Research Article Adv. Mat. Lett. 2011, **2**(5), 373-376 ADVANCED MATERIALS *Letters*

www.vbripress.com, www.amlett.com, DOI: 10.5185/amlett.2011.3075am2011

Photoluminescence studies of trichloro-DPQ organic phosphor

S.B. Raut, S.J. Dhoble*, R.G. Atram

Department of Physics, RTM Nagpur University, Nagpur 440033, India

*Corresponding author. E-mail:rautsonia4@rediffmail.com, bsjdhoble@rediffmail.com, ramdasatram@yahoo.co.in

Received: 26 April 2011, Revised: 22 July 2011 and Accepted: 26 July 2011

ABSTRACT

A new blue emitting material containing quinoline is designed, synthesized and characterized. The material has been prepared by well-known reaction such as Friedlander condensation reaction at 140 °C. The blended thin films of Trichloro-DPQ with poly (methyl methacrylate) (PMMA) at different weight % concentrations such as 10, 5, 1 and 0.1 weight % have been prepared. The structural characterization has been done by FTIR spectra. The synthesized polymeric compound demonstrates emission in blue region at 460 nm in powder form. At different weight % concentrations, there is emission at 444 nm with varying intensity. The light emitting and optoelectronic property of polymeric compound may find application in electroluminescence, OLED and sensors. Copyright © 2011 VBRI press.

Keywords: Organic phosphors; OLED; photoluminescence; XRD; FTIR.

S.B. Raut is research student at Department of Physics, R. T. M. Nagpur University, Nagpur, India. She is working on organic light emitting materials for different opto-electronic applications.

S.J. Dhoble obtained M.Sc. degree in Physics from Rani Durgavati University, Jabalpur, India in 1988. He obtained his Ph.D. degree in 1992 on Solid State Physics from Nagpur University, Nagpur. Dr.S.J. Dhoble is presently working as an Associate Professor in Department of Physics, R.T.M. Nagpur University, Nagpur, India. During his research carrier, he is involved in the synthesis and characterization of solid state lighting nanomaterials as well as development of radiation dosimetry phosphors using thermoluminescence, mechanoluminescence and lyoluminescence techniques. Dr. Dhoble published several research papers in International reviewed journals on solid-state lighting, LEDs, radiation dosimetry and laser materials. He is an executive member of Luminescence Society of India.

R. G. Atram served as a lecturer in Dr. Ambedkar College, Nagpur, India, from 1990 to 2004 and then as an Associate Professor in Department of Physics, R.T.M. Nagpur University, Nagpur, India, during 2004 to 2008. Dr. Atram obtained his Ph.D. degree in 2004 from R.T.M. Nagpur University, Nagpur. He is presently working as Principal, Ismail Yusuf College, Mumbai, India. His research interest is in synthesis and characterization of organic and inorganic materials for lighting applications.

Introduction

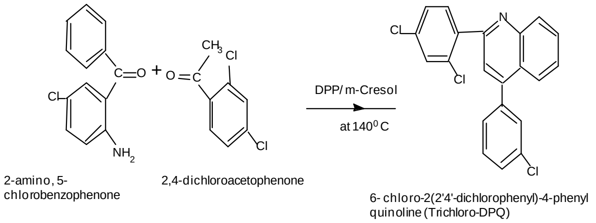
Organic polymers are promising materials for use as in bendable displays, solar panels, and smart materials [**1-6**] as the active layer in optoelectronic devices such as field-effect transistors (FET) [**7**], light-emitting diodes (LEDs) [**8**] and photovoltaic cells [**9**]. Most organic semiconductors are based on π-conjugated molecules, ranging in size from small molecules to polymers. Organometallic compounds with π-conjugated bridges are showing great potential building blocks for carbon-rich networks that are relevant to the development of new optical materials and optoelectronic devices [**10**]. Their organic nature allows for the fabrication of flexible, lightweight materials that can be processed very conveniently, particularly for low power, low cost applications [**11**]. Important advantages of using organic materials rather than inorganic semiconductors are the relatively low production and processing costs, flexibility and a low weight. Organic semiconductors can often be processed from solution, using techniques such as spin coating or ink-jet printing.

