Electronic Supporting Information for

Crystalline 3D open-framework halogeno(cyano)cuprates synthesized in ionic liquids

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Materials and Methods:

All reagents of A. R. grade employed were commercially available and used without further purification. The FT-IR spectra (KBr pellets) were recorded on a Nicolet Avatar 360 FT-IR Spectrometer in the range of 4000–400 cm^{-1}. C, H, and N elemental analyses were determined on an Elementar Vario EL III elemental analyzer. Thermal stability studies were carried out on a NETSCHZ STA–449 C thermoanalyzer under nitrogen atmosphere (40–800 ^{o}C range) at a heating rate of 10 ºC min^{-1}. The solid-state fluorescence spectra were measured at room temperature using a Cary Eclipse fluorescence spectrophotometer. The excitation slit and emission slit both were 2.5 nm. Powder X-ray diffraction (PXRD) pattern was measured on a Rigaku DMAX 2500 powder diffractmeter at 40 kV and 100 mA using Cu-Kα (λ = 1.54056 Å), with a scan speed of 0.2 s/step and a step size of 0.02°. The simulated powder pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury 2.3 program provided by the Cambridge Crystallographic Data Centre.

Table S1. Crystal data and structure refinements for **1** and **2** (SQUEEZE).

Empirical formula	$C_{25}Br_2Cu_6N_{13}H_{33}$	$C_{29}Br_2Cu_7N_{14}H_{39}$
Formula weight	1056.70	1188.34
Temperature (K)	293(2)	293(2)
Crystal system, Space group	Orthorhombic, *Pnma*	Triclinic, *P*-1
Unit cell dimensions	*a* = 17.0461(6) Å□ *b* = 21.6229(9)Å *c* = 9.8505(4) Å *V* = 3630.8(2) Å^3	*a* = 7.0962(2) Å□ *b* = 12.4549(7) Å *c* = 13.1580(5) Å *V* = 1065.68(8) Å^3
Z, Density(cal.)	4, 1.933 g/cm^3	1, 1.852 g/cm^3
Absorption coefficient	5.689 mm^{-1}	5.339 mm^{-1}
F(000)	2072	584
Crystal Size (mm)	0.46 × 0.38 × 0.29	0.42 × 0.30 × 0.20
Theta range for data collection	3.04 to 26.37	2.84 to 26.37
Limiting indices	-17<=h<=21, -21<=k<=26, -5<=l<=12	-8<=h<=6, -15<=k<=10, -16<=l<=16
Reflections collected / unique	10296 / 3810 [R(int) = 0.0663]	7154 / 4353 [R(int) = 0.0309]
Data Completeness measured	99.6 %	99.9 %
Refinement Method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Parameter/Restraints/Data(obs.)	3810 / 0 / 103	4353 / 0 / 115
Goodness-of-fit	1.010	1.007
Final R indices ($I > 2\sigma(I)$)	R1 = 0.0595, wR2 = 0.1401	R1 = 0.0537, wR2 = 0.1558
R indices (all)	R1 = 0.0860, wR2 = 0.1507	R1 = 0.0735, wR2 = 0.1687
Largest difference peak	1.226 and -0.968 e·A^{-3}	0.673 and -0.548 e·A^{-3}

[a] $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1** and **2**.

