Electronic Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information for MS:

Reversible Crystal-to-Crystal Transformation of a 3D-3D Coordination Polymer by Solid State Anion-replacement with No Change in Nano-particles Morphology

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Experimental Section:

Crystallographic measurements were made at 298K for compounds **1** using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromataed Mo–K_α radiation. The structures were solved by direct methods and refined by full–matrix least–squares techniques on F^2. Structure solution and refinement was accomplished using SIR97, SHELXL97 and WinGX. Crystal data for **1**: orthorhombic space group $Pna2_1$, a = 8.4799(14) Å, b = 15.706(3) Å, c = 5.7500(10) Å, α = 90, β = 90, γ = 90°, V = 765.8(2) $Å^3$, Z = 4, T = 298(2) K. The refinement of 106 parameters on the basis of 1439 independent reflections (of a total of 3929) converged at R1 = 0.0237, wR2 = 0.0528.

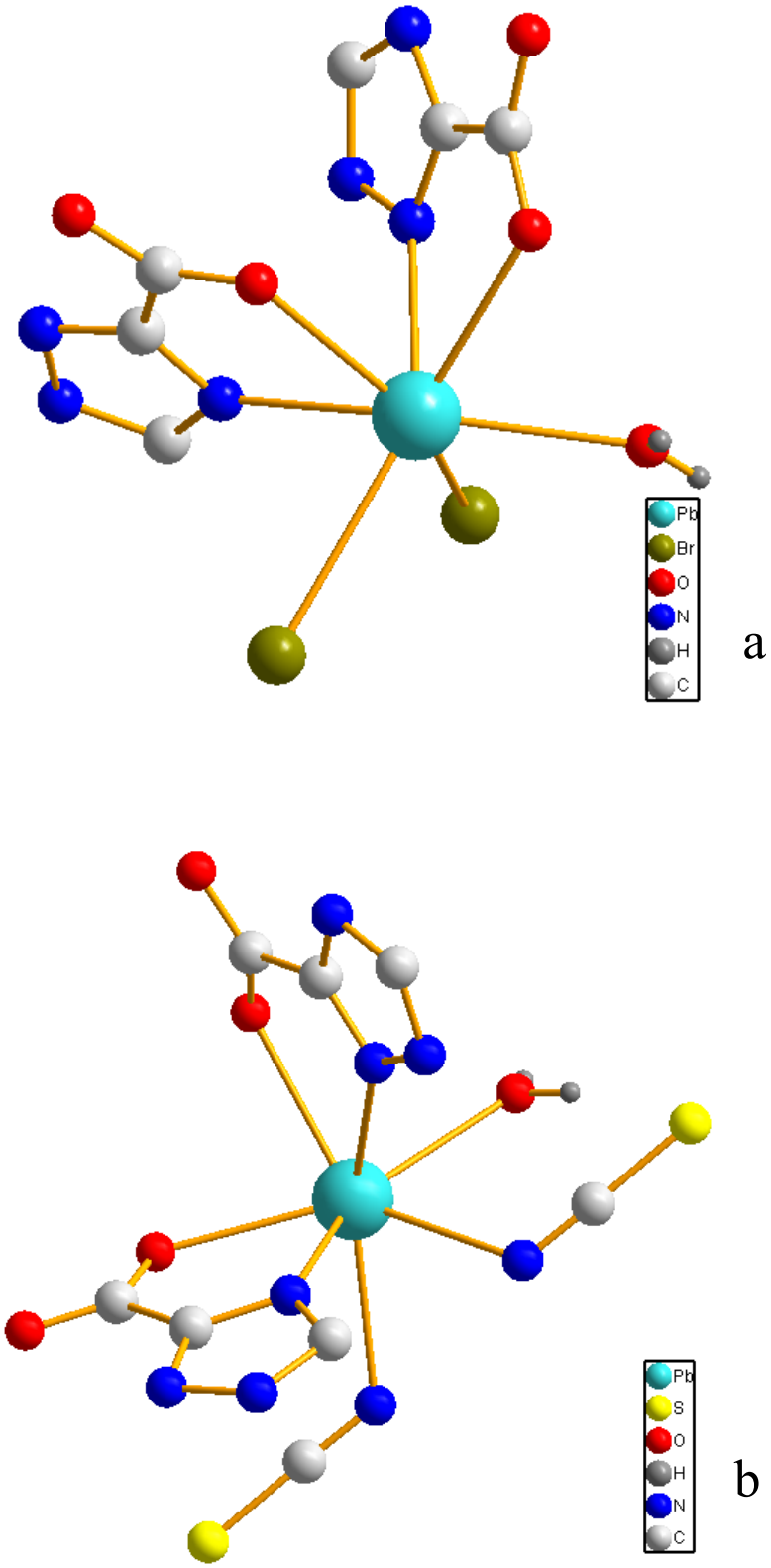

Fig. S1. The coordination environments of the (a) compound $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (**1**) and (b) compound $[Pb(L)(\mu_{1,1}\text{-}NCS)(H_2O)]_n$ (**2**).

