Electronic Supplementary Information (ESI)

for

Gyroidal Metal-Organic Frameworks by Solvothermal Subcomponent Self-assembly

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Experimental Section

General: Reagents and solvents employed were commercially available and used as received. Infrared spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000-400 cm^{-1}; abbreviations used for the IR bands are w = weak, m = medium, b = broad, vs = very strong. Thermogravimetric measurements were performed on a TA Instruments Q50 Thermogravimetric Analyzer under nitrogen flow of (40 $mL \cdot min^{-1}$) at a typical heating rate of 5 $°C \cdot min^{-1}$. X-ray powder diffraction (XRPD) experiments were performed on a D8 Advance X-ray diffractometer. Gas sorption experiments were carried out on a Micromeritics ASAP 2020 surface area and pore size analyzer. Prior to the measurement, the sample was dried by using the "outgas" function of the surface area analyzer for 12 hours at 150 °C.

Synthesis of STU-1: A mixture of $ZnCl_2$ (5.4 mg, 0.04 mmol), 4-formylimidazole (7.6 mg, 0.08 mmol), hydrazine monohydrate (2.0 mg, 0.04 mmol), and DMF (2.5 mL) were sealed in a Pyrex glass tube and heated in an oven at 100 °C for 3 days. After cooling to room temperature at a rate of 5 °C /h, the Light yellow polyhedral crystals were collected by

filtration and washed with DMF 3 times (2.0 mL each time, yield: 5.2 mg). IR (KB pellet, cm^{-1}): 2919.7(w), 2849.0(w), 1665.7(s), 1615.7(vs), 1586.3(s), 1506.8(m), 1471.5(w), 1453.8(w), 1389.0(vs), 1344.9(w), 1324.3(w), 1280.1(w), 1259.5(m), 1247.8(w), 1215.4(m), 1112.4(s), 1038.8(m), 1009.3(m), 971.1(m), 838.6(m), 809.2(m), 656.1(m), 620.8(w), 541.3(w), 497.1(m).

Synthesis of STU-2: A mixture of $Mn(NO_3)_2$ (11.5 mg, 0.04 mmol water solution: concentration 50%), 4-formylimidazole (7.6 mg, 0.08 mmol), hydrazine monohydrate (2.0 mg, 0.04 mmol), and DMF/ethanol mixed solvent (2.5 mL, 4:1, v/v) were sealed in a Pyrex glass tube and heated in an oven at 120 °C for 3 days. After cooling to room temperature at a rate of 5 °C /h, the purple-red polyhedral crystals were collected by filtration and washed with DMF 3 times (2.0 mL each time, yield: 4.6 mg). IR (KBr pellet, cm^{-1}): 2952.1(w), 2925.6(w), 2849.1(w), 1655.6(s), 1612.8(vs), 1539.2(s), 1503.8(m), 1459.7(w), 1383.2(m), 1349.5(s), 1250.7(s), 1203.6(m), 1112.4(s), 1027.0(m), 962.2(m), 873.9(w), 835.7(m), 818.0(m), 794.4(m), 659.0(s), 620.8(m), 497.1(m).

Synthesis of STU-3: A mixture of $CuCl_2 \cdot 2H_2O$ (6.8 mg, 0.04 mmol), 4-formylimidazole (7.6 mg, 0.08 mmol), hydrazine monohydrate (2.0 mg, 0.04 mmol), and DMF/ethanol mixed solvent (2.5 mL, 4:1, v/v) were sealed in a Pyrex glass tube and heated in an oven at 100 °C for 3 days. After cooling to room temperature at a rate of 5 °C /h, the blue block-like crystals were collected by filtration and washed with DMF 3 times (2.0 mL each time, yield: 5.6 mg). IR (KBr pellet, cm^{-1}): 2922.7(w), 2855.0(w), 1609.8(vs), 1568.6(s), 1498.0(w), 1469.0(w), 1400.8(w), 1350.8(w), 1259.5(vs), 1206.5(w), 1115.3(s), 1047.6(m), 1012.3(m), 959.3(w), 841.5(m), 815.0(m), 653.2(m), 541.3(w), 503.0(w).

Synthesis of STU-5: A mixture of $Cd(AC)_2 \cdot 2H_2O$ (10.6 mg, 0.04 mmol), 2-methyl-4-formylimidazole (8.8 mg, 0.08 mmol), hydrazine monohydrate (2.0 mg, 0.04 mmol), and DMF/ethanol mixed solvent (3.0 mL, 2:1, v/v) were sealed in a Pyrex glass tube and heated in an oven at 140 °C for 3 days. After cooling to room temperature at a rate of 5 °C /h, light yellow polyhedral crystals were collected by filtration and washed with DMF 3 times (2.0 mL each time, yield: 6.2 mg). IR (KBr pellet, cm^{-1}): 3400 (m), 2926 (w), 1615 (vs), 1495 (s), 1460 (w), 1395 (vs), 1294 (s), 1260(vs), 1154 (vs), 1036 (s), 1012 (m), 812 (vs), 670 (s), 591 m), 497 (m).

