Synthesis, Crystal Structure and Reversible Solid-State Crystal-to-Crystal Transformation of Three Isostructural Lead(II) Halide Coordination Polymers with different luminescence properties in bulk and nano scale

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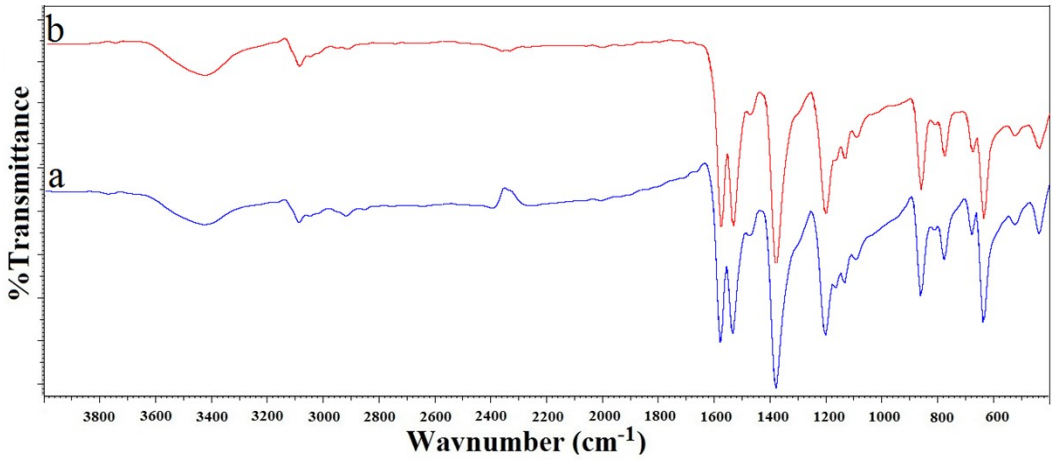
Table S1. Selective Bond Lengths (Å) and Angles (deg) for Complexes **1**-**3**.

