Electronic Supplementary Information

Electrochemical hydrogen evolution reaction catalysed by a dinuclear cobalt complex with doubly N-confused hexaphyrin

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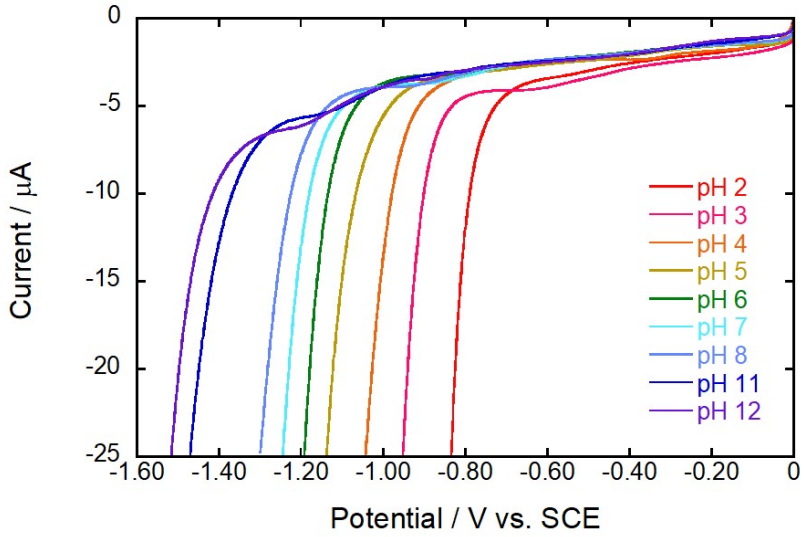


Fig. S1 LSVs using the complex-modified electrode in 0.10 M phosphate buffer solutions (pH 2.0, 3.0, 6.0-12) and 0.10 M acetic acid buffer solutions (pH 4.0, 5.0). $\nu = 0.10$ Vs^{-1}. Working electrode: glassy carbon (0.071 cm^2) modified with 35 μg cm^{-2} of MW-CNT and 2.8 nmol cm^{-2} of **Co_2DNCH**, temp: 295 K, under Ar atmosphere.

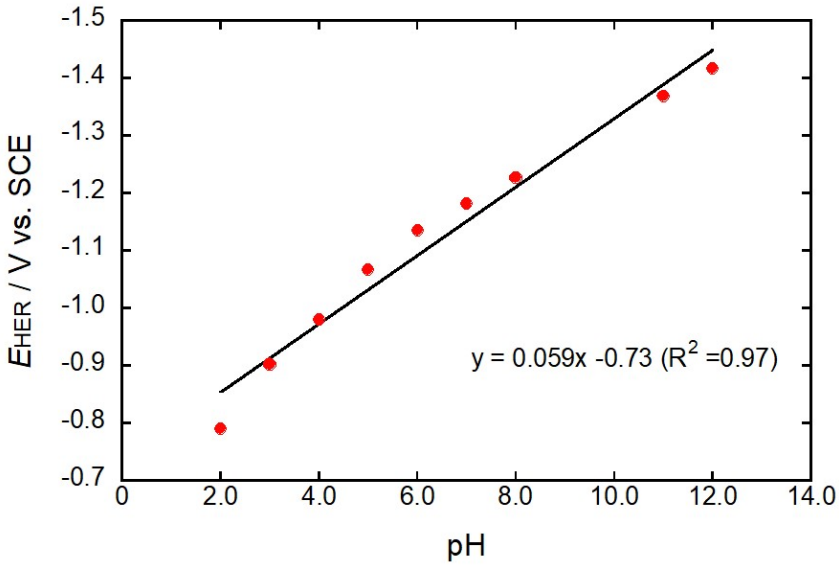


Fig. S2 A plot of E_{HER} for **Co_2DNCH** vs. pH of phosphate buffer solutions.

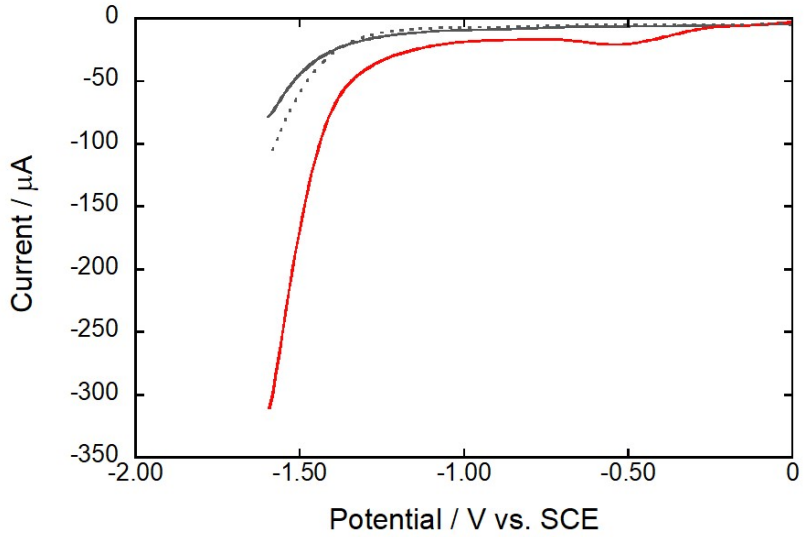


Fig. S3 LSVs using the complex-modified electrodes in a 0.10 M phosphate buffer solution (pH 7.0). Working electrode: grassy carbon electrode (0.071 cm^2) modified with **Co_2DNCH** and MW-CNT (red), MW-CNT (grey), MW-CNT after measurement of LSV using the **Co_2DNCH** modified electrode and rinsing the electrode with acetone (dashed line).

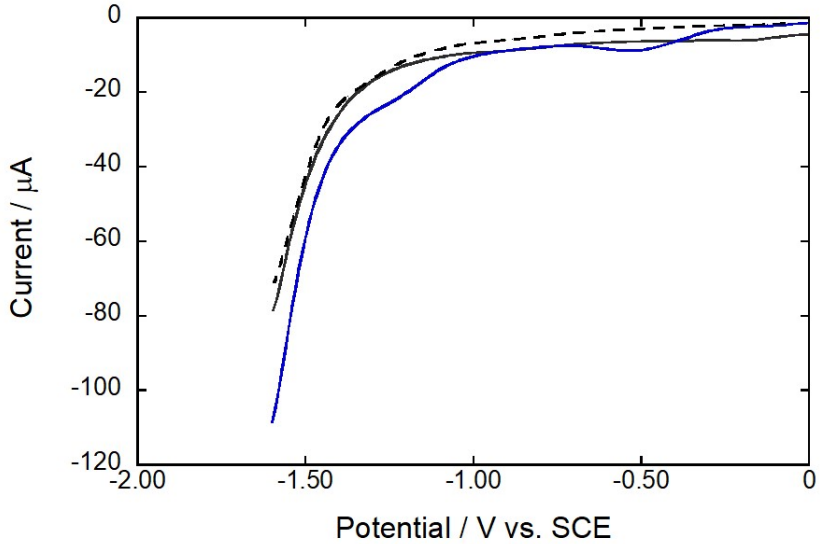


Fig. S4 LSVs using the complex-modified electrodes in a 0.10 M phosphate buffer solution (pH 7.0). Working electrode: grassy carbon electrode (0.071 cm^2) modified with **$CoPF_5$** and MW-CNT (blue), MW-CNT (grey), MW-CNT after measurement of LSV using the **$CoPF_5$** modified electrode and rinsing the electrode with acetone (dashed line).

