Photoluminescent studies of 2, 2’-dihydroxybiphenyl, ethylenediamine - formaldehyde copolymer

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Abstract. Polymer resin-II (2,2’-DBPEDF) synthesized by the condensation polymerization of 2,2’-dihydroxybiphenyl (DBP), ethylenediamine (ED) and formaldehyde (F) in acidic medium with molar ratio 2:1:3 of monomer and refluxing in oil bath at 120°C for 5 hr. Synthesized copolymer as a ligand is combined with metal particles such as Ni\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+} ions is in 2:1 molar proportion to get metal complex. The reaction has been finished with refluxed at 60°C for three hour. Composition and structure of organic polymer resin-II have been determined by elemental analysis and molecular weight determination by non-aqueous conductometric titration. The UV-visible, FTIR, proton nuclear magnetic resonance and surface feature and crystalline behaviour of ligand and its complexes were analysed by SEM. Newly synthesized copolymer with metal complexes with copper and zinc metal may be used as supporting material for luminescence 2,2’-DBPEDF-Cu show higher photoluminescence than 2,2’-DBPEDF-Zn.

Keywords. Synthesis, condensation, ethylenediamine, photoluminescence, copolymer, metal-complex.

1. Introduction

Impressive interest has been appeared in the synthesis and investigation of coordination complex polymers containing N, S and O donor atoms on polymeric interface. In recent years, polymeric compounds have a lot of consideration and significance, because of fundamental significance in industries. The polymer can be utilized as dyes, surface covering, retardants, adhesives, antibacterial, semiconductors, ion exchanger, rectifiers, battery-powered, glow, and so forth. Electrical conductivity and thermal studies of polymers is aid for polymer scientist because of pertinence at raised temperature next to challenges that need to confront attributable to appropriate electrical conductivity, warm soundness and low processability. In association with similar numerous collaborators attempted to modify the warm strength by changing the monomer arrangement in polymer union [1-4]. The most recent examination progress in fluorescent polymers is centred around the arrangement and photoluminescence of fluorescent polymers with new engineering different strategies for plan and amalgamation of fluorescent materials have additionally been created. Organic polymer which shows fluorescence can be combined by polymerization of starting monomers, utilizing fluorescent mixes as initiator fluorescent mixes as chain move specialist’s material holding between fluorescent gatherings and copolymers and polymerization of nonfluorescent monomers [5].

Photoluminescent supra molecular architecture has recently attracted much interest because of their potential applications in photoelectronic devices or as fluorescence sensors and probes. Polymers have started to find use in making LEDs, liquid crystals and as sensors for metal ion warfare agents, bacteria and biomolecules. Most of the photoluminescent materials are pi-conjugated semiconducting materials much interest is being shown in the synthesis and exploration of the structure-property relationship of pi conjugated polymers due to vital importance in electrical industries. Coordination mixes are entrancing class of particles that have wide applications in numerous fields, for example, light producing diodes (LEDs), follow metal investigation, metal flagging, plan of optical gadgets and sensor atoms [6]. As compared to blue, green and red luminescent complexes most stable luminescent complex is blue which is useful for electroluminescent displays [7]. LECs, supra molecular assemblies, solar energy conversion scheme [8], biological probing and oxygen sensing [9-10]. Luminescent coordination polymers are as of now accepting a lot of consideration because of their expected applications in different fields, for example, natural light radiating diodes [11].
The manuscript reports the synthesis, characterization and photo luminescent property of polymer derived from 2,2'-dihydroxybiphenyl, formaldehyde and ethylenediamine.

2. Materials and Methods
All the chemicals used are of AR grade.

2.1. Synthesis of 2,2'-DBPEDF polymer
Polymer was synthesized by condensation of 2,2'-dihydroxybiphenyl (DBP), ethylenediamine (ED) and formaldehyde (F) in presence of HCl as a catalyst in 2:1:3 proportion to 120°C in an oil bath with occasional shaking, to ensure thorough mixing for about 5 Hrs. The orange-colored resinous product was obtained. The product obtained was washed several times with warm water and alcohol to remove biphenyl-formaldehyde copolymer which may be present along with 2,2'-DBPEDF polymer. The polymer obtained was dried, powdered and afterward extricated with diethyl ether. The orange resinous mass was taken out from the flask. The structure of polymer resin is shown in Fig.1.

2.2. Synthesis of 2,2'-DBPEDF-II Copolymer-Metal Complex
Polymer metal complex has been synthesized by using polymer as ligand with Ni²⁺, Cu²⁺ and Zn²⁺. The copolymer taken in 2M concentration and Ni²⁺, Cu²⁺ and Zn²⁺ was taken in 1M concentration to form complex. The polymer 2,2'-DBPEDF-II (2g) was taken in flask and ethanol solution is added to allow it 2h for swelling. The nickel nitrate (1g) was dissolved in ethanol and then transfer into the flask with stirrer in condenser. The reaction takes place with an effective reflux at 60°C for 3h. Resultant mass was filtered and washed with ether to remove impurities. The resultant sample was dried and kept in vacuum desiccator. The procedure was repeated with Ni²⁺ and Zn²⁺.
metal ion. The scheme of preparation of the 2,2-DBPEDF-II complexes with Ni (II), Cu (II) and Zn (II) metal ion as shown in Fig. 2.

