Supplementary Material

Zinc-Containing Coordination Polymer as a Suitable Precursor for Solid State Synthesis of ZnO

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Experimental
**Materials and apparatus**

All chemicals and solvents were obtained from Acros, Alfa-Aesar and Sigma-Aldrich and used as received unless otherwise noted.

The CHN elemental analyses were done by a Perkin-Elmer 2400 SERIES II. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was conducted on the SPECTRO ARCOS FHE 12 ICP-OES analyzer. \(^1\)H 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. Field-emission scanning electron microscopy (FE-SEM) images were taken on MIRA3TESCAN-XMU and MIRA2TESCAN-XMU scanning electron microscopes. High resolution transmission electron microscopy (HR-TEM) images were recorded on FEL-Tecnai F20 TEM. Atomic force microscopy (AFM) was employed to characterize surface morphology using Ara-Research AFM full plus in the non-contact mode. 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\(^{-1}\) under static air. XRD patterns were recorded on a Rigaku D-max CIII X-ray diffractometer using Ni-filtered Cu K\(_\alpha\) radiation. The electronic spectra were taken on a Cintra 101 spectrometer. The emission spectra of the ligand and coordination polymer were taken on a Jasco FP-6500 spectrofluorometer.

**Synthesis of the ligand**

**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 Et\(_2\)O. The organic phases were washed with saturated aqueous
NaHCO$_3$, NaCl, and then dried over Na$_2$SO$_4$. Evaporation of the solvent afforded 5-(chloromethyl)-2-hydroxybenzaldehyde (A) as a wet solid that was washed with diethyl ether several times (6 g, 47% yield, m.p. 86-87 °C). Elemental anal. Calc. for C$_8$H$_7$O$_2$Cl: C, 56.33; H, 4.14. Found: C, 56.72; H, 4.08. $^1$H NMR (CDCl$_3$): δ = 11.07 (s, 1H, OH), 9.89 (s, 1H, CHO), 7.57 (dd, 1H, H$_{aromatic}$), 7.54 (d, 1H, H$_{aromatic}$), 6.99 (d, 1H, H$_{aromatic}$), 4.59 (s, 2H, CH$_2$Cl) ppm. FT-IR (KBr, cm$^{-1}$): 3223 (υ$_{O-H}$), 3042 (υ$_{C-H-aromatic}$), 2964 (υ$_{C-H-aliphatic}$), 2876, 2751 (υ$_{C-H-aldehyde}$), 1659 (υ$_{C=O}$), 1623, 1484 (υ$_{C=C}$).

**Sodium (3-formyl-4-hydroxy-benzylthio)-acetate (B)**

A solution of 1.08 g (11.72 mmol) thioglycolic acid in 10 mL acetonitrile was added gradually to a dispersed solution of 0.94 g (23.50 mmol) sodium hydroxide in 40 mL acetonitrile. After 2 hours, 2g (11.72 mmol) of (A) in 20 mL acetonitrile was added slowly to above solution and refluxed for 48 hours. The color of reaction mixture was changed to yellow at initial hours. The yellow precipitate of sodium (3-formyl-4-hydroxy-benzylthio)-acetate was collected and washed with acetonitrile several times. The product was dissolved in methanol, filtered to remove NaCl by product during reaction and the solvent was removed (1.8 g; 62% yield). Elemental anal. Calc. for C$_{10}$H$_9$O$_4$Na: C, 48.39; H, 3.65. Found: C, 47.99; H, 3.55. $^1$H NMR (D$_2$O): δ = 9.83 (s, 1H, CHO), 7.58 (s, 1H, H$_{aromatic}$), 7.50 (dd, 1H, H$_{aromatic}$), 6.89 (d, 1H, H$_{aromatic}$), 3.68 (s, 2H, Ar-CH$_2$-S), 3.01 (s, 2H, S-CH$_2$-COO) ppm. FT-IR (KBr, cm$^{-1}$): 3201 (υ$_{O-H}$), 3059 (υ$_{C-H-aromatic}$), 2964(υ$_{C-H-aliphatic}$), 2742 (υ$_{C-H-aldehyde}$), 1663 (υ$_{C=O-aldehyde}$), 1580, 1412 (υ$_{C=O-acid}$), 1486 (υ$_{C=C}$); (carboxylic acid groups frequencies of functionalized aldehyde in acidic form: 1730 (υ$_{C=O-acid}$), 1647 (υ$_{C=O-aldehyde}$)).

**Synthesis of Schiff base ligand (C)**
Sodium (3-formyl-4-hydroxy-benzylthio)-acetate, compound (B), (1.5 g, 6.04 mmol) was suspended in 20 mL dry acetonitrile. Then, 0.224 g (3.02 mmol) of 1,3-diaminopropane in 5 mL dry acetonitrile was added dropwise to the suspension and the resulting mixture refluxed for 24 hours. The solvent was removed by filtration, and the prepared Schiff base (C) washed with acetonitrile several times and dried under vacuum (1.4 g; 87% yield). Elemental anal. Calc. for C_{23}H_{24}N_{2}S_{2}O_{6}Na_{2}: C, 51.68; H, 4.53; N, 5.24. Found: C, 51.55; H, 4.23; N, 5.03. \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}): \( \delta = 13.40 \) (s, 2H, OH), 8.48 (s, 2H, HC=N), 7.34 (d, 2H, H\textsubscript{aromatic}), 7.24 (dd, 2H, H\textsubscript{aromatic}), 6.81 (d, 2H, H\textsubscript{aromatic}), 3.63 (s, 4H, Ar-CH\textsubscript{2}-S), 3.61 (t, 4H, NCH\textsubscript{2}), 2.81 (s, 4H, S-CH\textsubscript{2}-COO), 2.03 (quintet, 2H, CH\textsubscript{2}) ppm. FT-IR (KBr, cm\textsuperscript{-1}): 3435 (\( \nu_{\text{O-H}} \)), 3044 (\( \nu_{\text{C-H-aromatic}} \)), 2918 (\( \nu_{\text{C-H-aliphatic}} \)), 1636 (\( \nu_{\text{C=N}} \)), 1580, 1394 (\( \nu_{\text{C=O-acid}} \)), 1495 (\( \nu_{\text{C=C}} \)); (carboxylic acid groups frequencies of functionalized aldehyde in acidic form: 1713 (\( \nu_{\text{C=O-acid}} \)), 1641 (\( \nu_{\text{C=N}} \))).

![Chart S1](image)

**Chart S1.** Proposed structure of Zn-based infinite coordination polymer.