



Phosphorescent Blue Organic Light-Emitting Diodes with New Bipolar Host Materials

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We report narrow band gap bipolar host materials, CbPr-3 (9,9'-[(3,3'-Biphenyl-3,3'-yl-bipyridine)-1,3-biphenyl]bis-9H-carbazole) and Bim-4 (9,9'-[5-(1-phenyl-1H-benzimidazol-2-yl)-1,3-phenylene]bis-9H-carbazole), for blue phosphorescent OLEDs application. These two bipolar hosts have high triplet energy of ≥ 2.9 eV, capable of reducing the driving voltages and improving efficiencies. Significant low driving voltages of 7.4 and 6.6 V were obtained for CbPr-3 and Bim-4 hosts, compared with 9.0 V of the commonly used host, mCP (1,3-bis(9-carbazolyl)benzene). At a given constant luminance of 1000 cd/m², the power efficiency of both the bipolar host devices was enhanced by 2.5 times.

Keywords: Phosphorescent OLED, Bipolar Host, Triplet Energy.

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) in recent decades have proven their potential with superior properties for low power consumption displays, lightings and printed electronics industry.^{1,2} OLED lifetime has been dramatically improved over the last ten years with excellent progress in OLED materials and device technologies. On the other hand, power efficiency improvement in blue OLEDs is not so rapid. In order to improve power efficiency, high internal quantum efficiency with phosphorescent emitter and more importantly techniques to give low driving voltage in the devices are required. In the past, several approaches were employed to enhance power efficiency of phosphorescent OLEDs (PHOLEDs), which include doping or designing charge transporting layer,^{3,4} mixed host emissive layer,⁵ high triplet energy host material⁶ etc. Generally, unbalance hole and electron currents in the devices makes the recombination zone narrower, thereby shifting it either close to hole transport layer (HTL) or electron transport layer (ETL). Thus narrower charge recombination zone in PHOLEDs are prone to triplet-triplet exciton quenching due to local high density of the triplet excitons and also long diffusion of the triplet excitons.^{7,8} Therefore, bipolar host molecules capable of transporting both charges can meet the requirement of balancing the charge density for simplification of high performance PHOLEDs. Although several bipolar host materials are available for green and

red PHOLEDs but the blue phosphorescent bipolar host is still a challenge that can lead to excellent performance of the devices.

Over the past few decades, a very few blue host materials based on pyridine or phosphine oxide derivatives have been reported with the ideal EQE value of $\sim 20\%$. Recently, highly efficient phosphine oxide derivatives, SPPO1,⁹ BCPO¹⁰ for sky blue, and PPO21¹¹ for deep blue PHOLED application have been demonstrated successfully. The devices based on these materials have shown the EQE of about 20.5%, 23.5%, and 19.2%, respectively. Other pyridine containing bipolar host, 26DCzPPy¹² has been reported with 25% EQE for sky blue PHOLED applications. Although these materials were used to obtain high quantum efficiencies, but, there are some deficiencies that hampered their further applicability, such as operational stability, color chromaticity, thermal and morphological instability etc.

Herein, we report the new bipolar host materials, CbPr-3 (9,9'-[(3,3'-Biphenyl-3,3'-yl-bipyridine)-1,3-biphenyl]bis-9H-carbazole) and Bim-4 (9,9'-[5-(1-phenyl-1H-benzimidazol-2-yl)-1,3-phenylene]bis-9H-carbazole) for blue PHOLED applications. In CbPr-3 and Bim-4, pyridine moieties and imidazole moieties were inserted to enhance electron transporting capability, whereas carbazole moieties functions as hole transport units. Both these materials possess high triplet energies and narrow band gap resulting in good device efficiency and low driving voltage characteristics in blue PHOLEDs.

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2. EXPERIMENTAL DETAILS

2.1. Material Synthesis

The compound, CbPr-3 was synthesized according to the procedure shown in Figure 1. The synthesis of Bim-4 was done as described previously.¹³ Molecular structure of Bim-4 can be seen inset of Figure 2.

Step 1 Synthesis of intermediate (A): Carbazole 5.1 g, 1,3,5-tribromobenzene 19.1 g, cuprous chloride 0.8 g and potassium carbonate 16 g was suspended in 40 ml of dimethyl sulfoxide (DMSO), and heated and refluxed for 8 hours. The reaction fluid was cooled to room temperature and re-crystallized with methanol. The precipitated crystals were separated by water filtration and the obtained residue was purified by silica gel column chromatography, providing 7.3 g of the intermediate (A) (yield 50%).