Synthesis of Cu(BImED)NO_3: A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (4.8 mg, 0.02 mmol), 4-formylimidazole (3.8 mg, 0.04 mmol), ethlenediamine (0.6 mg, 0.01 mmol), and DMF/ethanol mixed solvent (2.5 mL, 4:1, v/v) were sealed in a Pyrex glass tube and heated in an oven at 120 °C for 3 days. After cooling to room temperature at a rate of 5 °C /h, the blue block-like crystals were collected by filtration and washed with DMF 3 times (2.0 mL each time, yield: 2.50 mg). IR (KBr pellet, cm^{-1}): 3428 (m), 3102 (w), 3002 (s), 1627 (vs), 1548 (w), 1468 (w), 1386 (vs), 1109(s), 1050 (w), 1029 (w), 956 (w), 659 (w), 620 (w).

Crystallographic study. Single Crystals of STU-5 and Cu(BImED)NO_3 were mounted on a glass fiber. Data collection were performed on an Agilent Technologies Gemini A System (Cu Kα, λ = 1.54178 Å) at 293 K (STU-4, 100 K). The data were processed using CrysAlis[Pro.1]. The structures were solved by direct methods and refined by full-matrix least-squares refinements based on F^2. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The crystallographic calculations were conducted using the SHELXL-97 programs. The treatment for the guest molecules in the STU-5 involves the use of the SQUEEZE program of PLATON.

Table S1 The unit-cell parameters of single crystals of STU-1, -2 and -3 obtained via solvothermal subcomponent self-assembly and reported data.

MOFs	Solvothermal subcomponent self-assembly			reported data		
	a (Å)	*V*(Å^3)	Space group	*a*(Å)	*V*(Å^3)	Space group
STU-1	34.54	41148	$Ia\bar{3}d$	34.65	41591	$Ia\bar{3}d$
STU-2*	34.78	42453	$Ia\bar{3}d$	35.80	45863	$Ia\bar{3}d$
STU-3	34.24	40079	$Ia\bar{3}d$	34.29	40316	$Ia\bar{3}d$

*STU-2 is seem more flexible than other STU MOFs, the unit cell parameters can vary in a wide range, but the space group is not change. The detail study for the flexible property is carrying out.

Table S2 Summary of the Crystal Data and Structure Refinement Parameters for STU-5 and $Cu(BImED)NO_3$.

Parameter	STU-5	$Cu(BImED)NO_3$
Chemical formula	$C_{16.25}H_{26.67}CdN_{7.04}O_{2.60}$	$C_{10}H_{11}N_7CuO_3$
Formula weight	*474.76*	*340.80*
Crystal system	*Cubic*	*Monoclinic*
Space group	$Ia\bar{3}d$	*P21/c*
a (Å)	*37.8124(1)*	*8.9680(3)*
b (Å)	*37.8124(1)*	*9.0543(3)*
c (Å)	*37.8124(1)*	*16.5808(5)*
α (deg)	*90*	*90*
β (deg)	*90*	*97.998(3)*
γ (deg)	*90*	*90*
V (Å^3)	*54063.3(2)*	*1333.25(8)*
Z	*96*	*4*
D_{Calcd} *(g·cm^{-3})*	*1.400*	*1.698*
μ (mm^{-1})	*7.989*	*1.661*
Reflections collected	*22548*	*5526*
Unique reflections	*4479*	*2338*
R_{int}	*0.0415*	*0.0290*
Goodness-of-fit on F^2	*1.072*	*1.038*
R_1 [a] *[I > 2σ(I)]*	*0.0444*	*0.0322*
wR_2 [b] *[I > 2σ(I)]*	*0.1119*	*0.724*
R_1 [a] *[all refl.]*	*0.0701*	*0.0447*
wR_2 [b] *[all refl.]*	*0.1246*	*0.0811*

[a] $R_1 = \sum(||F_0| - |F_c||)/\sum|F_0|$; [b] $wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

