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Cobalt Corrole Catalyzed Hydrogen Evolution Reaction: Surprising Electronic Effects and Characterization of Key Reaction Intermediates

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Supplementary Information

Materials.

All solvents and reagents were of high purity grades and purchased from Sigma-Aldrich and from Merck. The corroles Ga-H_8,[1] Ga-Br_8,[2] Co-H_8,[3] Co-F_8,[4] Co-Cl_8[5] were prepared according to the published procedures.

Nuclear magnetic resonance spectroscopy

^{19}F NMR spectra were recorded on a Bruker Avance 400 spectrometer (operating at 400 M Hz for ^1H and 376.7 M Hz for ^{19}F NMR) and Bruker Avance 200 spectrometer (operating at 200 M Hz for ^1H and 188 M Hz for ^{19}F NMR). Chemical shifts in the ^1H NMR spectra are reported in ppm relative to residual hydrogen in the deuterated solvents, and relative to $CFCl_3$ (δ= 0.00) in the ^{19}F NMR spectra.

Mass spectroscopy

HR-MS was obtained by LCT Premier from Waters under ESI condition for mass direct probe in positive and negative modes, for compounds dissolved in acetonitrile:water (70:30).

UV-vis spectroscopy

Spectral measurements were carried out with a HP8453 Diode Array Spectrophotometer.

Synthesis:

Co-Br_8: A solution of bromine (200 µL, 3.9 mmol) and Co-H_8[3] (50 mg, 49.9 µmol) in benzene (40 mL) was stirred for 18 hr, after which the benzene and excess bromine were removed under vacuum. 20 ml of benzene which contains 200µL pyridine were added and the mixture was stirred for 5 min (during this time the color solution changed from brown to green). Column chromatography on silica gel 60 (eluent: hexanes/ethyl acetate/pyridine 9:1:0.1) and recrystallization from mixtures of dichloromethane/n-hexane and drop of pyridine resulted in 67 mg (82 yield) of Co-Br_8. The spectral properties of the product were consistent with literature data.[6]

Ga-Cl_8: *N*-chlorosuccinimide (NCS, 100 mg, 0.75 mmol) and Ga-H_8[1] (60 mg, 63.7 μmol) in 5 mL *o*-dichlorobenzene were heated at 150 °C for 15 min under N_2. After which three portions of 70 mg NCS were added in intervals of 15 min with continuous heating (150 °C) under N_2. The mixture was heated for another 15 min then cooled to RT, filtered and evaporated. The residue was dissolved in 10 mL benzene and ethanol solution of $NaBH_4$ (100 mg, 2.6 mmol, in 5 mL,) was added. The reaction mixture was stirred for 5 min then the solvents were filtrated and removed under vacuum. The residue was dissolved in ether (50 mL), washed twice with 100 ml of water and dried over Na_2SO_4. Column chromatography (silica; ethyl acetate for the by-products and 3:1 ethyl acetate/ethanol for the product) and recrystallization from mixtures of benzene/n-heptane and drop of pyridine resulted in 30 mg (38% yield) of Ga-Cl_8. ^{19}F NMR (188 MHz, CD_3OD): δ, ppm= -140.3 (dd, ^3J(F,F) = 23.0 Hz, ^4J(F,F) = 7.3 Hz, 2F; *ortho*-F), -140.7 (dd, ^3J(F,F) = 23.5 Hz, ^4J(F,F) = 7.7 Hz, 4F; *ortho*-F), -155.8 (t, ^3J(F,F) = 19.9 Hz, 2F; *para*-F), -156.0 (t, ^3J(F,F) = 22.3 Hz, 1F; *para*-F), -166.3 (m, 4F; *meta*-F), -166.8 (m, 2F; *meta*-F). UV/Vis (benzene): λ_{max}, nm (ε, $M^{-1}cm^{-1}$)= 409 ($4.4x10^4$), 433 ($2.2x10^5$), 581 ($2.1x10^4$), 607 ($1.9x10^4$). HR(ESI)-MS in negative ion mode (M^-) (M+OH-2pyridine= $C_{37}N_4F_{15}Cl_8Ga\cdot OH$): calcd. for *m/z*= 1150.6675, obsd. 1150.6633.

Ga-F_8: A solution of 2,3,7,8,12,13,17,18-octafluoro-5,10,15-tris(pentafluorophenyl)corrole[4] (15 mg, 15.9 μmol) in pyridine (10 mL) was added to a flask that contains a large excess (about 0.2 g) of $GaCl_3$, and the reaction mixture was heated to reflux for 1 h under N_2, followed by evaporation of the solvent. Column chromatography on silica gel 60 (eluent: dichloromethane/CH_3CN 10:0→3) afforded 12 mg (65% yield) of Ga-F_8 as red crystals. ^{19}F NMR (376.7 MHz, C_6D_6): δ, ppm= -140.1 (dd, ^3J(F,F) = 22.6 Hz, ^4J(F,F) = 7.5 Hz, 2F; *ortho*-F), -140.4 (dd, ^3J(F,F) = 22.6 Hz, ^4J(F,F) = 7.5 Hz, 4F; *ortho*-F), -149.2 (d, 6.2 Hz, 2F; β-*pyrr*-F), -150.6 (t, ^3J(F,F) = 18.8 Hz, 2F; *para*-F), -151.1 (t, ^3J(F,F) = 22.6 Hz, 1F; *para*-F), -151.2 (d, 7.5 Hz, 2F; β-*pyrr*-F), -154.7 (d, 7.5 Hz, 2F; β-*pyrr*-F), -159.0 (d, 6.2 Hz, 2F; β-*pyrr*-F), -162.2 (m, 4F; *meta*-F), -162.8 (m, 2F; *meta*-F). λ_{max}, nm (ε, $M^{-1}cm^{-1}$)= 384 ($6.6x10^4$), 404 ($3.2x10^5$), 548 ($2.7x10^4$), 570 ($3.2x10^4$). HR(ESI)-MS in negative ion mode (M^-) (M+OH-2pyridine= $C_{37}N_4F_{15}F_8Ga\cdot OH$): calcd. for *m/z*= 1022.9039, obsd. 1022.9077.

Chemical reduction of Co-Cl_8 by:

1. Co(Cp*)$_2$: 5 mg (15.1 μmol) bis(pentamethylcyclopentadienyl)cobalt(II) (Co(Cp*)$_2$) and 8.7 mg Co-Cl_8 (7.7 μmol, without axial ligands) were dissolved in 1 mL THF-d_8 at RT under N_2 in glove box. The mixture was stirred for 5 min, during which the solution color changed from green to red. The solution was used for NMR measurements, still under N_2.

2. NaBH$_4$: 5 mg (4 μmol) of Co-Cl_8 were dissolved in 0.75 mL THF-d_8 under nitrogen in glove box. Excess of $NaBH_4$ were added (5 mg, 132 μmol) and the solution was stirred until its color changed from green to brown red. The solution was used for NMR and epr measurements, still under N_2.

3. NaBH(OAc)$_3$: 8.7 mg Co-Cl_8 (7.7 μmol, without axial ligands) were dissolved in 0.75 mL THF-d_8 under nitrogen in glove box. Excess of Sodium triacetoxyborhydride $NaHB(OAc)_3$ were added (10 mg, 47 μmol) and the solution was stirred until its color changed from green to brown red. The solution was used for NMR and epr measurements, still under N_2.

