Multivariant synthesis, crystal structures and properties of four nickel coordination polymers based on flexible ligands

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Contents

Table S1. Selected bond distances (Å) and angles (º) for compounds **1-4**

Compound **1**					
N(1)-Ni(1)	2.131(4)	O(9)-Ni(2)-N(2)#4	94.02(13)	O(1)-Ni(1)-N(1)	93.75(13)
N(2)-Ni(2)#1	2.107(4)	O(3)-Ni(2)-O(9)	91.41(12)	O(1)#2-Ni(1)-N(1)	86.25(13)
Ni(1)-O(1)	2.032(3)	O(1)#2-Ni(1)-O(8)	88.14(12)	O(8)-Ni(1)-N(1)	90.93(14)
Ni(1)-O(8)	2.096(3)	O(9)-Ni(2)-O(9)#3	180.0	O(8)#2-Ni(1)-N(1)	89.07(14)
Ni(2)-O(3)	2.048(3)	O(3)-Ni(2)-N(2)#4	90.55(14)	N(1)-Ni(1)-N(1)#2	180.00(18)
Ni(2)-O(9)	2.084(3)	O(3)#3-Ni(2)-O(9)	88.59(12)	O(9)#3-Ni(2)-N(2)#4	85.98(13)
O(1)-Ni(1)-O(8)	91.86(12)	O(3)-Ni(2)-O(3)#3	180.00(16)	O(3)#3-Ni(2)-N(2)#4	89.45(14)
O(1)-Ni(1)-O(1)#2	180.0				

Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z, #2 -x+1,-y,-z, #3 -x+1,-y+1,-z+1, #4 -x+1,-y,-z+1, #5 x,y+1,z for **1**.

Compound **2**					
N(1)-Ni(1)	2.103(5)	O(9)#2-Ni(1)-O(1)	94.53(14)	O(6)#3-Ni(1)-N(2)#1	86.81(17)
N(2)-Ni(1)#1	2.136(4)	O(9)#2-Ni(1)-O(6)#3	90.43(15)	O(4)#2-Ni(1)-N(2)#1	85.37(15)
Ni(1)-O(9)#2	1.994(3)	O(1)-Ni(1)-O(6)#3	89.74(16)	N(1)-Ni(1)-N(2)#1	93.05(19)
Ni(1)-O(1)	2.057(4)	O(9)#2-Ni(1)-O(4)#2	95.23(13)	O(2)#4-Ni(2)-O(2)	90.8(2)
Ni(1)-O(6)#3	2.065(4)	O(1)-Ni(1)-O(4)#2	169.81(15)	O(2)#4-Ni(2)-O(9)#2	173.46(14)
Ni(1)-O(4)#2	2.069(4)	O(6)#3-Ni(1)-O(4)#2	87.23(16)	O(9)-Ni(3)-O(7)#6	88.35(14)
Ni(2)-O(2)#4	2.048(4)	O(9)#2-Ni(1)-N(1)	89.74(17)	O(9)#2-Ni(2)-O(8)	87.08(15)
Ni(2)-O(9)#2	2.052(3)	O(1)-Ni(1)-N(1)	93.11(17)	O(9)#2-Ni(2)-O(9)#5	81.23(19)
Ni(2)-O(8)	2.103(4)	O(6)#3-Ni(1)-N(1)	177.11(17)	O(2)#4-Ni(2)-O(8)	88.99(17)
Ni(3)-O(9)	2.042(3)	O(4)#2-Ni(1)-N(1)	89.89(17)	O(9)-Ni(3)-O(3)	96.71(14)
Ni(3)-O(3)	2.084(3)	O(9)#2-Ni(1)-N(2)#1	177.15(17)	O(3)-Ni(3)-O(3)#4	85.2(2)
Ni(3)-O(7)#6	2.091(4)	O(1)-Ni(1)-N(2)#1	84.75(15)	O(3)-Ni(3)-O(7)#6	89.10(14)
O(8)-Ni(2)-O(8)#4	173.4(2)	O(9)-Ni(3)-O(9)#4	81.72(18)	O(9)#4-Ni(3)-O(7)#6	95.52(14)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y,-z+1/2, #2 x,y-1,z, #3 -x+1,-y+1,-z+1, #4 -x+3/2,y,-z+1/2, #5 -x+3/2,y-1,-z+1/2, #6 x+1/2,-y+2,z-1/2, #7 -x+1,-y+2,-z+1, #8 x,y+1,z for **2**.

