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Spectroscopic characterization of dichloro-DPQ with PMMA and PS blended films

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ABSTRACT

For the application in organic light-emitting diodes, the efficient new derivative of 2, 4-diphenyl quinoline i.e., 2(2',4'dichloro phenyl)-4-phenyl quinoline (dichloro-DPQ) has been synthesized by Friedlander condensation at 140 °C. Blended films of dichloro-DPQ with poly (methyl methacrylate) (PMMA) and polystyrene (PS) at different weight % concentrations like 10, 5 and 1 wt% have been prepared. Structural and optical characterization techniques were used to characterize the crystalline powder. The photoluminescence in synthesized dichloro-DPQ polymeric compound shows emission peak in blue region at 462 nm in powder form and PL emission in dichloro-DPQ with PMMA and PS with different wt%; we get hypsochromic shift. Optical properties of dichloro-DPQ make it possible candidate material as blue organic phosphor for the field of light industry. Copyright © 2012 VBRI Press.

Keywords: Light-emitting diodes; dichloro-DPQ; photoluminescence; PMMA; PS.



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Introduction

Since the breakthrough discovery by Tang and van Slyke in organic light emitting diodes (OLEDs), research into OLEDs has been pursued intensively because of their potential use in information displays with the advantages of self-luminescence, wide viewing angle (>160°), prompt response time ($\sim 1 \mu s$), low operating voltage (3–10 V), high luminance efficiency, high color purity, and easy to be made on various substrates [1]. Recently, organic light emitting diodes and polymeric light emitting diodes have been applied to display technologies [2]. In recent years, the design and synthesis of novel organic-inorganic hybrid materials have provoked significant interest owing to their enormous fascinating properties as well as great potential application [3]. Polymeric guest-host systems have been emerged as strong candidates for many modern technologies such as optoelectronic devices in comparison to their inorganic counterparts due to their advanced properties [4].

Red, green, and blue emissions with high efficiencies are required for full color displays [5-9]. Accordingly, a systematic study on molecular structure that can effectively prevent intermolecular interactions is needed for the material to be used as a highly efficient and pure blue emitting material [10]. Studies on blue OLEDs are very important for potential applications in full color flat-panel displays and white OLEDs [11]. The potential applications of blue OLEDs have driven extensive efforts to fabricate various kinds of OLEDs with high efficiency, good color stabilization and long lifetime [12]. Molecules containing aromatic heterocyclic (electron rich) like quinoline based molecules have been suggested as electron transport and hole blocking materials for electrolumines-cent devices [13–17]. Conjugated polymers have novel class of semiconductors with their interesting optical and electronic properties [18].

Quinolines constitute an important class of heterocycles as the quinoline structural unit is prevalent in naturally occurring quinoline alkaloids, therapeutics and synthetic analogues with important biological activities [19] and antiproliferative activities [20]. To synthesize highly conducting organics for the possible high temperature applications, we selected the most thermal oxidative stable polycondensed aromatic polymers for The immobilization and photoluminescent study. properties of Tris (8-hydroxyquinoline) aluminium (Alq₃) in the pores of mesoporous silica [21] and absorption and photoluminescence of derivatives of 1,3-dimethyl-1H-Pyrazolo[3,4-b] quinoline (DMPQ) [22] i.e., quinoline conjugated derivatives were studied. The electron transporting properties of copolymers bearing fluorene and quinoline units with conjugation confinement varied with the chain rigidity and conjugation length and proved to be useful in double and triple layer devices.

One class of such polymers is polyquinoline and its derivatives. Polyquinolines are emerging as very promising blue emitting materials due to their unique combination of high thermal stability, easy processibility and high photoluminescence (PL) quantum yields **[23]**. In case of application it is necessary to have a material system that is easy to produce on large scale and thus inexpensive. Hence, quinoline conjugated derivatives have generated considerable interest as blue emitting material. We are currently engaged in the study of a derivative of Diphenyl Quinoline in different wt % concentrations such as 10, 5, 1 and 0.1 wt% in both PMMA and PS.

Experimental

Dichloro substituted 2, 4-diphenylquinoline (DPQ) was synthesized according to Figure 1. 2-aminobenzophenone reacts with 2,4-dichloroacetophenone in presence of diphenyl phosphate and m-Cresol at 140 °C, water vapours come out, and finally undergoes crystallization and gives 2 (2', 4'- dichloro phenyl)-4- phenyl quinoline, (dichloro-DPQ). 2 g of 2-aminobenzophenone (99.5%, USA, Lancaster make) and 2 g of 2, 4-dichloroacetophenone (99%, Germany, Aldrich make) were added along with 2 g of diphenyl phosphate (99%, Germany, Aldrich make) and 3 ml of m-cresol (97%, USA, Lancaster make) in a glass reactor fitted with mechanical stirrer for the temperature at 140 °C for 4 h. After cooling, methylene chloride (100 ml) and 10% NaOH (100 ml) were added to reaction mixture. The organic layer shown in the inset of **Fig. 1** was separated and washed with distilled water (50 ml x 5 times) until it was neutral. Then it was dried over an MgSO₄ and evaporated under the natural condition to yield an off-white solid. The crude product then washed with hexane (25 ml x 5 times) to afford crystalline solid (2.65 g).

