Novel Blue Fluorescent Dopants Based on Imidazole-Containing Compound for Organic Electroluminescent Devices

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Abstract

We report the synthesis of bis-imidazole derivatives [1,4-bis-(2-(4-benzoylphenyl)-5-R-1H-4-imidazolyl)benzene] BSIB-1 (R = phenyl) and BSIB-2 (R = p-tolyl) by a simple one-step reaction of the corresponding substituted tetraone, substituted benzaldehyde and ammonium acetate and the use of these organic compounds as dopant emitters in electroluminescent devices. The physical properties of BSIBs were thoroughly investigated. A general device structure of the devices is ITO/NPB (20 nm)/CBP (20 nm)/BSIB:TPBI (X%, Y nm)/TPBI (20 nm)/Mg:Ag (10:1; 55 nm)/Ag (100 nm), where NPB, CBP and TPBI stand for 4,4’-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl, 4,4’-dicarbazolyl-1.1’-biphenyl and 2,2’,2”-(1,3,5-phenylene) tris-[1-phenyl-1H-benzimidazole], respectively. Efficient blue-green to blue emission from the devices with luminance ranging from 2500-5000 cd/m² was obtained. The efficiencies of the devices and the nature of the emitting color depended substantially on the concentration of the dopant and thickness of the emitting layer. The Förster mechanism is suggested to account for the transfer of energy from host TPBI to the dopant and emission from the dopant.

Key Words: Electroluminescent, Imidazole Derivatives, OLED, Blue-Light Emitting Dopants, Blue Light

1. Introduction

During the last decade organic light emitting diodes (OLEDs) has become a subject of interest among the researchers throughout the world due to its potential application in flat panel displays [1]. Since the first report by Tang et al. [2], scientists are engaged in searching for new materials for OLEDs. A substantial amount of work has been carried out in the discovery of new materials, innovation in device fabrication, uses of different electrodes etc., during this period [3-5]. Efficient red, green and blue electroluminescent (EL) emitters are obligatory for the design and construction of high-quality full-color display devices [6]. A number of fluorescent dyes and charge carriers have been developed; yet the effort is still going on in terms of color tuning, higher efficiency and durability. Compared to those of the green-emitting devices, the EL characteristics of blue and red-emitting ones require further improvement particularly the efficiency and color purity for full color application. It is more difficult to produce a pure blue emission due to its inherent wide band gap irrespective of the type of materials.
Although several reports on blue OLEDs are available in literature [7-8], only a very limited number of materials are practically useful. Among the various techniques developed so far to improve the efficiency of the OEL devices, the doping of the host emitter with an emitting material is a very valuable method [9]. The doping technique can be successfully used for tuning the color, to improve efficiency and durability of the devices. In addition, this method can be employed for using materials that are not suitable as the host emitter in electroluminescent devices. In this paper we wish to report the synthesis of derivatives of 1,4-bis-[2-(4-benzoylphenyl)-5-aryl-1\(H\)-4-imidazolyl] benzene (BSIB) and their application in organic electroluminescent devices. A very interesting feature of these compounds is that they hardly emit light in the solid state but emit bright blue-green light in solution. By exploiting this characteristic, we fabricated efficient OEL devices using BSIBs as dopants.

2. Experimental

2.1 General Information

The melting points were determined in a Fargo MP-2D melting point apparatus and were not corrected. The thermal data were obtained from a Seiko SII-EXSTAR 6000-DSC-6200 differential scanning calorimeter. BSIB compounds were heated at 20 °C/min under nitrogen atmosphere until complete melting and then cooled rapidly. A second heating scan was performed at the same rate to detect the glass transition temperature \(T_g\), the crystallization temperature \(T_c\) and the melting temperature \(T_m\) [10]. Absorption and emission measurement were carried out using a Hitachi U-3300 absorption spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. The redox potentials of the compounds were determined by cyclic voltammetry (CV) using an electrochemical analyzer CHI600A. A conventional three-electrode cell system was used with glassy carbon, platinum wire and Ag/AgCl as the working, counter and reference electrode, respectively. CV measurements were carried out in dry dichloromethane solutions of the compounds with 0.10 M tetra-n-butylammonium hexafluorophosphate as electrolyte medium. The HOMO levels were calculated from the oxidation-reduction potentials, which were obtained from the cyclic voltammetry (CV) curves. The LUMO levels were estimated based on the HOMO energy levels and the lowest-energy absorption edges of the UV-vis absorption spectra [11].

