Supporting Information

First Design of Novel Three-dimensional Coordination Polymers Based on Triangular Trinuclear Copper 1,2,4-triazolate Units

Quan-Guo Zhai, Can-Zhong Lu*, Shu-Mei Chen, Xin-Jiang Xu, Wen-Bin Yang

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences,

Fuzhou, Fujian, 350002, P.R. China.

*Corresponding author

E-mail: *czlu@ms.fjirsm.ac.cn*; Fax: +86-591-83714946; Tel.: +86-591-83705794.

Supplementary Index

Table S1. Bond lengths (Å) and angles (°) for **1** ……S3

Table S2. Bond lengths (Å) and angles (°) for **2**…….……S4

Table S3. Bond lengths (Å) and angles (°) for **3**……..……...S5

Figure S1.Channels formed in **1** viewed along [-1 0 1] axis ...……..…….S6

Figure S2. The infinite Cu^{II} chains in **2**……...……... S6

Figure S3. 2D inorganic sheet in **3** viewed from different directions.……..……...S7

Figure S4. Linking modes between triazole ligands and inorganic layers in **3**……....S7

Figure S5. FT-IR spectra...……..……...…...S8

Figure S6. TGA curves of **1**, **2** and **3**……..…….…….….S8

Figure S7. Powder XRD patterns for **1**…….…… S9

Figure S8. ESR spectra and magnetic data for **1**, **2** and **3**…….S10

Table S1. Bond lengths (Å) and angles (°) for **1**

Cu(1)-O(3)	1.9850(9)	N(1)#1-Cu(1)-N(1)	177.0(2)
Cu(1)-N(1)#1	1.992(5)	O(3)-Cu(1)-N(2)	180.0
Cu(1)-N(1)	1.992(5)	N(1)#1-Cu(1)-N(2)	91.50(12)
Cu(1)-N(2)	2.009(6)	N(1)-Cu(1)-N(2)	91.50(12)
C(1)-N(1)#2	1.307(7)	N(1)#2-C(1)-N(2)	112.7(5)
C(1)-N(2)	1.337(7)	C(1)#3-N(1)-N(1)#4	106.0(3)
N(1)-C(1)#3	1.307(7)	C(1)#3-N(1)-Cu(1)	132.7(4)
N(1)-N(1)#4	1.368(8)	N(1)#4-N(1)-Cu(1)	120.89(14)
N(2)-C(1)#1	1.337(7)	C(1)#1-N(2)-C(1)	102.7(6)
O(3)-Cu(1)#5	1.9850(9)	C(1)#1-N(2)-Cu(1)	128.7(3)
O(3)-Cu(1)#6	1.9850(9)	C(1)-N(2)-Cu(1)	128.7(3)
		Cu(1)-O(3)-Cu(1)#5	120.0
O(3)-Cu(1)-N(1)#1	88.50(12)	Cu(1)-O(3)-Cu(1)#6	120.0
O(3)-Cu(1)-N(1)	88.50(12)	Cu(1)#5-O(3)-Cu(1)#6	120.0

Symmetry transformations used to generate equivalent atoms:

