Electronic Supplementary Information for MS:

Mechanochemical solid-state transformations from a 3D lead(II) chloride triazole carboxylate coordination polymer to its bromide/thiocyanate analogs via anion-replacements; precursors for the preparation of lead(II) chloride/bromide/sulfide nanoparticles

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‡ Experimental section:

Synthesis of coordination polymers 1, 2 and 3:

Crystals of **1** were prepared by a branched tube method,[20] 1H-1,2,4-triazole-3-carboxylic acid (0.117 g, 1 mmol), potassium chloride (0.074 g, 1 mmol) and lead(II) nitrate (0.331 g, 1 mmol) were placed in the arm to be heated. Water was carefully added to fill both arms, and then the arm to be heated was placed in a bath at 60 °C. After 3 days, colorless crystals were deposited in the cooler arm which were filtered off, washed with water and air dried. (0.21 g, yield 57%), m.p. >300 °C. (Found C, 9.88; H, 1.12; N, 11.47. calculated for $C_3H_4ClN_3O_3Pb$; C: 9.67, H: 1.08, N: 11.27%). IR (cm^{-1}) selected bands: 560(s), 663(s), 1094(s), 1302(m), 1468(m), 1595(vs), and 3407(br). The 3D $[Pb(L)(\mu_2\text{-}Cl)(H_2O)]_n$ (**1**) polymerizes on grinding the solid with KBr and KSCN for 20 min in an agate mortar and pestle to form 3D coordination polymers, $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (**2**)[19a] and $[Pb(L)(\mu_{1,1}\text{-}NCS)(H_2O)]_n$ (**3**),[21] respectively. These powder samples separated by washing. In the case of **2**, yield: 70% (m.p > 300 °C). Found C, 8.55; H, 0.99; N, 10.43. calculated for $C_3H_4BrN_3O_3Pb$; C: 8.63, H: 0.96, N: 10.07%. In **3**, yield: 64% (m.p > 300 °C). Found; (C, 12.22; H, 0.79; N, 14.25%. calcd. for $C_4H_4N_4O_3PbS$; C, 12.19; H, 0.77; N, 14.21%).

Synthesis of $PbCl_2$, $PbBr_2$ and PbS 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 (1.35 ml) to form homogenous emulsion solutions. These solutions were degassed for 20 min and then heated to 200 °C for 2 h. At the end of the reaction, white precipitates for precursor **1**-**2** and black precipitates for precursor **3** were formed. A small amount of toluene and a large excess of MeOH were added to the all of three reaction solutions and $PbCl_2$, $PbBr_2$ and PbS nanoparticles were separated by centrifugation for the precursors **1**, **2** and **3**, respectively. The solids were washed with EtOH and dried under air atmosphere.

$PbCl_2$ 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); $PbBr_2$ with the lattice parameters (a = 8.062 Å, b = 9.5393 Å, c = 4.7348 Å, S.G. = Pnam (62) and z = 4); PbS with the lattice parameters (a = 5.9362 Å, S.G. = Fm3m (225) and z = 4)

