Contents lists available at ScienceDirect

Organic Electronics



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

A new *N*-fluorenyl carbazole host material: Synthesis, physical properties and applications for highly efficient phosphorescent organic light emitting diodes

Min-Gi Shin^{a,1}, K. Thangaraju^{a,1}, Seul-ong Kim^a, Jong-Won Park^a, Yun-Hi Kim^{b,*}, Soon-Ki Kwon^{a,*}

^a School of Materials Science, Engineering & Engineering Research Institute (ERI), Gyeongsang National University, Jinju-660 701, South Korea ^b Department of Chemistry and Research Institute of Natural Sciences (RINS), Gyeongsang National University, Jinju-660 701, South Korea

ARTICLE INFO

Article history: Received 24 November 2010 Received in revised form 14 February 2011 Accepted 15 February 2011 Available online 26 February 2011

Keywords: Organic light emitting diodes N-fluorenyl carbazole derivative High triplet energy state High thermal stability Green electrophosphorescence High efficiency

ABSTRACT

A new *N*-fluorenyl carbazole material, 9,9'-bis-(9,9-dimethyl-9H-fluoren-2-yl)-9H,9'H-[3,3']bicarbazolyl (BDFC), was synthesized by bromination, Ullmann and Yamamoto coupling reactions and confirmed using various spectroscopic studies. Thermogravimetric analysis and differential scanning calorimetry studies show the thermal stability ($\Delta T_{5\%}$) of 494.7 °C with high glass transition temperature ($T_{\rm g}$) of 177.8 °C. The photophysical and electrochemical studies of BDFC show the photoluminescence at 408 nm and a band gap of 3.01 eV with higher triplet energy of 2.72 eV. The phosphorescent organic light emitting diode using BDFC as host, ITO/di-[4-(*N*,*N*-ditolyl-amino)-phenyl]cyclohexane (TAPC)/host: fac-tris(2-phenylpyridine)-iridium [Ir(ppy)₃] (5%)/1,3,5-tris(m-pyrid-3-yl-phenyl)benzene (TmPyPB)/LiF/Al, shows the effective confinement of triplet excitons and efficient energy transfer to the guest emitter in the emissive layer, resulted in the higher device efficiencies of 56.3 cd/A, 18.1% and 21.3 lm/W compared with that (48.1 cd/A, 15.3% and 16.3 lm/W) of device based on (4,4'-*N*,*N*-dicarbazole)biphenyl (CBP) as host. The results show that the new host material BDFC could be useful for the efficient organic light emitting diodes.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The organic light emitting diodes (OLEDs) have been attracted very much attention in the recent past for the nextgeneration flat-panel displays, solid state lighting and other applications due to its self-emission, high luminous efficiency, high contrast ratio, fast response time, and wide color gamut [1,2]. In particular, studies with respect to phosphorescent materials have been an essential focus on the OLED research, which efficiently improve the electroluminescent (EL) efficiency due to the harvesting of both singlet- and triplet-excitons for the light emission [3,4]. Hence, the tremendous efforts have recently been made in the development of highly efficient phosphorescent organic light emitting diodes (PHOLEDs) [5-10]. In PHOLEDs, phosphorescent materials are often doped into a host matrix as guest triplet emitters, in order to reduce aggregation quenching and triplet-triplet annihilation. For the efficient electrophosphorescence from the triplet guests in a host matrix, HOMO-LUMO (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital) energy gap (E_g) and the triplet energy level of the host material must be higher than those of the guest to facilitate exothermic energy transfer from the host to guest and to prohibit reverse energy transfer from the guest back to the host (i.e., to effectively confine triplet



^{*} Corresponding authors. Tel.: +82 55 751 5296 (Y.-H. Kim), tel.: +82 55 751 5296; fax: +82 753 6311 (S.-K. Kwon).

E-mail addresses: ykim@gnu.ac.kr (Y.-H. Kim), skwon@gnu.ac.kr (S.-K. Kwon).

¹ These authors are equally contributed to this work.

^{1566-1199/\$ -} see front matter \odot 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.orgel.2011.02.014

excitons to the guest molecules) [11–15]. The host materials for electrophosphorescence reported thus far are limited to a few functionalities, including carbazoles and phenylsilanes [13–16]. The carbazole derivatives, which possess sufficiently large triplet energies and carrier transport properties, are widely used as host materials in PHOLEDs [17-19]. Examples of these materials include 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP), 1,3-bis(9-carbazolyl)benzene (mCP) and 3,5-bis(9-carbazolyl)tetraphenylsilane (SimCP). The most commonly used host material CBP has been shown useful for green- and redlight-emitting PHOLEDs [20–26]. However, CBP has several problems such as low T_{g} and low triplet energy state which deteriorate efficiency and longevity of the device. It has been reported that fluorene derivatives have been important materials for OLEDs because of their high quantum vield of photoluminescence (PL), electroluminescence (EL) efficiencies and high thermal stability [27-29]. However, it has been reported that the extension of the carbazole conjugation, which decreases the triplet energy of the carbazole as in the case of CBP, can be minimized by altering the linkage group to carbazole unit, while also maximizing the thermal stability of the material [18,30]. Thus, the research directed towards the design and synthesis of new carbazole derivatives with high triplet energy and thermal stability has not been limited [31,32].

