

Supporting Information

Capturing the Organic Species Derived from the C-C Cleavage In-Situ Oxidation of 1,2,3,4-Tetra(pyridin-4-yl)cyclobutane by [CuCN]_n-Based MOFs

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Table S1. Selected Bond Lengths (Å) and Angles (deg) for 1.

Cu(1)-C(25)	1.920(4)	C(25)-Cu(1)-C(25)#1	124.0(3)
Cu(1)-C(25)#1	1.920(4)	C(25)-Cu(1)-N(2)#2	117.55(16)
Cu(1)-N(2)#2	2.154(4)	C(25)#1-Cu(1)-N(2)#2	102.63(16)
Cu(1)-N(2)#3	2.154(3)	C(25)-Cu(1)-N(2)#3	102.63(15)
Cu(2)-N(5)	1.885(5)	C(25)#1-Cu(1)-N(2)#3	117.55(16)
Cu(2)-N(6)	1.906(5)	N(2)#2-Cu(1)-N(2)#3	87.0(2)
Cu(2)-N(3)	2.110(4)	N(5)-Cu(2)-N(6)	147.49(17)
Cu(3)-C(26)	1.879(4)	N(5)-Cu(2)-N(3)	111.53(16)
Cu(3)-N(7)	1.893(4)	N(6)-Cu(2)-N(3)	100.89(15)
Cu(3)-N(4)#4	2.075(3)	C(26)-Cu(3)-N(7)	144.07(18)
Cu(4)-C(27)	1.872(4)	C(26)-Cu(3)-N(4)#4	109.33(16)
Cu(4)-N(8)	1.902(4)	N(7)-Cu(3)-N(4)#4	106.60(16)
Cu(4)-C(28)	1.902(4)	C(27)-Cu(4)-N(8)	146.21(19)
Cu(4)-N(1)#5	2.084(4)	C(27)-Cu(4)-C(28)	146.21(19)
N(1)-Cu(4)#5	2.084(4)	C(27)-Cu(4)-N(1)#5	112.85(17)
N(2)-Cu(1)#2	2.154(3)	N(8)-Cu(4)-N(1)#5	100.94(16)
N(4)-Cu(3)#6	2.075(3)	C(28)-Cu(4)-N(1)#5	100.94(16)

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

Table S2. Selected Bond Lengths (Å) and Angles (deg) for 2.

Cu(1)-N(5)	1.764(6)	N(5)-Cu(1)-C(29)#1	140.4(3)
Cu(1)-C(29)#1	1.878(3)	N(5)-Cu(1)-N(1)	107.5(2)
Cu(1)-N(1)	2.079(2)	C(29)#1-Cu(1)-N(1)	109.88(11)
Cu(2)-N(6)	1.858(3)	N(6)-Cu(2)-N(7)	160.86(12)
Cu(2)-N(7)	1.863(3)	N(6)-Cu(2)-N(2)	98.67(10)
Cu(2)-N(2)	2.225(2)	N(7)-Cu(2)-N(2)	100.46(10)
Cu(3)-N(8)	1.744(7)	N(8)-Cu(3)-C(27)#2	138.3(3)
Cu(3)-C(27)#2	1.860(4)	N(8)-Cu(3)-N(3)	107.9(3)
Cu(3)-N(3)	2.056(2)	C(27)#2-Cu(3)-N(3)	112.94(12)
Cu(4)-C(26)#3	1.861(3)	C(26)#3-Cu(4)-N(9)	139.06(12)
Cu(4)-N(9)	1.885(3)	C(26)#3-Cu(4)-N(4)	111.10(11)
Cu(4)-N(4)	2.066(2)	N(9)-Cu(4)-N(4)	109.52(10)
C(29)-Cu(1)#4	1.878(3)		
C(27)-Cu(3)#2	1.860(4)		
C(26)-Cu(4)#5	1.861(3)		

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

Table S3. Selected Bond Lengths (Å) and Angles (deg) for **3**.

