Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(4):2118-2121

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Photoluminescence Study of Terpolymer Metal Complex Synthesized From 4-hydroxybenzophenone, Biuret and Formaldehyde

Wasudeo B. Gurnule[1*] and Deepti B. Patle[2]

[1]Department of Chemistry, Laxminarayan Institute of Technology, Nagpur, India
[2]Department of Chemistry, Kamla Nehru College, Sakkardara, Nagpur, India
Rashtrasant Tukadoji Maharaj, Nagpur University, Nagpur, India

---

ABSTRACT

In the present study, we report the synthesis and photoluminescence properties of 4-HBPBF-Cu and HBPBF-Zn terpolymer metal complexes. These terpolymer metal complexes have been prepared using the synthesized copolymer as ligand with two transition metal ions Cu^{2+} and Zn^{2+} ions at 60 °C. The terpolymer resins (4-HBPBF) have been synthesized by the condensation of 4- hydroxybenzaldehyde (4-HBP) and biuret (B) with formaldehyde (F) in the presence of acid catalyst and using 2:1:3 molar proportions of the reacting monomers at 126±2°C. A terpolymer composition has been determined on the basis of their elemental analysis and the number average molecular weight of this terpolymer was determined by conductometric titration in non-aqueous medium. The viscosity measurement in dimethyl sulphoxide (DMSO) has been carried out with a view to ascertain the characteristic functions and constants. The newly synthesized terpolymer resin was characterized by UV-visible

Keywords: Terpolymer; co-ordination; synthesis; photoluminescence; emission. spectra, FT-IR spectra, ^{13}C NMR and ^{1}H NMR spectra. The surface morphology of the terpolymer resin was examined by scanning electron microscopy and it establishes the transition state between crystalline and amorphous nature. The room-temperature photoluminescence study showed a sharp band at 510 nm for excitation and a strong emission at 768 nm.

INTRODUCTION

Photoluminescence is emission of light from a material that has absorbed light energy. In this process, the material's electrons are promoted to excited states by absorption of photons of light energy. The emitted light is the result of those electrons which relax back to the ground state by emitting photons. Both the wavelength of light required to cause photoluminescence and the wavelength of light emitted depend on the energy difference between the ground and excited electron states i.e. the band gap energy is a key parameter in photoluminescence. The relationship between energy and wavelength is given by:

$$E = \frac{hc}{\lambda} \quad ---------- (1)$$

where *h* is Planck's constant,
c is the speed of light,
λ is the wavelength of light.

Most organic photoluminescent materials are π-conjugated semiconducting materials. They are molecules that feature alternating single and double or single and triple bonds. The energies of electrons in the resulting π molecular orbitals are usually higher than in (σ) orbital's. Therefore, the energy gap between the highest occupied molecular (π-bonding) orbital (HOMO) and the lowest unoccupied (π* antibonding) orbital (LUMO) is small, making the materials semiconductors [1-2]. Small band gap (1.3 - 3 eV) allows photoluminescence with small

energy input (light of wavelengths in the near UV to near infrared range). In the case of organic π-conjugated polymers, the p-orbital is delocalized over the length of the chain.

