Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information for MS:

Solid State Structural Transformation of Bromide Coordination Polymer to Chloride by Anion Replacement; New Precursors for Preparation of $PbBr_2$ and $PbCl_2$ Nanoparticles

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‡ Experimental section:

Synthesis of coordination polymers 1, 2 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-bpdb (1 mmol, 0.210g), 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 3-4 days, crystals deposited in the cooler arm that were isolated, filtered off and dried. M.P.=228°C. Found; C, 24.89; H, 1.78; N, 9.72%, calculated for $C_{12}H_{10}Br_2N_4Pb$; C, 24.94; H, 1.73; N, 9.70%. IR (cm^{-1}) selected bonds: ν = 530(w), 815(m), 1055(m), 1205(m), 1315(m), 1410(s), 1543(s) and 1595(m) .

Single crystals of compound **2** suitable for X-ray diffraction were prepared by a thermal gradient method in branched tube. The ligand 4-bpdb (1 mmol, 0.210g), lead(II) nitrate (0.331g, 1mmol) and KCl (2 mmol 0.150g) 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.>300°C. Found; C, 29.51; H, 2.02; N, 11.46%, calculated for $C_{12}H_{10}Cl_2N_4Pb$; C, 29.49; H, 2.05; N, 11.47%. IR (cm^{-1}) selected bonds: ν = 513(w), 819(m), 1000(m), 1203(m), 1304(m), 1379(s), 1548(s) and 1601(m) .

Synthesis of coordination polymers 1, 2 with mechanochemical maner:

In mechanochemical manner compound **1** could be synthesized from grinding of row materials for 20 minutes in an agate mortar. Compound **2** could be synthesized from grinding of 1mmol of compound **1** with 2 mmol of KCl and these processes could be reversible by using of 2 mmol KBr for converting compound **2** to **1**. Compound **2** could be synthesized from grinding of row materials for 20 minutes in an agate mortar too. For purification of coordination polymers with mechanochemical maner after each stage washing with water, thrice time, has been done until extra KBr, KCl or KNO_3 removed.

Elemental analysis data for compounds **1** and **2** prepared with mechanochemical method:

Compound 1: C, 24.91; H, 1.75; N, 9.73 **Compound 2:** C, 29.50; H, 2.04; N, 11.48%

Synthesis of $PbBr_2$ and $PbCl_2$ nanoparticles by thermal decomposition of coordination polymers 1 and 2, respectively, at oleic acid as a surfactant:

Precursors **1** and **2** (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 180 °C for 2 h. At the end of the reaction, black precipitates for precursor **1** and **2** were formed. A small amount of toluene and a large excess of EtOH were added to the all of three reaction solutions and $PbBr_2$ and $PbCl_2$ nanoparticles were separated by centrifugation for the precursors **1** and **2**, respectively. The solids were washed with EtOH and dried under air atmosphere (yield: 63 and 64% for $PbBr_2$ and $PbCl_2$ respectively).

$PbBr_2$ 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.

$PbCl_2$ with the lattice parameters (a = 7.6222(5) Å, b = 9.0448(7) Å, c = 4.5348(4) Å, S.G. = Pnam (62) and z = 4) which are in JCPDS card file No. 26-1150.

Table S1 Crystal data and structure refinements for compound **1** and **2**.

Identification code	**$[Pb(4\text{-}bpdb)Br_2]_n$ (1)**	**$[Pb(4\text{-}bpdb)Cl_2]_n$ (2)**
Empirical formula	$C_{12}H_{10}Br_2N_4Pb$	$C_{12}H_{10}Cl_2N_4Pb$
Formula weight	577.25	488.33
Temperature(K)	100(2)	100(2)
Wavelength	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
Unit cell dimensions	a = 4.1774(5) Å	a = 4.0721(11) Å
	b = 9.2283(12) Å	b = 8.784(2) Å
	c = 10.8275(14) Å	c = 10.982(3)Å
	α = 108.661(2)°	α = 110.278(5)°
	β =95.978(2)°	β =95.380(9)°
	γ = 91.459(2)°	γ = 90.369(10)°
Volume	392.54(9) $Å^3$	366.53(17) $Å^3$
Z	1	1
Density (calculated)	2.442 Mg/m3	2.212 Mg/m3
F(000)	262	226
Theta range for data collection	2.33 to 30.00°	1.99 to 30.00°
Index ranges	$-5 \le h \le 5$	$-5 \le h \le 4$
	$-12 \le k \le 12$	$-12 \le k \le 12$
	$-15 \le l \le 15$	$-15 \le l \le 15$
Reflections collected	6789	4551
Independent reflections	2255 [R(int) = 0.0244]	2110 [R(int) = 0.0327]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2255 / 0 / 88	2110 / 0 / 88
Goodness-of-fit on F^2	1.004	1.014
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0139$, $wR_2 = 0.0327$	$R_1 = 0.0254$, $wR_2 = 0.0539$
R Indices (all data)	$R_1 = 0.0139$, $wR_2 = 0.0327$	$R_1 = 0.0254$, $wR_2 = 0.0539$

