

Electronic Supplementary Information

Distorted octahedral Cobalt(II)-Acylpyrazolone complex with tunable lattice-strain structure - An efficient electrocatalyst for overall water splitting

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Synthesis of acylpyrazolone Schiff base ligands

Synthesis of HPMAP: 1-phenyl-3-methylpyrazolone (0.1 mol, 17.5g) was dissolved in 90-100 mL of DMF in a RB flash equipped with a stirrer and condenser. Calcium hydroxide (0.2 mol, 14.81 g) was added to the yellow solution after 2-5 min and stirring for 2h. Then, acetyl chloride (0.1 mol, 7.85g) was added to the resultant yellow pale mixture and refluxed for 2-3 hours and the reaction was followed by TLC. The formed calcium complex was decomposed by pouring the mixture into HCl solution (2N, 200mL) which gave brown colorless solid. The brown solid after filtration was washed several times with distilled water and dried in oven at 80°C. The obtained product was soluble in chloroform, ethanol, acetonitrile and insoluble in n-hexane. Yield= 56.01%: Yield: (1.1g, 56%); mp: 72-75°C

Synthesis of HPMBP: HPMBP was prepared analogously from 1-phenyl-3-methylpyrazolone (0.1 mol, 17.5g), Calcium hydroxide (0.2 mol, 14.81 g) and benzoyl chloride (0.1 mol, 14.05g) using the same procedure as followed for HPMAP synthesis. Yield: (17.55g, 80%); Mp: 85-88°C.

Synthesis of HPMTP: HPMTP was prepared analogously from 1-phenyl-3-methylpyrazolone(0.1 mol, 17.5g), Calcium hydroxide (0.2 mol, 14.81 g) and toluoyl chloride(0.1 mol, 14.49g) using the same procedure procedure as followed for HPMAP synthesis. Yield: (19.85g, 78%); mp: 82-85°C.

NMR spectrum of acylpyrazolone ligands

1-phenyl-3-methyl-4-benzoylpyrazolone (HPMBP)

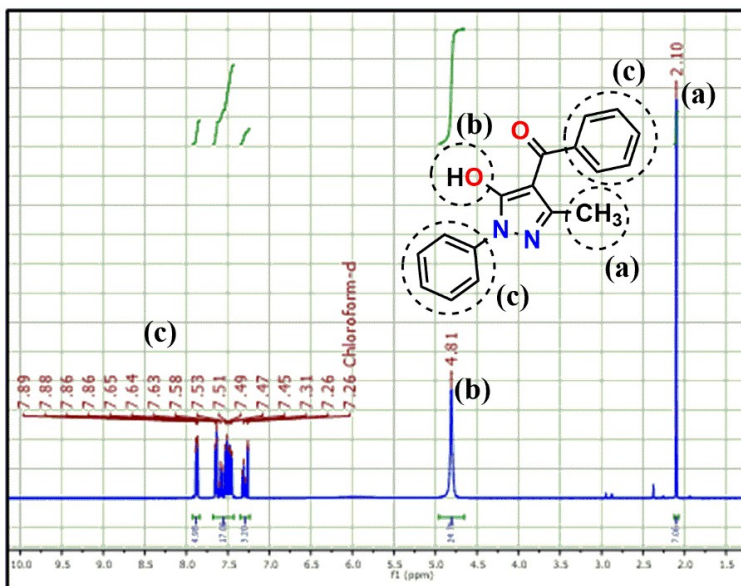


Fig. S1 ¹H NMR Spectrum of HPMBP

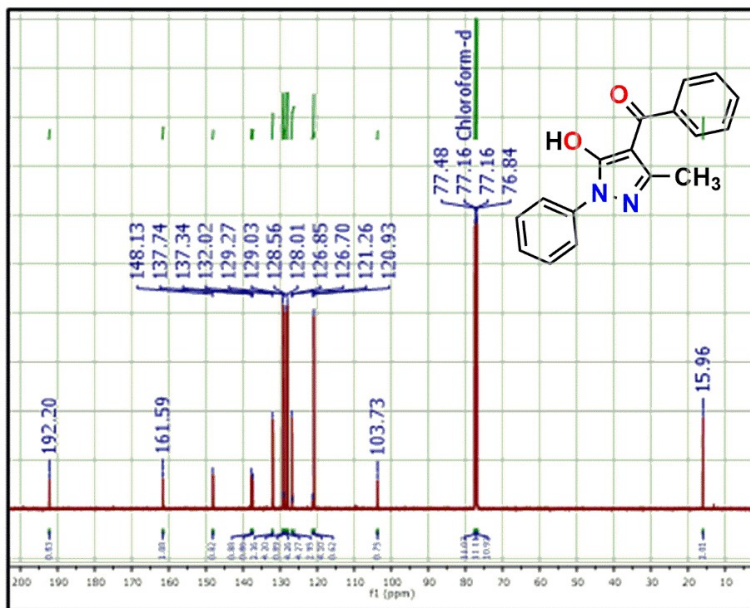


Fig. S2. ¹³C NMR Spectrum of HPMBP

¹H NMR (CDCl₃): Rf=0.57 (CH₂Cl₂: MeOH 9:1), δ= 2.10s (C₃-CH₃), 4.84s(O-H) 7.91d, 7.89-7.86dd, 7.66-7.63dd, 7.60-7.57m, 7.53-7.45m 7.33-7.29t (10H, H-ar. of HPMBP).

¹³CNMR (CDCl₃): δ=15.96s (C₃-CH₃), 103.73s(C=C-OH), 120.93s, 121.26s, 126.85, 128.01s, 128.56, 129.27s, 132.08, 137.34s, 137.74s (C-ar of HPMBP), 148.13s (C=N), 161.59s (C-OH),

192.20(C=O).¹⁻³

1-phenyl-3-methyl-4-toluoylpyrazolone (HPMTP)

