THE IMPACT OF ORTHO,META AND PARA METHOXY GROUP SUBSTITUTION ON PHOTOLUMINESCENT PROPERTIES OF 2,4-DIPHENYL QUINOLINE

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Abstract

Using a structure–property relationship for the position and number of methoxy group(s) to tune the optical properties of Diphenyl Quinoline derivatives. Based on our previously synthesized DPQ we systematically design some novel derivatives with tuned optical properties. For instance, the rotation of methoxy ($-OCH_3$) group substitutions at three different possible ortho, meta, and para positions on phenyl ring show significant changes in optical properties of quinoline derivatives. Three new polymeric compounds o-DPQ,m-DPQ, and p-DPQ consisting of 2,4-diphenylquinoline (DPQ) with a $–OCH_3$ group at ortho (o)/meta (m)/para (p) positions of the metalatedphenyl ring, respectively, as the main ligands were synthesized . We realized that $–OCH_3$position extremely affects the crucial photophysical and electronic properties such as emission color, photoluminescence quantum yield(PLQY) and energy levels of these polymeric compounds resulting in $–OCH_3$ position-dependent performance of their PhOLEDs. These compounds may be used for solution-processed easily accessible blue emitter in phosphorescent organic light-emitting diodes (PhOLEDs).. Thus, our investigation reveals that the DPQ derivatives with para-methoxy phenyl groups possess reasonably large amplitudes of their first hyper polarizability and good optical transparency, which can make them attractive candidates for nonlinear optical applications.

Keywords: DPQ,Photoluminescence ,hyper polarizability

1. Introduction

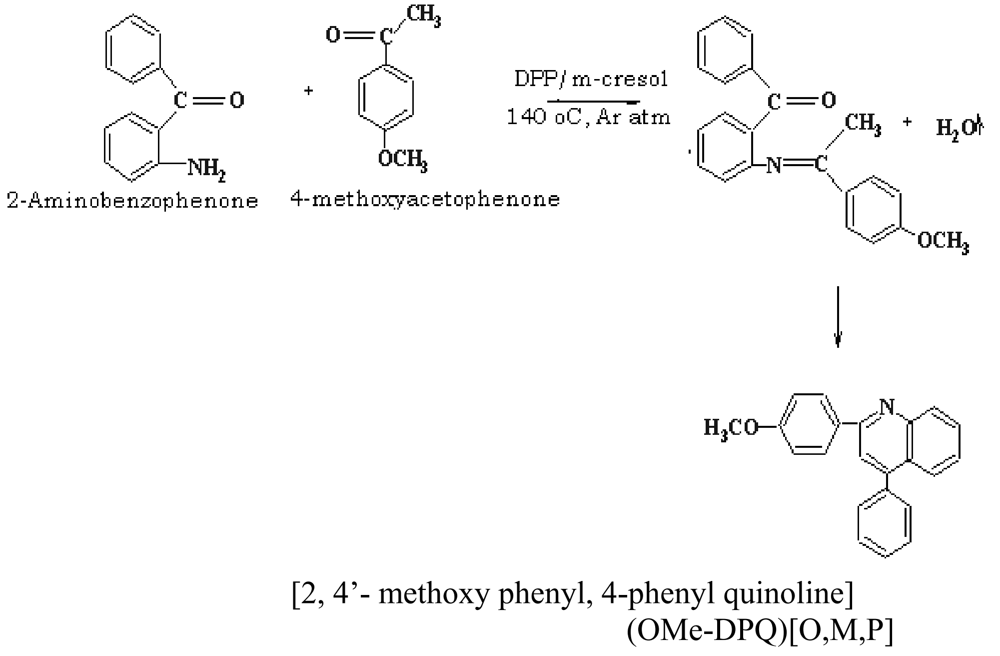
Owing to their excellent properties, optical materials are playing a crucial role in modern day hi-tech applications. The field of optical material designing has got further momentum since the use of a photon as a carrier of information[1]. Over the past few decades a huge variety of optical materials have been proposed, synthesized, and characterized using different experimental techniques . The organic class remains as the front-runner for designing efficient optical materials because of their huge structural diversity, larger optical coefficients as well as their ease of fabrication, etc. [2]. Different structural modification strategies have been used to modulate their optical response of several organic and polymeric compounds including donor-π-conjugated acceptor configuration[3]. The family of Diphenyl Quinoline [DPQ] derivatives has been significantly studied over recent years for their potential optical applications [4]. Several DPQ derivatives have attracted significant attention due to their efficient optical properties and good transparency through blue emission. G. Lee, et al. [5], have synthesized and grown yellow color crystals of DPQ derivatives with methoxy phenyl terminal groups. R. Wang et al. [6], also reported single crystals of pyridine based DPQ derivatives that have found transparent in entire visible and blue range with efficient optical properties[7].We have synthesized and reported methoxy substituted DPQ derivatives including o, m, p-methoxy phenyl groups. Considering these methoxy phenyl groups as terminal donors, these derivatives with push-pull configuration are expected as good candidates for potentialoptical materials[8,9]. In the present investigation, we aim to perform a systematic probe for optical properties, primarily based on the exploitation of number and position effects of methoxy groups with a subsequent substitution to tune the push-pull effects for possible future syntheses .

