Supporting Information for

A Luminescent Metal-Organic Framework for Sensing Methanol in Ethanol Solution

Zhao Jin,[a] Hongming He,[b] Huanyu Zhao,[a] Tsolmon, Borjigin,[b] Fuxing Sun,[b] and Guangshan Zhu*[ab]

a Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan QLD 4111 Australia, g.zhu@griffith.edu.au

b State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University, Changchun 130012 (China) Fax: (+86) 431-8516-8331

*To whom correspondence should be addressed, E-mail: g.zhu@griffith.edu.au

General Methods: All the chemicals and solvents used without further purification. Powder X-ray diffraction (XRD) data were collected on Scintag X1 diffractometer with Cu-Kα (λ = 1.5418Å) at 40kV, 35mA. A Perkin-Elmer TGA 7 thermogravimetric analyzer was used to obtain thermogravimetric analysis (TGA) curve in air with a heating rate of 5ºC/min. Luminescence spectra were measured using a HITACHI F-7000 fluorescence spectrometer.

Luminescence Measurements: The luminescence properties of **1** were investigated in the solid state and in various solvent emulsions at room temperature. The **1**–solvent emulsions were prepared by introducing 60 mg of **1** powder into 1.00 mL of methanol, ethanol and water. For sensing properties tests, the standard emulsion was prepared by introducing 120 mg of **1** powder into 0.5 mL ethanol. Different amounts of methanol were added into the standard **1** emulsion in ethanol. The photomultiplier tube voltage was 700 V, the scan speed was 1200 nm min^{-1}, and the slit widths were 5.0 nm.

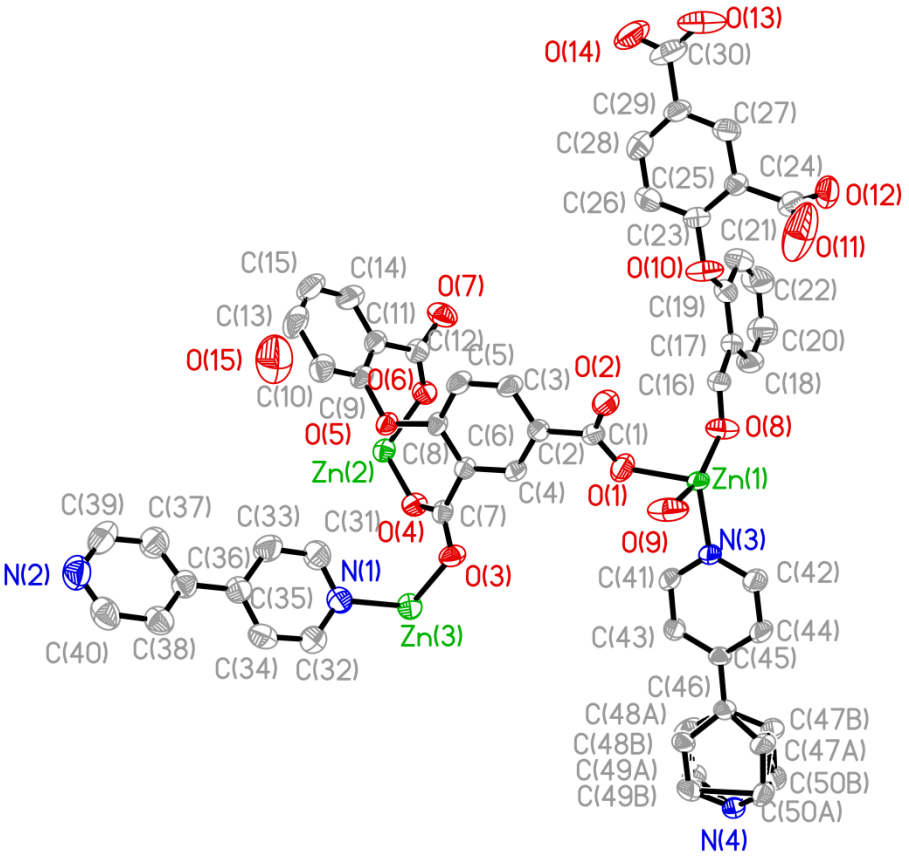

Fig. S1 The asymmetric unit of complex **1** is comprised of three crystallographically independent Zn(II) atoms, two fully deprotonated cpiop^{3-} ligands, two 4,4′-bpy ligands and one guest H_2O molecular.

