Supporting Information

for

From 2D→3D Inclined Polycatenation to 2D→3D Parallel Polycatenation: a Central Metal Cationic Induce Strategy

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Experiment Section

Materials and general methods: A piperazine-pyridine ligand, 1,4-bis (pyridin-4-ylmethyl)piperazine (bpmp), was prepared according to a previously reported procedure.[11d] All commercially available reagents and starting materials were of reagent-grade quality and used without further purification. Elemental analyses (C, H, N) were carried out on an Elementar Vario EL III analyzer. Infrared (IR) spectra were recorded on PerkinElmer Spectrum One as KBr pellets in the range 4000-400 cm^{-1}. Thermogravimetric analysis was recorded with a NETZSCH STA 449C unit at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. X-ray Powered diffraction (XRPD) patterns of the samples were recorded by an X-ray diffractometer (MiniFlex2 goniometer).

Synthesis of [Co(bpmp)(mip)(H_2O)] •3H_2O (1): A mixture of $Co(NO_3)_2$ •6H_2O (29.1mg, 0.1 mmol), bpmp (26.8mg, 0.1mmol), H_2mip (18.0mg, 0.10 mmol) and NaOH (8.00mg 0.2mmol) in deionized water (6 mL), sealed in a 25 mL Teflon-lined stainless steel autoclave, and heated at 130 ^oC for 72 hours, then slowly cooled to room temperature during 24 hours. Red rod crystals were recovered by filtration, washed by distilled water, and dried in air at ambient temperature. Yield: 47% (based on bpmp). Calcd for $C_{25}H_{32}N_4O_8Co_1$ (577.49):: C 52.18, H 5.60, N 9.74; found: C 52.11, H 5.56, N 9.85. IR (KBr, cm^{-1}): 3399 (s, br), 3067 (m), 2943 (m), 2820 (m), 2685 (w), 1825 (w), 1619 (vs), 1578 (s), 1427 (s), 1376 (s), 1300 (s), 1215 (m), 1117 (m), 1007 (m), 926 (w), 724 (w), 623 (w), 488 (w).

Synthesis of [Zn(bpmp)(mip)]·4H_2O (2): Compound **2** was prepared in the same way as that for **1** but using $Zn(NO_3)_2$ •6H_2O (22.8mg, 0.1mmol) as metal source. Colorless rod

crystals were recovered by filtration, washed by distilled water, and dried in air at ambient temperature. (51%, based on bpmp). Elemental analysis (%): calcd. for $C_{25}H_{35}ZnN_4O_8$ (584.98): C 51.33, H 6.03, N 9.58; found: C 51.39, H 6.09, N 9.57. IR (KBr, cm^{-1}): 3422 (s, br), 3070 (m), 2933 (m), 2811 (m), 2693 (w), 1815 (w), 1632 (vs), 1583 (s), 1421 (s), 1340 (s), 1298 (s), 1219 (m), 1119 (m), 1013 (m), 847 (w), 776 (m), 733(m), 620 (w), 495 (w).

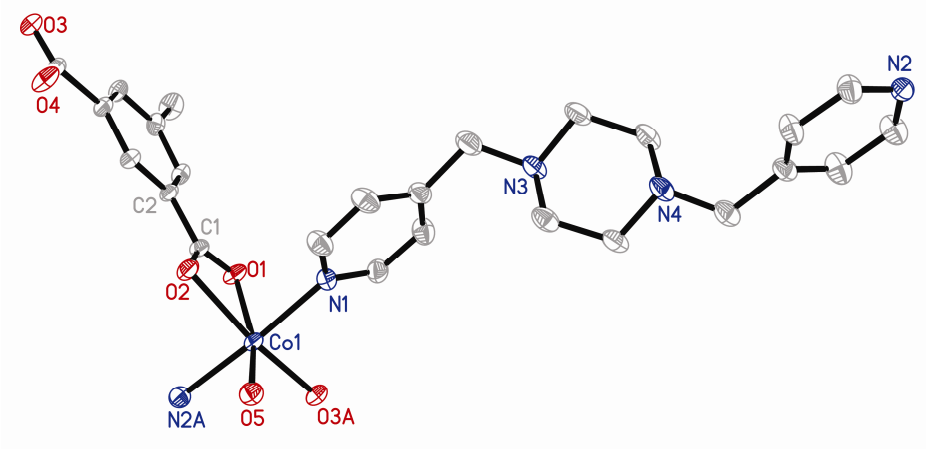


Figure S1 ORTEP drawing of the basic building block in complex **1**, showing the coordination environment around the cobalt atom with thermal ellipsoids at 30% probability.