Step 2 Synthesis of intermediate (B): 7.3 g of the intermediate (A) was dissolved in 40 ml of tetrahydrofuran, then 10 ml (1.6 M) of *n*-butyl lithium hexane solution (1.6 M) was added at -70°C . The obtained solution was agitated at -70°C to 40°C for one hour. And 5 ml of isopropyl tetramethyl dioxaborolane was slowly added. The obtained solution was heated to room temperature, and then agitated for 6 hours. To the obtained reaction solution, 20 ml of water was added and agitated for 20 minutes. The reaction solution was separated into two liquid layers, and organic layer thereof was dried with anhydrous sodium sulfate. After removing the organic solvent under a reduced pressure, the obtained residue was purified with the silica gel column chromatography to provide 5.4 g of the intermediate (B) (yield 67%).

Step 3 Synthesis of intermediate (C): 5.4 g of the intermediate (B), 3.3 g of 1,3,5-tribromobenzene, and 0.3 g of tetrakis-(triphenyl phosphine) palladium were suspended

in the 20 ml of tetrahydrofuran and 20 ml of toluene, then added with a solution of 20 wt% of tetraethyl ammonium hydroxide dissolved in 20 ml of water. The mixture obtained was heated and refluxed for 9 hours. The reaction fluid was separated into the two layers, and an organic layer thereof was cleaned with a sodium chloride saturated aqueous solution and later dried with anhydrous sodium sulfate. Subsequently, the organic solvent was removed by distillation under reduced pressure. The residue was purified by silica gel column chromatography to provide 4.5 g of the intermediate (C) (yield 70%).

Step 4 Synthesis of CbPr-3: 4.5 g of the intermediate (C), 2.0 g of 3-pyridineboronic acids, and 0.2 g of tetrakis-(triphenyl phosphine) palladium were suspended in 20 ml of tetrahydrofuran and 20 ml of toluene, then added with a solution of 20 wt% of tetraethyl ammonium hydroxide dissolved in 20 ml of water. The obtained mixture was heated and refluxed for 9 hours. The reaction fluid was separated into two layers, and an organic layer thereof was cleaned with a sodium chloride saturated aqueous solution and dried with anhydrous sodium sulfate. Subsequently, the organic solvent was removed by distillation under reduced pressure, and the residue was purified with silica gel column chromatography to provide 2.9 g of the CbPr-3 (yield 60%). Mass spectroscopy analysis data of CbPr-3 is as follows: MS (ESI) m/z 639.18($M+H$)⁺. Calc. for $\text{C}_{46}\text{H}_{30}\text{N}_4$: 638.78, ^1H NMR (300 MHz, CDCl_3) δ (ppm) 8.9(d, 2H), 8.65 (d, 2H), 8.18 (d, 4H), 8.21–7.88 (m, 7H), 7.81 (s, 1H), 7.6 (m, 4H), 7.50–7.48 (m, 4H), 7.42–7.32 (m, 2H), 7.31–7.29 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) 149.29, 148.41, 143.99, 141.22, 140.55, 140.09, 139.96, 135.84, 134.59, 126.29, 126.10, 125.84, 124.60, 123.70, 120.57, 120.52, 109.64.

Thermal properties of CbPr-3 and Bim-4 were investigated by thermogravimetric analysis (TGA) and differential

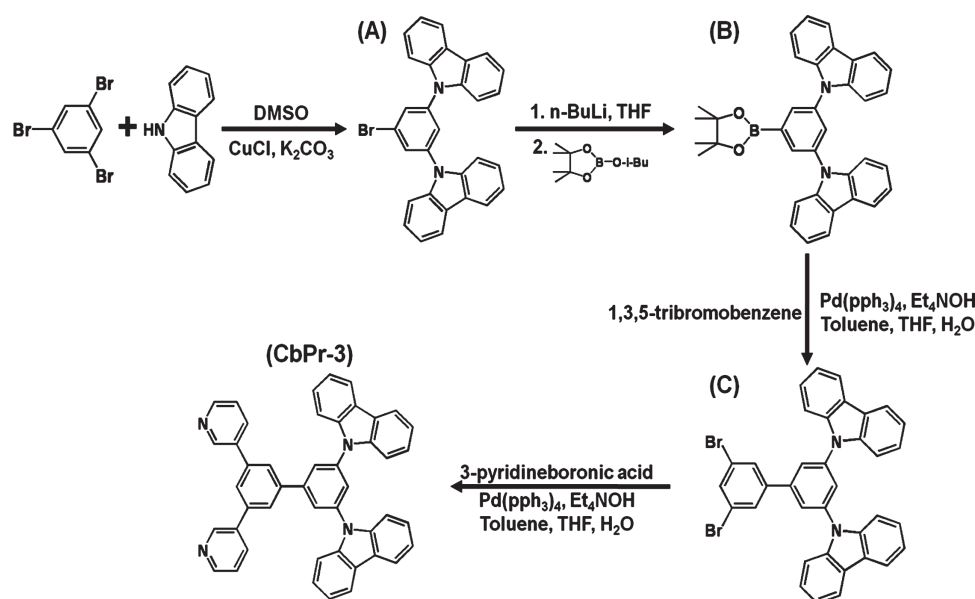


Fig. 1. Synthetic method of CbPr-3.

scanning calorimetry (DSC). Both these compounds exhibit high thermal-decomposition temperatures (T_d) of about 350 and 511 °C. Their glass transition temperatures (T_g) are about 120 and 139 °C which are higher than that of mCP.¹⁴ The high value of T_d and T_g proves excellent thermal and morphological stability, enabling the preparation of homogenous and stable thin film.

