Supplementary Information

Nonanuclear Ni(II) Complexes in a [1-7-1] Formation Derived from Asymmetric Multidentate Ligands: Magnetic and Electrochemical Properties

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Physical Measurement

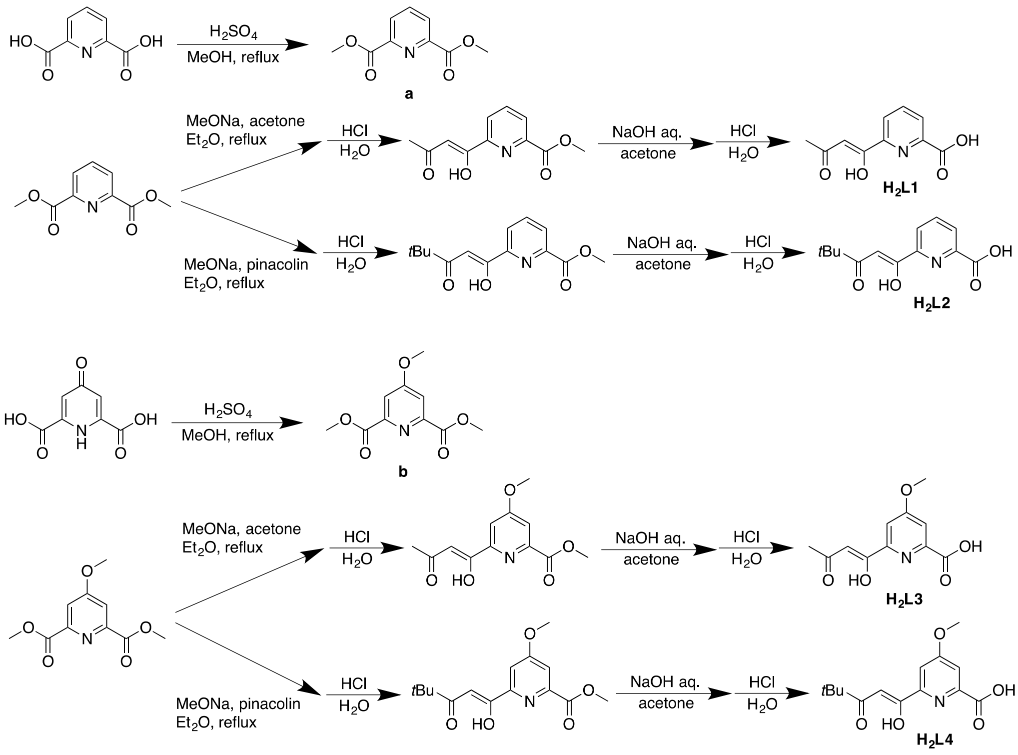
Elemental analyses of carbon, hydrogen and nitrogen were carried out by the staff of technical support division graduate school of science, Kyushu University. UV-Vis absorption was measured by JASCO V-630. Infrared spectra were measured with a JASCO FT/IR-4200 using ATR method. Cyclic voltammogram was recorded on an ALS 612D electrochemical analyzer and all electrodes used was purchased from BAS. Platinum electrode was used as counter electrode and glassy carbon electrode was used as working with electrode which was polished with 0.05 μm polishing alumina. As the reference electrode, RE-7 nonaqueous reference electrode (Ag^+/Ag) was used. Tetrabutylammonium perchlorate used as an electrolyte was recrystallized from ethanol. In the bulk electrolysis measurement, Porous carbon electrode was used as working electrode. The magnetic susceptibilities of all samples were measured on Quantum Design MPMS-XL5R SQUID susceptometer in the temperature range of 2-300 K in an applied DC field of 1000 Oe. The samples were put into a gelatin capsule, placed in a plastic straw, and then fixed to the end of the sample transport rod. Diamagnetic correction was calculated by using Pascal constant. The molar magnetic susceptibility, χ_M, was corrected for the diamagnetism of the constituent atoms and the sample tube.

Single-crystal X-ray diffraction

All Single-crystal X-ray diffraction data were collected on a Bulker SMART APEX II ULTRA CCD-detector Diffractometer, a rotating-anode (Bruker Tourbo X-ray source) with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) was used. Computations were carried out on a APEX2 crystallographic software package and OLEX2 software.[1] A single crystal was mounted on a polymer film with liquid paraffin and the temperature kept –173 ºC under flowing N_2 gas. All of the structures were solved by direct method or intrinsic method. All the structures were expanded using Fourier techniques. Fullmatrixleast-squares refinements were carried out with anisotropic thermal parameters for all non-disordered and non-hydrogen atoms. The hydrogen atoms were attached based on the difference Fourier map and calculation geometrically. The SQUEEZE program was used to remove the contribution of the highly disordered solvent molecules from the structural calculations.

Preparations

All chemicals were purchased from commercial sources and used without further purification. Dimethyl pyridine 2,6-carboxylate (**a**) and dimethyl 4-methoxypyridine-2,6-dicarboxylate (**b**) were prepared according to literature procedures.[2,3] The preparation of the 6-acetoacetyl-2-pyridinecarboxylic acid (H_2L1) and its derivatives were carried out in three steps including a Claisen condensation with reference to the literature method.[4] Synthetic scheme of the ligand is shown in **scheme 1**.



Scheme 1. Synthetic scheme of 6-acetoacetyl-2-pyridinecarboxylic acid and its derivatives.

Dimethyl pyridine-2, 6-dicarboxylate (a) [2]

Pyridine-2, 6-dicarboxylic acid (33.42 g, 0.20 mol) and concentrated sulfuric acid (6.0 g) was added to MeOH (100 ml). The mixture was refluxed for 3 h, and then cooled to room temperature with stirring. The white crystals of dimethyl pyridine-2,6-dicarboxylate was filtrated and washed with MeOH and dried *in vacuo*.

