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Electronic Supplementary Information

Benzene Absorption in a Protuberant-Grid-Type Zinc(II)−Organic Framework Triggered by the Migration of Guest Water Molecules

Tien-Wen Tseng,*[a] Tzuoo-Tsair Luo,[b] Chang-Hsiu Tsai,[ab] Chun-Chi Chen,[b] Gene-Hsiang Lee,[c] Chih-Chieh Wang,*[d] and Kuang-Lieh Lu*[b]

[a] Department of Chemical Engineering, National Taipei University of Technology, Taipei 106, Taiwan
Fax: +886-2-2731-7117; E-mail: f10403@ntut.edu.tw

[b] Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan. Fax: +886-2-27831237;
E-mail: kuanglieh@gmail.com

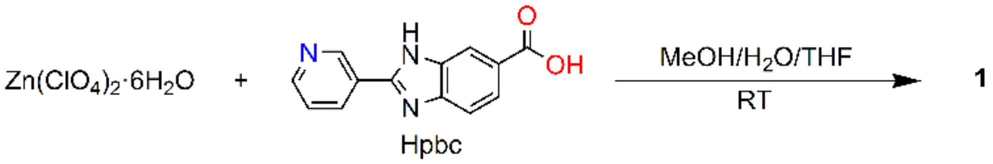
[c] Instrumentation Center, National Taiwan University, Taipei 106, Taiwan

[d] Department of Chemistry, Soochow University, Taipei 100, Taiwan

1. Experimental Section

Materials and Physical Techniques

The reagents and solvents were commercially available and were used as received without further purification. IR spectra were recorded in the range of 4000−450 cm^{-1} on a Perkin-Elmer Paragon 100 FT-IR spectrometer using the KBr disc technique. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Thermogravimetric analysis (TGA) for the single phase polycrystalline sample was performed on a Perkin-Elmer TGA-7 analyzer under N_2 atmosphere, in the temperature range of 30−800 °C at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were recorded on a Phillips X'Pert Pro diffractometer operating at a voltage of 40 kV and a current of 30 mA with Cu-Kα radiation (λ = 1.5406 Å). The 2-(3'-Pyridineyl)-benzimidazole-5-carboxylic acid (Hpbc) ligand was synthesized according to literature methods[1] and checked by ^{1}H-NMR and Mass spectroscopy.



Scheme S1. Synthesis of compound $\{[Zn(pbc)_2]\cdot 2CH_3OH\cdot 6H_2O\}_n$ (**1**).

Syntheses of Compounds 1 3

Synthesis of $\{[Zn(pbc)_2]\cdot 2CH_3OH\cdot 6H_2O\}_n$ (1). A solution of $Zn(ClO_4)_2\cdot 6H_2O$ (37.2 mg, 0.10 mmol) in MeOH (5 mL) was carefully layered on top of a bilayer solution comprised of an aqueous solution of 2-(3'-pyridineyl)-benzimidazole-5-carboxylic acid (Hpbc, 48.6 mg, 0.20 mmol) on the bottom and a buffer solvent of THF (10 mL) on the top. ***Caution***: *perchlorate salts are potentially explosive and should be handled with care.* The system was allowed to stand at room temperature for two weeks, whereupon yellow plate-shaped crystals of **1** were produced (yield: 41.0 mg, 0.057 mmol, 57.4% based on $Zn(ClO_4)_2\cdot 6H_2O$). The solid product was washed with deionized water and MeOH, and dried in air. Elemental analysis calcd (%) for **1**, $C_{56}H_{72}N_{12}O_{24}Zn_2$: C, 47.10; H, 5.08; N, 11.77; found: C, 47.14; H, 4.34; N, 12.33. IR (KBr pellet): 3093 (m), 1599 (m), 1559 (s), 1491 (m), 1372 (vs), 1199 (m), 1127 (m), 1060 (m), 818 (m), 786 (m), 694 (s) cm^{-1}.

Synthesis of compounds {[Zn(pbc)$_2$]·C_6H_6·0.5CH_3OH·7.5H_2O}$_n$ (2) and {[Zn(pbc)$_2$]·0.5C_7H_8·0.5CH_3OH·6.5H_2O}$_n$ (3). When yellow crystals of **1** were immersed in benzene or toluene, respectively, for three days at room temperature, the colour of the crystals changed to light-yellow. Upon the immersion treatment, compounds **2** and **3** were prepared and collected merely by simple filtration, and dried in air. The obtained compounds, formulated as {[Zn(pbc)$_2$]·C_6H_6·0.5CH_3OH·7.5H_2O}$_n$ (**2**) or {[Zn(pbc)$_2$]·0.5C_7H_8·0.5CH_3OH·6.5H_2O}$_n$ (**3**), respectively. IR of **2** (KBr pellet): 3095 (m), 1599 (s), 1558 (s), 1484 (m), 1456(m), 1372 (vs), 1198 (m), 1127 (m), 1059 (m), 818 (m), 782 (s), 695 (s) cm^{-1}. IR of **3** (KBr pellet): ν = 3094 (m), 1600 (s), 1558 (s), 1491 (m), 1456 (m), 1372 (vs), 1198 (m), 1127 (m), 1060 (w), 819 (m), 782 (m), 694 (s) cm^{-1}.

Crystallographic Data Collection and Refinement. The suitable single crystals of compounds **1**−**3** were mounted on the tip of a glass fibre and placed onto the goniometer head for indexing and intensity data collection using a Bruker SMART CCD diffractometer with a graphite-monochromatic Mo K_α radiation (λ = 0.71073 Å). The raw frame data for **1** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects with the Denzo program.[2] An empirical absorption correction was applied by using the Multi scan method. The structure of **1** was solved by direct methods and refined against F^2 by the full-matrix least-squares technique, using the WINGX,[3] PLATON,[4] and SHELX[5] software packages. The hydrogen atoms were calculated and refined as a riding model. The hydrogen atoms on the nitrogen atoms of the ligand pbc$^-$ group were found in the difference Fourier map but were placed in the calculated position and refined as a riding model. On the other hand, the water and benzene molecules of **2** have been subjected to anisotropic refinement (using the constraint "AFIX 66" on the benzene ring). The hydrogen atoms of partial solvated water molecules as well as those of the methanol molecules in the crystal lattice cannot be located from the difference Fourier map because of the severe disorders. An attempt to add hydrogen atoms was not successful. Some minor residual electrons have been assigned to the oxygen atoms of water molecules, but easily diverge after isotropic refinement. The toluene, methanol and some water molecules of **3** have been subjected to anisotropic refinement. Crystal data and structure refinement data for **1**–**3** are summarized in Table S1, and the selected bond lengths and angles are listed in Table S2. CCDC 1010281 (**1**), 1010282 (**2**), and 1010283 (**3**) 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.

