Electronic Supplementary Information

New metalloligands suitable for the construction of polynuclear complexes and coordination polymers with exposed metal sites

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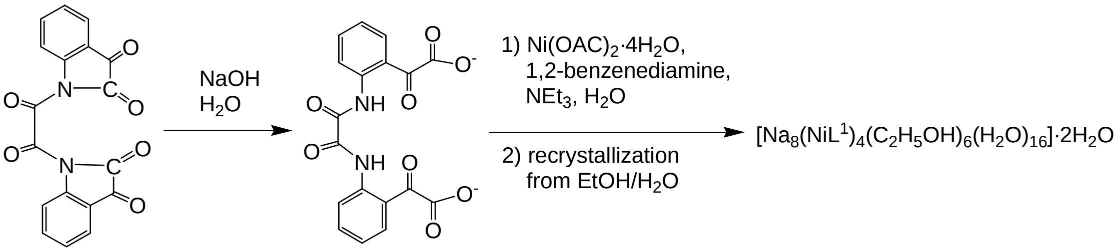
Materials and Measurements. All starting materials and solvents were purchased commercially and were used as received. 1,1'-oxalylbisisatin was prepared by the literature method,[1] and its ring opening in NaOH solution was carried out following the principle mentioned in the same literature. Infrared spectra were obtained from KBr pellets on a BIO-RAD 3000 infrared spectrophotometer in the 400-4000 cm^{-1} region. Elemental analyses of C, H and N were determined with a Perkin-Elmer 240 Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a STA-409PC equipment at a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/max 2500v/pc X-ray powder diffractometer (Cu Kα, 1.5418 Å).

Synthesis of $[Na_8(NiL^1)_4(C_2H_5OH)_6(H_2O)_{16}]\cdot 2H_2O$ (1).



A mixture of 1,1'-oxalylbisisatin (3.4827 g, 10.0 mmol) and the solution of 0.8000g (20.0 mmol) NaOH in 60 ml water was stirred at 40 °C for 2 h to give a yellow solution. To the solution was added $Ni(OAC)_2\cdot 4H_2O$ (2.4884 g, 10.0 mmol) and triethyl amine (2.89 ml). To the above solution was then added drop by drop a solution of 1,2-benzenediamine (1.0814 g, 10.0 mmol) in 20 ml water in 2 h under stirring at 75 °C, and the solution was kept stirring for another 6 h at 75 °C. The resulting mixture was then cooled to room temperature and filtered. The filtrate was evaporated by heating on a water bath of 60 °C to afford a dark red paste. The mixture of the paste and 20 ml ethanol was stirred for 30 min and then filtered under vacuum. The solid was dried in the air to afford a dark red powder (4.6750 g).

A mixture of the dark red powder (4.6750 g), ethanol (233 ml) and water (11.5 ml) was stirred and heated at 60 °C for 30 min, and then filtered. The filtrate of the mixture was stored over night and deep red crystals suitable for X-ray single crystal analysis were obtained. Yield: 1.4912 g (21.09%). Anal. Calc. for $C_{108}H_{120}N_{16}Na_8Ni_4O_{48}$: C 45.85, H 4.28, N 7.92%. Found: C 45.30, H 4.25, N 7.91%. IR (KBr, cm^{-1}): 3395(m), 1646(s), 1618(s), 1593(s), 1532(s), 1439(m), 1387(s), 1323(m), 1252(m), 1208(m), 1168(m), 769(m), 747(m).

Synthesis of $\{[Fe(NiL^1)(CH_3OH)(H_2O)_2]_4{\cdot}4CH_3OH{\cdot}4H_2O\}_n$ (2). A mixture of **1** (0.0690 g, 0.0244 mmol), $FeSO_4{\cdot}7H_2O$ (0.0274 g, 0.0985 mmol), methanol (60 ml) and water (120 ml) was stirred to form a red solution. The filtrate of the solution was then stored at room temperature for 7 days, and deep red crystals suitable for X-ray single crystal analysis were formed. Yield: 0.0360 g (53.8%, calculated on the amount of **1**). Anal. Calc. for $C_{104}H_{104}Fe_4N_{16}Ni_4O_{44}$: C 45.59, H 3.83, N 8.18%. Found: C 45.31, H 4.00, N 8.41%. IR (KBr, cm^{-1}): 3575(m), 3050(m), 1602(s), 1585(s), 1538(s), 1484(m), 1461(m), 1440(m), 1381(s), 1350(m), 1322(m), 1240(m), 1209(m), 1168(m), 765(m), 751(m).