Yield 35.70 g (91.5 %) ^1H NMR (600 MHz, $CDCl_3$ δ in ppm): 8.30 (d, 2H, *J*=7.8 Hz, py), 8.01 (dd, 1H, *J*=8.1Hz, py), 4.01 (s, 1H, OMe). Elemental analysis (%); Calcd. for $C_9H_9NO_4$: C 55.39, H 4.65, N 7.18; found: C 55.31, H 4.60, N 7.16. FT-IR (cm^{-1}); 1739, 1290, 1163, 996, 755, 694

Dimethyl 4-methoxypyridine-2,6-dicarboxylate (b) [3]

Chelidamic acid monohydrate (16.09 g, 80 mmol) was refluxed in methanol (800 mL) in presence of sulfuric acid (16 mL) for 10 days. The solvent was concentrated to dryness, and the crude product dissolved in water and neutralized by saturated $NaHCO_3$ solution. White precipitate was extracted by dichloromethane, and the organic phase was dried over Na_2SO_4 and evaporated to dryness. White solid of crude product was purified by column chromatography on silica gel with $CHCl_3$ / MeOH (20:1), and the solvent evaporated to give dimethyl 4-methoxypyridine-2,6-dicarboxylate.

Yield 12.07 g, (67.0 %). ^{1}H NMR (600 MHz, $CDCl_3$ δ in ppm): 7.80 (s, 2H, py), 4.00 (s, 6H, CO_2Me), 3.97 (s, 3H, OMe). Elemental analysis (%); Calcd. for $C_{10}H_{11}NO_5$: C 53.33, H 4.92, N 6.22; found: C 53.28, H 4.93, N 6.18. FT-IR (cm^{-1}); 1716, 1604, 1431, 1362, 1268, 1107, 1048, 993, 887, 786

6-acetoacetyl-2-pyridinecarboxylic acid (H_2L1) and its derivatives (H_2L2, H_2L3, H_2L4)

Compound **a** (9.76 g, 0.05 mol for **H_2L1** and **H_2L2**) or compound **b** (11.26 g, 0.05 mol for **H_2L3** and **H_2L4**), and 28 % sodium methoxide methanol solution (9.65 g, 0.05 mol) was added to diethyl ether (150 ml) and then, acetone (4.36 g, 0.075 mol for **H_2L1** and **H_2L3**) or pinacolin (7.51 g, 0.075 mol for **H_2L2** and **H_2L4**), in 30 ml of diethyl ether was added dropwise under reflux for 4 h. The yellow precipitate was filtered and washed with diethyl ether and dried *in vacuo*. After that, yellow powder was dissolved in 100 ml of water and pH was adjusted to 1 by 5M HCl. Stirring 12 h and yellowish white powder of methyl ester was filtrate and wash with water and dried *in vacuo*.

30 % aqueous NaOH (15 ml) was added to a solution of each compound in acetone (150 ml) under stirring at room temperature for 12 h. The yellow solid was collected by filtration and washed with acetone and dried *in vacuo*. After that, yellow powder was dissolved in 100 ml of water and pH was adjusted to 1 by 5M HCl. Yellowish white powder formed was filtered and wash with water and dried *in vacuo*.

6-acetoacetyl-2-pyridinecarboxylic acid (H_2L1)

H_2L1 was recrystallized from hot EtOH. Yield 7.70 g (54.4 %). ^{1}H NMR (600 MHz, $CDCl_3$ δ in ppm): 15.64 (s, H, C=C—OH), 8.33-8.35 (m, 2H, py) 8.12 (dd, 1H, *J*=7.8 Hz, py), 6.74 (s, 1H, —CH=), 2.29 (s, 3H, —CH_3). Elemental analysis (%); Calcd. for $C_{10}H_9NO_4$: C 57.97, H 4.38, N 6.76; found: C 57.83, H 4.31, N 6.72. FT-IR (cm^{-1}); 1706, 1617, 1580, 1460, 1422, 1327, 1300, 1249, 942, 779

6-(4,4-dimethyl-3-oxopentanoyl)picolinic acid (H_2L2)

Yield 7.52 g (56.3 %). ^{1}H NMR (600 MHz, $CDCl_3$ δ in ppm): 16.05 (s, H, C=C—OH), 8.35-8.33 (m, 2H, py) 8.12 (dd, 1H, *J*=7.8 Hz, py), 6.84 (s, 1H, —CH=), 1.28 (s, 9H, —*t*Bu). Elemental analysis (%); Calcd. for $C_{13}H_{17}NO_5$ (monohydrated): C 58.42, H 6.41, N 5.24; found: C 58.52, H 6.34, N 5.24. FT-IR (cm^{-1}); 1685, 1576, 1317, 1263, 1237, 785, 755, 687

4-methoxy-6-(3-oxobutanoyl)picolinic acid (H_2L3)

Yield 9.22 g (77.7 %). ^{1}H NMR (600 MHz, $CDCl_3$ δ in ppm): 15.61 (s, H, C=C—OH), 7.81 (s, 2H, py), 6.71 (s, 1H, —CH=), 4.00 (s, 3H, —OMe), 2.28 (s, 3H, CH_3). Elemental analysis (%);

Calcd. for $C_{11}H_{11}NO_5$: C 55.70, H 4.67, N 5.90; found: C 55.80, H 4.82, N 5.42. FT-IR (cm^{-1}); 1702, 1583, 1236, 1042, 704

6-(4,4-dimethyl-3-oxopentanoyl)-4-methoxypicolinic acid (H_2L4)