Thus, we designed highly twisted N-fluorenyl carbazole as a new host material. The introduction of fluorene unit, possessing high photoluminescence and electroluminescence efficiencies, to carbazole unit is to inhibit the extension of conjugation and improve the thermal stability of the material, which is suitable for host in the efficient electroluminescent devices. Moreover, the highly twisted structure due to coupling of N-fluorenylated carbazole would increase its glass transition temperature and molecular rigidity as well as inhibited intermolecular interaction. In the present study, we report on the synthesis and characterization of a new carbazole derivative BDFC in which fluorene-coupled at 3-position of carbazole unit. A new N-fluorenyl carbazole material BDFC shows the higher thermal stability ($\Delta T_{5\%}$) of 494.7 °C (CBP: 447 °C) with high glass transition temperature (T_g) of 177.8 °C (CBP: 62 °C) and a band energy gap of 3.01 eV with high triplet energy of 2.72 eV (CBP: 2.56 eV) for use as host material in the efficient organic light emitting diodes. We fabricate green-emitting phosphorescent organic light emitting diodes using the new BDFC as host and Ir(ppy) as guest emitter and report its higher device performances compared with that of the device based on widely used CBP host.

2. Experimental

2.1. Materials

All reagents and solvents were purchased from Aldrich Chemical Co. and Fluka. All the solvents were freshly distilled over appropriate drying reagents before use. The spectroscopic grade CHCl₃ (Aldrich) was used to measure UV-visible absorption and photoluminescence spectra of the samples. All other compounds were used as received. All the materials used in the phosphorescent organic light emitting diodes were purchased from Lumtec corp., Taiwan.

2.2. Synthesis

2.2.1. Synthesis of 9-(9',9'-dimethyl-9H-fluoren-2-yl)-9H-carbazole (1)

A mixture of activated copper powder (11.4 g, 0.120 mol), K₂CO₃ (16.53 g, 0.120 mol), 9H-carbazole (20 g, 0.120 mol), 2-bromo-9',9'-dimethyl-9H-fluorene (35.94 g, 0.132 mol) and 18-crown-6(4.74 g, 0.0179 mol) in dichlorobenzene (200 mL) was heated to 200 °C for 30 h. After that, the reaction mixture was filtered with methylene chloride (MC). After dichlorobenzene was removed by vacuum distillation, the crude product was purified by column chromatography (using MC/hexane: 1/5 as eluent) and recrystallization with ethanol. Yield: 38.33 g (89.15%). ¹H NMR (300 MHz, CDCl₃) δ: 8.21-8.18 (d, 2H), 7.96-7.93 (d, 1H), 7.84-7.81 (t, 1H), 7.65-7.64 (d, 1H), 7.58-7.54 (dd, 1H), 7.51-7.39 (m, 7H), 7.35-7.30 (m, 2H), 1.58-1.55 (d, 6H). ¹³C NMR (300 MHz, CDCl₃) δ : 155.16, 153.85, 141.03, 138.49, 138.45, 136.62, 127.60, 127.25, 125.96, 125.87, 123.38, 122.77, 121.46, 121.09, 120.36, 120.20, 119.89, 109.87, 47.16, 27.16. M⁺: 359.

2.2.2. Synthesis of 3-bromo-9-(9',9'-dimethyl-9H-fluoren-2yl)-9H-carbazole (**2**)

N-Bromosuccinimide (13.37 g, 0.097 mol) was added to the solution of 9-(9',9'-dimethyl-9H-fluoren-2-yl)-9H-carbazole (1) (35 g, 0.097 mol) and silica-gel (18 g) in methylene chloride (400 mL). The reaction mixture was stirred at room temperature. Before extraction with water and Methylene chloride, the reaction mixture was filtered with Methylene chloride. The mixture of reaction was purified by column chromatography (using MC/hexane: 1/5 as eluent) and recrystallization with ethanol. Yield: 40.59 g (95.10%). ¹H NMR (300 MHz, CDCl₃), δ : 8.29–8.28 (d, 1H), 8.14-8.12 (d, 1H), 7.96-7.93 (d, 1H), 7.60-7.59 (d, 1H), 7.53-7.52 (d, 1H), 7.51-7.50 (t, 3H), 7.47-7.33 (m, 6H), 1.57–1.56 (d, 6H). ¹³C NMR (300 MHz, CDCl₃) δ: 155.56, 153.82, 141.36, 139.71, 138.83, 138.27, 136.08, 128.63, 127.72, 127.27, 126.68, 125.79, 125.08, 123.06, 122.77, 122.27, 121.35, 121.18, 120.52, 120.29, 120.24, 112.61, 111.37, 110.09, 47.18, 27.13. M⁺: 439.

