Electronic Supplementary Material (ESI) for Dalton Transactions.

Metallosupramolecular Ni_2L_3 and Ni_4L_6 complexes of bis-bidentate pyridine-containing ligands: X-ray structures and catalytic proton reduction

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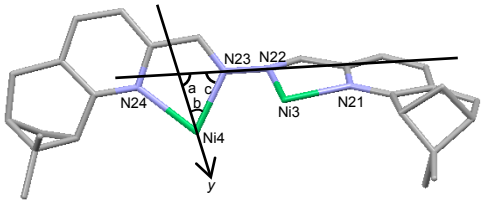
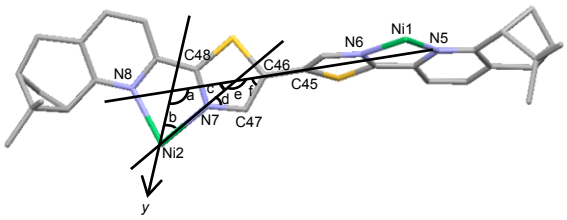
Supporting Information



The coordination vector *y* is the resultant coordination vector of Ni4–N23 and Ni4–N24 and is assumed that it is passed through the mid-point of the distance of N23 and N24 bisecting the bite angle of N23–Ni4–N24.

The directional angle ∠a is defined by the resultant coordination vector y and the interannular N22–N23 bond between the bidentate pyridyl-imine binding domains.
∠b = ∠(N23–Ni4–N24)/ 2 = 77°/ 2 = 38.5°
∠c = 180° − ∠(Ni4–N23–N22) = 180° − 123° = 57°
∠a = 180° − ∠b − ∠c = 84.5°

Figure S1. Graphical representation of directional angle of the bidenate pyridyl-imine binding domain of **L1** and its determination.



The coordination vector y is the resultant coordination vector of Ni2–N8 and Ni2–N7 and is assumed that it is passed through the mid-point of the distance of N8 and N7 bisecting the bite angle of N8–Ni2–N7.

The directional angle ∠a is defined by the resultant coordination vector y and the interannular C45–C46 bond between the bidentate pyridyl-thiazole binding domains.
∠b = ∠(N8–Ni2–N7)/ 2 = 79°/ 2 = 39.5°
∠d = 180° − ∠(Ni2–N7–C47) = 180° −136° = 44°
∠f = 180° − ∠(C47–C46–C45) = 180° − 129° = 51°
∠e = 360° −∠d −∠f − ∠(N7–C47–C46) = 360° − 44° − 51° − 115° = 150°
∠c = 180° − ∠e = 30°
∠a = 180° − ∠b − ∠c = 110.5°

Figure S2. Graphical representation of directional angle of the bidenate pyridyl-thiazole binding domain of **L2** and its determination.

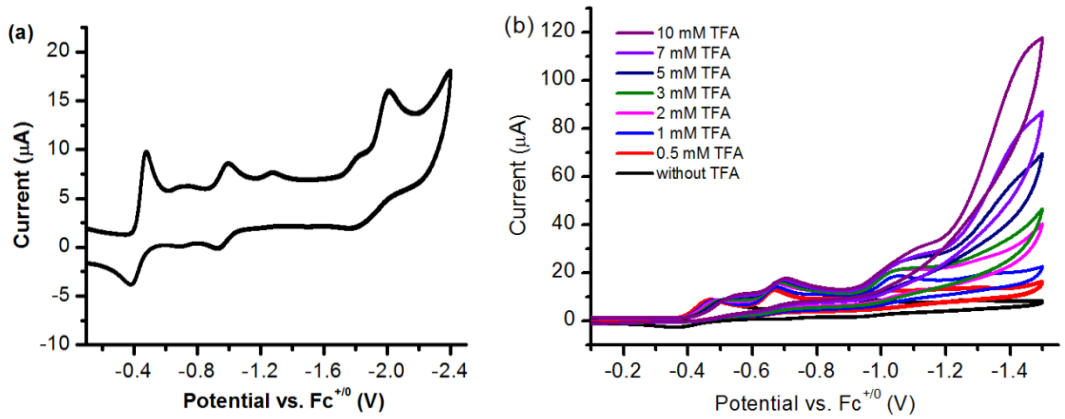


Figure S3. (a) Cyclic voltammogram of 0.25 mM of $[Ni_2(\mathbf{L1})_3](ClO_4)_4$. (b) Cyclic voltammogram of 0.25 mM $[Ni_2(\mathbf{L1})_3](ClO_4)_4$ in the absence and presence of TFA.

