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Photoluminescence studies of copolymer metal complexes with 8-hydroxyquinoline, hexamethylenediamine and formaldehyde

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ABSTRACT

This current research article provides the information on the synthesis of 8-HQHMDAF resinous copolymer and co-polymeric metal complexes prepared from it. 8-HQHMDAF resinous copolymer was incorporated with formaldehyde through refluxed-condensation of 8-hydroxyquinoline and 1, 6-diamino hexane in fixed molar ratio for 5 hrs using two molar acidic catalyst that is hydrochloride. Reaction maintained at 124 ± 2 ^{0}C constant temperatures. The newly developed copolymer 8-HQHMDAF resin functioned as ligands to form co-ordination polymer complex in a molar ratio of 2:1 with three transition metal ions Cu^{2+}, Ni^{2+} and Zn^{2+}. The reaction conducted for 3hrs with an efficient reflux maintained at 60 °C temp. Elemental composition of 8-HQHMDAF-M copolymeric metal complexes was analyzed by elemental analysis method. FT-IR and ^{1}H NMR Spectroscopic technique describe the structure of 8-HQHMDAF-M complex. The photoluminescence properties of newly synthesized copolymer metal complex samples were recorded on RF-501 (PC) S CE (LVD) MODEL PL spectrometer is used to records the photoluminescence spectra of synthesized copolymer metal complexes of three transition metal ion. Aim of the whole current study is the development new polymeric metal complexes to investigate its photo luminescent property and significant contributions from active researchers in the field.

Selection and peer-review under responsibility of the scientific committee of the International Conference on Advanced Functional Materials (Innovations in Chemical, Physical and Biological Sciences).

1. Introduction

Photoluminescence often referred (PL) spectroscopy is effective tool commonly used to classify and detect structures, to analyze optical properties electronic structure, semi-insulated and semiconductor structures. Emission of light radiation from a material that has absorbed light energy is called photoluminescence. In this process, energy is supplied externally in the form of light energy; the electrons of a material absorb light of suitable wavelength gets excited, promoted to higher energy states. Electrons of this excited molecules or material will give out light energy to go back to ground state. The energy difference between the ground and excited electron is also known as the band gap is the main factor which decides the wavelength of light needed to induce phenomenon of photoluminescence.

Advances in field of coordination compound gives idea that copolymer metal complexes are an interesting category of molecules with wide-ranging uses in many fields including light emitting diodes (LED 'S), trace metal processing, metal sensing, solar cells, solid state lighting, plasma display, optical system architecture, bio marker and sensor molecules, [1]. They're just green conscious, affordable, fascinating forms of coordination, and shows excellent luminescent properties. Between green, blue and red, stable blue luminescent complexes indeed uncommon, effective for electroluminescent displays, are still uncommon [2]. Because of the need for responsive and versatile chemo sensors for in vivo and in vitro applications, the design and preparation of blue luminescent transition metal complexes seems to be a very important field of research in recent years [3,4]. Luminescent copolymer metal complexes are at present attracting significant interest because of their future applications Because of their possible applications in diverse area such as organic light-emitting diodes (OLEDs) [5], light-emitting electrochemical cells (LECs), supramolecular frameworks, chemical sensors, solar energy transformation schemes [6], biological

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processing and oxygen signaling, luminescent copolymer metal complexes are presently gaining considerable interest.

Recent work in field of luminescence polymeric material Shows that several of these complexes were observed to be luminescent and that their emission activity differs with the frameworks and the steric properties of coordinated ligands [7]. Michael K Danquah and co-workers [8] prove persistent porosity plays an important role in fluorescent-polymer. A porous beta cyclodextrin-based terpolymer fluorescence sensor was designed for identification of Trinitrophenol in situ. Yanyan Zhang, Xiaohong Guo with his coworker established an effective, simple and direct and green procedure for preparing highly luminescent water soluble Ag nanoclusters for convertible temperature and pH nano-sensors [9]. A novel amorphous poly acrylamide copolymer is synthesized by Fan Gu, Chengjie Zhang, and Xiang Ma [10] which is capable of emitting fluorescence with tuneable colour including white light. J. Solanki and K. Surati, reported the synthesis, characterization and photoluminescence properties of heteroleptic Zn (II) complexes [11]. D. Singh, V. Nishal, and his colleagues also reported the luminescence properties of metal complexes prepared from 8-hydroxy quinoline [12]. W. B. Gurnule and co-workers also reported the synthesis of copolymer metal complexes using 8-hydroxyquinoline 5-sulphonic acid and studied their photoluminescence behaviour [13,14,15].