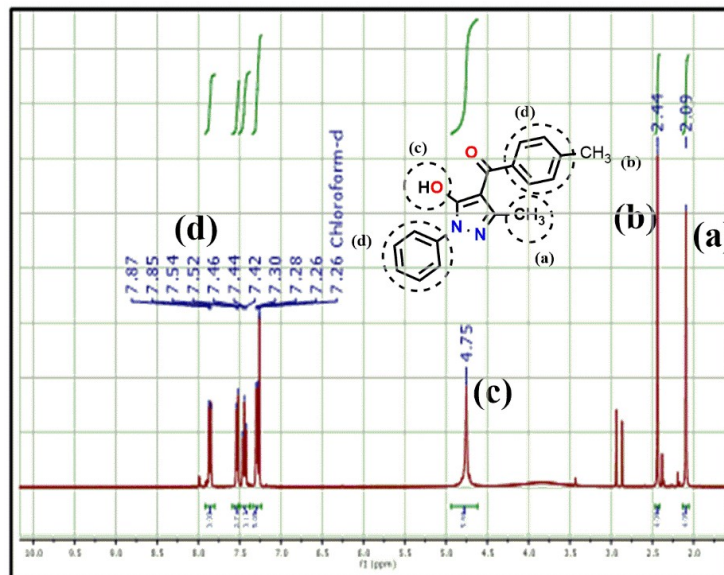


Fig. S3 ¹H NMR Spectrum of HPMTP

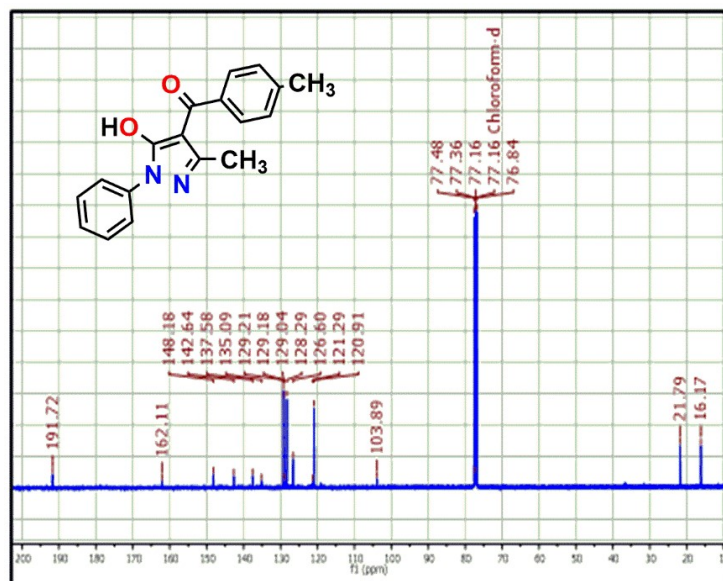


Fig. S4 ¹³C NMR Spectrum of HPMTP

¹H NMR (CDCl₃): Rf=0.78 (CH₂Cl₂:MeOH 9:1), δ=2.09s (C3-CH₃), δ=2.44s (C4-CH₃), 4.75s(O-H), 7.91-7.89d, 7.84-7.82d, 7.46-7.44d, 7.40-7.36t, 7.24-7.22d (9H, H-ar of HPMTP).

¹³CNMR (CDCl₃): δ=16.17s (C3-CH₃), δ= 21.79s (C4-CH₃), 103.89s (C=C-OH),120.91s, 121.29s, 126.60s, 128.29s, 129.04s, 129.18s, 135.09s, 137.58s, 142.64s (C-ar of HPMTP), 148.18s

(C3), 162.11s (C-OH), 191.72(C=O).^{4,5}

1-phenyl-3-methyl-4-acetylpyrazolone (HPMAP)

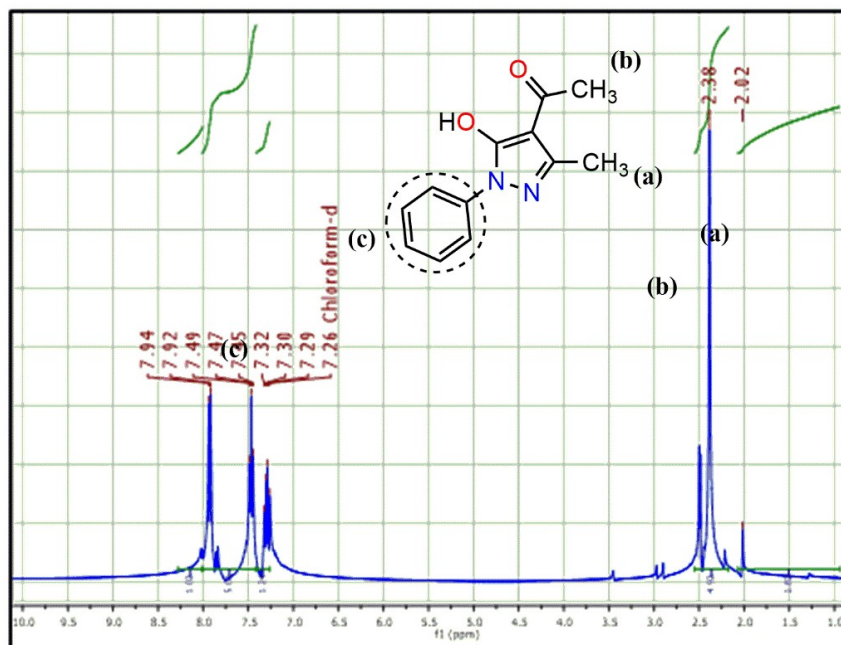


Fig. S5 ¹H NMR Spectrum of HPMAP

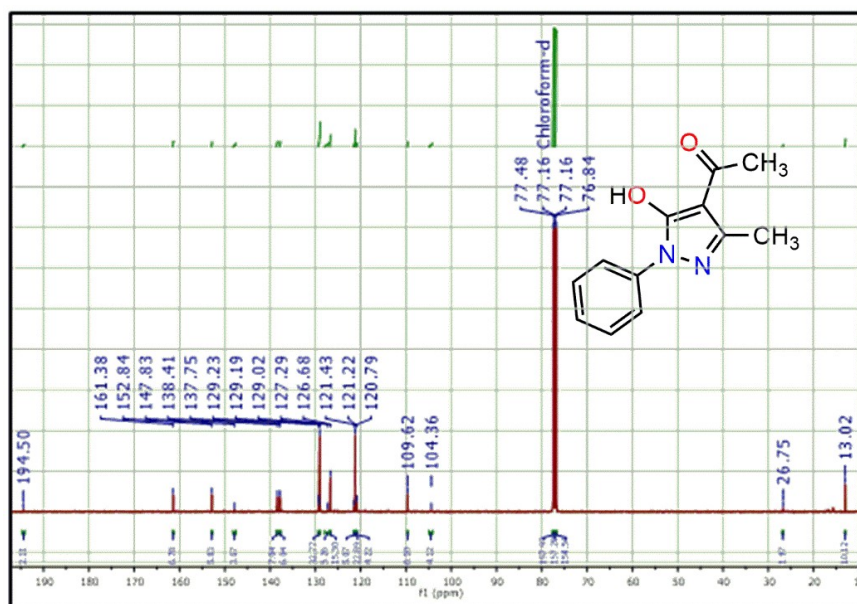


Fig. S6 ¹³C NMR Spectrum of HPMAP

FT-IR spectra of acylpyrazolone ligands

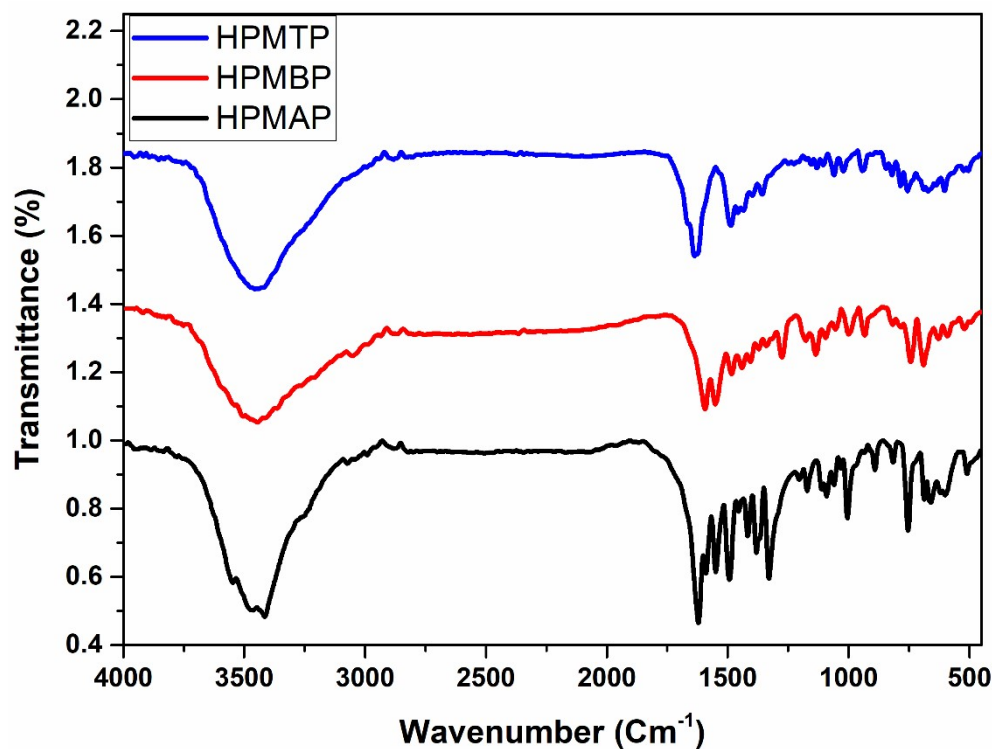


Fig. S7 FT-IR spectra of acylpyrazolone ligands: HPMAp, HPMBP and HPMTp

Table. S1 Infrared vibrational frequencies (cm^{-1}) of the acylpyrazolone ligand derivatives and their peak assignments