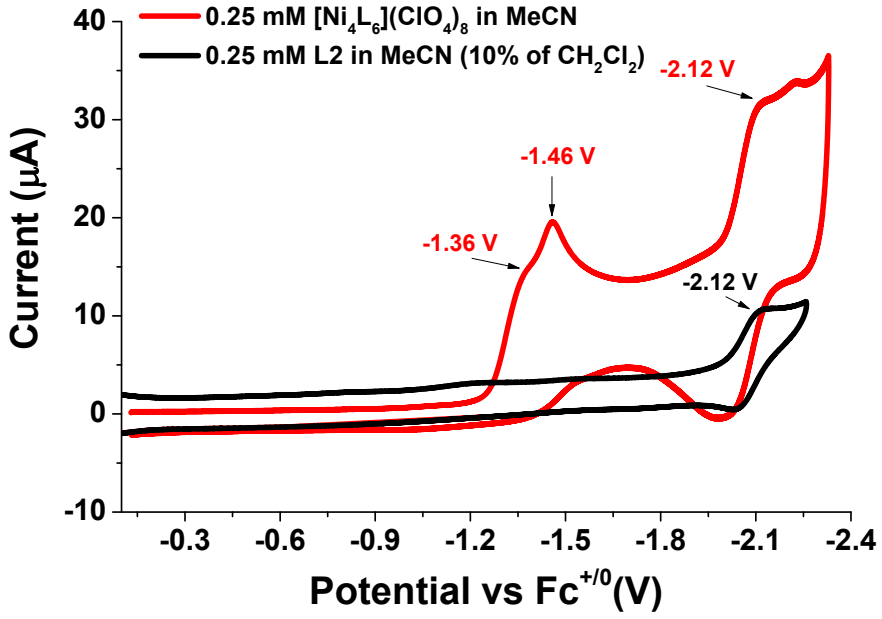


Figure S4. Cyclic voltammogram of 0.25 mM of $[Ni_4(\mathbf{L2})_6](ClO_4)_8$ in MeCN (red) and 0.25 mM of **L2** in the mixture of dichloromethane and MeCN (10% volume of CH_2Cl_2 in MeCN) (black).

Table S1. Crystal data, data collection, and refinement parameters of $[Ni_2(\mathbf{L1})_3](ClO_4)_4$ and $[Ni_4(\mathbf{L2})_6](ClO_4)_8$ [a]

Compound	$[Ni_2(\mathbf{L1})_3](ClO_4)_4$	$[Ni_4(\mathbf{L2})_6](ClO_4)_8$
Formula	Ni2 C87 H103.5 N16.5 Cl4 O16	Ni4 C181.75 H183 Cl9.50 N24.50 O32 S12
M_r	1895.58	4178.86
Color, habit	Yellow, oblique	Colorless, rectangular
Lattice type	Triclinic	Trigonal
Space group	P1	P3
a [Å]	12.5581(5)	26.2992(4)
b [Å]	12.6724(4)	26.2992(4)
c [Å]	29.7591(9)	19.8472(5)
α [°]	89.099 (2)	90.00
β [°]	81.233 (3)	90.00
γ [°]	76.182 (3)	120.00
V [Å^3]	4544.0(3)	11888.2(4)
Z	2	2
D_x [g m^{-3}]	1.385	1.167
F_{000}	1986	4333
Radiation used	CuKα	CuKα
μ [mm^{-1}]	2.204	2.833
θ range [°]	3.0032°–71.6697°	3.3582°–71.53°
Unique reflections measured	20270	15399
Unique reflections observed, $I > 2\sigma(I)$	20982	18122
R	0.0514	0.0553
wR^2	0.1502	0.1527

[a] Details in common: graphite monochromatic radiation, 173 K, Oxford Diffraction CrystAlisPro, refinement based on F^2.

Table S2. Selected bond lengths and bond angles of $[Ni_2(\mathbf{L1})_3](ClO_4)_4$

Bond length (Å)			
Ni3–N13	2.213(4)	Ni4–N15	2.092(4)
Ni3–N14	2.089(4)	Ni4–N16	2.171(4)
Ni3–N19	2.092(3)	Ni4–N17	2.191(4)
Ni3–N20	2.163 (4)	Ni4–N18	2.096(4)
Ni3–N21	2.192(3)	Ni4–N23	2.103(4)
Ni3–N22	2.095(4)	Ni4–N24	2.198(4)
Bond angles (°)			
N13–Ni3–N19	91.5(2)	N17–Ni4–N18	76.7(2)
N19–Ni3–N20	76.9(2)	N17–Ni4–N124	104.2(2)
N20–Ni3–N21	104.8(2)	N16–Ni4–N24	105.7(2)
N21–Ni3–N22	76.1(2)	N16–Ni4–N23	91.6(2)
N14–Ni3–N22	86.2(2)	N15–Ni4–N23	86.1(2)
N14–Ni3–N19	86.0(2)	N15–Ni4–N18	86.3(2)
N13–Ni3–N14	76.6(2)	N23–Ni4–N224	76.6(2)

Table S3. Selected bond lengths and bond angles of $[Ni_4(\mathbf{L2})_6](ClO_4)_8$

Bond length (Å)			
Ni1–N1	2.183(6)	Ni2–N7	2.080(4)
Ni1–N2	2.067(6)	Ni2–N8	2.196(5)
Ni1–N3	2.176(7)	Ni2–N7a	2.080(4)
Ni1–N4	2.102 (5)	Ni2–N8a	2.196(5)
Ni1–N5	2.206(4)	Ni2–N7b	2.080(4)
Ni1–N6	2.082(4)	Ni2–N8b	2.196(5)
Bond angles (°)			
N2–Ni1–N4	90.5(2)	N8–Ni2–N7	78.7(2)
N2–Ni1–N1	78.7(2)	N7–Ni2–N7a	91.6(2)
N1–Ni1–N5	104.9(2)	N7a–Ni2–N8a	78.7(2)
N5–Ni1–N3	103.9(2)	N8a–Ni2–N7b	84.9(2)
N3–Ni1–N6	84.3(2)	N8a–Ni2–N8b	103.9(2)
N6–Ni1–N4	91.5(2)	N8b–Ni2–N7b	78.7(2)
N4–Ni1–N1	84.0(2)	N8–Ni2–N8a	103.9(2)