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<Supporting Information>

Long-range magnetic ordering in a metal-organic framework based on octanuclear nickel(II) clusters

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Experimental Section

Materials and Methods

All reagents were commercially available and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. X-ray powder diffraction patterns were recorded on a D/max-γ A rotating anode X-ray diffractometer with Cu sealed tube (λ =1.54178 Å). The thermogravimetric analyses were carried out on a Perkin-Elmer-7 thermal analyzer at a heating rate of 10°C/min from 25 to 800 °C. Magnetic susceptibility data on crushed single crystals were collected over the temperature range 1.8–300.0 K using a Quantum Design MPMS-5S super-conducting quantum interference device (SQUID) magnetometer.

Synthesis

A mixture of benzene-1,2,4-tricarboxylic acid(H_3BTC) (1.0 mmol), $NiSO_4 \cdot 6H_2O$ (2.0 mmol), 1,3-bi(4-pyridyl)propane (bpp) (0.67 mmol), NaOH (0.5 mol/L, 6 mL) and distilled water (10 mL) was stirred for 2h. The mixture was then transferred to a 25 mL Teflon-lined steel autoclave and kept at 160 °C for 5 days under autogenous pressure. After the mixture had been slowly cooled down to room temperature, green block crystals of **1** were obtained and washed with distilled water. Yields: ca. 26% (based on Ni) for **1**. The general chemical formula sum is $C_{44}H_{42}N_4Ni_3O_{16}$ (1058.90). Anal. Calcd(%): C, 49.91; H, 4.00; N, 5.29. Found: C, 49.50; H, 4.36; N, 4.93. IR (cm^{-1}, KBr pellet): 3496(s), 3390(s), 3067(s), 1599(s), 1550(s), 1505(m), 1489(s), 1427(s), 1397(s), 1344(s), 1255(w), 1225(w), 1172(w), 1139(w), 1073(w), 1024(m), 987(w), 919(w), 827(s), 813(s), 785(s), 736(m), 716(m), 767(m), 618(m), 571(m), 525(m), 493(w).

X-ray crystal structure determination

X-ray single crystal diffraction data for **1** was collected on a Bruker Apex-II CCD detector with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) using SMART and SAINT programs. Routine Lorentz and polarization corrections were applied. The structures were solved by direct methods of SHELXS-97 and refined by full-matrix least-squares method using the SHELXL-97 program package. All of the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. Hydrogen atoms were assigned to calculated positions using a riding model with appropriately fixed isotropic thermal parameters. Details of crystallographic data for **1** were given in Table S1.

Table S1. Crystal data for polymer **1**

Chemical formula	$C_{44}H_{42}N_4Ni_3O_{16}$
Formula weight	1058.94
Temperature (K)	273(2)
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	*P*3c1
Unit cell dimensions	a = 19.403(2) Å
	b = 19.403(2) Å
	c = 21.606(5) Å
	γ = 120.00°
Volume (Å^3)	7044(2)
Z	6
Density (calculated)	1.498 g cm^{-3}
F(000)	3276
μ	1.264
θ range for data collection	2.30–25.05
Index ranges	$-20 \le h \le 23$, $-22 \le k \le 23$, $-25 \le l \le 25$
Reflections collected	33281
Independent reflections	4123 [R_{int} = 0.0638]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4123/30/322
Goodness of fit on F^2	1.014
Final R indices [$I \ge 2\sigma(I)$]	0.0709/0.1544
R indices (all data)	0.0955/0.1619
Largest diff. peak and hole	2.501 and –0.859 eÅ^{-3}

Table S2. Selected bond lengths (Å) for polymer **1**

Bond	length	bond	length
Ni(1)–O(1)	2.063(5)	Ni(1)–O(1W)	2.093(5)
Ni(1)–O(4A)	2.069(5)	Ni(3)–O(2)	2.413(7)
Ni(1)–N(1)	2.070(6)	Ni(2)–O(6)	2.297(6)
Ni(1)–O(3)	2.077(5)	Ni(2)–O(5)	2.313(5)
Ni(1)–N(2B)	2.084(6)		

Symmetry codes A: $x - y, -1 + x, 1 - z$; B: $1 - y, x - y, z$.

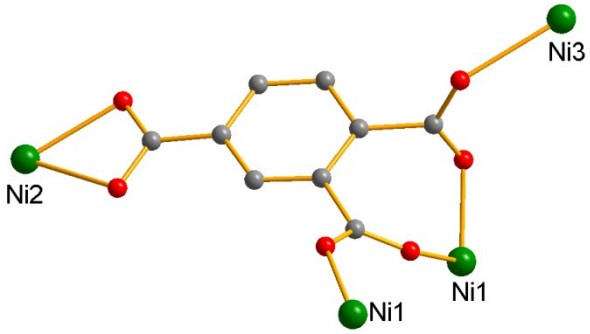
Table S3. Selected bond angles (°) for polymer **1**

