Supporting Information

General Information. Commercially available reagents were used as received without further purification. Elemental analyses (C, H, N) were performed with a PerkinElmer 240 elemental analyzer. Thermal gravimetric analysis (TGA) was performed under N_2 on a PerkinElmer TGA 7 instrument.

Synthesis of complex 1. 4,5-dicyanoimidazole (5 mg, 0.04 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (15 mg, 0.05 mmol), 4,4'-bipy (2.5 mg, 0.02 mmol) and tetrabutylammonium bromide (1 mg, 0.003 mmol) were dissolved in H_2O/dmf (v/v = 2:1, 1.5 mL) and sealed in a glass tube, slowly heated to 150℃ from room temperature in 5 hrs, kept at 150℃ for 3 days. The colourless crystals were obtained (yield：50%). Elemental analysis calcd (%) for **1**: C 27.79, H 2.33, N 13.65; found: C 28.15, H 2.94, N 12.59 %.

Synthesis of complex 2. A mixture of 4,5-dicyanoimidazole (5 mg, 0.04 mmol), $ZnCl_2$ (20 mg, 0.15 mmol) and NaN_3 (10 mg, 0.15 mmol) was suspended in the solution (6 mL) of CH_3CN (2 mL) and H_2O (4 mL). Upon addtion of a drop of HBF_4, a colourless solution was formed, which was heated in a teflon-lined steel bomb at 130℃ for 3 days. Colorless prism-like crystals formed were collected (yield: 45%). Elemental analysis calcd (%) for **2**: C 20.39, H 1.71, N 47.55; found: C 21.05, H 1.54, N 46.89 %.

Crystal structure determination of 1 and 2: Single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source ($Mo_{K\alpha}$ radiation, graphite monochromated). Structures were solved by direct methods using SHELXTL and were refined by full-matrix least-squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom.

Table S1. Crystal Data Collection and Structure Refinement for **1** and **2**.

	1	**2**
empirical formula	$C_{30}H_6N_{12}O_{25}Zn_8$	$C_5HN_{10}OZn$
formula weight	1457.43	282.53
temp (K)	173(2)	298(2)
crystal system	cubic	Orthorhombic
space group	*Fm*-3	$P2_12_12_1$
a (Å)	22.0003(7)	8.6429(6)
b (Å)	22.0003(7)	8.8848(6)
c (Å)	22.0003(7)	15.4504(10)
α(deg)	90	90
β(deg)	90	90
γ(deg)	90	90
V (Å^3)	10648.4(6)	1186.44(14)
Z	8	4
ρcalc (g/cm^3)	1.818	1.582
F(000)	5680	556
data/restraints/params	1107/0/62	2699/0/158
GOF on *F*2	1.163	1.207
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.1289, wR2 = 0.3774	R1 = 0.0389, wR2 = 0.1274

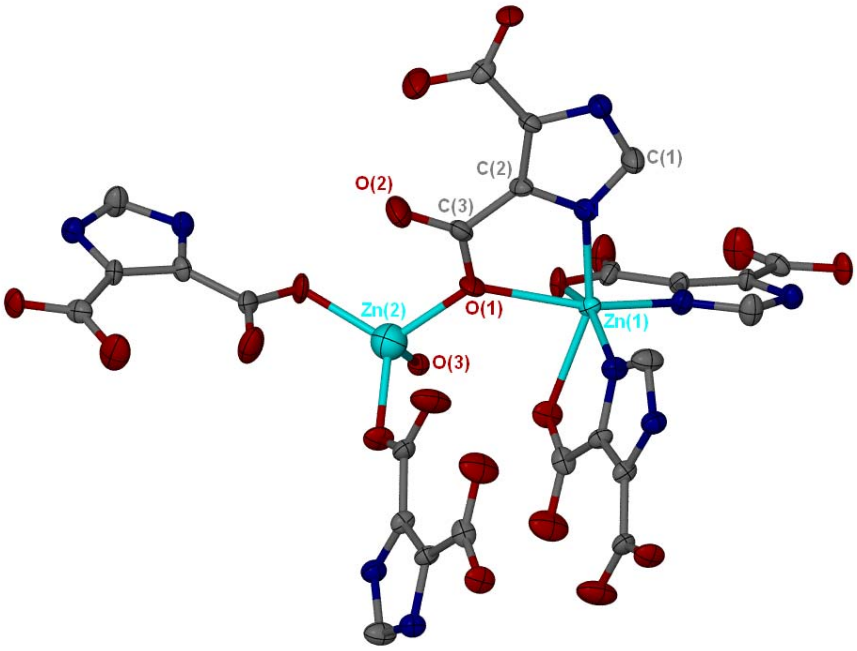

Figure S1. The coordination environment of zinc ions in **1**.