HPMAp	HPMBP	HPMTp	Assignments
3415.16 br	3452.95br	3476.30br	ν -OH enol form of ligand
1621.17br	1602.95br	1634.24br	ν C=O
1549.64s	1580.43s	1555.83s	ν C=N of Pyrazole ring stretching
1493.02m	1492.57m	1490.59w	ν C=C of phenyl and pyrazole
1381.46m	1349.53m	1212.42	ν as C-N of pyrazole ring
1059.99s	1140.79s	1167.31s	ν as C-O
1030.92m, 1004.49m	1033.49m, 1008.73m	1062.29m, 1025-40m	C-H in plane deformation and CH ₃ rocking
890.44br, 753.69br	791br, 791br	753.73br 943.36br,	Chelating deformation

509.91	637.13,	688.36	Chelating ring vibration
Legend = br = Broad, S = strong, W = weak, vas = Asymmetric stretching, vs = Symetric stretching			

Table. S2 CHNS analysis data and physical properties of the synthesized acylpyrazolone ligands and their Cobalt complexes

Compounds, empirical formula	Calculated (Experimental) (%)			Melting Point °C
	C	N	H	
HPMBP C ₁₇ H ₁₄ N ₂ O ₂	73.29 (71.90)	10.06 (10.3)	5.03 (6.14)	85-88
HPMTP C ₁₈ H ₁₆ N ₂ O ₂	73.95 (72.30)	9.58 (8.84)	5.52 (5.66)	82-85
HPMAP C ₁₂ H ₁₂ N ₂ O ₂	66.59 (67.75)	12.94 (14.73)	5.54 (4.80)	72-75
[(OH ₂) ₂ (PMBP) ₂ Co] C ₃₄ H ₃₀ N ₄ O ₆ Co	62.67 (60.16)	8.60 (8.60)	4.91 (5.05)	Carbonized between 130-140 °C
[(OH ₂) ₂ (PMTP) ₂ Co] C ₃₆ H ₃₄ N ₄ O ₆ Co	63.62 (62.89)	8.24 (8.14)	5.30 (5.74)	

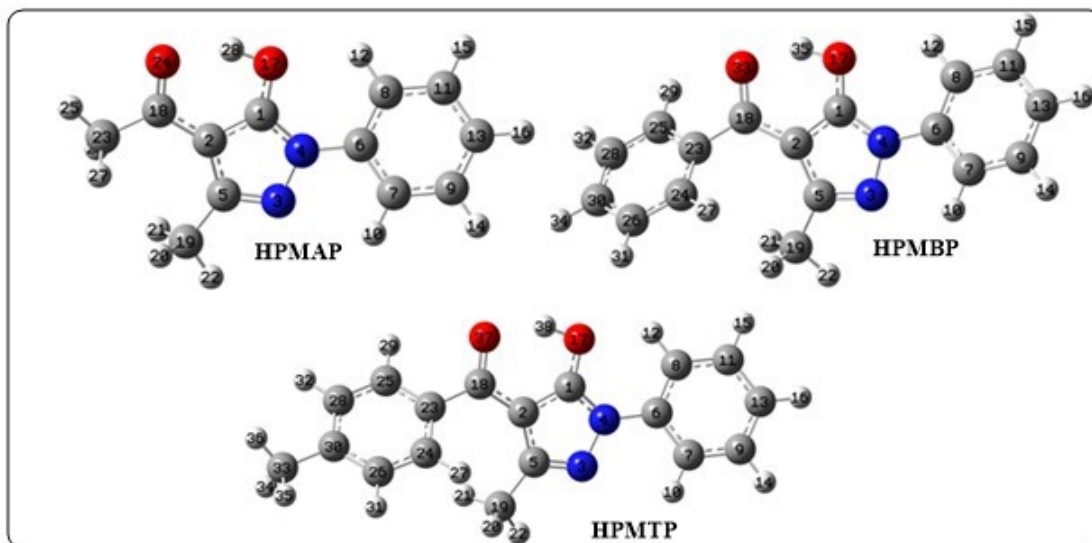


Fig. S8 Optimized structures of HPMAP, HPMBP and HPMTMP (B3LYP/6-31G(d, p) basis set.)

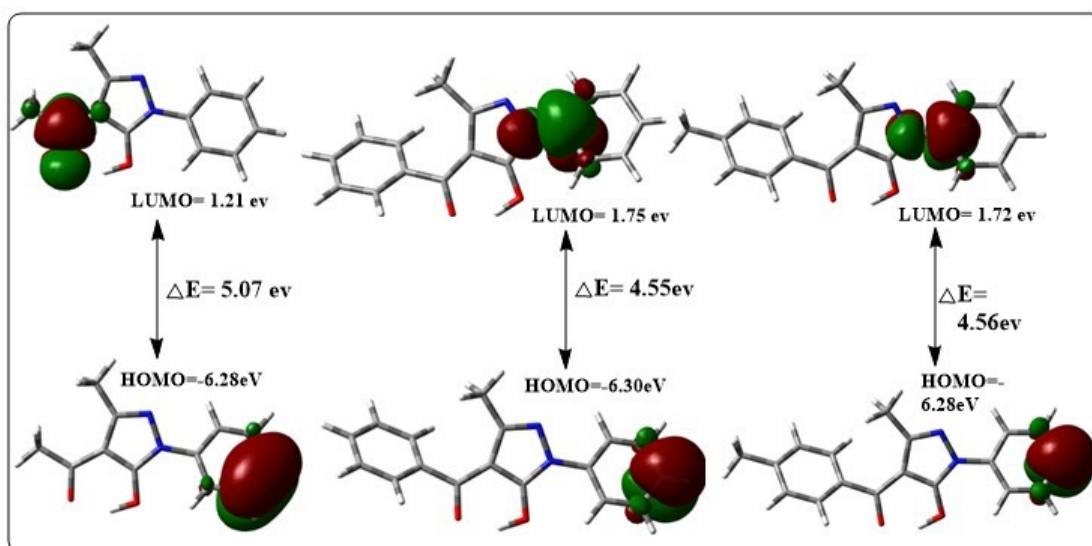


Fig. S9 HOMO and LUMO distribution of HPMAP, HPMBP and HPMTMP

Table. S3 Frontier orbital energies, Ionization potential, electron Affinity, Softness and Chemical hardness of HPMAP, HPMBP and HPMTTP ligands

Ligands	E(HOMO) (eV)	E(LUMO) (eV)	ΔE (eV)	I (eV)	A (eV)	η (eV)	S (eV)
HPMAP	-6.287	-1.216	5.071	6.287	1.216	2.535	0.395
HPMBP	-6.306	-1.758	4.558	6.306	1.758	2.274	0.439
HPMTTP	-6.289	-1.728	4.561	6.289	1.728	2.280	0.438

Table. S4 NBOs and hybridization states of HPMAP, HPMBP and HPMTTP obtained at B3LYP/6-31G (d,p) level

