



Preparation of monodispersed metal-based infinite coordination polymer nanostructures and their good capability for metal oxide preparation



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ABSTRACT

Two coordination polymer particles (Zn-CPP and Pb-CPP) were synthesized by reaction of metal(II) acetates with the sodium {3-[(4-carboxy-phenylimino)-methyl]-4-hydroxy-benzylsulfanyl}-acetate. The composition of CPPs was determined by elemental analyses which confirmed the presence of two metal ions per one organic linker in each monomeric unit. Photoluminescence studies of the prepared CPPs showed good correlation between the structure of CPPs and emission wavelengths. The calcination of Zn-CPP produced zinc oxide nanoparticles with large band gap and well defined morphology and composition.

1. Introduction

Crystal engineering, the design and synthesis of supramolecular coordination polymers with flexible frameworks is a frontier field in research, not only for their variety of architectures and interesting molecular topologies but also because of their potential applications such as zeolite-like catalysts [1,2], host-guest chemistry [3], gas storage [4–6], ion exchange [7], molecular recognition [8], photonic materials [9], and magnetic [10], electronic [11], and optical devices [11].

In comparison with the s, d, or f metal coordination polymers which has been mainly focused on up to now, less consideration has been given to the p block heavy metals as coordination centers, despite their important applications in electroluminescent devices, fluorescence, sensors, photovoltaic converters, and organic light-emitting diodes [12–15]. Lead(II) frameworks [16] have additionally attracted great interest because of variable coordination number, large ion radius, and the novel network topologies [17]. According to the hard-soft acid-base theory, the intermediate coordination ability of lead(II) means that it can flexibly coordinate small nitrogen or oxygen atoms as well as large sulfur atoms [18].

In the past, the vast majority of coordination polymer materials, including metal–organic frameworks (MOFs), were focused on macro-scaled crystalline products. Recently, methodologies for the preparation of nano- and micro-scaled coordination polymer particles (CPPs) have been demonstrated by several research groups [19–25]. For the first time, Mirkin [19] and Wang [20] independently developed the preparation of spherical Infinite Coordination Polymer (ICP) particles. Mirkin and coworkers [19] introduced bis-metallotridentate Schiff base ligands as linkers and metal cations as nodes to prepare nanosized ICPs.

Wang [20] utilized p-phenylenediamine and a hexachloroplatinate salt to prepare related structure with similar morphologies. Our group has also reported a fast precipitation method for the production of a variety of CPPs [26–29]. Furthermore, CPPs can be converted to metal oxides through the simple calcination process [30,31]. To expand our long-term interest in preparation of coordination compounds [32–36], herein we report the preparation of sphere-shaped Zn-CPP and Pb-CPP. In addition, prepared Zn-CPP is used to synthesis zinc oxide nanoparticles via calcination.

2. Experimental

2.1. Materials and apparatus

All solvents and other chemicals were obtained from commercial sources and used without further purification.

The CHN elemental analyses were done by Perkin-Elmer 2400 SERIES II. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was conducted on a SPECTRO ARCOS FHE 12 ICP-OES analyzer. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer. Fourier-transform infrared spectra of solid samples (KBr pellets) were obtained on a Perkin-Elmer Spectrum RXI FT-IR spectrometer. All FE-SEM images were taken on a MIRA3TESCAN-XMU scanning electron microscope. Thermogravimetric analysis (TGA) was conducted on a NETZSCH TG 209 F1 Iris thermogravimeter in the temperature range from room temperature to 700 °C at a heating rate of 10 °C min⁻¹ in air. XRD pattern was recorded on a Rigaku D-max CIII X-ray diffractometer using Ni-filtered Cu K α radiation. The electronic spectra were taken on a Cintra 101 spectrometer. The