References

1. M. H. Jung, J. M. Park, I. Y. C. Lee and M. Ahn, *J. Heterocycl. Chem.*, 2003, **40**, 37−44.
2. Z. Otwinowski, W. Minor, "*Processing of X-ray Diffraction Data Collected in Oscillation Mode*", *Methods in Enzymology*, *Macromolecular Crystallography, part A*, 1997, **276**, 307–326.
3. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
4. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
5. G. M. Sheldrick, *A Short History of SHELX*, *Acta Cryst.*, 2008, **A64**, 112.

2. Figs. S1–S21

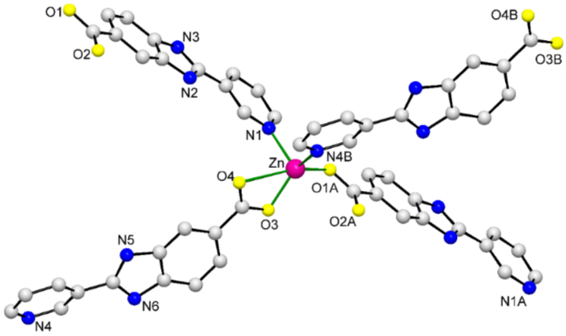


Fig. S1 The coordination environment of the Zn atom in **1**. Hydrogen atoms were omitted for clarity.

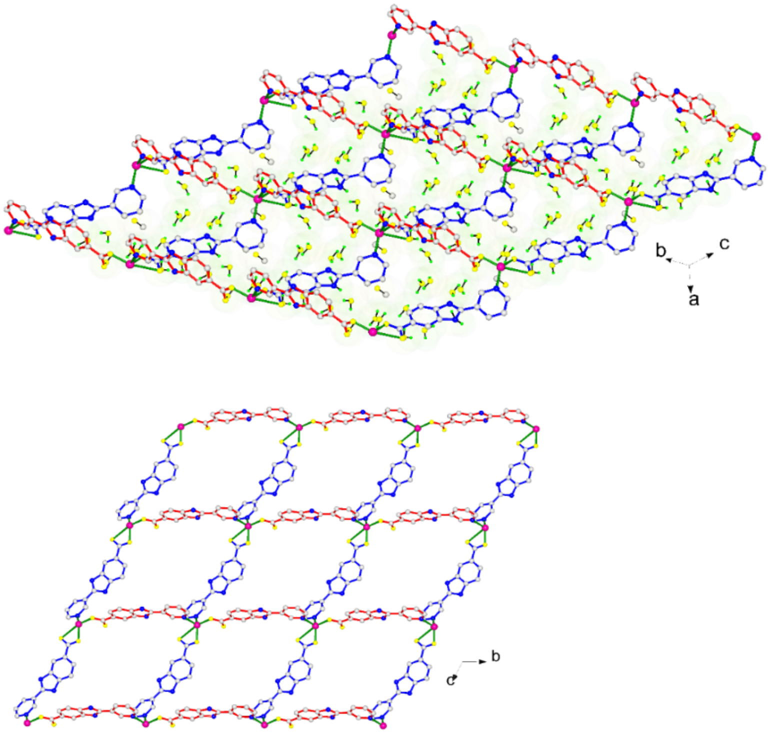


Fig. S2 A perspective view showed a 2D protuberant-grid-type network of **1** (up). Showing a 2D network with a (4,4)-**sql** topology (down).

