Electronic Supplementary Information (ESI) for

Unprecedented copper(I)-catalyzed *in situ* double cycloaddition reaction based on 2-cyanopyrimidine

Tian Wen, Mian Li, Xiao-Ping Zhou and Dan Li*

Department of Chemistry, Shantou University, Guangdong 515063, P. R. China.

E-mail: dli@stu.edu.cn

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, s = strong. Solid-state photoluminescence spectra were performed on a Perkin-Elmer LS 55 luminescence spectrometer. Thermal analyses were carried in the temperature range of 25–900 °C by means of a Rigaku standard TG-DTA analyzer in N_2 with an increasing temperature rate of 10 °C/min.

Synthesis of complexes 1, **2 and 3**: A mixture of Cu_2O (0.0143 g, 0.1 mmol), 2-cyanoprimidine (0.0105 g, 0.1 mmol), NaN_3 (0.0325 g, 0.5 mmol) in ethanol solvent (9.0 mL) adding a few drops of $NH_3{\cdot}H_2O$ was stirred for 15 min. It was then transferred and sealed in a 13 mL Teflon-lined stainless steel reactor, which was heated in an oven to 140 °C for 72 h and then cooled to room temperature at a rate of 3 °C 0.5 h^{-1}. Red block crystals of **1** were obtained as the main product (44% yield). Complex **2** was prepared using the method similar to that of complex **1** except without adding $NH_3{\cdot}H_2O$. Red block crystals were collected and dried in air (30% yield). Complex **3** was also prepared using the method of that similar to that of complex **1** except without adding NaN_3. Needle crystals were obtained as the main product (35% yield). IR for complex **1** (KBr pellet, cm^{-1}): 2092m, 1568vs, 1560m, 1490s, 1497w,1383vs, 822w; for **2**: 2115m, 1625s, 1576s, 1392vs, 1483w, 1413w, 810w, for **3**: 2100m, 1593m, 1490w, 1396vs, 1388vs, 818m, 645m. Complexes **1** and **3** are air-stable and insoluble in common solvents; and complex **2** is unstable in air and the color of the crystals change to blue after several days at room temperature.

Crystal Data Section

Crystallography: Suitable crystals of **1**, **2** and **3** were mounted with glue at the end of a glass fiber, respectively. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα, λ = 0.71073 Å) using SMART [Bruker AXS, Madison, WI, USA, **1997**]. Reflection intensities were integrated using SAINT software and absorption correction was applied semi-empirically [Bruker AXS, Madison, WI, USA, **1997**]. 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 (C–H = 0.960 Å). The crystallographic calculations were conducted using the SHELXL-97 programs.[1] The orientation of the bridging cyanide group in **2** was found to be disordered, and the C and N atoms were refined with a 50 % probability of being C or N. Parameters for data collection and refinement of complexes **1**, **2** and **3** are summarized in Table S**1**. Selected bond lengths and angles for complexes **1**, **2** and **3** are given in Table S**2**.

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[1] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.

Table S1. Summary of the Crystal Data and Structure Refinement Parameters for **1**, **2** and **3**.

Parameter	**1**	**2**	**3**
Chemical formula	$C_{16}H_9Cu_3N_{14}$	$C_{11}H_6Cu_2N_{13}$	$C_{22}H_{12}Cu_4N_{16}$
Formula weight	587.99	447.39	754.68
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*-1	*C*2/*c*	*P*-1
a (Å)	9.7029(6)	16.0392(2)	8.3754(15)
b (Å)	10.1842(6)	9.0345(7)	10.891(2)
c (Å)	11.1003(7)	14.6031(19)	14.418(3)
α (deg)	107.2920(10)	90	96.696(3)
β (deg)	91.1910(10)	111.974(2)	101.866(3)
γ (deg)	109.5120(10)	90	96.275(3)
V (Å^3)	978.34(10)	1962.3(4)	1266.2(4)
Z	2	4	2
T (K)	293(2)	293(2)	293(2)
D_{Calcd} (g cm^{-3})	1.996	1.514	1.979
μ(mm^{-1})	3.272	2.190	3.363
Reflections collected	5707	5450	8878
Unique reflections	3367	1709	4375
R_{int}	0.0222	0.0226	0.0206
$R1$ [I > 2σ(I)]	0.0466	0.0716	0.0436
$wR2$ [I > 2σ(I)]	0.1135	0.2172	0.1111
$R1$ [all refl.]	0.0689	0.0815	0.0528
wR2 [all refl.]	0.1496	0.2287	0.1183
ρ_{fin} (max/min) (e Å^{-3})	0.764/-0.477	1.149/-0.661	1.830/-1.167

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) for Complexes **1**, **2** and **3**.

