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Novel Br-DPQ blue light-emitting phosphors for OLED

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ABSTRACT: A new series of blue light-emitting 2,4-diphenylquinoline (DPQ) substituted blue light-emitting organic phosphors namely, 2-(4-methoxy-phenyl)-4-phenyl-quinoline (OMe–DPQ), 2-(4-methyl-phenyl)-4-phenylquinoline (M-DPQ), and 2-(4-bromo-phenyl)-4-phenylquinoline (Br-DPQ) were synthesized by substituting methoxy, methyl and bromine at the 2-para position of DPQ, respectively by Friedländer condensation of 2-aminobenzophenone and corresponding acetophenone. The synthesized phosphors were characterized by different techniques, e.g., Fourier transform infra-red (FTIR), differential scanning calorimeter (DSC), UV-visible absorption and photoluminescence spectra. FTIR spectra confirms the presence of chemical groups such as C=O, NH, or OH in all the three synthesized chromophores. DSC studies show that these complexes have good thermal stability. Although they are low-molecular-weight organic compounds, they have the potential to improve the stability and operating lifetime of a device made out of these complexes. The synthesized polymeric compounds demonstrate a bright emission in the blue region in the wavelength range of 405–450 nm in solid state. Thus the attachment of methyl, methoxy and bromine substituents to the diphenyl quinoline ring in these phosphors results in colour tuning of the phosphorescence. An electroluminescence (EL) cell of Br-DPQ phosphor was made and its EL behaviour was studied. A brightness–voltage characteristics curve of Br-DPQ cell revealed that EL begins at 400 V and then the brightness increases exponentially with applied AC voltage, while current–voltage (I–V) characteristics revealed that the turn on voltage of the fabricated EL cell was 11 V. Hence this phosphor can be used as a promising blue light material for electroluminescent devices. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: DPQ; electroluminescence cell; phosphor; quinoline; OLED

Introduction

Recently, much attention has been paid in the field to white organic lighting emitting diodes (WOLEDs) as a light source for the next-generation general illumination due to the high brightness, long lifetime, low power consumption, and environmentally friendly characteristics promised by solid-state lighting (1,2). To generate white light, the most common and simple method is to combine tri-colour red–green–blue (RGB) phosphor or bi-colour yellow–blue phosphor as luminescent materials for applications in flat panel displays (3–5), Hg-free lamps and solid-state lighting. The basic units of modern electronic appliances can be made from both traditional inorganic semiconductors and organic semiconductors, i.e. hydrocarbon molecules that combine semiconducting properties with some mechanical properties such as easy processing ability and flexibility (6). Pyrazoloquinoline derivatives (7), distyrylenes, anthracene derivative, spirofluoreres are demonstrated to be blue emitting materials for fabricating blue organic lighting emitting diodes (OLEDs). Incorporating deep-blue phosphors as emissive material in the effective device architectures of cOLEDS is one of the key challenges as they usually require large triplet energy hosts to prevent the reverse energy transfer from dopants to hosts (8). π-conjugated rigid polyquinolines have been extensively investigated as thermally stable, photoconductive, photo luminescent, and nonlinear polymeric materials (9–13). Of the hetero-aromatic polymers, quinoline-based polymers are of interest as these are reported to exhibit n-type onductivity upon doping and possess excellent thermal as well as oxidative stability (14–17). The present work deals with synthesis and characterization of blue-light-emitting 2-(4-methoxy-phenyl)-4-phenyl-quinoline (OMe-DPQ), 2-(4-methyl-phenyl)-4-phenylquinoline (M-DPQ), and 2-(4-bromo-phenyl)-4-phenylquinoline (Br-DPQ) phosphors and the fabrication and characterization of blue-light-emitting electroluminescence (EL) cells of Br-DPQ phosphors.

