Accepted Manuscript

Thermally-stable 2,3-diphenylated benzotiophene containing host materials for red phosphorescent organic light-emitting diodes

Joon Ho Jeon, Nam-Jin Lee, Ji-Hoon Lee, Min Chul Suh

PII: S0143-7208(14)00226-5

DOI: 10.1016/j.dyepig.2014.06.002

Reference: DYPI 4410

To appear in: Dyes and Pigments

Received Date: 2 April 2014

Revised Date: 22 May 2014

Accepted Date: 2 June 2014

Please cite this article as: Jeon JH, Lee N-J, Lee J-H, Suh MC, Thermally-stable 2,3-diphenylated benzotiophene containing host materials for red phosphorescent organic light-emitting diodes, *Dyes and Pigments* (2014), doi: 10.1016/j.dyepig.2014.06.002.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.







CHIP HIM

Thermally-stable 2,3-diphenylated benzotiophene containing host materials for red phosphorescent organic light-emitting diodes

Joon Ho Jeon^{a,†}, Nam-Jin Lee^{b,†}, Ji-Hoon Lee^{b,*}, and Min Chul Suh^{a,*} ^aDepartment of Information Display, Kyung Hee University, Dongdaemoon-Gu, Seoul 130-701, Republic of Korea ^bDepartment of Polymer Science and Engineering & Department of IT Convergence, 50 Daehak-ro, Chungju-Si, Chungbuk 380-702, Republic of Korea

Abstract

This study reports a series of benzo[b]thiophene (BT) derivatives with good electronic properties as host materials for red phosphorescent organic light-emitting diodes (PHOLEDs). We applied thermally-stable materials for red PHOLEDs which contain BT and carbazole moieties which also provide a good charge transport ability, as well as a good charge confinement effect ($T_1 > 2.25 \text{ eV}$). To control the appropriate charge transporting ability, two different structures having one or two carbazole units connected to the single BT moiety were prepared. Using this approach, we found that the material with a single carbazole and a single BT unit showed the best current efficiency and external quantum efficiency (up to 23.6 cd/A and 12.8%, respectively). The results of the experiment also suggest that BT could be used as an electron-transporting unit when utilized with carbazole moiety, although it has previously been utilized as a *p*-type material.

Keywords: Host materials; Red phosphorescent OLED; Benzothiophene; Carbazole; Lower lying LUMO level.

[†]Both authors have equally contributed to this work.

^{*}Corresponding authors. Tel : +82-43-841-5427/ +82-2-961-0694; Fax: +82/43-841-5420/+82-2-968-6924 E-mail: <u>jihoonli@ut.ac.kr</u> (Prof. J.-H. Lee), <u>mcsuh@khu.ac.kr</u> (Prof. M.C. Suh)

1. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have attracted much attention because of their high quantum efficiency as compared to conventional fluorescent OLEDs through utilizing both singlet and triplet excitons for emission [1-5]. In fact, red phosphorescent materials have already been applied in the main-display mode of commercial mobile phones since 2007. Green PHOLEDs have been utilized in the same application as well. More specifically, there has been progress in research on the external quantum efficiency (EQE) of PHOLEDs. Kim and co-authors reported that their extremely high efficiency (>30% of EQE) could be achieved if horizontally-oriented emitters are used [6]. Hence, numerous attempts have been undertaken to combine this extremely high efficiency with high device stability. To make such devices, many ideas are still needed on how to extract the internally trapped emission on a waveguide or a substrate mode. However, the development of thermally or electrochemically stable host materials to improve lifetime and internal quantum efficiency still needs to realize highly stable PHOLEDs, because PHOLEDs generally have a much shorter lifetime compared to fluorescent ones. Indeed, PHOLEDs normally need a more or less complicated evaporation system, such as mixed host approach, to obtain a much longer lifetime, although a very high efficiency could sometimes be achieved from a single host system. [7,8] Thus, many research groups focus on the elaboration of ideal host materials with bipolar characteristics, as a minute change in mixing the ratio of hole transport type and electron transport type host materials could change the resultant device characteristics, as well as negatively impact the reliability of active matrix OLED products. To synthesize the bipolar host material, attempts have been made to combine the hole transport type functional groups, with the electron transport type functional groups, As a result of these efforts, improvements of the PHOLED device efficiency by using certain bipolar host materials have been reported [9-13].

