Supporting Information for

A new strategy for the construction of single-walled metal-organic nanotubular framework: utilizing "T"-shaped building unit with ligand modification

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Experimental Details

General: All solvents and starting materials were purchased commercially and used as received. Elemental analyses (EA) were performed by a Perkin-Elmer 240 elemental analyzer (C, H, N). Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα). Thermogravimetric (TGA) measurements were performed on a TA Instruments Q50 Thermogravimetric Analyzer under nitrogen flow of (40 mL·min^{-1}) at a typical heating rate of 10 °C·min^{-1}. N_2 and CO_2 sorption for **2** measurements were performed using a Micromeritics ASAP 2020 M instrument.

Synthesis of 1: A mixture of Cu_2O (0.0074 g, 0.05mmol), Hpim (0.0145 g, 0.1000 mmol), H_2O (4.0 mL) and $NH_3·H_2O$ (25%, 2.0 mL) was put into a 15-mL Teflon-lined stainless autoclave and heated to 180 ºC for three days. This was then slowly cooled to room temperature. Purple crystals of **1** were obtained in about 30% yield. Elemental Analysis (%) for $C_8H_6CuN_3$ (calc: C, 46.26; H, 2.91; N, 20.23; found: C, 46.19; H, 3.02; N, 20.28).

Synthesis of 2: A mixture of CuI (0.0100 g, 0.05mmol), H_2ppt (0.0180 g, 0.10 mmol), THF (4.0 mL) and $NH_3·H_2O$ (25%, 2.5 mL) was put into a 15-mL Teflon-lined stainless autoclave and heated to 140 ºC for three days. This was then slowly cooled to room temperature. Purple crystals of **2** were obtained in about 40% yield. Elemental Analysis (%) for $C_7H_7Cu_2N_4SO_{1.5}$ (calc: C, 25.45; H, 2.14; N, 16.96; found: C, 25.49; H, 2.11; N, 17.01).

X-ray Crystallography. All single crystals of both complexes were carefully selected under an optical microscope and glued to thin glass fibers. Structural measurement for **1** was performed on a computer-controlled Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 294 K; for **2**, the structure determination was performed on Gemini Atlas CCD diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) at 294 K. Absorption corrections were applied by using the multiscan program SADABS. Structural solutions and full-matrix least-square refinements based on F^2 were performed with the SHELX-97 program packages, respectively. Anisotropic thermal parameters were applied to all non-hydrogen atoms. All the hydrogen atoms were generated geometrically. Crystal data as well as details of data collection and refinements for the complexes are described in the note of manuscript. Selected structural characteristics are given in Table S1. The compound **2** crystallized in a chiral space group $P4_2$, but the refinement of the structure gave the value of the flack parameter approaching 0.5 indicating a twin structure. The formula of **2** in the refinement result contains one water molecule less than that in the product based on elemental analysis (EA) and thermogravimetric analysis (TGA). It may be due to the loss of water before performing structural measurement and the former is determining just one crystal whereas the latter for the bulk of product.

Table S1 Selected bond lengths [Å] and angles [°] for **1** and **2**

Compound 1			
Cu(1)-N(2)#1	1.929(6)	N(2)#1-Cu(1)-N(1)	150.0(3)
Cu(1)-N(1)	1.932(6)	N(2)#1-Cu(1)-N(3)#2	101.8(3)
Cu(1)-N(3)#2	2.177(7)	N(1)-Cu(1)-N(3)#2	104.6(2)

Symmetry codes: #1 x-1,y,z; #2 x-1/2,-y+3/2,z+1/2.			
Compound 2			
Cu(1)-N(2)#1	1.898(5)	N(2)#1-Cu(1)-N(3)	155.53(15)
Cu(1)-N(3)	1.927(5)	N(2)#1-Cu(1)-N(4)#2	101.1(2)
Cu(1)-N(4)#2	2.197(3)	N(3)-Cu(1)-N(4)#2	101.2(2)
Cu(2)-N(1)#1	2.017(5)	N(1)#1-Cu(2)-S(1)	138.06(15)
Cu(2)-S(1)	2.261(3)	N(1)#1-Cu(2)-S(1)#3	103.46(15)
Cu(2)-S(1)#3	2.464(2)	S(1)-Cu(2)-S(1)#3	106.00(8)
Cu(2)-S(1)#4	2.481(2)	N(1)#1-Cu(2)-S(1)#4	107.19(14)
S(1)-Cu(2)-S(1)#4	105.43(8)	S(1)#3-Cu(2)-S(1)#4	83.03(7)
Cu(2')-N(1')#7	2.160(7)	N(1')#7-Cu(2')-S(1')	142.7(3)
Cu(2')-S(1')	2.272(14)	N(1')#7-Cu(2')-S(1')#6	99.8(4)
Cu(2')-S(1')#6	2.458(10)	S(1')-Cu(2')-S(1')#6	105.0(4)
Cu(2')-S(1')#5	2.460(10)	N(1')#7-Cu(2')-S(1')#5	105.6(4)
S(1')-Cu(2')-S(1')#5	105.0(4)	S(1')#6-Cu(2')-S(1')#5	82.2(3)
Cu(1)-Cu(2)	2.925(1)	Cu(1)-Cu(2')#1	2.902(4)
Symmetry codes: #1 x,y,z+1; #2 -y+1,x,z+1/2; #3 y+1,-x+1,z+1/2; #4 -y+1,x-1,z+1/2; #5 -y+1,x-1,z-1/2; #6 y+1,-x+1,z-1/2; #7 x,y,z-1.			

