Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Structures and magnetic studies of four new Ni(II) coordination polymers built by symmetrical tetracarboxylate and N-donor linkers

Contents

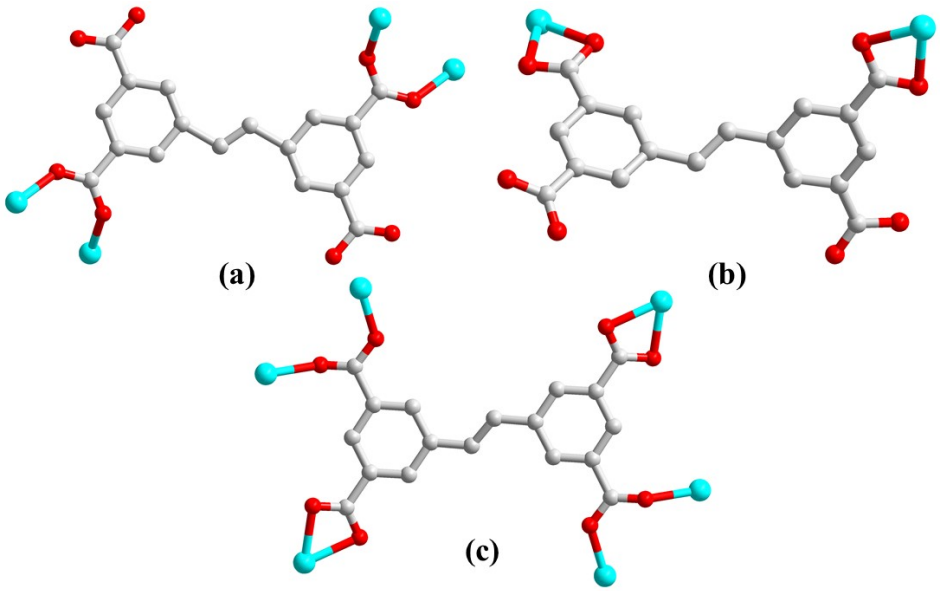
PXRD and Thermogravimetric Analysis

To examine the crystalline purities of complexes **1-4**, powder X-ray diffraction (PXRD) experiments were conducted at room temperature. The patterns of the experiment are consistent with the simulated ones. The result shows that bulk products of the three compounds exhibit phase purity (Fig. S2). The slightly different diffraction intensities can be attributed to the preferred orientation effects.

The thermal stability of **1-4** was studied by thermal gravimetric analysis (TGA, Fig. S4). For **1**, the first step of the weight loss corresponds to the release of two coordination water molecules in the range of 150-220 °C (found 4.2%; calculated 4.5%).

The weight loss of more than 360 °C can be ascribed to the collapse of the lattice structure, and the decomposition of the organic linker. For **2**, the weight loss around 90 °C is 5.5%, which is ascribed to the release of two lattice water molecules (calcd. 5.8%). The weight loss of more than 390 °C can be contributed to the collapse of the lattice structure, and the decomposition of the organic linker. For **3**, the first weight loss occurs from 140 to 230 °C, which is due to the release of one lattice water molecule (found 4.5%; calculated 3.7%). The organic components disintegrated above 410 °C.

For **2**, the TG curve shows a first weight loss from 100 to 200 °C, which corresponds to the loss of coordinated water molecules, and upon further heating, the structure is stable up to 340 °C, and then the structure decomposed at 350 °C.



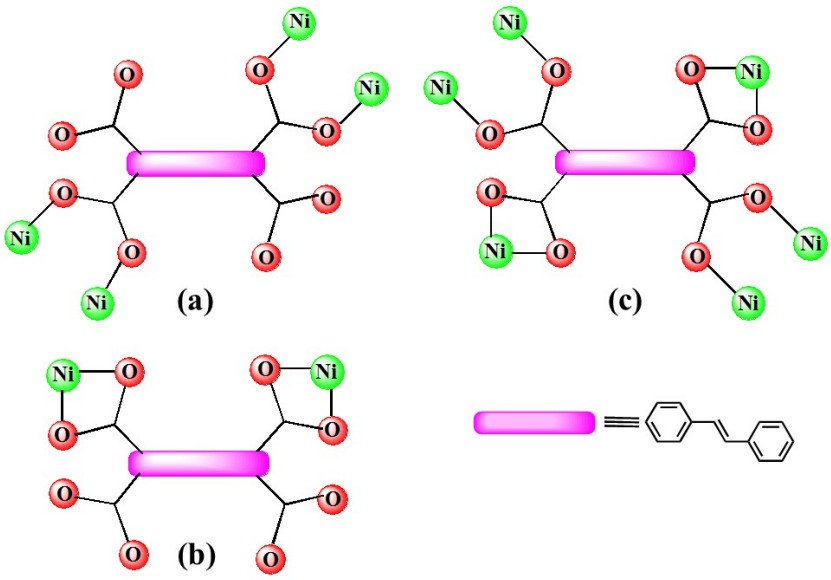


Figure S1. The coordination modes of **L** in **1-4**.

