



Synthesis and characterization of 2-(4-Ethoxy-phenyl)-4 Diphenyl quinoline (OEt- DPQ) Blue Emitting Organic Phosphors For OLED

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Abstract

The blue light emitting OEt-DPQ organic phosphor based on a pyrazoloquinoline derivatives was synthesized by using the acid-catalyzed Friedlander reaction. The synthesized organic phosphors were characterized by FTIR, TGA & DTA, UV-vis absorption and emission spectroscopy. The synthesized OEt-DPQ organic phosphor demonstrates emission in blue region at 391 nm in powder when excited at 368 nm. Thermal analysis showed that the good thermal stability upto 301 °C. Because of good thermal stability the synthesized phosphor may be efficiently used as the emitter materials in Organic Light-Emitting Diodes OLEDs.

Hence, the synthesized blue emitting 2-(4-Ethoxy phenyl)-4-Diphenylquinoline (OEt-DPQ) has generated considerable interest owing to their good photoluminescence efficiencies.

Keywords: Synthesis, OEt-DPQ, Photoluminescence, OLED

1. Introduction

In the last few years technologies like flat panel displays and solid state lighting from organic materials received lots of interest in academic and industrial research. Organic electronics became an important keystone of such modern technologies because the fabrication gets cheaper by the use of organic materials compared to established semiconductor techniques.

OLED displays are on the way to establish themselves in the market and the technology has a good chance to expand in the near future even for larger and high resolution displays. Organic light-emitting devices (OLEDs) from the polymeric materials has considerable interest in developing highly efficient, full color, and flat panel display. To achieve full color emission, three basic colours emission are needed i.e red, green and blue emission. In organic light emitting diodes (OLEDs), blue organic emitters have attracted considerable attention [1,2]. The poor stability, unbalanced charge injection and transport existing in these blue materials are obstacles to their development. Our main aim for blue emitting materials, to increase their electron affinities to realize balanced charge injection and transport [3-8]. Materials containing aromatic heterocyclic segments, viz., pyridine [9], quinoline [10-12], and oxadiazole [13-14], had been reported to exhibit better electron injection and transport ability. In the past three decades, a large number of poly (quinoline)s and their copolymers were synthesized and successfully used as electron-

transporting and emitting materials in OLEDs, selective luminescent sensors, and nonlinear optical materials. Derivatives of 2-4 Diphenyl quinoline are a phosphorescent materials, which are environmentally sensitive and are of great interest owing to their excellent photoluminescence (PL) quantum efficiency, good photo-stability and film-forming properties as well as desirable chemical and thermal stabilities [15-16]. To achieve good electron affinity, the electron donating groups substituted at the 2nd position of 2-4 diphenyl quinoline.

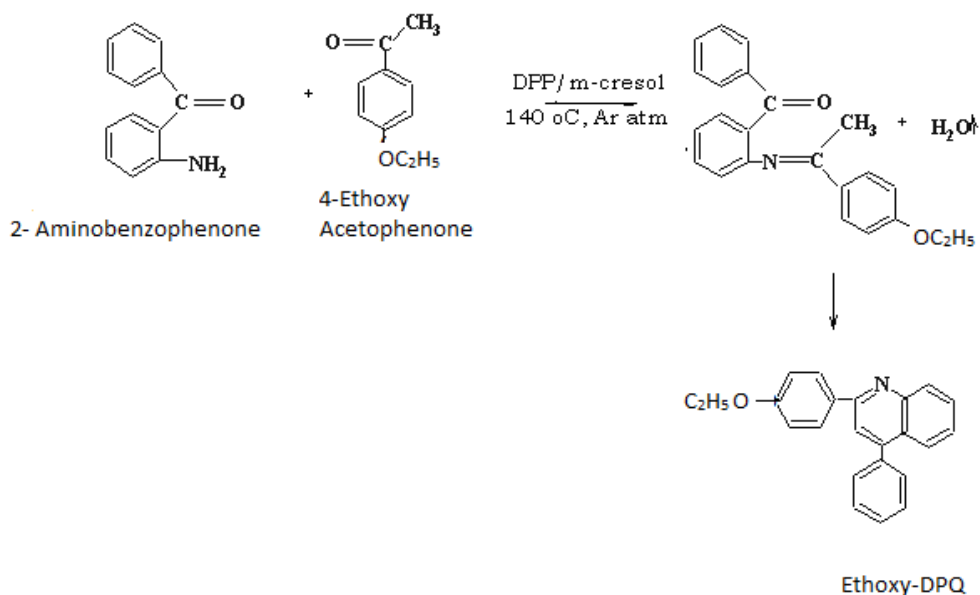
In this paper, we have synthesized blue emitting 2-(4-Ethoxy phenyl)- 4 Diphenyl quinoline (OEt- DPQ) and their photo physical, thermal and Structural properties were analyzed in detail.

