Supplementary Information

Water soluble binuclear aquo Cu(II) complex with amide ligand as electro catalyst for OER, HER and CO2RR activity

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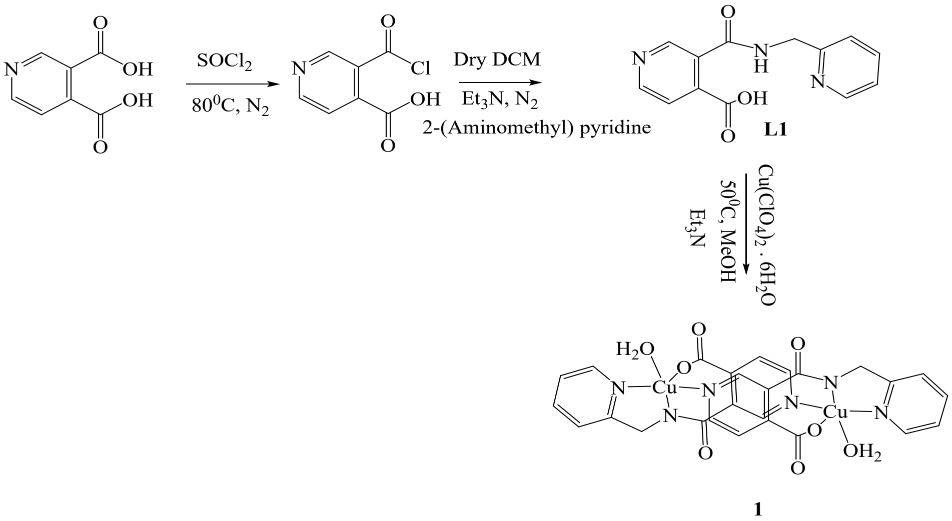
Synthesis and Structural analysis

Pyridine-3,4-dicarboxylic acid (3 mmol, 501.36 mg) was refluxed with 7 ml of Thionyl choride at 80^0C for 6 hours under inert atmosphere. Grey solid compound was separated from Thionyl choride using short path distillation. In the next step 2-(Aminomethyl) pyridine (3mmol, 282.33 mg) was added to an R.B with (4.5 mmol, 454.95 mg) Triethylamine ,15 ml of dry DCM and stirred for 20 minutes. Later the chlorinated compound was added to the R.B under inert atmosphere and refluxed at 40^0C for 8 hours. Dark brown crystalline ligand was filtered and dried in *vacuo*.[1-2] 1mmol (257 mg) of the ligand was dissolved in methanol with 1.5 mmol of Et_3N (1mmol, 151.65 mg) afterwards (370.53 mg) of copper perchlorate hexahydrate was added in the solution. Green precipitate was observed suddenly. The reaction mixture was refluxed for 2 hours at 50^0C. Green solid crystalline complex was filtered and washed with methanol and dissolved in water for all the analysis. NMR of the **L** was done on dissolution in $CDCl_3$ (Figure-S4). The exact mass of the ligand was calculated to be 257.08. Whereas the (+ESI-MS) observed on the Mass spectroscopy of ligand (**L1**) and **1** are 258.27 (Figure S1). A binuclear complex was also observed on the mass spectra showing an +ESI mass of 673.39 (Figure S3) in mass grade H_2O.



Scheme 1- Synthetic procedure for preparation of Ligand **L1** and Cu-complex **(1)** .

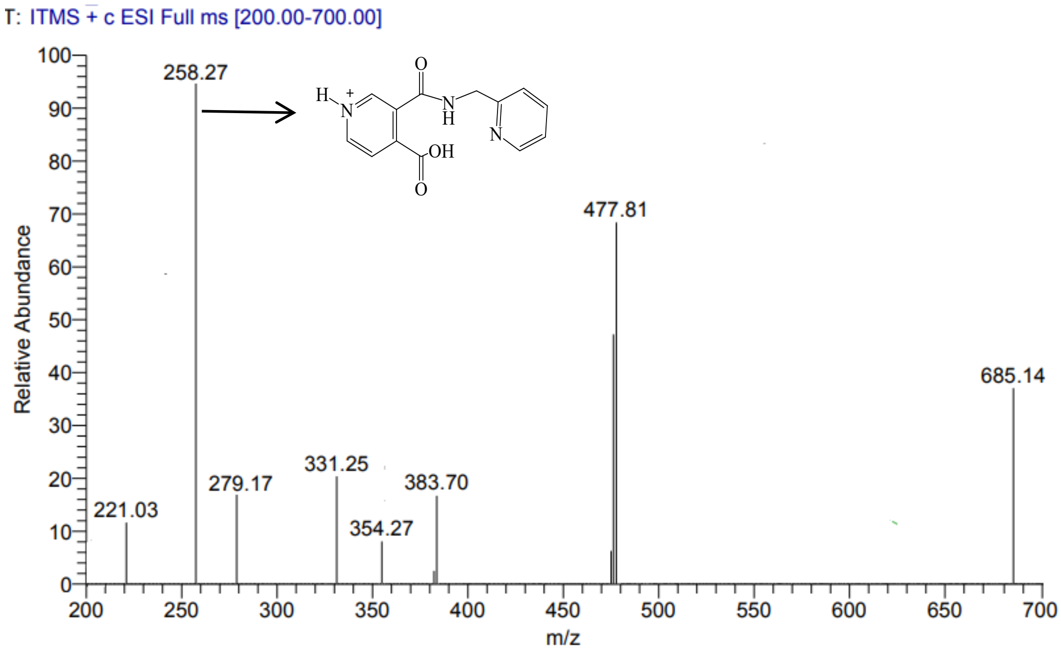


Figure S1- Mass spectrum of ligand.

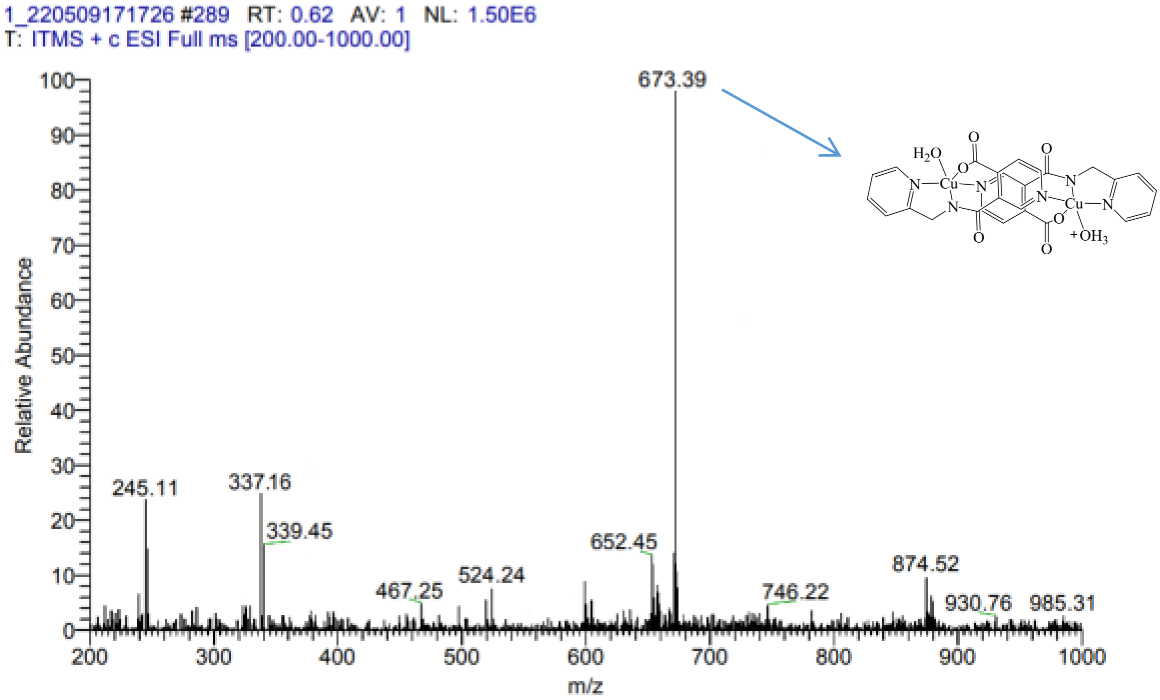
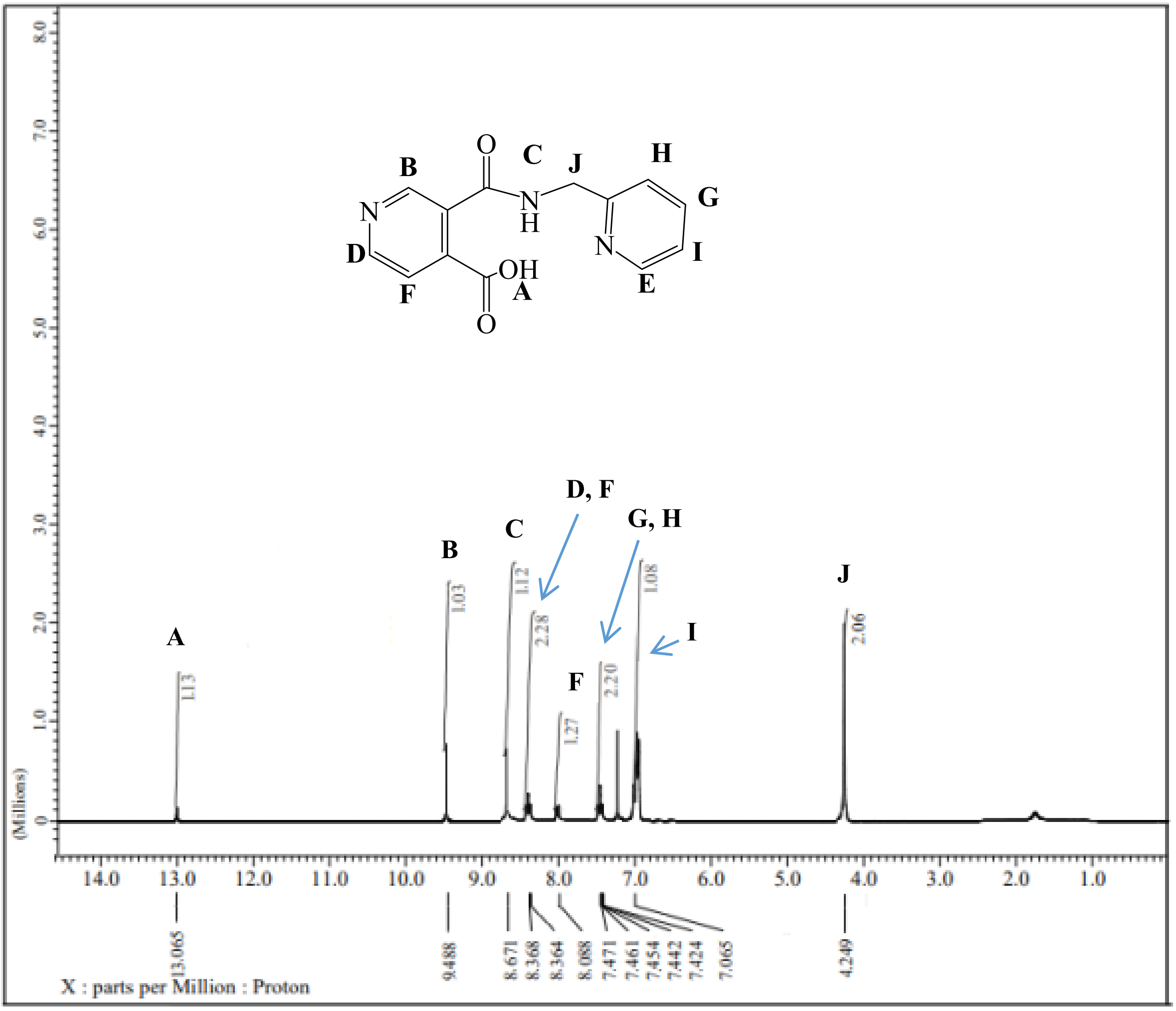


Figure S2- Mass of complex **1** recorded in Water .


O
B
C
J
H
N
N
H
G
D
N
I
OH
A
E
F
O
D, F
G, H
C
B
F
I
A
J
1.13
1.03
1.12
2.28
1.27
2.20
1.08
2.06
(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
13.065
9.488
8.671
8.368
8.364
8.088
7.471
7.461
7.454
7.442
7.424
7.065
4.249
X : parts per Million : Proton

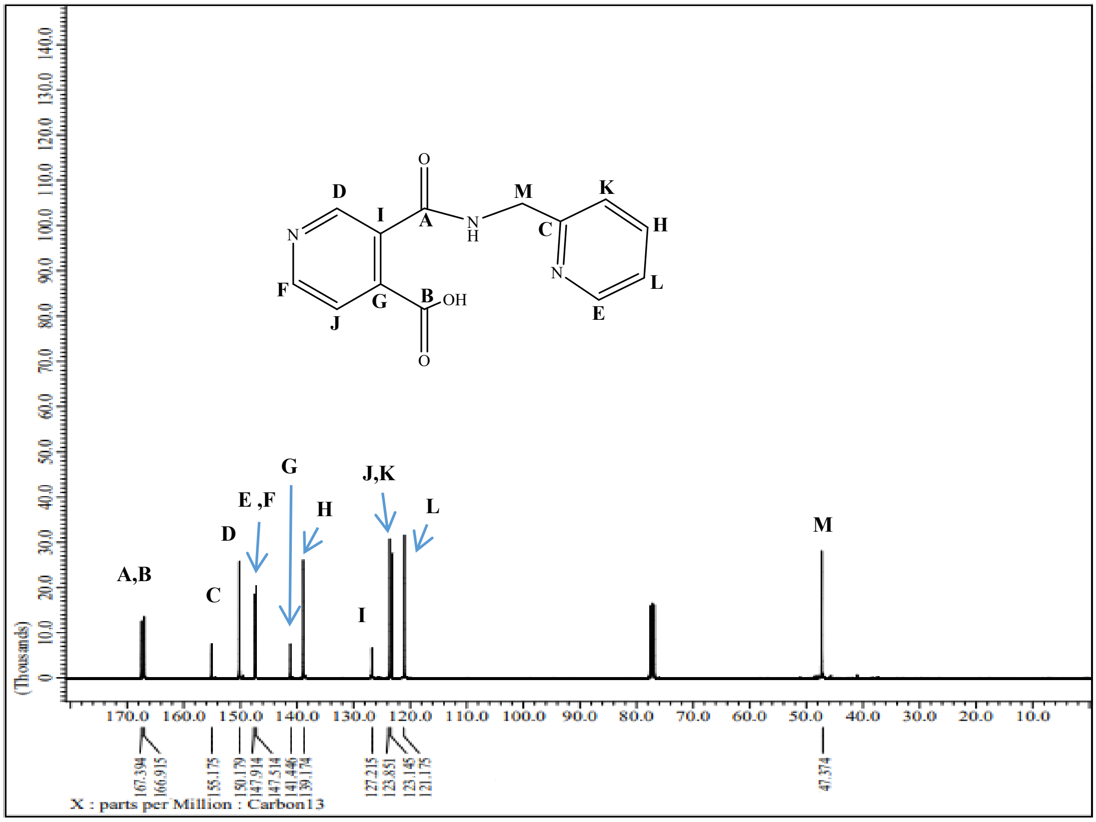


Figure S3- NMR spectrum of L in $CDCl_3$

Table S1.1- Crystal data and structure refinement for L

Identification code	SNAD1
Empirical formula	$C_{13}H_{15}N_3O_5$
Formula weight	293.28
Temperature/K	298.15
Crystal system	triclinic
Space group	P-1
a/Å	8.3624(6)
b/Å	8.5232(8)
c/Å	9.6931(8)
α/°	92.749(7)
β/°	92.290(6)
γ/°	96.721(7)
Volume/Å^3	684.61(10)
Z	2
ρ_{calc}g/cm^3	1.423
μ/mm^{-1}	0.111
F(000)	308.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.616 to 49.986