#1 y-1/4, x+1/4, -z #2 -y+1/2, -z+1/2, -x #3 -z, -x+1/2, -y+1/2

#4 -x, z+1/4, y-1/4 #5 z+0, -x+1/4, -y+1/4 #6 -y+1/4, -z+1/4, x+0

Table S2. Bond lengths (Å) and angles (°) for **2**

Cu(1)-N(1)#1	1.945(5)	O(1)-Cu(1)-Cl(1)	180.0
Cu(1)-N(1)	1.945(5)	N(2)-Cu(2)-N(2)#2	120.0
Cu(1)-O(1)	2.0151(10)	N(2)-Cu(2)-N(2)#3	120.0
Cu(1)-Cl(1)	2.347(2)	N(2)#2-Cu(2)-N(2)#3	120.0
Cu(2)-N(2)	1.966(7)	N(2)-Cu(2)-Cu(2)#4	90.0
Cu(2)-N(2)#2	1.966(7)	N(2)#2-Cu(2)-Cu(2)#4	90.0
Cu(2)-N(2)#3	1.966(7)	N(2)#3-Cu(2)-Cu(2)#4	90.0
Cu(2)-Cu(2)#4	2.9820(4)	N(2)-Cu(2)-Cu(2)#5	90.0
Cu(2)-Cu(2)#5	2.9820(4)	N(2)#2-Cu(2)-Cu(2)#5	90.0
N(1)-C(1)	1.312(7)	N(2)#3-Cu(2)-Cu(2)#5	90.0
N(1)-N(1)#6	1.375(9)	Cu(2)#4-Cu(2)-Cu(2)#5	180.0
N(2)-C(1)	1.347(7)	C(1)-N(1)-N(1)#6	106.1(3)
N(2)-C(1)#6	1.347(7)	C(1)-N(1)-Cu(1)	131.0(4)
O(1)-Cu(1)#7	2.0151(10)	N(1)#6-N(1)-Cu(1)	122.94(14)
O(1)-Cu(1)#8	2.0151(10)	C(1)-N(2)-C(1)#6	102.5(6)
		C(1)-N(2)-Cu(2)	128.7(3)
N(1)#1-Cu(1)-N(1)	174.1(3)	C(1)#6-N(2)-Cu(2)	128.7(3)
N(1)#1-Cu(1)-O(1)	87.06(14)	Cu(1)#7-O(1)-Cu(1)#8	120.0
N(1)-Cu(1)-O(1)	87.06(14)	Cu(1)#7-O(1)-Cu(1)	120.0
N(1)#1-Cu(1)-Cl(1)	92.94(14)	Cu(1)#8-O(1)-Cu(1)	120.0
N(1)-Cu(1)-Cl(1)	92.94(14)	N(1)-C(1)-N(2)	112.7(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+y, -x, z #2 -y, x-y, z #3 -x, -y, -z #4 -x, -y, -z+1
#5 -y+1, -x+1, z #6 x, x-y, z #7 -y+1, x-y, z #8 -x+y+1, -x+1, z

Table S3. Bond lengths (Å) and angles (°) for **3**

Cu(1)-N(2)	1.931(5)	N(1)-Cu(2)-Cl(1)#4	88.27(8)
Cu(1)-Cl(1)#1	2.2849(15)	N(1)#2-Cu(2)-Cl(1)#4	91.73(8)
Cu(1)-Cl(1)	2.2849(15)	Cl(1)#3-Cu(2)-Cl(1)#4	180.00(4)
Cu(2)-N(1)	1.935(3)	N(1)-Cu(2)-Cl(1)#2	91.73(8)
Cu(2)-N(1)#2	1.935(3)	N(1)#2-Cu(2)-Cl(1)#2	88.27(8)
Cu(2)-Cl(1)#3	2.5789(13)	Cl(1)#3-Cu(2)-Cl(1)#2	82.79(6)
Cu(2)-Cl(1)#4	2.5789(13)	Cl(1)#4-Cu(2)-Cl(1)#2	97.21(6)
Cu(2)-Cl(1)#2	2.5789(13)	N(1)-Cu(2)-Cl(1)	88.27(8)
Cu(2)-Cl(1)	2.5789(13)	N(1)#2-Cu(2)-Cl(1)	91.73(8)
Cl(1)-Cu(2)#4	2.5789(13)	Cl(1)#3-Cu(2)-Cl(1)	97.21(6)
C(1)-N(1)	1.325(5)	Cl(1)#4-Cu(2)-Cl(1)	82.79(6)
C(1)-N(2)#5	1.340(5)	Cl(1)#2-Cu(2)-Cl(1)	180.0
N(1)-N(1)#4	1.367(7)	Cu(1)-Cl(1)-Cu(2)#4	106.81(5)
N(2)-C(1)#5	1.340(5)	Cu(1)-Cl(1)-Cu(2)	106.81(5)
N(2)-C(1)#6	1.340(5)	Cu(2)#4-Cl(1)-Cu(2)	81.94(5)
		N(1)-C(1)-N(2)#5	111.9(4)
N(2)-Cu(1)-Cl(1)#1	128.62(4)	C(1)-N(1)-N(1)#4	106.3(2)
N(2)-Cu(1)-Cl(1)	128.62(4)	C(1)-N(1)-Cu(2)	132.4(3)
Cl(1)#1-Cu(1)-Cl(1)	102.76(8)	N(1)#4-N(1)-Cu(2)	121.37(10)
N(1)-Cu(2)-N(1)#2	180.00(9)	C(1)#5-N(2)-C(1)#6	103.7(5)
N(1)-Cu(2)-Cl(1)#3	91.73(8)	C(1)#5-N(2)-Cu(1)	128.1(2)
N(1)#2-Cu(2)-Cl(1)#3	88.27(8)	C(1)#6-N(2)-Cu(1)	128.1(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y+3/2, z #2 -x+1/2, -y+1/2, -z+1/2 #3 x+1/2, y, -z+1/2

