Organic Electronics 42 (2017) 66-74

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Synthesis and device properties of mCP analogues based on fused-ring carbazole moiety



^a Department of Nanobiomedical Science and BK21 PLUS NBM Global Research Center, Dankook University, Cheonan 31116, Republic of Korea ^b Department of Chemistry, Dankook University, Cheonan 31116, Republic of Korea

ARTICLE INFO

Article history: Received 5 August 2016 Received in revised form 5 December 2016 Accepted 15 December 2016 Available online 18 December 2016

Keywords: Phosphorescence OLED Sky blue Benzofurocarbazole High triplet energy Benzothienocarbazole Blue host

ABSTRACT

Novel mCP analogues consisting of blue phosphorescent host materials with fused-ring, 1,3-bis(5*H*-benzofuro[3,2-*c*]carbazol-5-yl)benzene (BFCz) and 1,3-bis(5*H*-benzo[4,5]thieno[3,2-*c*]carbazol-5-yl) benzene (BTCz) were designed and synthesized using benzofurocarbazole and benzothienocarbazole donor moieties. BFCz and BTCz exhibit high glass transition temperatures of 147 and 157 °C, respectively, and high triplet bandgaps of 2.94 and 2.93 eV, respectively. To explore the electroluminescence properties of these materials, multilayer blue phosphorescent organic light-emitting diodes (PHOLEDs) were fabricated in the following device structure: indium–tin-oxide (ITO)/PEDOT:PSS/4,4'-cyclohexylidene bis [*N*,*N*-bis(4-methylphenyl)aniline] (TAPC)/1,3-bis(*N*-carbazolyl) benzene (mCP)/host:FIrpic/diphenyl-phosphine oxide-4-(triphenylsilyl)phenyl (TSPO1)/LiF)/Al. The PHOLEDs with BTCz exhibited efficient blue emission with luminous and quantum efficiencies of 30.9 cd/A and 15.5% at 1000 cd/m², respectively.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

In 1998, an organic light emitting diode (OLED) was successfully developed with phosphorescent materials three to four times more effective than existing fluorescent organic materials, thus achieving 100% quantum efficiency of the organic electroluminescence display [1–4]. This phosphorescence works through a mechanism by which, after electronic excitation, singlet excitons become triplet excitons by intersystem crossing. These triplet excitons then start to emit light as they return to the ground state. To improve the color purity and efficiency, instead of using a single material, this light-emitting structure uses a host-dopant system in which excitons produced at a host are doped to produce light [5–8].

In the case of phosphorescent organic light-emitting diodes (PHOLEDs), the selection of the phosphorescent light-emitting host material has a direct impact on the luminous efficiency. The luminosity of the phosphorescent material arises from its triplet energy. Therefore, the higher the triplet energy of the host is in comparison to that of the dopant, the more easily it can be transferred from the host material to the dopant material [9–12]. In addition, the triplet

* Corresponding author.

E-mail address: chili@dankook.ac.kr (C.W. Lee).

energy is typically approximately 1 eV lower than the singlet energy, which is why it is preferable to use a host material whose highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap is greater than that of a fluorescent material [3]. In other words, if the host's triplet energy is lower than that of the dopant's phosphorescent material, an endothermic energy transfer occurs, lowering the external light emission efficiency. However, if the host's triplet energy is greater than the dopant's, an exothermic energy transfer occurs instead, increasing the light emission efficiency. Therefore, to increase the light emission efficiency, the triplet energy of the host material must be high [13,14].

In recent years, tremendous efforts have been devoted to developing host materials with desirable characteristics [15–17]. Carbazole-based materials are widely used as hosts in PHOLEDs to improve device efficiency [3,18–27]. The material most commonly used as the blue phosphorescent host is 1,3-bis(*N*-carbazolyl)benzene (mCP). Because of the high triplet energy of mCP (2.9 eV), a minimum of 20% quantum efficiency has been reported in most blue PHOLEDs in which mCP has been used as the host [28–32]. However, it is not easy to use this material in industrial applications because of its low thermal stability (Tg = 55 °C) and short lifetime. In short, it is necessary to create thermally stable compounds with high triplet energies to develop new host materials [33,34]. Benzofurocarbazole and benzothienocarbazole are better suited for use

http://dx.doi.org/10.1016/j.orgel.2016.12.027

1566-1199/© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).







as host materials than carbazole because of their electron donor moiety and thermal stability, which improves their quantum efficiency [35,36].

