Electronic Supplementary Information

Effect of metal ion substitution on the catalytic activity of a pentanuclear metal complex

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Materials and Methods

Materials

$Co(CH_3COO)_2 \cdot 4H_2O$, $NaBF_4$, NaOH, $Ir(ppy)_3$, aqueous solutions of NaOH and HCl, and all the solvents except for *N,N*-dimethylacetamide (DMA) were purchased from FUJIFILM Wako Pure Chemical Corporation. 3,5-Bis(2-pyridyl)pyrazole, 2-phenylbenzimidazole, tetra-*n*-butylammonium perchlorate (TBAP), methyl iodide and DMA were purchased from Tokyo Chemical Industry Co., Ltd. $NaBH_4$ was purchased from Aldrich. $Zn(OAc)_2 \bullet 2H_2O$ was purchased from Kanto Chemical Co., Inc. All the reagents were of highest quality available and were used as received except for TBAP. TBAP was recrystallised from absolute ethanol. H_2O was purified using a Millipore MilliQ purifier. 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (BIH) was synthesized using the slighly modified procedure reported in the literature[1]. Synthesis of $[\{Zn^{II}(\mu\text{-bpp})_3\}_2Zn^{II}_3(\mu\text{-OH})](BF_4)_3$ (**Zn5**$(BF_4)_3$) was performed by modifiying the procedure reported in the literatures[2,3].

Electrochemical studies

Cyclic voltammetry was performed with a Bio-Logic-Science Instruments potentiostat interfaced to a computer with SP-50 software, at room temperature under Ar or CO_2 using one-compartment cell with a standard three-electrode configuration, which consisted of a glassy carbon disk (diameter 3 mm, from BAS Inc.), a Ag/Ag^+ couple, and a platinum wire as the working, reference and auxiliary electrodes, respectively. The working electrode was treated between scans by means of polishing with 0.05 μm alumina paste (from BAS Inc.) and washing with purified H_2O. Ferrocene was used as an internal standard, and all potentials reported within this work are referenced to the ferrocenium/ferrocene couple at 0 V.

Photocatalytic reaction

For a typical run, a mixed solution of DMA/TFE (17:3, v/v) (2.0 mL) containing 30 μM **Co5**, 150 μM $Ir(ppy)_3$ and 0.10 M BIH was purged with CO_2 for 15 minutes unless otherwise stated. The solution was then irradiated with a blue LED (wavelength $\lambda = 420$ nm) at 20 °C in a custom made aluminium box with cooling system. The amount of CO and H_2 produced at the headspace of the cell was quantified by a Shimadzu GC-8A with a TCD detector equipped with a packed column with Molecular Sieve 13X-S 60/80 (He carrier gas, 40 °C) and a Shimadzu GC-2014 with a TCD detector equipped with a packed column with Molecular Sieve 5A (Ar carrier gas, 40 °C). Additionally, liquid product was quantified by using a Shimadzu LC-20AD with SPD-20A and RID-10A detectors equipped with a Shim-pack

SCR102H column. Calibration curves were obtained by sampling known amounts of H_2, CO, and HCOOH.

$^{13}CO_2$ labelling experiment.

A mixed solution of DMA/TFE (17:3, v/v) (2.0 mL) containing 30 µM **Co5**, 150 µM $Ir(ppy)_3$ and 0.10 M BIH was purged with Ar for 15 min, followed by $^{13}CO_2$ bubbling for 15 min. The $^{13}CO_2$ gas was produced by adding 2.0 M HCl to solid $Ba^{13}CO_3$ (98 atom % 13C, Sigma Aldrich). The evolved CO was detected by a GCMS-QP2020 (Rt-Msieve 5A (30 m, 0.53 mm ID, 50 µm d_f) He carrier gas, 40 °C).

Synthesis

Synthesis of [Co$^{II}_5$OH(bpp)$_6$](BF$_4$)$_3$ (Co5(BF$_4$)$_3$)

Aqueous solution of NaOH (1 M, 0.48 mL) was added to the methanol solution (4 mL) of 3,5-bis(2-pyridyl)pyrazole (Hbpp, 0.48 mmol, 107 mg). $Co(CH_3COO)_2 \cdot 4H_2O$ (40 mmol, 100 mg) was then added to the reaction mixture and stirred at 40 °C for 10 minutes. A few drops of saturated aqueous $NaBF_4$ solution was added to the reaction mixture, and a small portion of water was added to the solution. The solution was kept in a refrigerator for 1 h to generate a brown precipitate. The precipitate was collected by filtration, washed with water and dried under vacuum. The obtained precipitate was dissolved in acetonitrile and subjected to vapor diffusion in diethyl ether to afford brown crystals of [Co$^{II}_5$OH(bpp)$_6$](BF$_4$)$_3$·2H$_2$O. The crystals were collected by filtration and dried under vacuum. Yield 80 mg (52 %). Elemental analysis calcd. (%) for $C_{78}H_{59}Co_5F_{12}N_{24}O_3B_3$: C, 48.40; H, 3.07; N, 17.37. Found: C, 48.35; H, 3.13; N, 17.32.