Cu(1)-C(13)	1.868(7)	C(13)-Cu(1)-C(14)	131.5(3)
Cu(1)-C(14)	1.917(7)	C(13)-Cu(1)-N(10)#1	114.6(3)
Cu(1)-N(10)#1	2.102(6)	C(14)-Cu(1)-N(10)#1	102.8(3)
Cu(1)-N(2)	2.154(6)	C(13)-Cu(1)-N(2)	103.3(3)
Cu(2)-N(3)#2	1.824(7)	C(14)-Cu(1)-N(2)	98.6(2)
Cu(2)-N(3)	1.824(7)	N(10)#1-Cu(1)-N(2)	100.7(2)
Cu(3)-N(4)	1.936(9)	N(3)#2-Cu(2)-N(3)	176.8(4)
Cu(3)-N(5)	1.946(7)	N(4)-Cu(3)-N(5)	136.7(3)
Cu(3)-N(9)#3	2.125(6)	N(4)-Cu(3)-N(9)#3	112.3(3)
Cu(3)-N(1)#4	2.153(6)	N(5)-Cu(3)-N(9)#3	98.7(3)
Cu(4)-C(15)	1.872(8)	N(4)-Cu(3)-N(1)#4	101.3(3)
Cu(4)-N(6)	1.899(7)	N(5)-Cu(3)-N(1)#4	98.5(2)
Cu(4)-N(8)#5	2.080(6)	N(9)#3-Cu(3)-N(1)#4	105.4(2)
Cu(5)-C(16)	1.873(8)	C(15)-Cu(4)-N(6)	143.7(3)
Cu(5)-N(12)	1.885(7)	C(15)-Cu(4)-N(8)#5	109.9(3)
Cu(5)-C(17)	1.885(7)	N(6)-Cu(4)-N(8)#5	106.3(3)
Cu(5)-N(7)	2.067(6)	C(16)-Cu(5)-N(12)	144.8(3)
N(1)-Cu(3)#6	2.153(6)	C(16)-Cu(5)-C(17)	144.8(3)
N(8)-Cu(4)#1	2.080(6)	C(16)-Cu(5)-N(7)	113.7(3)
N(9)-Cu(3)#3	2.125(6)	N(12)-Cu(5)-N(7)	101.5(3)
N(10)-Cu(1)#5	2.102(6)	C(17)-Cu(5)-N(7)	101.5(3)

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

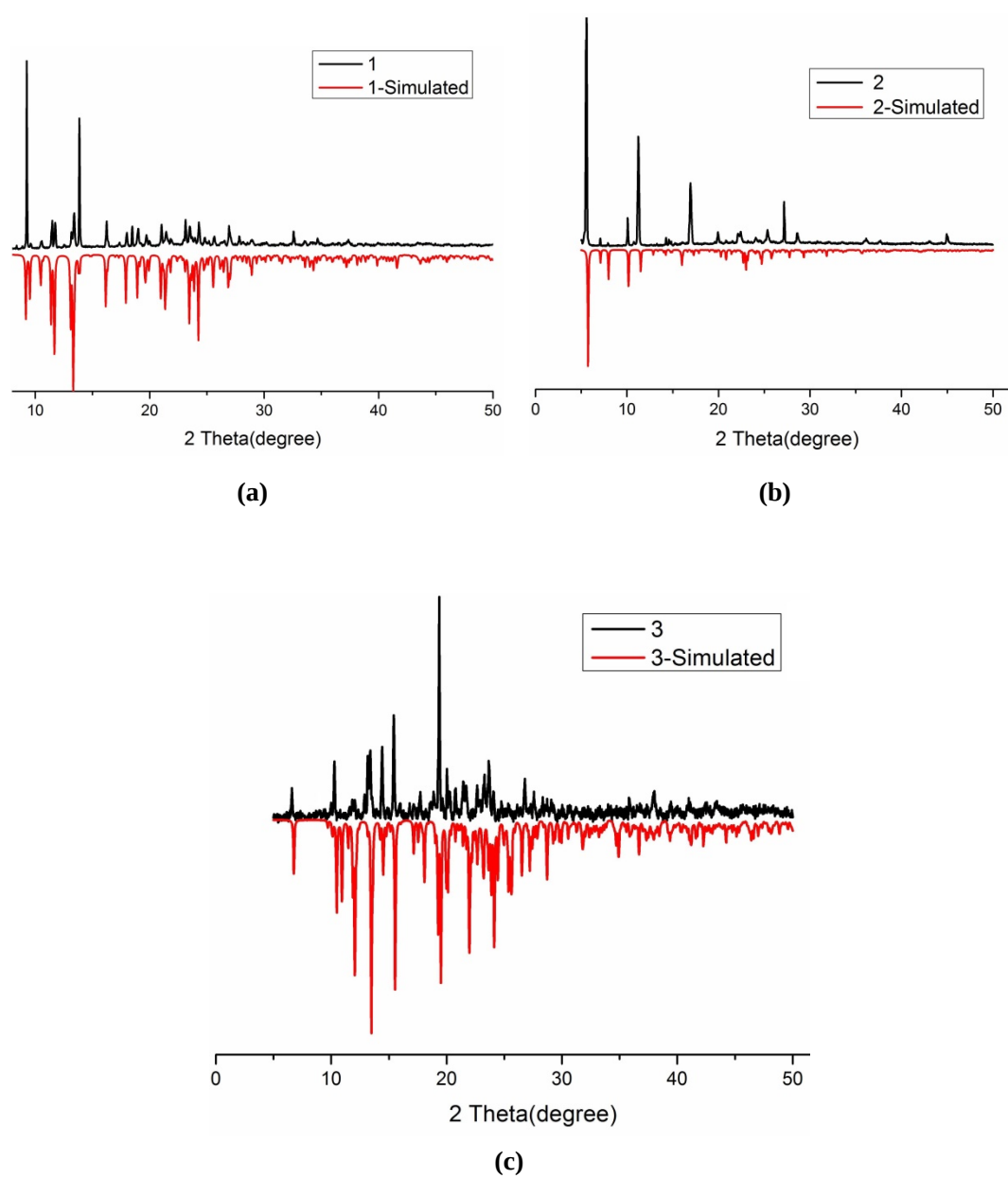
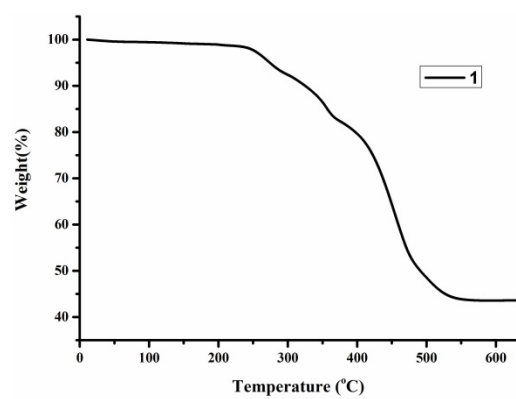
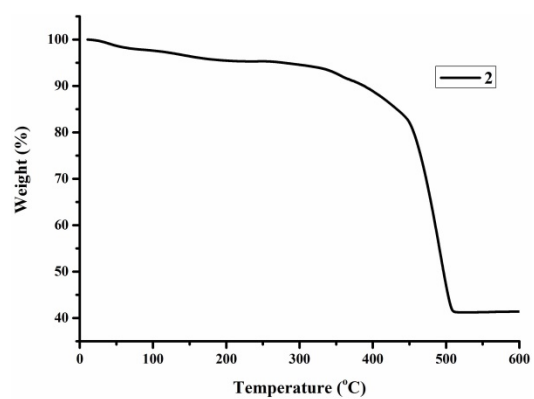