Yield 6.44 g (51.7 %). ^1H NMR (600 MHz, $CDCl_3$ δ in ppm): 16.02 (s, H, C=C—OH), 7.81 (s, 2H, py), 6.81 (s, 1H, —CH=), 4.00 (s, 3H, —OMe), 1.27 (s, 9H, *t*Bu). Elemental analysis (%); Calcd. for $C_{14}H_{17}NO_5$: C 60.21, H 6.14, N 5.02; found: C 59.92, H 6.13, N 4.94. FT-IR (cm^{-1}); 1694, 1585, 1464, 1334, 1044, 932, 738

$[Ni_9(L1)_6(OH)_6(H_2O)_6]$ (Ni_9L1)

H_2L1 (207 mg, 1.0 mmol) and Et_3N (416 μl) were dissolved in 15 ml of MeOH. Then, $NiSO_4 \cdot 6H_2O$ (526 mg, 2.0 mmol) in water (5 ml) was added in the methanol solution and stirred for 12 hours. Green solution was concentrated under ambient condition. Green crystals formed within 2 weeks were collected by filtration and washed with MeOH/H_2O and diethyl ether and dried *in vacuo.*

Yield 110 mg (33.8 %), Elemental analysis (%); Calcd. for $C_{60}H_{60}Ni_9N_6O_{36}$ $[Ni_9(L1)_6(OH)_6(H_2O)_6]$: C 36.59, H 3.07, N 4.27; found: C 36.67, H 2.66, N 4.37. Formula weight 1969.39 FT-IR (cm^{-1}); 1621, 1591, 1515, 1469, 1410, 1370, 1291, 1145

$[Ni_9(L2)_6(OH)_6(H_2O)_6] \cdot 2H_2O$ (Ni_9L2)

H_2L2 (498 mg, 2.0 mmol) and Et_3N (831 μl) were dissolved in 20 ml of MeOH. Then, $NiSO_4 \cdot 6H_2O$ (1.052 g, 4.0 mmol) in water (5 ml) was added in the methanol solution and stirred for 12 hours. Green solution was concentrated under ambient condition. Green crystals formed within two weeks were collected by filtration and recrystallized from 25 ml of MeOH/H_2O (*v* : *v* = 4 : 1). Green crystals formed were collected and washed with H_2O and dried *in vacuo.*

Yield 110 mg (14.6 %), Elemental analysis (%); Calcd. for $C_{78}H_{100}Ni_9N_6O_{38}$ $\{[Ni_9(L2)_6(OH)_6(H_2O)_6] \cdot 2H_2O\}$: C 41.49, H 4.46, N 3.72; found: C 41.05, H 4.09, N 3.82. Formula weight 2257.90. FT-IR (cm^{-1}); 1623, 1594, 1510, 1468, 1413, 1372, 1293, 1116

$[Ni_9(L3)_6(OH)_6(H_2O)_6]$ (Ni_9L3)

H_2L3 (237 mg, 1.0 mmol) and Et_3N (416 μl) were dissolved in 18 ml of MeOH. Then, $NiSO_4 \cdot 6H_2O$ (526 mg, 2.0 mmol) in water (2 ml) was added in the methanol solution and reflux for 24 hours. Green solution was concentrated under ambient condition. Green crystals formed within three weeks were collected by filtration and washed with H_2O and dried *in vacuo.* Yield 115 mg (32.1 %), Elemental analysis (%); Calcd. for $C_{66}H_{72}N_6Ni_9O_{42}$ $[Ni_9(L3)_6(OH)_6(H_2O)_6]$: C 36.88, H 3.38, N 3.91; found: C 37.38, H 3.20, N 4.01. Formula weight 2149.54. FT-IR (cm^{-1}); 1601, 1512, 1469, 1416, 1363, 1231, 1170, 1061

$[Ni_9(L4)_6(OH)_6(MeOH)_2(H_2O)_4]$ (Ni_9L4)

H_2L4 (279 mg, 1.0 mmol) and Et_3N (416 μl) were dissolved in 40 ml of MeOH. Then, $NiSO_4 \cdot 6H_2O$ (526 mg, 2.0 mmol) in water (10 ml) was added in the methanol solution and stirred for 12 hours. Green solution was concentrated under ambient condition. Green crystals formed within 7 days were collected by filtration and washed with MeOH and diethyl ether and dried *in vacuo.*

Yield 242 mg (89.6 %), Elemental analysis (%); Calcd. for $C_{60}H_{92}Ni_9N_6O_{52}$

$[Ni_9(L4)_6(OH)_6(MeOH)_2(H_2O)_4]$: C 42.51, H 4.65, N 3.46; found: C 42.54, H 4.45, N 3.50. Formula weight 2430.08. FT-IR (cm^{-1}); 1598, 1512, 1469, 1416, 1366, 1146, 1106, 1060

Crystal Structure

In the crystal structure, a lot of lattice water molecules are found, and they formed hydrogen bond-network and some of them form the hydrogen-bonded networks with carboxylate of the ligand. These solvent molecules had been removed from calculations using SQUEEZE. Approximately 10-20 water molecules could be seen as Q peaks on the difference map. The number of solvent water of the dried sample was determined by elemental analysis.

