Synthesis and Photoluminescence of a New Blue emitting Chlorine-amino-DPQ for OLEDs

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Abstract :- For the application in organic light-emitting diodes (OLEDs), the efficient new blue emitting organic polymer 6-chloro-2-(4-Amino-phenyl)-4-phenyl-quinoline (Cl-Amino-DPQ) were synthesized by substituting amino, at 2-para position of DPQ, by Friedlader condensation method. The Optical, structural and thermal properties of the Chlorine -Amino-DPQ has been studied. The UV-vis absorption and photoluminescent properties of the polymer were investigated. The CL-A-DPQ exhibits the photoluminescence (PL) peaks at 440 nm when excited at 380 nm. in powder, at 422 and 420 nm when excited at 365 in chloroform and THF solution respectively. It is proposed that the synthesized polymer may be efficiently used as the emitter materials in Organic Light-Emitting Devices OLEDs. It is promising candidates for potential applications in organic light-emitting diodes OLEDs, light-emitting electrochemical cells and solid-state organic lighting applications.
Keywords: Polymer,Photoluminescence, Synthesis, OLED

I. INTRODUCTION

Since the first demostration of efficient multilayer organic light-emitting devices (OLEDs) and the discovery of electroluminescence (EL) from the polymeric materials,there has been considerable interest in developing highly efficient, full color, and flat panel display. In order to achieve full color emission, red,green and blue emission are needed .However up to now, the blue light-emitting materials for commercial use are still limited .So there is great interest in developing efficient and stable blue OLEDs.Organic light-emitting diodes (OLED) have attracted considerable attention due to their various potential applications such as full-color flat panel displays, backlight for liquid crystal display (LCD), and next-generation light sources [1]. The past two decades have witnessed the great development of conjugated organic materials for electronic applications such as OLEDs, organic solar cells and organic thin-film transistors, which are promising candidates for display and solid-state lighting applications [2]. The basic units of modern electronic appliances may be made not only from traditional inorganic semiconductors, but also from organic semiconductors, i.e. hydrocarbon molecules that combine semiconducting properties with some mechanical properties such as easy processability and flexibility [3]. A precise and considerable amount of work has been devoted in the past decade to the development of multilayer OLEDs, chemical sensors, scintillators, field effect transistors [4]. In addition to the medicinal importance, Multi-substituted quinolines are valuable synthons used not only for the preparation of nano- and mesostructures with enhanced electronic and photonic properties [5] but also for the important biological activities [6]. For OLEDs containing fluorescent dopants, only singlet excitons can generate light; while for OLEDs containing phosphorescent dopants, both singlet and triplet excitons can generate light [7-8]. Pyrazole-containing derivatives, distyrylenes, anthracene derivative, spirofluoreres are demonstrated to be blue emitting materials for fabricating blue OLEDs [9-10]. For OLEDs incorporating deep-blue phosphors, one of the key challenges is the acquisition of effective device architectures. Deep-blue phosphors usually require large triplet energy hosts to prevent the reverse energy transfer from dopants to hosts [11]. There is a development in series of pyrazoloquinoline derivatives, which give bright blue EL emission [12]. π-Conjugated rigid poly (quinoline)s have been extensively investigated as thermally stable, photoconductive, photoluminescent, and nonlinear polymeric

materials [13–20]. Our choice of the phenylquinoline moiety as the acceptor was based on previous work that showed good electron transport properties in quinoline dendrimers, oligoquinolines and polyquinolines for OLEDs [21]. Of the heteroaromatic polymers, quinoline based polymers are of interest as these are reported to exhibit n-type conductivity upon doping and possess excellent thermal as well as oxidative stability [22]. Recently, quinoline conjugated derivatives have generated considerable interest as blue-emitting materials [23–26]. The blue emitting phenylated quinoline based organic phosphor materials have generated considerable interest owing to their high photoluminescence efficiencies. The main aim of the present work is to synthesize and characterize blue emitting organic luminescent phosphor material's derivative which is based on phenylated quinoline.