Synthesis of $\{[Ni(NiL)(H_2O)_3]{\cdot}C_2H_5OH{\cdot}2H_2O\}_n$ (3). A mixture of **1** (0.0690 g, 0.0244 mmol), $Ni(ClO_4)_2{\cdot}6H_2O$ (0.0360 g, 0.0984 mmol), ethanol (80 ml) and water (80 ml) was stirred to form a red solution. The filtrate of the solution was then stored for 28 days at room temperature, and red crystals suitable for X-ray single crystal analysis were formed. Yield: 0.0311 g (45.1%, calculated on the amount of **1**). Anal. Calc. for $C_{26}H_{28}N_4Ni_2O_{12}$: C 44.24, H 4.00, N 7.94%. Found: C 44.45, H 3.76, N 8.23%. IR (KBr cm^{-1}): 3579(s), 3309(m), 3062(m), 2900(m), 1606(s), 1586(s), 1540(s), 1483(m), 1460 (m), 1441(m), 1380(s), 1351(m), 1322(m), 1241(m), 1208(m), 1167(m), 765(m), 752(m).

Synthesis of $\{[Zn_2(NiL^1)_2(H_2O)_6]{\cdot}8H_2O\}_n$ (4). A mixture of **1** (0.1796 g, 0.0635 mmol), $Zn(OAC)_2{\cdot}2H_2O$ (0.0562 g, 0.256 mmol), DMF (50 ml) and water (150 ml) was stirred to form a red solution. The filtrate of the solution was then stored at room temperature for 6 days, and red crystals suitable for X-ray single crystal analysis were formed. Yield: 0.1581 g (89.6%, calculated on the amount of **1**). Anal. Calc. for $C_{48}H_{52}N_8Ni_2O_{26}Zn_2$: C 41.03, H 3.73, N 7.97%. Found: C 41.31, H 3.79, N 7.72%. IR (KBr cm^{-1}): 3578(m), 3406(m), 3010(m), 2896(m), 1603(s), 1587(s), 1538(s), 1483(m), 1461(m), 1440(m), 1380(s), 1350(m), 1324(m), 1240(m), 1209(m), 1169(m), 766(m), 751(m).

Synthesis of $\{[Cd(NiL^1)(H_2O)_2]{\cdot}2DMF]\}_n$ (5). A mixture of **1** (0.1070 g, 0.0378 mmol),

$Cd(NO_3)_2 \cdot 4H_2O$ (0.0469 g, 0.152 mmol) and water (100 ml) was stirred to form a red solution. The filtrate of the solution was stored overnight at room temperature to form red crystalline plates. To the mixture was added 100 ml DMF, and then the new mixture was heated at 80 °C to form a red solution. The filtrate of the solution was stored for 28 days at room temperature, and red crystals suitable for X-ray single crystal analysis were obtained. Yield: 0.0950 g (78.0%, calculated on the amount of **1**). Anal. Calc. for $C_{30}H_{30}CdN_6NiO_{10}$: C 44.72, H 3.75, N 10.43%. Found: C 44.50, H 3.90, N 10.23%. IR (KBr cm^{-1}): 3405(m), 1669(s), 1620(s), 1540(s), 1440(m), 1370(s), 1332(m), 1250(m), 1205(m), 1167(m), 766(m), 754(m)

Synthesis of $\{[Cd(NiL^1)(C_2H_5OH)]_2 \cdot H_2O\}_n$ (6). A mixture of **1** (0.0690 g, 0.0244 mmol), $CdCl_2 \cdot 1.5H_2O$ (0.0224 g, 0.0984 mmol), ethanol (170 ml) and water (170 ml) was stirred to form a red solution. The filtrate of the solution was then stored for 10 days at room temperature, and red crystals suitable for X-ray single crystal analysis were formed. Yield: 0.0313 g (47.3%, calculated on the amount of **1**). Anal. Calc. for $C_{52}H_{38}Cd_2N_8Ni_2O_{15}$: C 46.02, H 2.82, N 8.26%. Found: C 46.10, H 2.87, N 8.19%. IR (KBr cm^{-1}): 3305(m), 3129(m), 1629(s), 1608(s), 1590(s), 1534(s), 1439(m), 1375(s), 1325(m), 1253(m), 1207(m), 1169(m), 765(m), 749(m)。

