Electronic Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information for MS:

Solid State Structural Transformation of 1D to Intermediate 2D and then to 3D Porous Coordination Polymer by Anion Replacement; New Precursors for Preparation of $PbCl_2$, $Pb_3O_2Cl_2$ and PbO Nanoparticles

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‡ 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 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 one week, crystals deposited in the cooler arm that were isolated, filtered off and dried. M.p =250 °C. Found; C, 32.51; H, 2.70; N, 10.86%, calculated for $C_{14}H_{14}Cl_2N_4Pb$; C, 32.53; H, 2.71; N, 10.84%. 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 KCl (1 mmol 0.075g) 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 four days, crystals deposited in the cooler arm that were isolated, filtered off and dried. M.p =270 °C. Found; C, 30.74; H, 2.40; N, 12.85%, calculated for $C_{14}H_{14}ClN_5O_3Pb$; C, 30.94; H, 2.58; N, 12.89%. 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 $C_{14}H_{14}C_{l0}N_6O_7Pb$; 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:

In mechanochemical manner compound **1** could be synthesized from grinding of row materials for 20 minutes in an agate mortar. Compound **2** and **3** could be synthesized from grinding of 1mmol of compound **1** with 1 and 2 mmol of $NaNO_3$ respectively and these processes could be reversible by using of 1 and 2 mmol KCl for converting compound **3** to **2** and **1** respectively. For purification of coordination polymers with mechanochemical maner after each stage washing with water, thrice time, has been done until extra $NaNO_3$ or KCl removed.

Synthesis of $PbCl_2$, $Pb_3O_2Cl_2$ and PbO 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 $PbCl_2$, $Pb_3O_2Cl_2$ and PbO nanoparticles were separated by centrifugation for the precursors **3**, **2** and **1**, respectively. The solids were washed with EtOH and dried under air atmosphere (yield: 63, 60 and 64% for $PbCl_2$, $Pb_3O_2Cl_2$ and PbO respectively).

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; Orthorhombic $Pb_3O_2Cl_2$ with a = 9.52Å, z = 4 and S.G = $P2_12_12_1$ which are in JCPDS card file No. 23-0332; $PbCl_2$ 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	**1**	**2**
Empirical formula	$C_{14}H_{14}Cl_2N_4Pb$	$C_{14}H_{14}ClN_5O_3Pb$
Formula weight	516.39	542.94
Temperature(K)	293(2)	291(2)
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 12.805(1) Å	a = 14.0972(11)Å
	b = 4.0989(3) Å	b = 8.2977(8)Å
	c = 16.246(1) Å	c = 15.9525(14)Å
	β = 96.729(1)°	β =104.203(7)^o
Volume	846.8(1) Å3	1809.0(3)Å^3
Z	2	4
Density (calculated)	2.025 Mg/m3	1.994 g/m^3
F(000)	484	1024
Theta range for data collection	1.60 to 26.00°	2.45 to 27.48 ^{o}
Index ranges	$-15 \le h \le 15$	$-17 \le h \le 17$
	$-5 \le k \le 4$	$-10 \le k \le 10$
	$-20 \le l \le 20$	$-16 \le l \le 20$
Reflections collected	6148	3532
Independent reflections	1654	2575
Absorption correction	multi-scan	multi-scan
Refinement method	Full-matrix least-squares on F^2	$F^2 > 2\text{sigma}(F^2)$
Data / restraints / parameters	1654 / 0 / 96	3532 / 0 / 219
Goodness-of-fit on F^2	1.060	1.111
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0155$ and $wR_2 = 0.0388$	R_1= 0.0777 and wR_2= 0.1703
R Indices (all data)	$R_1 = 0.0157$ and $wR_2 = 0.0389$	R_1= 0.1070 and wR_2= 0.1821