Compound **3**					
N(1)-Ni(1)	2.070(3)	O(3)#3-Ni(1)-O(5)	98.89(9)	O(3)#3-Ni(1)-N(2)#4	90.23(10)
N(2)-Ni(1)#2	2.086(3)	O(3)#3-Ni(1)-N(1)	87.86(10)	O(5)-Ni(1)-N(2)#4	92.79(10)
N(5)-Ni(2)	2.081(3)	O(5)-Ni(1)-N(1)	87.85(10)	N(1)-Ni(1)-N(2)#4	178.06(10)
Ni(1)-O(3)#3	2.021(2)	O(3)#3-Ni(1)-O(1)	160.82(9)	O(5)-Ni(1)-O(1)	100.25(9)
Ni(1)-O(5)	2.054(2)	N(1)-Ni(1)-O(1)	91.84(10)	N(2)#4-Ni(1)-O(1)	89.86(10)
Ni(1)-O(1)	2.099(2)	O(3)#3-Ni(1)-O(2)	99.66(9)	O(5)-Ni(1)-O(2)	161.42(8)
Ni(1)-O(2)	2.202(2)	N(1)-Ni(1)-O(2)	91.92(10)	N(2)#4-Ni(1)-O(2)	88.06(10)
Ni(2)-O(18)#5	2.098(2)	O(17)#5-Ni(2)-O(17)	180.0	N(5)-Ni(2)-N(5)#5	180.0
Ni(2)-O(17)#5	2.106(2)	N(5)-Ni(2)-O(18)#5	92.18(10)	O(18)#5-Ni(2)-O(18)	180.0
O(1)-Ni(1)-O(2)	61.18(8)	N(5)-Ni(2)-O(17)#5	87.45(10)	O(18)-Ni(2)-O(17)#5	89.84(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1, #2 x,y,z+1, #3 x-1,y,z, #4 x,y,z-1, #5 -x+1,-y,-z+1, #6 x+1,y,z for **3**.

Compound **4**					
N(1)-Ni(1)	2.078(4)	O(3)#2-Ni(1)-O(8)	94.82(15)	O(3)#2-Ni(1)-N(1)	93.32(15)

N(2)-Ni(1)#1	2.085(4)	O(8)-Ni(1)-N(1)	90.00(15)	O(3)#2-Ni(1)-N(2)#3	90.60(15)
Ni(1)-O(3)#2	2.010(3)	O(8)-Ni(1)-N(2)#3	88.92(16)	N(1)-Ni(1)-N(2)#3	176.01(16)
Ni(1)-O(8)	2.075(4)	O(3)#2-Ni(1)-O(2)	159.90(14)	O(8)-Ni(1)-O(2)	104.81(15)
Ni(1)-O(2)	2.127(4)	N(1)-Ni(1)-O(2)	91.00(15)	N(2)#3-Ni(1)-O(2)	85.56(15)
Ni(1)-O(1)	2.132(4)	O(3)#2-Ni(1)-O(1)	98.49(14)	O(8)-Ni(1)-O(1)	166.58(14)
N(1)-Ni(1)-O(1)	90.91(16)	N(2)#3-Ni(1)-O(1)	89.25(16)	O(2)-Ni(1)-O(1)	61.79(13)

Symmetry transformations used to generate equivalent atoms: #1 x+1,y,z, #2 -x,y-1/2,-z+1/2, #3 x-1,y,z, #4 -x,y+1/2,-z+1/2 for **4**.

Table S2. The different products of different metal-ligand-bpe ratio

Metal-ligand-bpe Ratio	1:1:1	1:2:1	x:2:1(x≥2)
140℃, 0.2ml 1M NaOH(aq)	**3**	**1**	**2**

Table S3. The different products of different pH at the ratio of metal-ligand-bpe is 1:2:1

Different pH	5.5	~	6.5
140℃	**1**	**1**+**3**	**3**

Table S4. The different products of different solvent ratio (NMP/H_2O)

Different solvent ratio (NMP/H_2O)	0:8	0.5:7.5	2:6	4:4	6:2
140℃	**1**+amorphous	**4**+amorphous	**4**	**4**+amorphous	amorphous

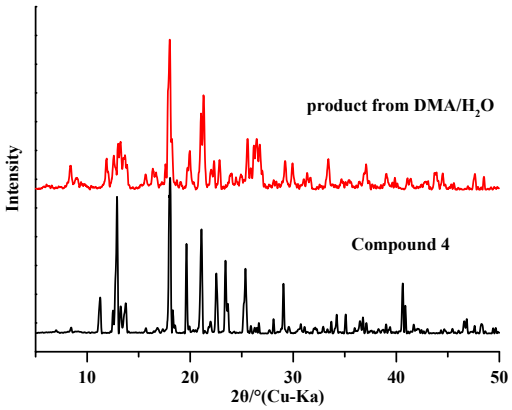


Figure S1. The PXRD parttern of product from DMA/H_2O system and compound **4**.

