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Supporting Information

Electrocatalytic H_2 evolution using Binuclear cobalt complexes as electrocatalysts

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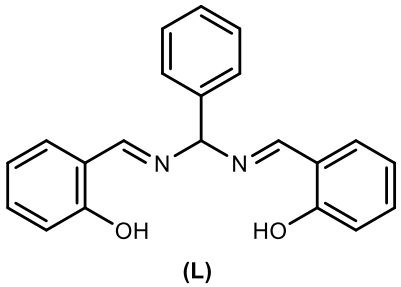
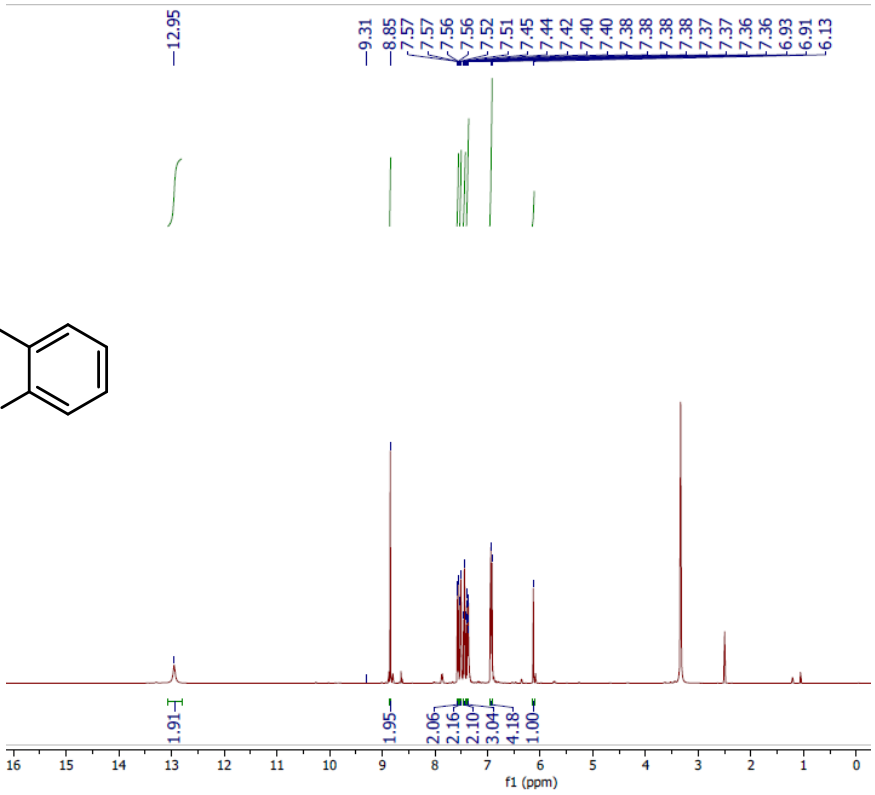
NMR spectra of Ligand (L) N,N’-Bis(salicylidene)-phenylmethanediamine



(L)



