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Synthesis and characterization of novel 2-(4- bromophenyl)-6-chloro-4- phenylquinoline, blue light emitting organic phosphor

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Abstract

This paper reflects the synthesis and charectarization of a blue light emitting novel 2-(4-bromophenyl)-6-chloro-4- phenylquinoline (Br-DPQ) emitting organic phosphor synthesised by Friedlander condensation reaction. Physical, chemical and optical properties of the synthesized organic phosphor were studied using X-ray diffraction (XRD), Thermo gravimetric and differential thermal analysis (TGA/DTA), Fourier Transform Infrared (FTIR) and photoluminescence (PL) spectra. Well resolved distinct peaks in the XRD pattern of the sample confirm its crystalline nature. The TGA curve infers that the complex maintains its properties unchanged till 100 °C. DTA curve displays two endothermic peaks, one centred at 98°C, corresponding to the distortion of water from the synthesized complex. Other peak at 188.24 ^{0}C, corresponding to the evaporation of residual moisture. Around 300.22°C and 439.09°C, exothermic peaks were observed in the DTA curve, which can be attributed to the decomposition process of the residual organic materials. FTIR spectra of Br-DPQ confirms that the synthesized polymer belongs to bromo group of DPQ family. The PL spectrum illustrates strong excitation at 373nm with emission centred at 422 nm, which lie in the blue region of the electromagnetic spectrum. The color coordinates of the complex was found to be (0.1603, 0.0509), corresponding to near blue region.

Keywords:- Friedlander condensation reaction, organic phosphor, OLEDs, Solid state lighting.

1. 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 become part of vast literature on organic light emitting diodes (OLEDs). One of the major concerns in the fabrication of full colour OLEDs is the equal performance of the three primary colours of red, green and blue. Colour purity and stability of blue colour remains a challenge[1,2]. Few low molecular blue emitting materials such as distyrylaylenes, 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 lifetime as compared to red or green emitting material due to trouble in hole and electron injection with larger band gap [3]. Materials with good optical non-linearity and spectral characteristics are required for high-level mechanics such as optical switching, information processing, telecommunications and data storage [4] and displays [5]. Due to their unique combination of high thermal stability, easy process ability and high photoluminescence (PL) quantum yields, Polyquinoline (PQ) conjugated derivatives have attracted major interest as very promising blue emitting materials [6-10]. Many PQ'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. [11]. In

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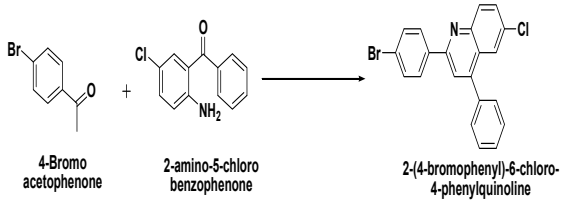
recent times, phenylated quinoline and their derivatives are used in OLED as carrier transporting as well as emitting materials [12]. On that account, an attempt has been made to synthesize and characterize 2-(4-bromophenyl)-6-chloro-4- phenylquinoline (Br-DPQ), by Friedlander condensation reaction.

2. Reagent and Solvents

Materials used for the synthesis of 2-(4-bromophenyl)-6-chloro-4- phenylquinoline complex are 4 Bromoacetophenone (C_8H_7BrO), [Loba chemie] melting range 49-52^{0}c, Molecular weight = 199.06 g/mol, Minimum Assay 98%, 2 amino 5 chloro benzophenone ($C_{13}H_{10}ClNO$) [Otto chemicals] Molecular weight = 231.68, assay 98%, melting point 96-98^{0}C(lit.), Diphenylphosphate $(C_6H_5O)_2P(O)OH$) [Sigma Aldrich]assay 99%, melting point 62-66^{0}C(lit.) Molecular weight = 250.19, mcresol [$CH_3C_6H_4OH$] Molecular weight 108.14, Minimum assay 98.0%, Wt. Per ml at 20^{0}C 1.033-1.035g, Dichloromethane(CH_2Cl_2) [Fisher scientific] Minimum assay 99%, Wt. Per ml at 20^{0}C 1.324-1.326g, Sodium hydroxide (NaOH) [Fisher scientific] Molecular weight 40.00, minimum assay 98.0%, Hexane ($CH_3(CH_2)_4CH_3$) [Loba chemie] Molecular weight 86.18, Assay min 85.0%, Wt. Per ml at 20^{0}C 0.66g and double distilled water.