Materials and methods

All reagents and solvents were used as received without further purification. All reactions were performed under an argon atmosphere. A BRUKER Fourier transform infra-red (FTIR) spectrometer was used to confirm the packing arrangements, chain conformational properties of OMe-DPQ, M-DPQ and Br-DPQ chromophores over the range 4000–600/cm by averaging 500 scans at a maximum resolution of 20/cm. Differential scanning calorimeter (DSC) analysis was carried out under nitrogen environment using the Mettler Tolledo System. The optical

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Abbreviations: DSC, differential scanning calorimeter; EL, electroluminescence; FTIR, Fourier transform infra-red; RGB, red–green–blue; UV, ultra-violet; WOLED, white organic lighting emitting diodes.

absorption spectrum of complex in dichloromethane was obtained on an Analytik Specord-50 spectrophotometer. The photoluminescence (PL) spectrum wass obtained by a SHIMADZU RF 5301 spectrofluorometer.

Synthesis of DPQ derivatives ((OMe-DPQ), (M-DPQ), (Br-DPQ))

The quinoline-derived ligand (OMe-DPQ) is synthesized according to Scheme 1(a) as shown in Fig. 1(a) from the condensation of 2-aminobenzophenone reaction with 4-methoxy acetophenone using the acid-catalyzed Friedländer reaction (18,19).

The 2-aminobenzophenone reacts with the corresponding 4-methxyacetophenone, in the presence of diphenyl phosphate as catalyst at 140°C in an argon atmosphere, water vapour is produced and finally undergoes crystallization giving the polymer OMe-DPQ. The crude product is then washed with hexane (25 ml × fives times) to produce a crystalline solid ($C_{22}H_{17}NO$), mol. wt. = 311.242 g; yield: 73%. Similarly, M-DPQ and Br-DPQ were synthesized by reacting 2-aminobenzophenone with the corresponding 4-methylacetophenone or 4-bromo acetophenone in the presence of diphenyl phosphate as catalyst at 140°C in the same atmosphere according to Scheme 1(b) and 1(c), respectively, with molecular formulae $C_{22}H_{17}NO$ and $C_{22}H_{17}N$, mol. wt. = 295.226 and 295.242 g offering the yields as 71% and 72%, respectively.