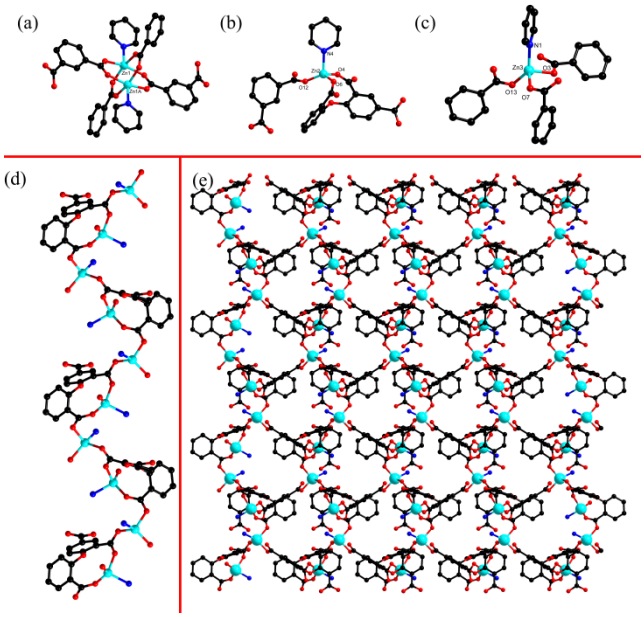

Fig. S2 Coordination environment of Zn1 (a); Zn2 (b); Zn3 (c); (d) 1D zig-zag chain consisted with Zn2, Zn3 and L1 along b-axis; (e) 2D layer formed by 1D zig-zag chains interconnecting with each other via L2. Zn: cyan, C: black, O: red. N: blue. H atoms omitted for clarity.

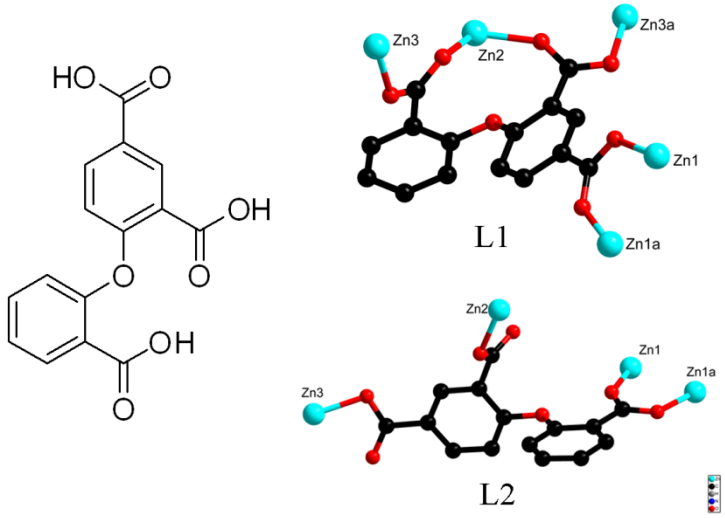

Fig. S3 ChemDraw-style picture of the ligand; (left) Coordination modes of $cpoip^{3-}$ ligand. (right)

