Electronic Supplementary Information

Ionothermal synthesis of novel Pb-OH-Cu-X (X = Cl, Br and I) quaternary heterometallic frameworks with tunable optical properties

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Table S1. Crystal data and structural refinements for compounds 1 to 3.

Compound	**1**	**2**	**3**
Empirical formula	$Pb_2CuCl_3O_2H_2$	$Pb_2CuBr_3H_2O_2$	$Pb_2CuI_3H_2O_2$
Formula weight	618.28	751.66	892.67
T (K)	298(2)	298(2)	298(2)
Crystal system	*I*41/*acd*	*I*41/*acd*	*Fddd*
Space group	tetragonal	tetragonal	orthorhombic
a (Å)	13.7547(11)	14.1711(10)	16.6743(15)
b (Å)	13.7547(11)	14.1711(10)	20.8855(18)
c (Å)	15.3654(13)	15.8493(15)	20.8865(19)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
V ($Å^3$)	2907.0(4)	3182.9(4)	7273.7(11)
Z	8	8	16
D_{calcd}($g \cdot cm^{-3}$)	5.561	6.274	6.521
F(000)	4192	5056	11840
Reflections collected	5483	6046	8811
Independent reflections	646	706	1610
GOF on F^2	1.140	1.127	1.097
R_1, wR_2 ($I > 2\delta(I)$)	0.0400/0.0892	0.0485/0.1315	0.0456/0.1124
R_1, wR_2 (all data)	0.0572/0.0948	0.0620/0.1367	0.0554/0.1166

Table S2. Selected bonded lengths (Å) and angles (°) for compound **1**.

Pb(1)-O(1)#1	2.336(10)	O(1)#1-Pb(1)-O(1)#2	68.8(4)
Pb(1)-O(1)#2	2.377(10)	O(1)#1-Pb(1)-O(1)	71.9(6)
Pb(1)-O(1)	2.424(9)	O(1)#2-Pb(1)-O(1)	71.2(4)
Pb(1)-Cl(2)#3	3.419(5)	Cl(1)#3-Cu(1)-Cl(1)	115.9(2)
Pb(1)-Cl(1)#4	3.3581(34)	Cl(1)#3-Cu(1)-Cl(2)	103.39(16
Pb(1)-Cl(1)#5	3.2804(43)	Cl(1)-Cu(1)-Cl(2)	112.24(12)
Pb(1)-Cl(2)	3.2792(42)	Cl(1)-Cu(1)-Cl(2)#4	103.39(16)
Pb(1)-Cl(1)#6	3.1459(43)	Cl(2)-Cu(1)-Cl(2)#4	109.9(2)
Pb(1)-Cl(1)	3.262(4)	Cu(1)-Cl(2)-Cu(1)#5	142.1(2)
Cu(1)-Cl(1)	2.334(4)	Pb(1)#2-O(1)-Pb(1)#1	109.4(4)
Cu(1)-Cl(2)	2.370(2)	Pb(1)#2-O(1)-Pb(1)	105.4(4)
		Pb(1)#1-O(1)-Pb(1)	104.1(4)
		Pb(1)-Cl(1)-Cu(1)	78.26(8)
		Pb(1)#2-Cl(1)-Cu(1)	124.72(2)
		Pb(1)#5-Cl(1)-Cu(1)	106.69(4)
		Pb(1)#4-Cl(1)-Cu(1)	109.98(2)
		Pb(1)#3-Cl(2)-Cu(1)	134.67(5)
		Pb(1)-Cl(2)-Cu(1)	77.44(4)

Symmetry codes: #1 y+1/4,-x+3/4,-z+1/4; #2 -y+3/4,x-1/4,-z+1/4; #3 y+1/4,x-1/4,-z+7/4; #4 y+1/4,-x+5/4,z-1/4; #5 -y+5/4,x-1/4,z+1/4.

Table S3. Selected bonded lengths (Å) and angles (°) for compound **2**.