Complex **1**			
Cu(1)-N(14)	1.893(5)	N(14)-Cu(1)-N(5)	112.3(2)
Cu(1)-N(9)	1.963(4)	N(14)-Cu(1)-N(9)	133.8(2)
Cu(1)-N(5)	2.028(5)	N(9)-Cu(1)-N(5)	113.79(19)
Cu(2)-C(16)#1	1.885(6)	C(16)#1-Cu(2)-N(10)	135.1(2)
Cu(2)-N(10)	2.018(5)	C(16)#1-Cu(2)-N(8)	129.9(3)
Cu(2)-N(8)	2.126(5)	N(10)-Cu(2)-N(8)	79.2(2)
Cu(2)-C(16)#2	2.367(6)	C(16)#1-Cu(2)-C(16)#2	106.3(2)
Cu(2)-Cu(2)#3	2.5776(16)	N(10)-Cu(2)-C(16)#2	101.9(2)
Cu(3)-N(6)#4	1.955(4)	N(8)-Cu(2)-C(16)#2	96.5(2)
Cu(3)-N(11)	2.010(5)	C(16)#1-Cu(2)-Cu(2)#3	61.77(19)
Cu(3)-N(13)	2.129(5)	N(10)-Cu(2)-Cu(2)#3	135.10(16)
Cu(3)-N(2)#4	2.199(5)	N(8)-Cu(2)-Cu(2)#3	124.95(17)
N(11)-Cu(3)-N(13)	80.79(19)	N(6)#4-Cu(3)-N(11)	144.5(2)
N(6)#4-Cu(3)-N(2)#4	79.94(18)	N(6)#4-Cu(3)-N(13)	127.49(19)
N(11)-Cu(3)-N(2)#4	105.54(18)	N(13)-Cu(3)-N(2)#4	120.33(19)
Complex **2**			
Cu(1)-C(7)	1.870(4)	C(7)-Cu(1)-N(4)#1	122.78(15)
Cu(1)-N(2)	2.039(4)	N(2)-Cu(1)-N(4)#1	97.98(15)
Cu(1)-N(4)#1	2.126(3)	C(7)-Cu(1)-N(6)#1	127.14(16)
Cu(1)-N(6)#1	2.134(3)	N(2)-Cu(1)-N(6)#1	109.79(13)
C(7)-Cu(1)-N(2)	112.62(15)	N(4)#1-Cu(1)-N(6)#1	79.56(13)
Complex **3**			
Cu(1)-N(15)	1.929(6)	Cu(4)-N(13)	2.158(4)
Cu(1)-N(16)	1.956(4)	Cu(3)-N(9)	1.953(3)
Cu(1)-N(2)	2.127(3)	Cu(3)-N(12)	2.382(4)
Cu(1)-N(3)	2.149(3)	Cu(2)-N(4)	1.958(3)

Cu(4)-N(11)	2.111(4)	Cu(2)-N(10)	2.000(3)
Cu(2)-N(8)	2.241(4)	N(5)#2-Cu(3)-N(12)	114.88(14)
Cu(2)-N(6)	2.431(4)	N(9)-Cu(3)-N(12)	80.99(13)
N(15)-Cu(1)-N(16)	122.57(18)	N(4)-Cu(2)-N(10)	136.06(15)
N(15)-Cu(1)-N(2)	130.72(17)	N(4)-Cu(2)-N(8)	123.86(15)
N(16)-Cu(1)-N(2)	99.11(15)	N(10)-Cu(2)-N(8)	80.03(13)
N(15)-Cu(1)-N(3)	109.56(16)	N(4)-Cu(2)-N(6)	75.85(13)
N(2)-Cu(1)-N(3)	77.48(13)	N(11)-Cu(4)-N(13)	77.83(14)

[a] Symmetry codes for **1**: #1 x,y+1,z #2 -x+1,-y+2,-z+1 #3 -x+1,-y+3,-z+1 #4 -x,-y+2,-z+1; for **2:** #1 -x+1/2,y+1/2,-z+1/2 #2 -x+1/2,y-1/2,-z+1/2 #3 -x,-y+1,-z; for **3**: #1 -x+1,-y+2,-z+1

