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SYNTHESIS, CHARACTERIZATION AND PHOTOLUMINESCENT STUDIES OF ORGANIC COPOLYMER DERIVED FROM 2, 2'-DIHYDROXYBIPHENYL AND PROPYLENEDIAMINE

S. S. Rahangdale[1], S. P. Chakole[2], K. S. Vajpai[3]and W. B. Gurnule[2]*

[1]Department of Chemistry, Jagat Arts, Commerce and IndirabenHariharbhai Patel Science College, Goregaon-441801, Maharashtra, India

*[2]Post Graduate Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur- 440024, Maharashtra, India.

[3]Department of Chemistry, Govt. Bilasa Girls P.G. College, Bilaspur-495001, Chattisgarh, India

Email: wbgurnule@gmail.com

Abstract :Copolymer (2,2'-BPPDF) synthesized by the condensation polymerization of 2,2'-dihydroxybiphenyl (BP), propylenediamine (PD) and formaldehyde (F) in acidic medium with molar proportion 3:1:5 of monomer and refluxing in oil bath at 120^0C for 5 hr. Assimilated copolymer as a ligand is joined with metal particles, for example, Ni^{2+}, Cu^{2+} and Zn^{2+} particles is in 2:1 molar extent to get metal complex. The response has been done with refluxed at 60^0C for three hour. Structure and composition of organic copolymer have been dictated by basic examination and sub-atomic weight assurance by non-aqueous conductometric titration. The UV-visible, FTIR, ^{1}H-NMR and surface morphologyas wellcrystalline nature of ligand and its complex were analysed by SEM. Newly integrated copolymer with complex with copper and zinc metal might be utilized as supporting material for luminescence 2,2'-BPPDF-Zn show higher photoluminescence than 2,2'-BPPDF-Cu.

Index Terms: Synthesis, condensation, propylenediamine, copolymer, photoluminescence, metalcomplex

I. INTRODUCTION

Great premium has been showed up in the blend and examination of coordination complex polymers containing N, S and O contributor molecules on polymeric interface. Lately, polymeric compounds have a great deal of thought and importance, in light of essential importance in ventures. The polymer can be used as colours, surface covering, retardants, glues, antibacterial, semiconductors, particle exchanger, rectifiers, battery-fueled, sparkle, etc. Electrical conductivity what's more, warm investigations of polymers is help for polymer researcher on account of congruity at raised temperature close to provokes that need to stand up to owing to suitable electrical conductivity, warm adequacy and low process ability. In relationship with comparable various teammates endeavoured to alter the warm strength by changing the monomer plan in polymer association [1-4]. The most late assessment progress in fluorescent polymers is revolved around the course of action and photoluminescence of fluorescent polymers with new designing various techniques for plan and mixture of fluorescent materials have furthermore been made. Natural polymer which shows fluorescence can be joined by polymerization of beginning monomers, using fluorescent blends as initiator fluorescent blends as chain move expert's material holding between fluorescent social occasions furthermore, copolymers and polymerization of nonfluorescent monomers [5].

Photo luminescent supra sub-atomic design has as of late pulled in much interest due to their possible applications in photo electronic gadgets or as fluorescence sensors and tests. Polymers have begun to discover use in making LEDs, fluid gems and as sensors for metal particle fighting specialists, microbes and biomolecules. A large portion of the photoluminescent materials are pi-formed semiconducting materials much interest is being displayed in the blend and investigation of the design property relationship of pi formed polymers because of fundamental significance in electrical enterprises. Coordination blends are spellbinding class of particles that have wide applications in various fields, for instance, light delivering diodes (LEDs), follow metal examination, metal hailing, plan of optical devices and sensor particles. When contrasted with blue, green and red radiant buildings most stable brilliant complex is blue which is valuable for electroluminescent shows [6,7]. LECs, supra sub-atomic gatherings, sunlight based energy change conspire [8], organic testing and oxygen detecting [9,10]. Radiant coordination polymers are at this point tolerating a great deal of thought as a result of their normal applications in various fields, for instance, normal light transmitting diodes [11].

The current review manages the synthesis, characterizationand photoluminescence property of copolymer resulting from 2,2'-dihydroxybiphenyl, propylenediamine and formaldehyde which have yet not been accounted for so far in writing.