2. Materials and methods

2.1. Chemicals

The monomers utilized during synthesis are 8-hydroxyquinoline; hexamethylene diamine and formaldehyde were of AR grade purchased from centre scientific company Nagpur, India. Metals ions used for complexation that are zinc nitrate, cupric nitrate, nickel nitrate, and other chemical such as Hydrochloride become available from Kamla Nehru Mahavidyalaya (Post Graduate Department of chemistry, Nagpur, India).

2.2. Method for synthesis of copolymer (8-HQHMDAF) metal complex

8-HQHMDAF Copolymer resin which act as ligand in complex formation procedure has been prepare by refluxed-condensation of monomers for 5 hrs maintained at 124 ± 2°C constant temperature. Monomers which are used are 8-hydroxyquinoline, hexamethylene diamine with formaldehyde in 1:1:2 M reactant concentrations. 2 M acid hydrochoride is required for polymerization catalyst. Newly developed copolymer 8-HQHMDAF resin functioned as ligand to form co-ordination polymer with three transition metal ion Cu^{2+}, Ni^{2+} and Zn^{2+} ions. 2 M 8-HQHMDAF copolymer was taken and 1 M transition metal ions (Cu^{2+}, Ni^{2+} and Zn^{2+}) was taken which means reactant are in 2:1 M proportions for the copolymer complex formation reaction. A weighed amount of polymer sample (2 g) was dissolved in ethanol solvent in round bottom (RB) flask and set aside for 2 h to allow it to swell. 1 g of zinc nitrate was weighed and dissolves in ethyl alcohol in separate beaker and gradually added to RB flask containing polymer. RB flask is installed with a reflux condenser and equipped mechanical stirrer kept in oil bath. The complexation reaction has proceeds with occasional shaking to make sure rigorous mixing. Temperature was maintained at 60 °C up to 3 hrs with appropriate reflux. Final product settled at bottom of the RB flask was observed. Precipitate were separated and filtered. To remove the impurities it is washed with ether then ethyl alcohol. For obtained final purified copolymer metal complex repeated purification has

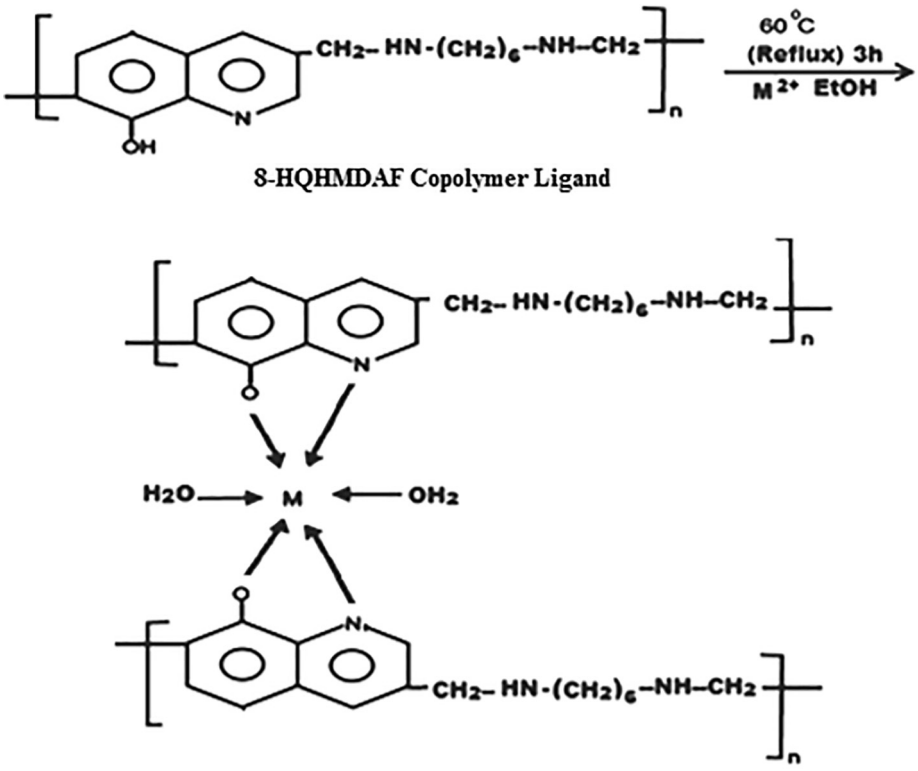

Fig. 1. Synthesis of 8-HQHMDAF-M copolymer metal complexes.