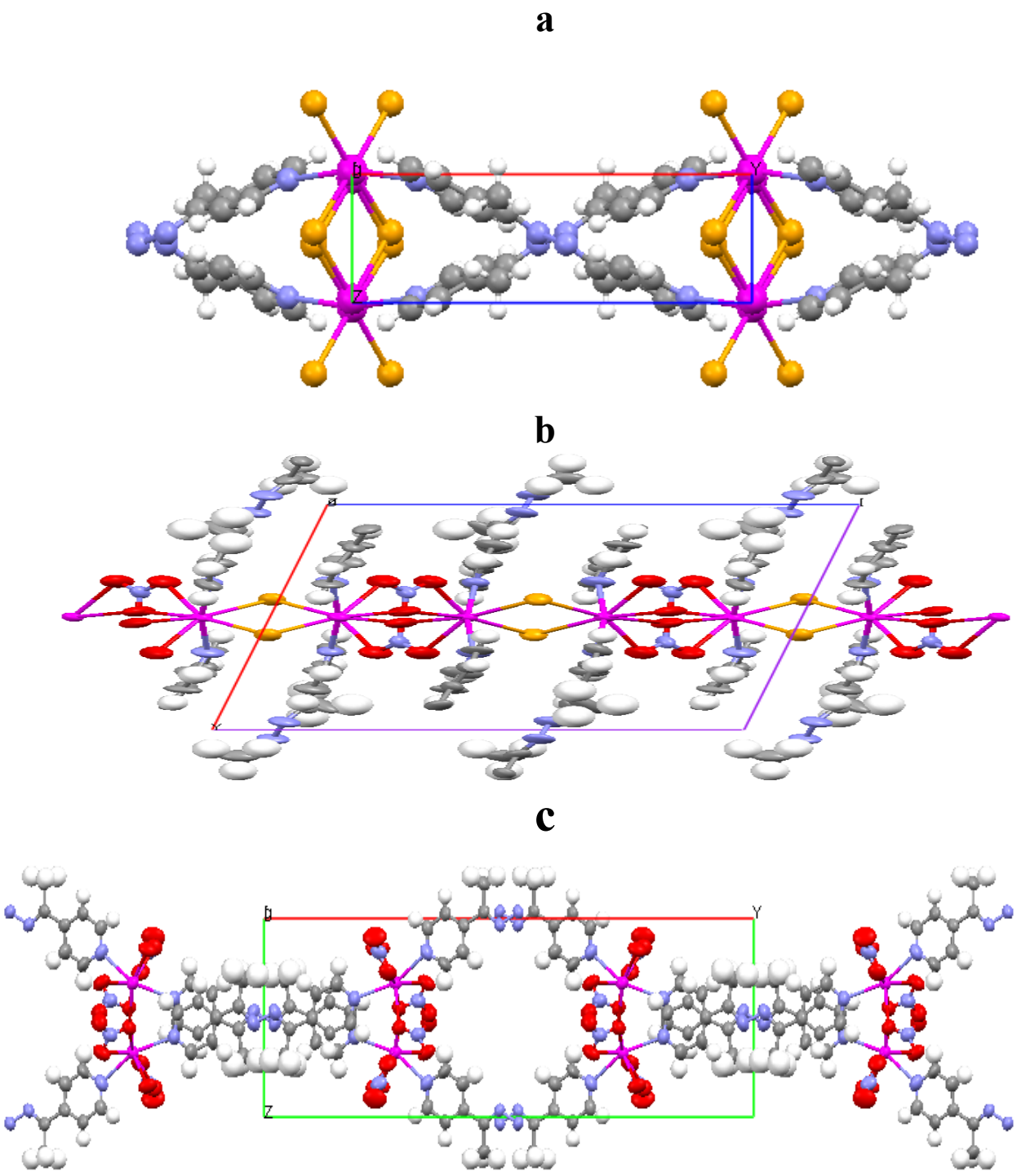

Fig. S1 The coordination environments and unit cell of (a) compound $[Pb(4\text{-bpdh})(Cl)_2]_n$ (**1**) (b) compound $[Pb(4\text{-bpdh})(Cl)(NO_3)]_n$ (**2**) and (c) compound $[Pb(4\text{-bpdh})(NO_3)_2(H_2O)]_n$ (**3**) (Pb= violet, O = red, C = gray and N= blue Cl= orange and H= white).