2. Materials and Methods:

2,2'- dihydroxybiphenyl and propylenediamine utilized in the current examination of insightful grade immaculateness were bought from Sigma Aldrich Chemicals. Formaldehyde (37%), cupric nitrate, nickel nitrate, zinc nitrate.

2.1. Synthesis of Copolymer

2,2'-BPPDF copolymer was ready by gathering 2, 2'-dihydroxybiphenyl (BP), propylenediamine (PD) and formaldehyde (F) within the sight of 2M Hydrochloric acid as an impetus in 3:1:5 molar extents at temperature 120°C in an oil bath with intermittent shaking, to guarantee exhaustive blending, for about 5hrs. The orange coloured hued product was obtained. The item acquired was washed with hot distilled water and methanol to eliminate the overabundance of biphenyl-formaldehyde copolymer which may be available alongside 2, 2'-BPPDF copolymer. The appropriately washed copolymer was dried, powdered and afterward extricated with diethyl ether and afterward with emollient ether. The orange earthy coloured shading resinous item was quickly eliminated from theflagon when response period was finished and afterward cleansed. The response and recommended structure of 2, 2'- BPPDF is displayed in Fig. 1

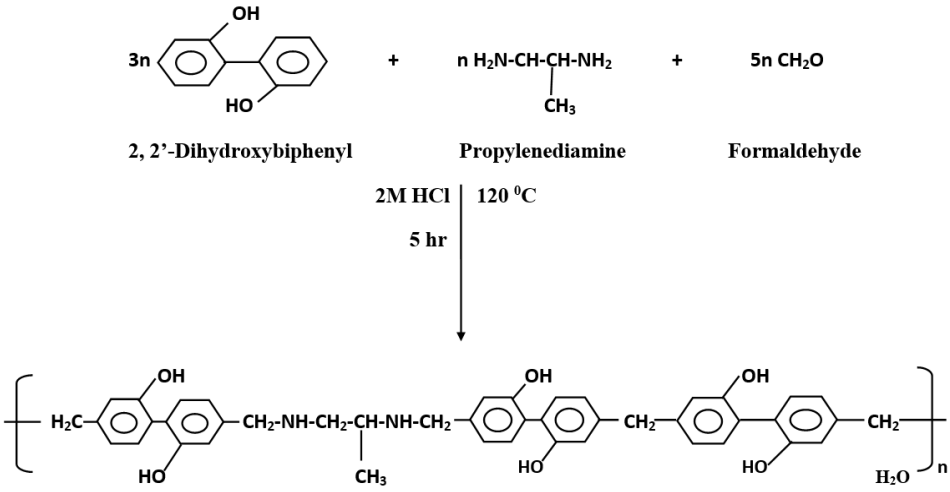
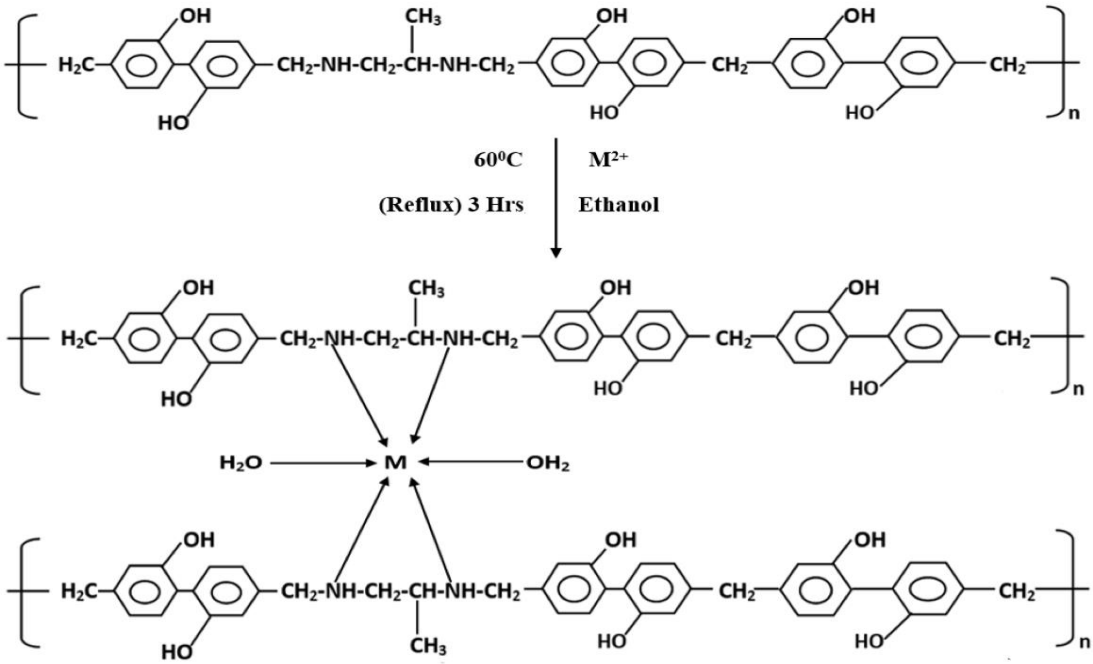