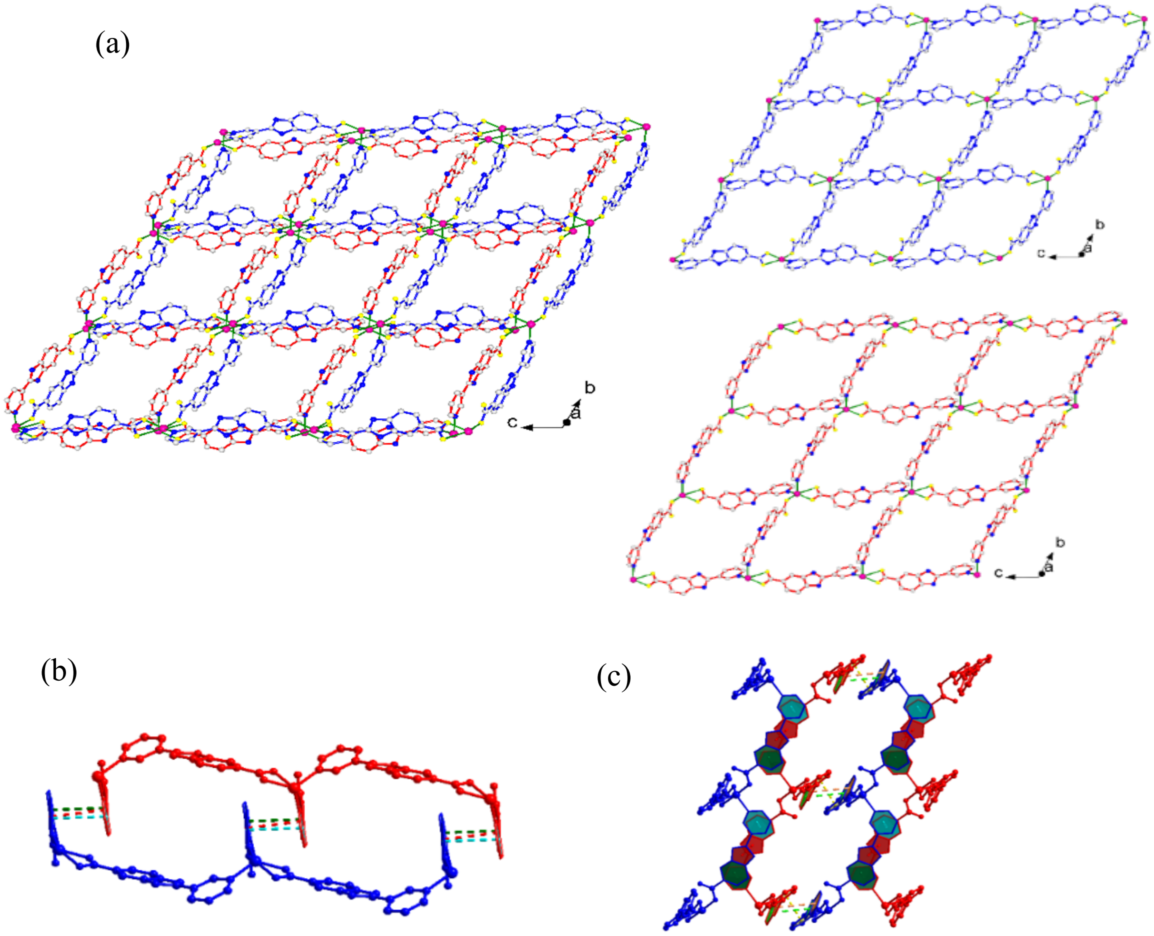


Fig. S3 (a) A view of an interdigitated bilayer (left); the twisted pbc$^-$ ligands feature Λ (up) and Δ (down) comformations. (b) A view of the π–π interactions (face-to-face) between the planar pbc$^-$ ligands in **1** along the *b* axis. (c) Showing the π–π interactions (face-to-face) between the nonplanar pbc$^-$ ligands view along the *c* axis.

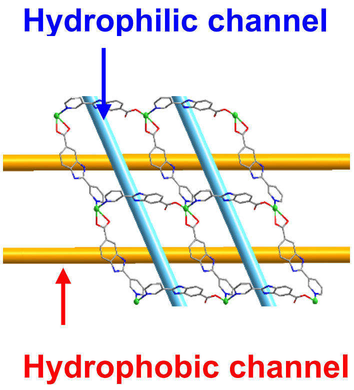


Fig. S4 A perspective view showing the hydrophilic channels and hydrophobic channels that are present in the bilayer structure of **1** along the *b* axis.

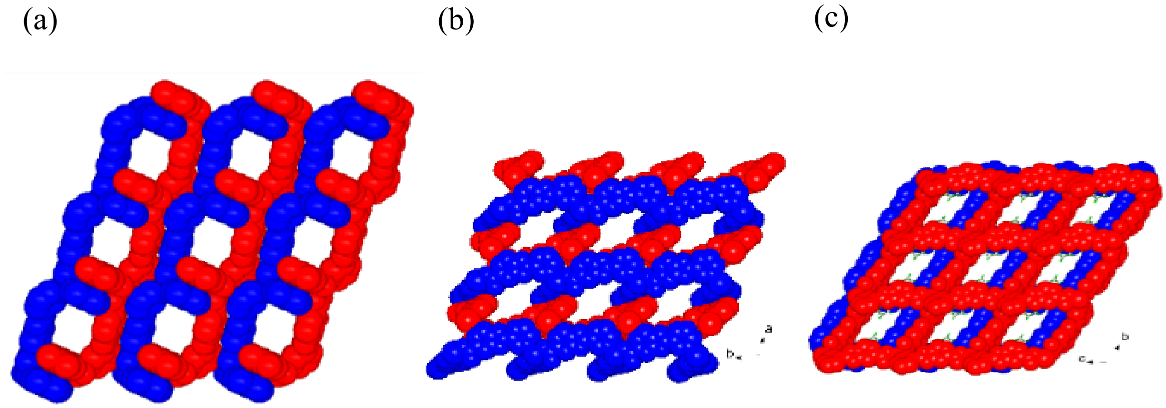


Fig. S5 The intersecting

channel system

ng the *c* axis.

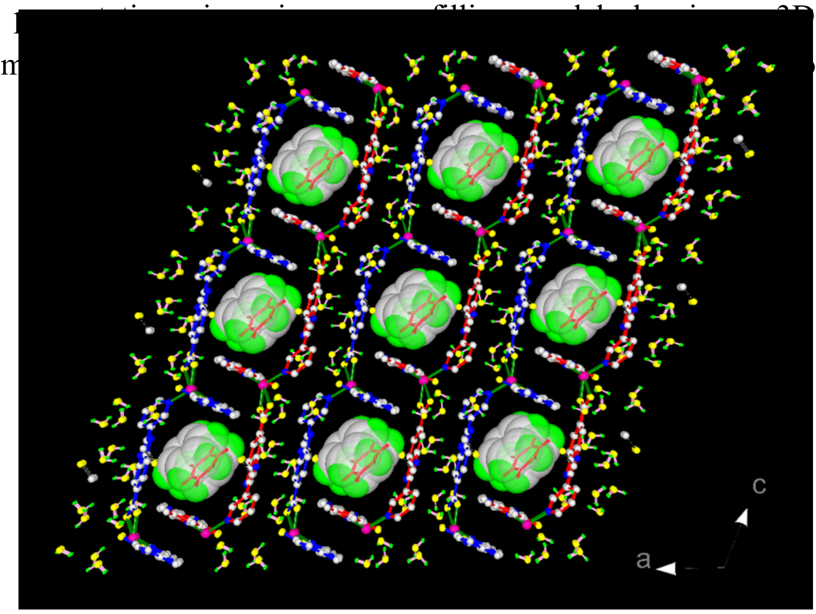


Fig. S6 A view of interlayer in **2** that was filled with methanol and guest water aggregates and the included benzene molecules located in the bilayer in the space-filling model along the *b* axis.

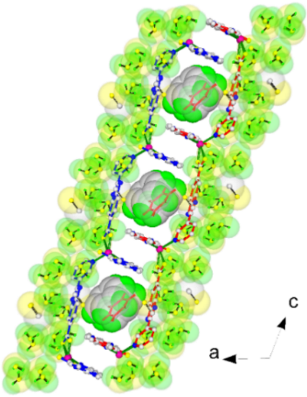


Fig. hydrophobic

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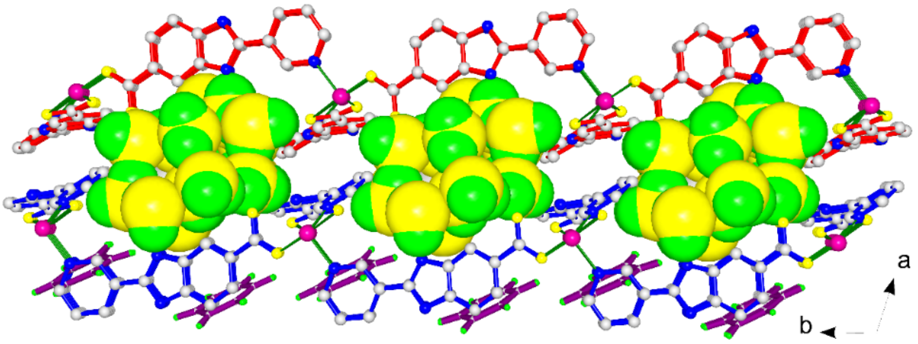

Fig. S8 Top view of the water channels in **2**.

