Electronic Supplementary Information for MS:

Mechanochemical Solid State Anion-exchange of Lead(II) Coordination Polymer via Intermediate Coordination Polymer; New Precursors for Preparation of $PbBr_2$/ $Pb_3O_2Br_2$, PbBr(OH) and PbO Nanoparticles

Lida Hashemi[a] , Ali Morsali[a*], Sang Woo Joo[b*]

[a]Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Islamic Republic of Iran
[b]School of Mechanical Engineering, WCU Nano Research Center, Yeungnam University, Gyongsan 712–749, South Korea

‡ Experimental section:

Synthesis of coordination polymers 1, 2 and 3 with branched tube method:

Single crystals of compound **1** suitable for X-ray diffraction were prepared by a thermal gradient method in branched tube. The ligand 4-bpdh (1 mmol, 0.238g), lead(II) nitrate (0.331g, 1mmol) and KBr (2 mmol 0.119g) were placed in the main arm of a branched tube. Methanol was carefully added to fill both arms. The tube was sealed and the ligand-containing arm immersed in an oil bath at 60°C while the other arm was kept at ambient temperature. After 4 days, crystals deposited in the cooler arm that were isolated, filtered off and dried. M.p =240 °C. Found; C, 27.71; H, 2.40; N, 9.26%, calculated for $C_{14}H_{14}Br_2N_4Pb$; C, 27.75; H, 2.31; N, 9.25%. IR (cm^{-1}) selected bonds: ν= 574(w), 821(s), 1062(m), 1217(w), 1291(w), 1415(m), 1600(vs) and 3435(m) .

Single crystals of compound **2** suitable for X-ray diffraction were prepared by a thermal gradient method in branched tube. The ligand 4-bpdh (1 mmol, 0.238g), lead(II) nitrate (0.331g, 1mmol) and KBr (1 mmol 0.119g) were placed in the main arm of a branched tube. Methanol was carefully added to fill both arms. The tube was sealed and the ligand-containing arm immersed in an oil bath at 60°C while the other arm was kept at ambient temperature. After 3 days, crystals deposited in the cooler arm that were isolated, filtered off and dried. M.p =250 °C. Found; C, 28.55; H, 2.40; N, 11.70%, calculated for $C_{28}H_{28}Br_{2.16}N_{9.84}O_{5.50}Pb_2$; C, 28.53; H, 2.37; N, 11.69%. IR (cm^{-1}) selected bonds: ν= 576(m), 824(s), 1059(w), 1297(m), 1394(s), 1590(vs) and 3031(w) .

Single crystals of compound **3** suitable for X-ray diffraction were prepared by a thermal gradient method in branched tube. The ligand 4-bpdh (1 mmol, 0.238g) and lead(II) nitrate (0.331g, 1mmol) were placed in the main arm of a branched tube. Methanol was carefully added to fill both arms. The tube was sealed and the ligand-containing arm immersed in an oil bath at 60°C while the other arm was kept at ambient temperature. After 2-3 days, crystals deposited in the cooler arm that were isolated, filtered off and dried. M.p =290 °C. Found; C, 28.65; H, 2.40; N, 14.35%, calculated for $C_{14}H_{14}C_{10}N_6O_7Pb$; C, 28.69; H, 2.39; N, 14.34%. IR (cm^{-1}) selected bonds: ν = 575(w), 825(s), 1055(m), 1293(s), 1372(vs), 1544(w), 1599(s) and 3384(m) .

Synthesis of coordination polymers 1, 2 and 3 with mechanochemical maner:

Compound **3** is synthesized from grinding of row materials for 20 minutes in an agate mortar. the 3D $[Pb(4\text{-}bpdh)(NO_3)_2(H_2O)]_n$ (**3**) polymerizes on grinding the solid with 1 and 2 mmol of KBr for 20 min in an agate mortar and pestle to form 3D coordination polymer, $[Pb(4\text{-}bpdh)(Br)(NO_3)]_n$ (**2**) and 1D coordination polymer $[Pb(4\text{-}bpdh)(Br)_2]_n$ (**1**), respectively. These powder samples separated by washing.

Synthesis of PbO, PbBr(OH), $Pb_3O_2Br_2$ and $PbBr_2$ nanoparticles by thermal decomposition of coordination polymers 1, 2 and 3, respectively, at oleic acid as a surfactant:

Precursors **1-3** (0.1 mmol) were dispersed in oleic acid (1.58 ml) to form homogenous emulsion solutions. These solutions were degassed for 20 min and then heated to 190 °C for 2 h. At the end of the reaction, black precipitates for precursor **1-3** were formed. A small amount of toluene and a large excess of EtOH were added to the all of three reaction solutions and $PbBr_2$, PbBr(OH), $Pb_3O_2Br_2$ and PbO nanoparticles were separated by centrifugation for the precursors **1**, **2** and **3**, respectively. The solids were washed with EtOH and dried under air atmosphere.

Orthorhombic PbO structure with the lattice parameters of a = 5.4903Å, c = 4.7520Å, Z = 4 and S.G = Pcam which are in JCPDS card file No. 38-1477 after calcination of compound **3**; Orthorhombic PbBr(OH) with a = 7.3850 Å and z = 4 which are in JCPDS card file No. 30-0697 and Orthorhombic $Pb_3O_2Br_2$ with a = 12.2520 Å and z = 4 which are in JCPDS card file No. 87-1185 after calcination of compound **2**; $PbBr_2$ with the lattice parameters (a = 8.062 Å, b = 9.5393 Å, c = 4.7348 Å, S.G. = Pnam (62) and z = 4) which are in JCPDS card file No. 31-0679 after calcination of compound **1** .

Table S1 Crystal data and structure refinements for compounds 1-3.