Among the several issues, one of the major concerns in the fabrication of full color OLEDs is the equal performance of the three primary colors of red, green and blue. Color purity and stability of blue color remains a challenge. Several low molecular blue emitting materials such as distyrylaylenes, metal chelates, anthracene derivatives, spirofluorenes, pyrazoloquinolines, silones, etc. were used for fabricating blue OLEDs. However, blue emitting material accompanies serious problems of lower efficiency and shorter lifetime compared to red or green emitting material due to difficulty in hole and electron injection with larger band gap [**12**]. Full-color displays incorporating high efficient white organic light emitting diodes with color filters can circumvent issues of high-resolution shadow masking for fine patterning the organic thin films, making it more feasible for fabrication of large-area OLED displays [**13**].

Quinolines are heterocyclic compounds, which are worth to study for many reasons, chief among them being their prevalence among biologically active molecules [**14**]. Recently quinolines conjugated derivatives have generated considerable interest as blue emitting material [**15, 16**]. 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. Poly (quinoline) s have been shown to combine excellent electron-transport abilities and photochemical stabilities with good mechanical and thermal properties. However, one major limitation at this point is the limited solubility of poly (quinoline) s in organic solvents. If the solubility of poly(quinoline)s in common organic solvents can be improved without compromising the physical and optical properties, they posses great potential as active elements in other electronic and opto-electronic devices such as thin film transistors, photovoltaic cells, electrochromic cells, and biosensors.

Experimental

Trichloro substituted 2, 4-diphenyl quinoline has been synthesized by Friedlander condensation of 2-amino, 5-cholobenzophenone and 2, 4-dichloroacetophenone. Trichloro-DPQ was synthesized as shown in scheme 1. 2-aminobenzophenone reacts with 2,4-dichloroacetophenone in presence of diphenyl phosphate at 140 °C, water vapors comes out and finally, undergoes crystallization and gives Trichloro substituted 2, 4 diphenyl quinoline.



Scheme 1. Synthesis of 6-chloro-2(2’4’- dichlorophenyl)-4-phenylquinoline (Trichloro-DPQ).

2-amino, 5-cholobenzophenone (2 gm, 8.1 mmol) and 2, 4-dichloroacetophenone (2 gm, 13.3 mmol) were added along with 2 gms of diphenyl phosphate and 3 ml of m-cresol in a glass reactor fitted with mechanical stirrer for the temperature at 140 ^{o}C for 4 h. After cooling, methylene chloride (100 ml) and 10% NaOH (100 ml) were added to reaction mixture. The organic layer was separated and washed with distilled water (50 ml x 5 times) until it was neutral. Then it was dried over $MgSO_4$ 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 gm). The presence of a chloro group strongly increases the reactivity of the aromatic ring and favour substitution at 2 and 4 positions.

Blends of different polymers potentially offer materials with an attractive combination or balance of properties; however, most polymer pairs are immiscible and many have weak interfacial interactions that lead to an unstable morphology and poor mechanical performance, i.e., they are not able to exist i.e. incompatible. In such cases, compatibilization can be achieved by block (or graft) copolymers located at the domain interface that produce a fine and stable morphology and improved mechanical properties [**17**]. To prepare the composite blended films, PMMA was selected as the host material because PMMA is hard, optically and electrically inert and also has good film forming property with glass transition temperature at about 105 °C. It also exhibits good linear optical transmittance, optical stability, thermal stability and moreover better compatibility with organics [**18**]. A light emitting polymer blended with a photonically inert polymer such as poly (methyl meth-acrylate) (PMMA) often yields a higher PL intensity on photoexcitation due to the dilution effect. Blended films of Trichloro-DPQ in PMMA 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.