2.1. Experimental

2-(4- bromophenyl)-6-chloro-4-phenylquinoline (Br-DPQ) was synthesized by Friedlander condensation reaction. 2D and 3D synthesis scheme of 2-(4- bromophenyl)-6-chloro-4- phenylquinoline is as shown in Fig.1 and 2, respectively. The experimental set up of the synthesis process is well demonstrated in Fig.3.



(C_8H_7BrO) ($C_{13}H_{10}ClNO$) ($C_{21}H_{13}BrClN$)

Where, C=63.90%, H=3.32%, Cl= 8.98%, Br= 20.24%, N=3.55%

Fig.1 2D- Synthesis scheme of 2-(4-bromophenyl)-6-chloro-4- phenylquinoline.

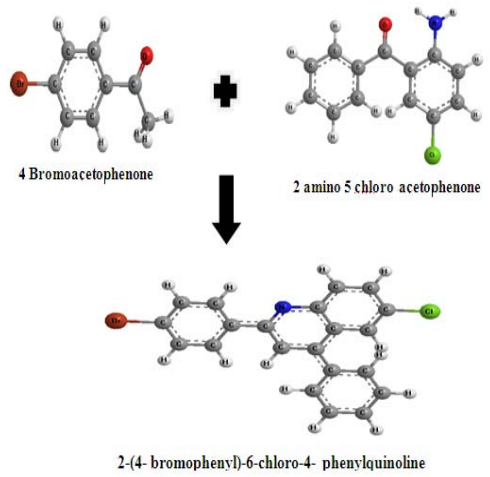


Fig.2: 3D- Synthesis scheme of 2-(4-bromophenyl)-6-chloro-4- phenylquinoline.

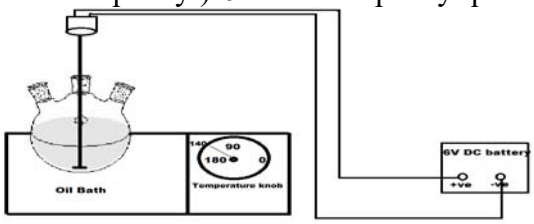


Fig.3: Schematic diagram of synthesis process

2.2. Synthesis procedure

Synthesis of Br-DPQ by Friedlander condensation reaction involves, the following steps-

Step 1: 2 Amino-5- Chloro Benzo phenone ($C_{13}H_{10}ClNO$), (2gm), 4 Bromo acetophenone (C_8H_7BrO) (2gm), Diphenyl phosphate 2 gm and M-cresol of 3ml were used as the starting materials for the reaction of the polymer. The mixture of these materials are added in a round 3 neck flask and fixed the glass stirrer from the middle neck of round flask for stirring the compound.

Step 2: The temp of oil bath was maintained at constant temperature at 90^{0}C for 1 hr and then at 140^{0}C for 4 hr.

Step 3: After completing the heating and stirring process, the flask was taken out of the oil bath for cooling.

Step 4: In the purification process, 60 ml dichloromethane (Methylne chloride) and then 60 ml NaOH solution with a 10 % NaOH concentration were added and the mixture was kept for 8 hr.

Step 5: Two layers were formed in the flask. These layers were separated by the funnel and then washed with 20 ml distilled water (3 times) [13]. When distilled water is added in order to

lower the temperature of the layers, they became cold, revealing that it is an endothermic reaction.

Step 6: Later, the resulting precipitate was kept on the hot plate at 40^0C for removing water from the synthesized complex.

Step 7: It is again washed with 20 ml of hexane (3 times) and again kept the sample on hot plate increasing 5^0 temp. above room temperature.

Step 8: The powder precipitate was collected on butter paper, and dried at room temp for removing the moisture of the powder if any left. Finally, milky white colour powder with compound weight 2.61gm was obtained.

3. Results and discussion

Physical and chemical properties of the synthesized 2-(4- bromophenyl)-6-chloro-4-phenylquinoline phosphor were characterized by photoluminescence (PL) spectra on RF5301 Spectro fluorometer, Thermo gravimetric analysis (TGA), Differential Thermal Analysis (DTA) on Perkin Elmer diamond, Fourier Transform Infrared (FTIR) spectra on Bruker and X-ray diffraction on X-ray Diffractometer (PAN analytical) [14-16].

3.1. XRD Spectra

The X-Ray diffraction analysis of 2-(4-bromophenyl)-6-chloro-4-phenylquinoline (Br-DPQ) in solid state was probed by XRD spectra. The diffractogram of the synthesized complex displays few sharp and strong diffraction peaks, indicating the crystalline nature of the complex as shown in Fig.4. Maximum relative intensity (100%) was observed at 2θ value of 19.53^0, corresponding to interplanar distance of $4.54057A^0$.