	atom	*x*	*y*	*z*	*U*(eq)
	Cu(1)	6684(1)	5782(1)	799(1)	41(1)
	Cu(2)	4323(1)	6646(1)	3148(1)	45(1)
	Cu(3)	4404(1)	5480(1)	2956(1)	49(1)
	C(1)	4862(4)	5114(3)	4555(6)	49(2)
	C(2)	6045(4)	4948(3)	-1475(6)	35(1)
	C(3)	5270(4)	6255(3)	2376(6)	37(2)
1	C(4)	8335(4)	6221(3)	1355(6)	39(2)
	N(1)	6311(4)	5249(3)	-664(6)	54(2)
	N(2)	5786(4)	6106(3)	1917(6)	46(1)
	N(3)	7777(4)	6050(3)	1183(5)	44(1)
	N(4)	4862(4)	5114(3)	4555(6)	49(2)
	Br(1)	4665(1)	7500	4842(1)	43(1)
	Br(2)	3871(1)	7500	1296(1)	38(1)
	Br(1)	5120(1)	7914(1)	3381(1)	62(1)
	Cu(1)	5000	15000	5000	132(1)
	Cu(2)	3177(1)	9790(1)	2511(1)	68(1)
	Cu(3)	4803(1)	13692(1)	1966(1)	63(1)
	Cu(4)	6860(1)	9330(1)	1623(1)	68(1)
	C(1)	5047(10)	14482(8)	3873(5)	76(2)
	C(2)	4488(9)	12114(6)	2269(5)	55(2)
2	C(3)	10772(8)	9506(6)	2233(6)	66(2)
	C(4)	5378(8)	9831(6)	375(4)	59(1)
	C(5)	4931(10)	14715(6)	445(4)	69(2)
	N(1)	4955(10)	14187(6)	3155(5)	83(2)
	N(2)	4122(8)	11223(7)	2379(5)	77(2)
	N(3)	9315(10)	9419(6)	2020(6)	86(2)
	N(4)	5378(8)	9831(6)	375(4)	59(1)
	N(5)	4931(10)	14715(6)	445(4)	69(2)

Table S3. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

		1	
Cu(1)-N(1)	1.951(7)	N(1)-Cu(1)-N(3)	128.2(2)
Cu(1)-N(3)	1.989(6)	N(1)-Cu(1)-N(2)	111.2(2)
Cu(1)-N(2)	2.012(6)	N(3)-Cu(1)-N(2)	120.5(2)
Cu(2)-C(4)#1	1.979(6)	C(4)#1-Cu(2)-C(3)	126.4(3)
Cu(2)-C(3)	1.975(7)	C(4)#1-Cu(2)-Br(1)	111.56(19)
Cu(2)-Cu(3)	2.5314(12)	C(3)-Cu(2)-Br(1)	111.92(18)
Cu(2)-Br(1)	2.5572(10)	Cu(3)-Cu(2)-Br(1)	139.09(4)
Cu(2)-Br(2)	2.7085(11)	C(4)#1-Cu(2)-Br(2)	103.94(19)
Cu(3)-C(2)#3	1.889(6)	C(3)-Cu(2)-Br(2)	105.34(18)
Cu(3)-C(1)	1.928(6)	Br(1)-Cu(2)-Br(2)	90.67(3)
Cu(3)-C(3)	2.307(6)	C(2)#3-Cu(3)-C(1)	126.4(3)
Cu(3)-C(4)#1	2.520(7)	C(2)#3-Cu(3)-C(3)	115.1(2)
C(1)-N(4)#2	1.111(11)	C(1)-Cu(3)-C(3)	103.9(2)
C(1)-C(1)#2	1.111(11)	C(2)-Cu(3)-C(4)#1	103.1(2)
C(2)-N(1)	1.125(8)	C(1)-Cu(3)-C(4)#1	109.5(3)
C(3)-N(2)	1.039(8)	C(3)-Cu(3)-C(4)#1	93.9(2)
C(4)-N(3)	1.034(8)	Cu(2)-Br(1)-Cu(2)#5	92.53(5)
		Cu(2)#5-Br(2)-Cu(2)	86.02(4)
Symmetry transformations used to generate equivalent atoms: #1 x-1/2,y,-z+1/2; #2 -x+1,-y+1,-z+1; #3 -x+1,-y+1,-z; #4 x+1/2,y,-z+1/2; #5 x,-y+3/2,z.			
		2	
Cu(1)-C(1)	1.820(6)	Cu(2)-Br(1)-Cu(4)	66.62(3)
Cu(2)-C(3)#2	1.894(5)	C(1)-Cu(1)-C(1)#1	180
Cu(2)-N(2)	1.935(8)	C(3)#2-Cu(2)-N(2)	130.7(3)
Cu(2)-Br(1)	2.4786(11)	C(3)#2-Cu(2)-Br(1)	109.6(2)
Cu(3)-C(2)	1.895(7)	N(2)-Cu(2)-Br(1)	119.23(17)
Cu(3)-N(1)	1.902(7)	C(2)-Cu(3)-N(1)	119.1(3)
Cu(3)-C(5)	1.931(6)	C(2)-Cu(3)-C(5)	117.3(3)
Cu(4)-N(3)	1.907(7)	N(1)-Cu(3)-C(5)	123.6(3)
Cu(4)-C(4)	1.912(5)	N(3)-Cu(4)-C(4)	141.1(3)
Cu(4)-Br(1)	2.6235(11)	N(3)-Cu(4)-Br(1)	106.7(2)
C(1)-N(1)	1.144(8)	C(4)-Cu(4)-Br(1)	112.02(17)
C(2)-N(2)	1.128(9)		
C(3)-N(3)	1.133(8)		
C(4)-N(4)#3	1.091(10)		
C(5)-N(5)#4	1.122(11)		
Symmetry transformations used to generate equivalent atoms: # 1 -x+1,-y+3,-z+1; #2 x-1,y,z; #3 -x+1,-y+2,-z; #4 -x+1,-y+3,-z; #5 x+1,y,z.			