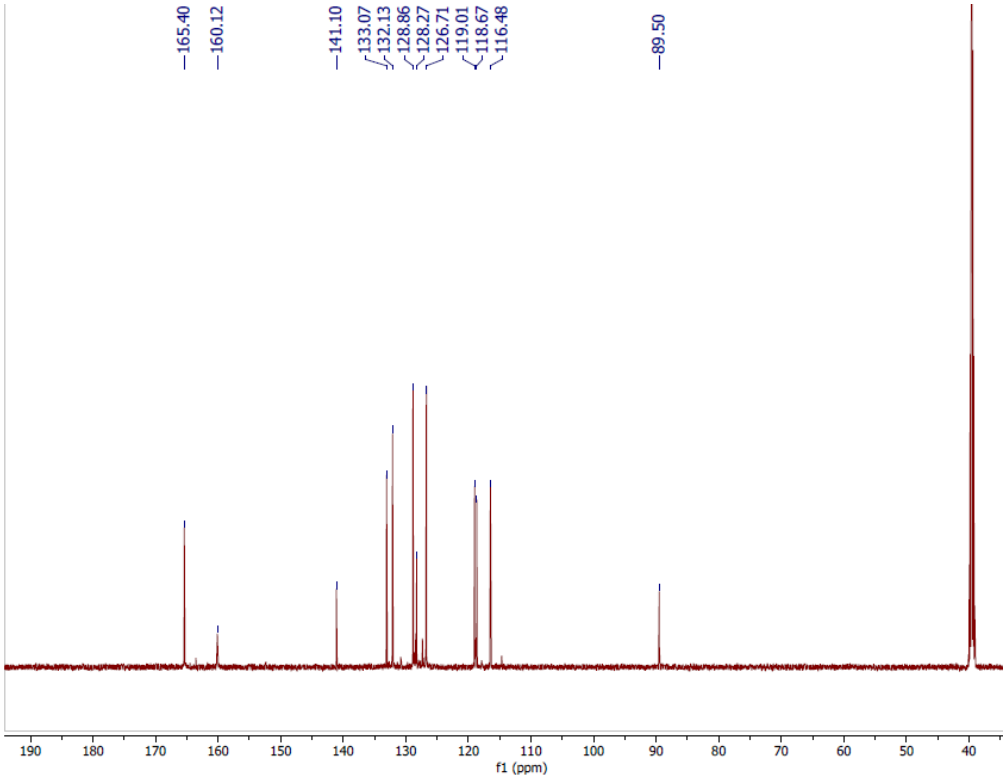


Table S1. X-ray structure data collection and refinement parameters

	2
Formula	$C_{52}H_{42}O_4N_6Co_2I_3$
M_w	1313.47
Crystal system	Monoclinic
a (Å)	15.9062(16)
b (Å)	19.149(2)
c (Å)	17.2316(18)
α (°)	90
β (°)	105.992(3)
γ (°)	90
V (Å^3)	105.992(3)
Space group	C2/c
Z	4
D_{calc} (g cm^{-3})	1.729
μ (mm^{-1})	2.543
No. of reflections	33797
No. of independent	4970
R_{int}	0.0550
No. parameters	305
R_1/wR_2	0.0622/
	0.1314
GOF	1.060

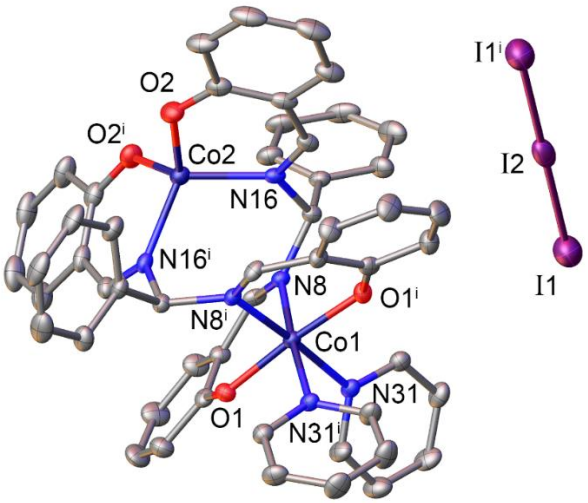


Table S2. Selected bond length in complex **2**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
I2	I1	2.9152(10)	Co1	N8^2	1.962(4)
I2	I1^1	2.9152(10)	Co1	N8	1.962(4)
Co1	O1^2	1.869(4)	Co2	N16	1.985(5)
Co1	O1	1.869(4)	Co2	N16^2	1.985(5)
Co1	N31	1.981(5)	Co2	O2	1.896(5)
Co1	N31^2	1.981(5)	Co2	O2^2	1.896(5)
Co1	Co2	4.175(5)			
^{1}1/2-X,1/2-Y,1-Z; ^{2}1-X,+Y,1/2-Z					

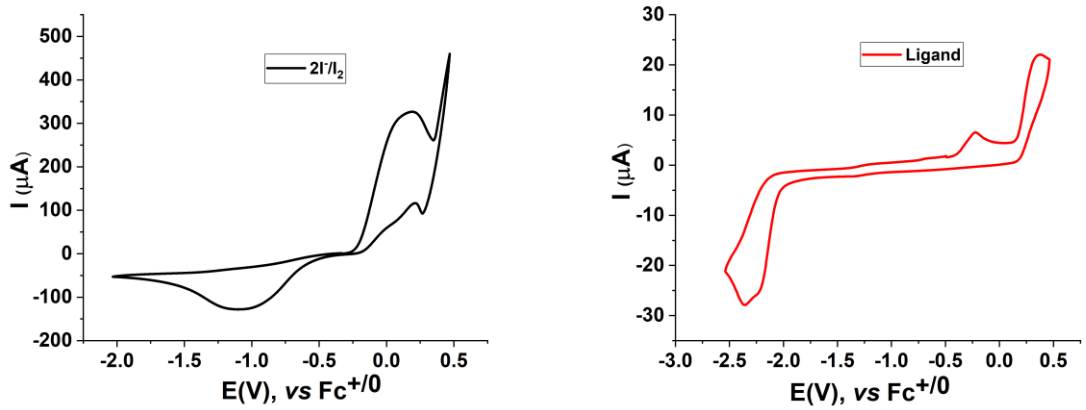


Figure S1: Cyclic voltammograms of **I^-/I couple** (black line) and **ligand** (redline) recorded at a stationary glassy carbon electrode in DMF with a potential scan rate of 50 $mV.s^{-1}$