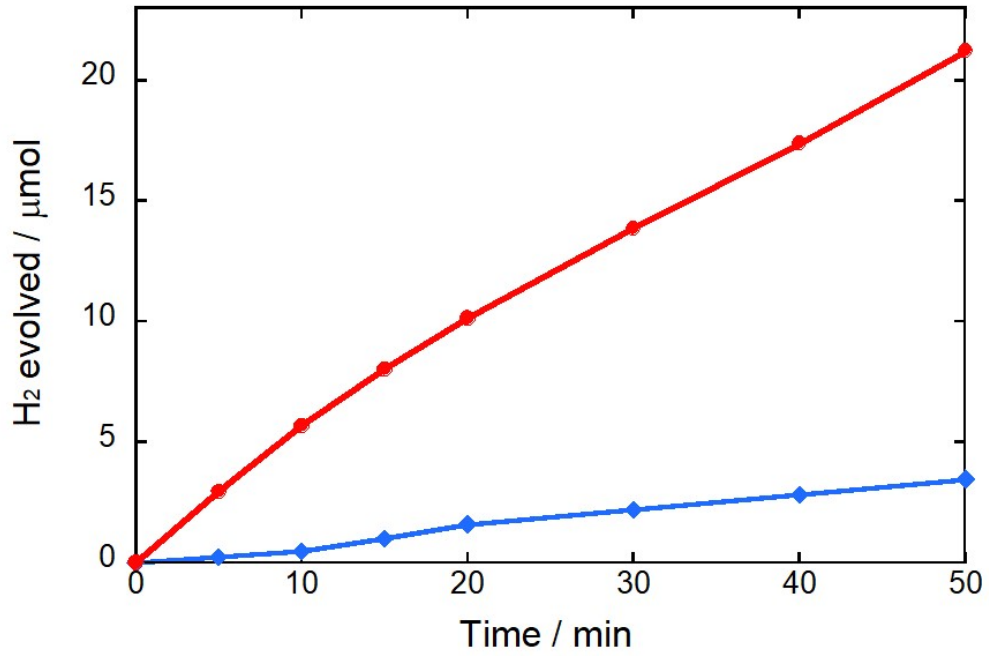


Fig. S5 Electrochemical H_2 evolution from 0.10 M phosphate buffer solution (pH 7.0) using **Co_2DNCH** (red) and **$CoPF_5$** (blue) modified onto a glassy carbon electrode at -1.1 V.

Table S1 Redox potentials of **Co_2DNCH** and **$CoPF_5$** in DMF

	Potential (V *vs*. SCE)			
	-1/0	-2/-1	-3/-2	-4/-3
$CoPF_5$	-0.60	-1.59		
Co_2DNCH	-0.47	-0.80	-1.49	-1.65

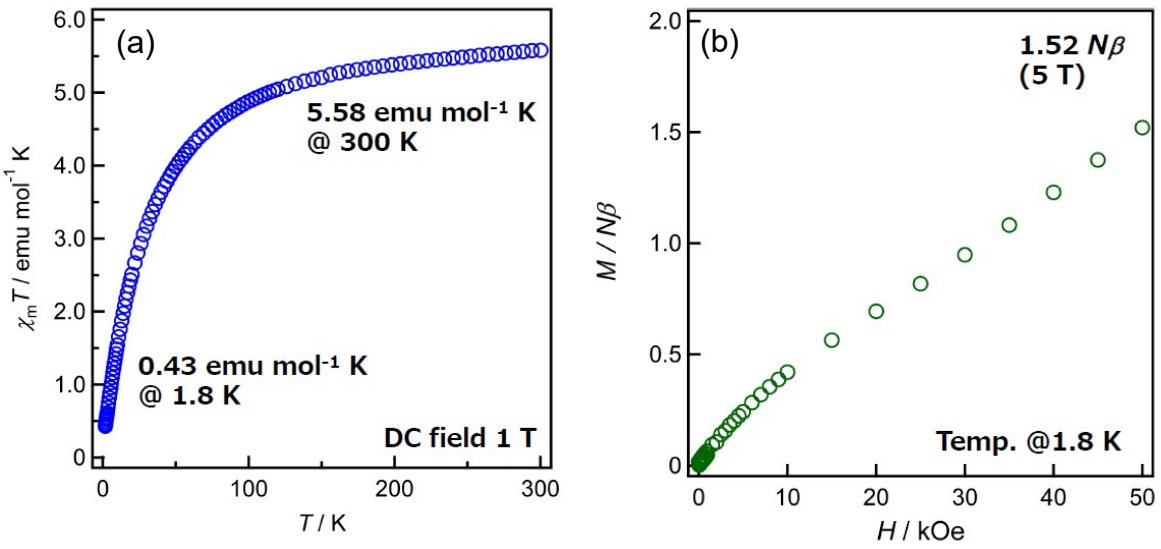


Fig. S6 Plots of (a) $\chi_m T$ vs. T and (b) M - H curve for a dried sample of **Co_2DNCH**.

DFT calculation

Furuta et al. have reported the crystal structure of **Co_2DNCH** in which the five-coordinated geometry of two Co^{2+} ions are coordinated by DNCH and aqua.[1] The two aqua ligands on Co ions bond to two THF molecules by hydrogen bonds, respectively. Based on this crystal structure, three initial structure models: (**a**) [$Co_2(OH_2)_2$DNCH] + 4THF, (**b**) [$Co_2(OH_2)_2$DNCH], and (**c**) [Co_2DNCH]) were prepared and optimised calculations were performed with the calculation methods described in the experimental section of the main text. The models **a** and **c** reproduced well the bond lengths and bond angles between the central metal and ligands in the crystal structure (Table S2, Fig. S8). The structure optimization calculations for **b** resulted in a dominant intramolecular hydrogen bond between the ketone moiety in DNCH and the aqua ligand (Fig. S8). This is because of the absence of THF, which forms an intermolecular hydrogen bond with the aqua ligand in the crystal. The most stable spin state from singlet to septet was estimated to be the septet (2S+1 = 7) in all computational models (Table S3). In addition to the high reproducibility of the crystal structure in models **a** and **c**, the septet state is by far the most stable compared to the other spin states, supporting the results of the magnetic measurements. Therefore, the influence of the aqua ligand on the results of the energy and structure calculations is insignificant. Furthermore, the aqua ligand on Co ions of **Co_2DNCH** would be labile in DMF solution. For these reasons, the model in **c** was used in the following calculations.