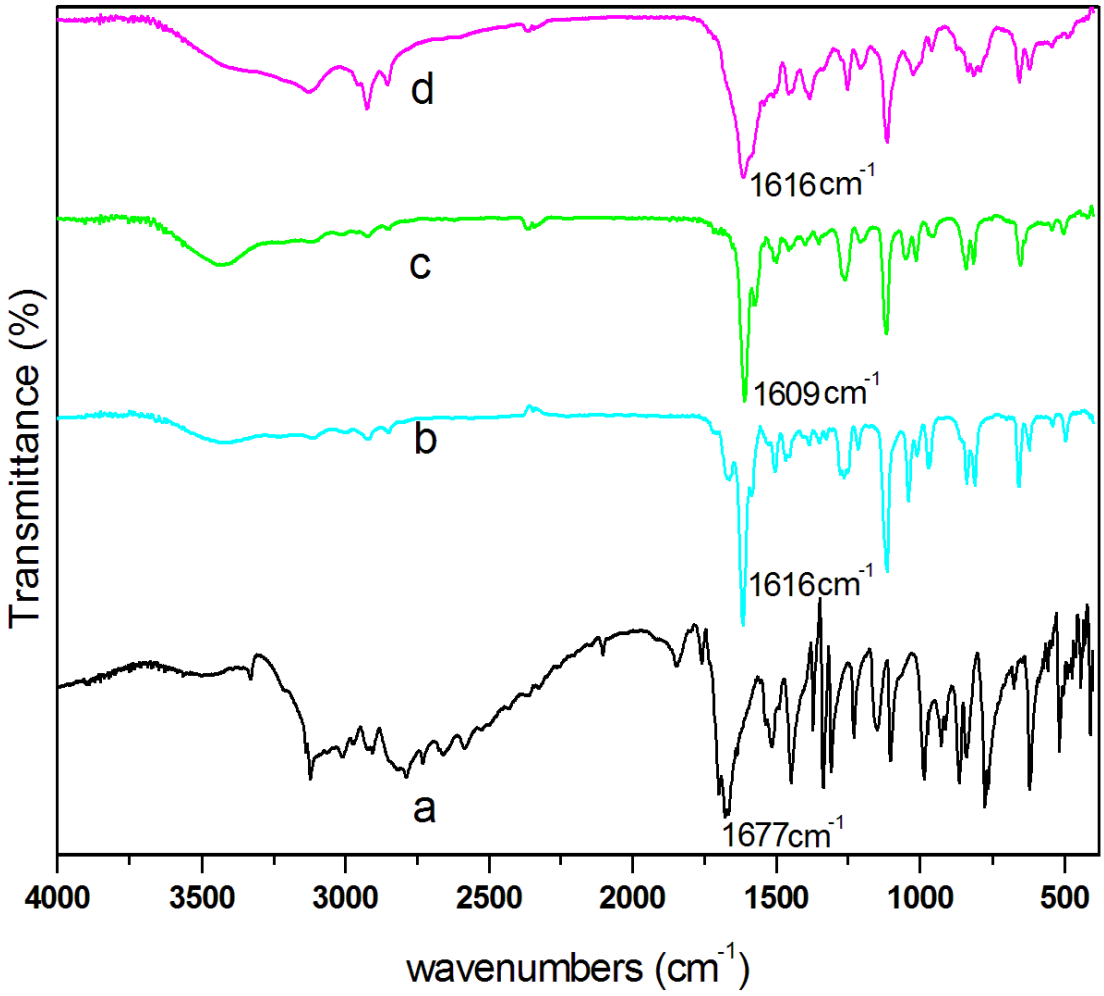

Fig. S1 IR spectra of 4-formylimidazole (a), STU-1 (b), STU-2 (c), and STU-3 (d)，all MOFs were obtained by solvothermal supramolecular self-assembly.

Note: The feature C=O peak (around 1677 cm^{-1}) of formylimidazole disappeared, and a strong absorption at around 1610 cm^{-1} is presented, indicating that the dynamic imine bonds and BIm were formed in these compounds