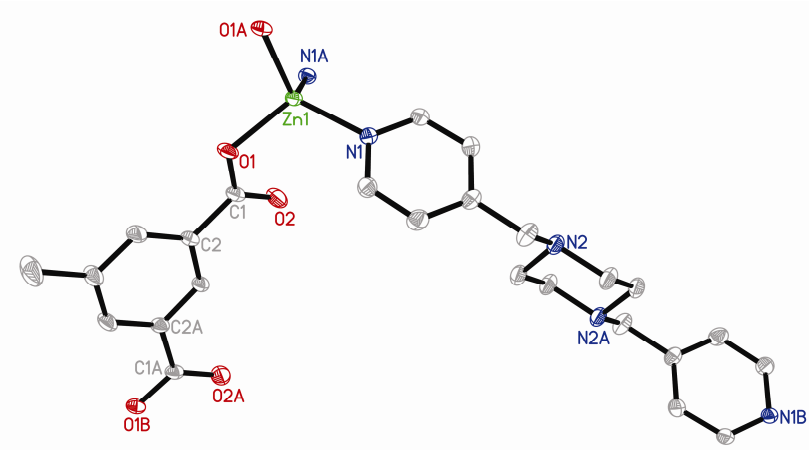


Figure S2 ORTEP drawing of the basic building block in complex **2**, showing the coordination environment around the Zinc atom with thermal ellipsoids at 30% probability.

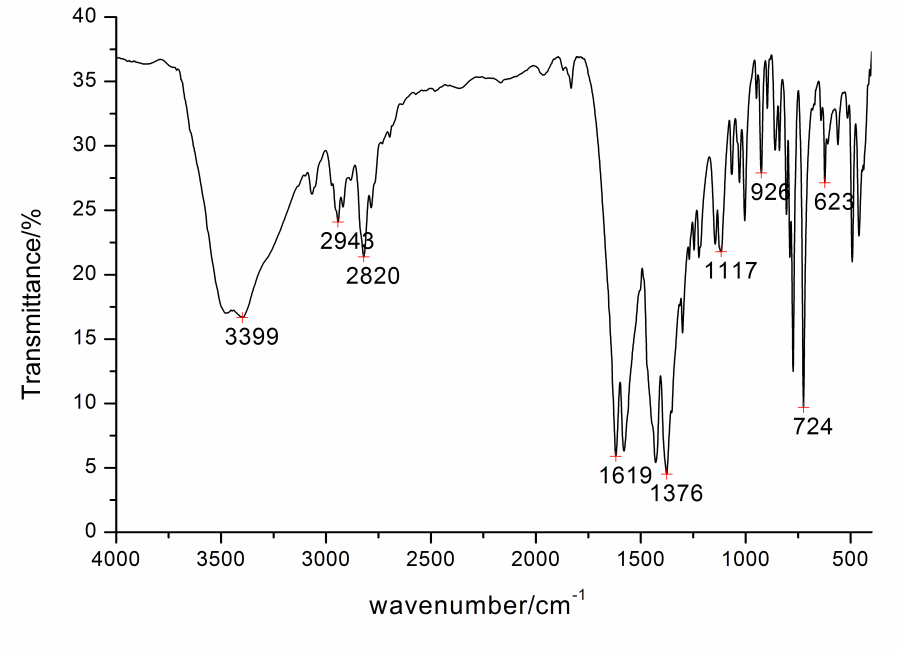


Figure S3 IR spectrum of complex **1**.

