Optical study of blue emitting Methoxy substituted 2, 4-Diphenyl uinoline

B.M. Bahirwar¹, J.G. Mahakhode², G.D. Zade³, R.B. Pode⁴

¹Guru Nanak College of Science, Ballarpur. (M.S.) 442701, ²D.B.Science College, Gondia. (M.S.) 441614 ³Jawaharlal Neharu College, Wadi, (M.S.). ⁴ Department of Physics. RTM Nagpur Uni, Nagpur India 440033.

Abstract: Blue-emitting phenylated quinoline conjugated derivatives in liquid and solid phases have generated considerable interest owing to their high photoluminescence (PL) quantum vields. A blue lightemitting material. Methoxy (OCH3) substituted Diphenvl *Quinoline (2,4'-Methoxy Phenyl ,4 - Phenyl Quinoline)* has been synthesized and characterized by FT-IR, UV-VIS absorption and Photoluminescence measurements. Two absorption peaks at 270 and 330 nm due to conjugated side and π - π^* transition of the conjugated main chains, respectively are reported. The synthesized polymeric compound demonstrate a bright emission in blue region at 434 nm in the solid state and at 431 and 461 nm in Chloroform and Acetic acid solutions, respectively. Results reveal a promising blue emitter with a much simpler architecture for high efficiency OLEDs (organic light-emitting devices).

Keywords: Blue emitting material; FT-IR; UV-VIS absorption

Introduction

Organic light-emitting devices (OLEDs) based on small molecule and conjugated polymers are being developed for full color flat panel displays [1, 2]. Efficient and bright red, green, and blue emissions are essential for achieving the full color displays. However, blue emitting materials have a poor color purity and stability due to the intrinsic characteristic of a wide band gap irrespective of the type of materials. In recent years, attempts have been made to develop blue light emitters for full color displays [3]. Several low molecular blue emitting materials such as distyrylaylenes, metal chelates, anthracene derivatives, spirofluorenes, pyrazoloquinolines, siloles, etc. were used for fabricating blue OLEDs [4]. Recently, quinoline conjugated derivatives have generated considerable interest as blue-emitting materials [5, 6]. π – conjugated polyquinolines and related polyquinoxalines have demonstrated excellent electron-transport and electroluminescent properties in OLEDs [9,10]. Polyquinolines are emerging as very promising blue emitting materials due to their unique combination of high thermal stability, easy processability and high photoluminescence (PL) quantum yields [11]. Chiang et al. [12] have developed a series of polyquinolines containing 9, 9-spirobifluorene units, having high thermal stability, good solubility in common solvents and high PL quantum efficiency.

In the present work, we have synthesized methoxy moity substituted 2, 4-diphenyl quinoline (OMe-DPQ). The structure of methoxy substituted 2,4-DPQ is as shown



Figure 1 structure of Methoxy substituted 2, 4 – DPQ (OMe-DPQ)

The molecular structure was confirmed by FT-IR spectra. The synthesized complex was characterized using absorption and optical measurements in solid as well as liquid phases.

Synthesis of Methoxy-DPQ

Methoxy substituted 2,4-diphenylquinoline (DPQ) was synthesized according to Scheme 1 as shown in Fig. 2. 2aminobenzophenone reacts with 4-methoxy acetophenone in the presence of diphenyl phosphate at 140 °C in an Argon atmosphere, resulting in water vapors and finally crystallization gives a Methoxy 2,4diphenyl quinoline. 2-Aminobenzophenone (2 gm, 8.1 mmol, Lancster make) and acetophenone (2 gm, 13.3 mmol, SRL make) were added along with 2 gms of diphenyl phosphate (Aldrich make) and 3 gm of m-cresol (Lancster make) in a glass reactor fitted with a mechanical stirrer and two glass inlets.



Figure 2 Synthesis scheme of Methoxy 2, 4-Diphenyl Quinoline

B.M. Bahirwar

The reaction mixture was purged with a Argon gas (purity: 99.9 %) for 20 min and then temperature was gradually raised to 90 °C under the argon atmosphere for 1 h and later to 140 °C for 4 h. After cooling to room temperature, methylene chloride (100 ml, SRL make) and 10% NaOH (100 ml) were added to the reaction mixture. The organic layer was separated and washed with distilled water (50 ml x 5 times) until a neutral solution was obtained. Later, it was dried over a MgSO4 and evaporated under the natural condition to yield an off-white solid powders. The crude product was then washed with hexane (25 ml x 5 times), resulting a crystalline solid (2.45 gm).