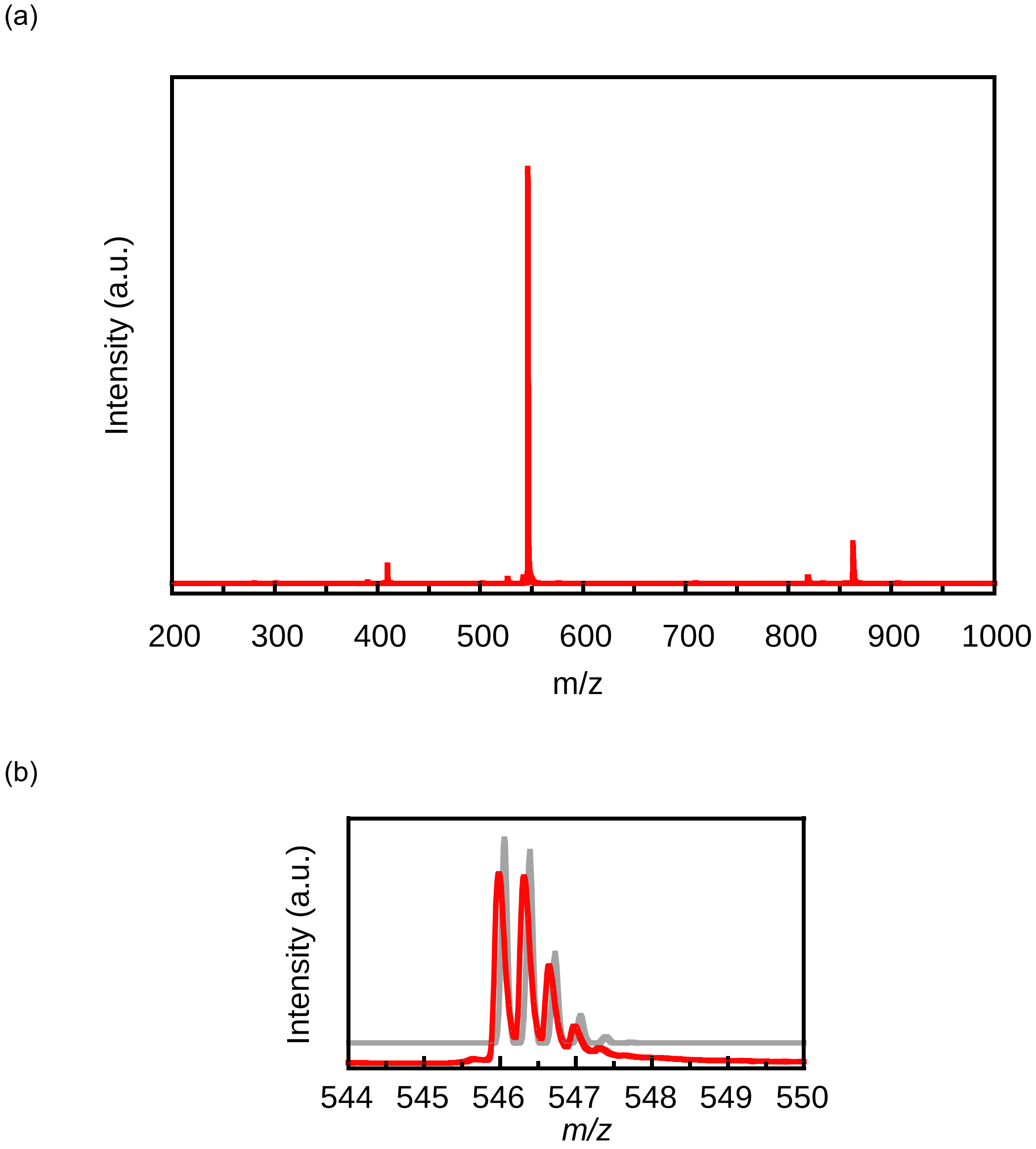

Figure S1. (a) An ESI-TOF mass spectrum of (a) **Co5** (b) An enlarged ESI-TOF mass spectrum of **Co5** (red line) and the simulated pattern for $[Co_5OH(bpp)_6]^{3+}$ (grey line). Analyses were carried out on a JEOL JMS-T100LP mass spectrometer.