Polymer binder materials are ideally convenient for the fabrication of EL cells and OLEDs. Polymeric materials can exhibit high transparency in the visible region of the spectrum, adequate resistance to heat and humidity variations, as well as high mechanical strength [24].

They also provide very good host environment for organic dye molecules. We have utilized commercially available poly (methyl meth-acrylate) (PMMA) and polystyrene (PS) for blended thin films which are optically and electrically inert and also have good film forming property with a glass transition temperature of 105 °C and 95 °C respectively. The organic compounds when used as electronics material are often in forms of thin films [25]. Blended films of dichloro-DPQ in PMMA and PS matrix at 10, 5, 1, 0.1 weight % have been prepared. The films were made by casting the dichloromethane solution on to clean glass or good quality stainless steel plates as substrate.

The Fourier Transform Infrared (FT-IR) spectrum was measured with a SHIMADZU Model 8101A infrared spectrophotometer. The blended films of dichloro-DPO with PMMA and PS matrix were prepared at different concentrations. The optical absorption spectra of blended thin films were obtained on SHIMADZU Model UV-2401PC spectrophotometer. The photoluminescence HITACHI spectra were obtained bv F-4000 spectrofluorometer.



Fig. 1. Synthesis of [2(2',4'- dichloro phenyl)-4-phenyl uinolone] (dichloro-DPQ).

Results and discussion

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic materials. **Fig. 2** shows all the major peaks of dichloro-DPQ in powder form (**Table 1**).



Fig. 2. FTIR spectrum of dichloro-DPQ.

 Table 1. The wave numbers of various vibration peaks observed and the corresponding assignment of vibrations.

Wavenumber (cm ⁻)	As	Assignment of vibrations					
3100-3000	3000 C-H aromatic vibration stretch						
1600-1500	C-C aromatic stretch bands						
1500-1400	C =	C = N (imine) group and this is					
1360-1250	C-	C- N Stretching mode of					
800-700	С	C- Cl stretching of chloro group					
4.5 Apsorbance (O.D.) 3 0 0	K	a b c d	a = 10 wt% b = 5 wt% c = 1 wt% d = 0.1 wt%]			
200	300	400	500				

Fig. 3. Absorption spectra of dichloro-DPQ with PMMA at different weight % concentrations.

Wavelength (nm)

The absorption spectra were obtained by UV-2401PC spectrophotometer. The polymeric compound has nearly identical absorption maxima (λ_{max}) at 268 nm and 334 nm in both cases of dichloro-DPQ with PMMA and PS matrix as shown in **Fig. 3-4**, respectively

The absorption spectra are a superposition of the polymeric compound at different weight % concentrations. An effect of protonation on optical absorption has previously been observed in conjugated oligoquinolines. 268 nm is due to π - π * transition contributed by the conjugated quinoline backbone.

There is an additional absorption at 334 nm contributed by the phenyl side chains of the model compound. The absorption spectra of different weight % concentrations are similar, due to the presence of same chromophore. The UV-vis absorption spectra could provide a good deal of information on the electronic structures of the polymeric compound.



Fig. 4. Absorption spectra of dichloro-DPQ with PS at different weight % concentrations.



Fig. 5. PL spectra of dichloro-DPQ (powder) (a) emission spectra, excited by 370 nm, and (b) excitation spectra, monitored at 462 nm.

The photoluminescence spectra were obtained by HITACHI F-4000 spectrofluorometer. The luminescence of organic compounds is essentially based on localized π electron systems within individual organic molecules. The emissions are all in the blue region with the λ max ranging between 462 nm and 421 nm, depending on the concentrations of the materials. The excitation spectra of dichloro-DPQ in crystalline powder form shows peak at 370 nm. When the powder is excited at 370 nm, it emits intense blue light of wavelength 462 nm, as shown in **Fig. 5**. In case of diphenyl quinoline (DPQ), the PL spectrum shows emission at 434 nm when excited at 365 nm [26]. Hence red shift is observed in case of dichloro-DPQ in powder form. The red shift of 28 nm is found due dichloro group substitution as compared to 2, 4-DPQ. The full

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width of half maxima (FWHM) value of PL spectrum is 93 nm.



Fig. 6. PL Excitation and emission spectra of dichloro-DPQ in PMMA matrix when excited at 365 nm.



Fig. 7. PL Excitation and emission spectra of Dichloro-DPQ in PS matrix when excited at 355 nm.

The PL spectra of thin films of the dichloro-DPQ with PMMA and PS are investigated and shown in **Fig. 6-7**. The blue emission band is at the different location as the single chain emission of dichloro-DPQ in a matrix of PMMA and PS. The PL spectra of dichloro-DPQ with PMMA with different weight concentrations like 10, 5 and 1, when excited at 365 nm for all concentrations; we get emission in nm at 443, 438 and 435 nm, respectively (**Fig. 6**).