Table 1
Yield and melting point for 8-HQHMDAF-M copolymer metal complexes.

Copolymer metal complexes	Yield (%)	Melting point(K)
8-HQHMDAF-Zn	80.90	445–450
8-HQHMDAF-Cu	79.00	410–415
8-HQHMDAF-Ni	76.24	422–430

been processed. The final purified copolymer metal complex was dried in air to remove moisture, ground in to fine powdered form and placed in vacuum desiccators with silica gel. The above mentioned synthesis process was applied for the production of remaining copolymer complexes with Cu^{2+} and Ni^{2+} transition metal ion. The reaction scheme and possible structure of the 8-HQHMDAF-M co-ordination polymer with three transition metal ions Cu^{2+}, Ni^{2+} and Zn^{2+} is represented into Fig. 1.

3. Characterization

Characterization of copolymer metal complex is done with variety of experimental approaches. Physicochemical approaches and spectroscopic techniques applied for molecular characterization for polymeric metal complex. 8-HQHMDAF-M copolymer metal complex prepared using three transition metal ion Cu^{2+}, Ni^{2+} and Zn^{2+} ions. Products found to be greenish to yellowish in colour. Solubility behaviour shows that some copolymer metal complexes are soluble and some are partially dissolves in solvents like THF, HCl, DMSO and DMF while in all other organic solvents are largely insoluble. The yields for the copolymer metal complex and melting point for 8-HQHMDAF-M copolymer metal complex were presented in following Table 1.

4. Results and discussion

4.1. Elemental study

Elemental examination is a technique which decides the elemental composition (normally a weight percent of CHNX) in compound product. Microanalysis of of all 8-HQHMDAF-M copolymeric metal complexes with Cu^{2+}, Ni^{2+} and Zn^{2+} metal ion for carbon, hydrogen, nitrogen and metal component were carried out. The findings reported were considered to be in clear agreement for the measured values. The empirical weight of a single repeated component was determined from the empirical formulation. The quantity of metal ions present in the metal complexes suggests 1:2 M/L stoichiometry from the experimental results,

Table 2
Elemental description and empirical formulation for 8-HQHMDAF-M copolymer metal complex.

Copolymer metal complex	C % observed (cal.)	H % observed (cal.)	N % observed (cal.)	M % observed (cal.)	EmpiricalFormula for repeating unit	Formula Weight for repeating unit
8-HQHMDAF-Zn	66.39 (66.36)	7.15 (7.17)	12.51 (12.55)	9.73 (9.77)	$C_{34}H_{48}N_6O_4$. Zn	669.400
8-HQHMDAF-Cu	66.63 (66.51)	7.15 (7.19)	12.62 (12.58)	9.56 (9.51)	$C_{34}H_{48}N_6O_4$.Cu	667.546
8-HQHMDAF-Ni	66.96 (66.99)	7.18 (7.24)	12.63 (12.67)	8.82 (8.85)	$C_{34}H_{48}N_6O_4$. Ni	662.690

