.651514	15.181495	2.796823
H	7.766237	16.154429	3.279037
C	8.368614	14.850528	1.669252
H	9.075123	15.556719	1.224295
C	8.650971	11.859865	-0.561658
H	9.188628	11.514973	-1.450094

C	7.731827	10.979259	0.045813
H	7.563347	9.981660	-0.354770
C	8.892948	13.129829	-0.076308
H	9.610089	13.797552	-0.559715
C	2.850237	8.354333	4.680454
H	2.120703	8.106713	5.459014
C	4.483966	16.518467	5.417539
H	5.100640	16.380279	4.517074
H	4.479384	15.558965	5.959102
H	4.979461	17.260931	6.059129
C	2.535307	18.078591	5.694554
H	3.123100	18.600487	6.455902
C	1.259996	18.541349	5.374935
H	0.849317	19.411374	5.894624
C	0.521344	17.899629	4.380901
H	-0.474606	18.259951	4.109420
H	3.967084	12.313691	2.436692
H	3.723141	13.013870	3.078902