2.2 Fabrications and Measurements of Electroluminescent Devices

The OLED devices containing BSIB derivatives were fabricated by vacuum deposition (as shown in Figure 1). The substrate was an indium tin oxide (ITO) coated glass with a sheet resistance of 25 ohm/cm\(^2\). The ITO-coated glass was pretreated according to a regular chemical cleaning using detergent, DI water and alcohol in sequence, followed by ozone cleaning. The thermal evaporation of organic materials was carried out at chamber pressure of 10\(^{-6}\) Torr. The dopant and host materials were co-evaporated from different heating sources. The cathode consisting of Mg:Ag (10:1, 55 nm) was deposited by simultaneous evaporation of Mg and Ag metals at a deposition rate of 5-7 and 0.5-0.7 Ås\(^{-1}\), respectively. A thick silver-capping layer of 100 nm was deposited over the cathode, by evaporation of silver metal with a rate of 3-4 Ås\(^{-1}\). The deposition rate of the organic compounds is in between 1-2 Ås\(^{-1}\). The effective area of the emitting diode was 9.00 mm\(^2\). Current-Voltage-Luminance \((I-V-L)\) measurements were made simultaneously using a Keithly 2400 Source meter and a Newport 1835-C optical meter equipped with a Newport 818-ST silicon photo diode. The electroluminescent (EL) spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The measurements were made at room temperature under ambient conditions.

2.3 General Procedure for the Synthesis of Imidazole Derivatives

A mixture of tetraone (1-[4-(2-oxo-2-phenylacetyl)phenyl]-2-phenyl-1,2-ethanediene) (0.98 g, 2.87 mmol), 4-benzoylbenzaldehyde (1.20 g, 5.73 mmol) and ammonium acetate (1.10 g, 14.33 mmol) in glacial acetic acid (14 mL) were refluxed for 10 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into methanol (100 mL) with stirring, the separated solid was filtered off, washed with methanol and dried. The dried crude product was purified by vacuum sublimation technique at 3–5x10\(^{-3}\) Torr to gave product BSIB-1. The other derivative BSIB-2 was prepared according to the above procedure from the corresponding tetraone. The yields and important spectral data are given below.
1.4-Bis-[2-(4-benzoylphenyl)-5-phenyl-1H-4-imidazolyl]benzene (BSIB-1):
Yield: 70 %. Mp. = 350 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.26–7.38 (m, 6H), 7.47-7.70 (m, 14H), 7.78-7.82 (m, 4H), 7.88 (d, $J$ = 8.32 Hz, 4H), 8.23 (d, $J$ = 8.32 Hz, 4H). $^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ 125.6, 128.1, 128.5, 129.1, 130.5, 131.2, 132.9, 135.4, 137.6, 138.9, 145.9, 195.4.

1.4-Bis-[2-(4-benzoylphenyl)-5-(p-tolyl)-1H-4-imidazolyl]benzene (BSIB-2):
Yield: 66 %. Mp. = 320 °C. IR (KBr): 3278, 1770, 1642, 1277, 936, 822, 697 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.35 (s, 6H), 7.15-7.19 (m, 4H), 7.46-7.60 (m, 14H), 7.78-7.83 (m, 4H), 7.88 (d, $J$ = 8.46 Hz, 4H), 8.18 (d, $J$ = 8.46 Hz, 4H). $^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ 21.3, 125.5, 128.5, 129.1, 129.5, 130.0, 131.6, 132.3, 132.8, 135.5, 137.6, 139.1, 145.6, 195.3.