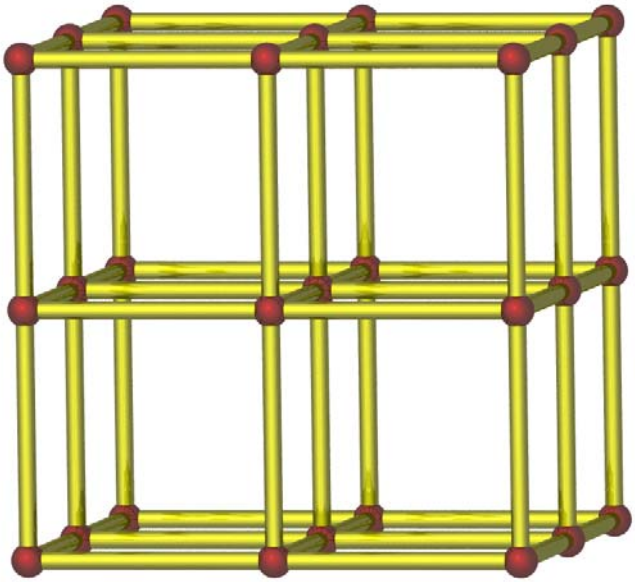

Figure S2. The cubic net of **1**.

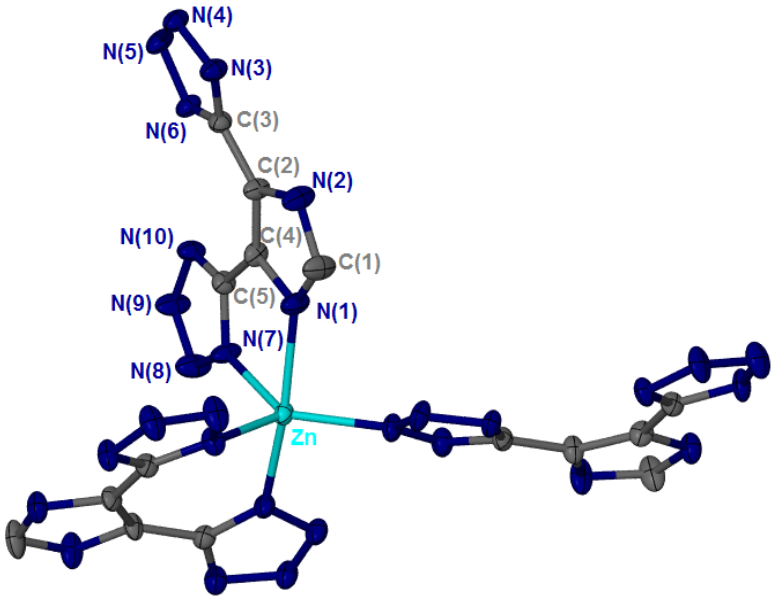

Figure S3. The coordination environment of zinc ion in **2**.

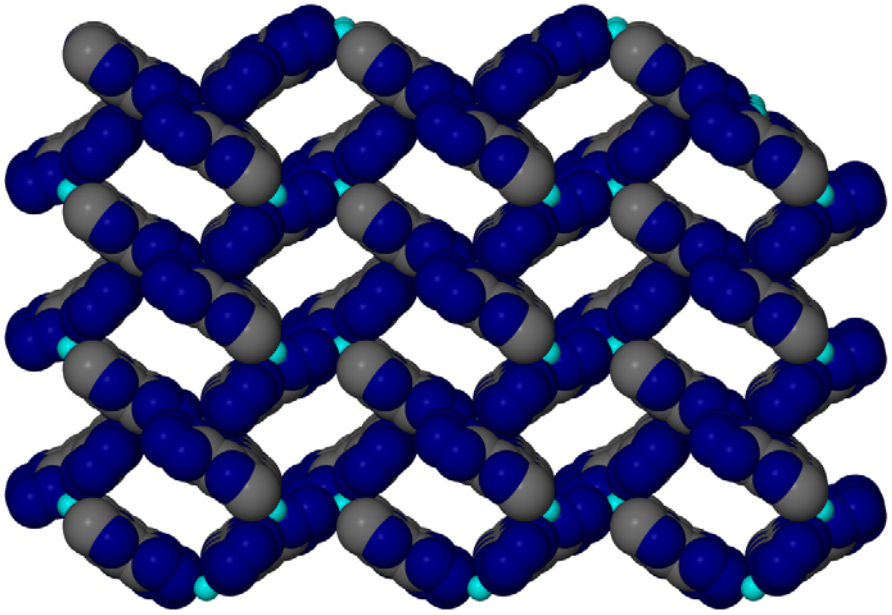

Figure S4. Space-filling representation of the 3D open framework of **2**, showing the rectangular channels.