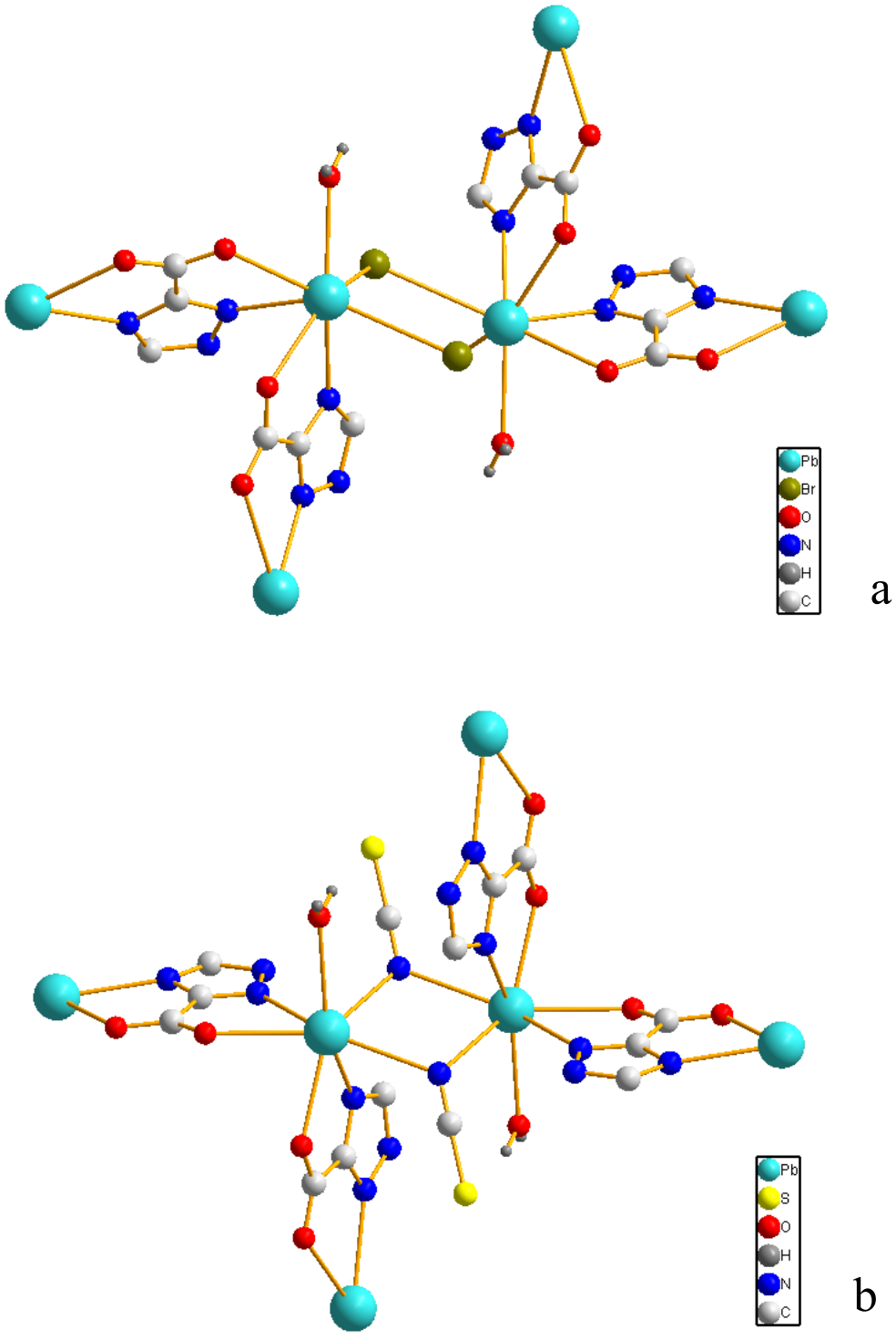

Fig. S2. (a) View of a section of the dimeric units by bridging of the Br^- anions via one sides in **1** and (b) View of a section of the dimeric units by bridging of the NCS^- anions via one sides in **2**.

