NJC

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Anion influence on transformations of nonporous 3D to porous 3D coordination polymer

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Abstract:

Reversible anion-exchange of nonporous 3D lead(II) coordination polymers with ligand 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh), from $[Pb(4\text{-}bpdh)(\mu\text{-}NCS)_2]_n$ (**1**) to intermediate 3D $[Pb(4\text{-}bpdh)(\mu\text{-}NCS)(NO_3)]_n$ (**2**) and then porous 3D coordination polymers of $[Pb(4\text{-}bpdh)(NO_3)_2(H_2O)]_n$ (**3**) and $[Pb(4\text{-}bpdh)(NO_3)_2]_n$ (**4**) by solid state anion-replacement processes under mechanochemical reactions, have been studied. The reversible solid state structural transformations of compound **1** to compound **2** and then **3** and **4** by anion-replacement have been verified by PXRD and IR spectroscopy. $Pb_5O_4SO_4$, $Pb_2(SO_4)O$ and PbO nanoparticles were obtained by thermal decomposition of compounds **1**, **2** and **3**, **4** at 600 °C under air atmosphere, respectively. These nanoparticles were characterized by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM).

Keywords: Anion-replacement; Coordination polymer; Solid state process; Nanoparticles

1. Introduction

Mechanochemistry, a burgeoning field in coordination polymers, has been utilized to synthesize various coordination polymers from the reactants without solvents or using liquid or ionic liquid assisted grinding (ILAG) [1]. Solid state crystal-to-crystal transformations of coordination polymers are interesting since they involve breaking and forming of coordination bonds in more than one direction. These kinds of solid state structural transformations with the retention of crystalline character directly reflect the relationship between the solids involved. To develop further our understanding of the supramolecular architecture, it is challenging to continue the investigations on the crystal-to-crystal transformations involving anion-replacement [2-13]. During the last two decades, the rational design and synthesis of novel coordination polymers has made considerable progress [14-18]. The importance of coordination polymers is based not only on their intriguing structural motifs, but they also exhibit a range of potentially useful applications. Studies on crystal-to-crystal transformations involving anion replacement in coordination polymers are more recent [19-25]. It is well known that the anions may have a major influence on constructing novel network geometries [26]. Solid state reactions by manual or mechanical grinding solid reactants together with either no added solvent or only nominal amounts for molecular synthesis have triggered much attention [27].

In this manuscript the main scope is preparation of new coordination polymers and preparation of porous 3D coordination polymer by a simple solid state grinding from a nonporous coordination polymer. In the second part the prepared lead (II) coordination polymers were used as precursors for preparation of different lead (II) nanoparticles. For the first scope, we report the crystal-to-crystal conversion of nonporous 3D lead(II) coordination polymers by solid-state reversible anion replacement, $[Pb(4\text{-bpdh})(\mu\text{-NCS})_2]_n$ (**1**) to $[Pb(4\text{-bpdh})(\mu\text{-NCS})(NO_3)]_n$ (**2**) then $[Pb(4\text{-bpdh})(NO_3)_2(H_2O)]_n$ (**3**) and $[Pb(4\text{-bpdh})(NO_3)_2]_n$ (**4**) {4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene}. To study the usage of coordination polymers as suitable precursors for the syntheses of metal nanostructures materials, coordination polymer **1** and the same samples after grinding with 1 and 2 mmol $NaNO_3$, compounds **2**, **3** and **4** used as precursors to preparation of $Pb_5O_4SO_4$/ $Pb_2(SO_4)O$ and PbO nanostructures by thermal decomposition in oleic acid as a surfactant, respectively.

2. Experimental Section

2.1. Materials and physical measurements

The materials: All chemicals were of reagent grade from Merck Company and were used as commercially obtained without further purification and the ligand 4-bpdh was prepared by reported method [28].

The usual characterization techniques: IR spectra were recorded on a SHIMADZU- IR460 spectrometer in a KBr matrix. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus. The samples were characterized by a scanning electron microscope (SEM) (Philips XL 30) with gold coating.

The PXRD: X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Cu-Kα radiation. The simulated XRD powder pattern based on single crystal data were prepared using Mercury software [29].

The X-ray diffraction: Crystallographic measurements were made at 293(2) K using a Bruker AXS SMART APEX CCD diffractometer. The intensity data were collected using graphite monochromated Mo–K_α radiation (λ=0.71073Å). Accurate unit cell parameters and orientation matrices were obtained from least–squares refinements using the programs Smart and Saint, and the data were integrated using Saint. The structures have been solved by direct methods and refined by full–matrix least–squares techniques on F^2 using SHELXTL. The molecular structure plots were prepared using the Diamond and Mercury programs.

2.2. Synthesis of coordination polymers 1, 2, 3 and 4 with thermal gradient method

Single crystals of compound **1-4** suitable for X-ray diffraction were prepared by a thermal gradient method in branched tube [30].