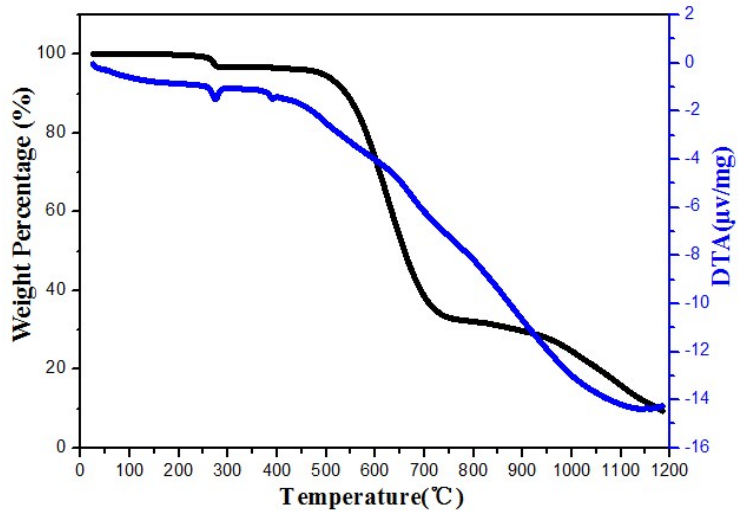
Pb(1)-O(1)#1	2.370(16)	Br(2)#3-Cu(1)-Br(2)	115.7(2)
Pb(1)-O(1)	2.394(16)	Br(2)#3-Cu(1)-Br(1)#4	104.59(9)
Pb(1)-O(1)#2	2.398(15)	Br(2)-Cu(1)-Br(1)#4	112.37(6)
Pb(1)-Br(2)#4	3.367(1)	Br(1)#4-Cu(1)-Br(1)	107.10(18)
Pb(1)-Br(2)#3	3.419(5)	Cu(1)#5-Br(1)-Cu(1)	138.46(17)
Pb(1)-Br(2)#5	3.287(8)	O(1)#1-Pb(1)-O(1)	69.5(7)
Pb(1)-Br(2)	3.393(5)	O(1)#1-Pb(1)-O(1)#2	71.9(6)
Pb(1)-Br(1)	3.373(8)	O(1)-Pb(1)-O(1)#2	71.5(6)
Cu(1)-Br(2)	2.441(3)	Pb(1)#1-O(1)-Pb(1)	108.7(6)
Cu(1)-Br(1)	2.480(3)	Pb(1)#1-O(1)-Pb(1)#6	105.2(6)
		Pb(1)-O(1)-Pb(1)#6	104.4(6)
		Pb(1)#2-Br(2)-Cu(1)	124.07(3)
		Pb(1)-Br(2)-Cu(1)	77.80(7)
		Pb(1)-Br(1)-Cu(2)	77.74(1)
		Pb(1)#6-Br(1)-Cu(1)	137.20(7)
		Pb(1)#5-Br(2)-Cu(1)	107.48(5)

Symmetry codes: #1 -x+2,-y+1/2,z+0; #2 -y+5/4,x-3/4,-z+3/4; #3 -y+5/4,-x+5/4,-z+1/4; #4 y-3/4, -x+5/4, z-1/4; #5 -y+5/4,x+3/4,z+1/4; #6 y+3/4,-x+5/4,-z+3/4.

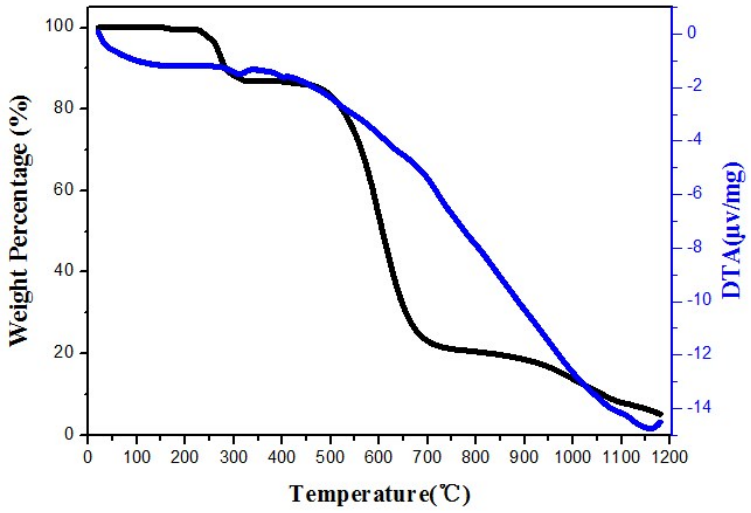
Table S4. Selected bonded lengths (Å) and angles (°) for compound **3**.