By using Bragg's law $2d\sin\theta = n\lambda$, λ was calculated as

$$\lambda = 2 \times 10.913x \text{ Sin } (4.047) = 1.540\ A^0$$

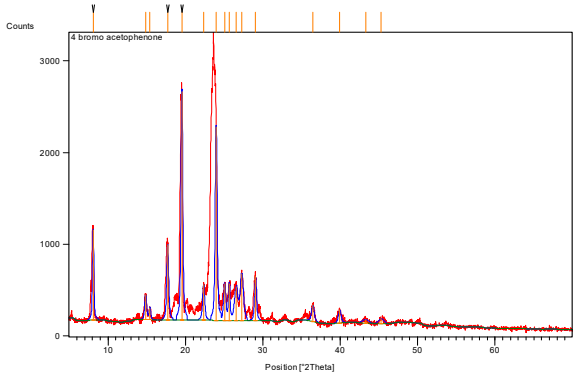


Fig. 4: X-ray diffractogram of 2-(4-bromophenyl)-6-chloro-4- phenylquinoline.

By using Scherrer's formula, grain size of the particle was calculated as

$$T = k\lambda/\beta\cos\theta = \frac{0.9 \times 1.540}{0.2040 \times \cos(4.047)}$$

$$= 6.811\ A^0$$

= 0.68 nm

Using Scherrer formula, the size of the particle is found to be less than 1nm.

3.2. Thermo gravimetric and Differential Thermal Analysis (TGA/DTA)

Thermal stability, chemical reactivity and phase transitions properties of Br-DPQ are evaluated by TGA and DTA in nitrogen atmosphere. These measurements can be made simultaneously on the sample to assess direct correlation of weight and heat changes as function of time and temperature in various gaseous environments with greater certainty than available with separate measurements.

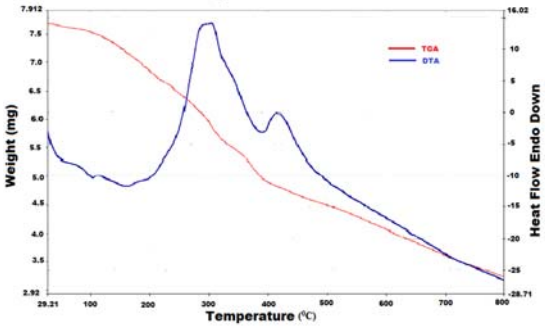


Fig. 5: TGA and DTA Spectra of 2-(4-bromophenyl)-6-chloro-4- phenylquinoline.

The TGA curve displays a horizontal plateau, indicating no much weight loss in the sample till 100 °C as indicated in Fig. 5. This infers that the complex has an ability to maintain its properties unchanged upon heating till 100 °C. With further increase in temperature, the thermogram takes curved portion, indicating decomposition or weight loss of the sample due to heating. DTA curve of Br-DPQ displays a combination of endothermic and exothermic peaks. Two endothermic peaks, one centred at 98°C, correspond to the distortion of water from the synthesized complex. Other peak at 188.24 ^{0}C corresponds to the evaporation of residual moisture. Exothermic peaks around 300.22°C,

439.09°C can be attributed to the decomposition process of the residual organic materials.

3.3. FTIR Spectra

The packing arrangements, chain conformational properties, and molecular structure of Br-DPQ chromophore are confirmed by FT-IR spectra over the range 4000–580/cm by averaging 500 scans at a maximum resolution of 20/cm as shown in Fig.6. As broad background with some asymmetric peaks were observed below 500 cm^{-1}, which may be due to scattering of crystalline nature of the phosphor and hence not recorded. In Fourier transform infrared (FTIR) - spectroscopy, IR radiation is passed through the sample. A part of infrared radiation is absorbed by the sample, while some part is transmitted.

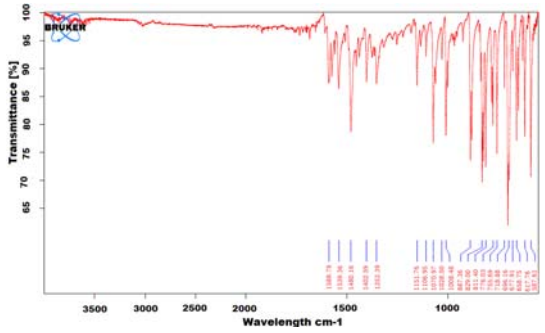


Fig. 6: FTIR Spectra of 2-(4- bromophenyl)-6-chloro-4- phenylquinoline.