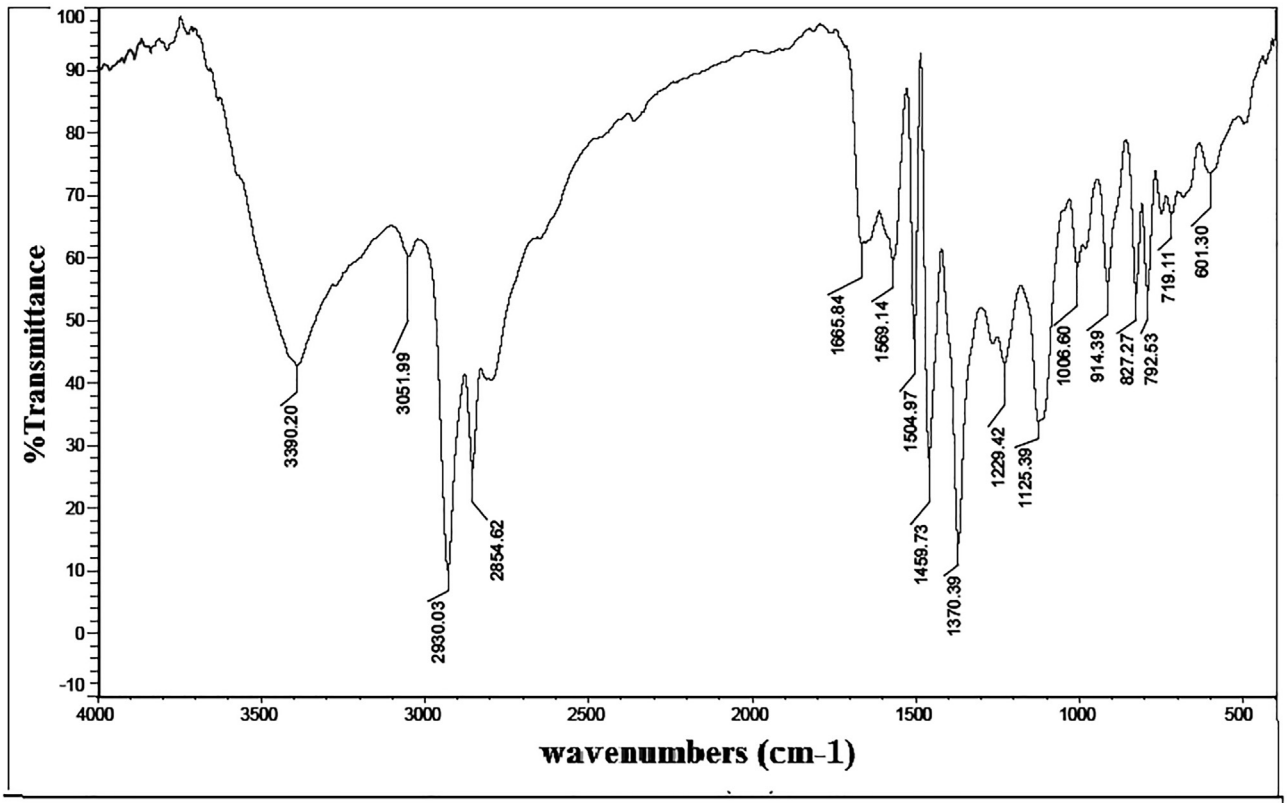

Fig. 2. FT-IR spectra of 8-HQHMDAF-Zn copolymer metal complex.

Table 3
FTIR spectral data of 8-HQHMDAF-M copolymer metal complex.

Assignment	Observed Frequencies cm^{-1}		
	8-HQHMDAF-Zn	8-HQHMDAF-Cu	8-HQHMDAF-Ni
C–H (stretching in ring)	3056(w)	3054(w)	3055(w)
C = N (quinoline ring)	1579(b)	1578(b)	1578(b)
$–CH_2$ (methylene bridge)	1374(sh,m)	1372(sh,m)	1372(m sh)
C–H (bending in $–CH_2$ group)	1464 (m)	1465 (m)	1464 (m)
>C-O (phenolic stretching)	1240(w)	1241(w)	1241(w)
>NH (stretching bridge)	2936(w)	2935(w)	2936(w)
2,3,5,8 substitution in ring	793,1042,1121,1223	794, 1046, 1119,1224	796, 1045, 1120,1224
O → M	601	544	560
N → M	515	463	480