2.2.3. Synthesis of 9,9'-bis-(9,9-dimethyl-9H-fluoren-2-yl)-9H,9'H-[3,3']bicarbazolyl (BDFC)

A mixture of bis(cyclooctadiene)nickel(0) (2.85 g, 10.37 mmol) and 2,2-bipyridyl (1.86 g, 11.92 mmol) in dimethylformamide (40 mL) and toluene (160 mL) was heated to 80 °C. After 30 min, cyclooctadiene (0.93 g, 8.64 mmol) and 3-bromo-9-(9',9'-dimethyl-9H-fluoren-2-yl)-9H-carbazole (**2**) (4 g, 9.12 mmol) in toluene (40 mL) were added to the reaction mixture and stirred for 144 h. The reaction mixture in HCl and Dioxane was stirred for 15 min and washed with HCl. The reaction mixture was purified by column chromatography (using CH_2Cl_2 /hexane: 1/10 as eluent) and recrystallization with methylene chloride and ethanol. Yield: 2.53 g (77.35%). FT-IR (KBr): 3043,

2954. ¹H NMR (300 MHz, CDCl₃) δ : 8.53–8.52 (s, 1H), 8.28–8.27 (d, 1H), 8.00–7.97 (d, 1H), 7.86–7.83 (m, 2H), 7.71 (s, 1H), 7.64–7.59 (m, 2H), 7.53–7.43 (m, 6H), 1.61–1.60 (d, 6H). ¹³C NMR (300 MHz, CDCl₃) δ : 155.50, 153.86, 141.50, 140.17, 138.50, 138.46, 136.70, 134.37, 127.61, 127.26, 126.10, 125.87, 125.81, 124.02, 123.62, 122.78, 121.39, 121.14, 120.48, 120.21, 120.00, 118.94, 110.15, 110.01, 47.19, 27.18. HRMS: calcd. for C₅₄H₄₀N₂: 716.3191, found: 716.3192.

2.3. Measurements

¹H nuclear magnetic resonance (NMR) spectra were recorded using DRX 300 MHz Bruker spectrometer and chemical shifts in spectra were reported in parts per million (ppm) units with tetramethylsilane as internal standard. Infrared (IR) studies of the samples were carried out using a Genesis II FT-IR spectrometer. A Jeol JMS-700 high-resolution mass spectrometer (HRMS) was used to obtain the mass spectra of the samples. Thermogravimetric analysis (TGA) was performed under nitrogen using a TA instrument 2025 thermogravimetric analyzer. The sample was heated from 50 °C to 800 °C with a heating rate of 10 °C/min. Differential scanning calorimeter (DSC) studies were carried out under nitrogen using a TA instrument 2100 differential scanning calorimeter. The sample was heated from 30 °C to 300 °C with a heating rate of 10 °C/ min. UV-visible absorption and photoluminescence (PL) studies at room temperature were carried out using Perkin Elmer LAMBDA-900 UV/VIS/NIR spectrometer and LS-50B luminescence spectrophotometer, respectively and the phosphorescence spectrum was recorded from the delayed emission of BDFC at 77 K. Cyclic voltammogram (CV) of the sample was recorded using a Epsilon E3



Fig. 1. The synthetic scheme of BDFC.



Fig. 2. FT-IR spectrum of BDFC.



Fig. 3. The molecular structure (determined by Spartan08 software) of BDFC.



Fig. 4. The UV-visible absorption, photoluminescence (at room temperature) and phosphorescence (at 77 K) spectra of BDFC in toluene $(1\times 10^{-5}\,M).$

at room temperature in a 0.1 M solution of tetrabutylammonium perchlorate (Bu₄NClO₄) in acetonitrile under nitrogen environment at a scan rate of 50 mV/s. The platinum rod was used as working and the counter electrode, and a Ag/AgNO₃ electrode was used as the reference electrode. The mobility of BDFC molecule was determined from the Time-of-Flight (ToF) experiment. For ToF experiment, a semitransparent aluminum (Al) layer of 20 nm thickness was deposited on the glass substrate as bottom electrode by thermal evaporation process. A thick BDFC film of 1 µm thickness was drop-casted on the bottom electrode using the BDFC solution (3 wt.% in toluene) by vacuum drying at 60 °C for 24 h. The thickness and flatness of drop-cast BDFC film were measured using an alphastepper (Alpha step 500, Tencor). The device for ToF experiment was completed by depositing a thin Al film of 20 nm thickness on the above prepared BDFC film for the top electrode. The ToF experiment was performed in a vacuum cryogenic chamber by illuminating the sample with N₂ laser (337 nm) pulses of duration 6 ns under a dc bias for the ToF photocurrent transients [33].