IR analysis of the sample products was carried out on Shimadzu FTIR instrument model 8101A. The pellets used for reading spectra were prepared by mixing 1 to 2 mg of the sample with a pinch of KBr. The spectrum in the range of 400 to 4600 cm^{-1} was recorded at room temperature. The photoluminescence spectra (excitation and emission) of trichloro-DPQ in powder and blended films with PMMA at different weight % concentrations were recorded in the Hitachi F4000 spectrofluorophotometer having photomultiplier as detector (Model R372 F) and 150 W xenon lamps with ozone self-dissociation function as a source. This spectrofluorophotometer provides corrected emission and excitation spectra in the 220–700 nm ranges having resolution at 1.5 nm wavelength accuracy.

Results and discussion

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic materials. **Fig.** 1 and 2, show the FTIR spectra of Trichloro-DPQ (powder) and trichloro-DPQ+PMMA (blended film).

From **Fig. 1**, we can conclude that, the aromatic CH vibration stretch which appears at 3100- 3000 cm^{-1}. The new strong bands between 1500 and 1400 cm^{-1} due to the imine (C = N) group and this is the characteristic of the quanoline ring. The C=N structure in the polymers gives the electron transporting characteristics. There are aromatic C-C stretch bands for the carbon- carbon bonds in the aromatic ring at about 1600-1500 cm^{-1}. The substitution pattern in an aromatic is identified by looking at the C-H out of plane bending bands and also from the combination bands (overtones) between 1650- 2000 cm^{-1}. A strong band in the region 750-700 cm^{-1} shows mono-substituted (Cl) benzene. The vibrational stretching for C=C appears at 1690- 1621 cm^{-1}. In **Fig. 2**, we obtained the same vibration stretching as in **Fig. 1**. In case of Trichloro-DPQ + PMMA blended film (10%), the C=O Stretching at 1734-1700 cm^{-1}

and C-O Stretching at 1300-1250 appear in **Fig. 2**. This confirms the fact that trichloro-DPQ has been dispersed as an interpenetrating network in the PMMA matrix.

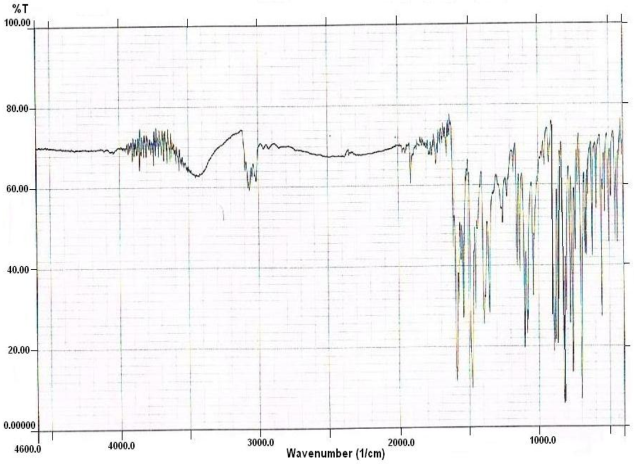


Fig. 1. FTIR spectra of Trichloro-DPQ in powder form.

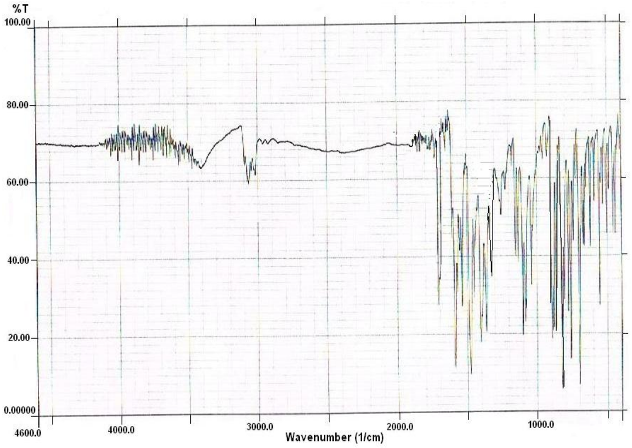


Fig. 2. FTIR spectra of Trichloro-DPQ in PMMA matrix at 10 wt%.