II.Experimental

2.1 Synthesis of **4-chloro-2-(4-Amino-phenyl)-4-phenyl-quinoline (Cl-A-DPQ).**

The quinoline-derived phosphors 6-Chloro-2-(4- Amino-phenyl)-4 Phenyl quinoline (Cl-A-DPQ)], were synthesized conveniently according to Scheme 2 from the condensation of 2-Amino, 5-Chlorobenzophenone and 4-amino acetophenone using the acid-catalyzed Friedlander reaction [27].

2-Amino, 5-Chlorobenzophenone (2gm), and 4-amino acetophenone (2gm), were added along with Di-phenyl Phosphate (DPP) (2 gm), and m-Cresol (3 ml), in a glass reactor fitted with mechanical stirrer, two glass inlets and one side arm. The reaction mixture was purged with argon for 20 min. and then the temperature was raised to 90 °C gradually under Argon atmosphere for 1 hour and subsequently to 140 °C for 4 hours. After cooling, dichloromethane–CH_2Cl_2, (50 ml) and 10 % NaOH (50 ml) were added to the reaction mixture.

The organic layer was separated and washed with distilled water (20 ml x 5) until it was neutral, then dried over $MgSO_4$ and evaporated under vacuum to yield an off- white solid with some radish liquid on top. The crude product was filtered and washed with hexane (5 ml x 3) to obtain crystalline solid of 6-Chloro-2-(4-Aminophenyl)-4Phenylquinoline. abbreviated as Cl-A-DPQ.
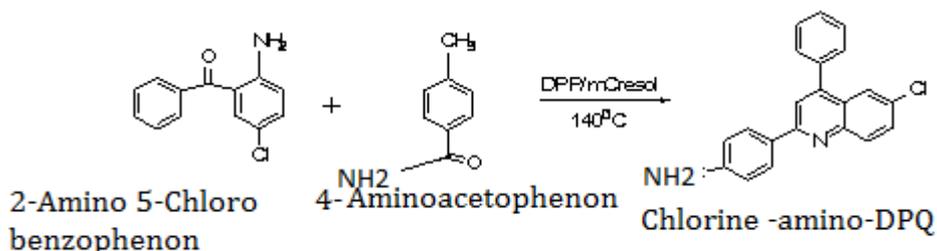
Scheme1: Synthesis of [6-chloro-2- (4- methoxy phenyl), 4-phenyl quinoline] (CL-A-DPQ)

III. Results and discussion

3.1. Synthesis and structural characterizations

Friedlander reaction [27] was used to synthesize of Cl-A-DPQ organic phosphor as shown in Scheme 1.Condensation of the ketone with the o-aminobenzophenone catalyzed by the acid gave corresponding quinolines in the yield of 64–75%.. The structures and purity of the polymer were characterized by ^{1}H NMR and elemental analysis. The mononuclear polymer is thermally stable up

to 300–385 ºC revealed by thermal gravimetric analysis (TGA). X-ray crystallographic studies have been carried out for (CL-A-DPQ).

3.2. *FTIR analysis*

The FT-IR spectra of the new Cl-Amino-DPQ chromophore is as shown in Fig. 1. On the basis of FT-IR spectra, the conversion of the reaction forming Cl-DPQ can be estimated. The IR bands characteristic of the functional groups of the monomers, two bands in the regions 3320-3340 and 3443-3460 cm^{-1} corresponding to primary amines and one strong band in the region 1624-1656 cm^{-1} corresponding to the carbonyl (C=O) group, are absent in the IR spectra of the polymeric compound. The aromatic CH vibration stretch appears at 3100-3000 cm^{-1}. There is an aromatic CC stretch band (for the carbon-carbon bonds in the aromatic ring) at about 1500 cm^{-1}. The strong FT-IR peaks at 1663 and 1656 cm^{-1} owing to the carbonyl groups are almost completely disappeared in Cl-Aamino-DPQ. Instead, new strong bands between 1600 and 1400 cm^{-1} due to the imine (C=N) group and characteristic of the quinoline ring were observed. The peak at 846 cm^{-1}, is characteristic of paradisubstitution of the benzene ring. This is usually an excellent confirmation of the completion of cyclization reaction forming quinoline rings.