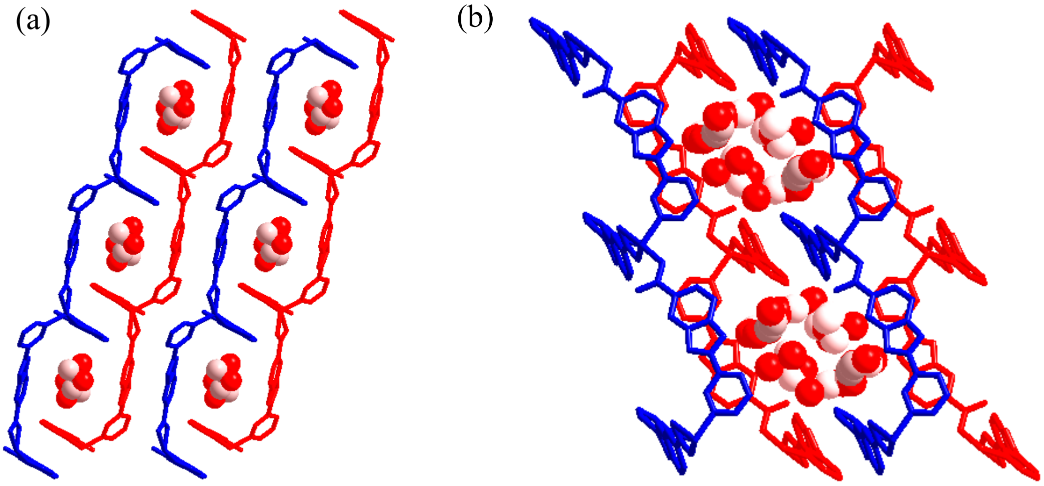

Fig. S9 Crystal str hydrophobic channels, and (b) hy

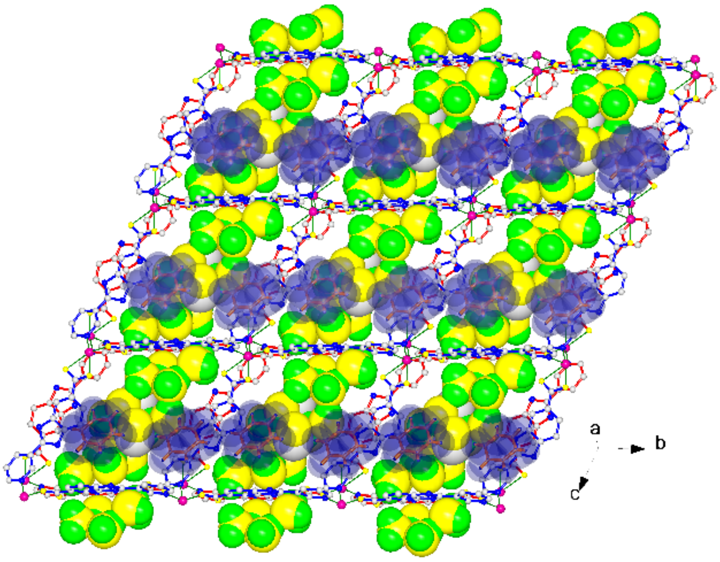

Fig. S10 A perspective view of self-assembled arrays of the benzene molecules (as highlighted in blue color), as well as the guest methanol molecules and water aggregates (O in yellow and H in green) in **2**.

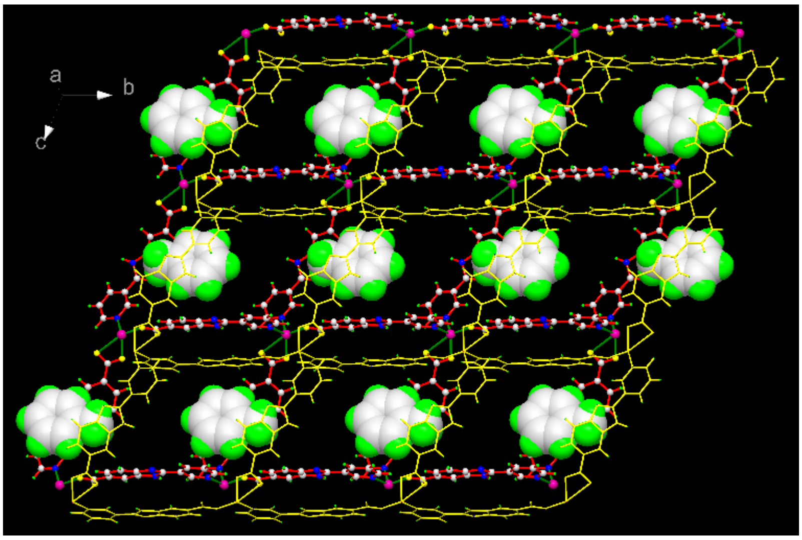

Fig. S11 An illustration of 1D arrays of toluene molecules that are encapsulated within the hydrophobic channels of compound **3**.

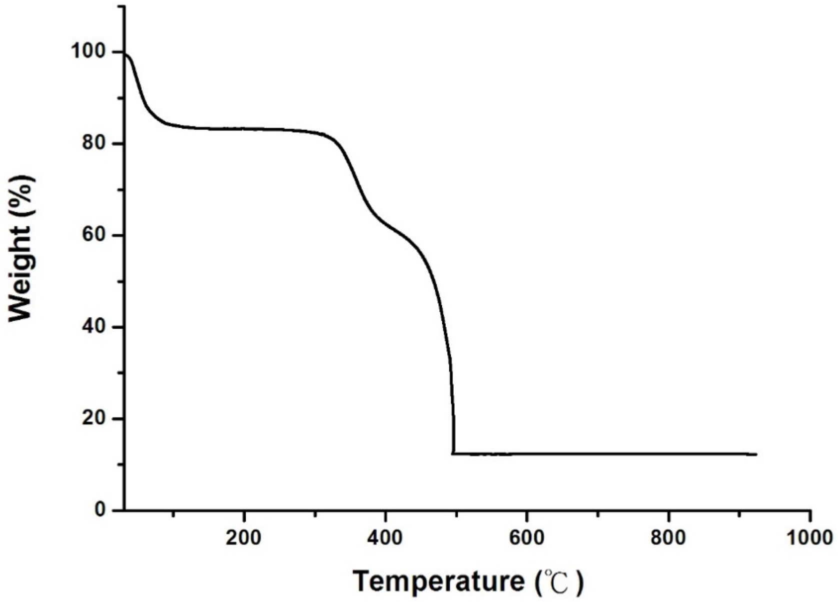

Fig. S12 The TGA diagram of compound **1**.

