Electronic Supporting Information (ESI) for

Bottom-up assembly of porous MOF based on nanosized nonanuclear zinc precursor for high selective gas adsorption

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Experimental Section

Materials and methods.

All chemicals were commercially purchased and used as received.

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at http://www.iucr.org. The thermogravimetric analysis (TGA) was done on a standard TG-DTA analyzer under air atmosphere at a heating rate of 10 °C/min for measurement. IR spectra were measured in the range of 400-4000 cm^{-1} on a Tensor 27 OPUS FT-IR spectrometer using KBr pellets (Bruker, German).

The $[Zn_9(Me_2bta)_{12}(NO_3)_6]\cdot 3DMF$ (denoted as $\{Zn_9\}$) precursor was prepared according to the literature.[S1]

Syntheses of 1 and **2:** A mixture of $\{Zn_9\}$ (136 g, 0.05 mmol), H_2bcpt·HCl (93 mg, 0.27 mmol) for **1**, 1,4-BDA·HCl (93 mg, 0.27 mmol) for **2**, and DMF (10 mL) was sealed in a 23 mL Teflonlined stainless steel container, which was heated at 120 °C for 2 days and then cooled to room temperature at a rate of 10 $°C\cdot h^{-1}$. Colorless block shaped crystals of **1** and **2** were collected. Yield: 22.6% (**1**) and 8.1% (**2**) based on Zn. Elemental analysis (%): Calcd. for $\mathbf{Zn_9Cl_2C_{129.5}H_{113.5}N_{42}O_{8.5}}$ (*Mr* = 3053.65) (**1**): C, 50.94; H, 3.75, N, 19.26. Found: C, 50.98; H, 3.68; N, 19.31. IR (KBr disk, cm^{-1}) as shown in Fig. S8.

X-ray Crystallography.

The crystallographic data of **1** were collected on a Rigaku SCX-mini diffractometer at 298(2) K with Mo-Kα radiation (λ = 0.71073 Å). The program SAINT[S2] was used for integration of the diffraction profiles. The crystal data were solved by direct methods and refined by a full-matrix least-square method on F^2 using the *SHELXL-97* crystallographic software package.[S3] For **1**, the solvents DMF molecules were highly disordered and could not be modeled properly, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules. The results were appended in the CIF file. The reported refinements are of the guest-free structures using the *.hkp files produced using the SQUEEZE routine.[S4] The number of located electrons, 49 + 49 in two voids per unit cell. These residual electron densities were assigned to two DMF molecules. So SQUEEZE removed two DMF molecules per unit cell.

This value calculated based upon volume/count_electrons analysis, combining with elemental analyses and TG analyses. (One DMF molecule would give 40 e). There are four formula units in one cell, so one formula unit contains 0.5 disordered DMF molecules.[S5] So the tentative formula for this compound is **{[$Zn_9Cl_2(bcpt)_2(Me_2BTA)_{12}$]·0.5DMF}$_n$**. So the solvents molecules cannot be added in the calculated positions. They were directly included in the final molecular formula. Further details of crystal data and structure refinement for **1** were summarized as follows. Selected bond lengths of **1** were given in Table S1. Full crystallographic data for **1** have been deposited with the CCDC (887425). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.[S6]

Reference

S1 S. Biswas, M. Tonigold, M. Speldrich, P. Kögerler, D. Volkmer, *Eur. J. Inorg. Chem.*, 2009, 3094.

S2 *Bruker AXS, SAINT Software Reference Manual*, Madison, WI, 1998.

S3 (a) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

S4 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Untrecht University, 2003.

S5 (a) O. V. Dolomanov, D. B. Cordes, N. R. Champness, A. J. Blake, L. R. Hanton, G. B. Jameson, M. Schroder and C. Wilson., *Chem. Commun.*, 2004, 642; (b) Y. Du, A. L. Thompson and D. O. Hare, *Chem. Commun.*, 2008, 5987; (c) Y. F. Bi, X. T. Wang, W. P. Liao, X. F. Wang, X. W. Wang, H. J. Zhang, and S. Gao, *J. Am. Chem. Soc.*, 2009, **131**, 11650; (d) W. X. Zhang, W. Xue, J. B. Lin, Y. Z. Zheng and X. M. Chen, *CrystEngComm*, 2008, **10**, 1770. and so on.