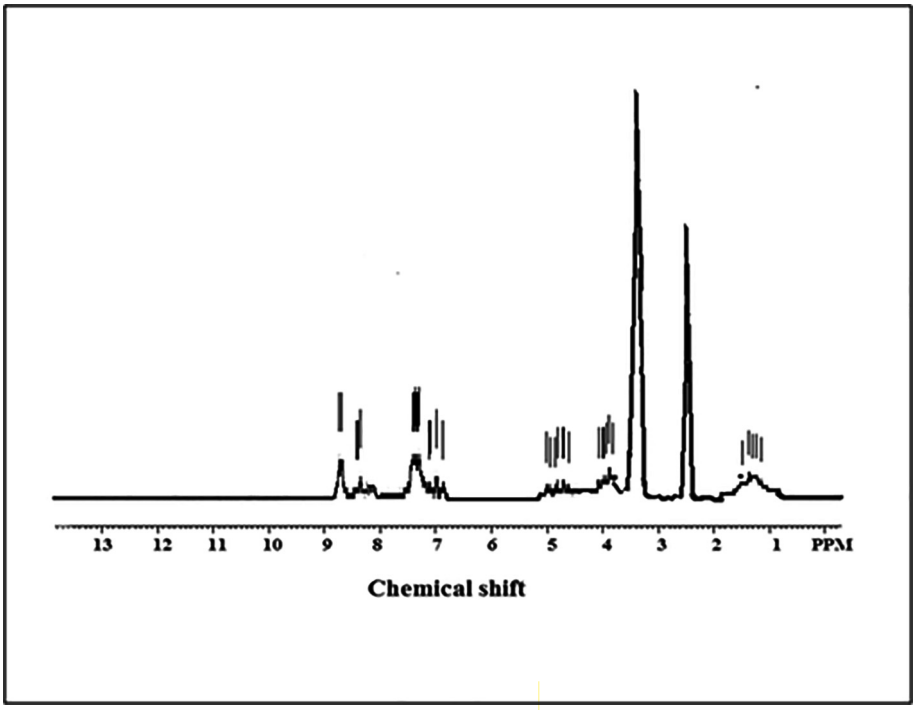

Fig. 3. Proton NMR study of 8-HQHMDAF-Zn copolymer metal complex.

which implies six coordination that included two coordinated water molecules for complexes 8-HQHMDAF-Cu; 8-HQHMDAF-Ni and 8-HQHMDAF-Zn. Analytical data for all 8-HQHMDAF-M copolymer metal complexes are presented within Table 2.

4.2. FT-IR spectra

In FTIR spectra of metal complexes of Zn (II) are given in Fig. 2. It shows that compared with the co-polymeric ligands metal complexes gives significantly extended signals. In the spectrum for polymeric metal complexes, bands corresponding to –C-N-C stretching vibration found in range of 1569 cm^{-1} is moved to the higher frequency region (1598 cm^{-1}) which indicates the coordination of the aromatic (C- N) group's nitrogen atom with metal ion present in center. Band corresponds to phenolic –OH not found in complex. Sharp band appearing compared to ligand in region 3430 cm^{-1} assigned to –OH group may be due to coordination of water molecule. Band at 3056 cm^{-1} shows C–H stretching in ring. Sharp medium peak at1374 cm^{-1} may be ascribed to $–CH_2$ methylene bridge in copolymer. Absorption signals corresponding to (C-O) of the phenolics stretching have been found in the region at (1232) cm^{-1} moved to lesser frequency (1217) cm^{-1}, signifying the chance of coordination of oxygen atom of phenolics, attached to quinoline ring with metal ion. Above data clearly indicates the involvement of oxygen and nitrogen atoms in the complexation. This is again explained by the presence of signals around (463–515) cm^{-1} and (544–601) cm^{-1} corresponds to (M−N) and (M−O) respectively. FTIR spectra for Cu (II) and (Ni II) are nearly similar. Data for all three copolymer metal complexes are represented in Table 3.

4.3. NMR spectra

8-HQHMDAF-Zn copolymer metal complex gives NMR (^1H) graph because of d^9 along with d^8 configuration. ^1H NMR analysis for copolymer metal complexes with Cu^{2+} and Ni^{2+} ions are more challenging than Zn and reported to justify linkages of the structure proposed. Proton NMR study of copolymer metal complex 8-HQHMDAF-Zn are presented in Fig. 3. Proton NMR spectra of copolymer resins 8-HQHMDAF shows pinnacle in 8.35 δ ppm region corresponds to phenolic (–OH) proton attached to quinoline ring. Because of intra-molecular hydrogen interaction in quinoline ring signals shifted to slightly downfield. In copolymer metal complex 8-HQHMDAF-Zn, the signal indication at 8.45 δ ppm region in

