ELECTRONIC SUPPLEMENTARY INFORMATION FOR

A New Family of 1D, 2D and 3D Frameworks Aggregated from Ni_5, Ni_4 and Ni_7 Building Units: Synthesis, Structure, and Magnetism

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The Discussion of Synthesis

Molar ratio: The various molar ratios of reactants (such as 1:2, 2:1, 3:1, 3:2 etc) have been tried in our recipes of synthesis. It turned out that 2:1 molar ratio of metal ion and ligand is the best choice for high purity and yield.

Crystallization methods: Since the H_3BPT ligand is poorly soluble to obtain crystals at room temperature, we employed solvothermal reactions giving high temperature and autogenous pressure to make the synthesis reaction occur. After attempting different reaction temperature and time, we found that maintaining the reaction at 433 K for 72 h is the best condition for the purity and crystallinity.

Solvents: The synthesis of the complexes was failed by using single solvent, thus we tried different mix-solvents, in which the polarity of each kind of solvents is different. So we speculated that the polarity of the solvent may be an important factor for the reaction.

Auxiliary ligands: We originally chose the auxiliary N-heterocyclic ligands 2,2′-bipy (as terminal ligand) and 1,4-bi(1H-imidazol-1-yl)benzene) (as extended ligand), respectively, to control the dimensionality of the complexes **2** and **3**. In the complex **3**, the 1,4-bi(1H-imidazol-1-yl)benzene) ligand coordinates with Ni^{2+} ions and extends the structure to 3D according to our design. To our surprise, the auxiliary ligand 2,2′-bipy in **2** mainly adjust the reaction process instead of preventing the further interconnection as terminal ligand . In order to study the role of 2,2′-bipy, we replaced it with triethylamine and ensured the same pH conditions before reaction. Then, the obtained crystal is the same to complex **2**. So, the 2,2′-bipy mainly acts as an environmental factor to adjust the deprotonation of H_3BPT.

Table S1. Selected Bond Lengths (Å) and Angles (deg) for 1 -3

Complex **1**					
Ni1–O13	2.008(8)	Ni1–O7	2.052(8)	Ni1–O1	2.090(8)
Ni1—O13^{i}	2.008 (8)	Ni1—O7^{i}	2.052 (8)	Ni1—O1^{i}	2.090(8)
Ni2–O13^{i}	2.004(8)	Ni2–O14	2.028(10)	Ni2–O15	2.057(9)
Ni2–O16	2.100(10)	Ni2–O17	2.107(9)	Ni2–O2	2.116(9)
Ni3–O8	2.019(9)	Ni3–O4^{ii}	2.039(9)	Ni3–O13	2.042(8)
Ni3–O19	2.053(10)	Ni3–O18	2.100(9)	Ni3–O17^{i}	2.126(9)
O13—Ni1—O13^{i}	179.998(2)	O13–Ni1–O7	89.2(3)	O13–Ni1–O7^{i}	90.8(3)
O13–Ni1–O1^{i}	92.9(3)	O13–Ni1–O1	87.1(3)	O7–Ni1–O7^{i}	179.998(2)
O7–Ni1–O1^{i}	89.8(3)	O7–Ni1–O1	90.2(3)	O1–Ni1–O1^{i}	179.998(2)