Table S2 Selected bond lengths (Å) and angles (°) of **Co_2DNCH** determined by X-ray analysis of the single crystal and DFT calculations.

		Model		
	crystal	**a**	**b**	**c**
$rCo_1–O_2$	1.932	2.023	2.089	2.035
$rCo_1–N_6$	2.139	2.169	2.143	2.006
$rCo_1–N_5$	2.007	2.035	2.036	2.052
$rCo_1–N_4$	2.052	2.119	2.119	2.071
$rCo_1–Co_{51}$	4.802	4.865	4.694	4.801
$\angle O_2–Co_1–N_5$	137.8	135.9	138.2	150.0
$\angle N_2–Co_1–N_4$	174.5	168.4	177.6	169.0
$\angle O_2–Co_1–O_3$	108.7	109.9	88.2	-
$\angle O_{27}–Co_{51}–O_{52}$	108.7	110.8	88.2	-

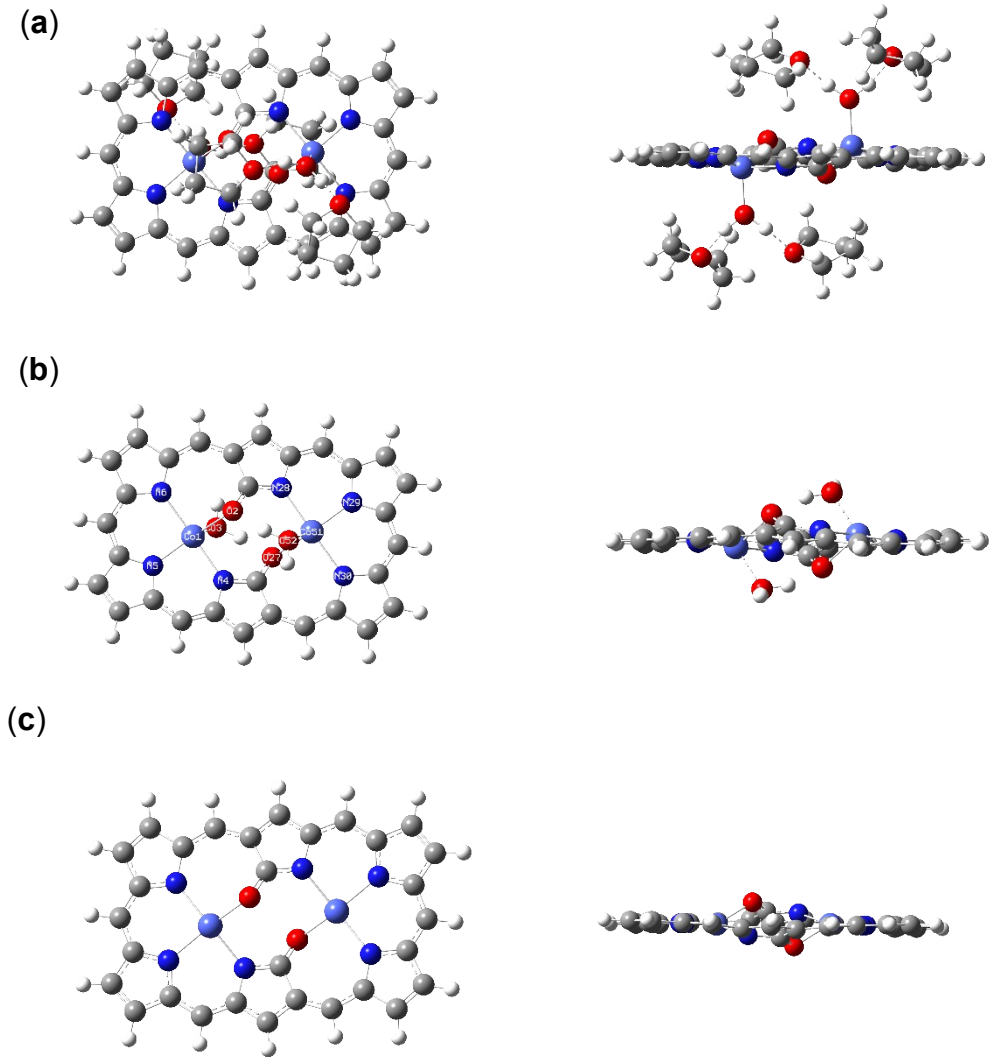


Fig. S7 Structure of geometry optimization using the initial structure models **a**, **b**, and **c** (2S+1 = 7).

Table S3 Relative energies of **Co_2DNCH** using different computational models.

	ΔE / kcal mol^{-1}			
models	Singlet	Triplet	Quintet	Septet
a	77.5	16.0	9.39	0.00
b	15.2	15.2	7.91	0.00
c	65.7	9.8	27.1	0.00

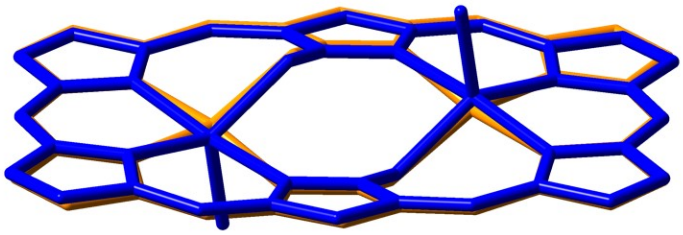


Fig. S8 Overlaid structures of crystal structure of **Co_2DNCH** (blue) and geometry optimization (2S+1 = 7) using **c** (orange).

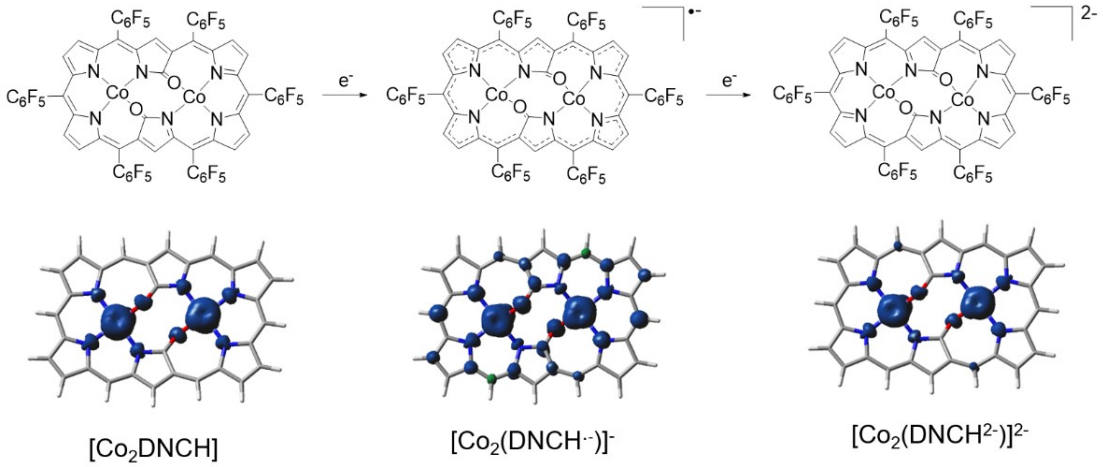


Fig. S9 DFT-derived spin density plots of **Co_2DNCH** and the one- and two-electron-reduced forms.