X-ray Crystallography

Data collection for **Co5** was performed at 123 K on a ROD, Synergy Custom system (Rigaku Oxford Diffraction) equipped with confocal monochromated Mo-Kα radiation, and data were processed using CrysAlisPro 1.171.39.43c (Rigaku Oxford Diffraction). The structure were solved by direct methods using SIR-97 and refined by the full-matrix least aquares techniques on F^2 (SHELXL-2014/3). All nonhydrogen atoms were refined anisotropically and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: CCDC deposition number; 1949862 for $\mathbf{Co_5}(BF_4)_3$. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Summary of crystallographic data for **Co5**(BF_4)$_3$.

	[$Co_5OH(bpp)_6$](BF_4)$_3$
formula	$C_{78}H_{55}B_3Co_5F_{12}N_{24}O$
crystal system	monoclinic
space group	$P\,2_1/n$
a /Å	15.2146(6)
b /Å	22.3485(8)
c /Å	26.8017(12)
β /°	102.122(4)
V /Å^3	8910.0(6)
Z	4
R_1	0.0720
wR_2	0.2172
GooF	1.027

Table S2. Selected bond lengths of **Co5**$(BF_4)_3$.

	bond	**length / Å**
d(M_{api}-N)	Co1-N1	2.198(5)
	Co1-N2	2.108(5)
	Co1-N5	2.186(5)
	Co1-N6	2.103(4)
	Co1-N9	2.182(5)
	Co1-N10	2.104(4)
	Co2-N13	2.195(5)
	Co2-N14	2.100(5)
	Co2-N17	2.175(5)
	Co2-N18	2.118(5)
	Co2-N21	2.195(5)
	Co2-N22	2.120(5)
average		**2.149(5)**
d(M_{core}-N)	Co3-N3	2.054(5)
	Co3-N4	2.072(5)
	Co3-N15	2.055(5)
	Co3-N16	2.086(4)
	Co4-N7	2.049(4)
	Co4-N8	2.073(5)
	Co4-N19	2.073(5)
	Co4-N20	2.070(5)
	Co5-N11	2.055(4)
	Co5-N12	2.084(4)
	Co5-N23	2.056(4)
	Co5-N24	2.072(5)
average		**2.067(5)**
d(M_{core}-O)	Co3-O1	1.997(4)
	Co4-O1	2.017(4)
	Co5-O1	2.014(4)
average		**2.009(4)**

Table S3. Selected angles of **Co5**(BF_4)$_3$.

	bond	**angle / deg**
core angle	Co3-O1-Co4	120.4(2)
	Co3-O1-Co5	120.3(2)
	Co4-O1-Co5	118.7(2)
average		**119.8(2)**

Electrochemical Measurements

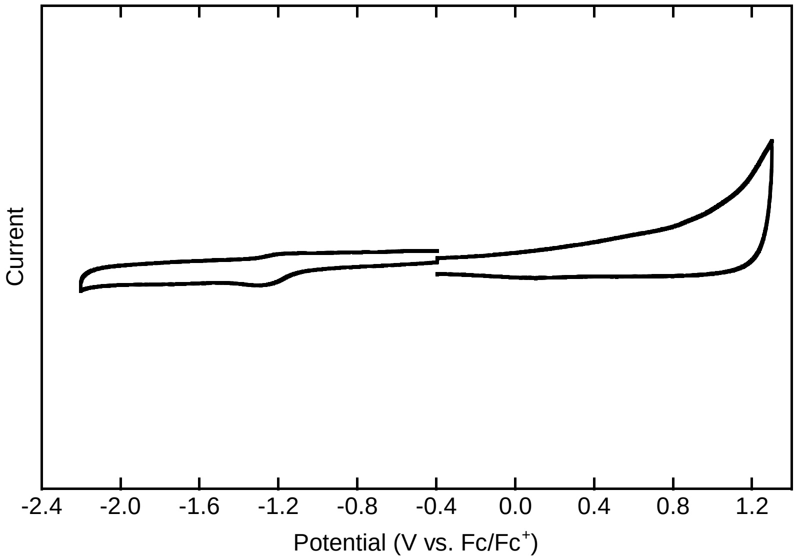

Figure S2. A cyclic voltammogram of a **Zn5** (0.2 mM) in an acetonitrile solution containing (n-Bu)$_4$NClO$_4$ (TBAP, 0.1 M) at a scan rate of 100 mV/s.