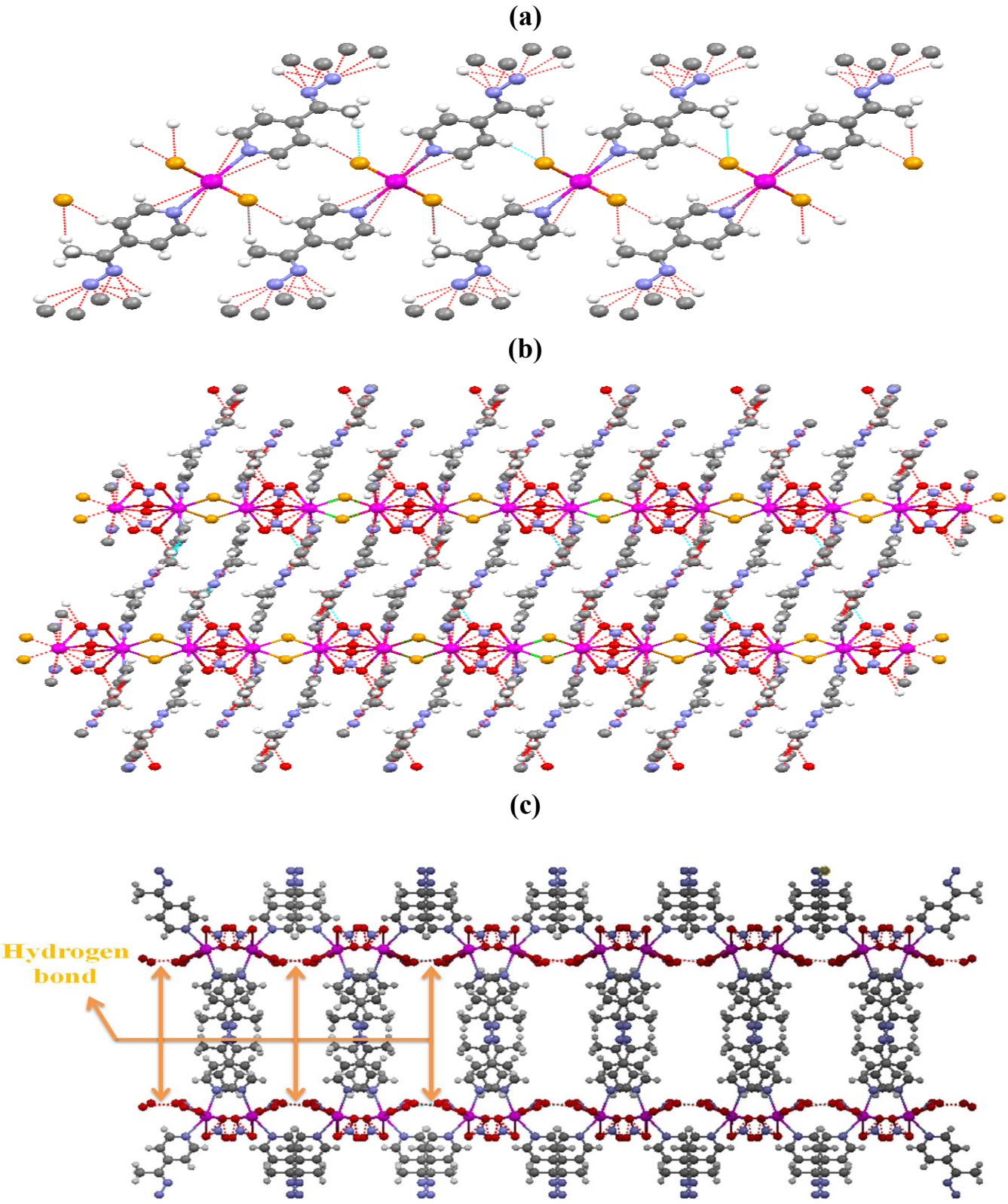

Fig. S2 A schematic diagram illustrating the interactions in polymeric chains of (a) compound **1** and (b) compound **2** and (c) compound **3**.