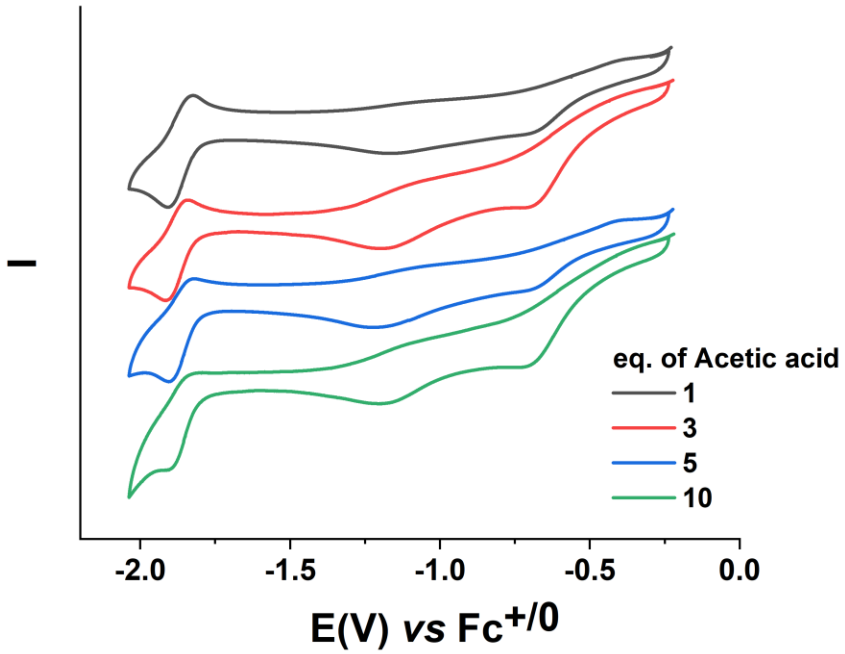


Figure S2: Cyclic voltammograms of a 1 mM solution of complex **2** with different equivalent of acetic acid recorded at a stationary glassy carbon electrode in DMF with a potential scan rate of 50 $mV.s^{-1}$