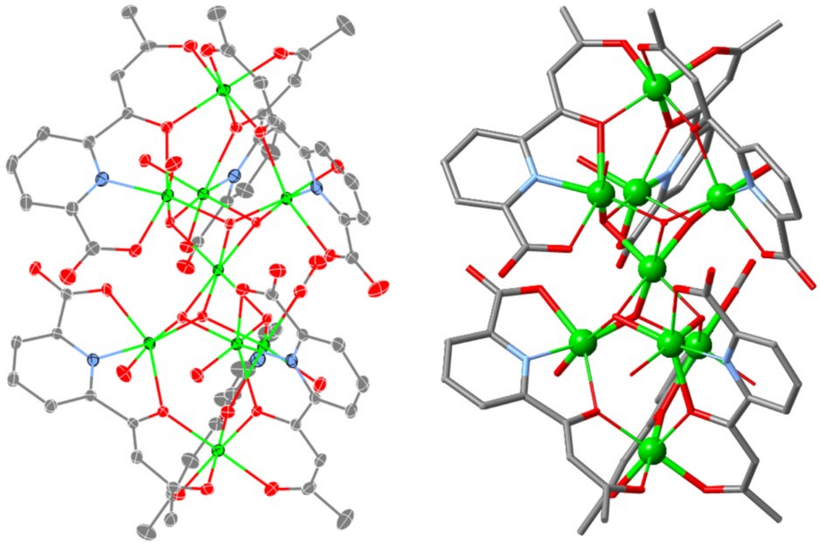


Fig. S1 An ORTEP drawing and schematic structure of **Ni$_9$L1**. H atoms are omitted for clarity. Ni: light green; C: gray; O: red; and N: light blue.

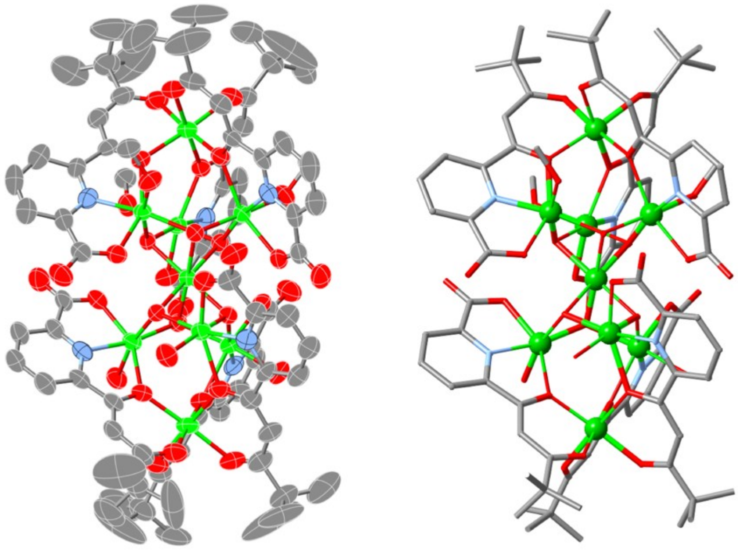


Fig. S2 An ORTEP drawing and schematic structure of **Ni$_9$L2**. H atoms are omitted for clarity. Ni: light green; C: gray; O: red; and N: light blue

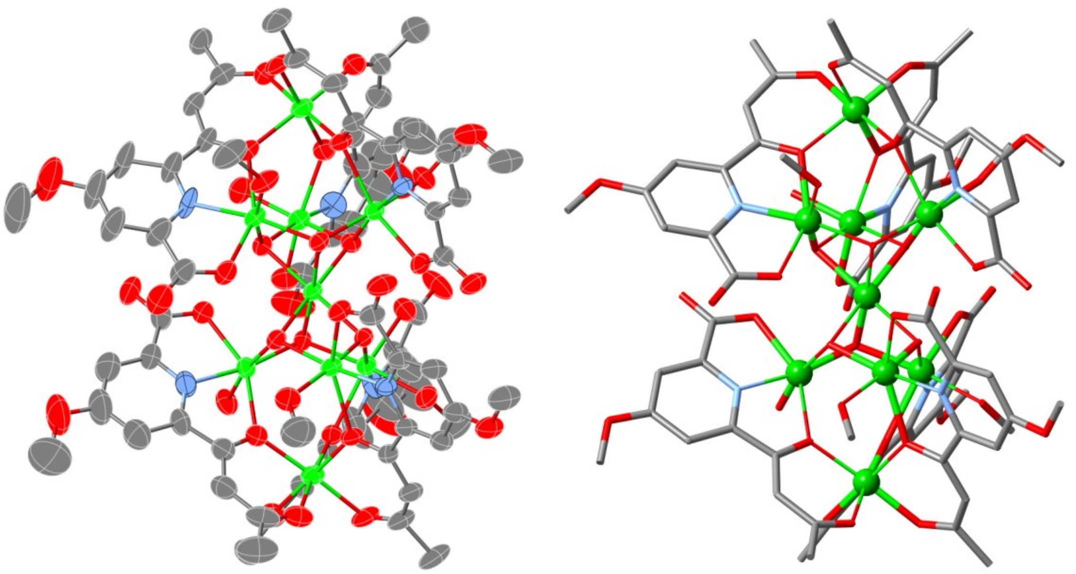


Fig. S3 An ORTEP drawing and schematic structure of **Ni$_9$L3**. H atoms are omitted for clarity. Ni: light green; C: gray; O: red; N: and light blue