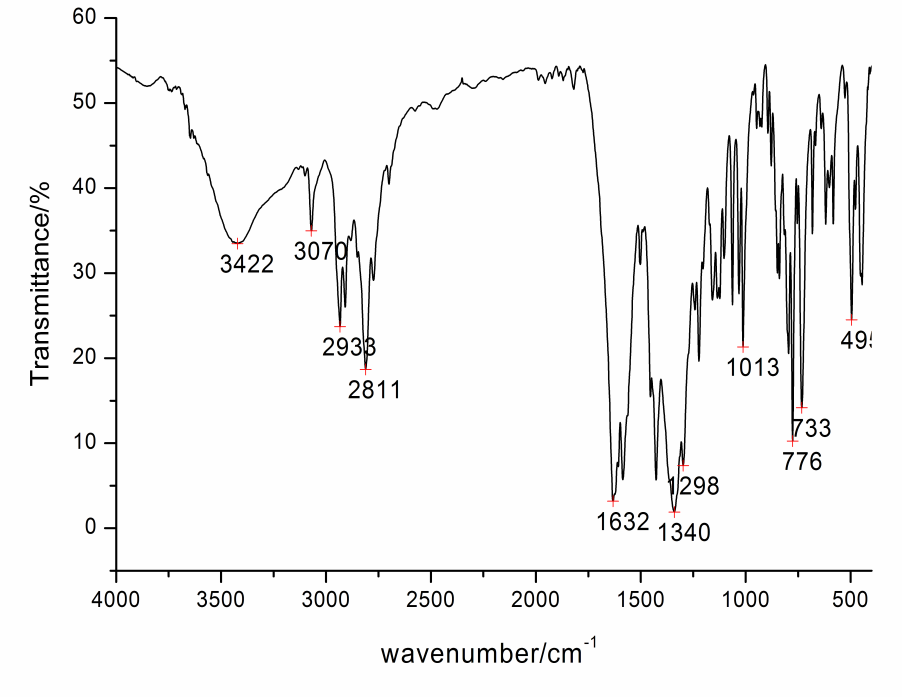


Figure S4 IR spectrum of complex **2**.