O13^{i}–Ni2–O14	175.8(4)	O13^{i}–Ni2–O15	93.7(4)	O13^{i}–Ni2–O16	84.9(4)
O13^{i}–Ni2–O17	82.0(3)	O13^{i}–Ni2–O2	94.1(3)	O14–Ni2–O15	89.7(4)
O14–Ni2–O16	92.8(4)	O14–Ni2–O17	94.4(4)	O14–Ni2–O2	88.3(4)
O15–Ni2–O16	86.4(4)	O15–Ni2–O17	173.1(4)	O15–Ni2–O2	92.3(4)
O16–Ni2–O17	87.8(4)	O16–Ni2–O2	178.3(4)	O17–Ni2–O2	93.4(3)
O8–Ni3–O4^{ii}	90.4(4)	O8–Ni3–O13	93.2(3)	O8–Ni3–O18	90.4(4)
O8–Ni3–O19	177.8(4)	O8–Ni3–O17^{i}	88.9(4)	O4^{ii}–Ni3–O13	167.6(4)
O4^{ii}–Ni3–O19	91.7(4)	O4^{ii}–Ni3–O18	94.6(4)	O4^{ii}–Ni3–O17^{i}	87.5(3)
O13–Ni3–O18	97.3(3)	O13–Ni3–O19	84.6(4)	O13–Ni3–O17^{i}	80.7(3)
O18–Ni3–O17^{i}	177.8(3)	O19–Ni3–O18	89.9(4)	O19–Ni3–O17^{i}	90.6(3)
Ni2^{i}-O13-Ni1	120.5(4)	Ni2^{i}-O13-Ni3	101.7(3)	Ni1-O13-Ni3	122.6(4)
Ni2-O17-Ni3^{i}	95.7(3)				

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$.

Complex **2**

Ni1–O1	2.107(2)	Ni1–O7	2.052(2)	Ni1-O7^{ii}	2.044(2)
Ni1–O3^{iii}	2.062(2)	Ni1-O5^{i}	2.029(2)	Ni1–O8	2.089(3)
Ni2-O2	1.996(2)	Ni2–O7	2.013(2)	Ni2–O9	2.108(2)
Ni2–O10	2.095(2)	Ni2–O3^{iii}	2.137(2)	Ni2–O6^{iv}	2.039(2)
O5^{i}–Ni1–O7^{ii}	99.37(9)	O5^{i}–Ni1–O7	93.99(9)	O7^{ii}–Ni1–-O7	80.87(9)
O5^{i}–Ni1–O3^{iii}	163.00(9)	O7^{ii}–Ni1–O3^{iii}	96.00(9)	O7–Ni1–O3^{iii}	81.28(9)
O5^{i}–Ni1–O8	90.84(10)	O7^{ii}–Ni1–O8	92.73(10)	O7–Ni1–O8	172.54(9)
O3^{iii}–Ni1–O8	95.66(10)	O5^{i}–Ni1–O1	80.85(9)	O7^{ii}–Ni1–O1	178.24(9)
O7–Ni1–O1	100.86(9)	O3^{iii}–Ni1–O1	84.01(9)	O8–Ni1–O1	85.51(10)
O2–Ni2–O7	95.22(9)	O2–Ni2–O6^{iv}	166.00(10)	O7–Ni2–O6^{iv}	98.66(9)
O2–Ni2–O10	82.41(10)	O7–Ni2–O10	176.58(9)	O6^{iv}–Ni2–O10	83.81(9)
O2–Ni2–O9	85.52(9)	O7–Ni2–O9	90.54(9)	O6^{iv}–Ni2–O9	92.46(9)
O10–Ni2–O9	91.72(9)	O2–Ni2–O3^{iii}	91.97(9)	O7–Ni2–O3^{iii}	80.37(9)
O6^{iv}–Ni2–O3^{iii}	92.19(9)	O10–Ni2–O3^{iii}	97.22(9)	O9–Ni2–O3^{iii}	170.33(9)
Ni2-O7-Ni1^{ii}	120.66(10)	Ni2-O7-Ni1	96.05(9)	Ni1^{ii}-O7-Ni1	99.13(9)
Ni1^{iii}-O3-Ni2^{iii}	92.06(9)				

Symmetry codes: (i) $-x, -y, -z+2$; (ii) $-x+1, -y, -z+1$;(iii) $-x+1, -y+1, -z+2$;(iv) $x+1, y, z-1$;(v) $x-1, y, z+1$;