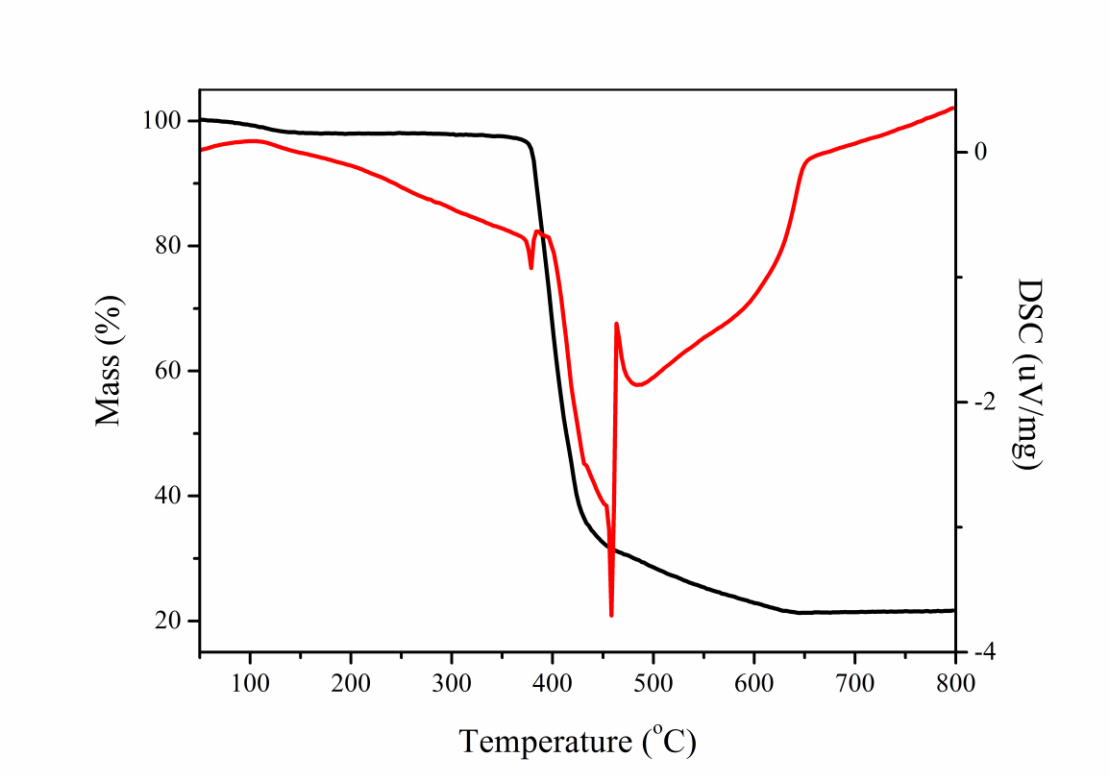

Fig S4 TGA and DSC measurements for as-synthesized **1**.