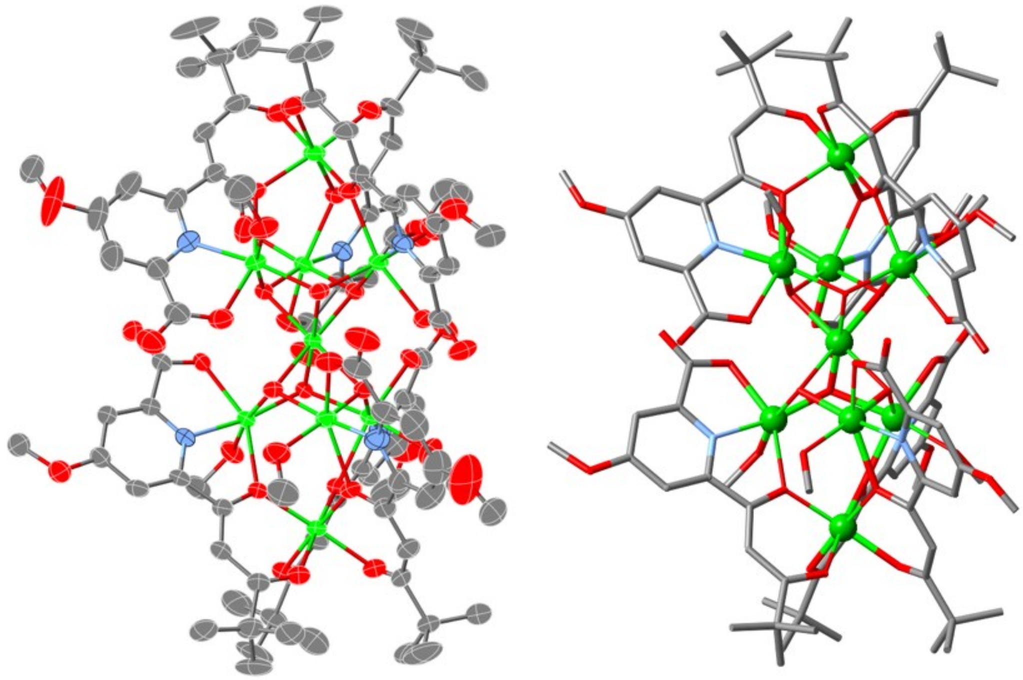


Fig. S4 An ORTEP drawing and schematic structure of **Ni$_9$L4**. H atoms are omitted for clarity. Ni: light green; C: gray; O: red; N: and light blue

Table S1. Crystallographic parameters

Complex	**Ni$_9$L1**	**Ni$_9$L2**
Formula	$C_{60.18}H_{60.18}N_6Ni_9O_{36}$	$C_{81}H_{102}N_6Ni_9O_{36}$
Formula weight	1971.90	2264.09
Temperature / K	100	100
Crystal size / mm	0.341 × 0.077 × 0.054	0.238 × 0.085 × 0.084
Crystal system	Monoclinic	Cubic
Space group	$P2_1$/n	*Pa*
a / Å	17.738(2)	28.0844(16)
b / Å	26.380(3)	28.0844(16)
c / Å	21.689(2)	28.0844(16)
α / °	90	90
β / °	95.9356(13)	90
γ / °	90	90
Volume / Å^3	10094.5(19)	22151.(4)
Z value	4	8
R_1	0.0294	0.0805
wR_2	0.0800	0.1998
Goodness of Fit	1.074	1.073

Complex	**Ni$_9$L3**	**Ni$_9$L4**
Formula	$C_{102}H_{99}N_9Ni_{13.5}O_{63}$	$C_{88.39}H_{99.67}N_6Ni_9O_{42.86}$
Formula weight	3251.48	2457.62
Temperature / K	100	100
Crystal size / mm	0.296 × 0.08 × 0.06	0.232 × 0.056 × 0.052
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/c	*C*2/c
a / Å	43.678(5)	22.931(2)
b / Å	35.508(4)	24.553(3)
c / Å	28.756(3)	21.426(2)
α / °	90	90
β / °	126.189(10)	106.2012(12)
γ / °	90	90
Volume / Å^3	35993(7)	11584.(2)
Z value	8	4
R_1	0.0803	0.0489
wR_2	0.2361	0.1461
Goodness of Fit	1.059	1.065

Table S2. Calculated value of valence for **$Ni_9L\boldsymbol{n}$** (V_i)

	Ni1	**Ni2**	**Ni3**	**Ni4**	**Ni5**	**Ni6**	**Ni7**	**Ni8**	**Ni9**
Ni_9L1	2.15	2.01	2.04	2.04	1.94	2.02	2.05	2.02	2.14
Ni_9L2	2.19	2.04	1.98	2.03	2.15				
Ni_9L3	2.17	2.06	2.03	2.04	1.97	2.02	2.02	2.06	2.18
Ni_9L4	2.17	2.04	2.02	2.02	1.95				
	Ni11	**Ni12**	**Ni13**	**Ni14**	**Ni15**				
Ni_9L3	2.16	2.03	2.04	1.91	1.97				

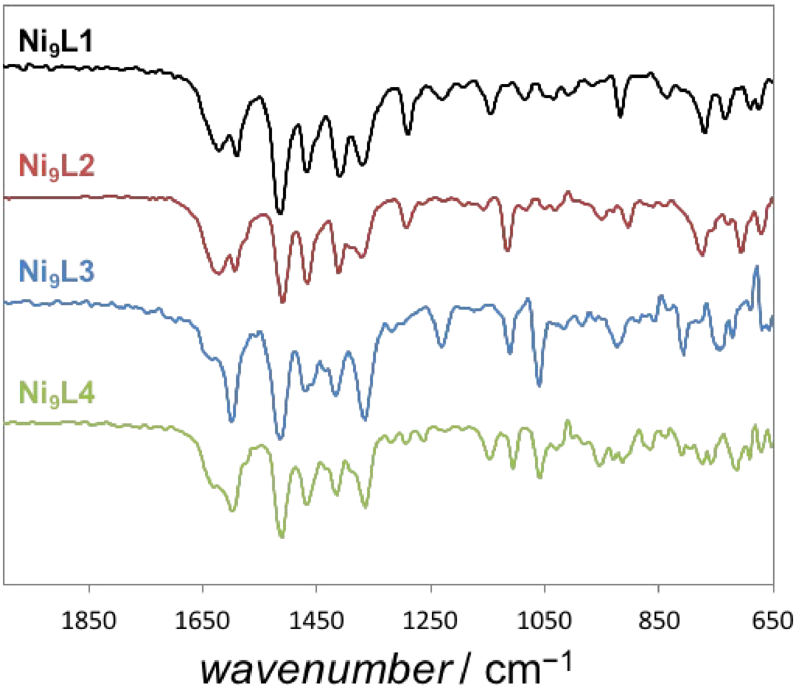


Fig. S5. FT-IR spectra of **$Ni_9L\boldsymbol{n}$**.