Identification code	**1**	**2**	**3**
Empirical formula	$C_{14}H_{14}Br_2N_4Pb$	$C_{28}H_{28}Br_{2.16}N_{9.84}O_{5.50}Pb_2$	$C_{14}H_{14}C_{l0}N_6O_7Pb$
Formula weight	605.29	1177.72	585.50
Temperature(K)	298	180(2)	296
Wavelength	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2/c	P-1	P2/c
Unit cell dimensions	a = 15.179(4)Å	a = 8.3995(1) Å	a = 29.5578(14)Å
	b = 4.2189(10)Å	b = 17.9496(3) Å	b = 10.5995(6)Å
	c = 16.682(3)Å	c = 27.9998(5) Å	c = 7.5118(4)Å
	β =117.679(17)^{o}	β = 89.987(1)°	β =91.337(4)^{o}
Volume	946.0(4)Å^3	3578.0(1) Å3	2352.8(2)Å^3
Z	2	4	4
Density (calculated)	2.125 g/m^3	2.186 Mg/m3	1.653 g/m^3
F(000)	556	2195	1112
Theta range for data collection	2.45 to 25.29 °	1.71 to 26.00°	1.38 to 27.20 °
Index ranges	$-17 \le h \le 18$	$-10 \le h \le 10$	$-33 \le h \le 37$
	$-4 \le k \le 5$	$-22 \le k \le 22$	$-13 \le k \le 13$
	$-20 \le l \le 16$	$-34 \le l \le 34$	$-8 \le l \le 9$
Reflections collected	1789	46625	4870
Independent reflections	1689	14031	3215
Absorption correction	Integration	Multi-scan	Integration
Refinement method	$F^2 > 2sigma(F^2)$	Full-matrix least-squares on F^2	$F^2 > 2sigma(F^2)$
Data / restraints / parameters	1789 / 0 / 97	14031 / 14 / 630	4870 / 24 / 255
Goodness-of-fit on F^2	1.216	1.022	0.985
Final *R* indices [$I>2\sigma(I)$]	R_1= 0.0466 and wR_2= 0.1077	$R_1 = 0.0346$ and $wR_2 = 0.0787$	R_1= 0.0443 and wR_2= 0.0884
R Indices (all data)	R_1= 0.0530 and wR_2= 0.1235	$R_1 = 0.0651$ *and* $wR_2 = 0.0926$	R_1= 0.0792 and wR_2= 0.0963

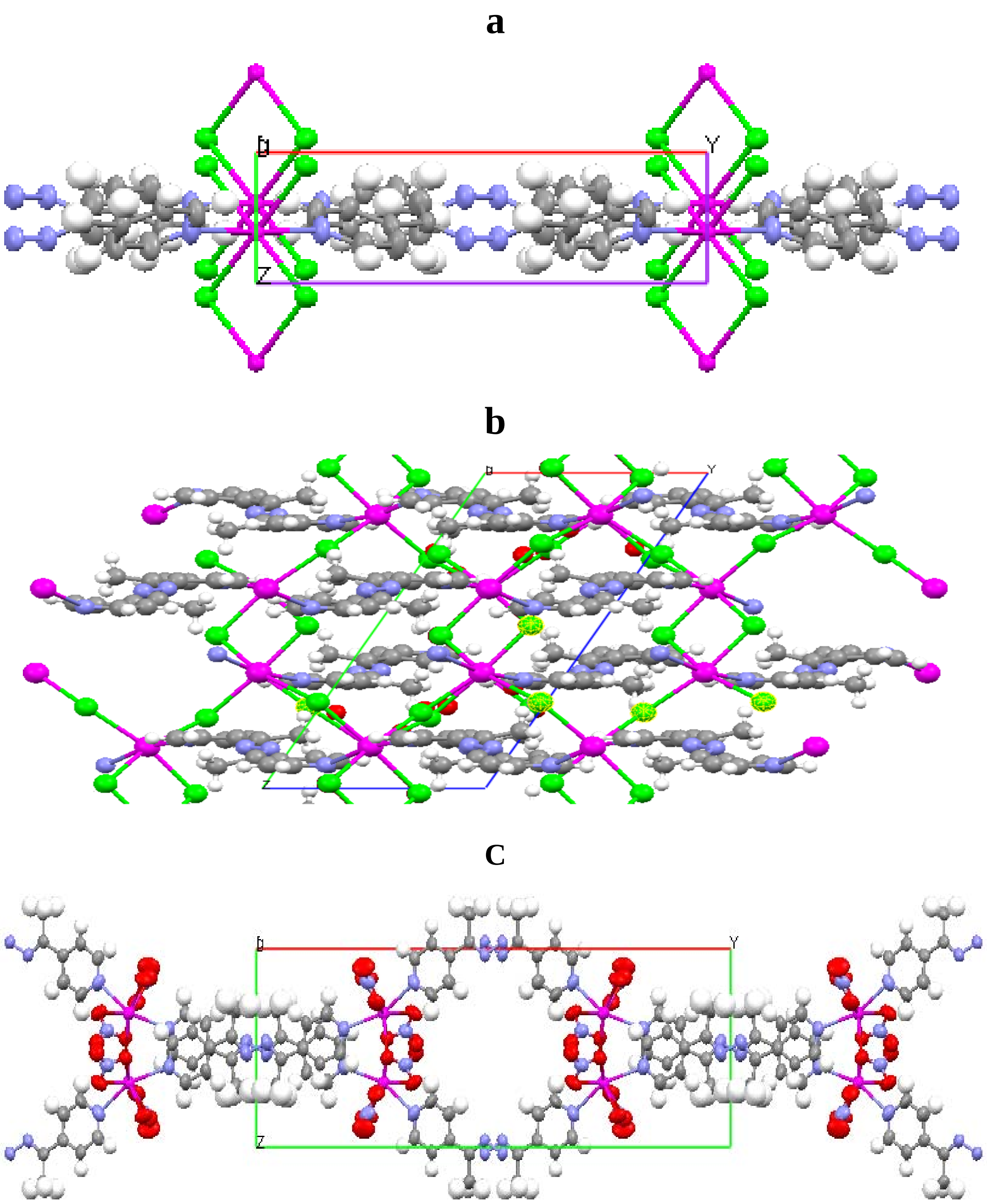

Fig. S1 The coordination environments and unit cell of (a) compound $[Pb(4\text{-bpdh})(Br)_2]_n$ (**1**) (b) compound $[Pb(4\text{-bpdh})(Br)(NO_3)]_n$ (**2**) and (c) compound $[Pb(4\text{-bpdh})(NO_3)_2(H_2O)]_n$ (**3**) (Pb= violet, O = red, C = gray and N= blue Br= green and H=white).

