Electronic supplementary information

Nickel coordination polymers with $\{4^8.6^2\}$ and bnn topologies constructed from common square-pyramidal 5-connected nodes

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Experimental Section

General Information. Solvents were dried with standard procedures. Starting chemicals were purchased from commercial source and used as received. Infra-red spectra were acquired from a Bio-Rad FTS-185 infra-red spectrophotometer. Elemental analyses were performed on a Thermo Flash 2000 CHN-O elemental analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 6. Thermogravimetric Analyzer under flowing N_2 gas (20 mL/min), and the heating rate was 20 °C/min. Powder X-ray diffraction (PXRD) measurements were recorded on Shimadzu Lab-X XRD-6000 diffractometer with Cu Kα, λ= 1.54060 Å.

Synthesis of $[Ni(oba)(dia)_{1.5}(H_2O)]\cdot H_2O$ (1). $Ni(NO_3)_2\cdot 6H_2O$ (0.094 g, 0.322 mmol), dia (0.100 g, 0.322 mmol), and H_2oba (0.0833 g, 0.322 mmol) were placed in H_2O (10 mL) in a 100 mL Teflon-lined stainless reactor. The pH of the solution was adjusted by the addition of triethylamine until the final pH is 9~10. The reactor was tightly closed and heated up to 140 °C in 12 h and maintained at the same temperature for 72 h. Afterwards, the reaction mixture was allowed to cool down to room temperature at a rate of -4.17 °C/h. Green crystals were separated by filtration, washed with deionized water, dichloromethane, and DMF and dried in air. Yield: 0.13 g, 75 %. Anal. Calcd for $C_{44}H_{31}N_6NiO_6{\cdot}H_2O$: C, 64.73; H, 4.07; N, 10.29. Found: C, 64.78; H, 4.26; N, 10.21. IR (KBr/pellet cm^{-1}): 2823 (w br), 1718 (s br), 1577 (s), 1531 (w), 1508 (w), 1448 (s), 1400 (w), 1340 (w), 1263 (s), 1172 (s), 1118 (s), 1112 (s), 1068 (w), 1045 (s), 1018 (w), 948 (w), 920 (w), 892 (w), 862 (w), 792 (s), 734 (s), 703 (s), 690 (s), 673 (s), 609 (w), 595 (w), 580 (w), 435 (w, br).

Synthesis of $[Ni(Hsip)(dia)_{1.5}(H_2O)]{\cdot}H_2O$ (2). $Ni(NO_3)_2{\cdot}6H_2O$ (0.374 g, 1.28 mmol), dia (0.100 g, 0.322 mmol) and NaH_2sip (0.086 g, 0.322 mmol) were placed in H_2O (10 mL) in a 100 mL Teflon-lined stainless reactor. The reactor was tightly closed and heated up according to the same temperature program as that of **1.** Green crystals were separated by filtration, washed with deionized water, dichloromethane, and DMF and dried in air. Yield: 0.07 g, 81 %. Anal. Calcd for $C_{38}H_{27}N_6NiO_8S{\cdot}H_2O$: C, 56.74; H, 3.63; N, 10.45. Found: C, 56.36; H, 3.44; N, 10.30. IR (KBr/pellet cm^{-1}): 3413 (br), 3120 (s), 1685 (s), 1618 (s) 1556 (w), 1500 (s), 1421 (s), 1416 (s), 1360 (w), 1315 (w), 1240 (w), 1227 (s), 1169 (s), 1157 (s), 1103 (s) , 1086 (w), 1041 (s), 939 (w), 912 (w), 868 (w), 837 (w), 816 (w), 814 (w), 767 (s), 741 (s), 670 (w). 658 (s), 613 (s), 536 (w).