The characteristic peaks of FT-IR spectra of Cl-DPQ are 3110, 3080, 3035, 2998, 2928, 2590, 1952, 1840, 1813, 1614, 1545, 1488, 1445, 1418, 1330, 1294, 1234, 1123, 1094, 1014, 950, 927, 867, 843, 810, 742, 677, 639, 630, 581, 539, 486, 454 cm^{-1}.
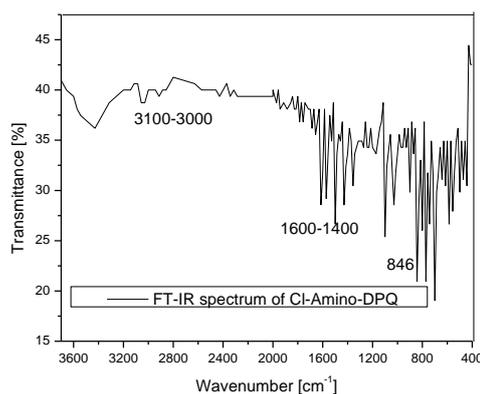
Figure 1. FT-IR spectra of Cl-Amino-DPQ

3.3 *X-ray diffraction analysis:*

The X-Ray diffraction pattern of Chlorine-amino - Diphenyl Quinoline (Cl-Amino– DPQ) are shown in Fig.2. From the X-ray diffraction analysis, the powder Cl-amino – DPQ have many strong, sharp diffraction peaks and some diffused background. This indicates the crystalline character of the compound. These spacings correspond to the chain distances of a well-organized molecular layer structure. A much weaker diffraction peak indicates lower crystallinity or orientation. In addition, its higher volume fraction of insulating side chains may also contribute to its low field-effect mobility. However, too much crystallinity causes brittleness. The crystallinity parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak (halo).
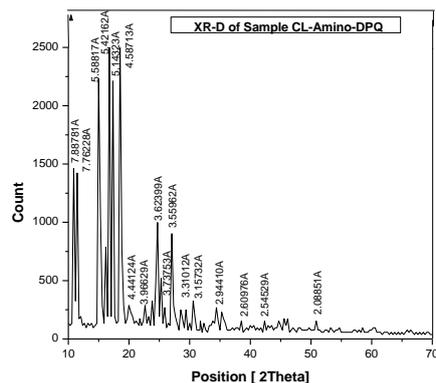
Figure 2: XRD pattern of Cl-Amino-DPQ

3.4 Thermal propertiesanalysis

(a)Thermogravimetric (TGA) Analysis of Cl-Amino-DPQ:

Thermal stability, chemical reactivity and phase transitions properties of materials are evaluated by TGA and DTA. The TGA is used for precise measurement of specimen weight changes as function of time and temperature in various gaseous environments. This experimental method is very useful for investigation of reactivity and stability. Thermal decomposition and nitridation reactions are typical examples. DTA is used for measuring changes in specimen heat content during solid-state transformations and gas – solid reactions. Data can be acquired during heating and cooling cycles. Endothermic and exothermic events can be identified easily. TGA and DTA measurements can be made simultaneously on the sample to allow direct correlation of weight and heat change events with greater certainty than available with separate measurements.
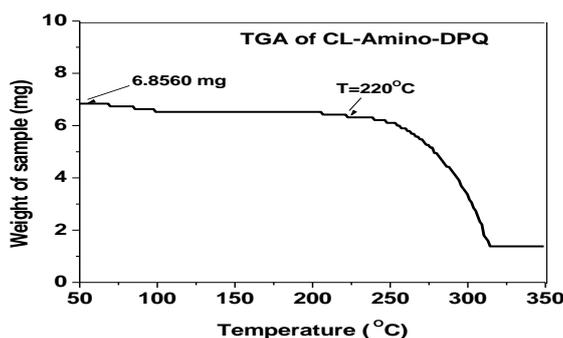

*Figure 3. Thermo gravimetric analysis curve.*

The dynamic (non-isothermal) thermo gravimetric analysis of Cl-Amino-DPQ has been carried out in air atmosphere with a heating rate $4\ ^{0}$ C / min. in a platinum crucible. The thermocouple used was Chromel - alumel in the temperature range $30 – 400\ ^{0}$C. The TGA and SDTA curve obtained from Mettler STARe Thermo Gravimetric Analyzer, TGA/sDTA851e is shown in Fig. 3
From the TGA curve it is clear that

(a) No weight loss was observed in the first step of temperature range from 38 to 68 ^{0} C. i.e. there is no effect of temperature on a sample up to 68 ^{0}C.