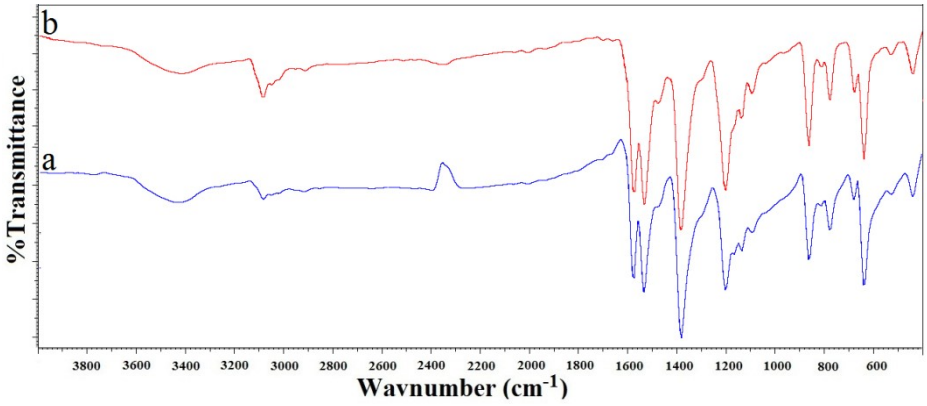
1		**2**		**3**	
Pb(1)-O(3)	2.508(4)	Pb(1)-O(3)#1	2.518(3)	Pb(1)-O(2)	2.527(3)
Pb(1)-O(3)#1	2.587(4)	Pb(1)-O(1)	2.566(3)	Pb(1)-O(1)#1	2.565(3)
Pb(1)-O(2)	2.592(4)	Pb(1)-O(3)	2.588(3)	Pb(1)-O(1)#2	2.617(3)
Pb(1)-O(1)#2	2.604(4)	Pb(1)-O(2)	2.631(3)	Pb(1)-O(3)#3	2.687(3)
Pb(1)-O(1)	2.724(5)	Pb(1)-O(2)#2	2.706(3)	Pb(1)-O(3)	2.724(3)
Pb(1)-Cl(1)#3	2.8388(19)	Pb(1)-Br(1)	2.9771(5)	Pb(1)-I(1)	3.1654(4)
Pb(1)-Cl(1)	2.9503(17)	Pb(1)-Br(1)#3	3.1067(5)	Pb(1)-I(1)#4	3.3132(3)
O(3)-Pb(1)-O(3)#1	92.53(9)	O(3)#1-Pb(1)-O(1)	72.95(9)	O(2)-Pb(1)-O(1)#1	72.43(11)
O(3)-Pb(1)-O(2)	73.17(14)	O(3)#1-Pb(1)-O(3)	89.32(6)	O(2)-Pb(1)-O(1)#2	80.68(11)
O(3)#1-Pb(1)-O(2)	76.79(14)	O(1)-Pb(1)-O(3)	78.56(10)	O(1)#1-Pb(1)-O(1)#2	84.35(6)
O(3)-Pb(1)-O(1)#2	157.77(13)	O(3)#1-Pb(1)-O(2)	156.94(9)	O(2)-Pb(1)-O(3)#3	117.35(10)
O(3)#1-Pb(1)-O(1)#2	108.75(14)	O(1)-Pb(1)-O(2)	117.01(10)	O(1)#1-Pb(1)-O(3)#3	154.93(10)
O(2)-Pb(1)-O(1)#2	117.10(14)	O(3)-Pb(1)-O(2)	112.57(10)	O(1)#2-Pb(1)-O(3)#3	119.14(11)
O(3)-Pb(1)-O(1)	121.62(13)	O(3)#1-Pb(1)-O(2)#2	121.80(9)	O(2)-Pb(1)-O(3)	49.47(10)
O(3)#1-Pb(1)-O(1)	82.16(13)	O(1)-Pb(1)-O(2)#2	49.33(9)	O(1)#1-Pb(1)-O(3)	121.29(10)
O(2)-Pb(1)-O(1)	48.91(14)	O(3)-Pb(1)-O(2)#2	86.43(9)	O(1)#2-Pb(1)-O(3)	92.99(10)
O(1)#2-Pb(1)-O(1)	69.32(15)	O(2)-Pb(1)-O(2)#2	69.00(10)	O(3)#3-Pb(1)-O(3)	69.48(11)
O(3)-Pb(1)-Cl(1)#3	74.63(10)	O(3)#1-Pb(1)-Br(1)	75.73(6)	O(2)-Pb(1)-I(1)	105.30(9)
O(3)#1-Pb(1)-Cl(1)#3	164.14(10)	O(1)-Pb(1)-Br(1)	106.74(8)	O(1)#1-Pb(1)-I(1)	77.04(7)
O(2)-Pb(1)-Cl(1)#3	107.43(12)	O(3)-Pb(1)-Br(1)	161.44(6)	O(1)#2-Pb(1)-I(1)	157.40(7)
O(1)#2-Pb(1)-Cl(1)#3	83.30(11)	O(2)-Pb(1)-Br(1)	81.36(7)	O(3)#3-Pb(1)-I(1)	78.05(8)
O(1)-Pb(1)-Cl(1)#3	112.35(10)	O(2)#2-Pb(1)-Br(1)	110.69(7)	O(3)-Pb(1)-I(1)	107.54(7)
O(3)-Pb(1)-Cl(1)	82.63(11)	O(3)#1-Pb(1)-Br(1)#3	81.11(7)	O(2)-Pb(1)-I(1)#4	142.90(8)
O(3)#1-Pb(1)-Cl(1)	71.59(9)	O(1)-Pb(1)-Br(1)#3	141.05(8)	O(1)#1-Pb(1)-I(1)#4	78.66(7)
O(2)-Pb(1)-Cl(1)	138.94(12)	O(3)-Pb(1)-Br(1)#3	72.48(6)	O(1)#2-Pb(1)-I(1)#4	73.70(6)
O(1)#2-Pb(1)-Cl(1)	97.71(10)	O(2)-Pb(1)-Br(1)#3	98.13(7)	O(3)#3-Pb(1)-I(1)#4	98.63(7)
O(1)-Pb(1)-Cl(1)	145.33(11)	O(2)#2-Pb(1)-Br(1)#3	149.16(7)	O(3)-Pb(1)-I(1)#4	155.45(8)
Cl(1)#3-Pb(1)-Cl(1)	97.11(5)	Br(1)-Pb(1)-Br(1)#3	94.037(14)	I(1)-Pb(1)-I(1)#4	89.996(9)

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



(c)