In this study, instead of mCP with carbazole, 1,3-bis(5*H*-benzo-furo[3,2-*c*]carbazol-5-yl)benzene (BFCz) and 1,3-bis(5*H*-benzo[4,5] thieno[3,2-*c*]carbazol-5-yl)benzene (BTCz) were synthesized using benzofurocarbazole and benzothienocarbazole, respectively. BFCz and BTCz exhibit high triplet energies (2.94 eV and 2.93 eV, respectively) and are very suitable for use as blue phosphorescent host materials. In addition, they exhibit high thermal stability and have glass transition temperatures of 147 °C (BFCz) and 157 °C (BTCz), respectively. The PHOLED with BTCz exhibited high quantum efficiency (16.1%) and good color stability, between 100 cd/m² and 3000 cd/m², with increasing voltage.

2. Materials and methods

2.1. Materials and instruments

Dibenzo[b,d]furan-4-ylboronic acid, dibenzo[b,d]thiophen-4ylboronic acid. 1-bromo-2-nitrobenzene, (\pm) -trans-1,2cyclohexanediamine, copper(I) iodide, 1,3-diiodobenzene, tripotriethylphosphite, tassium phosphate, tetrakis(triphenylphosphine)palladium(0), and tripotassium phosphate (Aldrich Chem. Co. St. Louis, MO, USA) were used without further purification. Potassium carbonate, toluene, dichloromethane, ethyl acetate. *n*-hexane. 1.4-dioxane. and ethanol (Duksan Chem. Co. Seoul, Korea) were used as received. The solvents were dried and degassed following standard procedures.

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Varian, Unity Inova (300 MHz) system. Fourier transform infrared (FT-IR) spectra were obtained with a Varian 640 FT-IR device. Gas chromatography (GC) mass spectra were recorded using a Jeol (JMS-AX505WA) and HP 5890 Series II (Brea, CA, USA) in fast atom bombardment (FAB) mode. Elemental analyses were performed using a CE Instruments EA1110 device (Hindley Green, Wigan, UK). The ultraviolet-visible (UV-vis) spectra were recorded on a UV-vis spectrophotometer (Shimadzu, UV-1601PC; Tokyo, Japan) and photoluminescence (PL) spectra were obtained using a fluorescence spectrophotometer (Jasco FP-6500; Tokyo, Japan). Differential scanning calorimetry (DSC) measurements were performed on a Shimadzu DSC-60 under nitrogen at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 at a heating rate of 10 °C/min. Cyclic voltammetry measurements were carried out in an acetonitrile solution with 0.1-M tetrabutylammonium perchlorate. Silver (Ag) metal was used as the quasi-reference electrode, Pt wire was used as a counter electrode, and polished glassy carbon was used as the working electrode.

2.2. Preparation of 4-(2-nitrophenyl)dibenzo[b,d]furan

Dibenzo[*b*,*d*]furan-4-ylboronic acid (10.00 g, 47.16 mmol), 1bromo-2-nitrobenzene (7.94 g, 39.31 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.59 g, 1.38 mmol) were dissolved in a solution of 2-M potassium carbonate (70 mL) and toluene (200 mL). The reaction mixture was refluxed under nitrogen for 24 h. The mixture was diluted with dichloromethane and washed with distilled water. The organic layer was treated with anhydrous magnesium sulfate and evaporated *in vacuo* to yield the crude product, which was purified by column chromatography using dichloromethane/*n*-hexane to obtain a yellow powder. The results are as follows:

Yield 85%. ¹H NMR (300 MHz, CDCl₃) δ 8.12–8.15 (m, 2H), 7.82–7.84 (d, 1H), 7.64–7.61 (d, 1H), 7.58–7.51 (d, 1H), 7.49–7.41 (m,

3H), 7.35–7.31 (t, 3H). Mass (FAB) m/z 290 $[(M+1)^+]$. Anal. Calcd. for C₁₈H₁₁NO₃: C, 74.73%; H, 3.83%; N, 4.84%; O, 16.59%. Found: C, 74.9%; H, 3.40%; N, 4.43%; O, 16.12%.

2.3. Preparation of 5H-benzofuro[3,2-c]carbazole

4-(2-Nitrophenyl)dibenzo[*b*,*d*]furan (10.00 g, 34.57 mmol) was dissolved in triethylphosphite (100 mL) and refluxed for 10 h. The reaction mixture was cooled to room temperature and extracted with ethyl acetate and distilled water. The organic layer was treated with anhydrous magnesium sulfate, and the solvent was removed by rotary evaporation. Impurities were removed by column chromatography on silica gel using dichloromethane/*n*-hexane to obtain a yellowish powder. The results are as follows:

Yield 95%. ¹H NMR (300 MHz, CDCl₃) δ 11.8 (s, 1H), 8.32–8.35 (d, 1H), 7.82–7.84 (d, 1H), 7.64–7.61 (d, 1H), 7.58–7.51 (d, 1H), 7.49–7.41 (m, 3H), 7.35–7.31 (t, 3H). Mass (FAB) m/z 257 [(M+1)⁺]. Anal. Calcd. for C₁₈H₁₀NO: C, 87.36%; H, 3.93%; N, 5.47%; O, 6.24%. Found: C, 87.7%; H, 3.4%; N, 5.03%; O, 6.41%.