For preparation of compound **1**, the ligand 4-bpdh (1 mmol, 0.238g) and lead(II) thiocyanate (0.076g, 1mmol) were placed in the main arm of a branched tube. Methanol/H_2O (1:1) 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 a few days, crystals deposited in the cooler arm that were isolated, filtered off and dried. M.P.= 310 °C.

Found; C, 34.24; H, 2.50; N, 14.86, calculated for $C_{16}H_{14}N_6PbS_2$; C, 34.18; H, 2.49; N, 14.95%. IR (cm^{-1}) selected bonds: ν = 574(w), 825(m), 1053(w), 1213(w), 1283(w), 1410(m), 1596(s), 2055(vs) and 3385(w).

For preparation of compound **2**, the ligand 4-bpdh (1 mmol, 0.238g), lead(II) nitrate (0.331g, 1mmol) and NH_4SCN (1 mmol 0.076g) 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 a few days, crystals deposited in the cooler arm that were isolated, filtered off and dried. M.P.= 325 °C. Found; C, 31.74; H, 2.40; N, 14.83%, calculated for $C_{15}H_{14}N_6O_3PbS$; C, 31.82; H, 2.47; N, 14.85%. IR (cm^{-1}) selected bonds: ν = 575(w), 827(m), 1048(w), 1217(w), 1326(vs), 1367(vs), 1596(s), 2066(vs) and 3384(w).

Compounds **3** and **4** were prepared according to reported method [31, 32].

2.3. Synthesis of coordination polymers 1, 2, 3 and 4 with mechanochemical method

In mechanochemical method compound **1** could be synthesized from grinding of raw materials for 20 minutes in an agate mortar. Compounds **2** and **3, 4** 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 reaction of 1 and 2 mmol NH_4SCN with compounds **3, 4** to **2** and **1,** respectively. For purification of coordination polymers with mechanochemical manner after each stage washing with water, thrice time, has been done until extra $NaNO_3$ or NH_4SCN removed.

Elemental analysis data for compounds **1-4** prepared with mechanochemical method:

Compound 1: C, 33.93; H, 2.59; N, 14.92 **Compound 2:** C, 31.69; H, 2.45; N, 14.82%

Compound 3: C, 28.68; H, 2.36; N, 14.37% **Compound 4:** C, 30.15; H, 2.70; N, 15.44%.

2.4. Synthesis of $Pb_5O_4SO_4$, $Pb_2(SO_4)O$ and PbO nanoparticles by thermal decomposition of coordination polymers 1, 2, 3 and 4, respectively.

$Pb_2(SO_4)O/Pb_5O_4SO_4$, $Pb_2(SO_4)O/PbSO_4$ and PbO nanoparticles were obtained by thermal decomposition of compounds **1**, **2** and **3, 4** at 600 °C under air atmosphere, respectively. Monoclinic $Pb_2(SO_4)O$ with a = 13.746(3) Å, z = 4 and S.G = C2/m which are in JCPDS card file No. 33-1486; monoclinic $Pb_5O_4SO_4$ structure with the lattice parameters of a = 11.532 Å, Z = 4 and S.G = $P2_1/a$ which are in JCPDS card file No. 23-0333; orthorhombic $PbSO_4$ with a = 6.9575(5) Å, z = 4 and S.G. = Pbnm which are in JCPDS card file No. 36-1461 and 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.

3. Results and discussion

In this manuscript we report the crystal-to-crystal conversions of nonporous 3D lead(II) coordination polymers by solid-state reversible anion replacement, $[Pb(4\text{-bpdh})(\mu\text{-NCS})_2]_n$ (**1**) to $[Pb(4\text{-bpdh})(\mu\text{-NCS})(NO_3)]_n$ (**2**) then $[Pb(4\text{-bpdh})(NO_3)_2(H_2O)]_n$ (**3**) and $[Pb(4\text{-bpdh})(NO_3)_2]_n$ (**4**) {4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene}. Single crystals of compounds **1, 2** were prepared by a branched tube method [30] and structure of compounds **3, 4** has been reported previously [31-32]. In mechanochemical manner compound **1** could be synthesized from grinding of raw materials for 20 minutes in an agate motor. Compounds **2, 3** and **4** could be synthesized from grinding of 1mmol of compound **1** with one and two mmol of $NaNO_3$ respectively. For preparation of compound **3** one drop of water was added to starting material in the grinding stage. These processes could be reversible by using of one and two mmol NH_4SCN for converting of compounds **3, 4** to **2** and **1**, respectively. Determination of the structure of compounds **1-4** by X–ray crystallography (Table 1 and Figures S1, S2) shows interesting substantial structural changes on anion-replacement between compound **1** with **2** and **3**, **4**.

