

Synthesis and Photoluminescence Properties of New Conjugated Oligoquinolines 2, 2'-Bis (4-phenylquinoline) 1, 4 Phenylene

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Abstract: A novel 2,2'-Bis(4-Phenylquinoline) 1,4 phenylene (BPQ-P) organic phosphor was synthesized in Argon (Ar) and Nitrogen (N₂) atmosphere at 140°C by using Friedlander Condensation reaction. Based on our previously synthesized DPQ, we systemically designed some novel derivatives with tuned optical properties & the compound showed blue emission under a UV source. The synthesized organic phosphor is assessed by various characterization techniques such as FTIR and NMR spectroscopy. Using excitation and emission spectra were analysed the properties of PL in organic compounds. The synthesized organic phosphors show bright emission in the blue region, with the peaks at 483nm for 4-phenylquinoline. The physical and photoluminescence properties of these organic compounds reveal promising blue emitters for high efficiency organic light emitting diodes (OLEDs) and it may also find device applications as n-type semiconductors.

Keywords: Synthesis, Photoluminescence, NMR, UV-absorption, OLEDs, n-type semiconductor

I. INTRODUCTION

Now a day, organic materials have several advantages with respect to inorganic materials among them, ease of synthesis and handling and very high emission quantum efficiency. One of the most fascinating advantages of organic materials is the possibility of a wide range of emission colours in the blue region.

Developing blue light emitters is essential for the development of full color displays [1, 2]. It is much more difficult to produce blue emission due to the intrinsic characteristic of having wide band gap irrespective of the type of materials [3]. Because of their high solution and solid-state photoluminescence (PL) quantum yields, recently much research into blue emitting materials has centred on fluorine-conjugated derivatives [4]. More recently, some pyrene derivatives have been used in OLEDs in order to improve hole-transporting ability because of its electron-rich property [5], yet the performance of those OLEDs is not satisfactory in brightness and efficiency. Polyquinolines, which were developed by Still et al. In the 1970s are synthesized by the acid-catalysed Friedlander condensation reaction between monomers containing Bis (o-aminoketone) and Bis (ketomethylene) functional moieties. Based on their optical and electronic properties for these polymers have recently been investigated as potentially useful materials in optoelectronic applications such as electroluminescent [1-5] and non-linear optical devices. Oligoquinolines, Polyquinolines and copolymers have been proposed as electron transport materials (or emitters) for LED devices because of the electron deficient nature of the quinoline ring [6-7]. In the light of these observations, we also studied the optical, luminescent and electrochemical properties of the new Oligoquinolines.

The synthesis, electronic structure and optical, non-linear optical and charge transport properties of numerous conjugated oligomers [8] of polyenes, acenes [9], thiophene [10], pyrrole [11], p-phenylene and p-phenylene vinylene [8] has been extensively investigated both as P type (hole transport) organic semiconductors and as structurally well-defined model systems for the corresponding conjugated polymers [12-17] are known. We report here in synthesis, NMR structures and photoluminescence properties of new conjugated oligoquinolines. The oligomers are promising

model systems for elucidating the structure property relationships of conjugated polyquinolines and may also be useful as N type semiconductors for device applications.

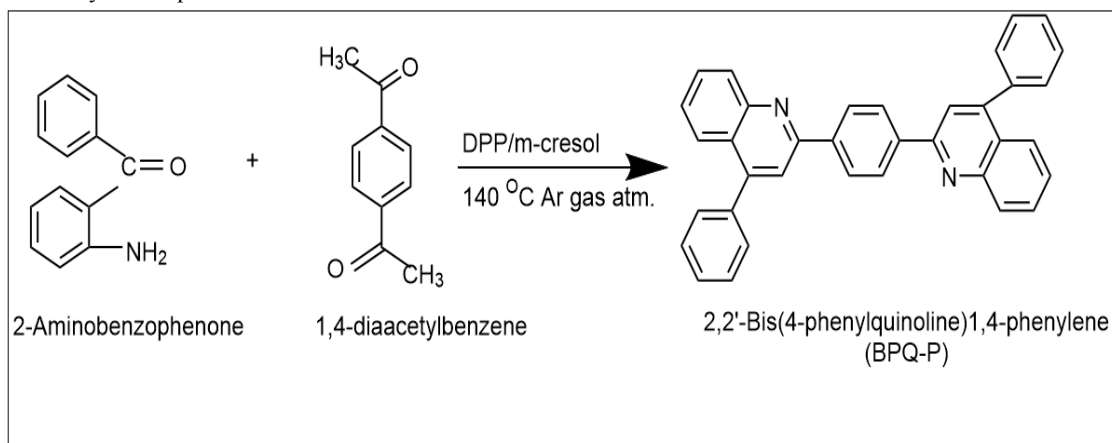
The N-type conjugated polymers by virtue of their electron transport, high electron affinity and interesting Photophysical properties are of growing interest in electronic and optoelectronic devices,