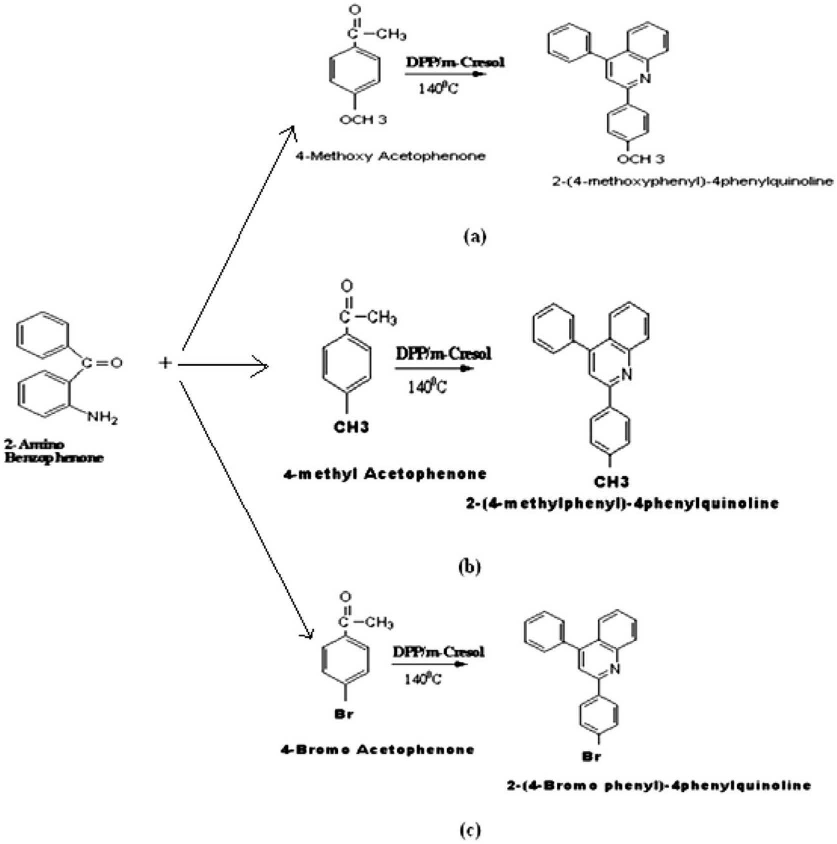
Results and Discussion

Fourier transform infra-red (FTIR) characterization

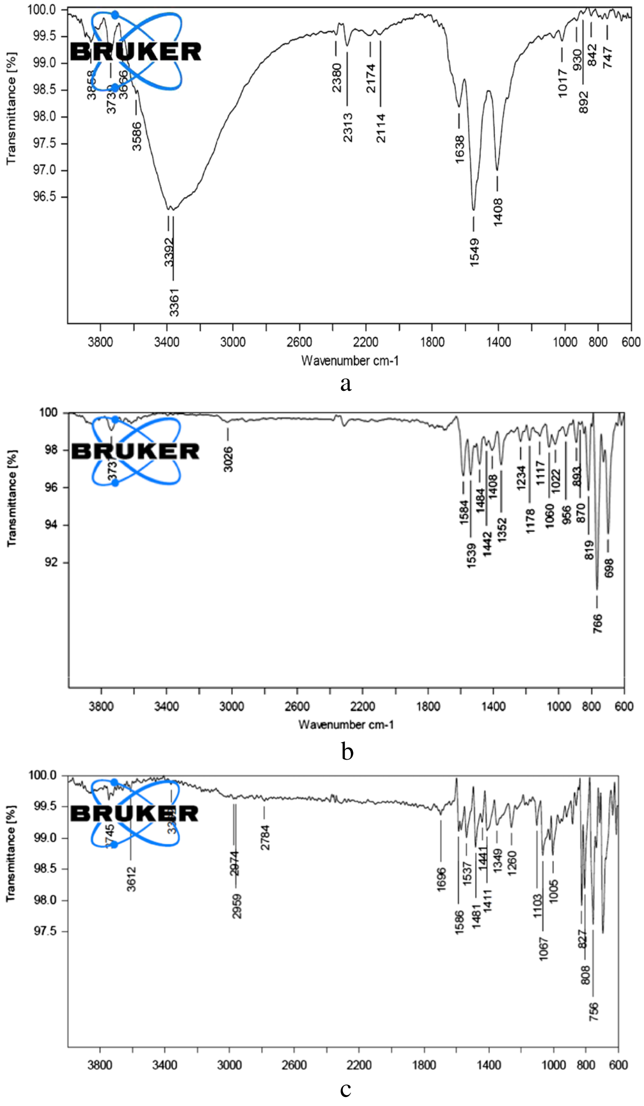
FTIR spectra of OMe-DPQ, M-DPQ and Br-DPQ display a broad background with some asymmetric peaks observed below 600 cm^{-1} as shown in Fig. 1(a), (b) and (c). This may be due to scattering resulting from the crystalline nature of the phosphor and hence not recorded. In OMe-DPQ, a broad peak in the range of 3590–3000 reveals the presence of O–H bonding, while small stretching peaks in the range 2300–2100 confirms the presence of a methoxy (O–CH_3) group. Aromatic CC stretch bands were from the carbon–carbon bonds in the aromatic ring and due to the imine (C=N) group in the range of the quinoline ring. This was found to be a characteristic of the quinoline ring (19).

Differential scanning calorimetry (DSC)

Thermal properties of OMe-DPQ, Br-DPQ and Br-DPQ were evaluated by DSC measurements. The DSC trace of these polymeric compounds containing quinoline showed no crystallization but only melting and glass transitions peaks. This clearly indicates that the incorporation of the rigid quinoline unit into the phenyl backbone reduces the segmental mobility and effectively suppresses the tendency of the polymer chains to densely pack. This improved thermal resistance of the copolymers bodes well for stable blue emission from light-emitting diodes (LEDs) made from them. Thermally induced phase transitions were observed, these typical thermal characteristics are similar to the previous reports (22). These results show that these compounds have good thermal stability, although they are low-molecular-weight organic compounds, they in turn improve the stability and operating lifetime of the device. Figure 2 (a) indicates that OMe-DPQ undergoes a glass transition at 41°C, followed by crystallization at 88°C and crystalline