Table S5. Crystallographic data for compound **3'**

Compound	**3'**
Formula	$C_{34}H_{35}N_3O_{11}Ni_{1.5}$
Formula weight	749.71
Crystal system	Triclinic
Space group	*P-1*

a(Å)	10.162(16)
b(Å)	13.36(2)
c(Å)	13.36(2)
α(º)	72.61(3)
β(º)	83.85(2)
γ(º)	82.09(3)
V (Å^3)	1710(5)
Z	2
Dc (g cm^{-3})	1.456
F(000)	780
GOF on F^2	0.882
R_1,wR_2[I >2σ(I)]	0.0819,0.1764
R_1,wR_2 (all data)	0.1647,0.2147
R_{int}	0.0594

Table S6. Selected bond distances (Å) and angles (º) for compound **3'**

Compound **3'**					
N(1)-Ni(1)	2.107(10)	N(3)#4-Ni(2)-O(10)	92.7(3)	O(8)-Ni(1)-N(1)	92.5(3)
N(2)-Ni(1)#3	2.074(10)	O(10)-Ni(2)-O(10)#4	180.0	N(2)#5-Ni(1)-N(1)	176.7(5)
N(3)-Ni(2)	2.087(10)	N(3)#4-Ni(2)-O(9)	87.6(3)	O(4)-Ni(1)-O(5)#6	161.6(3)
Ni(2)-O(10)	2.094(7)	O(10)-Ni(2)-O(9)	91.1(3)	O(8)-Ni(1)-O(5)#6	99.8(3)
Ni(2)-O(9)	2.098(8)	N(3)#4-Ni(2)-O(9)#4	92.4(3)	N(2)#5-Ni(1)-O(5)#6	92.5(3)
Ni(1)-O(4)	1.992(8)	O(9)-Ni(2)-O(9)#4	180.0	N(1)-Ni(1)-O(5)#6	90.3(4)
Ni(1)-O(8)	2.054(7)	O(4)-Ni(1)-O(8)	98.6(3)	O(4)-Ni(1)-O(6)#6	99.4(3)
Ni(1)-O(5)#6	2.120(8)	O(4)-Ni(1)-N(2)#5	86.6(4)	O(8)-Ni(1)-O(6)#6	162.0(3)
Ni(1)-O(6)#6	2.194(7)	O(8)-Ni(1)-N(2)#5	88.6(3)	N(2)#5-Ni(1)-O(6)#6	92.1(3)
N(3)#4-Ni(2)-N(3)	180.0	O(4)-Ni(1)-N(1)	90.2(4)	N(1)-Ni(1)-O(6)#6	87.8(3)
		O(5)#6-Ni(1)-O(6)#6	62.2(3)		

Symmetry transformations used to generate equivalent atoms: #1 x+1,y,z, #2 -x,-y+2,-z, #3 x,y,z+1, #4 -x,-y+1,-z, #5 x,y,z-1, #6 x-1,y,z, for **3'**.

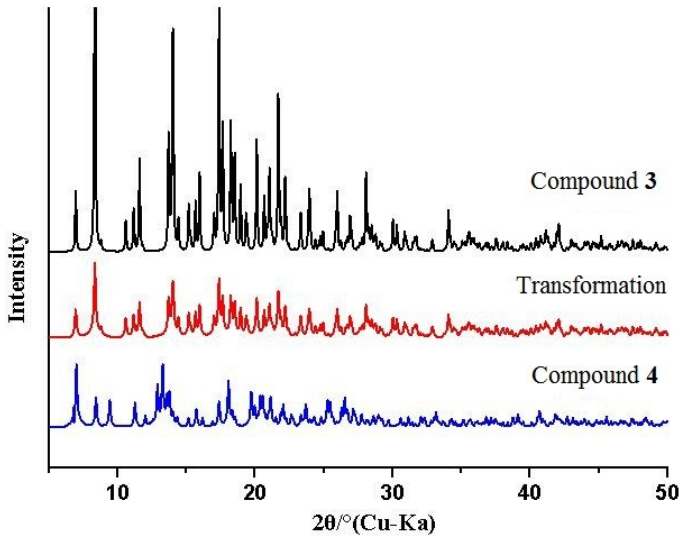


Figure S2. The simulated patterns of compound **3** (top) and compound **4** (bottom), the experimental patterns of **3'** by step-wise synthesis (middle).