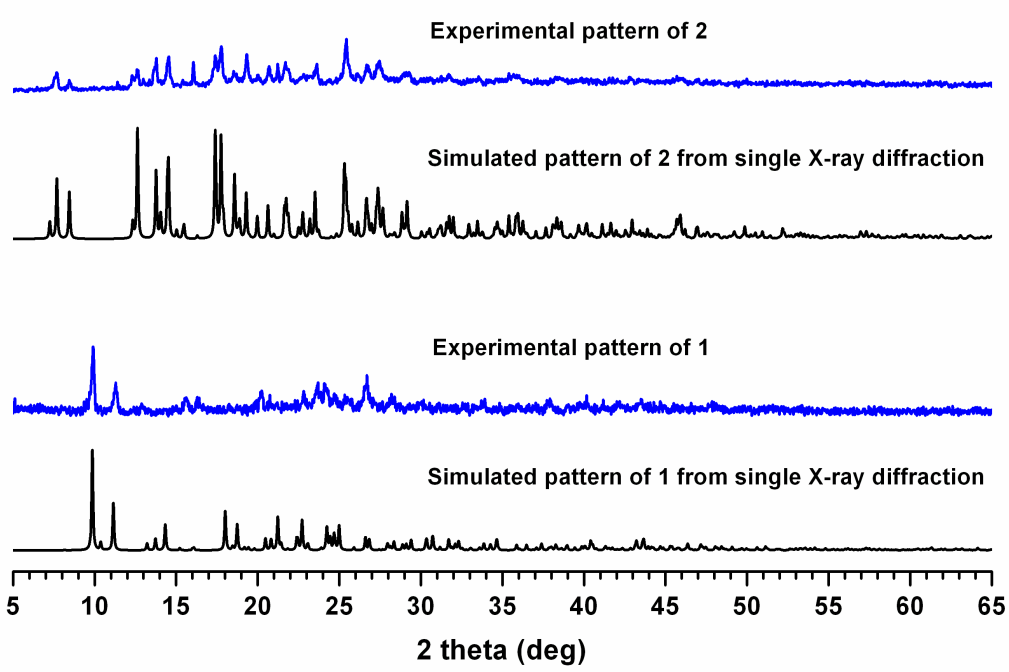

Fig. S1 X-ray powder diffraction patterns for **1** and **2**.