Index ranges	$-9 \le h \le 9$, $-10 \le k \le 10$, $-10 \le l \le 11$
Reflections collected	5220
Independent reflections	2396 [R_{int} = 0.0253, R_{sigma} = 0.0372]
Data/restraints/parameters	2396/0/200
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0461, wR_2 = 0.1162
Final R indexes [all data]	R_1 = 0.0654, wR_2 = 0.1333
Largest diff. peak/hole / e Å^{-3}	0.22/-0.25

Table S1.2- Bond Angles of L1

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C7	N2	C8	120.19(17)	O3	C7	C4	121.34(18)
C13	N3	C9	122.12(17)	N2	C7	C4	116.68(17)
C1	N1	C5	117.05(18)	N3	C9	C8	115.13(16)
O2	C6	C3	116.93(16)	N3	C9	C10	119.09(17)
O1	C6	O2	124.44(18)	C10	C9	C8	125.79(17)
O1	C6	C3	118.63(17)	N2	C8	C9	114.45(16)
C3	C4	C7	123.77(17)	C1	C2	C3	120.01(19)
C3	C4	C5	118.02(18)	C9	C10	C11	119.12(19)
C5	C4	C7	118.19(17)	N1	C5	C4	123.75(19)
C4	C3	C6	122.03(16)	N1	C1	C2	123.28(19)
C2	C3	C6	120.09(17)	N3	C13	C12	120.5(2)
C2	C3	C4	117.88(18)	C12	C11	C10	120.4(2)
O3	C7	N2	121.90(18)	C13	C12	C11	118.79(19)

Table S1.3 Bond Angle of L1

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O2	C6	1.260(2)	C4	C3	1.387(3)
O1	C6	1.234(2)	C4	C7	1.493(3)
O3	C7	1.228(2)	C4	C5	1.387(3)
N2	C7	1.325(2)	C3	C2	1.380(3)
N2	C8	1.443(2)	C9	C8	1.496(3)
N3	C9	1.337(2)	C9	C10	1.371(3)
N3	C13	1.335(3)	C2	C1	1.364(3)
N1	C5	1.337(3)	C10	C11	1.372(3)
N1	C1	1.327(3)	C13	C12	1.351(3)
C6	C3	1.507(3)	C11	C12	1.370(3)

Table -S 2.1 Crystal data and structure refinement for Cu Complex

Identification code	Amide 2 Cu
Empirical formula	$C_{13}H_{15}CuN_3O_6$
Formula weight	371.81
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.5673(3)
b/Å	10.4935(4)
c/Å	16.3022(7)
α/°	90
β/°	97.043(3)
γ/°	90
Volume/Å^3	1454.52(10)
Z	4
ρ_{calc}g/cm^3	1.698
μ/mm^{-1}	1.538
F(000)	760.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.88 to 49.994
Index ranges	$-8 \le h \le 10$, $-11 \le k \le 12$, $-19 \le l \le 13$
Reflections collected	5941
Independent reflections	2540 [R_{int} = 0.0213, R_{sigma} = 0.0278]
Data/restraints/parameters	2540/0/219
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0727
Final R indexes [all data]	R_1 = 0.0337, wR_2 = 0.0759
Largest diff. peak/hole / e Å^{-3}	0.30/-0.33

Table S-2.2 Selective Bond Angle for Cu-Complex

Atom	**Atom**	**Atom**	**Angle**
O4	Cu1	N2	95.70(8)
O4	Cu1	O1	85.27(8)
O4	Cu1	N3^1	91.87(8)
N1	Cu1	O4	175.89(8)
N1	Cu1	N2	82.76(8)
N1	Cu1	O1	92.72(8)
N1	Cu1	N3^1	92.24(7)
N2	Cu1	O1	128.72(8)
N2	Cu1	N3^1	114.00(8)
O1	Cu1	N3^1	117.22(7)

Table S-2.3 Selective bond length for Cu- Complex

Atom	**Atom**	**Length/Å**
Cu1	O4	1.9530(18)
Cu1	N1	1.9446(19)
Cu1	N2	2.0111(18)
Cu1	O1	2.0506(17)
Cu1	N3^{1}	2.1861(19)

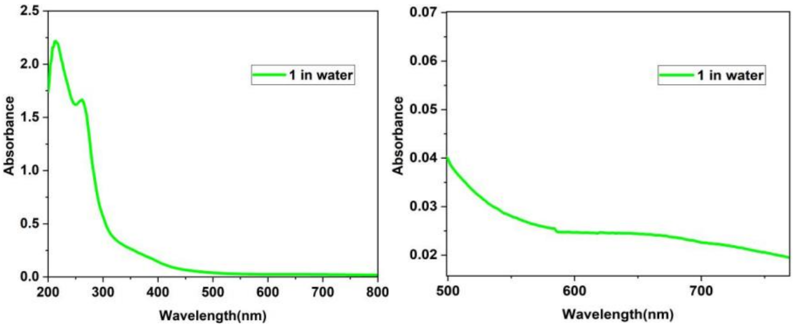
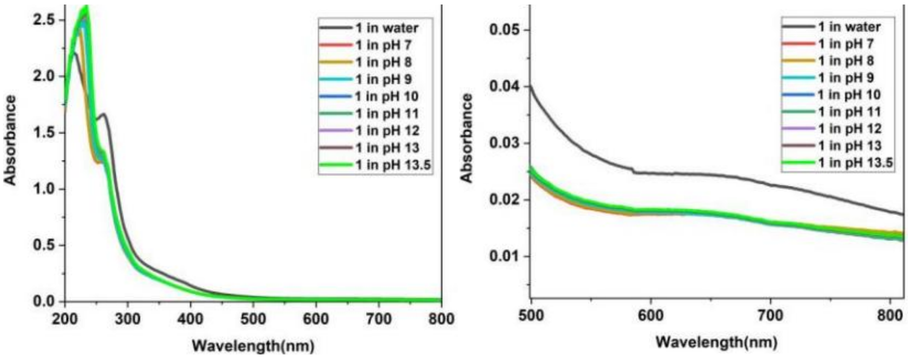


Figure S4- UV-Visible spectrum of 0.5 mM Complex **1** in water.

UV-Visible spectroscopic analysis of the complex after dissolving it in distilled water (Figure S4) reveals the presence of a broad absorption of λ_{max} at 650 nm which is a characteristic feature of Cu(II) centre d-d transition. [1-2] whereas Peak at 262 nm is designated as an $n-\pi^*$ transition.[3] Peak at 213 m can also be designated to a characteristic ligand based $\pi-\pi^*$transition.[4]



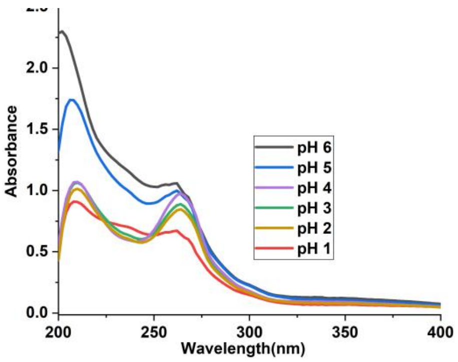


Figure S5- UV- visisble spectra of 0.5 mM complex **1** in water with pH 7-13.5, Complex **1** at pH 7-13.5 and Complex **1** at pH 1-6.

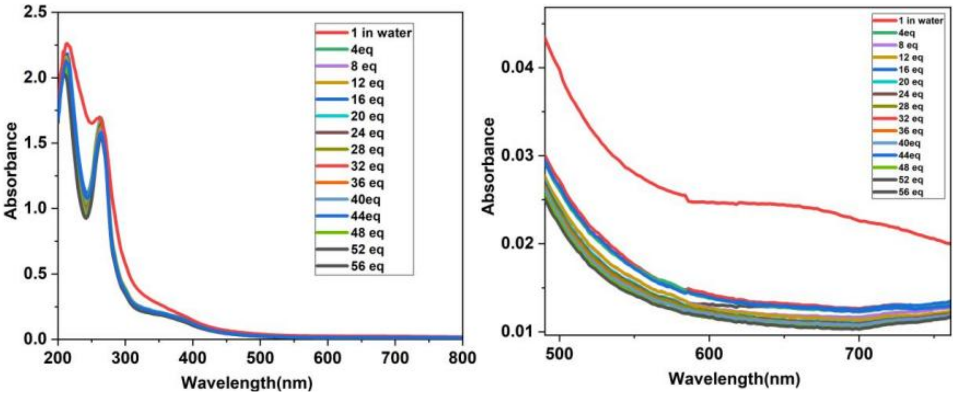


Figure S6- 0.5 mM complex **1** in water and 4-56 equivalent of Perchloric acid.

UV-Visible spectroscopic analysis of 0.5 mM complex **1** was done at pH 7-13.5 (Figure S5) where the observation are conclusively proving the higher stability of the **1** . Peak at 650 nm assigned for d-d transition acutely decreases at pH 7 whereas increases from pH 7-13.5. Same phenomenon is observed at 262 nm without any deviation in the peak. With increase in the basicity of the solution peak at 213 nm starts to shift 5-7 nm everytime the basicity of the complex solution is enhanced by using phospahte buffer solution.[5]Similarly, 0.5 mM complex solution was spectrochemically analyzed on UV-Visible spectroscopy to observe the characteristic change and stability at acidic conditions. At 650 nm a decrease in the absorbance is observed with addition of acid, this externally added acid to the system gets bonded to the metal centre, likewise at 262 nm and 213 nm the absorption decreases with increase in the acidity (4-56 equivalent perchloric acid) of the complex aqua solution (Figure S6). The addition of the proton to the metal centre[6] facilitates the metal centre to be highly involved in HER and further in reduction of proton.

Electrocatalytic Proton Reduction, Carbon dioxide Reduction and water oxidation

Typical three electrode system with glassy carbon as working , Platinum as counter and Ag/AgCl (aqs.) as reference electrodes were used. 3 M KCl was prepared and used in the counter electrode during all the electrochemical analysis. A fixed scan rate of 100 mV/s was maintained during all electrochemical experiments for cathodic and anodic scans otherwise provided.

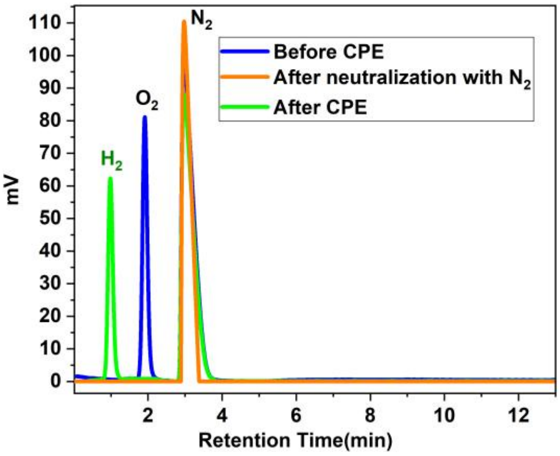


Figure S7- GC trace of H_2 for complex **1** after 2 hours of CPE at -1.6 V.

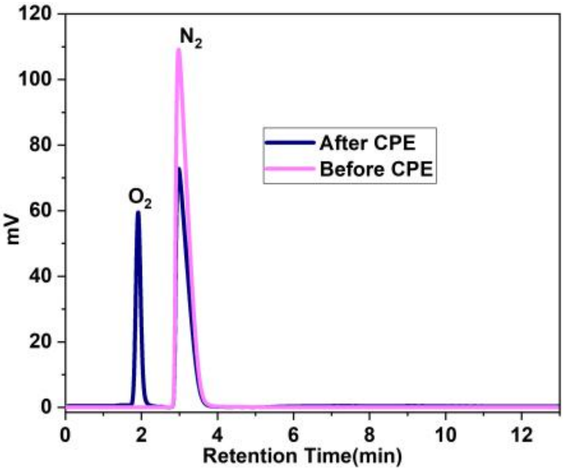
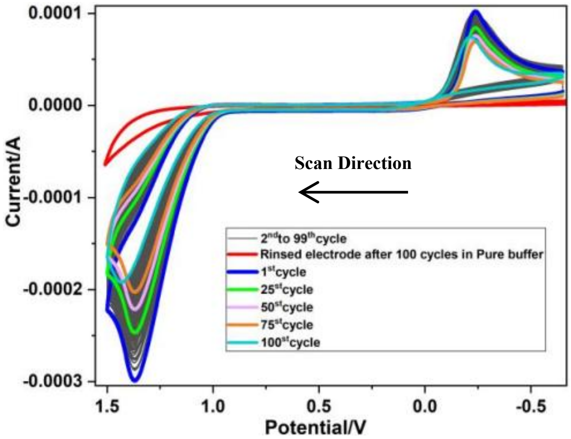
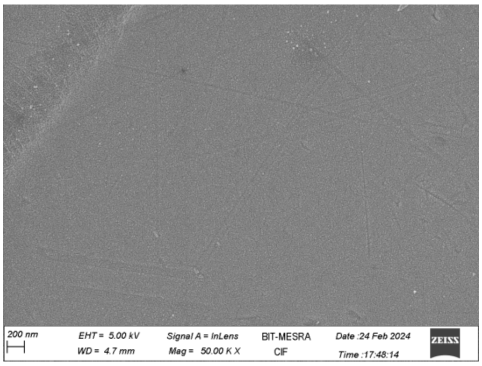
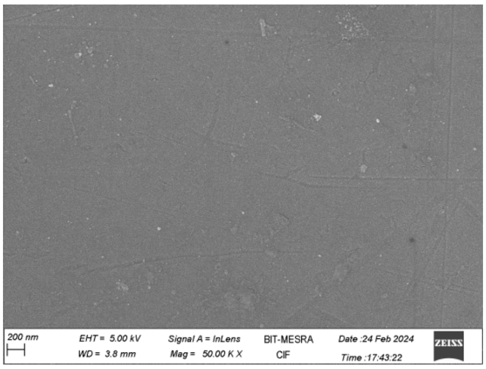


Figure S8- GC trace of O_2 after 2 hours of CPE at +1.45 V.