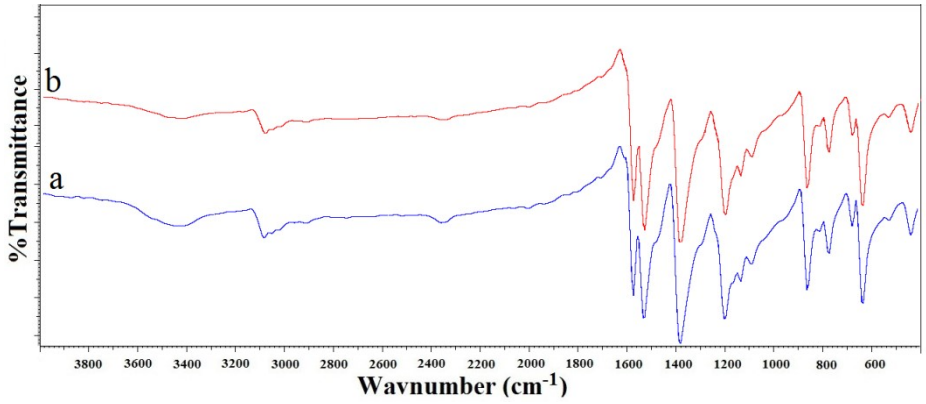
Single crystal of **1**: m.p. > 300 ˚C; yield 61% based on Pb(II); $C_6H_4ClNO_3Pb$: calcd. C, 18.93; H, 1.06; N, 3.67%; found: C, 18.86; H, 1.10; N, 3.58%. FT-IR (KBr cm^{-1}): 679 cm^{-1} (s, ν (Pb–O)), 778 cm^{-1} (m, ν_{oop} $(C–H)_{ring}$), 862 cm^{-1} (s, ν (C–C)), 1136 cm^{-1} (m, ν $(C–H)_{ring}$), 1205 cm^{-1} (vs, ν $(N–O)_{N\text{-}oixde}$), 1382 cm^{-1} (m, ν $(C=C)_{Ar}$), 1537 cm^{-1} (vs, ν_{sym} $(CO_2–Pb)$), 1580 cm^{-1} (s, ν_{asym} $(CO_2–Pb)$), 3092 cm^{-1} (w, ν_{sym} (C–H)).



(d)

Single crystal of **2**: m.p. > 300 ˚C; yield 73% based on Pb(II); $C_6H_4BrNO_3Pb$: calcd. C, 16.95; H, 0.95; N, 3.29%; found: C, 16.87; H, 1.10; N, 3.18%. FT-IR (KBr cm^{-1}): 678 cm^{-1} (s, ν (Pb–O)), 776 cm^{-1} (m, ν_{oop} $(C–H)_{ring}$), 861 cm^{-1} (s, ν (C–C)), 1135 cm^{-1} (m, ν $(C–H)_{ring}$), 1201 cm^{-1} (vs, ν

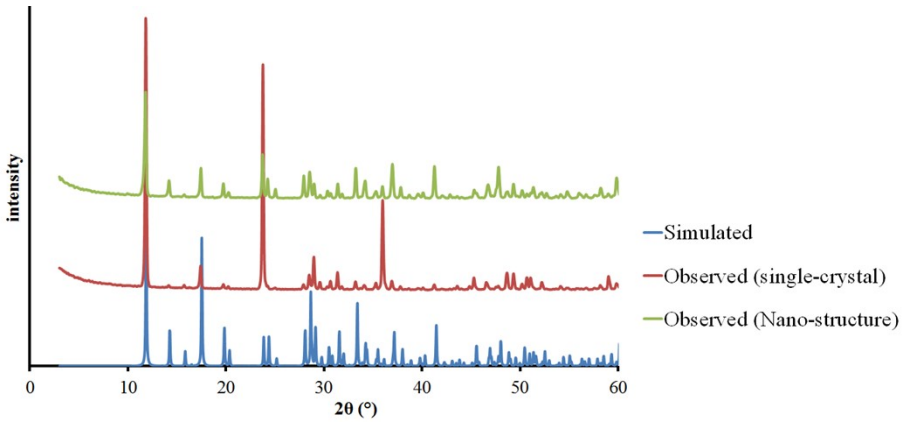
$(N–O)_{N\text{-}oixde}$), 1382 cm^{-1} (m, ν $(C=C)_{Ar}$), 1533 cm^{-1} (vs, ν_{sym} $(CO_2–Pb)$), 1577 cm^{-1} (s, ν_{asym} $(CO_2–Pb)$), 3085 cm^{-1} (w, ν_{sym} (C–H)).



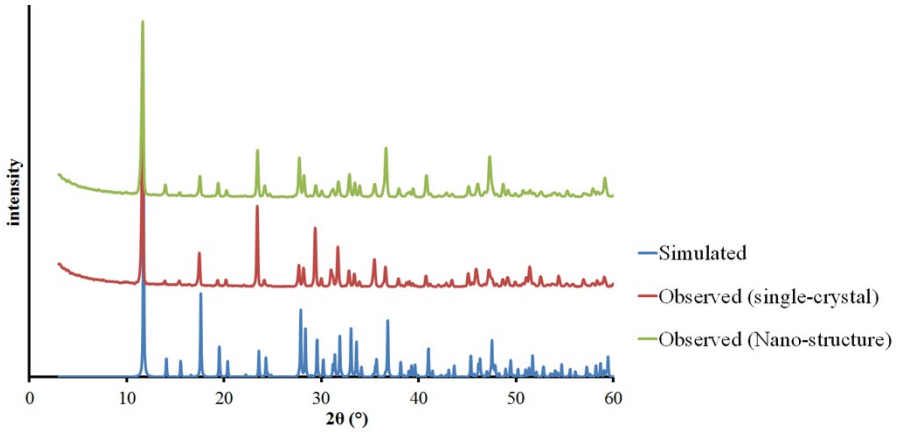
(e)

