



What can only occur in supramolecular systems; first solid-state conversion of micro to nanostructures without any treatment in environmental conditions



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ABSTRACT

The sonochemical reaction between lead acetate and 5-chloro-8-hydroxyquinoline resulted in formation of one-dimensional pencil shaped $[Pb_2(5-Clq-8-ol)_2(OAc)_2]_n$ (**1**) supramolecular polymer microrods. After three months, these crystalline microrods convert to amorphous nanoparticles of **1** without any treatment in environmental conditions. In the absence of ultrasonic waves, bulk sample of **1** with microrods morphology was obtained again. Surprisingly, these microrods convert to nanorods of **1** with more crystalline structure after three months. It seems that the sonochemical prepared sample of **1** has less crystalline stability than the bulk sample. Although conversion of bulk to nanostructures is very rare in other materials, existence of weak secondary interactions in supramolecular systems, become it possible.

1. Introduction

In the last two decades, design and syntheses of coordination supramolecular compounds, which involve a great number of interactions and self-assembly of organic ligands with functional groups and metal ions with specific directionality, has produced appreciable progress within the field of supramolecular chemistry and crystal engineering [1–7]. Recently the self-assembly approach has become one of the most widely used techniques for the preparation of many functional materials, due to its potential to translate molecular building blocks into well-defined solid-state systems with relatively facile manner [8–10]. The variety of self-assembled structures relies largely on the presence of suitable metal ligand interactions and supramolecular contacts (hydrogen bonding and other weak interactions) [11]. Until now, many single-, double-, triple- and higher-order stranded supramolecular polymers have been generated by a self-assembly process [12–16]. Nevertheless, it is still a huge challenge to reasonably construct the expected architectures with unique properties [17–19]. To the best of our knowledge, few papers are discussed the morphology controlling of compounds and checking out their changes. They have only studied on different compounds such as micro crystals [20], HA films on highly ordered nanotubular [21], a new asymmetric quaterthiophene [22], Mn(III) metalloporphyrins that contain size controlled amorphous and

crystalline nano- and micro sized coordination polymer aggregates [23], diarylethene single crystal [24] and copper–zinc-10,15,20-tetra (4-pyridyl) porphyrin coordination polymer [25]. In another interesting study, we looked at; they have demonstrated a comprehensive morphology evolution from the porphyrin derivative by droplet templating on a hydrophilic substrate by just changing the assembly temperature [26]. But in this work we wish to report the first solid-state conversion of Pb(II) supramolecular polymers with 5-chloroquinolin-8-ol ligand with microrods morphology to nanorods and nanoparticles of it without any treatment in environmental conditions.

2. Experimental

2.1. Materials and physical techniques

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. The molecular structure plots were prepared using Mercury. PARSONIC 15S ultrasonic bath (with the frequency 28 kHz) was used for the ultrasonic irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using an Equinox 55 FT-IR spectrometer (Bruker, Bremen, Germany) in ATR form, in the range of 400–4000 cm^{-1} with 4.0 cm^{-1} resolution and the 16 scan's

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numbers. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer manufactured by Philips with monochromatized $\text{CuK}\alpha$ radiation and simulated XRD powder patterns based on single crystal data were prepared using the Mercury software. The samples were characterized with a scanning electron microscope (Philips XL 30) with gold coating.

2.2. Synthesis two samples of $[\text{Pb}_2(5\text{-Clq-8-ol})_2(\text{OAc})_2]_n$ (**1**) by sonochemical process and as the bulk sample

To synthesis of **1** by a sonochemical process, we used ultrasonic bath with 0.075:0.075 M concentrations of initial reagents (H5-Clq-8-ol:Pb(OAc)₂) and the power of 28 kHz for 1 h. To the solution of H5-Clq-8-ol in MeOH (20 mL), a solution of Pb(OAc)₂ in MeOH (20 mL) was added in a drop wise manner under the ultrasonic irradiation. The obtained precipitates were filtered, subsequently washed with water and then dried. d.p. = 270 °C, Yield: 0.821 g (61.5% based on final product). To synthesis the bulk sample of **1**, 0.075 M solution of H5-Clq-8-ol in MeOH (20 mL) was heated and stirred with 0.075 M solution of Pb(OAc)₂ (in 20 mL MeOH) for an hour, yellow precipitate was formed. The obtained precipitate was filtered, subsequently washed with water and then dried. d.p. = 273 °C, Yield: 0.724 g (54.2% based on final product).