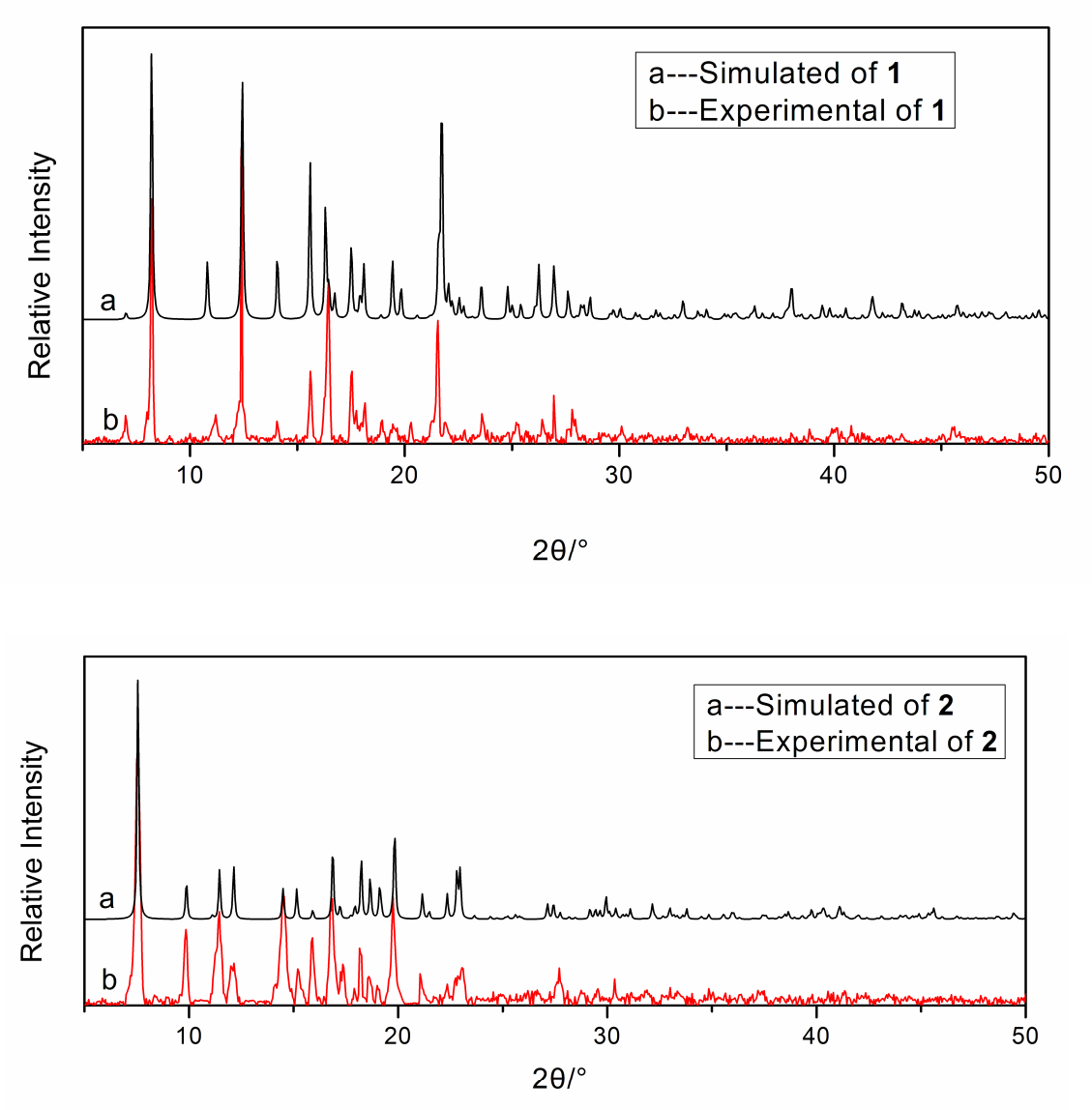


Figure S5 X-Ray powder diffraction patterns of **1** and **2**.

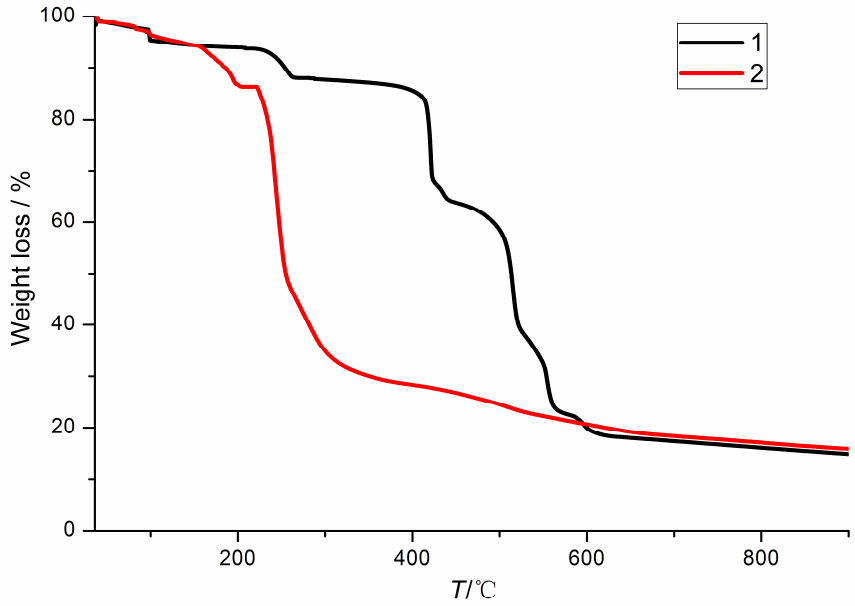
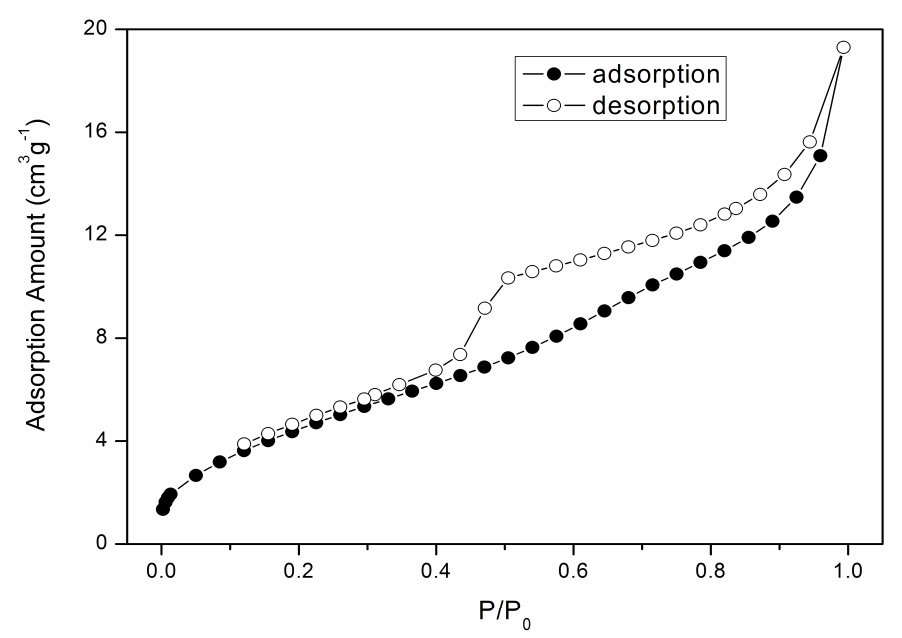