EPR spectroscopy

The EPR spectra were recorded on a Bruker EMX-10/12 X-band (ν = 9.3 GHz) digital EPR spectrometer, equipped with a Bruker N_2-temperature controller. EPR spectra processing and simulation were performed with the Bruker WIN-EPR and SimFonia softwares.

Cyclic voltammetry (CV)

Electrochemical apparatus and Procedures.

All electrochemical experiments under heterogeneous conditions were performed using a CH Instruments (model CHI710D Electrochemical Analyzer). Ag/AgCl and Pt wire were used as reference and counter electrodes respectively in all the electrochemical experiments until otherwise mentioned. Biopotentiostat, electrodes, were purchased from CH Instruments. The rotating ring disk electrochemical (RRDE) set up from Pine Research Instrumentation (E6 series ChangeDisk tips with AFE6M rotor) was used to obtain the RRDE data. For studying electrocatalytic hydrogen production the catalyst was physiabsorbed on EPG in or modified**.**

The cyclic voltamograms in homogeneous solution was utilized by a WaveNow USB potentiostat Galvanostat (Pine Research Instrumentation), using Pine AfterNath Data Organizer software. A three electrode system was used, consisting of a mini glassy carbon electrode (diameter of the active zone: 2.8 mm; Metrohm) working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. The CV measurements were performed in acetonitrile solutions (HPLC Grade), 0.1 M in tetrabutylammonium perchlorate (TBAP, Fluka, recrystallized twice from methanol), and 1 mM substrate under N_2 atmosphere at ambient temperature. Scan rates of 10-1000 mV/s were applied. The $E_{1/2}$ value for the ferrocene/ferrocenium couple under these conditions was 0.47 V. The mini-glassy carbon electrode was cleaned by using a polishing set for cleaning solid-state electrodes (Metrohm).

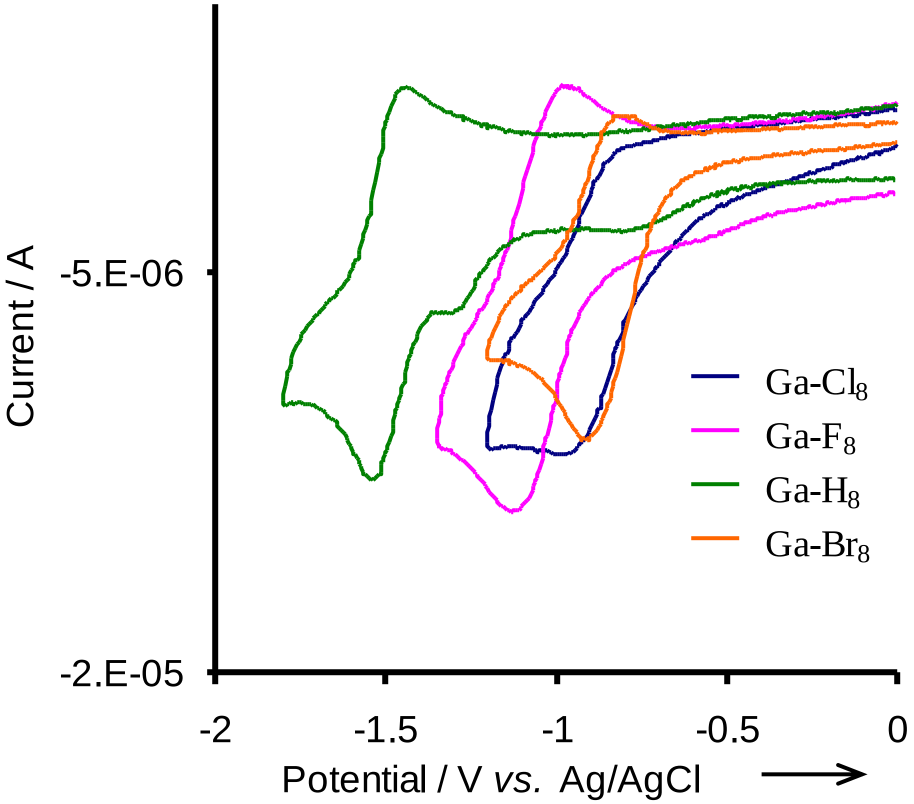


Fig. S1 Cyclic voltammograms of 1 mM Ga-X_8 complexes, in acetonitrile solutions (HPLC grade) with 0.1 M TBAP as electrolyte (Fluka, recrystallized twice from methanol), and under a N_2 atmosphere. Scan rate: 100 mVs^{-1}; glassy carbon working electrode. The mini-glassy carbon electrode was cleaned by using a polishing set for cleaning solid-state electrodes (Metrohm).

Table S1. First oxidation and first reduction potentials (V vs. Ag/AgCl) of Ga-X_8.

	First oxidation	**First reduction**
Ga(tpfc)(py)	0.70	-1.49
Ga(tpfc)(F8)(py)	1.13	-1.06
Ga(tpfc)(Cl8)(py)	1.16	-0.89
Ga(tpfc)(Br8)(py)	1.11	-0.86
Ferrocene	0.46	

Density Functional Theory Calculations:

All of the calculations were performed on the Inorganic-HPC cluster at IACS using the Gaussian 03 software package. The geometries were optimized with the spin-unrestricted formalism using both the BP86 functionals[7-9] and the 6-311G* basis set for Co and 6-31G* basis set for other atoms. Frequency calculations were performed on each optimized structure using the same basis set to ensure that it was a minimum on the potential energy surface. Total energy calculations were performed using the 6-311+G* and 6-31+G* basis set in water solvent[10] and a convergence criterion of 10^{-8} hartree. Basis-set superposition error has been reported to be minimal (~1 kcal/mol) for anion binding at this level of theory.