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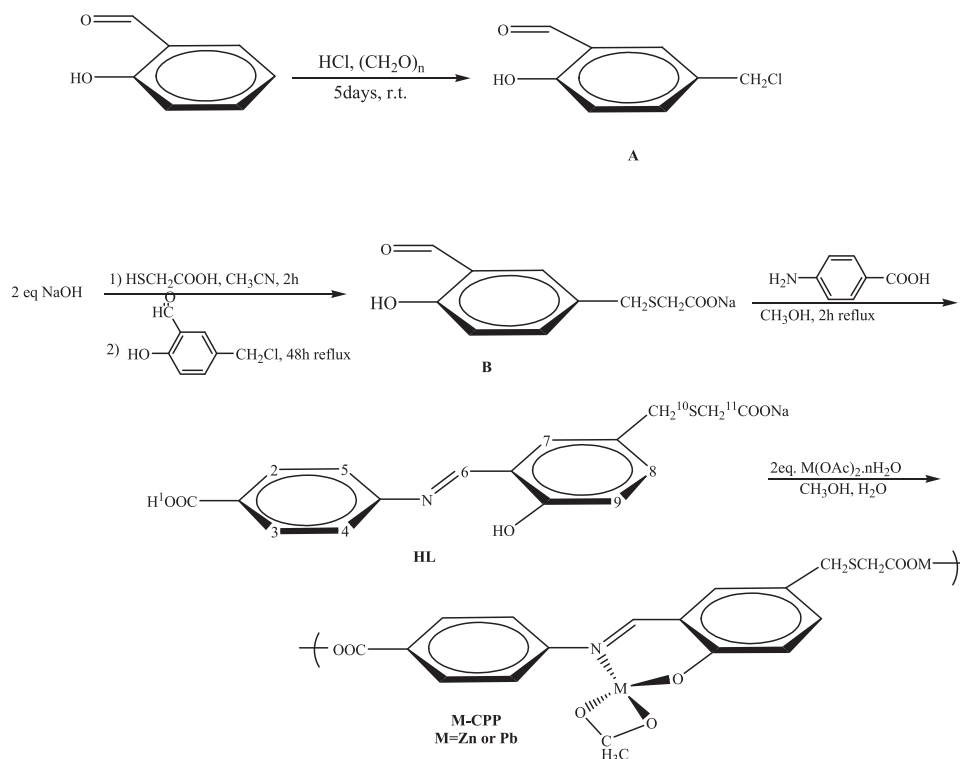


Fig. 1. Schematic synthetic routes to synthesis metal based Coordination Polymers Particles (M-CPP).

emission spectra of the ligand and coordination polymer were taken on a Jasco FP-6500 spectrofluorometer.

2.1.1. Synthesis of the ligand

Fig. 1 shows all of the steps involved in the synthesis of the ligand and CPPs.

2.1.2. 5-(chloromethyl)-2-hydroxybenzaldehyde (**A**)

9.18 g (75.17 mmol) of salicylaldehyde was treated with 5.0 g of paraformaldehyde in 50 mL of conc. HCl. After 5 days of stirring at room temperature, the reaction mixture was repeatedly extracted with Et₂O. The organic phase was washed with saturated aqueous NaHCO₃, NaCl, and then dried over Na₂SO₄. Evaporation of the solvent afforded (**A**) as a wet solid that was washed with diethyl ether several times (6 g, 47% yield, m.p. 86–87 °C) [27,37]. Elemental anal. Calc. for C₈H₇O₂Cl: C, 56.33; H, 4.14. Found: C, 56.72; H, 4.08. ¹H NMR (CDCl₃): δ = 11.07 (s, 1 H, OH), 9.89 (s, 1 H, CHO), 7.57 (dd, 1 H, H_{aromatic}), 7.54 (d, 1 H, H_{aromatic}), 6.99 (d, 1 H, H_{aromatic}), 4.59 (s, 2 H, CH₂Cl) ppm. FT-IR (KBr, cm⁻¹): 3223 (ν_{O-H}, H₂O), 3042 (ν_{C-H-aromatic}), 2964 (ν_{C-H-aliphatic}), 2876, 2751 (ν_{C-H-aldehyde}), 1659 (ν_{C=O}), 1623, 1484 (ν_{C=C}).