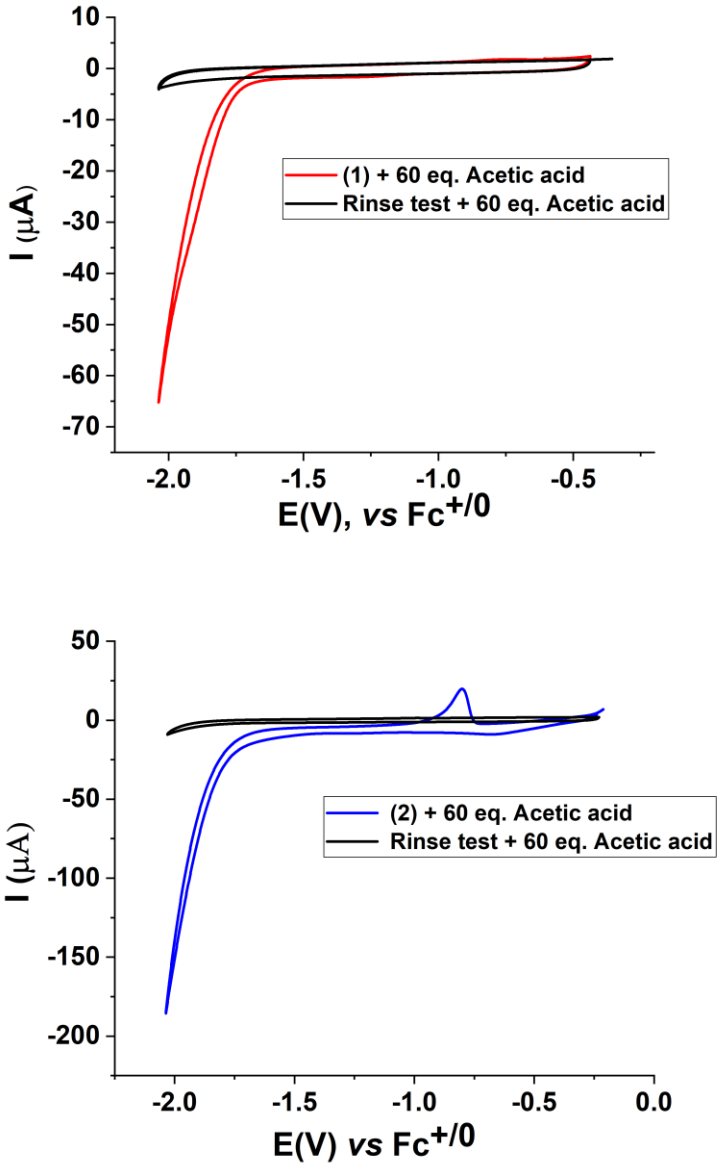


Figure S3: "Rinse test" control experiments of two complexes: The glassy carbon electrode, after participating the proton reduction in the presence of catalysts with 60 mM concentration of AA (red line and blue line), was cleaned by DMF solvent washing and used as the working electrode in the proton reduction without catalysts (black line). (DMF solution; 50 $mV.s^{-1}$ scan rate).

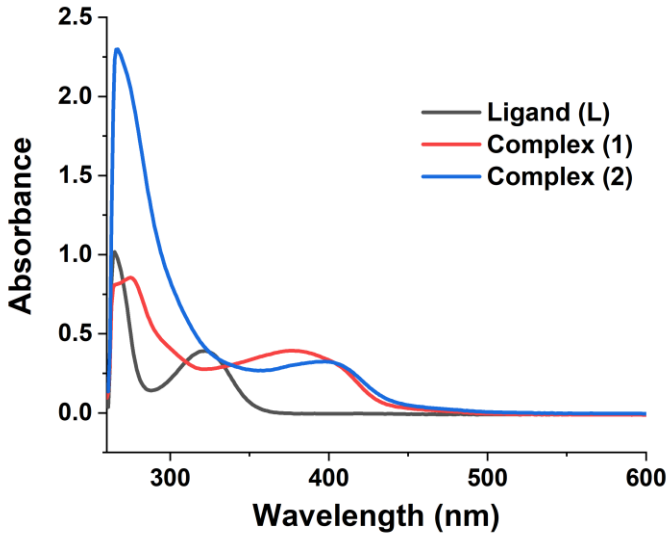


Figure S4: UV-Vis spectra of Ligand and complexes **1** and **2** recorded in DMF

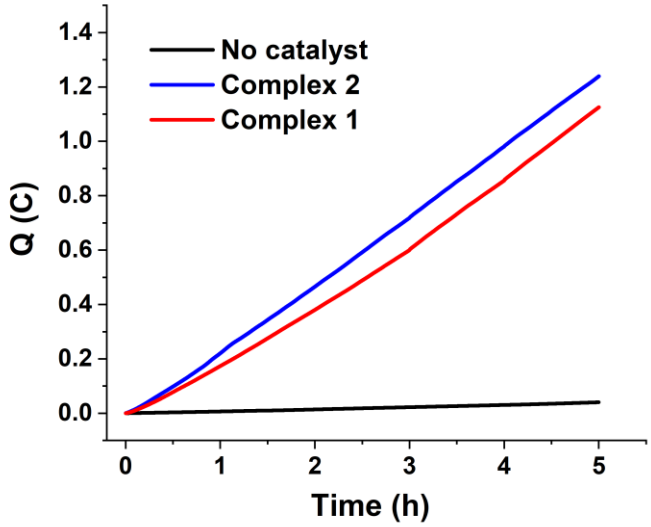


Figure S5: Coulometry for bulk electrolysis at -1.93 V *vs*. $Fc^{+/0}$. The electrolytic solution contains 0.1 M TBATBF in DMF, 60 mM Acetic acid: without catalysts (black line) or 1 mM of **1** (red line) or 1 mM of **2** (blue line)