#4 -x, -y+1/2, z #5 -x, -y+1, -z #6 x, y+1/2, -z

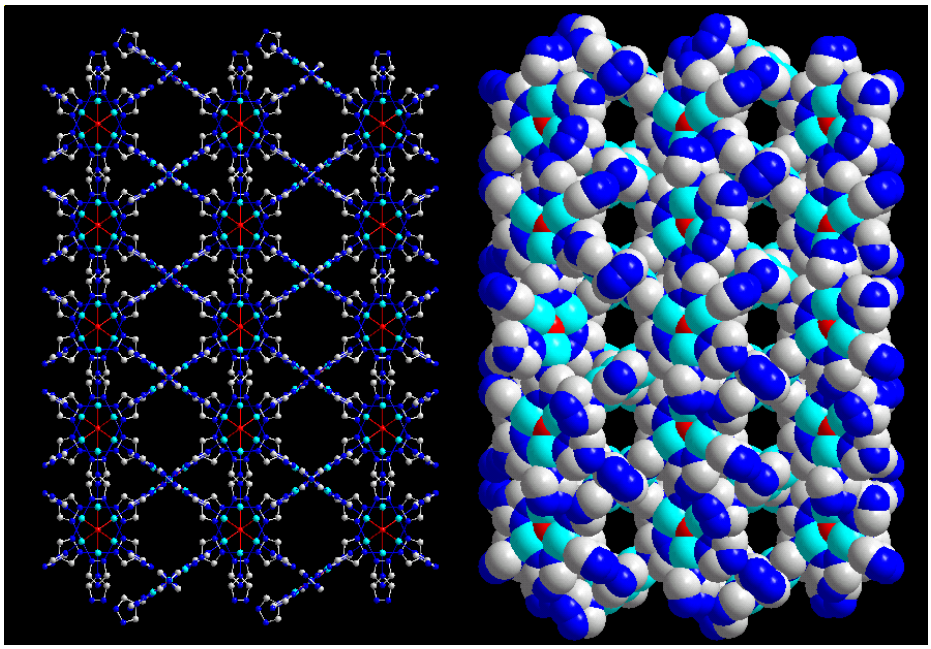


Figure S1. Ball-and-stick representation (left) and space-filling diagram (right) of the channels formed in **1** viewed along [-1 0 1] axis.

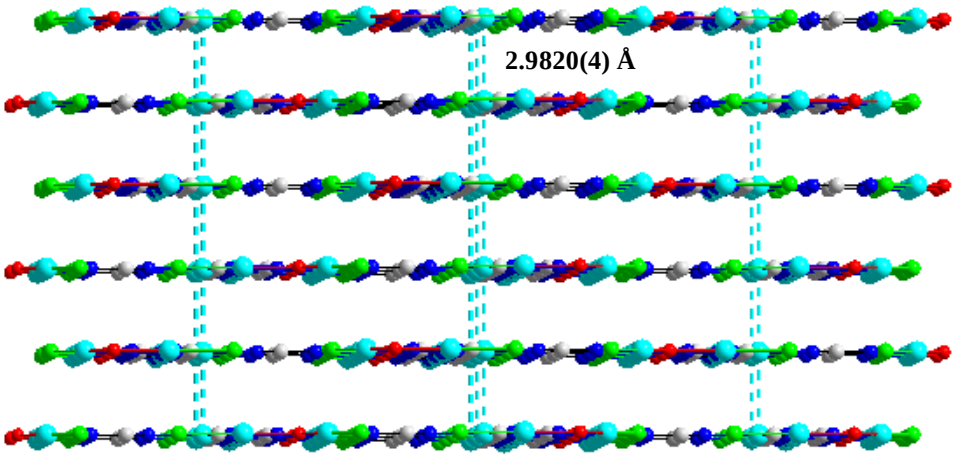


Figure S2. The infinite Cu^{II} chains in **2**.