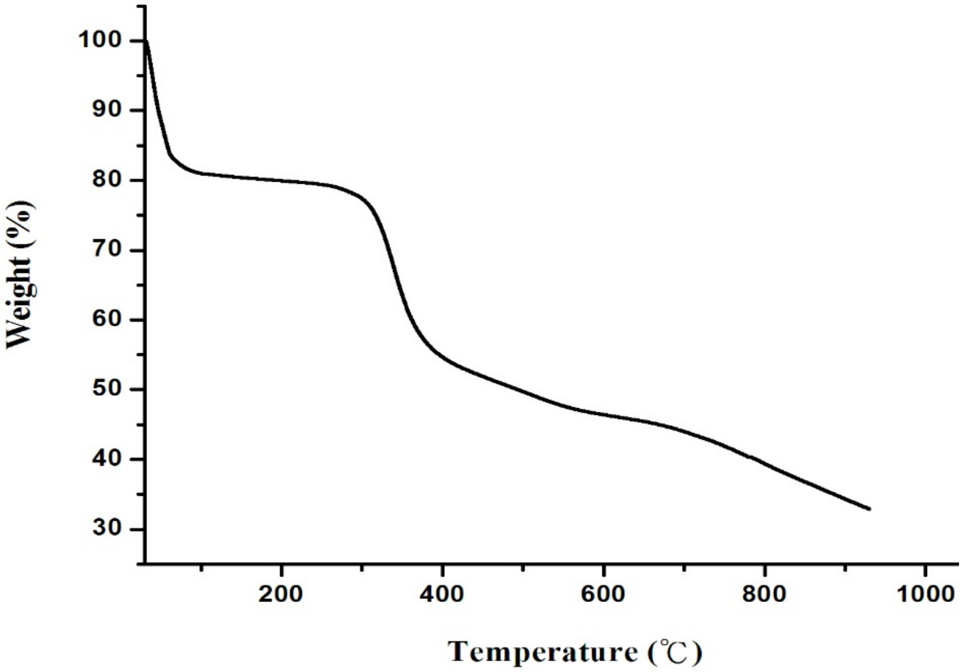

Fig. S13 The TGA diagram of compound **2**.

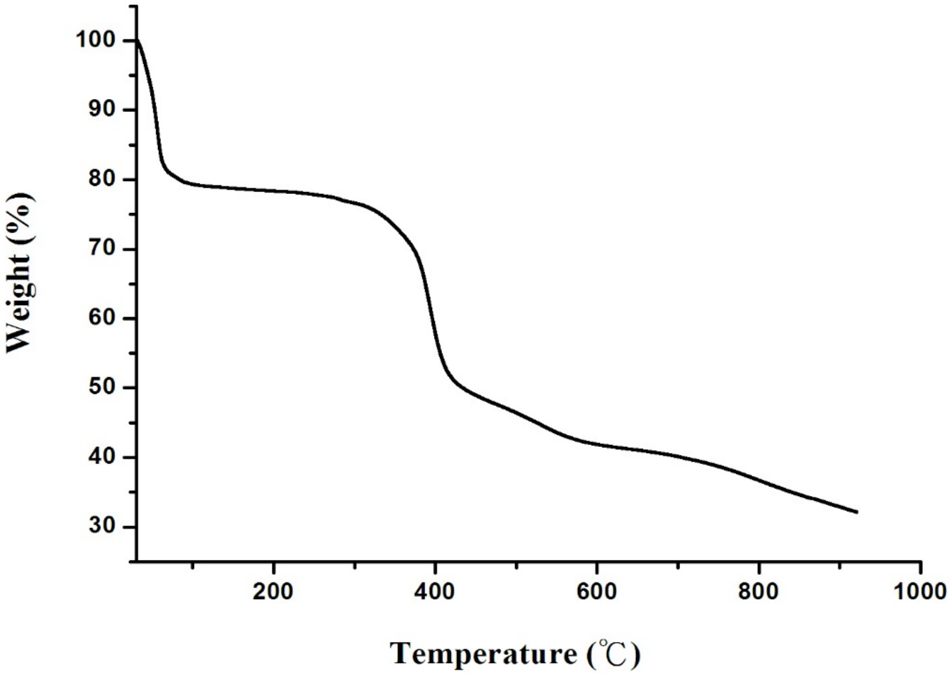

Fig. S14 The TGA diagram of compound **3**.

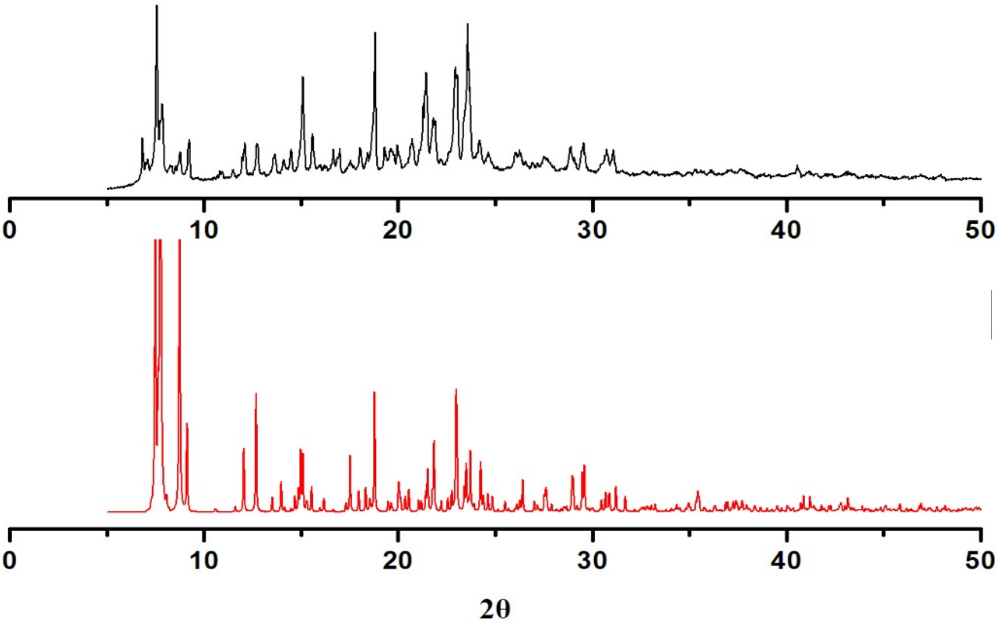

Fig. S15 The PXRD patterns of compound **1** (black, as-synthesized; red, simulated).