Table S2 Mulliken Atomic Charge Distribution for Co-F_8

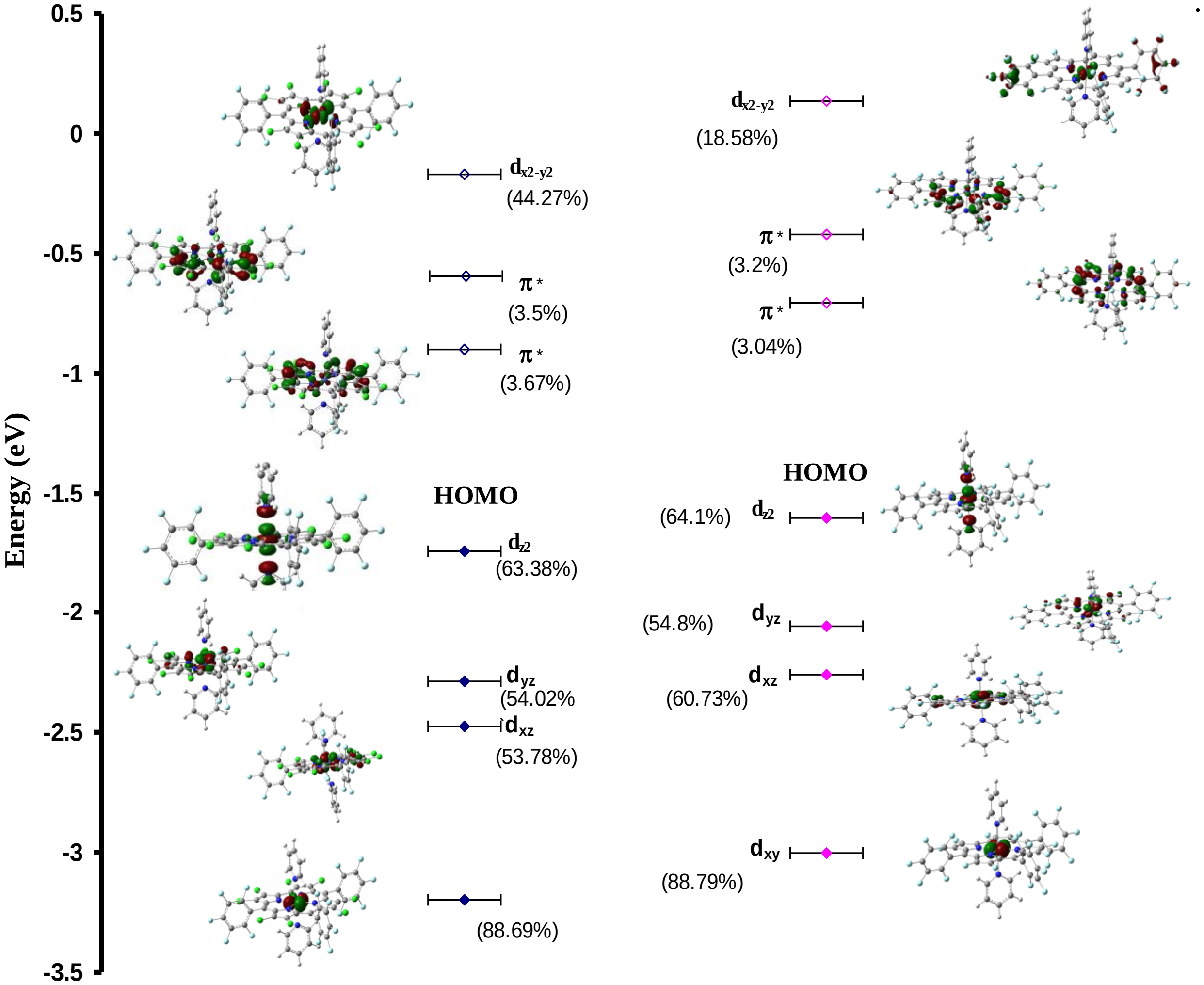
Co-F_8	**Atom**	**Mulliken atomic charges**	**Total charge in Corrole ring**
1	Co	1.18	-2.18
2	N	-0.65	
3	N	-0.68	
4	N	-0.68	
5	N	-0.65	
6	F	-0.27	
7	F	-0.28	
8	F	-0.28	
9	F	-0.28	
10	F	-0.28	
11	F	-0.28	
12	F	-0.28	
13	F	-0.27	
14	C	0.17	
15	C	0.19	
16	C	0.18	
17	C	0.24	
18	C	0.0	
19	C	0.21	
20	C	0.21	
21	C	0.21	
22	C	0.24	
23	C	-0.01	
24	C	0.23	
25	C	0.21	
26	C	0.21	
27	C	0.22	
28	C	0.0	
29	C	0.23	
30	C	0.18	
31	C	0.19	
32	C	0.18	
33	C	-0.20	
34	C	-0.21	
35	C	-0.22	
36	N	-0.39	
37	C	0.018	
38	C	-0.15	
39	C	-0.12	
40	C	-0.15	
41	C	0.02	
42	H	0.14	
43	H	0.14	
44	H	0.14	
45	H	0.17	

46	H	0.17
47	C	0.33
48	C	0.23
49	C	0.24
50	C	0.24
51	C	0.33
52	F	-0.26
53	F	-0.27
54	F	-0.27
55	F	-0.27
56	F	-0.27
57	C	0.32
58	C	0.23
59	C	0.24
60	C	0.23
61	C	0.32
62	F	-0.27
63	F	-0.27
64	F	-0.27
65	F	-0.27
66	F	-0.26
67	C	0.32
68	C	0.23
69	C	0.24
70	C	0.23
71	C	0.32
72	F	-0.27
73	F	-0.27
74	F	-0.27
75	F	-0.27
76	F	-0.26
77	N	-0.39
78	C	0.02
79	C	-0.15
80	C	-0.12
81	C	-0.14
82	C	0.02
83	H	0.17
84	H	0.14
85	H	0.13
86	H	0.14
87	H	0.17

Table S3 Mulliken Atomic Charge Distribution for Co-Cl_8.

Co-Cl_8	**Atom**	**Mulliken atomic charges**	**Total charge in Corrole ring**
1	Co	1.18	-2.21
2	N	-0.63	
3	N	-0.67	
4	N	-0.67	
5	N	-0.63	
6	Cl	0.02	
7	Cl	0.0	
8	Cl	0.01	
9	Cl	0.01	
10	Cl	0.01	
11	Cl	0.01	
12	Cl	0.0	
13	Cl	0.02	
14	C	0.23	
15	C	-0.16	
16	C	-0.21	
17	C	0.32	
18	C	-0.02	
19	C	0.28	
20	C	-0.16	
21	C	-0.17	
22	C	0.30	
23	C	-0.02	
24	C	0.0	
25	C	-0.17	
26	C	-0.16	
27	C	0.28	
28	C	-0.02	
29	C	0.32	
30	C	-0.21	
31	C	-0.16	
32	C	0.23	
33	C	-0.26	
34	C	-0.26	
35	C	-0.27	
36	N	-0.40	
37	C	0.02	
38	C	-0.15	
39	C	-0.12	
40	C	-0.15	
41	C	0.02	
42	H	0.14	
43	H	0.14	
44	H	0.15	

45	H	0.17
46	H	0.18
47	C	0.35
48	C	0.24
49	C	0.25
50	C	0.24
51	C	0.36
52	F	-0.26
53	F	-0.27
54	F	-0.27
55	F	-0.27
56	F	-0.26
57	C	0.35
58	C	0.24
59	C	0.25
60	C	0.24
61	C	0.35
62	F	-0.26
63	F	-0.27
64	F	-0.27
65	F	-0.27
66	F	-0.26
67	C	0.35
68	C	0.24
69	C	0.25
70	C	0.24
71	C	0.35
72	F	-0.26
73	F	-0.27
74	F	-0.27
75	F	-0.27
76	F	-0.25
77	N	-0.40
78	C	0.02
79	C	-0.15
80	C	-0.11
81	C	-0.14
82	C	0.02
83	H	0.17
84	H	0.15
85	H	0.14
86	H	0.14
87	H	0.18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-2
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π*
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π*
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HOMO
d_{z2}
(63.38%)
d_{yz}
(54.02%
d_{xz}
(53.78%)
(88.69%)
d_{x2-y2}
(18.58%)
π*
(3.2%)
π*
(3.04%)
HOMO
(64.1%)
d_{z2}
(54.8%)
d_{yz}
d_{xz}
(60.73%)
d_{xy}
(88.79%)

Table S4 Observed bond distances of Co-F_8 by optimized geometry and by crystal structure.[4]

Observed bond distances	**Optimized geometry**	**Crystal structure**
Co-$N_{corrole}$ (Å)	**1.89, 1.89, 1.91, 1.91**	**1.87, 1.88, 1.90, 1.90**
Co-N_{py} (Å)	**1.98, 1.99**	**2.01, 2.00**