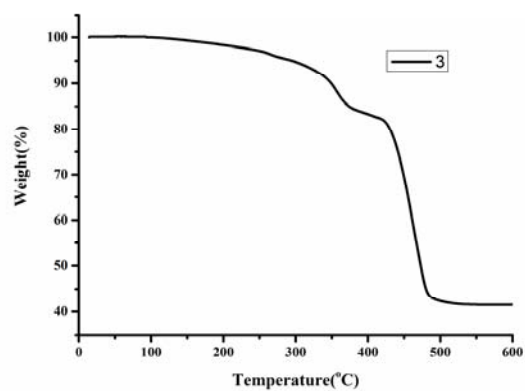
Figure S1. Experimental (black) and simulated (red) PXRD patterns for **1**(a), **2** (b) and **3** (c).



(a)



(b)



(c)

Figure S2. The TGA curves for **1** (a), **2** (b) and **3** (c).

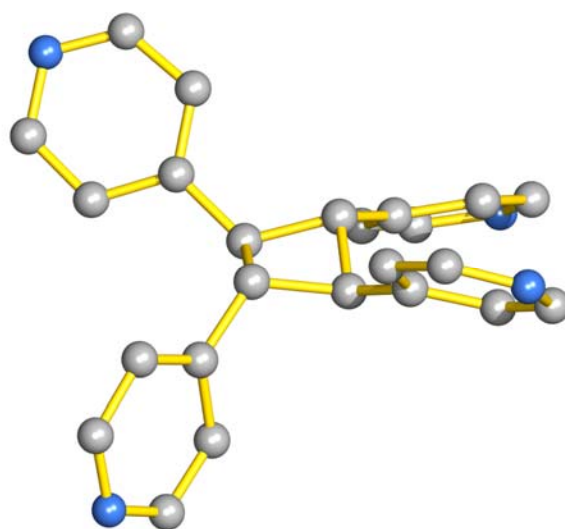


Figure S3. View of the tpcb ligand in **1**.