S6 The checkcif program available at: http://journals.iucr.org/services/cif/checkcif.html.

Crystal data for 1: **$Zn_9Cl_2C_{129.5}H_{113.5}N_{42}O_{8.5}$**, *Mr* = 3053.65; Monoclinic, *C2/c*; *a* = 48.197(10) Å, *b* = 17.145(3) Å, *c* = 27.248(5) Å, *β* = 117.37(3)°; *V* = 19995(7) Å^3; *Z* = 4; D_{calc} = 1.006 g/cm^3; *T* = 298(2) K.; Reflections collected/unique = 83704/17591, R_{int} = 0.1249; *R1* = 0.0647, *wR2* = 0.1609 (I > 2θ(I)); *R1* = 0.1141, *wR2* = 0.1834 (all data) and *GOF* = 1.001.

Crystal data for 2: **{[Zn_9Cl_4(1,4-BDA)$(Me_2BTA)_{12}$]·xG}$_n$** (G = Guest solvents),

$C_{104}H_{100}N_{36}O_4Cl_4Zn_9$, *Mr* = 2648.64; Triclinic, *P*-1; *a* = 14.226(3) Å, *b* = 21.948(4) Å, *c* = 25.055(5) Å, α= 64.25(3) Å, *β* = 74.61(3)°, γ = 71.82(3)°; *V* = 6617(2) $Å^3$; *Z* = 4. The structures of **2** are shown in Fig. S4 and Fig. S5 in the Supporting Information.

Sorption Measurements.

Gas adsorption/desorption measurements were carried out using a Micrometrics ASAP 2020 M volumetric gas adsorption instrument. UHP-grade gases were used in measurements. Before the measurement, the sample of **1** were soaked in pure methanol (CH_3OH) for 3 days to remove DMF and H_2O solvent molecules in the channels, and then filtrated, and activation of the methanol-exchanged **1** at 100 °C under high vacuum (less than 10^{-5}Torr) overnight led to the formation of activated sample **1a**. About 60.3 mg of the desolvated sample were used for the entire adsorption/desorption measurements. The H_2 adsorption/desorption isotherms were collected at 77 K in a liquid nitrogen bath and 87 K in a liquid argon bath. The CO_2, CH_4 and N_2 adsorption/desorption isotherm measurements were carried out at 195 K in a carbon dioxide ice bath, respectively.

Figures in Supporting Information

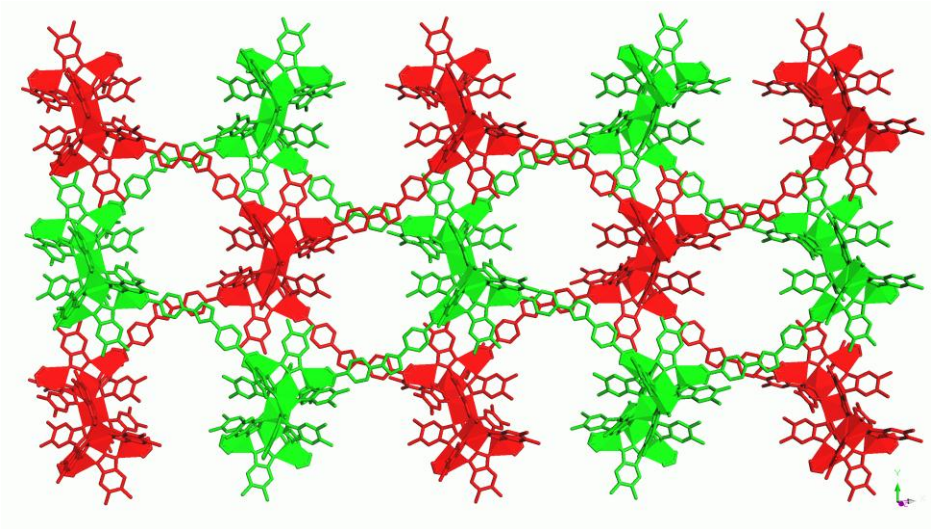

Fig. S1. Two identical sets of 2D layers in **1** are interlocked with each other to form a two-fold interpenetration framework. (All solvent and hydrogen atoms are omitted for clarity).