The FT-IR spectra of 2-(4- bromophenyl)-6-chloro-4- phenylquinoline displays maximum absorption bands peaks in the finger print region (1600-1350 cm^{-1}), which are generally due to intra molecular phenomena, and are highly specific for each material as shown in Fig.6. Aromatic CC stretch bands (for the carbon–carbon bonds in the aromatic ring are due to the imine (C=N) group was found to be the characteristic of the quinoline ring. A peak at 1353.39 cm^{-1} predicts aromatic ring stretching and the presence of nitro compounds. The peaks between the range 1000 - 600cm^{-1} reveals the bending of phenyl group. Two prominent peaks in the lower range 829, 696.16 and 587.61 cm^{-1} are due to C-H alkaline bonding. This spectrum confirms the presence of quinoline and the formation of the desired phosphors.

3.4. Photoluminescence (PL) spectra

Upon excitation of Br-DPQ main chain in solid state at 373 nm, the emission spectrum displays a sharp emission peak at 422 nm as shown in Fig.7. Thus the synthesized polymeric compounds demonstrate a bright emission in blue region [17] of electromagnetic spectrum .Hence this phosphor might be useful as a promising blue light material for electroluminescent devices.

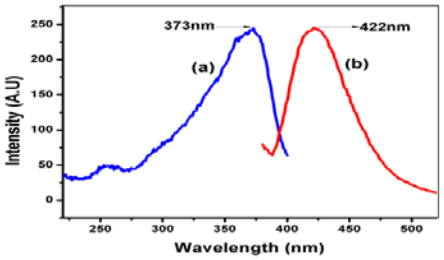


Fig.7: (a) Excitation and (b) Emission spectra of 2-(4- bromophenyl)-6-chloro-4- phenylquinoline organic complex.

3.5. CIE coordinates

The color of a light source is typically characterized in terms of Commission International de l'Eclairage (CIE) system. Any color can be expressed by the chromaticity coordinates x and y on the CIE chromaticity diagram. Radiant imaging is the color calculator program [18], by using which the chromatic co-ordinates (X,Y) can be calculated. For 2-(4-bromophenyl)-6-chloro-4- phenylquinoline (Br-DPQ) the chromaticity co-ordinates are found to be (0.1603, 0.0509), corresponding to near blue region as shown in Fig. 8

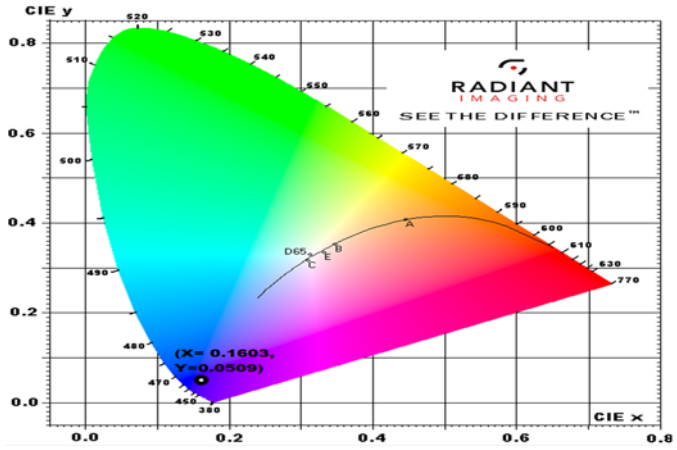


Fig.8: CIE 1931 (x,y) diagram showing emission color coordinates of 2-(4- bromophenyl)-6-chloro-4- phenylquinoline.

4. Conclusions

An organic phosphor 2-(4- bromophenyl)-6-chloro-4- phenylquinoline, belonging to DPQ family was synthesised by Friedlander condensation reaction. Well resolved distinct peaks in the XRD pattern of the sample confirm its crystalline nature. Maximum relative intensity (100%) was observed at 2θ value of 19.53^0, corresponding to interplanar distance of $4.54057A^0$. The TGA curve infers that the complex has an ability to maintain its properties unchanged upon heating till 100 °C. DTA curve displays two endothermic peaks, one centered at 98°C, corresponds to the distortion of water from the synthesized complex. Other peak at 188.24 ^{0}C, corresponds to the evaporation of residual moisture. DTA curve displays two exothermic peaks around 300.22°C, 439.09°C, which can be attributed to the decomposition process of the residual organic materials. FTIR spectra of Br-DPQ confirms that the synthesized polymer belongs to bromo group of DPQ family. The PL spectrum illustrates strong excitation at 373nm with emission centred at 422 nm, which lie in the blue region of the electromagnetic spectrum. CIE coordinates of Br-DPQ are found to be (0.1603, 0.0509). Hence, the synthesized organic phosphor can be useful for blue organic light emitting diodes (OLEDs) and solid state lighting.

5. References

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