

## Supporting Information

### Product control by halide ions of ionic liquids in the ionothermal syntheses of Ni-(H)BTC metal-organic frameworks

Ling Xu,<sup>a</sup> Shihai Yan,<sup>a</sup> Eun-Young Choi,<sup>a</sup> Jin Yong Lee,<sup>a</sup> and Young-Uk Kwon<sup>\*a</sup>

<sup>a</sup> *Department of Chemistry, BK21 School of Chemical Materials Science, Institute of Basic Science SKKU  
Advanced Institute of Nanotechnology Sungkyunkwan University, Suwon, 440-746, Korea.*

#### Experimental materials

##### Characterization methods

Elemental analyses (C, H and N) were performed on an EA1110 elemental analyzer. The good agreement between the experimental and theoretical data indicates that the new compounds in this study are synthesized as single phases. FT-IR spectra were obtained on a Bruker Tensor27 FT-IR spectrometer using KBr pellets dispersed with sample powders in the range of 4000–400 cm<sup>-1</sup>. Thermogravimetric (TG) analyses were carried out on a TA4000/SDT 2960 instrument in flowing N<sub>2</sub> with a heating rate of 10 °C·min<sup>-1</sup>. X-ray powder diffraction data were recorded on a Rigaku D/max-RC diffractometer at 30 KV, 40 mA for CuK $\alpha$ , ( $\lambda = 1.5406 \text{ \AA}$ ) with a scan speed of 2 °min<sup>-1</sup> and a step size of 0.02 ° in 2 $\theta$ .

Crystallographic data were collected at 173(2) K on Bruker CCD diffractometers in different locations. The structures were solved by the direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in the final stages of the refinements on calculated positions bonded to their carrier atoms. The calculations were performed using the SHELXTL, version 5.1, software package.<sup>1</sup>

##### Syntheses of the ILs

All chemicals were commercially purchased and used without further purification. The ILs except [EMI]Cl (Aldrich) were prepared according to the literature method. [EMI]Br

(white solid, m.p. = 80-82 °C, yield: 92%), [EMI]I (white solid, m.p. = 80-82 °C, yield: 72%), [PMI]Br (pale yellow oil, yield: 80%), [PMI]I (pale brown oil, yield: 78%), [PMI]Cl (pale yellow oil, yield: 60%). [BMI]Br (pale yellow oil, yield: 78%), [BMI]I (brown oil, yield: 75%), [BMI]Cl (white solid, m.p. = 68-70 °C, yield: 72%).

### Preparation of the compounds

**[EMI]<sub>2</sub>[Ni<sub>3</sub>(BTC)<sub>2</sub>(OAc)<sub>2</sub>] (A1).** Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.5–4.0 mmol with a step of 0.5 mmol) and H<sub>3</sub>BTC (0.5 mmol), were mixed with 1.0 g [EMI]X (X = Cl, Br, I) in a 25 mL Teflon-lined stainless steel autoclave. The mixtures were heated at 180 °C for 3 days in a furnace and cooled naturally to obtain suitable crystals. The series of reactions gave the same green crystals of **A1**. Yield based on H<sub>3</sub>BTC: 63%. No further characterization of Compound **A1** was performed because it was reported previously.<sup>2a</sup>

**[PMI]<sub>2</sub>[Ni<sub>3</sub>(BTC)<sub>2</sub>(OAc)<sub>2</sub>] (A2).** Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.0–3.0 mmol with a step of 0.5 mmol) and H<sub>3</sub>BTC (0.5 mmol), were mixed with 1.0 mL [PMI]X (X = Cl, Br) in a 25 mL Teflon-lined stainless steel autoclave. The mixtures were heated at 180 °C for 3 days in a furnace and cooled naturally to obtain suitable crystals. The series of reactions gave the same green crystals of **A2**. Yield based on H<sub>3</sub>BTC: 60%. Elemental analysis found: C, 44.50; H, 4.03; N, 5.55. Calc. for C<sub>36</sub>H<sub>38</sub>N<sub>4</sub>Ni<sub>3</sub>O<sub>16</sub>: C, 45.10; H, 3.99; N, 5.84%. IR data (in KBr, cm<sup>-1</sup>): 3429(m), 3173(m), 3142(m), 3054(s), 2975(s), 2935(m), 2879(w), 2415(w), 1925(w), 1900(s), 1621(s), 1582(s), 1542(s), 1447(s), 1375(m), 1168(m), 1088(m), 1049(w), 1017(w), 953(w), 877(w), 771(m), 730(m), 682(m), 651(m), 619(m), 531(w).

**[BMI]<sub>2</sub>[Ni<sub>3</sub>(BTC)<sub>2</sub>(OAc)<sub>2</sub>] (A3).** Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.5 mmol, 0.373 g) and H<sub>3</sub>BTC (0.5 mmol, 0.105 g), were mixed with 1.0 g [BMI]Cl in a 25 mL Teflon-lined stainless-steel autoclave. The mixtures were heated at 180 °C for 3 days in a furnace and cooled naturally to obtain suitable green crystals of **A3**. Yield based on H<sub>3</sub>BTC: 62%. Elemental analysis found: C, 45.55; H, 4.08; N, 5.72. Calc. C<sub>38</sub>H<sub>42</sub>N<sub>4</sub>Ni<sub>3</sub>O<sub>16</sub>: C, 46.25; H, 4.30; N, 5.69%. IR data (in KBr, cm<sup>-1</sup>): 3427(m), 3176(m), 3147(m), 3049(s), 2975(s), 2938(m), 2875(w), 2467(w), 1892(w), 1619(s), 1590(s), 1545(s), 1439(s), 1378(s), 1174(m), 1093(m), 1044(m), 1013(m), 951(w), 938(w), 880(w), 820(w), 771(m), 728(m), 715(m), 690(m), 654(m), 623(m), 611(m), 585(w), 524(w).

**[PMI]<sub>2</sub>[Ni<sub>3</sub>(HBTC)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] (B1)**. Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.5–4.0 mmol with a step of 0.5 mmol) and H<sub>3</sub>BTC (0.5 mmol) were mixed with 1.0 mL [PMI]I in a 25 mL Teflon-lined stainless steel autoclave. The mixtures were heated at 180 °C for 3 days in a furnace and cooled naturally to obtain green crystals. Yield based on H<sub>3</sub>BTC: 40%. Elemental analysis found: C, 46.87; H, 3.57; N, 3.55. Calc C<sub>50</sub>H<sub>42</sub>N<sub>4</sub>Ni<sub>3</sub>O<sub>26</sub>: C, 46.52; H, 3.28; N, 4.34%. IR data (in KBr, cm<sup>-1</sup>): 3541(s), 3113(w), 3095(w), 2975(w), 2945(w), 2365(w), 2339(w), 1702(s), 1627(s), 1587(s), 1438(s), 1361(s), 1317(w), 1301(w), 1225(w), 1168(m), 1125(w), 957(w), 931(w), 906(w), 799(w), 784(w), 763(w), 715(w), 696(w), 677(w), 624(w), 545(w), 533(w).