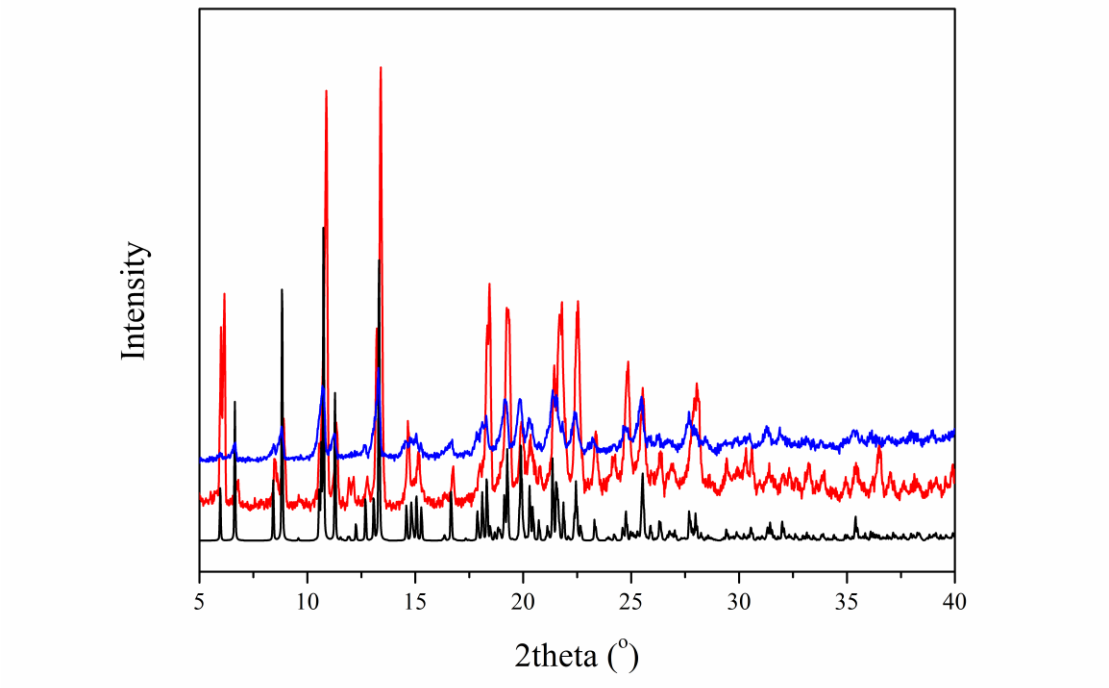

Fig S5 PXRD of the compound **1**. After sensing tests (blue, upper); As-synthesis (red, middle); Simulated (black, below)

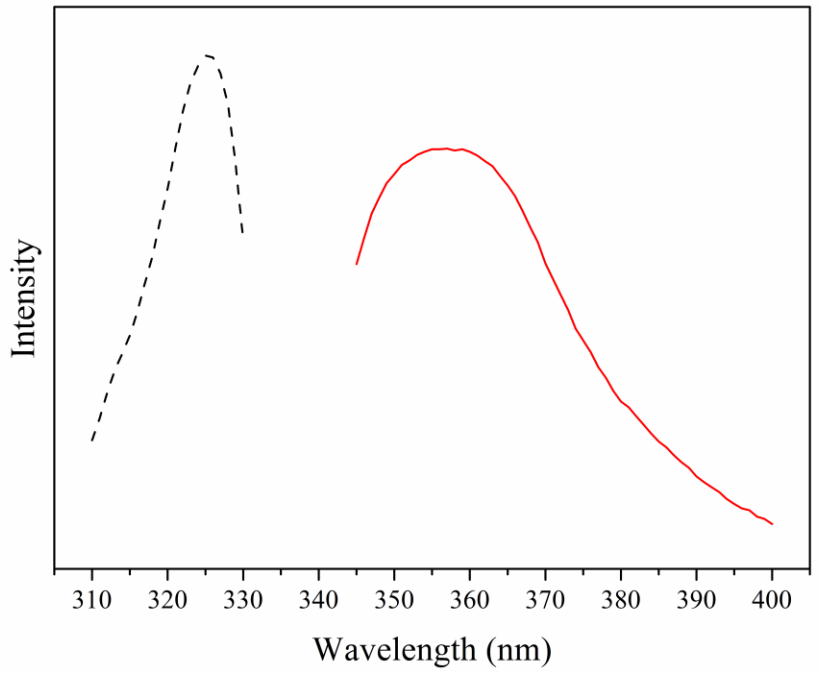

Fig S6 Emission spectrum of the H_3cpoip ligand in solid state exhibits a broad peak centered at 357 nm when exited at 325 nm.

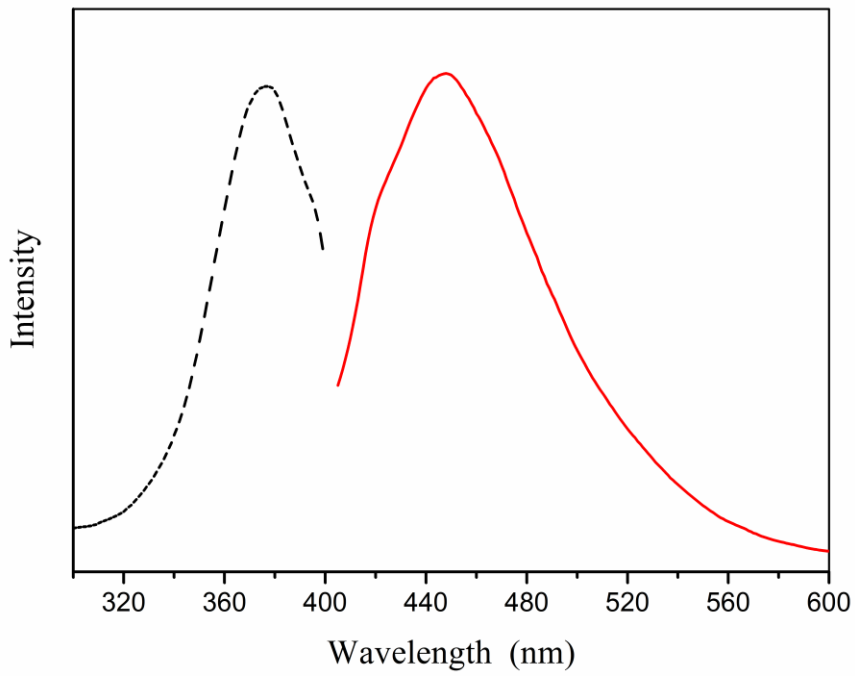

Fig S7 Emission spectrum of **1** in solid state.