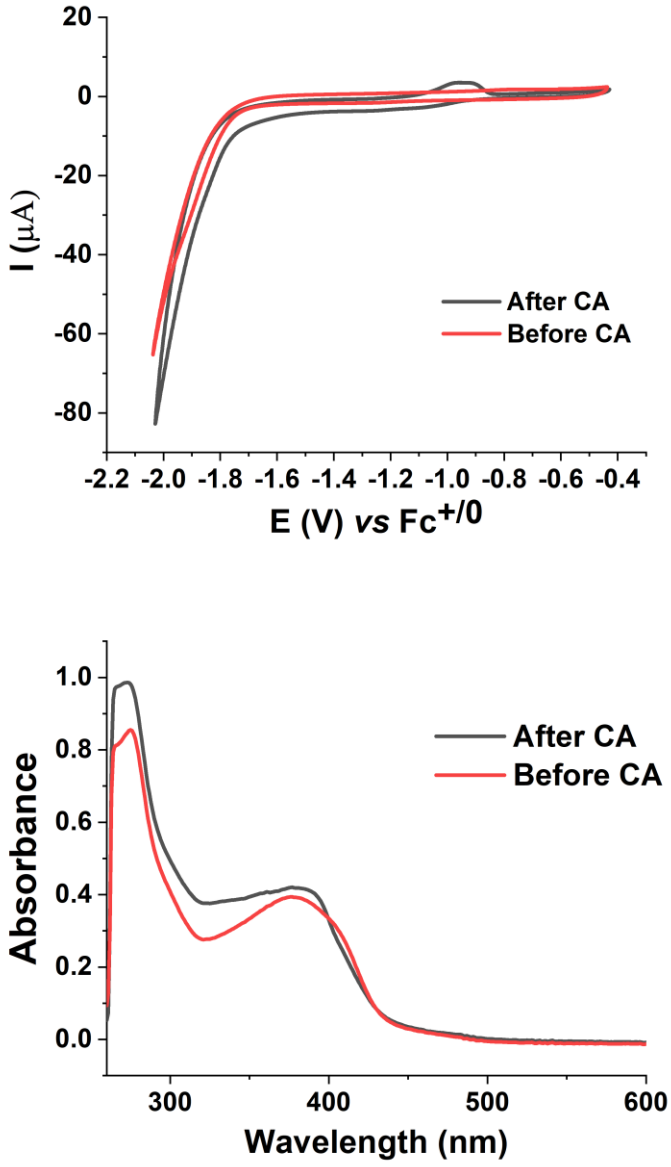


Figure S6: Cyclic voltammograms and UV-Vis spectra of a 1 mM solution of complex **1** in DMF in the presence of 60 mM of Acetic acid before and after 5-hour bulk electrolysis performed at – 1.93 V *vs*. $Fc^{+/0}$