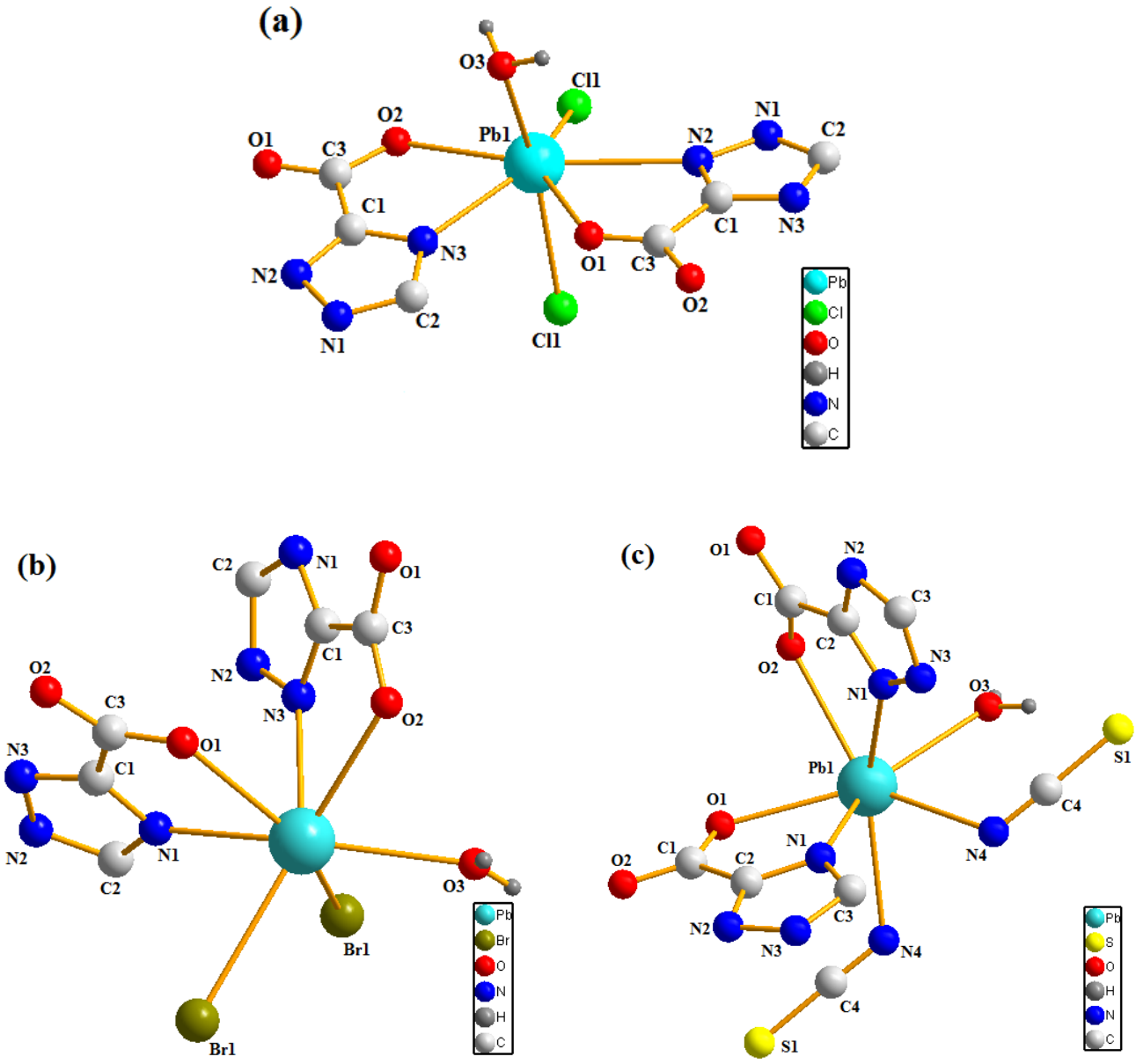

Fig. S1 The coordination environments of the (a) compound $[Pb(L)(\mu_2\text{-}Cl)(H_2O)]_n$ (**1**) (b) compound $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (**2**) and (c) compound $[Pb(L)(\mu_{1,1}\text{-}NCS)(H_2O)]_n$ (**3**).