X-ray Diffraction Studies. Reflection data were collected on a Bruker APEX II equipped with a CCD area detector and a graphite monochromater utilizing MoKα radiation ($\lambda = 0.71073$ Å) at

150(2) K. The unit cell parameters were obtained by least-squares refinement. The data were integrated via SAINT.[1] Lorentz and polarization effect and multiscan absorption corrections were applied with SADABS.[2] The structures were solved by direct methods and refined by full-matrix least squares methods against F^2 with SHELXTL.[3] All non-H atoms were refined anisotropically. All H-atoms, except those of water, were fixed at calculated positions and refined with the use of a riding model. H-atoms of the water solvent molecule in **1** was not located but included in the molecular formula. H-atoms of the water molecules in **2** were located from difference electron density map and not refined. One of the anthracene rings is disordered. The relevant atoms with 50% of site occupancy, C2A, C3A, and C4A, were located from the electron density map. CCDC-857273 (**1**) and -857274 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

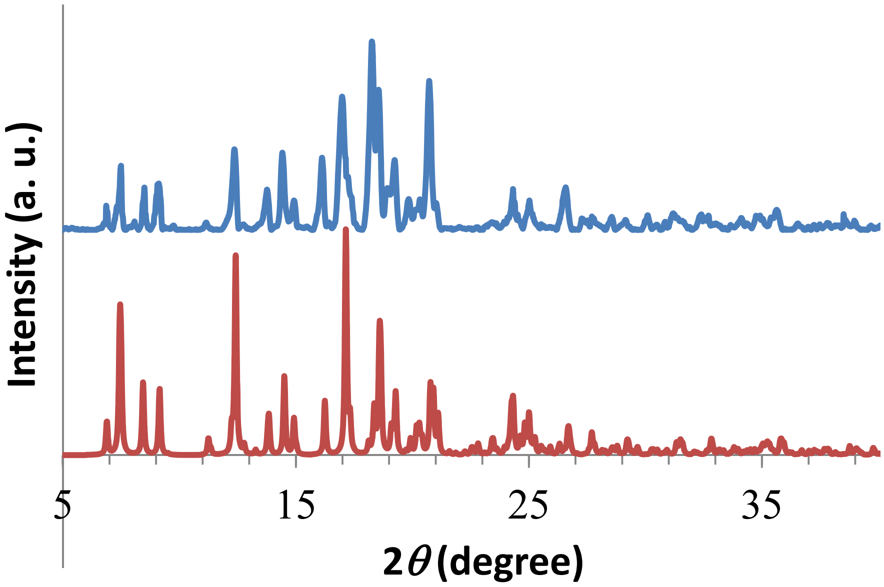

Figure S1. Comparison of the experimental PXRD patterns for as-asynthesized **1** (upper trace) and the simulated pattern from single-crystal X-ray diffraction data (lower trace).

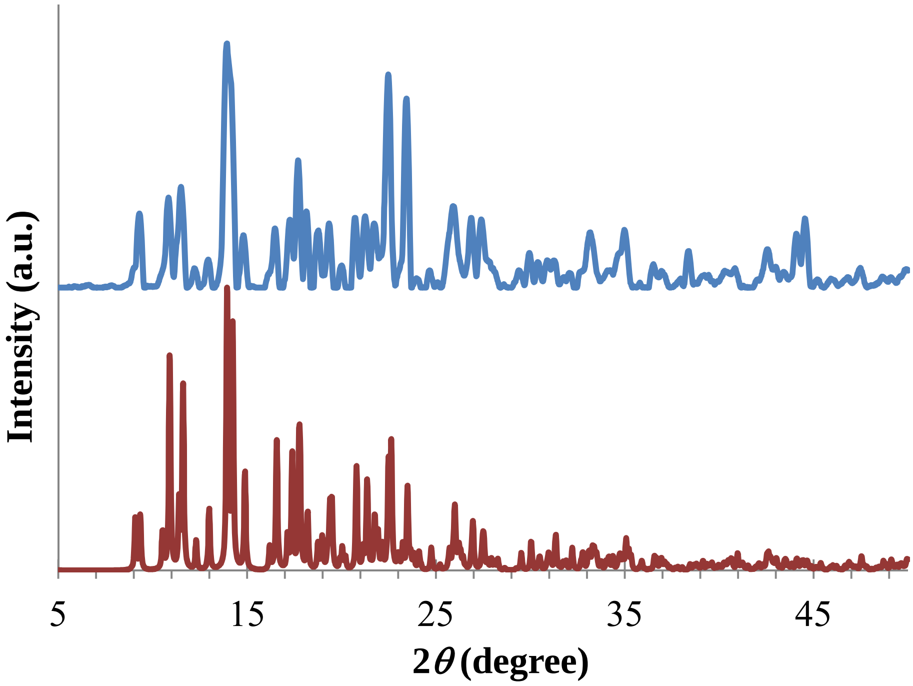

Figure S2. Comparison of the experimental PXRD patterns for as-asynthesized **2** (upper trace) and the simulated pattern from single-crystal X-ray diffraction data (lower trace).