Fig. 5. (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) studies of BDFC. Inset shows the glass transition temperature (T_g) of BDFC.

2.4. Device fabrication

The phosphorescent organic light emitting diodes were fabricated as shown in Fig. 6. The device structure was as follows: indium-tin-oxide (ITO)/1,1-bis[di-4-tolylami-no]phenyl]cyclohexane (TAPC) as the hole transport layer (HTL) (30 nm)/emissive layer (EML) (30 nm)/1,3,5-tris (m-pyrid-3-yl-phenyl)benzene (TmPyPB) as the electron

transport layer (ETL) (30 nm)/LiF (1 nm)/Al (120 nm). The (4,4'-N, N'-dicarbazole)biphenyl (CBP) host for device A or 9,9'-Bis-(9,9-dimethyl-9H-fluoren-2-yl)-9H,9'H-[3,3']bicarbazolvl (BDFC) host for the device B doped with 5% green-emitting phosphorescent dopant, fac-tris(2-phenvlpyridine)iridium [Ir(ppy)₃] was used as emissive layer (EML). The CBP host based device was fabricated for the comparison of the device performances with that of BDFC host based device. The patterned ITO (anode) coated glass substrates were ultrasonically cleaned in acetone for 10 min followed by isopropyl alcohol, dried in each step at 90 °C for 10 min and UV treated for 10 min before loading into the deposition chamber for the device fabrication. All organic layers were deposited by thermal evaporation process under a vacuum of ${\sim}5\times10^{-6}\,\text{Torr}$ and LiF as electron injection layer and Al cathode were deposited without breaking the chamber vacuum. The fabricated devices were transferred into the glove-box for the encapsulation of the devices with moisture getter using UV curable epoxy. The current density-voltage (I-V) characteristics of all devices were measured using Keithley 236 source meter. The electroluminescence and luminescence characteristics of the devices were recorded using Spectrascan PR655 spectroradiometer under ambient condition.

3. Results and discussion

The new *N*-fluorenyl carbazole material, 9,9'-bis-(9,9dimethyl-9H-fluoren-2-yl)-9H,9'H-[3,3']bicarbazolyl (BDFC),



Fig. 6. Cyclic voltammogram of BDFC.

Та	bl	e	1	

The physical properties of BDFC.

was prepared as depicted in Fig. 1. The BDFC was synthesized via manifold chemical reactions such as bromination, Ullmann and Yamamoto coupling reactions as described below. The compound **1** was obtained by Ullmann coupling reaction of 9H-carbazole and 2-bromo-9',9'-dimethyl-9H-fluorene using activated copper powder, K₂CO₃ and 18-crown-6. BDFC was prepared by Yamamoto coupling reaction of compound **2** obtained from mono-bromination of compound **1**. The structure of BDFC was confirmed by ¹H NMR, IR and HRMS. In the IR spectrum, we confirmed the structure from disappearing of aromatic C–Br stretching at 1060 cm⁻¹ (Fig. 2). The angle of 126° between carbazole and fluorene units in the highly twisted structure of BDFC molecule was determined by Spartan08 software as shown in Fig. 3.

The UV-visible absorption, photoluminescence and phosphorescence (at 77 K) spectra of BDFC in toluene $(1 \times 10^{-5} \text{ M})$ are shown in Fig. 4. From the UV-visible absorption spectrum of BDFC, the absorption bands between 294 nm and 330 nm are assigned for S_0 to S_2 and S_0 to S_1 electronic transitions of the BDFC molecule [30]. BDFC showed the photoluminescence (PL) at 408 nm in toluene, indicating the emission from its lowest exited state. The phosphorescence spectrum of BDFC was obtained from the delayed emission of BDFC in toluene $(1 \times 10^{-5} \text{ M})$ at 77 K. From the phosphorescence spectrum of BDFC molecule, the triplet energy (T_1) was estimated from the highest energy peak (455 nm) to be 2.72 eV, which is higher than that $(T_1: 2.56 \text{ eV})$ of CBP host [19,34]. The mobility of BDFC was determined from the Time-of-Flight (ToF) experiment. It was calculated using the equation $\mu = \frac{d^2}{Vt}$, where *d* is the thickness of the film, *V* is the applied dc bias voltage and t is the measured transit time [33]. The ToF mobility of BDFC host was found to be $3.4 \times 10^{-4} \text{ cm}^2/\text{Vs}$ at bias voltage of 28.26 mV and transit time of 10.45 µs. The thermal properties of BDFC sample were determined by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) measurements. From the DSC data (Fig. 5b), the glass transition temperature (T_{α}) was observed at 177.8 °C, which is much higher than that (62 °C) of CBP, and the melting temperature (T_m) was observed at 259.62 °C as a sharp endothermic peak [19]. In TGA curve of BDFC (Fig. 5a), 5% weight loss was observed at 494.7 °C, showing the higher thermal stability compared with that (447 °C) of CBP. The higher