bond angle	degree	Bond angle	degree
O(1)–Ni(1)–O(4A)	175.5(2)	O(1)–Ni(1)–O(1W)	82.6(2)
O(1)–Ni(1)–N(1)	91.2(2)	O(4A)–Ni(1)–O(1W)	93.1(2)
O(4A)–Ni(1)–N(1)	90.4(2)	N(1)–Ni(1)–O(1W)	92.0(2)
O(1)–Ni(1)–O(3)	89.2(2)	O(3)–Ni(1)–O(1W)	82.7(2)
O(4A)–Ni(1)–O(3)	88.8(2)	N(2B)–Ni(1)–O(1W)	173.1(2)
N(1)–Ni(1)–O(3)	174.6(2)	O(6D)–Ni(2)–O(6)	98.6(2)
O(1)–Ni(1)–N(2B)	96.1(2)	O(6)–Ni(2)–O(5D)	132.3(2)
O(4A)–Ni(1)–N(2B)	88.0(2)	O(6)–Ni(2)–O(5)	56.7(2)
N(1)–Ni(1)–N(2B)	94.8(2)	O(6C)–Ni(2)–O(5)	123.2(2)
O(3)–Ni(1)–N(2B)	90.5(2)	O(5D)–Ni(2)–O(5)	100.2(2)

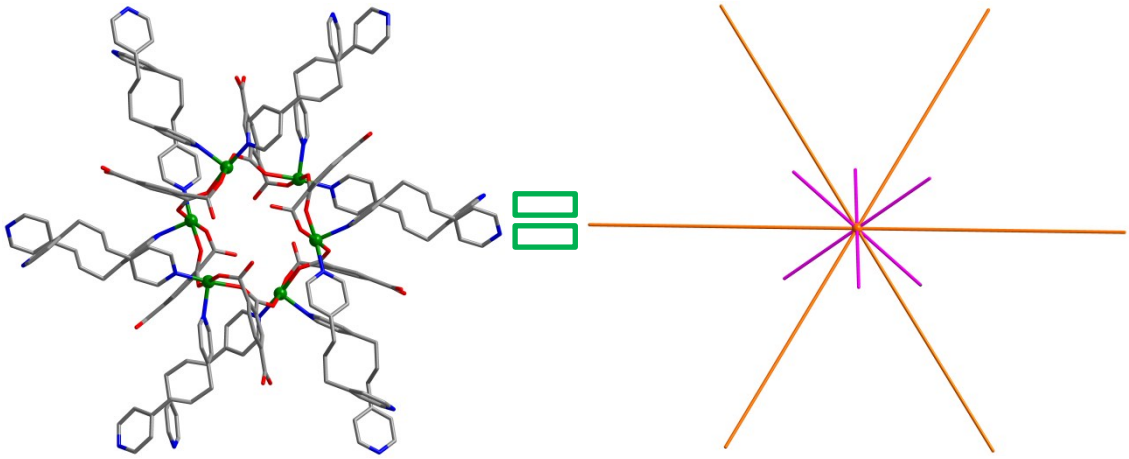
Symmetry codes A: $x - y$, $-1 + x$, $1 - z$; B: $1 - y$, $x - y$, z; C: $2 - y$, $x - y$, z; D: $2 - x + y$, $2 - x$, z.

Table S4. Hydrogen bonding interactions (Å, º) of polymer **1**

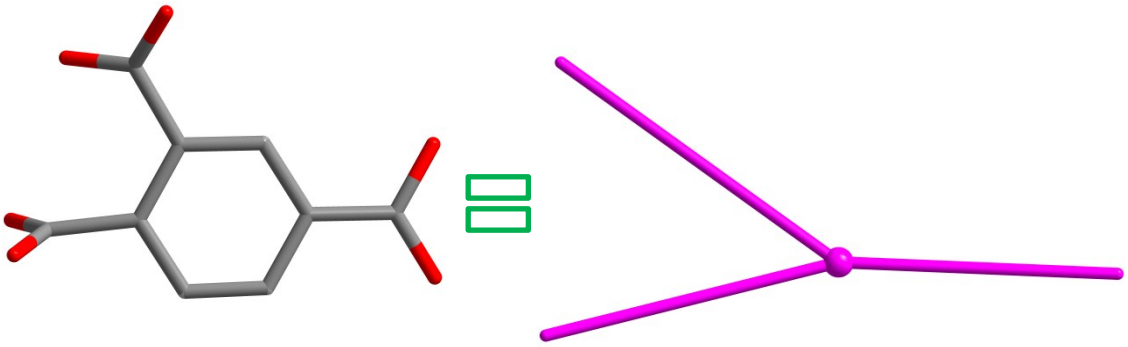
D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	∠(DHA)	Symmetry Transformation for A
O(1W)–H(1WC)···O(2)	0.85	2.39	3.196(9)	158	$1 - y, -1 + x - y, z$
O(1W)–H(1WD)···O(3)	0.85	1.84	2.638(7)	156	$x - y, -1 + x, 1 - z$
C(9)–H(9A)···O(1)	0.93	2.48	3.359(9)	158	$2 - x, 1 - x + y, 1/2 - z$
C(21)–H(21A)···O(4)	0.93	2.51	3.022(10)	115	$y, 1 - x + y, 1 - z$



Scheme S1. Coordination modes of BTC^{3-} anion in polymer **1**.