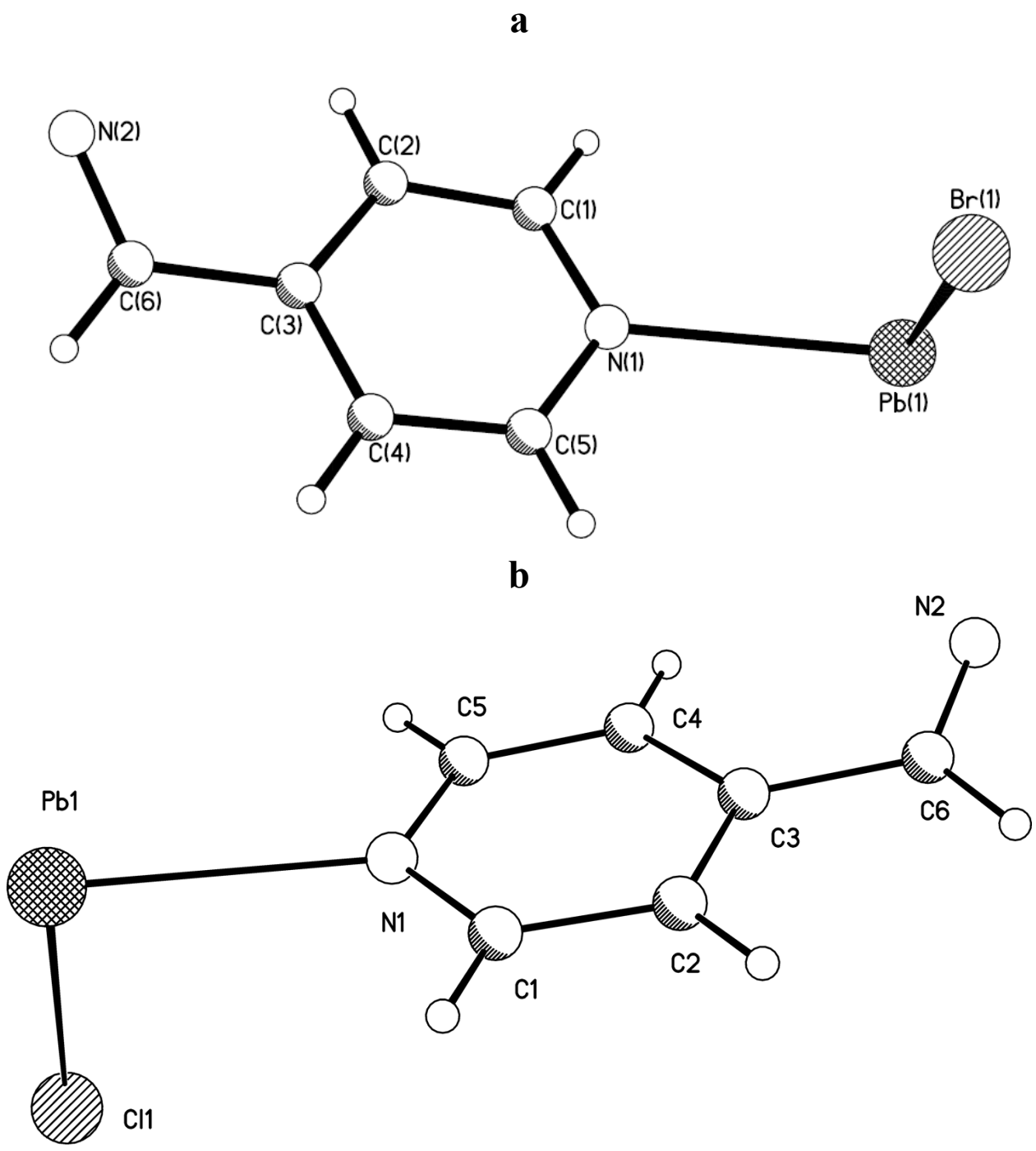

Fig. S1 Molecular view of independent part of unit cell (a) compound $[Pb(4\text{-bpdh})(Br)_2]_n$ (**1**) (b) compound $[Pb(4\text{-bpdh})(Cl)_2]_n$ (**2**).