Absorption ^a	Emission						
λ_{abs} (nm)	λ_{PL}^{b} (nm)	λ _{Phos} c (nm) (at 77 K)	$T_{\rm d}^{\rm d}/T_{\rm g}^{\rm e}/T_{\rm m}^{\rm f}$ (°C)	HOMO (eV)	LUMO (eV)	Eg ^g (eV)	T_1^h (eV)
294,305,330	408	455	494.7/177.8/259.6	5.38	2.37	3.01	2.72

^a The major UV-visible absorption band peaks are listed.

^b Photoluminescence (PL) maximum measured in tolune at room temperature.

 $^{\rm c}\,$ The highest energy peak of the phosphorescence spectrum in tolune at 77 K.

 d T_{d} – Temperature corresponding to a 5% weight loss in thermogravimetric analysis.

^e T_g – Glass transition temperature from differential scanning calorimetry (DSC) studies.

^f $T_{\rm m}$ – Melting temperature from DSC studies.

 g E_{g} – Band gap energy calculated from the equation $E_{g} = hc/\lambda = 1241/\lambda$, where λ is the edge wavelength (nm) of UV-visible absorption spectrum.

^h T_1 – Triplet energy is estimated from the higher energy peak of the phosphorescence spectrum.

triplet energy and thermal stability of BDFC compared with CBP reveal the decreased conjugation of carbazole unit by fluorene unit coupled to it [18,30]. The electrochemical properties of BDFC sample was investigated by cyclic voltammetric (CV) studies. The CV curve of BDFC is shown in Fig. 6. It shows the reversible oxidation potential characterized by E_{onset} value at 0.88 V. The estimated ionization potential (IP = E_{onset} + 4.54 = HOMO level) was 5.38 eV. The higher HOMO energy level of BDFC can be useful for the efficient hole-injection and transport. The LUMO energy level of BDFC was calculated to be 2.37 eV from the edge wavelength of UV-visible absorption spectrum. BDFC having the band gap of 3.01 eV with high triplet energy of 2.72 eV could be suitable for use as host material for the efficient organic light emitting diodes. The thermal, photophysical and electrochemical properties of BDFC are listed in Table 1.

To investigate the new *N*-fluorenyl-carbazole material (BDFC) as host in organic light emitting diodes (OLEDs), the phosphorescent organic light emitting diodes (PHOL-EDs) based on BDFC as host and green phosphorescent



Fig. 7. The device structures of the devices A and B.

dopant, fac-tris(2-phenylpyridine)iridium $[Ir(ppy)_3]$, as guest emitter were fabricated as shown in Fig. 7 and characterized. PHOLED based on widely used CBP was fabricated for the comparison. The energy level diagram and the structure of materials used in the devices are shown in Fig. 8 [19,34-38]. The PHOLEDs were fabricated using the following device structure: ITO/1.1-bis/di-4-tolvlamino]phenyl]cyclohexane (TAPC) $(30 \text{ nm})/\text{host: Ir}(ppy)_3$ with optimized concentration of 5% (30 nm)/1,3,5-tris(m-pyrid-3-yl-phenyl)benzene (TmPyPB) (30 nm)/LiF/Al. The CBP was used as host in the device A and BDFC host was used in device B. TAPC with LUMO energy level of 2.0 eV (LUMO: 2.6 eV for CBP; 2.37 eV for BDFC) and higher triplet energy (T_1) of 2.9 eV $(T_1: 2.56 \text{ eV for CBP}; 2.72 \text{ eV for BDFC};$ 2.46 eV for $Ir(ppy)_3$) was used as hole transport layer (HTL), while TmPyPB with HOMO energy level of 6.68 eV (HOMO: 5.9 eV for CBP; 5.38 eV for BDFC) and higher triplet energy of 2.78 eV compared with that of host and dopants was used as electron transport layer (ETL) in the devices for the effective confinement of charge carriers and/or excitons within the emissive layer (EML). Fig. 9 shows the current density-voltage-luminescence (I-V-L)characteristics of devices A and B. From the I-V-L characteristics of device A, the drive voltages of 5 V for 100 cd/ m^2 and 8 V for 1000 cd/m^2 were observed and it showed a maximum luminescence of 23,250 cd/m² at 16 V. Device A showed the turn-on voltage (defined as an applied voltage required for the luminescence of 1 cd/m^2) of 3 V. Fig. 10 shows the current- and external quantum-efficiency characteristics of devices A and B. Device A based on CBP host showed the maximum current efficiency of 48.0 cd/A, external quantum efficiency of 15.3% and power efficiency of 16.3 lm/W. The electroluminescence spectra of devices A and B at 10.5 V are shown in Fig. 11. The device A showed the electroluminescence (EL) emission