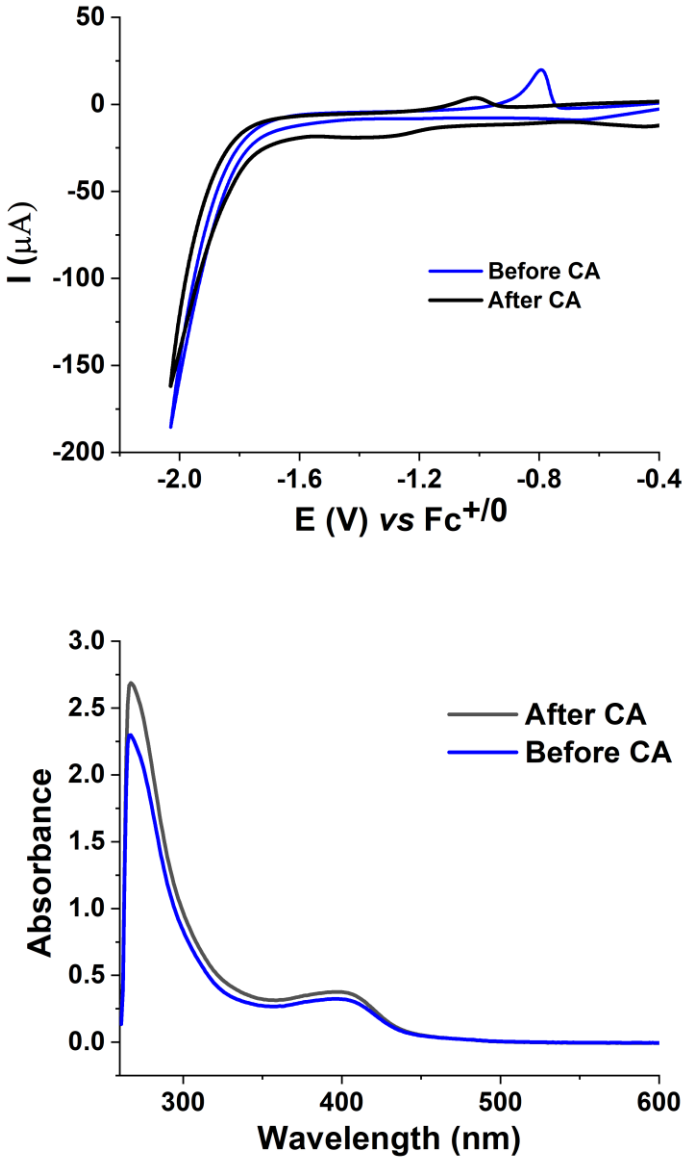


Figure S7: Cyclic voltammograms and UV-Vis spectra of a 1 mM solution of complex **2** in DMF in the presence of 60 mM of Acetic acid before and after 5-hour bulk electrolysis performed at – 1.93 V *vs*. $Fc^{+/0}$

- ***Overpotential determination***

Determine the standard potential of Acetic acid in DMF: based on the equation **(1)** [1]

$$E°(HA/A^-; H_2) = E°(H^+/H_2) - 2.303(RT/F)pKa_{(HA)} + \varepsilon_D - (RT/2F)\ln(C_o/C^o_{H2}) \quad \textbf{(1)}$$

$E°(H^+/H_2)$ = -0.662 V (*vs* $Fc^{+/0}$) [2]

pK_a of Acetic acid in DMF: 13.5

ε_D = 0.04 V

C_o: concentration of acetic acid

C^o_{H2}: concentration of dissolved hydrogen at standard condition = 1.9 mM.

- Complex [$\mathbf{Co^{II}_2L_2}$] **(1)** with 60 mM Acetic acid in DMF

$E°(HA/A^-; H_2) = E^T_{1/2}$ = (-0.662) – [(2.303x8.314x298)/96485]x13.5 + 0.04 – [(8.314x298)/(2x96485)]ln(60/1.9) = **- 1.46 V** (*vs* $Fc^{+/0}$)

Overpotential = $E^T_{1/2} – E_{cat/2}$ = -1.46 – (-1.92) = **0.46 V** (*vs* $Fc^{+/0}$)

- Complex [$\mathbf{Co^{II}Co^{III}L_2}$] **(2)** with 60 mM Acetic acid in DMF

$E°(HA/A^-; H_2) = E^T_{1/2}$ = **- 1.46 V** (*vs* $Fc^{+/0}$)

Overpotential = $E^T_{1/2} – E_{cat/2}$ = -1.46 – (-1.93) = **0.47 V** (*vs* $Fc^{+/0}$)