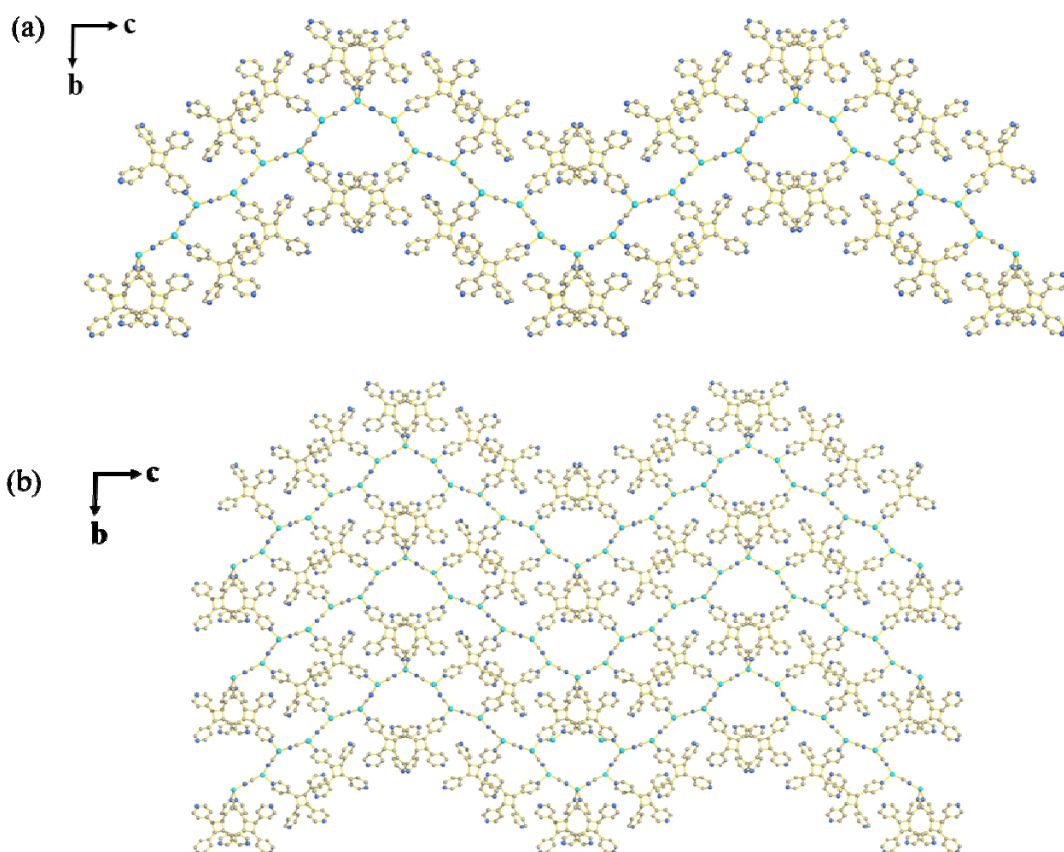


Figure S4. (a) View of a section of the 1D chain of **1** extending along the *c* axis. (b) View of the 2D network of **1** extending along the *bc* plane.