Although over several dozen polyquinolines have been reported in the last two decades [12-17] only one preliminary report discussed the crystal structure of a right-rod polyquinolines.

II. EXPERIMENTAL

In the present work, blue light emitting oligoquinolines 2,2'-bis (4-phenylquinoline) 1,4 phenylene (BPQ-P) was synthesized.

All the materials and the chemicals are of Analytical Reagent (AR) grade. According to Scheme I as shown below, 2-aminobenzophenone reacts with 1,4 diacetyl benzene in presence of diphenyl phosphate at 140⁰c, in an Aragon(Ar) atmosphere, water vapour comes out and finally undergoes crystallisation and gives 2,2'-bis(4-phenyl quinoline) 1,4 phenylene(BPQ-P).In reaction mixture 2-Aminobenzophenone(2gm, 8.1mmol, Aldrich make) & 1,4 diacetyl benzene(1gm, 6.16mmol, TCI America) were added along with diphenyl phosphate(DPP)(2gm,12.3mmol, Aldrich make) and 3ml of m-cresol (Alfa Aesar) in a round bottom glass reactor fitted with mechanical stirrer and two glass inlets. The synthesis process was conducted in oil bath.



Scheme I: Synthesis of oligoquinoline 2,2'- Bis (4- Phenylquinoline) 1,4 phenylene (BPQ-P)

The reaction mixture was heated to 90⁰c gradually under Aragon (Ar) gas atmosphere for 1 hour and subsequently to 140⁰c for 5 hours. After 6 hours, the solution was cooled and poured into a solution of 10% triethylamine in methanol (300ml) and the crude product was collected by filtration. The oligomers were purified by recrystallization from a 1:4 mixture of tetrahydrofuran (THF) and methanol. The solid crystallization powder was dissolved in organic solvents basic (THF) as well as in acidic (F.A.) in different mol concentration. The optical absorption spectra of solutions were obtained on UV-visible spectrophotometer SHIMADZU UV-1700. The photoluminescence spectra were obtained by HITACHI F-7000 AND F-7500 FL fluorescence spectrophotometer.

III. RESULTS AND DISCUSSION

3.1 NMR Spectra

In Fig.1 represents ¹H NMR spectra was recorded in 400 MHz to determine the structure of organic molecules in CDCl₃ solution of BPQ-P. It characterized the nature and the purity of phosphor. The chemical shifts observed from ¹H-NMR spectrum of BPQ-P were found to be δ (ppm)8.388(s,4H), δ 8.303(d,2H), δ 8.123(d,2H), δ 7.911(d,2H), δ 7.856(s,2H), δ 7.768(m,12H) where d, s and m stand for doublet, singlet and multiplet bands respectively as shown in fig.1. This spectrum conforms the presences of 24H-atom in synthesised phosphor. This peak can be assigned to the

aromatic protons which are corrected with the structure as described in fig.1. This indicates crystalline parts give sharp narrow resonances peaks and amorphous component gives a very broad and small peak (halo).