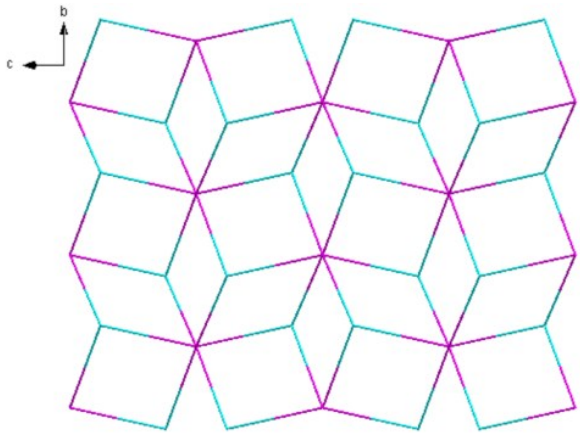


Figure S3. The topology net of **2**.

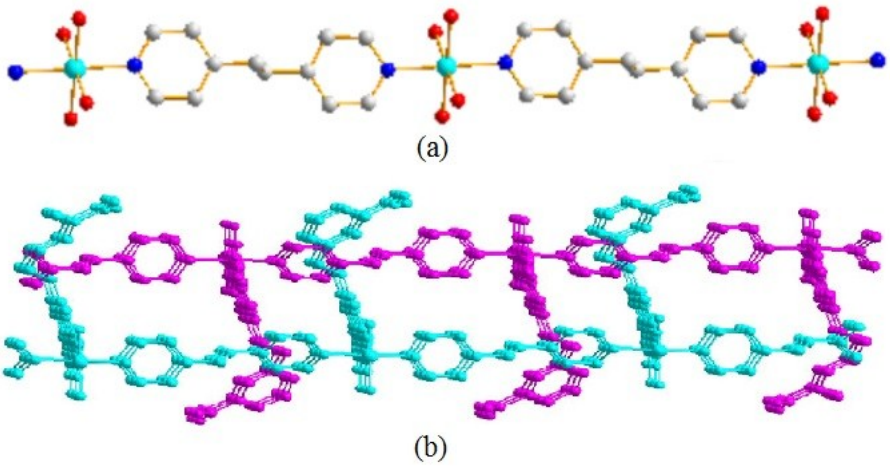


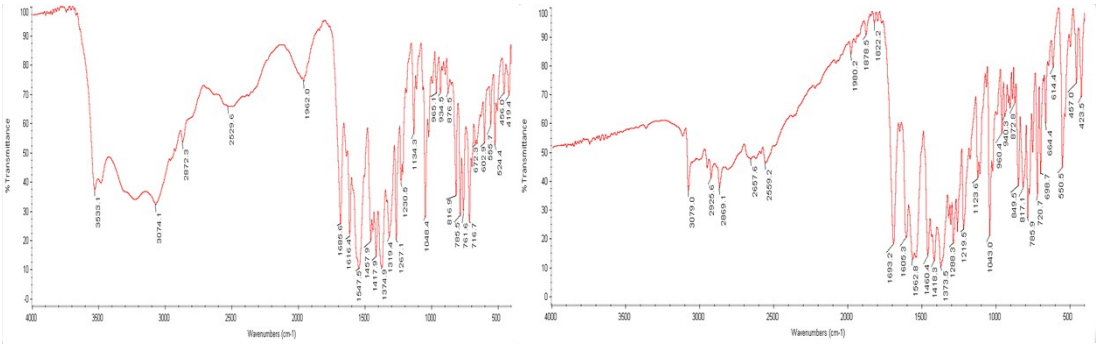
Figure S4. a) The 1D cation chain of $[Ni_{0.5}(bpe)_{0.5}(H_2O)_2]_n^{n+}$ in **3**, b) The two-fold interpenetrating architecture $[Ni(L)(bpe)(H_2O)]_n^{n-}$ constituted from 2D layers in **3**.