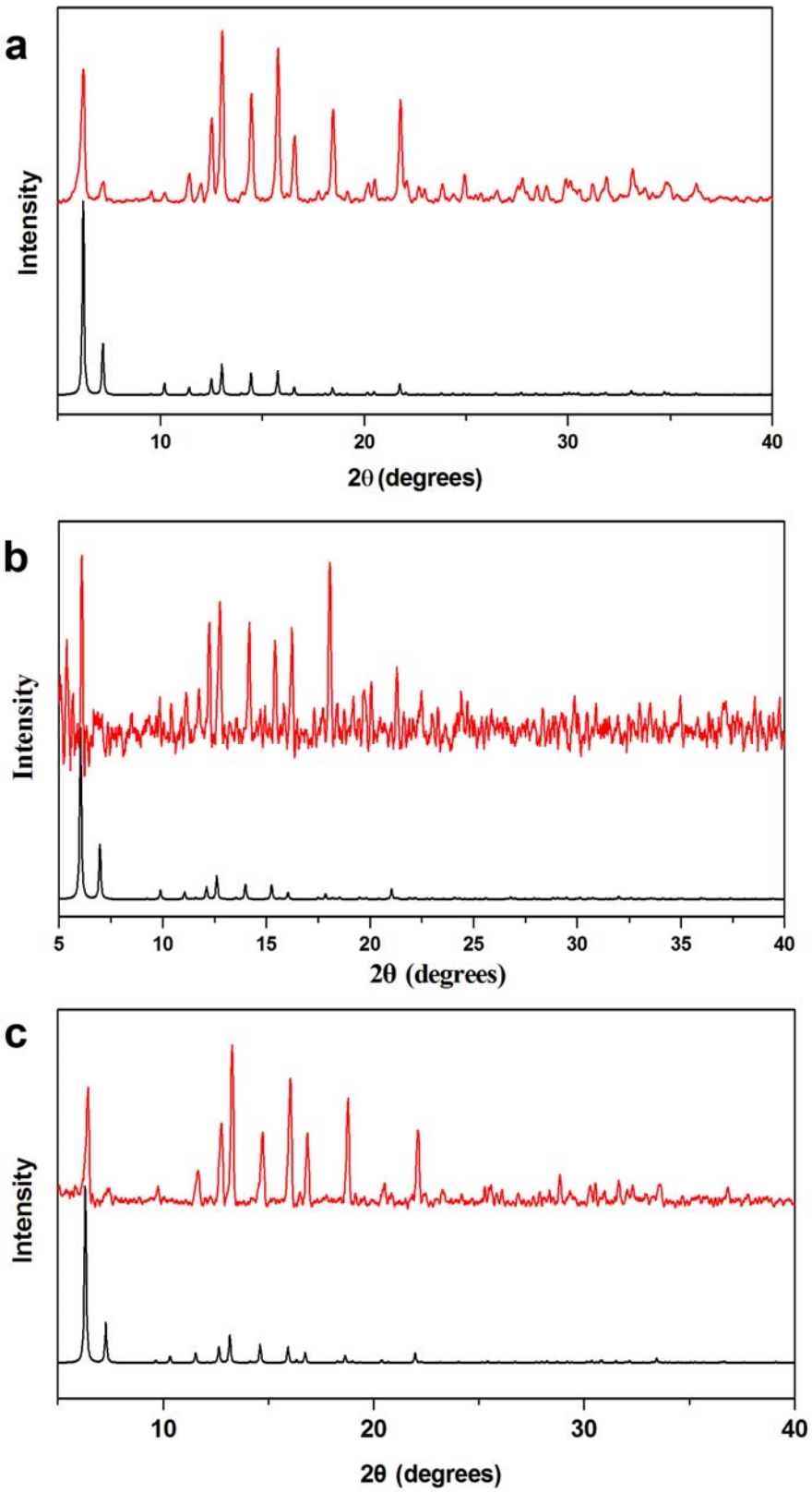

Fig. S2 Powder X-ray diffraction patterns (Cu Kα, λ=1.5418 Å) of MOFs STU-1 (a), STU-2 (b), STU-3 (c), which were all obtained by solvothermal subcomponent self-assembly. Black patterns: calculated pattern from the single crystal structure, red patterns: observed from an as-synthesized sample.

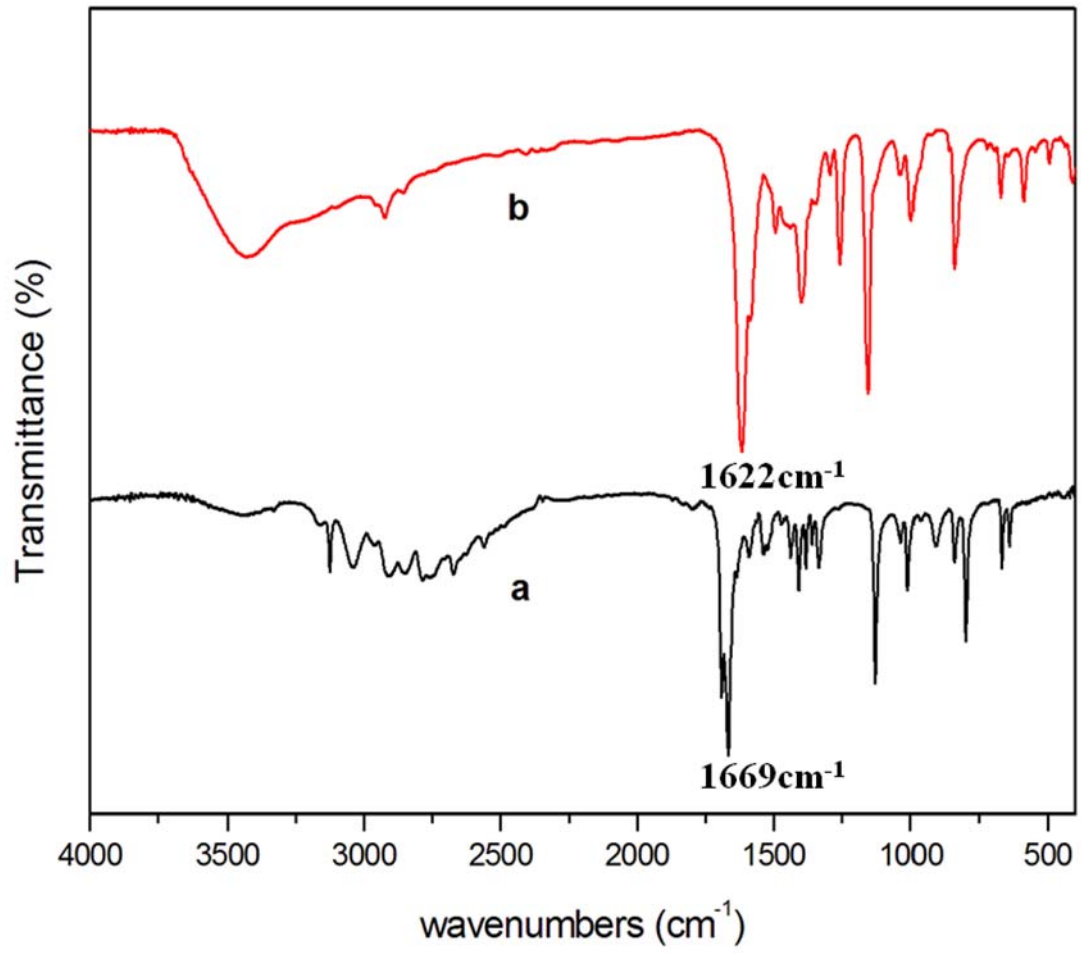

Fig. S3 IR spectra of 2-methyl-4-formylimidazole (a) and STU-5(b).