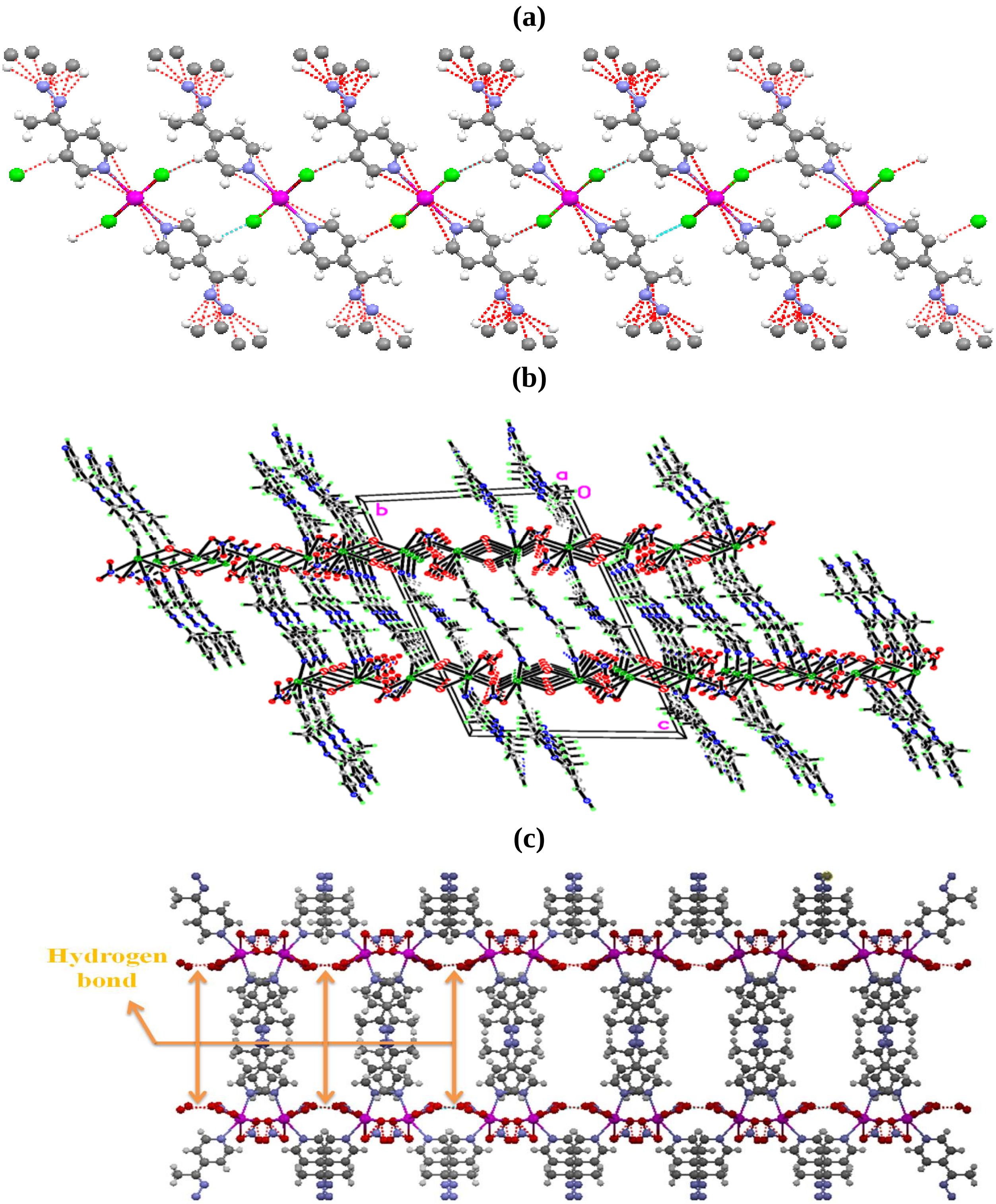

Fig. S2 A schematic diagram illustrating the interactions in polymeric chains of (a) compound **1** and (b) compound **2** and (c) compound **3**, (Pb= violet, O = red, C = gray and N= blue Br= green and H=white)