2.1.3. Sodium (3-Formyl-4-hydroxy-Benzylthio)-acetate (**B**)

In a 100 mL round bottom flask, 1.08 g (11.72 mmol) of thioglycolic acid in 10 mL acetonitrile was added gradually to a dispersed solution of 0.94 g (23.50 mmol) of fine powder sodium hydroxide in 40 mL acetonitrile. After 2 h, 2.0 g (11.72 mmol) of (**A**) in 20 mL acetonitrile was added slowly to above solution and refluxed for 48 h. The color of reaction mixture was changed to yellow at initial hours. The yellow precipitated of sodium (3-formyl-4-hydroxy-benzylthio)-acetate was collected and washed with acetonitrile several times. The product was dissolved in methanol, filtered and evaporated to remove NaCl byproduct which was formed during reaction (1.8 g; 62% yield). Elemental anal. Calc. for C₁₀H₉O₄SNa: C, 48.39; H, 3.65. Found: C, 47.99; H, 3.55. ¹H NMR (D₂O): δ = 9.83 (s, 1 H, CHO), 7.58 (s, 1 H, H_{aromatic}), 7.50 (dd, 1 H, H_{aromatic}), 6.89 (d, 1 H, H_{aromatic}), 3.68 (s, 2 H, Ar-CH₂-S), 3.01 (s, 2 H, S-CH₂-COO) ppm. FT-IR (KBr, cm⁻¹): 3201

(ν_{O-H}), 3059 (ν_{C-H-aromatic}), 2912 (ν_{C-H-aliphatic}), 2742 (ν_{C-H-aldehyde}), 1663 (ν_{C=O-aldehyde}), 1580, 1412 (ν_{C=O-acid}), 1486 (ν_{C=C}).

2.1.4. Synthesis of the Sodium {3-[(4-carboxy-phenylimino)-methyl]-4-hydroxy-benzylsulfany]-acetate (**L**)

10 mL methanolic solution of 1.1 g (8.10 mmol) para-aminobenzoic acid was added to 2.0 g (8.10 mmol) sodium (3-formyl-4-hydroxy-benzylthio)-acetate (**B**) which was dissolved in 20 mL methanol. The color of the solution was changed immediately from yellow to orange and the reaction mixture was refluxed for 2 h. Evaporation of the final solution gives the fine orange crystals of the product which was washed twice with cold methanol (2.1 g; 70% yield). Elemental anal. Calc. for C₁₇H₁₄NSO₅Na: C, 55.58; H, 3.84; N, 3.81. Found: C, 55.69; H, 3.50; N, 3.48. ¹H NMR (DMSO-*d*₆): δ = 12.90 (s, 1 H, COOH¹), 8.93 (s, 1 H, N = CH⁶), 7.93 (d, 2 H, H^{2,3}), 7.60 (dd, 1 H, H⁷), 7.37 (d, 1 H, H⁸), 7.35 (d, 2 H, H^{4,5}), 6.91 (d, 1 H, H⁹), 3.74 (s, 2 H, Ar-CH₂¹⁰-S), 3.38 (s, 2 H, S-CH₂¹¹-COO) ppm. FT-IR (KBr, cm⁻¹): 3438 (ν_{O-H}), 3043 (ν_{C-H-aromatic}), 2903 (ν_{C-H-aliphatic}), 1696 (ν_{C=O-acid}), 1622 (ν_{C=C}).

2.1.5. Synthesis of infinite coordination polymer (M-CPP; M = Zn or Pb)

A methanolic solution of M(OAc)₂·nH₂O (M = Zn or Pb; 6.81 mmol, 10 mL) was added slowly to a solution of Schiff base ligand (**L**) (1.0 g, 2.72 mmol) in 6:4 methanol:H₂O solution. A cloudy solution was observed and a large amount of precipitate produced within several minutes. The colloidal solution was further stirred and after one hour the precipitate was isolated and washed with H₂O and methanol several times via centrifugation and redispersion cycles. Each successive supernatant was decanted and replaced with distilled H₂O and methanol.

Zn-CPP: Yellow (1.1 g; 76% yield). Elemental anal. Calc. for C₁₉H₁₅NSO₇Zn₂·2H₂O: C, 40.16; H, 3.37; N, 2.47; Zn, 23.01. Found: C, 40.20; H, 3.02; N, 2.51; Zn, 22.87. FT-IR (KBr, cm⁻¹): 3419 (ν_{O-H}, H₂O), 3063 (ν_{C-H-aromatic}), 2918 (ν_{C-H-aliphatic}), 1620 (ν_{C=N}), 1590 (ν_{C=O-asymmetric}), 1390 (ν_{C=O-symmetric}).

Pb-CPP: Yellow (1.3 g; 58% yield). Elemental anal. Calc. for

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