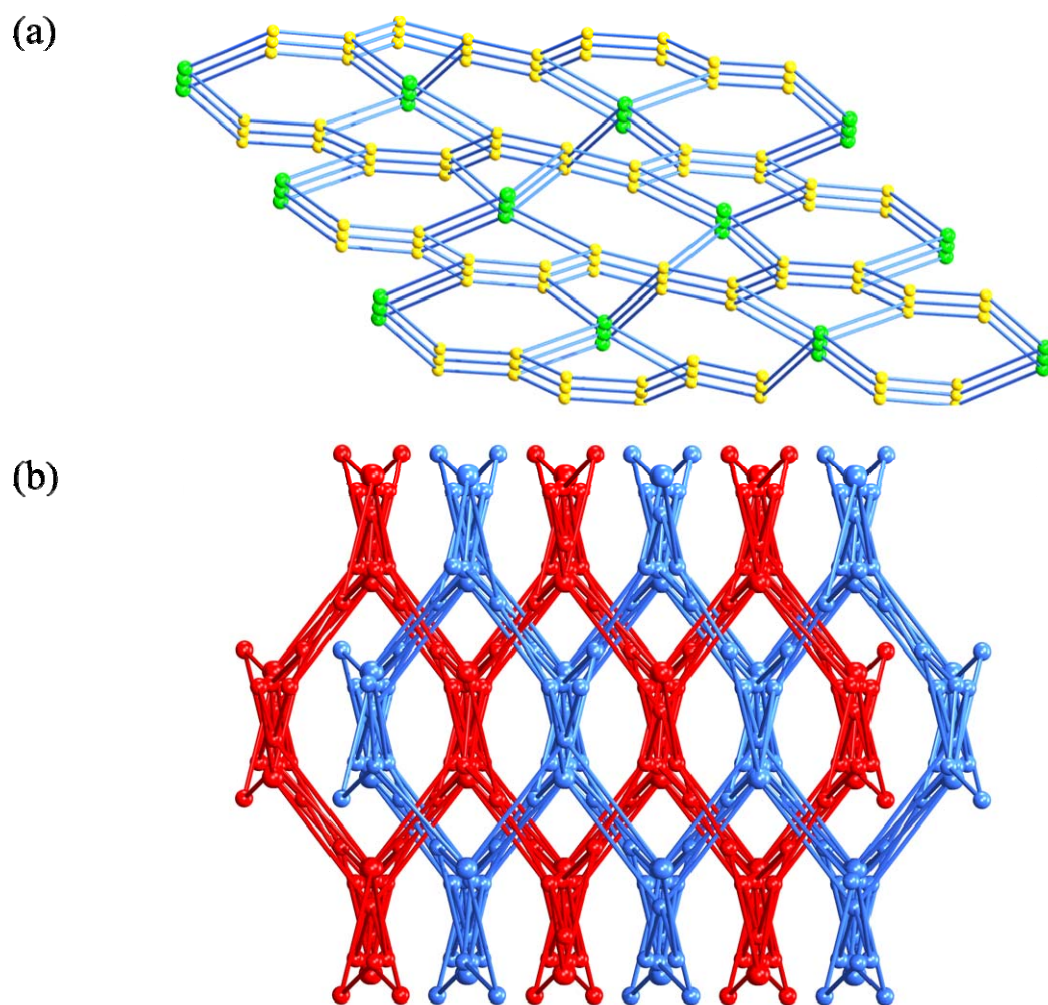


Figure S5. (a) View of the topological structure of **1**. The yellow and green spheres represent Cu centres and tpcb ligands, respectively. (b) Schematic view of the 2-fold interpenetrated network of **1**.

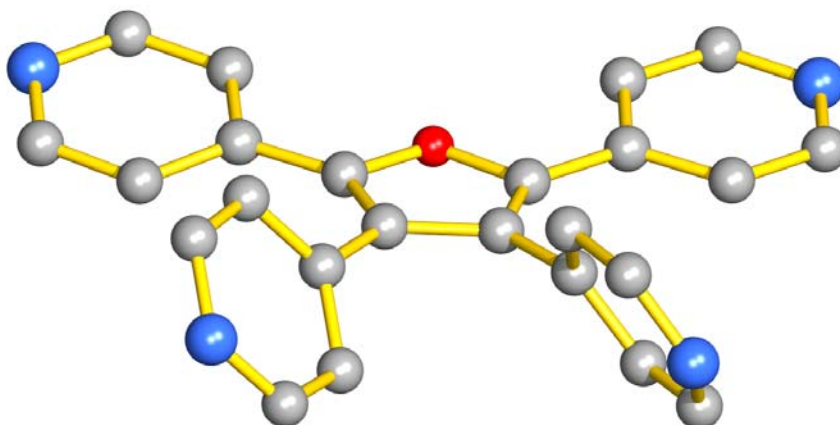


Figure S6. View of the tpyf ligand in **2**.

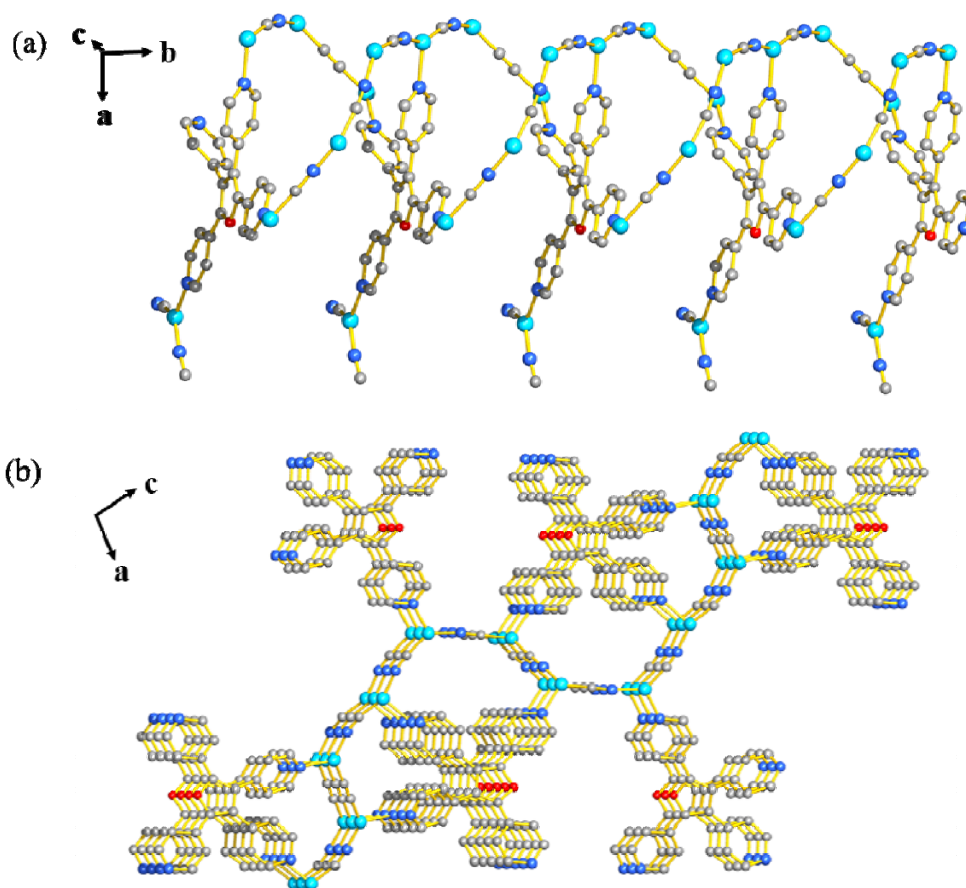
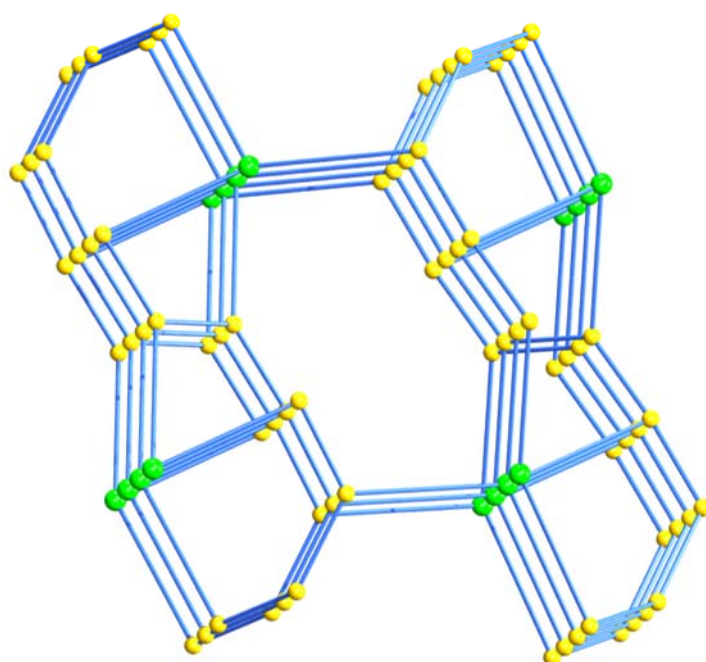