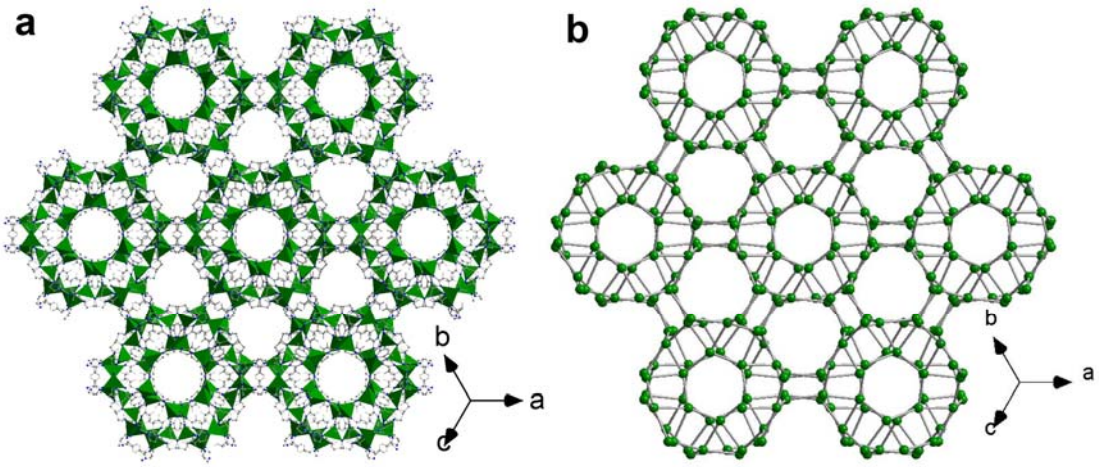

Fig. S4 The labyrinthine zeolitic imidazolate framework (a) and **gie** topology (b) of STU-5.

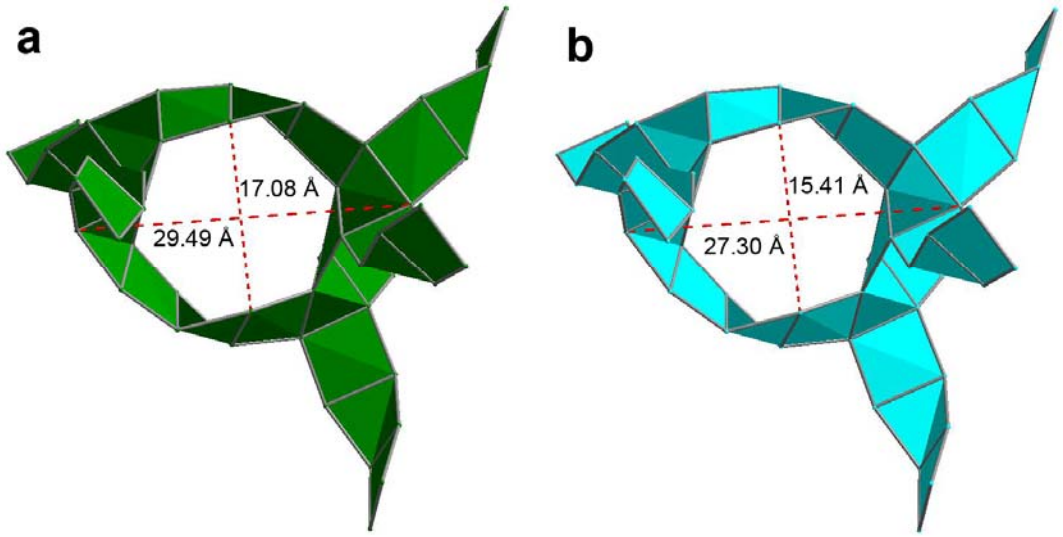

Fig. S5 The 12-ring windows formed by intersecting of three same handedness helical ribbons of STU-5 (a) and STU-1(b).