**[BMI]<sub>2</sub>[Ni<sub>3</sub>(HBTC)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] (B2)**. Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (2.0–4.0 mmol with a step of 0.5 mmol) and H<sub>3</sub>BTC (0.5 mmol) were mixed with 1.0 mL [BMI]X (X = Br, I) in a 25 mL Teflon-lined stainless steel autoclave. The mixtures were heated at 180 °C for 3 days in a furnace and cooled naturally to obtain suitable crystals. The series of reactions gave the same green crystals of **B2**. Yield based on H<sub>3</sub>BTC: 48%. No further characterization of Compound **B2** was performed because it was reported previously.<sup>2b</sup>

### Description of the crystal structures and comparison of the two structure types:

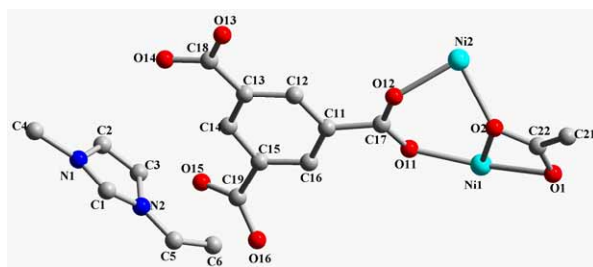
The crystallographic data of the five compounds (**A1**, **A2**, **A3**, **B1**, **B2**) in this study are shown in Table S1. Although the crystal structures of **A1** and **B2** were reported, we repeated their structure refinements at 173 K for direct comparison with the other crystal structures. The bond distances and angles of the compounds at 173 K are given in Table S2. The atom labels are with reference to those in Fig. S1, in which the asymmetric units and the coordination spheres around the Ni atoms are shown.

The five compounds were formed in two different types of 3D framework structures. Fig. S2 summarizes the reaction conditions of the compounds and compares the topologies of the two structure types. In both types, the structures show 3D frameworks constructed by interconnecting linear Ni<sub>3</sub> units through (H)BTC ligands with the IL cations occupying the empty space (cavity) (one cation per cavity) of the framework. It is worthy to note the protonated BTC ligands and monoprotinated HBTC ligands are verified by the charge balance and ref. 3(c) and 3(h).

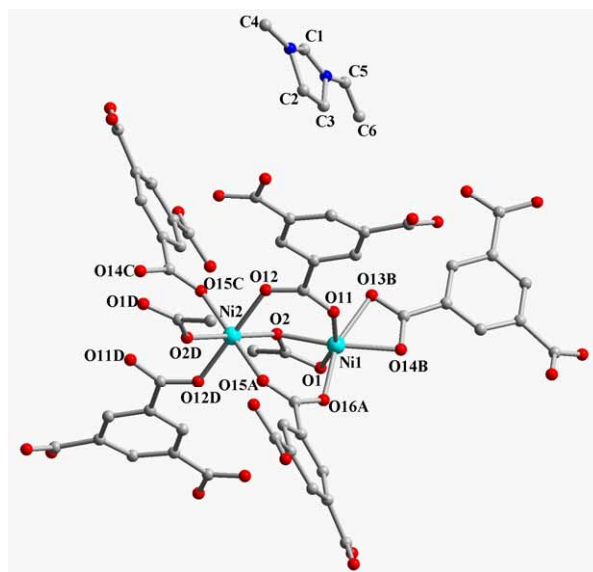
In addition to the different connectivity fashions of BTC ligands described in the main

text, there are a few difference between them: (i) In type **A**, one Ni<sup>2+</sup> atom and two symmetry-related Ni<sup>1+</sup> atoms are linked by four bidentate and two chelating COO<sup>-</sup> ligands and two chelating/bridging acetate ligands to generate a [Ni<sub>3</sub>(COO)<sub>6</sub>(OAc)<sub>2</sub>] SBU (Fig. S3a). In comparison, in type **B**, a trinuclear [Ni<sub>3</sub>(COO)<sub>10</sub>(μ<sub>2</sub>-O<sub>w</sub>)<sub>2</sub>] SBU is formed through two μ<sub>2</sub>-O<sub>1w</sub> and six monodentate COO<sup>-</sup> ligands replacing the two chelating/bridging OAc<sup>-</sup> and the two chelating COO<sup>-</sup> ligands of type **A** structure, respectively (Fig. S4a); (ii) In type **A** structure, four SBUs are connected through the anti-parallel BTC<sup>3-</sup> ligands with two carboxylic groups (O11/O12, O15/O16) by bidentate connectivity modes to form a quadrangle ring, whose propagation generates a 2D grid (Fig. S3b), whereas, in type **B**, the SBUs linked by anti-parallel μ<sub>3</sub>-HBTC<sup>2-</sup> ligands to form a 1D double chain along the *a*-direction (Fig. S4b) and by μ<sub>4</sub>-HBTC<sup>2-</sup> to produce a 2D layer in the *bc* plane (Fig. S4c); (iii) the 3D networks of type **A** are fused by stacking 2D layers with a -ABAB- fashion through Ni<sup>1+</sup>-O13/O14 bonds with IL cations anchoring in the channels (Fig. S2), while, in type **B**, the layers are further connected via the 1D double chains through the same SBUs as nodes to generate 3D frameworks with corresponding cations of ILs locating in the channels (Fig. S2).

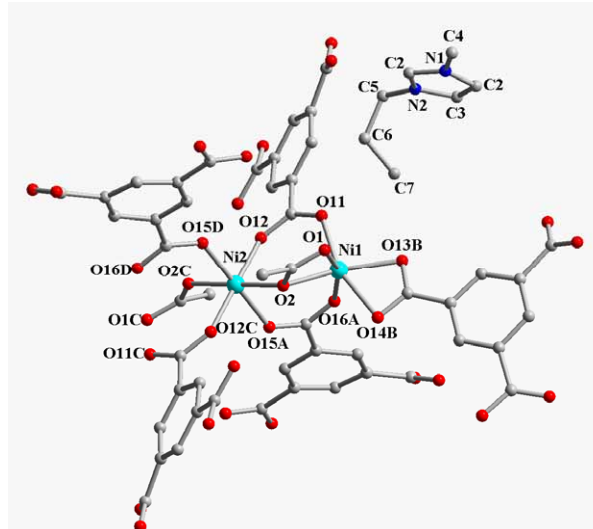
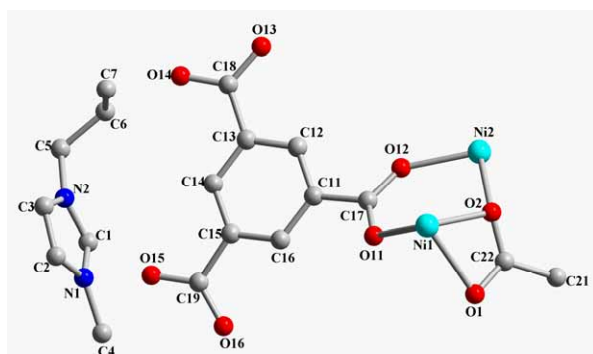
**A1** Asymmetric units



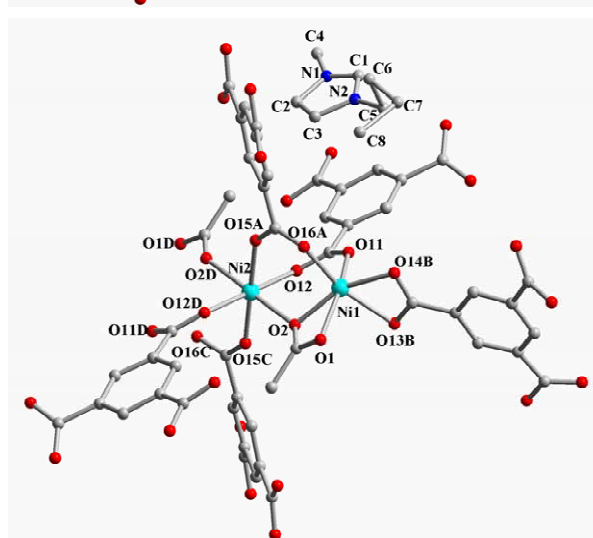
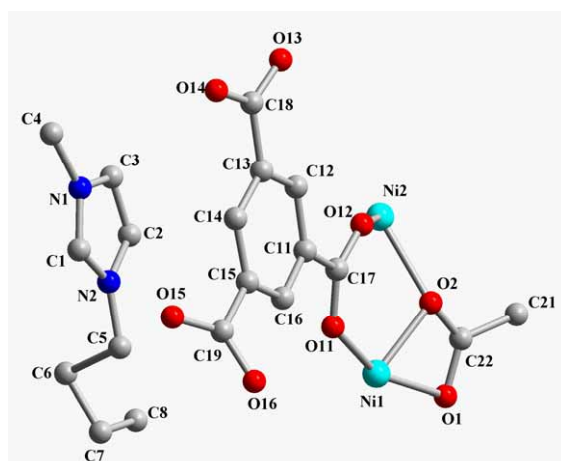
coordination spheres