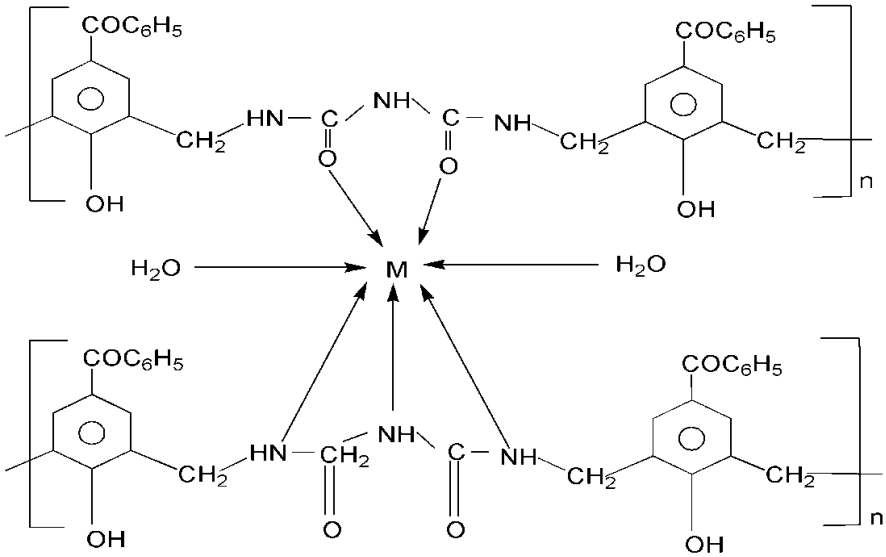
Five new conjugated terpolymers containing 9, 9-dihexylfluorene, 10-hexylphenothiazine (HPT) donor, and 9-fluorenone (FLO) acceptor were synthesized by Suzuki copolymerization and used to study the effects of competing energy and intramolecular charge transfer processes on the photoluminescence (PL) and electroluminescence (EL) of multichromophore copolymers by Abhishek P. Kulkarni et. al. [3]. Hung-Ju Yen and Guey-Sheng Liou [4] prepared two novel poly(amine-hydrazide)s from the polycondensation reactions of the dicarboxylic acid, 9-[N,N-di(4 carboxyphenyl)amino]anthracene (1), with terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH) via the Yamazaki phosphorylation reaction, respectively. All these polymers exhibited high Tg values, good thermal stability, and lower HOMO energy levels with good photoluminescent and electrochromic characteristics. The optical absorption, photoluminescence (PL) and electrical conductivity of the films have been investigated by Singh and coworkers [5]. They observed that the PL of the composite films is quenched significantly with the increase of SWNT concentration. Pradeep kar and co-workers [6] synthesized Poly(m-aminophenol) (PmAP) by the oxidative polymerization of m-aminophenol in sodium hydroxide medium. The photo physical behavior of benzophenone (BP) in poly (methyl methacrylate) (PMMA) has been studied as a function of temperature by John R. Ebdon et. al [7]. They studied the Luminescence of polymer matrices of Phosphorescence of benzophenone dispersed in poly (methyl methacrylate). Recently, we studied the synthesis and optical properties of M-C σ-bonded transition metal poly (aryleneethynylene)s [8-13].

In this paper, our emphasis is mainly focus on the photoluminescence study of terpolymer metal complexes synthesized by 4-hydroxy benzophenone-biuret-formaldehyde as a ligand with Cu^{2+} and Zn^{2+} ions. The absorption and photoluminescence spectra discussed in result and discussion part.

EXPERIMENTAL SECTION

Preparation of Terpolymer-Metal Complexes

The terpolymer metal complexes have been prepared using the synthesized terpolymers as ligand with two transition metal ions i.e. $Cu^{2+}$and Zn^{2+} ions. The terpolymer was taken in 2 M and the transition metal ions (Cu^{2+} and Zn^{2+}) was taken in 1 M for the complex formation reaction. The 4-HBPBF terpolymer (2 g) was taken in round bottom (RB) flask and immersed in ethanol solution to allow it for swelling in 2 h. The Copper nitrate (1 g) was dissolved in ethanol solution and then poured into round bottom flask with equipped mechanical stirrer and a reflux condenser. The reaction has been carried out with an effective reflux at 60°C for 3 h. The colloidal precipitate was observed in the flask and separated out. The product was filtered off and washed with ether and ethanol to remove the impurities. The purification has been done repeatedly to separate the purified product. The resultant purified sample was air dried, powdered and kept in vacuum desiccator with silica gel. The same procedure was also followed for the preparation of 4-HBPBF complexes with Zn^{2+} metal ion. The scheme of preparation of the 4-HBPBF complex with Cu(II) and Zn(II) meal ions is shown in Scheme 1.