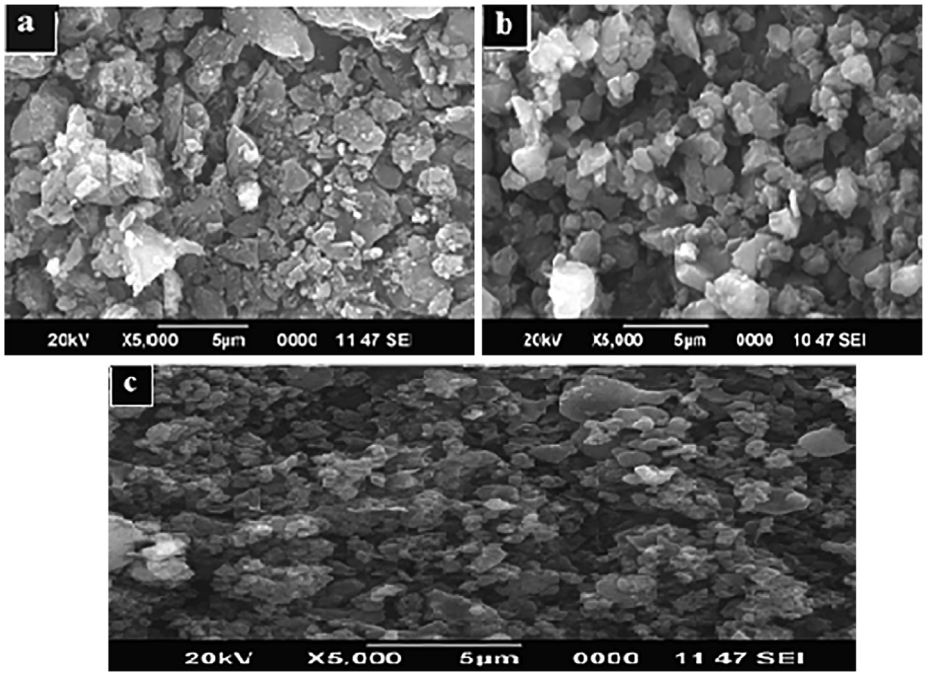

Fig. 4. (a): SEM Images of 8-HQHMDAF-Cu. (b): SEM Images of 8-HQHMDAF-Ni, (c): SEM Images of 8-HQHMDAF-Zn.

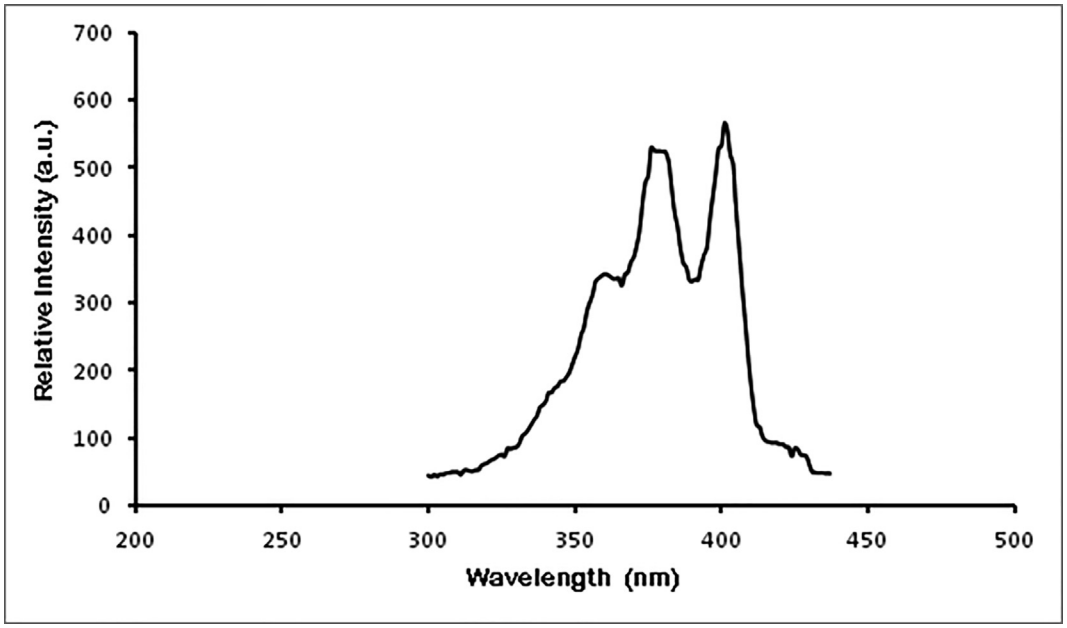

Fig. 5. PL Spectra 8-HQHMDAF-Cu copolymer metal complex.

ligand is ascribe to phenolic group is completely vanished. It provides strong indication that metal ion bond formation with ligand takes place via oxygen atom in –OH group of quinoline ring. All aromatic quinoline ring proton gives poor asymmetrical multiplate type signal in the area 6.34 δ ppm. A modest singlet signal given in range 3.83 δ ppm allocated for protons of methelenic bridge (Ar-CH_2-N) category. Triplets in 9.12 δ ppm region can assigned for proton of –SO_3H group. In metal complex as the nitrogen atom deactivates the pyridine ring, of quinoline ring hence all aromatic protons signals of ring are slightly shifted to upfield δ ppm indicates Zn–N bond formation. Proton NMR spectra of copolymer resins 8-HQHMDAF-Zn are presented in Figs. 3 & 4.