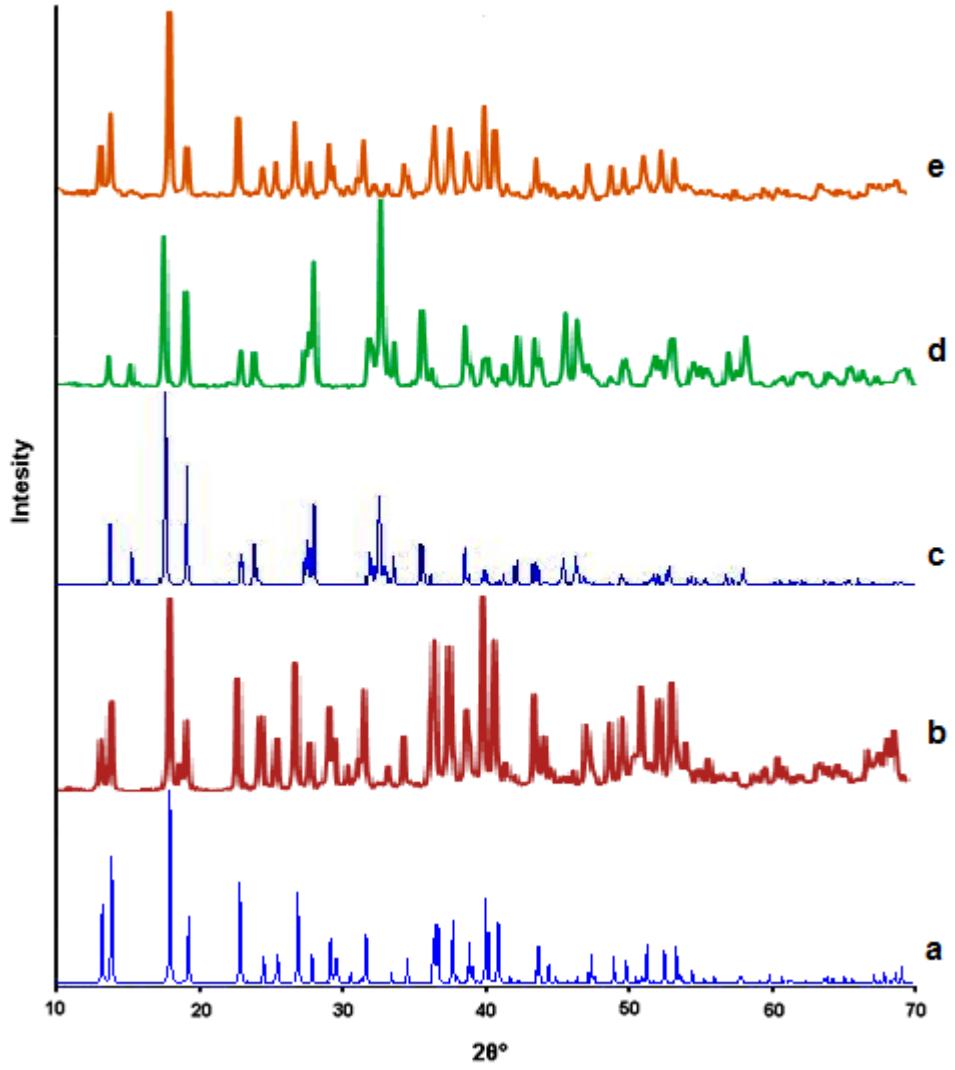

Fig. S3. The XRD patterns of (a) simulated from single crystal X-ray data of compound **1**, (b) bulk materials as synthesized of compound **1**, (c) simulated from single crystal X-ray data of compound **2**, (d) bulk materials obtained by solid state anion-replacement of compound **1**, (e) the reversed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