Table 1. Crystal data and structure refinements for compounds **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{16}H_{14}N_6PbS_2$	C_{15} $H_{14}N_6O_3PbS$
Formula weight	561.64	565.57
Temperature(K)	293	296
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	triclinic
Space group	P 21/c	$P\bar{1}$
Unit cell dimensions	a = 16.3972(5)Å	a = 7.8060(4)Å
	b = 14.1233(3)Å	b = 12.1582(6)Å
	c = 20.3576(6)Å	c = 20.5067(10)Å
	α = 90.00	α = 90.072(4)
	β =109.200(2)^o	β =91.404(4)^o
	γ = 90.00	γ = 108.250(4)
Volume	4452.2(2)Å^3	1847.69(16)Å^3
Z	4	2
Density (calculated)	1.676g/m^3	2.033g/m^3
F(000)	2128	1072
Theta range for data collection	1.95to 26.50^o	1.76to 28.03 ^{o}
Index ranges	$-20 \leq h \leq 20$	$-9 \leq h \leq 9$
	$-17 \leq k \leq 17$	$-15 \leq k \leq 15$
	$-25 \leq l \leq 25$	$-25 \leq l \leq 25$
Reflections collected	9223	7593
Independent reflections	7257	6362
Absorption correction	Integration	integration
Refinement method	$F^2 > 2$sigma(F^2)	$F^2 > 2$sigma(F^2)
Data / restraints / parameters	9223 / 0 /527	7593 / 0 / 473
Goodness-of-fit on F^2	1.168	1.009
Final *R* indices [$I>2\sigma(I)$]	R_1= 0.0566 and wR_2= 0.1014	R_1= 0.0278 and wR_2= 0.0626
R Indices (all data)	R_1= 0.0789 and wR_2= 0.1080	R_1= 0.0381 and wR_2= 0.0658

Compound **1** is 3D coordination polymer and the lead(II) atoms are linked by two nitrogen of 4-bpdh ligands and two nitrogen of μ-NCS anion, so lead(II) atoms are four coordinate. Compound

2 is 3D coordination polymer but lead(II) atoms are linked by two nitrogen of 4-bpdh ligands, three nitrogen of nitrate anions (one in monodentate mode and the other one in bridge mode), one nitrogen of μ-NCS anion and one sulfur atom of μ-SCN anion, so lead(II) atoms are seven coordinate. The coordination polymer **3** is a porous 3D neutral metallopolymer bridged by NO_3^-, 4-bpdh ligand and one H_2O molecule, thus forming an infinite framework, as illustrated in Fig. 1, down. Compound **4** is a 3D porous coordination polymer bridged by $NO_3^-$and 4-bpdh ligand. Crystals of **1** upon grinding with 1 and 2 mmol of solid $NaNO_3$ for 20 minutes in an agate motor lead to formation of compound **2** and **3**, respectively. These processes being accompanied without a color changes (Fig. 1). Compound **3** crystallizes in the monoclinic P2/c space group, while the compound **2** and **1** crystallizes in the triclinic P$\bar{1}$ and monoclinic P21/c space group, respectively. Compound **4** crystallizes in the monoclinic C2/c space group. Results found for the compounds **1**, **2** and **3**, **4** providing us with one of the few examples of crystal-to-crystal conversions along with anion-replacement. Upon grinding the compounds **3** and **4** with 1 and 2 mmol of NH_4SCN, these compounds transform from nitrate to coordination polymers with thiocyanate /nitrate and then full thiocyanate, compounds **2** and **1**, respectively. The samples have been washed after mechanochemical reactions and before analysis, so the samples are free from any NaN_3 or NH_4SCN or other inorganic salts. The structural conversions from 3D coordination polymer **1** (up) to 3D coordination polymers **2** (middle) and 3D coordination polymers **3**, **4** (bottom) by solid state reversible anion-replacement are shown in Figure 1 and Figure 2. In other hand these process could be reversible by using of one and two mmol NH_4SCN for converting of compounds **3** and **4** to **2** and **1,** respectively. In all four coordination polymers, each Pb(II) ion is in the holo-directed geometry but coordination numbers are different. The environment of lead(II) atoms is PbN_4 in compound **1**, and in compounds **2**, **3** and **4** are PbN_6S, PbN_2O_5 and PbN_2O_6, respectively.