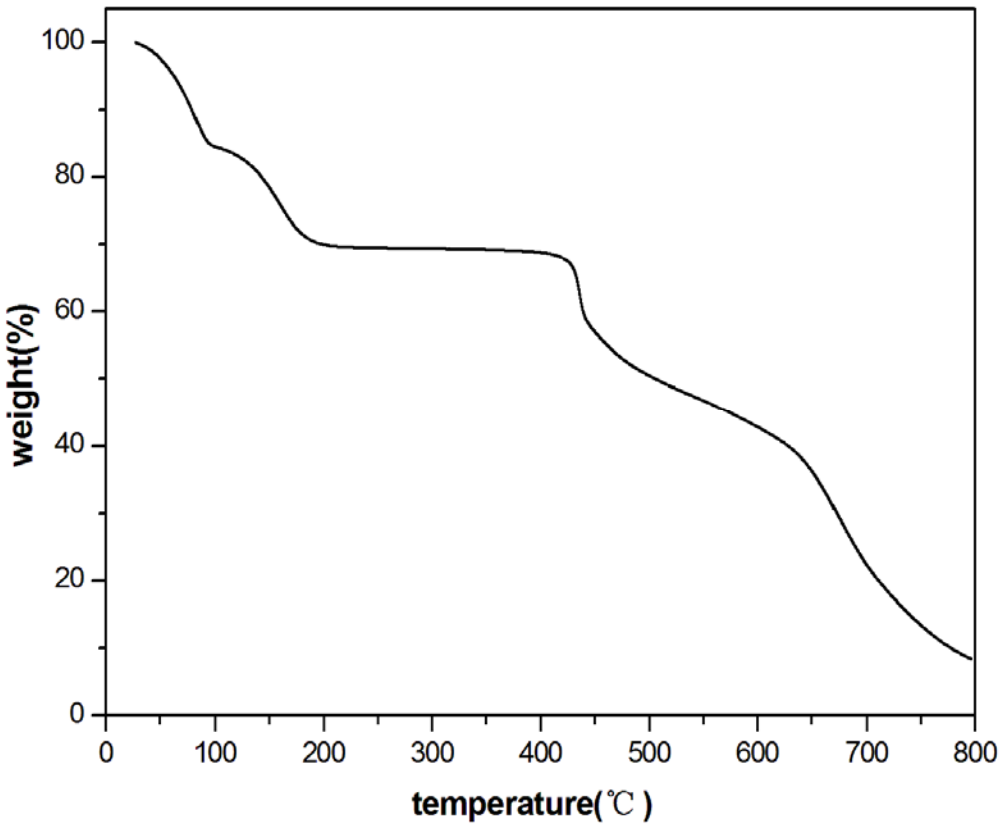

Fig. S6 The TGA plot of STU-5 with DMF and ethanol guests under N_2 atmosphere.

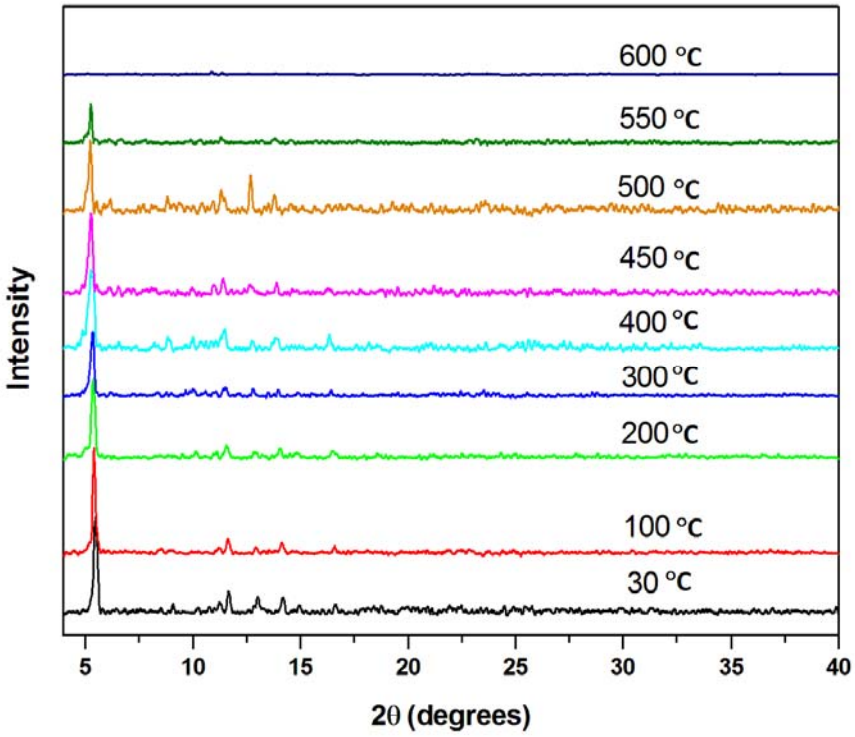

Fig. S7 The variable-temperature powder X-ray diffraction patterns of STU-5.