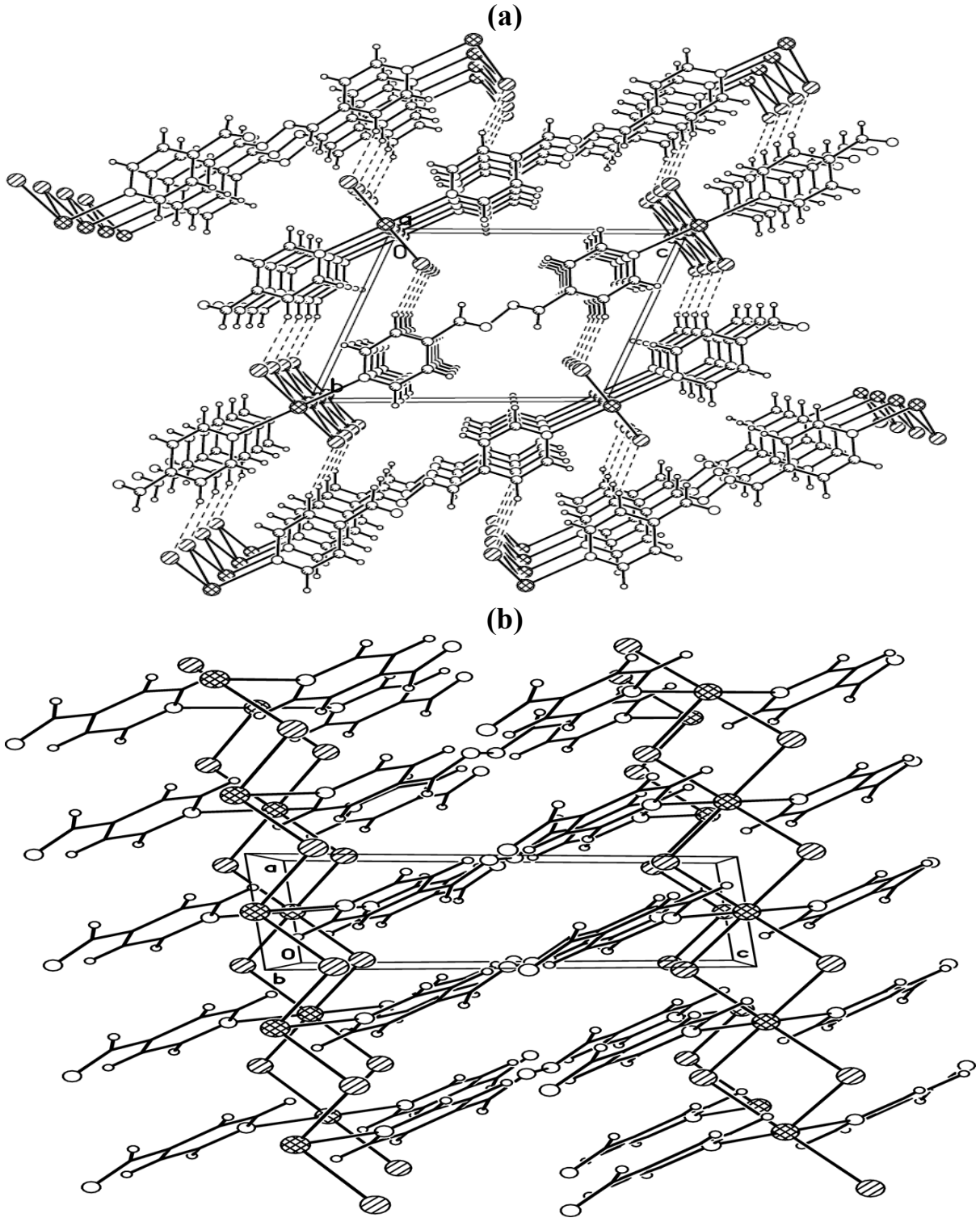

Fig. S2 Fragment of crystal packing (a) compound $[Pb(4\text{-bpdh})(Br)_2]_n$ (**1**) (b) compound $[Pb(4\text{-bpdh})(Cl)_2]_n$ (**2**).