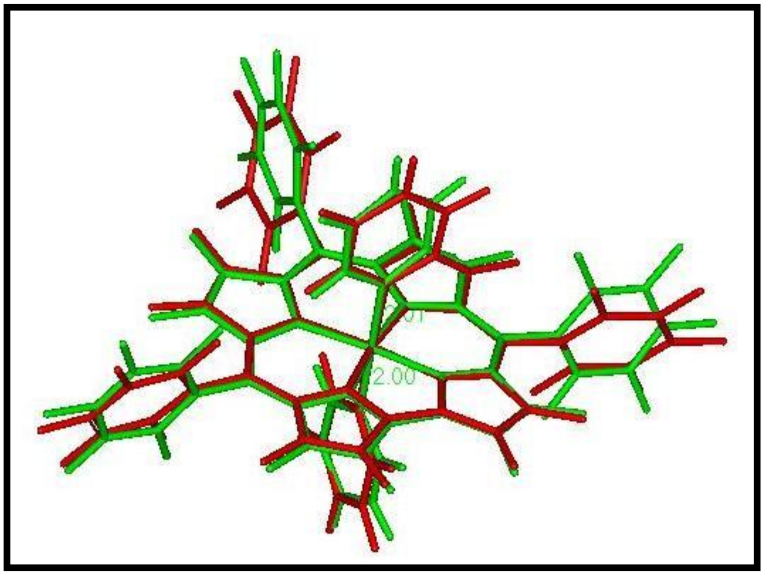


Fig. S3 Overlay of the optimized geometry (Red) with the crystal structure (Green) of Co-F_8.[4]

1. Catalytic Hydrogen Production: Heterogeneous Catalysis

a) Physiadsorption of the catalyst on Pyrolytic Graphite Electrode (EPG) Surface

The graphite electrode surface was first cleaned using grit paper and inserted into the RRDE tip. A chloroform solution of the catalysts was prepared. 50 μL of the catalyst was dropcasted onto the EPG surface and kept for 10 minutes. Then it was washed with chloroform, ethanol and double distilled water respectively and sonicated in water for a while. Then it was dried under Ar atmosphere.

b) Electrochemical hydrogen production by Co-X_8 adsorbed on EPG in aqueous H_2SO_4

The shaft bearing the EPG electrode and the Pt ring is vertically inserted to the water jacket cell and the cell is purged with N_2 for 30-60 minutes. Hydrogen generation experiments have been investigated in thoroughly degassed solutions (freeze-pump-thaw) to eliminate any electrocatalytic O_2 reduction. Background scans are performed under same conditions with bare electrodes. Linear sweep voltammetry (LSV) is performed at 300 rpm (rotations per minute) to investigate electrocatalytic H_2 generation.

c) Detection of catalytic proton reduction

The platinum ring was electrochemically cleaned and the Pyrolytic Graphite Electrode (EPG) was inserted into the RRDE tip and the catalyst was loaded which is then mounted on the rotor and immersed into a cylindrical glass cell which is equipped with Ag/AgCl reference and Pt counter electrodes. Scan rate and rotation speed was maintained at 50 mV/s and 300 rpm respectively. The potential (+0.7 V) at which the ring was held during the collection experiments for detecting H_2 was obtained from literature.[4]

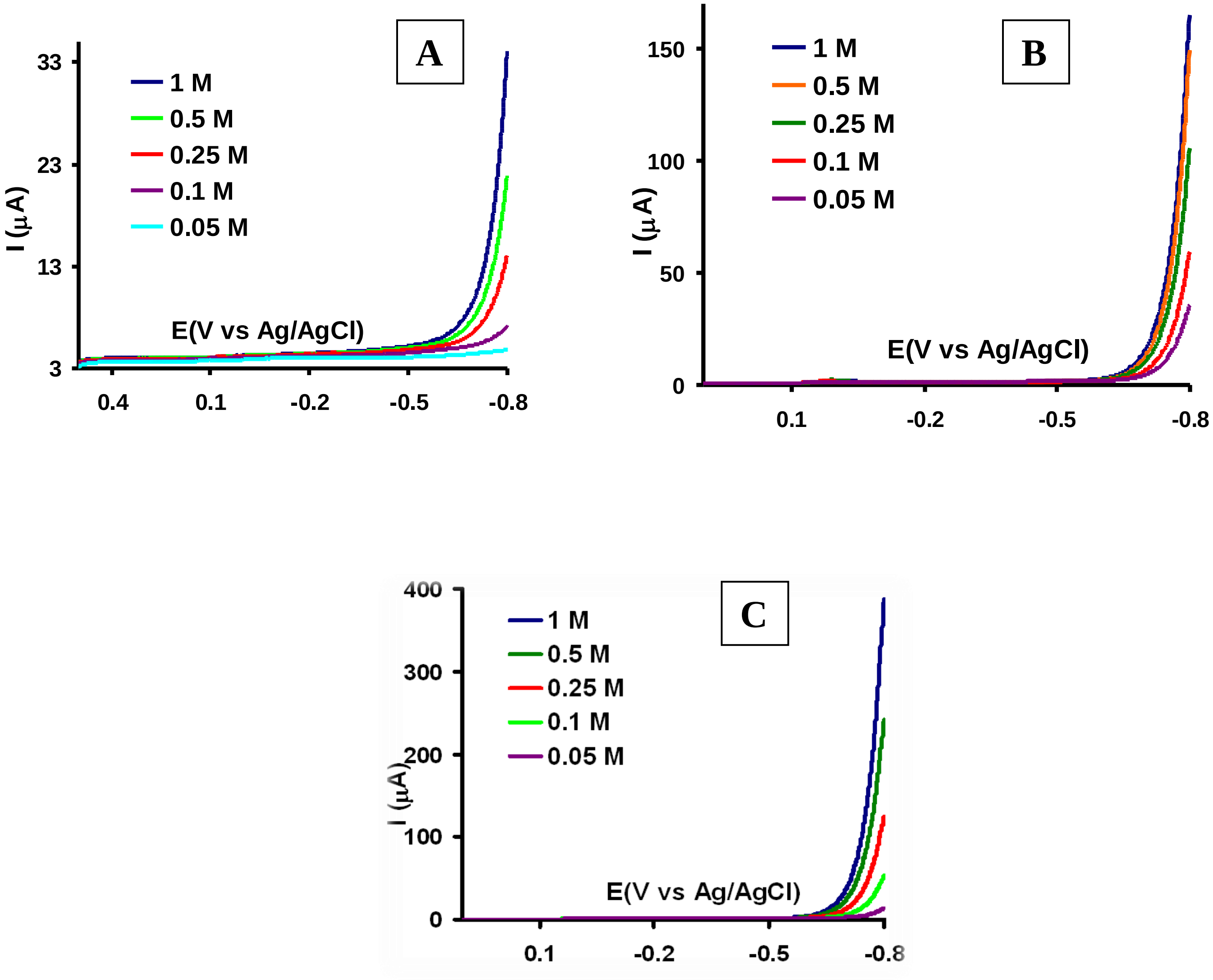
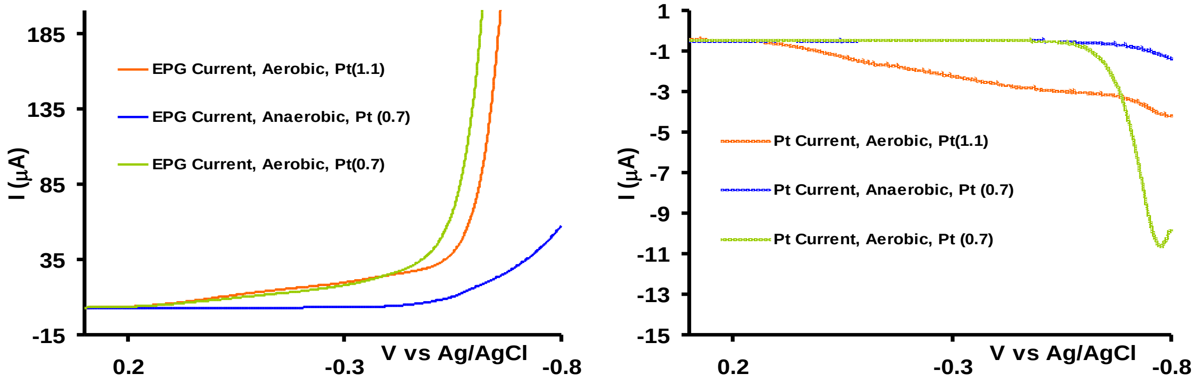
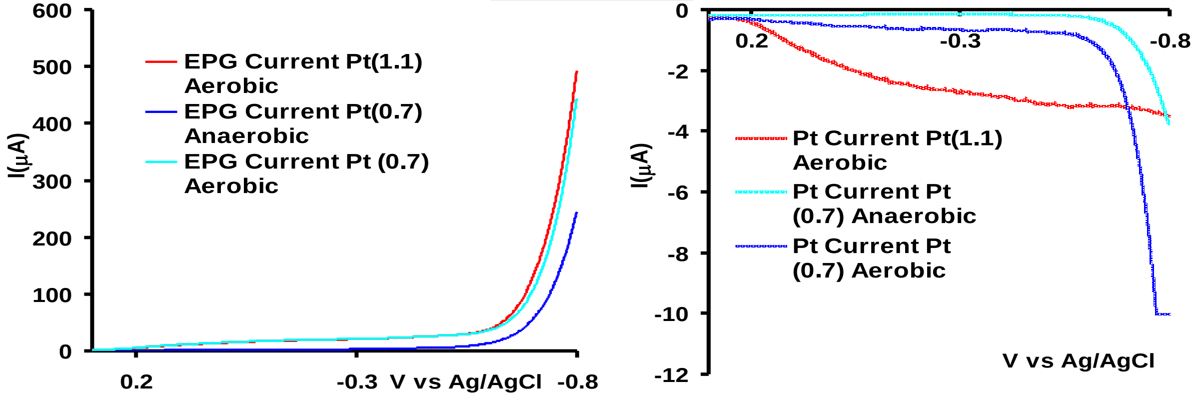