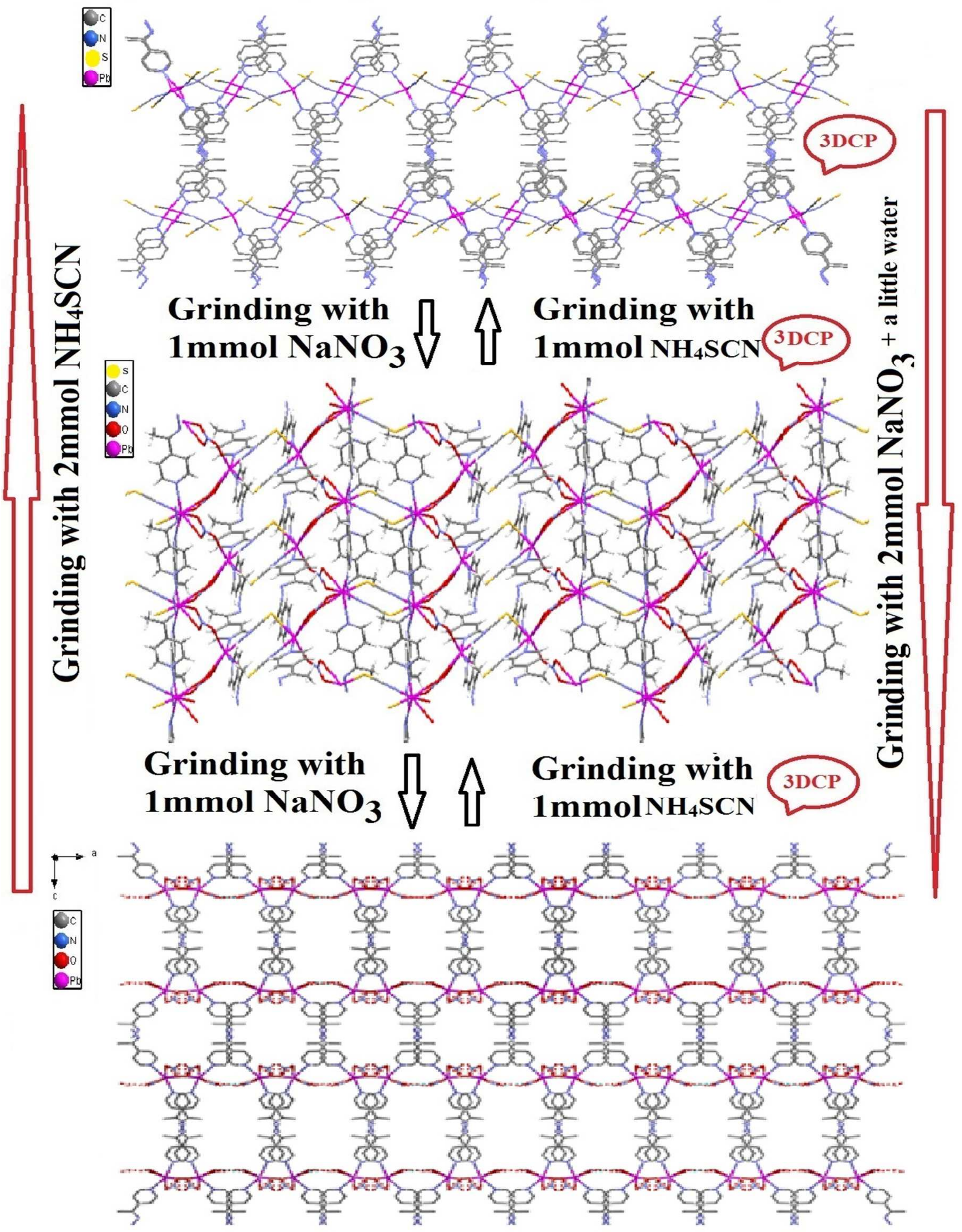


Fig. 1 A schematic diagram illustrating the structural conversions from nonporous 3D coordination polymer **1** (up) to 3D coordination polymers **2** (middle) and porous 3D coordination polymer **3** (bottom) by solid state reversible anion-replacement.