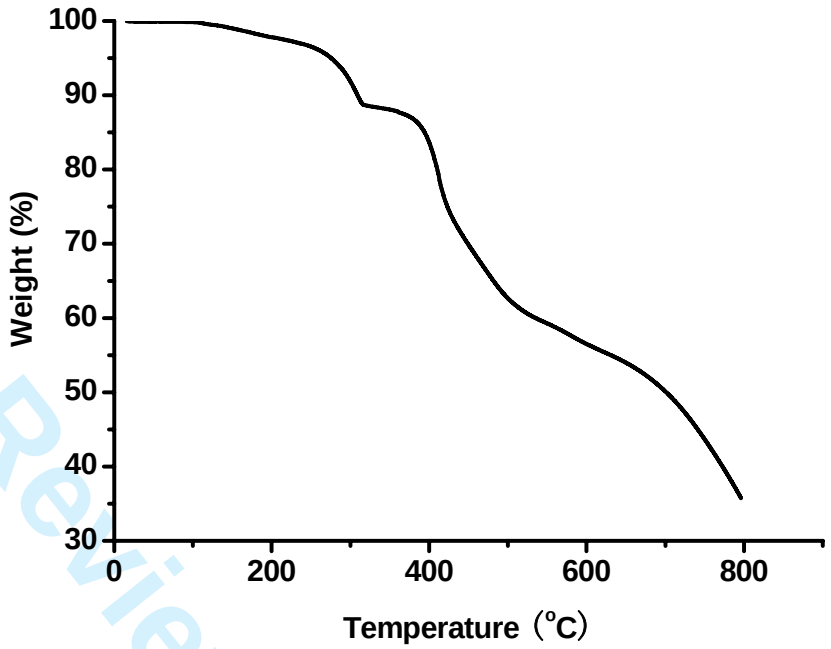

Figure S5. TGA for **1.**

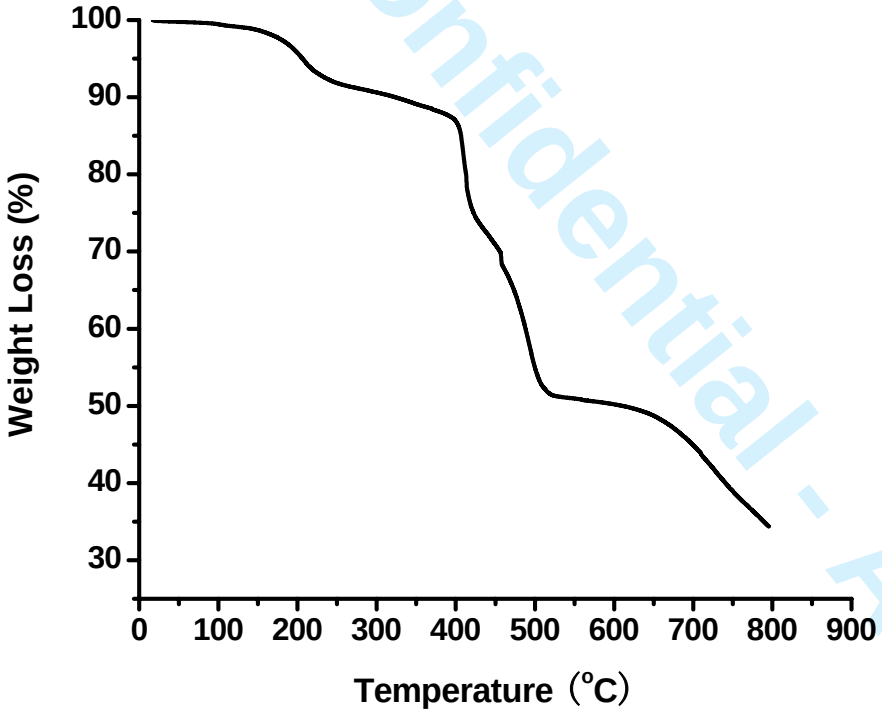

Figure S6. TGA for **2**.

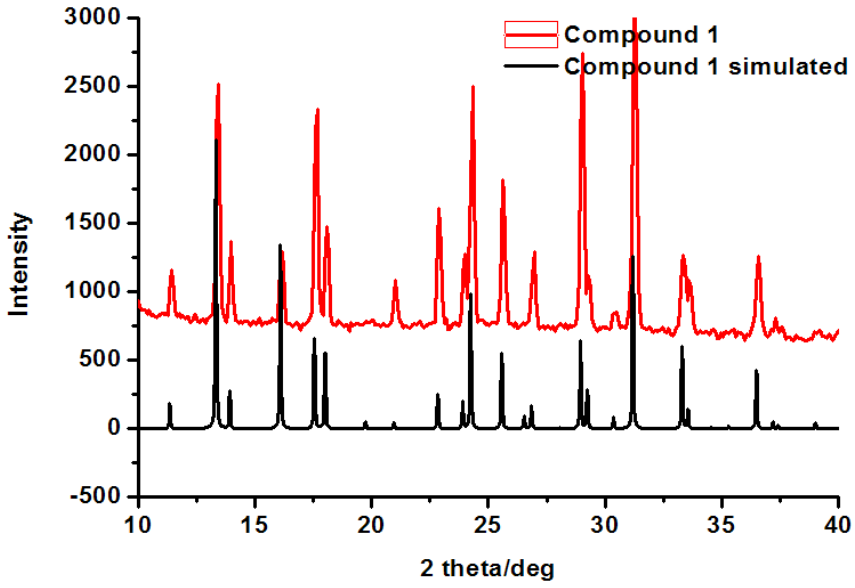

Figure S7. PXRD for **1**.