4.4. Surface analysis

The SEM analysis has provided great application in characterization, recognizing surface properties, and particle size of material. The morphology of all the 8-HQHMDAF-M copolymer metal complexes was analyzed by scanning electron micrographs Scanning electron microscope Joel 6390 LV at STIC, Cochin at different magnification. SEM study for 8-HQHMDAF-M copolymer metal complexes shows somewhat distinct morphology from its coordinating ligand. The SEM photograph represent coarse, firm with closely packed arrangement on surface. The voids which observed on ligands surface were absent on surface of copolymer

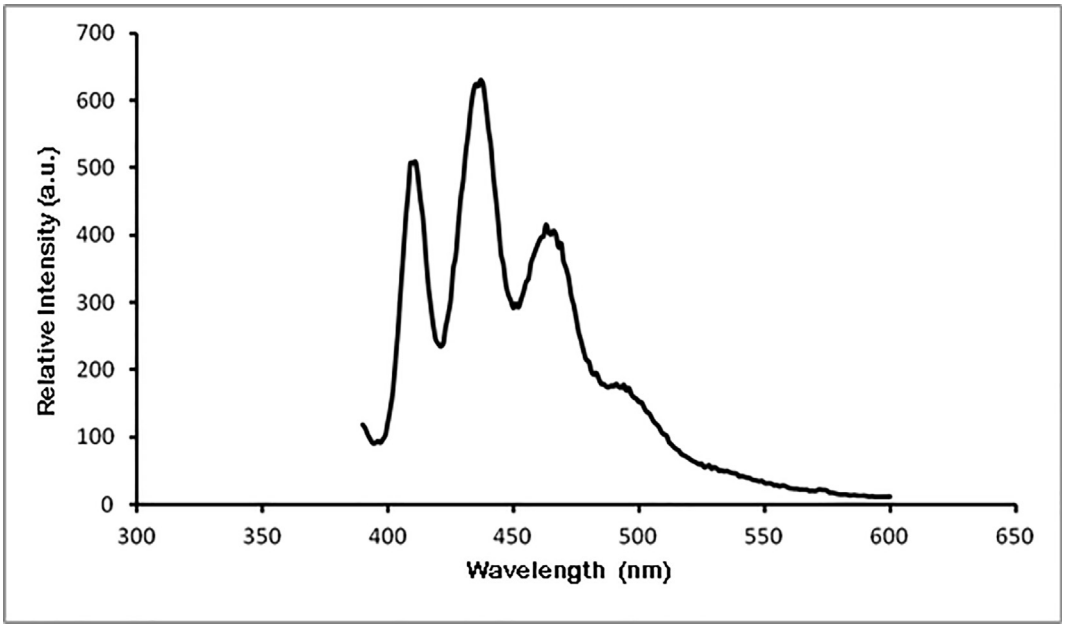

Fig. 6. PL Spectra 8-HQHMDAF–Zn copolymer metal complex.