Figure 1.Chemical Structure of 2,2'-BPPDF Copolymer

Synthesis of 2, 2'-BPPDF Copolymer Metal Complexes

The copolymer metal complexes have been arranged utilizing the integrated copolymer as ligand with three change metal particles for example Cu^{2+}, Ni^{2+} and Zn^{2+} particles the copolymer taken in 2M and he change metal particles (Cu^{2+} Ni^{2+} and Zn^{2+}) was taken in 1M for the perplexing development response. The 2,2'- BPPDF copolymer (2g) was taken in round base flask and submerged in ethanol answer for permit it for expanding in 2h. The Copper nitrate (1g) was break up in ethanol arrangement and then, at that point filled round base flask with prepared mechanical stirrer and a refluxed condenser. The response has been completed with a compelling reflux at 60^0C for 3 hrs. The colloidal encourage was seen in the cup and separate out. The item was separated off and washed with ether and ethanol to eliminate pollutions. The resultant purified test was dried, powdered and in vacuum desiccator with silica gel. A similar technique was likewise followed for the arrangement of 2, 2'-BPPDF complexes with Ni^{2+} and Zn^{2+} metal particle. The plan of readiness of the 2, 2'-BPPDF edifices with Cu (II), Ni (II) and Zn (II) metal particle as displayed in Fig.2.



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

Figure 2.Synthesis of 2, 2'-BPPDF Copolymer metal complex.

3. Characterization of Copolymer

Recently integrated and filtered copolymer was exposed to natural investigation for carbon, hydrogen, nitrogen, on Perkin Elmer 2400 Elemental Analyzer instrument and bright noticeable spectra of copolymer in dimethyl sulfoxide (DMSO) dissolvable recorded on Varian Carry 5000 UV-Visible spectrophotometer in the reach from 200 to 800nm. An infra-red range of copolymer gum was recorded on Perkin-Elmer-983 spectrophotometer in KBr beds in the reach from of 4000 - 400 cm^{-1} Spectrophotometer,^{1}H-NMR and study was acted in DMSO as dissolvable on Bruker Advance-II 400 NMR spectrophotometer at Sophisticated Test and Instrumentation Centre Cochin, University of Science and Technology, Cochin. The photoluminescence properties of recently combined copolymer metal complex examples were recorded on RF-501 (PC) S CE (LVD) Model. SEM was utilized to set up the surface morphology and nature of the copolymer.

3.1 ConductometricTitraion

Sub-atomic weight($\overline{Mn}$) ofcopolymer was constrained by non-aqueous conductometric titration strategy by utilizing ethanolic KOH as a titrant. The level of polymerization and sub-atomic weight ($\overline{Mn}$)of the polymer have been settled using the condition. This perception is in acceptable concurrence with the pattern seen by before laborers [12].

$$(\overline{DP}) = \frac{\text{Total milliequivalents of base required for complete neutralization}}{\text{Milliequi,of base required for smallest interval}}$$

$(\overline{Mn})$ = $(\overline{DP})$ X weight of repeating unit (monomer)

3.2 Theoretical Consideration for Photoluminescence Study

Photoluminescence is emanation of light from a material that has retained light energy. In this interaction, the materials electrons are elevated to invigorated state by retaining photon of light energy. The transmitted light is the consequence of those electrons which unwind back to the ground state by radiating photons. Both the frequency of light needed to cause photoluminescence and the wave length of lightemitted relies upon the energy distinction between ground state and invigorated state electrons for example the band hole energy is a critical boundary in photoluminescence. The relationship among energy and frequency is given by

$E = hc/\lambda$

Where, h is Planks steady

c is the speed of light

λ is the frequency of light

4. Results and Discussion

4.1 Elemental Analysis

2, 2'- BPPDF copolymer was examined for the C, H and N content. Experimental equation of copolymer has been proposed and organized in Table 1. The synthesis of copolymer acquired was observed to be in acceptable connection.