Figure S7. (a) View of a part of the 1D chain of **2** extending along the *b* axis. (b) View of the 2D network of **2** extending along the *ac* plane.

(a)



(b)

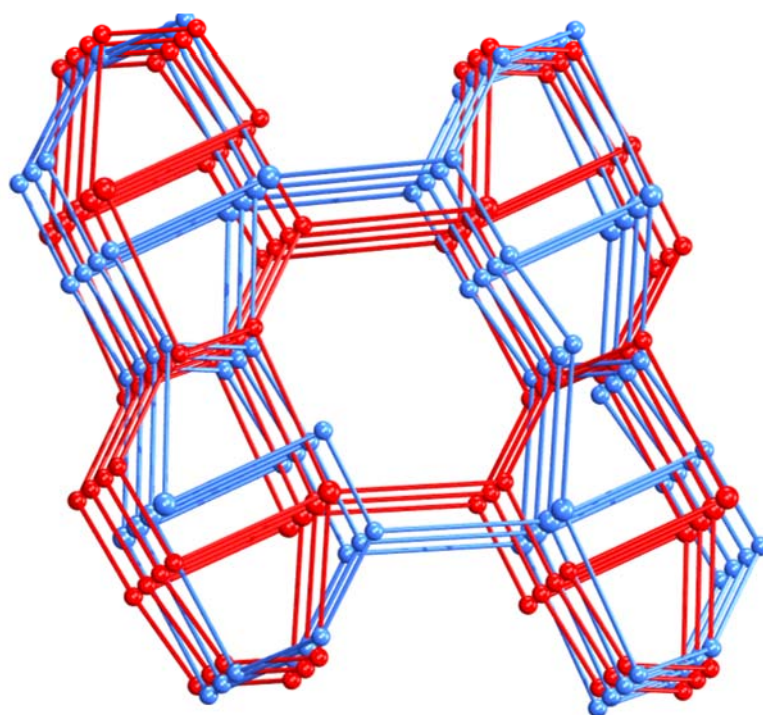


Figure S8. (a) View of the topological structure of **2**. The yellow and green spheres represent the Cu centres and tpyf ligands, respectively. (b) Schematic view of the 2-fold interpenetrated network of **2**.