2. Experimental :

2.1. Synthesis of 2-(4-Ethoxy-phenyl)-4-Diphenyl-quinoline (OEt - DPQ)

The quinoline-derived ligand 2-(4-Ethoxy phenyl)- 4 Diphenyl quinoline (OEt-DPQ) were synthesized conveniently according to Scheme-I from the condensation of 2-aminobenzophenone and 4-Ethoxyacetophenone using the acid-catalyzed Friedlander reaction [17].

2-Aminobenzophenone (2 g, 8.1 mmol) and 4-Ethoxyacetophenone (2 g, 13.3 mmol) were added along with 2 g of diphenyl phosphate and 3ml of m-cresol in a glass reactor fitted with mechanical stirrer. Heat the reaction mixture at 90 °C for 1 h and then for 4 h at 140 °C.



Scheme 1: Synthesis of 2-(4-Ethoxy phenyl)-4 Diphenyl quinoline (OEt-DPQ)

After cooling, methylene chloride (100 ml) and 10% NaOH (100 ml) were added to reaction mixture. The organic layer was separated and collect this layer on watch glass to evaporate remaining dichloromethane. Then washed with distilled water (20 ml x 5) until it was neutral. It dried in oven up to 60°C and after that washed with hexane (5 ml x 3) to obtain crystalline solid of Ethoxy- Diphenylquinoline abbreviated as OEt-DPQ, relative molar mass = 325.40gm.

2.2. Measurements

The FTIR spectra were recorded on Bruker-Apha at room temperature. UV-Vis absorption was recorded on a UV-visible Spectrophotometer, SHIMADZU at room temperature. The photoluminescence study were carried out on a SHIMADZU RF 5301 spectrofluorometer. TGA & DTA measurement was recorded on SHIMADZU thermo gravimetric analyzer.