Table 1. Elemental analysis and empirical formula of copolymer

Copolymer	Percentage C Found (cal.)	Percentage H Found (cal.)	Percentage N Found (cal.)	Percentage O Found (cal.)	Empirical formula	Formula weight
2,2'-BPPDF	76.10 (76.08)	6.12 (6.05)	3.98 (4.04)	13.80 13.83	$C_{44}H_{42}O_{06}N_2.H_2O$	712

4.2 NonaqueousConductometric Titration Method

Atomic load of recommended polymer has been dictated by this strategy in DMSO dissolvable. A chart is plotted between explicit conductance and milliequivalents of ethanolic KOH needed for balance of 100g every copolymer. Atomic weight($\overline{Mn}$)of copolymer could be obtained by increasing the normal level of polymerization ($\overline{DP}$) by recipe weight of rehashing unit. It is seen that the atomic load of polymer ascends with the ascent in ethylenediamine. The bend acquired is displayed in figure 3 and informations are classified in table 2.

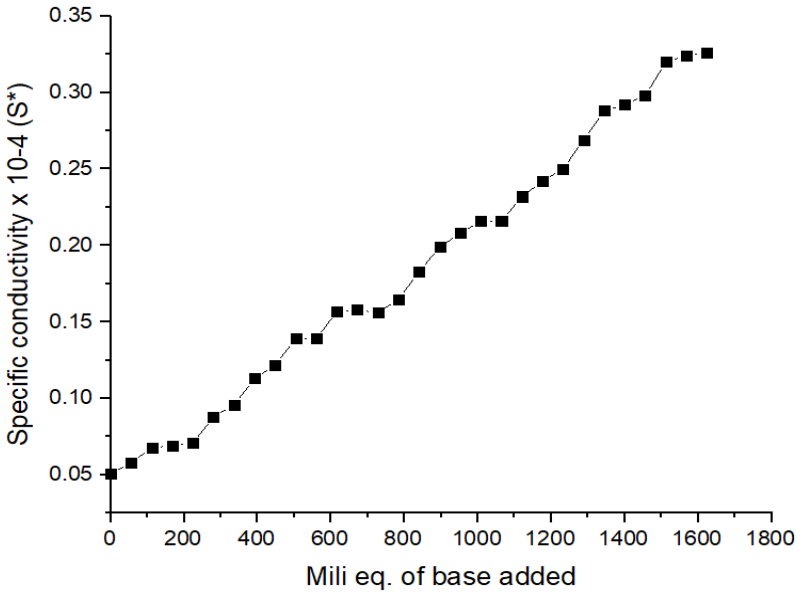


Figure 3. Titration curve of 2,2'-BPPDF copolymer

Table 2. Molecular weight determination of 2,2'-BPPDF copolymer

Copolymer	1st phase of neutralisation	Final stage of neutralisation (Meq/100g sample)	Degree of polymerization ($\overline{DP}$)	Empirical weight (g)	Number average molecular weight($\overline{Mn}$)
2,2'-BPPDF	110	1512	13.75	712	9790

4.3 FTIR Spectra

The FTIR range of 2, 2'-BPPDF copolymer shows a wide retention band showed up in the district 3446cm^{-1} might be relegated to the extending vibrations of phenolic hydroxyl (-OH group) bunches showing intermolecular hydrogen holding. The top, at 1564.27cm^{-1} demonstrate the presence of - NH extending (imides). The top at 1450cm^{-1} demonstrate the presenceof sweet-smelling ring. The groups showed up at 1388cm^{-1} might be credited to methylene bunch. The band at 1076cm^{-1} shows the presence of methylene bridge[13].The 2,4,2',4' substitution of aromatic benzene ring recognized by the medium / weak absorption bands appeared at 756-758, 815-817, 929-960 and 1093-1099 cm^{-1} respectively [14]