Fig. S4 RDE of Co-X_8 ctalysts physiadsorbed on EPG electrode on increasing H_2SO_4 concentration. Scan rate = 50 mV/s. Rotation Speed = 300 rpm. X = Br (A), Cl (B), F (C).

Co-Cl$_8$



Co-F$_8$



Co-Br$_8$

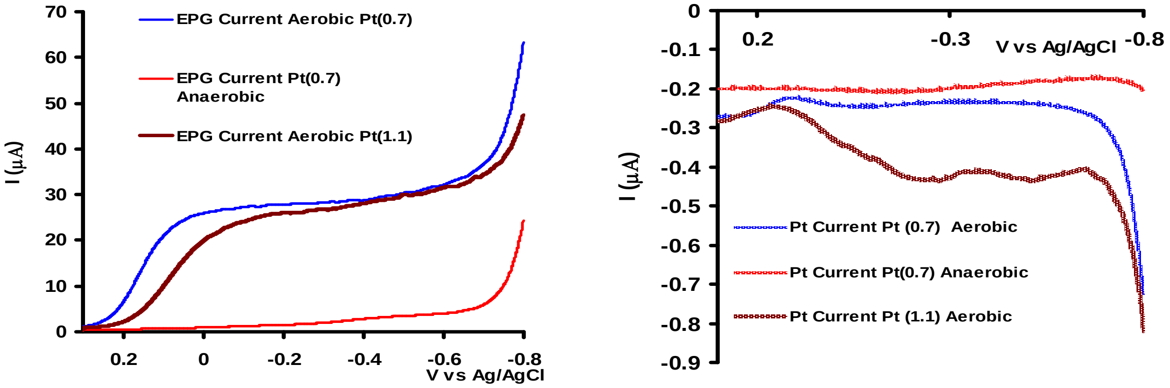


Fig. S5 Catalytic Hydrogen Production and Detection under Aqueous Condition in Anaerobic and Aerobic Conditions (under heterogeneous conditions).

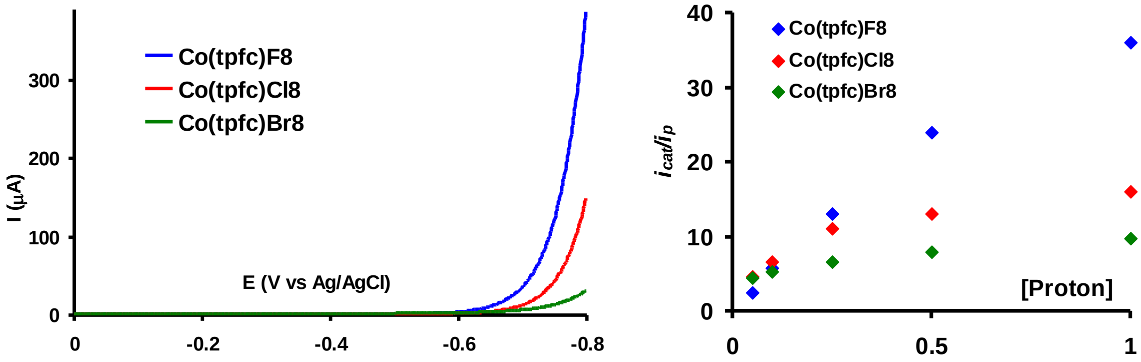


Fig. S6 A) LSV of EPG with catalysts Co-X_8 in deoxygenated 1N H_2SO_4 under N_2 atmosphere using Ag/AgCl as reference and Pt wire as counter electrodes. Scan rate = 50 mV/s. Rotation speed = 300 rpm. X = Br (green line), F (blue line), Cl (red line). b) Plot of i_{cat}/ip at – 0.7 V *vs*. [proton] for Co-X_8 compounds, X = Cl (red cube), Br (green cube), F (blue cube)

Table S5 Catalytic Onset Potential for Proton Reduction of Cobalt corroles in 1 N H_2SO_4 (under heterogeneous conditions).

