Electronic supplementary information (ESI)

Cluster- and chain-based magnetic MOFs derived from 3*d* metal ions and 1,3,5-benzenetricarboxylate

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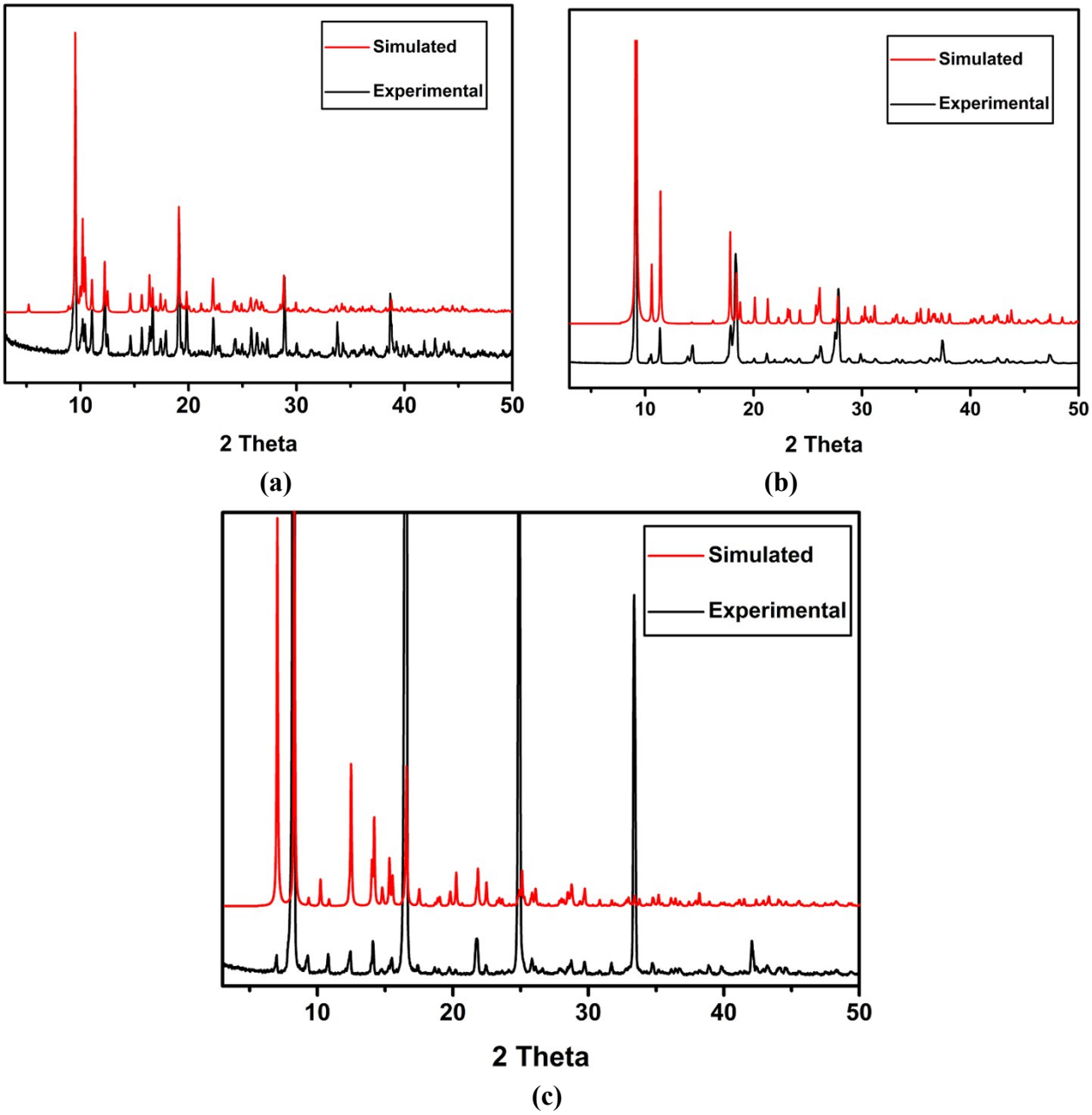

Fig. S1 X-ray powder diffraction (PXRD) patterns of (a) **1**, (b) **2** and (c) **3**.