Crystallography for 1, 2, 4 and 5. The diffraction data were collected at 113(2) K with a Rigaku Saturn CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with ω and φ scans. Absorption corrections were carried out utilizing CrystalClear routine.[2] The structures were solved by the direct methods and refined by full-matrix least-squares refinements based on F^2.[3] Crystal data of **1**: $C_{108}H_{120}N_{16}Na_8Ni_4O_{48}$, $M_r = 2828.88$, $T = 113(2)$ K, monoclinic $C2/c$, $a = 34.433(12)$ Å, $b = 12.141(3)$ Å, $c = 30.332(8)$ Å, $\beta = 106.958(7)°$, $V = 12129(6)$ Å^3, $Z = 4$, $D_c = 1.549$ g cm^{-3}, $\mu = 0.738$ mm^{-1}, $R_{int} = 0.0776$, final $R_1 = 0.0806$, $wR_2 = 0.2000$ ($I \geq 2\sigma$), $S = 1.141$. Crystal data of **2**: $C_{26}H_{26}FeN_4NiO_{11}$, $M_r = 685.04$, $T = 113(2)$ K, monoclinic $P2_1/n$, $a = 15.932(3)$ Å, $b = 8.8699(19)$ Å, $c = 19.240(4)$ Å, $\beta = 91.679(4)°$, $V = 2717.7(10)$ Å^3, $Z = 4$, $D_c = 1.675$ g cm^{-3}, $\mu = 1.296$ mm^{-1}, $R_{int} = 0.0285$, final $R_1 = 0.0481$, $wR_2 = 0.1434$ ($I \geq 2\sigma$), $S = 1.065$. Crystal data of **4**: $C_{48}H_{52}N_8Ni_2O_{26}Zn_2$, $M_r = 1405.14$, $T = 113(2)$ K, triclinic $P\bar{1}$, $a = 8.9653(18)$ Å, $b = 15.482(3)$ Å, $c = 19.932(4)$ Å, $\alpha = 90.78(3)°$, $\beta = 91.84(3)°$, $\gamma = 91.97(3)°$, $V = 2763.2(10)$ Å^3, $Z = 2$, $D_c = 1.689$ g cm^{-3}, $\mu = 1.625$ mm^{-1}, $R_{int} = 0.0602$, final $R_1 = 0.0620$, $wR_2 = 0.1398$ ($I \geq 2\sigma$), $S = 1.074$. Crystal data of **5**: $C_{30}H_{30}CdN_6NiO_{10}$, $M_r = 805.71$, $T = 113(2)$ K, monoclinic $P2_1/n$, $a = 11.1075(17)$ Å, $b = 14.004(2)$ Å, $c = 19.542(3)$ Å, $\beta = 92.756(3)°$, $V = 3036.2(8)$ Å^3, $Z = 4$, $D_c = 1.763$ g cm^{-3}, $\mu = 1.391$ mm^{-1}, $R_{int} = 0.0280$, final $R_1 = 0.0221$, $wR_2 = 0.0563$ ($I \geq 2\sigma$), $S = 1.030$.

Crystallography for 3 and 6. The diffraction data were collected at 296(2) K with a Bruker SMART

CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with φ and ω scans. Absorption corrections were carried out utilizing SADABS routine.[4] The structures were solved by the direct methods and refined by full-matrix least-squares refinements based on F^2.[3] Crystal data of **3**: $C_{26}H_{28}N_4Ni_2O_{12}$, M_r = 705.91, T = 296(2) K, monoclinic $P2_1/c$, a = 15.3667(10) Å, b = 9.0896(6) Å, c = 24.9074(12) Å, β = 126.332(3)°, V = 2802.7(3) Å^3, Z = 4, D_c = 1.673 g cm^{-3}, μ = 1.416 mm^{-1}, R_{int} =0.0180, final R_1 = 0.0276, wR_2 = 0.0699 ($I \geq 2\sigma$), S = 1.038. Crystal data of **6**: $C_{52}H_{38}Cd_2N_8Ni_2O_{15}$, M_r = 1357.11, T = 296(2) K, monoclinic $C2/c$, a = 11.3958(17) Å, b = 18.9334(17) Å, c = 22.595(3) Å, β = 96.522(3)°, V = 4843.5(11) Å^3, Z = 4, D_c = 1.862 g cm^{-3}, μ = 1.715 mm^{-1}, R_{int} =0.0235, final R_1 = 0.0499, wR_2 = 0.0968 ($I \geq 2\sigma$), S = 1.110.

References

1 D. S. C. Black and G. I. Moss, *Aust. J. Chem.,* 1987, **40**, 129.

2 Crystal Structure 3.7.0 and Crystalclear 1.36: Crystal Structure Analysis Package. Rigaku and Rigaku/MSC (2000-2005), The Woodlands, TX.

3 G. M. Sheldrick, SHELXL-97, program for the refinement of the crystal structures. University of Göttingen, Germany, 1997.