![Synthesis of 2,2'-DBPEDF-II Copolymer -metal complex](image)

**Figure 2.** Synthesis of 2,2'-DBPEDF-II Copolymer -metal complex

2.3. Conductometric Titration

Molecular weight \( (M_n) \) of polymer was controlled by non aqueous conductometric titration method by using ethanolic KOH as a titrant. The degree of polymerization and molecular weight \( (M_n) \) of the polymer have been resolved utilizing the equation. This observation is in good agreement with the trend observed by earlier workers [12].

\[
(D_p) = \frac{\text{Total milliequivalents of base required for complete neutralization}}{\text{Milliequils of base required for smallest interval}} = \frac{\text{Total milliequivalents of base required for complete neutralization}}{(\text{Mn}) = (D_p) \times \text{weight of repeating unit}}
\]

3. Results and Discussion

3.1. Elemental Analysis

2,2'-DBPEDF-II polymer was analyzed for the C, H and N content. Empirical formula of polymer has been suggested and tabulated in Table 1. The composition of polymer obtained was found to be in good correlation.
Table 1. Elemental analysis and empirical formula of copolymer resin

| Polymer          | Percentage C Found (cal.) | Percentage H Found (cal.) | Percentage N Found (cal.) | Empirical Formula | Formula Weight |
|------------------|---------------------------|---------------------------|---------------------------|-------------------|----------------|
| 2,2’-DBPEDF-II   | 68.27 (65.71)             | 7.27 (7.78)               | 7.8 (8.07)                | C_{29}H_{27}O_{4}N_{2} | 347            |

3.2. **Non-aqueous conductometric Titration Method**
Molecular weight of suggested polymer has been determined by this method in DMSO solvent. A graph is plotted between specific conductance and milliequivalents of ethanolic KOH required for neutralization of 100g each polymer. Molecular weight (Mn) of polymer could be obtained by multiplying the average degree of polymerization (Dp) by formula weight of repeating unit. It is seen that the molecular weight of polymer rises with the rise in ethylenediamine. The curve obtained is shown in figure 3 and data are tabulated in table 2.

![Figure 3. Titration curve of 2,2’-DBPEDF polymer](image)

Table 2. Molecular weight determination of 2,2’-DBPEDF-II polymer

| Polymer          | 1st phase of neutralization | Final phase of neutralization (Meq/100g sample) | Degree of polymerization (Dp) | Empirical weight (g) | Number average molecular weigh (Mn) |
|------------------|-----------------------------|-----------------------------------------------|-------------------------------|----------------------|-------------------------------------|
| 2,2’-DBPEDF-II   | 140                         | 1288                                         | 9.2                           | 347                  | 3192.4                              |

3.3. **FTIR Spectra**
The FTIR spectrum of 2,2’-DBPEDF-II polymer shows a broad absorption band appeared in the region 3407cm\(^{-1}\) may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intermolecular hydrogen bonding. The peak, at 2922cm\(^{-1}\) indicate the presence of -NH stretching (imides). The peak at 1614cm\(^{-1}\) indicate the presence
of aromatic ring. The bands appeared at 1466 cm$^{-1}$ may be ascribed to methylene group. The band at 1076 cm$^{-1}$ indicates the presence of methylene bridge[13].

![Figure 4. FTIR Spectrum of 2,2'-DBPEDF-II polymer](image)

**Table 3. FTIR Data of 2,2'-DBPEDF-II Polymer**

| Obs. frequencies (cm$^{-1}$) | Assignment      | Exp. frequencies (cm$^{-1}$) |
|------------------------------|-----------------|------------------------------|
| 3407 (b, st)                 | - OH group      | 3200-3750                    |
| 2922(s)                      | -NH, Stretching | 3500-2800                    |
| 1614(s)                      | Aromatic ring   | 1600-1800                    |
| 1466(st)                     | -CH$_2$ Stretching | 1400-1550                   |
| 1076(s)                      | -CH$_2$ bridge  | 800-1150                     |

**3.4. Proton NMR Spectra**

Proton NMR Spectrum of the 2,2'-DBPEDF-II recorded in DMSO-$d_6$ (Fig. 5). The signal appearing at the region of 6.95 ($\delta$) ppm is due to hydroxyl proton. The signal appeared at 6.7 ppm is due to amino proton of -CH$_2$-NH-CH$_2$- group. Aromatic amine proton Ar-NH$_2$ gives singlet at 4.55 ppm. Proton of Ar-CH$_2$- linkage gives triplet at 4.1 ppm. A medium signal appeared at 3.66 ($\delta$) ppm may be assigned to methylene protons of Ar-CH$_2$N group and signal at 2.77 ($\delta$) ppm is proton of Ar-CH$_2$.