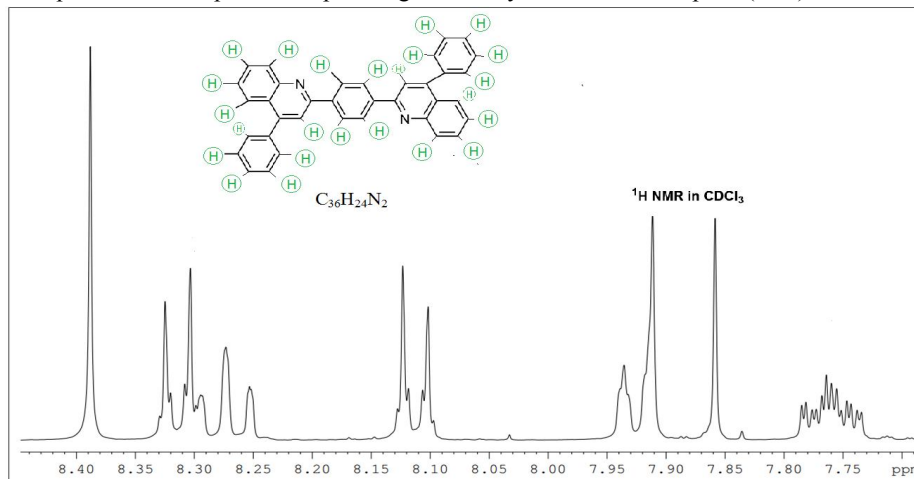


Figure 1: NMR spectra of 2, 2'-Bis (4-phenylquinoline) 1, 4-phenylene (BPQ-P)

3.2 FT-IR Spectra

The FT-IR of new conjugated polymer is shown in fig.2. The peak at 762 cm^{-1} is a characteristic of paradiistribution of the benzene ring. The strong FT-IR peaks at 1678 and 1583 cm^{-1} of carbonyl groups are completely disappeared in 2,4 DPQ derivative. Instead, new strong bands between 1590 & 1480 cm^{-1} due to imines ($\text{C}=\text{N}$) group and characteristic of the quinoline ring was observed. The aromatic CH vibration stretch appears at 3152 & 3100 cm^{-1} and aromatic C-C bonds in the aromatic ring (C-C stretch bonds) at about 1500 cm^{-1} . FT-IR find the results that the confirm the formation of double benzene ring substituted 2, 4 DPQ

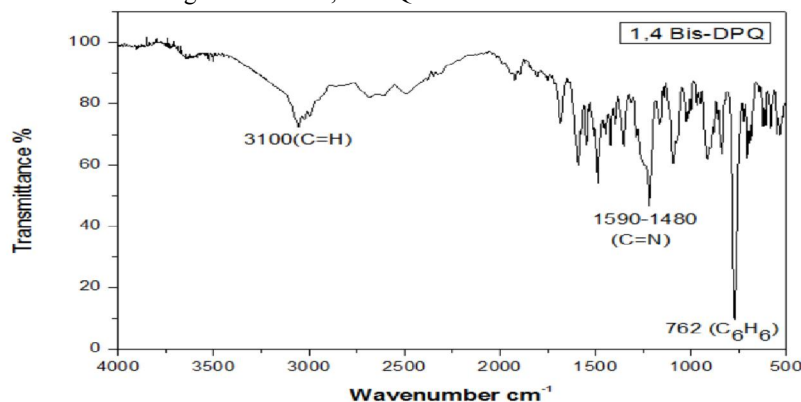


Figure 2: FT-IR spectra of 2, 2'-Bis (4-phenylquinoline) 1, 4-phenylene (BPQ-P)

3.3 Optical Study

A. Absorption Spectra

The absorption spectrum of synthesized BPQ-P in THF & Formic acid solution at room temperature is shown in Fig.3 & Fig.4 results the absorbance in different concentration of oligoquinolines polymer in both solution. Two absorption peaks in synthesized organic compound at 288 , 340 & 359 nm in THF due to conjugated side chains and $\pi-\pi^*$ transition of the conjugated polymer main chains, respectively are observed. Optical absorption spectra of this polymeric compound is bathochromically shifted by $15-20\text{ nm}$ indicating that a blue light emitting is promisable to

determine the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Similarly, in Formic acid solution the two absorption peaks of synthesized chromophore at 282 & 360 nm. Thus, the absorption spectra has found that $\lambda_{\max}=360$ nm.