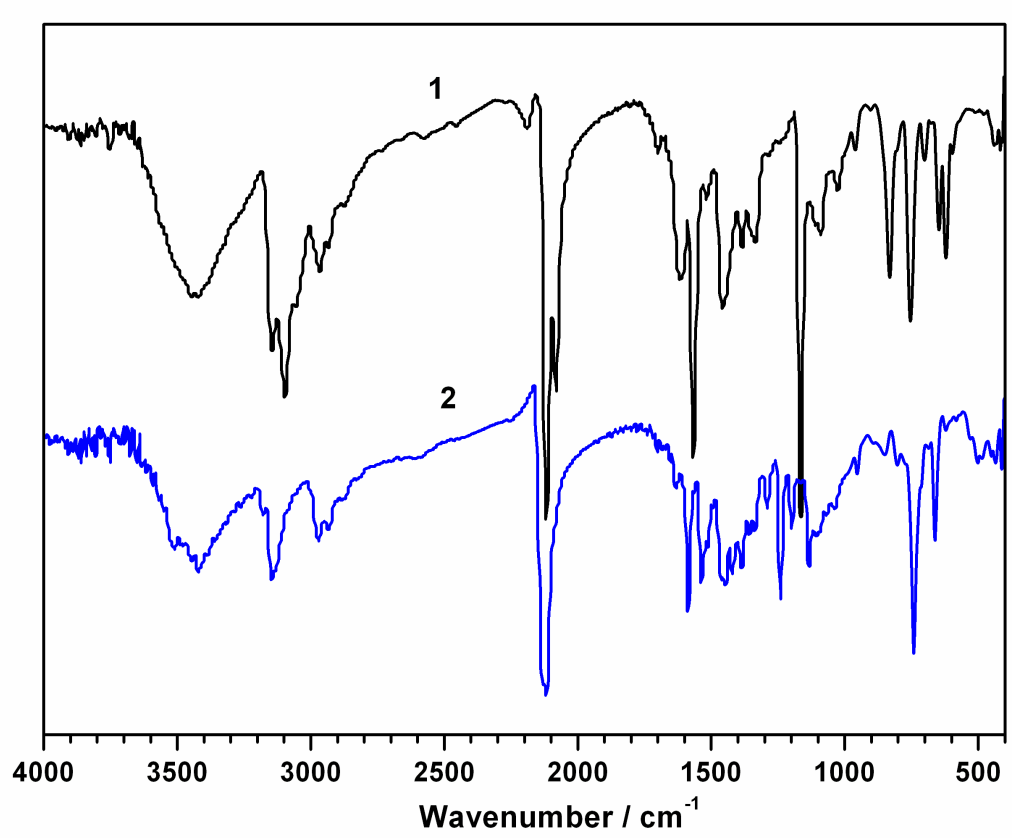

Fig. S2 IR spectra for **1** and **2**.

