

“Synthesis, Characterization & Comparative study of Organic Derivatives of Di-phenyl-quinoline (DPQ) Phosphors for Light Emitting Diodes (OLED)”

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Abstract:

An Organic Light Emitting Diode (OLED) is a special type of light-emitting diode (LED) in which, the emissive layer comprises a thin-film of certain organic compounds. These polymers are found growing applications in electronics and optoelectronics, including light-emitting diodes, photovoltaic cells, thin film transistors, and sensors. Primary colours Red, green, and blue emissions with high efficiencies are required for full-colour displays. New series of blue light emitting di-phenyl-quinoline (DPQ) & its derivatives Methyl (M-DPQ), Chlorine-Methyl (Cl-M-DPQ), Chlorine-Methoxy (Cl-MO-DPQ), 2-(4-Bromo-Phenyl)-6-Chloro-4-Phenyl-quinoline (Br-DPQ), (P-Acetyl biphenyl-Cl-DPQ), P - Hydroxy DPQ, OMe - DPQ and 4 - (6-Chloro-4-Phenyl-quinolin-2-yl) Phenol phosphor were synthesized in Argon atmosphere at 140 °C by Friedlander condensation. All samples in different organic solvents were studied. Structural characterization was made by FTIR. Ultraviolet, fluorescence and excitation spectroscopy were used for analysis of photo physical properties. Thermal properties were characterized by TGA and SDTA. The TGA and SDTA characterization show not only the DPQ but also its derivatives have good thermal stability even though they are low molecular weight organic compounds, which may in turn improve the stability and operating lifetime of the device. The physical and chemical properties of these polymers are useful as a blue emitting organic material for OLED's and solid state lightning.

Keywords: Di-phenyl-quinoline (DPQ), Synthesis, Characterizations, Comparative study.

Introduction:

As compared to inorganic ones, organic materials have several advantages like easy handling and synthesis of organic materials with very high emission quantum efficiency. In wide research drill, the invention of efficient blue electroluminescence in organic and conjugated polymer has come out in a vast literature on organic light emitting diodes (OLEDs). Among the several issues, one of the major concerns in the fabrication of full colour 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 [1-3]. Few low molecular blue emitting materials such as distyrylarylenes, metal chelates, anthracene, derivatives, spirofluorenes, pyrazoloquinolines, silones, etc. were used for building blue OLEDs. However, these materials accompanies serious problems of lower efficiency and shorter life time as compared to red or green emitting materials due to trouble in hole and electron injection with larger band gap [4]. Materials with good optical non-linearity and spectral characteristics are required for high-level mechanics such as optical switching, information processing, telecommunication and data storage [5] and displays [6]. Due to their unique combination of high thermal stability, easy process ability and high photoluminescence (PL) quantum yields, Polyquinoline (PQ) conjugated derivatives have accomplished major interest as very promising blue emitting materials [7-11]. Many DPQ's were developed and their spectroscopic and optical properties were examined by choosing a proper doping molecule and the concentration so as to modify carrier transport properties [12]. In recent times, phenylated quinolone and their derivatives are used in OLED as carrier transporting as well as emitting materials [13]. On that account, an attempt has been made to synthesize Methyl

(M - DPQ), Chlorine-Methyl (Cl-M-DPQ), Chlorine-Methoxy (Cl-MO-DPQ), 2- (4-Bromo - Phenyl)-6 -Chloro-4-Phenyl-quinoline (Br-DPQ), (P-Acetyl biphenyl-Cl -DPQ), P - Hydroxy DPQ, OMe - DPQ and 4 - (6-Chloro -4-Phenyl-quinolin-2-yl) Phenol, by Friedlander Condensation Reaction and analyse their structural, thermal and optical properties.