(b) A small weight loss of about 1.62 % was observed in the second step of temperature ranges from 68 ^{0}C to 84 ^{0}C.The weight of the sample reduces to 6.735 mg.

(c) The total weight loss of about 3.15 % was observed in the third step of temperature range from 84 to 97 ^{0}C. In this step, the sample weight becomes 6.63 mg.

No further weight loss was observed up to the temperature of 205^{0}C. (sample weight was 6.63 mg). Above 205 ^{0}C significant weight loss was observed and it continues up to 314 ^{0}C. The sample weight becomes 1.38 mg 212 ^{0}C is the degradation temperature. At this temperature there was a weight loss of 5 % of the starting mass and is a convenient benchmark for comparing anti-oxidant efficiency.

(b)Differential Scanning Calorimetry(DSC)

We investigated the thermal properties of CL-Amino-DPQ by differential scanning calorimetry (DSC) DSC measurement are recorded on Mettler Tolledo System. The DSC trace of the polymeric compound containing quinoline showed no crystallization but only melting and glass transitions peaks. This clearly indicates that the incorporation of the rigid quinoline unit into the phenyl backbone reduces the segmental mobility and effectively suppresses the tendency of the polymer chains to densely pack. This improved thermal resistance of the copolymers bodes well for stable blue emission from LEDs made from them.The DSC second heating scans of the polymeric compound are as shown in Fig. 4 Fig. 4 indicate that CL-Amino-DPQ undergoes a glass transition at 75 ^{0}C, following by melting point at 111 ^{0}C and degradation temperature at 393 °C.
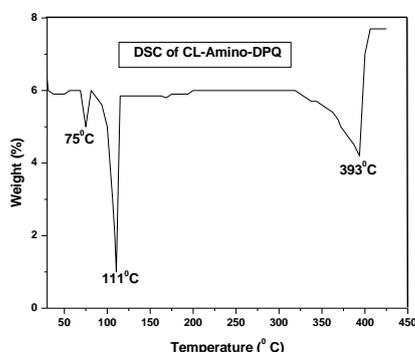
Figure 4. DSC scans of (a)CL-Amino– DPQ

3.5 Optical Properties

3.5.1 Absorption Spectra*: The optical properties of asymmetric Cl-Amino-DPQ were measured in basic solvents i.e. chloroform, dichloromethane solutions and in acids i.e. acetic acid and formic acid. However, the compound Cl-Amino-DPQ shows broad absorption band ranging from 240 to 390 nm with a λ_{max} at around 260 nm and a shoulder at 312 nm in both solutions.
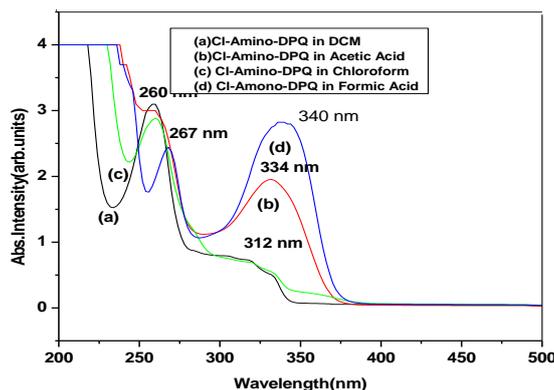
Fig.ure 5. :Absorption spectra of Cl-Amino-DPQ in (a) DCM (b)Acetic acid (c)Chloroform (d) Formic acid solution

Fig. 5 curve(c) shows the optical absorption spectra of Cl-Amino-DPQ in chloroform at room temperature. The polymeric compound have broad absorption at 260 nm (4.78 eV) due to π - π* transition and 312 nm (3.76 eV) due to intermolecular charge transfer in chloroform.