(a)



(b)

Fig.S1 (a) Schematic illustration of 12-connected $Ni(1)_6(COO)_{12}$ unit connected with six $Ni(1)_6(COO)_{12}$ units and six Ni(2) atoms; (b) Schematic illustration of 3-connected $BTC3^-$ ligand bonded to one $Ni(1)_6(COO)_{12}$ unit and two Ni(II) atoms (Ni(2) and Ni(3)).

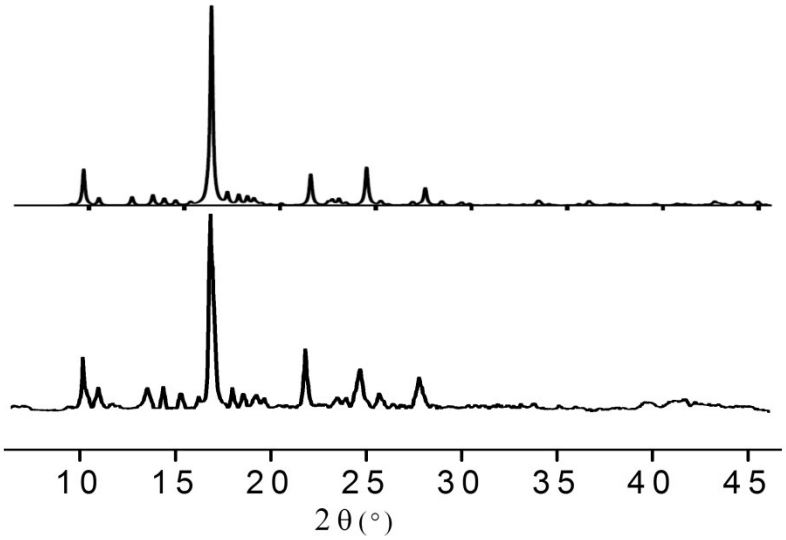


Fig. S2 The pattern calculated from the single-crystal data for **1** (top) and the powder X-ray diffraction pattern of the samples (bottom).

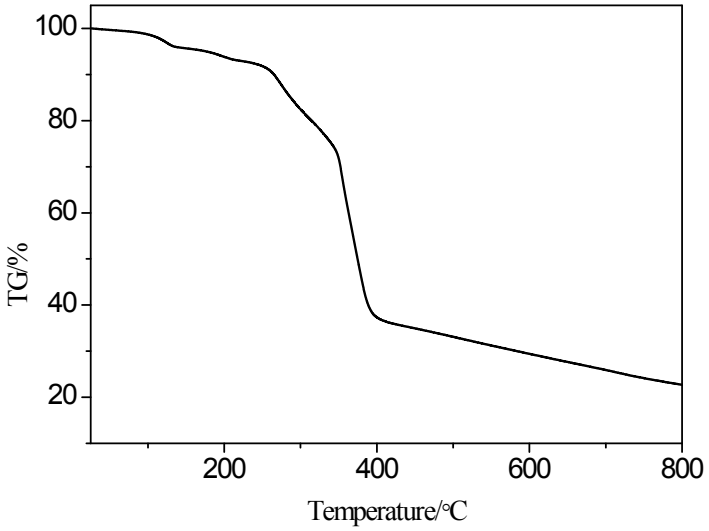


Fig. S3 Thermogravimetric analysis (TGA) curve for polymer **1**.

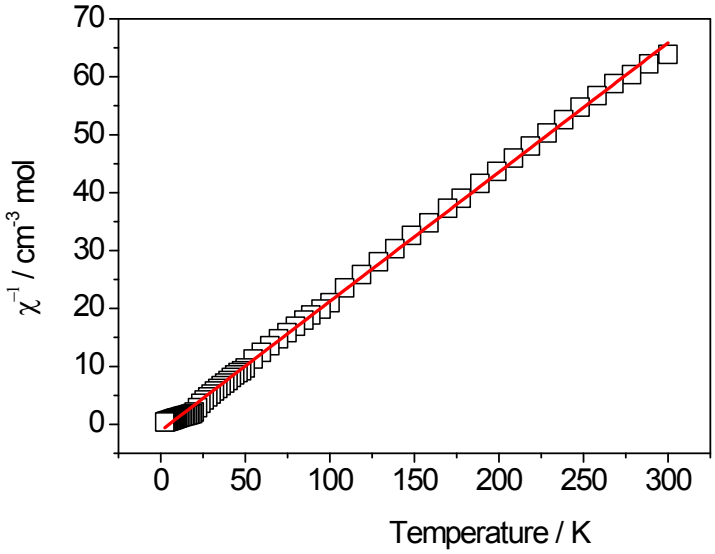


Fig. S4 Plot of χ^{-1} vs. T of **1**. The solid line is the best fit to the Curie-Weiss law.