3. Results and discussion

The reaction between lead acetate and 5-chloro-8-hydroxyquinoline resulted in formation of $[\text{Pb}_2(5\text{-Clq-8-ol})_2(\text{OAc})_2]_n$ (**1**) [27]. S. W. Ng, et al. did not consider the structure of **1** deeply in detail [27]. The Pb^{II} atoms in **1** are chelated by acetate and 5-Clq-8-ol⁻ anions; the O atoms of the 5-Clq-8-ol⁻ also bridge to another Pb^{II} ion which results in formation of five-coordinate metal center with PbO₄N hemidirected coordination sphere (Fig. S1a in the SI). In **1**, the lone pair of Pb(II) is 'active' in the solid-state and the arrangement of O-atoms suggest a gap or hole in coordination geometry around the Pb(II) coordination sphere (Figs. S1a and S2a in the SI), a gap possibly occupied by a 'stereo-active' electron lone pair. Hence, the geometry of the nearest coordination environment of every Pb(II)-atoms is likely to be caused by the geometrical constraints of coordinated O and N-atoms, and by the influence of a stereo-chemically 'active' electron lone pair. The 5-Clq-8-ol⁻ anions act in two different coordination modes; chelating, where one oxygen and one nitrogen atoms of the 5-Clq-8-ol⁻ coordinate to a Pb^{II} ion and bridging, where the oxygen atom of 5-Clq-8-ol⁻ bridges between two lead atoms, finally connects to two Pb^{II} ions (Fig. S2a in the SI). A search was also made generally for Pb...C approaches and it appears that the Pb^{II} ions are linked to three carbon atoms of the aromatic ring of 5-Clq-8-ol⁻ with distances of Pb(1)...C(1), Pb(1)...C(2) and Pb(1)...C(3) of 3.548, 3.444 and 3.667 Å, respectively (Fig. S1a in the SI). Also the Pb atoms in compound **1** may also be involved in an η^6 interaction with the aromatic ring of 5-Clq-8-ol⁻ ligand which results in formation of one-dimensional pencil shaped supramolecular polymer in **1** (Fig. S1b and S2b in the SI). To the best of our knowledge, one-dimensional pencil shaped supramolecular polymers are rarely seen [28]. It should be mentioned that 'stereo-active' electron lone pair in **1** is one of the effective factors which leads to formation of one-dimensional supramolecular polymer. Similar to Tl^I, Pb^{II} usually favors the formation of Pb...C secondary interactions especially on its vacant coordination site with stereo chemically active electron lone pair which indicates that Pb^{II} ion has the capacity to act as both a Lewis acid and a Lewis base [29]. Thus, the Pb^{II} coordination sphere is completed and rather than a PbO₄N coordination sphere, the complex could be considered to contain O₄NPb...C₆ coordination sphere with Pb... $\pi_{\text{(centroid)}}$ distance of 3.471 Å (Fig. S1a in the SI). The reported Pb...C separations range is 3.083–4.05 Å in $[\text{Pb}(\text{o-xylene})_2(\text{Cl}_2\text{AlCl}_2)_2]$, $[\text{Pb}(\eta^6\text{-C}_6\text{H}_6)(\text{Cl}_2\text{AlCl}_2)_2]\text{C}_6\text{H}_6$, $[\text{Pb}_2\{\text{SeC}_6\text{H}_2(\text{CF}_3)_3\}_4(\text{toluene})_2]$, $[\text{Pb}(\text{MPOA-c})_2(\text{H}_2\text{O})]_n$ and $[\text{Pb}_2(\text{DBM})_4]$ species [30]. Similar M...C interactions