3. Results And Discussion
Imidazole derivatives BSIB-1 and BSIB-2 were conveniently synthesized by a simple one step condensation reaction from the corresponding tetaone, 4-benzoylbenzaldehyde and ammonium acetate in refluxing acetic acid solution (eq. 1). The compounds were purified by vacuum sublimation and the structures were confirmed by various spectral methods. The melting points and other physical data are listed in Table 1. Both BSIB-1 and BSIB-2 give very intense blue-green fluorescence in solution but do not emit light in the solid state. In addition, these compounds show very high melting points and glass transition temperature. It is obvious from the photoluminescence (PL) properties that these compounds are not appropriate as the host emitter in OEL devices due to self-quenching in the solid state, but are potentially good dopant emitters in OEL devices.

![Figure 1. General device structure and molecular structures of materials used in this study.](image)
There are two well-established mechanisms for energy transfer from the host material to the dopant. One is the Förster energy transfer [12] in which the absorption spectra of the dopant should overlap with the emission spectra of the host. Another is the carrier trapping mechanism in which the HOMO/LUMO energy levels of the dopant should be in between those of the host. The absorption spectra of BSIB derivatives and the emission spectra of the TPBI and CBP thin films are shown in Figure 2, which clearly indicates that there are considerable overlapping of the absorption spectra of BSIBs with the PL spectra of TPBI and CBP. Thus, TPBI or CBP can be used as the host material in the OEL device based on BSIBs dopant. We choose the electron-transfer material TPBI as the host due to the fact it has been widely used. To make sure the energy is transferring from TPBI to BSIBs, we have taken few photoluminescence spectra of BSIBs doped TPBI thin films in different doping concentration as depicted in Figure 3. In low concentration of BSIB-1 (2%), the TPBI emission (~380 nm) is dominating, but at higher concentration of BSIB-1 (10%) the emission occurred mainly from BSIB-1 at 488 nm with little emission from TPBI. Similar results were observed for compound BSIB-2. Since BSIBs practically do not emit light in the solid states, we studied their photoluminescence property in solution. The PL spectra of BSIB-1 in different solvents are shown in Figure 4. The PL emission peaks are greatly changed in different solvents. For example, it emits at 454 nm in toluene solution, but at 539 nm in DMSO. The variation of the PL peak wavelengths in different solvents are likely due to the polarization-induced spectral shift [13]. As the polarity of the solvent increases, the spectrum shifts towards the red region. Similar spectral shift is also observed for BSIB-2 in different solvents.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tm (°C)</th>
<th>Tg (°C)</th>
<th>Tc (°C)</th>
<th>λ_{max}^{Abs} (nm)</th>
<th>λ_{max}^{Em} (nm)</th>
<th>HOMO/LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSIB-1</td>
<td>350</td>
<td>173</td>
<td>244</td>
<td>251, 371</td>
<td>486</td>
<td>5.46/2.68</td>
</tr>
<tr>
<td>BSIB-2</td>
<td>320</td>
<td>167</td>
<td>242</td>
<td>257, 375</td>
<td>497</td>
<td>5.58/2.62</td>
</tr>
</tbody>
</table>