Structural Description Section

Structure of 1

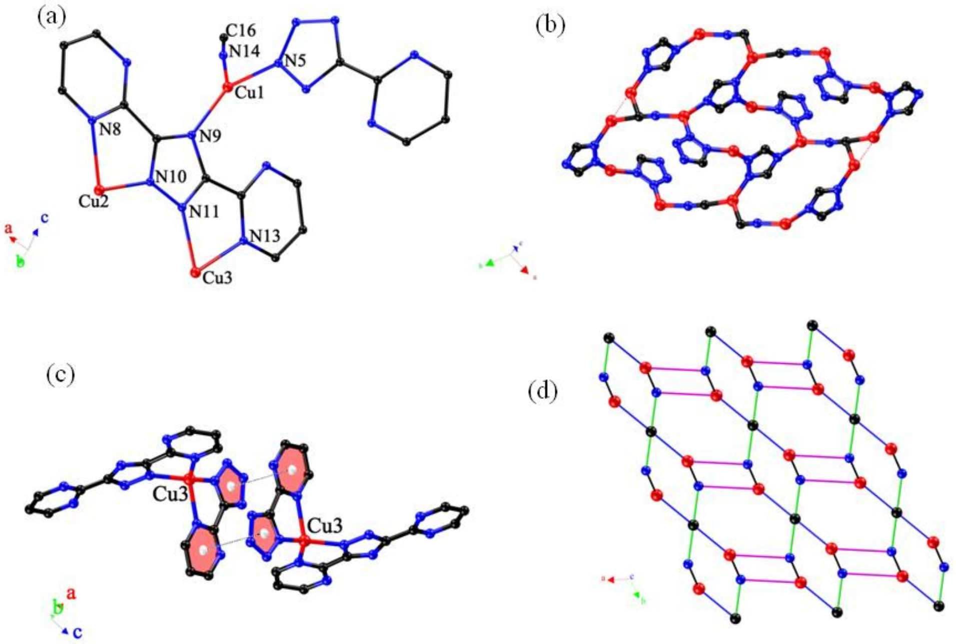


Fig. S1. (a) The asymmetry unit of **1**. (b) View of the 2D layer of **1**, wherein the shorter Cu···Cu contacts are highlighted in red dotted line, Cu atoms are shown in red, N in blue, C in black, H atoms and pyrimidine groups are omitted for clarity. (c) Schematic description of the $\pi\cdots\pi$ interaction of **1** (dotted line for $\pi\cdots\pi$ interaction). (d) Schematic description of the (3,3,4) connected $(4.6^2)(4.6^2)(6^4.10^2)$ net.

Complex **1** crystallizes in the space group of *P*-1, and contains three distinct Cu(I) ion, a CN^- linker, one ligand of 5-pyrimidyl-tetrazolate, as well as 3,5-bispyrimidyl-1,2,4-triazolate in the asymmetric unit (Fig. S**1**a). Cu1 atom is in a distorted trigonal-planar arrangement comprised of a cyanide group and one N5 donor from tetrazole ligand and one N9 donor from triazole ligand, and their angles are 112.3(1), 113.79(2), and 133.3(2) °, respectively. The Cu1–N14, Cu1–N5 and Cu1–N9 bond lengths are 1.893(5), 2.028(5), and 1.963(4) Å, respectively. The 3,5-bispyrimidyl-1,2,4-triazolate ligand chelates Cu2 and Cu3 (Fig. S**1**a), and the two Cu atoms exhibit similar distorted tetrahedral conformations (Fig. S1a). Interestingly, the pyrimidine rings of the two ligands only take part in the chelating coordination. Therefore, we can neglect pyrmidine when considering constructing coordination polymer, which results a two-dimensional net formed by tetrazolate, triazolate and cyano group (Fig. S1b). The Cu2 links two cyanide groups, the adjacent Cu2···Cu2 distances is 2.5776(16) Å. The face-to-face distance between the adjacent layers is 3.6754(1) Å, indicating the existence of weak π···π interactions (Fig. S1c). With the cyanide groups being considered as linkers, the Cu atoms being denoted as three-coordinate non-planar nodes, the whole framework are found to be trinodal (3,3,4) net with a Schläfli symbol of $(4.6^2)(4.6^2)(6^4.10^2)$ (Fig. S1d).