3. Result and Discussion

3.1. Structural Properties

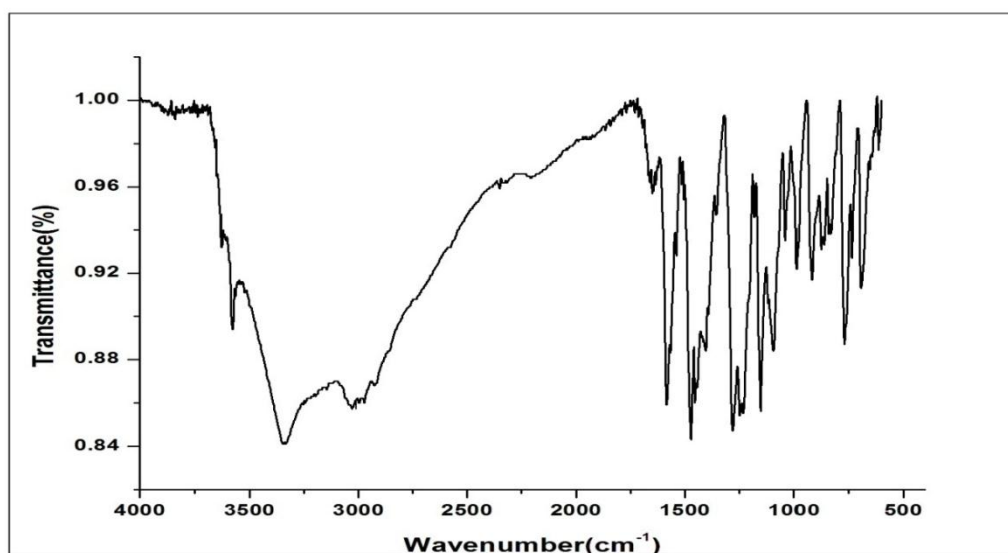


Fig. 1: FT-IR spectra of OEt-DPQ

By using FTIR spectra we can confirm that the presence of different molecules of polymeric compounds. Fig.1. shows FTIR spectra of OEt-DPQ. Above spectra shows the presence of the aromatic CH vibration peak appears at 3100-3000 cm^{-1} . The peak at 846 cm^{-1} , is characteristic peak of the benzene ring. For C=C stretching (the carbon-carbon bonds in the aromatic ring) absorption occurs 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 OMe-DPQ. Instead, new strong bands between 1600 and 1400 cm^{-1} due to the imines (C=N) group and characteristic of the quinoline ring were observed. This is usually an excellent confirmation of the completion of cyclization reaction forming quinoline rings. Peaks between 1600 and 1400 cm^{-1} due to the imine (C=N) group and this is characteristic of the quinoline ring.

The absorption corresponding to 3000-3200 cm^{-1} , indicates the presence of ethoxy (OCH_2CH_3)

3.3. Photophysical properties

In order to realize the functioning of organic materials in device applications, studying their photophysical properties is important. Under irradiation, the photophysical properties of synthesized molecules are generally dependent on the polarization of pyrazoloquinoline derivatives backbone. Usually, light absorption in synthesized molecules generate charge transfer between the substituents at the 4-position and carbonyl groups of the quinoline. Using UV-Vis absorption and photoluminescence (PL) spectroscopy, basic photophysical characteristics such as the absorption maxima (ν_{Abs}), optical band gaps ($E_{\text{g}}^{\text{opt}}$), Stokes shift ($\nu_{\text{Abs}} - \nu_{\text{Em}}$), of the molecules were determined.

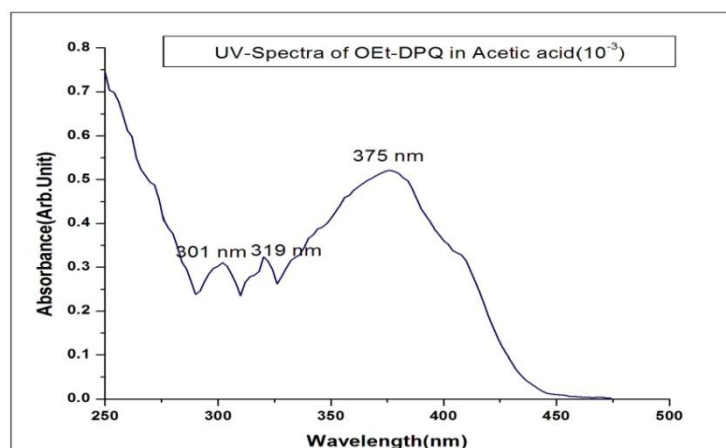


Fig. 2. Absorption spectra of OEt-DPQ in Acetic acid

The UV-vis absorption spectra of OEt-DPQ in acetic acid at room temperature are shown in Fig.1. Pure Acetic acid solutions show absorption shoulder at 263nm, with no absorption above 320 nm. As shown in curve(Fig.2.), the Absorption maxima of OEt-DPQ are found to be at 375 nm. Pure 2-4

diphenyl quinoline show strong absorption maxima at 333 nm. It is found that the absorption maxima for substituted electron-donating Ethoxy groups at the 4-position of 2-4 diphenyl quinoline, has been red shifted. This maximum peak suggesting strong π - π^* conjugation.