2.4. Preparation of 1,3-bis(5H-benzofuro[3,2-c]carbazol-5-yl) benzene (**BFCz**)

5*H*-benzofuro[3,2-*c*]carbazole (5.00 g, 19.43 mmol), 1,3diiodobenzene (3.05 g, 9.25 mmol), copper(I) iodide (0.18 g, 0.93 mmol), and tripotassium phosphate (4.32 g, 20.36 mmol) were dissolved in 1,4-dioxane (80 mL) and then added to the flask. After stirring for 1 h at room temperature under a nitrogen atmosphere, a (\pm)-*trans*-1,2-cyclohexanediamine (0.11 g, 0.93 mmol) was added. The reaction mixture was stirred for 48 h at 100 °C, and the reaction was quenched with toluene (300 mL). The solvent was removed by rotary evaporation, and the crude product was washed with water. Impurities were removed by column chromatography on silica gel using dichloromethane/*n*-hexane. Additionally, BFCz was purified by sublimation under a vacuum. As a result, the title compound was obtained as a white powder. The results are as follows:

Yield 45%. Mp: 298 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.61 (d, 2H), 7.95–8.03 (m, 4H), 7.91–7.94 (m, 2H), 7.84–7.88 (m, 2H), 7.62–7.67 (d, 2H), 7.5–7.59 (d, 2H), 7.42–7.48 (m, 4H), 7.44–7.48 (m, 4H), 7.38–7.43 (t, 2H). ¹³C NMR (300 MHz, CDCl₃) δ 156.2, 151, 141, 139.5, 138.5, 138, 132, 126.1, 125.8, 125.6, 125.4, 125.2, 125, 123.6, 122.4, 122.2, 121.6, 118.2, 118.1, 117, 111.5, 110, 109, 108, 107.5, 106. FT-IR (KBr, cm⁻¹) 3050, 3020 (aromatic C-H). Mass (FAB) m/z 588 [(M+1)⁺]. Anal. Calcd. for C₄₂H₂₄N₂O₂: C, 85.70%; H, 4.11%; N, 4.76%; O, 5.44%. Found: C, 84.22%; H, 4.01%; N, 4.71%; O, 4.30%.

2.5. Preparation of 4-(2-nitrophenyl)dibenzo[b,d]thiophene

The method used to synthesize 4-(2-nitrophenyl)dibenzo[b,d] thiophene was the same as that for 4-(2-nitrophenyl)dibenzo[b,d] furan, except that dibenzothiophene-4-boronic acid (10.76 g, 47.16 mmol) was used instead of dibenzofuran-4-boronic acid. The results are as follows:

Yield 80%. ¹H NMR (300 MHz, CDCl₃) δ 8.39–8.38 (d, 2H), 8.14–8.11 (m, 2H), 7.72–7.69 (d, 1H), 7.67–7.64 (t, 1H), δ 7.57–7.46 (m, 3H), δ 7.39–7.35 (m, 2H). Mass (FAB) m/z 306 [(M+1)⁺]. Anal. Calcd. for C₁₈H₁₁NO₂S: C, 70.80%; H, 3.63%; N, 4.59%; O, 10.48%; S, 10.50%. Found: C, 70.4%; H, 3.22%; N, 4.43%; O, 10.8%; S, 10.0%.

2.6. Preparation of 5H-benzo[4,5]thieno[3,2-c]carbazole

The method used to synthesize 5H-benzo[4,5]thieno[3,2-c] carbazole was the same as that for 5H-benzofuro[3,2-c]carbazole, except that 4-(2-nitrophenyl)dibenzo[b,d]thiophene (10.56 g, 34.57 mmol) was used instead of 4-(2-nitrophenyl)dibenzo[b,d]

furan. The results are as follows:

Yield 90%. ¹H NMR (300 MHz, CDCl₃) δ 11.8 (s, 1H), 8.39–8.38 (d, 2H), 8.14–8.11 (m, 2H), 7.72–7.69 (d, 1H), 7.67–7.64 (t, 1H), 7.57–7.46 (m, 3H), 7.39–7.35 (m, 1H). Mass (FAB) m/z 273 [(M+1)⁺]. Anal. Calcd. for C₁₈H₁₁NS: C, 79.38%; H, 3.70%; N, 5.14%; S, 11.77%. Found: C, 79.04%; H, 3.82%; N, 5.30%; S, 11.0%.