Compounds	**Catalytic Onset Potential (V *vs* Ag/AgCl)**	**i_{cat}/ip at -0.7 V *vs* Ag/AgCl in 1 N H_2SO_4**
Co-F_8	-0.64	36
Co-Cl_8	-0.69	16
Co-Br_8	-0.73	9.7

2. Catalytic Hydrogen Production: Homogeneous Catalysis

CV measurements were performed in acetonitrile solutions (HPLC grade) containing: 0.1 M in tetrabutylammonium perchlorate (TBAP, Fluka, recrystallized twice from methanol), 1 mM catalyst (Co-X_8) and increasing amounts of TFA under N_2 atmosphere at ambient temperature. Scan rates of 100 mV/s, a mini glassy carbon electrode (diameter of the active zone: 2.8 mm; Metrohm) working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode.

Table S6. Catalytic rates, peak E_{cat}, catalytic onset potentials (E_{onset}), $E_{1/2}$ and Overpotentials for electrocatalytic H_2 production by Co-X_8 in homogeneous acetonitrile solution containing TFA [a]

	Co-F_8		Co-Cl_8		Co-Br_8	
	b	c	b	c	b	c
i_{cat}/i_p	11.6	25	5.5	12	3	7
peak E_{cat}	-1.06	-1.13	-1.30	-1.33	-0.93	-1.23
E_{onset}	-0.63	-0.60	-0.57	-0.54	-0.41	-0.42
$E_{1/2}$	-0.90	-0.91	-1.15	-1.15	-0.85	-1.05
Overpotential[d]	0.40	0.41	0.65	0.65	0.35	0.55
Overpotential[e]	0.60	0.60	0.85	0.86	0.55	0.76

(a) Potentials are in V *vs.* Ag/AgCl; i_{cat}/i_p for a scan rate of 100 mV/s; (b) [TFA]= 4 Mm; (c) [TFA]= 10 mM; (d) Ref. 11; (e) Calculated by taking account the homoconjugation that may increase the effective acidity of TFA (ref. 12).

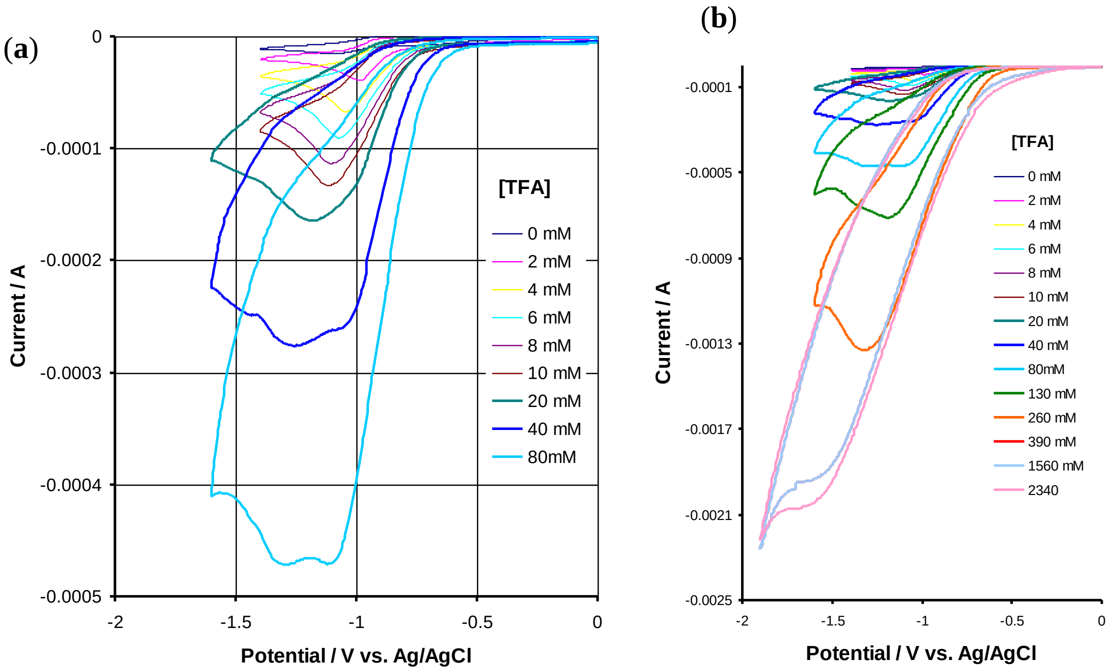


Fig. S7 Cyclic voltammograms of 1 mM Co-F_8 in homogeneous acetonitrile solutions containing 0.1 M TBAP and: a) 0 – 80 mM TFA; b) 0-2340 mM TFA. Scan rate: 100 mV/s, Working electrode: glassy carbon electrode.

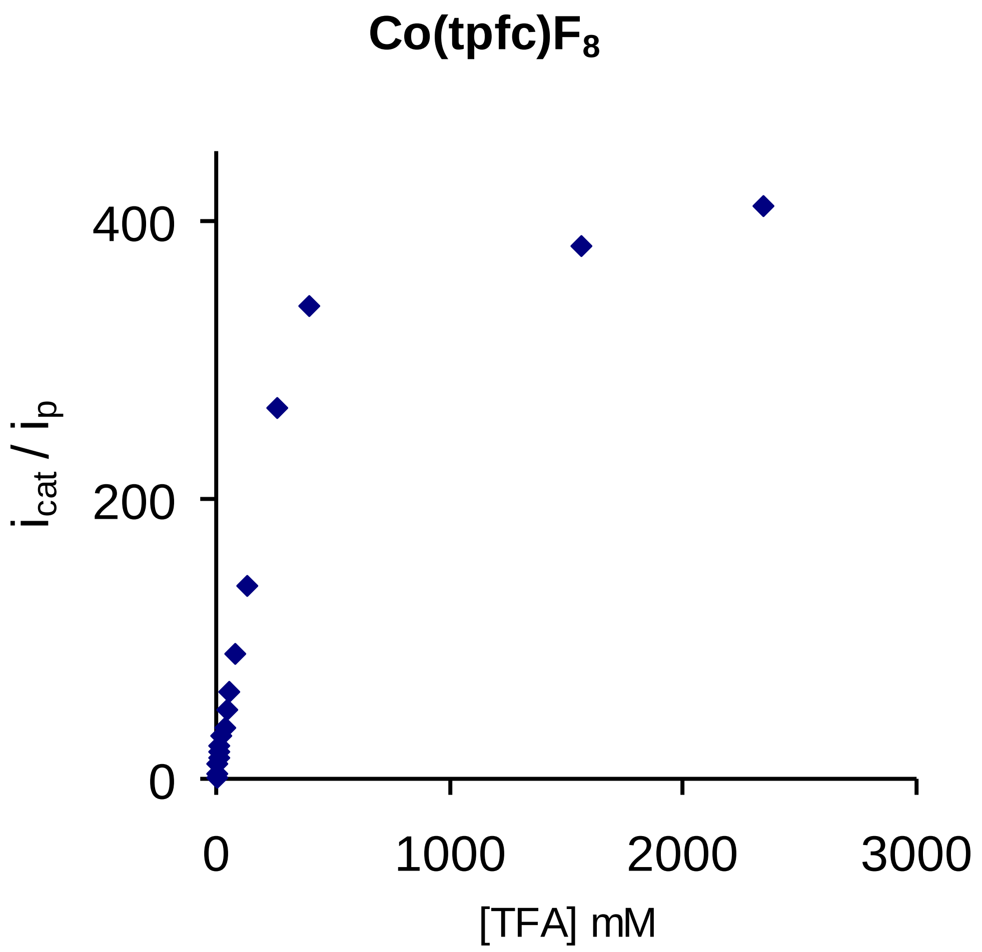


Fig. S8 Depending of i_{cat}/i_p for Co-F_8 on the concentration of TFA in acetonitrile. Scan rate: 100 mV/s, Working electrode: glassy carbon electrode. At 0.39 M TFA i_{cat}/i_p= 340 which corresponding to a turnover frequency of 22,400 s^{-1}, with an over potential of 415 mV.