Fig. 8. The energy level diagram and molecular structures of the materials used in the devices.



Fig. 9. The current density–voltage–luminescence (*J*–*V*–*L*) characteristics of devices A and B.



Fig. 10. (a) The current efficiency-current density- and (b) external quantum efficiency-current density-characteristics of the devices A and B.

peak at 512 nm with shoulder peak at 539 nm with CIE color coordinates of (0.31, 0.61), originating from $Ir(ppy)_3$ dopant [36,39–41]. No emissions from the host and/or



Fig. 11. The electroluminescence spectra of the devices A and B at 10.5 V.

adjacent charge transporting layers were observed, indicating the effective confinement of charge carriers and/or excitons and complete energy transfer to guest emitter in the EML of the device A.

Device B based on BDFC host showed the drive voltages of 8.5 V for 100 cd/m^2 and 13.5 V for 1000 cd/m^2 , and a maximum luminescence of 22,930 cd/m² at 20 V as shown in Fig. 9. The turn-on voltage is increased to 3.5 V compared with that (3 V) of device A. The increased energy barrier of 0.41 eV for electron injection at BDFC/TmPyPB interface of the device B than that (0.18 eV) of device A using CBP host resulted in the higher operating voltage than that of device A. The device B using BDFC host exhibited the higher current efficiency of 56.8 cd/A, external quantum efficiency of 18.1% and power efficiency of 21.3 lm/W compared with that (48.1 cd/A, 15.3% and 16.3 lm/W) of device A using CBP host, resulting from the efficient energy transfer and the higher triplet energy (T_1 : 2.72 eV) of BDFC host (T_1 : 2.56 eV for CBP). The device B showed the higher quantum efficiency roll-off (17% at 8.3 mA/cm^2) for the increasing current densities compared with that (2% at 8.3 mA/cm²) of the device A using CBP



Fig. 12. The electroluminescence spectra of the device B at different voltages.

Table 2			
The electroluminescence	characteristics	of th	e devices. ^a

Device ^b	Turn-on	L	η _c	η _{ext}	$\eta_{ m p}$	EL ^c	CIE
	voltage (V)	(cd/m ² , V)	(cd/A, V)	(%, V)	(lm/W, V)	(nm)	(x, y)
A	3	23,250, 16.0	48.0, 10.5	15.3, 10.5	16.3, 9.0	512	(0.31, 0.61)
B	3.5	22,930, 20.0	56.8, 10.5	18.1, 10.5	21.3, 8.0	512	(0.30, 0.61)

^a The data for brightness (*L*), current efficiency (η_c), external quantum efficiency (η_{ext}) and power efficiency (η_p) are the maximum values of the corresponding device. The turn-on voltage for all the devices was defined as voltage required for luminescence of 1 cd/m².

^b The device structure is ITO/TAPC (30 nm)/Host: Ir(ppy)₃ (5%) (30 nm)/TmPyPB (30 nm)/LiF/Al with CBP host for device A and BDFC host for device B. ^c The peak emission wavelength of the EL spectrum of corresponding device.