Table S1. Crystallographic data.

	1	**2**
empirical formula	$C_{44}H_{31}N_6NiO_6 \cdot H_2O$	$C_{38}H_{27}N_6NiO_8S \cdot H_2O$
formula weight	816.46	795.43
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
A, Å	11.1502(3)	9.2237(18)
B, Å	13.5449(2)	11.182(2)
c, Å	14.6921(2)	19.434(5)
α, deg	113.808(1)	99.623(18)
β, deg	101.505(1)	94.382(19)
γ, deg	100.238(1)	114.218(12)
V, Å^3	1904.99(6)	1778.7(7)
T, K	150(2)	150(2)
D, g/cm^3	1.420	1.485
Z	2	2
no. of unique data	9821	7361
no. of params refined	551	497
$R_1{}^a$ $[I > 2\sigma I]$	0.0464	0.0570
$wR_2{}^b$ (all data)	0.1216	0.1592

Table S2. Important bond distances (Å) and Angles (°) of **1** and **2**.

1		**2**	
Ni1–N1A	2.0798(17)	Ni1–N2	2.064(3)
Ni1–N4	2.1370(17)	Ni1–N3	2.085(3)
Ni1–N5	2.0735(17)	Ni1–N5	2.089(3)
Ni1–O2	2.0327(15)	Ni1–O3	2.105(3)
Ni1–O3W	2.1369(15)	Ni1–O12W	2.083(3)
Ni1–O4	2.0894(14)	Ni1–O5B	2.052(3)
N1A–Ni1–O4	90.65(6)	N3–Ni1–O5B	91.97(13)
N1A–Ni1–O2	98.54(7)	N3–Ni1–O3	91.19(13)
N1A–Ni1–N5	88.84(7)	N3–Ni1–N5	90.13(13)
N1A–Ni1–O3W	83.41(6)	N3–Ni1–O12W	86.10(14)
N4–Ni1–O4	85.83(6)	N2–Ni1–O5B	86.87(12)
N4–Ni1–O2	84.77(7)	N2–Ni1–O3	90.04(12)

N4–Ni1–O3W	88.15(6)	N2–Ni1–O12W	92.03(14)
N4–Ni1–N5	99.30(7)	N2–Ni1–N5	91.81(13)
O4–Ni1–O3W	89.59(6)	O5B–Ni1–O12W	91.55(12)
O4–Ni1–N5	86.23(7)	O5B–Ni1–N5	92.35(12)
O2–Ni1–N5	96.01(7)	O3–Ni1–N5	85.62(12)
O2–Ni1–O3W	89.37(6)	O3–Ni1–O12W	90.68(12)
N1A–Ni1–N4	170.88(7)	N3–Ni1–N2	177.78(13)
N5–Ni1–O3W	171.16(6)	N5–Ni1–O12W	174.67(13)
O2–Ni1–O4	170.57(6)	O3–Ni1–O5B	176.25(10)

Symmetry code: A = x, 1+y, z; B = x, y-1,z; B = 1+x, 1+y, z

Table S3. Classical hydrogen bonds between the two interpenetrating nets in **2** [Å and °]

D-H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(12)-H(12B)···O(1)#1	0.97	2.00	2.878(5)	148.7
O(2)-H(2A)···O(7)#2	1.04	1.64	2.679(4)	171.5
O(2)-H(2A)···O(4)#2	1.04	2.52	3.170(5)	120.1

Symmetry transformations used to generate equivalent atoms: #1: x+1, y, z; #2: x-1, y, z

References

1. *SAINT*, Bruker AXS Inc.:Madison, Wisconsin, USA., 2007.

2. G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, 1996.

3. G. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.