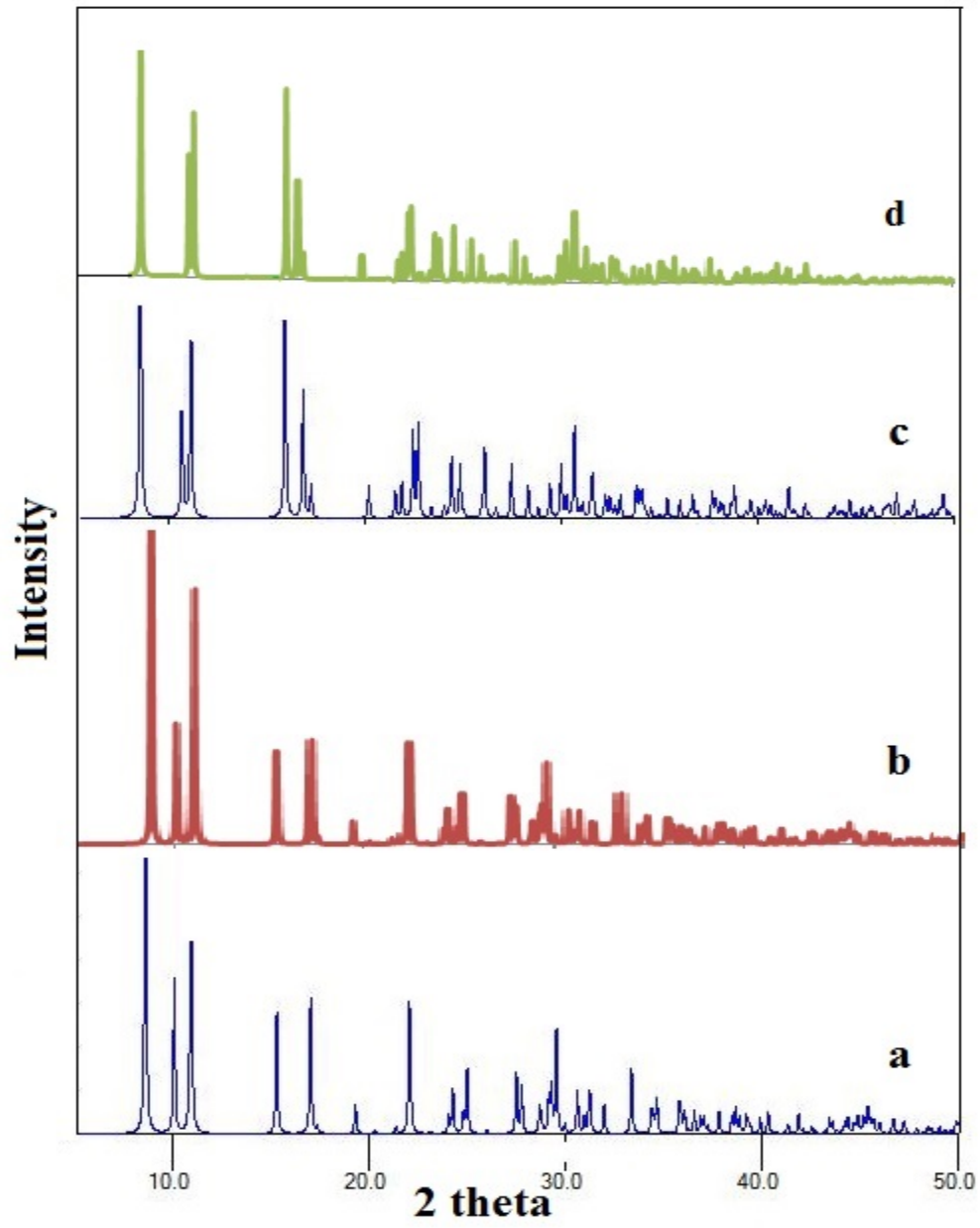

Fig. S3 The XRD patterns of (a) simulated from single crystal X-ray data of compound **1**, (b) bulk materials obtained by solid state anion-replacement of compound **2** with 2 mmol KBr**,** (c) simulated from single crystal X-ray data of compound **2**, (d) bulk materials obtained by solid state anion-replacement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