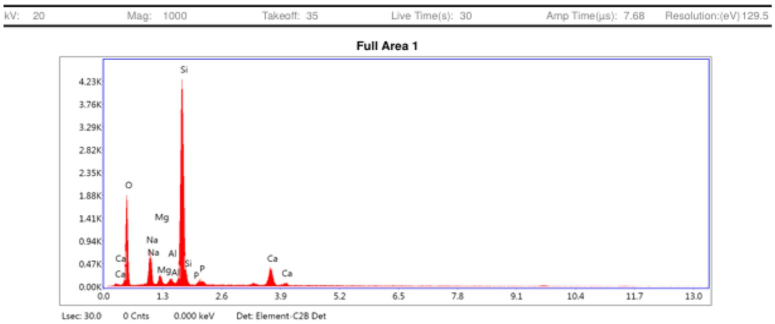


Before 100 Cycles

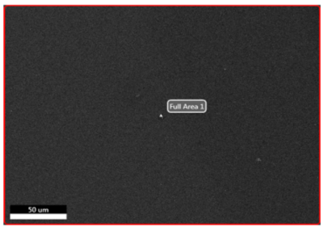


After 100 Cycles

Before 100 Cycles

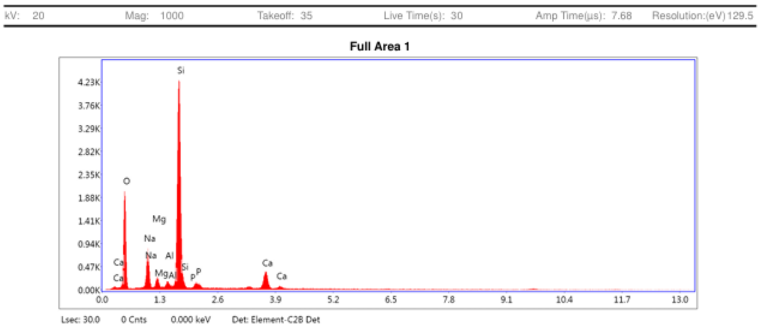


eZAF Smart Quant Results

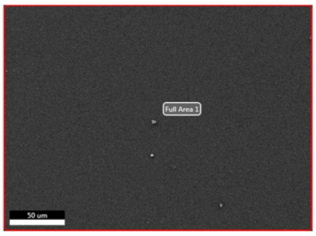


Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
O K	39.00	52.71	353.74	9.39	0.1107	1.0597	0.9690	0.2680	1.0000
NaK	10.75	10.11	150.96	8.90	0.0451	0.9636	0.9954	0.4327	1.0069
MgK	1.49	1.32	30.08	14.66	0.0074	0.9803	1.0031	0.5018	1.0128
AlK	0.46	0.37	11.17	33.41	0.0028	0.9442	1.0103	0.6334	1.0233
SiK	40.77	31.39	1156.25	4.05	0.2978	0.9651	1.0171	0.7539	1.0037
P K	0.22	0.15	3.67	22.15	0.0011	0.9271	1.0235	0.5451	1.0060
CaK	7.31	3.95	121.99	5.64	0.0623	0.9116	1.0505	0.9179	1.0172

After 100 Cycles

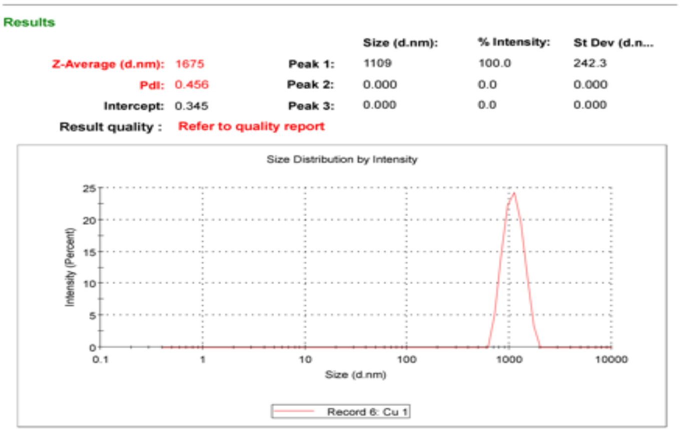


eZAF Smart Quant Results



Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
O K	39.73	53.40	385.31	9.28	0.1152	1.0588	0.9696	0.2738	1.0000
NaK	10.89	10.19	159.52	8.87	0.0456	0.9628	0.9960	0.4317	1.0068
MgK	1.66	1.47	35.12	14.33	0.0083	0.9795	1.0036	0.5000	1.0125
AlK	0.48	0.38	12.14	28.85	0.0029	0.9434	1.0108	0.6300	1.0228
SiK	40.02	30.65	1181.72	4.08	0.2908	0.9642	1.0176	0.7508	1.0037
P K	0.24	0.17	4.31	22.40	0.0012	0.9263	1.0240	0.5481	1.0059
CaK	6.98	3.74	121.85	5.63	0.0594	0.9108	1.0509	0.9191	1.0174

DLS



Results

			Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	1675	Peak 1:	1109	100.0	242.3
PdI:	0.456	Peak 2:	0.000	0.0	0.000
Intercept:	0.345	Peak 3:	0.000	0.0	0.000

Result quality : Refer to quality report

Figure S9- 100 cycles of consecutive CV at pH 13.5 for complex **1** and CV of rinsed working electrode (glassy carbon) in pH 13.5 buffer. FESEM images of glassy carbon before 100 Cycles of CV and after 100 cycles of CV at pH 13.5. EDS images of glassy carbon before 100 Cycles of CV and after 100 cycles of CV at pH 13.5(ITO only for FESEM and EDS). DLS of the catalytic solution after 2 hours of CPE at +1.45 V vs Ag/AgCl at pH 13.5 using glassy carbon.

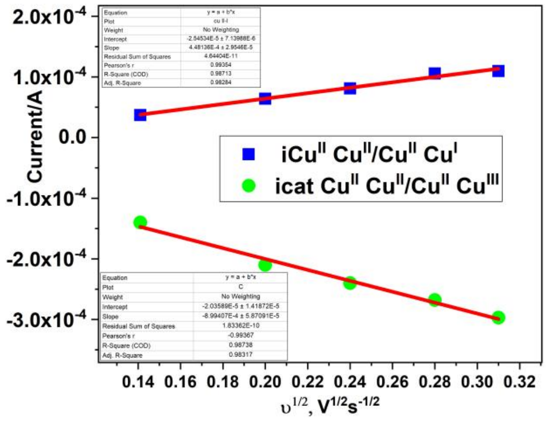
Since the design of the FESEM/EDX machine doesn't allowed us to mount the glassy carbon on for analysis, ITO glass was used in the rerun of 100 cycles of CV at pH 13.5 and analyze for any metal oxide nano-particles.

Calculation of K_{cat} for water oxidation through peak current method

The slope of peak current of complex **1** Cu^{II} Cu^{II}/Cu^{II} Cu^{I} couple at different scan rate *vs* square root of the respective scan rate results in the calculation of diffusion coefficient when used against the Randles-Sevcik relation (eq S1). The scan rate dependent measurements revealed that the Cu^{II} Cu^{II}/Cu^{II} Cu^{I} is diffusion controlled. Thus, a diffusion coefficient of 9.15x 10^{-7} cm^2s^{-1} is calculated which is reasonable in water as the solvent[2].

$$i_p = 0.446nFA[Cu]\left(\frac{\upsilon nFD_{Cu}}{RT}\right)^{1/2} \qquad \text{eq S1}$$

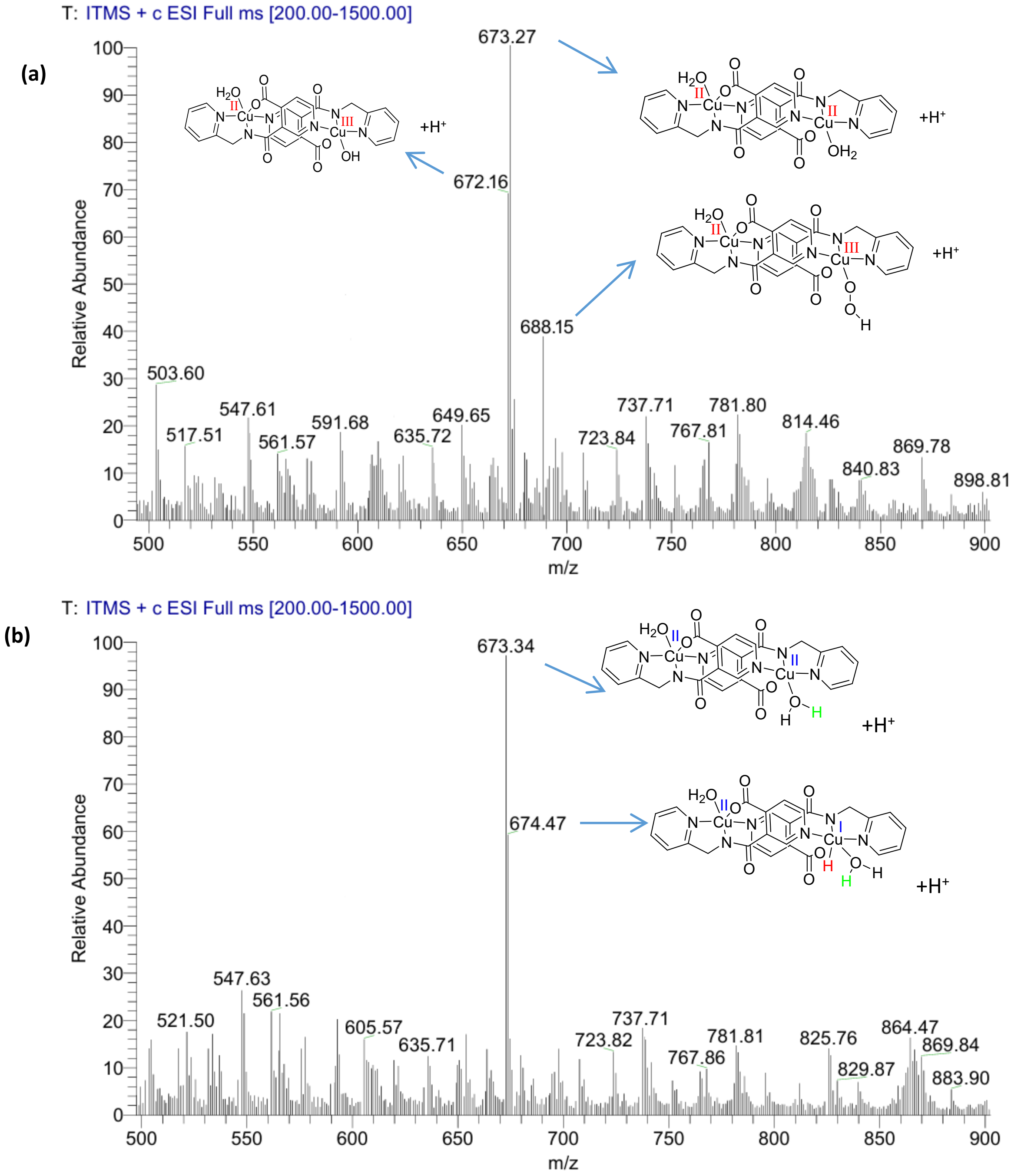
$$i_{cat} = n_{cat}FA[Cu](k_{cat}D_{Cu})^{1/2} \qquad \text{eq S2}$$



Equation	y = a + b*x
Plot	cu II-I
Weight	No Weighting
Intercept	-2.54534E-5 ± 7.13988E-6
Slope	4.48136E-4 ± 2.9546E-5
Residual Sum of Squares	4.64404E-11
Pearson's r	0.99354
R-Square (COD)	0.98713
Adj. R-Square	0.98284

Equation	y = a + b*x
Plot	C
Weight	No Weighting
Intercept	-2.03589E-5 ± 1.41872E-5
Slope	-8.99407E-4 ± 5.87091E-5
Residual Sum of Squares	1.83362E-10
Pearson's r	-0.99367
R-Square (COD)	0.98738
Adj. R-Square	0.98317

Figure S10- The plot of i_{cat} Cu^{II} Cu^{II}/Cu^{II} Cu^{III} and iCu^{II} Cu^{II}/Cu^{II} Cu^{I} vs the square root of the scan rate.