Scheme 1. Synthesis of (a) OMe-DPQ; (b) M-DPQ; and (c) Br-DPQ organic phosphors.



a

b

c

Figure 1. FTIR spectra of (a) OMe-DPQ, (b) M-DPQ, and (c) Br-DPQ organic phosphors. In the wave number range less than 1000 cm^{-1}, phenyl group bending can be observed. While in the characteristic spectra of M-DPQ and Br-DPQ, a broad absorption peak below 3000 cm^{-1} disappeared and the sharp peaks shifted towards lower wave number. The absorption bands in the finger print region (1600–1350 cm^{-1}) are generally due to intra-molecular phenomena, and are highly specific for each material. They predicted aromatic ring stretching, revealing the presence of a C=C group. A strong peak at 1352 cm^{-1} predicts aromatic ring stretching and the presence of nitro compounds. The peaks between the range 1000–600 cm^{-1} revealed the bending of a phenyl group. Two prominent peaks in the lower range between 766 and 698 cm^{-1} are due to C–H alkaline bonding. These spectra confirm the formation of the desired phosphors.

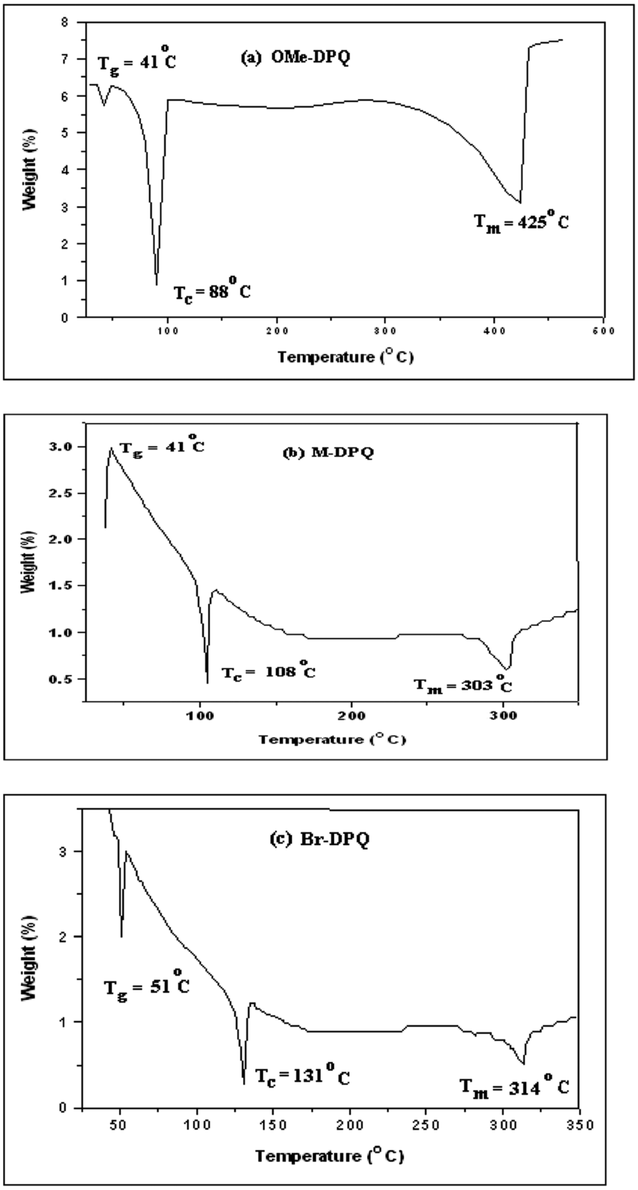


Figure 2. DSC scans of (a) OMe-DPQ, (b) M-DPQ and (c) Br-DPQ organic phosphors. Figure 2(c) indicates that Br-DPQ undergoes a glass transition at 51°C, followed by crystallization at 131°C and crystalline melting point at 314°C, proving their efficiency in their use as blue light-emitting phosphors in the fabrication of blue OLEDs and displays for solid-state lighting.

melting point at 425°C. Figure 2(b) indicates that M-DPQ undergoes a glass transition at 41°C, followed by crystallization at 108°C and crystalline melting point at 303°C.