Table S4 Relative energies (kcal mol^{-1}) of the different spin states of **Co_2DNCH** and the one- and two-electron reduced forms.

Spin state	[Co_2DNCH]	[Co_2(DNCH$^{\cdot-}$)]$^{-}$	[Co_2(DNCH^{2-})]$^{2-}$
singlet	65.7	-	45.0
triplet	9.78	-	14.4
quintet	27.1	-	29.9
septet	0.00	-	0.00
nonet	18.9	-	25.8
doublet	-	17.0	-
quintet	-	12.5	-
sextet	-	33.3	-
octet	-	0.00	-

Cartesian coordinates of optimized geometries

[Co_2DNCH] (**c**, 2S + 1 = 7)

SCF done: E(UB3LYP) = -1921.87444321

Co	-2.05441400	0.27315000	1.21155300
O	-1.00272500	0.94601100	-0.39601300
N	-0.27623200	-0.17115400	2.16223800
N	-2.92477900	0.61912400	3.03758900
N	-3.89548100	0.32588600	0.26525800
C	-0.90296600	0.40746600	-1.53500300
C	-2.03970800	0.02543900	-2.43348900
C	-3.42161700	0.01580700	-2.20058200
C	-4.22911600	0.17212800	-1.07037600
C	-5.66945900	0.19687100	-1.21659300
H	-6.19137900	0.09308700	-2.15963000
C	-6.19843500	0.39500700	0.02173000
H	-7.24030400	0.48430600	0.30257900
C	-5.08858400	0.47337300	0.94065200
C	-5.25965200	0.69184100	2.31349100
C	-4.26431400	0.77805700	3.28414600
C	-4.47499400	1.03684600	4.69125700
H	-5.43996900	1.19518700	5.15628900
C	-3.24311600	1.03763400	5.28169800
H	-3.00156400	1.19438900	6.32549100
C	-2.27906300	0.75918800	4.24109200
C	-0.89832300	0.64470000	4.42448700
C	0.03690300	0.27139300	3.46019800
C	1.43548000	0.32300800	3.64255000
H	1.93656200	0.63775400	4.54988700
O	1.00272500	-0.94601100	0.39601300
N	0.27623200	0.17115400	-2.16223800
N	2.92477900	-0.61912400	-3.03758900
N	3.89548100	-0.32588600	-0.26525800
C	0.90296600	-0.40746600	1.53500300
C	2.03970800	-0.02543900	2.43348900
C	3.42161700	-0.01580700	2.20058200
C	4.22911600	-0.17212800	1.07037600
C	5.66945900	-0.19687100	1.21659300
H	6.19137900	-0.09308700	2.15963000
C	6.19843500	-0.39500700	-0.02173000
H	7.24030400	-0.48430600	-0.30257900
C	5.08858400	-0.47337300	-0.94065200
C	5.25965200	-0.69184100	-2.31349100
C	4.26431400	-0.77805700	-3.28414600
C	4.47499400	-1.03684600	-4.69125700
H	5.43996900	-1.19518700	-5.15628900
C	3.24311600	-1.03763400	-5.28169800
H	3.00156400	-1.19438900	-6.32549100
C	2.27906300	-0.75918800	-4.24109200
C	0.89832300	-0.64470000	-4.42448700
C	-0.03690300	-0.27139300	-3.46019800
C	-1.43548000	-0.32300800	-3.64255000
H	-1.93656200	-0.63775400	-4.54988700
Co	2.05441400	-0.27315000	-1.21155300

H	-4.00494300	-0.17568500	-3.10006300
H	0.51175200	-0.87624700	-5.41286500
H	6.28431400	-0.81239000	-2.65261400
H	4.00494300	0.17568500	3.10006300
H	-0.51175200	0.87624700	5.41286500
H	-6.28431400	0.81239000	2.65261400

$[Co_2(DNCH^{-})]^{-}$ (**c**, 2S + 1 = 8)
SCF Done: E(UB3LYP) = -1922.04825811

Co	-2.06292100	0.28495800	1.20989600
O	-1.00871400	1.00267000	-0.39523800
N	-0.27097500	-0.18809400	2.15689400
N	-2.94101300	0.62428100	3.03680500
N	-3.91608700	0.31694700	0.26914300
C	-0.91353100	0.43503400	-1.53712200
C	-2.03824700	0.04575600	-2.42021300
C	-3.43873000	0.05257600	-2.20193300
C	-4.24580100	0.18669700	-1.08022600
C	-5.69157500	0.21015000	-1.22287600
H	-6.21407100	0.12024500	-2.16807700
C	-6.22247700	0.38402900	0.01769600
H	-7.26627400	0.46556800	0.29713900
C	-5.11183500	0.45602100	0.94739300
C	-5.28798900	0.66633600	2.31688800
C	-4.27910900	0.76744100	3.29172200
C	-4.48383200	1.03066100	4.69417500
H	-5.44725800	1.18127600	5.16684700
C	-3.23923600	1.04972400	5.28232400
H	-2.99789700	1.21606300	6.32573400
C	-2.28277400	0.77817900	4.24584000
C	-0.89797400	0.66911000	4.41105900
C	0.03479600	0.28045200	3.44888500
C	1.43720600	0.33473100	3.62304200
H	1.94362400	0.66515400	4.52342800
O	1.00871400	-1.00267000	0.39523800
N	0.27097500	0.18809400	-2.15689400
N	2.94101300	-0.62428100	-3.03680500
N	3.91608700	-0.31694700	-0.26914300
C	0.91353100	-0.43503400	1.53712200
C	2.03824700	-0.04575600	2.42021300
C	3.43873000	-0.05257600	2.20193300
C	4.24580100	-0.18669700	1.08022600
C	5.69157500	-0.21015000	1.22287600
H	6.21407100	-0.12024500	2.16807700
C	6.22247700	-0.38402900	-0.01769600
H	7.26627400	-0.46556800	-0.29713900
C	5.11183500	-0.45602100	-0.94739300
C	5.28798900	-0.66633600	-2.31688800
C	4.27910900	-0.76744100	-3.29172200
C	4.48383200	-1.03066100	-4.69417500
H	5.44725800	-1.18127600	-5.16684700
C	3.23923600	-1.04972400	-5.28232400
H	2.99789700	-1.21606300	-6.32573400