Single crystal of **3**: m.p. > 300 ˚C; Yield 80% based on Pb(II); $C_6 H_4 I N O_3 Pb$: calcd. C, 15.26; H, 0.85; N, 2.97%; found: C, 15.17; H, 1.01; N, 3.07%. FT-IR (KBr cm^{-1}): 678 cm^{-1} (s, ν (Pb–O)), 774 cm^{-1} (m, ν_{oop} $(C–H)_{ring}$), 861 cm^{-1} (s, ν (C–C)), 1135 cm^{-1} (m, ν $(C–H)_{ring}$), 1200 cm^{-1} (vs, ν $(N–O)_{N\text{-}oixde}$), 1382 cm^{-1} (m, ν $(C=C)_{Ar}$), 1531 cm^{-1} (vs, ν_{sym} $(CO_2–Pb)$), 1574 cm^{-1} (s, ν_{asym} $(CO_2–Pb)$) , 3085 cm^{-1} (w, ν_{sym} (C–H)).

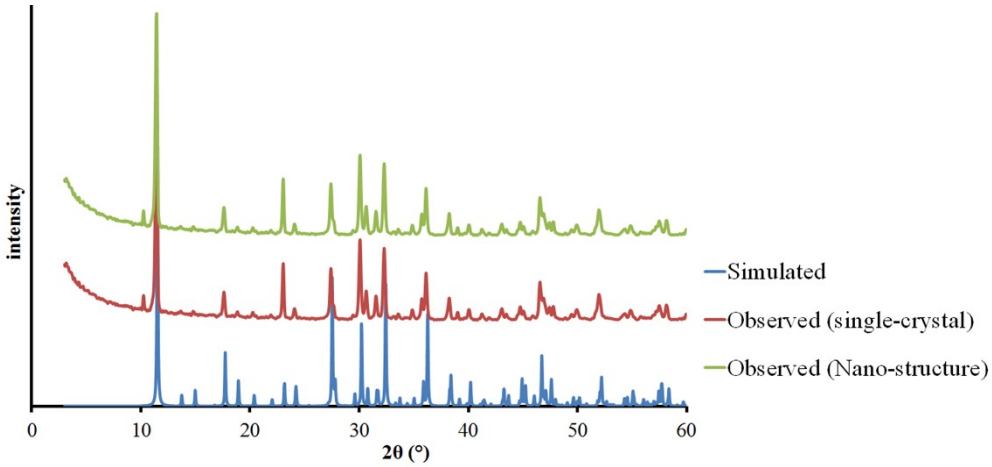
Figure S1: The IR spectrum of compound **1-3** (c-e): a) single-crystal synthesized by branched-tube method, b) nano structures synthesized by sonochemical method.



(a)



(b)



(c)

Figure S2. Experimental and simulated powder X-ray diffraction (PXRD) patterns for compounds **1**-**3** (a-c).

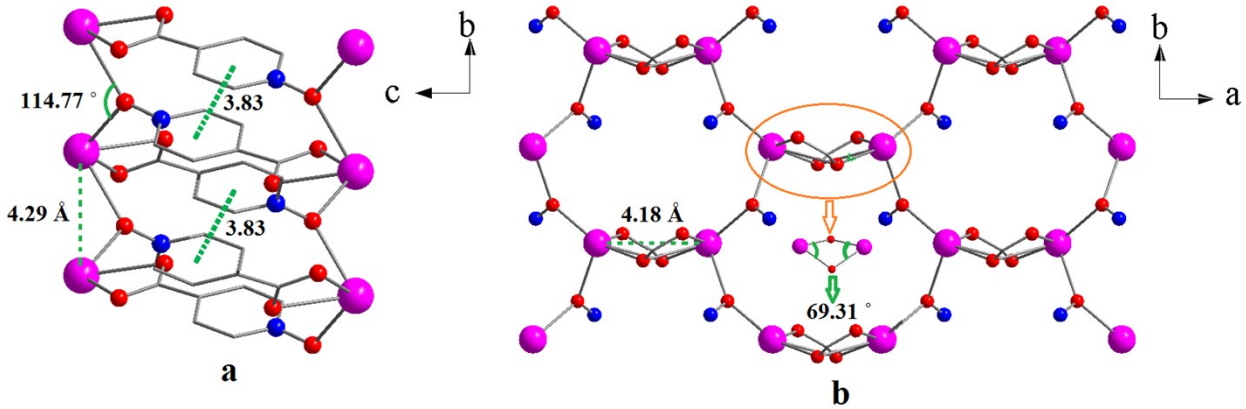


Figure S3. View of distances and angles of compound **1**: a) 1D zigzag chain and the π–π interactions; b) [Pb_2O_2] unit; (Cl ions and H atoms are omitted for clarity).

