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ARTICLE TYPE www.rsc.org/xxxxxx | XXXXXXXX

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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Abstract: A reversible anion-exchange of 2D lead(II) coordination polymers with the ligand 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb), from 2D $[Pb(4\text{-bpdb})Br_2]_n$ (**1**) to 2D $[Pb(4\text{-bpdb})Cl_2]_n$ (**2**) coordination polymer by solid state anion-replacement processes under mechanochemical reactions, have been studied. The reversible solid state structural transformations of compound **1** to compound **2** by anion-replacement have been verified by PXRD and IR spectroscopy. $PbBr_2$ and $PbCl_2$ nanoparticles were obtained by thermal decomposition of compounds **1**and **2** in oleic acid as surfactant at 180 °C under air atmosphere, respectively. These nanoparticles were characterized by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM).

During the last two decades, the rational design and synthesis of novel coordination polymers has made considerable progress initiating a remarkable advance in the fields of supramolecular chemistry and crystal engineering[1-7]. The importance of coordination polymers is based not only on their intriguing structural motifs, but they also exhibit a range of potentially useful applications in catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence, and molecular sensing. Studies on transformations involving anion replacement in coordination polymers are more recent [8-20]. It is well known that the anions may have a major influence on constructing novel network geometries[21]. 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 lots of attention.[22,23] Mechanochemical synthesis, 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).[24,25] To develop further our understanding of the supramolecular architecture, it is challenging to continue the investigations on the transformations involving anion-replacement using mechanochemical manner.[26] During the course of the syntheses of the coordination polymers from ligand 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb), we observed the solid state structural transformations of 2D lead(II) coordination polymers by solid-state reversible anion-replacement, $[Pb(4\text{-bpdh})Br_2]_n$ (**1**) to $[Pb(4\text{-bpdh})Cl_2]_n$ (**2**). The ligand 4-bpdb was prepared by reported method.[27] Single crystals of compounds **1** and **2** were prepared by a branched tube method [28] from reaction between 4-bpdb and lead(II) nitrate with ratio (1:2) of KBr and KCl, respectively. The compounds **1** and **2** could be prepared by grinding of 4-bpdb and lead(II) nitrate with ratio (1:2) of KBr and KCl too. 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, respectively, and these processes could be reversible by using of 2 mmol KBr for converting compound **2** to **1**. For purification of coordination polymers with mechanochemical maner after each stage washing with water, three times, have been done until extra KBr, KCl or KNO_3 removed. Determination of the structures of compounds **1**-**2** by X–ray crystallography (Table S1 and Figures S1,S2) shows interesting substantial structural changes on anion-replacement between compound **1** and **2**. Compounds **1** and **2** are 2D coordination polymers and the lead(II) atoms are linked by two nitrogen atoms of 4-bpdb ligands and two Br anions in compound **1** and two nitrogens of 4-bpdb ligands and two Cl anions in compound **2** (Figure S1 and S2).

Crystals of **1** upon grinding with 2 mmol of solid KCl for 20 minutes in an agate mortar lead to formation of compound **2**. These processes being accompanied without a color changes and reversible with grinding with 2 mmol of solid KBr (Fig. 1). Compound **1** and compound **2** both, crystallizes in the triclinic Pī space group and providing us with one of the examples of solid state structural transformations along with anion-replacement.

The structural conversions from 2D coordination polymer **1** (up) to 2D coordination polymer **2** (bottom) by solid state reversible anion-replacement are shown in Fig. 1. In two polymers, each Pb^{II} ion is in the holo-directed geometry[29] and coordination numbers are same**.** The environment of lead (II) atoms is PbN_2Br_4 in compound **1**, and PbN_2Cl_4 in compounds **2**.

Reversible solid state structural transformations with anion-replacement from compound **1** to **2** 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 **2** to **1**, 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 **2** with 2 mmol KBr (Fig. S3b).

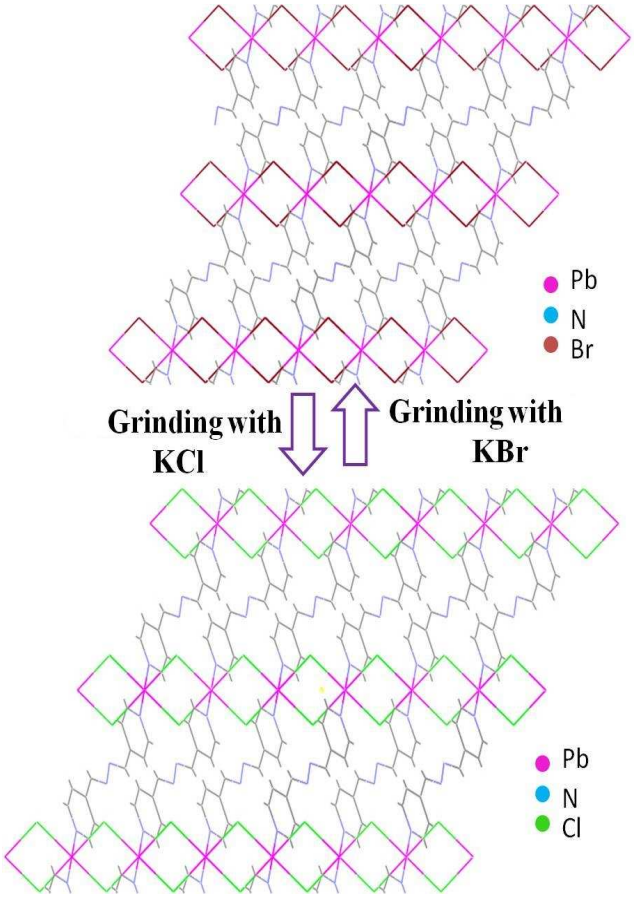

Fig. 1 A schematic diagram illustrating the structural conversions from 2D coordination polymer **1** (up) to 2D coordination polymers **2** (bottom) by solid state reversible anion-replacement.

