Optik 127 (2016) 4329–4332

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Synthesis and characterization of terepthalaldehyde–thiocarbohydrazide polymer doped with Cu(II) and Zn(II) Metal ions for solar cell applications

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ARTICLE INFO

Article history:
Received 31 December 2015
Accepted 25 January 2016

Keywords:
Thiocarbohydrazide
Band gap
Polymers
Fluorescence

ABSTRACT

A convenient synthesis method and the properties of a polynuclear Cu(II) and Zn(II) terapthaldehyde-thiocarbohydrazide polymeric metal complexes has been discussed in this work. A product of terepthalaldehyde–thiocarbohydrazide as condensed polymer (TThP) was synthesized by polycondensation reaction of terepthalaldehyde with thiocarbohydrazide. Two polymeric metal complexes of the condensed product $[(C_{15}H_{12}N_4S)_2CuCl_2]_n$ (TThP–$CuCl_2$) and $[(C_{15}H_{12}N_4S)_2ZnCl_2]_n$ (TThP–$ZnCl_2$) were prepared with $CuCl_2$ and $ZnCl_2$ metal salts separately and compared for property evaluation. Structural analysis was carried out by elemental analysis, SEM and FTIR, thermal analysis with the help of TGA and optical properties was carried with UV–visible and fluorescence techniques. TThP shows fluorescence at 424 nm at an excitation wavelength of 435 nm and its polymer complexes TThP–$CuCl_2$ and TThP–$ZnCl_2$ show fluorescence at the same wavelength with higher intensity. The band gap of the synthesized polymer metal complexes decrease from 3.3 to 2.6 eV as metals varied from M = Cu(II)–Zn(II). This confirms the successful inclusion of metals in polymer back bone.

1. Introduction

Currently researchers explore organic compounds as new electroluminescent materials for optical properties [1]. π-Conjugated molecules have many attractive properties such as fluorescence emission, light absorption, and charge transport, which leads to optoelectronic device applications including light-emitting diodes, field-effect transistors and solar cells [2]. Various organic and inorganic compounds condense themselves to provide a polymer type structure that carries the ability to coordinate with metal ions to improve the properties in different fields like luminescence and sensor technology, sewage treatment, catalysis and biological application [3,4]. Polymer ligand extended the utility for formation of polymer type metals complexes and shows advantage than the small organic compounds such as prominent luminescence efficiency, easy film forming capacity, desired thermal stability and low cost processibility [5,6]. various compounds like triphenylamine, 8-hydroxyquinolinate, 1,10-phenanthroline, terepthalaldehyde-based compounds are known as hole/electron transporting as well as thermally and photolytically stable and emitting materials, which are applied in molecular-based OLEDs [7,8]. π-Conjugated molecules [9,10] have attracted the attention because of the rigid and coplanar structure with limited conformational change that gives rise to interesting properties such as intense luminescence [11] and remarkable hole/electron mobility [12]. From last few decades Cu(II) and Zn(II) coordinated polymer metal complexes carries better injection effectiveness, lower operating voltage and better quantum yield. In this view huge no of such π-conjugated polymer metal complexes as light emitting material in the field of electroluminescence [13]

In this study the ligand is composed of terapthaldehyde and thiocarbohydrazide which act as hole/electron transporting material. The ligand is coordinated with metal to form the metal complex. The inclusion of metal in ligand backbone facilitates the electron mobility due to back π bonding between the metal and the ligand. The polymeric metal complexes have acceptor–donor–acceptor sites in the back bone. The acceptor–donor–acceptor repetitive sites carry symmetric intermolecular energy transfer ability, which can develop the luminescence clarity [6].

In view of the above, we have designed and synthesised two polymer metal complexes by condensation reaction between terepthalaldehyde with thiocarbohydrazide and tune its backbone with Cu(II)–Zn(II) salts to prepare polymer metal complexes and

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http://dx.doi.org/10.1016/j.ijleo.2016.01.199
0030-4026/

these synthesized complexes have been studied with optical properties with a direct band gap.

2. Experimental procedure

2.1. Reagents

All chemicals purchased were of analytical grade. Terepthalaldehyde and thiocarbohydrazide was purchased from S.D. Fine-CHEM Ltd. India. Cupric Choloride and Zinc Choloride (hydrated), Silica Gel, Ethanol, DMF, Ether, DMSO, ethyl alcohol, acetone and other solvents procured from Merck India Ltd. Copper and zinc ion solution were prepared by dissolving in double distilled water.

2.2. Synthesis of terapthaldehyde–thiocarbohydrazide polymer ligand (TThP)

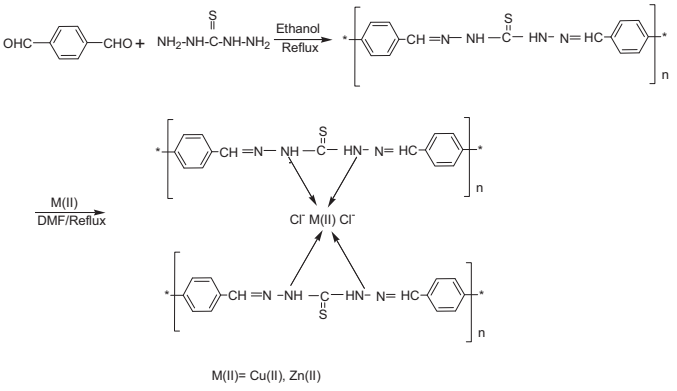
TThP ligand was prepared by adding (0.2 g, 1.9 mmol) thiocarbohydrazide with hot ethanolic solution of terapthaldehyde containing (0.5 g, 3.8 mmol) in 1:2 molar ratio. The reaction mixture was heated for 2–3 h on hot water bath and yellow precipitate was obtained. The product was filtered and thoroughly washed with water to remove the unreacted moieties. The product was recrystallized in ethanol and the reaction was monitored by TLC. The product was then dried in vacuum at 40 °C for 30 h to yield TThP. The yield of the sample is (85–87%).