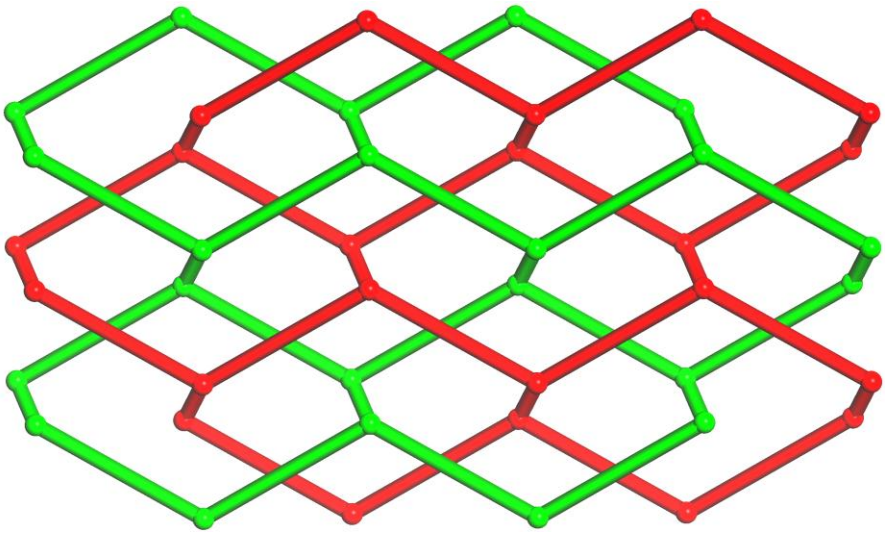

Fig. S2. The simplification network shows two identical sets of 2D layers interlocked with each other to form a two-fold interpenetration topology of **1**. The two colours represent the two sets of 2D layers. The {Zn_9} clusters are abstracted as four-connected roding nodes.

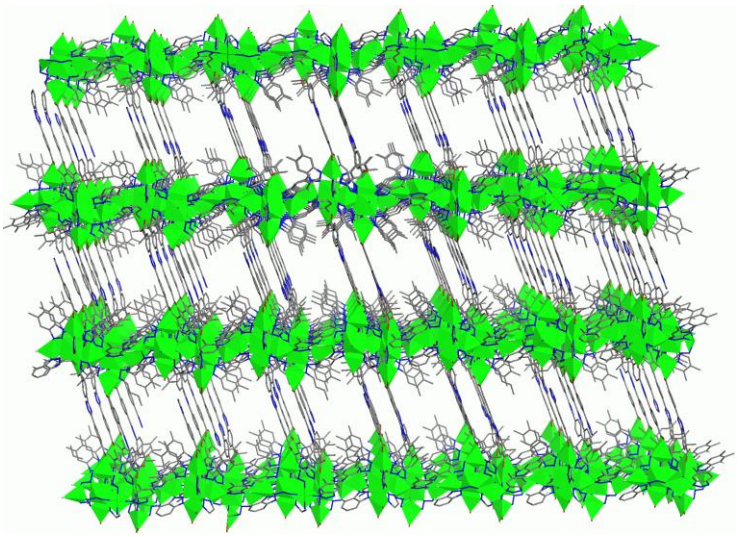

Fig. S3. The 3D packing structure of **1** shows 1D open channel along the *b* axis. (All solvent and hydrogen atoms are omitted for clarity).

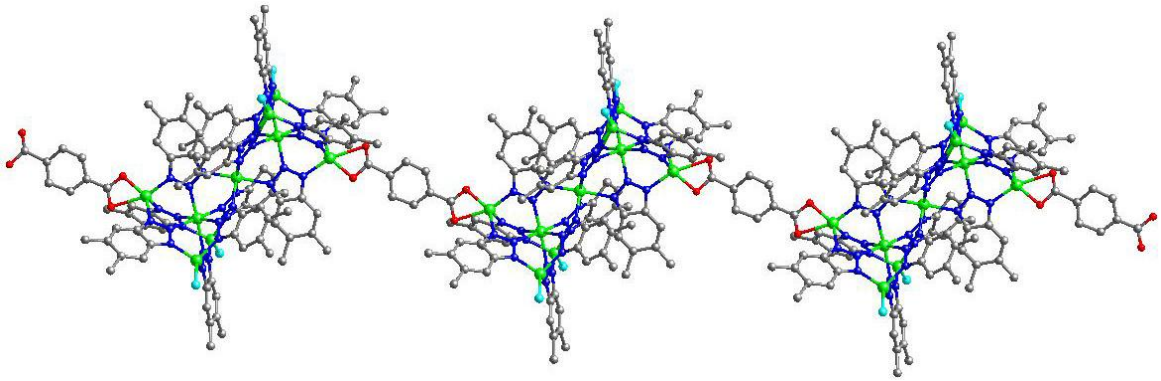

Fig. S4. The 1D chain structure of compound **2**.