Experimental:

In the present work, blue emitting polymers was synthesized in nearly quantitative yield by **Friedlander Condensation Reaction**. All the materials and the chemicals used are of Analytical Reagent (AR Grade). The materials used for the synthesis of polymers are –

1. FOR- Methyl (M - DPQ), →
 - 2-Amino, 5- Chlorobenzo phenone.
 - P-Methyl Acetophenon,
 - Diphenyl Phosphate (DPP)
 - m – Cresol
2. FOR- Chlorine-Methyl (Cl – M - DPQ)→
 - 2-Amino, benzo phenone.
 - P-Methyl Acetophenon
 - Diphenyl Phosphate (DPP)
 - m – Cresol
3. FOR - Chlorine-Methoxy (Cl – MO - DPQ) →
 - 2-Amino, 5- Chlorobenzo phenone.
 - 4-Methoxy Acetophenon
 - Diphenyl Phosphate (DPP)
 - m – Cresol
4. FOR- 2- (4-Bromo - Phenyl) – 6 – Chloro – 4 – Phenyl-quinoline (Br-DPQ),
 - 2-Amino, 5- Chlorobenzo phenone.
 - 4 Bromoacetophenone
 - Diphenyl Phosphate (DPP)
 - m – Cresol

The materials used for purification are –

1. Dichloromethane (CH_2Cl_2)
2. Sodium hydroxide (NaOH)
3. Hexane ($\text{CH}_3(\text{CH}_2)_4\text{CH}_3$)

Synthesis Scheme:

The experimental arrangement used for the synthesis of all the four polymers by Friedlander Condensation Reaction involves the following steps-

Step 1: Materials/ chemicals used as mentioned above for four polymers were used as the starting materials with proper proportion for the reaction of the polymer. The mixture of these materials are added in a round triple neck flask and fixed the glass stirrer from the middle neck of round flask for stirring the compound.

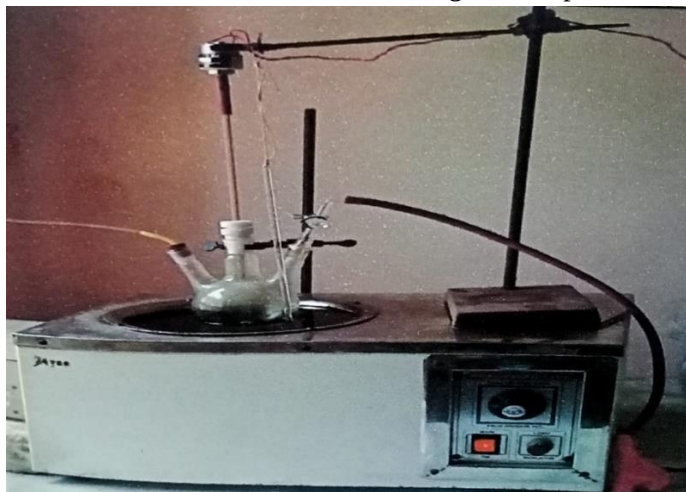


Fig. 1 Experimental arrangement for the synthesis

Step 2: The temperature of oil bath was maintained at constant value at 90⁰ for one hour and then at 140⁰ for four hours.

Step 3: After completing the heating and stirring process, the flask was taken out from the oil bath and cooled for two hours.

Step 4: In the purification process, 60 ml dichloromethane (Methylne chloride) and then 60 ml NaOH solution with 10 % NaOH concentration were added and the mixture was kept for cooling up to eight hours. Two organic layers were observed in the flask as shown in figure 2.

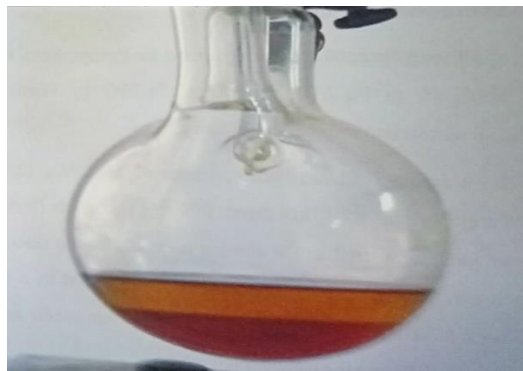


Fig. 2 Organic layers obtained after cooling

Step 5: These layers were separated by the funnel and then washed with 20 ml distilled water (3 times) [14].

Step 6: Later, the resulting precipitate was kept in the hot air oven at 40⁰C for drying the synthesized polymeric compound.

Step 7: It is again washed with 20 ml of hexane (3 times).

Step 8: Later, the powder precipitated was collected on butter paper and dried at room temperature.

Step 9: It was kept in hot air oven at 40⁰ C. Finally, milky white color powder with various compound weights for each derivatives of DPQ polymer were obtained.

The representation of structural scheme of the derivatives of DPQ are shown if figure below.