Controlled Potential Electrolysis

Controlled Potential Electrolysis was performed in a gas-tight two-compartment electrochemical cell as in Figure S3. In the first compartment, the carbon plate working electrode and a leakless Ag/AgCl reference electrode (Innovative Instrument, Inc.) were immersed in 0.1 M TBAP/MeCN (5mL) containing **Co5** and trifluoroethanol. In the second compartment, the Pt auxiliary electrode was immersed in 0.1 M TBAP/MeCN (5 mL) containing ferrocene (40 mM) as a sacrificial reductant. The two compartments were separated by an anion exchange membrane (Selemion DSV). The solution was purged with CO_2 for 30 min prior to electrolysis. The electrolysis was performed for 1 h with constant stirring. The amount of CO and H_2 produced at the headspace of the cell was quantified by a Shimadzu GC-8A with a TCD detector equipped with a packed column with Molecular Sieve 13X-S 60/80 (He carrier gas, 40 °C) and a Shimadzu GC-2014 with a TCD detector equipped with a packed column with Molecular Sieve 5A (Ar carrier gas, 40 °C). Additionally, liquid product was quantified by using a Shimadzu LC-20AD with SPD-20A and RID-10A detectors equipped with a Shim-pack SCR102H column. Calibration curves were obtained by sampling known amounts of H_2, CO, and HCOOH.

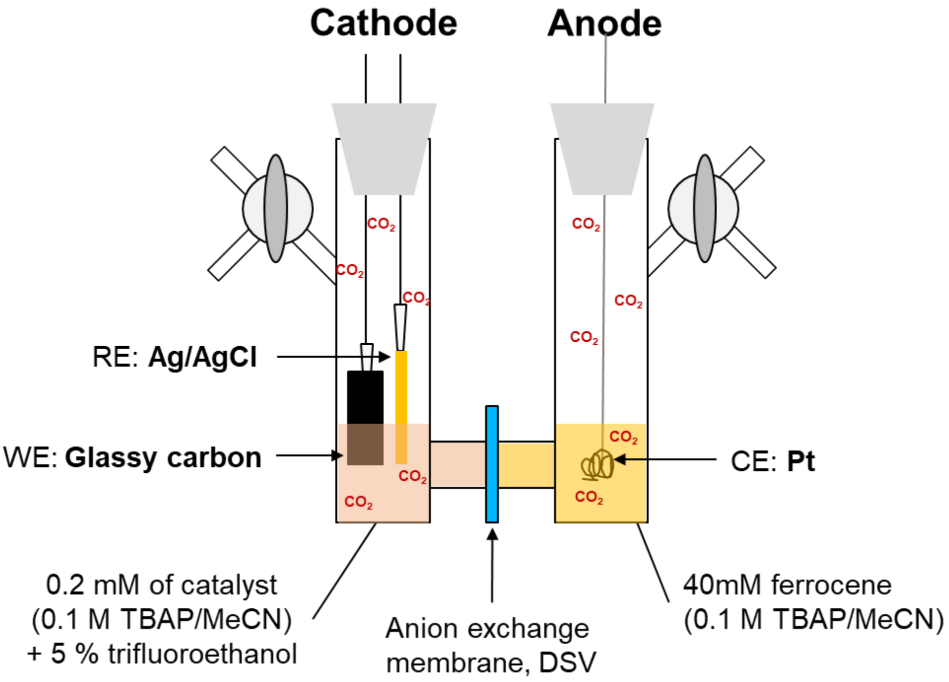

Figure S3. General setup for controlled-potential electrolysis performed in this work.

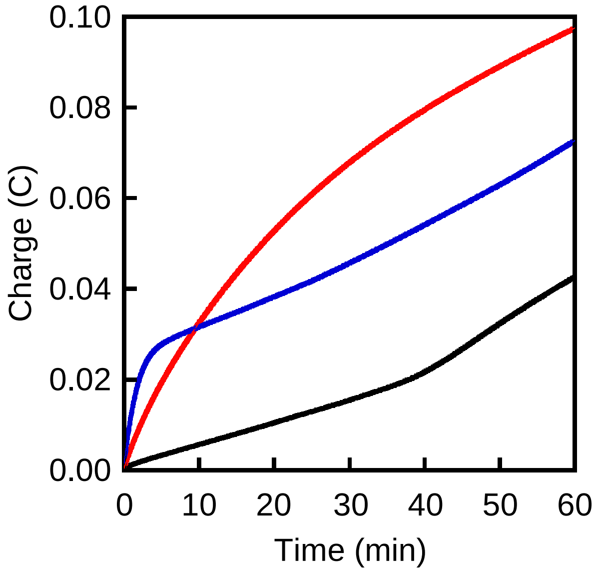

Figure S4. The results of CPE of 0.2 mM **Co5** (red line), **Co5** in the presence of 5 % trifluoroethanol (blue line) and in the absence of **Co5** (black line) in 0.1 M TBAP/MeCN under CO_2 at −2.5 V (vs. Fc/Fc^+) for 1 h. The CPE experiments were carried out using a GC plate as a working electrode.