(All solvent and hydrogen atoms are omitted for clarity)

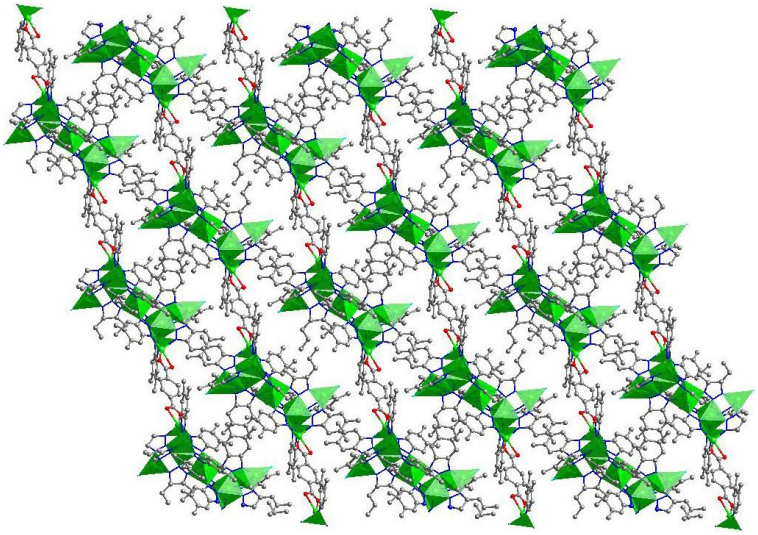

Fig. S5. The 3D packing structure of **2** shows no enough room for more BDA ligands connecting each other in *bc* plane. (All solvent and hydrogen atoms are omitted for clarity).

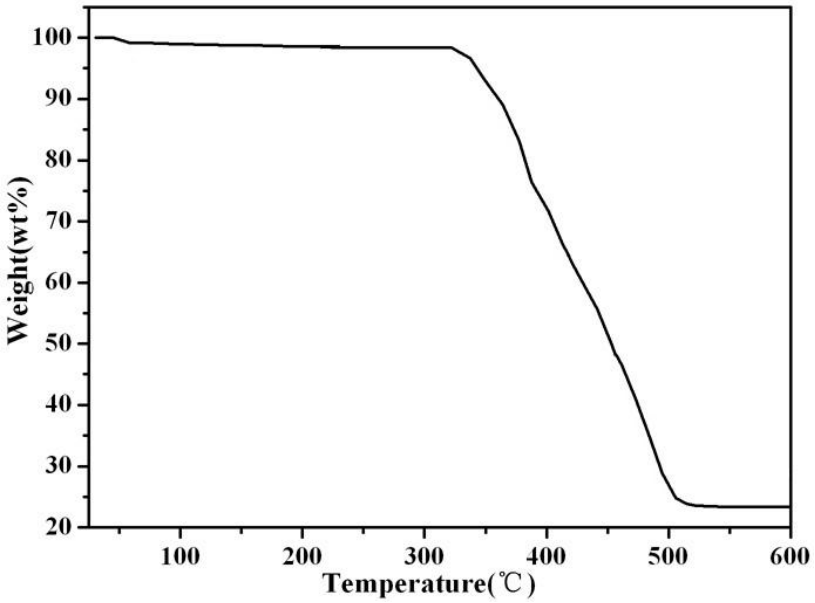

Fig. S6. TG curves of compound **1**.