1. Methyl (M - DPQ)-

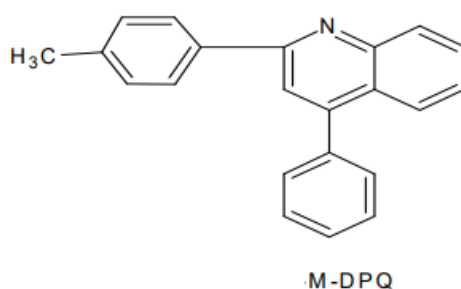


Fig. 3 Chemical structure of M- DPQ polymer

2. Chlorine-Methyl (Cl – M - DPQ)-

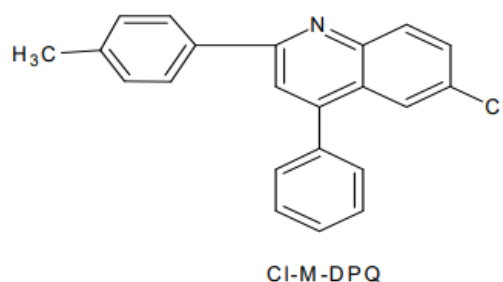


Fig. 4 Chemical structure of Cl – M - DPQ polymer

3. Chlorine-Methoxy (Cl – MO - DPQ)-

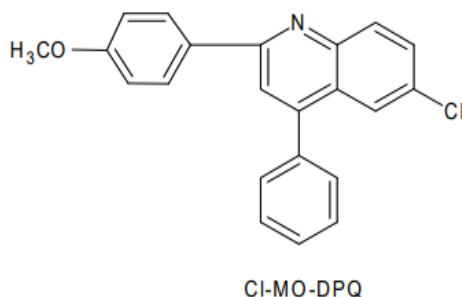


Fig. 5 Chemical structure of Cl – MO - DPQ polymer

4. Phenyl-Quinoline (Br-DPQ)-

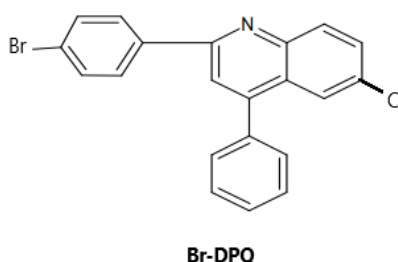


Fig. 6 Chemical structure of Br - DPQ polymer

Characterization:

Structural, thermal and optical properties of the newly synthesized polymeric compound were probed by various characterization techniques such as Fourier Transformation Infrared (FTIR) spectroscopy, X- Ray diffraction (XRD), Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Photoluminescence (PL) spectroscopy.

- FTIR Spectra → To determine the chemical compositions [15]
- XRD Spectra → To determine the crystalline structure of polymers.
- TGA Curve → To study the thermal properties of the sample. [16,17]
- DTA Curve → To determine the melting point of the material
- PL- Spectra → To study the emission and excitation phenomena.

Result & Discussion:

Materials in solid state or even solvated materials can be used to record the photoluminescence spectra. The photoluminescence spectroscopy is a contactless and non-destructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and impart excess energy into the material in a process called photo excitation. This excess energy can be dissipated by the sample through the emission of light (luminescence). The excitation and emission of the derivatives of DPQ are summarised in table 1.

Table – 1 Excitation and emission of derivatives of DPQ

S. No.	Derivatives of DPQ	Excitation (nm)	Emission (nm)
1.	M-DPQ	385	468
2.	Cl-M-DPQ	365	442
3.	Cl-MO-DPQ	365	440
4.	Br-DPQ	373	422