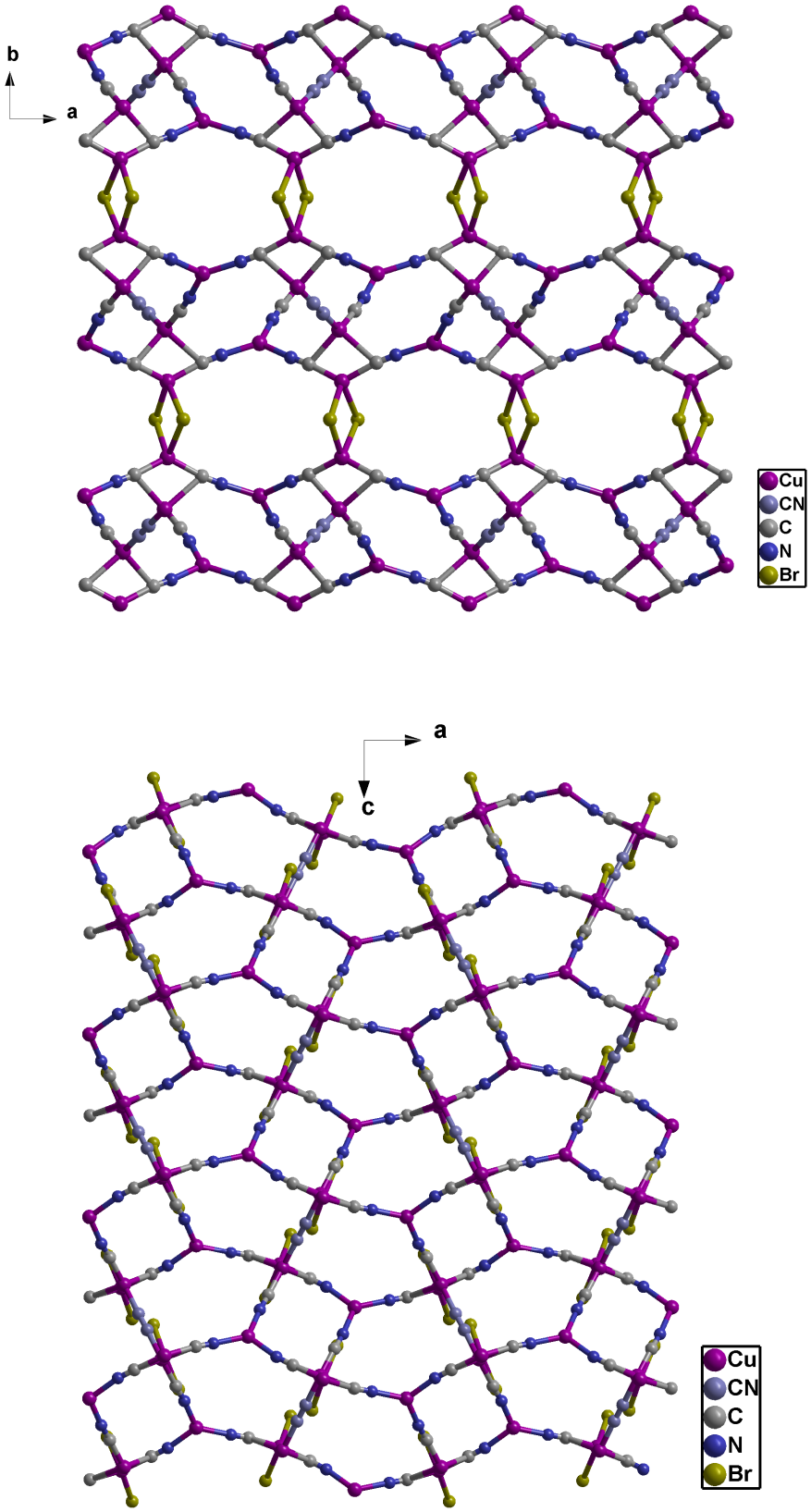

Fig. S3 3D open-framework of **1** viewed along the *b*- and *c*-axis directions.