C	2.28277400	-0.77817900	-4.24584000
C	0.89797400	-0.66911000	-4.41105900
C	-0.03479600	-0.28045200	-3.44888500
C	-1.43720600	-0.33473100	-3.62304200
H	-1.94362400	-0.66515400	-4.52342800
Co	2.06292100	-0.28495800	-1.20989600
H	-4.01356700	-0.11348100	-3.11288100
H	0.50159200	-0.91474700	-5.39388800
H	6.31331000	-0.77457500	-2.66058500
H	4.01356700	0.11348100	3.11288100
H	-0.50159200	0.91474700	5.39388800
H	-6.31331000	0.77457500	2.66058500

$[Co_2(DNCH^{2-})]^{2-}$ (**c**, 2S + 1 = 7)
SCF Done: E(UB3LYP) = -1922.14903113

Co	-2.08389400	0.29985900	1.21302800
O	-1.00795600	1.02288300	-0.40260500
N	-0.27898500	-0.17772200	2.15195800
N	-2.96265400	0.63169300	3.04937800
N	-3.91516000	0.31873000	0.27764000
C	-0.90950900	0.44694600	-1.54481500
C	-2.03317500	0.06471500	-2.42565900
C	-3.45030700	0.10363500	-2.20523000
C	-4.24328400	0.21008900	-1.08088200
C	-5.69831100	0.22305600	-1.21790200
H	-6.21934700	0.14518600	-2.16583000
C	-6.23133600	0.36472900	0.02027300
H	-7.27787700	0.42765600	0.29759700
C	-5.12474700	0.43935400	0.96439800
C	-5.31462600	0.63852500	2.31862500
C	-4.30315100	0.75941300	3.31327900
C	-4.50217400	1.02494500	4.70109400
H	-5.46286500	1.16920500	5.18300200
C	-3.23873600	1.06349500	5.28696400
H	-2.99601000	1.23644500	6.32995200
C	-2.29680700	0.80360400	4.25496400
C	-0.89499700	0.70172500	4.39674400
C	0.02118000	0.29740000	3.44326100
C	1.43918800	0.33803700	3.61138300
H	1.94754800	0.66976200	4.51154400
O	1.00795600	-1.02288300	0.40260500
N	0.27898500	0.17772200	-2.15195800
N	2.96265400	-0.63169300	-3.04937800
N	3.91516000	-0.31873000	-0.27764000
C	0.90950900	-0.44694600	1.54481500
C	2.03317500	-0.06471500	2.42565900
C	3.45030700	-0.10363500	2.20523000
C	4.24328400	-0.21008900	1.08088200
C	5.69831100	-0.22305600	1.21790200
H	6.21934700	-0.14518600	2.16583000
C	6.23133600	-0.36472900	-0.02027300
H	7.27787700	-0.42765600	-0.29759700
C	5.12474700	-0.43935400	-0.96439800

C	5.31462600	-0.63852500	-2.31862500
C	4.30315100	-0.75941300	-3.31327900
C	4.50217400	-1.02494500	-4.70109400
H	5.46286500	-1.16920500	-5.18300200
C	3.23873600	-1.06349500	-5.28696400
H	2.99601000	-1.23644500	-6.32995200
C	2.29680700	-0.80360400	-4.25496400
C	0.89499700	-0.70172500	-4.39674400
C	-0.02118000	-0.29740000	-3.44326100
C	-1.43918800	-0.33803700	-3.61138300
H	-1.94754800	-0.66976200	-4.51154400
Co	2.08389400	-0.29985900	-1.21302800
H	-4.02721400	-0.02919300	-3.12080200
H	0.48695400	-0.97087100	-5.36987100
H	6.34423300	-0.72664900	-2.65800800
H	4.02721400	0.02919300	3.12080200
H	-0.48695400	0.97087100	5.36987100
H	-6.34423300	0.72664900	2.65800800

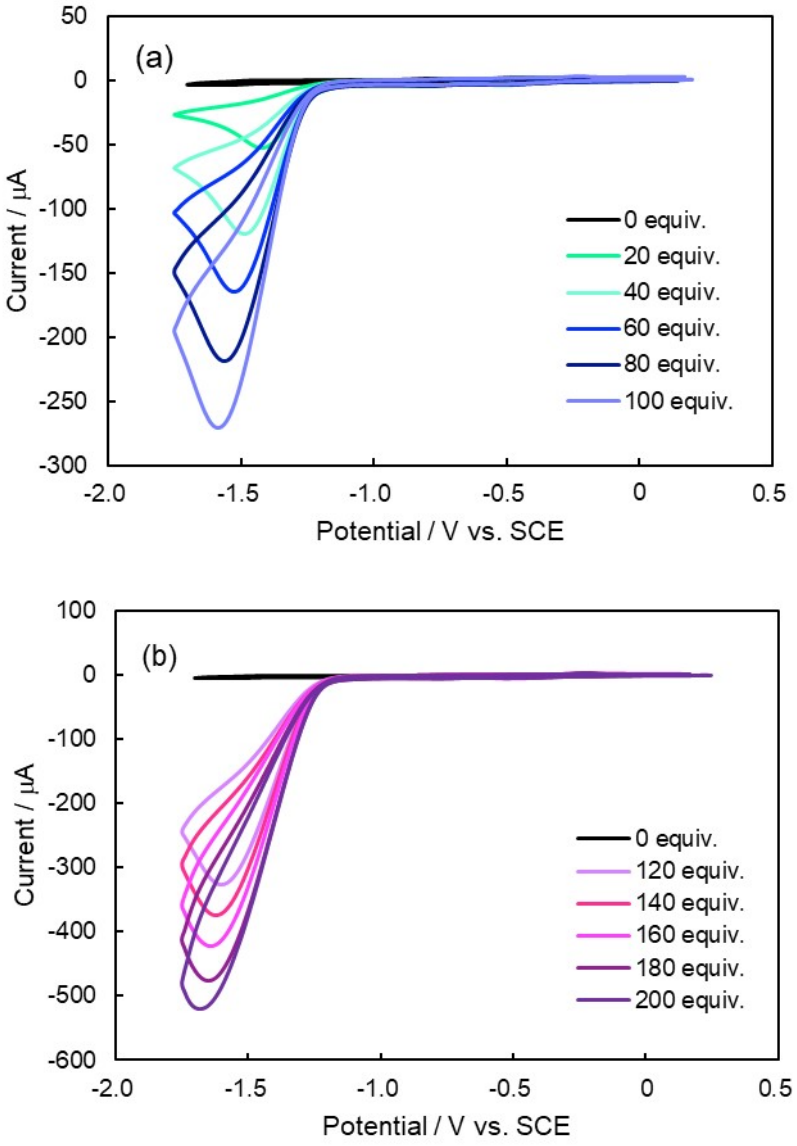


Fig. S10 CVs of **Co_2DNCH** (0.25 mM) in DMF solutions in the absence (black) and presence of 20-100 equivalents (a) and 120-200 equivalents (b) of Et_3NHCl. Working electrode: grassy carbon (0.071 cm^2), counter electrode: Pt wire, reference electrode: $Ag/AgNO_3$, scan rate: 0.10 V s^{-1}, electrolyte: *n*-Bu_4NClO_4 (100 mM), temp: 295 K, under Ar atmosphere. All potentials were converted to voltages *vs*. SCE.