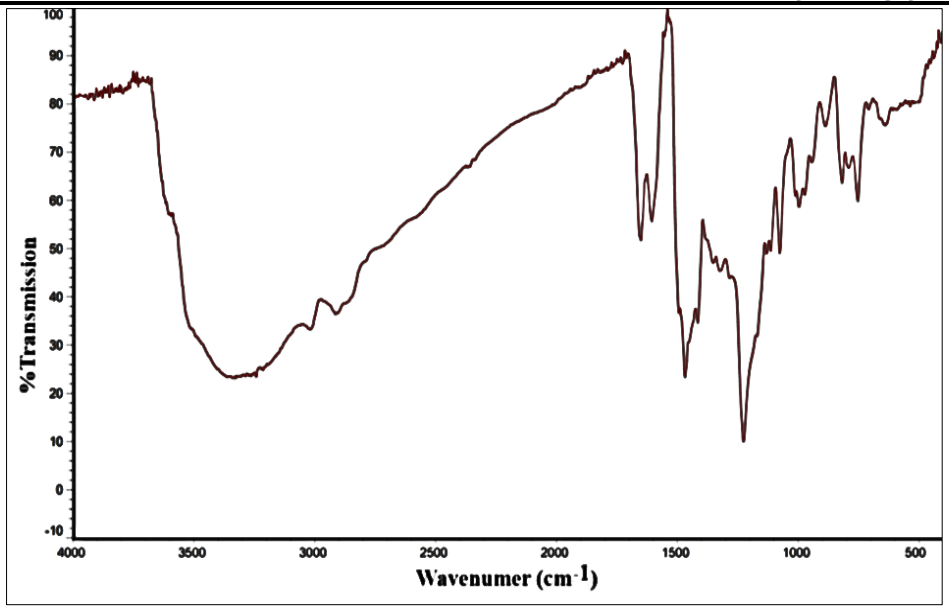


Figure 4. FTIR Spectrum of 2, 2'-BPPDF copolymer

Table 3. FTIR Data of 2, 2'-BPPDF copolymer

Obs. frequencies (cm^{-1})	**Assignment**	**Exp. frequencies (cm^{-1})**
3446 (b)	-OH Intermolecular H-bonding	3400-3200
2947.23 (w)	CH_2 linkage	2860- 2950
1564.27 (m)	NH bending	1540-1950
1450 (sh, m)	Aromatic ring Substituted	1600-1450
1388 (sh, m)	CH_2 methylene bridge	1390-1270
1288 (m)	C-N stretching (Ar-NH)	1200-1500
758 (m)	2, 4, 2', 4'-Substitution in benzene skeleton	750-800
815 (m)		800-840
960 (m)		940-970
1099 (m)		1098-1050

4.4^{1}H NMR Spectra

^{1}H NMR Spectrum of the 2, 2'-BPPDF recorded in DMSO-d6 (Fig. 5). The sign showing up at the district of 8.27 (δ) ppm is because of hydroxyl proton. The sign showed up at 4.98 ppm is because of amino proton of - CH_2-NH-CH_2-bunch. Sweet-smelling amine proton Ar-NH_2 gives singlet at 7.88 ppm. Proton of Ar-CH_2-linkage gives trio at 2.41 ppm. A medium sign showed up at 3.65 (δ) ppm might be allocated to methylene protons of Ar-CH_2N gathering and sign at 2.77 (δ) ppm is proton of Ar-CH_2 [15-17].