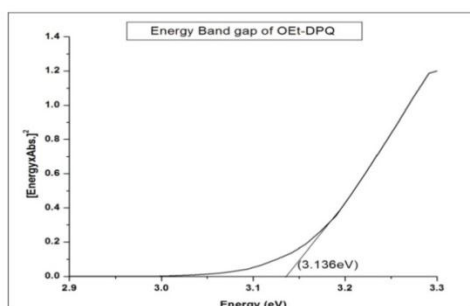


Fig.3. Determination of Energy band gap E_{g} of OEt-DPQ in Acetic acid

Optical band gap (E_g) for the derivatives calculated by using the procedure described by Morita et al., [18] from the solid-state absorption spectra (fig. 2). The calculated energy band gap for is Ethoxy-DPQ found to be $E_g = 3.136$ eV in Acetic acid solution.

The PL spectra of Ethoxy-DPQ in powder form (Fig. 4) displayed blue phosphorescence, which may be ascribed to the charge transfer

between the electron-donating substituent at the 4-position and the electron accepting carbonyl groups. The excitation band in powder is centered at 368 nm and the polymeric chromophore emits blue emission of wavelength 391 nm, due to the presence of electron-withdrawing Ethoxy -substituent in 2-4 diphenyl quinoline.

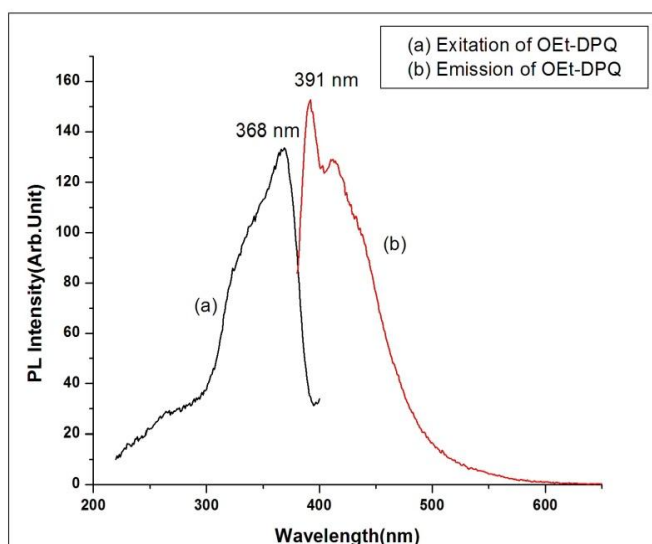


Fig.4: (a) Excitation & (b) Emission spectra of OEt- DPQ

Stokes shift ($V_{Abs} - V_{Em}$) indicates the difference in the structure and properties of the phosphorescent molecules between the ground and the excited states [19-21]. The Stokes' shifts (cm^{-1}) were determined by Eq. (1).

$$(V_{Abs} - V_{Em}) = (1/\lambda_{Abs} - 1/\lambda_{Em}) \times 10^7 \text{ cm}^{-1} \dots (1)$$

The molecules show Stokes shifts are high with values of 1100 cm^{-1} ensuring that there is no re-absorption of the emitted radiation

3.3. Thermal properties

The stability and the lifetime of the devices can be improved by possessing materials with high thermal stability. The thermal properties of the derivatives were determined by TGA.

Thermal stability was evaluated by TGA and was carried out in the temperature range of

30–300 °C. A constant heating was used to melt and decompose the molecules under nitrogen atmosphere. TGA curve of OEt-DPQ as shown in Fig. 5. TGA curve of OEt-DPQ shows that the molecules exhibited high thermal stabilities with minimum weight loss at lower temperature. Some weight loss was observed at around the temperature of 100 °C is due to some volatile impurities or moisture present in material. The decomposition temperatures corresponding to 5% and 10% weight losses were in the temperature range 100°C–145°C and 145°C–214°C respectively. Up to 300 °C, 25% of weight losses and then after continues heating at 300 °C there is a gradual loss of weight.