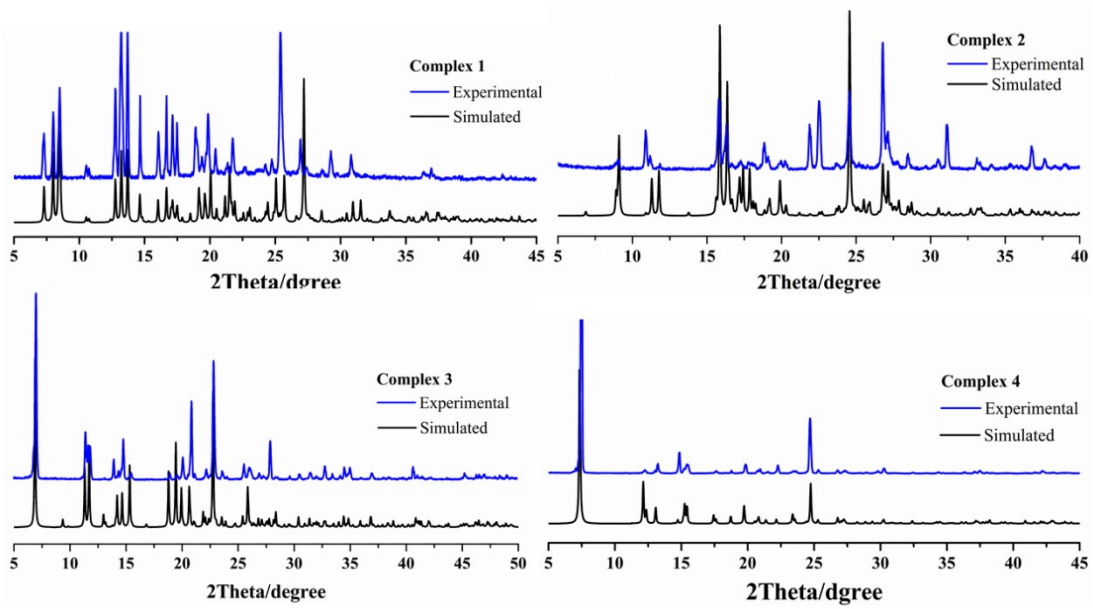


Figure S2. Simulated and observed PXRD patterns of complexes **1-4**.

