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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. 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. 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 Ka 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 Et₂O. The organic phases were washed with saturated aqueous

NaHCO₃, NaCl, and then dried over Na₂SO₄. 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 C₈H₇O₂Cl: C, 56.33; H, 4.14. Found: C, 56.72; H, 4.08.¹H NMR (CDCl₃): $\delta = 11.07$ (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, CH₂Cl) ppm. FT-IR (KBr, cm⁻¹): 3223 (vo-H), 3042 (vc-H-aromatic), 2964 (vc-Haliphatic), 2876, 2751 (vc-H-aldehyde), 1659 (vc=o), 1623, 1484 (vc=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-hydroxybenzylthio)-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 C₁₀H₉O₄SNa: C, 48.39; H, 3.65. Found: C, 47.99; H, 3.55. ¹H NMR (D₂O): δ = 9.83 (s, 1H, CHO), 7.58 (s, 1H, Haromatic), 7.50 (dd, 1H, Haromatic), 6.89 (d, 1H, Haromatic), 3.68 (s, 2H, Ar-CH₂-S), 3.01 (s, 2H, S-CH₂-COO) ppm. FT-IR (KBr, cm⁻¹): 3201 (vo-H), 3059 (vc-H-aromatic), 2912(vc-H-atiphatic), 2742 (vc-H-aldehyde), 1663 (vc=o-aldehyde), 1580, 1412 (vc=o-acid), 1486 (vc=c); (carboxylic acid groups frequencies of functionalized aldehyde in acidic form: 1730 (vc=o-acid), 1647 (vc=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 C₂₃H₂₄N₂S₂O₆Na₂: C, 51.68; H, 4.53; N, 5.24. Found: C, 51.55; H, 4.23; N, 5.03.¹H NMR (DMSO-d₆): $\delta = 13.40$ (s, 2H, OH), 8.48 (s, 2H, HC=N), 7.34 (d, 2H, H_{aromatic}), 7.24 (dd, 2H, H_{aromatic}), 6.81 (d, 2H, H_{aromatic}), 3.63 (s, 4H, Ar-CH₂-S), 3.61 (t, 4H, NCH₂), 2.81 (s, 4H, S-CH₂-COO), 2.03 (quintet, 2H, CH₂) ppm. FT-IR (KBr, cm⁻¹): 3435 (ν _{C-H}), 3044 (ν _{C-H-aromatic}), 2918 (ν _{C-H-aliphatic}), 1636 (ν _{C=N}), 1580, 1394 (ν _{C-G-acid}), 1495 (ν _{C=C}); (carboxylic acid groups frequencies of functionalized aldehyde in acidic form: 1713 (ν _{C=O-acid}), 1641 (ν _{C=N})).

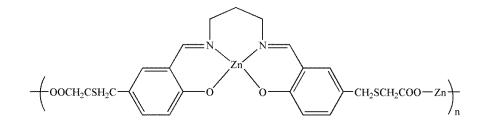


Chart S1. Proposed structure of Zn-based infinite coordination polymer.