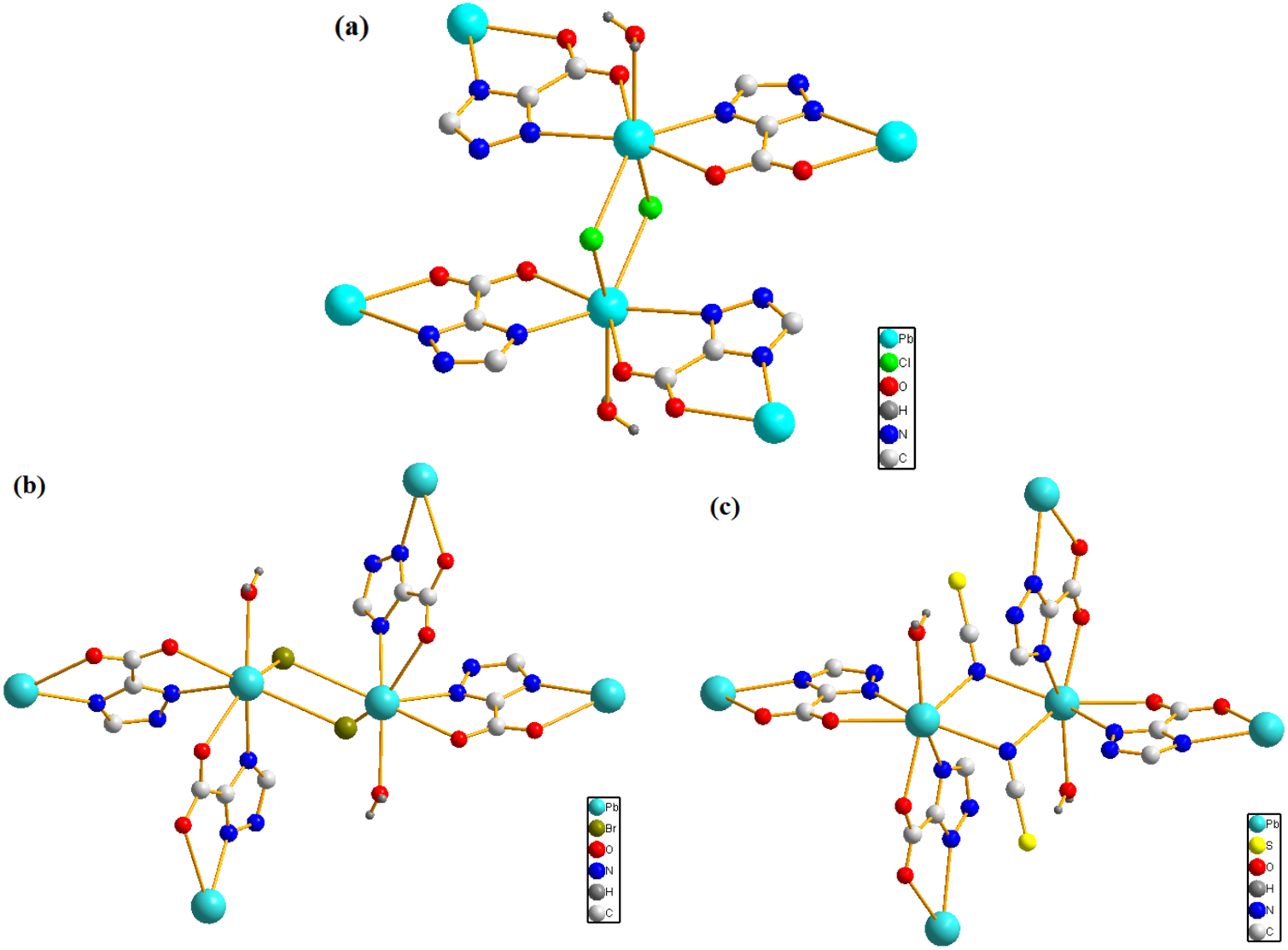

Fig. S2 (a) View of a section of the dimeric units by bridging of the Cl^- anions via one sides in **1** (b) View of a section of the dimeric units by bridging of the Br^- anions via one sides in **2** and (c) View of a section of the dimeric units by bridging of the NCS^- anions via one sides in **3**.