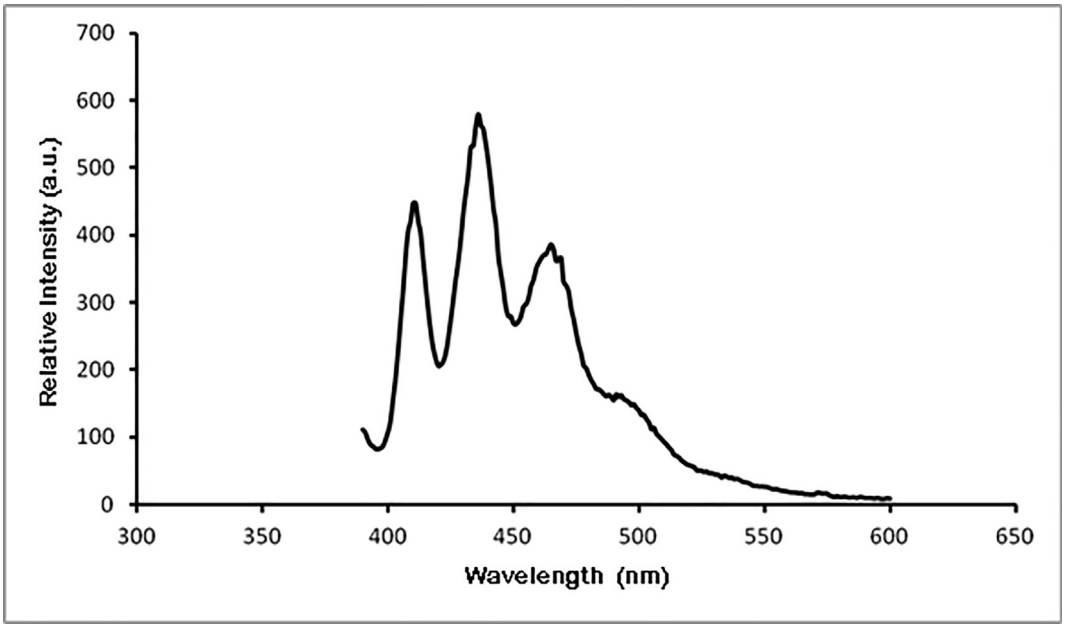

Fig. 7. PL Spectra 8-HQHMDAF -Ni copolymer metal complex.

metal complex. This may emerge from the filling of the voids by the helpful commitment of the complexation of metal ions with co-polymeric ligand or the vanishing of the voids in the revamp of copolymer chains during complexation with metal ion. Increase of crystalline character of complex compared to the copolymer ligand.

5. Photoluminescence study of copolymer metal complexes

Synthesis method for green color 8-HQHMDAF-M copolymer metal complex and photoluminescence characterizations were described in current research work. A central factor of photoluminescence study is to discuss the luminescent behavior of the interpreted copolymer metal complex. It should be remembered that the copolymer metal complex utilized Photoluminescence examination is prepared by condensation process. In addition, the respective peak intensities for each and every peak often based on the resulting proficiency of a radiative recombination. Therefore, the Photoluminescence spectral analysis of these samples shows that the product developed has certain quality to be used precursor for semi-conducting and optical device research. Shimadzu RF-5301 Photoluminescence spectrophotometer is used to study the Photoluminescence nature of co-polymeric metal complexes which is 8-HQHMDAF-Cu, HQHMDAF-Zn, and 8-HQHMDAF-Ni at Kamla Nehru Mahavidyalaya, Nagpur. Photoluminescence spectra of 8-HQHMDAF-Cu, HQHMDAF-Zn,

and 8-HQHMDAF-Ni copolymer metal complex were represented in following Figs. 5, 6 and 7 respectively.

Photoluminescence spectra of 8-HQHMDAF-Cu copolymer metal complex represents in Fig. 5 which shows the emission bands at 380 nm and at 401 along with blue colour emission in UV region and 8-HQHMDAF-Cu metal complex get excited at 324 nm, the intensity of peak found to be 565.568 (a.u). Fig. 6 represents photoluminescence spectra for 8-HQHMDAF-Zn copolymer metal complex get excited at wavelength 379 nm and shows three emission peak in UV region at 409 nm, 437 nm and 463 nm. In8-HQHMDAF-Zn polymer metal complex gives peak at 437 nm is more intense along with blue color with intensity 631.142 (a.u.). Fig. 7 represent photoluminescence spectra of 8-HQHMDAF-Ni polymer metal complex which shows three emission band of which two emission peaks at 411 nm and 436 nm are longer and one small peak at 466 nm in UV region. The peak at 436 nm is more intense along with blue color with intensity 579.796 (a.u.). The excitation wavelength for 8-HQHMDAF -Ni polymer metal complex found to be 372 nm.

From above study 8-HQHMDAF-M copolymer metal complexes act as good photoluminescence material. It can be used inexpensive basic material for the chemical production of the various emitters of copolymer metal complexes, and its convenience makes this type of material preferable. Consequently, Photoluminescence spectral study of all these samples reveals that the material produced has some quality to be used as base material for light emitting device and semiconducting devices research.

6. Conclusion

A copolymer metal complex by using 8-HQHMDAF copolymer as a ligand with three transition metal ions Cu^{2+}, Ni^{2+} and Zn^{2+} are successfully prepared by using poly condensation method. Physicochemical methods and spectroscopic methods used for molecular characterization. FT-IR and (^{1}H) NMR spectroscopic analysis are helpful to propose the structure of the 8-HQHMDAF-M copolymer metal complex. Photoluminescence study indicates that 8-HQHMDAF-M copolymer metal complexes act as good photoluminescence material. It can be use as supporting material, and starting materials for various light emitting devices and semiconducting device.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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