(a)
T: ITMS + c ESI Full ms [200.00-1500.00]
Relative Abundance
m/z
673.27
672.16
688.15
503.60
517.51
547.61
561.57
591.68
635.72
649.65
723.84
737.71
767.81
781.80
814.46
840.83
869.78
898.81
+H+
(b)
T: ITMS + c ESI Full ms [200.00-1500.00]
Relative Abundance
m/z
673.34
674.47
521.50
547.63
561.56
605.57
635.71
723.82
737.71
767.86
781.81
825.76
829.87
864.47
869.84
883.90
+H+

(c)

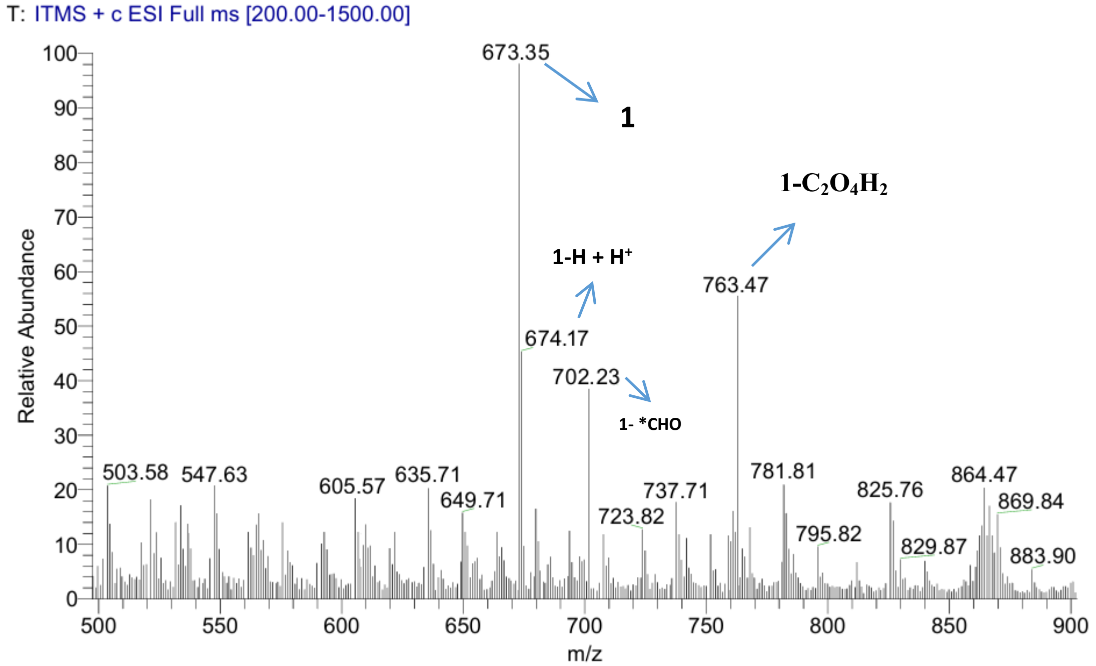


Figure S11 (a)- Mass spectrum of Complex **1** after 2 hours of CPE at +1.45 V vs Ag/AgCl, pH 13.5 Phosphate buffer and 0.5 mM concentration. (b)- Mass spectrum of 0.5 mM concentration Complex **1** after 2 hours of CPE at -1.6 V vs Ag/AgCl with 56 eq. Perchloric acid. (c) Mass spectrum of 0.5 mM concentration Complex **1** after 4.5 hours of CPE at -2.15 V vs Ag/AgCl with 8 eq. Perchloric acid and purging CO_2 for 60 minutes (see Figure-10).

Calculation of Faradaic Efficiency and TON

F.E for Hydrogen generation

Controlled Potential Electrolysis at -1.6 V vs Ag/AgCl was done for complex **1** where 4.92 C of total charge was observed with a change of 0.4 cm (h) in the height of displaced volume of catalytic solution in the cell holding glassy carbon. With a radius of 1.1 cm of the cell , volume of the gas generated was calculated using $V = \pi(r)^2h$. Thus , V= 1.05 cm^3 or 1.05 ml was calculated. Converting it into the number of moles using conversion factor of 24.0 L per mole of any ideal gas we get 0.0437 x 10^{-3} moles *i.e* the moles of H_2 generated experimentally.

Now , Total Charge = $Charge_{cat.}$-$Charge_{blank}$
= 10.22-0.007 C
= 10.21 C

Theoretical Moles of Hydrogen Made via Total Charge: 10.21 C x (1 mol e / 96485 C) x (1 mol H_2 / 2 mol e^-) = 5.29 x 10^{-5} moles H_2 theoretical

Faradaic Efficiency = (Experimental moles of H_2) / (moles of H_2 calculated theoreticaily) x 100%

= (0.0000437/0.0000529) x 100
= 83 %

TON of 1 for H_2 Generation

The Bulk electrolysis for 2 hours at -1.6 V vs Ag/AgCl with 56 eq. of perchloric acid produces 1.05 ml of Hydrogen. Catalytic loss during this timeline was calculated using the UV-Visible spectroscopic analysis of **1** before and after CPE which was ~8%. Using these values a TON was deduced.

$(1.05/22400) \times (10^3 / 0.5 \times 10^{-3} \times 2) \times (100/8)$

$\mathrm{TON}_{\mathrm{Hydrogen}} = \sim 586$

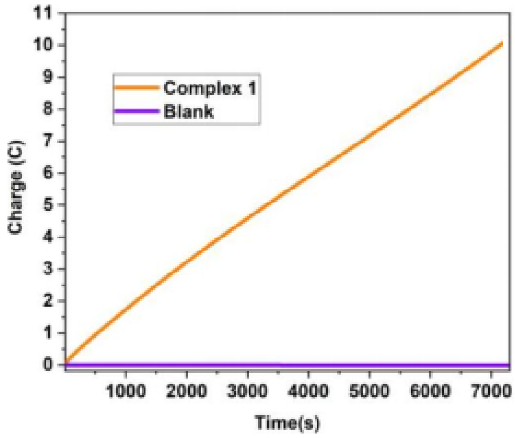


Figure S12(a)- Total charge accumulated after 2 hours of CPE of complex **1** at -1.6 V vs Ag/AgCl.

F. E for Oxygen generation

$$\mathrm{F.\ E} = 4 \times \text{amount of } O_2 \text{ (moles)} \times 100 / n \text{ (moles of electron)}$$
$$n = Q \text{ (charge)} / F \text{ (Faraday Constant)}$$

The total charge accumulated after 2 hours of CPE was found to be 10.40 C which is used to calculate the number of moles of electrons. While during the CPE a change of 0.2 cm of height in the catalytic solution was observed in the cell containing working electrode. Thus, using the formula $V = \pi(r)^2h$, a volume of 0.52 cm^3 or ml was observed . Later dividing it by 24.0 L per mole of any ideal gas we get 0.021×10^{-3} moles of O_2 generated electrochemically (experimentally). Using the above formula we get.

$= (4 \times 0.000021/ 0.00010) \times 100$

$= 84\ \%$

TON of 1 for OER

The bulk electrolysis produces 0.52 ml of O_2 in 2 hours at +1.45 V vs Ag/AgCl. CV taken after the CPE exhibits that the catalytic loss is around 17.56%. Employing the catalytic concentration and these data we can calculate the TON of **1** .

$(0.52/22400) \times (10^3/0.5 \times 10^{-3} \times 4) \times (100/17.56)$

$\mathrm{TON}_{\mathrm{Oxygen}} = 66$

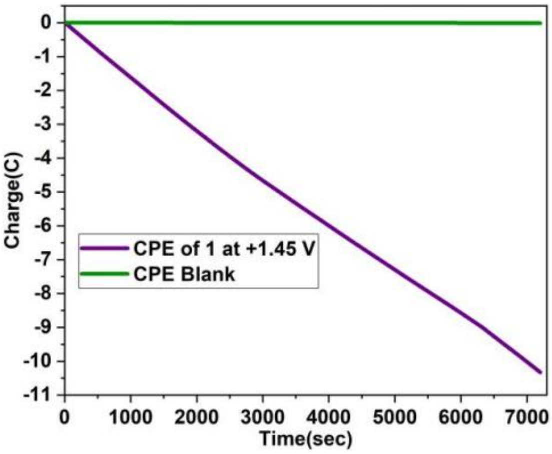


Figure S12(b)- Total charge accumulated after 2 hours of CPE of complex **1** at +1.45 V vs Ag/AgCl.

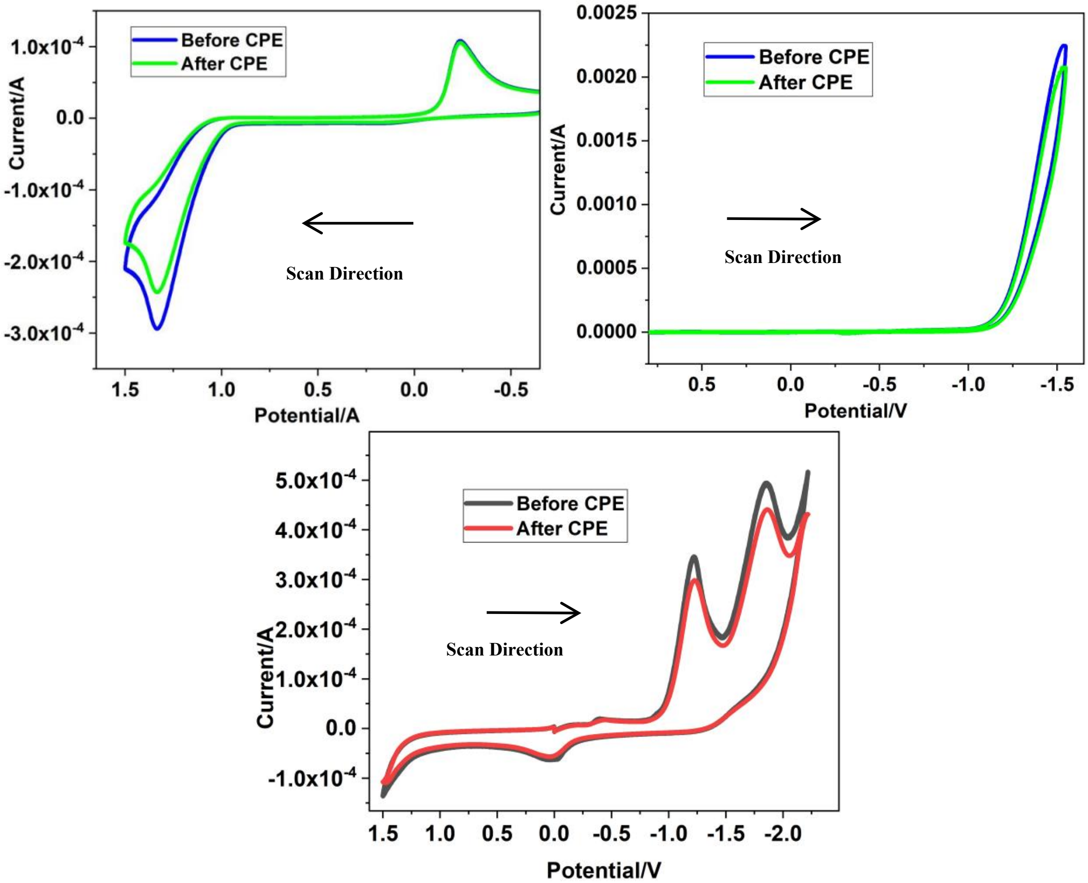


Figure S13- (A) CV of Complex **1** in phosphate buffer solution at pH 13.5 before CPE and after 2 hours of CPE with 0.5 mM conc. at +1.45 V vs Ag/AgCl **(B)** CV of **1** before and after CPE with 0.5 mM conc. at -1.6 V vs Ag/AgCl for 2 hours **(C)** CV of **1** before and after CPE with 0.5 mM conc. at -2.15 V vs Ag/AgCl for 4.5 hours.

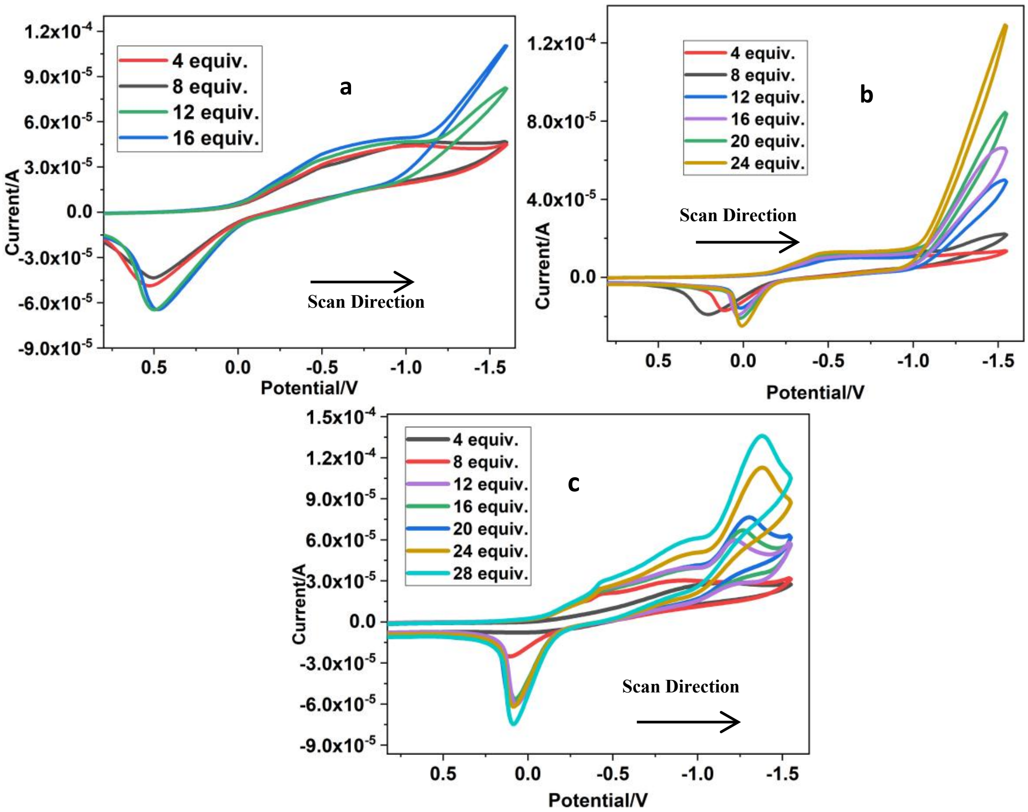


Figure S14- CV of cathodic segment **1** in water, c = 0.5 mM, Scan rate =100 mV/s, internal reference Ag/AgCl (Aqueous), Working electrode-glassy Carbon in different acids. (a) Acetic acid (b) orthophospheric acid (c) Hydrochloric acid.