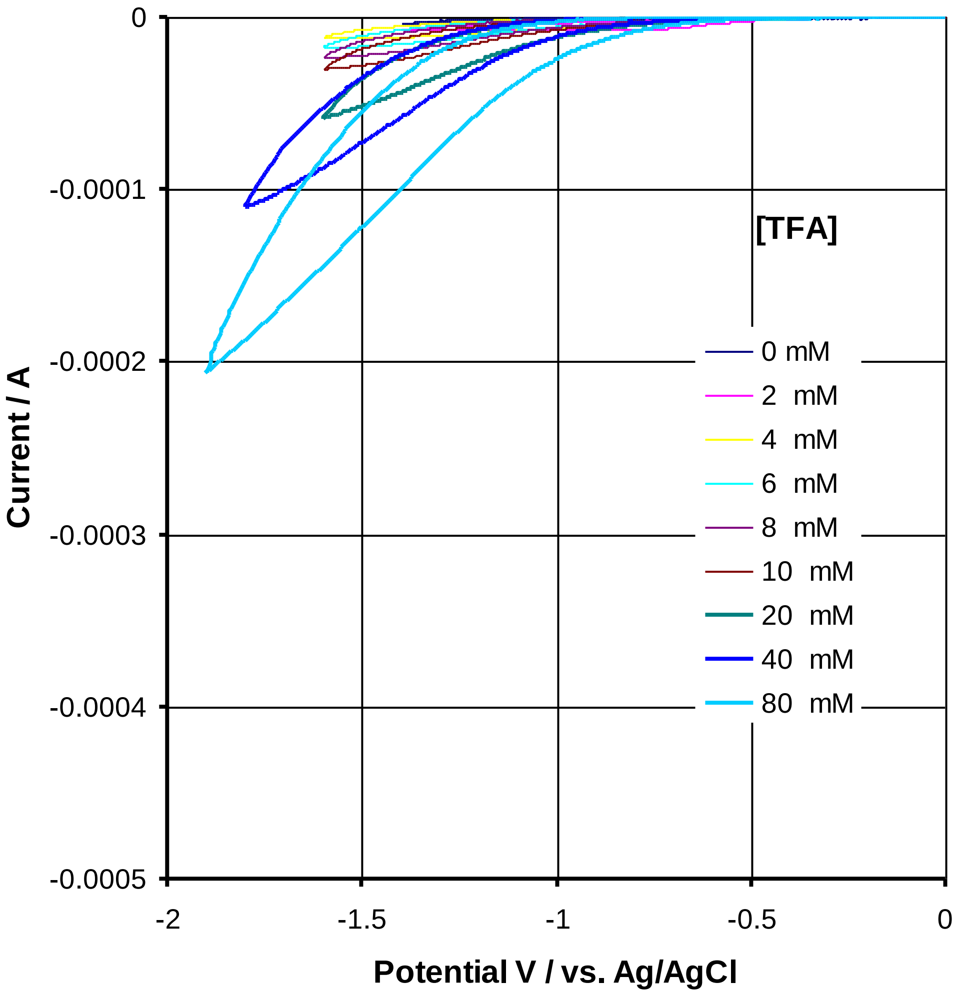
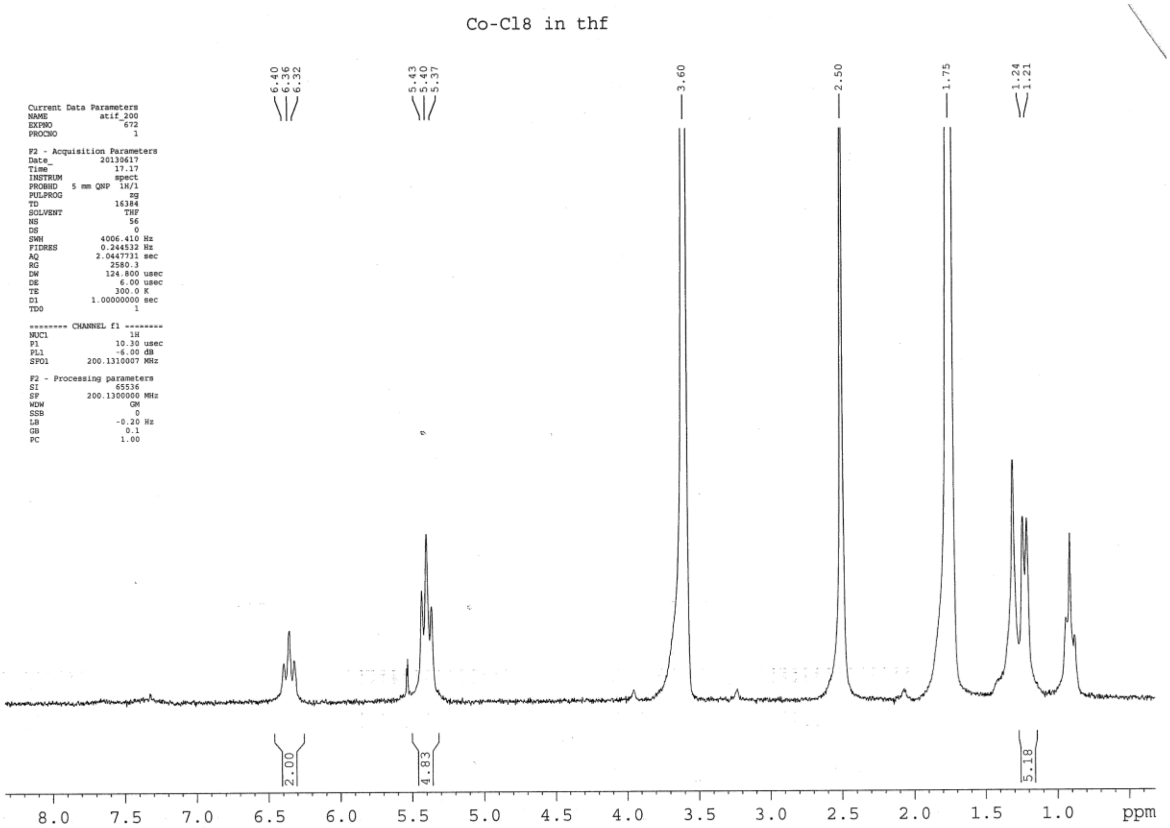


Fig. S9 Cyclic voltammograms of homogeneous acetonitrile solutions containing 0.1 M TBAP and 0 – 80 mM TFA. Scan rate: 100 mV/s, Working electrode: glassy carbon electrode.