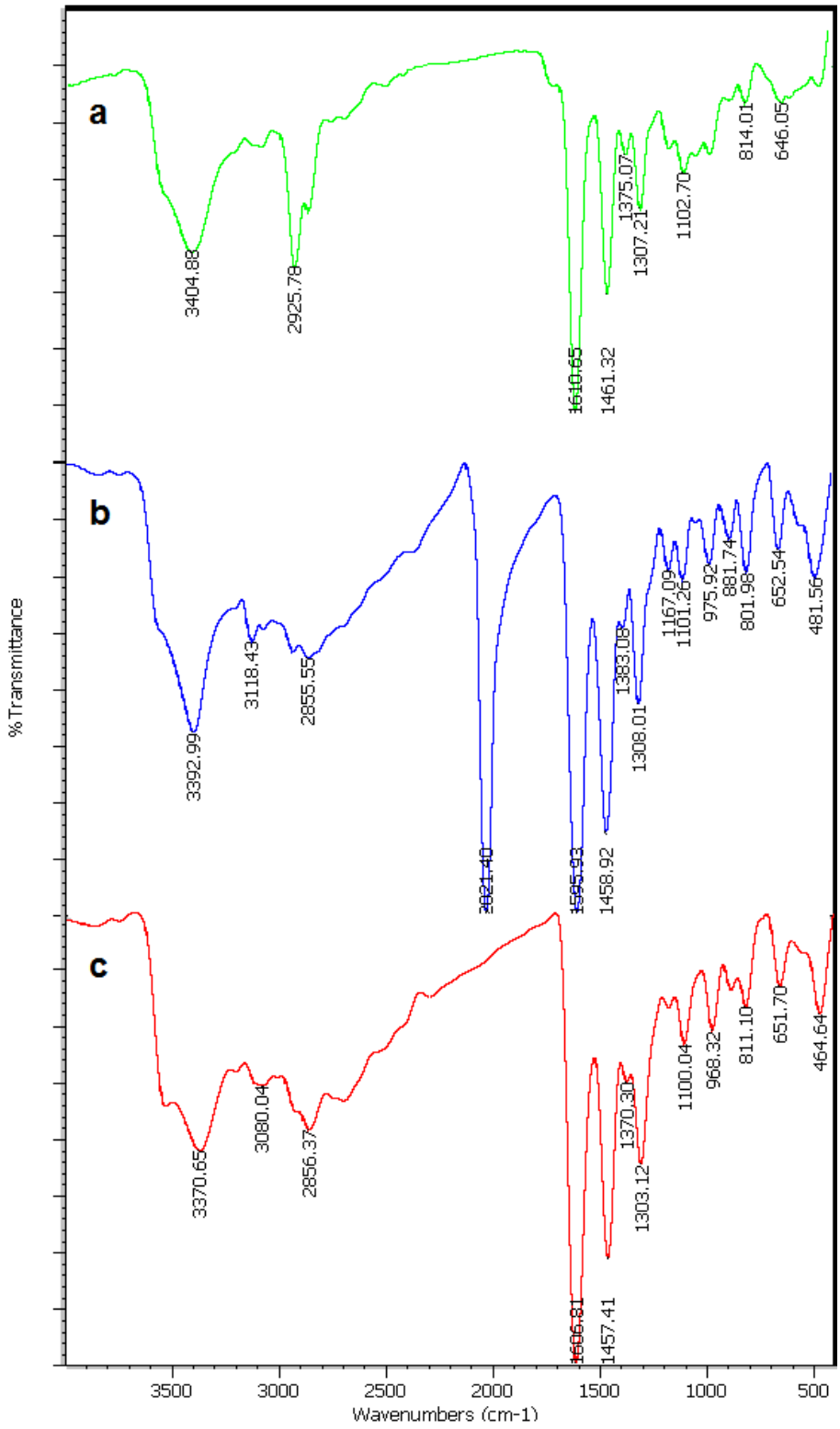

Fig. S4. IR spectra of (a) compound **1**, (b) bulk materials obtained by solid state anion-replacement of compound **1** and (c) the reversed species obtained by solid state anion-replacement of compound **2**.

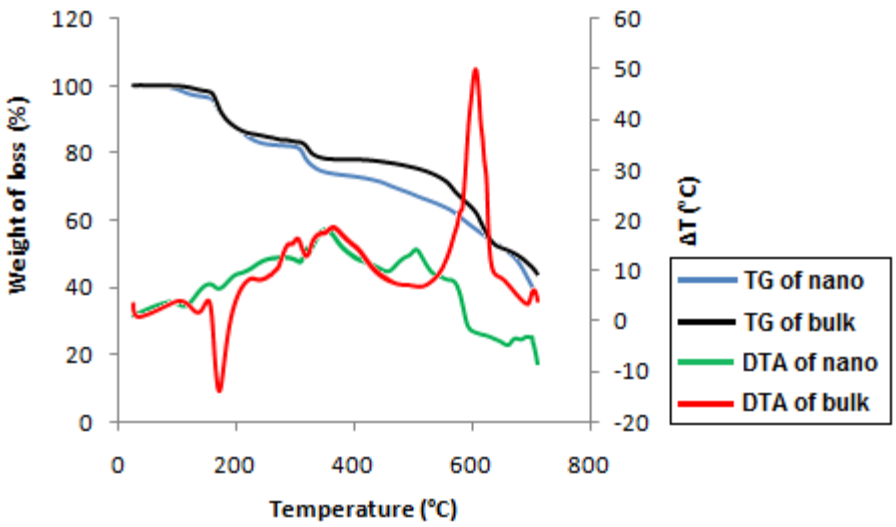

Fig. S5. Thermal behaviour of compound **1** as bulk and nanoparticles.