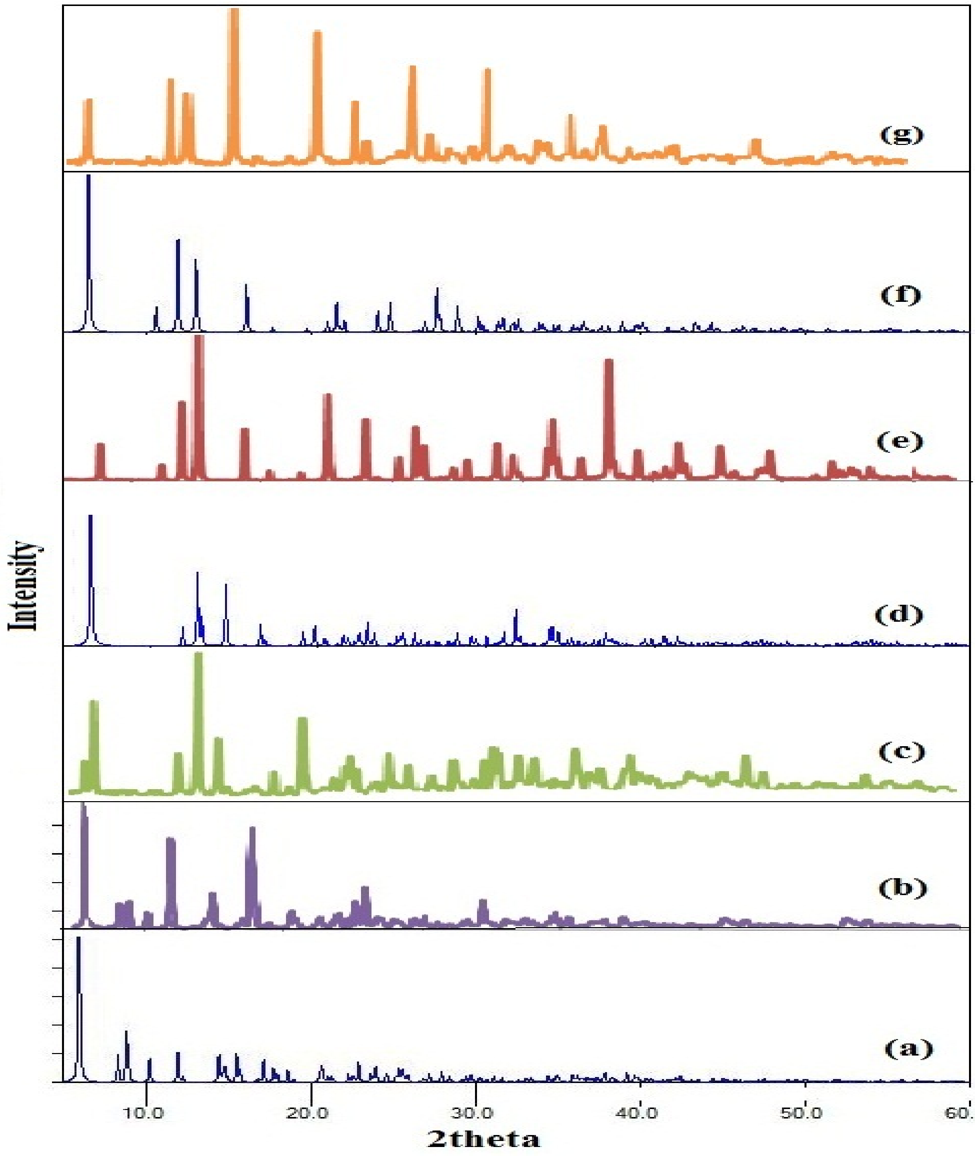

Fig. S3 The XRD patterns of (a) simulated from single crystal X-ray data of compound **3**, (b) bulk materials as synthesized of compound **3**, (c) bulk materials obtained by solid state anion-replacement of compound **3** with 1 mmol KBr, (d) simulated from single crystal X-ray data of compound **2,** (e) bulk materials obtained by solid state anion-replacement of compound **2** with 1 mmol KBr, and (f) simulated from single crystal X-ray data of compound **1**, (g) compound **1** obtained by solid state anion-replacement of compound **3** with 2 mmol KBr.