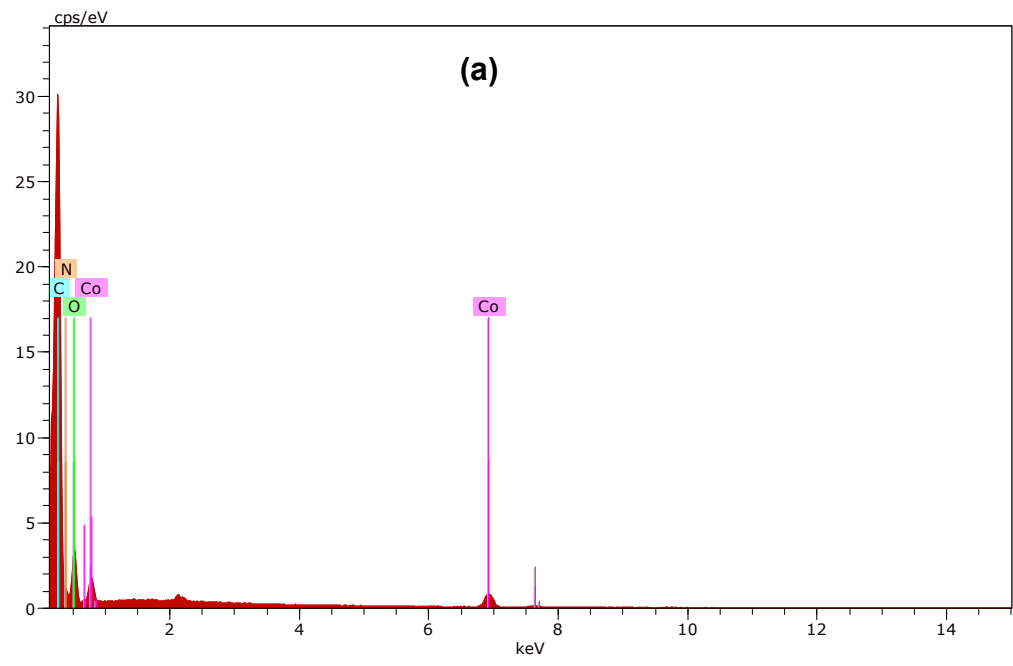
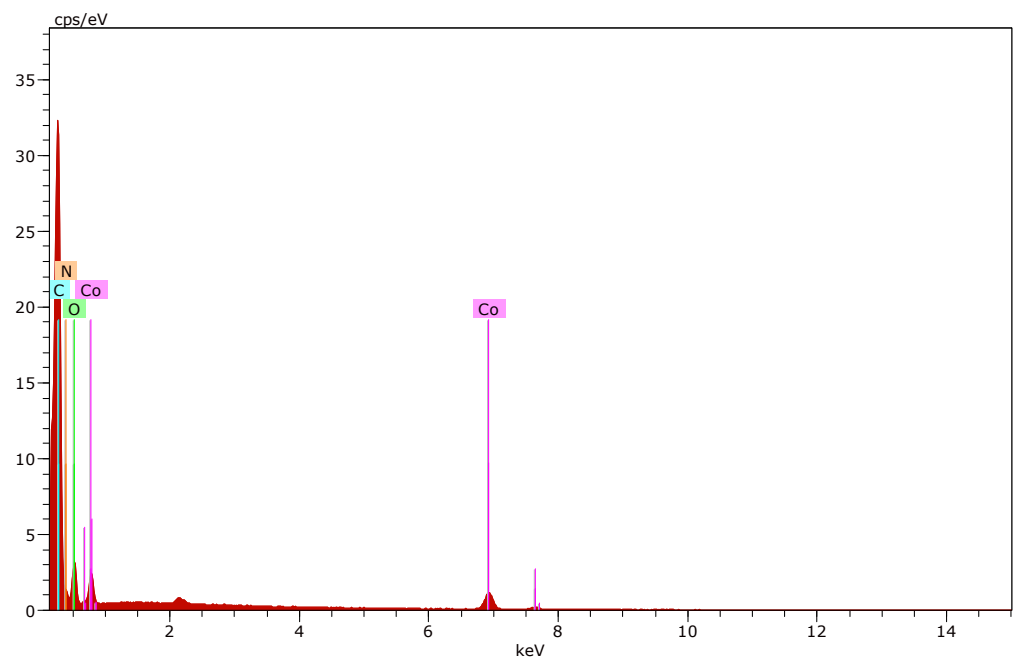
HPMAP		HPMBP		HPMTTP	
Donors NBO	Hybrid	Donors NBO	Hybrid	Donors NBO	Hybrid
δ (1) C1- O17	sp ^{2.40} (C1) sp ^{1.83} (O17)	δ (1) C1-O17	sp ^{2.39} (C1) sp ^{1.82} (O17)	δ (1) C1- O17	sp ^{2.39} (C1) sp ^{1.82} (O17)
δ (1) C18 -O24	sp ^{2.47} (C18) sp ^{1.46} (O24)	δ (1) C18 -O33	sp ^{2.55} (C18) sp ^{1.53} (O33)	δ (1) C18 -O37	sp ^{2.55} (C18) sp ^{1.53} (O37)
LP (1) O17	sp ^{1.38}	LP (1) O17	sp ^{1.39}	LP (1) O17	sp ^{1.39}
LP (1) O24	Sp ^{0.84}	LP (1) O33	sp ^{0.90}	LP (1) O37	sp ^{0.91}
-----	-----	LP (1) C13	p ¹	LP (1) C13	p ¹

Table. S5 Infrared vibrational frequencies (Cm^{-1}) of the acylpyrazolone ligands and its cobalt complexes, and their assignments

HPMBP	HPMTP	Complex 1	Complex 2	Assignments
-----	-----	3450-3700	3450-3700	$\sqrt{\text{-OH}}$ of water
1602.95br	1634.24br	1611.25 br	1609.89 br	$\sqrt{\text{C=O}}$
1580.43s	1555.83s	1484.45-1300m	1487.31-1300 w	$\sqrt{\text{C=N}}$ of Pyrazole ring stretching
1492.57m	1490.59w			$\sqrt{\text{C=C}}$ of phenyl and pyrazole
1349.53m	1212.42			$\sqrt{\text{as C-N}}$ of pyrazole ring
1140.79s	1167.31s	1021.32-1059.61s	1030.69-1062.14s	$\sqrt{\text{as C-O}}$
	-----	552.26 - 438.01w	527.43-441.61w	Co-O
		839.36 w	842.20 w	coordinated water molecule

Table. S6 UV-visible absorption wavelengths (nm) of acylpyrazolone ligands derivatives and its cobalt complexes, and their assignments

HPMBP	HPMTP	Complex 1	Complex 2	Assignments
285	293	280	285	$\pi \rightarrow \pi^*$
346	368	340	347	$n \rightarrow \pi^*$



(b)

Fig. S10 EDAX spectra of (a) complex (1) and (b) complex (2)

Table. S7 XPS Binding Energies Data, FWHM of the Co 2p_{3/2}, Co 2p_{1/2} and their satellite of Co-complexes and Co(II) chloride hexahydrate

	Cobalt chloride hexahydrate		Complex (1)		Complex (2)	
	B.E (eV)	FWHM (eV)	B.E (eV)	FWHM (eV)	B.E (eV)	FWHM (eV)
Co2p _{3/2}	780.65	3.07	778.74	2.93	778.47	2.58
Co 2p _{3/2} satellite	785.79	6.52	782.72	6.58	782.20	6.56
Co 2p _{1/2} satellite	802.57	5.05	798.91	5.51	798.29	6.91
O 1s	531.28	2.88	533.98	1.67	533.80	1.58
			529.43	2.54	529.38	1.78
			529.34	1.18	529.07	1.11
			528.85	1.28	528.69	1.21
N 1s	-----	-----	398.15	1.21	398.18	1.14
			396.68	1.67	396.72	1.58
C 1s	----- -----	-----	289.21	1.58	289.00	1.52
			284.42	1.46	284.50	1.02
			282.66	1.31	282.51	1.43
			282.11	1.02	282.05	0.98
Spin-orbital splitting	$\Delta E_{1a}= 15.96$		$\Delta E_{1b}=15.79$		$\Delta E_{1c}=15.94$	
	$\Delta E_{2a}= 16.78$		$\Delta E_{2b}=16.19$		$\Delta E_{2c}=16.09$	