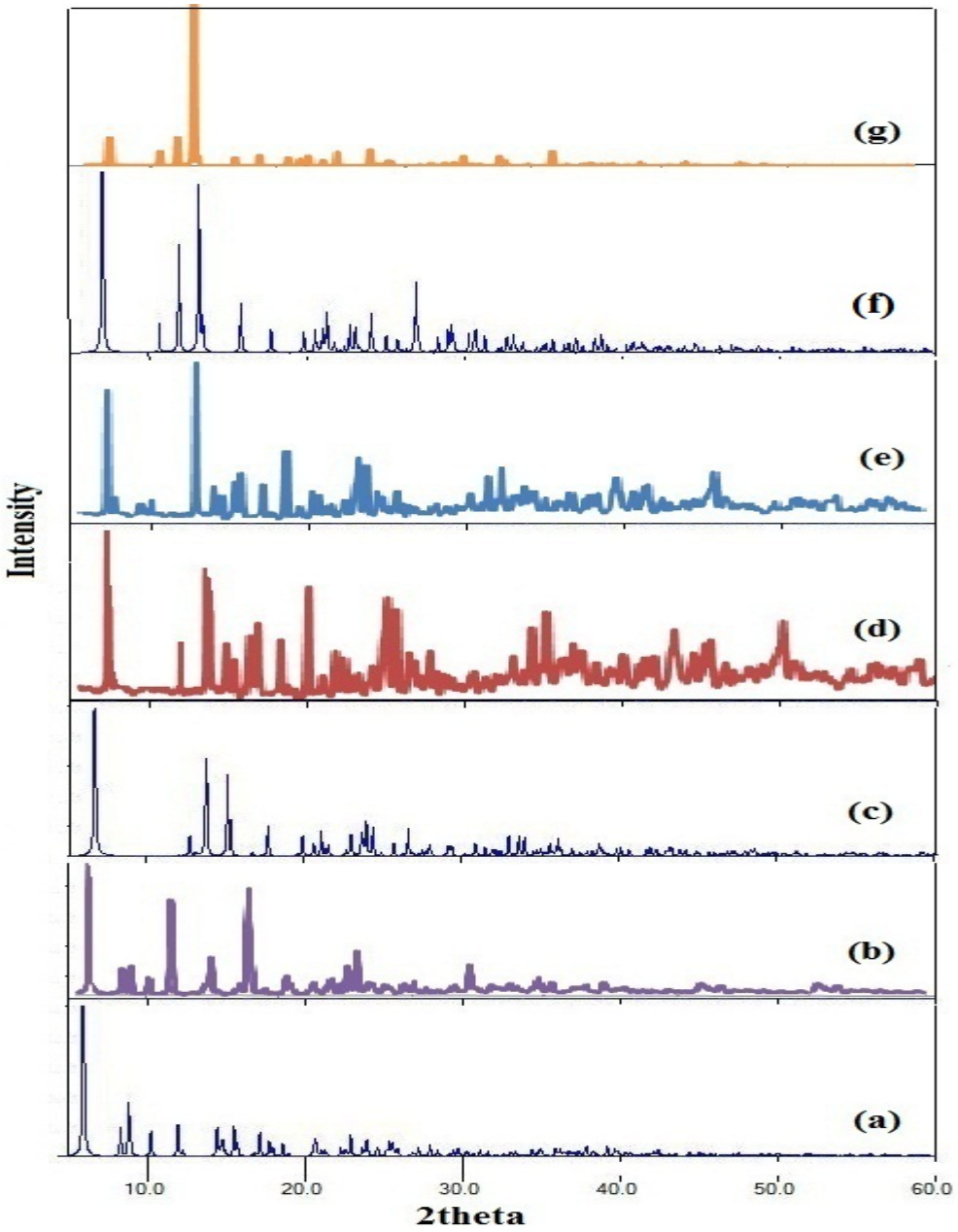

Fig. S3 The XRD patterns of (a) simulated from single crystal X-ray data of compound **3**, (b) bulk materials as synthesized of compound **3**, (c) simulated from single crystal X-ray data of compound **2**, (d) bulk materials obtained by solid state anion-replacement of compound **3** with 1 mmol KCl**,**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