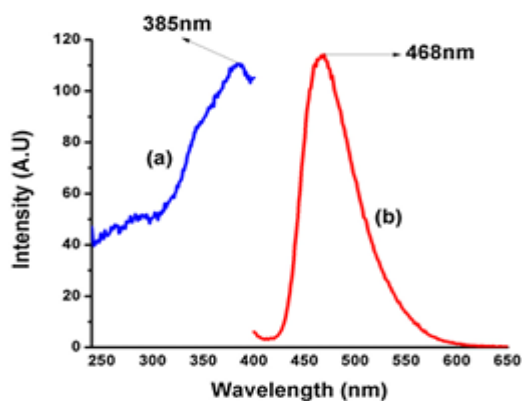


Figure-7 (a) Excitation and (b) Emission Spectra of Excitation of M-DPQ

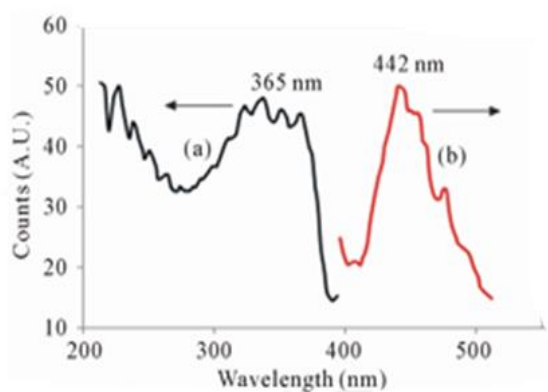


Figure-8 (a) Excitation and (b) Emission Spectra of Excitation of Cl-M-DPQ

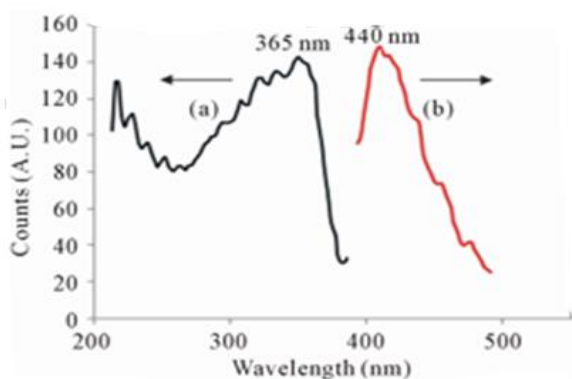


Figure-9 (a) Excitation and (b) Emission Spectra of Excitation of Cl-MO-DPQ

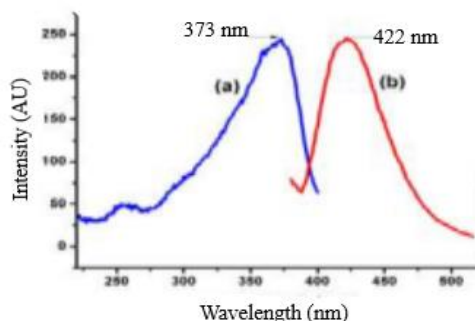


Figure-10 (a) Excitation and (b) Emission Spectra of Excitation of Br-DPQ

Fourier Transform Infra-Red (FTIR) spectroscopy has been a workhorse technique for materials analysis in the laboratory. No two compounds produce the exact infrared spectrum, due to the fact that every material is a unique combination of atoms. Therefore, infrared spectroscopy can result in a positive identification of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. The FTIR spectra of all the derivatives of DPQ are summarised below.

Table-2 Analysis form FTIR spectra

S. No.	Derivatives of DPQ	Fingerprint region/ (Max Transmission)	Cause
1.	M-DPQ	1600-1500 cm^{-1}	Aromatic ring C–C stretching bands.
2.	Cl-M-DPQ	3100 - 3000 cm^{-1}	Aromatic CH vibration stretch
3.	Cl-MO-DPQ	1700 cm^{-1} 2820 - 2815 cm^{-1}	C = O stretching O - CH ₃ group
4.	Br-DPQ	1600-1350 cm^{-1} 829, 696.16 & 587.61 cm^{-1}	C = N group C - H alkaline bonding

The FTIR spectra shows the aromatic CH vibration stretch which appears at 3100 - 3000 cm^{-1} . A strong absorption band in the region around 1700 cm^{-1} is due to C=O stretching. There are aromatic CC stretch bands for the carbon- carbon bonds in the aromatic ring at about 1500 - 1600 cm^{-1} . A small stretching peak appears at 2820 - 2815 cm^{-1} which confirms the presence of methoxy (O-CH₃) group. The strong FT-IR peaks at 1663 and 1656 cm^{-1} owing to the carbonyl groups have almost completely disappeared as in 2, 4-DPQ. 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. We observe the asymmetric C-H stretch of the methyl group (2960 cm^{-1}) occurring at slightly higher frequency than symmetric vibrations (2875 cm^{-1}) for methyl.