2. Experimental

Synthesis of ortho,meta,and para substituted [2, 4’- methoxy phenyl, 4-phenyl quinoline] (OMe – DPQ)

Methoxy substituted 2, 4-diphenylquinoline[2, 4’- methoxy phenyl, 4-phenyl quinoline (OMe-DPQ) was synthesized according to Scheme 1 as shown below. 2 - Aminobenzophenone reacts with 4-methoxy acetophenone in presence of diphenyl phosphate at 140 ^{o}C, in an Argon atmosphere, water vapours come out, and finally undergoes crystallization and gives Methoxy 2, 4 - diphenyl quinoline.2-Aminobenzophenone (2 gm, 8.1 mmol, Lancaster make) and 2,3,and 4- methoxy acetophenone [ortho,meta and para](2 gm, 13.3 mmol, SRL make) were added along with 2 gms of diphenyl phosphate (Aldrich make) and 3 ml of m-cresol (Lancaster make) in a glass reactor fitted with mechanical stirrer and two glass inlets. The reaction mixture was purged with an Argon gas (purity: 99.9 %) for 20 min. and then temperature was raised to 90 ^{o}C gradually under the argon atmosphere for 1 h and then to 140 ^{o}C for 4 h.

After cooling, methylene chloride (100 ml, SRL make) and 10% NaOH (100 ml) were added to reaction mixture. The organic layer (fig.4.2) was separated and washed with distilled water (50 ml x 5 times) until it was neutral. Then it was dried over an $MgSO_4$ 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 [$C_{22}H_{17}NO$] (2.45 gm), mol. wt. = 311.242 gm.



[2, 4’- methoxy phenyl, 4-phenyl quinoline]
(OMe-DPQ)[O,M,P]

Fig.:-1 Synthesis of [2, 4’- methoxy phenyl, 4-phenyl quinoline] (OMe-DPQ)[Orto,Meta,Para]

3. Result and discussion:

3.1 FT-IR Characteristics

On the basis of FT-IR spectra, the conversion of the reaction forming OMe-DPQ can be estimated. The peak at 846 cm^{-1}, is characteristic of ortho, meta and para disubstitution of the benzene ring (15).The aromatic CH vibration stretch appears at 3100-3000 cm^{-1}. The absorption corresponding to 2820 cm^{-1}, indicates the presence of methoxy (OCH_3) group. There are aromatic CC stretch bands (for the carbon-carbon bonds in the aromatic ring) at about 1500 cm^{-1}. The strong FT-IR peaks at 1663 and 1656 cm^{-1} owing to the carbonyl groups is almost completely disappeared in all OMe-DPQ. Instead, new strong bands between 1600 and 1400 cm^{-1} due to the imines (C=N) group and characteristic of the quinoline ring were observed. This is usually an excellent confirmation of the completion of cyclization reaction forming quinoline rings.