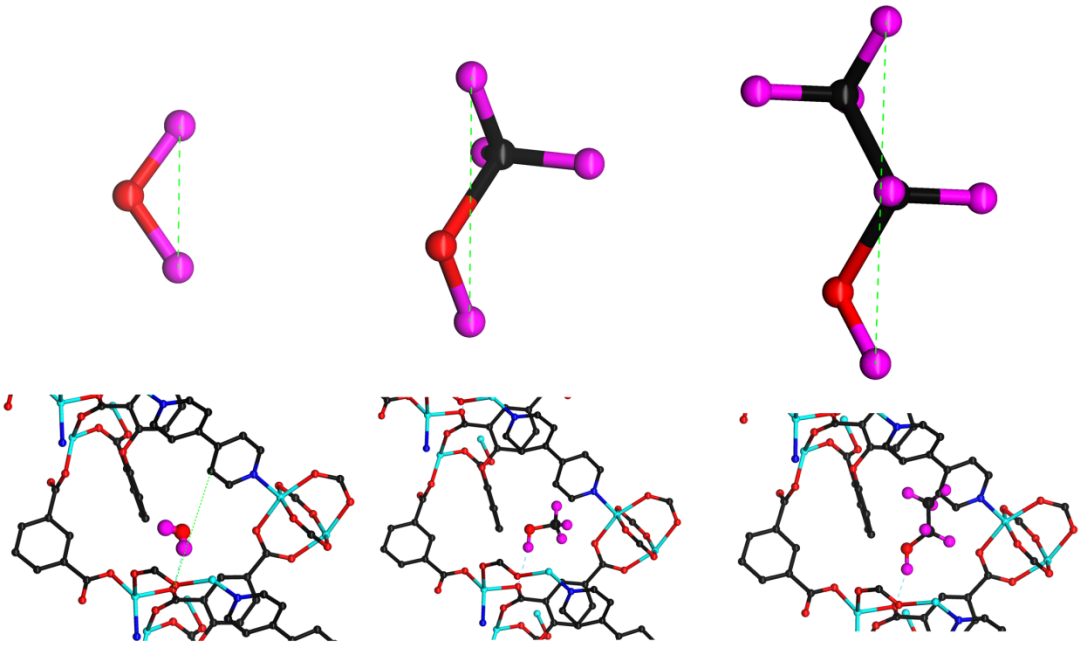

Fig S8 water, methanol and ethanol molecules, their size are defined by the two H atoms with the largest distance. (upper) Simulation for comparison of pore size and the size of these molecules in MS (below), indicates that methanol molecular can go through the channel and exchange the guest water molecular. In contrast, ethanol molecular is too big to get into the channel to exchange the guest water molecular. So, the emission of **1** in water and ethanol are the same, but the emission of **1** in methanol displays obvious change.