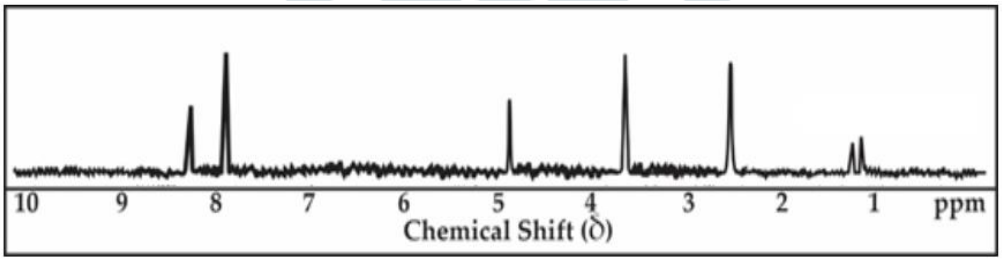


Figure 5. NMR spectrum of copolymer

Table-4: ^{1}H-NMR spectral data of 2, 2'-BPPDF copolymer

Chemical Shift (δ) ppm of 2,2'-BPPDF	Nature of proton assigned	Expected chemical shift
8.27	Proton of -OH group	7.5-8.5
4.98	proton of -NH linkage	4.0-8.0
7.88	Aromatic proton (unsymm. Pattern)	6.5-8.5
3.65	Methylene proton of Ar - CH_2 - N - linkage	3-5.5
2.41-2.51	Methylene proton of Ar - CH_2 - Ar linkage	1.5-5.5

4.5 Scanning Electron Microscopy (SEM)

Surface investigation discovered incredible use in understanding the surface provisions of the materials. The SEM photos got in various amplifications for 2, 2'-BPPDF copolymer tar are displayed in Fig. 5. It demonstrates that the 2, 2'-BPPDF copolymer shows spherulites with profound groove [18]. Spherulites are regular translucent arrangement and they fill in high gooey and concentrated arrangement. In the current case, the spherulites are mind boggling polycrystalline arrangement made out of easiest primary equation having smoothest surface free from deformities of development. The precious stones are more modest in surface region with less firmly stuffed structure. Hence, the spherulites morphology of copolymer show translucent design of pitch with profound groove which is plainly noticeable in SEM photos of pitch. These confirmations demonstrate that pretty much the sap shows formless person with less close stuffed surface having profound pits. In this manner, SEM concentrate on shows that 2,2'-BPPDF copolymer has glasslike and a few undefined characters. Hence, it has the progress structure among translucent and formless.

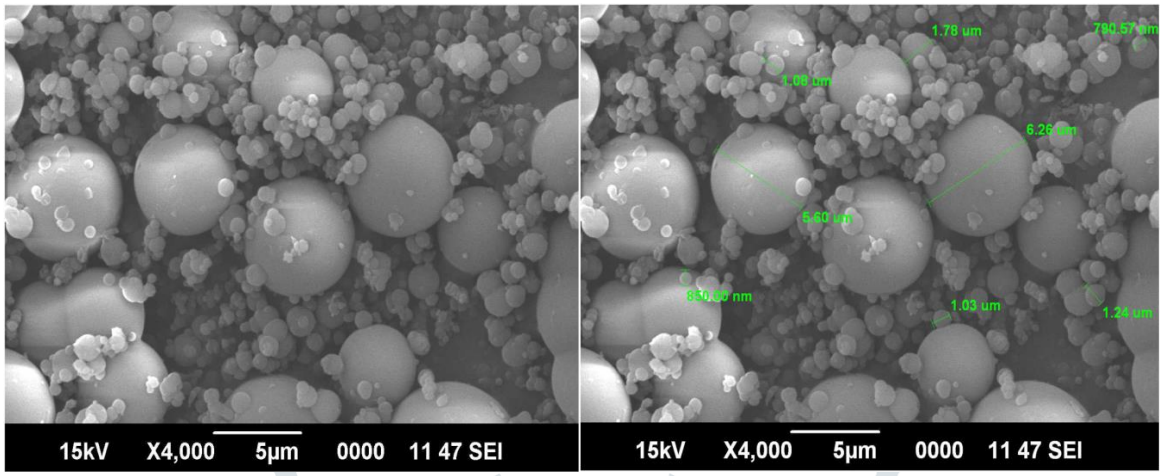


Figure 6.Surface Morphology of 2,2'-BPPDF copolymer

4.6 PL Spectra of complexes

The apparent range in the PL-range of co-appointment polymer of 2, 2'-BPPDF copolymer with Ni (II), Cu (II), Zn (II) metal particle are displayed underneath in Fig.7, Fig.8 and Fig.9. A photoluminescence range introduced in Fig.7 addresses on discharge band at a 436 nm for 2, 2'-BPPDF-Ni in the apparent locale. The power of this pinnacle is observed to be at 52 (a.u.). Fig.8 addresses one discharge band at 444 nm, alongside blue tone for 2, 2'-BPPDF-Zn polymer metal complex. It is to be noticed that the power of this pinnacle is observed to be at 65. One more finding of Fig.9 shows the photoluminescence spectra of 2, 2'-BPPDF-Cu which can't discharge any radiance in the apparent area. Fig.9 addresses discharge band at 410 nm alongside blue shading it is to seen that force of this pinnacle is observed to be at 47. Photoluminescence spectra of these coordination polymer show that delivered substance has quality be utilized in the semiconductor gadgets[18]. This shows that the combined coordination polymer can be utilized as photoluminescent material for different application and additionally as a supporting material for light discharging gadgets [19-21].