Table S4. Summary of CPE experiments.[a]

No.	Catalyst	TFE (%)	Charge (C)	CO (μmol)	H_2 (μmol)	HCOOH (μmol)
1	**Co5**	5	0.073	0.11	0.19	0.08
2	**Co5**	-	0.098	0.09	0.05	0.22
3	-	-	0.043	0	0.01	0

[a] Conditions: 0.2 mM **Co5**, applied voltage: −2.5 V (vs. Fc/Fc^+), duration: 1 h.

Photocatalytic Experiment

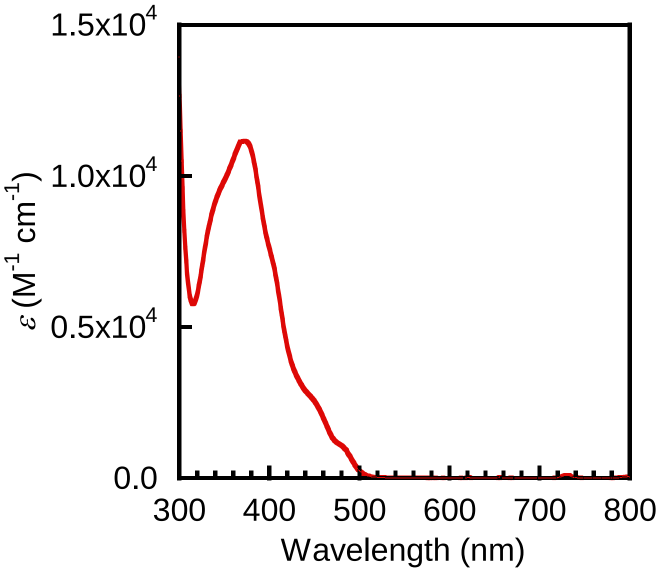

Figure S5. The absorption spectrum 30 μM Ir(ppy)$_3$ in acetonitrile.

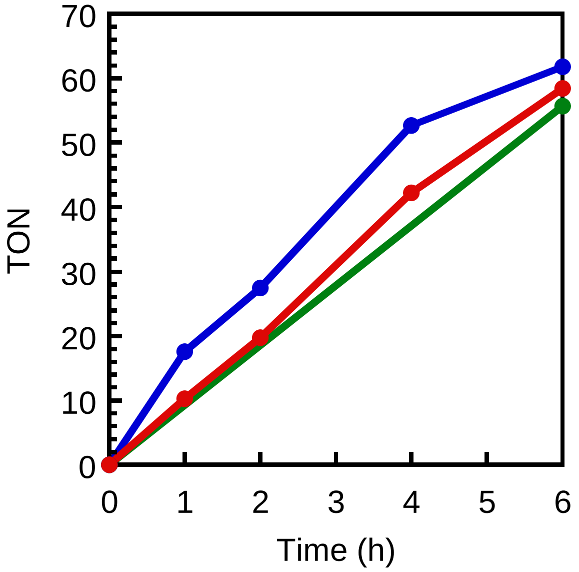

Figure S6. Photocatalytic production of CO (red line), H_2 (blue line) and HCOOH (green line) in a CO_2-saturated DMA/TFE (17:3, v/v) solution containing 1 μM **Co5,** 150 μM $Ir(ppy)_3$ and 0.1 M BIH under visible-light irradiation (225 W Xe lamp equipped with 420 nm long pass filter (Edmund Industrial Optics) and CM-1 cold mirror, wavelength 420 ≤ λ ≤ 750 nm).

Reference

1. D. Hong, Y. Tsukakoshi, H, Kotani, T. Ishizuka and T. Kojima, *J. Am. Chem. Soc.*, 2017, **139**, 6538.

2. J.-Z. Hou, M. Li, Z. Li, S.-Z. Zhan, X.-C Huang,. and D. Li, *Angew. Chem. Int. Ed.,* 2008, **47**, 1711.

3. S. Romain, J. Rich, C. Sens, T. Stoll, J. Benet-Buchholz, A. Llobet, M. Rodriguez, I. Romero, R. Clérac, C. Mathonière, C. Duboc, A. Deronzier, and M.-N. Collomb, *Inorg. Chem.* 2011, **50**, 8427.