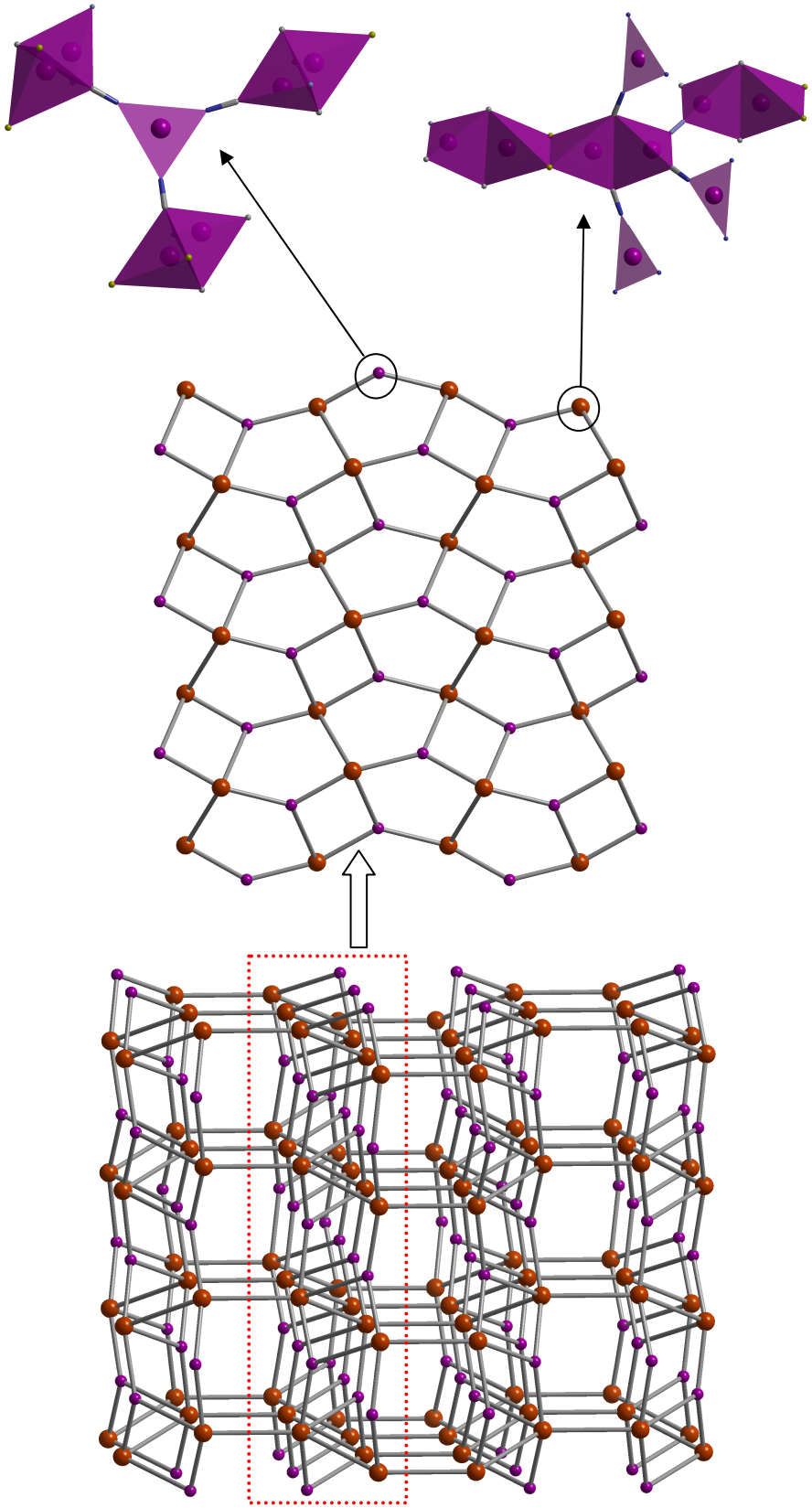

Fig. S4 The 3,5-connected topological net of **1**.