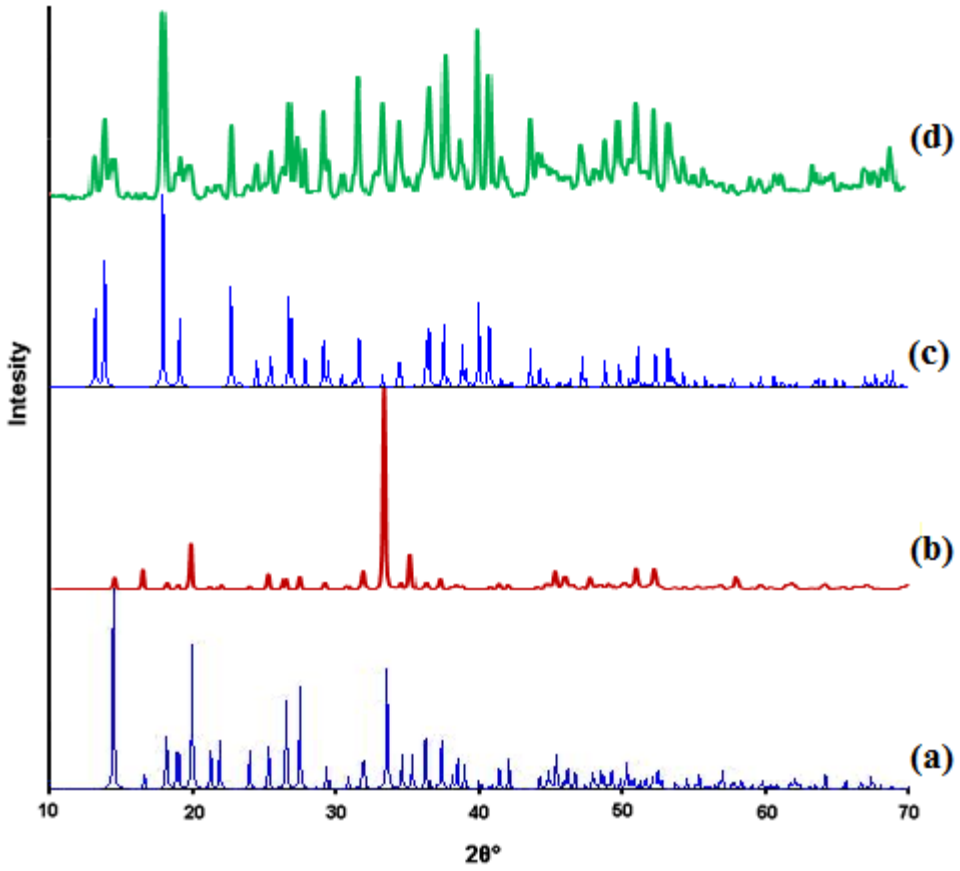

Fig. S3 The XRD patterns of (a) simulated from single crystal X-ray data of compound **1**, (b) bulk materials as synthesized of compound **1**, (c) simulated from single crystal X-ray data of compound **2** and (d) bulk materials obtained by solid state anion-replacement of compound **1**.

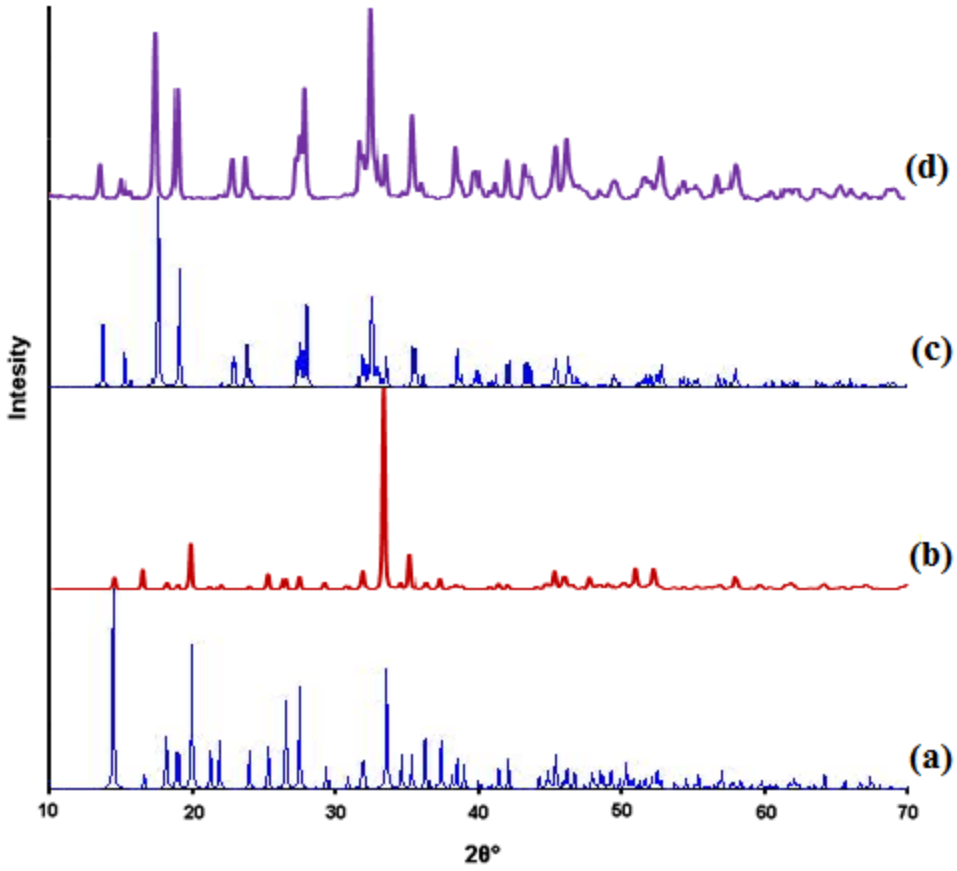

Fig. S4 The XRD patterns of (a) simulated from single crystal X-ray data of compound **1**, (b) bulk materials as synthesized of compound **1**, (c) simulated from single crystal X-ray data of compound **3** and (d) bulk materials obtained by solid state anion-replacement of compound **1**.