Absorption spectra

The UV-visible light absorption spectra of 10^{-4} M solutions of OMe-DPQ, M-DPQ and Br-DPQ, pure DPQ in dichloromethane (DCM) at room temperature are shown in Fig. 3 (a), (b), (c) and (d), respectively. M-DPQ exhibits two absorption peaks in the UV region, one at 268 nm and the other at 345 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition, respectively. Br-DPQ exhibits two absorption peaks in the UV region, one at 270 nm and the other at 326 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition, respectively. DPQ exhibits two absorption peaks in the UV region, one at 254 nm and the other at 327 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition, respectively. OMe-DPQ exhibits two absorption peaks in the UV region, one at 272 nm and the other at 333 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition, respectively. Peak positions of both the bands lies at the same wavelength for all the compounds synthesized, indicating the role of DPQ in the complex. Thus the synthesized phosphors have good solubility in DCM.

Photoluminescence spectra

Upon excitation of OMe-DPQ, M-DPQ or Br-DPQ main chains in solid state at 378 nm, the emission spectrum displays two

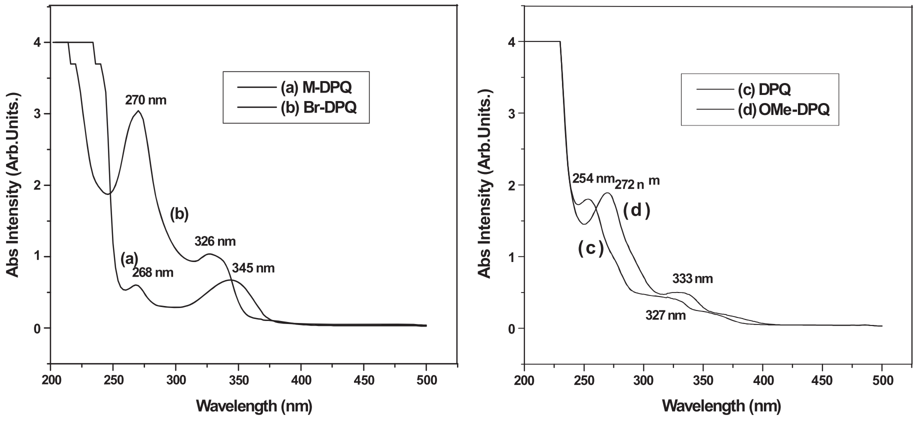


Figure 3. Absorption spectra of (a) M-DPQ, (b) Br-DPQ , (c) DPQ and (d) OMe-DPQ, organic phosphors in DCM solution.

unresolved bands at 428 and 405 nm with some vibronic structure as shown in Fig. 4(a). M-DPQ also displays two unresolved bands around 435 and 415 nm as shown in Fig. 4 (b), while Br-DPQ PL spectra display a sharp peak at 450 nm and a weak shoulder at 431 nm as shown in Fig. 4(c). Thus the synthesized polymeric compounds demonstrate a bright emission in blue region in the wavelength range of 405–450 nm in solid state. Attachment of methyl and methoxy substituents to the diphenyl quinoline ring results in colour tuning of phosphorescence. Hence these phosphors can be used as a promising blue light material for electroluminescent devices.

Development and characterization of EL cells

In order to study the EL characteristics of the synthesized materials EL cells have been prepared by placing Br-DPQ phosphor between two electrodes as shown in Fig. 5. One of the