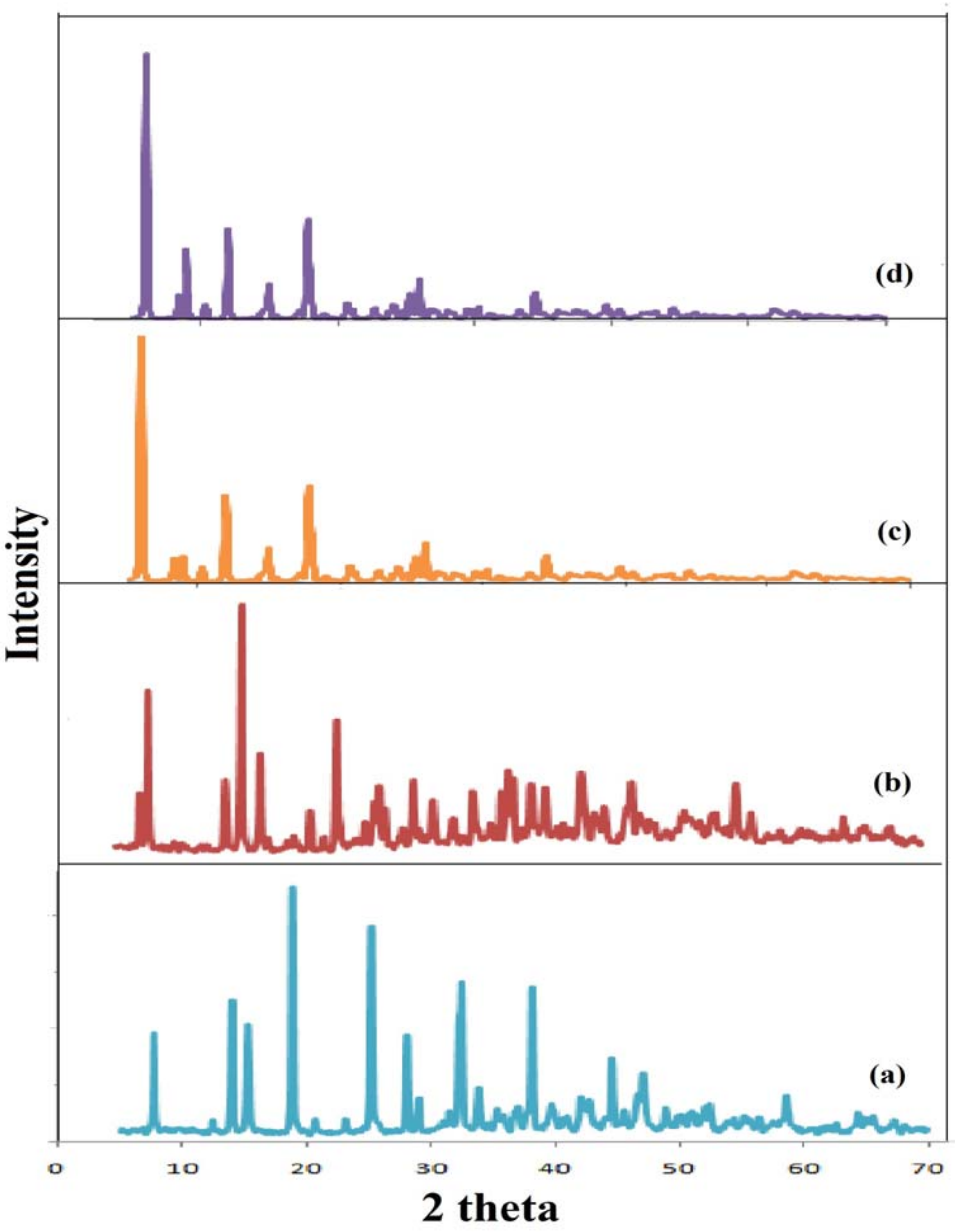

Fig. S4 The XRD patterns of (a) compound **1** that obtained by solid state anion-replacement of compound **3** with 2 mmol KBr (b) compound **2** obtained by solid state anion-replacement of compound **1** with 1 mmol $NaNO_3$, (c) compound **3** obtained by solid state anion-replacement of compound **2** with 1 mmol $NaNO_3$, (d) compound **3** obtained by solid state anion-replacement of compound **1** with 2 mmol $NaNO_3$.

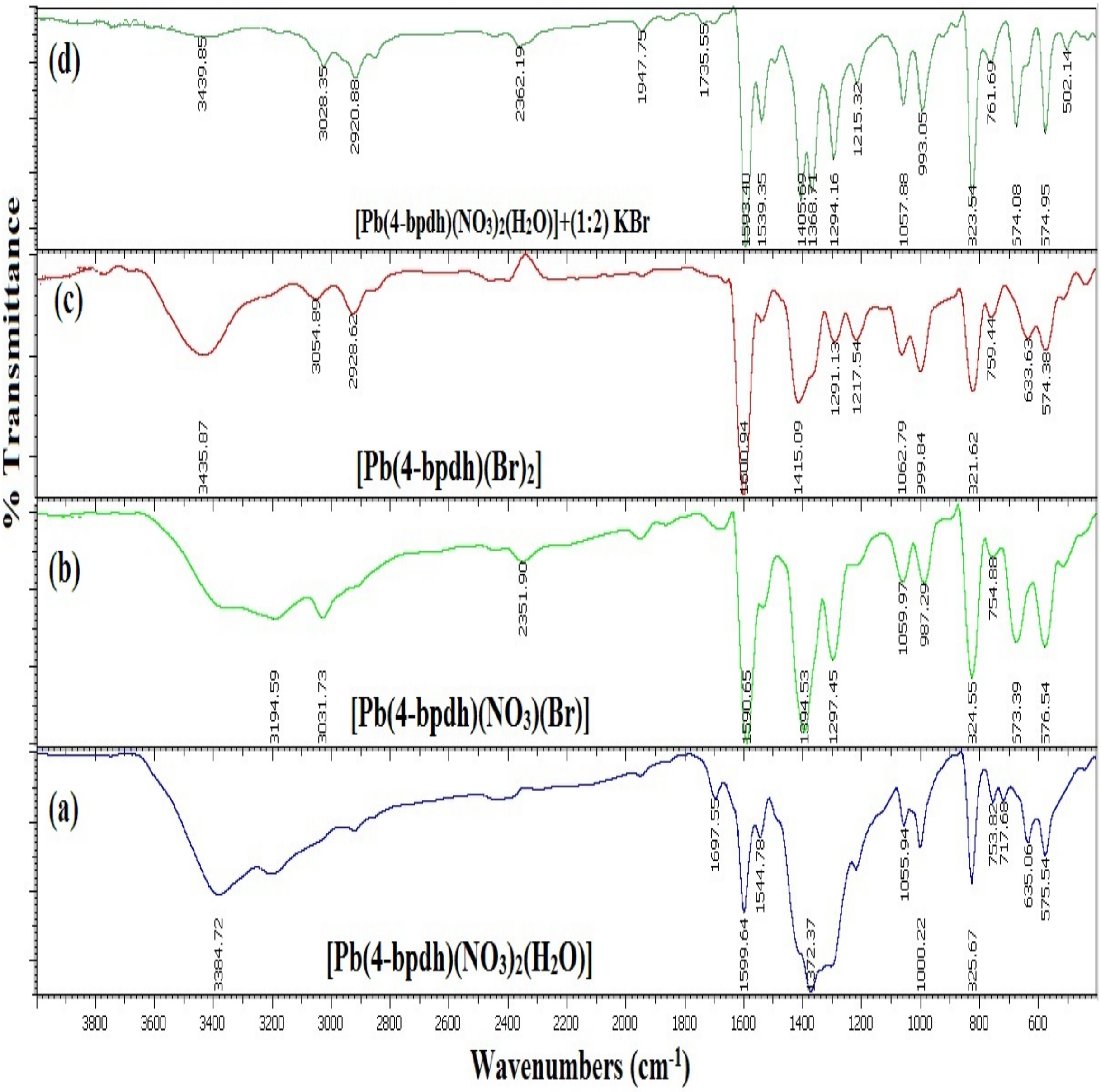

Fig. S5 IR spectra of (a) compound **3**, (b) bulk materials obtained by solid state anion-replacement of compound **3** by grinding with 1 mmol KBr**,** (c) bulk materials obtained by solid state anion-replacement of compound **2** by grinding with 1 mmol KBr and (d) bulk materials obtained by solid state anion-replacement of compound **1** by grinding with 2 mmol KBr.