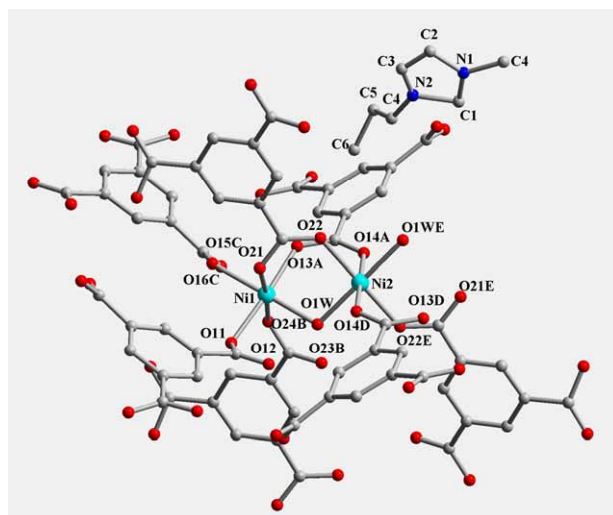
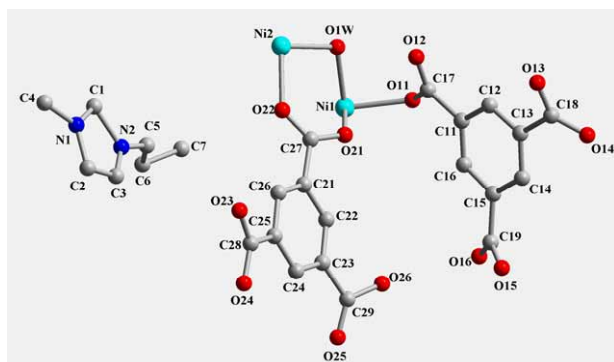
**A2**



**A3**



**B1**



**B2**

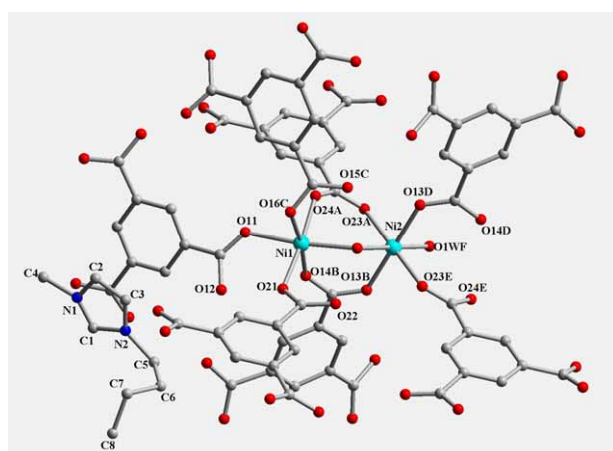
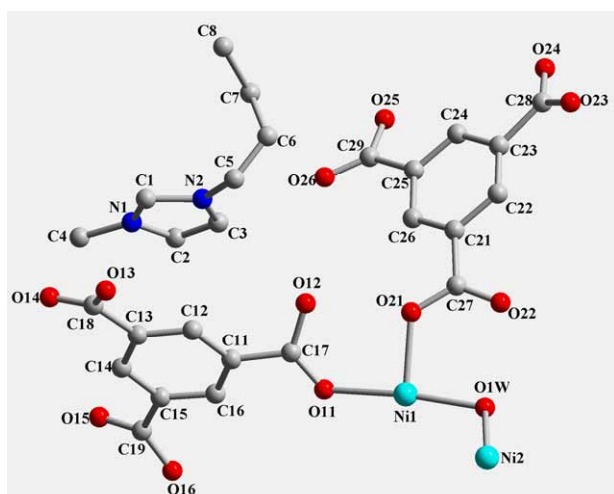


Fig. S1. Asymmetric units and coordination spheres of compounds A1, A2, A3, B1, and B2.

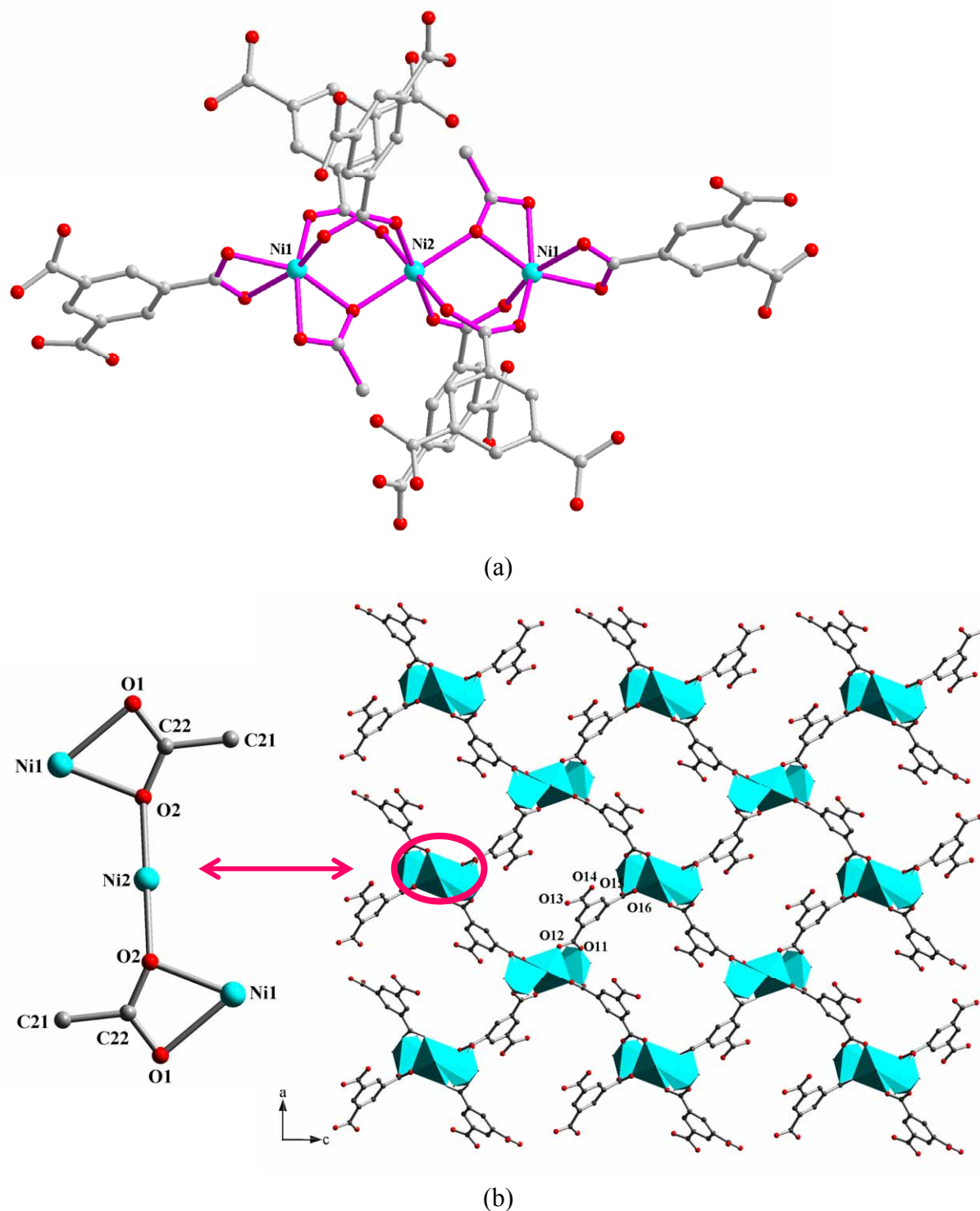


Fig. S2. The structure of type A. (a) Atom labels and the local structure around the linear trinuclear  $[\text{Ni}_3(\text{COO})_6(\text{OAc})_2]$  second building unit (SBU) (shown in purple) and (b) the structure of a 2D grid formed by connecting the trinuclear  $[\text{Ni}_3(\text{COO})_6(\text{OAc})_2]$  SBUs through the benzene-rings of the BTC ligands.