Structure of 2

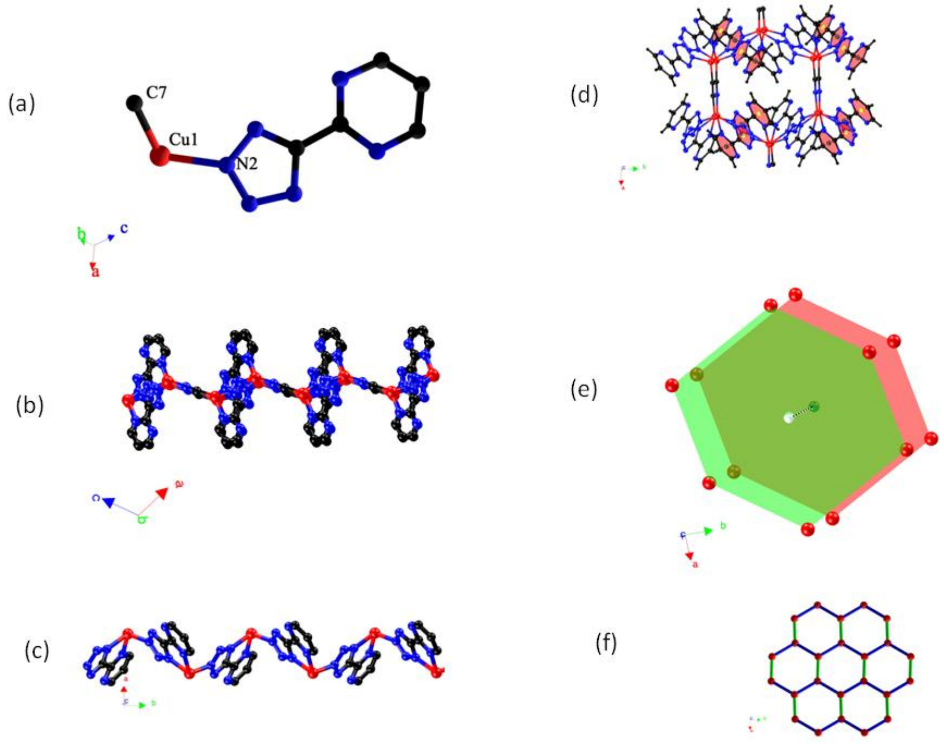


Fig. S2. (a) The asymmetry unit of **2**. (b) Schematic description of the 1D chain in **2**. (c) Schematic description of the zigzag chain in **2** after neglecting CN^-. (d) C-H$\cdots\pi$ and $\pi\cdots\pi$ interaction between neighboring 2D layers. (e) View of the two 6-membered shortest circuits interlayer (dotted line for central distance). (f) View of the (6,3) net. Cu atoms are shown in red, N in blue, C in black, H atoms are omitted for clarity.

Complex **2** crystallizes in the space group of *C*2/*c*, and only contains one Cu(I) ion, a μ_2-CN linker, as well as one ligand of 5-pyrimidyl-tetrazolate in the asymmetric unit (Fig. S2a). Similar to Cu2 and Cu3 in **1**, the Cu atom is in a distorted tetrahedral arrangement comprised of one C/N atom from cyanide groups [Cu–C/N = 1.870(4) Å] and a N donor from tetrazole ligand and two chelating N atoms from pyrimidine tetrazole [Cu–N = 2.039(4)–2.134(3) Å], with the angles varying from 79.56(13) to 127.14(16) °. The Cu–$N_{\text{tetrazole}}$ distance (2.122(4) Å) is shorter than the Cu–$N_{\text{pyrimidine}}$ distance (2.135(4) Å) as it originates from the partly deprotonated tetrazole ring, whereas the pyrimidine ring fulfills the coordination of the metal ion. Complex **2** can be regarded as one chain along the b axis (Fig. S2b). Interestingly, if we omit the cyanide groups linker, the 5-pyrimidyl-tetrazolate ligands link the Cu atoms into a one-dimensional zigzag chain along the *c* axis (Fig. S2c). These chains are then interconnected by cyanide group linker to give the resulting two-dimensional structure. The central distances of the tetrazole and the pyrimidine rings between the parallel adjacent layers are 4.0624(1) Å. The distances of the H atoms of the pyrimidine ring and the tetrazole central are 3.4809(1), 3.9254(1) and 4.3224(1) Å. These distances indicate the existence of weak π···π and the C–H···π interactions between the layers (Figure S2d). The neighbouring central distances of hexagon are 7.301(5) Å (Fig. S2e). The structure contains interesting hexagonal 1D channel with no solvent molecule embedded. The structure clearly exhibits (6,3) network, in which Cu atoms act as 3-connected nodes while CN^- and 5-pyrimidyl-tetrazolate ligands are defined as two kinds of linkers (Fig. S2f).