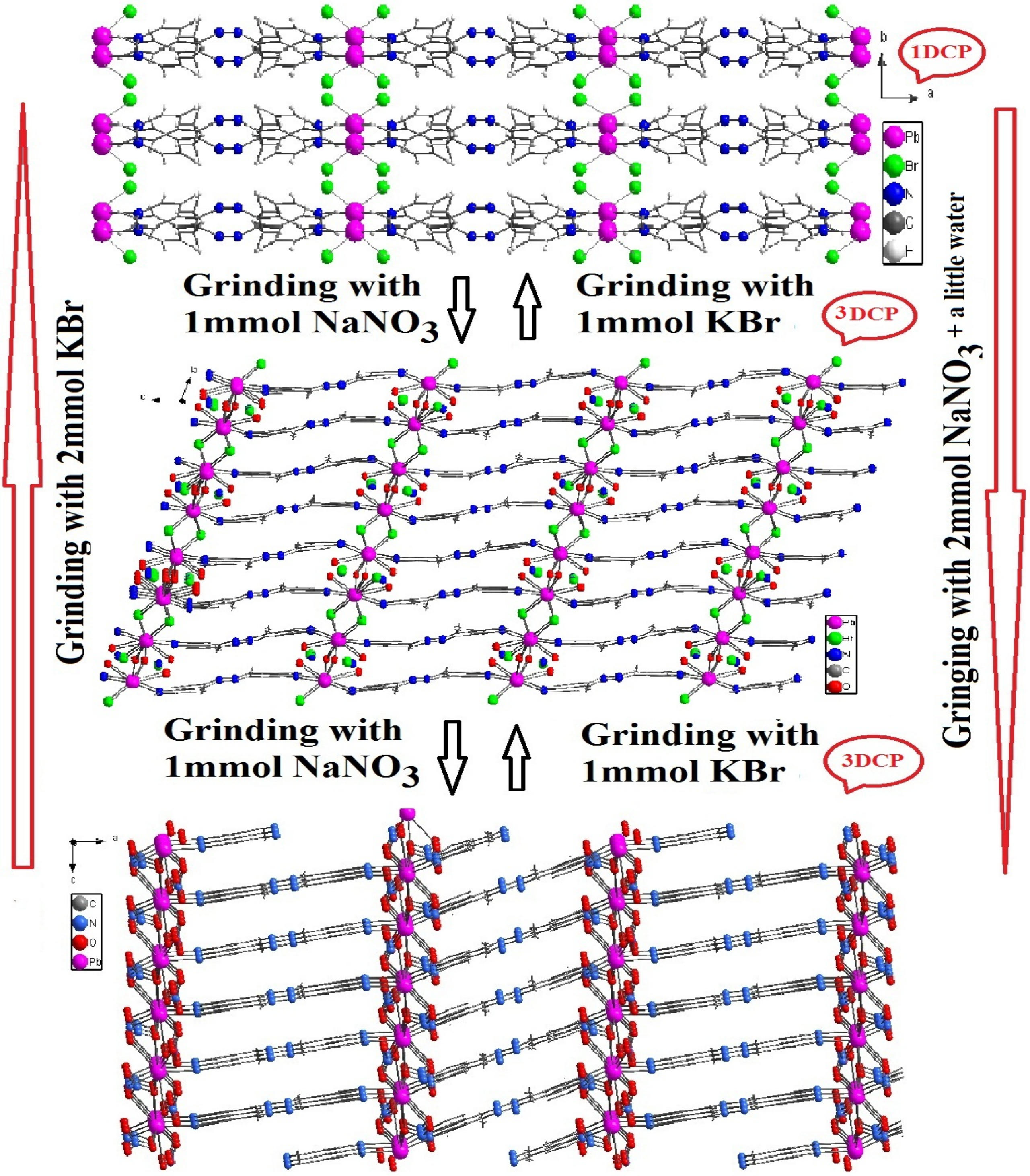

Fig. S6 A schematic diagram illustrating the structural conversions from 1D coordination polymer **1** (up) to 2D coordination polymers **2** (middle) and 3D coordination polymer **3** (bottom) by solid state reversible anion-replacement.

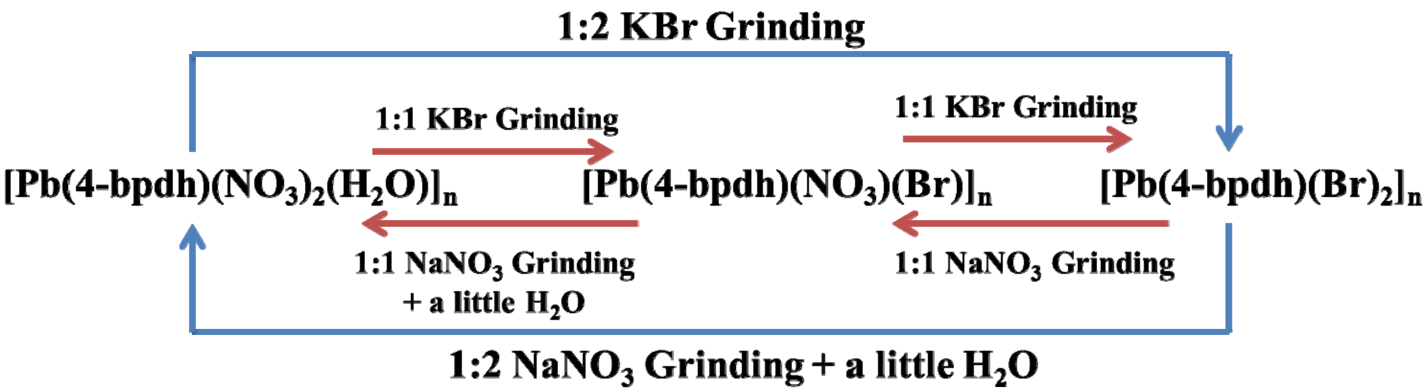

Fig. S7 schematic diagram for this Solid State Crystal to Crystal Conversions.