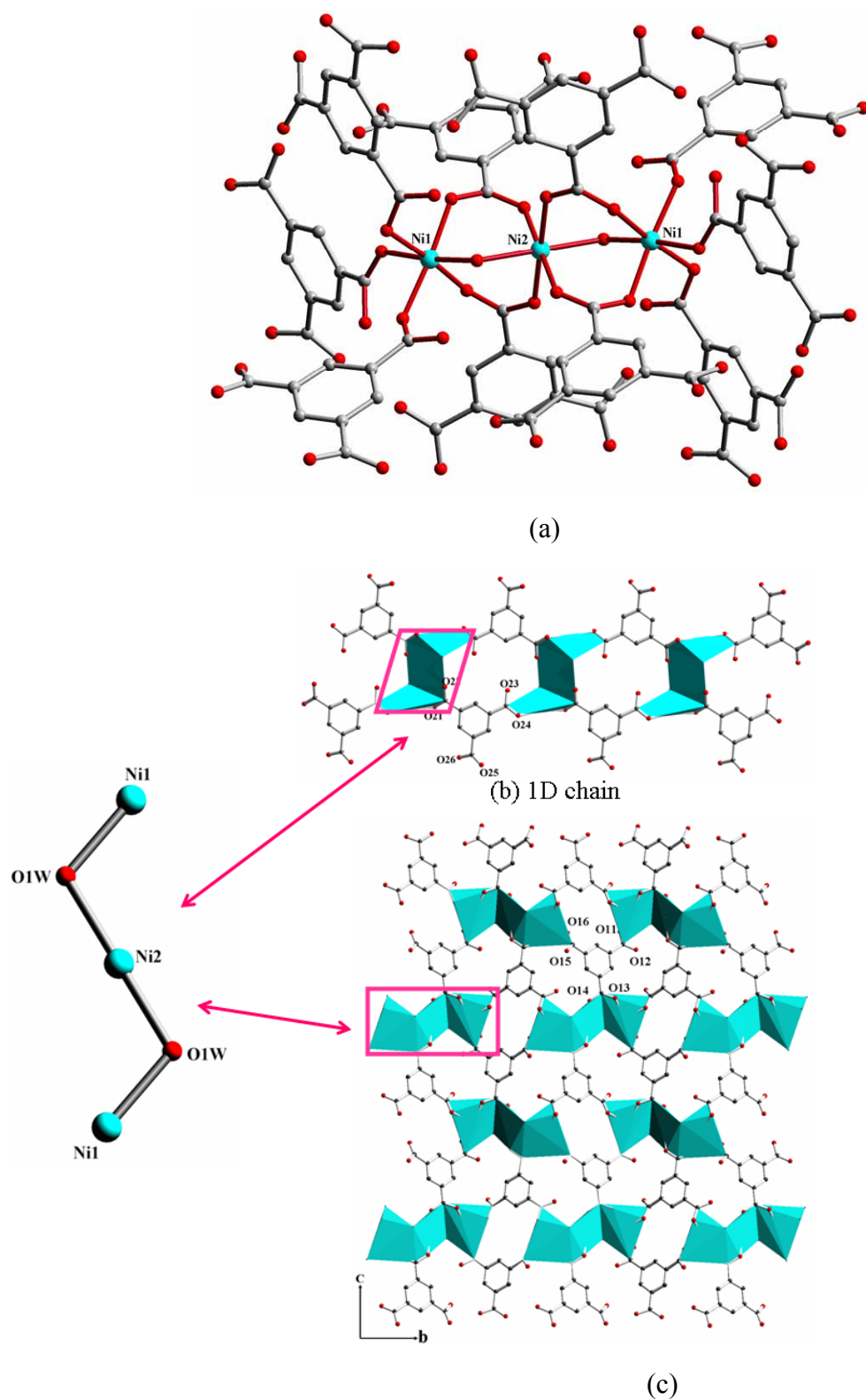
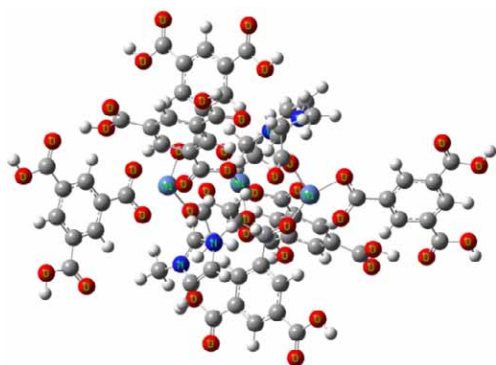
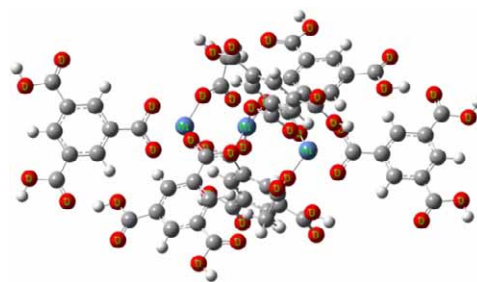


Fig. S3. The structure of type **B**. (a) Atom labels and the local structure around the linear trinuclear  $[\text{Ni}_3(\text{COO})_{10}(\mu_2\text{-O}_w)_2]$  second building unit (SBU) (shown in mauve) and the structures of (b) a 1D chain and (c) a 2D layer formed by connecting the trinuclear  $[\text{Ni}_3(\text{COO})_{10}(\mu_2\text{-O}_w)_2]$  SBUs through the benzene-rings of the BTC ligands.