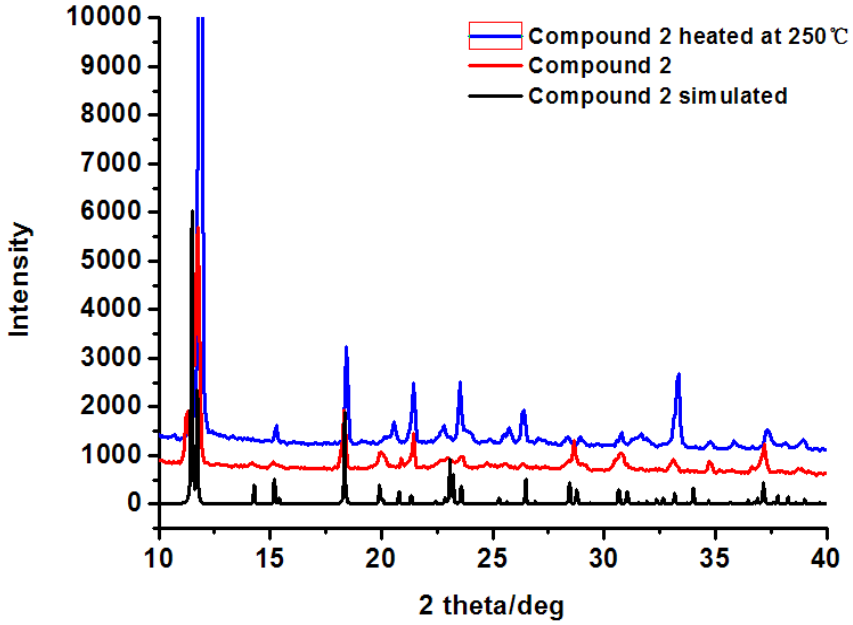

Figure S8. PXRD for **2**.

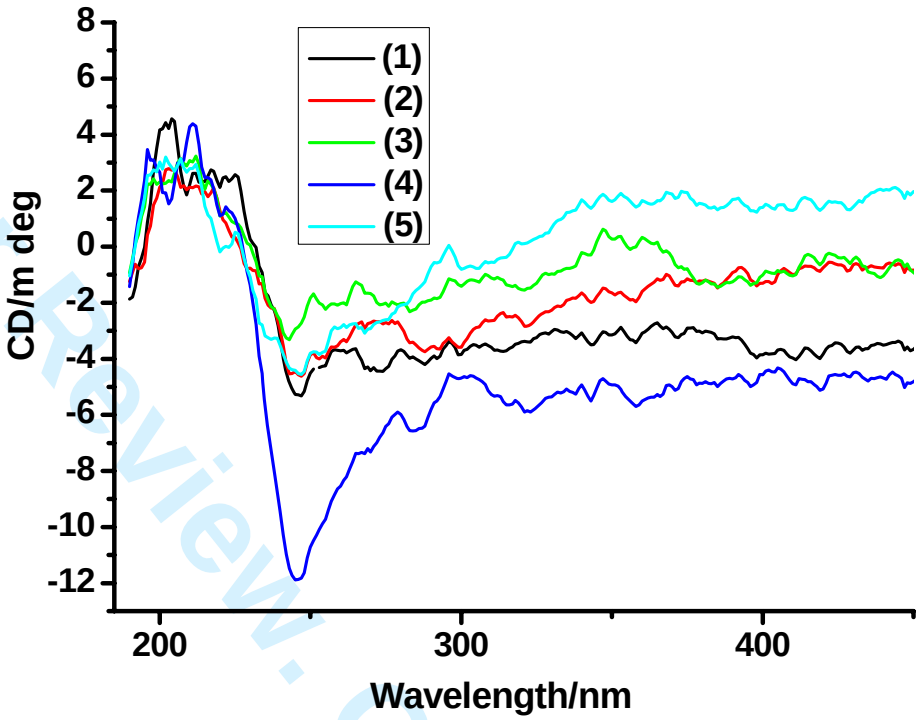

Figure S9. CD spectrum for **2**. The bulk samples were sperated into five parts. The measurement for the samples showed the similar signals.