2.2. OLED Fabrication and Measurement

1,4-Bis(1-naphthylphenylamino)-biphenyl (NPB) and mCP as the hole transporting material or host were commercially available. Other bipolar hosts, CbPr-3 or Bim-4, were synthesized in the laboratory. The phosphorescent dopant material iridium(III)bis(4,6-(difluorophenyl)pyridinato-*N,C'*picolate) (Firpic), and electron transporting material, 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) were commercially available. The details of fabrication and measurement has been described elsewhere.¹⁵

3. RESULTS AND DISCUSSION

The photophysical properties of both the host materials were measured using UV-visible absorption and photoluminescence spectra as shown in Figure 2.

The absorption spectrum of CbPr-3 and Bim-4 have absorption bands from 230 to 370 nm which could be from π - π^* transitions of the conjugated π -electron system. The PL emission maxima for CbPr-3 and Bim-4 in a solution were observed around 391 and 400 nm. The low temperature phosphorescent spectrum of the both materials was measured in 2-methyl tetrahydrofuran and methylene chloride mixed solution at 77 K, revealed the phosphorescent sub-band of two peaks. From the first peak, triplet energies of 2.9 and 3.0 eV were calculated. It confirms that CbPr-3 and Bim-4 triplet energies are in a good agreement in transferring excitons from the bipolar hosts to the Firpic dopant having triplet energy of 2.65 eV.¹² Cyclic voltammetry experiments were performed to know HOMO levels of CbPr-3 and Bim-4. The HOMO energy levels for CbPr-3 and Bim-4 were estimated to be 5.8 eV by

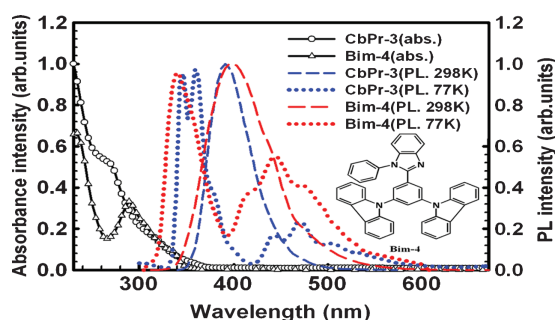


Fig. 2. Absorption and photoluminescence spectra of CbPr-3 and Bim-4. Inset shows the molecular structure of Bim-4.

Table I. A summary of energy levels.

	mCP	CbPr-3	Bim-4
HOMO (eV)	5.9	5.8	5.8
LUMO (eV)	2.4	2.6	2.4
Band gap (eV)	3.5	3.2	3.4
Triplet energy (eV)	2.8	2.9	3.0

cyclic voltammogram. The LUMO energy levels of both the hosts are at 2.6 and 2.4 eV which can be deduced from the calculation of band gaps. Table I summarizes the experimentally obtained energy levels.

A series of the devices were fabricated and evaluated for their J - V and L - V output characteristics. The devices were fabricated using CbPr-3, Bim-4, respectively. For comparison, mCP type of host device with 10 wt% of Firpic in similar experimental conditions was also fabricated. These devices were fabricated on the ITO with a multilayered structure of ITO/NPB (40 nm)/mCP (15 nm)/Host: 10 wt% Firpic dopant (30 nm)/TPBI (25 nm)/LiF (1 nm)/Al (100 nm). Here NPB improves the hole injection. The operating condition and characteristics of these devices are compared and summarized in Table II. The mCP, CbPr-3, and Bim-4 host devices are named as device A, B, and C.

Figure 3 shows the current density-voltage (J - V) and luminance-voltage (L - V) characteristics of all the three devices. The devices B and C have lower driving voltages compared with the reference device A. It was observed that driving voltages to reach 1000 cd/m² were found to be 7.4 and 6.6 V for the devices B and C, lower than 9.0 V for mCP based device. The reduction in driving voltage in device B and C is attributed to minimization of charge trapping by dopant molecules in a narrow band gap host emitting layer and lower injection barrier to the emitting layer. In case of mCP as a host material, its hole transportation is faster than that of electron, and its wide band gap introduces charge trapping by dopant molecules at deep sites. Therefore, there is unbalancing of charges which make the recombination zone narrower, thereby shifting more towards electron transporting layer. This can

Table II. A summary of device characteristics.