Table S7. The dihedral angels and torsion angels of the H_3L ligand in Compounds **1-4**

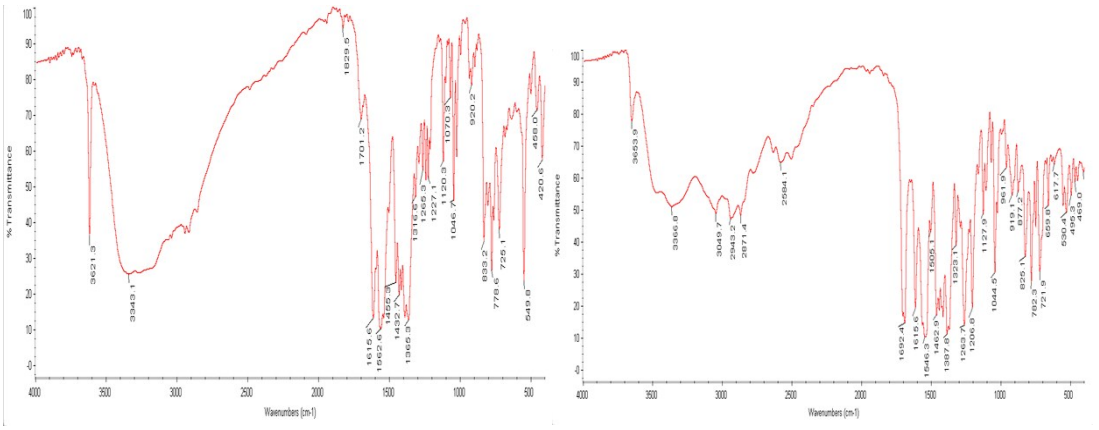
	dihedral angle (°)	Torsion angle (°)
1	69.872(25)	179.802(69)
2	71.590(11)	-173.615(28)
3	78.222(20)	109.289(50)
4	76.822(5)	-171.468(21)

Table S8. The dihedral angels and torsion angels of the bpe in Compounds **1-4**

	dihedral angle (°)	Torsion angle (°)
1	52.714(25)	55.104(86)
2	46.722(10)	67.013(34)
3 (2D)	28.058(16)	-179.141(39)
3 (1D)	0.000(24)	-180.000(39)
4	47.924(10)	174.81(2)

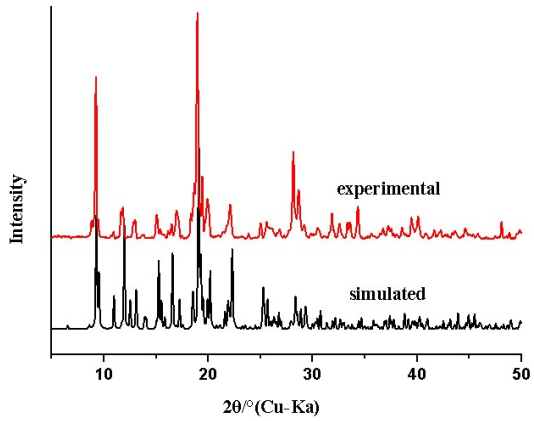


1 2



3 4

Figure S5. The FT-IR Spectra of H_4L ligand and compounds **1-4**.



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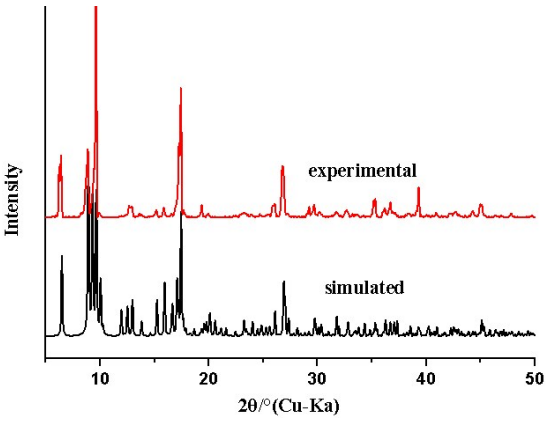

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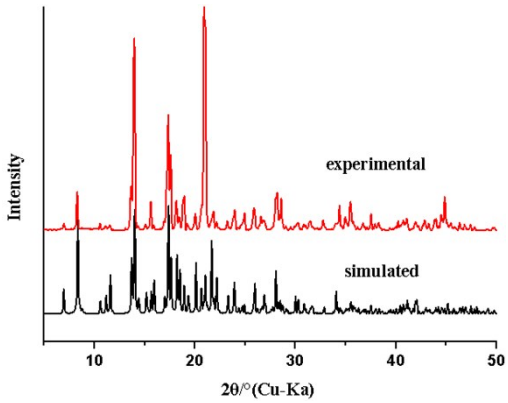