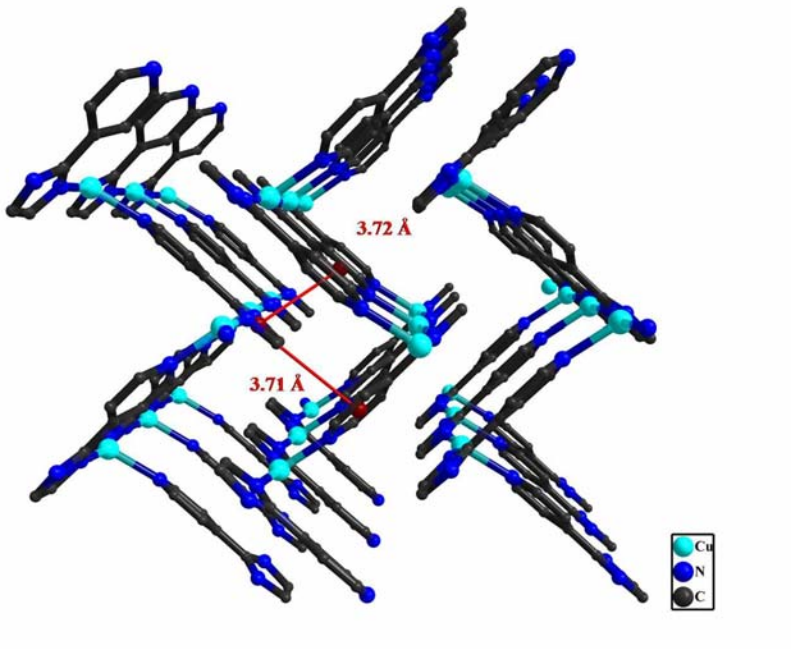

Fig. S1 3D structure of **1**.

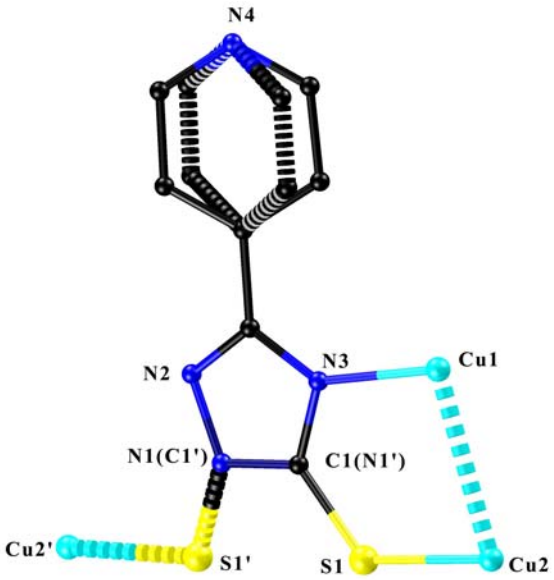

Fig. S2 The asymmetric unit in **2**.

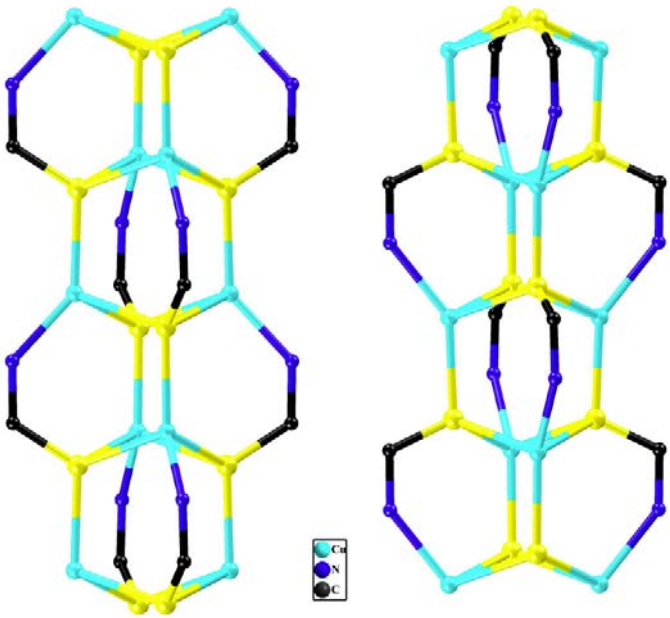

Fig. S3 Two kinds of "CuSCN" chains in **2** constructed by two disordered parts: Cu2, S1, C1, N1 (left) and Cu2', S2', C1', N1' (right), respectively, showing different chirality.