host. The higher efficiency roll-off of the device B can be explained by the imbalance of charge carriers in the EML due to the higher HOMO (5.38 eV) and LUMO (2.37 eV) energy levels of BDFC host than that (HOMO: 5.9 eV; LUMO: 2.6 eV) of CBP host. In other words, the higher HOMO energy level of BDFC host in the device reduces the hole injection barrier, which is much favorable for hole injection, while the higher LUMO level increases the electron injection barrier, less favor for election injection, compared with that of CBP host in device and which in turn makes the charge imbalance in the EML of the device B based on BDFC, leading to the increased efficiency roll-off compared with that of device A based on CBP. The device B showed the characteristic dopant emission at 512 nm with shoulder peak at 539 nm with CIE color coordinates of (0.30, 0.61) at 10.5 V (Fig. 11). The device B based on BDFC host exhibits the EL emission at 512 nm with CIE color coordinates of (0.30, 0.62), (0.30, 0.61), (0.30, 0.61) and (0.31, 0.61) at 5 V, 10 V, 15 V and 20 V, respectively as shown in Fig. 12. The small residual emission of device B around 408 nm at higher operating voltage is attributed to the BDFC host emission. The device based on BDFC host showed the effective confinement of triplet excitons and efficient energy transfer to the guest emitter in the EML of the device, resulted in the higher device efficiencies compared with that of CBP based device. The characteristics of the devices A and B are summarized in Table 2. The higher thermal stability (BDFC; $\Delta T_{5\%}$: 494.7 °C and $T_{\rm g}$: 177.8 °C, CBP; $\Delta T_{5\%}$: 447 °C and $T_{\rm g}$: 62 °C), higher triplet energy (T₁: 2.72 eV for BDFC and 2.56 eV for CBP) for the effective confinement of triplet excitons to the emitter, and the higher device performances of BDFC host could make the new N-fluorenyl carbazole (BDFC) host superior than widely used CBP host for the efficient organic light emitting diodes.

4. Conclusion

A new *N*-fluorenyl carbazole (BDFC) host material was synthesized and characterized. The thermal stability $(\Delta T_{5\%})$ of 494.7 °C with the high glass transition temperature (T_g) of 177.8 °C was observed from TGA and DSC studies. The physical studies of BDFC showed the emission at 408 nm and a band energy gap of 3.01 eV with high triplet energy of 2.72 eV. The highly efficient PHOLEDs employing BDFC as host have been fabricated using the structure: ITO/ Di-[4-(*N*,*N*-ditolyl-amino)-phenyl]cyclohexane (TAPC)/ BDFC (host): fac-tris(2-phenylpyridine)iridium [Ir(ppy)₃] (5%)/1,3,5-tris(m-pyrid-3-yl-phenyl)benzene (TmPyPB)/

LiF/Al. The device showed the effective confinement of triplet excitons and efficient energy transfer to the guest emitter in the EML, resulted in the higher current efficiency of 56.3 cd/A, external quantum efficiency of 18.1% and power efficiency of 21.3 lm/W compared with that (48.1 cd/A, 15.3% and 16.3 lm/W) of the device based on CBP host. The results show that the new host material BDFC could be useful for the efficient organic light emitting diodes.

Acknowledgements

This research was financially supported by MKE and KIAT through the Workforce Development Program in Strategic Technology, by Strategic Technology under Ministry of Knowledge Economy of Korea and by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0000310).

References

- [1] C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. 51 (1987) 913.
- [2] J.H. Burroughes, D.D.C. Bradley, A.R. Broun, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B. Holms, Nature 347 (1990) 539.
- [3] M.A. Baldo, D.F. O Brien, Y. You, A. Shoustikov, S. Silbey, M.E. Thampson, S.R. Forrest, Nature 395 (1998) 151.
- [4] C. Adachi, M.A. Baldo, M.E. Thampson, Appl. Phys. Lett. 77 (2000) 904.
- [5] S.O. Jung, Q. Zhao, J.-W. Park, S.O. Kim, H.-Y. Oh, S.-K. Kwon, Y.J. Kang, Org, Electron. 10 (2009) 1066.
- [6] Y.-S. Park, J.-W. Kang, D.M. Kang, J.-W. Park, Y.-H. Kim, S.-K. Kwon, J.-J. Kim, Adv. Mater. 20 (2008) 1957.
- [7] S.O. Jung, Y.J. Kang, H.-S. Kim, Y.-H. Kim, C.-L. Lee, J.-J. Kim, S.-K. Lee, S.-K. Kwon, Eur. J. Inorg. Chem. 2004 (2004) 3415.
- [8] D.M. Kang, H.-D. Park, Y.-H. Kim, S.C. Shin, J.-J. Kim, S.-K. Kwon, J.-W. Kang, J.W. Park, S.O. Jung, S.-H. Lee, Adv. Mater. 20 (2008) 2003.
- [9] S.O. Jung, Y.-H. Kim, S.-K. Kwon, H.-Y. Oh, J.-H. Yang, Org. Electron. 8 (2007) 349.
- [10] S.-O. Jung, Y.-H. Kim, H.-S. Kim, S.-K. Kwon, H.-Y. Oh, Mol. Cryst. Liq. Cryst. 444 (2006) 95.
- [11] D.-S. Leem, S.O. Jung, S.-O. Kim, J.-W. Park, J.W. Kim, Y.-S. Park, Y.-H. Kim, S.-K. Kwon, J.-J. Kim, J. Mater. Chem. 19 (2009) 8824.
- [12] C. Adachi, M.A. Baldo, M.E. Thampson, S.R. Forrest, J. Appl. Phys. 90 (2001) 5048.
- [13] J. Holmes, S.R. Forrest, Y.-J. Tung, R.C. Kwong, J.J. Brown, S. Garon, M.E. Thampson, Appl. Phys. Lett. 82 (2003) 2422.
- [14] S.-J. Yeh, M.-F. Wu, C.-T. Chen, Y.-H. Song, Y. Chi, M.-H. Ho, S.-F. Hsu, C.-H. Chen, Adv. Mater. 17 (2005) 285.
- [15] X. Ren, J. Li, R.J. Holmes, P.I. Djurovich, S.R. Forrest, M.E. Thampson, Chem. Mater. 16 (2004) 4743.
- [16] M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, Y. Taga, Appl. Phys. Lett. 79 (2001) 156.
- [17] K. Brunner, A. Van Dijken, H. Borner, J.J.A.M. Bastiaansen, N.M.M. Kiggen, B.M.W. Langeveld, J. Am. Chem. Soc. 126 (2004) 6035.
- [18] 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.