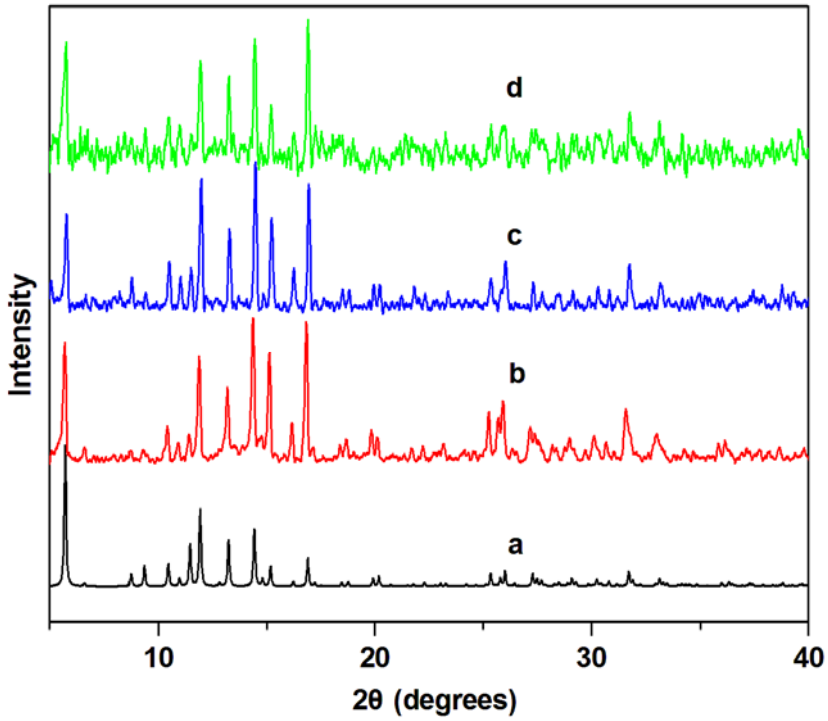

Fig. S8 X-ray diffraction patterns (Cu Kα, λ=1.5418 Å) of compound STU-5. (a) Calculated pattern from the single crystal structure; (b) observed from an as-synthesized sample; (c) observed from solid sample of (b) treated in boiling water for 24 hours; (d) observed from solid sample of (b) treated in boiling methanol for 24 hours.

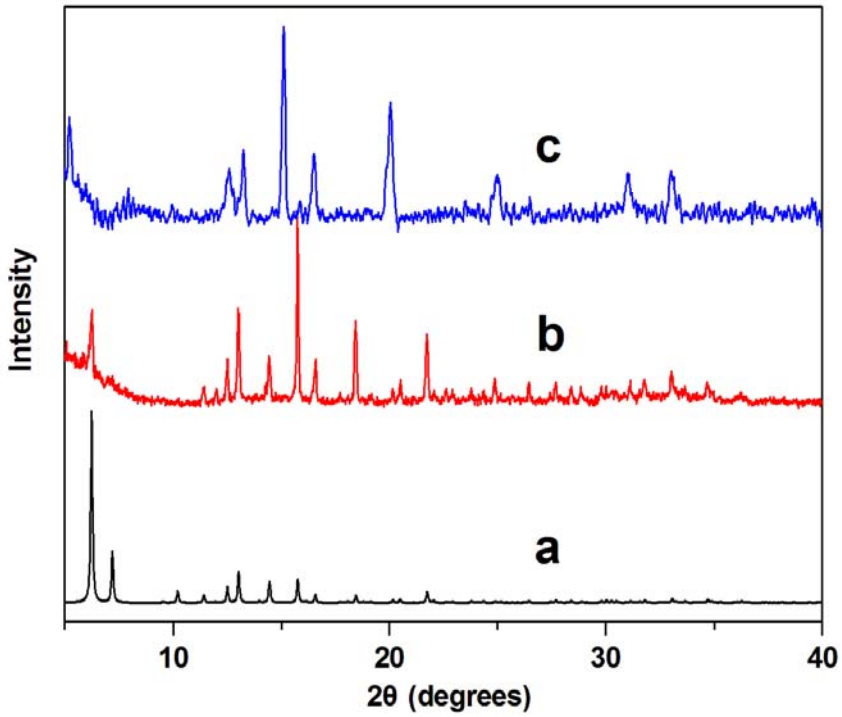

Fig. S9 X-ray diffraction patterns (Cu Kα, λ=1.5418 Å) of compound STU-1. (a) Calculated pattern from the single crystal structure; (b) observed from an as-synthesized sample; (c) observed from sample of (b) treated in boiling water for 24 hours.

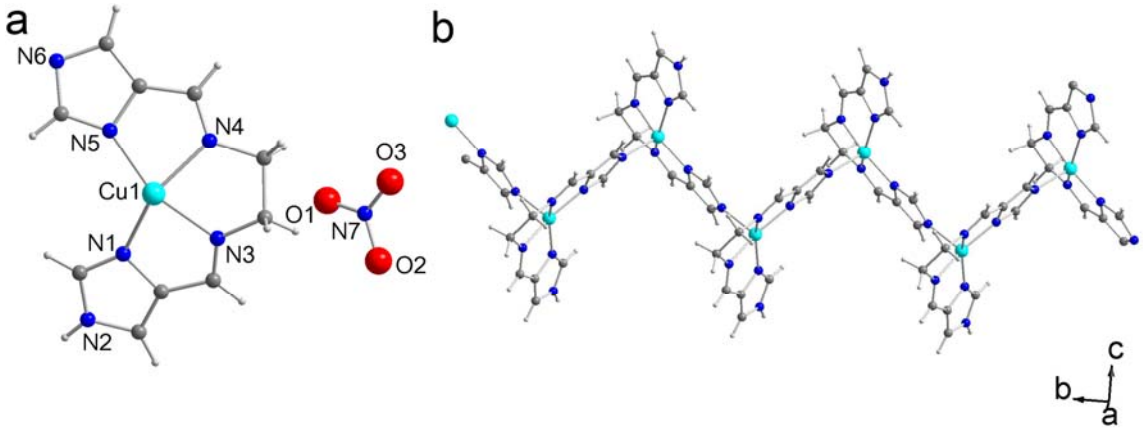

Fig. S10 Crystal structure of compound Cu(BImED)NO_3: (a) asymmetric unit, (b) 1D zig-zag coordination polymer structure.