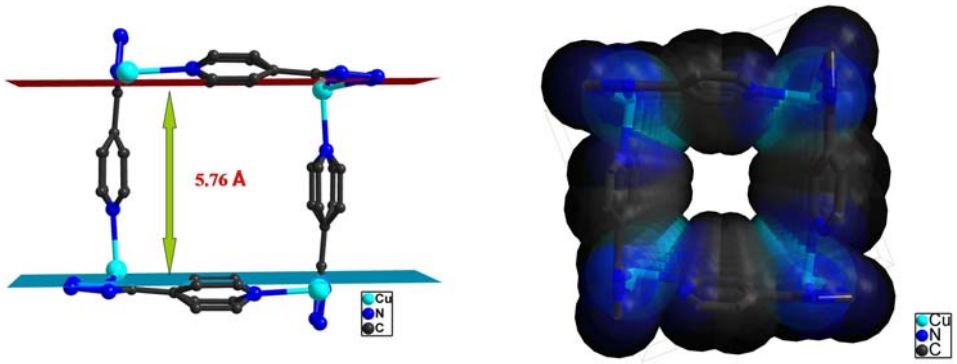

Fig. S4 View of 1D channel, the diameter (left) and stick model superposed by space filling model (right) in **2**.

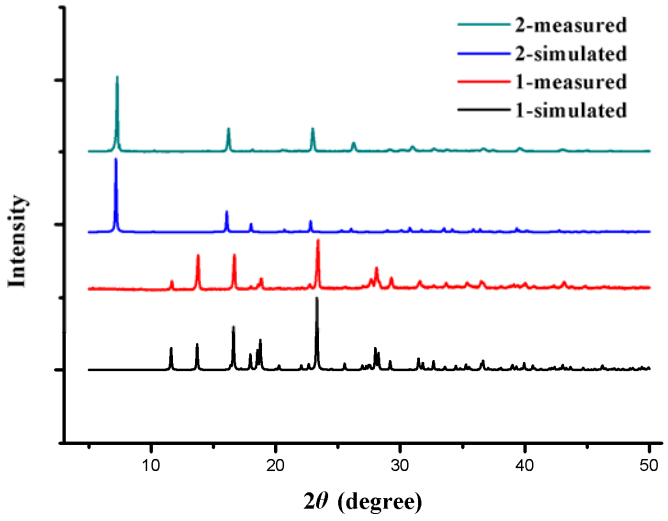

Fig. S5 PXRD patterns of **1** and **2**.

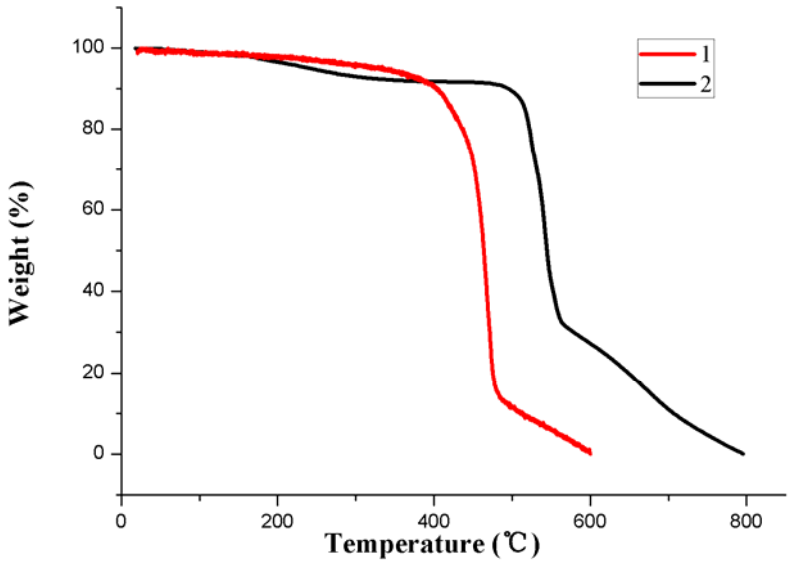

Fig. S6 TGA of **1** and **2**.

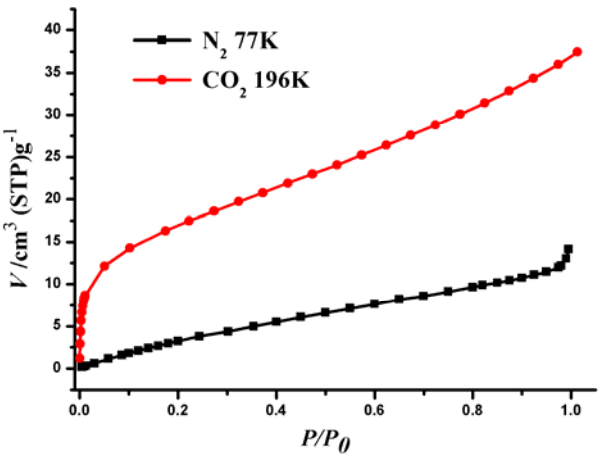

Fig. S7 Adsorption isotherms of CO_2 (red) and N_2 (black) at low temperature (195K for CO_2 and 77K for N_2) for activated **2** (desorption isotherms are omitted for clarity).