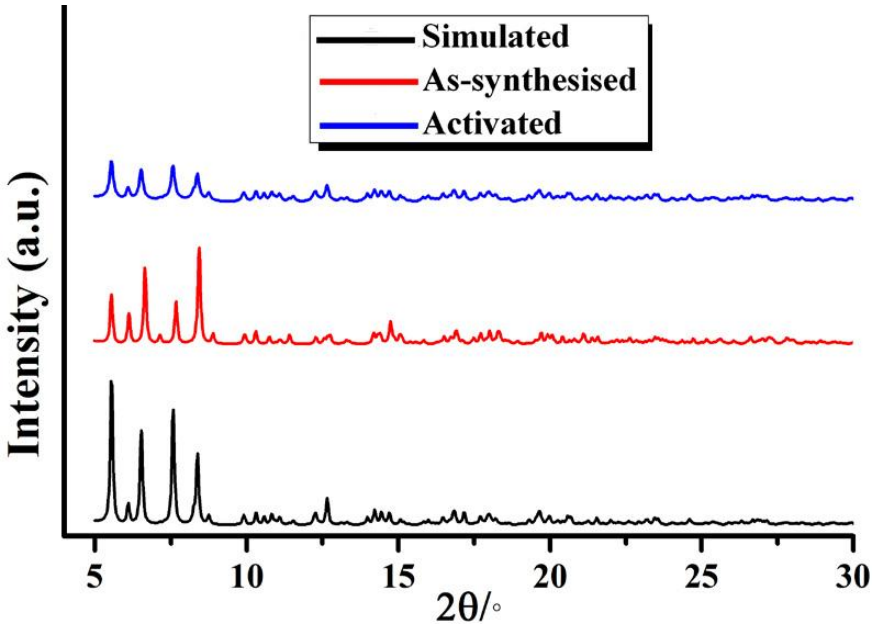

Fig. S7. XRPD patterns for simulated, **1**, and **1a**.

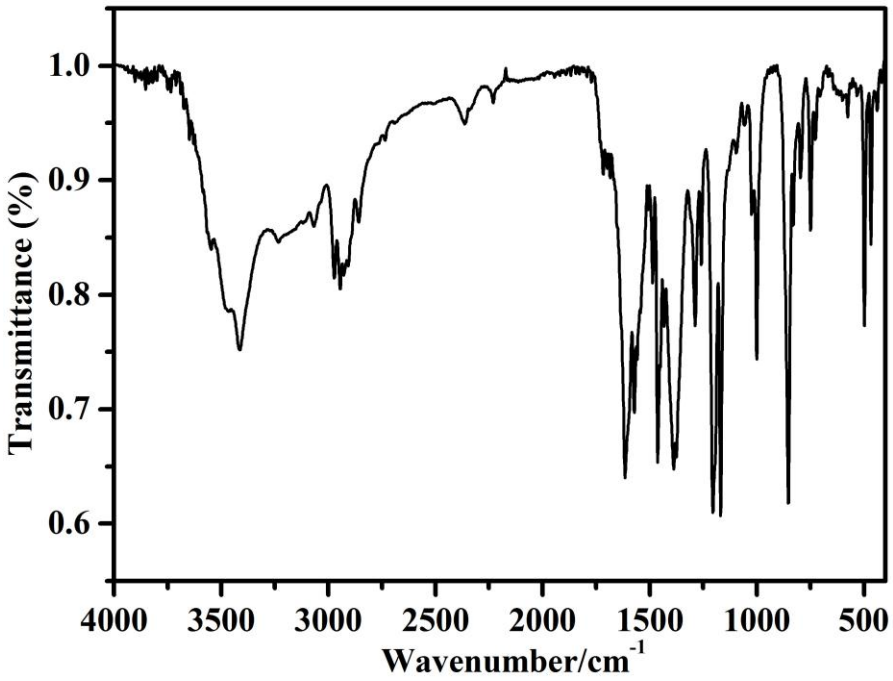

Fig. S8. IR spectra of compound **1**.