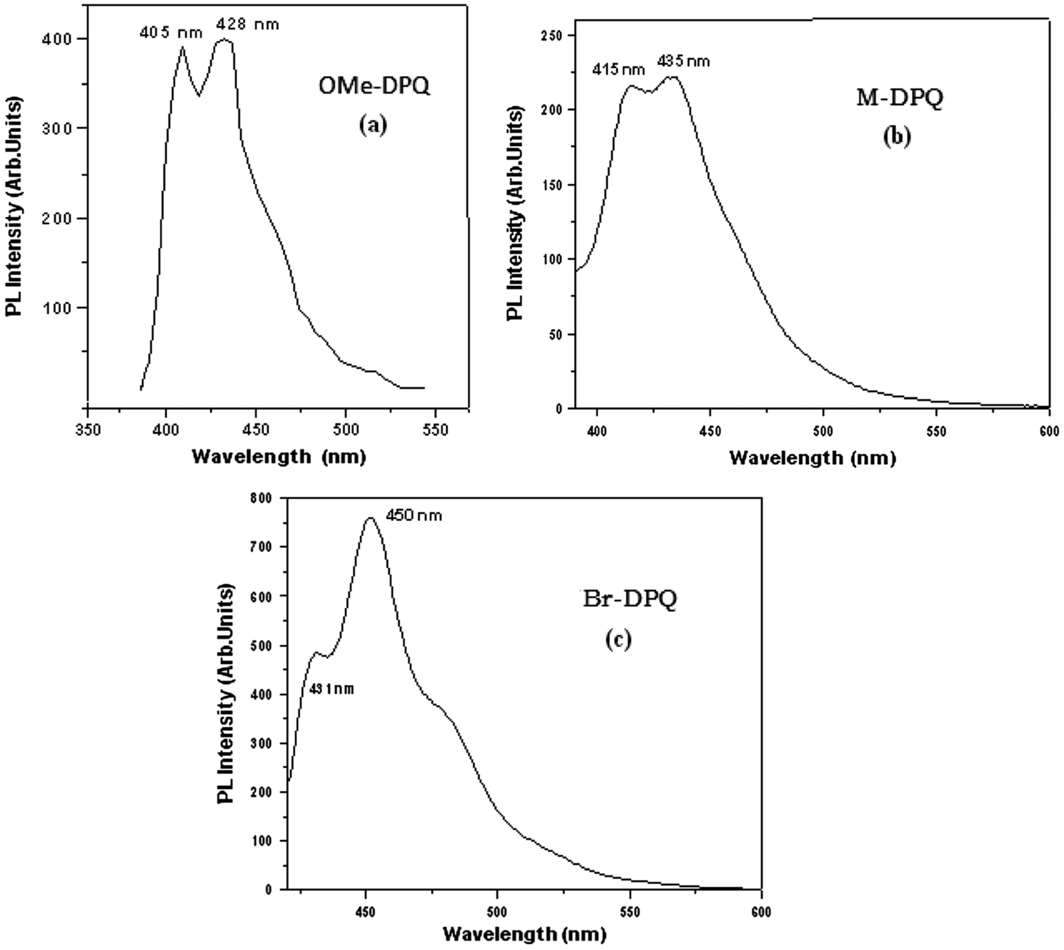


Figure 4. Photoluminescence (PL) spectra of (a) OMe-DPQ, (b) M-DPQ, and (c) Br-DPQ organic phosphors.

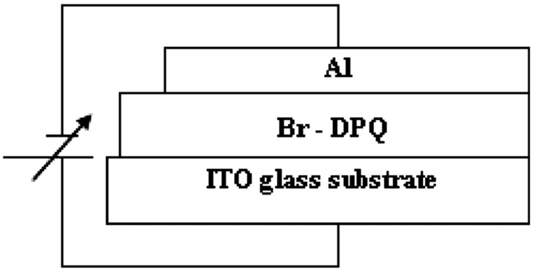


Figure 5. Anatomy of fabricated EL cell.

electrodes is transparent, made up of a thin conducting layer of SnO_2 coated on glass plates and the other electrode is simply aluminum foil. The emission of light can be observed through the transparent electrode under applied AC voltage, measured by a photomultiplier tube. In the present investigations, we have restricted our study to the EL measurements brightness versus voltage and current versus voltage.

Voltage–brightness characteristics. To obtain the voltage–brightness characteristics of a given EL cell, the frequency of function generator was fixed at 600 Hz and then AC voltage of fixed frequency across the cell was increased and the corresponding brightness was recorded with the help of photomultiplier tube by means of a pico ammeter. The brightness–voltage characteristics curve of Br-DPQ cell revealed that EL begins at 400 V and then after brightness increases exponentially with applied AC voltage as shown in Fig. 6. By increasing the applied electric field, injection of electrons and holes from cathode and anode are enhanced, they recombine immediately and emit more photons and hence the EL intensity or brightness of blue colour increases with electric field.