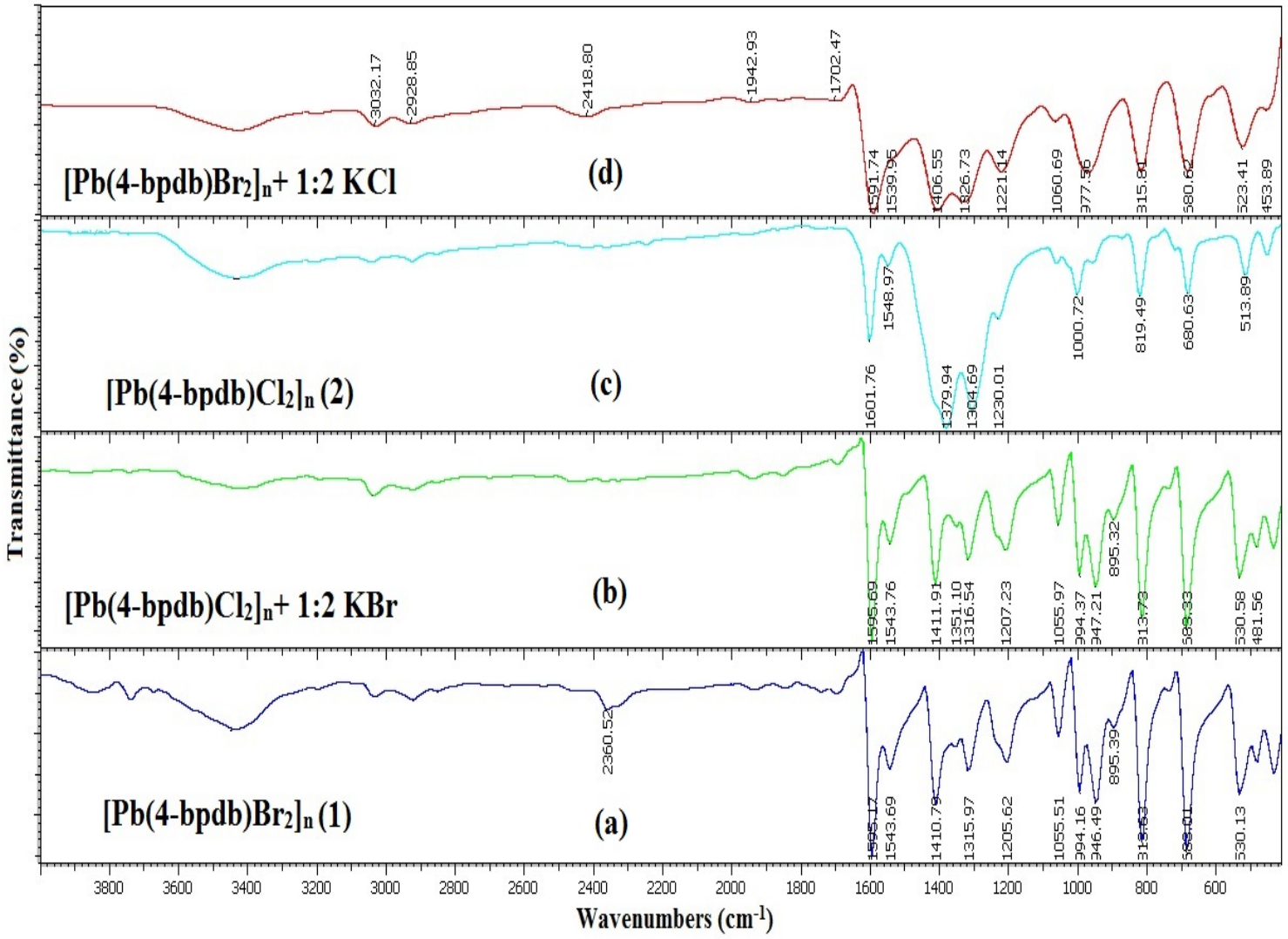

Fig. S4 IR spectra of (a) compound **1**, (b) bulk materials obtained by solid state anion-replacement of compound **2** by grinding with 2 mmol KBr**,** (c) compound **2** and (d) bulk materials obtained by solid state anion-replacement of compound **1** by grinding with 2 mmol KCl.