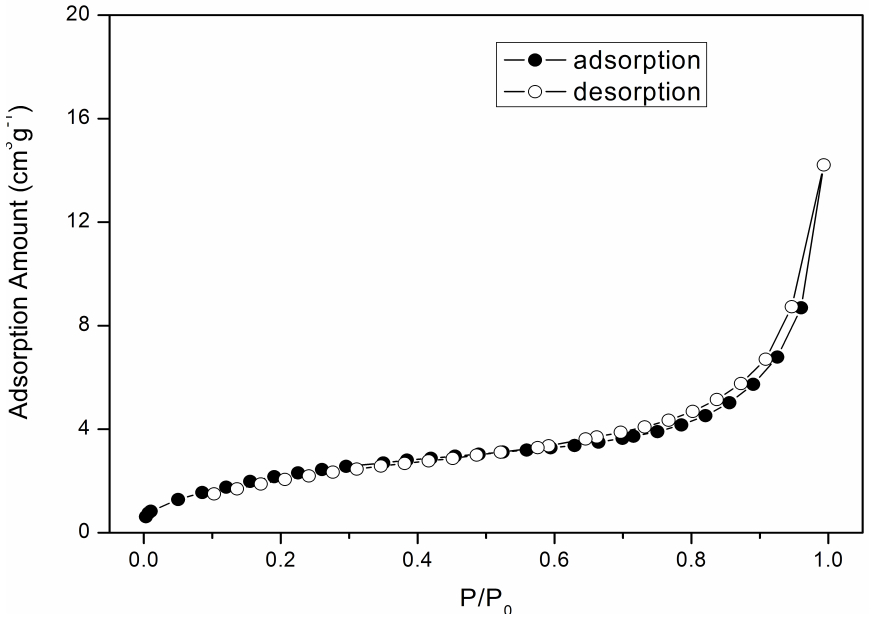
Figure S6 TGA curve for compounds **1** and **2**.

As shown in Figure **S6**, compound **1** exhibits two significant weight losses. The first weight loss of 12.67% occurs between 50℃ to 260℃ corresponds to the removal of the three noncoordinated water and one coordinated water molecules (calcd: 12.52%). From 358℃ to 770℃, the weight loss of 73.57% (calcd: 74.46%)suggests the decomposition of compound **1**. The residue weight of 13.76% is ascribed to CoO (cacld: 13.02%).

The TGA curve of **2** (Figure **S6**) indicates two obvious weight loss stages, 13.16% between 50℃ to 195℃, and 73.08% between 225℃ to 755℃. The former is in accordance with the loss of the guest water molecules (cacld: 12.32%). The latter arises from the decomposition of the organic ligands (cacld: 73.76%). The residue weight of 14.76% is ascribed to ZnO (cacld: 13.92%)



(a)



(b)

Figure S7 Reversible nitrogen gas adsorption（●)–desorption（○) isotherm for **1**(a) and **2**(b).