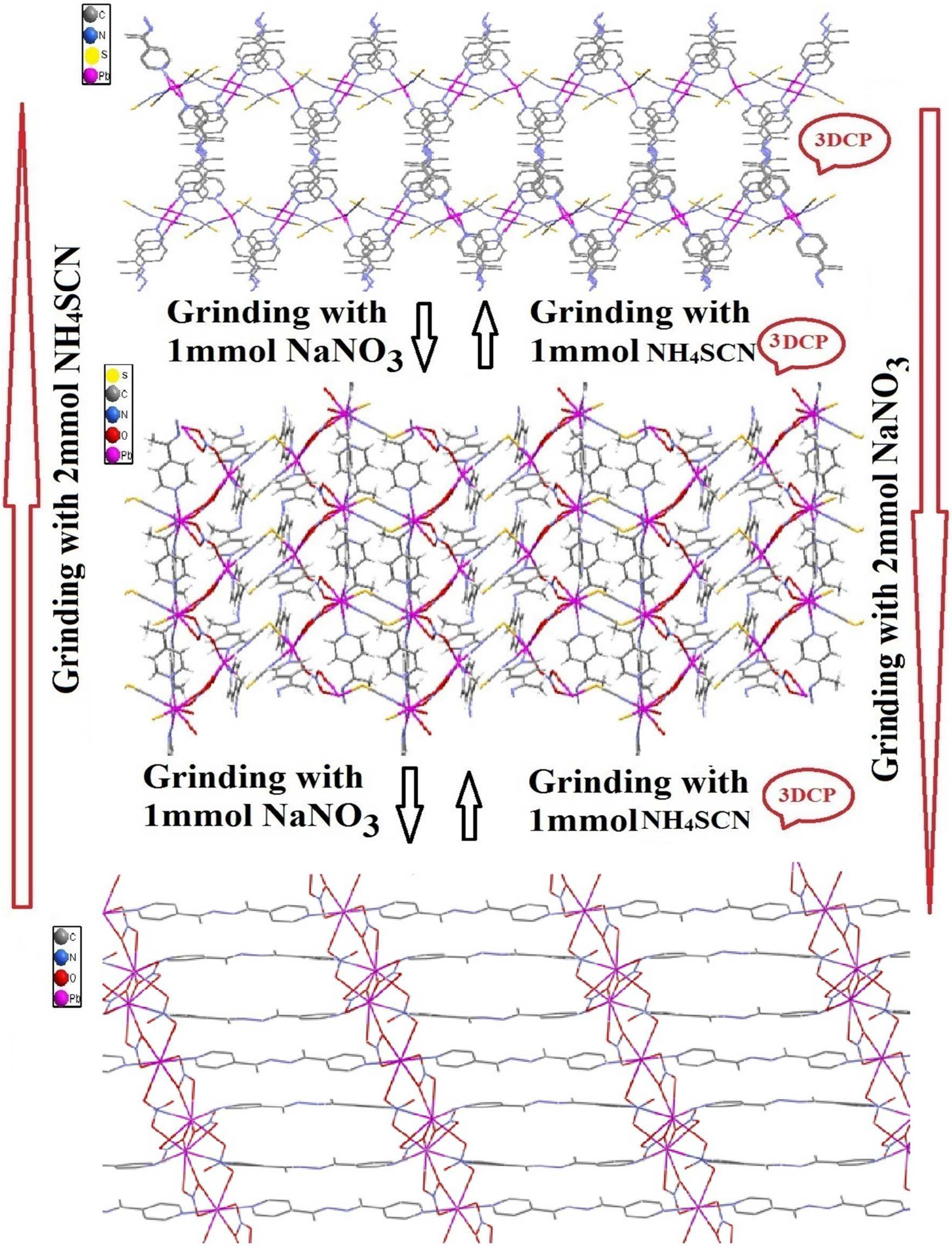
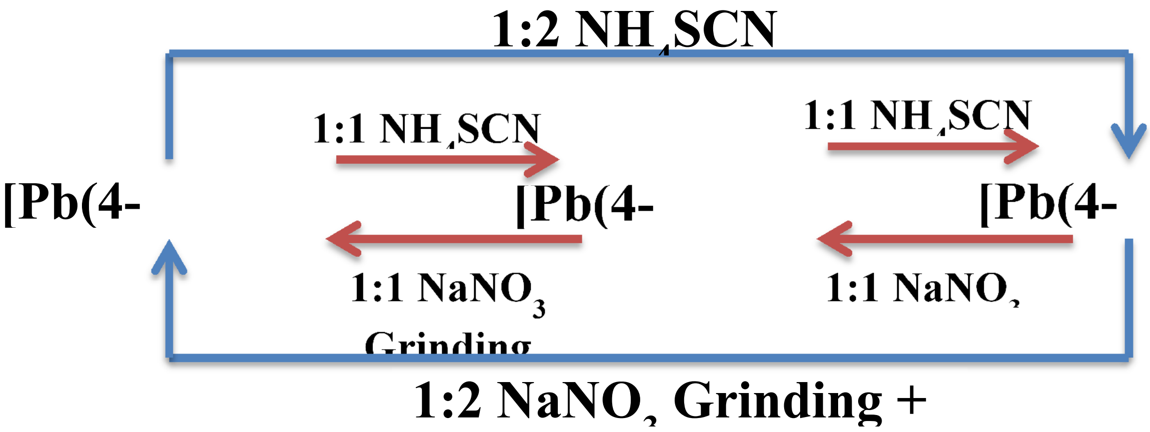


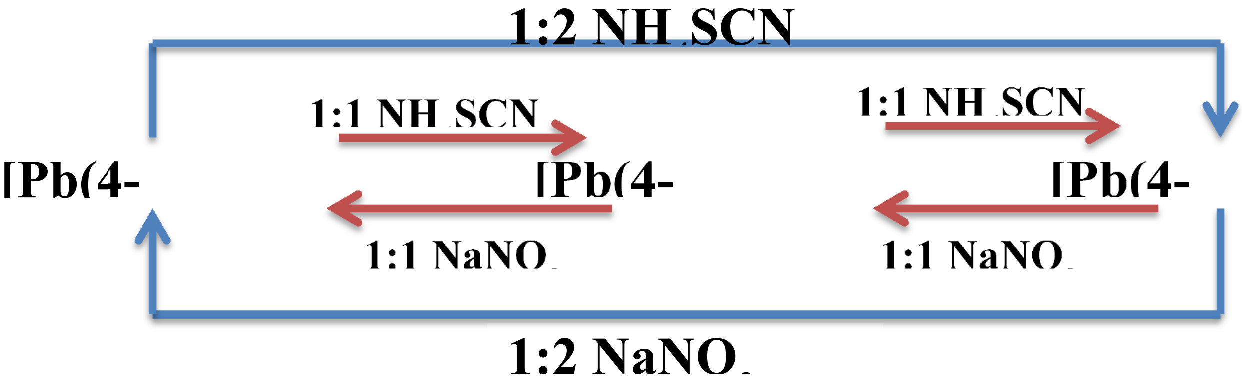
Fig. 2 A schematic diagram illustrating the structural conversions from nonporous 3D coordination polymer **1** (up) to 3D coordination polymers **2** (middle) and porous 3D coordination polymer **4** (bottom) by solid state reversible anion-replacement.