Structure of 3

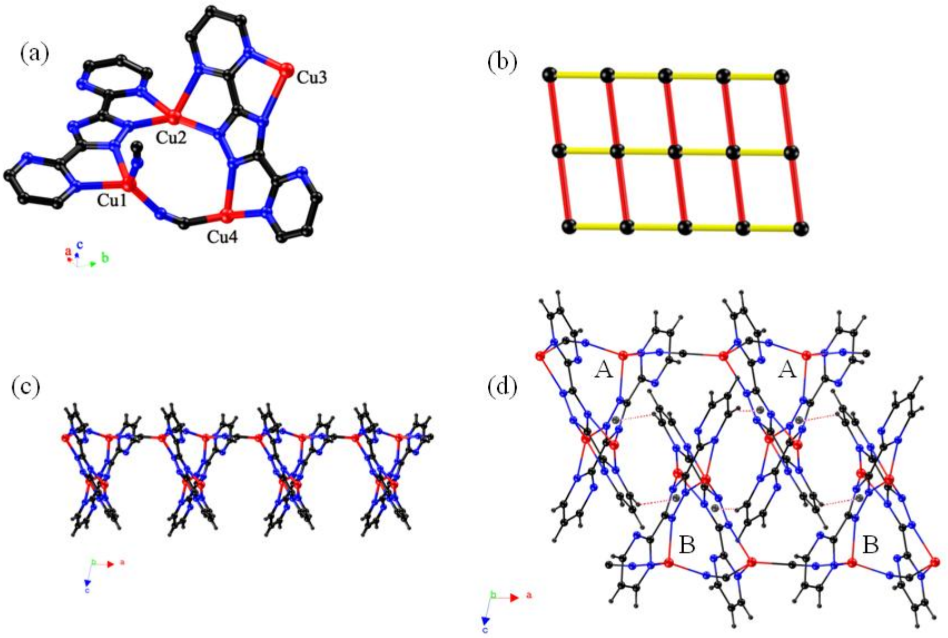


Fig. S3. (a) The asymmetry unit of **3**. (b) View of the (4,4) grid net (black ball for the complex). (c) Schematic description of the 1D chain in **3**. (d) 2D packing diagram of inter-layers in **3** (dotted line for C–H···π interactions). Cu atoms are shown in red, N in blue, C in black, H atoms of pyrimidine rings are omitted for clarity.

Complex **3** crystallizes in the space group of *P*-1, and contains four Cu(I) ions, two CN^- linker, as well as two ligands of 3,5-bispyrimidyl-1,2,4-triazolate in the asymmetric unit (Fig. S3a). There is a distorted 9-membered ring therein. Regarding the 3,5-bispyrimidyl-1,2,4-triazolate and Cu atoms as a four-connected node, the framework can be abstracted into a uniform four-connected 2D (4,4) rectangle lattice network (Fig. S3b). Complex **3** can be regarded as one chain along the *b* axis (Fig. S3c). Interestingly, the neighbouring layers exhibit two arrangements (A and B) and are interconnected via C–H···π (3.2814(2)-4.107(3) Å) interactions (Fig. S3d).