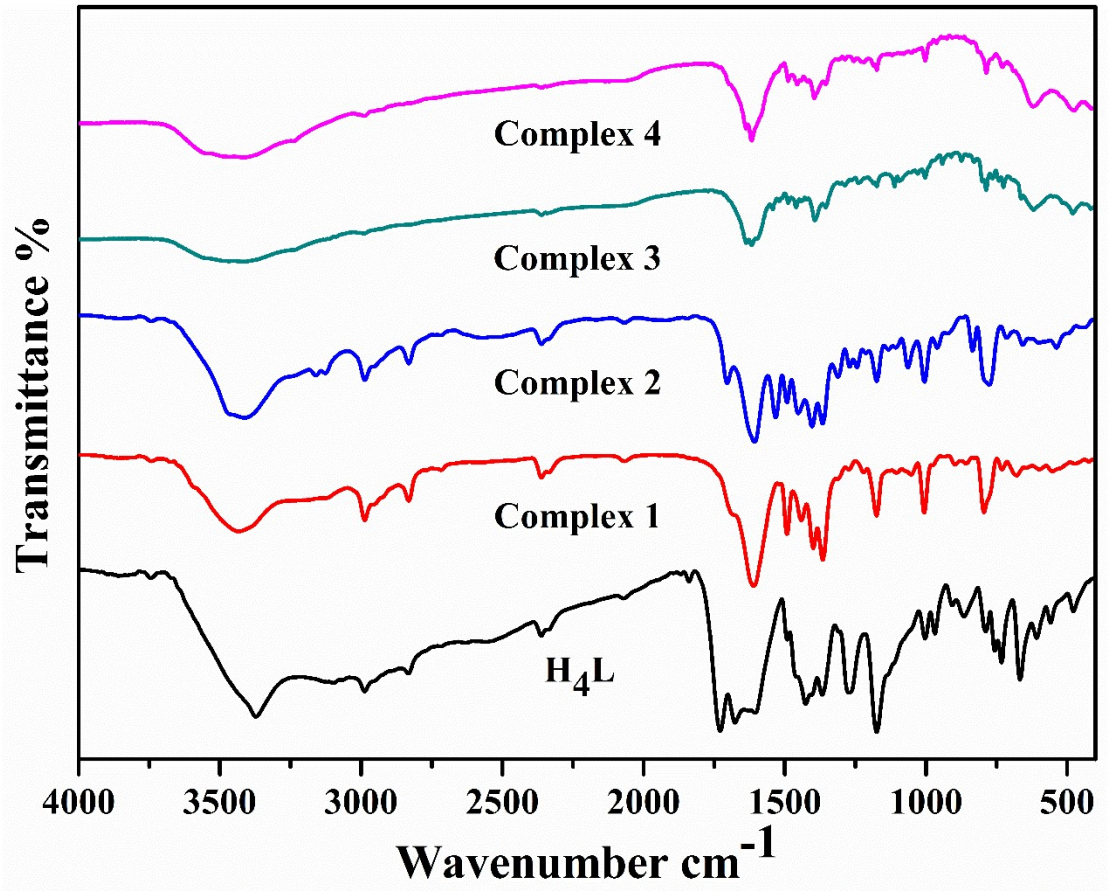


Figure S3. Infrared spectra of complexes **1-4**.

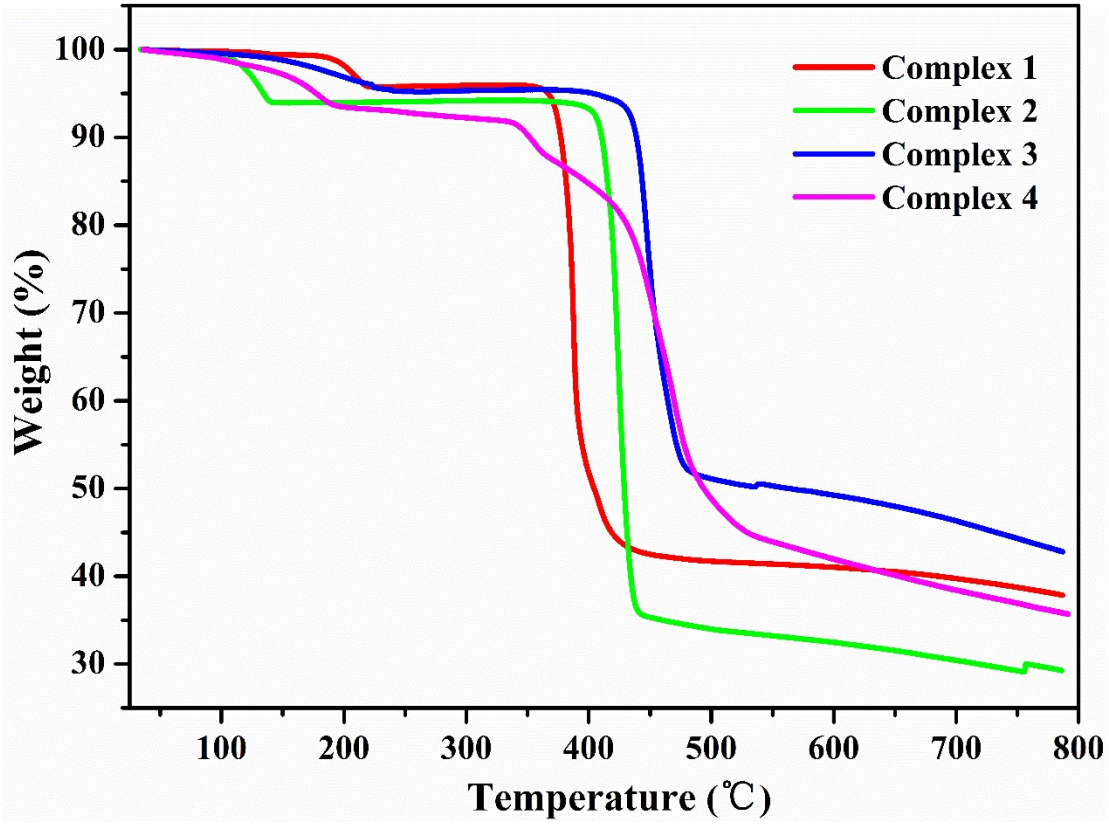


Figure S4. The TG curves of complexes **1**-**4**.