Reversible crystal-to-crystal conversions along with anion-replacement from compound **1** to **2** and **3** were confirmed by powder X-ray diffraction patterns. The structures of the bulk materials for the compounds were confirmed by matching their powder X-ray diffraction patterns with those generated from the corresponding single-crystal structures (Fig. S3). In the case of conversion **1** to **2**, acceptable match was observed between the patterns simulated from single-crystal X-ray data (Fig. S3a) and that measured by powder X-ray diffraction for the bulk crystalline sample as obtained from the synthesis of compound **1** (Fig. S3b). Transformation of compound **1** to compound **2** by solid state anion-replacement (Figure S3a-d) results in a change of the powder pattern. Figure S3c-d shows matches between patterns of prepared **2** with calculated from the single-crystal X-ray data. The observation of a new pattern of peaks implies complete disappearance of **1** and formation of a new compound **2** during the solid state reaction with $NaNO_3$. The same procedure was observed for transformation of **2** to **3**. Those powder X-ray diffraction patterns are shown in Fig. S3c-f. According to the Fig.S3g compound **3** obtained by solid state anion-replacement of compound **1** with two mmol $NaNO_3$. These reactions are reversible and polymers **3** and **2** are converted back to **1** by solid state grinding with NH_4SCN (Fig S4a-c) and in other hand compound **3** could be converted to compound **1** by solid state grinding with two mmol NH_4SCN and this process will be reversible by grinding of compound **1** with two mmol of $NaNO_3$ (Fig S3g and Fig S4d).

To further confirm the reversible anion-replacement from compound **1** to **2** and **3**, **4** IR spectra were recorded for **3** and for the same samples after grinding with one and two mmol $NaNO_3$ (Fig. S5). For the IR spectrum of **3**, absorption bands with a variable intensity in the frequency range 1205–1585 cm^{-1} corresponded to vibrations of the pyridine rings, NO_3^- vibrations at 1380-1400 cm^{-1} indicates that the nitrate groups coordinate to the lead(II) centers in a bridging mode. The $\nu_{O\text{-}H}$ vibration of the coordinated water molecule is observed as a strong band centred at 3384 cm^{-1}(Fig. S5c). The IR spectra of compounds **1**, **2** and **3** is similar but it can clearly be seen that after grinding the solid **3** by one and two mmol NH_4SCN, the characteristic strong absorption band centred at 1380 cm^{-1}, which originates from the NO_3^- anion, become weak in compound **2** (Fig. S5b) and disappeared in the spectrum of compound **1** (Fig. S5a). It indicates that the NO_3^- anions in **3** were completely exchanged by μ-NCS anions. Figure S5d and S5e shows that compound **1** could be converted to compound **3** with two mmol $NaNO_3$ grinding without pass from intermediate **2** and compound **3** could be converted to compound **1** with two mmol NH_4SCN grinding without pass from intermediate **2**. Anion-replacement from compound **1** to **2** and **4** were confirmed by IR spectroscopy too (Figure S6). Scheme 1 and 2 shows a schematic diagram for these solid state crystal to crystal Conversions.



Scheme 1. Schematic diagram for solid state crystal to crystal conversion between compounds **1**, **2** and **3**.



Scheme 2. Schematic diagram for solid state crystal to crystal conversion between compounds **1**, **2** and **4**.

To study the usage of coordination polymers as suitable precursors for the syntheses of metal nanostructures materials [33] 3D coordination polymers, $[Pb(4\text{-bpdh})(\mu\text{-NCS})_2]_n$ (**1**) and the same samples after grinding with one and two mmol $NaNO_3$, $[Pb(4\text{-bpdh})(\mu\text{-NCS})(NO_3)]_n$ (**2**), $[Pb(4\text{-bpdh})(NO_3)_2(H_2O)]_n$ (**3**) and $[Pb(4\text{-bpdh})(NO_3)_2]_n$ (**4**) used as precursors to preparation of $Pb_5O_4SO_4$/ $Pb_2(SO_4)O$ and PbO nanostructures by thermal decomposition at 600 °C, respectively. Fig. S7 provides the XRD patterns of the residues obtained from thermal decomposition of coordination polymers **1**, **2**, **3** and **4** at 600 °C under air atmosphere for 4h. The obtained patterns match with the standard patterns of $Pb_2(SO_4)O/Pb_5O_4SO_4$, $Pb_2(SO_4)O/PbSO_4$ and PbO (for compounds **3** and **4**) which are the same as the reported values, JCPDS card numbers 33-1486/23-0333, 23-0332/36-1461 and 38-1477, respectively. Figure 3 shows the SEM images of $Pb_5O_4SO_4$/ $Pb_2(SO_4)O$ and PbO nanoparticles obtained by thermolysis of compounds **1**-**3**, respectively.