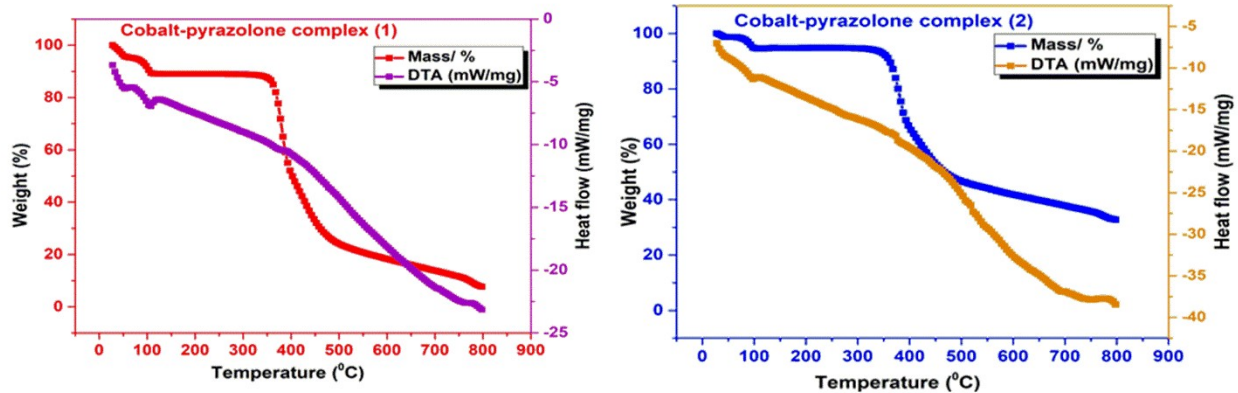


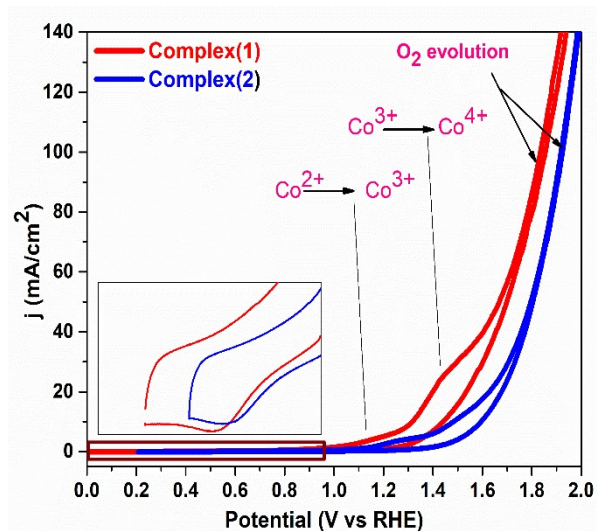
Fig. S11 TGA/DTA curves of the cobalt-acylpyrazolone complexes under N₂ atmosphere

Table. S8 Comparison of cobalt complexes towards OER with literature reported
Cobalt and transition metal based electrocatalysts in 1M KOH

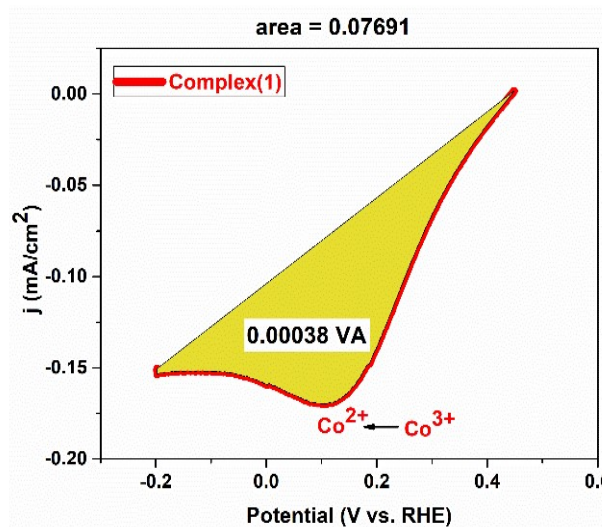
Electrocatalysts	Current density (mA/cm ²)	Overpotential (mV)	Tafel slope (mV/dec)	Reference
CoSe ₄	10	320	61.6	6
[Co(L1)] H ₂ L1: N,N0- bis(salicylidene)-4-chloro-1,2-phenyldiamine	10	316	75	7
[Co(L2)]N,N0 H ₂ L ₂ : N,N0-bis(salicylidene)-4-bromo-1,2-phenyldiamine		247	50	
CoOOH	0.1	385	94.6	8
([Co1.5(tib)(dcpna)]·6H ₂ O) 1,3,5-tris(1-imidazolyl)-benzene (tib), 5-(30 ,50 -dicarboxylphenyl)nicotinic acid (H3dcpna)	10	360	89	8
Co ₃ O ₄ /NRGO (N-doped reduced graphene oxide (NRGO))	10	420	83	9
[CoIII(LN ₂ O ₃)H ₂ O]	10	500	No data	10
CoP		400	57	11
[CoL ₂) (H ₂ L = 4-chloro-1,2-bis [2-hydroxy-5-(phenylazo)benzylideneamino]benzene	10	360	No data	12
[CoL ₂) L2:Bis[Salicylydene]-1,2-Iminophenylenediamine	2	140	84	12
[Co(L) (CH OH)] L2: Soduim (E)-4-(2-hydroxylnaphtalene-1-yl)diazinyl benzenesulfonate	0.5	520	No data	12
	5.0	720		
NiCo LDHs/GF	20	249	108.02	13
3D-Ni-MOF/NF with 4,4'-biphenyl dicarboxylic acid	20	350		14
Complex (1)	10	140	50	Present work
Complex (2)	10	320	90	

Table. S9 Comparison of EIS data of cobalt complexes towards OER with literature reported Cobalt based electrocatalysts

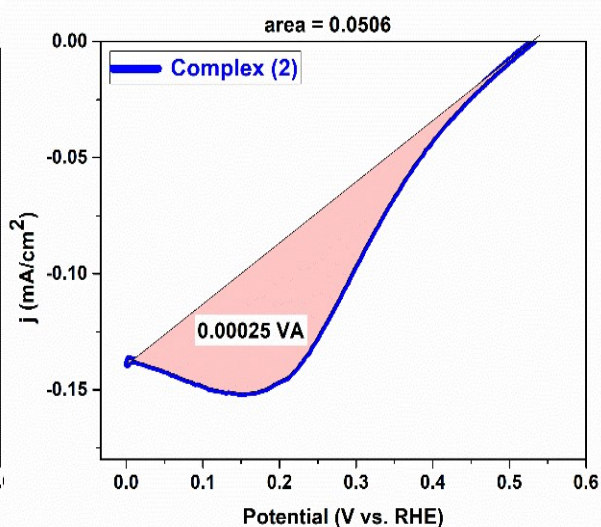
Compounds	Rs (ohm)	Rct (ohm)	Cdl	Reference
([Co _{1.5} (tib)(dcpna)]·6H ₂ O)	13.4	247.0	118	6
Co ₃ O ₄	14.1	408.6	0.56	
CoSe ₄	No data	180	No data	8
Complex (1)	48.37	174.09	No data	Present work
Complex (2)	39.6	265.28	No data	



(a)



(b)



(c)

Fig. S12 (a) CV curves of Cobalt acylpyrazolone complex (1) and (2), (b) Calculated area of complex 1 and (c) Calculated area of complex 2 with reduction of Co³⁺ to Co²⁺.