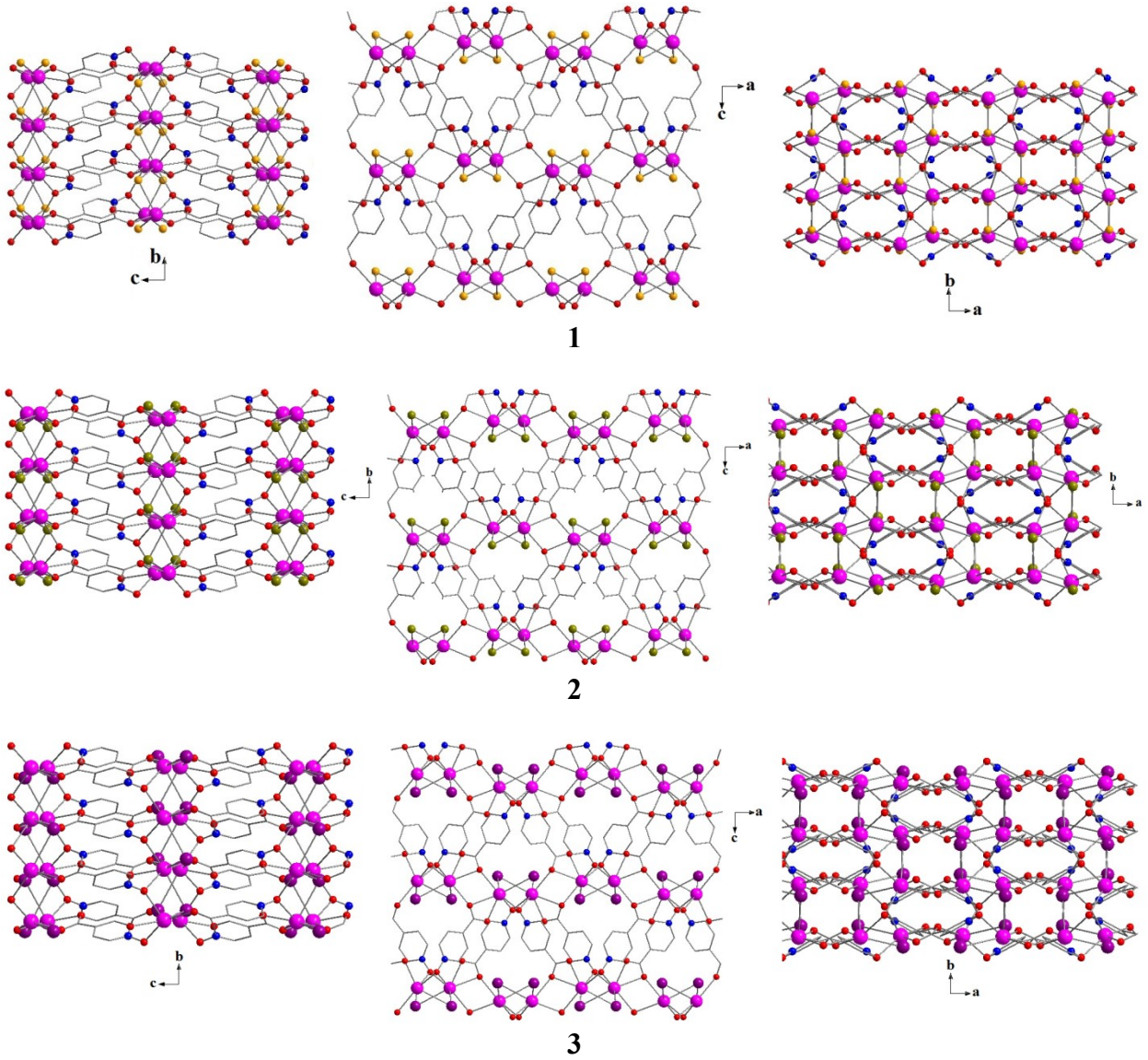
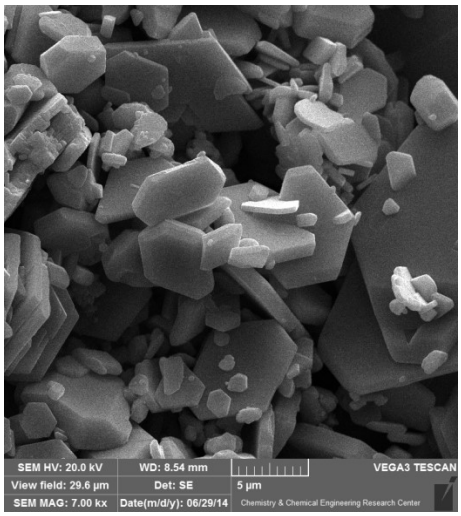
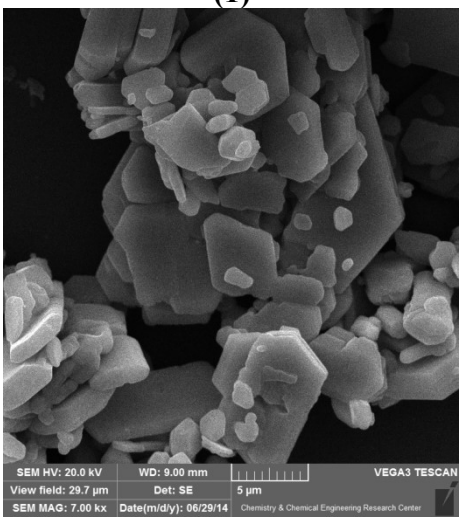