2.7. Preparation of 1,3-bis(5H-benzo[4,5]thieno[3,2-c]carbazol-5-yl)benzene

The method used to synthesize BTCz was the same as that for BFCz, except that 5*H*benzo[4,5]thieno[3,2-*c*]carbazole (5.31 g, 19.43 mmol) was used instead of 5*H*-benzofuro[3,2-*c*]carbazole. The results are as follows:

Yield 40%. Mp: 300 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.35–8.39 (d, 2H), 8.21–8.28 (m, 4H), 8.0–8.05 (m, 2H), 7.91–7.99 (m, 2H),

7.82–7.85 (d, 2H), 7.66–7.71 (m, 4H), 7.42–7.59 (m, 8H). 13 C NMR (300 MHz, CDCl₃) δ 139, 138.5, 138.6, 136, 133, 128, 126.5, 126, 125, 124.1, 122, 121, 120.5, 120, 119.5, 117, 111, 108. FT-IR (KBr, cm⁻¹) 3050, 3020 (aromatic C-H). Mass (FAB) m/z 621 [(M+1)⁺]. Anal. Calcd. for C₄₂H₂₄N₂S₂: C, 81.26%; H, 3.90%; N, 4.51%; S, 10.33%. Found: C, 81.62%; H, 4.04%; N, 4.76%; S, 10.30%.

2.8. Device fabrication and measurement

Blue PHOLED devices were fabricated by thermal deposition using BFCz and BTCz as hosts with a configuration of ITO (120 nm)/ PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/host:FIrpic (25 nm)/TSPO1 (35 nm)/LiF (1 nm)/Al (200 nm), where ITO, PEDOT:PSS, TAPC, mCP, FIrpic, and TSPO1 are indium tin oxide, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), 4,4'cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)aniline], 1,3-bis(*N*-



Fig. 1. Energy diagram of the blue PHOLEDs using BFCz and BTCz host. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

carbazolyl)benzene, iridium(III) bis[(4,6-difluorophenyl)pyridinato- N,C^2]picolinate and diphenylphosphine oxide-4-(triphenylsilyl)phenyl, respectively. FIrpic was doped in the BFCz and BTCz hosts at doping concentrations of 3, 5, and 10%. Electrical measurements of the blue PHOLEDs and single-carrier devices were performed using Keithley 2400 source measurement unit and luminance measurements were carried out using a CS 2000 spectroradiometer under ambient conditions after encapsulation of the devices. The device structures and chemical structures of the organic materials are shown in Fig. 1.

3. Results and discussion

3.1. Synthesis and characterization

To synthesize the benzofurocarbazole and benzothienocarbazole donors using our established method for ring-fused hetero aromatic compounds, dibenzo[b,d]furan-4-ylboronic acid and dibenzo[b,d]thiophen-4-ylboronic acid first had to be reacted with 1-bromo-2-nitrobenzene by Suzuki coupling. Cyclization reactions of the resulting 4-(2-nitrophenyl)dibenzo[b,d]furan and 4-(2-nitrophenyl)dibenzo[b,d]furan and 4-(2-nitrophenyl)dibenzo[b,d]furan and 4-(2-nitrophenyl)dibenzo[b,d]thiophene in the presence of triethyl-phosphine produced the corresponding 5*H*-benzofuro[3,2-*c*] carbazole and 5*H*-benzo[4,5]thieno[3,2-*c*]carbazole, respectively. The two fused-ring heteroaromatic donor moieties were incorporated in 1,3-diiodobenzene by a tripotassium phosphate-mediated coupling reaction to produce BFCz and BTCz at synthetic yields of 45% and 40%, respectively.

The synthesis scheme for BFCz and BTCz is shown in Scheme 1. The chemical structures and compositions of the resulting precursor and bipolar phosphorescence host compounds were characterized by ¹H NMR, ¹³C NMR, FT-IR, GC-MS, and elemental analysis. The results of the elemental analysis and mass spectroscopy also support the formation of BFCz and BTCz and agreed well with the calculated values.