Table S1. Crystal data and structure refinement for complexes **1**-**4.**

Complex	1	2	3	4
Empirical formula	$C_{39}H_{28}N_2NiO_{14}$	$C_{30}H_{23}N_4NiO_{10}$	$C_{23}H_{20}N_4NiO_5$	$C_{14}H_{10}N_2NiO_5$
Formula weight	807.34	658.23	491.14	344.95
Temperature (K)	293	293	293	190
Wavelength (Å)	1.54184	1.54184	1.54184	1.34139
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
Unit cell dimension				
a (Å)	11.5719(10)	11.2470(8)	8.1814(6)	8.0206(3)
b (Å)	11.9790(12)	11.3626(8)	10.0230(7)	9.7574(3)
c (Å)	14.2548(15)	12.9121(7)	14.0209(8)	13.0392(4)
α (°)	68.685(10)	86.947(5)	70.905(6)	110.763(1)
β (°)	66.871(9)	84.530(5)	73.353(6)	90.633(2)
γ (°)	88.769(8)	60.884(7)	80.145(6)	112.746(2)

V (Å^3)	1675.8(3)	1434.97(18)	1037.13(13)	866.89(5)
Z	2	2	2	2
D_{calc} (Mg m^{-3})	1.600	1.523	1.573	1.322
μ (mm^{-1})	1.54	1.56	1.75	6.24
F(000)	832	678	508	352
Crystal size (mm)	0.12 × 0.11 × 0.11	0.14 × 0.11 × 0.07	0.08 × 0.08 × 0.07	0.16 × 0.16 × 0.14
θ range (°)	3.7 to 70.9	5.4 to 69.8	4.7 to 71.2	4.5 to 54.0
Index ranges	-13 ≤ h ≤ 13,	-13 ≤ h ≤ 12,	-7 ≤ h ≤ 9,	-7 ≤ h ≤ 9,
	-14 ≤ k ≤ 14,	-12 ≤ k ≤ 13,	-11 ≤ k ≤ 11,	-11 ≤ k ≤ 11,
	-17 ≤ l ≤ 12	-15 ≤ l ≤ 15	-12 ≤ l ≤ 16	-12 ≤ l ≤ 16
Reflections collected	10807	9126	6388	3097
Independent reflection	5991 [R_{int} = 0.033]	5131 [R_{int} = 0.069]	3685 [R_{int} = 0.033]	3097 [R_{int} = 0.040]
Data/restraints/parameters	5991/1472/519	5131/0/413	3685/0/298	3097/0/204
Final R_1, wR_2 indices [$I > 2\sigma(I)$]	0.049, 0.122	0.082, 0.251	0.041, 0.104	0.082, 0.225
R_1, wR_2 indices (all data)	0.064, 0.135	0.090, 0.256	0.050, 0.112	0.092, 0.231
GOF	1.05	1.10	1.05	1.02
$\Delta\rho_{max,min}$ (e Å^{-3})	0.42/-0.42	1.69/-0.77	0.39/-0.47	1.00/-0.62

Table S2. Selected Bond Lengths (Å) and angles (°) for complexes **1-4**.

Complex 1					
Ni1-O14	2.027 (2)	Ni1-O14	2.027 (2)	Ni1-N2	2.087 (2)
Ni1-O1	2.038 (2)	Ni1-O1	2.038 (2)	Ni1-O13	2.195 (2)
O14-Ni1-O1		93.77 (9)	N1-Ni1-N2		80.42 (9)
O14-Ni1-N1		175.67 (9)	O2#1-Ni1-N2		88.46 (10)
O1-Ni1-N1		90.56 (9)	O14-Ni1-O13		83.71 (9)
O14-Ni1-O2#1		94.28 (8)	O1-Ni1-O13		79.97 (9)

O1-Ni1-O2#1	100.46 (9)	N1-Ni1-O13	97.01 (9)
N1-Ni1-O2#1	84.97 (9)	O2#1-Ni1-O13	177.97 (8)
O14-Ni1-N2	95.30 (9)	N2-Ni1-O13	91.46 (10)
O1-Ni1-N2	166.77 (9)		

Symmetry codes for #1 −x+1, −y+2, −z+1; #2 −x, −y+2, −z+2.