UV-vis Spectra

All UV-vis spectra for **Ni$_9$L*n*** showed one intense band around 350 nm which could be attributed to in the ligand origin. The intensity of this band overlap of the charge transfer bands of Ni–μ-OH. The d-d transition absorption band was observed around 660 nm in both spectra. This band supposed to be involved with $^3A_2 \rightarrow {}^3T_1$ for the octahedral Ni(II) center.

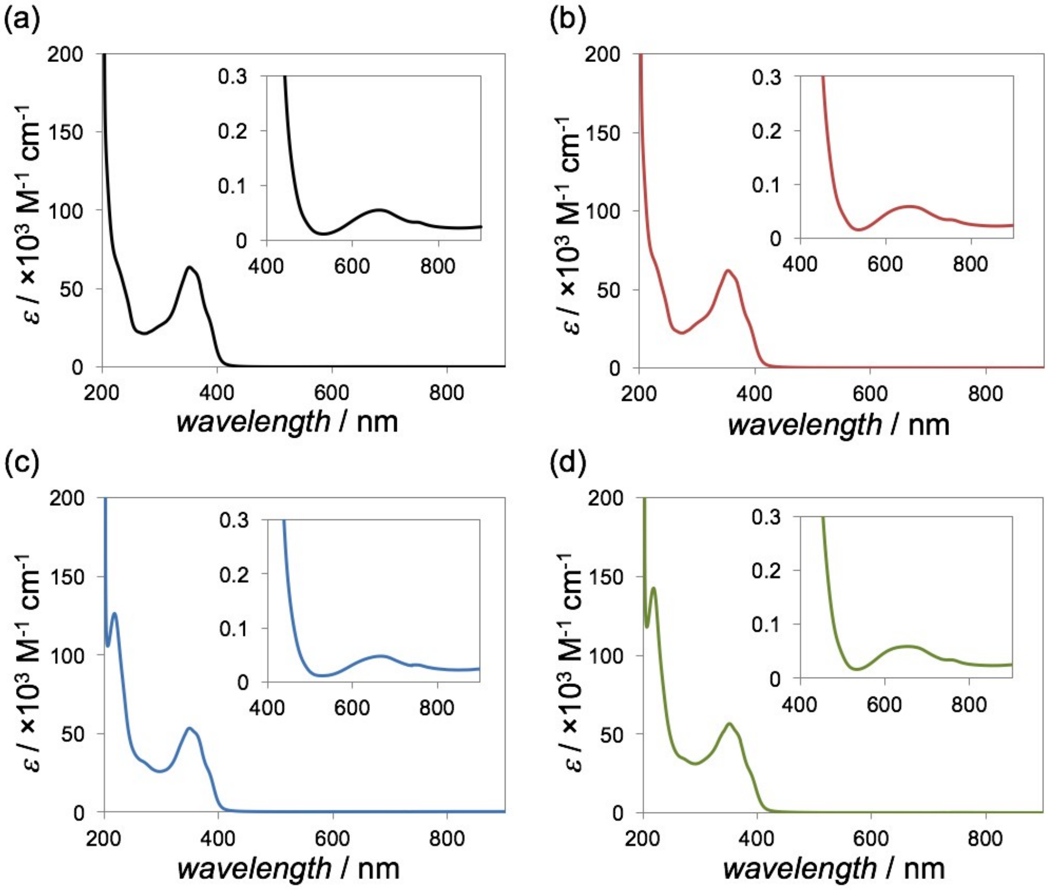


Fig. S6. UV-vis spectra of **Ni$_9$L1** (a), **Ni$_9$L2** (b), **Ni$_9$L3** (c), **Ni$_9$L4** (d), in Acetonitrile/MeOH.

Bulk electrolysis experiment

The bulk electrolysis measurement was run by holding the potential of the working electrode at 0.696 V *vs*. Fc^+/Fc until the ratio of the average current of each interval to the average current of the first interval reaches at 6 %. Integration of the current showed the passage of 0.585 C, which is comparable to 1.01 electrons per molecule of **Ni_9L1**.

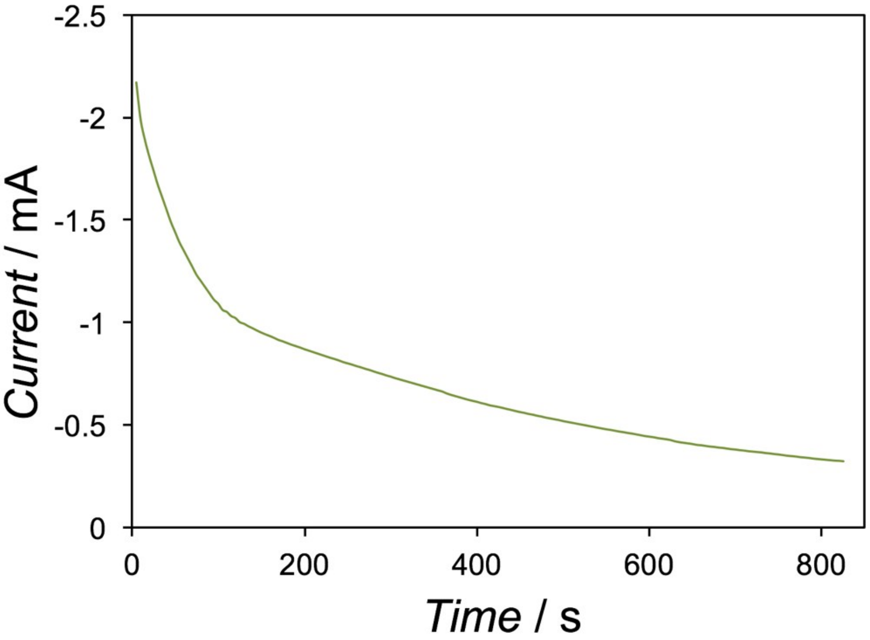


Fig. S7. The result of bulk electrolysis measurement of **Ni_9L1**. (0.1 mM **Ni_9L1,** in 60 ml of Acetonitrile/MeOH with 0.1 M TBAP electrolyte.)