3.2. Thermal properties

The thermal properties of BFCz and BTCz were analyzed using DSC. DSC scan curves for BFCz and BTCz are presented in Fig. 2. The BFCz and BTCz had melting points (T_m) of 298 and 300 °C, respectively. The glass transition temperatures (T_g) were measured from the inflection points of the endothermic curves obtained by DSC and were 147 and 157 °C for BFCz and BTCz, respectively. The T_m and T_g of BTCz were slightly higher than those of BFCz because of its larger molecular size and the rigidity of dibenzothiophene. The rigidity of the fused ring heteroaromatic core increased the T_g of the host materials. The initial decomposition temperatures were 381 °C for BFCz and 373 °C for BFCz, and 10% weight losses were observed at 497 °C and 487 °C for BFCz and BTCz, respectively. The basic thermal and photophysical properties of BFCz and BTCz are summarized in Table 1.

3.3. Molecular simulation and energy level

Molecular simulation of BFCz and BTCz was carried out to investigate the HOMO and LUMO distributions of BFCz and BTCz, as shown in Fig. 3 The HOMO of BFCz and BTCz was distributed over the fused ring heteroaromatic core, and the LUMO was localized over the phenyl unit, because of electron-rich fused-ring heteroaromatic moiety. The bipolar character of BFCz and BTCz separated the HOMO and LUMO of BFCz and BTCz, which may reduce the bandgap of the BFCz and BTCz host materials.

3.4. Electrochemical properties

The ionization potential and electron affinity of BFCz and BTCz were analyzed using cyclic voltammetric oxidation and reduction scans. The oxidation and reduction curves were measured separately because of the irreversibility of the oxidation and reduction of the BFCz and BTCz hosts. Fig. 4 shows the oxidation and reduction curves of BFCz and BTCz. The oxidation potential and reduction



Scheme 1. Synthetic scheme of BFCz and BTCz: (a) Pd (PPh₃)₄, K₂CO₃, D.W, toluene, 90 °C, 24 h; (b) triethylphosphite, 120 °C, 10 h; (c) Cul, K₃PO₄, (±)-*trans*-1,2-cyclohexanediamine, 1,4-dioxane, 100 °C, 48 h.



Fig. 2. DSC and TGA thermogram of (a) BFCz and (b) BTCz.

potential were 1.35 V and -2.52 V, respectively, for BFCz and 1.29 V and -2.53 V, respectively, for BTCz, which corresponded to ionization potentials of -6.18 eV for BFCz and -6.12 eV for BTCz. Therefore, the HOMO and LUMO can be estimated to be -6.18 and -2.76 eV, respectively, for BFCz and -6.12 and -2.70 eV, respectively, for BTCz, based on the ionization potential and electron affinity.

3.5. Photophysical properties

The photophysical properties of BFCz and BTCz were analyzed using UV–vis and photoluminescence (PL) spectrometers. The UV–vis and PL spectra of BFCz and BTCz are presented in Fig. 5. The two host materials absorbed UV–vis light strongly at short wavelengths, below 310 nm, by π – π * transition, and weakly at long wavelengths, between 310 nm and 365 nm, by n– π * absorption.

Table 1

Basic thermal and photophysical properties of the devices obtained from BFCz and BTCz hosts.

Properties			Materials	
			BFCz	BTCz
Purity	HPLC	(%)	99.7	99.7
Thermal analysis	DSC (°C)	Tg	147	157
		Tm	298	300
Optical analysis	UV (THF)	Max (nm)	362.2	361.9
		Bg (eV) ^a	3.42	3.42
	PL (THF) (nm)	Max	353	354
		FWHM ^b	23.0	25.0
	PL (Solid) (nm)	Max	365	362
		FWHM ^b	43.0	46.0
	LT PL	T ₁	2.94	2.93
	PLQY		0.115	0.089
	PLQY (Firpic 10%)		0.865	0.755
Electrical analysis	CV (eV)	HOMO ^c	-6.18	-6.12
		LUMOd	-2.76	-2.70

^a Bandgap.

^b Full width at half maximum.

^c Highest occupied molecular orbital.

^d Lowest unoccupied molecular orbital.



Fig. 3. HOMO and LUMO distribution of BFCz and BTCz host materials.



Fig. 4. Electrochemical oxidation and reduction curves of BFCz and BTCz.

The use of benzofurocarbazole and benzothienocarbazole instead of carbazole extended the UV–vis absorption to 360 nm, which is good for energy transfer from the host material to the dopant material. The solution PL of BFCz and BTCz was measured in



Fig. 5. UV-vis and PL spectra of (a) BFCz and (b) BTCz.

tetrahydrofuran, and their maximum emission peaks were observed at 353 and 354 nm, respectively. The emission peaks of BFCz and BTCz were shifted to 365 and 362 nm, respectively, after dispersion in solid polystyrene. These results can be explained by the flexibility of the benzofurocarbazole moiety of BFCz decreasing energy levels more than the benzothienocarbazole moiety of BTCz. The first phosphorescent peak positions of the low-temperature PL emissions were 421 nm and 423 nm, respectively. The triplet energies calculated from the low-temperature PL spectra were 2.94 eV for BFCz and 2.93 eV for BTCz.