Determination of active sites from the redox curves

		- Co
Calculated area	= 0.077 mVA = 0.000077 VA	Complex (1)
Scan rate	200 mV/s = 0.2 V/s	
The associated charge is	= 0.000077 VA / 0.2 Vs ⁻¹ = 0.00038 As = 0.00038 C	Since, the oxidation of Co ²⁺ to Co ³⁺ is a
The number of electrons transferred is	= 0.00038 C / 1.602 × 10 ⁻¹⁹ C = 2.40 × 10 ¹⁵	single electron transfer reaction,

- Complex 2

Calculated area	= 0.0506 mVA = 0.0000506 VA	
Scan rate	200 mV/s = 0.2 V/s	
The associated charge is	= 0.0000506 VA / 0.2 Vs ⁻¹ = 0.00025 As = 0.00025 C	
The number of electrons transferred is	= 0.00025 C / 1.602 × 10 ⁻¹⁹ C = 1.56 × 10 ¹⁵	

the number electron calculated above is exactly the same as the number of surface-active sites. Hence, the surface concentration of Co atom participated in OER is **2.40 × 10¹⁵** and **1.56 × 10¹⁵** for complex (1) and (2) respectively.

Determination of Turnover Frequency (TOF) from OER overpotentials

TOF was calculated by calibrating the surface-active Co atoms that undergone redox reaction before onset of OER only participated in OER electrocatalysis.

Therefore, TOF can be calculated by,

$$\text{TOF} = j \times \text{NA} / F \times n \times \Gamma \dots\dots\dots (S1)$$

Where,

j = current density

NA= Avogadro number

F = Faraday constant

n = Number of electrons

Γ = Surface concentration

For Complex (1)

$$\text{TOF}_{1.52\text{V}} = [(40.70 \times 10^{-3}) (6.023 \times 10^{23})] / [(96485) (4) (0.240 \times 10^{16})]$$

TOF_{1.61V} = 26.46 s⁻¹

For Complex (2)

$$\text{TOF}_{1.52\text{V}} = [(18.30 \times 10^{-3}) (6.023 \times 10^{23})] / [(96485) (4) (0.156 \times 10^{16})]$$

TOF_{1.61V} = 18.30 s⁻¹

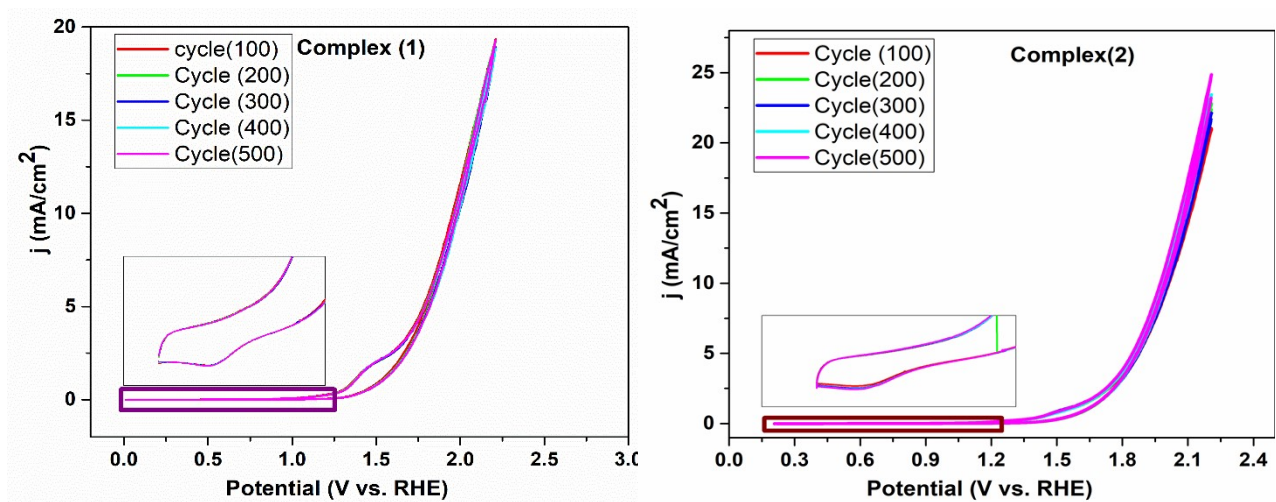


Fig. S13 Selected cycle CV curve of Complex (1) and (2) taken at a scan rate of 200 mV/se

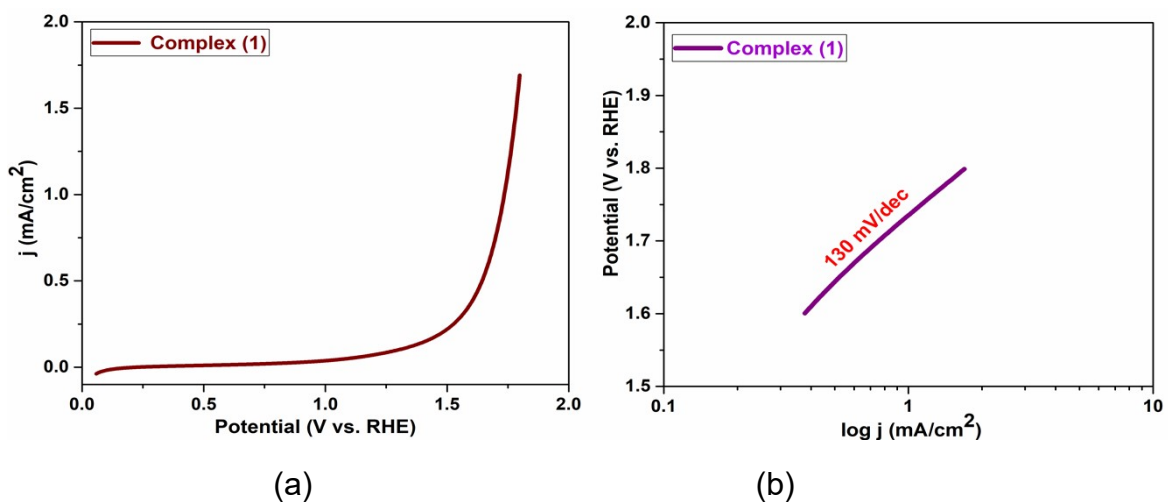
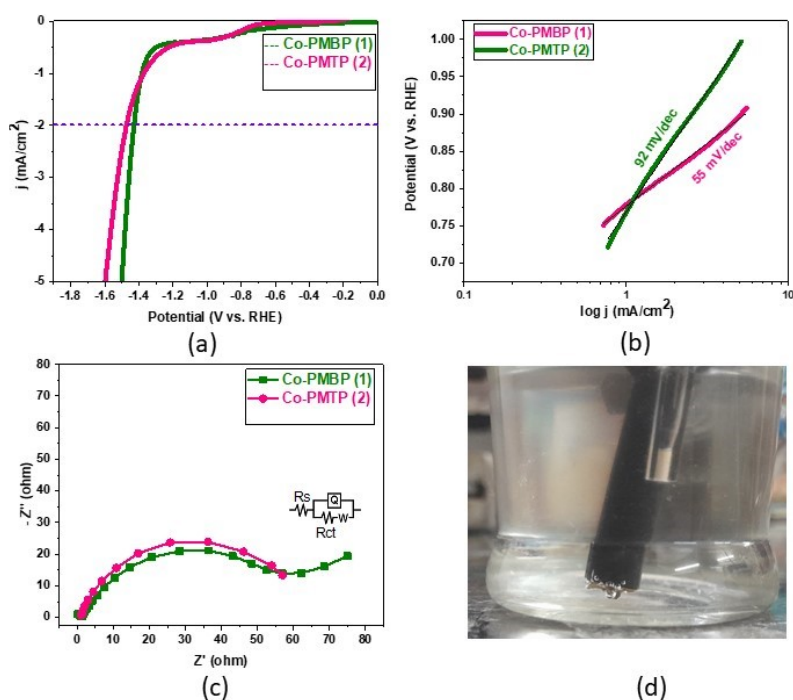