Pb(1)-O(1)#1	2.410(10)	I(3)#2-Cu(1)-I(3)	115.93(13)
Pb(1)-O(1)	2.421(10)	I(3)#2-Cu(1)-I(2)	106.70(3)
Pb(1)-O(2)	2.428(10)	I(3)-Cu(1)-I(2)	114.21(3)
Pb(2)-O(2)	2.362(10)	O(2)-Pb(2)-O(1)	73.6(4)
Pb(2)-O(1)	2.384(10)	O(1)#1-Pb(1)-O(1)	68.9(5)
Pb(2)-O(2)#1	2.396(10)	O(1)#1-Pb(1)-O(2)	71.8(4)
Pb(1)-I(2)#3	3.588(1)	Pb(2)-O(2)-Pb(2)#1	108.6(5)
Pb(1)-I(2)#4	3.594(9)	Pb(2)-O(1)-Pb(1)	103.4(3)
Pb(1)-I(3)#5	3.599(1)	Pb(1)#1-O(1)-Pb(1)	109.5(5)
Pb(1)-I(1)#4	3.597(7)	Pb(2)#2-I(3)-Cu(1)	107.3(7)
Pb(2)-I(1)#2	3.610(1)	Pb(1)-I(3)-Cu(1)	120.79(5)
Pb(2)-I(3)#2	3.554(4)	Pb(2)-I(3)-Cu(1)	68.879(25)
Pb(2)-I(3)#6	3.460(2)		
Cu(1)-I(3)#2	2.617(2)		
Cu(1)-I(2)	2.678(2)		
Cu(2)-I(3)	2.614(2)		
Cu(2)-I(1)#2	2.643(2)		

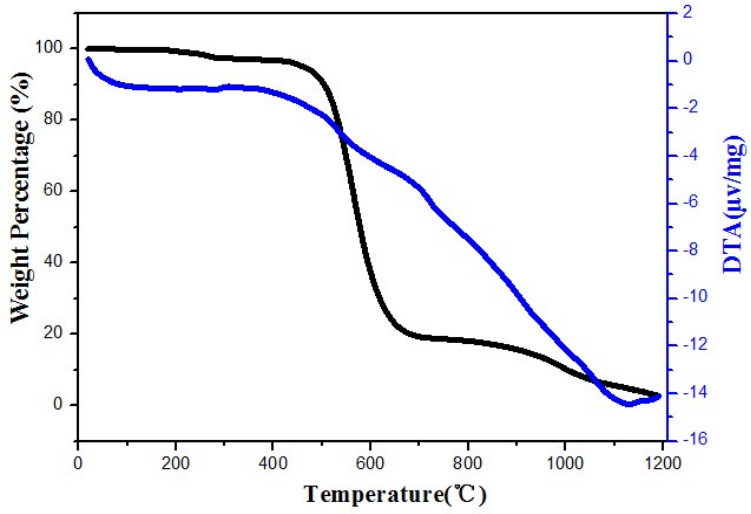
Symmetry codes:#1 -x, 0.75-y, 0.75-z; #2 0.25+x, 0.25+y, 1-z; #3 0.25-x, 0.25-y, z; #4 0.5+x, 0.25-y, 0.75-z; #5 0.25+x, 0.5-y, -0.25+z; #6 -0.25-x, 0.75-y, z; #7 -0.25-x, y, 0.75-y; #8 -0.25+x, -0.25+y, 1-z.



(a)

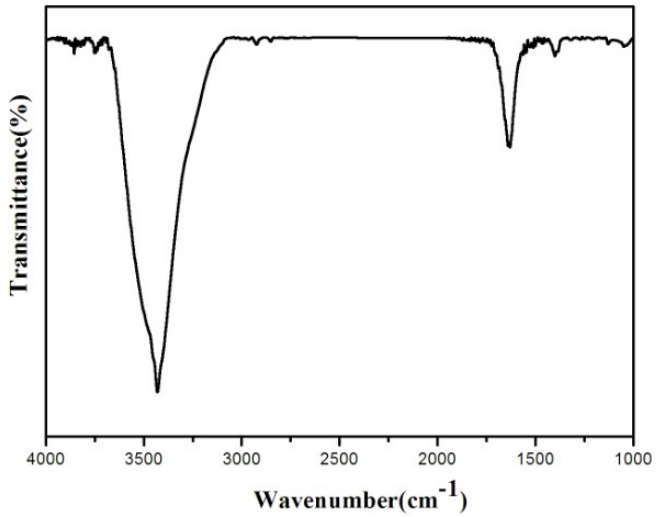


(b)