3.6. Device properties

Fig. 6 shows current density—voltage characteristics of hole and electron only devices of BFCz and BTCz. Hole only device with a configuration of ITO (50 nm)/PEDOT:PSS (10 nm)/BFCz or BTCz (100 nm)/TAPC (5 nm)/Al (200 nm) and electron only device with a structure of ITO (50 nm)/Ca (5 nm)/BFCz or BTCz (100 nm)/LiF (1 nm)/Al (200 nm) were fabricated. Hole mobility is mainly affected by the carbazole unit, both BFCz and BTCz show similar characteristics. However, higher electron mobility in BFCz than that of BTCz was measured because BFCz possesses a strong tendency to attract the electrons due to the higher electronegativity of the oxygen atom in BFCz than that of the sulfur atom in BTCz.

Fig. 7 shows the current density—voltage—luminance curves of deep-blue PHOLEDs fabricated with BFCz and BTCz hosts. FIrpic was used as the blue dopant material for BFCz and BTCz. The doping



Fig. 6. Current density-voltage curves of hole-only(a) and electron only (b) devices.

concentration of the FIrpic was varied from 3% to 10% to optimize the performance of the BFCz and BTCz devices. The current density of the BFCz and BTCz devices was rather high at a 3% doping concentration and slightly increased at 5% and 10% doping concentrations. The increase in the current density at the higher doping concentrations was due to better charge hopping between the dopant materials as a result of the reduced hopping distance. Holes and electrons can be trapped by dopant materials in the BFCz– or



Fig. 7. Current density-voltage and luminance-voltage curves of devices using BFCz and BTCz hosts.



Fig. 8. Current efficiency of the devices using BFCz and BTCz hosts.

BTCz-FIrpic emitting layer because of the difference in the HOMO and LUMO levels between the host and the FIrpic. In particular, there were small LUMO-level differences between the host and FIrpic of 0.40 eV for BFCz and 0.46 eV for BTCz, as shown in the energy level diagram in Fig. 1. Therefore, electrons are trapped by dopant materials, and the current density is enhanced by the FIrpic dopant. As the current density is increased by doping, the electron transport between the dopant materials is enhanced by electron hopping at high doping concentrations, leading to high current densities at high doping concentrations [37-39]. The luminance followed the same trend as the current density, because the luminance depends on the current density and recombination efficiency. The current density and luminance of the blue BTCz device exhibited trends similar to those of the BFCz device. However, the current density and luminance of the BTCz were lower than those of the BFCz, despite their similar triplet energies (2.94 eV for BFCz and 2.93 eV for BTCz), because the BTCz is more charge balanced than the BFCz as shown Fig. 6.

Fig. 8 illustrates the dependence of the current efficiency on the luminescence of the BFCz and BTCz devices at different doping concentrations. The maximum current efficiency of the blue PHOLED was obtained at a doping concentration of 10%. As a result, the maximum current efficiencies of the BFCz and BTCz devices



Fig. 9. Quantum efficiency and power efficiency of the devices using BTCz and BFCz hosts.

Devices	Properties	Properties						
	1000 cd m ⁻² (max)							
	QE ^a [%]	PE^{b} [lm W ⁻¹]	CE^{c} [cd A^{-1}]	Voltage [V]	Color coordinate			
BFCz 3%	13.3 (14.1)	12.8 (18.7)	26.0 (27.4)	7.09	0.16, 0.36			
BFCz 5%	12.9 (14.1)	12.7 (20.8)	25.4 (27.7)	6.98	0.16, 0.37			
BFCz 10%	14.2 (15.0)	14.9 (21.8)	28.6 (30.2)	6.67	0.16, 0.38			
BTCz 3%	13.6 (16.3)	12.8 (24.1)	26.4 (31.3)	7.19	0.16, 0.36			
BTCz 5%	15.3 (16.2)	14.2 (22.0)	30.0 (31.5)	7.34	0.16, 0.36			
BTCz 10%	15.5 (16.1)	14.8 (23.2)	30.9 (31.9)	7.27	0.16, 0.37			

 Table 2

 The characteristics of PHOLEDs of BFCz and BTCz hosts doped with 3, 5, and 10% Firpic dopant.

^a QE, quantum efficiency.

^b PE, power efficiency.