2.3. Syntheses of TThP metal complexes

The synthesis of two polymer metal complexes were prepared by adding two metal salts, $CuCl_2$ or $ZnCl_2$ (0.01 mol) with TThP (0.02 mmol) in the molar ratio of 1:2 in presence of DMF as shown in Scheme 1. The reaction mixture was refluxed for 5 h to yield TThP–$CuCl_2$ and TThP–$ZnCl_2$. The products were filtered washed with ether and acetone, dried in vacuum at room temperature. The products were confirmed by FT-IR and Elemental analysis (Yield is 80%).

3. Characterization

The formation of terepthalaldehyde–thiocarbohydrazide polymer (TThP) and their respective polymer metal complexes were confirmed by using various analytical techniques. FT-IR spectra were recorded in the 4000–350 cm^{-1} regions using Bruker Tensor 37 spectrophotometer. The chemical analysis was conducted (C, H, N, and S) by Vario EL-III elemental analyzer and the percentages of carbon, hydrogen, nitrogen, and sulfur were estimated. Surface morphology was observed using an S-4800 (Hitachi, Japan) FESEM. Samples were sputter-coated with gold and were analyzed. The thermal stability was studied with thermogravimetric analysis (TGA), carried out in a nitrogen atmosphere using (Shimadzu TGA-50 Model) thermal analyzer. Ultravoilet visible (UV–vis) spectra were taken on Lambda 25 spectrophotometer. The fluorescence spectral analyses were performed on an Agilent technologies Cary eclipse fluorescence spectrophotometer.



Scheme 1. Proposed scheme for the preparation of TThP, TThP–$CuCl_2$ and TThP-$ZnCl_2$.

4. Results and discussion

4.1. Elemental analysis

The formulas of TThP, TThP–$CuCl_2$ and TThP–$ZnCl_2$ are $(C_{15}H_{12}N_4S)_n$, $[(C_{15}H_{12}N_4S)_2\ Cu]_n\ Cl_2$ and $[(C_{15}H_{12}N_4S)_2\ Zn]_n\ Cl_2$ are obtained on the basis of elemental analysis, respectively. The synthesis route of the polymer TThP, polymeric metal complexes TThP–$CuCl_2$ and TThP–$ZnCl_2$ is presented in Scheme 1. Both Cu(II) and Zn(II) are coordinated with four nitrogen atoms.

Elemental analysis of TThP: C, 50.90%, N, 25.75% and H, 4.24%. Found: C, 50.89%, N, 25.45% and H, 4.24%

Elemental analysis of TThP–$CuCl_2$: C, 36.67%, N, 18.34% and H, 3.25%. Found: C, 36.62%, N, 18.30% and H, 3.05%.

Elemental analysis of TThP–$ZnCl_2$: C, 36.47%, N, 18.18% and H, 3.11%. Found: C, 36.45%, N, 18.30% and H, 3.04%

4.2. FTIR analysis

The assignment of the FTIR spectra is useful for determining the absorption peaks corresponding to functional groups in polymeric ligand and complexes TThP, TThP–$CuCl_2$ and TThP–$ZnCl_2$, respectively, as shown in Fig. 1. The FTIR spectra of the metal complexes possess similar absorption peaks but with considerable shifts compared with that of the ligand. Most of the peaks in the polymeric metal complexes of Cu(II) and Zn(II) have been shifted because of the coordination of ligand with metal. The bands in the region 3100–3400 cm^{-1}, attributed to the NH_2 frequencies in the spectra of the ligands, shift to 3160–3310 cm^{-1} in those of the complexes, as a result of the coordination of the nitrogen (NH_2) group with metal ions [14]. The C=N bands of the thiosemicarbazide at 1593 cm^{-1} [15] shift to 1600–1580 cm^{-1} in the spectra of the complexes [16]. The peak at 1078 cm^{-1} is assigned for C=S [17]. In case of coordination of sulphur with metal (M–S), M–S stretching vibrations are observed below 500 cm^{-1}[18,19], such peak is not present in the spectrum. The non-involvement of sulphur in coordination with metal is proved by observing C=S vibration at similar position 1078 cm^{-1} in case of ligand as well in complexes. This confirms the sulphur is not take part in bonding with Cu(II) and Zn(II).

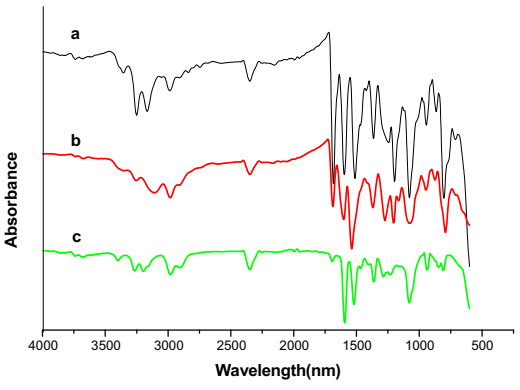


Fig. 1. FTIR of (a) TThP, (b) TThP–$CuCl_2$ (c) TThP–$ZnCl_2$.