Complex **3**

Ni1–O1	2.031(6)	Ni1–O4 ^{i}	2.052(7)	Ni1–N1	2.059(7)
Ni1–O7	2.062(6)	Ni1-O9^{ii}	2.066(6)	Ni1–O10 ^{ii}	2.169(6)
Ni2–O9^{ii}	1.993(6)	Ni2– O8^{iii}	2.020(7)	Ni2–O2	2.064(6)
Ni2–N4^{iv}	2.076 (8)	Ni2–O7	2.093 (6)	Ni2–O11^{i}	2.156 (6)
Ni3–O9^{v}	1.992 (7)	Ni3–O9	1.992 (7)	Ni3–O3 ^{v}	2.029 (7)
Ni3–O3	2.029 (7)	Ni3–O10^{v}	2.105 (6)	Ni3–O10	2.105 (6)
Ni4–O8^{vi}	2.043 (6)	Ni4–O8	2.049 (6)	Ni4–O7^{vii}	2.057 (7)
Ni4–O6	2.107 (6)	Ni4–O5	2.123 (6)	Ni4–O11^{viii}	2.147 (7)
O1–Ni1–O4^{i}	89.4 (3)	O1–Ni1–N1	90.9 (3)	O4^{i}–Ni1–N1	90.1 (3)
O1–Ni1–O7	93.0 (3)	O4^{i}–Ni1–O7	173.6 (2)	N1–Ni1–O7	95.8 (3)
O1–Ni1–O9^{ii}	94.5(3)	O4^{i}–Ni1–O9^{ii}	91.7 (2)	N1–Ni1–O9^{ii}	174.4 (3)
O7–Ni1–O9ii	82.2 (2)	O1–Ni1–O10^{ii}	171.4 (2)	O4^{i}–Ni1–O10^{ii}	85.6 (3)
N1–Ni1–O10^{ii}	96.2 (3)	O7–Ni1–O10^{ii}	91.3 (3)	O9^{ii}–Ni1–O10^{ii}	78.7 (2)
O9^{ii}–Ni2–O8^{iii}	167.2 (3)	O9^{ii}–Ni2–O2	89.0 (3)	O8^{iii}–Ni2–O2	94.8 (3)
O9^{ii}–Ni2–N4^{iv}	97.5 (3)	O8^{iii}–Ni2–N4^{iv}	94.7 (3)	O2–Ni2–N4^{iv}	90.1 (3)
O9ii–Ni2–O7	83.2 (2)	O8^{iii}–Ni2–O7	84.5 (3)	O2–Ni2–O7	92.2 (2)
N4^{iv}–Ni2–O7	177.6 (3)	O9^{ii}–Ni2–O11^{i}	95.5 (3)	O8^{iii}–Ni2–O11^{i}	80.1 (2)
O2–Ni2–O11^{i}	174.3 (3)	N4^{iv}–Ni2–O11^{i}	92.8 (3)	O7–Ni2–O11^{i}	84.8 (2)

O9^{v}–Ni3–O9	180.0 (4)	O9^{v}–Ni3–O3	88.6 (3)	O9–Ni3–O3	91.4 (3)
O9^{v}–Ni3–O3^{v}	91.4 (3)	O9–Ni3–O3^{v}	88.6 (3)	O3–Ni3–O3^{v}	89.5 (4)
O9^{v}–Ni3–O10	81.9 (2)	O9–Ni3–O10^{v}	98.1 (2)	O3–Ni3–O10^{v}	90.6 (3)
O3^{v}–Ni3–O10^{v}	173.2 (3)	O9^{v}–Ni3–O10	98.1 (2)	O9–Ni3–O10	81.9 (2)
O3–Ni3–O10	173.2 (3)	O3^{v}–Ni3–O10	90.6 (3)	O10^{v}–Ni3–O10	90.0 (4)
O8^{vi}–Ni4–O8	83.7 (3)	O8^{vi}–Ni4–O7^{vii}	84.8 (3)	O8–Ni4–O7^{vii}	92.7 (3)
O8^{vi}–Ni4–O6	167.1 (3)	O8–Ni4–O6	109.2 (3)	O7^{vii}–Ni4–O6	93.9 (3)
O8^{vi}–Ni4–O5	104.7 (3)	O8–Ni4–O5	169.5 (3)	O7^{vii}–Ni4–O5	94.3 (3)
O6–Ni4–O5	62.6 (3)	O8^{vi}–Ni4–O11^{viii}	95.1 (2)	O8–Ni4–O11^{viii}	79.6 (2)
O7^{vii}–Ni4–O11^{viii}	172.3 (3)	O6–Ni4–O11^{viii}	88.0 (3)	O5–Ni4–O11^{viii}	93.2 (3)