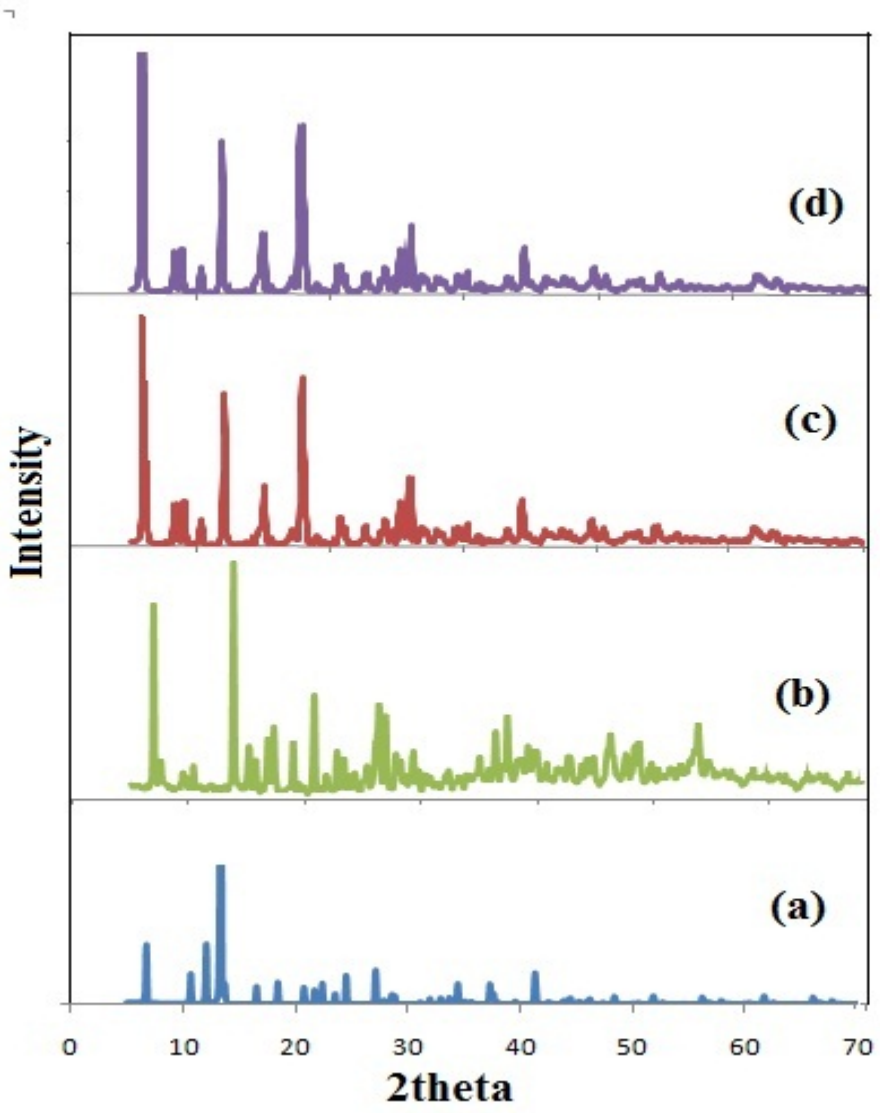

Fig. S4 The XRD patterns of (a) compound **1** that obtained by solid state anion-replacement of compound **3** with 2 mmol KCl (b) compound **2** obtained by solid state anion-replacement of compound **1** with 1 mmol $NaNO_3$, (c) compound **3** obtained by solid state anion-replacement of compound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