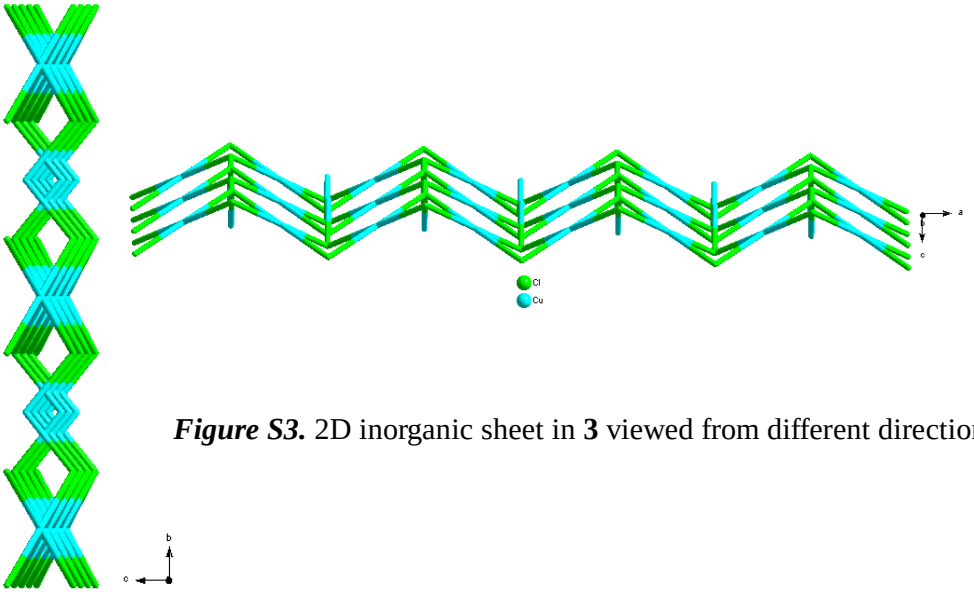


Figure S3. 2D inorganic sheet in **3** viewed from different directions

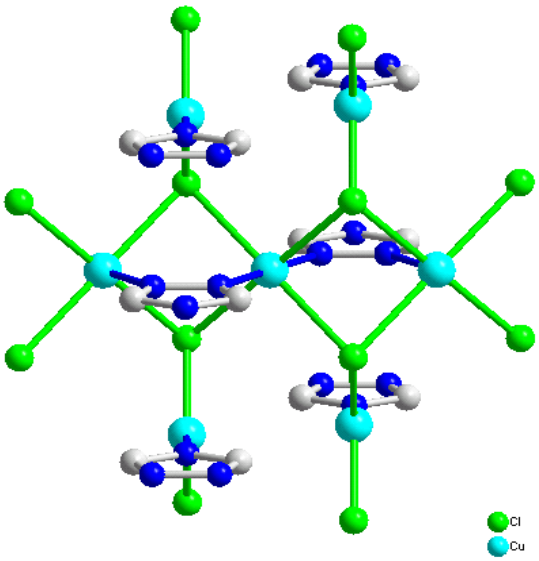


Figure S4. Basic linking modes between triazole ligands and 2D inorganic layers in **3**