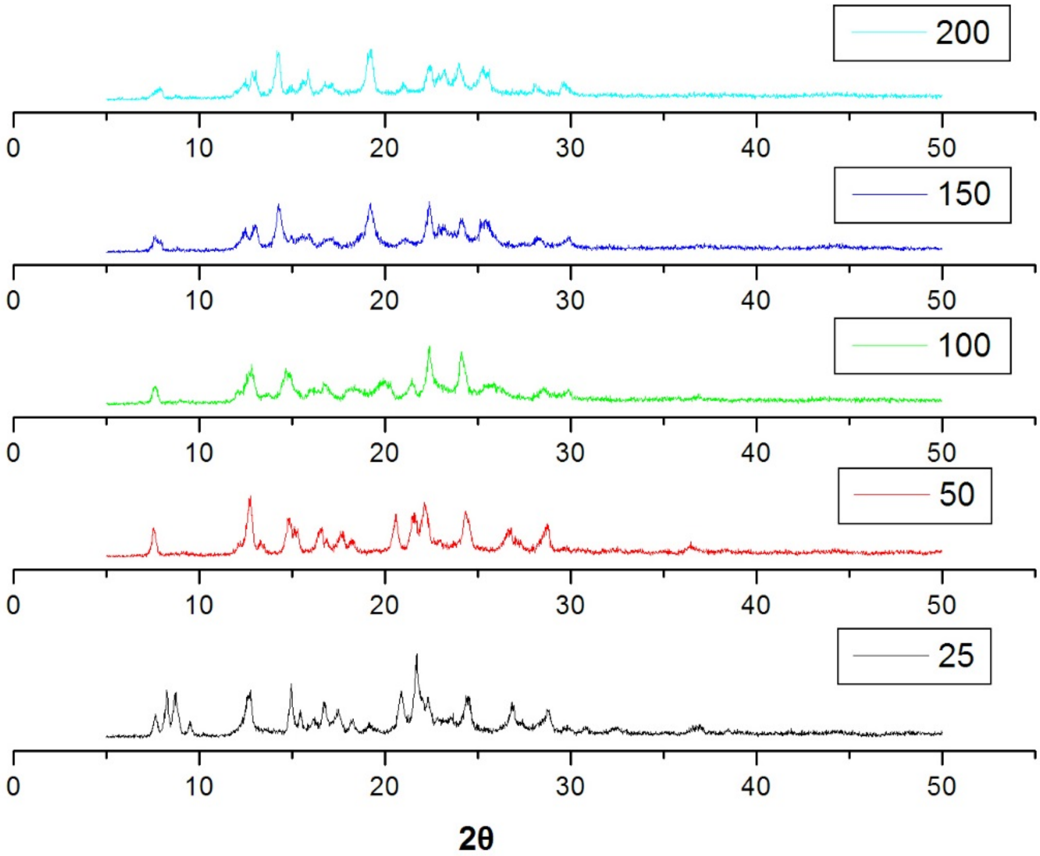

Fig. S16 The PXRD patterns of variable temperatures (°C) dependence for compound **1**.

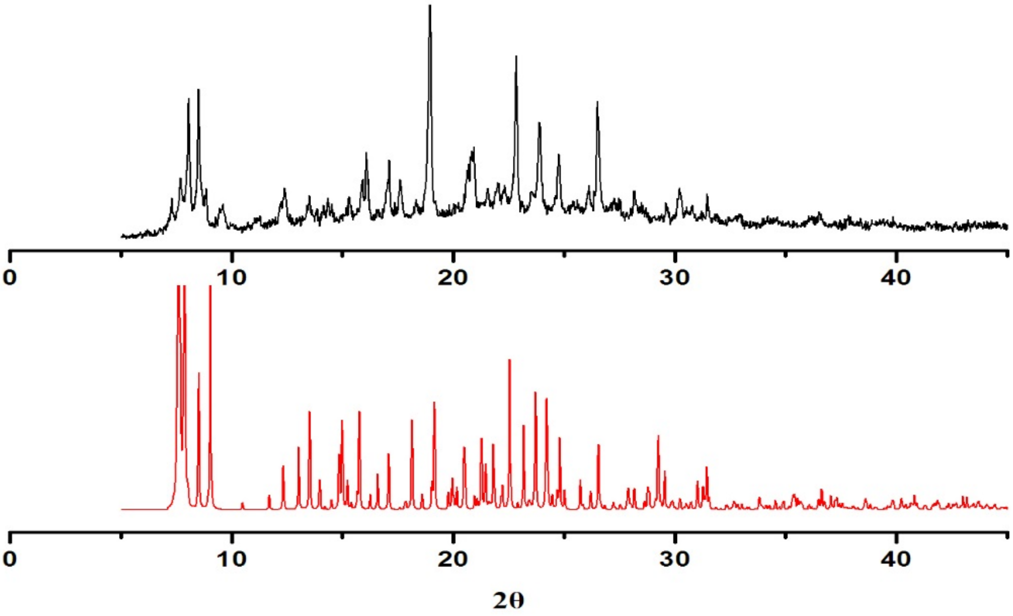

Fig. S17 The PXRD patterns of compound **2** (black, as-synthesized; red, simulated).