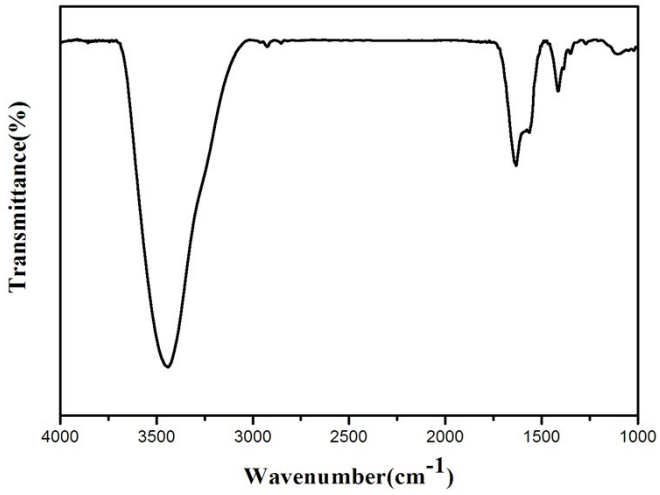


(c)

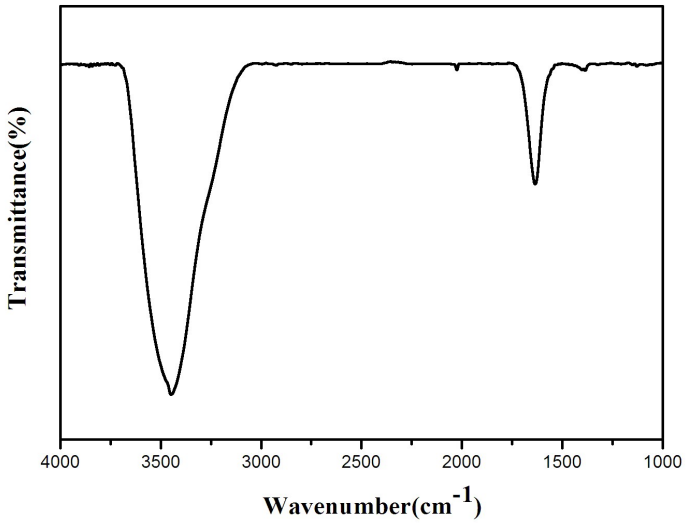
Figure S1. Thermogravimetric curves for compounds **1**-**3** (a-c).



(a)

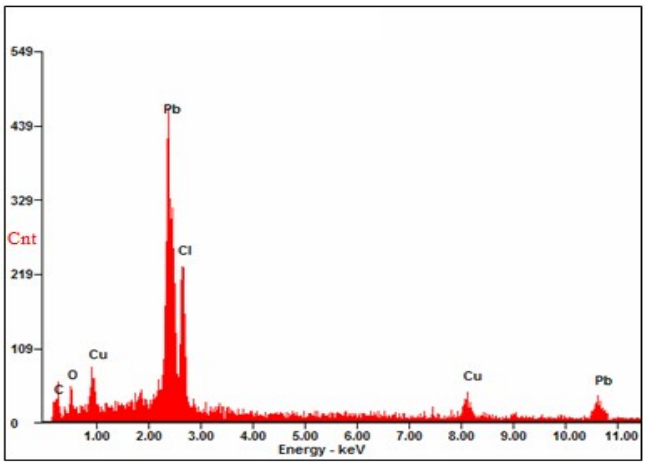


(b)