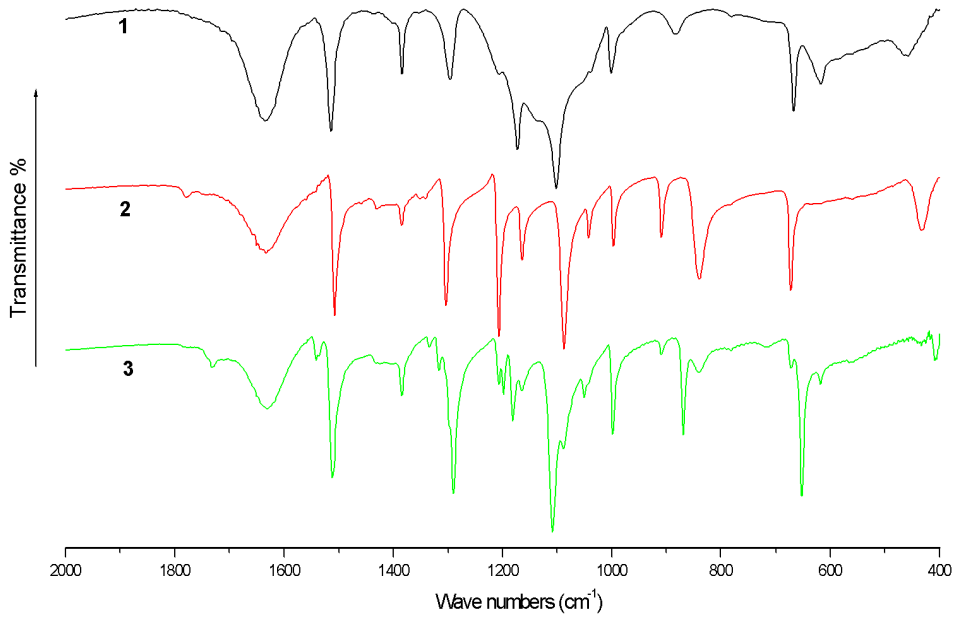


Figure S5. FT-IR spectra of **1**, **2** and **3**

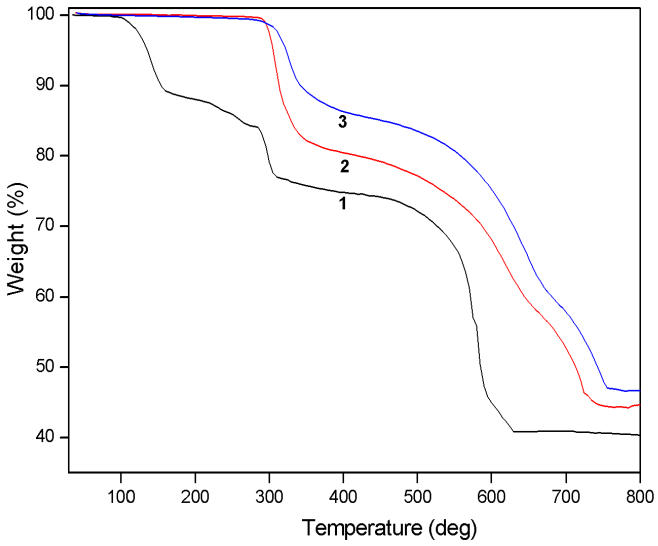


Figure S6. TGA curves for **1**, **2** and **3**. The weight loss in the temperature range 300-750 ^{o}C is 54.05 % for **2** and 51.46 % for **3**, which corresponding to the decomposition of organic components and chlorine (calcd: 53.49 % for **2** and 52.28 % for **3**).