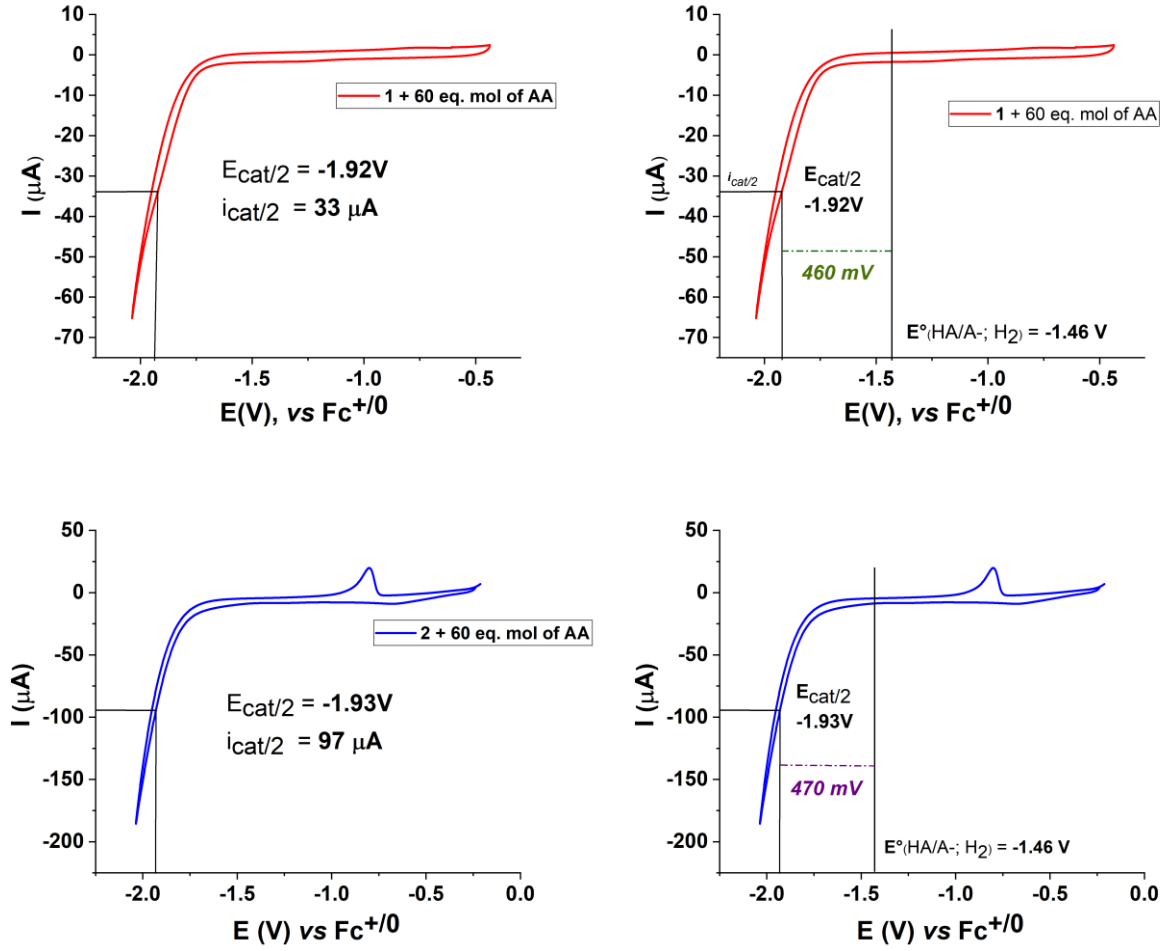


Figure S8: Determination of $i_{cat/2}$; $E_{cat/2}$ and overpotential of complexes **1** and **2**

- **Diffusion coefficient determination**

Using the the Randles-Sevcik equation[3]:

$$\boldsymbol{i_p} = 0.4463 \times n^{3/2} \times F^{\mathbf{3/2}} \times \boldsymbol{A} \times [cat] \times (RT)^{-1/2} \times D^{1/2} \times \boldsymbol{\vartheta^{1/2}}$$

Where i_p is the cathodic peak current (A), R = 8.314 J/mol K, T = 299K, F = 96485 C/mol, ν is scan rate (V/s), A is the surface area of electrode (m^2), n is the number of electrons transferred, [cat] is the concentration of catalyst (M) and D is the diffusion coefficient (m^2/s). The plot of i_p versus the square root of scan rate is the linear regression equation and the diffusion coefficient can be extracted from the slope of such linear fitting. As a result, the values of D of complex **1** and **2** were **7.48 x 10^{-7} cm^2/s** and **3.32 x 10^{-6} cm^2/s**, respectively.

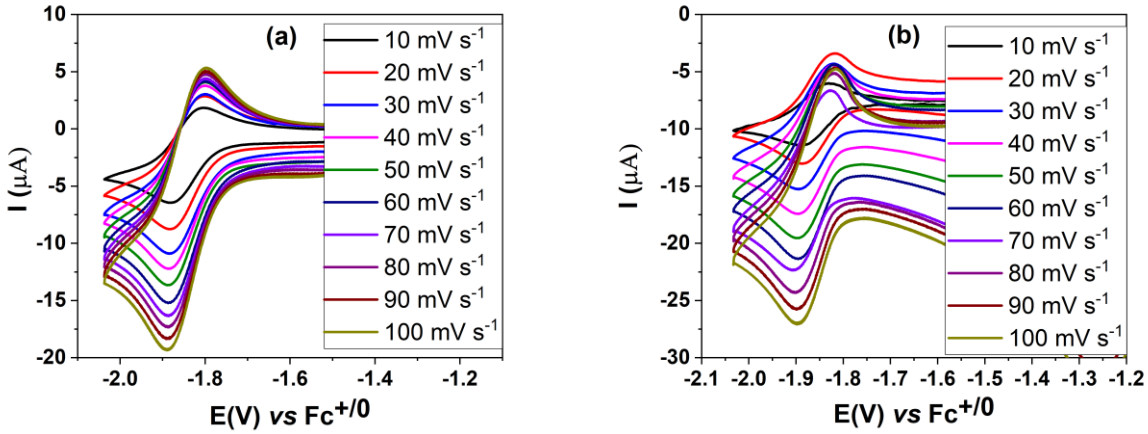


Figure S9: Cyclic voltammograms of complex **1 (a)** and **2 (b)** at various scan rates