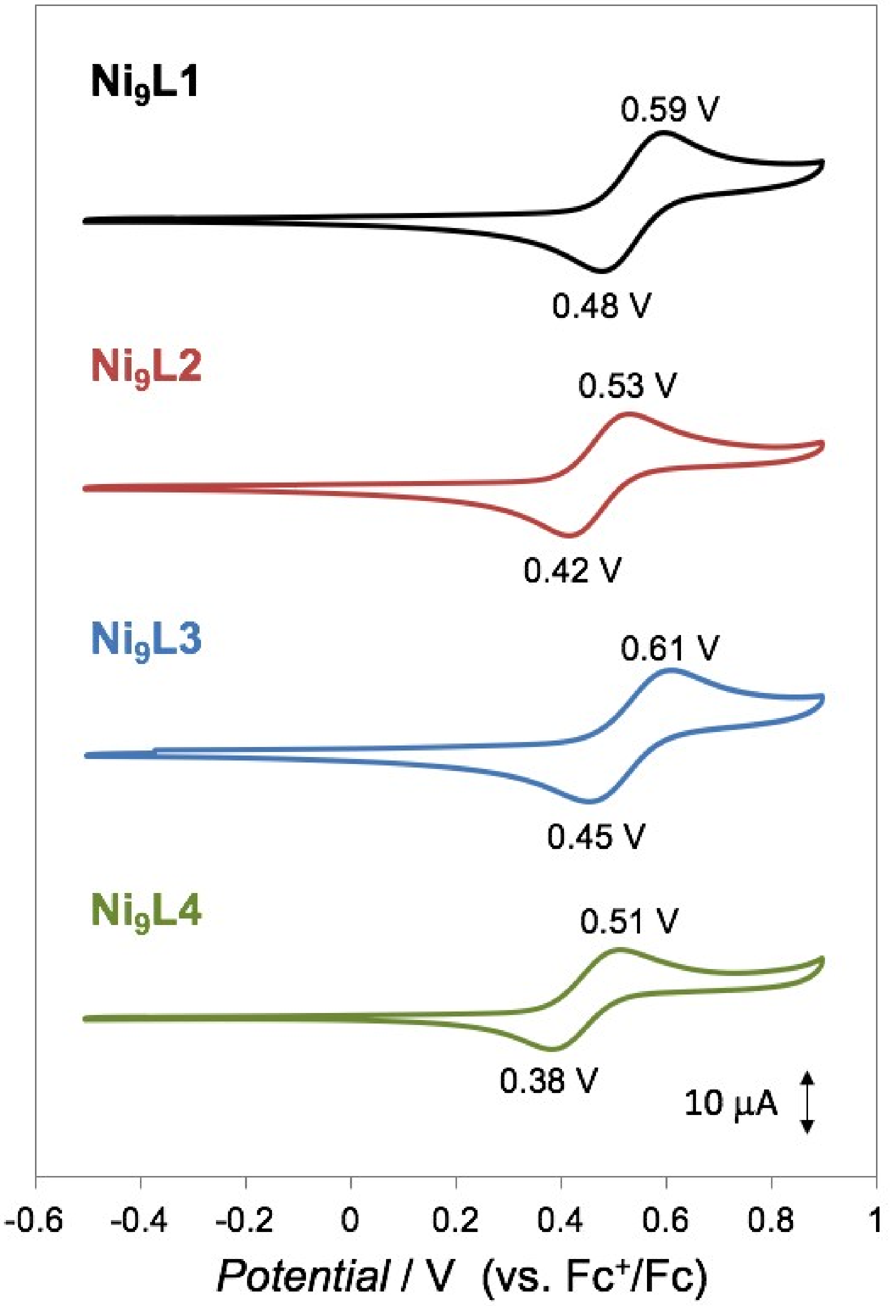


Fig. S8. Cyclic voltammograms (100 mV/s) of 1 mM **Ni_9L*n*** in Acetonitrile/MeOH with 0.1 M TBAP electrolyte.

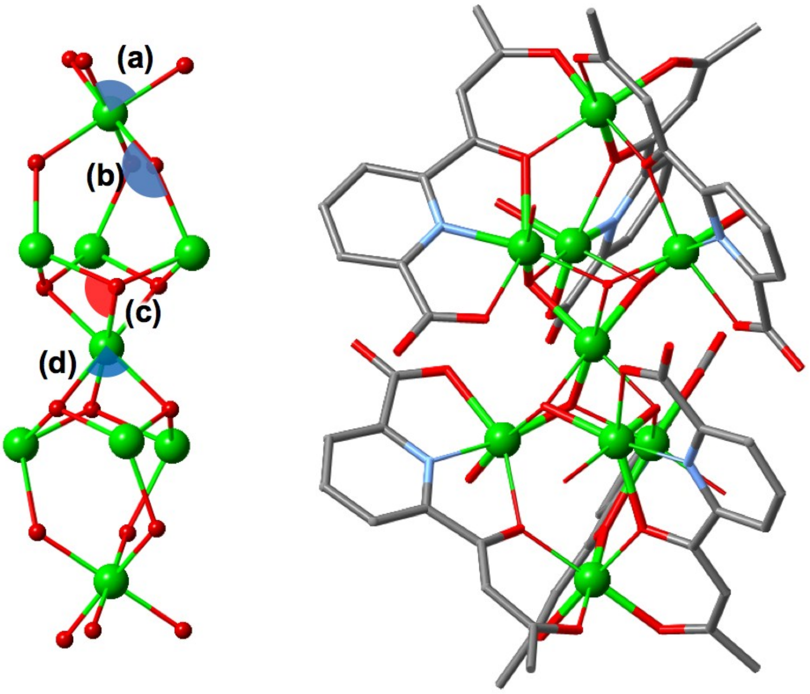


Fig. S9. Ni-O-Ni or O-Ni-O angles changed by introduction of *t*-butyl group. (red and blue represent expanded angle and contracted angle respectively. Numeric data were summarized in Table S3)

Table S3. Electrochemical and structural data of **Ni$_9$L*n***.