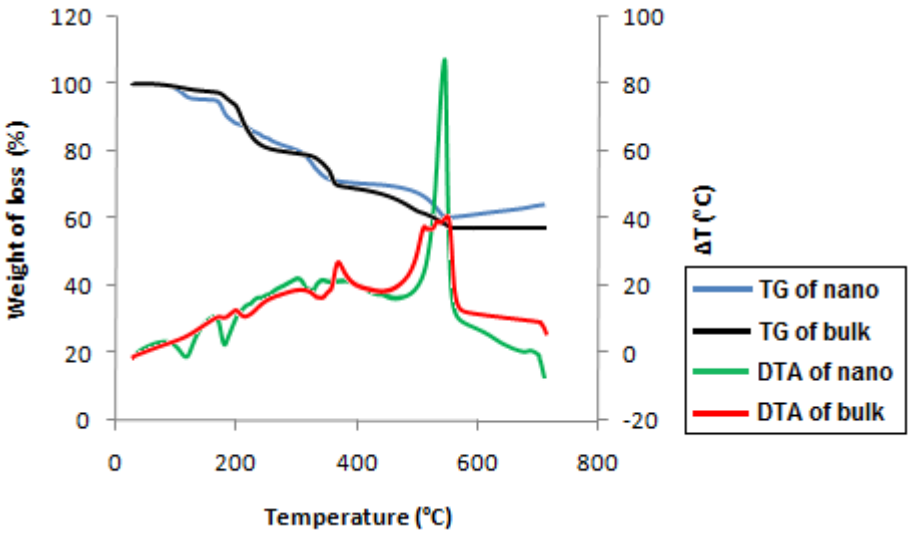

Fig. S6. Thermal behaviour of compound **2** as bulk and nano-particle.

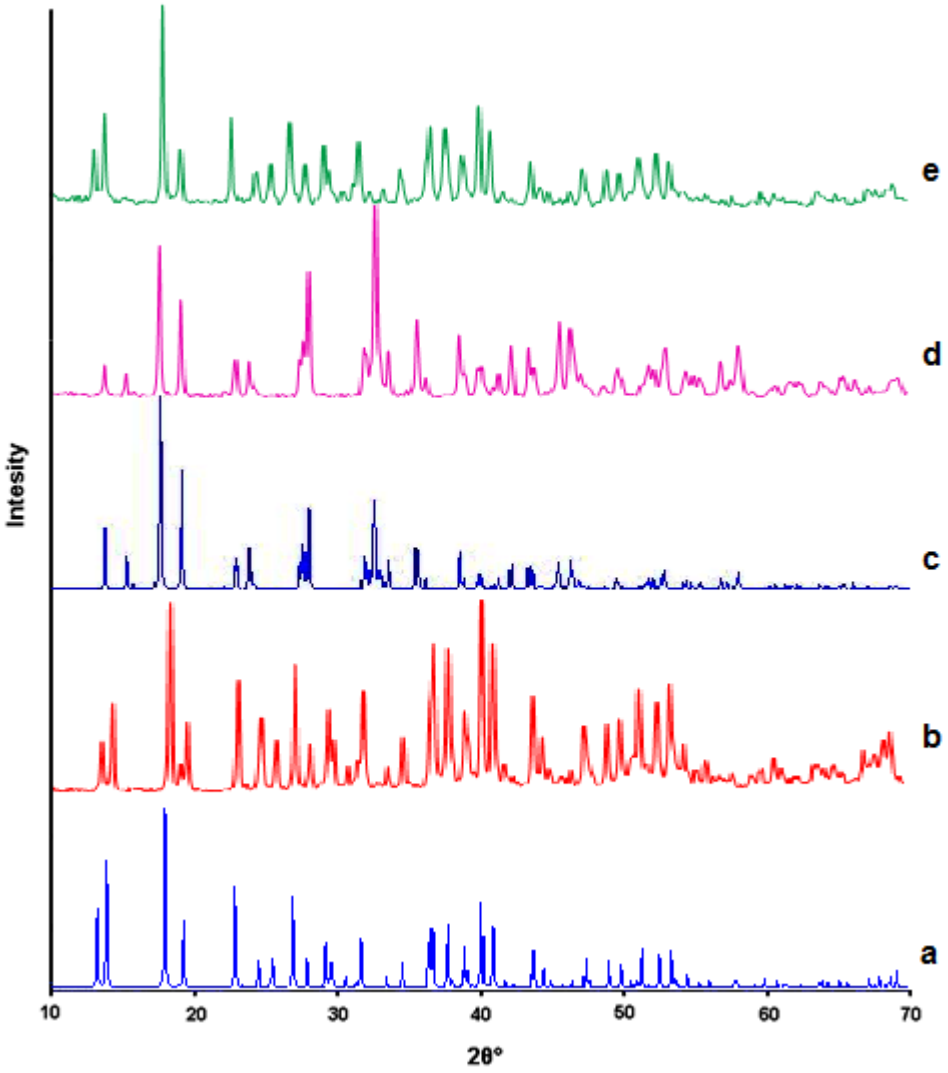

Fig. S7. The XRD patterns of (a) simulated from single crystal X-ray data of compound **1**, (b) nanoparticles of compound **1**prepared by sonochemical process, (c) simulated from single crystal X-ray data of compound **2**, (d) nanoparticles obtained by solid state anion-replacement of compound **1**, (e) the reversed species obtained by solid state anion-replacement of compound **2**.