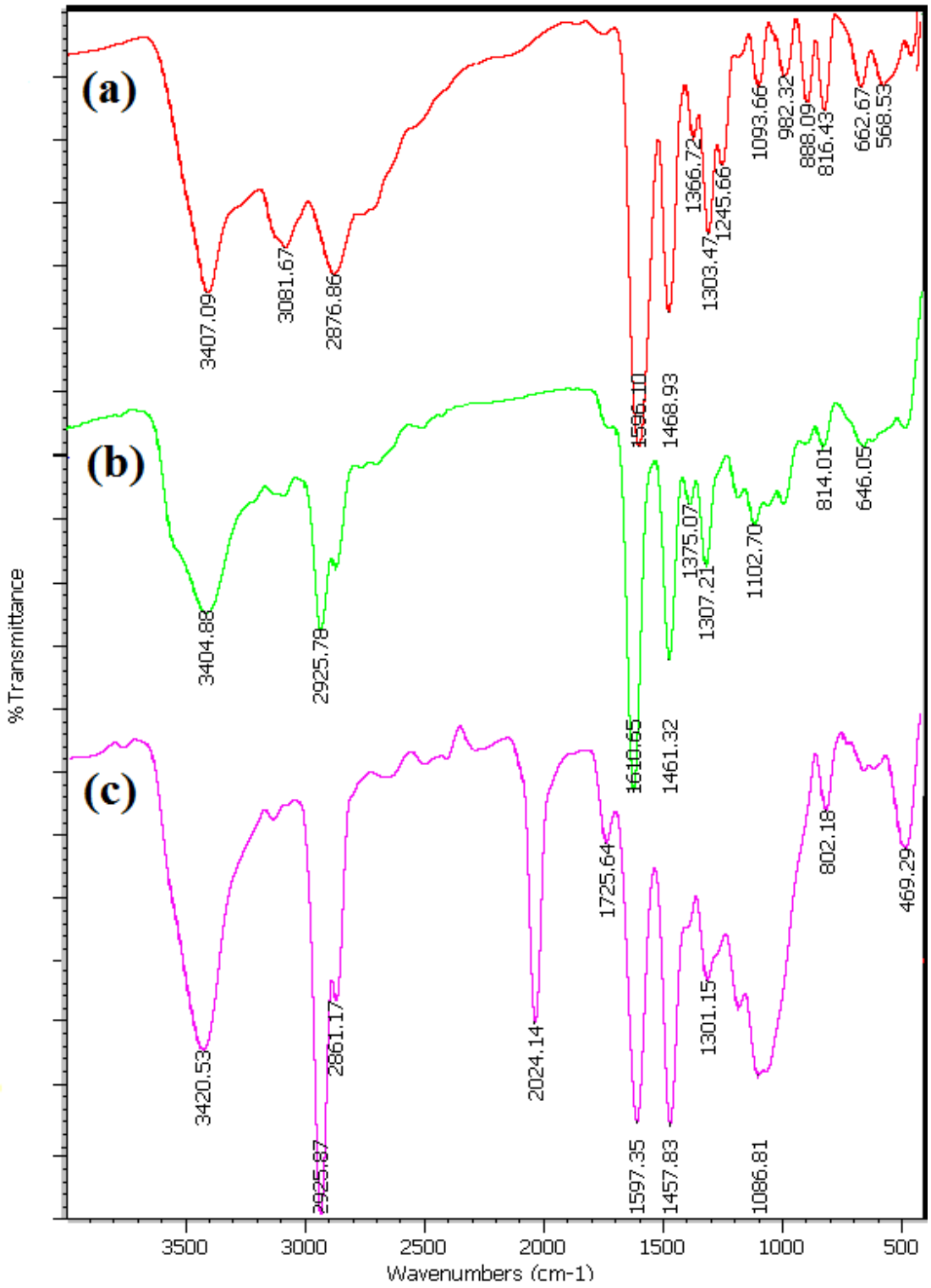

Fig. S5 IR spectra of (a) compound **1**, (b) bulk materials obtained by solid state anion-replacement of compound **1** by grinding with KBr and (c) bulk materials obtained by solid state anion-replacement of compound **1** by grinding with KSCN.