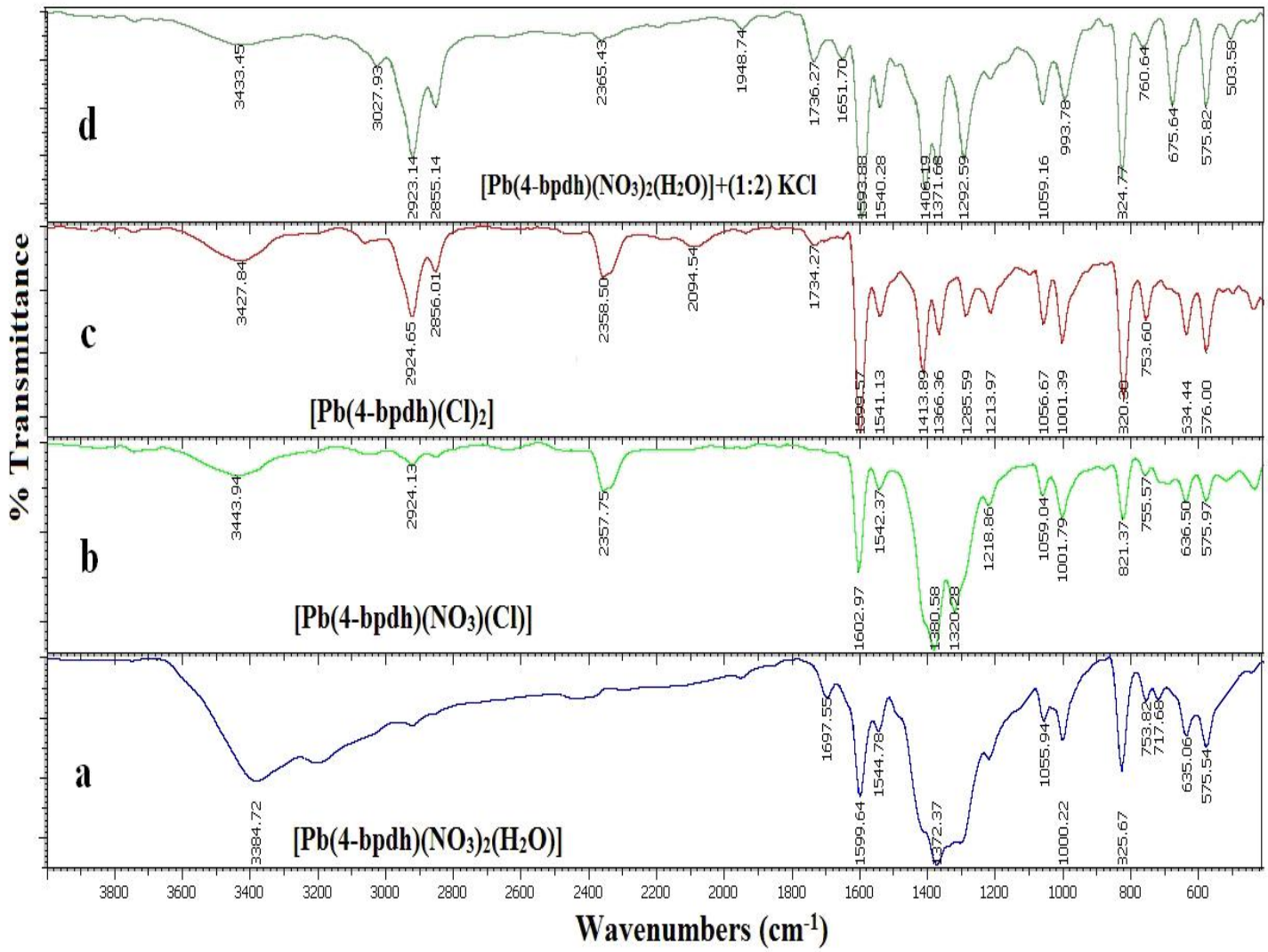

Fig. S5 IR spectra of (a) compound **3**, (b) bulk materials obtained by solid state anion-replacement of compound **3** by grinding with 1 mmol KCl**,** (c) bulk materials obtained by solid state anion-replacement of compound **2** by grinding with 1 mmol KCl and (d) bulk materials obtained by solid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