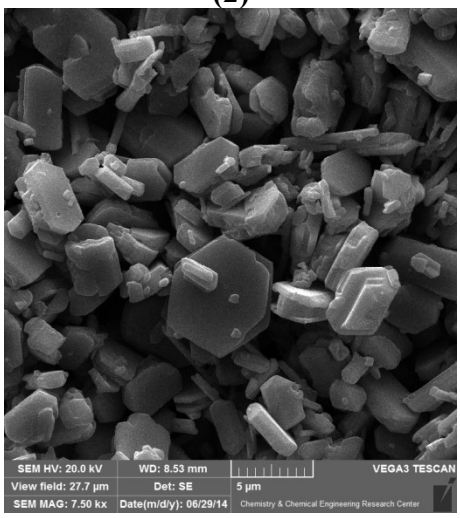
Figure S4. Crystal packing of isostructural 3D CPs **1**-**3** along *a*, *b* and *c* directions, Color code: pink, Pb; red, O; blue, N; gray, C; yellow, Cl; green, Br and violet, I atoms.



(1)



(2)



(3)

Figure S5. SEM images of the synthesized compounds by sonochemical methods.

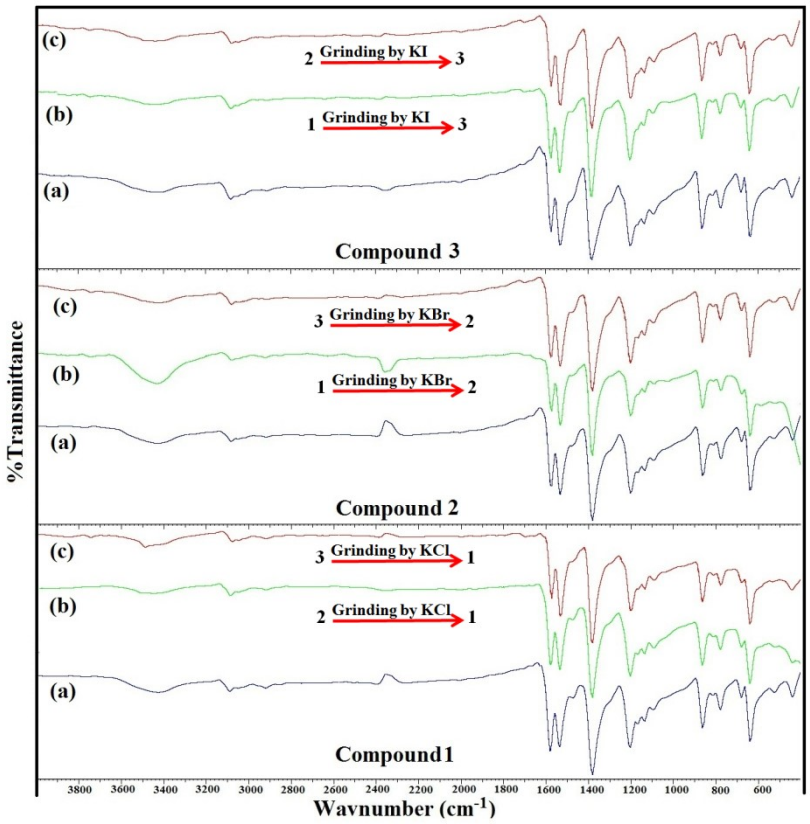


Figure S6. IR spectra of **1**-**3**: a) single crystal, b and c) prepared from mechanochemical solid state transformations.