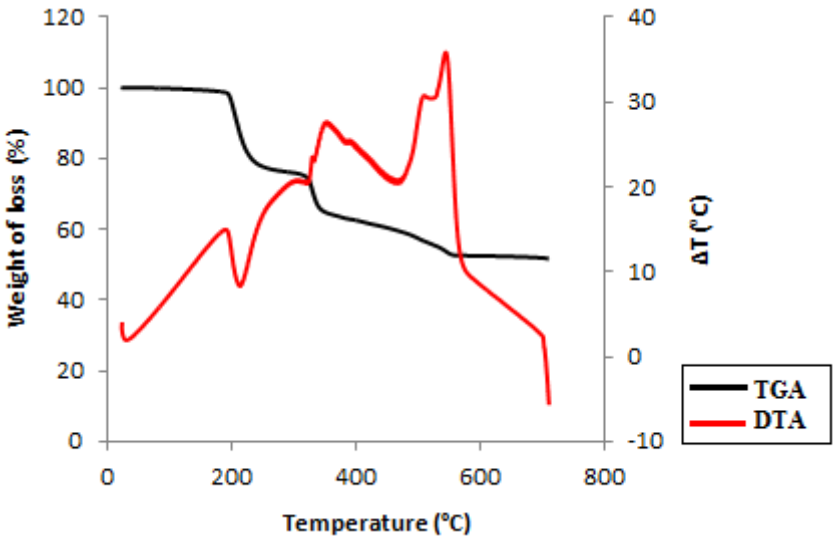

Fig. S6 Thermal behaviour of compound **1**.

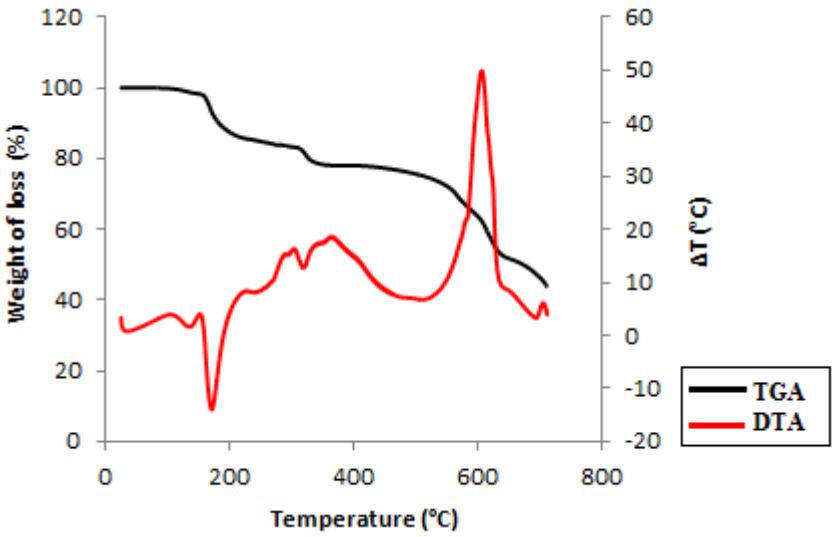

Fig. S7 Thermal behaviour of compound **2**.

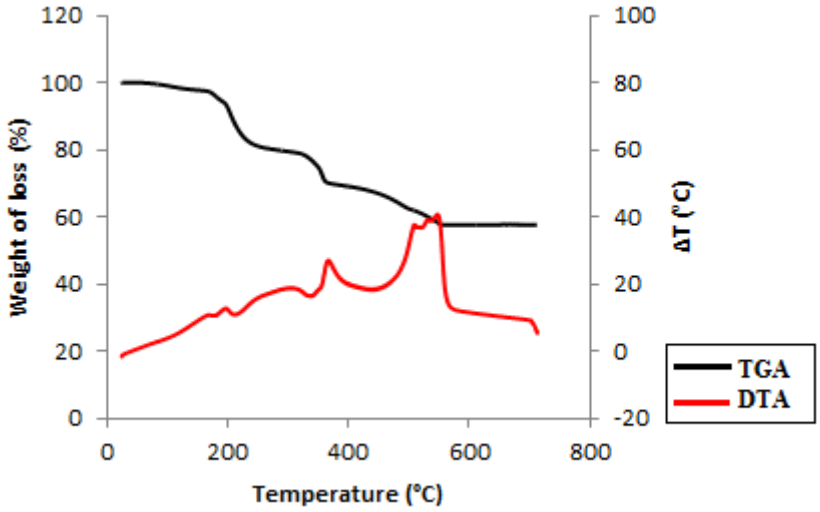

Fig. S8 Thermal behaviour of compound **3**.