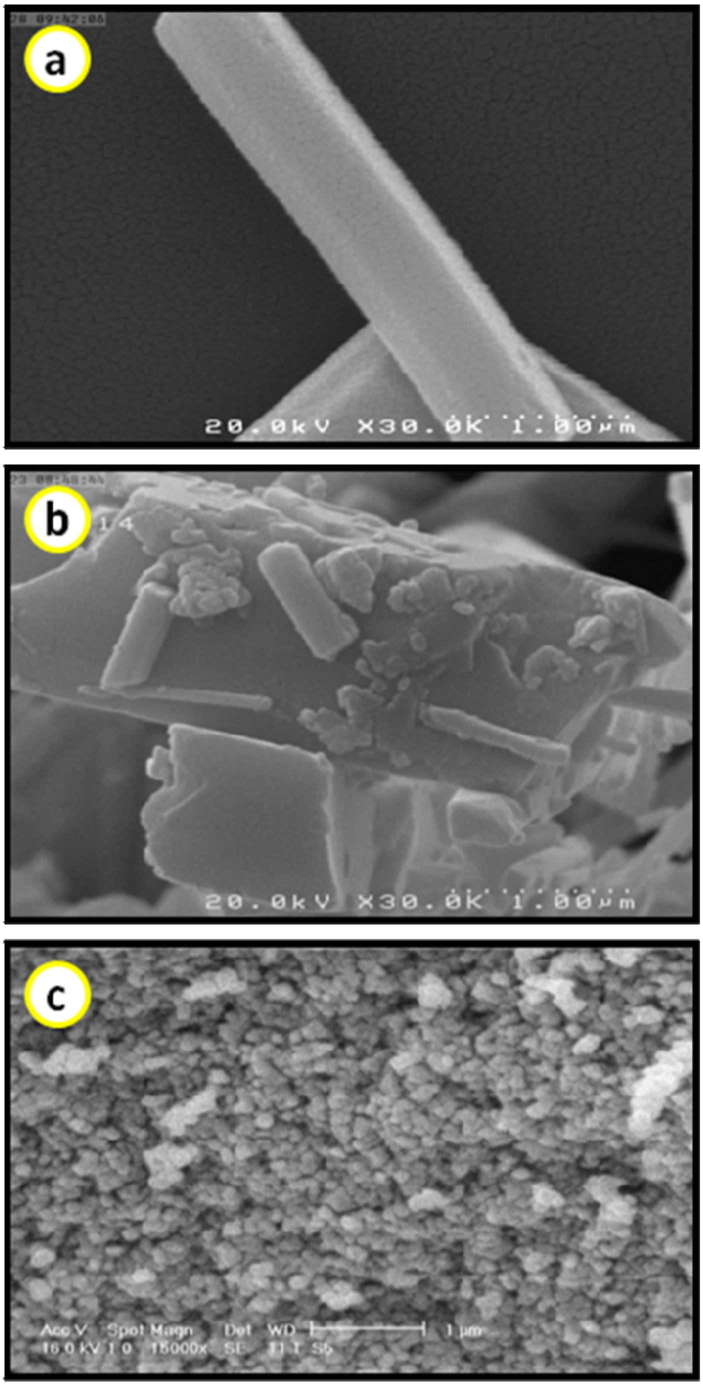

Fig. S8 SEM images for as synthesized (a) compound 1, (b) compound 2 and (c) compound 3; before thermolysis.