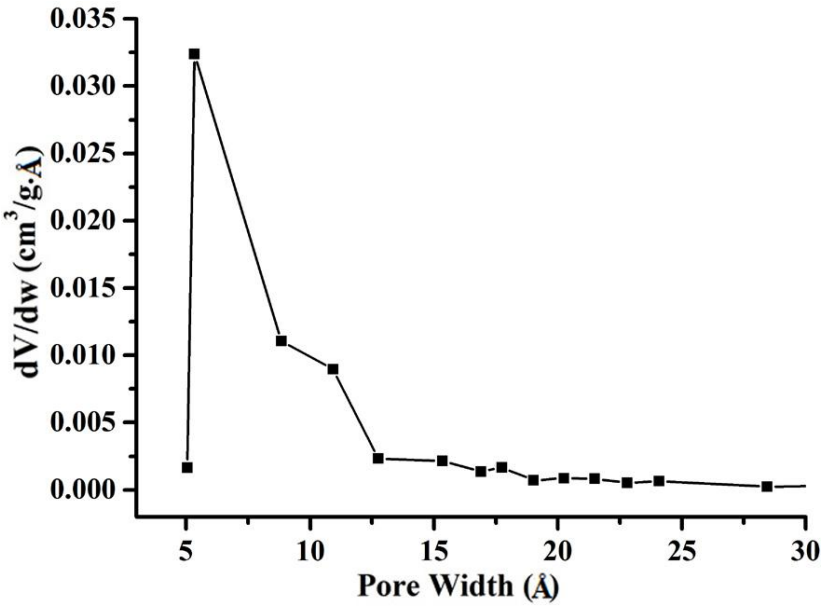

Fig. S9. Pore size distribution of **1a**.

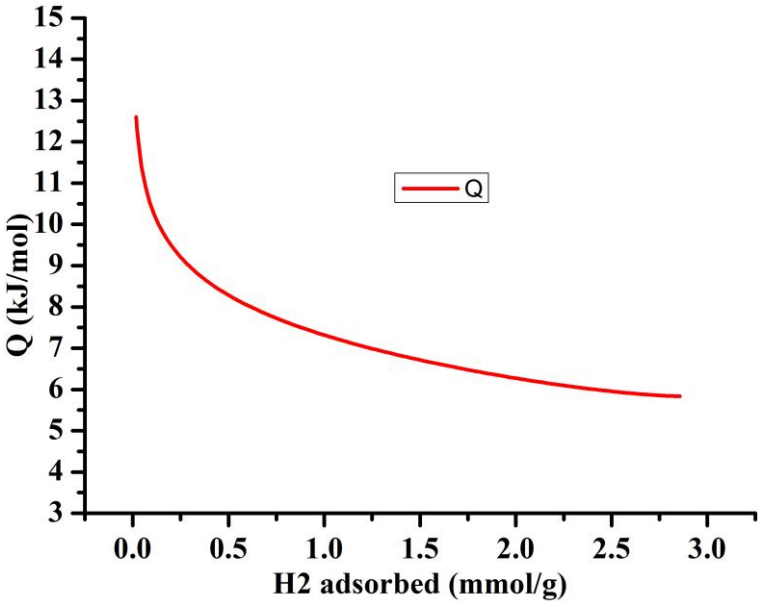

Fig. S10. H_2 adsorption enthalpy for **1** calculated from the H_2 adsorption isotherms at 77 K and 87 K.

Table S1 The selected bond lengths [Å] and angles [º] of compound **1**.