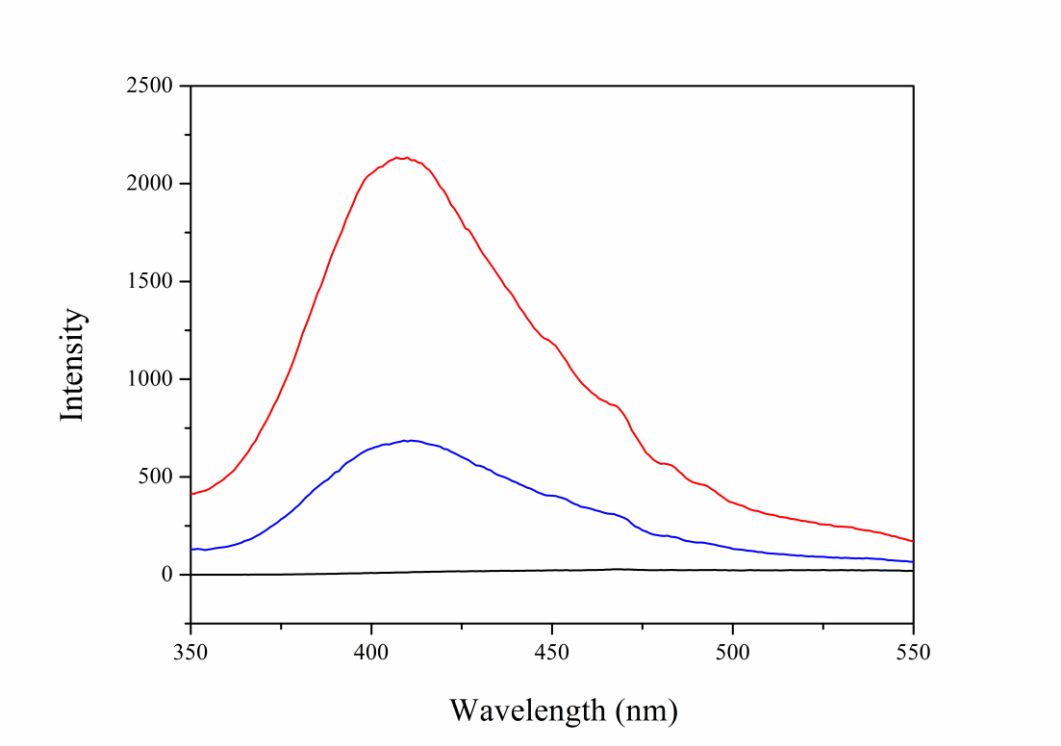

Fig S9 Emissive response spectra of 1 for methanol in H_2O solution with different methanol volume concentration. (v/v; 2×10^{-7}, black and below; 1×10^{-4}, blue and middle; 1×10^{-1}, red and upper)