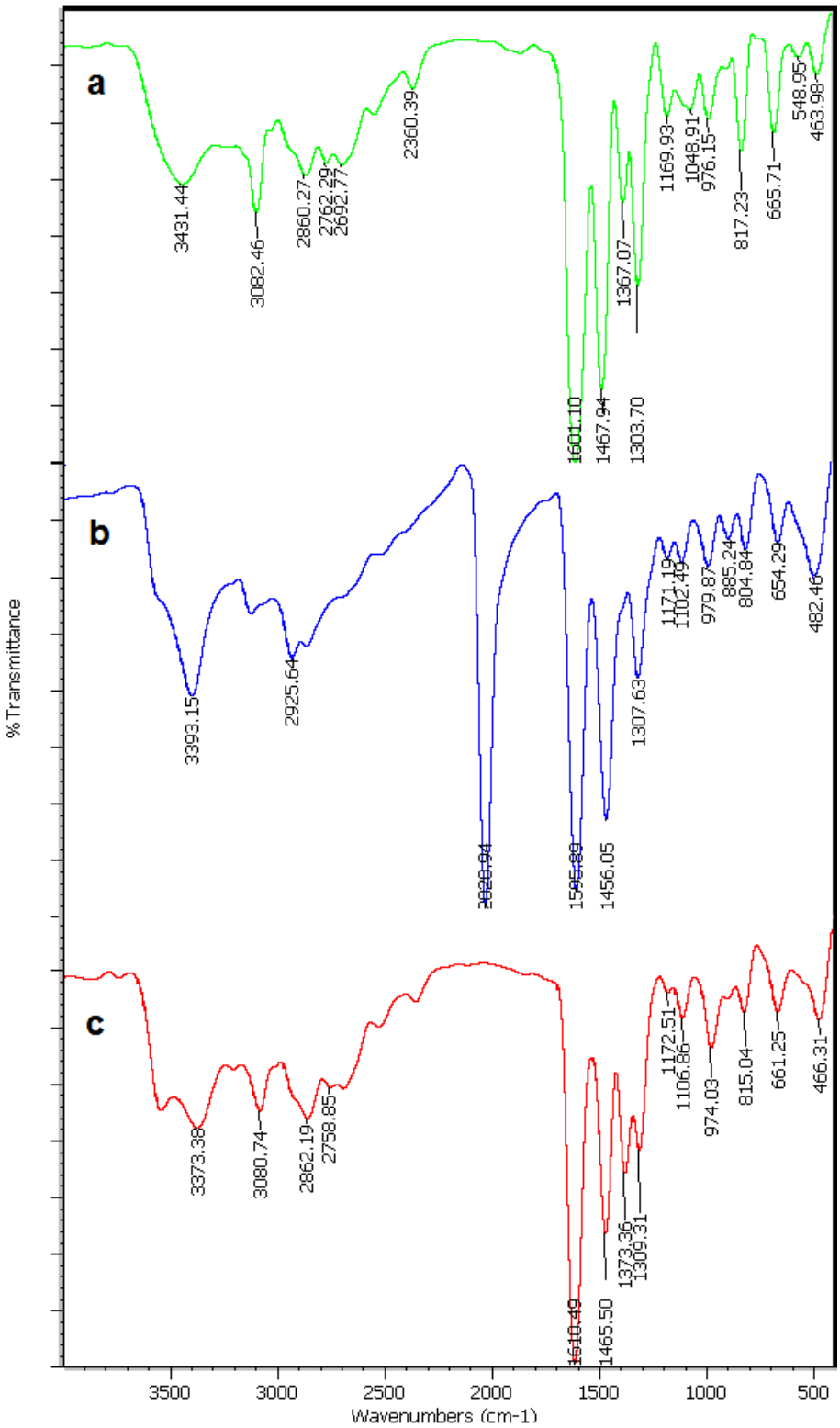

Fig. S8. IR spectra of (a) nano-particles of compound **1** produced by sonochemical method**,** (b) nano-particles of compound **2** obtained by solid state anion-replacement of compound **1** and (c) the reversed nano-particles obtained by solid state anion-replacement of compound **2**.