4 G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Germany, 1996.

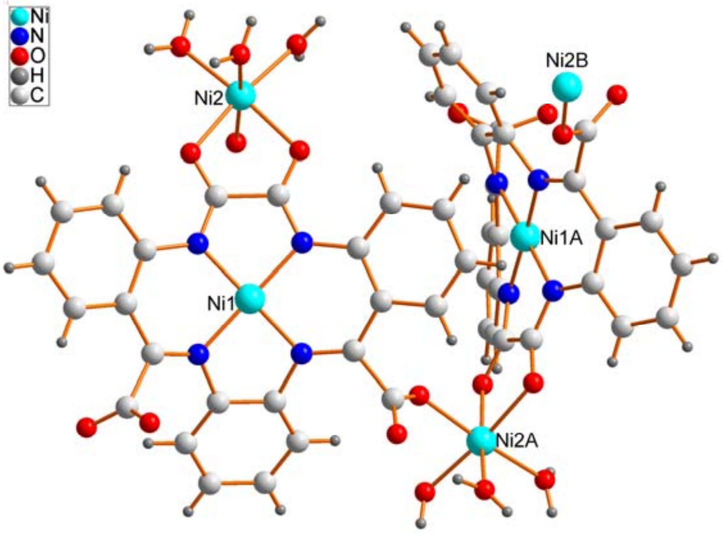


Fig. S1 Plot showing the coordination environments of Ni atoms, and the coordination mode and "head-to-tail" arrangement of NiL^1 in **3** (The additional "A" and "B" letters in the atom labels indicate that these atoms are at (-x, 1/2+y, 3/2-z) and (x, 1+y, z), respectively).

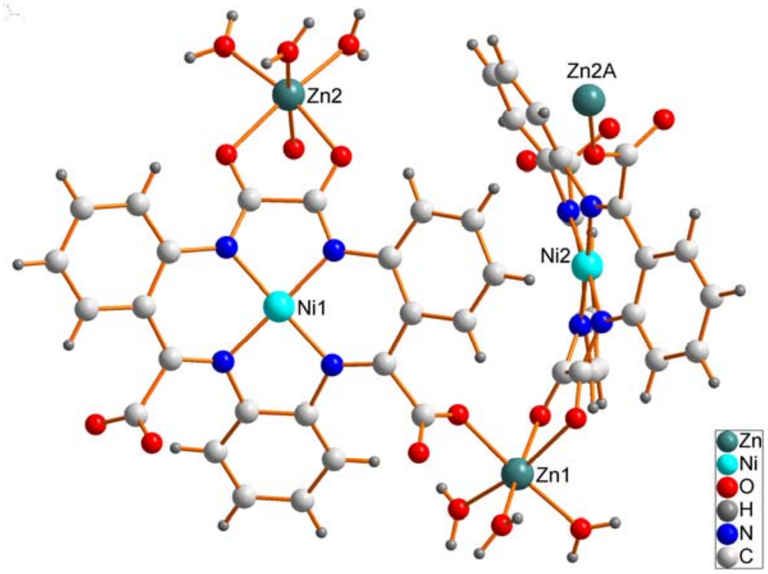


Fig. S2 Plot showing the coordination environments of Ni and Zn atoms, and the coordination mode and "head-to-tail" arrangement of NiL^1 in **4** (The additional "A" letter in the atom label indicates that this atom is at (1+x, y, z)).