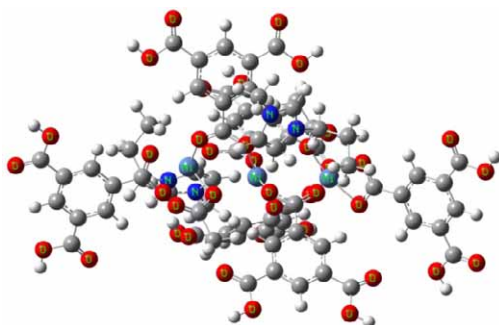




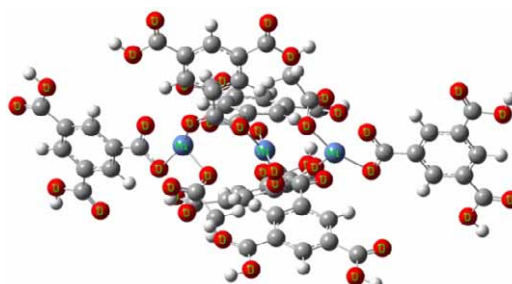
**A1 (Crystal)**



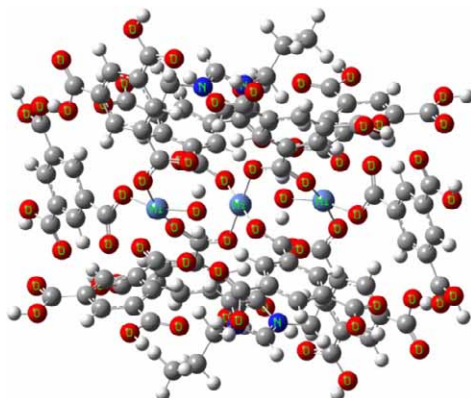
**A1 (Framework)**



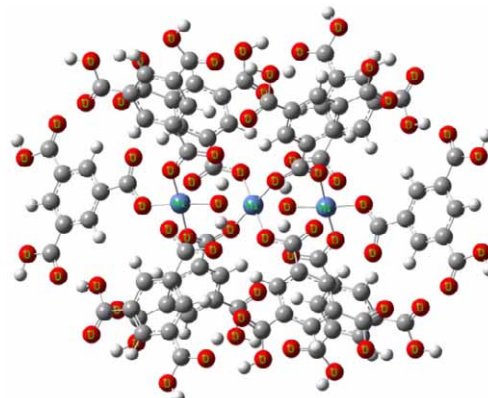
**A2 (Crystal)**



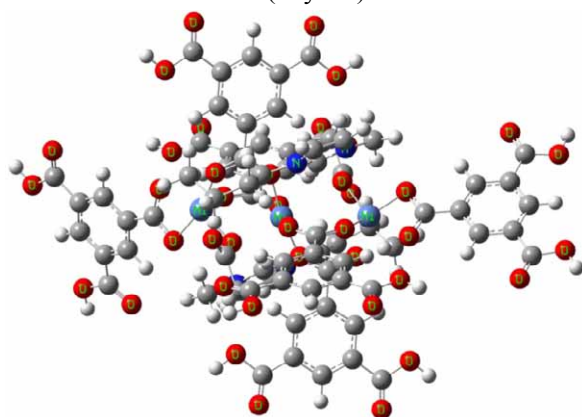
**A2 (Framework)**



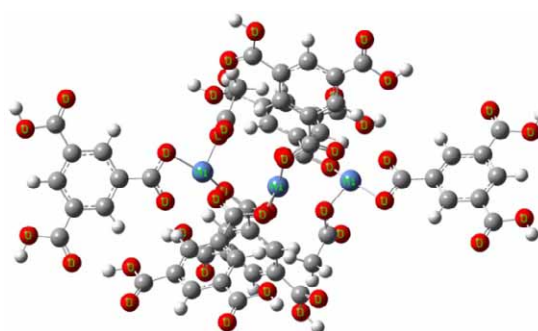
**B1 (Crystal)**



**B1 (Framework)**



**A3 (Crystal)**



**A3 (Framework)**

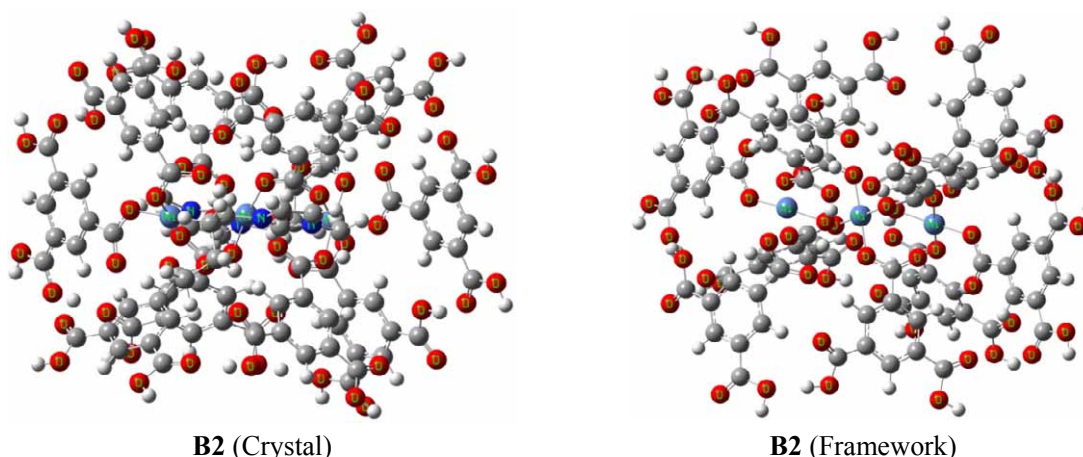


Fig. S4. The optimized structures of the MOFs (right column) and their complexes with cations (EMI, PMI, and BMI) (left column).\* In each of the complexes, two cations are included.

**\*A brief description for the structures shown in Figure S4.**

In all cases, one carboxyl group of every ligand participates in the coordination with the Ni nuclei, and the other two carboxyl groups are saturated with the protons. In good agreement with the experimental data, the tri-nuclei Ni<sub>3</sub> units in all of the optimized structures are almost in one line. Compared with the MOFs of **A1**, **A2**, and **A3**, the inclusion of the cations (EMI, PMI, and BMI) makes the corresponding cavity increased and the neighboring room decreased because of the steric effect. Each included cation interacts with two adjacent ligands. On the other hand, for **B1** and **B2**, the inclusion of the cations makes little effect on the cavity size because their MOFs are already very compact. The interactions can be found between every inserted cation and four proximate ligands. This may be the reason why the interaction energy between the frameworks and the cation for **B1/B2** is larger than that for **A2/A3**.