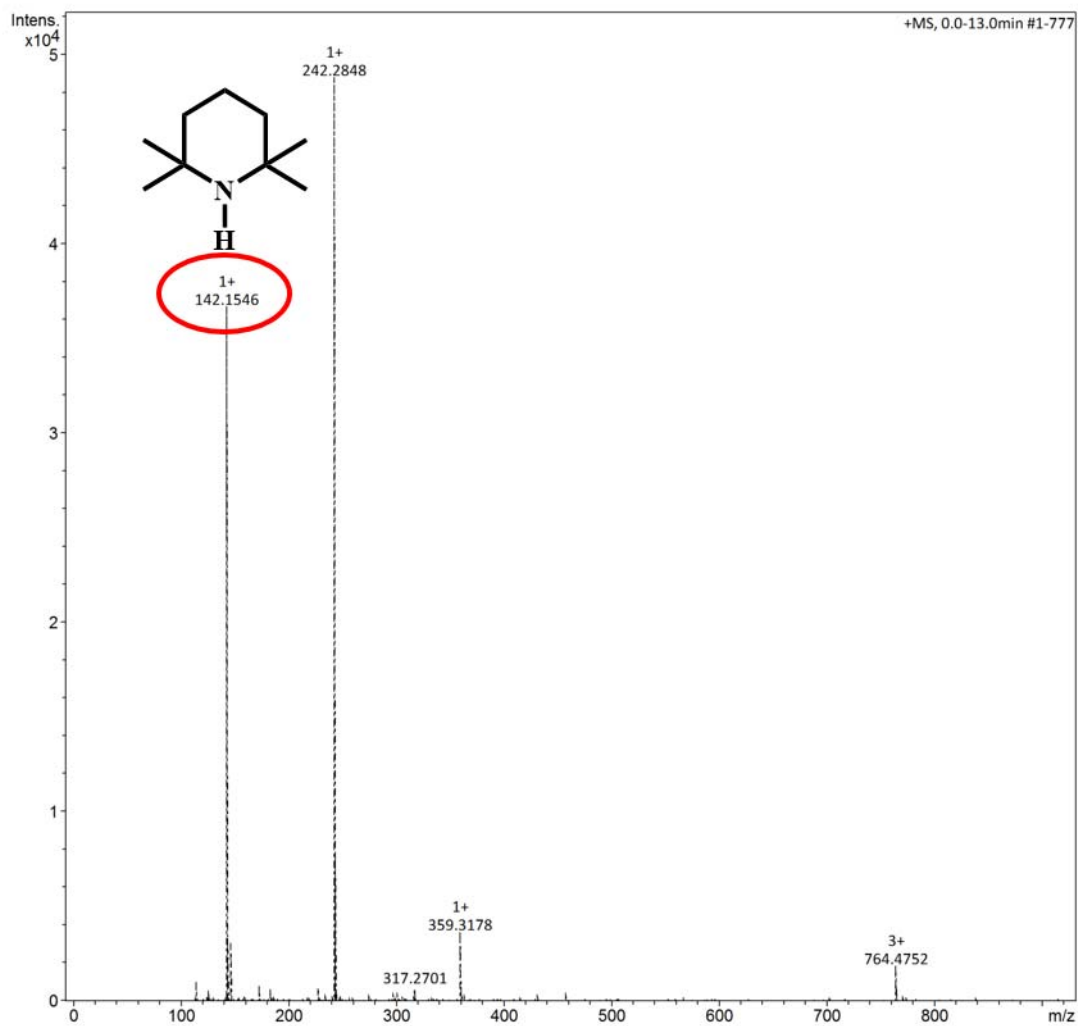


Figure S9. The mass spectrum of the supernatant solution during the synthesis of **3**.

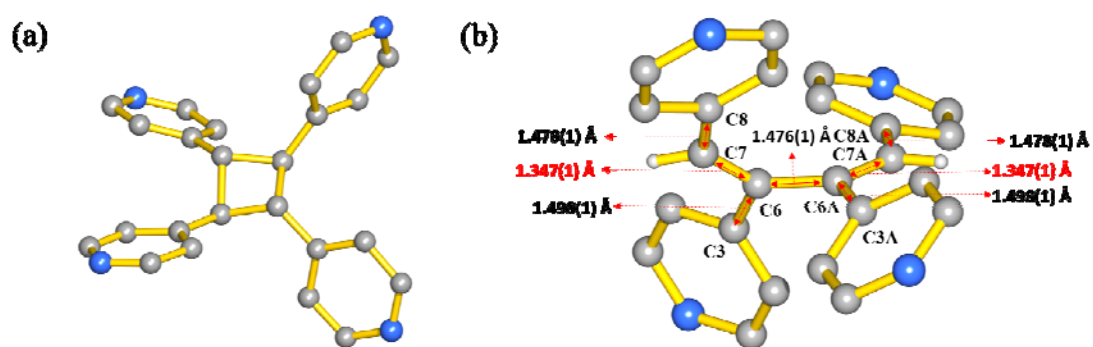


Figure S10. (a) View of the tpcb ligand in **3**. (b) View of the tpyb ligand in **3**.