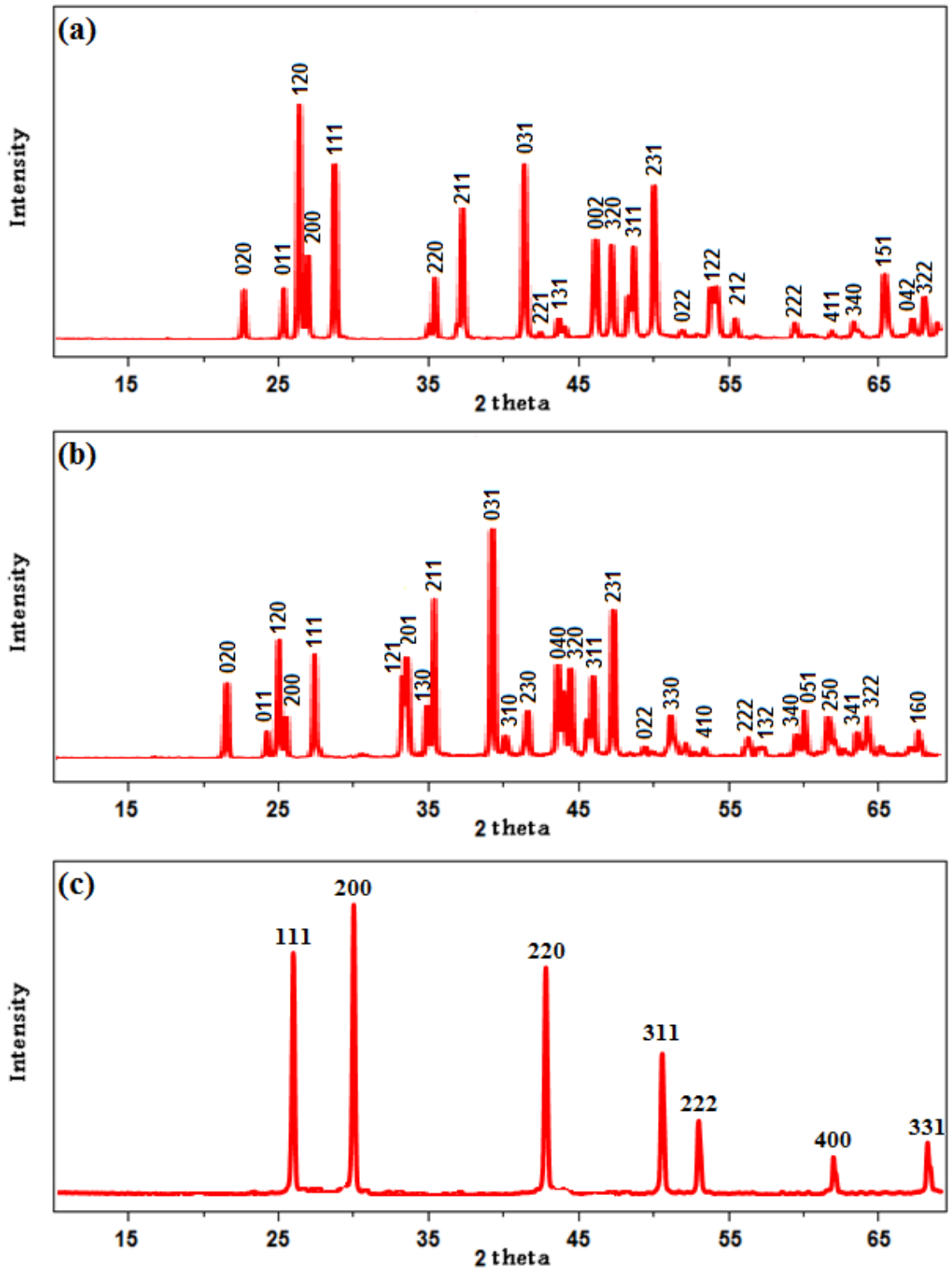

Fig. S9 XRD patterns of (a) $PbCl_2$, (b) $PbBr_2$ and (c) cubic-shaped PbS nanoparticles prepared by thermolysis of compounds **1**, **2** and **3** in oleic acid at 200 °C under air atmosphere for 2 h, respectively