Fig. S5 schematic diagram for these Solid State structural transformation.

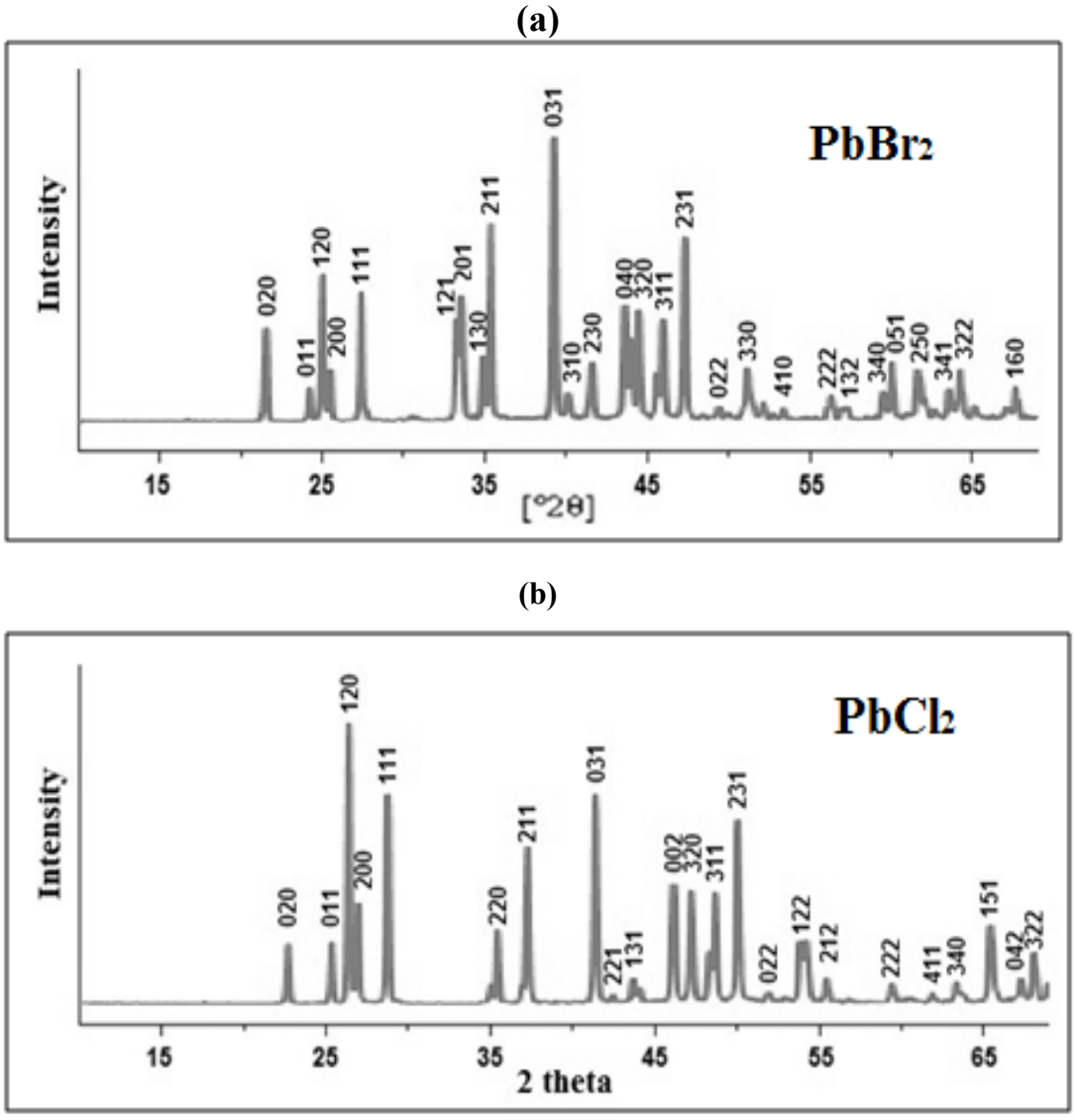

Fig. S6 XRD patterns of (a) $PbBr_2$ and (b) $PbCl_2$ nanoparticles prepared by thermolysis of compounds **1** and **2** in oleic acid at 180 °C under air atmosphere for 2 h, respectively.