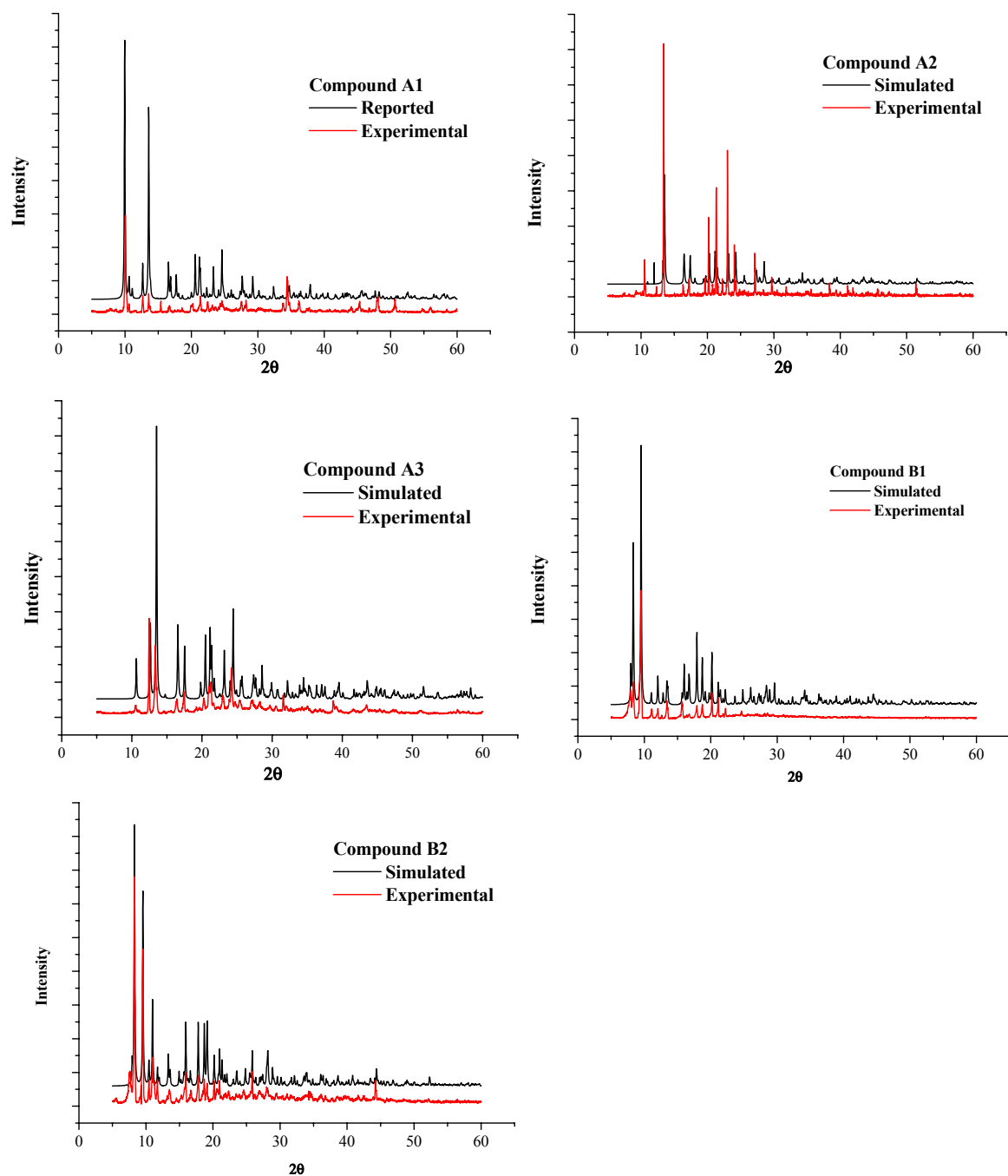


Fig. S5. Experimental and stimulated XRD powder patterns for compounds **A1**, **A2**, **A3**, **B1**, **B2**.

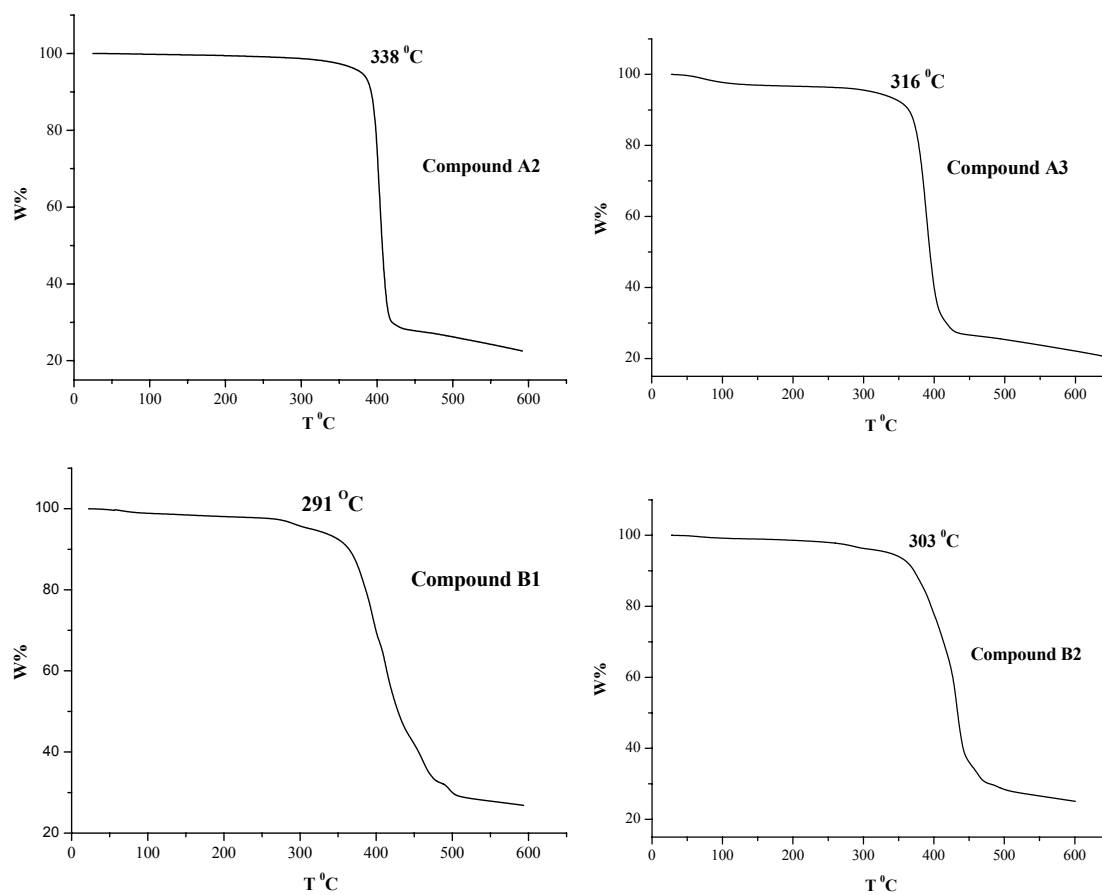


Fig. S6. TG curves of compounds A2, A3, B1, B2.

Table S1. Crystallographic data for compounds **A1**, **A2**, **A3**, **B1**, **B2** at 173(2) K.

	<b>A1</b>	<b>A2</b>	<b>A3</b>	<b>B1</b>	<b>B2</b>
Color	Green	Green	Green	Green	Green
Empirical formula	C <sub>34</sub> H <sub>34</sub> N <sub>4</sub> Ni <sub>3</sub> O <sub>16</sub>	C <sub>36</sub> H <sub>38</sub> N <sub>4</sub> Ni <sub>3</sub> O <sub>16</sub>	C <sub>38</sub> H <sub>42</sub> N <sub>4</sub> Ni <sub>3</sub> O <sub>16</sub>	C <sub>50</sub> H <sub>42</sub> N <sub>4</sub> Ni <sub>3</sub> O <sub>26</sub>	C <sub>52</sub> H <sub>46</sub> N <sub>4</sub> Ni <sub>3</sub> O <sub>26</sub>
Crystal Size	0.25*0.15*0.10	0.18*0.15*0.13	0.25*0.20*0.15	0.30*0.15*0.12	0.30*0.15*0.12
<i>F</i> <sub>w</sub>	930.78	958.83	986.89	1291.01	1319.06
crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
space group	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>P2</i> <sub>1</sub> / <i>c</i>	<i>P2</i> <sub>1</sub> / <i>c</i>
<i>a</i> /Å	14.0636(6)	14.1349(5)	14.009(2)	10.7110(9)	10.781(3)
<i>b</i> /Å	15.9152(7)	16.2961(5)	16.332(2)	13.7963(12)	13.903(4)
<i>c</i> /Å	16.5858(7)	16.5240(5)	16.622(2)	18.7511(16)	18.740(5)
$\beta$ /°	-	-	-	98.158(2)	98.170(5)
<i>V</i> /Å <sup>3</sup>	3712.3(3)	3806.2(2)	3802.8(9)	2742.9(4)	2780.4(12)
<i>Z</i>	4	4	4	2	2
<i>D</i> <sub>c</sub> /g·cm <sup>-3</sup>	1.665	1.665	1.724	1.563	1.576
$\mu$ /cm <sup>-1</sup>	15.86	15.42	15.54	11.11	10.98
<i>F</i> (000)	1912	1976	2040	1324	1356
$\theta$ /°	2.29-28.30	2.27-28.29	2.27-26.56	2.19-28.22	2.20-28.12
total reflections	25715	26404	26315	19663	19885
unique reflections	4593, $R_{\text{int}} = 0.0559$	4672, $R_{\text{int}} = 0.0596$	4671, $R_{\text{int}} = 0.0635$	6684, $R_{\text{int}} = 0.0608$	6830, $R_{\text{int}} = 0.0757$
obs. reflections	3226	3419	3445	4365	4142
<i>GOF</i>	1.095	1.063	1.084	1.084	1.002
$R_1, wR_2$ (obs.) [ <i>I</i> > 2σ( <i>I</i> )]	0.0605, 0.1616	0.0365, 0.0908	0.0675, 0.1645	0.0658, 0.1741	0.0703, 0.1732
$R_1, wR_2$ (all)	0.0899, 0.1905	0.0653, 0.1172	0.1015, 0.1988	0.1120, 0.2144	0.1225, 0.2142
Largest and Mean $\Delta/\sigma$	0.002, 0.000	0.001, 0.000	0.005, 0.000	0.002, 0.000	0.021, 0.000
$\Delta\rho$ (e.Å <sup>-3</sup> )	1.759, -1.127	0.804, -0.640	1.460, -1.596	1.813, -0.975	1.786, -0.887

Table S2. Selected bond distances (Å) and angles (°) of compounds **A1-A3** and **B1-B2**.