*aObtained from DSC measurement.
*bMeasured in a CH2Cl2 Solution.
*cMeasured in a THF solution.
*dMeasured in a TPBI thin film doped with BSIB-1 or 2 (10%, 50 nm).
To understand the electroluminescent properties of compounds BSIBs, we have fabricated several organic light emitting devices with BSIBs as the dopant and TPBI as the host. Based on our experiences and reports in literature [8], a general device structure, ITO/NPB (20 nm)/CBP (20 nm)/BSIB-1:TPBI (X%, Y nm)/TPBI (20 nm)/Mg:Ag (10:1; 55 nm)/Ag (100 nm), was employed. Device A having 3% BSIB-1 in TPBI emits light at 445 nm with a shoulder at around 375 nm. The peak at 445 nm seems to be from NPB, while the shoulder at ~375 nm is from TPBI. This result indicates that there is no energy transfer from TPBI to BSIB-1 occurred in this case. By increasing the dopant concentration to 5% in B, the device emits light at 484 nm with a trace emission from TPBI indicative of successful energy transfer from TPBI to BSIB-1 in this case. Device B has a turn on voltage of 5.5 V, maximum luminance of 4152 cd/m² at voltage 20 V, external quantum efficiency (EQE) of 1.11% and current efficiency of 2.16 cd/A. The CIE coordinates for this device are located at (X = 0.15, Y = 0.28). Encouraged by the result of device B, we have fabricated devices C-F by systematically changing the concentration of BSIB-1 dopant in the devices. The performance data of devices C-F are tabulated in the Table 2.
Examination of the data in Table 2 reveals that as the concentration of the dopant increases, the external quantum efficiency, current efficiency and power efficiency decrease while the turn-on voltages increase. The maximum luminance of the devices is not much affected with change of dopant concentration. For device C where the dopant concentration is 7%, the maximum brightness is 4364 cd/m²; the EQE and current efficiency are 0.97% and 1.76 cd/A, respectively. Device C emits light at 481 nm with CIE coordinates of (X = 0.15, Y = 0.25). The EL emission peaks for devices C-F are in the region 480-491 nm clearly indicating that the energy is transferred from TPBI to BSIB-1 and the emission is coming from the dopant material. The normalized EL spectra of devices B-F is shown in Figure 5, while the current-voltage-luminance (I-V-L) curves of devices B-F measured at room temperature and ambient conditions are shown in Figure 6. The CIE coordinates of the devices C-F indicate that they emit blue-green light rather than pure blue light. The emission peaks and the CIE coordinate values of devices C-F do not change significantly with the applied voltage as shown by the EL spectra of device D at different voltage in Figure 7.
Figure 5. EL spectra of devices B-K [ITO/NPB (20 nm)/CBP (20 nm)/BSIB-1:TPBI (X%, Y nm)/TPBI (20 nm)/Mg:Ag (10:1; 55 nm)/Ag (100 nm)] at 10 V.

Figure 6. (a) Luminance-voltage (L-V) and (b) current density--voltage (CD-V) characteristics for devices B-K.
The devices properties are also influenced substantially by the thickness of the emitting layer. Devices G-K were constructed by varying the thickness of the emitting layer. The key performance data of these devices are also listed in Table 2. In devices G-I, the thickness of the emitting layer is reduced to 20 nm with dopant concentrations of 5, 7 and 10%, respectively. The turn-on voltages of devices G-I are clearly lower than the corresponding devices with emitting-layer thickness of 40 nm. The external quantum efficiencies are not changing significantly, but the maximum luminance is reduced by around 1000 cd/m² for all the devices. There are very little variations in current and power efficiency. The most important change for devices G-I is the emission peak shifting to blue region by 20-30 nm. For example, device G emits light at 450 nm with a shoulder of host TPBI emission at around 375 nm. The maximum luminance, EQE, current and power efficiencies for device G are 3417 cd/m², 1.2%, 1.1 cd/A and 0.48 lm/W, respectively, while the CIE coordinates are located at (X = 0.15, Y = 0.012) very close to the CIE values of the NTSC standard blue color (X = 0.14, Y = 0.09). Similar type of changes was also observed for devices H and I compared with the corresponding devices C and D with thickness of 40 nm. The EL spectra of devices G-I are also included in the Figure 5, while the current-voltage-luminance (I-V-L) measurements for G-I are shown in the Figure 6.