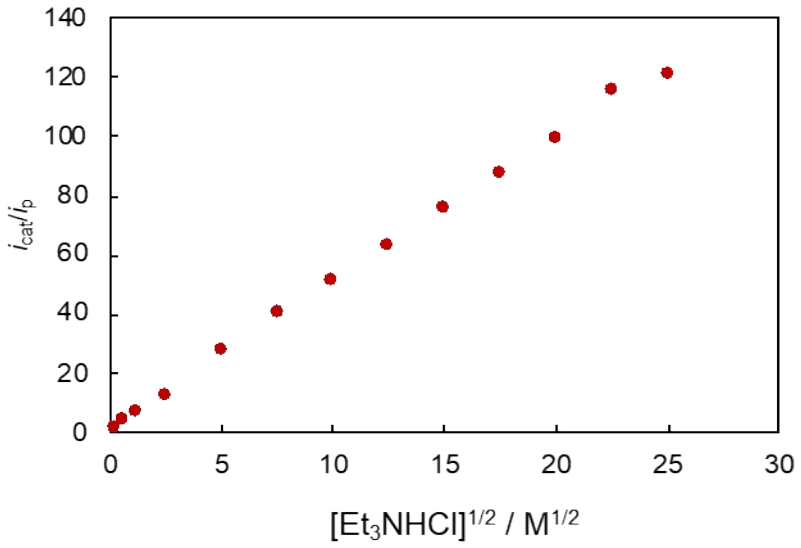


Fig. S11 Plots of i_{cat}/i_p of **Co_2DNCH** *vs.* square root of the concentration of Et_3NHCl. Measurements were performed in DMF of 0.25 mM **Co_2DNCH** (a) and **$CoPF_5$** (b) with several amount of Et_3NHCl (0.5-50 mM). Working electrode: glassy carbon (0.071cm^2), counter electrode: Pt, reference electrode: $Ag/AgNO_3$, electrolyte: *n*-Bu_4NClO_4 (100 mM), temp: 295 K, under Ar atmosphere.

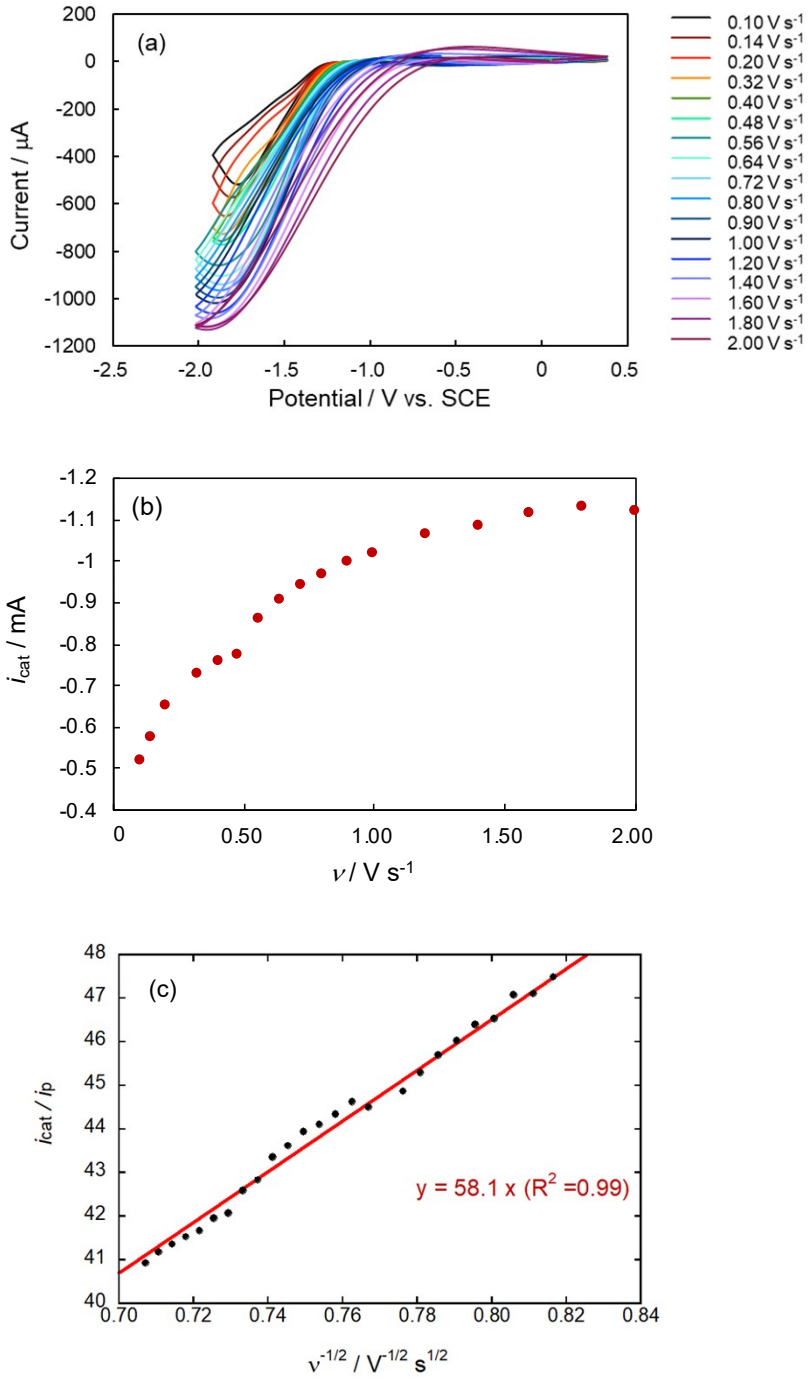


Fig. S12 (a)CVs of **Co_2DNCH** (0.25 mM) in DMF solutions in the absence (black) and presence of 200 equivalents of Et_3NHCl. (b) A plot of i_{cat} *vs. v.* Measurements were performed in DMF of 0.25 mM **Co_2DNCH** (c) A plot of the ratio of i_{cat} to i_p as a function of the inverse of the square root of the scan rate obtained from CVs of DMF solutions containing 0.25 mM of **Co_2DNCH** Working electrode: grassy carbon (0.071 cm^2), counter electrode: Pt wire, reference electrode: $Ag/AgNO_3$, scan rate: 0.10-2.00 V s^{-1}, electrolyte: *n*-Bu_4NClO_4 (100 mM), temp: 295 K, under Ar atmosphere. All potentials were converted to voltages *vs*. SCE.