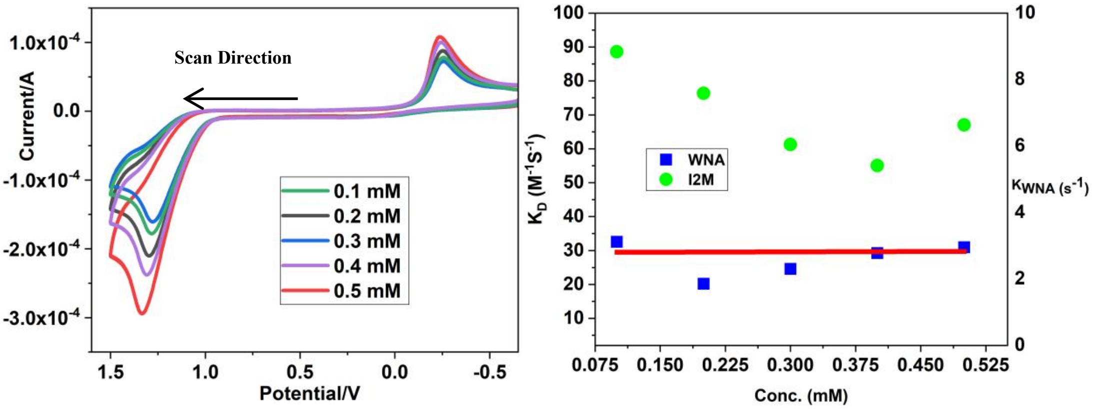
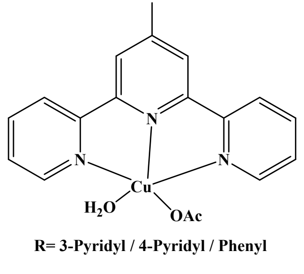


Figure S15- CV of complex **1** with concentration 0.1 mM to 0.5 mM in pH 13.5 phosphate buffer solution with scan rate of 100 mV/s and glassy carbon working electrode .

Table S3- of comparative catalytic efficiency

Catalyst	Efficiency	Experimental Condition	Working Electrode	Process	Ref.
1	TOF- H_2 = 1679 s^{-1}	Perchloric acid in Water	Glassy Carbon	Electrochemical	This work

	TOF- O_2 = 31 s^{-1}	Sodium phosphate buffer, pH 13.5	Glassy Carbon	Electrochemical	This work
	TOF-CO_2RR = 4 h^{-1}	CO_2+ Perchloric acid in Water	Glassy Carbon	Electrochemical	This work
2-4	TOF- H_2 = 1473 s^{-1},700 s^{-1},926 s^{-1}	AcOH in 95:5 (v/v) DMF/H_2O	Glassy Carbon	Electrochemical	3
5	TOF- O_2 = 8.03 s^{-1}	KOH in water	Boron-doped diamond	Electrochemical	4
6	TOF- O_2 = 0.12 s^{-1}	Phosphate buffer, pH 12.0	Glassy Carbon	Electrochemical	5
7	TOF- O_2 = 0.4 s^{-1}	pH 12.4, 0.1 M NaOH/NaOAc	Glassy Carbon	Electrochemical	6
8-10	TOF- O_2 = 88 s^{-1},1462 s^{-1},10 s^{-1}	0.1M phosphate buffer at pH13.0	Glassy Carbon	Electrochemical	7
11	TOF- O_2 = 100 s^{-1}	0.1M aqueous electrolyte (NaOAc,NaOH),pH=11.8–13.3	Glassy Carbon	Electrochemical	8
12	TON- H_2 = 364	phosphate buffer at pH 7, solvent water	Glassy Carbon	Electrochemical	9
13	TOF- H_2 = 303 s^{-1}	TFA,0.1 M $(Bu_4N)PF_6$	Glassy Carbon	Electrochemical	10
14-15	F.E = 72% and 84%	DMF using 0.1M TBAP	Glassy Carbon	Electrochemical	12
16	TOF = 1.6194 X $10^{-2}h^{-1}$	ACN 0.1M Bu4NClO4	Glassy Carbon	Electrochemical	13



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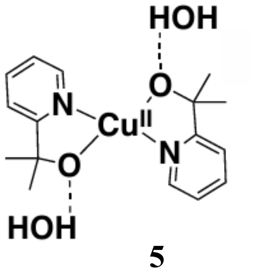

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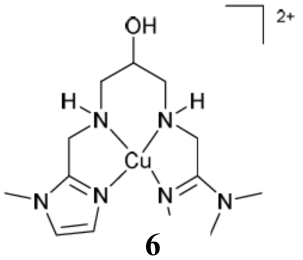

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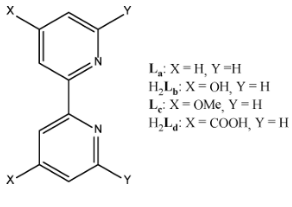

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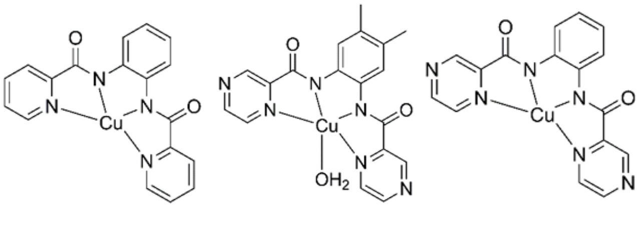

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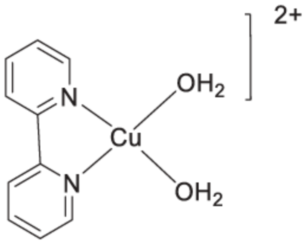

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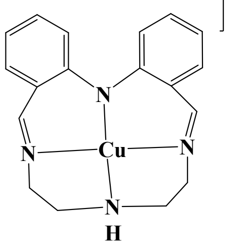

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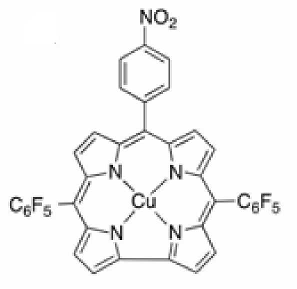

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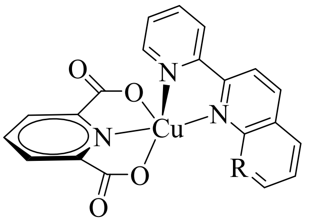
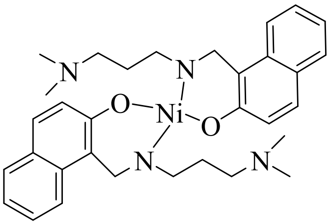


R= N=14
R= CH=15



16

Figure S16- Copper based proton reducing and water oxidizing catalysts

Elemental Analysis

The CHNS analysis was done to determine the % composition of C, N, H and S in the parent complex Dinuclear Cu-complex: **$Cu_2L_2.2H_2O$** which further disintegrates into **1**. Thus, the Anal.Calc.for Chemical Formula: $C_{26}H_{22}Cu_2N_6O_8$ (%) : C 46.36; H 3.29; Cu 18.87; N 12.48; O, 19.00. Found: C 46.38; H 3.307; N 12.43, S 0.007.

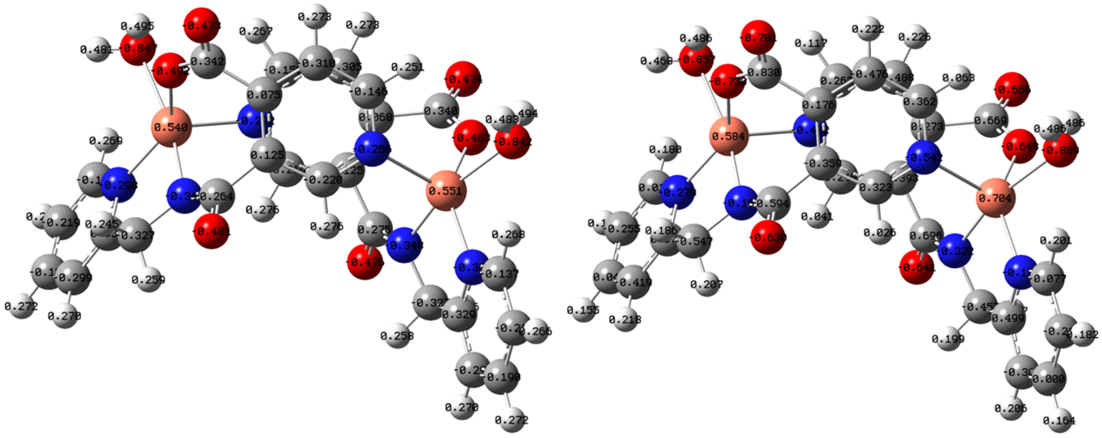


Figure S 17- (a) Atomic charges obtained using the Mulliken population analysis (b) Electrostatic Potential Charges (ESP) on respective atoms for complex **1**.

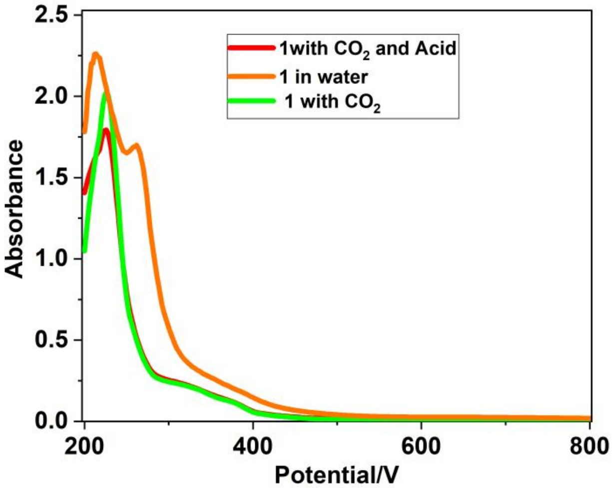


Figure S 18- UV-Visible spectra of 0.5 mM of **1**, **1** after purging CO_2 for 60 minutes and with 8 eq of perchloric acid.

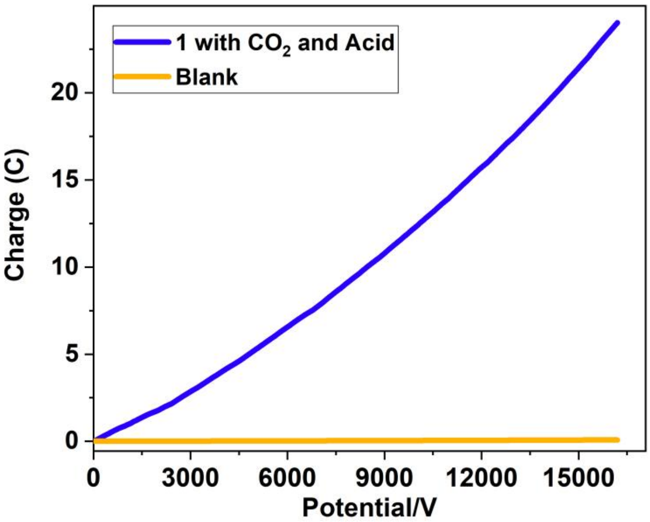
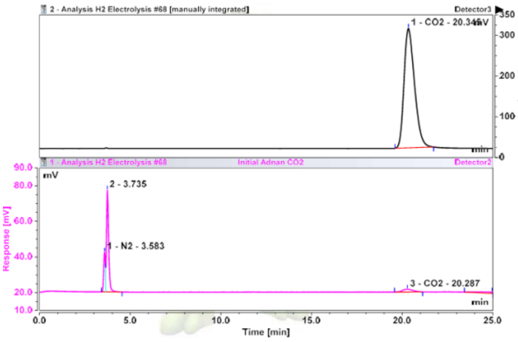
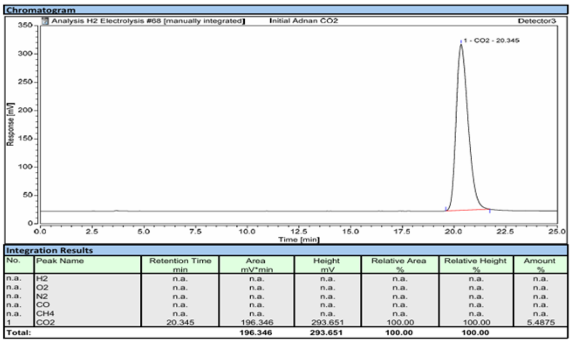


Figure S 19- 270 minutes of CPE of **1** after purging CO_2 for 60 minutes with 8 eq of perchloric acid and 0.5 mM of **1** at 2.15 V vs Ag/AgCl and CPE of blank solution withpurging CO_2 for 60 minutes with 8 eq of perchloric acid at 2.15 V vs Ag/AgCl.