	Ni$_9$L1	**Ni$_9$L2**	**Ni$_9$L3**	**Ni$_9$L4**
$E_{1/2}$ / V	0.54	0.47	0.53	0.45
(a)$_{\text{(ave.)}}$ / °	88.95	87.55	88.67	86.30
(b)$_{\text{(ave.)}}$ / °	123.62	123.35	123.58	123.06
(c)$_{\text{(ave.)}}$ / °	95.29	95.44	95.33	95.56
(d)$_{\text{(ave.)}}$ / °	78.98	78.85	78.98	78.86
Ni$_{\text{(central)}}$-O$_{\text{(ave.)}}$. / Å	2.071	2.065	2.066	2.070

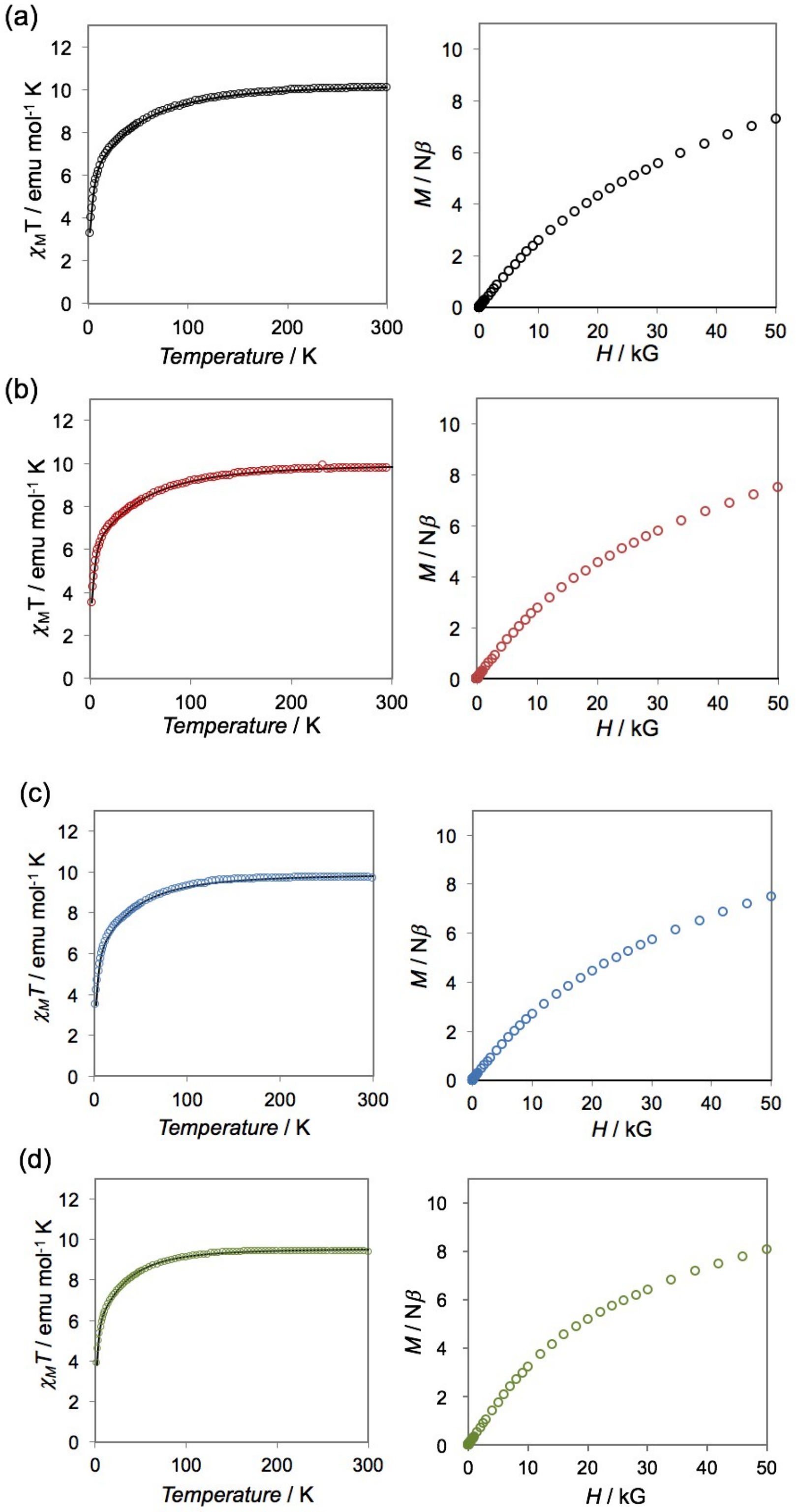


Fig. S10. $\chi_M T$ vs. *T* curves and magnetization curves of **Ni$_9$L1** (a), **Ni$_9$L2** (b), **Ni$_9$L3** (c), **Ni$_9$L4** (d) at 2 K (The solid lines represent the theoretical curves.).

References

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