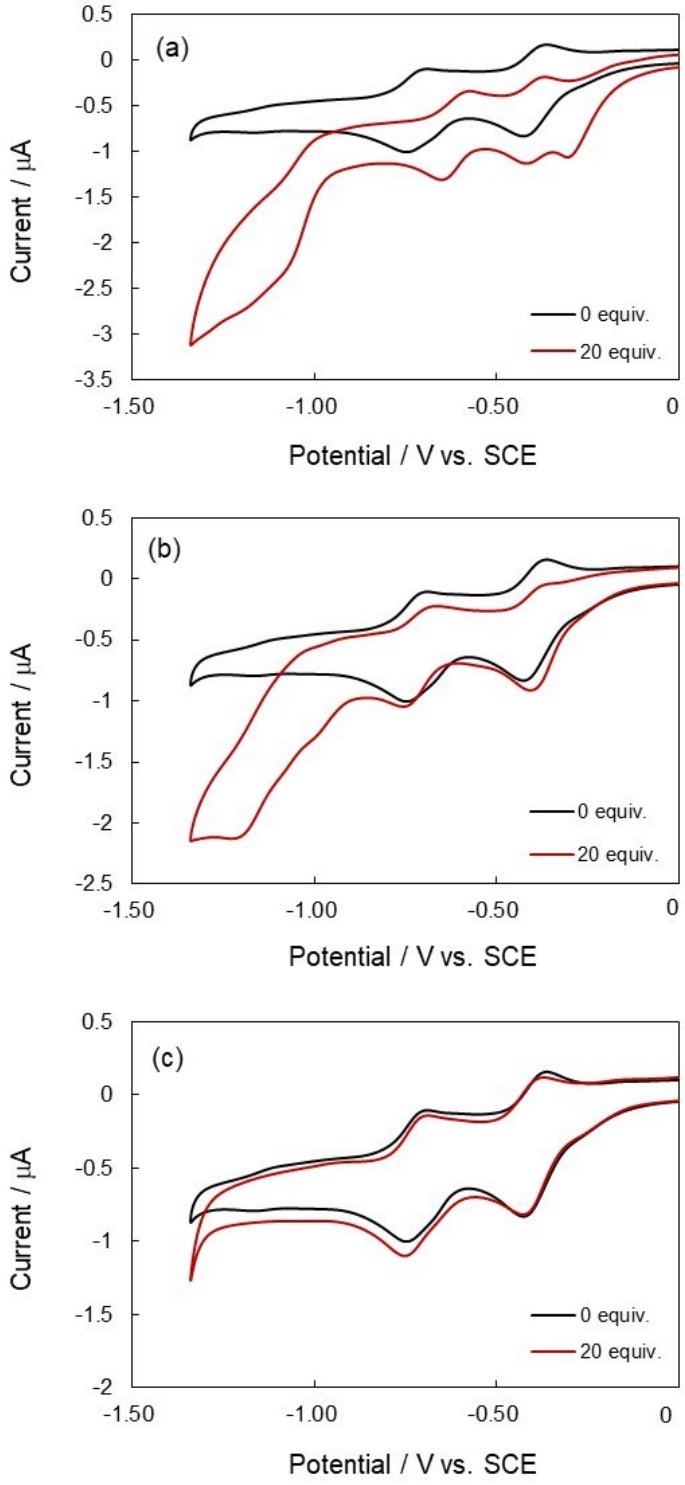


Fig S13 CVs of **Co_2DNCH** (0.25 mM) in DMF solutions in the absence (black) and presence of 20 equivalents of (a)Et_3NHCl, (b) AcOH and (c) PhOH. Working electrode: grassy carbon (0.071 cm^2), counter electrode: Pt wire, reference electrode: $Ag/AgNO_3$, scan rate: 5.00 mV s^{-1}, electrolyte: *n*-Bu_4NClO_4 (100 mM), temp: 295 K, under Ar atmosphere. All potentials were converted to voltages *vs*. SCE.

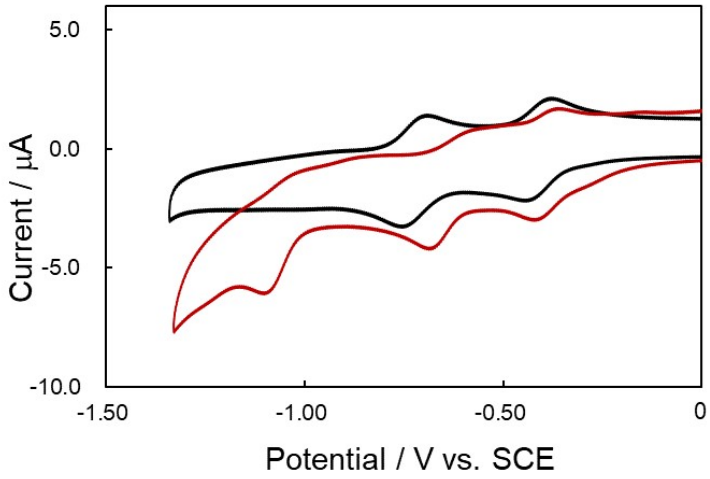


Fig S14 CVs of **Co_2DNCH** (0.25 mM) in DMF solutions in the absence (black) and presence of 20 equivalents of Et_3NHCl (red). Working electrode: grassy carbon (0.071 cm^2), counter electrode: Pt wire, reference electrode: $Ag/AgNO_3$, scan rate: 100 mV s^{-1}, electrolyte: *n*-Bu_4NClO_4 (100 mM), temp: 295 K, under Ar atmosphere. All potentials were converted to voltages *vs*. SCE.

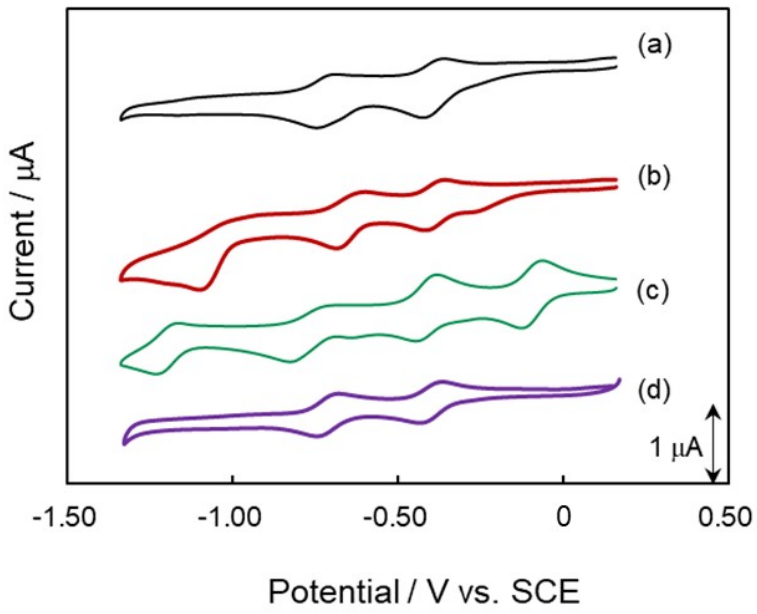


Fig. S15 CVs of DMF solutions containing **Co_2DNCH** (a), **Co_2DNCH** in the presence of 2 eq. of Et_3NHCl (b), **H_4DNCH** (c), and **Co_2DNCH** in the presence of 20 eq. of Et_4NCl. Working electrode: glassy carbon (0.071 cm^2), counter electrode: Pt, reference electrode: $Ag/AgNO_3$, Complex: 0.25 mM, electrolyte: *n*-Bu_4NClO_4 (100 mM), scan rate: 5 mV s^{-1}, temp: 295 K. All potentials were converted to voltages *vs*. SCE.