Fig. S14 LSV curve at a scan rate of 50 mV/s, (b) Tafel slope at overpotential of 597 mV of cobalt-acylpyrazolone complexes (1) in 0.5 M Na₂SO₄

Table. S10 Comparison of cobalt complexes towards HER with literature reported

Cobalt based electrocatalysts in 1M KOH

Compounds	Current density (mA/cm ²)	Over potential (mV)	Tafel slope(mV/dec)	reference
CoP@PC-750	10	85mv	-----	
Co-NCNTs	2 10	104 170	97	15
Co-Phosphine	2 10	65 110	93	16
Co-NRCNTs(N- riche doped carbon nanotubes)	2 10	380 540	No data	17
Co(BFAC)CNT S	0.8 mA/cm ⁻²	800	No data	18
Complex (2)	2	573	129	Present work

**Fig. S15** (a) LSV curves at a scan rate of 50 mV/s, (b) Tafel slope and (c) EIS spectra of complex (1) and

(2)/GC in neutral condition; (d) H₂ bubbles on the electrode of Cobalt-pyrazolone complex (2)/GC

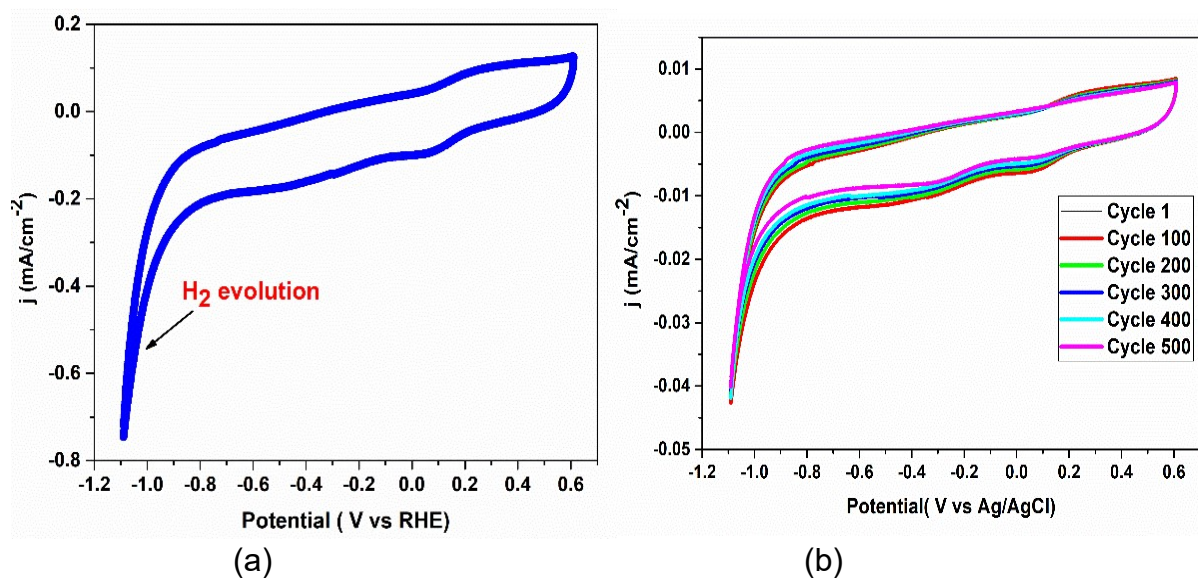


Fig. S16 (a) CV curves and (b) Selected cycle CV curve of complex (1) taken at a scan rate of 200 mV/sec.

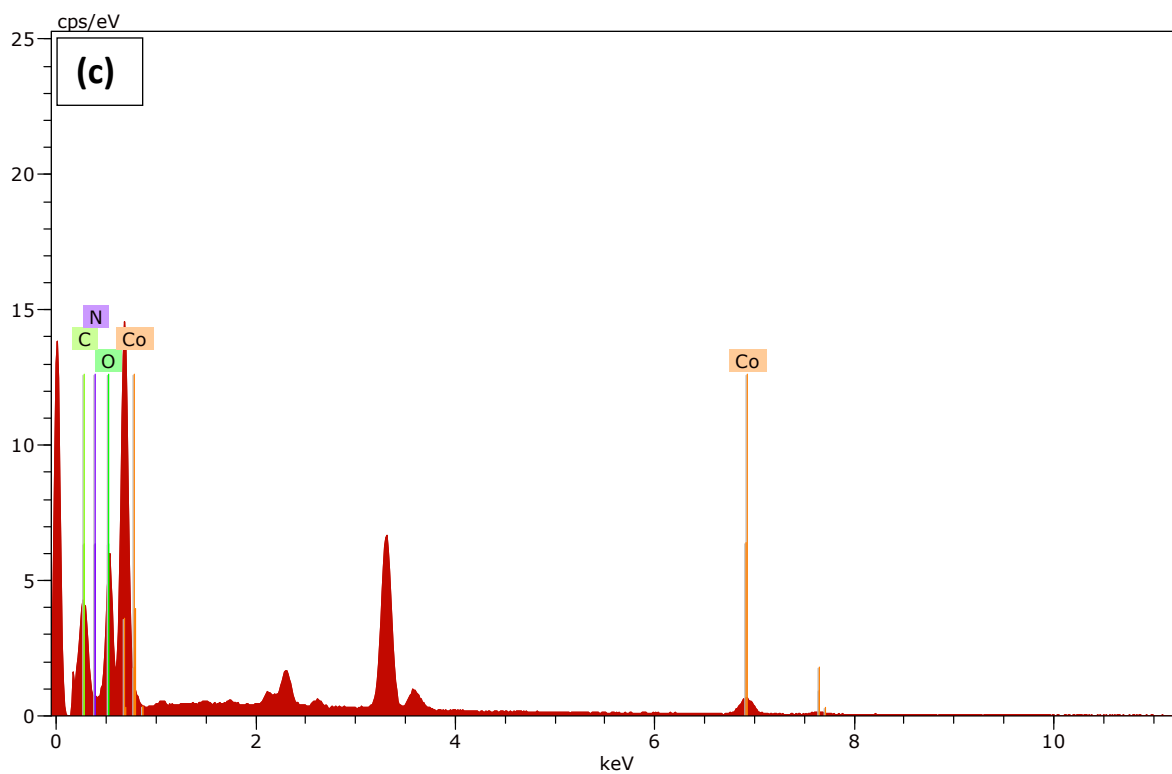
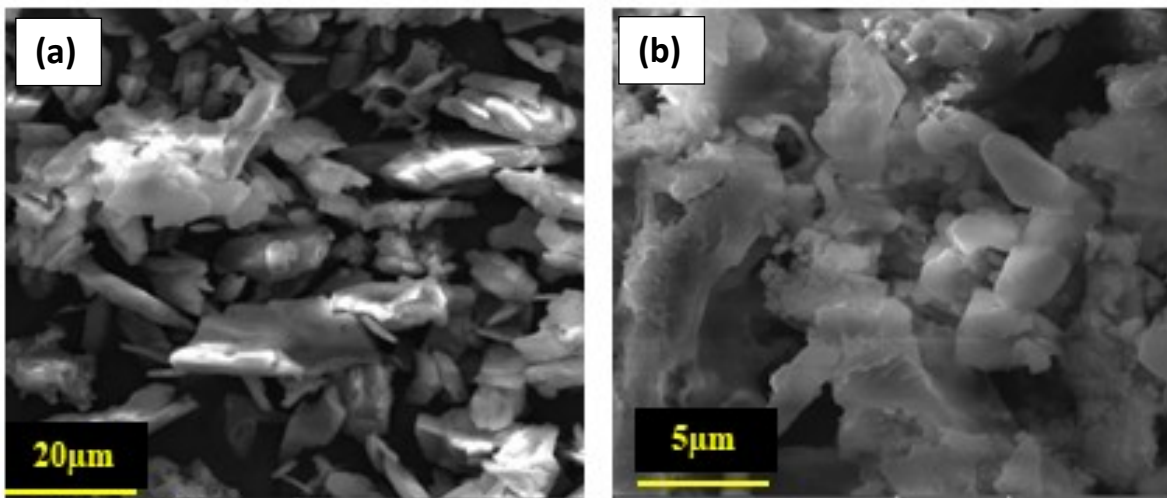


Fig. S17 (a), (b) SEM images and corresponding (c) EDAX spectra of complex (2) after continuous electrolysis at 1.6 V vs RHE.