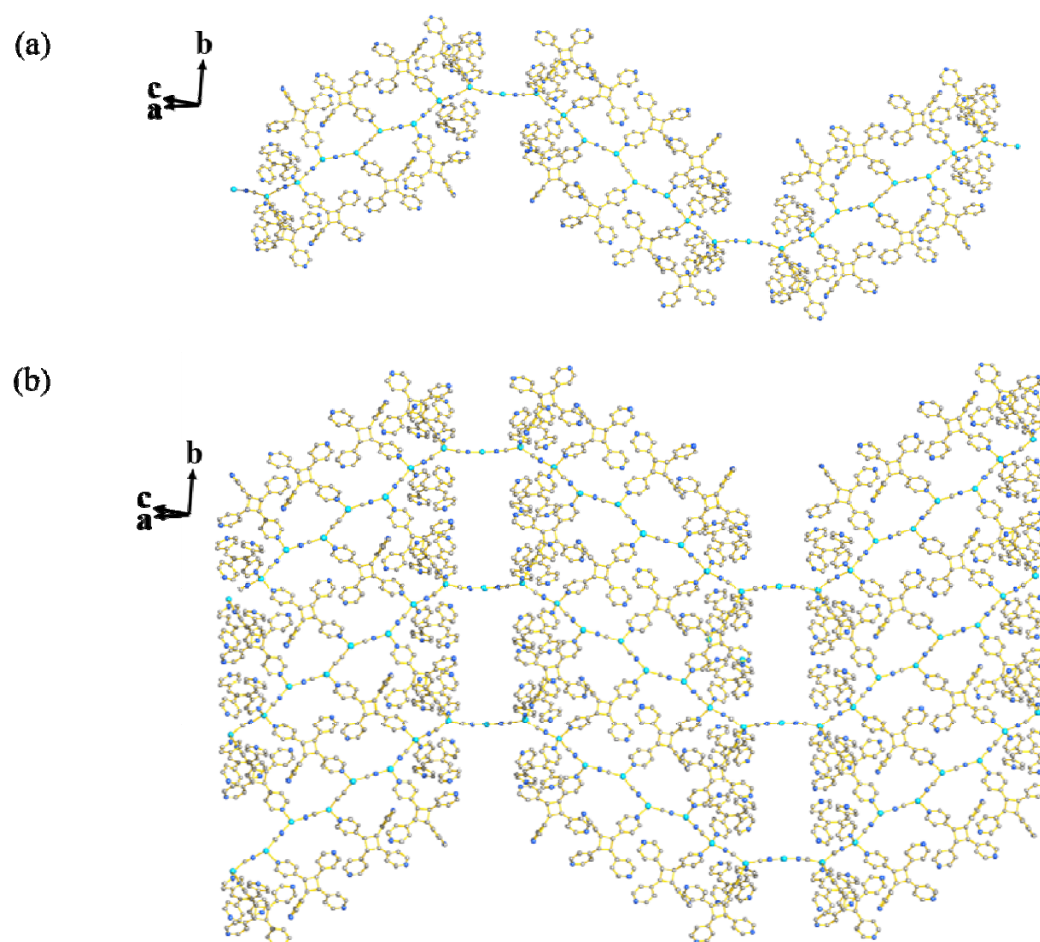


Figure S11. (a) View of a portion of the 1D chain of **3** extending along the [101] direction. (b) View of the 2D network of **3** extending along the (101) plane.

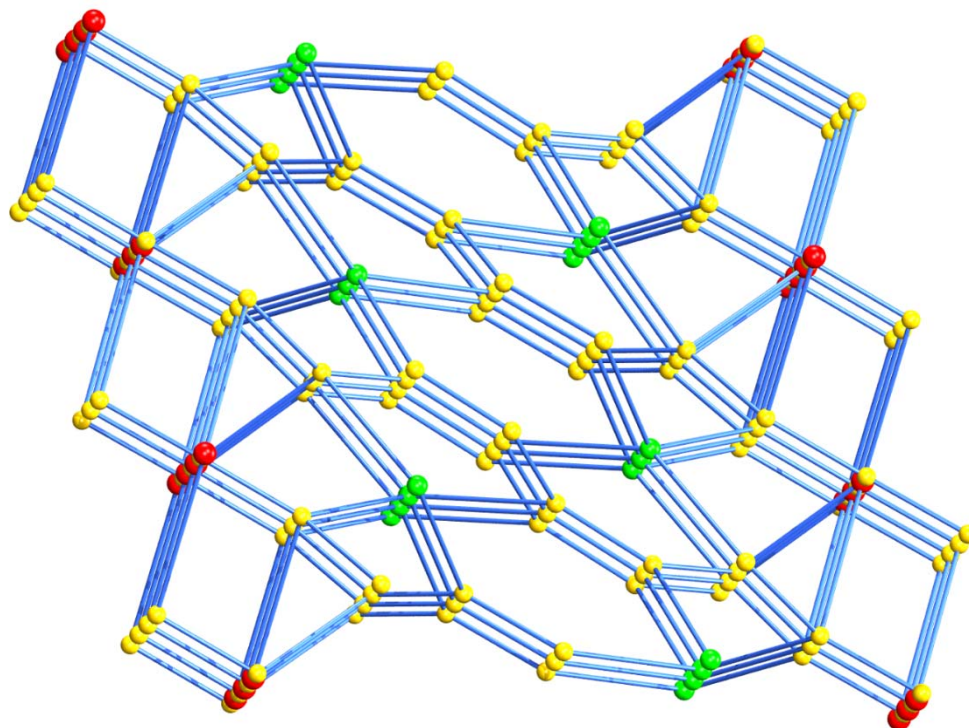


Figure S12. View of the topological structure of **3**. The yellow, green and red spheres represent the Cu centres, tpcb and tpyb ligands, respectively.