The reason for the observed blue shifts of devices G-I is not yet clear. The EL spectra of these devices change considerably with applied voltage. An example of the change of the EL spectrum (device I) with applied voltage is depicted in Figure 8. Two other devices J and K with emitting-layer thickness 30 nm having dopant concentration of 10% and 15% respectively were constructed. The key performance data of J-K are listed in Table 2, while the EL spectra and I-V-L measurement curves are shown in Figures 5 and 6, respectively. Device J has a turn-on voltage of 5.2 V with maximum luminance of 3752 cd/m² at 17.5 V. The EL emission peak of J is at 471 nm with CIE coordinates at (X = 0.14, Y = 0.23). As indicated by the EL spectrum of device J, there is no contribution from TPBI emission and not much change of spectrum was observed with applied voltage (Figure 9). Comparison of the performance of devices D, I and J reveals that the turn-on voltage, the wavelength of emission peak and the Y values in the CIE coordinates vary systematically with the thickness of the emitting layer. Similar trend is also found in devices E and K.
Figure 8. EL spectra of device I [ITO/NPB (20 nm)/CBP (20 nm)/BSIB-1:TPBI (10%, 20 nm)/TPBI (20 nm)/Mg:Ag (10:1; 55 nm)/Ag (100 nm)] at different voltages

Figure 9. EL spectra of device J [ITO/NPB (20 nm)/CBP (20 nm)/BSIB-1:TPBI (10%, 30 nm)/TPBI (20 nm)/Mg:Ag (10:1; 55 nm)/Ag (100 nm)] at different voltages

We have also fabricated several devices L-P using BSIB-2 as the dopant in TPBI and measured the physical properties of these devices. A general device structure ITO/NPB (20 nm)/CBP (20 nm)/BSIB-2:TPBI (X%, Y nm)/TPBI (20 nm)/Mg:Ag (10:1; 55 nm)/Ag (100 nm) was employed for these studies. In devices L-O the concentration of the dopant (BSIB-2) in TPBI were varied systematically. The key performance data of L-P are listed in Table 3. Device L (5% dopant, 40 nm thickness) has a turn-on voltage of 5.5 V, maximum brightness of 4991 cd/m² at 20.0 V and EQE, current and power efficiencies of 1.19%, 2.77 cd/A and 0.90 lm/W, respectively. The device emits blue-green light at 492 nm having CIE coordinates at (X = 0.17, Y = 0.37). The performance data in the Table 3 reveals that as the concentration of the dopant BSIB-2 increases, the efficiencies of devices decrease. This can be attributed to concentration quenching at higher dopant concentrations. Red shifts in the EL emission peaks (Figure 10) of devices L-O were observed as the dopant concentrations increase. This phenomenon can be explained by the increasing dielectric constant of the medium as a consequence of an increasing amount of polar dopant [14]. To investigate the effect of the thickness of the emitting layer on the properties of the devices, we have constructed device P with 10%
dopant concentration and 30 nm emitting-layer thickness. Comparison of the performance data of
device M (10%, 40 nm) and P (10%, 30 nm), shows that P is marginally better than M with respect to
efficiencies (Table 3). The EL emission spectrum of
device P (487 nm) has a blue shift with respect to
device M (496 nm), and accordingly the CIE coordinates are also shifted toward the blue region.

Figure 10. EL spectra of devices L-P [ITO/NPB (20 nm)/CBP (20 nm)/BSIB-2:TPBI (X%, Y nm)/TPBI (20
nm)/Mg:Ag (10:1; 55 nm)/Ag (100 nm)] at 10 V

Figure 11. (a) Luminance-voltage (L-V) and (b) current density–voltage (CD-V) characteristics for devices L-P
Table 3. Performance of the electroluminescent devices based on BSIB-2 dopant.\(^a\)