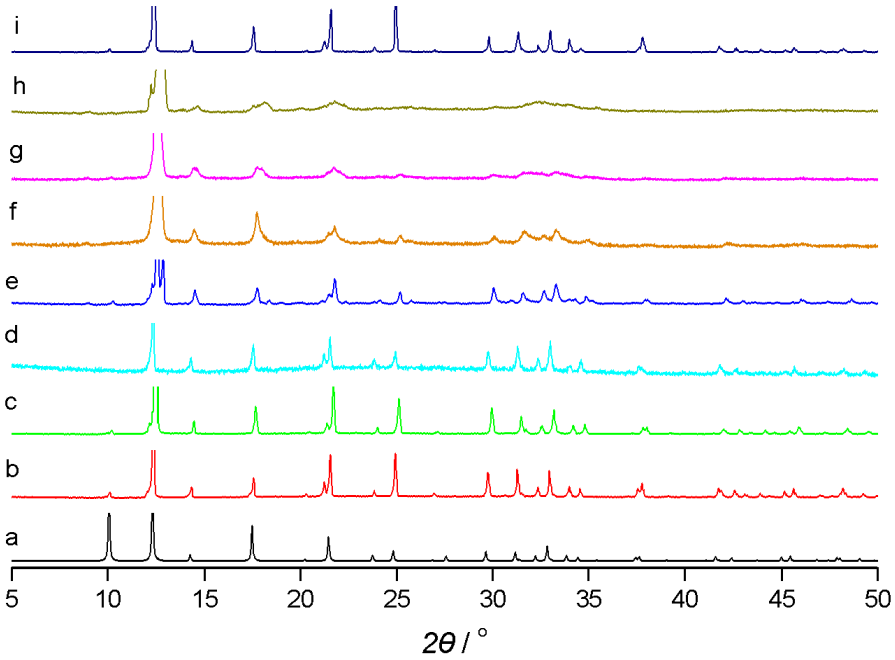
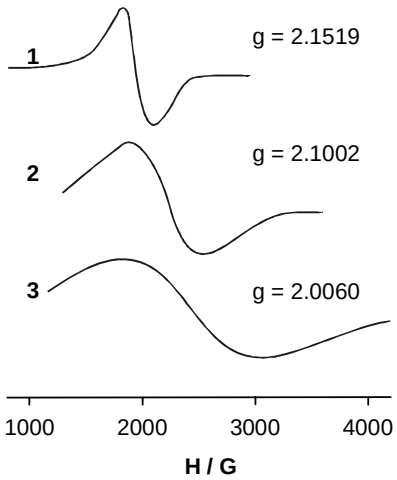
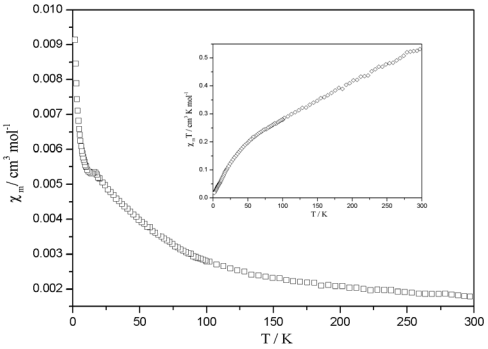


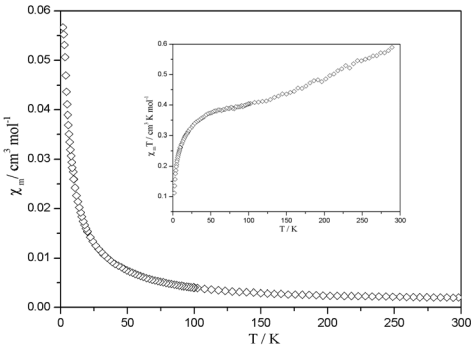
Figure S7. XRPD patterns for **1**: (a) calculated on the basis of the structure determined by single-crystal X-ray diffraction; (b) taken at room temperature; (c) after heating at 100 ^{o}C for 30min; (d) after heating at 200 ^{o}C for 30min; (e) after heating at 300 ^{o}C for 30min; (f) after heating at 350 ^{o}C for 30min; (g) after heating at 400 ^{o}C for 30min; (h) after heating at 450 ^{o}C for 30min; (i) after rehydration of sample (f) for 24 h.



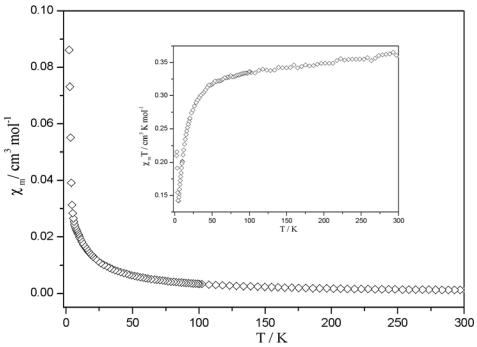
(a)



(b)



(c)



(d)

Figure S8. ESR powder spectra at 298 K (a) and temperature dependence of the magnetic susceptibility recorded in a field of 5K Oe (b - **1**, c - **2**, d - **3**). The insets show the corresponding variation of the $\chi_M T$ products.