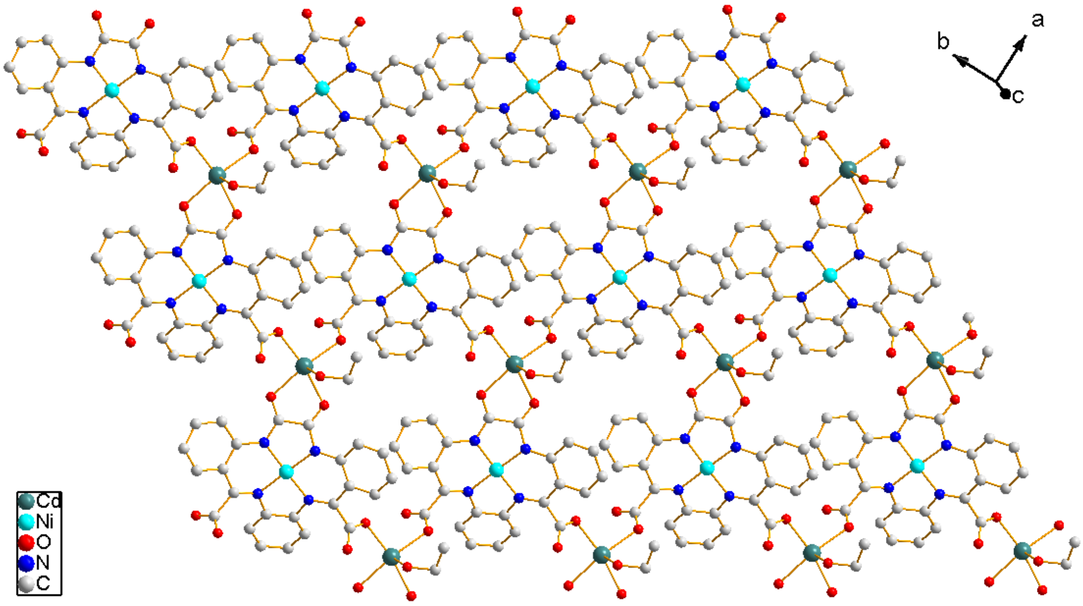


Fig. S3 Plot showing the coordination environments of Ni and Cd atoms, coordination mode of NiL^1 and layered structure in **6**. Hydrogen atoms have been omitted for clarity.

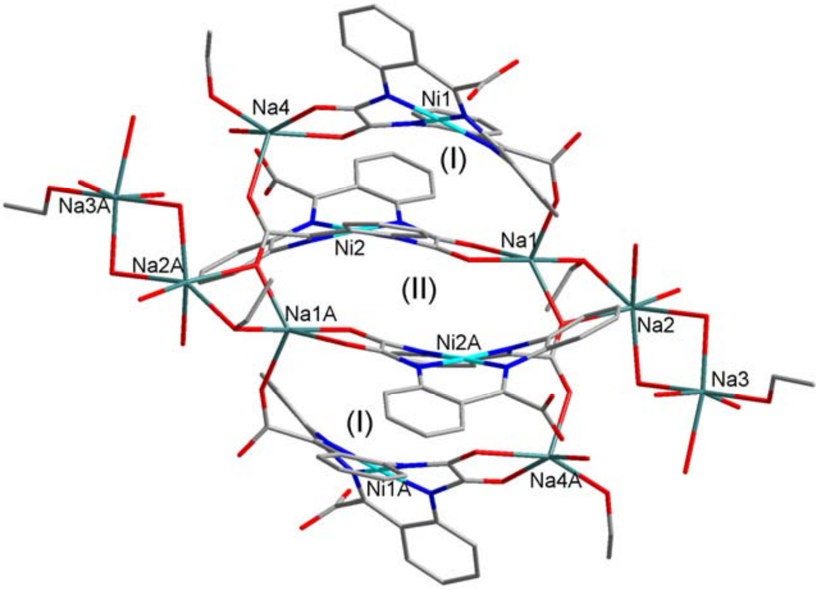


Fig. S4 Plot showing the two kinds of $Na_2(NiL^1)_2$ metallomacrocylces ((I) and (II)) in the dodecanuclear complex of **1**. Hydrogen atoms have been omitted for clarity (sodium, pine green; nickel, cyan; nitrogen, blue; oxygen, red; carbon, grey. The additional "A" letters in the atom labels indicate that these atoms are at (2-x, 1-y, 2-z)).

Table S1 Atom-to-atom distances shorter than 3.80 Å between the two $\mathrm{NiL^1}$ ligands in each of the two kinds of $\mathrm{Na_2(NiL^1)_2}$ metallomacrocycles in the dodecanuclear complex of **1.**

metallomacrocylce (I)		metallomacrocylce (II)	
Ni1···C46	3.696(6)	N7···O7 [a]	3.720(5)
Ni1···C47	3.659(7)	N8···C47 [a]	3.609(9)
N1···N8	3.678(7)	N8···O7 [a]	3.720(5)
N1···C48	3.593(7)	O7–C41 [a]	3.290(6)
N2···C47	3.464(8)	O7–C43 [a]	3.086(7)
O2···C41	3.395(8)	O7–C44 [a]	3.536(7)
O2···C43	3.426(7)	O7–C48 [a]	3.252(7)
O2···C48	3.632(6)	O7–N7 [a]	3.720(5)
O2···Ni2	3.254(4)	O7–N8 [a]	3.777(6)
O2···N7	3.403(7)	C25–C43 [a]	3.692(8)
O2···N8	3.543(5)	C25–C47 [a]	3.566(9)
C2···C43	3.462(8)	C25–C48 [a]	3.531(8)
C2···C48	3.494(8)	C41–O7 [a]	3.290(6)
C2···N8	3.685(7)	C43–O7 [a]	3.086(7)
C3···N8	3.721(7)	C44–O7 [a]	3.536(7)
C4···C27	3.575(8)	C48–O7 [a]	3.252(7)
C4···N5	3.541(8)	C43–C25 [a]	3.692(8)
C5···N5	3.659(8)	C47–C25 [a]	3.566(9)
C5···C27	3.212(9)	C48–C25 [a]	3.531(8)
C5···C28	3.245(8)		
C5···C29	3.559(8)		
C5···C32	3.689(8)		
C6···C27	3.736(9)		
C6···C28	3.284(9)		
C6···C29	3.665(8)		
C7···O8	3.726(8)		
C8···C25	3.741(9)		
C9···O7	3.710(7)		
C11···C46	3.595(9)		
C11···C47	3.564(9)		
C16···C46	3.600(9)		