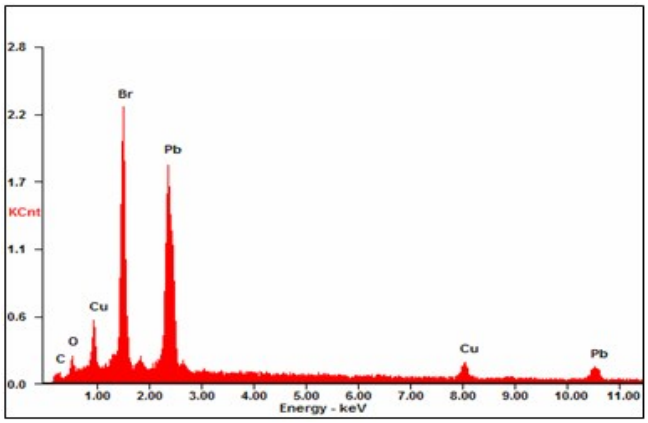


(c)

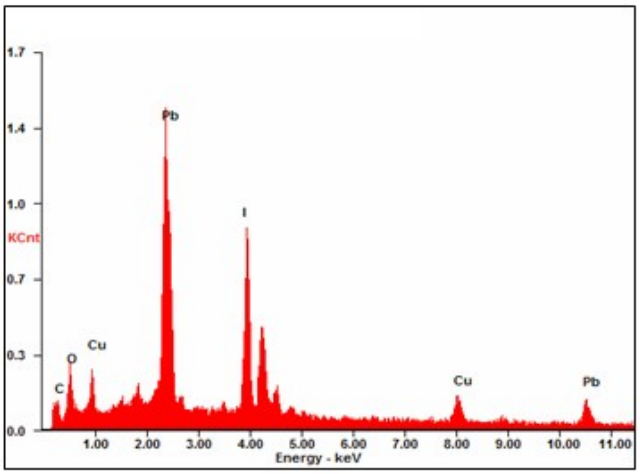
Figure S2. FT-IR spectra of compounds **1**-**3** (a-c).



(a)



(b)



(c)

Figure S3. EDX for compounds **1**-**3** (a-c).