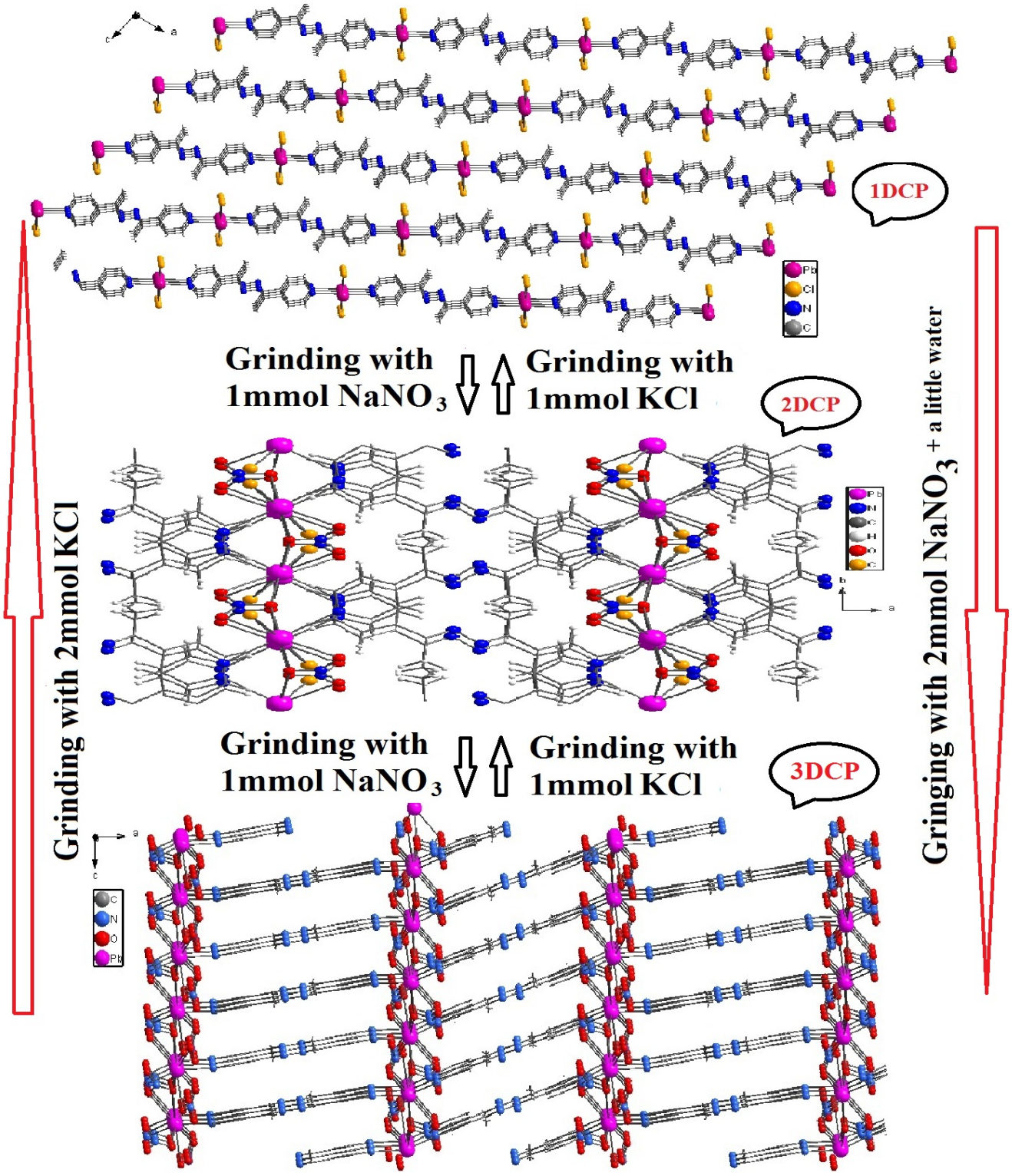

Fig. S6 A schematic diagram illustrating the structural conversions from 1D coordination polymer **1** (up) to 2D coordination polymers **2** (middle) and 3D coordination polymer **3** (bottom) by solid state reversible anion-replacement.

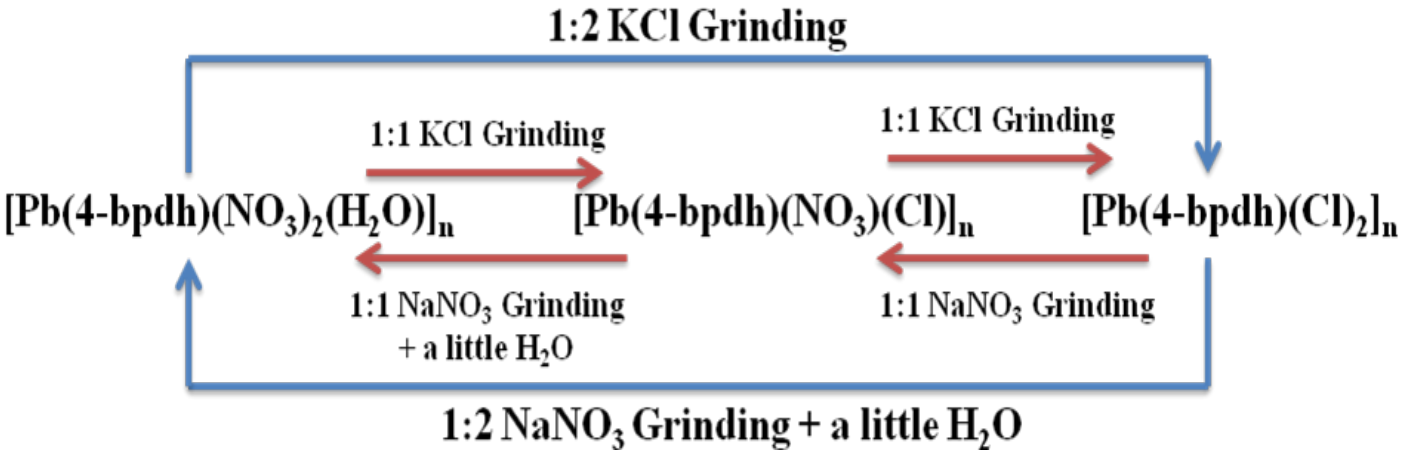

Fig. S7 schematic diagram for these Solid State Crystal to Crystal Conversions.