[a] 1-x,-y,2-z

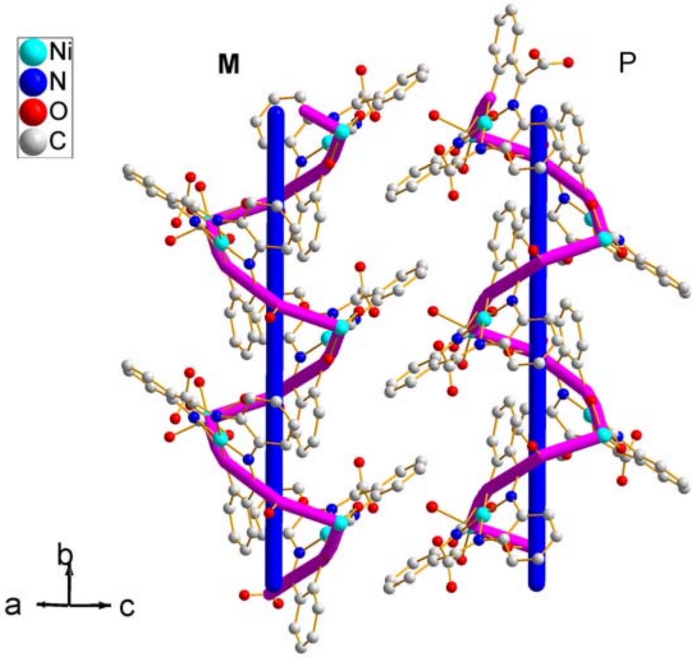


Fig. S5 Left- (M) and right-handed (P) helical chains in **3.** Hydrogen atoms and coordinated solvent molecules have been omitted for clarity.

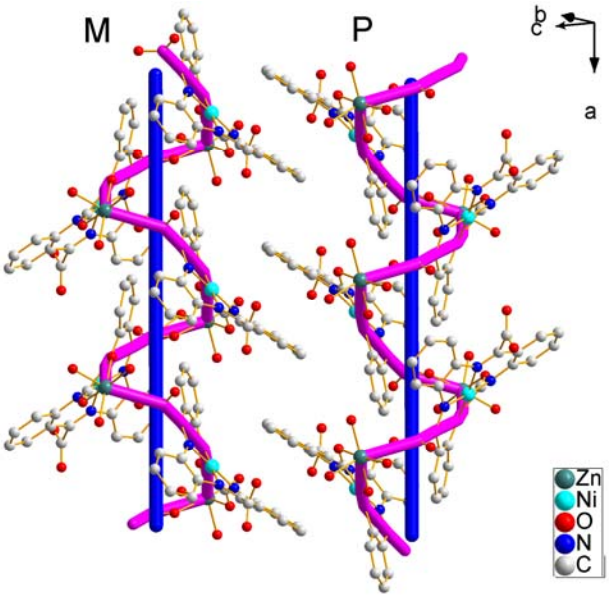


Fig. S6 Left- (M) and right-handed (P) helical chains in **4.** Hydrogen atoms and coordinated solvent molecules have been omitted for clarity.