- [19] M.-H. Tsai, Y.-H. Hong, C.-H. Chang, H.-C. Su, C.-H. Wu, A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, J.V. Grazulevicius, C.-P. Hsu, Adv. Mater. 19 (2007) 862.
- [20] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, J. Am. Chem. Soc. 123 (2001) 4304.
- [21] W.Y. Wong, C.L. Ho, Z.Q. Gao, B.X. Mi, C.H. Chen, K.W. Cheah, Z.Y. Lin, Angew. Chem. Int. Ed. 45 (2007) 7800.
- [22] A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, J. Am. Chem. Soc. 125 (2003) 12971.
- [23] Y.-J. Su, H.-L. Huang, C.-L. Li, C.-H. Chien, Y.-T. Tao, P.-T. Chou, S. Datta, R.-S. Liu, Adv. Mater. 15 (2003) 884.
- [24] W.S. Huang, J.T. Lin, C.H. Chien, Y.T. Tao, S.S. Sun, Y.S. Wen, Chem. Mater. 16 (2004) 2480.
- [25] C.L. Li, Y.J. Su, Y.T. Tao, P.T. Chou, C.H. Chien, C.C. Cheng, R.S. Liu, Adv. Funct. Mater. 15 (2005) 384.
- [26] S.G. Jung, Y.J. Kang, H.S. Kim, Y.H. Kim, C.L. Lee, J.J. Kim, S.K. Lee, S.K. Kwon, Eur. J. Inorg. Chem. 16 (2004) 3415.
- [27] K.S. Kim, Y.M. Jeon, J.W. Kim, C.W. Lee, M.S. Gong, Org. Electron. 9 (2008) 797.
- [28] A. Farcas, N. Jarroux, V. Harabagiu, P. Guégan, Eur. Polym. J. 45 (2009) 795.

- [29] Y.-H. Kim, S.-J. Park, J.-W. Park, J.H. Kim, S.-K. Kwon, Macromol. Res. 15 (2007) 216.
- [30] 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.
- [31] T. Tsuzuki, S. Tokito, Adv. Mater. 19 (2007) 276.
- [32] Z.Q. Gao, M. Luo, X.H. Sun, H.L. Tam, M.S. Wong, B.X. Mi, P.F. Xia,
- K.W. Cheah, C.H. Chen, Adv. Mater. 21 (2009) 688.
 [33] D.S. Chung, S.J. Lee, J.W. Park, D.B. Choi, D.H. Lee, J.W. Park, S.C. Shin, Y.-H. Kim, S.-K. Kwon, C.E. Park, Chem. Mater. 20 (2008) 3450.
- [34] J. Lee, J.-I. Lee, K.-I. Song, S.J. Lee, H.Y. Chu, Appl. Phys. Lett. 92 (2008) 203305
- [35] B.D. Chin, C. Lee, Adv. Mater. 19 (2007) 2061.
- [36] S.H. Kim, J. Jang, J.Y. Lee, Appl. Phys. Lett. 90 (2007) 223505.
- [37] .J.Y. Lee, Appl. Phys. Lett. 89 (2006) 153503.
- [38] N. Chopra, J. Lee, Y. Zheng, S.-H. Eom, J. Xue, F. So, Appl. Mater. Interface 1 (2009) 1169.
- [39] Y. Zhang, G. Cheng, Y. Zhao, J. Hou, S. Liu, Appl. Phys. Lett. 86 (2005) 011112.
- [40] G. Cheng, F. Li, Y. Duan, J. Feng, S. Liu, S. Qiu, D. Lin, Y. Ma, S.T. Lee, Appl. Phys. Lett. 82 (2003) 4224.
- [41] Y. Wang, Appl. Phys. Lett. 85 (2004) 4848.