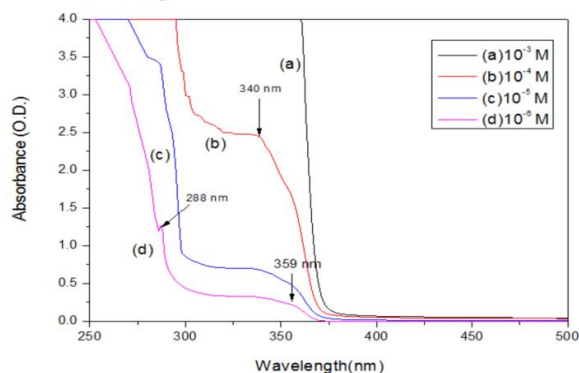


Figure 3: Absorption spectra of BPQ-P in THF

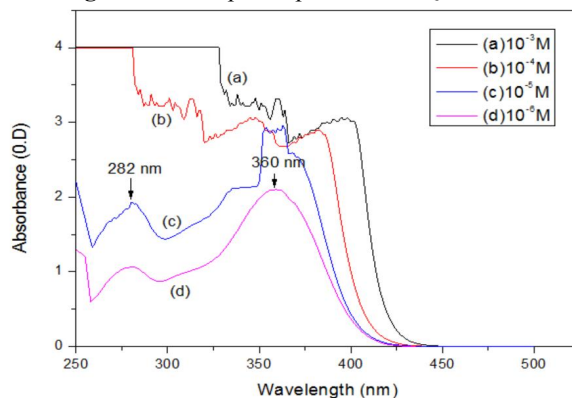


Figure 4: Absorption spectra of BPQ-P in Formic acid

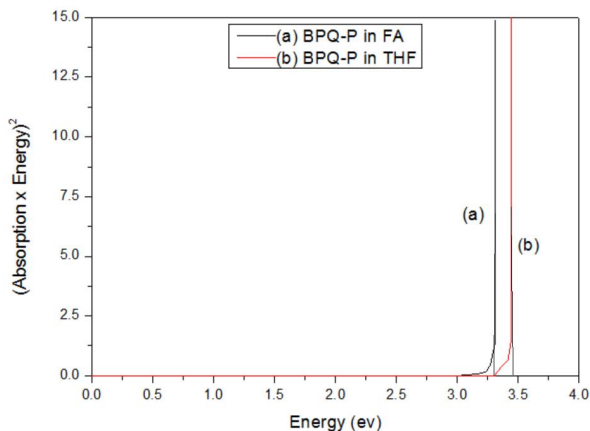


Figure 5: Optical energy band gap of BPQ-P in formic acid

The determination of energy band gap of BPQ-P using the literature processor was found to be 3.28 eV and 3.34 eV in formic acid and THF respectively as shown in above fig.5.