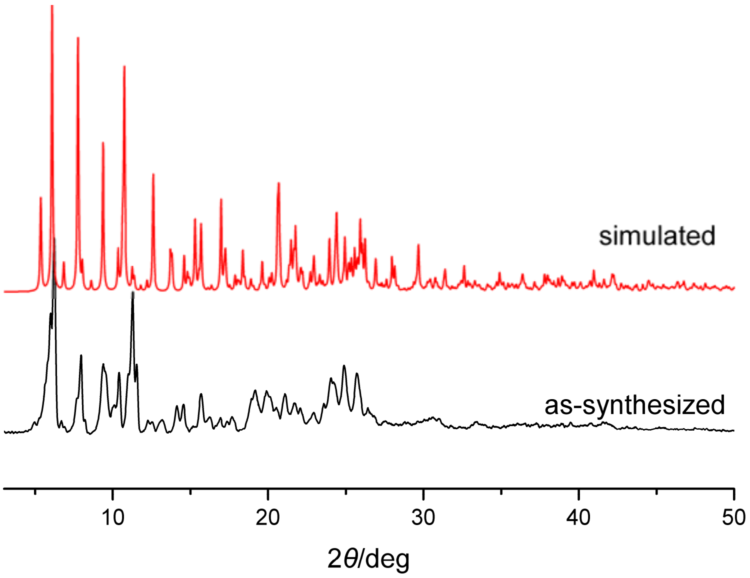


Fig. S7 PXRD patterns of **1** simulated from the X-ray single-crystal structure and as-synthesized samples.

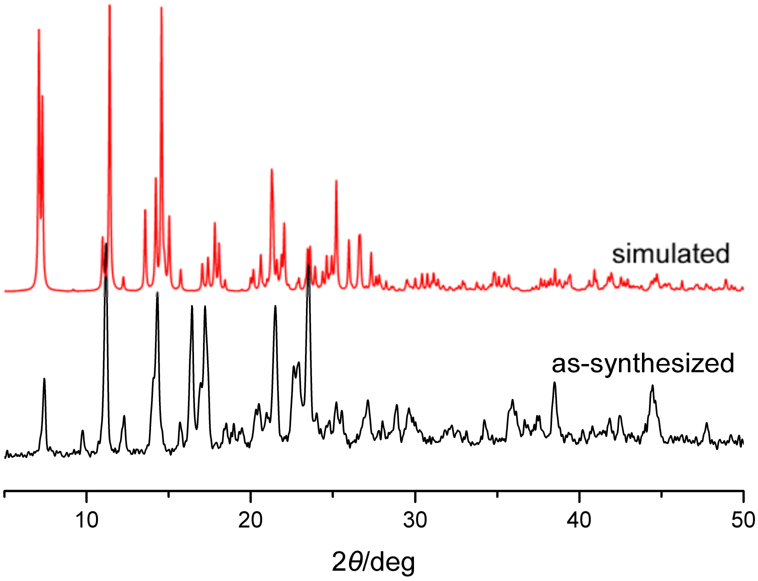


Fig. S8 PXRD patterns of **2** simulated from the X-ray single-crystal structure and as-synthesized samples.

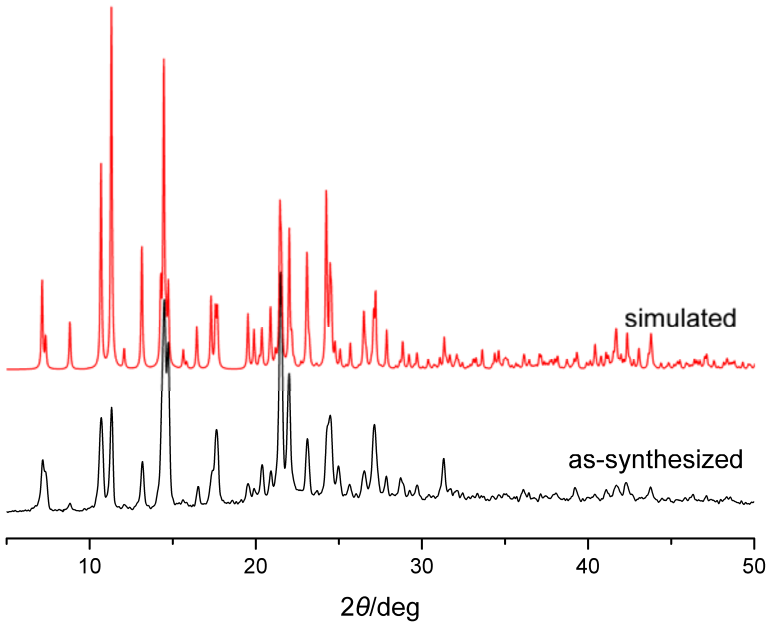


Fig. S9 PXRD patterns of **3** simulated from the X-ray single-crystal structure and as-synthesized samples.