Both the void percentage of complexes **1** and **2** have been calculated with Calc all/PLATON, and the results are 15.8% for **1** and 17.4% for **2** after remove off the lattice water. The N2 isotherms for **1** and **2** were measured using the ASAP 2020 surface area analyzer at 77K. The Brunauer-Emmett-Teller (BET) surface areas for **1** and **2** are 17.8 m^2/g and 8.6 m^2/g respectively (Figure S7)

Table S1. Crystallographic data for complexes 1-2

	1	**2**
Formula	$C_{25}H_{34}N_4O_8Co_1$	$C_{25}H_{35}N_4O_8Zn_1$
Fw	577.49	584.94
Crystal size (mm)	0.15×0.13×0.12	0.20×0.16×0.13
Crystal system	Monoclinic	Monoclinic
Space group	*P*c	*C*2/c
a/Å	11.290(3)	18.105(6)
b/Å	12.609(4)	15.467(5)
c/Å	10.281(3)	10.115(3)
β/º	107.231(6)	97.760(5)
V/Å^3	1397.8(7)	2806.6(15)
Z	2	4
D_c/g cm^{-3}	1.353	1.365
μ/mm^{-1}	0.666	0.927
F(000)	590	1196
T/K	298(2)	298(2)
λ(MoKα)/Å	0.71073	0.71073
Reflections collected	10803	10699
Unique reflections	5631	3204
Parameters	329	164
S on F^2	1.100	1.098
R_1 (I > 2σ(I))[a]	0.0415	0.0453
$_wR_2$ (I > 2σ(I))[b]	0.1058	0.1339
R_1 (all data)[a]	0.0575	0.0528
$_wR_2$ (all data)[b]	0.1337	0.1484
$\Delta\rho_{max}$ and $_{min}$ [e/Å^3]	0.579 and -0.457	0.135 and -0.767

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths (A°) and angles (deg) for complexes 1-2

Compound **1**			
Co1-O1	2.137(3)	Co1-O2	2.160(3)
Co1-O3^{i}	2.047(3)	Co1-N1	2.184(3)
Co1-O5	2.083(3)	Co1-N2^{ii}	2.175(3)
O3^{i}-Co1-O5	95.19(12)	O3^{i}-Co1-N1	90.74(13)
O1-Co1-N1	86.23(13)	O1-Co1-N2^{ii}	89.98(13)
O5-Co1-O2	98.97(11)	N1-Co1-N2^{ii}	176.02(16)
O1-Co1-O2	61.28(10)	N1-Co1-O5	92.65(12)
O2-Co1-O3^{i}	165.77(11)	O5-Co1-N2^{ii}	90.50(13)
O3^{i}-Co1-O1	104.54(11)	O3^{i}-Co1-N2^{ii}	91.41(13)
Compound **2**			
Zn1-N(1)	2.037(2)	Zn1-N(1)^{i}	2.037(2)
Zn1-O1	1.9890(18)	Zn1-O1^{i}	1.9890(18)
O1-Zn1-O1^{i}	94.41(11)	O1-Zn1-N1^{i}	118.61(8)
O1^{i}-Zn1-N1^{i}	108.15(8)	O1-Zn1-N1^{i}	108.15(8)
O1^{i}-Zn1-N1	118.61(8)	N1^{i}-Zn1-N1	107.27(12)

Symmetry code for **1**: i x,y,z+1; ii x+1,y+1,z;

Symmetry code for **2**: -x,y,-z+1/2;

Table S3 Hydrogen-bonding distance (A°) and angles (deg) for complexes 1-2

D-H···A	*d*(H···A)	∠DHA	*d*(D···A)	Symmetry transformation for A
Compound **1**				
O5-H5A···O4	1.920	146.96	2.673	x, y, z+1
O5-H5B···O6	1.939	149.65	2.707	
O6-H6A···O4	2.263	114.53	2.727	x, -y, z+1/2
O6-H6B···O7	2.235	112.18	2.674	x, -y, z+1/2
O7-H7A···O2	2.299	112.55	2.739	
O7-H7B···O6	2.102	124.21	2.674	x, -y, z-1/2
O8-H8A···O6	2.203	128.24	2.810	x-1, y, z
O8-H8B···N3	2.198	132.79	2.845	
Compound **2**				
O3-H3A···O1	2.059	165.03	2.890	
O4-H4A···N2	2.361	120.62	2.887	-x+1/2, y+1/2, -z+1/2