This study reports two different types of new host materials for red PHOLEDs having high triplet (>2.25 eV) with thermally-stable benzo[b]thiophene (BT) moieties to improve their

electron transport ability. As a result of using BT moieties at host material, PHOLEDs devices that have novel host materials showed an improved EQE (up to 12.8%).

2. Results and Discussion

2.1. Materials

Two bipolar host materials to realize a highly efficient thermally-stable red PHOLEDs were prepared. Due to its frequent occurrence in nature and useful properties in material science, BT moiety was selected as a basic functionality [14-17]. In particular, the triplet energy level of BT (~2.99 eV) is similar to that of 9-H or 9-phenyl carbazole (~3.01 eV) [18-21]. This is a very useful merit for making new host materials and tuning their triplet energy levels. On the other hand, these BT derivatives including multiply arylated benzo[b]thiophenes and further π -extended benzo[1,2-b;4,5-b']dithiophenes have recently aroused considerable interest in the field of organic electronics[22-24]. However, to the best of our knowledge, no OLEDs using host materials based on BT moiety have been investigated to date.

Scheme. 1 shows the schematic diagram of the synthetic route to prepare such compounds. Herein the 2,3-diphenylated BT derivative was used as an electron-transporting functionality. Indeed, there have scarcely been any attempts to make new bipolar host materials that do not contain any electron-transporting moieties, such as pyridine, triazine, benzimidazole, phosphine oxide, and so on. Meanwhile, we changed the numbers of carbazole moiety connected to the central benzene core unit which act as hole transporting functional units.

Fig. 1 shows the geometries of the core parts of the two resultant host materials obtained from the simulation at a DNP/GGA(PBE) level of theory using Dmol3 module (Material Studio 7.0, Accelrys). BT moieties were rather twisted to the core benzene unit (dihedral angles ca. $38.75 \sim 42.05^{\circ}$) which could expectedly arouse a broken conjugation so that these materials can be used as red host materials (T₁ > 2.25 eV). In addition, the molecular orbital distribution of *Synthesis of* 9,9'-(5-(triphenylen-2-yl)-1,3-phenylene)bis(9H-carbazole) (BTmCP), and Synthesis of 9-(4-(2,3-diphenylbenzo[b]thiophen-5-yl)phenyl)-9H-carbazole (BT- PC) are also shown in Fig. 1. As expected from the molecular structures, the electrons in lowest unoccupied molecular orbital (HOMO) were localized on the N-phenylcarbazole (PC) or 1,3-phenylene)bis(9H-carbazole) (mCP) units, while the electrons in lowest unoccupied molecular orbital (LUMO) were dispersed over the 2,3-diphenylbenzo[b]thiophene core units. In other words, the hole carriers injected from the hole transport layer (HTL) could move through PC or mCP units, while the electrons injected from the electron transporting layer (ETL) could be transported through BT moieties.

Fig. 2(a) shows the UV-Vis absorption and photoluminescence spectra of new host material. The band gap (E_g) of BT-mCP was slightly larger than that of BT-PC (BT-mCP 3.48eV, BT-PC: 3.39eV). Both compounds showed vibronic fine structures in their emission spectra, especially at low temperature (77 K). The triplet energies (T_1) of new host materials determined by the first phosphorescence peak from the shorter wavelength region were 2.26, 2.26 eV for BT-mCP and BT-PC, respectively. The energy level of HOMO was collected from cyclic voltammetry while E_g was determined from the band edge of UV-visible absorption spectrum (see Table 1). The LUMO level of material was determined from the HOMO level and E_g . Fig. 2(b) and 2(c) shows the thermal stability behavior of the materials synthesized in this study. Novel host materials with benzothiophene moieties have high thermal stability. BT-mCP and BT-PC showed the decomposition temperature (T_d) of 430, 393°C as shown in Fig. 2(c). The representative results are also summarized in Table 1.