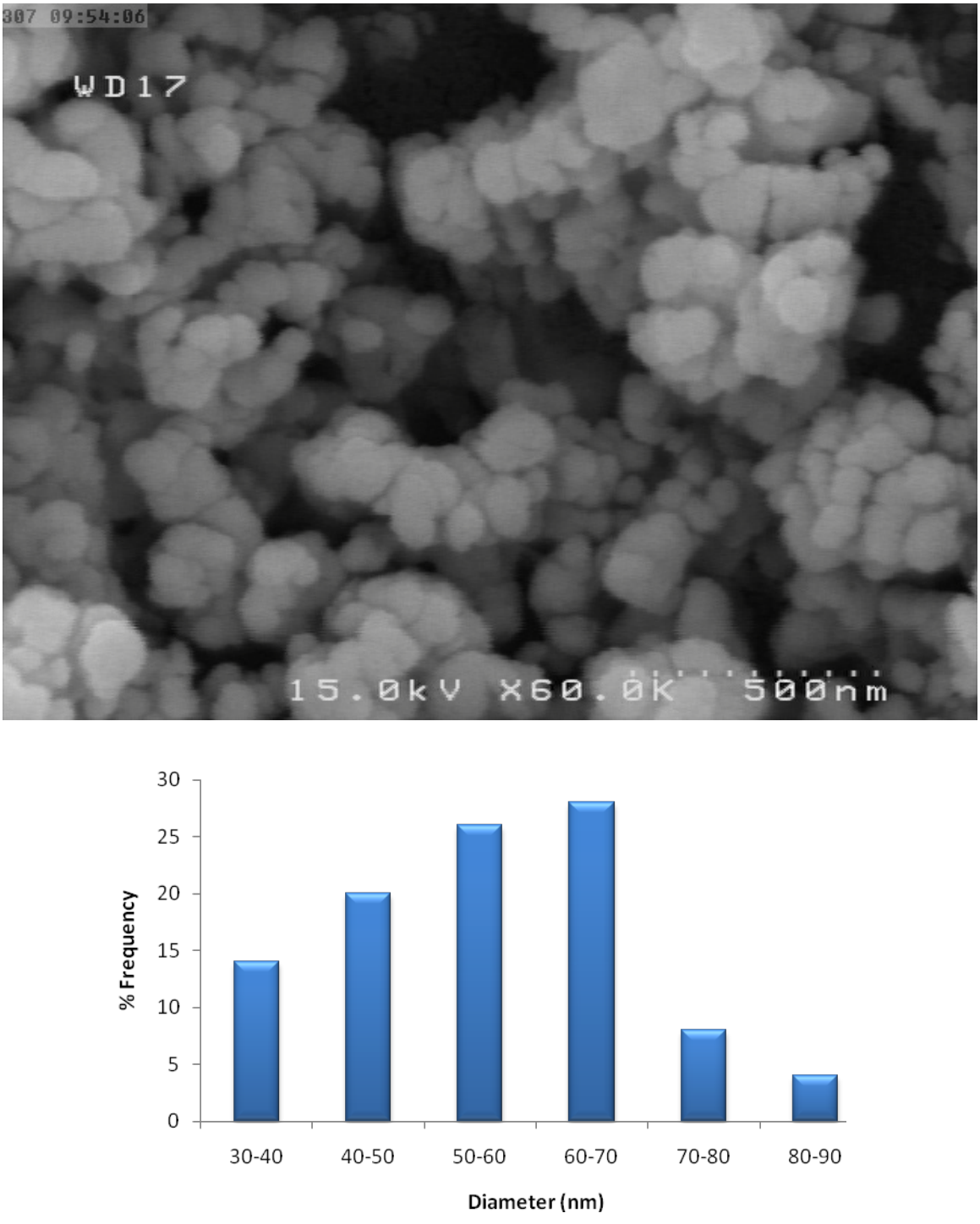

Fig. S9. The SEM image and the corresponding particle size distribution histogram of the reversed species obtained by solid state anion-replacement of compound **2**.

Table S1. Crystal data and structure refinement of $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (**1**) and $[Pb(L)(\mu_{1,1}\text{-}NCS)(H_2O)]_n$ (**2**).

Identification code	Compound **1**	Compound **2**
Empirical formula	$C_3H_4Br\,N_3O_3Pb$	$C_4H_4N_4O_3PbS$
Formula weight	417.19	394.35
Temperature	298(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$	$P\,2_1/c$
Unit cell dimensions	a = 8.4799(14) Å	a = 6.9672(9) Å
	b = 15.706(3) Å	b = 13.4568(16) Å
	c = 5.7500(10) Å	c = 9.6163(12) Å
	α= 90°	α = 90.00°
	β= 90°	β = 110.715(2)°
	γ = 90°	γ = 90.00°
Volume	765.8(2) $Å^3$	843.302 $Å^3$
Z	4	4
Density (calculated)	3.618 Mg/m^3	3.106 $g.cm^{-3}$
Absorption coefficient	27.209 mm^{-1}	20.233 mm^{-1}
F(000)	736	708
Crystal size	0.35 × 0.21 × 0.18 mm^3	0.28 × 0.24 × 0.22 mm^3
Theta range for data collection	2.59 to 25.74°	2.72 to 30.33°
Index ranges	-10≤ h ≤8	-8≤ h ≤8
	-17≤ k ≤19	-16≤ k ≤10
	-7≤ l ≤6	-10≤ l ≤11
Reflections collected	3929	4158
Independent reflections	1439 [R(int) = 0.0307]	1486[*R*(int)=0.0354]
Absorption correction	Semi-empirical from equivalents	Integration
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1439 / 4 / 106	1486 / 0 / 119
Goodness-of-fit on F^2	1.021	1.101
Final R. [I>2sigma(I)]	R_1 = 0.0237, wR_2 = 0.0528	R_1= 0.0244, wR_2= 0.0618
R indices (all data)	R_1 = 0.0260, wR_2 = 0.0534	R_1= 0.0256, wR_2= 0.0624
Largest diff. Peak, hole	1.343 and -1.659 $e.Å^{-3}$	1.563 and -2.173 $e.Å^{-3}$