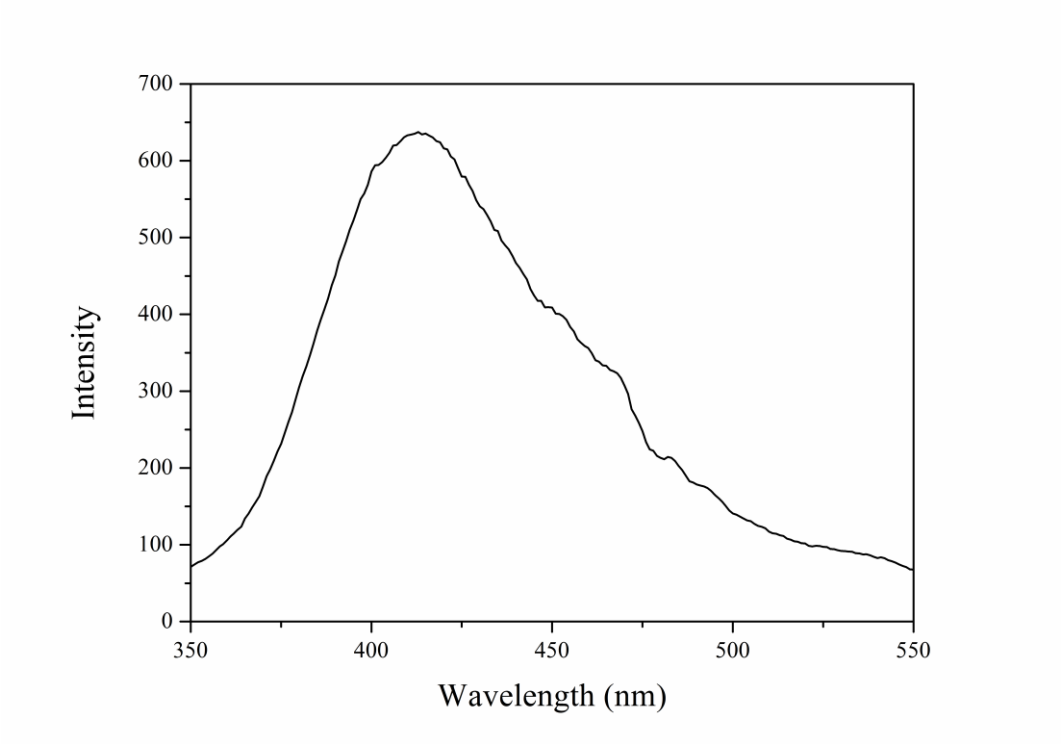

Fig S9 Emissive response spectra of **1** for methanol in imitated alcoholic beverage. Methanol concentration here is 1×10^{-4} according to the results obtained from emissive response spectra of **1** in methanol/ethanol binary system.

Table. S1 Crystallographic Data for compounds **1**

Compound	1
Chemical formula	$Zn_3C_{50}H_{28}N_4O_{15}$
Formula weight	1120.87
Crystal system	Monoclinic
Space group	P21/c
a (Å)	10.235(2)
b (Å)	14.898(3)
c (Å)	30.275(6)
α (º)	90
β (º)	101.897(6)
γ (º)	90
V (Å^3)	4517.2(16)
Z	4
D_c/g cm^{-3}	1.648
reflections collected / unique	28285 / 10948
Completeness to theta = 25.00	96.3 %
[a]R_1 [$I > 2\sigma(I)$]	0.0564
[b]$_wR_2$ [$I > 2\sigma(I)$]	0.1398
GooF on F^2	1.027

Table. S2 Selected Bond lengths [Å] and angles [º] for compound 1

Zn(1)-O(8)	2.015(2)	Zn(2)-O(6)	1.9377(18)
Zn(1)-O(9)	2.024(2)	Zn(2)-O(4)	1.9775(19)
Zn(1)-N(3)	2.0385(19)	Zn(2)-N(4)#3	2.043(2)
Zn(1)-O(2)#1	2.0426(19)	Zn(3)-O(13)#4	1.955(2)
Zn(1)-O(1)	2.048(2)	Zn(3)-O(7)#5	1.976(2)
Zn(1)-Zn(1)#1	2.9332(7)	Zn(3)-O(3)	2.0245(18)
Zn(2)-O(12)#2	1.921(2)	Zn(3)-N(1)	2.027(2)
O(8)-Zn(1)-O(9)	158.25(8)	O(12)#2-Zn(2)-O(4)	101.20(9)
O(8)-Zn(1)-N(3)	109.33(8)	O(6)-Zn(2)-O(4)	109.39(8)
O(9)-Zn(1)-N(3)	92.38(8)	O(12)#2-Zn(2)-N(4)#3	113.91(9)
O(8)-Zn(1)-O(2)#1	88.64(9)	O(6)-Zn(2)-N(4)#3	104.27(8)
O(9)-Zn(1)-O(2)#1	86.55(10)	O(4)-Zn(2)-N(4)#3	95.53(8)
N(3)-Zn(1)-O(2)#1	99.14(8)	O(13)#4-Zn(3)-O(7)#5	96.94(10)
O(8)-Zn(1)-O(1)	89.03(9)	O(13)#4-Zn(3)-O(3)	104.29(10)
O(9)-Zn(1)-O(1)	88.21(10)	O(7)#5-Zn(3)-O(3)	103.41(8)
N(3)-Zn(1)-O(1)	100.61(8)	O(13)#4-Zn(3)-N(1)	136.42(11)
O(2)#1-Zn(1)-O(1)	159.75(7)	O(7)#5-Zn(3)-N(1)	107.79(10)
O(12)#2-Zn(2)-O(6)	127.75(8)	O(3)-Zn(3)-N(1)	104.07(8)

Symmetry mode for **1**: #1 -x,-y+1,-z+2; #2 x,-y+1/2,z-1/2; #3 -x-1,y-1/2,-z+3/2; #4 x-1,-y+1/2,z-1/2; #5 -x,y+1/2,-z+3/2; #6 x+1,-y+1/2,z+1/2; #7 -x-1,y+1/2,-z+3/2; #8 -x,y-1/2,-z+3/2; #9 x,-y+1/2,z+1/2;