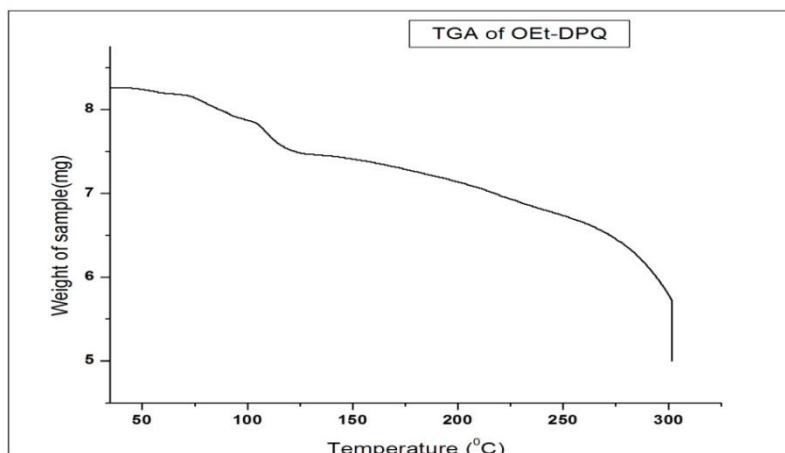


Fig. 5: TGA curve of OEt-DPQ

Differential thermal analysis (DTA), the technique of recording the difference in temperature between a substance and a reference material against either time or temperature. Generally, sharp endothermic peaks give ideas of changes in crystallinity or fusion processes whereas broad endothermic

peak signifies dehydration reactions. DTA curve allows the detection of every physical or chemical change or not in sample, accompanied by a change in weight. DTA result of OEt-DPQ shows the melting temperature at about 81 °C and glass transition temperature is at 114 °C.

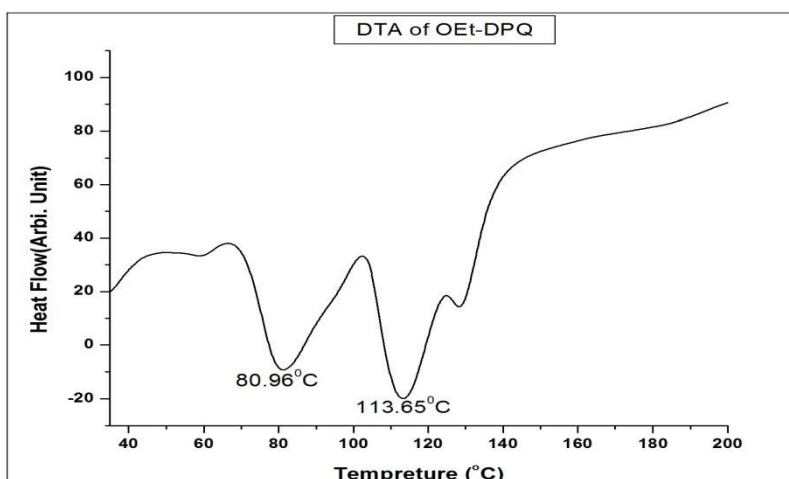


Fig.6. DTA curve for OEt-DPQ

4. Conclusions

We have successfully synthesized a new blue emitting phosphore 2-(4-Ethoxyphenyl)-4 Diphenyl quinoline (OEt-DPQ) in solid crystalline powder form. Synthesized OEt-DPQ has high electron affinity with desired wide band gap required for blue light emission. Structural, Optical and thermal studies of the Ethoxy-DPQ (OEt-DPQ) phosphor were investigated using UV-Vis absorption spectrometry, PL spectrometry, TGA, DTA and FTIR. The FTIR spectra confirmed the molecular and structural characteristics of our synthesized sample. The UV-Vis absorption

spectra of the synthesized phosphor showed broad-bands as compared 2-4 Diphenyl quinoline. The Ethoxy-DPQ showed excellent PL properties with large Stokes shifts. Thermal properties revealed that Ethoxy-DPQ have high melting points and good thermal stabilities.

This results indicate that the synthesized Ethoxy-DPQ (OEt-DPQ) is very promising for applications in flexible organic devices and to be more cheaper and more saving energy efficient

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