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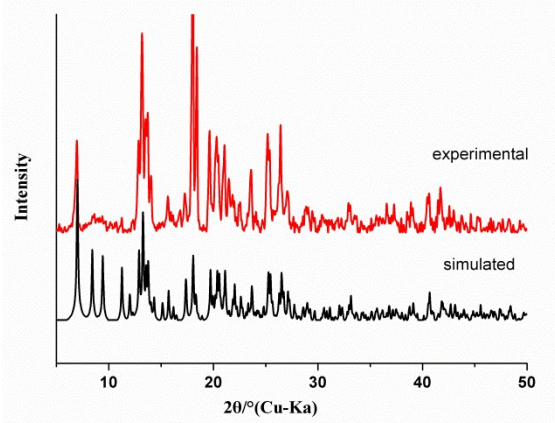
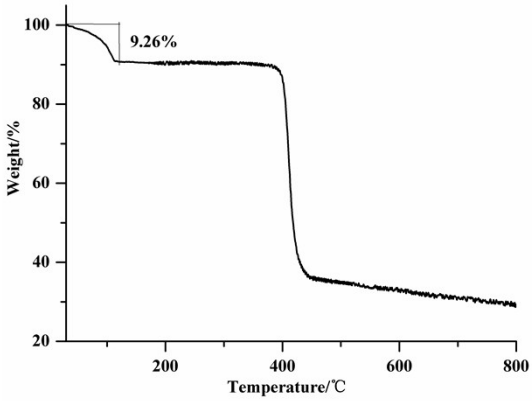
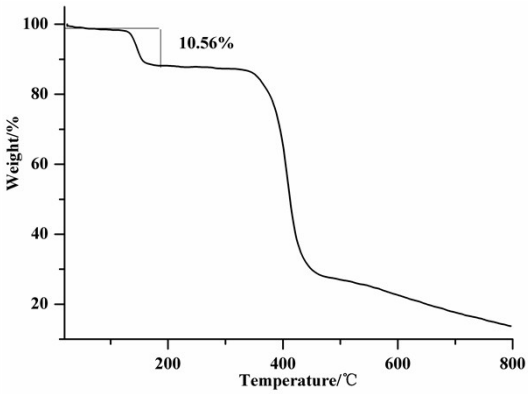


4

Figure S6. The PXRD patterns of compounds **1-4** and the simulated spectra.



1



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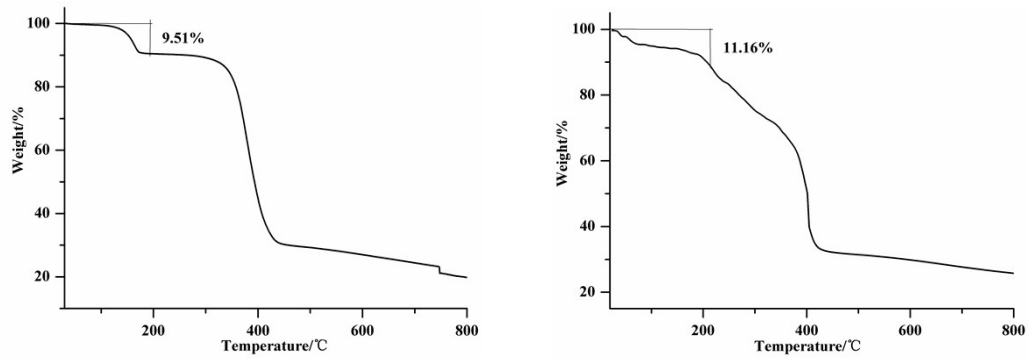
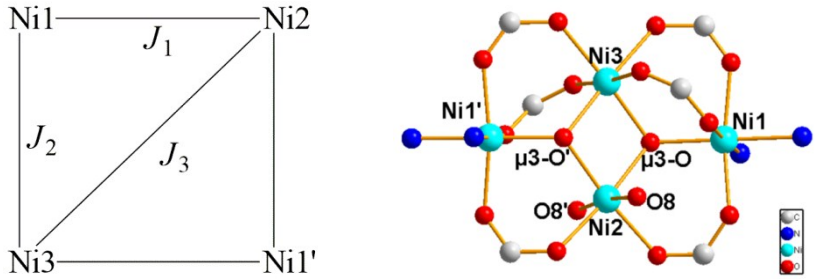


3 4

Figure S7. TGA-DTA curves for **1-4**.



Scheme S1. Schematic representation of magnetic mode in **2**.