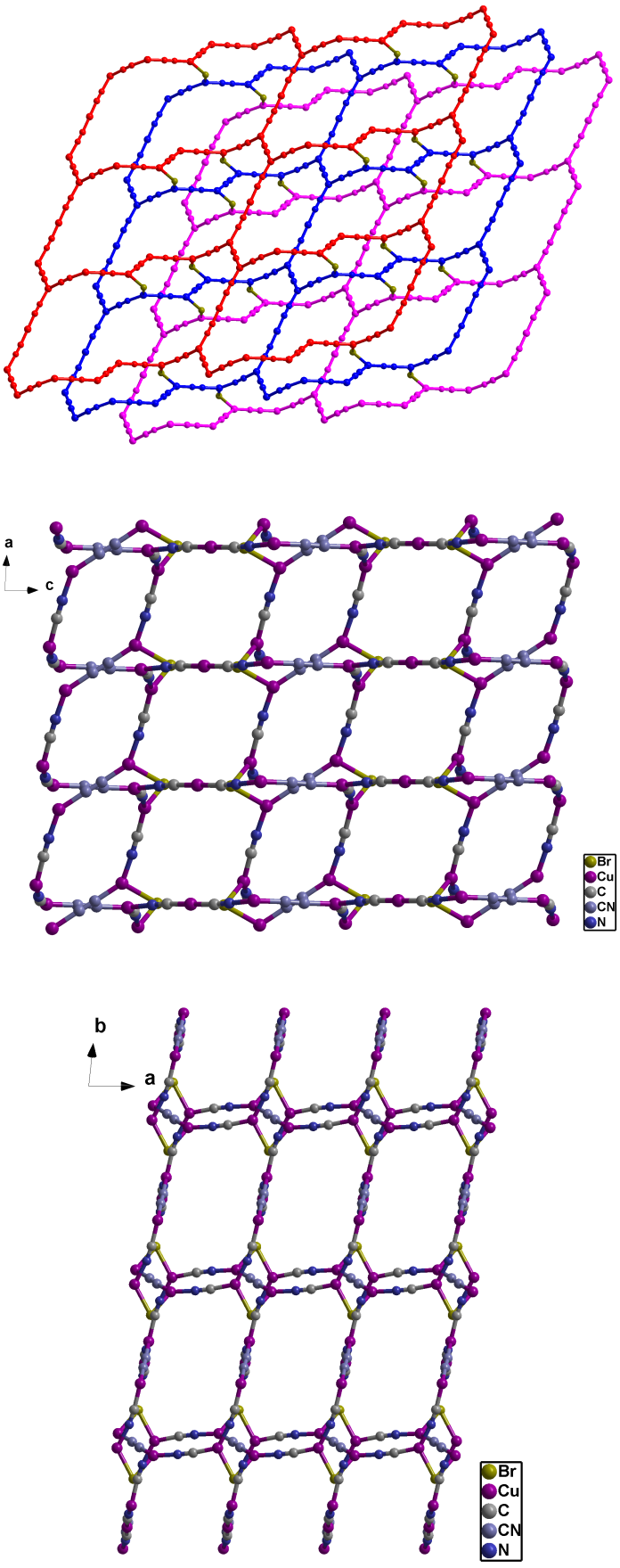

Fig. S5 3D open-framework of **2** viewed along different directions.

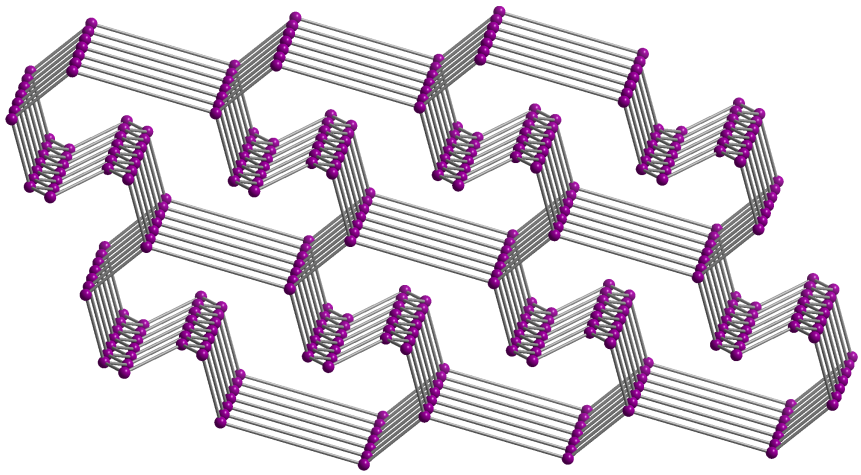

Fig. S6 The 3-connected 3,3,3T9 topological net of **2**.