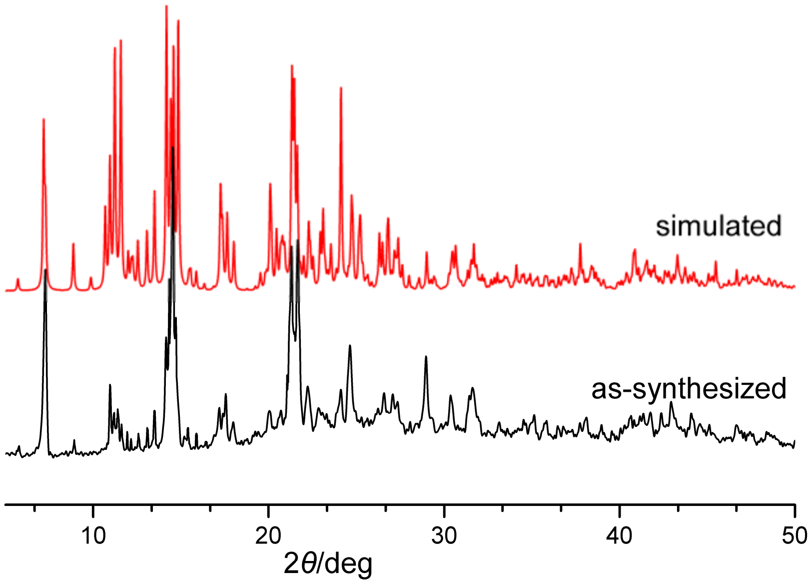


Fig. S10 PXRD patterns of **4** simulated from the X-ray single-crystal structure and as-synthesized samples.

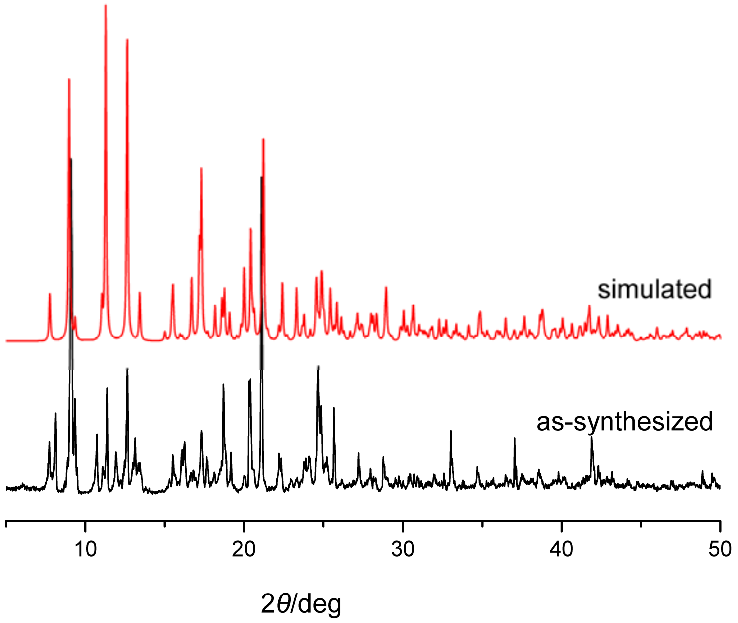


Fig. S11 PXRD patterns of **5** simulated from the X-ray single-crystal structure and as-synthesized samples.

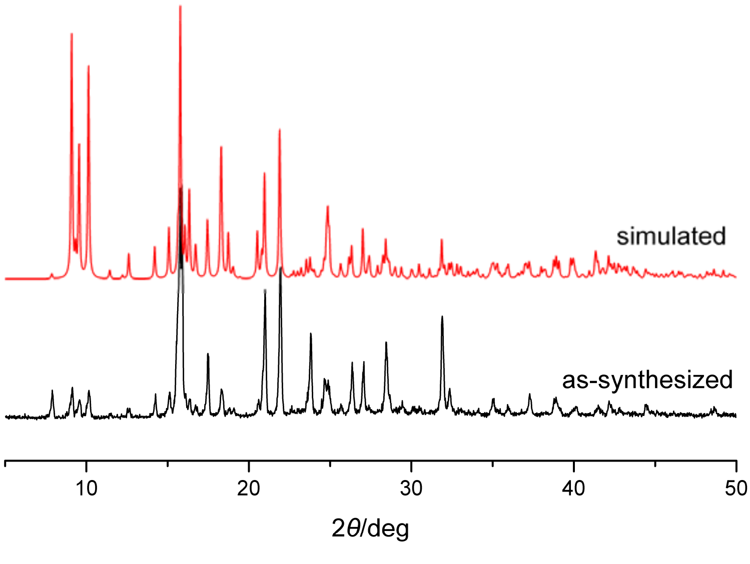


Fig. S12 PXRD patterns of **6** simulated from the X-ray single-crystal structure and as-synthesized samples.