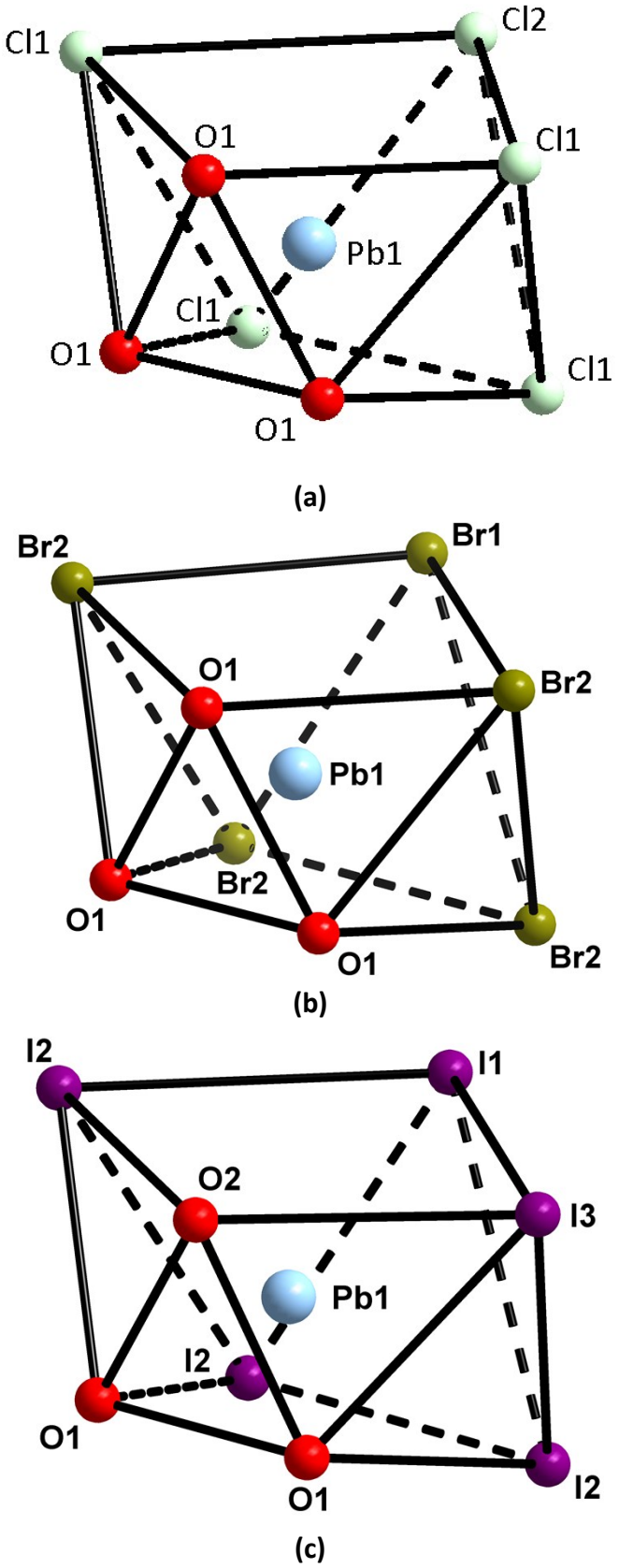


Figure S4. The eight-coordinated $[PbCl_5O_3]$ (a), $[PbBr_5O_3]$ (b) and $[PbI_5O_3]$ (c) sphere in compounds **1**-**3**.