![Figure 5. NMR spectrum of polymer](image)
3.5. Surface Morphology
SEM gives information about the nature and surface morphology of the polymer. SEM images acquired in various amplifications for the of 2,2’-DBPEDF-II polymer are given in Fig. 6. The 2,2’-DBPFDF-II polymer shows spherulites with deep corrugation [16-17]. In the current case, the spherulites are mind boggling polycrystalline arrangement made out of most straight forward underlying equation having smoothest surface liberated from imperfections of development. Consequently, morphology show glasslike structure with profound folding which is obviously noticeable in SEM photos pitch. Accordingly, SEM study shows that 2,2’- DBPEDF-II polymer pitch has translucent and some formless nature.

![SEM images of 2,2’-DBPEDF-II polymer](image)

**Figure 6.** Morphology of 2,2’-DBPEDF-II polymer

3.6. PL Spectra of Polychelates
The visible spectrum in the PL- spectrum of co-ordination polymer of 2,2’-DBPEDF-II copolymer with Ni (II), Cu (II), Zn (II) metal ion are shown below in Fig.7, Fig.8 and Fig.9. A photoluminescence spectrum presented in Fig.7 represents emission band at a 470 nm for 2,2’- DBPEDF-II-Ni in the visible region. The intensity of this peak is found to be at 52 (a.u.). Fig.8 represents one emission band at 474 nm, along with blue colour for 2,2’DBPEDF-II - Cu polymer metal complex. It is to be observed that the intensity of this peak is found to be at 65. Another finding of Fig.9 shows the photoluminescence spectra of 2,2’-DBPEDF-II-Zn which is not able to emit any luminescence in the visible region. Fig.9 represents emission band at 470 nm along with blue colour it is to observed that intensity of this peak is found to be at 47.

Photoluminescence spectra of these coordination polymer demonstrate that produced substance has quality be used in the semiconductor devices. This shows that the synthesized coordination polymer can be used as photoluminescent material for various application & also as a supporting material for light emitting devices [18].
Figure 7. PL Spectra of 2,2'-DBPEDF-II-Ni polymer metal complex

Figure 8. PL Spectra of 2,2'-DBPEDF-II-Cu polymer metal complex
4. Conclusion

Polymer has been synthesized by polymerization technique using three monomers. Coordination polymers of copolymer with metal ions in the ratio 2:1 also been synthesized. These coordination polymers have been characterized by FTIR and proton NMR spectrum of the 2,2'-DBPEDF-II polymer. A basic and easy technique, to be specific, changed substance shower testimony (M-CBD), was used for the blend of new metal polymer buildings. Primary examinations indicated that these co appointment polymers have semi glasslike conduct. PL spectra of polymer metal buildings exhibit some quality to be utilized in the exploration of electronic gadgets and can be as photoluminescence material for strong state lighting application and furthermore as a supporting material for light producing gadgets.

5. References

[1] Singh I, Mathur P C, Bhatnagar P K, 2009 Int. J. Nanotechnol, 2 1
[2] Kar P, Pradhan C N, Adhikari B, 2010 Synth. Metal, 160 1524
[3] Date R W, Bruce D W, 2003 J. Am. Chem. Soc. 125 9
[4] Gurnule W B, Das N C, 2019 Materials Today Proceedings 15 611
[5] Kohad C G, Gurnule W B, 2019 Materials Today Proceedings 15 438
[6] Zang J, Xu L, Wong W Y, 2018 Coord. Chem. Rev. 355 180
[7] Seco J M, Antonio R D, Padro D, Gracia J A, Ucalde J M, 2017 Inorg. Chem. 56 (6) 3149
[8] Wang L, Zhu X, Wang W, Guo J, Li Z, 2005 J. Chem. Soc. Dalton Trans., 3235
[9] She B, Su Y, Zhang M H, Lu R, Zhao S, 2016 ACS Appl. Mater Interfaces, 8(17) 10717
[10] Jia W L, Mc-Cormick T. Tao Y, Lu J P, Wang S, 2005 Inorg. Chem., 44, 5706
[11] Bizzari C, Spuling E, Knol D M, Volz D, Brase S, 2018 Coord. Chem. Rev., 373 49
[12] Shrivastava A, 2018 Intro. Plst. Engg., 17
[13] Dhore M S, Zade A B, 2013, J. Eng. & Technoogy 2 (4) 2324
[14] Lusia R, Lecinia L G J, Adriana B, Claudia M G D, Paulo E A, Sofia M F, Hugh D, 2011 Dalton Trans, 40 11732
[15] J Khobragade J, Gurnule W B, Ahmed M, 2014 Rasayan J. Chem., 7(4) 413
[16] Singru R N, Gurnule W B, Khati V A, Zade A B, Dontulwar J R, 2010 Desalination 263(1-3)200
[17] Suzuki E, 2002 J. Microscopy 208 153
[18] Yang C, Luo J, Ma J, Lu M, Liang L, 2012 Dyes Pigm., 92 696

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