^c CE, current efficiency.

were 30.2 and 31.9 cd/A, respectively, and the luminance efficiencies at 1000 cd/m² were 28.6 and 30.9 cd/A, respectively.

Quantum efficiency-luminance-power efficiency curves for the BFCz and BTCz-FIrpic PHOLEDs are shown in Fig. 9. The quantum efficiencies of the BFCz and BTCz devices increased as the FIrpic doping concentration increased, and a high quantum efficiency was obtained at a doping concentration of 10%. The maximum quantum efficiencies of the BFCz and BTCz-FIrpic PHOLEDs were 15.0 and 16.1%, respectively, and the quantum efficiencies at 1000 cd/m² at a doping concentration of 10% were 14.2 and 15.5%, respectively. The quantum efficiency was not significantly reduced even at a high luminance of 3000 cd/m². The efficiency roll-off was less than 10% at 3000 cd/m^2 . The power efficiencies of the BFCz and BTCz devices at 1000 cd/m² were 14.9 and 14.8 lm/W. respectively. The high power efficiency of the FIrpic device is due to the high quantum efficiency and low driving voltage of the device. The quantum efficiency and power efficiency of the BFCz device was lower than those of the BTCz device. It is estimated that higher power efficiency, current efficiency and quantum efficiency of BTCz were derived from its optimized charge balance. The performance of the BFCz and BTCz—FIrpic blue PHO-LEDs is summarized in Table 2.

3.7. Electroluminescence properties

The electroluminescence (EL) spectra of the fused-ring BFCz and BTCz blue devices are shown in Fig. 10. The BFCz and BTCz devices exhibited blue emissions centered at 473 nm at a 10% doping concentration. The EL spectrum was slightly red-shifted at the high doping concentration (inset figure), but the maximum emission wavelength of the 10% FIrpic-doped device was still 473 nm for both the BFCz and BTCz devices. The increase of the shoulder peak was caused by dopant–dopant interaction at the high doping concentration because of the reduced molecular distance and recombination-zone shift, which affects the interference effect of light emission. The International Commission on Illumination (CIE) color coordinates of the 3%, 5%, and 10% FIrpic-doped BFCz and BTCz devices at 1000 cd/m² were (0.16, 0.36), (0.16, 0.37), and (0.16, 0.38), and (0.16, 0.36), (0.16, 0.36), and (0.16, 0.37), respectively.



Fig. 10. EL spectra of BFCz and BTCz devices.

4. Conclusions

Blue phosphorescent host materials BFCz and BTCz, which are analogous to mCP with fused-ring carbazole moiety, were designed and effectively synthesized. Their EL properties were investigated by fabrication of multilayered PHOLEDs. A device using the emitter BTCz as the emissive layer exhibited outstanding PHOLED performance, with CIE (x,y) coordinates of (0.16, 0.37) at 7 V and maximum luminous and quantum efficiencies of 31.9 cd/A and 16.1% at 0.295 mA/cm², respectively, because of the high triplet energy of the emitter BTCz.

Acknowledgements

The present research was conducted by the research fund of Dankook University in 2014.

References

- M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Nature 395 (1998) 151.
- [2] M.A. Baldo, D.F. O'Brian, M.E. Thompson, S.R. Forrest, Phys. Rev. B 60 (1999) 14422.
- [3] M.A. Baldo, M.E. Thompson, S.R. Forrest, Nature 403 (2000) 750.
- [4] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 75 (1999) 4.
- [5] C.W. Tang, S.A. VanSlyke, C.H. Chen, J. Appl. Phys. 65 (1989) 3610.
- [6] J. Shi, C.W. Tang, Appl. Phys. Lett. 70 (1998) 1665
- [7] L.S. Hung, C.H. Chen, Mater. Sci. Eng. R. 39 (2002) 143.
- [8] J. Shi, C.W. Tang, J. Appl. Phys. 80 (2002) 3201.
- [9] H. Inomata, K. Goushi, T. Masuko, T. Konno, T. Imai, H. Sasabe, J.J. Brown, C. Adachi, Chem. Mater. 16 (2004) 1285.
- [10] S.C. Dong, C.H. Gao, Z.H. Zhang, Z.Q. Jiang, S.T. Lee, L.S. Liao, Phys. Chem. Chem. Phys. 14 (2012) 14224.
- [11] S.C. Dong, C.H. Gao, X.D. Yuan, L.S. Cui, Z.Q. Jiang, S.T. Lee, L.S. Liao, Org. Electron 14 (2013) 902.
- [12] L.S. Cui, S.C. Dong, Y. Liu, Q. Li, Z.Q. Jiang, L.S. Liao, J. Mater. Chem. C 1 (2013) 3967.
- [13] T. Matsushima, C. Adachi, Appl. Phys. Lett. 92 (2008) 63306.