Gas Chromatography For CO_2RR

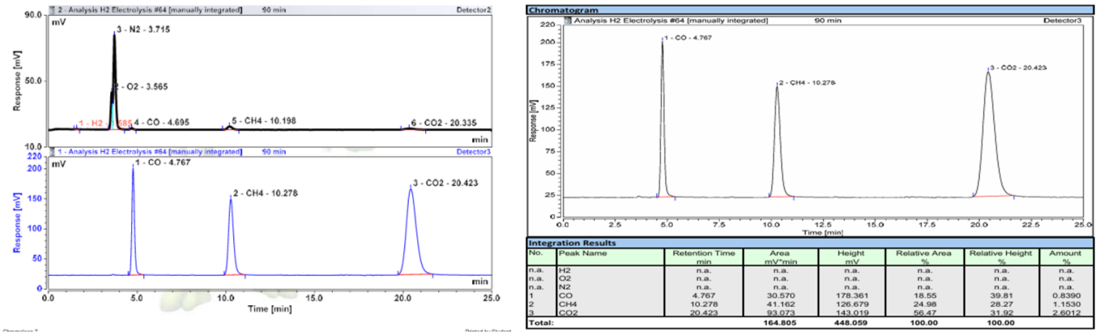




Integration Results

No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Relative Height %	Amount %
n.a.	H2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	O2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	N2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	CO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	CH4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	CO2	20.345	196.346	293.651	100.00	100.00	5.4875
Total:			**196.346**	**293.651**	**100.00**	**100.00**	

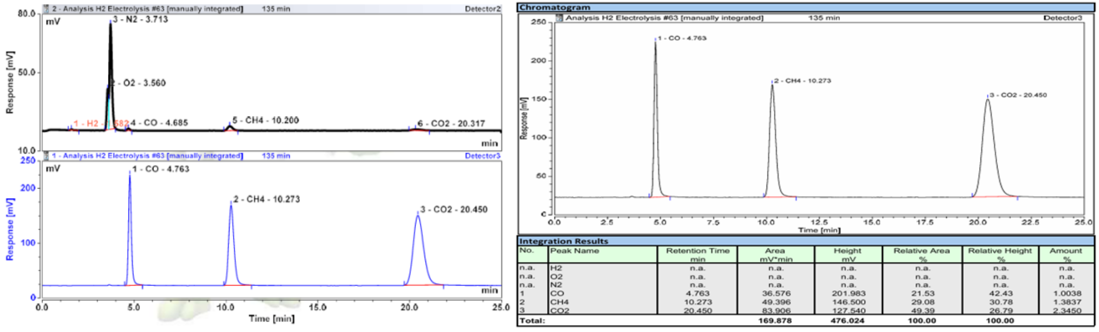
(a) Before CPE



Integration Results

No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Relative Height %	Amount %
n.a.	H2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	O2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	N2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	CO	4.767	30.570	178.361	18.55	39.81	0.8390
2	CH4	10.278	41.162	126.679	24.98	28.27	1.1530
3	CO2	20.423	93.073	143.019	56.47	31.92	2.6012
Total:			164.805	448.059	100.00	100.00	

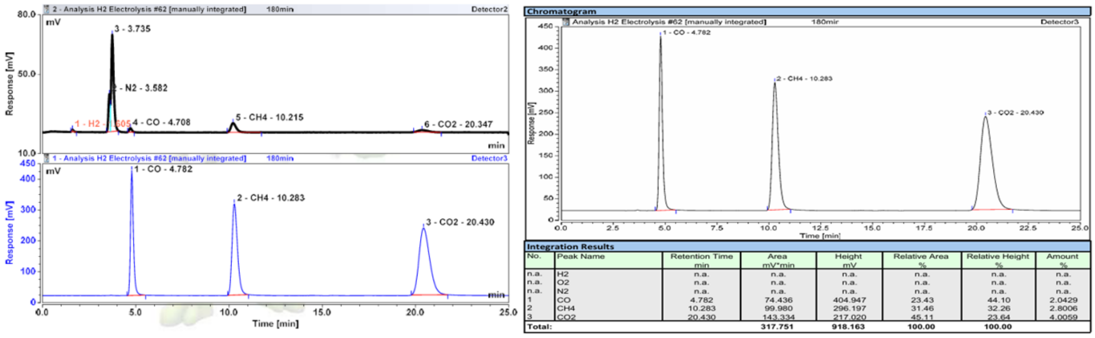
(b) After 90 min



Integration Results

No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Relative Height %	Amount %
n.a.	H2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	O2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	N2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	CO	4.763	36.576	201.983	21.53	42.43	1.0038
2	CH4	10.273	49.396	146.500	29.08	30.78	1.3837
3	CO2	20.450	83.906	127.540	49.39	26.79	2.3450
Total:			169.878	476.024	100.00	100.00	

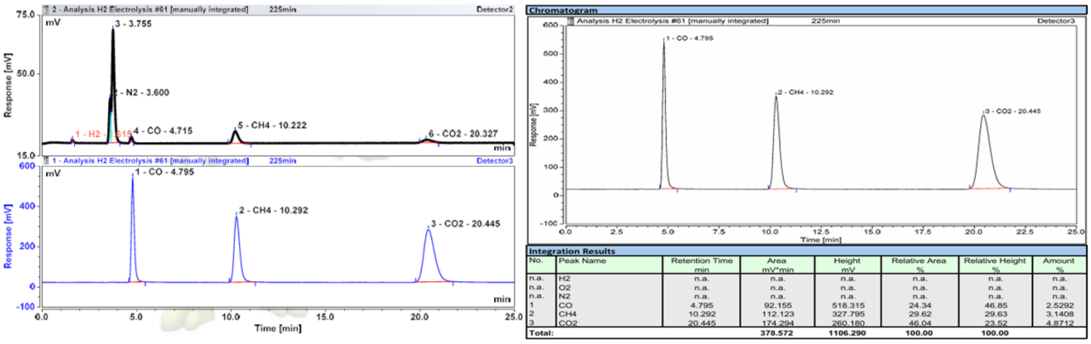
(c) After 135 min



Integration Results

No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Relative Height %	Amount %
n.a.	H2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	O2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	N2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	CO	4.782	74.436	404.947	23.43	44.10	2.0429
2	CH4	10.283	99.980	296.197	31.46	32.26	2.8006
3	CO2	20.430	143.334	217.020	45.11	23.64	4.0059
Total:			317.751	918.163	100.00	100.00	

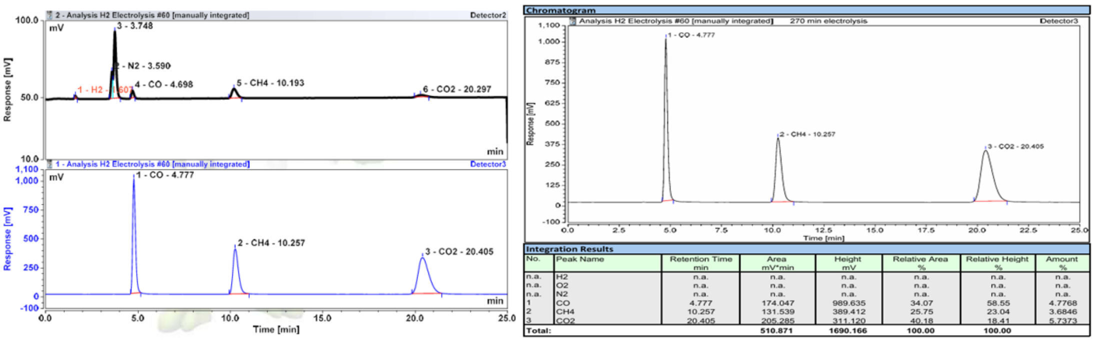
(d) After 180 min



Integration Results

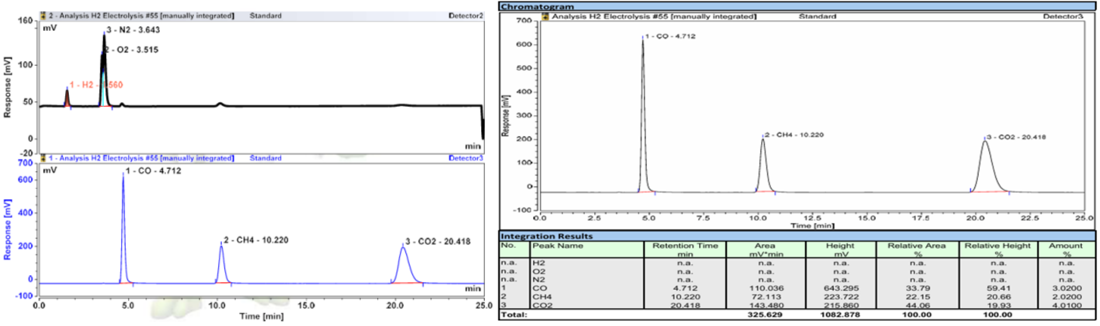
No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Relative Height %	Amount %
n.a.	H2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	O2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	N2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	CO	4.795	92.155	518.315	24.34	46.85	2.5292
2	CH4	10.292	112.123	327.795	29.62	29.63	3.1408
3	CO2	20.445	174.294	260.180	46.04	23.52	4.8712
Total:			378.572	1106.290	100.00	100.00	

(e) After 225 min



No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Relative Height %	Amount %
n.a.	H2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	O2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	N2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	CO	4.777	174.047	989.635	34.07	58.55	4.7768
2	CH4	10.257	131.539	389.412	25.75	23.04	3.6846
3	CO2	20.405	205.285	311.120	40.18	18.41	5.7373
Total:			510.871	1690.166	100.00	100.00	

(f) After 270 min



No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Relative Height %	Amount %
n.a.	H2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	O2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
n.a.	N2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	CO	4.712	110.036	643.295	33.79	59.41	3.0200
2	CH4	10.220	72.113	223.722	22.15	20.66	2.0200
3	CO2	20.418	143.480	215.860	44.06	19.93	4.0100
Total:			325.629	1082.878	100.00	100.00	

(h) Standard gas

Figure S20- GC trace after CPE for 270 minutes of CPE at -2.15 V vs Ag/AgCl with CO_2 and H^+.

K_{cat}, rate of formation, F.E and TON of Methane

Since in the standard gas the quantity of methane was 503 ppm which attributed to area under the curve as 72.113 mV min. Therefore, 1 ppm = 6.97 ppm/unit. This can be used to further calculate the amount (ppm) of gas produced during the 270 minutes of CPE.

Min	Area(mV min)	CH_4 (ppm) = area x 6.97
90	41.16	286.88
135	49.37	344.1
180	99.98	696.86
225	112.12	781.47
270	131.54	916.83

With 0.5 mM of catalyst and 3 ml of headspace we calculated.

$n = ppm/10^6 \times PV/RT$ (here, n= mole of CH_4)

Therefore, Moles of CH_4 = ppm x 1.22×10^{-10}

Min	Moles of CH_4 = ppm x 1.22×10^{-10}
0	0
90	3.5×10^{-8}
135	4.19×10^{-8}
180	8.50×10^{-8}
225	9.53×10^{-8}
270	11.18×10^{-8}

Now , the rate of generation of CH_4 = Δmol of CH4/ Δt

Rate = $(11.18- 0) \times 10^{-8} / 16200$

= 6.9×10^{-12} mol/s

Since, we used 0.5 mM of catalyst

$$\text{TON} = \frac{\text{Total moles of } CH_4}{[\text{cat}]}$$

$$= \frac{11.18 \times 10^{-8}}{5 \times 10^{-7}}$$

TON = 0.22

TOF = TON/ Time = 0.22 / 4.5 hours

$= 0.05\ h^{-1}$

Faradaic efficiency = n N F / Q ×100%

Q: the charge obtained from the test during CO_2 reduction (C), F: faradaic constant (96485 C/mol), N: the number of electrons required to generate the product, n: the moles of products (mol).

$$F.E_{CH4} = \frac{8 \times 11.18 \times 10^{-8} \times 96485}{24.1} \times 100 = 0.36\ \%$$

K_{cat}, rate of formation , F.E andTON of carbon monoxide

Since in the standard gas the quantity of methane was 500 ppm which attributed to area under the curve as 110.03 mV min. Therefore, 1 ppm = 4.54 ppm/unit. This can be used to further calculate the amount (ppm) of gas produced during the 270 minutes of CPE.

Min	Area(mV min)	CH_4 (ppm) = area x 4.54
90	30.57	138.78
135	36.57	166.02
180	74.43	337.91
225	92.15	418.36
270	174.04	790.14

With 0.5 mM of catalyst and 3 ml of headspace we calculated.

n= ppm/10^6 x PV/RT (here, n= mole of CH_4)

Therefore, Moles of CH_4 = ppm x 1.22×10^{-10}

Min	Moles of CH_4 = ppm x 1.22×10^{-10}
0	0
90	1.69×10^{-8}
135	2.02×10^{-8}
180	4.12×10^{-8}
225	5.1×10^{-8}
270	9.63×10^{-8}

Now , the rate of generation of CO = Δmol of CH4/ Δt

Rate = $(9.63- 0) \times 10^{-8} / 16200$

$= 5.9 \times 10^{-12}$ mol/s

Since, we used 0.5 mM of catalyst

$$\text{TON} = \frac{\text{Total moles of CO}}{[\text{cat}]}$$

$$= \frac{9.63 \times 10^{-8}}{5 \times 10^{-7}}$$

TON = 0.20

TOF = TON/ Time = 0.2 / 4.5 hours

$= 0.045\ h^{-1}$

Faradaic efficiency = n N F / Q ×100%

Q: the charge obtained from the test during CO_2 reduction (C), F: faradaic constant (96485 C/mol), N: the number of electrons required to generate the product, n: the moles of products (mol).

$$F.E_{CO} = \frac{2 \times 9.63 \times 10^{-8} \times 96485}{24.1} \times 100 = 0.08\ \%$$

HPLC

Detection of oxalic acid by HPLC process:-

Method for detection and measurement of oxalic acid by HPLC

Preparation of 10 mmol/l phosphate buffer (pH 2.5) for mobile phase

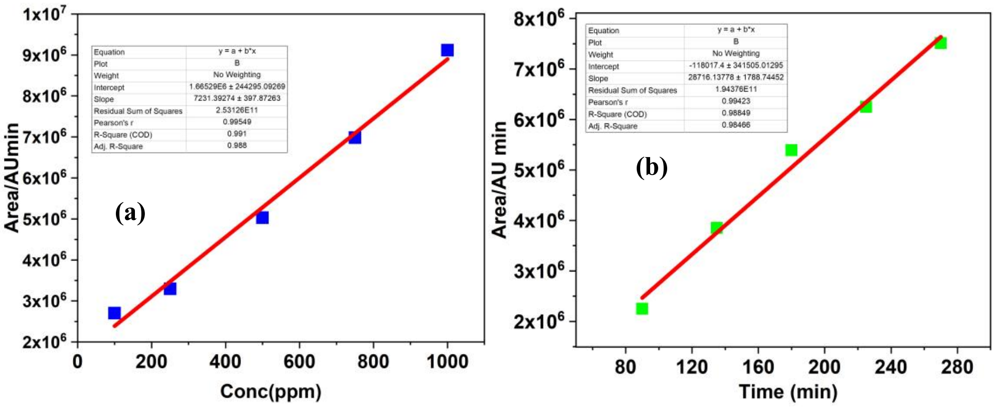
1. Preparation of 500 ml 10 mmol/l sodium dihydrogenphosphate aqueous solution in 0.005 M TBA Stock solution- 0.78g of sodium dihydrogenphosphate dihydraded was dissolved in 500 ml deionised water followed by addition of 0.848 g of TBA.
2. Preparation of 10 mmol/l phosphate aqueous solution: 0.49g of Phosphoric acid (Purity 85%) was dissolved in 500ml deionized water.
3. pH of stock solution was adjusted to 2.1 by mixing solution 1 with solution 2. Finally the solution was filtered through 0.45-µm EH filters to remove insoluble substances.

Preparation of standard oxalic acid solutions:

0.1 m Mol Oxalic acid solution was prepared by dissolving 1010.1 mg oxalic acid in 10 ml water. Solutions of different concentration were made from this stock solution by dilution with mobile phase solution.