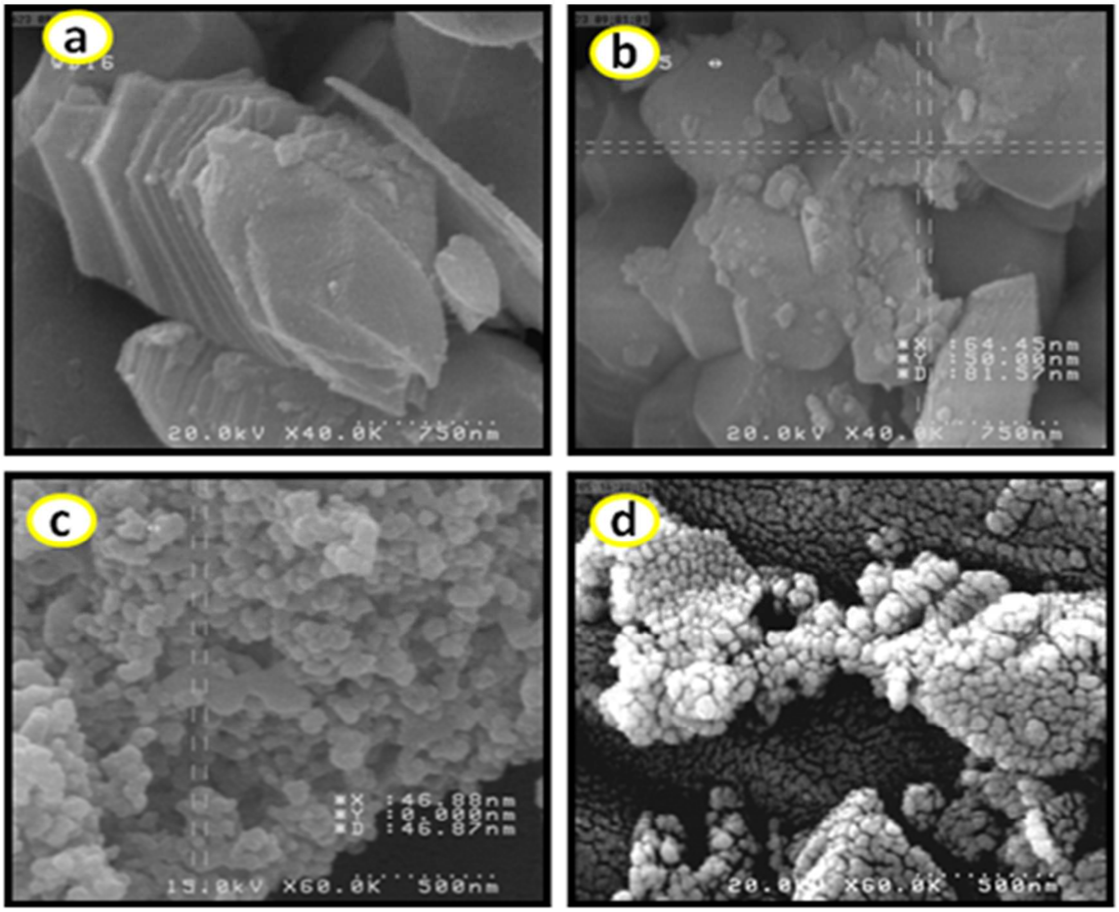


Fig. 3 The SEM images of (a) $Pb_2(SO_4)O/Pb_5O_4SO_4$, (b) $Pb_2(SO_4)O/PbSO_4$, (c) PbO and (d) PbO nanoparticles prepared by thermolysis of compounds **1**, **2** and **3**, **4** at 600 °C under air atmosphere, respectively.

4. Conclusion

In summary, a 3D nonporous lead(II) coordination polymer $[Pb(4\text{-bpdh})(\mu\text{-NCS})_2]_n$ (**1**) polymerize on grinding the solid with one and two mmol $NaNO_3$ to form the 3D coordination polymers, $[Pb(4\text{-bpdh})(\mu\text{-NCS})(NO_3)]_n$ (**2**) and porous coordination polymers $[Pb(4\text{-bpdh})(NO_3)_2(H_2O)]_n$ (**3**) and $[Pb(4\text{-bpdh})(NO_3)_2]_n$ (**4**), respectively. The difference between preparation of compound **3** and **4** from compound **1** is adding one drop of water in the grinding process of syntheses of compound **3**. This process could be reversible with grinding of compound **3** or **4** with one and two mmol NH_4SCN to introduce compound **2** and **1** respectively. $Pb_5O_4SO_4$/ $Pb_2(SO_4)O$ and PbO nanoparticles were obtained by thermolysis of compounds **1**, **2** and **3** at 600 °C under air atmosphere, respectively. This work is the first report about conversion of a nonporous coordination polymer to porous coordination polymer and however this work shows a new strategy for preparation of a porous metal-organic framework from nonporous coordination polymer by solid state reaction.