- [14] A. Chaskar, H.F. Chen, K.T. Wong, Adv. Mater. 23 (2011) 3876.
- [15] J.Y. Cho, K.S. Yook, J.Y. Lee, Adv. Mater. 26 (2014) 4050.
- [16] H.H. Chou, C.H. Cheng, Adv. Mater. 22 (2010) 2468.
- [17] Q. Wang, I.W. Oswald, X. Yang, G. Zhou, H. Jia, Q. Qiao, Y. Chen, J. Hoshikawa-Halbert, B.E. Gnade, Adv. Mater. 26 (2014) 8107.
- [18] S.L. Lin, L.H. Chan, R.H. Lee, M.Y. Yen, W.J. Kuo, C.T. Chen, R.J. Jeng, Adv. Mater. 20 (2008) 3947.
- [19] E. Mondal, W.Y. Hung, Y.H. Chen, M.H. Cheng, K.T. Wong, Chemistry 19 (2013) 10563.
- [20] J. Huang, J.H. Su, X. Li, M.K. Lam, K.M. Fung, H.H. Fan, K.W. Cheah, C.H. Chen, H. Tian, J. Mater. Chem. 21 (2011) 2957.
- [21] M.H. Tsai, H.W. Lin, H.C. Su, T.H. Ke, C.C. Wu, F.C. Fang, Y.L. Liao, K.T. Wong, C.I. Wu, Adv. Mater. 18 (2006) 1216.
- [22] M.H. Tsai, Y.H. Hong, C.H. Chang, H.C. Su, C.C. Wu, M.A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, J.V. Grazulevicius, C.P. Hsu, Adv. Mater. 19 (2007) 862.
- [23] J. He, H. Liu, Y. Dai, X. Ou, J. Wang, S. Tao, X. Zhang, P. Wang, D. Ma, J. Phys. Chem. C 113 (2009) 6761.
- [24] Y. Chen, W. Liang, W.H. Choi, J. Huang, Q. Dong, F. Zhu, J. Su, Dyes Pigments 123 (2015) 196.
- [25] T.L. Chiu, H.J. Chen, Y.H. Hsieh, J.J. Huang, M.K. Leung, J. Phys. Chem. C 119 (2015) 16846.
- [26] Y. Naqai, H. Sasabe, S. Ohisa, J. Kido, J. Mater. Chem. C 4 (2016) 9476.
- [27] J.J. Huang, Y.H. Hung, P.L. Ting, Y.N. Tsai, H.J. Gao, T.L. Chiu, J.H. Lee, C.L. Chen, P.T. Chou, M.K. Leung, Org. Lett. 18 (2016) 672.
- [28] V. Adamovich, J. Brooks, A. Tamayo, A.M. Alexander, P.I. Djurovich, B.W. D'Andrade, C. Adachi, S.R. Forrest, New. J. Chem. 26 (2002) 1171.
- [29] R.J. Holmes, S.R. Forrest, Y.J. Tung, R.C. Kwong, J.J. Brown, S. Garon, M.E. Thompson, Appl. Phys. Lett. 82 (2003) 2422.
- [30] H.H. Chou, C.H. Cheng, Adv. Mater. 22 (2010) 2468.
- [31] J.H. Lee, J.I. Lee, J.Y. Lee, H.Y. Chu, Appl. Phys. Lett. 94 (2009) 193305.
- [32] S. Tokito, T. Iijima, Y. Suzuri, H. Kira, T. Tsuzuki, F. Sato, Appl. Phys. Lett. 83 (2003) 569.
- [33] Y. Tao, C. Yang, J. Qin, Chem. Soc. Rev. 40 (2011) 2943.
- [34] D.E. Loy, B.E. Koene, M.E. Thompson, Adv. Funct. Mater. 12 (2002) 245.
- [35] D.R. Lee, S.H. Hwang, S.K. Jeon, C.W. Lee, J.Y. Lee, Chem. Comm. 51 (2015) 8105.
- [36] D.R. Lee, C.W. Lee, O.Y. Kim, S.H. Hwang, J.Y. Lee, SID Symposium Dig. Tech. Pap. 46 (2015) 502.
- [37] B.W. D'Andrade, M.A. Baldo, C. Adachi, J. Brooks, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 79 (2001) 1045.
- [38] M.G. Kim, J.Y. Lee, Chem. Asian J. 7 (2012) 899.
- [39] J.Y. Lee, Mol. Cryst. Liq. Cryst. 498 (2009) 131.