<table>
<thead>
<tr>
<th>Device</th>
<th>Compositions(^b)</th>
<th>(V_i)</th>
<th>(\eta_e (%)), V</th>
<th>(L) (cd/m(^2)), V</th>
<th>(\eta_p) (cd/A), V</th>
<th>(\eta_p) (lm/W), V</th>
<th>CIE (x, y), V</th>
<th>(\lambda_{\text{max EL}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>BSIB-2:TPBI (5%,40nm)</td>
<td>5.5</td>
<td>1.187, 10.5</td>
<td>4991, 20.0</td>
<td>2.771, 10.0</td>
<td>0.901, 9.5</td>
<td>(0.17,0.37), 10</td>
<td>492</td>
</tr>
<tr>
<td>M</td>
<td>BSIB-2:TPBI (10%,40nm)</td>
<td>6.0</td>
<td>0.795, 13.0</td>
<td>4093, 20.0</td>
<td>2.034, 13.0</td>
<td>0.502, 12.0</td>
<td>(0.18,0.42), 10</td>
<td>496</td>
</tr>
<tr>
<td>N</td>
<td>BSIB-2:TPBI (15%,40nm)</td>
<td>6.0</td>
<td>0.648,13.0</td>
<td>3574, 19.5</td>
<td>1.653, 13.0</td>
<td>0.424, 11.5</td>
<td>(0.18,0.41), 10</td>
<td>494</td>
</tr>
<tr>
<td>O</td>
<td>BSIB-2:TPBI (20%,40nm)</td>
<td>6.2</td>
<td>0.518, 15.0</td>
<td>3598, 20.0</td>
<td>1.453, 15.0</td>
<td>0.326, 13.0</td>
<td>(0.20,0.47), 10</td>
<td>501</td>
</tr>
<tr>
<td>P</td>
<td>BSIB-2:TPBI (10%,30nm)</td>
<td>5.0</td>
<td>0.979,10.5</td>
<td>4197,18.0</td>
<td>1.989, 10.5</td>
<td>0.615, 10.0</td>
<td>(0.15,0.30), 10</td>
<td>487</td>
</tr>
</tbody>
</table>

\(^a\)The values for the external quantum efficiency (\(\eta_e\)), brightness (L), current efficiency (\(\eta_p\)) and power efficiency (\(\eta_p\)) are the maximum for the devices.

\(^b\)The general device structure is ITO/NPB (20 nm)/CBP (20 nm)/BSIB-2:TPBI (X%, Y nm)/TPBI (20 nm)/Mg:Ag (10:1; 55 nm)/Ag (100 nm).

To understand the mechanism of energy transfer in the present studies, the PL spectrum of TPBI thin film doped with BSIB-1 and EL spectrum of one of the devices made from BSIB-1 dopant were compared. Device D in which the dopant concentration is 10% (40 nm) emits light at 489 nm (Figure 7). The PL peak wavelength of a TPBI thin film doped with 10% BSIB-1 is 488 nm as shown in Figure 3. The similarity of EL and PL emission spectrum of BSIB-1 under the same dopant concentration proves that the energy transferred from host to dopant in the device is occurring via a Förster energy transfer mechanism. Similarly, device M (10% BSIB-2, 40 nm) emits light at 496 nm, which is almost the same as the PL peak wavelength (494 nm) of a TPBI thin film doped with 10% BSIB-2. This also indicates that a Förster energy transfer mechanism operates in device M.

5. Conclusion

We have successfully prepared two imidazole derivatives (BSIB-1 and 2) by a simple one-step condensation reaction and used them as emissive dopants for multilayers electroluminescent devices. The BSIB derivatives have excellent physical properties such as high melting point and glass-transition temperature. They emit bright light in solution states but do not emit light in the solid states. The emission peak wavelengths are significantly affected by the properties of the solvents. Several devices have been fabricated with the general device configuration ITO/NPB (20 nm)/CBP (20 nm)/BSIB:TPBI (X%, Y nm)/TPBI (20 nm)/Mg:Ag (10:1; 55 nm)/Ag (100 nm) by changing the dopant concentration and thickness of the emitting layer. Under the above device configuration, a maximum luminance of more than 4000 cd/m\(^2\) for BSIB-1 and around 5000 cd/m\(^2\) for BSIB-2 could be obtained. The maximum EQE of more than 1%, current efficiency more than 2 cd/A and power efficiency of 0.9 lm/W were achieved for these EL devices. The EL devices based on BSIB derivatives emit light in the blue-green to blue region. The EL emission peaks and color can be tuned by adjusting the concentration of dopants and thickness of the emitting layer. The energy transfer from the TPBI host exciton to the dopants in the present case is operating according to the Förster energy transfer mechanism.

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References


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