Complex 2

Ni1-N3	2.015 (5)	Ni1-O1	2.110 (4)	Ni1-O6#1	2.117 (4)
Ni1-N1	2.031 (5)	Ni1-O5#1	2.113 (4)	Ni1-O2	2.141 (4)
N3-Ni1-N1		96.57 (19)	O1-Ni1-O6#1		93.74 (16)
N3-Ni1-O1		98.86 (18)	O5#1-Ni1-O6#1		62.51 (15)
N1-Ni1-O1		99.21 (18)	N3-Ni1-O2		159.79 (18)
N3-Ni1-O5#1		100.17 (18)	N1-Ni1-O2		93.31 (17)
N1-Ni1-O5#1		101.77 (17)	O1-Ni1-O2		62.05 (15)
O1-Ni1-O5#1		149.70 (16)	O5#1-Ni1-O2		94.99 (16)
N3-Ni1-O6#1		91.38 (18)	O6#1-Ni1-O2		83.80 (16)
N1-Ni1-O6#1		163.54 (17)			

Symmetry codes for #1 x, y, z+1; #2 x, y, z−1; #3 −x+2, −y−1, −z+1; #4 −x+3, −y, −z.

Complex 3

Ni1-O4#1	2.0136 (16)	Ni1-N4#3	2.064 (2)	Ni1-O1	2.1405 (16)
Ni1-O3#2	2.0546 (16)	Ni1-N1	2.070 (2)	Ni1-O2	2.1658 (16)
O4#1-Ni1-O3#2		102.91 (7)	O4#1-Ni1-O3#2		102.91 (7)
O4#1-Ni1-N4#2		89.56 (8)	O4#1-Ni1-N4#2		89.56 (8)
O3#2-Ni1-N4#2		84.99 (8)	O3#2-Ni1-N4#2		84.99 (8)
O4#1-Ni1-N1		95.94 (8)	O4#1-Ni1-N1		95.94 (8)
O3#2-Ni1-N1		91.28 (8)	O3#2-Ni1-N1		91.28 (8)
N4#2-Ni1-N1		173.94 (8)	N4#2-Ni1-N1		173.94 (8)
O4#1-Ni1-O1		156.16 (7)	O4#1-Ni1-O1		156.16 (7)

O3#2-Ni1-O1	100.51 (7)

Symmetry codes for #1 x, y+1, z; #2 −x, −y+1, −z+2; #3 x−1, y, z+1; #4 −x, −y, −z+3; #5 x, y−1, z; #6 x+1, y, z−1.

Complex 4					
Ni01-O1	2.014 (5)	Ni01-O2#1	2.056 (5)	Ni01-O3#2	2.085 (5)
Ni01-O5	2.050 (6)	Ni01-N1	2.069 (6)	Ni01-O4#2	2.213 (5)
O1-Ni01-O5		83.9 (2)	O2#1-Ni01-O3#2		96.11 (19)
O1-Ni01-O2#1		91.45 (19)	N1-Ni01-O3#2		94.4 (2)
O5-Ni01-O2#1		175.3 (2)	O1-Ni01-O4#2		94.08 (18)
O1-Ni01-N1		110.5 (2)	O5-Ni01-O4#2		90.4 (2)
O5-Ni01-N1		89.9 (3)	O2#1-Ni01-O4#2		89.47 (19)
O2#1-Ni01-N1		92.1 (2)	N1-Ni01-O4#2		155.3 (2)
O1-Ni01-O3#2		153.66 (19)	O3#2-Ni01-O4#2		60.91 (17)
O5-Ni01-O3#2		87.9 (2)			