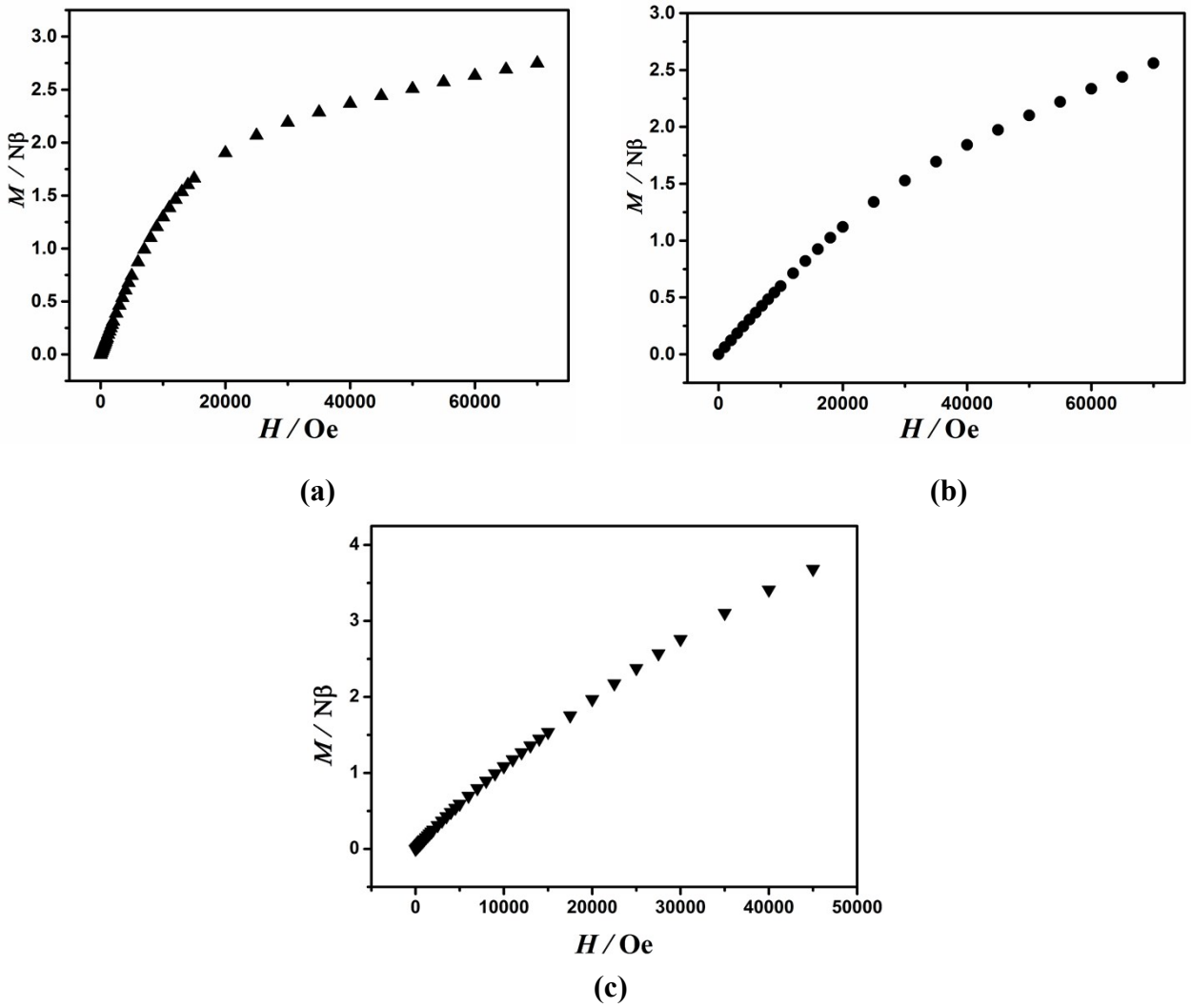

Fig. S2 The *M vs. H* plots for **1** (a), **2** (b) and **3** (c) measured at 2 K.

Table S1 Bond valences (s) calculated as $s = \exp[(r_0-r)/B]$ with B = 0.37, r_0 = 1.67 for Ni(II)–O pairs and B = 0.37, r_0 = 1.75 for Ni(III)–O pairs.

Ni1:

Nr	Bond	Dist	r_0	B	Sum	Diff
1	Ni(1)-O(6)	1.939	1.75	0.37	2.90	0.10
2	Ni(1)-O(1)	2.075	1.75	0.37		
3	Ni(1)-O(1)#5	2.075	1.75	0.37		
4	Ni(1)-O(1)#6	2.075	1.75	0.37		
5	Ni(1)-O(1)#3	2.075	1.75	0.37		
6	Ni(1)-O(5)	2.057	1.75	0.37		

Ni2:

Nr	Bond	Dist	r_0	B	Sum	Diff
1	Ni(2)-O(6)	1.957	1.67	0.37	2.16	0.16
2	Ni(2)-O(3)#6	2.010	1.67	0.37		
3	Ni(2)-O(3)	2.010	1.67	0.37		
4	Ni(2)-O(2)	2.021	1.67	0.37		
5	Ni(2)-O(2)#6	2.021	1.67	0.37		
6	Ni(2)-O(4)	2.110	1.67	0.37		