The Fourier transform infrared (FT-IR) spectra were measured using a 8101A SHIMADZU infrared spectrophotometer. The optical absorption spectra of OMe-DPQ in basic (chloroform) and acidic (acetic acid) organic solvents with different mol. concentration were obtained using Analytik Specord-50 spectrophotometer. The photoluminescence spectra were measured by HITACHI F - 4000 spectrofluorometer. All measurements were carried at room temperature.

Results and Discussion

The FT-IR spectra of the new OMe-DPQ chromophore is shown in Fig. 3 The peak at 846 cm⁻¹ is a characteristic of paradisubstitution of the benzene ring (7, 8). The aromatic CH vibration stretch appears at 3100-3000 cm⁻¹ and aromatic carbon-carbon bonds in the aromatic ring (C-C stretch bonds) at about 1500 cm⁻¹. The strong FT-IR peaks at 1663 and 1656 cm⁻¹ of carbonyl groups are completely disappeared in 2,4-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. FT-IR results confirm the formation of methoxy moity substituted 2, 4-diphenyl quinoline.



Figure 3. FT-IR spectra of synthesized OMe-DPQ solid complex

Absorption Spectra

The optical absorption spectra of asymmetric methoxy-DPQ were measured in. chloroform (basic medium) and acetic acid (acidic medium). Figure 4 shows the absorbance in different concentration of OMe - DPQ organic in chloroform. Two absorption peaks in synthesized polymeric compound at 270 and 330 nm due to conjugated side chains and π - π * transition of the conjugated polymer main chains, respectively, are observed.



Fig. 4 Absorption spectra of OMe-DPQ in chloroform

Red shift of absorption peaks in asymmetric Me-DPQ compared to 2- 4 DPQ (λ max = 254 nm) suggests a strong π - π * conjugation. These results are consistent with the recent study on the distinct photophysical properties observed in 2, 4-DPQ. Optical absorption of OMe-DPQ is bathochromically shifted by 10-15 nm, indicating that the methoxy substituent plays a significant role in determining the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Figure 5 shows the absorption spectra of OMe-DPQ in acetic acid solution. The absorbance of the polymeric compound OMe-DPQ in acetic acid is significantly modified, having a different line shape and shifts to high wavelength side compared to chloroform. Two strong absorption peaks centered at 278 and 360 nm are measured, accompanied with a weak shoulder in the UV region.



Figure 5. Absorption spectra of OMe-DPQ in acetic acid solution

Photoluminescence Spectra

The excitation and photoluminescence (PL) spectra of OMe - DPQ in powder form are as shown in Fig. 6. The excitation peak appears at 385 nm, accompanied with a weak shoulder at 270 nm, whereas emission curve indicates an intense blue light at 434 nm, excited at 385nm. A narrow full width at half maximum of 46 nm is measured.





Figure 7 shows the excitation and PL spectra of different concentrations of the OMe-DPQ in chloroform, excited at 367 nm. They show a typical fine structure in dilute solutions of OMe-DPQ. The PL peaks are appeared at 407nm and 430nm. Similar results are obtained with the



Figure 7. Excitation and PL spectra of OMe-DPQ in chloroform



Figure 8. Excitation and PL spectra of OMe-DPQ in acetic acid solution

B.M. Bahirwar

excitation of 374 nm light, except increase in PL emission intensity. A very narrow full width at halfmaximum (FWHM) value of 54 nm is measured. The FWHM of the PL emission spectra in chloroform solution and solid powder are comparable at 46-54 nm. Figure 8 (a) shows excitation and PL spectra of the polymeric compound Me-DPQ dissolved in acetic acid solution (concentration 1×10^{-6} M), excited at the wavelength of 358 nm, whereas results in 1x10⁻³ M concentration are displayed in Fig. 8(b), excited at the wavelength of 365nm. Main peak is appeared at 460nm in both solutions with a very broad full width at halfmaximum value of 105 nm. The Stokes' shift between absorption and emission in acetic acid is found be 101 nm.

Conclusion

We have synthesized a new blue emitting material, Methoxy Diphenyl Quinoline (OMe-DPQ). Methoxy moity in the synthesized polymeric compound reduces the interchain aggregates, resulting a good solubility in organic solvents and high optical stability. The intramolecular excimer emission dominates the luminescence of polymeric compound in acidic (acetic acid) solution compared to chloroform. A very narrow full width at half-maximum (FWHM) value of PL spectra is obtained. Results indicate a promising blue emitting material, Methoxy Diphenyl Quinoline (OMe-DPQ), for organic light emitting devices.

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