N(1)-Zn(1)	2.043(4)	N(15)-Zn(5)	2.146(4)
N(2)-Zn(4)	2.217(4)	N(16)-Zn(3)	2.010(4)
N(3)-Zn(2)	2.043(4)	N(17)-Zn(4)	2.188(4)
N(4)-Zn(2)	2.032(4)	N(18)-Zn(5)	2.190(4)
N(5)-Zn(4)	2.192(4)	O(1)-Zn(1)	1.976(4)
N(6)-Zn(3)	2.046(4)	O(2)-Zn(1)	2.430(5)
N(7)-Zn(3)	2.016(4)	O(3)-Zn(2)#1	2.011(4)
N(8)-Zn(4)	2.282(5)	O(4)-Zn(2)#1	2.308(4)
N(9)-Zn(1)	2.022(5)	Zn(2)-O(3)#2	2.011(4)
N(10)-Zn(1)	2.022(4)	Zn(2)-O(4)#2	2.308(4)
N(11)-Zn(4)	2.157(4)	Zn(2)-C(64)#2	2.483(6)
N(12)-Zn(5)	2.154(4)	Zn(5)-N(15)#3	2.146(4)
N(13)-Zn(2)	2.010(4)	Zn(5)-N(12)#3	2.154(4)
N(14)-Zn(4)	2.208(4)	Zn(5)-N(18)#3	2.190(4)
Cl(1)-Zn(3)	2.256(18)	Cl(2)-Zn(3)	2.02(2)
Cl(3)-Zn(3)	2.669(14)		
O(1)-Zn(1)-N(10)	124.11(18)	N(4)-Zn(2)-O(4)#2	96.38(18)
O(1)-Zn(1)-N(9)	127.4(2)	N(3)-Zn(2)-O(4)#2	159.28(17)
N(10)-Zn(1)-N(9)	100.56(18)	N(16)-Zn(3)-N(7)	100.37(18)
O(1)-Zn(1)-N(1)	100.57(18)	N(16)-Zn(3)-Cl(2)	124.2(11)
N(10)-Zn(1)-N(1)	99.84(17)	N(7)-Zn(3)-Cl(2)	121.8(10)
N(9)-Zn(1)-N(1)	97.20(19)	N(16)-Zn(3)-N(6)	98.95(18)
O(1)-Zn(1)-O(2)	57.72(17)	N(7)-Zn(3)-N(6)	99.40(18)
N(10)-Zn(1)-O(2)	94.99(17)	Cl(2)-Zn(3)-N(6)	107.4(9)
N(9)-Zn(1)-O(2)	95.65(19)	N(16)-Zn(3)-Cl(1)	119.7(6)
N(1)-Zn(1)-O(2)	158.21(17)	N(7)-Zn(3)-Cl(1)	114.7(5)
N(13)-Zn(2)-O(3)#2	137.55(19)	Cl(2)-Zn(3)-Cl(1)	12.8(13)
N(13)-Zn(2)-N(4)	104.60(18)	N(6)-Zn(3)-Cl(1)	120.0(5)
O(3)#2-Zn(2)-N(4)	111.63(19)	N(16)-Zn(3)-Cl(3)	99.7(3)
N(13)-Zn(2)-N(3)	95.87(17)	N(7)-Zn(3)-Cl(3)	96.7(3)
O(3)#2-Zn(2)-N(3)	100.53(19)	Cl(2)-Zn(3)-Cl(3)	45.3(9)
N(4)-Zn(2)-N(3)	97.41(18)	N(6)-Zn(3)-Cl(3)	152.6(3)
N(13)-Zn(2)-O(4)#2	95.53(17)	Cl(1)-Zn(3)-Cl(3)	32.6(6)
O(3)#2-Zn(2)-O(4)#2	59.84(18)	N(11)-Zn(4)-N(17)	92.11(15)

N(14)-Zn(4)-N(2)	89.30(16)	N(11)-Zn(4)-N(5)	177.16(16)
N(11)-Zn(4)-N(8)	88.87(16)	N(17)-Zn(4)-N(5)	87.49(15)
N(17)-Zn(4)-N(8)	91.41(16)	N(11)-Zn(4)-N(14)	91.47(16)
N(5)-Zn(4)-N(8)	88.33(16)	N(17)-Zn(4)-N(14)	91.27(16)
N(14)-Zn(4)-N(8)	177.29(16)	N(5)-Zn(4)-N(14)	91.35(16)
N(2)-Zn(4)-N(8)	88.01(16)	N(11)-Zn(4)-N(2)	89.95(15)
N(15)-Zn(5)-N(15)#3	180.00(16)	N(17)-Zn(4)-N(2)	177.84(16)
N(15)-Zn(5)-N(12)	92.93(16)	N(5)-Zn(4)-N(2)	90.42(16)
N(15)#3-Zn(5)-N(12)	87.07(16)	N(12)#3-Zn(5)-N(18)	87.14(16)
N(15)-Zn(5)-N(12)#3	87.07(16)	N(15)-Zn(5)-N(18)#3	88.64(16)
N(15)#3-Zn(5)-N(12)#3	92.93(16)	N(15)#3-Zn(5)-N(18)#3	91.36(16)
N(12)-Zn(5)-N(12)#3	180.0(3)	N(12)-Zn(5)-N(18)#3	87.14(16)
N(15)-Zn(5)-N(18)	91.36(16)	N(12)#3-Zn(5)-N(18)#3	92.86(16)
N(15)#3-Zn(5)-N(18)	88.64(16)	N(18)-Zn(5)-N(18)#3	180.0(2)
N(12)-Zn(5)-N(18)	92.86(16)		

Symmetry transformations used to generate equivalent atoms: #1: x+1/2, -y+1/2, z+1/2; #2: x-1/2, -y+1/2, z-1/2; #3: -x+1/2, -y+3/2, -z+1.