Table S2. The reaction results of the addition of assistant reagents

	1	**2**	**3**
NaCl	√	√	×
none	×	×	√
$NaNO_3$	√	√	×
KCl	×	×	×

Table S3. Selected bond lengths (Å) and angles (°) for **1**[a]

Co1—O1	1.992(7)	Co3—O8	2.038(7)
Co1—O9$^{\#1}$	2.038(9)	Co3—O10$^{\#1}$	2.117(9)
Co1—O13	1.978(6)	Co3—O11$^{\#4}$	2.207(6)
Co1—O15	2.053(10)	Co3—O12$^{\#4}$	2.189(7)
Co2—O2	2.081(7)	Co3—O13	2.037(6)
Co2—O3$^{\#2}$	2.112(6)	Na1A—O12	2.304(9)
Co2—O6$^{\#3}$	2.221(7)	Na1A—O16	2.377(14)
Co2—O7	2.068(7)	Na1A—O19	2.345(11)
Co2—O13	2.054(7)	Na1A—O19$^{\#5}$	2.593(10)
Co2—O14	2.102(7)	Na1A—O20	2.297(9)
Co3—O5$^{\#3}$	2.112(6)		
O1—Co1—O9$^{\#1}$	105.3(3)	O13—Co3—O11$^{\#4}$	94.3(2)
O1—Co1—O15	94.9(4)	O13—Co3—O12$^{\#4}$	153.1(2)
O9$^{\#1}$—Co1—O15	103.1(4)	O12—Na1A—O16	132.7(4)
O13—Co1—O1	120.6(3)	O12—Na1A—O19$^{\#5}$	80.0(3)
O13—Co1—O9$^{\#1}$	129.5(3)	O12—Na1A—O19	107.0(3)
O13—Co1—O15	93.2(3)	O16—Na1A—O19$^{\#5}$	65.7(4)
O2—Co2—O3$^{\#2}$	86.1(3)	O19—Na1A—O16	100.8(5)
O2—Co2—O6$^{\#3}$	88.4(3)	O19—Na1A—O19$^{\#5}$	83.8(3)
O2—Co2—O14	85.5(3)	O20—Na1A—O12	117.1(4)
O3$^{\#2}$—Co2—O6$^{\#3}$	168.6(3)	O20—Na1A—O16	97.5(5)
O7—Co2—O2	168.3(3)	O20—Na1A—O19$^{\#5}$	162.3(4)
O7—Co2—O3$^{\#2}$	90.0(3)	O20—Na1A—O19	94.7(4)
O7—Co2—O6$^{\#3}$	97.2(3)	O5$^{\#3}$—Co3—C18$^{\#4}$	134.7(3)
O7—Co2—O14	84.0(3)	O8—Co3—O5$^{\#3}$	92.1(3)
O13—Co2—O2	94.8(3)	O8—Co3—O10$^{\#1}$	169.5(4)
O13—Co2—O3$^{\#2}$	92.6(2)	O8—Co3—O11$^{\#4}$	93.7(3)
O13—Co2—O6$^{\#3}$	77.9(3)	O8—Co3—O12$^{\#4}$	87.5(3)
O13—Co2—O7	96.4(3)	O8—Co3—C18$^{\#4}$	93.0(3)
O13—Co2—O14	170.7(3)	O10$^{\#1}$—Co3—O11$^{\#4}$	87.0(3)
O14—Co2—O3$^{\#2}$	96.7(3)	O10$^{\#1}$—Co3—O12$^{\#4}$	83.8(3)
O14—Co2—O6$^{\#3}$	92.9(3)	O13—Co3—O5$^{\#3}$	99.7(2)
O5$^{\#3}$—Co3—O10$^{\#1}$	84.6(3)	O13—Co3—O8	102.9(3)
O5$^{\#3}$—Co3—O11$^{\#4}$	163.3(3)	O13—Co3—O10$^{\#1}$	87.4(3)
O5$^{\#3}$—Co3—O12$^{\#4}$	104.8(2)	O12$^{\#4}$—Co3—O11$^{\#4}$	59.9(2)

[a]Symmetry codes: #1: x+1/2, y−1/2, z; #2: −x+1, y, −z+1; #3: −x+3/2, y+1/2, −z+1; #4: −x+3/2, y−1/2, −z+2; #5: −x+1, y, −z+2

Table S4. Selected bond lengths (Å) and angles (°) for **2**[a]