[M=Cu(II), Zn(II)]

Scheme 1. Proposed Geometry of 4-HBPBF-Metal Complexes

RESULTS AND DISCUSSION

The Photoluminescence spectra were performed using Shimadzu RF-5301(PC) S CE(LVD) LS55 spectrophotometer at Sivaji Science College, Nagpur. The visible emission in the PL-spectrum of co-ordination polymer of 4-HBPBF terpolymer with Cu and Zn metal ion are shown below in Fig. 1 and Fig. 2.

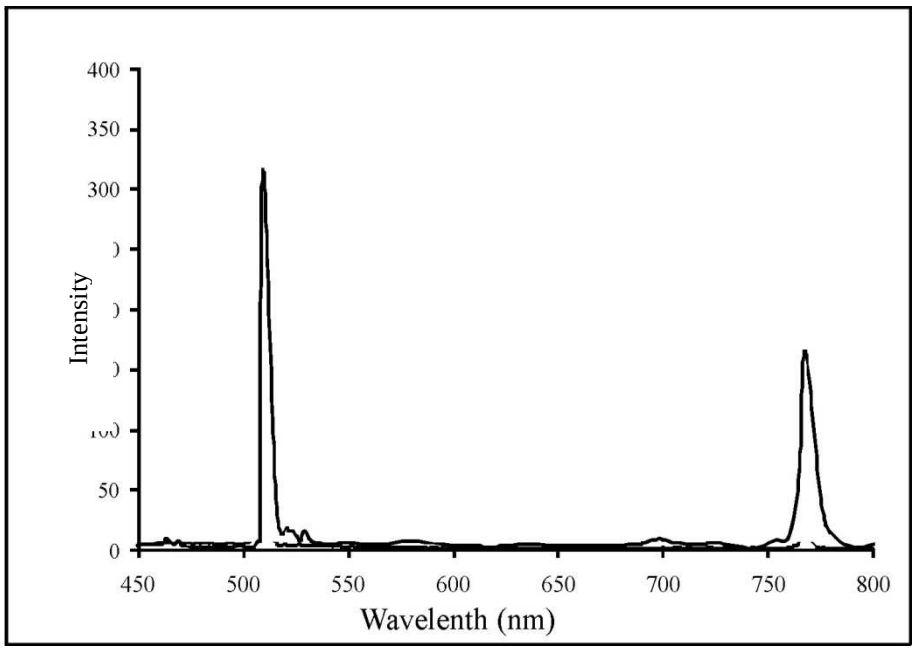


Fig. 1. PL Spectra of 4-HBPBF-Cu terpolymer metal complex (powder)