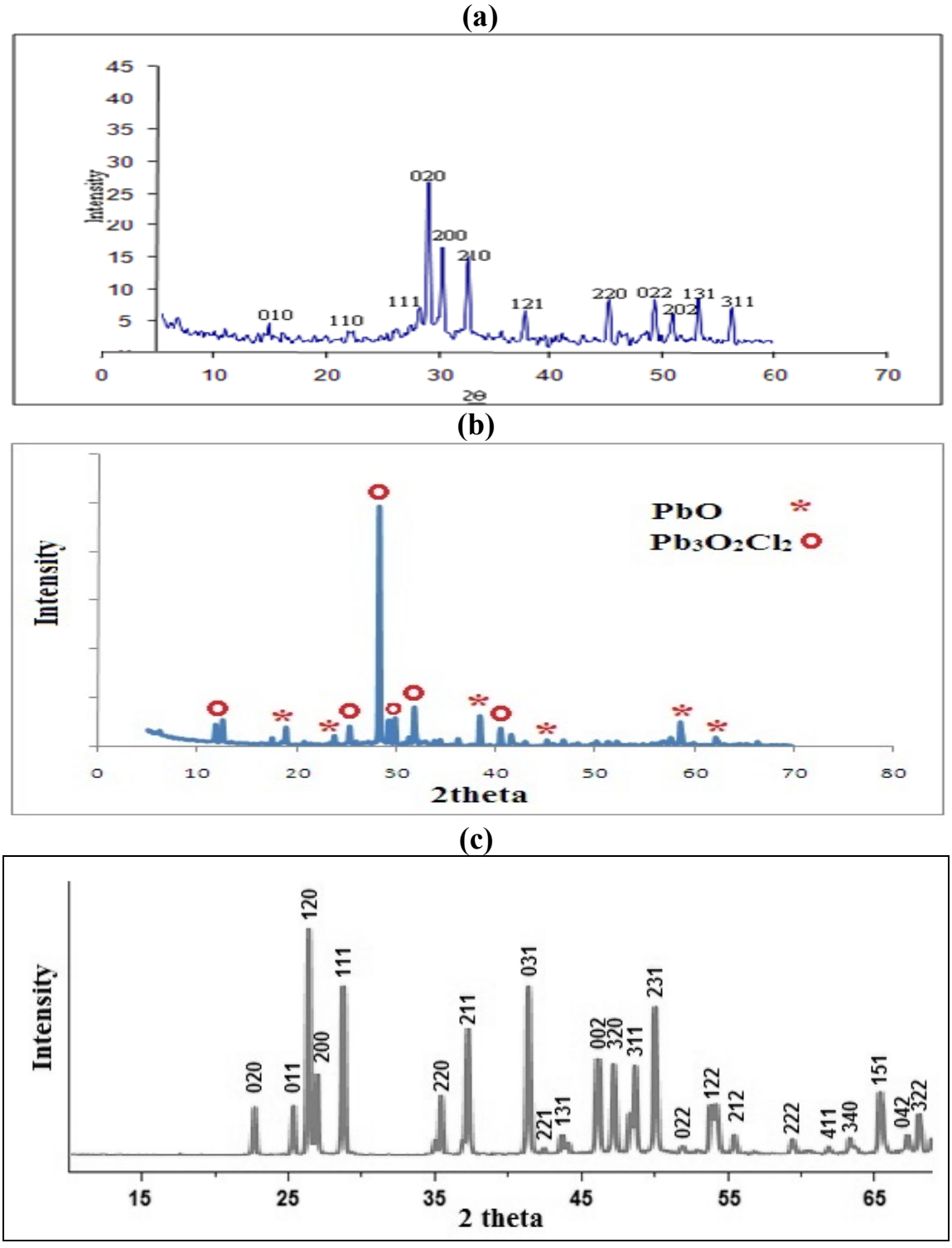

Fig. S8 XRD patterns of (a) PbO, (b) PbO/$Pb_3O_2Cl_2$ and (c) $PbCl_2$ nanoparticles prepared by thermolysis of compounds **3**, **2** and **1** in oleic acid at 180 °C under air atmosphere for 2 h, respectively.