Fig. 5 curve(a) shows the optical absorption spectra of Cl-Amino-DPQ in dichloromethane at room temperature. The polymeric compound have broad absorption at 260 nm (4.78 eV) and 312 nm (3.76 eV) due to π-π* transition intermolecular charge transfer in dichloromethane. The peak intensity decreases with increasing concentration of Cl-Amino-DPQ. No new absorption features were observed in the wavelength range 200 – 500 nm, suggesting that the material have no observable interaction in their electronic ground state.

Fig. 5 (Curve (b)) shows absorption spectra of Cl-Amino-DPQ in acetic acid as a function molar concentration. The absorption spectra of the compound in the different solvents are characterized by two bands, one near 267 nm (4.82 eV) and the other at around 334 nm (3.70 eV) for Cl-Amino-DPQ. The former band can be assigned to π-π* transition whereas the lowest-energy band, which is less intense, is largely of charge transfer character. The absorbance spectrum of the compound is characterized by a strong absorption peak centered at 334 nm and with a weak shoulder at 260 nm.

Fig. 5 (curve (d). the absorption spectra of the Cl-Amino-DPQ compound in formic acid are characterized by two bands, one near 267 nm (4.64 eV) and the other at around 340 nm (3.66 eV) for Cl-Amino-DPQ. The former band can be assigned to π- π* transition whereas the lowest-energy band, which is less intense, is largely of charge transfer character. The compounds show evidence of solvatochromism in which both the absorption wavelengths are red shifted slightly with increasing polarity of the solvent. In both polar solvents, the absorption bands are narrower and without any vibrational structure. The breadth of the absorption bands can be attributed to the decreased planarity of the molecules caused by the large steric interactions within the molecule. The peak intensity is always higher in formic acid compared to in acetic acid expect for high mol. concentration solutions as Amino-DPQ in formic acid enters in saturation region of absorption curve at lower concentration. It is this lowest-energy absorption band that is most sensitive to the solvent polarity and to the accepter Cl group.

3.5.2 Photophysical Properties: The PL emission spectra of the polymeric compound also showed a distinct solvent dependence. This effect was discussed in the PL spectra presented for dilute solutions in solvents where the polarity is varied. The relative intensity of the blue emission band was substantially reduced. This result indicates strong intermolecular interaction in the solid state.The emission peaks of the CL-Amino-DPQ in different solvents show clear differences as shown in Fig. 6. When the CL-Amino-DPQ is excited at 395 nm, it emits intense blue light of

wavelength peaks at around 422 nm in Chloroform, and 420 nm in CH_2Cl_2 (medium polarity) and 428 nm in acetic acid and 426 in formic acid.
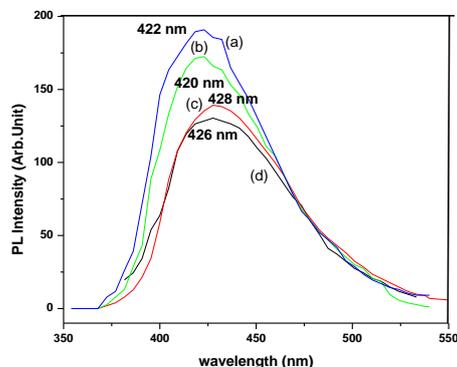

Fig.6 PL Spectra of CL-Amino-DPQ (a) in Chloroform (b) DCM (c) Acetic Acid (d) Formic Acid

IV. CONCLUSION

We have successfully synthesized a new blue emitting plolymer 6-chloro-2-(4-Amino-phenyl)-4-phenyl-quinoline (CL-Amino –DPQ.. The synthesized polymeris thermally very stable over a wide range of temperature and suitable for the use as a blue-emissive material in solution processed organic devices. In conclusion, the synthesized [(CL-Amiono-DPQ) polymer with the emission in the blue region at 428 nm is very promising for applications in flexible organic devices.

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