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PROCNO                  1

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DS                      0
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FIDRES           0.244532 Hz
AQ              2.0447731 sec
RG                 2580.3
DW                124.800 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
TD0                     1

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P1                  10.30 usec
PL1                 -6.00 dB
SFO1          200.1310007 MHz

F2 - Processing parameters
SI                  65536
SF            200.1300000 MHz
WDW                    GM
SSB                     0
LB                  -0.20 Hz
GB                    0.1
PC                   1.00
```

Fig. S10 ^{1}H NMR spectrum of Co-Cl_8 in THF-d_8. Note the high field resonances of the coordinated pyridine (1.22 (*o*-H), 5.4 (*m*-H), and 6.36 (*p*-H) ppm).

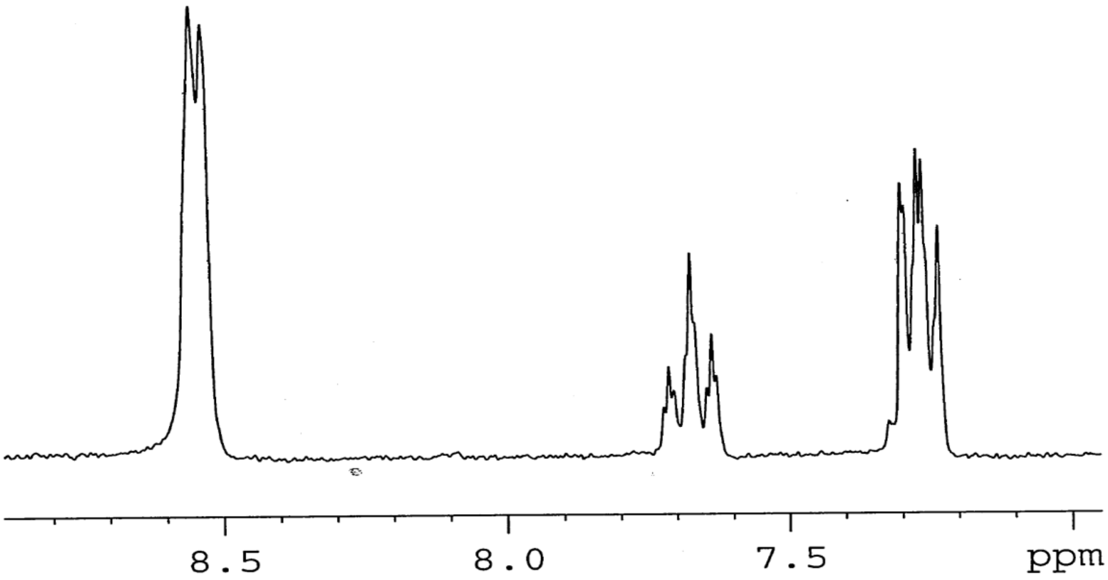

Fig. S11 ^{1}H NMR spectrum obtained upon reduction of Co-Cl_8 to [Co-Cl_8]$^{2-}$, in THF-d_8 under N_2 atmosphere. Note that the ^{1}H NMR spectrum displays only the resonances of non-coordinated pyridine (8.54 (*o*-H), 7.23 (*m*-H), and 7.65 (*p*-H) ppm).

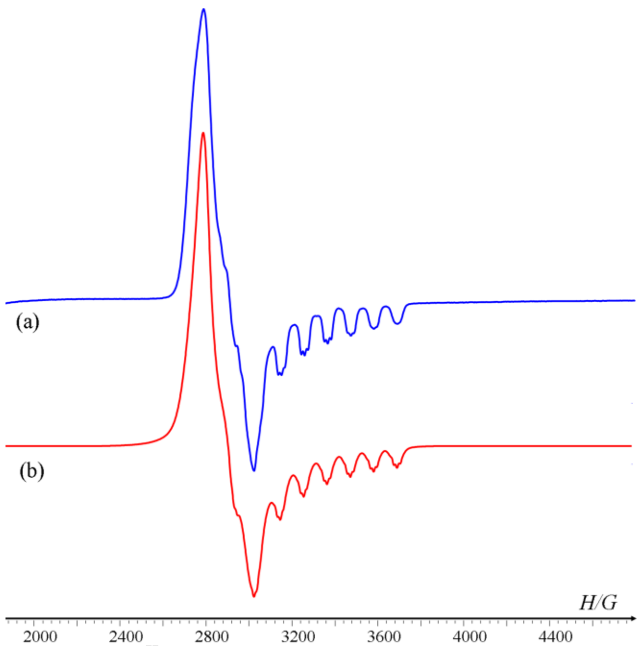

Fig. S12 (a) EPR spectrum of $[Co^{II}\text{-}Cl_8]^-$ in frozen THF glass at 140K with sodium borohydride as reducing agent. (b) Simulated spectrum with $g_1 = 2.320$, $g_2 = 2.270$, $g_3 = 1.996$; $A_1(^{59}Co) \approx 27.0$ G, $A_2(^{59}Co) \approx 23.0$ G, $A_3(^{59}Co) = 108.0$ G and $A_3(^{14}N) = 15.6$ G.

The EPR spectrum of $[Co^{II}\text{-}Cl_8]^-$ in frozen solvent glass is rhombic. The diagonal components of the g-tensor ($g_1 = 2.320$, $g_2 = 2.270$, and $g_3 = 1.996$) and hyperfine coupling tensor A with ^{59}Co [$A_1(^{59}Co) \approx 27.0$ G, $A_2(^{59}Co) \approx 23.0$ G, and $A_3(^{59}Co) = 108.0$ G] of $[Co^{II}\text{-}Cl_8]^-$ are consistent with Co(II) compounds in general. An additional hyperfine coupling with one ^{14}N nuclei of pyridine was observed [$A_3(^{14}N) = 15.6$ G].

References

1 J. Bendix, I. J. Dmochowski, H. B. Gray, A. Mahammed, L. Simkhovich and Z. Gross, *Angew. Chem. Int. Ed.*, 2000, **39**, 4048.

2 L. Wagnert, R. Rubin, A. Berg, A. Mahammed, Z. Gross and H. Levanon, *J. Phys. Chem. B*, 2010, **114**, 14303.

3 L. Simkhovich, A. Mahammed, I. Goldberg and Z. Gross, *Chem. Eur. J.*, 2001, **7**, 1041.

4 B. Mondal, K. Sengupta, A. Rana, A. Mahammed, M. Botoshansky, S. G. Dey, Z. Gross and A. Dey, *Inorg. Chem.*, 2013, **52**, 3381.

5 A. Mahammed, M. Botoshansky and Z. Gross, *Dalton Trans.*, 2012, **41**, 10938.

6 A. Mahammed, B. Tumanskii and Z. Gross, *J. Porphyrins Phthalocyanines*, 2011, **15**, 1275.

7 A. D. Becke, *Phys. Rev. A.*, 1988**, 38**, 3098.

8 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. A. Montgomery, Jr. J. E. 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 03,* C.02; *Gaussian, Inc.: Wallingford,* CT, 2004.

9 J. P. Perdew, *Phys. Rev. B*, 1986**, 33**, 8822.

10 S. Miertus, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981**, 55**, 117.

11 (a) G. A. N. Felton, R. S. Glass, D. L. Lichtenberger and D. H. Evans, *Inorg. Chem.*, 2006, **45**, 9181; (b) P. -A. Jacques, V. Artero, J. Pécaut and M. Fontecave, *Proc. Nat. Acad. Sci.*, 2009, **106**, 20627.

12 V. Fourmond, P. A. Jacques, M. Fontecave and V. Artero, *Inorg. Chem.* 2010, **49**, 10338.