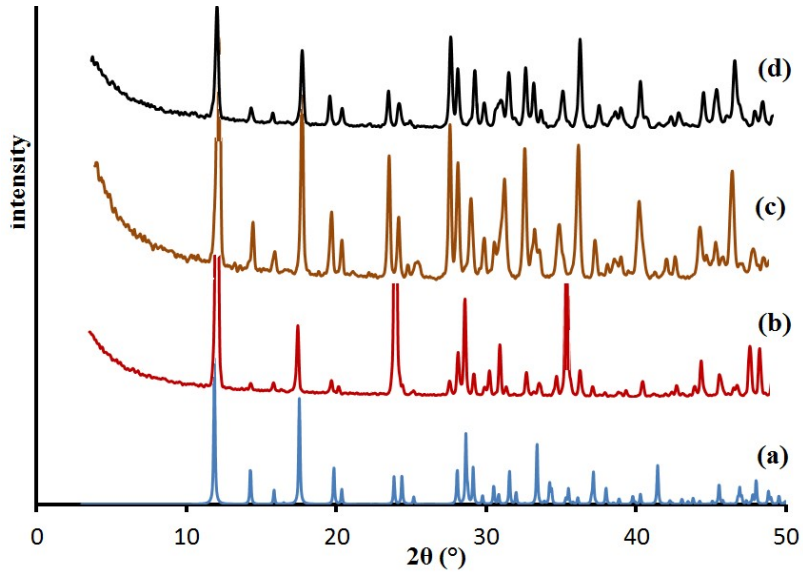


Figure S7. The PXRD patterns of **1**: a) simulation; b) experimental; c) ground product of **2** with KCl; d) ground product of **3** with KCl.

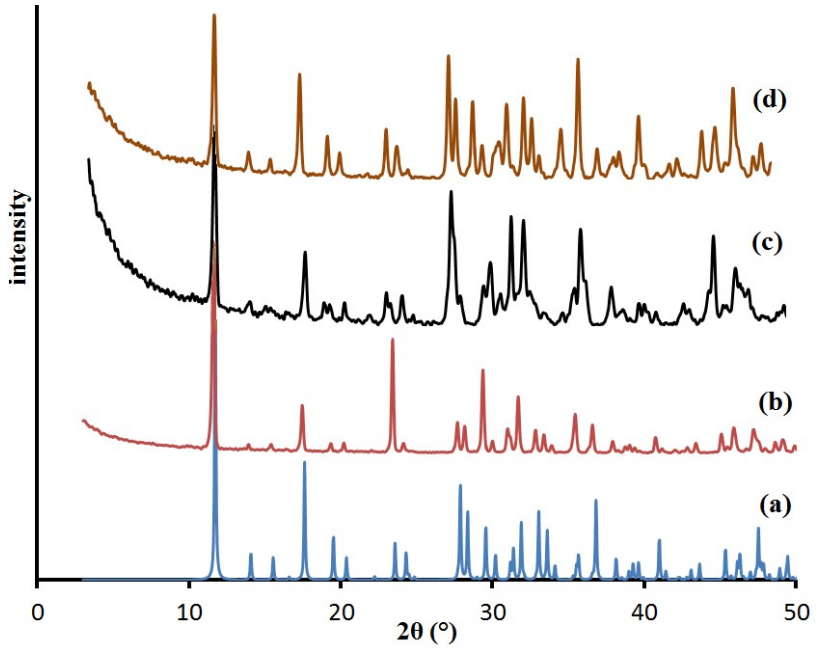


Figure S8. The PXRD patterns of **2**: a) simulation; b) experimental; c) ground product of **1** with KBr; d) ground product of **3** with KBr.