Supplementary material:

Crystallographic data for the structure reported in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC- 952823 for compound **1** and CCDC- 952822 for compound **2**.

Acknowledgements. Support of this investigation by Tarbiat Modares University and Iran National Science Foundation are gratefully acknowledged.

References:

[1] V. Strukil, L. Fabian, D.G. Reid, M.J. Duer, G.J. Jackson, M. Eckert-Maksic, T. Friscic, *Chem. Commun*. 2010**, 46**, 9191.

[2] A.M.P. Peedikakkal, J.J.Vittal, *Cryst. Growth Des*. 2011**, 11**, 4697.

[3] M. Hedayetullah Mir, J.J. Vittal, *Cryst. Growth Des*. 2008**, 8**, 1478.

[4] M. Nagarathinam, J.J. Vittal, *Chem. Commun*. 2008, 438.

[5] G. Mahmoudi, A. Morsali, *Cryst. Growth Des*. 2008**, 8**, 391.

[6] A. Aslani, A. Morsali, M. Zeller, *Dalton Trans*. 2008, 5173.

[7] H. Sadeghzadeh, A. Morsali, *Inorg. Chem*. 2009**, 48**, 10871.

[8] A. Aslani, A. Morsali, *Chem. Commun*. 2008, 3402.

[9] M. Nagarathinam, J.J. Vittal, *Angew. Chem.*, *Int. Ed*. 2006**, 45**, 4337.

[10] B. Rather, B. Moulton, R.D. Bailey Walsh, M.J. Zaworotko, *Chem. Commun*. 2002, 694.

[11] S. Khanjani, A. Morsali, P. Retailleau, *CrystEngComm* 2010**, 12**, 2173.

[12] M. Khanpour, A. Morsali, *Eur. J. Inorg. Chem.* 2010, 1567.

[13] K. Akhbari, A. Morsali, *CrystEngComm,* 2011**, 13**, 2047.

[14] N. Gimeno, R. Vilar, *Coord. Chem. Rev.* 2006, **250**, 3161.

[15] S. Kitagawa, R. Kitaura, S.-I., Noro, *Angew. Chem. Int. Ed*. 2004, **43**, 2334.

[16] C. J. Janiak, *Dalton Trans.* 2003, 2781.

[17] S. L. James, *Chem. Soc. Rev.* 2003, **32***,* 276.

[18] L. Carlucci, G. Ciani, D. Proserpio, *Coord. Chem. Rev.* 2003, **246**, 247.

[19] T. Sampanther, J.J. Vittal, *Cryst. Eng.* 2000**, 3**, 117.

[20] N.L. Toh, M. Nagarathinam, J.J. Vittal, *Angew. Chem. Int. Ed.* 2005**, 44**, 2237.

[21] X.D. Yang, D. Wu, J.D. Ranford, J.J. Vittal, *Cryst. Growth Des.* 2005**, 5**, 41.

[22] J.D. Ranford, J.J. Vittal, D. Wu, X. Yang, *Angew. Chem. Int. Ed.* 1999, **38**, 3498.

[23] J.J. Vittal, X.-D. Yang, *Cryst. Growth Des.* 2002, **2**, 259.

[24] J.D. Ranford, J.J. Vittal, D. Wu, *Angew. Chem. Int. Ed.* 1998, **37**, 1114.

[25] D.M. Shin, I.S. Lee, D. Cho, Y.K. Chung, *Inorg. Chem.* 2003, **42**, 7722.

[26] S.-I. Noro, R. Kitaura, K. Mitsuru, S. Kitagawa, T. Ishii, H. Matsizaka, M. Yamashita, *J. Am. Chem Soc.* 2002, **124**, 2568.

[27] M. Nagarathinam, A. Chanthapally, S. H. Lapidus, P. W. Stephens, J. J. Vittal, *Chem. Commun.*, 2012, **48**, 2585.

[28] D.M. Ciurtin, Y.-B. Dong, M. D. Smith, T. H.-C. Barclay, *Inorg. Chem*. 2001, **40**, 2825.

[29] Mercury 1.4.1, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, 2001-2005.

[30] B. Ding, E. C. Yang, J. H. Guo, X. J. Zhao, X. G. Wang, *Inorg. Chem. Commun.*, 2008, **11**, 1481.

[31] L. Hashemi, A. Morsali, *CrystEngComm*. 2012, **14**, 779.

[32] L. Hashemi, A. Morsali, *CrystEngComm*. 2012, **14**, 8349.

[33] M. Y. Masoomi, A. Morsali, *Coord. Chem. Rev.* 2012, **256**, 2921.

Table of Contents/ Graphic Abstract:

Anion influence on transformations of nonporous 3D to porous 3D coordination polymer Lida Hashemi, Ali Morsali*, Orhan Büyükgüngor	This work is a new strategy for preparation of porous metal-organic framework from nonporous coordination polymer by solid state reaction.