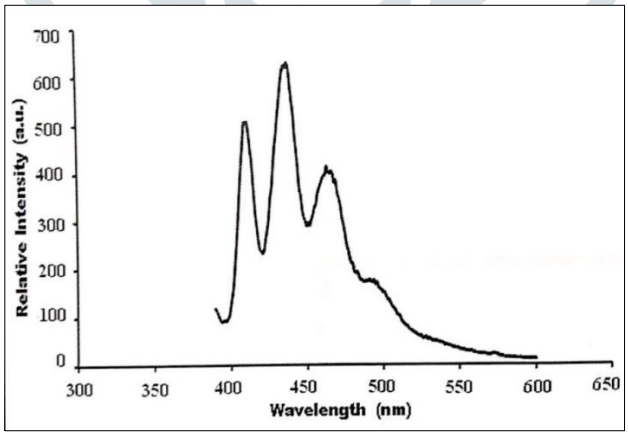


Figure7. PL Spectra of 2, 2'- BPPDF –Ni Copolymer Metal Complex

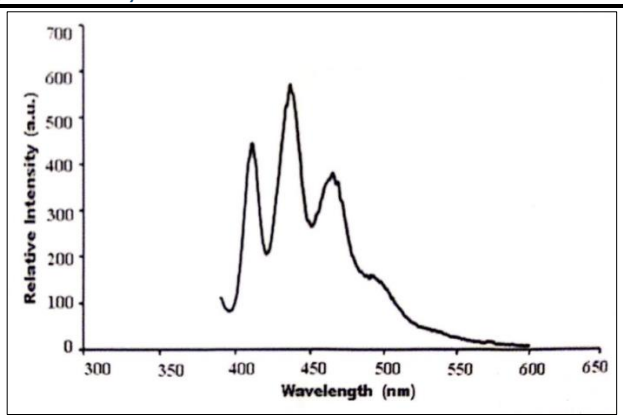


Figure8. PL Spectra of 2, 2'- BPPDF –ZnCopolymer Metal Complex

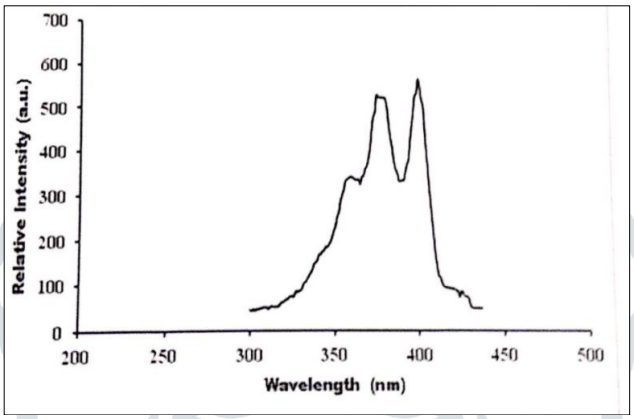


Figure9. PL Spectra of 2, 2'- BPPDF –CuCopolymer Metal Complex

Conclusions

Copolymer has been incorporated by polymerization procedure utilizing three monomers. Coordination polymers of copolymer with metal particles in the proportion 2:1 likewise been incorporated. These coordination polymers have been described by FTIR and proton NMR range of the 2,2'- BPPDF copolymer. A fundamental and straightforwardness method, to be explicit, changed substance shower declaration (M-CBD), was utilized for the mix of new metal polymer structures. Essential assessments showed that these co arrangement polymers have semi glasslike direct. PL spectra of polymer metal structures show some quality to be used in the investigation of electronic contraptions and can be as photoluminescence material for solid state lighting application and besides as a supporting material for light delivering gadgets.

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