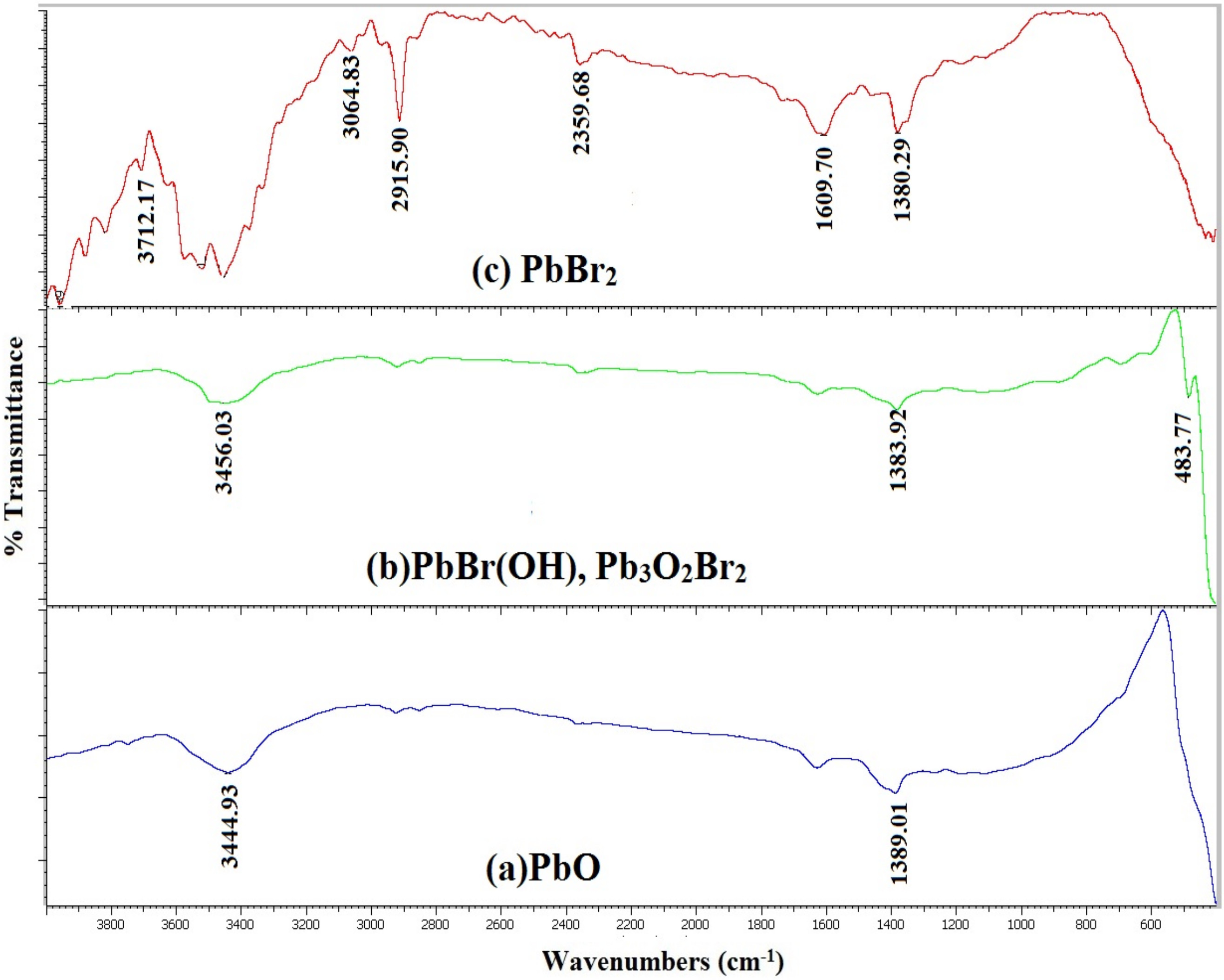

Fig. S9 IR data for (a) PbO, (b) ($PbBr(OH)$, $Pb_3O_2Br_2$) and (c) $PbBr_2$ nanoparticles.

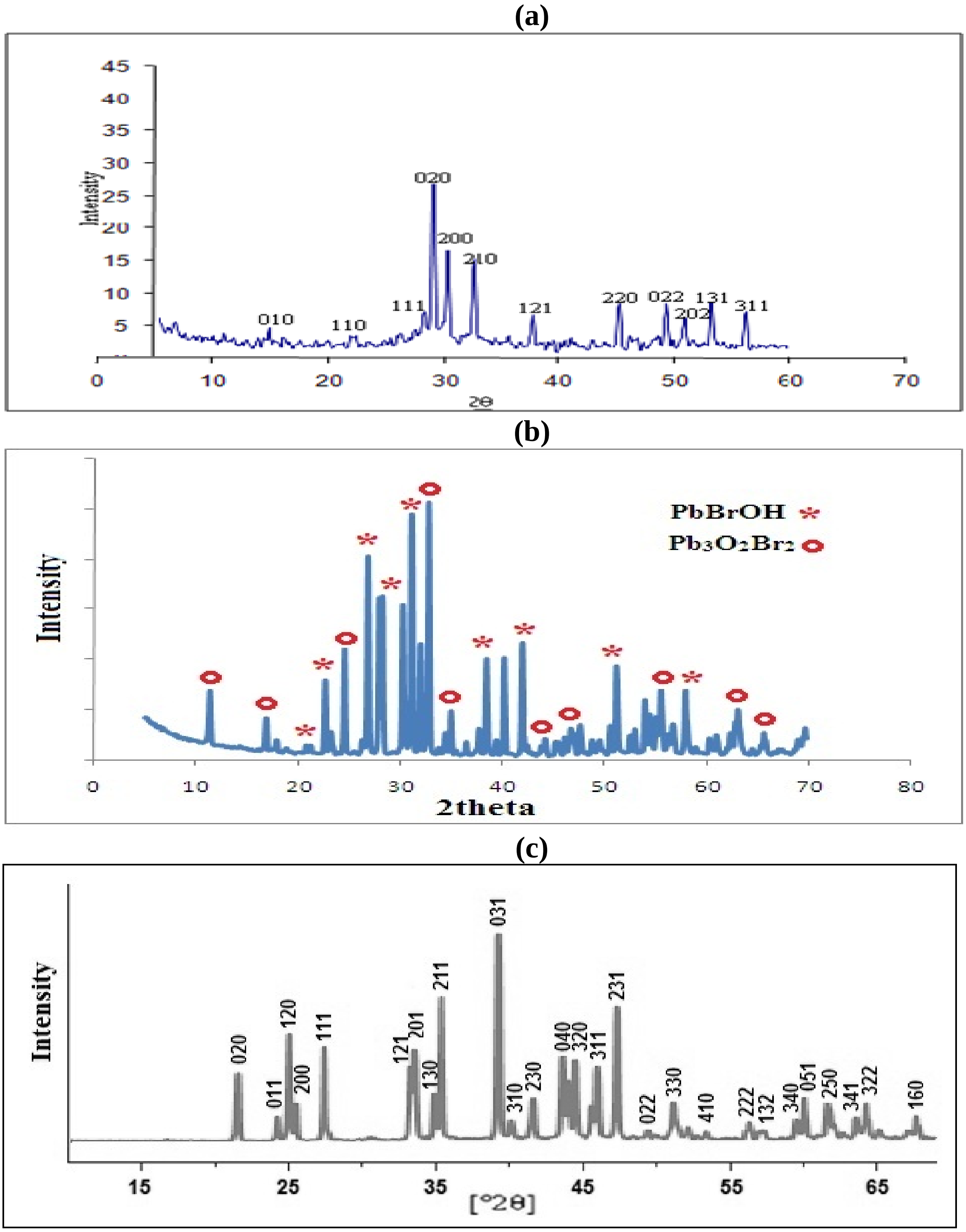

Fig. S10 XRD patterns of (a) PbO, (b) (PbBr(OH), $Pb_3O_2Br_2$) and (c) $PbBr_2$ nanoparticles prepared by thermolysis of compounds **1**, **2** and **3** in oleic acid at 180 °C under air atmosphere for 2 h, respectively.