Symmetry codes: (i) x, $-y+1$, $z+1/2$; (ii) $-x+1$, $-y+1$, $-z+1$; (iii) $x-1/2$, $y+1/2$, z; (iv) $x-1/2$, $-y+3/2$, $z-1/2$; (v) $-x+1$, y, $-z+1/2$; (vi) $-x+2$, $-y+1$, $-z+1$; (vii) $-x+3/2$, $-y+3/2$, $-z+1$; (viii) $x+1/2$, $-y+1/2$, $z+1/2$; (ix) x, $-y+1$, $z-1/2$; (x) $x+1/2$, $y-1/2$, z; (xi) $x-1/2$, $-y+1/2$, $z-1/2$; (xii) $x+1/2$, $-y+3/2$, $z+1/2$.

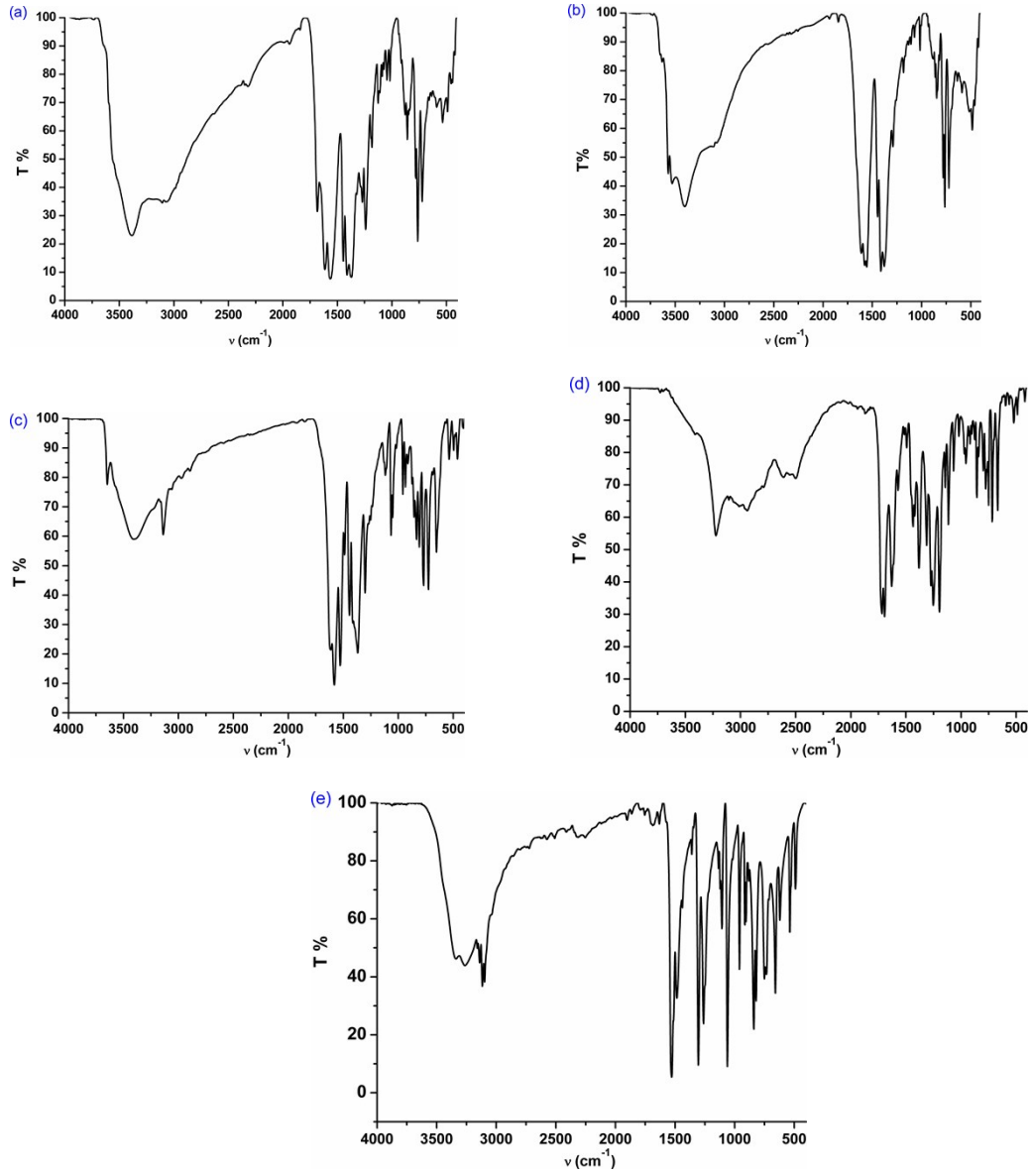

Fig. S1 The IR spectra of **1** (a), **2** (b) and **3** (c), H_3BPT(d) and 1,4-bib (e).

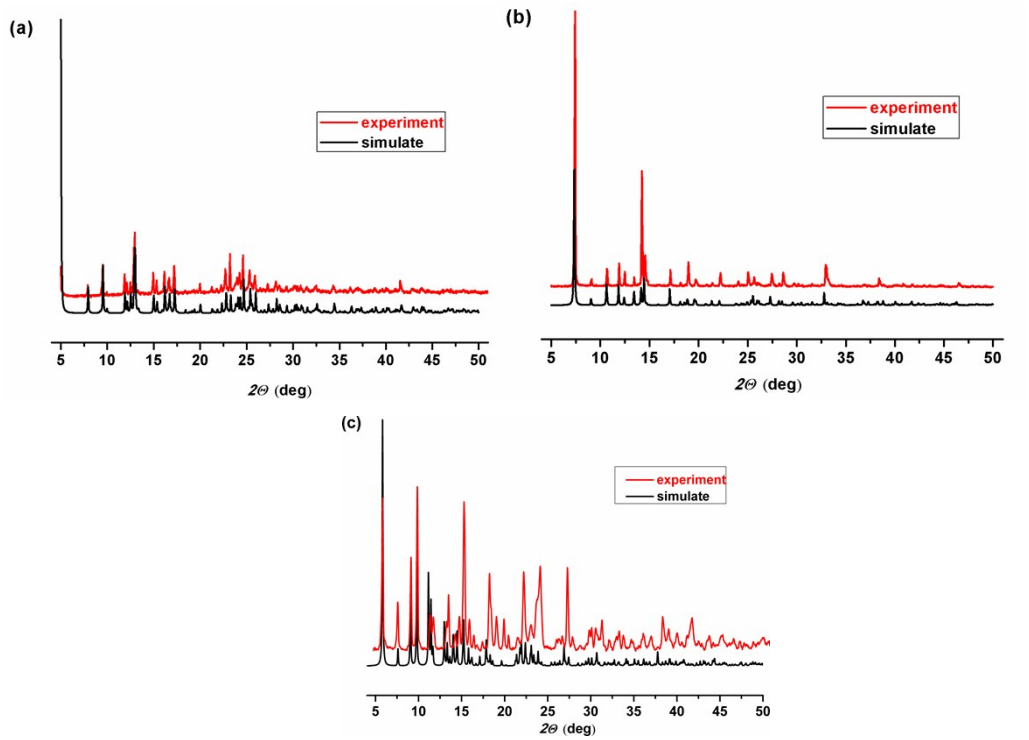

Fig. S2 Comparison of the simulated and experimental PXRD patterns of **1** (a), **2** (b) and **3** (c).