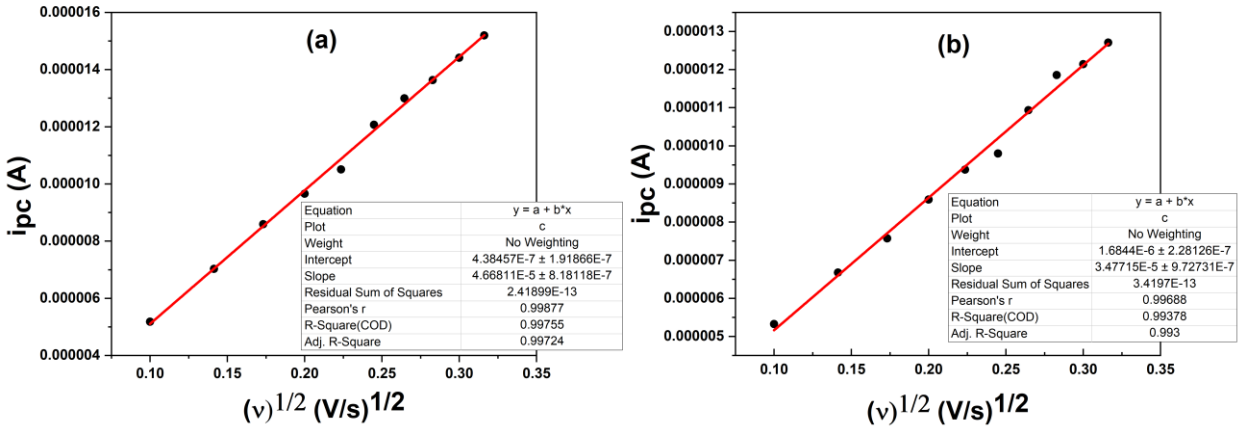


Figure S10: The plots of i_p versus the square root of scan rate of complex **1 (a)** and **2 (b)**

Table S3: The peak separation analysis of complex **1**

Scan rate (mV/s)	$\Delta E = \lvert E_{pc} - E_{pa} \rvert$ (mv)	The number of e
10	77	1.3
20	81	1.4
30	84	1.4
40	86	1.5
50	89	1.5
60	87	1.5
70	89	1.5
80	91	1.5
90	92	1.6
100	93	1.6

Table S4: The peak separation analysis of complex **2**

Scan rate (mV/s)	$\Delta E = \lvert E_{pc} - E_{pa} \rvert$ (mV)	The number of e
10	59	1.0
20	70	1.2
30	74	1.3
40	76	1.3
50	79	1.3
60	77	1.3
70	78	1.3
80	86	1.5
90	80	1.4
100	82	1.4

Table S5: The values of rate constants extracted from FOWA with various concentration of Acetic acid

Catalyst	Parameter	[AA] mM				
		39	69	109	159	219
Complex (**1**)	$slope_{FOWA}$	2.36129	3.6845	5.62887	9.08636	10.65935
	k_{obs}	0.53883	1.31192	3.06192	7.97869	10.98028
	k_{cat}	13.81611	19.01341	28.09104	50.18046	50.13825
Complex (**2**)	$slope_{FOWA}$	17.57088	22.10996	29.32824	45.11062	59.8623
	k_{obs}	30.45376	48.22029	84.84493	200.72963	353.47661
	k_{cat}	780.86555	698.84475	778.39383	1262.45047	1614.04844

Table S6: Comparison of two catalysts **(1)**; **(2)** with other published dicobalt complexes

Complexes	**Solvent**	**Proton Source**	**Overpotential mV (vs. $Fc^{+/0}$)**	**Faradaic Efficiency**	**Ref**
(1)	DMF	Acetic acid	460	95%	
(2)	DMF	Acetic Acid	470	85%	
Pyridazine dicobalt	DMF	2,6-dichloroanilinium tetrafluoroborate	n.i	n.i	[4]
Polypyridine-pyrazine dicobalt	CH_3CN	*p*-TsOH	n.i	40%	[5]
Glyoxime-[BO_4] dicoblat	DMF	Protonated DMF	954	88%	[6]
Tetrakis-Schiff Base Dicobalt	CH_3CN	Acetic acid	310	72-94%	[7]
Polypyridine-pyrazole dicobalt	CH_3CN	TFA	n.i	79%	[8]
Bis(thiosemicarbazone) dicobalt	DMF	Et_3NHBF_4	n.i	65%	[9]
Polypyridine-Amido bridge dicobalt	CH_3CN	Acetic acid	n.i	94%	[10]
n.i: no information					

References

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