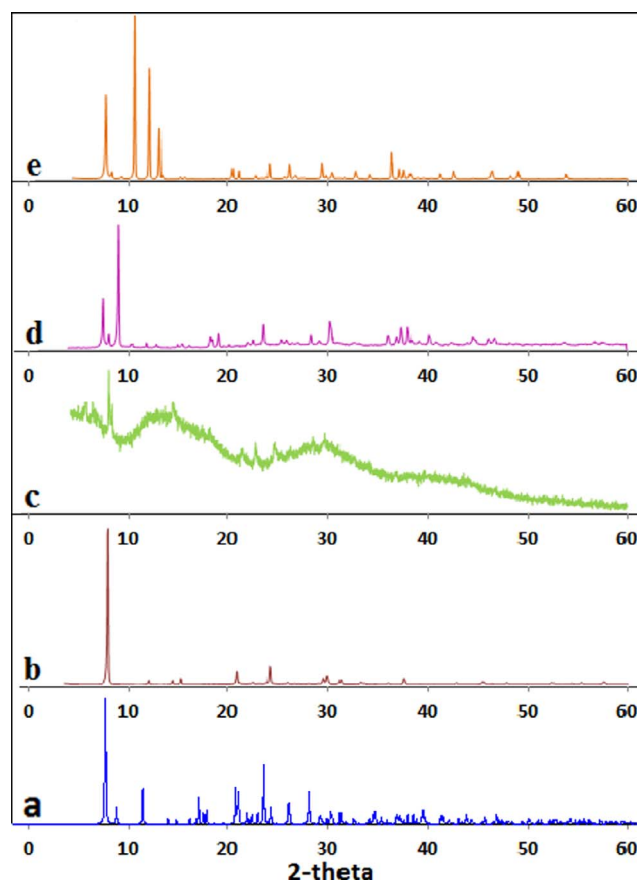


Fig. 1. XRD patterns; a) simulated pattern based on single crystal data of compound $[\text{Pb}_2(5\text{-Clq-8-ol})_2(\text{OAc})_2]_n$ (**1**), b) microrods of **1** prepared by sonochemical process, c) nanoparticles of **1** after three months, d) microrods of **1** as the bulk sample and e) nanorods of **1** after three months.

could be observed in other supramolecular compounds with $\text{M} = \text{Ag}^+$, Au^+ and Tl^+ [31–33]. From the sonochemical synthesis of **1** in methanol, yellow precipitates were obtained. Acceptable matches, with slight differences in 2θ , were observed between the simulated from single-crystal X-ray data pattern (Fig. 1a) and that from the experimental powder X-ray diffraction pattern of **1** (Fig. 1b). The result of XRD powder patterns indicates that the experimental data are in good agreement with the simulated XRD powder pattern based on single crystal data. The morphology and structure of the sample was investigated by Scanning Electron Microscopy (SEM). Fig. 2(top) indicates that microrods of **1** were prepared by sonochemical process. It is interesting for us that compound **1** is a one-dimensional pencil shaped supramolecular polymer in its crystalline structure too (Fig. 2b). After three months for some purposes we decided to consider the SEM image of this sample again. Surprisingly we observed that the sonochemical prepared sample after three months have comprised from nanoparticles of **1** (Fig. 2bottom). XRD pattern of it showed that the sample has approximately amorphous structure (Fig. 1c). Thus it seems that microrods of **1** with very good crystallinity converted to amorphous nanoparticles of **1**. To corroborate that the both samples have the same structure, we examined the FT-IR spectra of them (Fig. S3a, b in the SI). It is obvious that the sample prepared by sonochemical process has the same structure as it after three months. In the next step we decided to synthesis bulk sample of **1** without existence of ultrasonic waves. A comparison between the simulated XRD pattern from single crystal X-ray data of **1** (Fig. 1a) and the XRD pattern of the typical bulk sample of **1** (Fig. 1d) shows acceptable matches, with slight differences in 2θ , between the simulated from single-crystal X-ray data pattern (Fig. 1a) and that from the experimental powder X-ray diffraction pattern of **1**

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