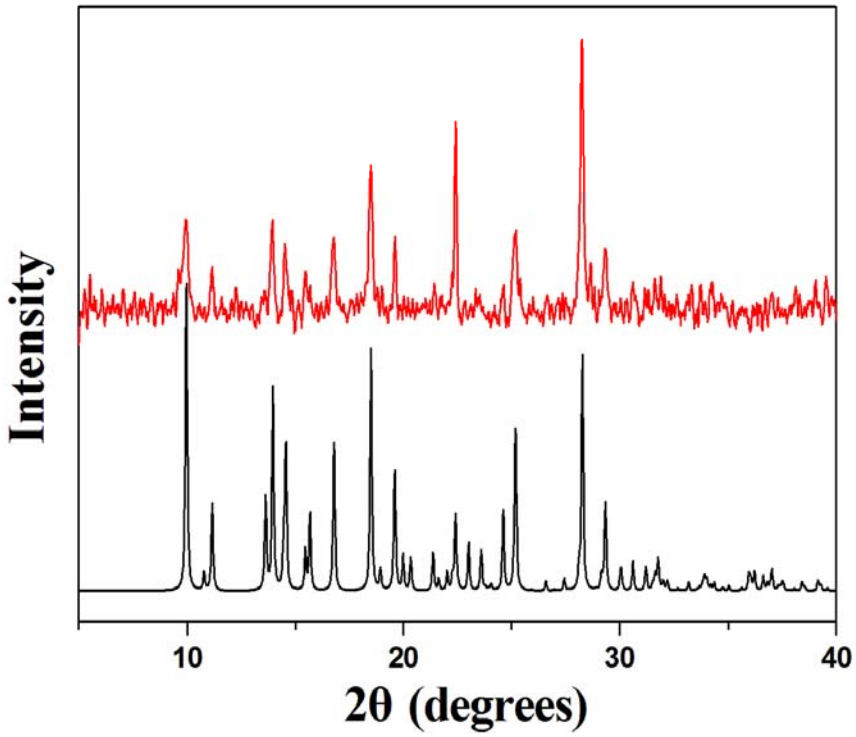

Fig. S11 X-ray diffraction patterns (Cu Kα, λ=1.5418 Å) of compound Cu(BImED)NO_3. (a) Calculated pattern from single crystal structure of Cu(BImED)NO_3; (b) observed from an as-synthesized sample of Cu(BImED)NO_3.

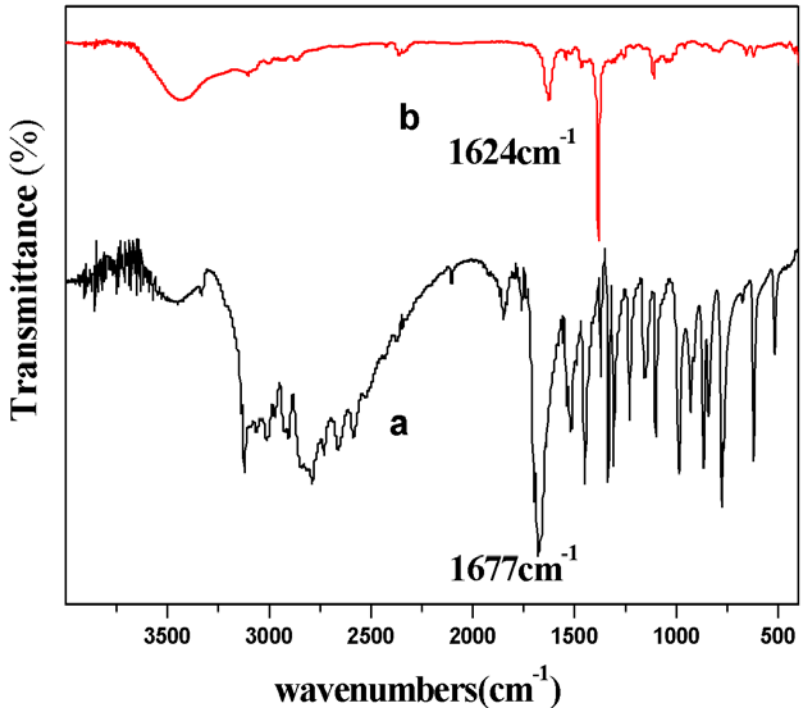

Fig. S12 IR spectra of 4-formylimidazole (a), Cu(BImED)NO_3 (b).