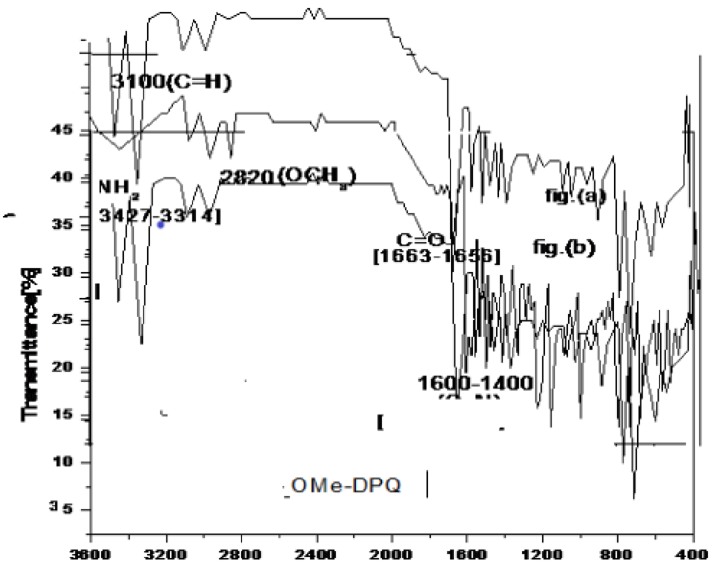


Fig. 2:- FT-IR Spectra of (a)Ortho,(b)Meta, and(c) para OMe-DPQ

3.2 The Photophysical properties

3.2.1 Absorption Spectra:

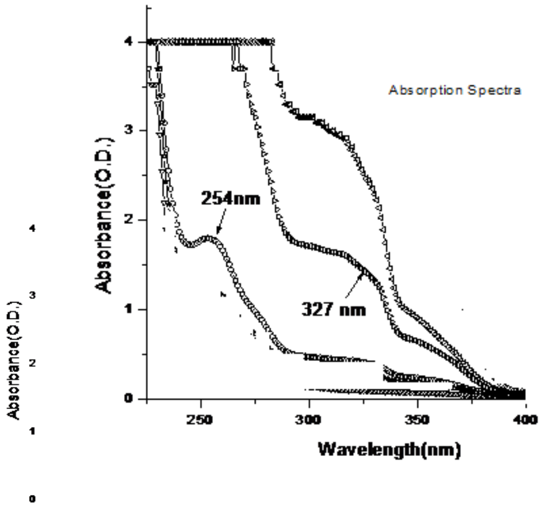


Fig.3:- ,UV-visible Spectra of (a) Ortho,(b)Meta, and(c) para OMe-DPQ

In order to examine the effect of OMe (OCH3) group position on the ground and excited state properties of this polymeric compound, UV-visible absorption spectra (Fig. 3). in $CHCl_3$ (10^{-5} M) at room temperature.The stronger absorption peaks between 265 and 350 nm mostly represent the ligand centered π–π* transitions. The weaker absorption peaks between 350 and520 nm are known to be the admixed ligand charge transfer transitions where the usually spin-forbidden transitions of the triplet states are allowed . The electroattracting character of the substituents present in ortho and meta OMe substitution diminish the intensity of UVVis absorption. As shown in Fig, the lower energy transition bands of meta position clearly blue shifted compared to the o- andp-analogs indicating the impact of –OCH3 substitution position on the ground state properties of the compound.

3.2.2 Photoluminescent spectra

The photoluminescence (PL) spectra (Fig.4) were measured in $CHCl_3$ (10^{-5} M) at room temperature.The position of the – OCH_3 on DPQ has marked changes in the emission wavelength s of both the compounds. The PL peaks are recorded at 460, 485, 490 nm , respectively. Similar to the lower energy bands in the absorption spectra, the PLmax of meta substituted is hypsochromically shifted around 37 nm and 9 nm compared to the ortho substituted DPQ and para substituted DPQ, respectively. The of – OCH_3 group at m-location lowers the highest occupied molecular orbital (HOMO)level of m-OMe DPQ leading to blue shift in emission.

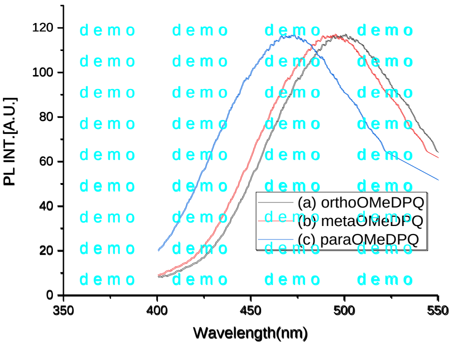


Fig. 4: PL spectra of of (a) Ortho,(b)Meta, and(c) para OMe-DPQ

The strong polarization effect and the large steric volume of the – OCH_3 substituent at o-position might be further reasons for variation in the electronic distribution of ortho-OMe DPQ when compared to para-OMeDPQ demonstrating the influence of – OCH_3 group position on emission color tuning.

4. Conclusions

In this work, we introduced a –OMe group at three different positions (o-/m-/p-) on the 2,4-diphenylquinoline (DPQ) cyclometalating ligand and synthesized series of highly soluble new polymeric compound complexes o-DPQ, m-DPQ, p-DPQ. We observed that introduction of – OMe into m-position greatly diminished the non-radiative relaxations and improved the PL emission .. The overall results of these blue OLEDs are among the best one solution-processed devices. These findings demonstrate a simple approach for fine-tuning the emissive properties of the polymeric compound in order to obtain highly efficient blue emitting PhOLEDs for practical application of the solution process.

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