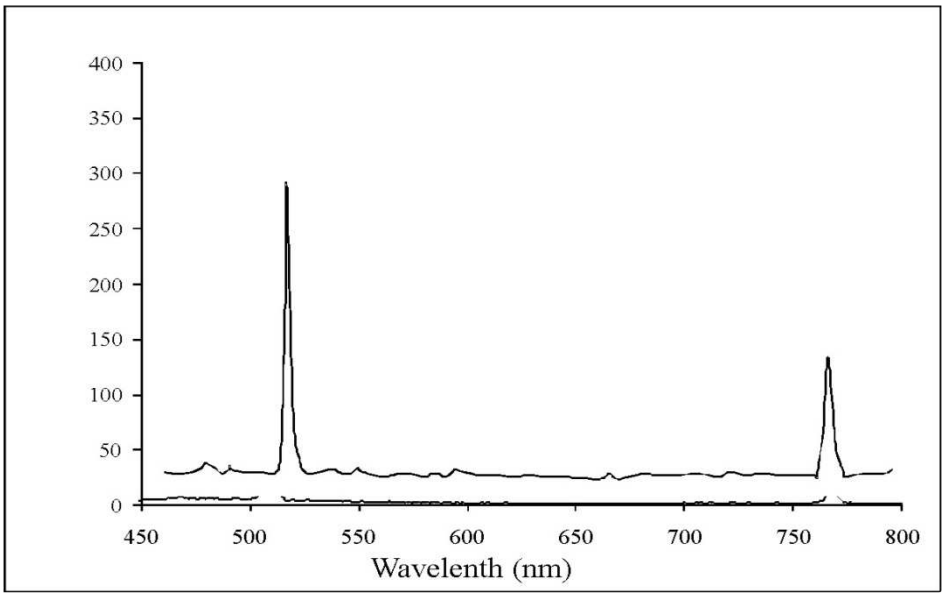


Fig. 2. PL Spectra of 4-HBPBF-Cu terpolymer metal complex (powder)

Fig. 1 and Fig. 2. shows the PL spectra of 4-HBPBF terpolymer metal complex. Fig. 1 represents one emission bands at 768 nm along with excitation at 510 nm. Fig. 2 represents one emission bands at 512 nm along with excitation at 765 nm. A central factor of this discussion is the nature of the characterized samples. Thus PL spectra of these terpolymer metal complexes demonstrate that the produced material has enough quality to be used in the research of semiconductor devices. The results reveal that the prepared co-ordination terpolymer resin can be used for photo luminescent liquid crystal display (PLLCD) and solid state lighting applications as a supporting material[14].

CONCLUSION

A simple and low cost method, namely, modified chemical bath deposition (M-CBD), was employed for the synthesis of new terpolymer-metal complexes. Structural studies showed that these co-ordination terpolymers have semi crystalline behavior. PL spectra of these polymers demonstrate that the produced material has some quality to be used in the research of semiconductor devices and as luminescent materials.

Acknowledgment
Authors are thankful to the Director, Laxminarayan Institute of Technology, Nagpur, India, for providing the necessary laboratory facilities and also thankful to SAIF, Punjab University, Chandigarh for carrying out spectral analysis. One of the author (W.B. Gurnule) thanks to UGC New Delhi for financial assistance.

REFERENCES

[1] J Shinar; V Savvateev; A Survey. New York: Springer- Verlag New York, **2004**, p. 5.
[2] SK Kapse; VV Hiwase; AB Kalambe; *J. Chem. Pharma. Res*., **2012**, 4(3), 1734-1739.
[3] P Abhishek . Kulkarni; Xiangxing Kong and Samson A. Jenekhe *Macromolecules*, **2006**, 39 (25), pp 8699–8711.
[4] Hung-Ju Yen and Guey-Sheng Liou, **9 FEB 2009** | DOI: 10.1002/pola.23258 www.interscience.wiley.com.
[5] Inderpreet Singh; P.C. Mathur and P.K. Bhatnagar, *Int. J. Nanotechnol*., **2009**, Vol.2, 1-8
[6] Pradip Kar; Narayan C. Pradhan; Basudam Adhikari, *Synthetic Metals*, **2010**, 160 pg. 1524-1529.
[7] John R. Ebdon; David M. Lucas; Ian Soutar**;** Anthony R. Lane; Linda Swanson, *Polymer*, **1995**, Volume 36, Issue 8, 1577-1584.
[8] M.Younus; A.Köhler; S. Cron; N. Chawdhury; *Chem. Int. Ed*. **1998**, 37, 30-36.
[9] N. Chawdhury; A. K. Köhler; RH Friend, *J. Chem. Phys*. **1999**, 110, 4963.
[10] RN Singru; *J. Chem. Pharma. Res;* **2012**, 4(1), 46-53.
[11] J S Wilson; N Chawdhury; A. Al-Mandhury; *J. Am. Chem. Soc*. **2001,** 123,9412.
[12] AR Ismaeel; KM Edbey*; J. Chem. Pharma Res*. **2010**, 2(2), 459-466.
[13] RS Bhandari; AK Chauhan; Goswami, *J. Chem. Pharma. Res*, **2011**, 3(2), 34-38.
[14] RN Singru; VA Khati; WB Gurnule; AB Zade; JR Dontulwar; *Desalination*, **2010,** 263, 200-210.