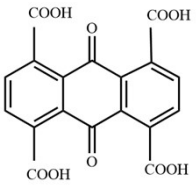
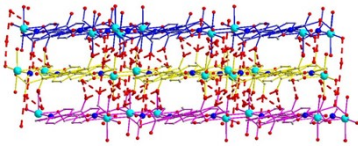
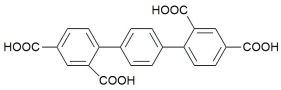
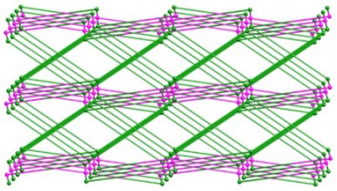
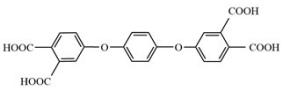
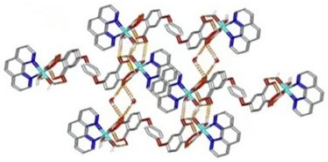
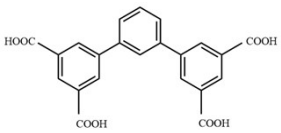
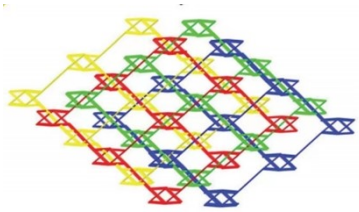
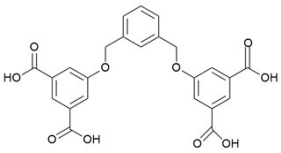
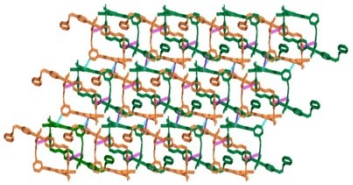
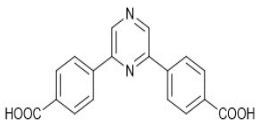
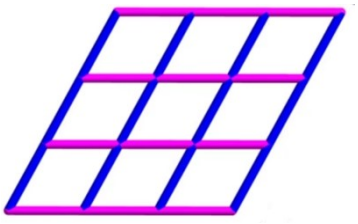
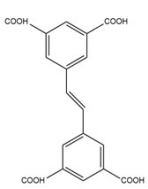
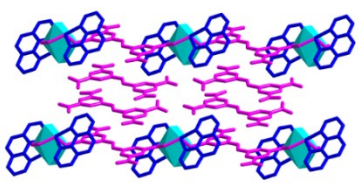
Symmetry codes for #1 −x+2, −y+2, −z+1; #2 x+1, y+1, z; #3 −x+1, −y+1, −z; #4 −x+2, −y+3, −z+2; #5 x−1, y−1, z.

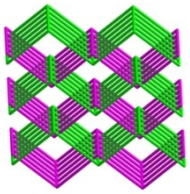
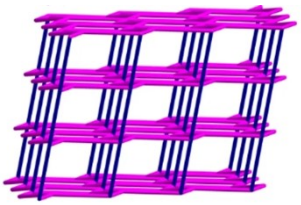
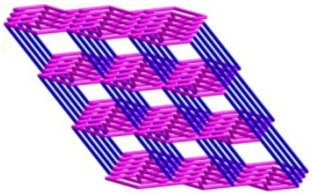
Table S3. Hydrogen bond parameters [Å, °] for complex **2**.

Compound 2				
D–H···A	D–H	H···A	D···A	D–H···A
O1S–H1S1···N2#2	0.98	2.39	3.1207(1)	131
O1S–H1S3···O1#4	0.98	2.19	2.9155(1)	129
O5–H5B···O3#1	0.98	1.66	2.6344(1)	169
O5–H5C···O3#2	0.96	1.78	2.6895(1)	157
O6–H6A···O4#3	0.97	1.70	2.6620(1)	167
O6–H6B···O1	0.97	1.61	2.5748(1)	169
O6–H6B···O2	0.97	2.42	2.8907(1)	109
C19–H19···O4#3	0.95	2.20	3.1473(1)	171

Symmetry code: #**1** 1-x, -y, -z; #**2** x, y, 1+z; #**3** -1+x, y, 1+z; #**4** 1+x, y, z.

Table S4. Structural comparison of various MOFs synthesized using the H_4L ligand.

Formula	Ligand	Ancillary ligand	structure	dimension	Ref
$C_{14}H_{14}NNiO_{10}$		bpy		3D	[1]
$C_{24}H_{23}NiN_2O_6$		bpp		3D	[2]
$C_{46}H_{42}Ni_2N_4O_{18}$		phen		3D	[3]
$C_{16}H_{13}NNiO_6$		4,4′-bpy		3D	[4]
$C_{50}H_{50}N_4Ni_2O_{14}$		bpp		3D	[5]
$C_{24}H_{19}N_4NiO_6$		dib		2D	[6]
$C_{39}H_{28}N_2NiO_{14}$		1,10-phen		1D	This work

$C_{30}H_{23}N_4NiO_{10}$		dib		2D	This work
$C_{23}H_{20}N_4NiO_5$		bix		3D	This work
$C_{14}H_{10}N_2NiO_5$		dpa		3D	This work

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