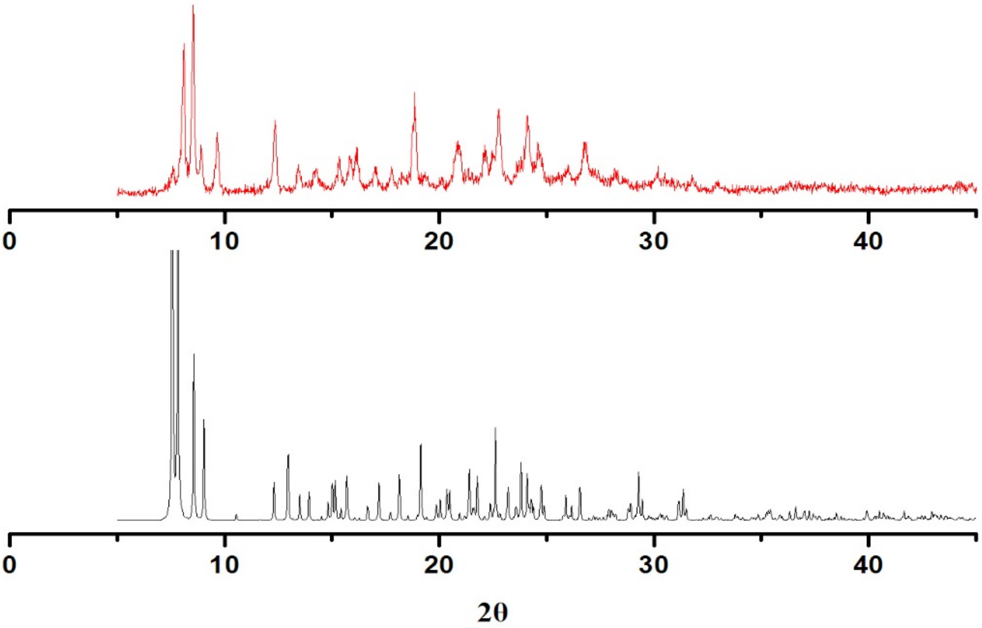

Fig. S18 The PXRD patterns of compound **3** (black, simulated; red, as-synthesized).

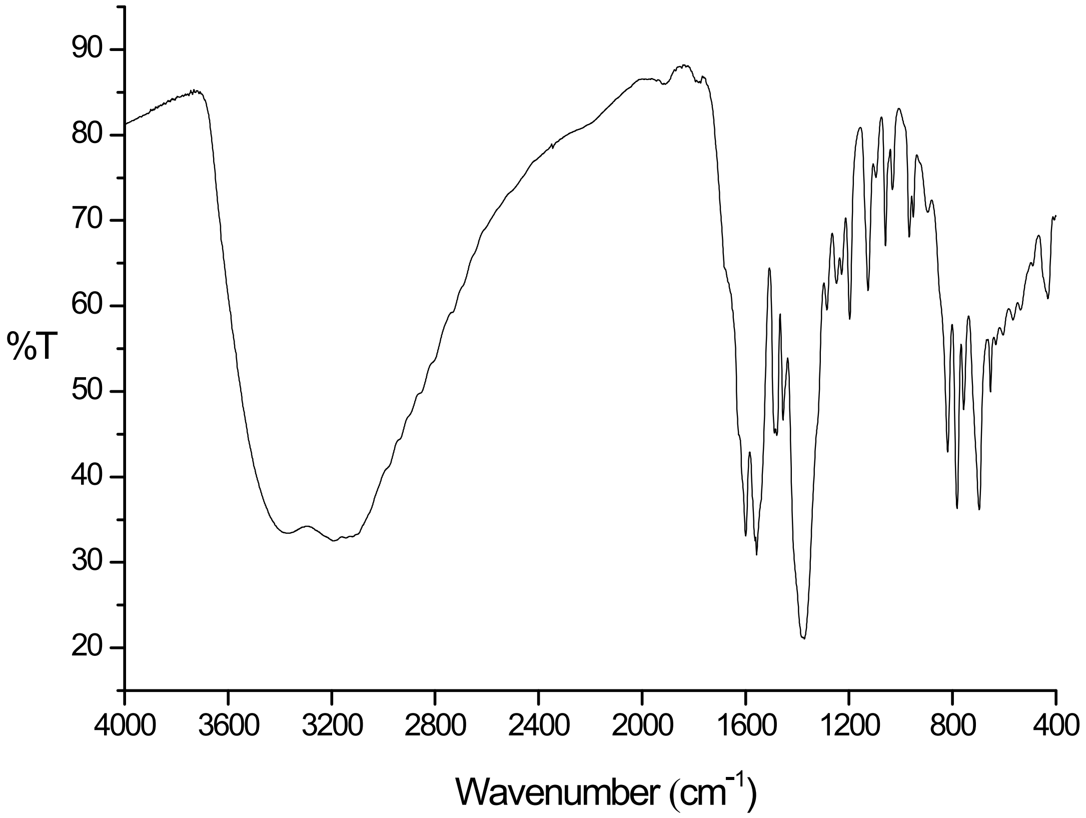

Fig. S19 The IR spectrum of **1**.

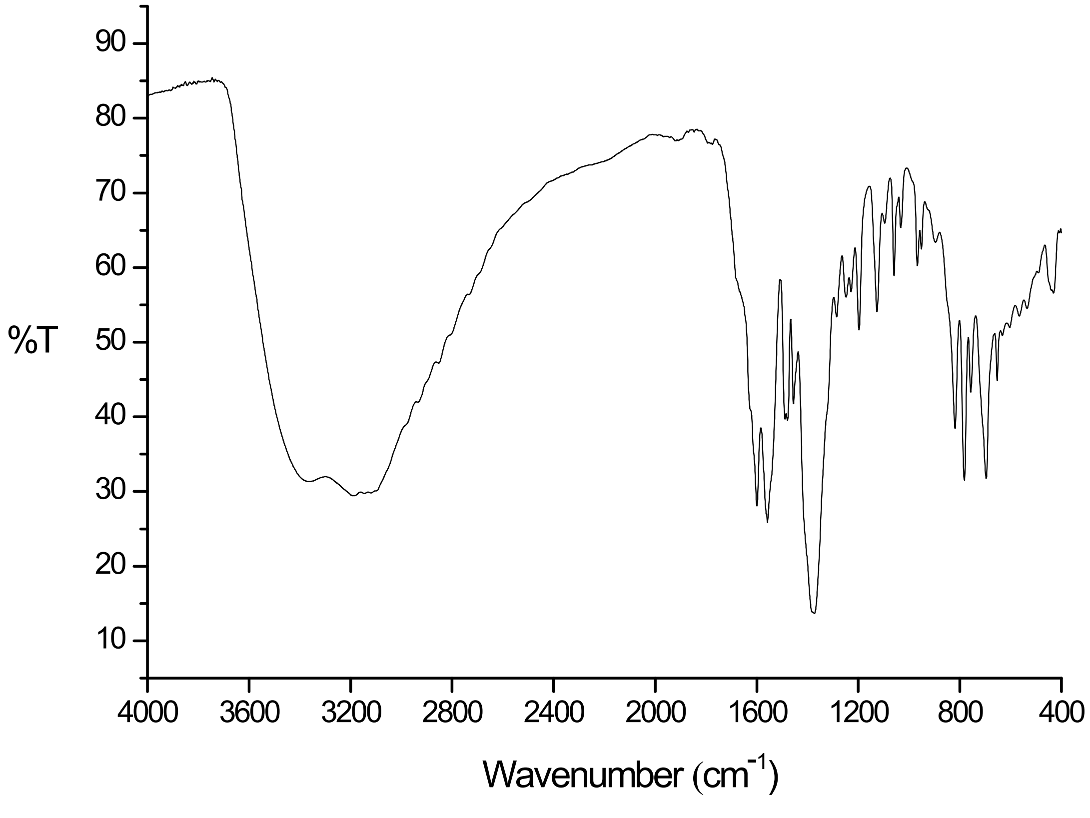

Fig. S20 The IR spectrum of **2**.