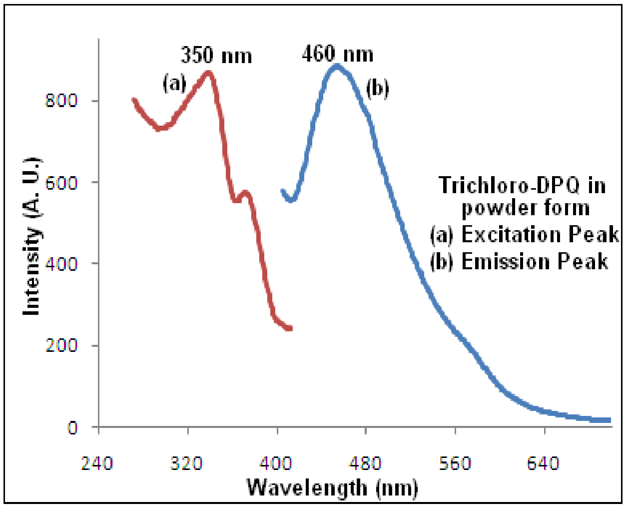


Fig. 3. PL emission and Excitation spectra of Trichloro-DPQ in Powder form, the emission peak was monitored at λ_{exc} = 350 nm.

The luminescence of organic compounds is essentially based on localized π-electron systems within individual organic molecules. The excitation spectra of Trichloro-DPQ in powder form and blended thin film form are shown in **Fig. 3** and **4** respectively. In case of methoxy substituted Diphenyl Quinoline, the PL spectrum shows emission at 434 nm when excited at 385 nm. Hence bathochromic shift by 26 nm is observed in case of Trichloro-DPQ in powder form as compared to the methoxy substituted diphenyl quinoline. The PL emissions are all in the blue region with the λ_{max} ranging in between 460 nm and 444 nm, depending on the concentrations of the material.

When the powder is excited at 350 nm, it emit intense blue light of wavelength 460 nm and is suitable for OLED as shown in **Fig. 3**. Thus the luminescent properties of the materials become interesting as they have received extensive attention for their potential applications in many aspects such as photonic crystal, optical glasses, and fluorescent or laser systems.

Fig. 4 shows the emission spectra blended thin films at 10, 5, 1 and 0.1 wt% concentrations in polymer matrix of PMMA. The PL spectra of Trichloro - DPQ with PMMA at different weight % concentrations we get emission at 444 nm when monitored at 350 nm. The blue emission band is at the different location as the single chain emission of Trichloro-DPQ in a matrix of PMMA. There is systematic blue shift in the emission peak maxima. This is due to molecular interaction between fluorescent material and polymer. The polar carbonyl side group of PMMA may be responsible for removing the degeneracy via interaction with the lone pairs of the nitrogen. In general, the blue-shift is observed when the conjugation length is shortening due to any kind of structural effects.

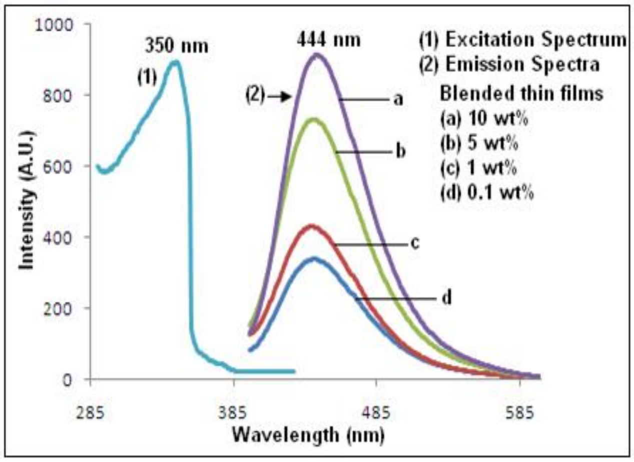


Fig. 4. PL emission and Excitation spectra of Trichloro-DPQ in blended thin films with PMMA matrix

Conclusion

The affordable starting materials for the chemical synthesis of the different quinoline emitters and its simplicity make this material class suitable. The organic compound is a blue light emitting chromophore in solid crystalline powder as well as in blended thin films. The FTIR spectra confirmed the molecular and structural characteristics of our sample. The blue emission band is observed in Trichloro-DPQ at different concentrations in a polymer matrix of PMMA.