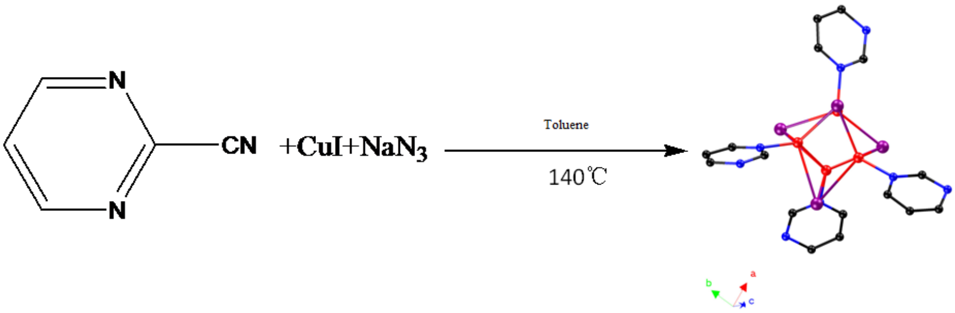
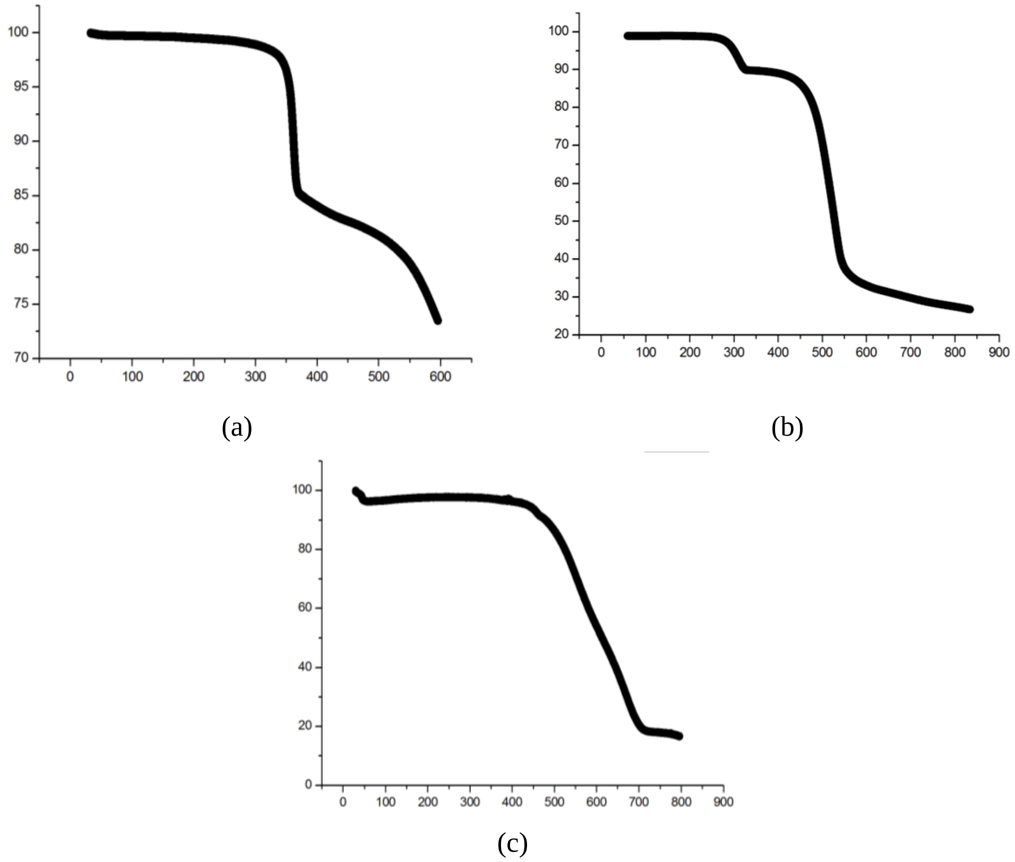


Fig. S4. Scheme showing carbon-carbon bond cleavage of 2-cyanopyrimidine which yields Cu_4I_4(pyrimidine)$_4$ cluster. Cu atoms are shown in red, N in blue, C in black, I atoms in purple, H atoms are omitted for clarity.

Physical Measurement Section



(a) (b)

(c)

Fig. S5. Thermogravimetric analysis plots of **1** (a), **2** (b) and **3** (c).

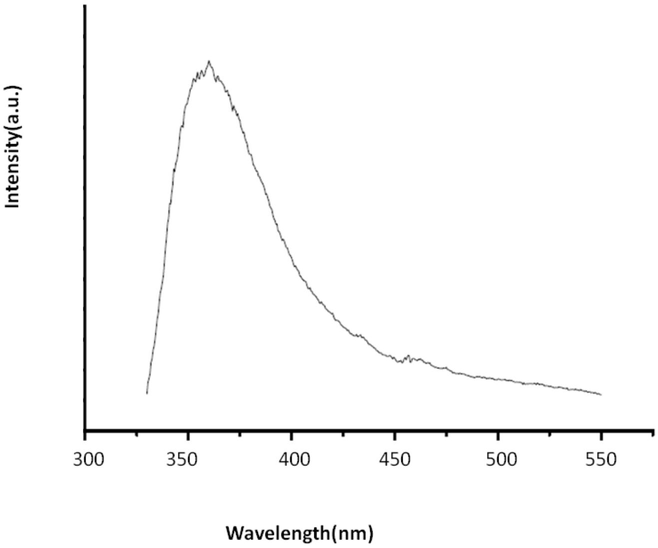


Fig. S6. Solid-state fluorescent emission spectra of **1**.