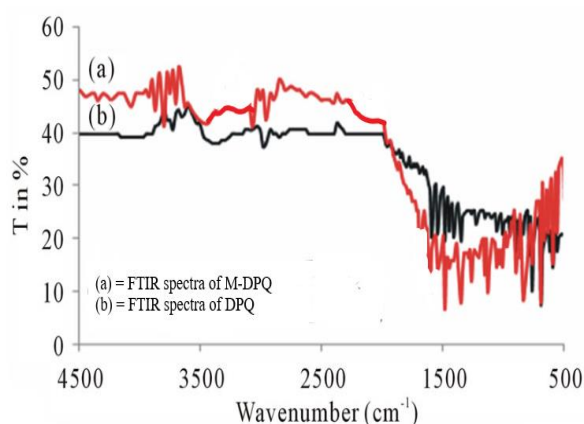


Figure-11 FTIR Spectra of M-DPQ

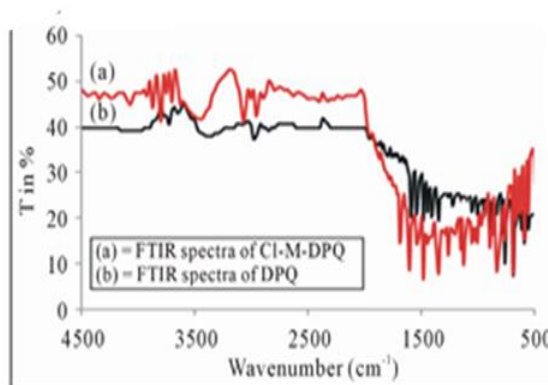


Figure-12 FTIR Spectra of Cl-M-DPQ

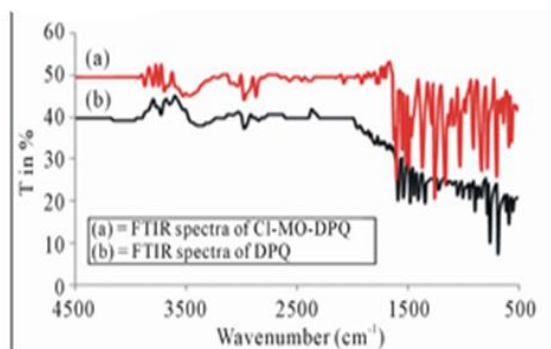


Figure-13 FTIR Spectra of Cl-MO-DPQ

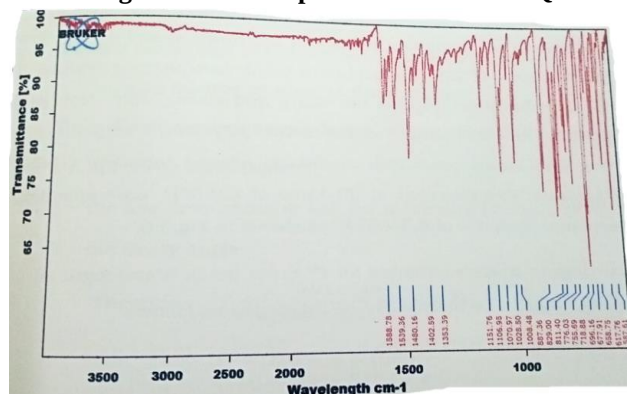


Figure-14 FTIR Spectra of Br-DPQ

Conclusion:

The physical, optical and chemical properties of blue emitting derivatives of DPQ materials like M-DPQ, Cl-M-DPQ, Cl-MO-DPQ and Br-DPQ were studied from the spectra's. As far as emissions are concerned, all the polymeric compounds have their band in the range of 422 - 468 nm. So, they emit better blue emission. In acid there is higher protonation of C = N group and shows emission of higher wavelength. Also, the polymeric compounds show two absorption peaks attributed to UV and visible region and emission in blue region.

In conclusion, the results of the present study show that the optical band gap of DPQ and its substituted derivatives varies in acids. The P-Acetyl biphenyl and P-Acetyl biphenyl Chloro substitution increases the solubility and shows appreciable blue emission in several solvents. The present results on the electronic structure and optical properties of all the polymers suggest that they can be expected to have improved nonlinear optical properties. Enhancement in PL intensity and spectral modification are observed in the new polymeric compounds. During the synthesis of all the polymeric compounds we used only 2 gm weight of catalyst Diphenyl Phosphate (DPP0. So, these compounds are very conomic. Thus, from the results of present study, all the polymeric compounds can have an applications in electroluminescence, OLED's, sensors, etc.

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