Ni1—O1	2.074(3)	Ni1—O5	2.056(6)
Ni2—O3	2.010(3)	Ni1—O6$^{\#5}$	1.937(6)
Ni2—O4	2.109(5)	Ni2—O2$^{\#6}$	2.021(3)
Ni2—O6	1.958(3)		
O1$^{\#4}$—Ni1—O1$^{\#3}$	171.3(2)	O2$^{\#6}$—Ni2—O2$^{\#7}$	88.1(2)
O1$^{\#3}$—Ni1—O1	90.9(2)	O2$^{\#7}$—Ni2—O4	86.36(15)
O1$^{\#4}$—Ni1—O1	88.4(2)	O2$^{\#6}$—Ni2—O4	86.36(15)
O1$^{\#4}$—Ni1—O1$^{\#2}$	90.9(2)	O1$^{\#3}$—Ni1—O1$^{\#2}$	88.4(2)
O1$^{\#2}$—Ni1—O1	171.3(2)	O3$^{\#8}$—Ni2—O2$^{\#6}$	170.53(14)
O5—Ni1—O1$^{\#2}$	85.64(10)	O3$^{\#8}$—Ni2—O2$^{\#7}$	89.48(16)
O5—Ni1—O1$^{\#3}$	85.64(10)	O3—Ni2—O2$^{\#7}$	170.53(14)
O5—Ni1—O1$^{\#4}$	85.64(10)	O3—Ni2—O3$^{\#8}$	91.4(2)
O6$^{\#5}$—Ni1—O1	94.36(10)	O3$^{\#8}$—Ni2—O4	84.36(14)
O6$^{\#5}$—Ni1—O1$^{\#3}$	94.36(10)	O3—Ni2—O4	84.36(14)
O6$^{\#5}$—Ni1—O1$^{\#2}$	94.36(10)	O6—Ni2—O2$^{\#6}$	92.30(15)
O6$^{\#5}$—Ni1—O1$^{\#4}$	94.36(10)	O6—Ni2—O2$^{\#7}$	92.30(15)
O6$^{\#5}$—Ni1—O5	180.0	O6—Ni2—O3	96.94(14)
O6—Ni2—O4	178.1(2)	O6—Ni2—O3$^{\#8}$	96.93(14)

[a]Symmetry codes: #1: −*x*+1, *y*, *z*; #2: −*x*+2, −*y*, *z*; #3: −*x*+2, *y*, *z*; #4: *x*, −*y*, *z*; #5: *x*+1/2, *y*−1/2, *z*+1/2; #6: −*x*+3/2, −*y*+1/2, *z*−1/2; #7: −*x*+3/2, *y*+1/2, *z*−1/2; #8: *x*, −*y*+1, *z*.

Table S5. Selected bond lengths (Å) and angles (°) for **3**[a]

O6—Mn1$^{\#1}$	2.191(5)	Mn2—O2	2.171(5)
Mn1—O2	2.505(7)	Mn2—O5	2.200(4)
Mn1—O5	2.245(5)	Mn1—O3	2.126(4)
Mn1—O1	2.246(5)	Mn1—O7$^{\#2}$	2.092(4)
Mn2—O4	2.088(4)		
O7$^{\#2}$—Mn1—O3	87.11(16)	O4—Mn2—O2$^{\#3}$	92.3(2)
O6$^{\#1}$—Mn1—O2	91.8(2)	O4$^{\#3}$—Mn2—O2$^{\#3}$	87.7(2)
O6$^{\#1}$—Mn1—O5	94.46(18)	O4$^{\#3}$—Mn2—O2	92.3(2)
O6$^{\#1}$—Mn1—O1	85.6(2)	O4$^{\#3}$—Mn2—O5	91.27(17)
O5—Mn1—O2	70.14(17)	O4$^{\#3}$—Mn2—O5$^{\#3}$	88.73(17)
O5—Mn1—O1	124.00(19)	O4—Mn2—O5$^{\#3}$	91.27(17)
O1—Mn1—O2	53.92(18)	O4—Mn2—O5	88.73(18)
O3—Mn1—O6$^{\#1}$	176.52(18)	O4—Mn2—O4$^{\#3}$	180.0
O3—Mn1—O2	89.98(18)	O2—Mn2—O5$^{\#3}$	102.5(2)
O3—Mn1—O5	88.95(18)	O2—Mn2—O5	77.5(2)
O3—Mn1—O1	93.0(2)	O2$^{\#3}$—Mn2—O5	102.5(2)
O7$^{\#2}$—Mn1—O6$^{\#1}$	90.19(18)	O2$^{\#3}$—Mn2—O5$^{\#3}$	77.5(2)
O7$^{\#2}$—Mn1—O2	159.97(18)	O5$^{\#3}$—Mn2—O5	180.0
O7$^{\#2}$—Mn1—O5	129.55(18)	O4—Mn2—O2	87.7(2)
O7$^{\#2}$—Mn1—O1	106.4(2)	O2—Mn2—O2$^{\#3}$	180.0

[a]Symmetry codes: #1: x, $-y+1/2$, $-z$; #2: $-x$, $y-1/2$, z; #3: $-x+1$, $-y+1$, $-z$.