Compound A1		
Bond distances	Bond angles	
Ni1-O11 = 2.010(2)	O11-Ni1-O16A = 95.08(9)	O15C-Ni2-O12D = 90.98(9)
Ni1-O16A = 2.019(2)	O11-Ni1-O2 = 100.00(9)	O15A-Ni2-O2D = 86.34(8)
Ni1-O2 = 2.041(2)	O16A-Ni1-O2 = 96.89(9)	O15C-Ni2-O2D = 93.66(8)
Ni1-O14B = 2.058(2)	O11-Ni1-O14B = 93.32(9)	O12-Ni2-O2D = 92.31(8)
Ni1-O13B = 2.168(2)	O16A-Ni1-O14B = 97.03(9)	O12D-Ni2-O2D = 87.69(8)
Ni1-O1 = 2.186(2)	O2-Ni1-O14B = 159.76(9)	O15A-Ni2-O2 = 93.66(8)
Ni2-O15A = 2.019(2)	O11-Ni1-O13B = 90.84(9)	O15C-Ni2-O2 = 86.34(8)
Ni2-O12 = 2.046(2)	O16A-Ni1-O13B = 159.29(9)	O12-Ni2-O2 = 87.69(8)
Ni2-O2D = 2.093(2)	O2-Ni1-O13B = 101.60(9)	O12D-Ni2-O2 = 92.31(8)
Ni2-O2 = 2.093(2)	O14B-Ni1-O13B = 62.76(9)	C1-N1-C2 = 97.1(7)
N1-C1 = 1.188(10)	O11-Ni1-O1 = 160.78(9)	C1-N1-C4 = 146.8(8)
N1-C2 = 1.455(9)	O16A-Ni1-O1 = 93.11(9)	C2-N1-C4 = 116.0(7)
N1-C4 = 1.470(11)	O2-Ni1-O1 = 61.70(9)	C1-N2-C5 = 138.4(10)
N2-C1 = 1.214(10)	O14B-Ni1-O1 = 102.90(9)	C5-N2-C3 = 124.3(9)
N2-C5 = 1.277(14)	O13B-Ni1-O1 = 87.56(9)	C6-C5-N2 = 128.1(16)
N2-C3 = 1.415(9)	O15A-Ni2-O12 = 90.98(9)	N1-C1-N2 = 128.4(8)
C6-C5 = 1.25(2)	O15C-Ni2-O12 = 89.02(9)	C3-C2-N1 = 107.3(6)
	O15A-Ni2-O12D = 89.02(9)	C2-C3-N2 = 109.5(7)
	Symmetry code: $A = x+1/2, y, -z+1/2$ ; $B = -x+1/2, y-1/2, z$ ; $C = -x+1/2, -y+2, z+1/2$ ; $D = -x+1, -y+2, -z+1$ .	
Compound A2		
Bond distances	Bond angles	
Ni1-O11 = 2.0146(14)	O11-Ni1-O16A = 94.56(6)	O12-Ni2-O2C = 85.97(5)
Ni1-O16A = 2.0193(14)	O11-Ni1-O2 = 97.61(6)	O12-Ni2-O2 = 94.03(5)
Ni1-O2 = 2.0325(13)	O16A-Ni1-O2 = 98.74(6)	O12C-Ni2-O2 = 85.97(5)
Ni1-O13B = 2.0622(14)	O11-Ni1-O13B = 97.50(6)	O15D-Ni2-O2 = 91.94(5)
Ni1-O14B = 2.1585(14)	O16A-Ni1-O13B = 97.18(6)	O15A-Ni2-O2 = 88.06(5)
Ni1-O1 = 2.2068(15)	O2-Ni1-O13B = 157.03(6)	C1-N1-C2 = 108.6(2)
Ni2-O12 = 2.0273(13)	O11-Ni1-O14B = 160.04(5)	C1-N1-C4 = 125.6(2)
Ni2-O15A = 2.0640(13)	O16A-Ni1-O14B = 91.21(6)	C2-N1-C4 = 125.7(2)
Ni2-O2 = 2.0682(14)	O2-Ni1-O14B = 100.37(5)	C1-N2-C3 = 107.8(2)
N1-C1 = 1.324(3)	O13B-Ni1-O14B = 62.77(5)	C1-N2-C5 = 125.9(2)
N1-C2 = 1.379(3)	O11-Ni1-O1 = 92.83(6)	C3-N2-C5 = 126.3(2)
N1-C4 = 1.456(4)	O16A-Ni1-O1 = 159.68(6)	N2-C1-N1 = 109.2(2)
N2-C1 = 1.318(3)	O2-Ni1-O1 = 61.47(6)	C3-C2-N1 = 106.2(2)
N2-C3 = 1.375(3)	O13B-Ni1-O1 = 100.59(6)	C2-C3-N2 = 108.2(2)
N2-C5 = 1.475(3)	O14B-Ni1-O1 = 88.22(6)	N2-C5-C6 = 112.1(2)
C2-C3 = 1.341(4)	O12-Ni2-O15D = 89.48(5)	C5-C6-C7 = 114.8(3)
C5-C6 = 1.490(4)	O12-Ni2-O15A = 90.52(5)	
C6-C7 = 1.505(4)	Symmetry code: $A = x-1/2, y, -z+1/2$ ; $B = -x, y+1/2, -z+1/2$ ; $C = -x, -y+1, -z$ ; $D = -x+1/2, -y+1, z-1/2$ .	