Table S2. Bond lengths /Å and angles /^{o} for $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$

Pb(1)-N(1)	2.591(6)
Pb(1)-N(3)#1	2.607(7)
Pb(1)-O(1)	2.675(6)
Pb(1)-O(3)	2.707(6)
Pb(1)-O(2)#1	2.745(6)
Pb(1)-Br(1)	2.9363(11)
Pb(1)-Br(1)#2	3.2340(10)
Br(1)-Pb(1)#3	3.2340(10)
O(2)-Pb(1)#4	2.745(6)
N(3)-Pb(1)#4	2.607(7)
N(1)-Pb(1)-N(3)#1	71.2(2)
N(1)-Pb(1)-O(1)	63.85(19)
N(3)#1-Pb(1)-O(1)	73.4(2)
N(1)-Pb(1)-O(3)	151.3(3)
N(3)#1-Pb(1)-O(3)	97.7(3)
O(1)-Pb(1)-O(3)	139.8(2)
N(1)-Pb(1)-O(2)#1	123.38(17)
N(3)#1-Pb(1)-O(2)#1	62.2(2)
O(1)-Pb(1)-O(2)#1	73.18(18)
O(3)-Pb(1)-O(2)#1	68.2(2)
N(1)-Pb(1)-Br(1)	77.86(16)
N(3)#1-Pb(1)-Br(1)	83.94(16)
O(1)-Pb(1)-Br(1)	139.94(13)
O(3)-Pb(1)-Br(1)	74.7(2)
O(2)#1-Pb(1)-Br(1)	124.16(13)
N(1)-Pb(1)-Br(1)#2	70.18(15)
N(3)#1-Pb(1)-Br(1)#2	140.58(15)
O(1)-Pb(1)-Br(1)#2	96.30(15)
O(3)-Pb(1)-Br(1)#2	112.6(2)
O(2)#1-Pb(1)-Br(1)#2	152.19(13)
Br(1)-Pb(1)-Br(1)#2	80.57(2)
Pb(1)-Br(1)-Pb(1)#3	107.58(3)
C(3)-O(1)-Pb(1)	120.4(5)
C(3)-O(2)-Pb(1)#4	118.6(5)
Pb(1)-O(3)-H(3A)	141(5)
Pb(1)-O(3)-H(3B)	99(5)
C(2)-N(1)-Pb(1)	140.4(5)
C(1)-N(1)-Pb(1)	116.0(5)
C(1)-N(3)-Pb(1)#4	116.8(6)
N(2)-N(3)-Pb(1)#4	135.6(5)

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

Table S3. Bond lengths /Å and angles /^{o} for [Pb(L)($\mu_{1,1}$-NCS)(H_2O)]$_n$ (**2**).

Pb(1)–N(1)	2.525(4)
Pb(1)–O(1)	2.621(4)
Pb(1)–N(2)#1	2.677(5)
Pb(1)–N(4)	2.699(5)
Pb(1)–N(4)#2	2.725(5)
Pb(1)–O(2)#1	2.746(4)
N(1)–Pb(1)–O(1)	64.69(12)
N(1)–Pb(1)–N(2)#1	75.22(15)
O(1)–Pb(1)–N(2)#1	105.97(15)
N(1)–Pb(1)–N(4)	72.49(14)
O(1)–Pb(1)–N(4)	135.20(13)
N(2)#1–Pb(1)–N(4)	73.89(13)
N(1)–Pb(1)–N(4)#2	74.23(15)
O(1)–Pb(1)–N(4)#2	81.36(13)
N(2)#1–Pb(1)–N(4)#2	141.42(14)
N(4)–Pb(1)–N(4)#2	74.87(16)
N(1)–Pb(1)–O(2)#1	109.27(13)
O(1)–Pb(1)–O(2)#1	76.27(12)
N(2)#1–Pb(1)–O(2)#1	61.79(12)
N(4)–Pb(1)–O(2)#1	132.52(13)
N(4)#2–Pb(1)–O(2)#1	152.57(13)

Symmetry transformations used to generate equivalent atoms: for #1 x, -y+1/2, z-1/2; #2 -x+2, -y, -z+1.