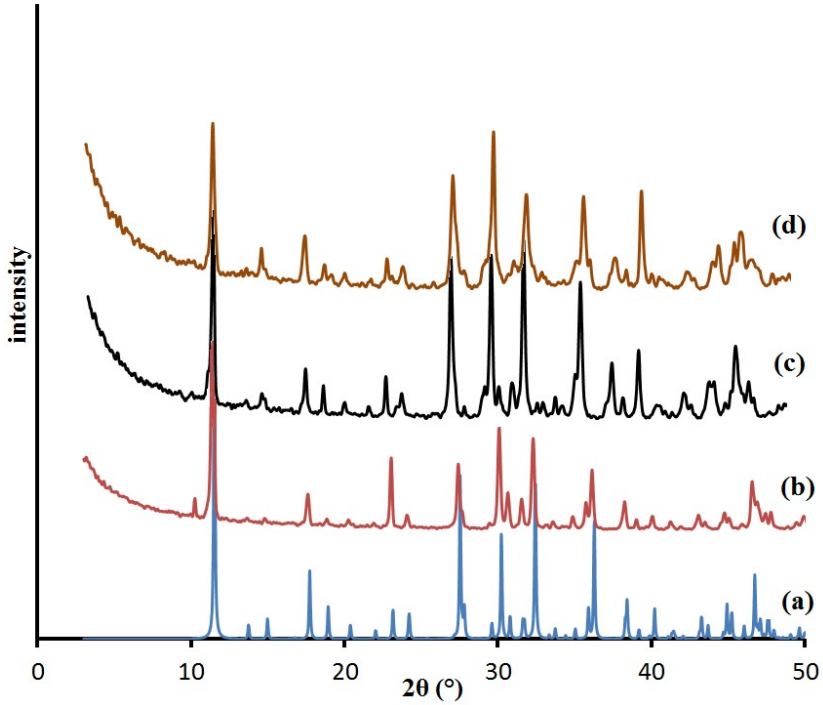
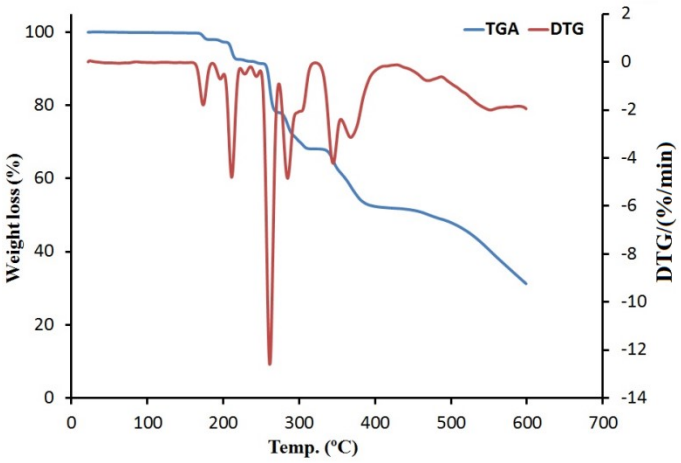
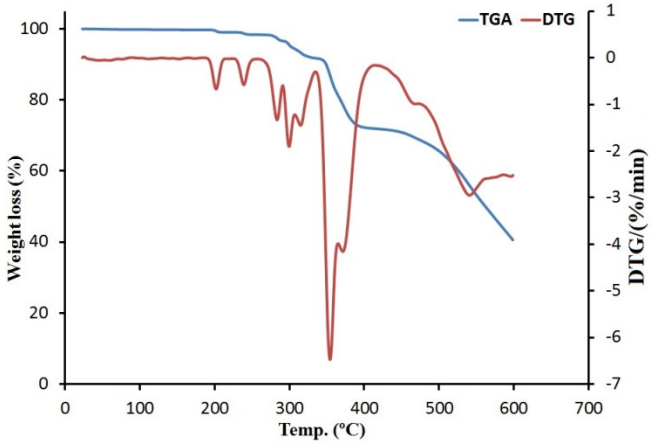


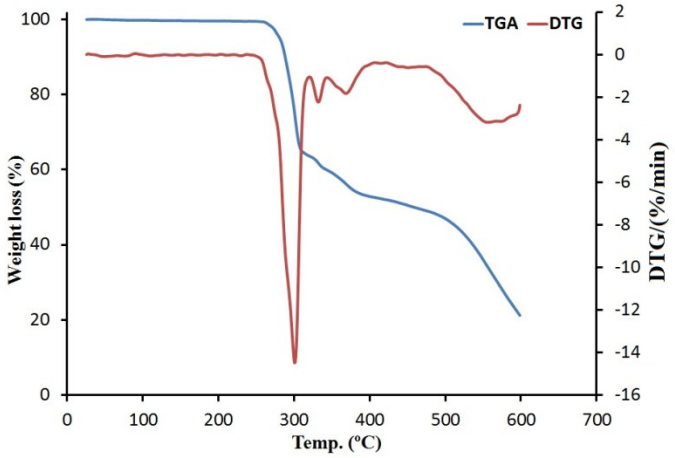
Figure S9. The PXRD patterns of **3**: a) simulation; b) experimental; c) ground product of **1** with KI; d) ground product of **2** with KI.



(1)



(2)



(3)

Figure S10. The TGA and DTG curves of **1**-**3**.