The PL spectra of dichloro-DPQ with PS with different weight concentrations like 10, 5 and 1, when excited at 355 nm for all concentrations; we get emission in nm at 422, 434 and 426 nm, respectively (**Fig. 7**). A small hypsochromic shift is observed in case of blended thin films of dichloro-DPQ+PMMA and dichloro-DPQ+PS at different decreasing weight % concentrations such as 10, 5 and 1 wt% as compared to the dichloro-DPQ powder. This type of emission with decreasing concentration may be due to molecular interactions. At higher concentrations molecules come close together and

can interact. This can result in lowering of the energy levels. It is quite possible that emission from higher excited state may get quenched due to cross relaxation. The derivative of DPQ such as amino-DPQ and their polymer blended films show the same hypsochromic shift [27]. As we see the PL spectra of dichloro-DPQ in PMMA and PS at 10 weight %, emission peak λ em in PMMA at 443 nm and in PS 422 nm as shown in **Fig. 8**.



Fig. 8. Comparison of Dichloro-DPQ in PMMA and PS at 10 wt% .



Fig. 9. Energy band gap of dichloro-DPQ+PMMA at different wt% concentrations.

The polar carbonyl side group of PMMA may be responsible for removing the degeneracy via interaction with the lone pairs of the nitrogen. This effect is not seen in the PS case possibly because the main chain group has a reduced interaction with the dopant. Hence there is change in intensity. In general the PL in organic materials is originated from the radiative recombination of singlet exciton, especially singlet polaron-exciton i.e., bound electron-hole pairs in polymers. It is generally true that the emission spectrum has much better resolved structure than is seen in the absorption spectrum. In the doped PMMA film the dopant-polymer interaction and possibly a more uniform dispersion [28].

A very narrow full width at half-maximum (FWHM) value of dichloro-DPQ powder 93 nm as well as blended thin films with both PMMA having 62, 48, 81 nm and PS

matrix having 102, 60, 52 nm of PL spectra at different weight % concentrations such as 10, 5, 1 wt % can be obtained respectively. The FWHM of the PL emission spectrum in solid powder is broadened as compared to PMMA matrix at all concentrations. In case of dichloro-DPQ+PS at 10 wt%, emission spectrum is broadened as compared to solid powder.

The energy band gap of dichloro-DPQ with PMMA and PS matrixes at different weight % concentrations are as shown in **Fig. 9-10** respectively. Optical excitation of electrons across the band gap is strongly allowed transition producing an abrupt increase in absorptivity at the wavelength corresponding to the gap energy. This feature in the absorption spectrum is known as the optical absorption edge.

The bandgap of material can be measured from absorption edge of UV-visible spectra. The procedure described by Morita et al. [29] is used for energy gap determination. Table 2 shows the spectral properties of dichloro-DPQ λ max, λ ex, λ em, energy gap and FWHM (PL).



Fig. 10. Energy band gap of dichloro-DPQ+PS at different wt% concentrations.

From CIE 1931 chromaticity diagram are shown in **Fig.11**. The chromatic coordinates (x, y) were calculated using the color calculator program radiant imaging [**30**].

Table 2. Spectral properties of dichloro-DPQ $\lambda_{max},\lambda_{ex},\lambda_{em}$ in nm, energy gap (eV) and FWHM (PL).

Compound	λ _{max} (nm)	λ _{ex} (nm)	λ _{em} (nm)	Energy gap (eV)	FWHM (PL)
Dichloro-DPQ		370	462		93
(powder)					
Dichloro-					
DPQ+PMMA					
10%	268, 334	365	443	3.20	62
5%	268, 334	365	438	3.64	48
1%	268, 334	365	435	3.38	81
Dichloro-					
DPQ+PS					
10%	268, 334	355	422	3.15	102
5%	268, 334	355	434	3.40	60
1%	268, 334	355	426	3.28	52

Generally, the color of the phosphorescence is represented by color coordinates which could be calculated from the emission spectrum using the chromaticity coordinate calculation method based on the CIE 1931 (Commission International d'Eclairage) system. In general, the color of any light source can be represented on the (x, y) coordinate in the color space. We calculated its chromaticity coordinates, which are (X= 0.1391, Y= 0.0352), are shown in **Fig. 11** by solid circle. From CIE 1931 chromaticity diagram, one can see that the colour of afterglow located at the blue region.



Fig. 11. CIE 1931 (x, y) diagram displaying emission color coordinates of dichloro-DPQ (X=0.1391, Y=0.0352).

Conclusion

We report about new easy-to-synthesize deep blue lightemitting organic materials. The organic materials are potential candidates because they can be well adjusted chemically to fit wide range of photonics and optoelectronics applications. The organic compounds are blue light emitting chromophore in solid crystalline powder as well as in blended films. From PL spectra of the films of compounds in PMMA and PS emit strong blue luminance. The excitation and emission spectra change significantly with the concentration in both shape and position of the peaks. The blended films are similar to solid solutions, which show concentration effects on the λ_{max} values of PL emissions, by showing hypsochromic shift in emission wavelengths. The luminescent properties of these materials become thus of interest for both fundamental and applied research. Thus, organic materials are good candidates as a blue organic phosphor which could be useful for the field of light industry.

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