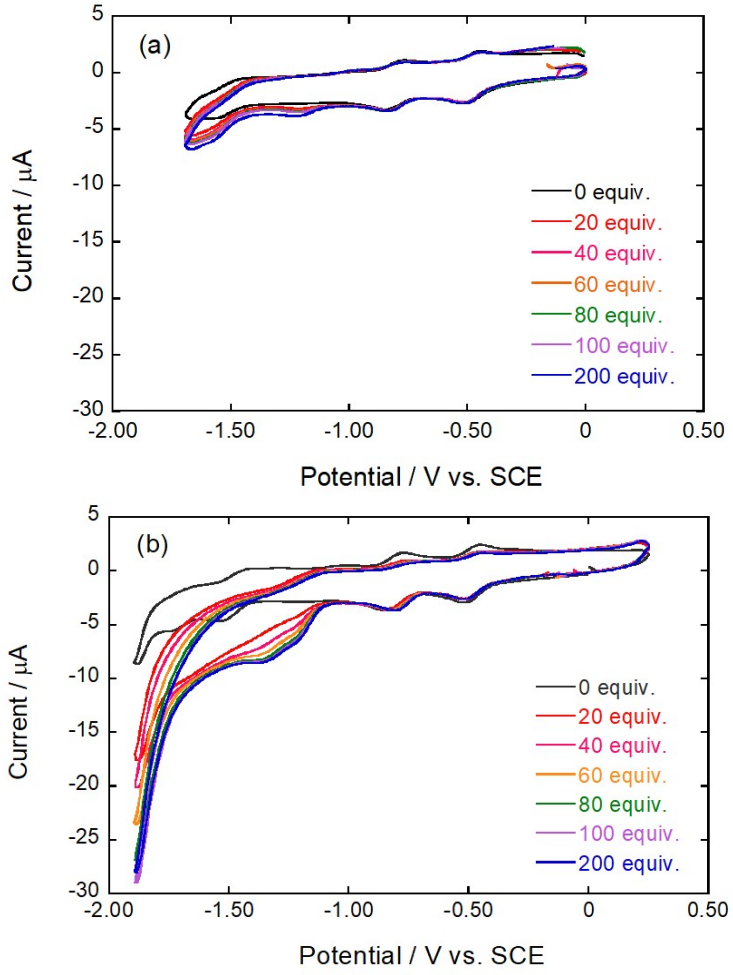


Fig. S16 CVs of **Co_2DNCH** (0.25 mM) in DMF solutions in the absence (black) and presence of several amounts of PhOH (a) or AcOH (b). Working electrode: grassy carbon (0.071 cm^2), counter electrode: Pt wire, reference electrode: $Ag/AgNO_3$, scan rate: 0.10 V s^{-1}, electrolyte: *n*-Bu_4NClO_4 (100 mM), temp: 295 K, under Ar atmosphere. All potentials were converted to voltages *vs*. SCE.

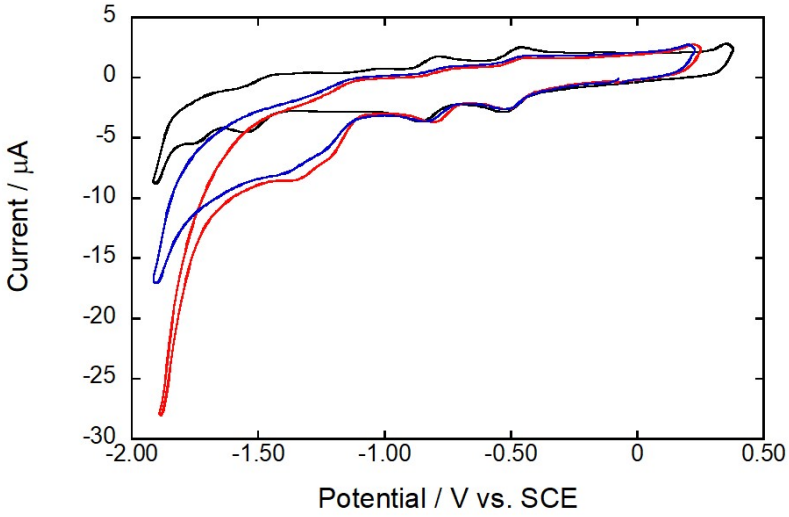
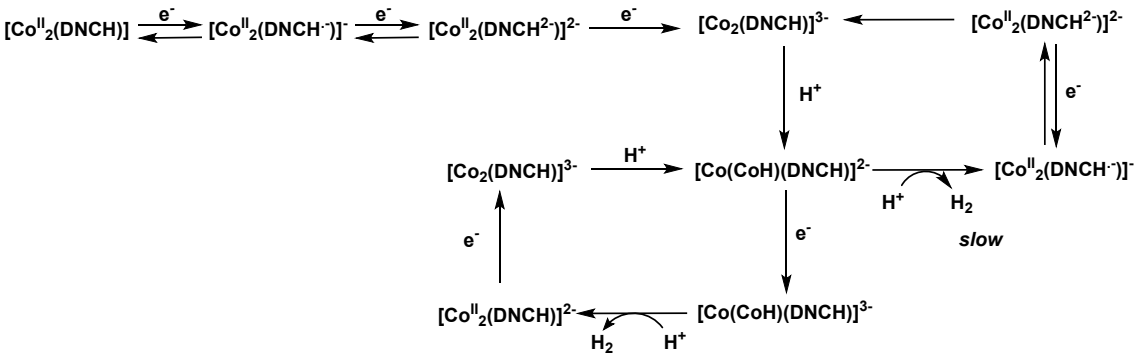


Fig. S17 CVs of **Co_2DNCH** (0.25 mM) in DMF solutions in the absence (black) and presence of 50 mM AcOH(red) or AcOD (blue). Working electrode: grassy carbon (0.071 cm^2), counter electrode: Pt wire, reference electrode: $Ag/AgNO_3$, scan rate: 0.10 V s^{-1}, electrolyte: *n*-Bu_4NClO_4 (100 mM), temp: 295 K, under Ar atmosphere. All potentials were converted to voltages *vs*. SCE.



Scheme S1 Proposed mechanism of **Co_2DNCH** with PhOH or AcOH as a proton source.

References

1. M. Suzuki, M. C. Yoon, D. Y. Kim, J. H. Kwon, H. Furuta, D. Kim and A. Osuka, *Chem. Eur. J.,* 2006, **12**, 1754-1759.