B. Photoluminescence Spectra

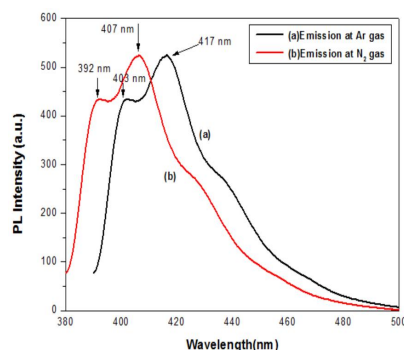


Figure 6: PL Spectra of BPQ-P in THF under Ar gas and N₂ gas

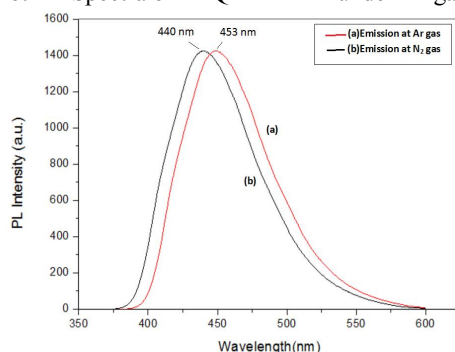


Figure 7: PL spectra of BPQ-P in Formic acid under Ar gas and N₂ gas

The PL spectra of BPQ-P were synthesized organic phosphor in THF and Formic acid solvents are shown in fig.6. & fig.7 at Ar and N₂ gas atmosphere. The excitation and emission spectra of the oligoquinolines show similar dependents on the size of the aromatic group that links the two quinoline moieties and the solvent environment. The emission spectrum of BPQ-P in THF show two peaks at 407 nm and 417 nm under N₂ and Ar gas atm. respectively when excited wavelength of 380 and 395 nm. The red shifted from the emission maxima is 10 nm. The emission spectrum of BPQ-P in F.A. show two peaks at 440 nm and 453 nm under N₂ and Ar gas atm. respectively when excited wavelength of 410 and 415 nm. The red shifted from the emission maxima is 13 nm. The shift in excitation and emission wavelength can be attributed due to the changes in the polarity of solvent. The shift was found larger in protic solvents as compare to aprotic and non-polar solvents.

C. Stokes Shift

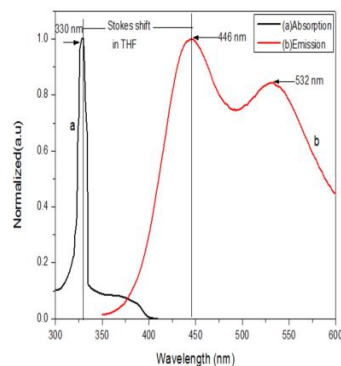


Figure 8 (a): Stokes shift of BPQ-P in THF

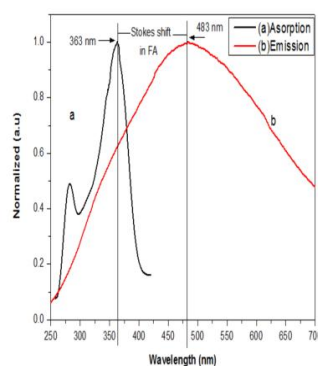


Figure 8 (b): Stokes shift of BPQ-P in formic Acid

The Stokes shift of 2, 2'-Bis (4-phenylquinoline) 1, 4 Phenylene (BPQ-P) was even larger [65-68 nm] in protic solvents in comparison with aprotic and non polar solvents. It indicates that increase in Stokes shift further support the view of intermolecular charge transfer interactions in the phosphor. Red shift towards higher wavelength is observed in formic acid as compared to THF. The shift of emission in solution increased with increase in solvent polarity. Fig.8 (a) & (b) shows the Stokes shift of BPQ-P in basic (THF) & acidic (Formic acid) solvents.

IV. CONCLUSION

We have successfully synthesized a new blue emitting phosphor 2, 2' Bis (4-phenylquinoline) 1, 4 phenylene (BPQ-P) in solid crystalline powder form. Synthesized BPQ-P has high electron affinity with desired wide band gap required for blue light emission. The investigated structural, optical and thermal stability studied of the synthesized phosphor using NMR spectroscopy, FT-IR spectra, UV-Vis absorption spectrometry, PL spectrometry and TGA/DTA. The change in polarity index of the solvent, the absorption peak shifted towards the long wavelengths, which may be due to protonation of the imines nitrogen of the quinoline ring. Emission spectra show better luminescence at 1 wt. %, 5wt. % and 10 wt. % with variation in optical density. The synthesized polymeric phosphor emits more intense blue light at lower wt. % concentration probably observing emission from isolated molecules. Its photoluminescence yield increases unusually in the solid-state over solution, 52%-60% respectively.

The Stokes shift was observed 65-68 nm larger in protic solvent in comparison with aprotic and non polar solvents. In term of applications, with inorganic or metallic materials, organic molecules and their derivatives have drawn many researchers' candidate materials for nanoscale electronic devices of next generation. These results reflect that the synthesized organic phosphor can be useful for developing organic luminescent devices, solar cell devices, or in chemical sensor and it may also find device applications as n-type semiconductors.

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