The blended films are similar to solid solutions, which show concentration effects on the aggregation of dopant emitters as well as the λ_{max} values of PL emissions. Hence, compared with pure powder form, the concentration effect of the PMMA in different weight % induces blue shift of PL in the blended films. The developments of organic light emitting materials are important as they may be one of the next inroads into the flat panel display market.

Reference

1. Mikroyannidisa, J. A.; Suresh, P; Sharma, G. D. *Synth. Met*. **2010**, 160, 932.
   DOI: 10.1016/j.synthmet.2010.02.003
2. Chauhan, V.; Yunus M.; Sankararamakrishnan, N. *Adv. Mat. Lett*. **2010**, 1, 225.
   DOI: 10.5185/amlett.2010.6135
3. Goyal, R. K.; Damkale, S. R.; Mulik, U. P.; Negi, Y. S.; Dadge, J. W.; Aiyer, R. C. *Adv. Mat. Lett*. **2010**, 1, 264.
   DOI: 10.5185/amlett.2010.8150
4. Shukla, S. K.; Bharadvaja, A.; Tiwari, A.; Parashar, G. K.; Dubey, G. C. *Adv. Mat. Lett*. **2010**, 1, 129.
   DOI: 10.5185/amlett.2010.3105
5. Kalyani, N. T.; Dhoble, S. J.; Pode, R. B. *Adv. Mat. Lett*. **2011**, 2, 65.
   DOI: 10.5185/amlett.2010.10169
6. Raut, S. B.; Dhoble, S. J.; Atram, R. G. *Synth. Met*. **2011**, 161, 391.
   DOI: 10.1016/j.synthmet.2010.12.016
7. Facchetti, *A. Mater. Today* **2007**, 10, 28.
   DOI: 10.1016/S1369-7021(07)70017-2
8. Gledhill, S. E.; Scott, B.; Gregg, B. A. *J. Mater. Res*. **2005**, 20, 3167.
   DOI: 10.1557/jmr.2005.0407
9. Spanggaard, H.; Krebs, F. C. *Sol. En. Mat. Sol. Cells* **2004**, 83, 125.
   DOI: 10.1016/j.solmat.2004.02.021
10. Wong, W. –Y.; Guo, Y.; Ho, C. –L. J. *Inorg. and Organometal. Poly. and Mat*. **2009**, 19, 46.
    DOI: 10.1007/s10904-008-9233-9
11. Baumgartner, T. J. *Inorg. and Organometal. Poly. and Mat*. **2005**, 15, 389.
    DOI: 10.1007/s10904-006-9013-3
12. Youngil Park, Chang-Hun Seok, Ji-Hoon Lee, Jongwook Park, *Synth. Met*. **2010**, 160, 845.
    DOI: 10.1016/j.synthmet.2010.01.031
13. Zhang, G.; Chou, H.; Jiang, X.; Sun, P.; Cheng, C. *Organic Electronics* **2010**, 11, 1165.
    DOI: 10.1016/j.orgel.2010.04.016
14. Redeckar, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *App. Phys. Lett*., **1998**, 73, 1565.
    DOI: 10.1063/1.122205
15. Lee, C. J.; Pode, R. B.; Moon, D.G.; Han, J. I. *Thin Solid Films* **2004**, 467, 201.
    DOI: 10.1016/j.tsf.2004.04.016
16. Zang, X.; Shetty, A. S.; Jenekhe, S.A. *Acta Polym*. **1998**, 49, 52.
    DOI: 10.1002/(SICI)1521-4044(199801)49:1<52::AID-APOL52>3.0.CO;2-V)
17. Tiwari, R. R.; Paul, D. R. *Polymer* **2011**, 52, 1141.
    DOI: 10.1016/j.polymer.2011.01.019
18. Poornesh, P.; Hegde, P. K.; Umesh, G.; Manjunatha, M. G.; Manjunatha, K. B.; Adhikari, A. V. *Optics & Laser Technology* **2010**, 42, 230.
    DOI: 10.1016/j.optlastec.2009.06.018