<b>Compound A3</b>		
Bond distances	Bond angles	
Ni1-O11 = 2.006(1)	O11-Ni1-O16A = 94.24(5)	O12C-Ni2-O2 = 91.37(5)
Ni1-O16A = 2.022(1)	O11-Ni1-O2 = 99.56(5)	O12-Ni2-O2 = 88.63(5)
Ni1-O2 = 2.038(1)	O16A-Ni1-O2 = 97.18(5)	O15A-Ni2-O2C = 85.38(5)
Ni1-O14B = 2.058(1)	O11-Ni1-O14B = 97.18(5)	O12C-Ni2-O2C = 88.63(5)
Ni1-O13B = 2.172(1)	O16A-Ni1-O14B = 97.45(5)	O12-Ni2-O2C = 91.38(5)
Ni1-O1 = 2.192(1)	O2-Ni1-O14B = 156.81(5)	C1-N1-C2 = 107.4(3)
Ni2-O15A = 2.034(1)	O11-Ni1-O13B = 91.42(5)	C1-N1-C4 = 132.2(4)
Ni2-O12 = 2.059(1)	O16A-Ni1-O13B = 159.59(5)	C2-N1-C4 = 120.3(3)
Ni2-O2 = 2.104(1)	O2-Ni1-O13B = 101.19(5)	C1-N2-C5 = 129.1(3)
N1-C1 = 1.309(5)	O14B-Ni1-O13B = 62.35(5)	C1-N2-C3 = 104.5(3)
N1-C2 = 1.418(5)	O11-Ni1-O1 = 159.87(5)	C5-N2-C3 = 126.4(3)
N1-C4 = 1.520(6)	O16A-Ni1-O1 = 94.08(5)	N2-C1-N1 = 113.7(3)
N2-C1 = 1.301(5)	O2-Ni1-O1 = 61.18(5)	C3-C2-N1 = 104.6(4)
N2-C5 = 1.410(5)	O14B-Ni1-O1 = 99.87(5)	C2-C3-N2 = 109.7(4)
N2-C3 = 1.418(5)	O13B-Ni1-O1 = 87.10(5)	N2-C5-C6 = 104.7(4)
C2-C3 = 1.349(6)	O15A-Ni2-O12C = 90.12(5)	C7-C6-C5 = 85.7(10)
C5-C6 = 1.646(10)	O15A-Ni2-O12 = 89.88(5)	C6-C7-C8 = 95.5(14)
C6-C7 = 1.44(3)	Symmetry code: $A = x+1/2, y, -z+3/2$ ; $B = -x+3/2, y+1/2, z$ ; $C = -x+2, -y,$	
C7-C8 = 1.78(3)	$-z+1$ ; $D = -x+3/2, -y, z-1/2$ .	
<b>Compound B1</b>		
Bond distances	Bond angles	
Ni1-O21 = 2.003(2)	O21-Ni1-O13A = 94.46(8)	O14A-Ni2-O22 = 90.83(8)
Ni1-O13A = 2.0165(19)	O21-Ni1-O24B = 175.29(8)	O22-Ni2-O1WE = 81.01(7)
Ni1-O24B = 2.0252(19)	O13A-Ni1-O24B = 88.18(8)	O14D-Ni2-O1W = 88.82(7)
Ni1-O11 = 2.0679(18)	O21-Ni1-O11 = 88.58(8)	O14A-Ni2-O1W = 91.18(7)
Ni1-O1W = 2.0687(19)	O13A-Ni1-O11 = 174.57(8)	O22-Ni2-O1W = 98.99(7)
Ni1-O16C = 2.1143(19)	O24B-Ni1-O11 = 88.49(8)	C1-N1-C2 = 118.6(7)
Ni2-O14A = 2.0309(19)	O21-Ni1-O1W = 88.30(8)	C1-N1-C4 = 124.5(6)
Ni2-O22 = 2.0639(19)	O13A-Ni1-O1W = 95.96(8)	C2-N1-C4 = 116.9(6)
Ni2-O1W = 2.0972(18)	O24B-Ni1-O1W = 95.32(8)	C3-N2-C5 = 131.1(11)
N1-C1 = 1.265(8)	O11-Ni1-O1W = 88.62(7)	C3-N2-C1 = 109.7(7)
N1-C2 = 1.369(11)	O21-Ni1-O16C = 86.95(8)	C5-N2-C1 = 119.2(10)
N1-C4 = 1.496(9)	O13A-Ni1-O16C = 86.77(8)	N1-C1-N2 = 94.5(6)
N2-C3 = 1.211(10)	O24B-Ni1-O16C = 89.30(8)	N2-C3-C2 = 114.7(10)
N2-C5 = 1.343(19)	O11-Ni1-O16C = 88.90(7)	N2-C5-C6 = 133.2(15)
N2-C1 = 1.520(9)	O1W-Ni1-O16C = 174.69(8)	C5-C6-C7 = 110.9(13)
C3-C2 = 1.240(13)	O14D-Ni2-O22 = 89.17(8)	C3-C2-N1 = 102.2(8)
C5-C6 = 1.44(2)	Symmetry code: $A = x, -y+1/2, z+1/2$ ; $B = x-1, y, z$ ; $C = -x+1, -y, 1-z$ ; $D =$	
C6-C7 = 1.570(12)	$-x+1, y+1/2, -Z+1/2$ ; $E = -x+1, -y+1, -z+1$ .	
<b>Compound B2</b>		
Bond distances	Bond angles	
Ni1-O24A = 1.9932(16)	O24A-Ni1-O14B = 96.18(6)	O23E-Ni2-O1WF = 98.17(6)

Ni1-O14B = 2.0130(14)	O24A-Ni1-O21 = 173.71(6)	O23A-Ni2-O1WF = 81.83(6)
Ni1-O21 = 2.0306(15)	O14B-Ni1-O21 = 88.65(6)	O13B-Ni2-O1W = 93.71(5)
Ni1-O16C = 2.0558(14)	O24A-Ni1-O16C = 86.33(6)	O13D-Ni2-O1W = 86.29(5)
Ni1-O1W = 2.0683(14)	O14B-Ni1-O16C = 173.32(6)	O23E-Ni2-O1W = 81.83(6)
Ni1-O11 = 2.1288(15)	O21-Ni1-O16C = 88.44(6)	O23A-Ni2-O1W = 98.17(6)
Ni2-O13B = 2.0215(15)	O24A-Ni1-O1W = 87.31(6)	Ni1-O1W-Ni2 = 111.61(6)
Ni2-O23A = 2.0686(14)	O14B-Ni1-O1W = 95.72(6)	C1-N1-C2 = 111.7(4)
Ni2-O1W = 2.1077(13)	O21-Ni1-O1W = 96.24(5)	C1-N1-C4 = 136.6(5)
N1-C1 = 1.252(6)	O16C-Ni1-O1W = 90.58(5)	C2-N1-C4 = 111.8(5)
N1-C2 = 1.353(6)	O24A-Ni1-O11 = 86.82(6)	C3-N2-C1 = 104.8(4)
N1-C4 = 1.478(9)	O14B-Ni1-O11 = 86.81(6)	C3-N2-C5 = 131.7(4)
N2-C3 = 1.318(6)	O21-Ni1-O11 = 89.43(6)	C1-N2-C5 = 123.4(4)
N2-C1 = 1.378(5)	O16C-Ni1-O11 = 87.15(6)	N1-C1-N2 = 108.5(4)
N2-C5 = 1.521(7)	O1W-Ni1-O11 = 173.83(6)	C3-C2-N1 = 103.7(4)
C2-C3 = 1.336(7)	O13D-Ni2-O23E = 91.23(6)	N2-C3-C2 = 111.3(4)
C5-C6 = 1.335(10)	O13D-Ni2-O23A = 88.77(6)	C6-C5-N2 = 120.2(7)
C6-C7 = 1.548(19)	O13B-Ni2-O1WF = 86.29(5)	C5-C6-C7 = 115.5(10)
C7-C8 = 1.58(2)	O13D-Ni2-O1WF = 93.71(5)	C6-C7-C8 = 101.4(11)

Symmetry code:  $A = x-1, y, z$ ;  $B = -x-1, y+1/2, -z-1/2$ ;  $C = -x-1, -y+1, -z$ ;  $D = x, -y+3/2, z+1/2$ ;  $E = -x, -y+2, -z$ ;  $F = -x-1, -y+2, -z$ .



Table S3. Calculations of the cavity volumes for the MOFs at 173K.

Compound	<b>A1</b>	<b>A2</b>	<b>A3</b>	<b>B1</b>	<b>B2</b>
Unit cell vol (V)	3712.3	3806.2	3802.8	2742.9	2780.4
Z	4	4	4	2	2
Vol. Per cavity (= V/Z)	928.08	951.55	950.7	1371.5	1390.2
Fraction of free vol. (F)	43.1	45.3	45.0	41.1	42.1
Cavity volume (F*V/Z)	400.0	431.05	427.82	563.67	585.27

Table S4. The calculated interaction energies of the frameworks with EMI (**A1**), PMI (**A2** and **B1**), and BMI (**A3** and **B2**).<sup>a</sup>

	MOF( <b>A1</b> )-EMI	MOF( <b>A2</b> )-PMI	MOF( <b>B1</b> )-PMI	MOF( <b>A3</b> )-BMI	MOF( <b>B2</b> )-BMI
Interaction	-223.0	-200.1	-216.3	-212.6	-228.8
Energy <sup>a</sup>			-16.2 <sup>b</sup>		-16.2 <sup>b</sup>

<sup>a</sup>Interaction energies are calculated by subtracting the energies of MOF (Type **A** or Type **B**) and Cations (EMI or PMI or BMI) from the energies of MOF-Cation complexes. Energies are in kcal/mol. <sup>b</sup>These values represent the relative stability of **B1/A2** with respect to **B2/A3**.

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