Standard detectable oxalic acid were 1000 µgm/ml, 750 µgm/ml, 500 µgm/ml,250 µgm/ml,100 µgm/ml. Each sample was chromatographed for 12 min and the retention time of oxalic acid was found to be ~4.25 min. A linear graph (Fig- S21) was obtained by plotting the peak area vs different oxalic acid concentration.

The Chromatographic condition: - flow rate = 0.3ml/min(0.15ml/min acetonitril, 0.15ml/min 2.00 pH buffer),oxalic acid was detected at 254 nm, injection volume was 20µl.On plotting the peak area vs. concentration of the standard oxalic acid a liner plot was obtained. From the calibration curve it is possible to quantify the amount of the acids produced in the bulk electrolysis.



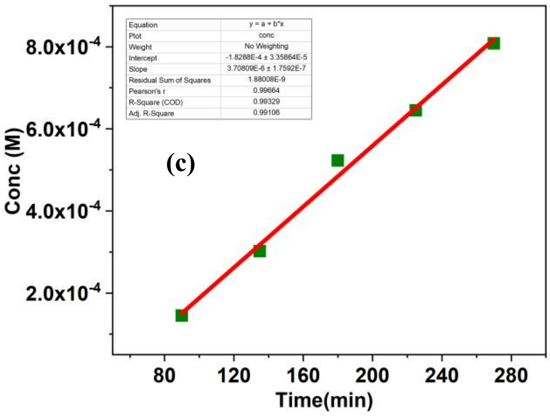


Figure S 21- (a) Area vs Concentration graph of standard solution (b) Area vs Time dependent HPLC data observed after every 45 minutes of interval (c) Concentration vs Time graph obtained from the Time dependent HPLC data observed after every 45 minutes of interval and the standard curve.

Min	ppm	mmol (ppm x 0.01/ 90.03)
90	121.87	0.01353
135	302.95	0.03363
180	516.57	0.05738
225	635.48	0.07058
270	811.21	0.09014

Rate of formation of oxalic acid

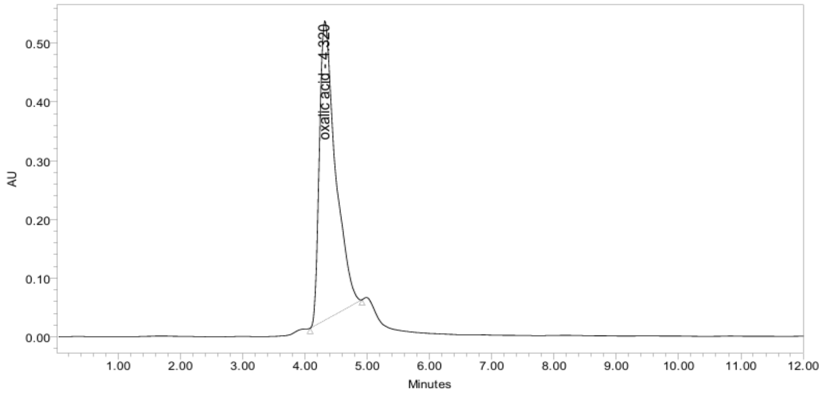
Min	Δmmol	Rate (mmol/s)
90-135	0.02	7.44×10^{-6}
135-180	0.023	8.80×10^{-6}
180-225	0.0133	4.48×10^{-6}
225-270	0.0195	7.24×10^{-6}

Since using the observed data 811.21 ppm of oxalic acid is formed in 270 minutes and we used 0.5 mM of catalyst.

Since, TON = Moles of product/ Moles of catalyst
= 9.014×10^{-3} moles/ 5×10^{-4} moles
$\text{TON}_{\text{oxalic acid}} = \sim 18$
TOF = TON/ Time = 18 / 4.5 hours
= 4 h^{-1}

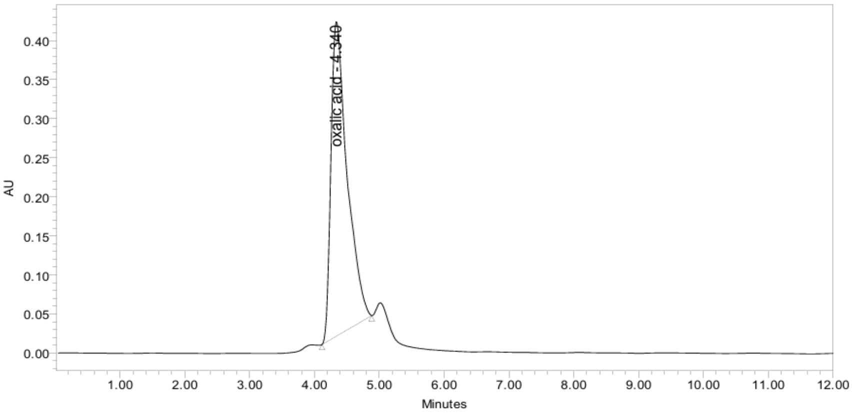
Therefore, overall rate of formation of oxalic acid = Δmmol of catalyst/ time
= 0.09013-0.01353 mmol/ 10800 s
= 7.10×10^{-6} mmol/s = 7.10×10^{-9} mol/s

HPLC plots
For Standard



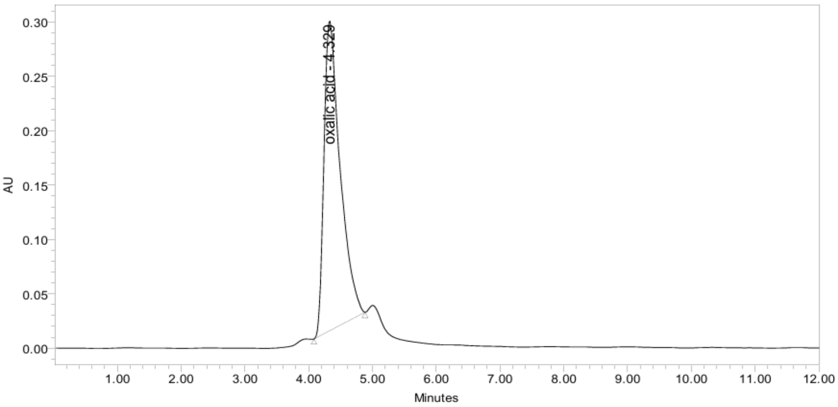
	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.320	9114850	100.00	510579

1000 ppm



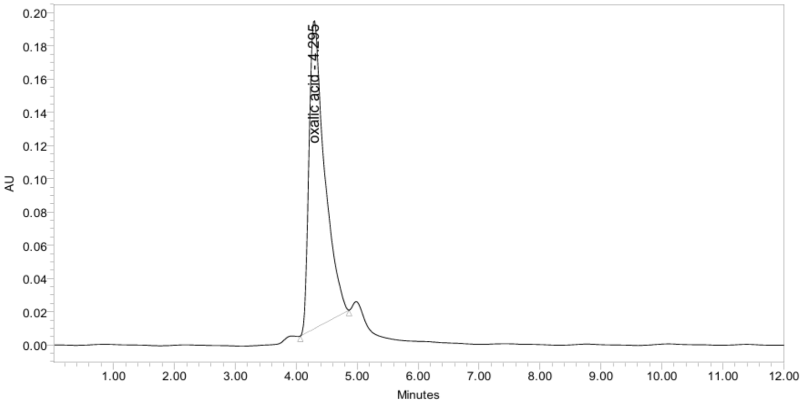
	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.340	6980700	100.00	403629

750 ppm



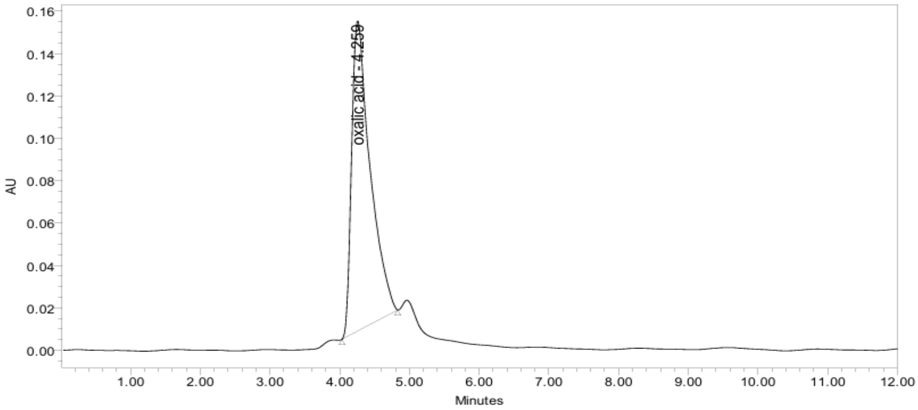
	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.329	5032819	100.00	285006

500 ppm



	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.295	3294511	100.00	185444

250 ppm

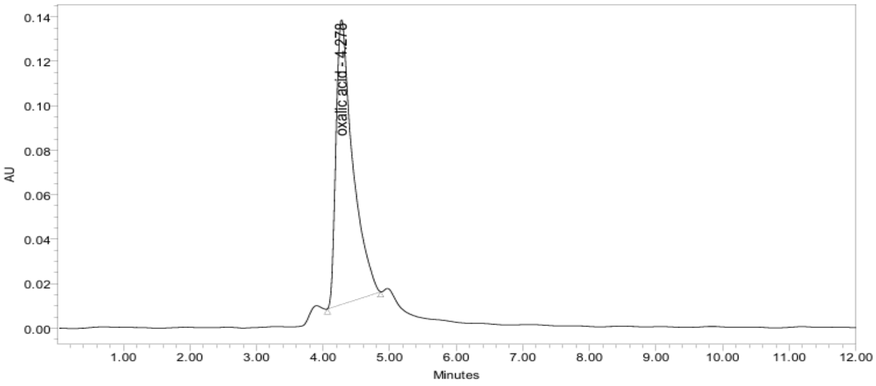


	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.259	2705196	100.00	146850

100 ppm

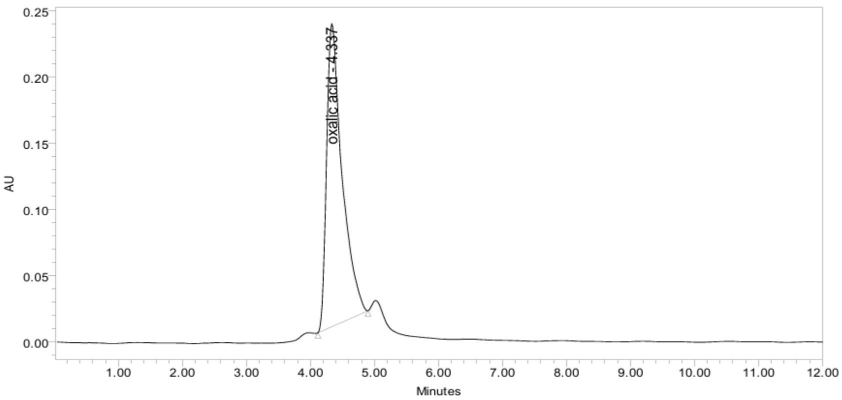
Figure S 22- HPLC plot of Standard oxalic solution with 100 ppm to 1000 ppm concentrartion.

Time dependent HPLC curve after 45 minutes of interval



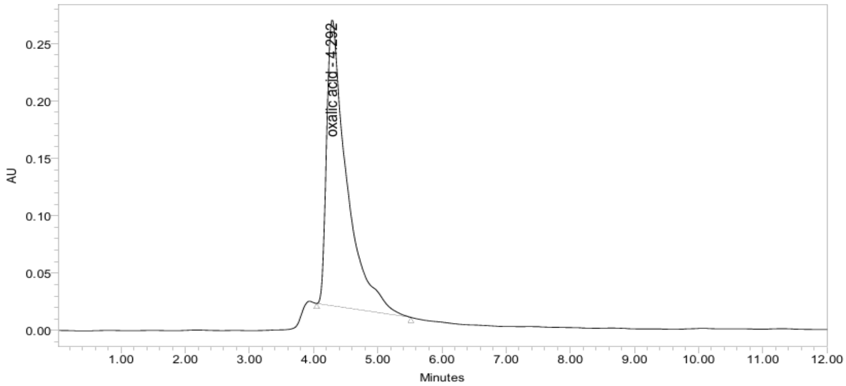
	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.278	2249880	100.00	128000

90 min



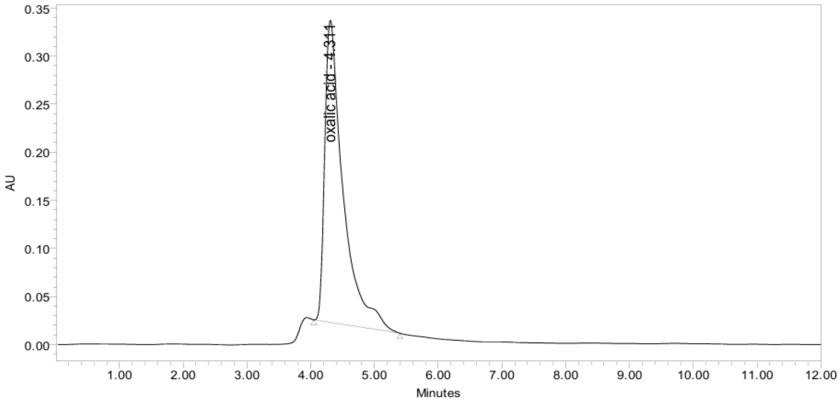
	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.337	3852853	100.00	229043

135 min



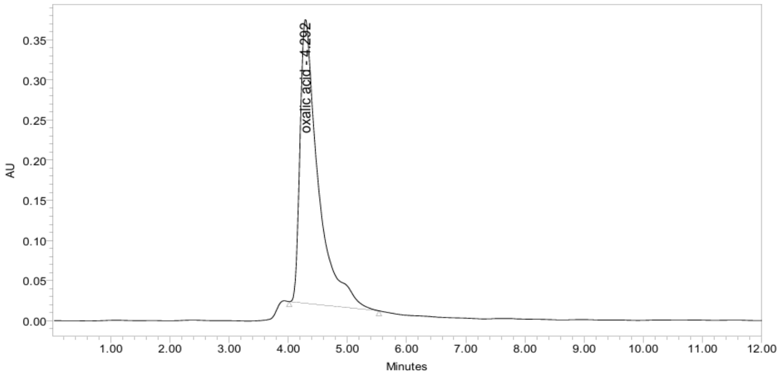
	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.292	5389679	100.00	249706

180 min



	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.311	6249175	100.00	314358

225 min



	Peak Name	RT	Area	% Area	Height
1	oxalic acid	4.292	7512850	100.00	354425

270 min

Figure S 23 - HPLC Plots observed after every 45 minutes of interval of CPE at -2.15 V after 270 minutes atarting from 90 minutes.

$$\mathrm{FE}(\%)_{\text{oxalic acid}} = \frac{n \times F \times N_{\text{produ}}}{Q_{\text{passed}}} \text{ X } 100$$

Where

n = electrons transferred per molecule of product

F = Faraday constant =96485 C mol^{-1}

N_{product} = moles of product formed

Q_{passed} = total charge passed in coulombs (C)

$Q_{\text{theoretical}} = n \times F \times N_{\text{product}}$

$Q_{\text{theoretical}} = 2 \times 96485 \times 1.1502 \times 10^{-4}$

$Q_{\text{theoretical}} = 22.175$ C

FE(%) = Qpassed / Qtheoretical×100

= 22.175 / 24.1 × 100

FE(%) = 91.99%

F.E = ~92 %

As K_{cat} , rate of formation and the TON all the products of electrochemical reduction of CO_2 is deduced. We can now calculate the selectivity[11] of the products.

$$\text{Selectivity} = n_1 / n_t \text{ x } 100$$

n_1 is the target product (in moles) generated during the CPE and n_t is the total product (in moles) generated during the CPE.