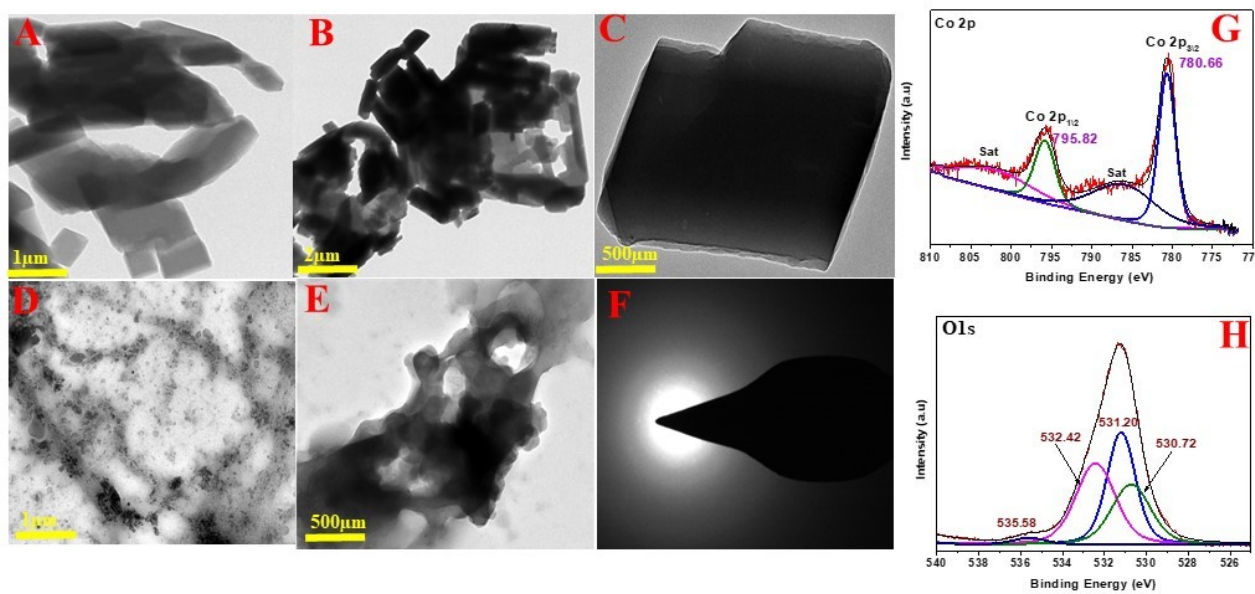


Fig. S18 (A–C) before and (D–E) Post-OER HR-TEM images of complex (2), (F) the corresponding SAED patterns of the post-OER sample and (G–H) High resolution spectra of Co2p and O1s for the post-OER of complex (2)

DFT Studies

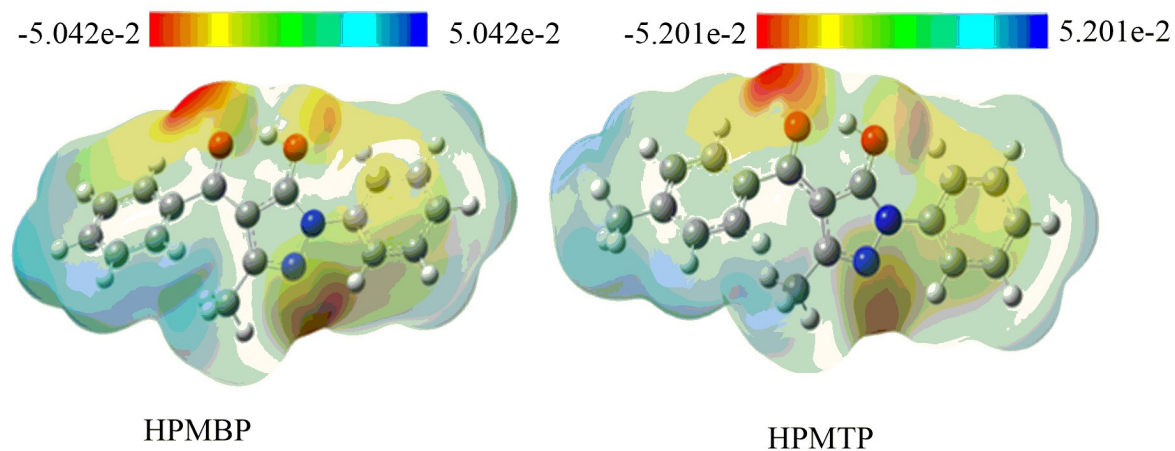


Fig. S19 Molecular electrostatic potential of acylpyrazolone ligands

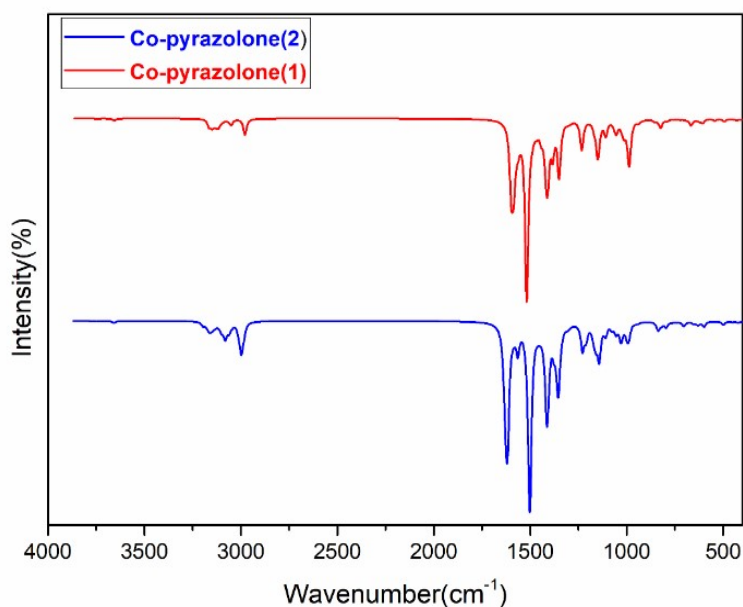


Fig. S20. Theoretical FT-IR spectra of cobalt-acylpyrazolone complexes

Table. S11 Occupancy of energy orbitals of Co(II) ions in complex (1) and (2)

		Complex (1)	Complex (2)		
	Occupancy	Energy (eV)	Energy (eV)	orbitales	
n=1 l=0	2.00	-7515.3151	-7515.5740	s	
n=2 l=0	2.00	-882.3445	-882.5902		
n=2 l=1	6.00	-765.9584	-766.2053	p	HOMOs
n=3 l=0	2.00	-99.2845	-99.5351	s	
n=3 l=1	6.00	-64.4929	-64.7435	p	
n=3 l=2	7.00	-7.9180	-8.1606	d	
n=4 l=0	2.00	-4.7864	-5.0375	s	
n=3 l=2	0.00	-35.9794	-35.9801	d	LUMOs
n=4 l=0	0.00	-20.6063	-20.6280	P	
n=4 l=1	0.00	-14.4467	-14.5301	S	
n=4 l=1	0.00	-6.9885	-7.2110	P	

References

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