	Device A (mCP)	Device B (cbpr-3)	Device C (Bim-4)
Turn-on voltage (at 1 cd/m ²)	4.4 V	3.4 V	3.0 V
Operating voltage (1000 cd/m ²)	9.0 V	7.4 V	6.6 V
Efficiency (1000 cd/m ²)	11.0 cd/A	17.5 cd/A	20.3 cd/A
Efficiency (maximum)	3.8 lm/W	9.4 lm/W	9.7 lm/W
External quantum efficiency (%)	15.0 cd/A	20.3 cd/A	22.0 cd/A
CIE(x, y)	7.8 lm/W	11.5 lm/W	15.0 lm/W
(1000 cd/m ²)	9.6%	13.0%	14.1%
	(0.17, 0.28)	(0.17, 0.29)	(0.17, 0.29)

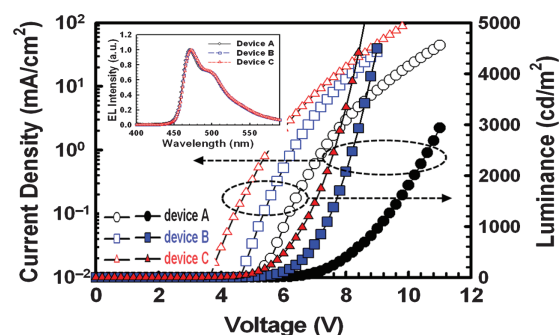


Fig. 3. J - V and L - V characteristics of the devices.

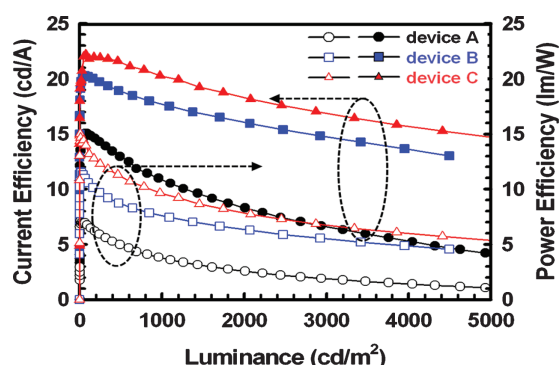


Fig. 4. Current and Power efficiencies of the devices.

enhance the possibility of triplet-triplet annihilation also. Thus the mCP host device exhibits poor performance as well as shows high driving voltage. Inset of Figure 3 also shows the EL spectra of all the three devices exhibiting emissions in the blue regions. It indicates complete energy transfer from the host materials to the guest due to confinement of triplet excitons at the Firpic dopant molecule. The EL spectral peaks and CIE_{xy} coordinates of all devices are summarized in Table II. At 1000 cd/m², the EL spectral peaks and CIE_{xy} coordinates of CbPr-3 and Bim-4 host devices are at 472 nm/(0.17, 0.29) which is found similar to mCP based device exhibiting a peak at 469 nm/(0.17, 0.28). The EL spectrum of each device does not change significantly with the applied voltage.

The current and power efficiencies of CbPr-3 and Bim-4 host devices are shown in Figure 4. At a given constant luminance of 1000 cd/m², the current and power efficiencies of the devices B and C were 17.5 cd/A, 9.4 lm/W, and 20.3 cd/A, 9.7 lm/W respectively, whereas device A exhibits of about 11.0 cd/A, 3.8 lm/W, respectively. Furthermore, the maximum current and power efficiencies obtained were 20.3 cd/A, and 11.5 lm/W for device C, and 22.0 cd/A, and 15.0 lm/W for device B while 15.0 cd/A, 7.8 lm/W were observed for device A. Due to good charge balance and wide emission zone, efficiency roll-off has been reduced in the device B and C, thus achieving high

power efficiency at a high current density. In a reference device, we have poor charge balance leading to low efficiency and steep efficiency roll-off. It clearly reveals that external quantum efficiency (EQE) for CbPr-3 and Bim-4 devices were 13.0% and 14.1% higher than mCP based device exhibiting EQE of about 9.6%.

4. CONCLUSION

In summary, we have demonstrated superior performance of CbPr-3 and Bim-4 as the bipolar narrow band gap hosts for blue PHOLED application. The minimized charge trapping by a dopant molecule and a low injection barrier to emitting layer were resulting into significant reductions in driving voltage and improvement of efficiencies. For CbPr-3 and Bim-4 hosts, the driving voltage was reduced about 1.6 and 2.4 V while their power efficiency at constant luminance of 1000 cd/m² was enhanced 2.5 times with low roll-off.

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