The same procedure was observed for transformation of **1** to **2**. Those powder X-ray diffraction patterns shown in Fig. S3c-d. These two reactions are reversible and polymers **1** is converted back to **2** by solid state grinding with 2mmol KCl (Fig S3d) that have acceptable match with the patterns simulated from single-crystal X-ray data for compound **2**.

To further confirm the reversible anion-replacement from compound **1** to **2** and **2** to **1**, IR spectra were recorded (Fig. S4). The IR spectra of compounds **1** and **2** are similar and the Cl^- anions in compound **2** were completely exchanged by Br^- anions (Fig. S4b). Figure S4d shows that compound **1** could be converted to compound **2** with 2 mmol KCl grinding and Br^- anions in compound **1** were completely exchanged by Cl^- anions. Figure S5 shows a schematic diagram for these solid state structural transformations.

To study the sufficiency of coordination polymers as suitable precursors for the syntheses of metal nanostructures materials,[30] coordination polymers, $[Pb(4\text{-bpdh})(Br)_2]_n$ (**1**) and the same samples after grinding with 2 mmol KCl, $[Pb(4\text{-bpdh})(Cl)_2]_n$ (**2**) used as precursors to preparation of lead(II) bromide and lead(II) chloride nanostructures by thermal decomposition in oleic acid as a surfactant, respectively. Fig. S6 provides the XRD patterns of the residues obtained from thermal decomposition of coordination polymers **1** and **2** in oleic acid at 180 °C under air atmosphere for 2h. The obtained patterns match with the standard patterns of $PbBr_2$ and $PbCl_2$ which are the same as the reported values, JCPDS card numbers 31-067 and 26-1150, respectively. Fig. 2 shows the SEM images of $PbBr_2$ and $PbCl_2$ nanoparticles obtained by thermolysis of compounds **1** and **2** in oleic acid, respectively. This method for preparation of nano-scale materials may have some advantages such as: it takes place in shorter reaction times, produces better yields and also it may do not need special conditions like high temperature, long reaction times and pressure control.

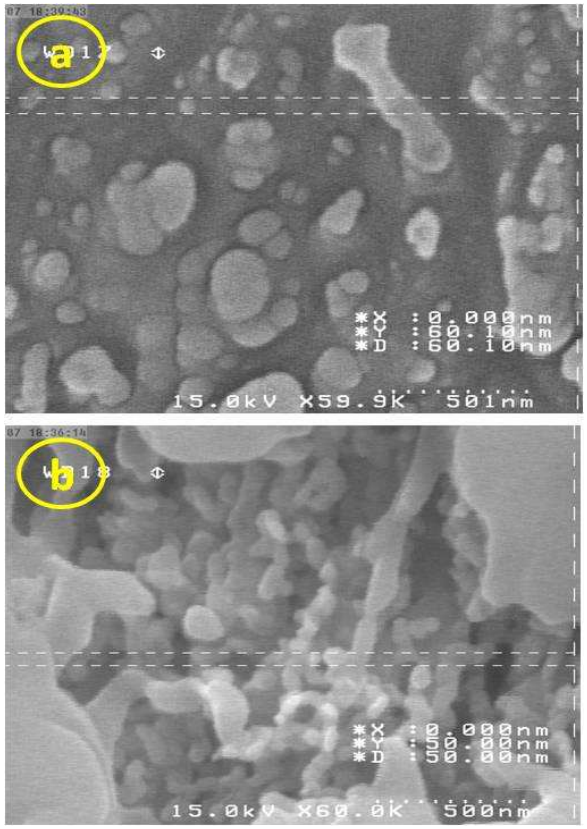

Fig. 2 The SEM images of (a) $PbBr_2$ and (b) $PbCl_2$ nanoparticles prepared by thermolysis of compounds **1**, **2** in oleic acid at 180 °C under air atmosphere for 2 h, respectively.

In summary, a 2D lead(II) coordination polymer $[Pb(4\text{-bpdb})(Br)_2]_n$ (**1**) polymerize on grinding the solid with 2 mmol KCl to form the 2D coordination polymers, $[Pb(4\text{-bpdb})(Cl)_2]_n$ (**2**) and this process could be reversible with grinding of compound **2** with 2 mmol KBr to produce compound **1**. $PbBr_2$ and $PbCl_2$ nanoparticles were obtained by thermolysis of compounds **1**, **2** in oleic acid as surfactant at 180 °C under air atmosphere, respectively. This work is one of the reports about conversion of a two-dimensional bromide coordination polymer to two-dimensional chloride polymer and shows one of the series for preparation of 2D coordination polymers 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- 983875 for compound **1** and CCDC-983876 for compound **2**.

Acknowledgements. Support of this investigation by Tarbiat Modares University and the Iran National Science Foundationis (INSF) are gratefully acknowledged.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental section, XRD patterns, IR spectra,]. See DOI: 10.1039/b000000x/

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Table of Contents:

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