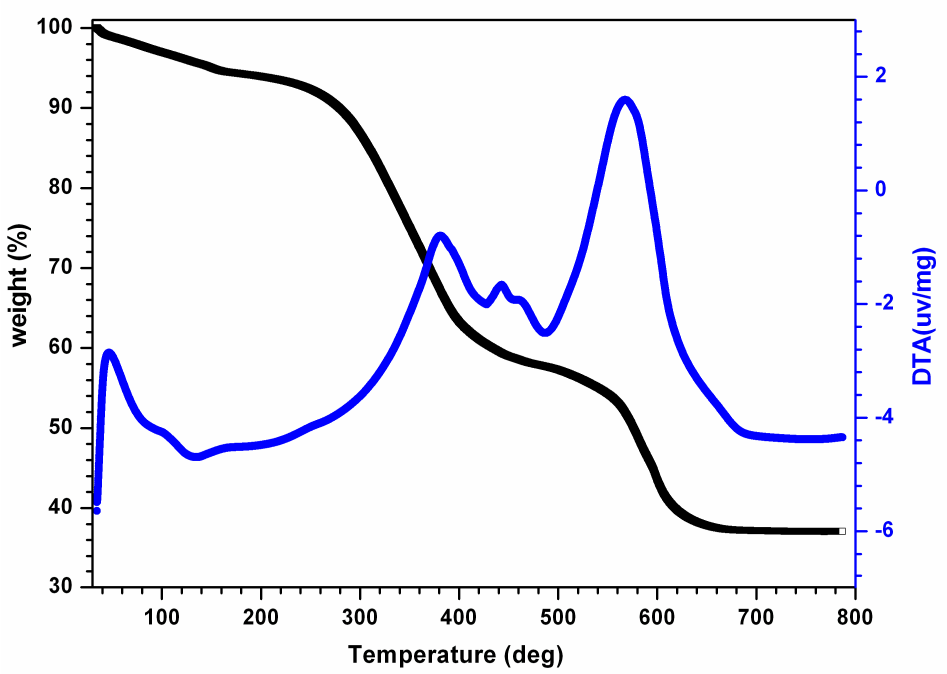

Fig. S7 TG/DTA curves of compound **1**.

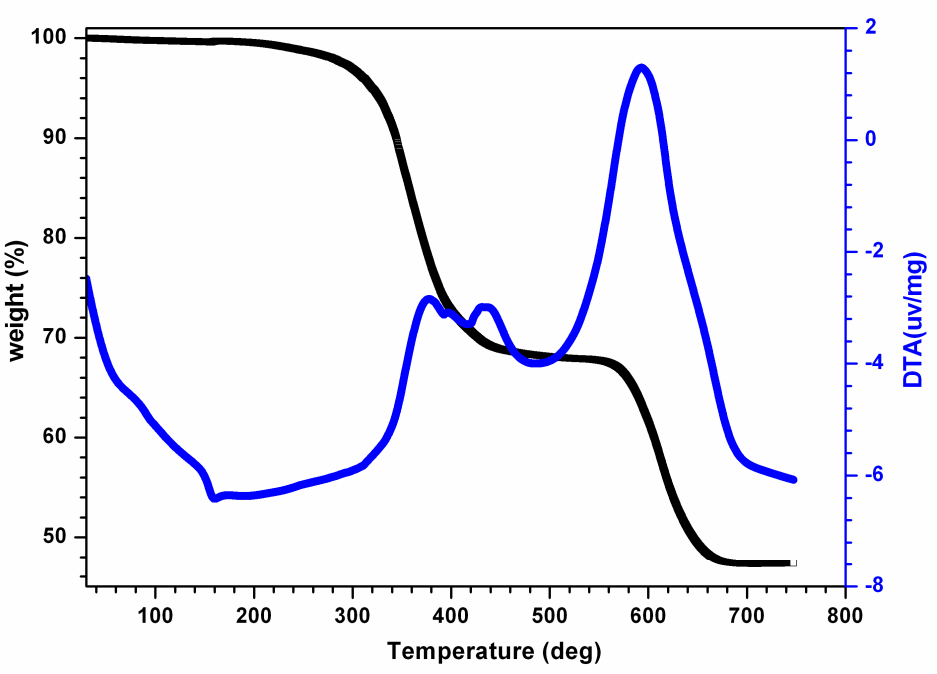

Fig. S8 TG/DTA curves of compound **2**.