Total mole of products = 9.014×10^{-3} moles (oxalic acid) + 11.18×10^{-8} (methane) + 9.63×10^{-8} (carbon monoxide)
= 9.014+0.0001118+0.0000963
= 9.0142081×10^{-3} mol

Now,

$$\text{Selectivity}_{CH4} = n_1/ n_t \times 100$$
$$= 11.18 \times 10^{-8} \text{ mol} / 9.0142081 \times 10^{-3} \text{ mol} \times 100$$
$$= 1.2408 \times 10^{-5} \%$$

$$\text{Selectivity}_{CO} = n_1/ n_t \times 100$$
$$= 9.63 \times 10^{-8} \text{ mol} / 9.0142081 \times 10^{-3} \text{ mol} \times 100$$
$$= 1.0681 \times 10^{-5} \%$$

$$\text{Selectivity}_{\text{(oxalic acid)}} = n_1/ n_t \times 100$$
$$= 9.014 \times 10^{-3} \text{ moles} / 9.0142081 \times 10^{-3} \text{ mol} \times 100$$

$$= \sim 99.9997\%$$

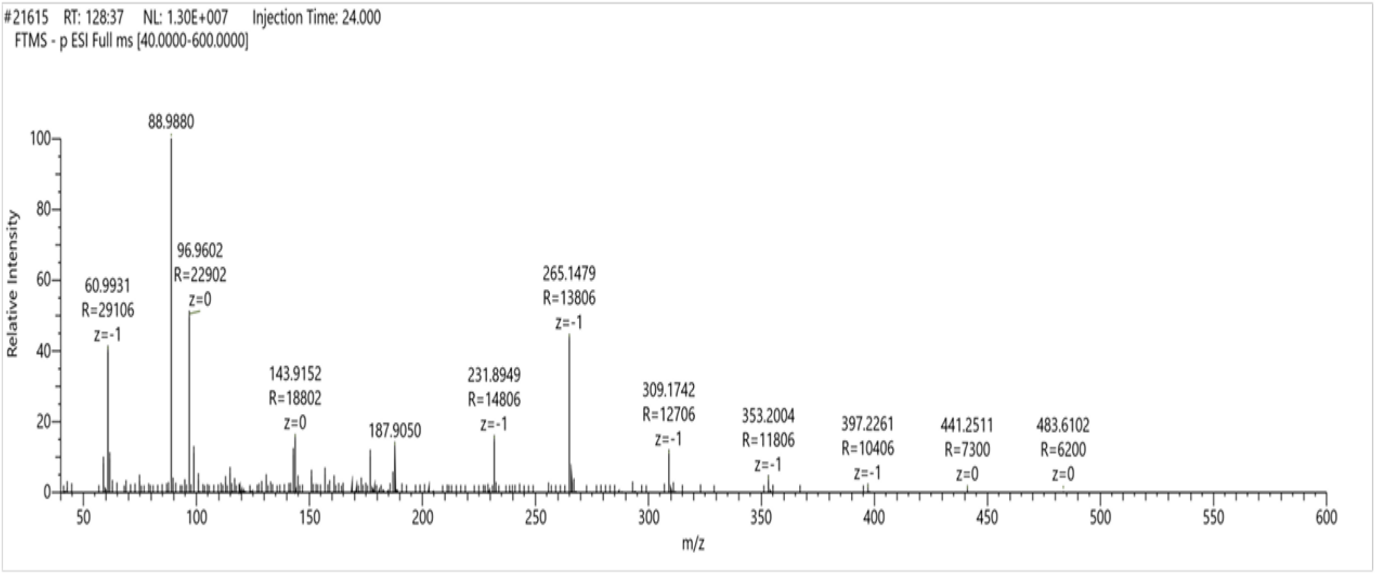


Figure S24- (a) HRMS spectra of catalytic solution after 270 minutes of CPE at -2.15 V using glassy carbon electrode in water with CO_2 and perchloric acid.

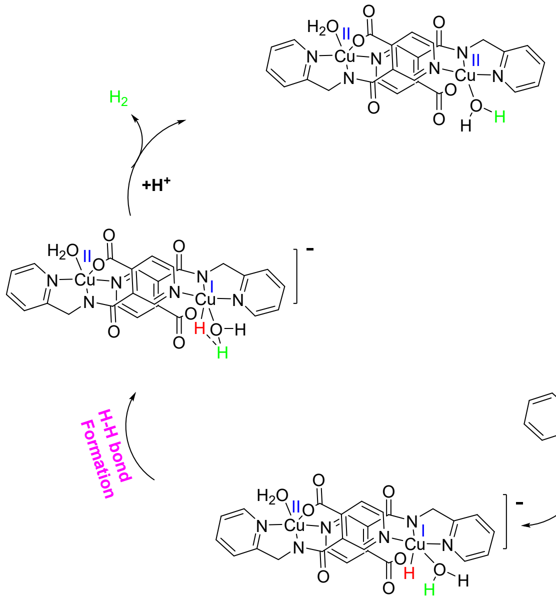


Figure S25 (a)- Plausible mechanism for Proton reduction by Complex **1**.

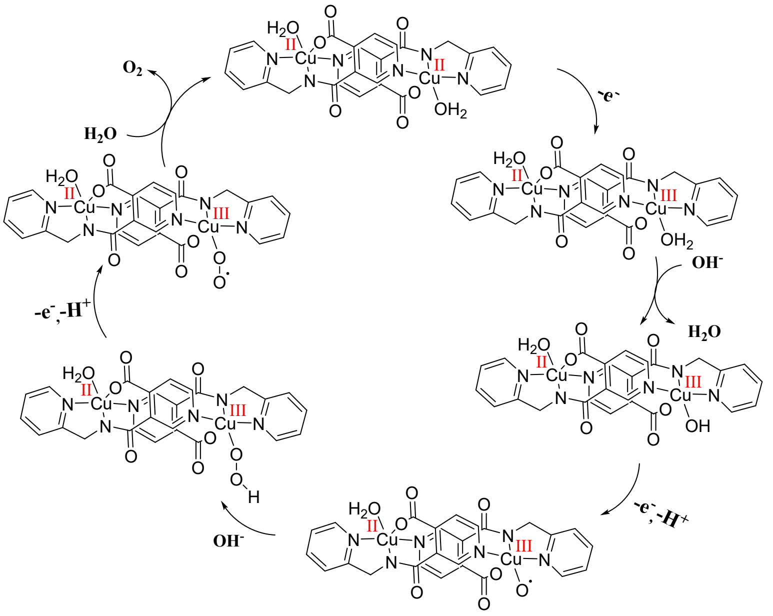


Figure S25 (b)- Plausible mechanism for Oxygen evolution reaction by Complex **1**.

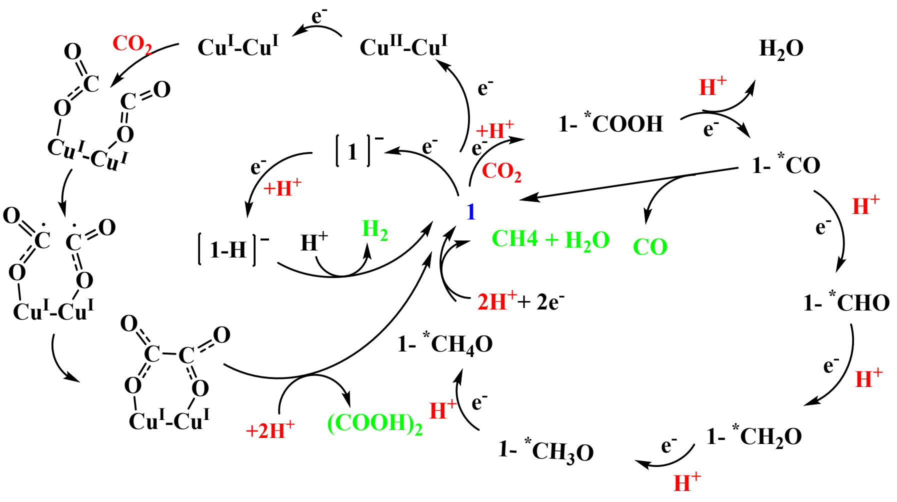


Figure S25 (c)- Plausible mechanism for the CO_2RR to $(COOH)_2$ with competitive reaction generating H_2, CO and CH_4 .

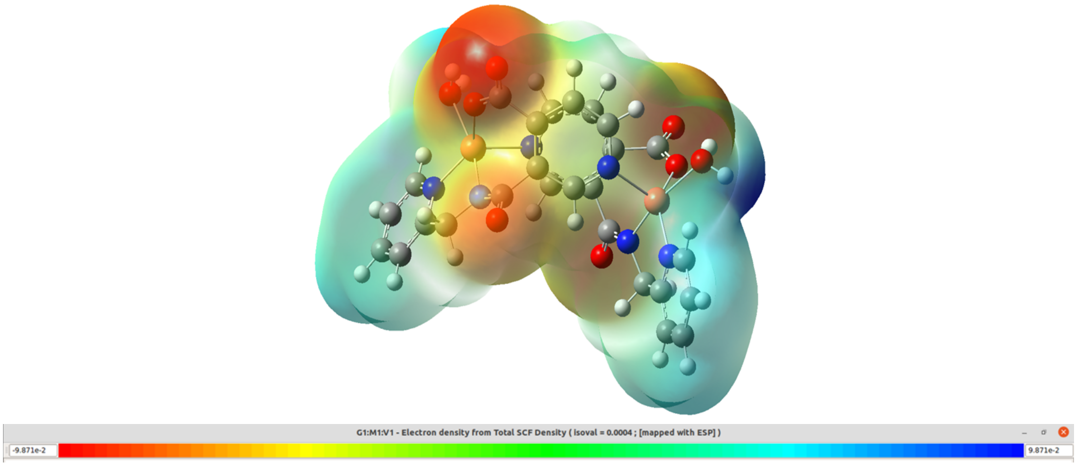


Figure S 26 - Electrostatic Potential Plots of complex **1**

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Cartesian Coordinate for Complex 1

E(UB3LYP)= -5215.150574 Hartree

C	-0.60756	-2.98214	0.34536
C	-1.63877	-1.95985	0.46634
C	-2.96385	-2.40419	0.51933
C	-3.23253	-3.75683	0.67419
C	-0.99695	-4.29364	0.40554
H	-3.76825	-1.7011	0.46025
H	-4.24115	-4.09983	0.77406
H	-0.27585	-5.06498	0.23253
N	-2.22348	-4.61766	0.7167
C	0.93002	-2.87162	0.16978
C	-1.50926	-0.40752	0.5432
O	1.54459	-3.78708	-0.43677
O	-2.51869	0.2862	0.25442
O	-0.44106	0.20374	0.90422
N	1.60566	-1.88175	0.66272
C	4.27894	2.0244	0.5745
C	3.2756	2.53511	1.4125
C	2.22404	1.69862	1.82721
C	3.16901	-0.10061	0.6743
C	4.22423	0.6792	0.19611
H	5.07396	2.65347	0.23229
H	3.3092	3.5558	1.7318
H	1.44989	2.08119	2.45904
H	4.97422	0.25705	-0.43967
C	3.01515	-1.59686	0.39466
N	2.19315	0.42135	1.42208
Cu	0.77591	-0.74621	1.82502
O	1.19732	-0.55163	3.59518
H	0.42011	-0.7281	4.13037
H	3.62741	-2.16006	1.06763
H	3.29208	-1.84071	-0.60969
H	1.49934	0.3454	3.75556

C	-1.56946	-4.06435	3.01864
C	-2.79772	-3.51111	3.04063
C	-2.9449	-2.13195	3.01926
C	-1.82165	-1.34987	2.68546
C	-0.47639	-3.29621	2.50008
H	-3.88979	-1.67579	3.2291
H	-1.91288	-0.28398	2.66359
H	0.44813	-3.76794	2.24011
N	-0.62759	-1.92233	2.38015
C	-1.50319	-5.52295	3.58813
C	-3.96814	-4.51976	3.02249
O	-1.63443	-5.73517	4.82153
O	-5.09623	-4.17414	3.46016
O	-3.79964	-5.76806	2.51159
N	-1.36934	-6.51927	2.77325
C	1.13015	-8.77779	-0.40826
C	0.26924	-8.10842	-1.292
C	-0.81358	-7.36687	-0.78524
C	-0.20021	-7.93609	1.40103
C	0.8927	-8.68814	0.96665
H	1.95578	-9.34723	-0.78104
H	0.43592	-8.16204	-2.3476
H	-1.47175	-6.85346	-1.45469
H	1.53248	-9.18231	1.6676
C	-0.56886	-7.71686	2.86481
N	-1.01982	-7.30554	0.53832
Cu	-2.45827	-6.33534	1.29599
H	0.30307	-7.58819	3.47153
H	-1.14021	-8.52764	3.26613
O	-3.594	-7.33073	0.26248
H	-4.39798	-7.51259	0.75455
H	-3.16916	-8.15858	0.02633