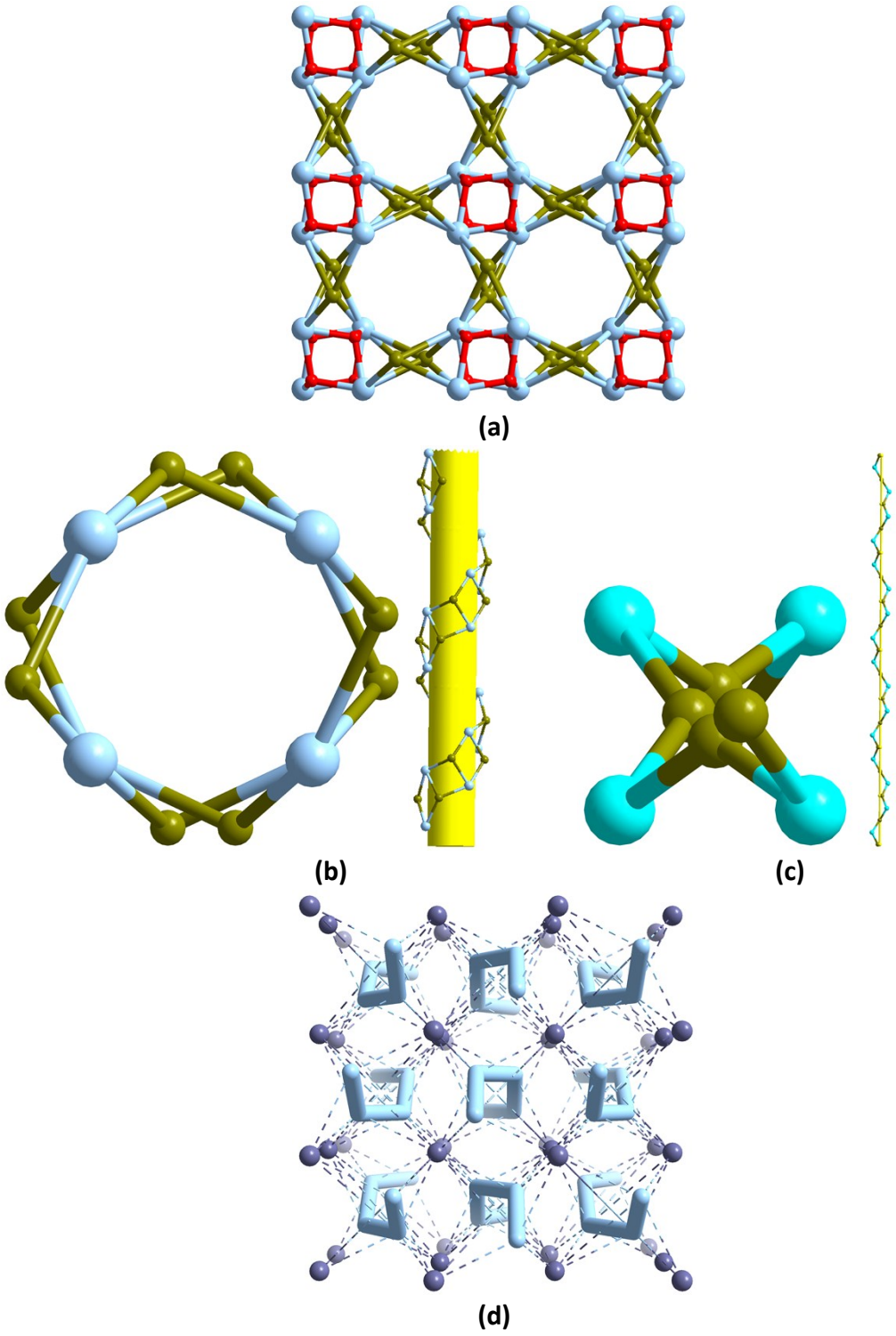


Figure S5. (a) The $[Pb_2Br_2(OH)_2]$ porous framework in **2** projected along the [001] direction; (b) the top and side-view of the right-handed helical $[Pb_2Br_2]$ ''ribbon''; (c) the top and side-view of the [CuBr] helical chain; (d) the schematic rod-packing network for **2**.

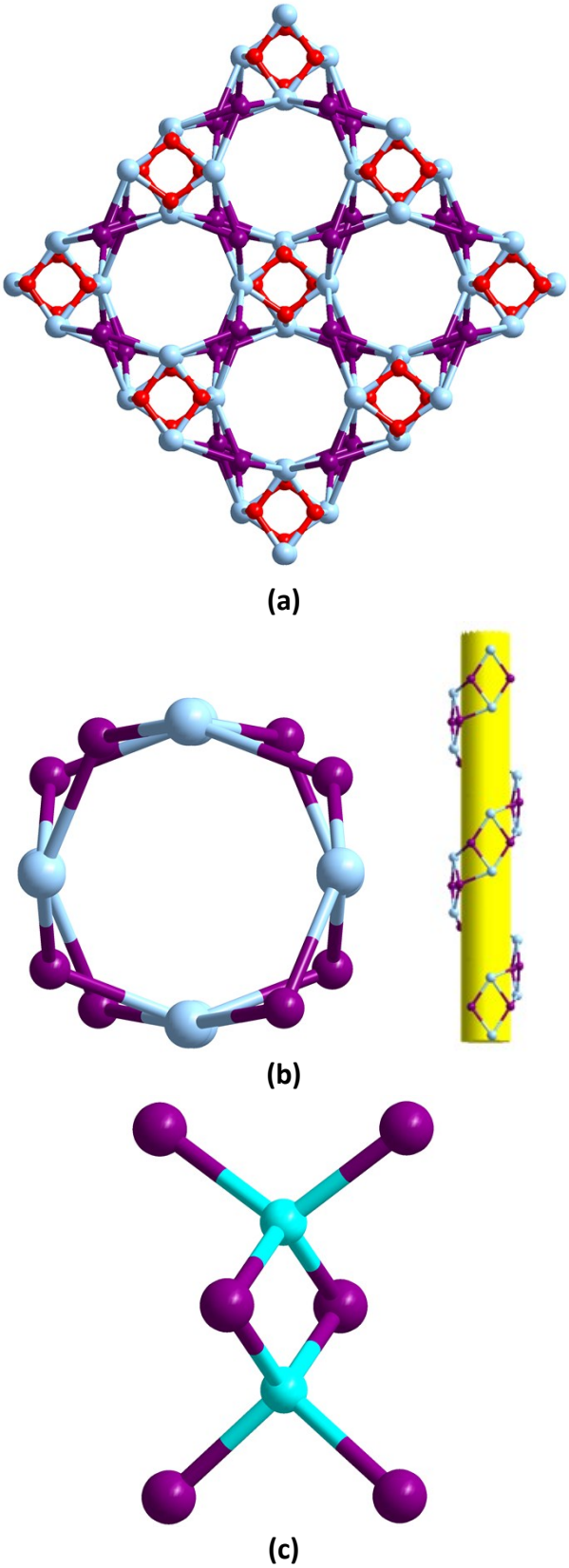


Figure S6. (a) The $[Pb_2I_2(OH)_2]$ porous framework in **3** projected along the [100] direction; (b) the top and side-view of the right-handed helical $[Pb_2I_2]$ ‘‘ribbon’’; (c) the $[Cu_2I_6]$ dinuclear cluster.