Voltage–current characteristics. In order to obtain voltage–current characteristics of a given EL cell, again AC voltage of fixed frequency across the cell was increased and the corresponding current through the EL cell was recorded by a micro ammeter. Figure 7. clearly shows a linear relation between current and voltage, indicating the ohmic nature of the device. Such ohmic behaviour can be attributed to the 'hoping' conductivity of electrons through a fine emissive layer. The turn-on voltage of the fabricated EL cell was found to be 11 V. By adding additional hole and electron transport and injection layers, the efficiency of the cell can be enhanced.

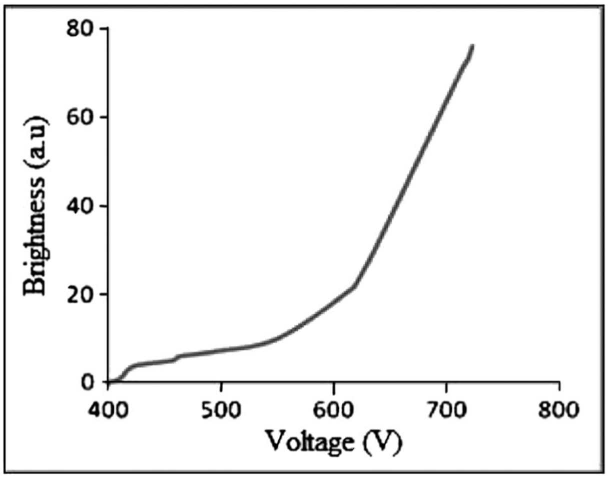


Figure 6. Brightness–voltage characteristics curve for Br-DPQ sample.

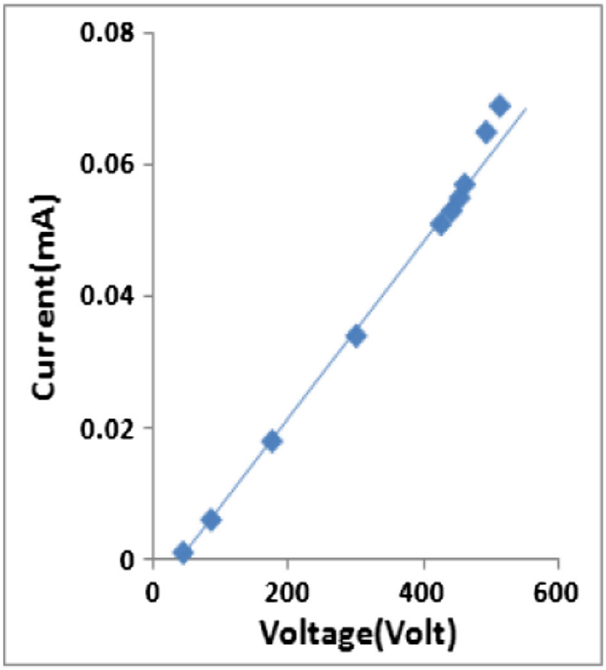


Figure 7. Current–voltage characteristics for the Br-DPQ sample.

Conclusion

DPQ-substituted blue emitting organic phosphor materials OMe-DPQ, M-DPQ and Br-DPQ have been synthesized in nearly quantitative yields by Friedländer condensation of 2- amino-benzophenone and corresponding acetophenone. FTIR spectra confirm the formation of the synthesized DPQ-substituted blue light-emitting organic complexes. DSC studies show that M-DPQ has 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 UV–vis absorption spectra in dichloromethane provided information on the electronic structures of the polymeric compound. The synthesized polymeric compounds demonstrate a bright emission in blue region in the wavelength range of 405–450 nm in solid state. Thus the attachment of methyl and methoxy substituents to the diphenyl quinoline ring in these phosphors results in colour tuning of phosphorescence. Brightness–voltage characteristics curve of the Br-DPQ EL cell revealed that EL begins at 400 V and then the brightness increases exponentially with applied AC voltage. The turn-on voltage of the fabricated EL cell was found to be 11 V. Hence this phosphor can be used as a promising blue light material for electroluminescent devices.

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