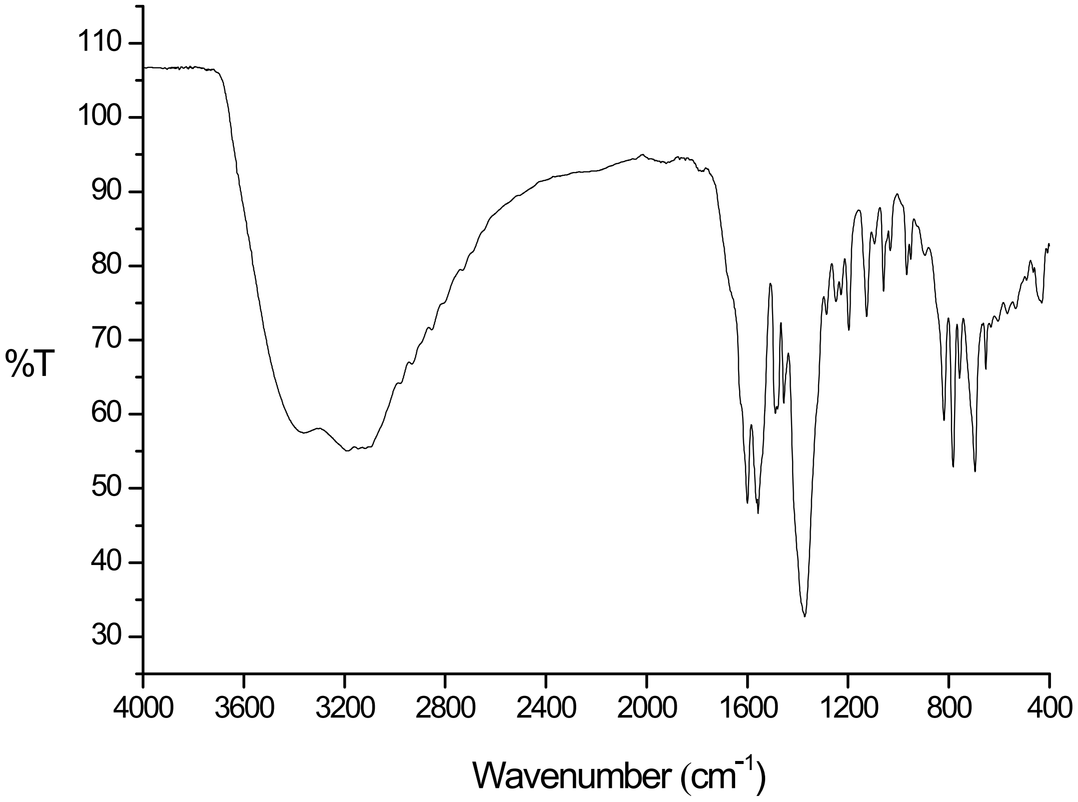

Fig. S21 The IR spectrum of **3**.

Table S1 Crystal data and refinement details for compounds **1**, **2**, and **3**

compound	**1**	**2**	**3**
chemical formula	$C_{56}H_{72}N_{12}O_{24}Zn_2$	$C_{65}H_{76}N_{12}O_{23}Zn_2$	$C_{60}H_{70}N_{12}O_{22}Zn_2$
formula mass	1428.02	1536.08	1442.02
crystal syst.	Triclinic	Triclinic	Triclinic
space group	$P\,-1$	$P\,-1$	$P\,-1$
a (Å)	12.4693(7)	12.5650(8)	12.4881(8)
b (Å)	13.2851(7)	13.2721(9)	13.2558(8)
c (Å)	13.1755(7)	13.2881(9)	13.2738(8)
α (deg)	112.301(1)	111.9938(14)	112.0191(15)
β (deg)	105.397(1)	107.5534(14)	107.4532(15)
γ (deg)	97.728(1)	97.9667(15)	98.2194(16)
V (Å^3)	1878.0(2)	1878.1(2)	1860.5(2)
Z	1	1	1
ρ_{calc}/g cm^{-3}	1.260	1.358	1.287
μ (mm^{-1})	0.718	0.720	0.720
T/K	150(2)	150(2)	150(2)
2θ range (deg)	3.56–55.0	3.54–55.0	3.58–55.0
total no. of data collected	24255	22071	24382
$R_{(sigma)}$	0.0613	0.0693	0.0655
no. of unique data collected	8587	8591	8536
no. of obsd data ($I > 2\sigma(I)$)	7105	6474	6662
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0870, 0.2423	0.0768, 0.2112	0.0710, 0.1987
R_1,[a] wR_2[b] (all data)	0.1023, 0.2544	0.1007, 0.2267	0.0908, 0.2117
no. of variable	420	466	473
GOF	1.104	1.059	1.099

[a] $R_1(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, [b] $wR_2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Bond lengths (Å) and angles (°) around the Zn(II) ion in **1**, **2**, and **3**[a]

	1	**2**	**3**
Zn–O(1)$_{\mathrm{i}}$	1.966(3)	1.957(3)	1.958(3)
Zn–O(3)	1.953(3)	1.958(4)	1.951(3)
Zn–N(4)$_{\mathrm{ii}}$	2.025(4)	2.024(4)	2.021(4)
Zn–N(1)	2.063(4)	2.069(5)	2.065(4)
O(1)$_{\mathrm{i}}$–Zn–O(3)	108.0(1)	107.3(2)	107.2(1)
O(1)$_{\mathrm{i}}$–Zn–N(4)$_{\mathrm{ii}}$	107.1(1)	107.9(2)	107.9(1)
O(3)–Zn–N(4)$_{\mathrm{ii}}$	125.2(1)	125.2(1)	127.7(1)
O(1)$_{\mathrm{i}}$–Zn–N(1)	95.9(1)	96.0(2)	96.0(1)
O(3)–Zn–N(1)	111.9(1)	109.4(2)	109.6(1)
N(4)$_{\mathrm{ii}}$–Zn–N(1)	104.7(1)	104.8(2)	103.9(1)

[a] Symmetry transformations used to generate equivalent atoms: i x, y - 1, z; ii x, y, z+1.