2.2. Device Characteristics

Bipolar characteristics of host materials with proper triplet energy levels are very important for the enhancement of efficiency, because they help to broaden the recombination zone inside the emission layer of PHOLEDs. In addition, the precisely controlled charge balance at the emission layer is also very important to improve the device stability, as well as its efficiency. To investigate the relative charge carrier transport ability of emission layer (EML), we prepared the hole only devices (HODs), as well as electron only devices (EODs) [25-27] of 4,4-N,N'-Dicarbazole-1,1'-biphenyl (CBP) and newly synthesized host materials by using molybdenum oxide (MoO₃) and lithium quinolate (LiQ) as charge carrier injection layers from indium tin oxide (ITO) and aluminum (Al) as follows.

HOD A: ITO / MoO₃ (0.75 nm) / CBP (100 nm) / MoO₃ (10 nm) / Al (100 nm) HOD B: ITO / MoO₃ (0.75 nm) / BT-mCP (100 nm) / MoO₃ (10 nm) / Al (100 nm) HOD C: ITO / MoO₃ (0.75 nm) / BT-PC (100 nm) / MoO₃ (10 nm) / Al (100 nm)

EOD A: Al (50 nm) / LiQ (1.5 nm) / CBP (100 nm) / LiQ (1.5 nm) / Al (100 nm) EOD B: Al (50 nm) / LiQ (1.5 nm) / BT-mCP (100 nm) / LiQ (1.5 nm) / Al (100 nm) EOD C: Al (50 nm) / LiQ (1.5 nm) / BT-PC (100 nm) / LiQ (1.5 nm) / Al (100 nm)

Fig. 3(a) shows energy band diagram of HODs and EODs of host materials utilized in this study. 0.75 nm of MoO₃ were deposited on the front and rear of host materials of HOD devices. MoO₃ helps the effective ohmic injection of hole carriers into the HOMO and block the flow of electrons from cathode to the LUMO [25]. At EODs, LiQ/Al were used to inject the electron into the LUMO of new host materials, because it has also been widely known as an effective cathode system towards tris(8-hydroxyquinolinato)aluminum [28]. The current density – voltage (J - V) characteristics obtained from the aforementioned HODs and EODs are shown in Fig. 4(a). Our results suggest that while the hole current density was significantly reduced in the order of HOD A (CBP) > HOD B (BT-mCP) > HOD C (BT-PC), the electron current density was reduced in the order of EOD C (BT-PC) > EOD A (CBP) \approx EOD B (BT-mCP). To estimate the charge balance when the materials were used as host materials in emission layer, we plotted the relative charge density of those devices by dividing the hole current density of HODs by electron current density of EODs [e.g. J(hole) / J(electron) where J — current density, mA/cm²] as shown in Fig. 4(b) [1]. From this plot, we could expect that BT-PC could give the most desirable device performance as the relative charge density value was very close to unity, although the differences of HOMOs and LUMOs between host and dopant materials should be additionally considered. Consequently,

from this result it could be expected that BT-PC would show the most efficient device behavior.

CBP was selected as a reference material to verify the effect of new synthetic host materials, because one of the major charge functional units of new host materials is carbazole moiety which is similar to those of CBP. Fig. 5 shows the perspective image of the OLED devices fabricated in this study. The chemical structures of the used materials are provided in Fig. 5. We used ITO as an anode, *N*,*N*'-bis(naphthalen-1-yl)-*N*,*N*'-bis(phenyl)benzidine (NPB) as a hole transport layer, 4,4',4''-tris(carbazol-9-yl)-triphenylamine (HATCN) as a charge generation layer, CBP and new materials synthesized in this study as host materials for EML and iridium(III) bis(2-Phenylquinoline) acetylacetonate ($Ir(phq)_2acac$) as a dopant material for EML, 4,7- diphenyl-1,10-phenanthroline (TpPyPB) as an electron transport layer, as well as a hole blocking layer, lithium fluoride (LiF) as an electron injection layer, Al as a cathode. The exact device configuration used in this work was as follows.

Device A: ITO / NPB (60 nm) / HATCN (5 nm) / NPB (60 nm) / CBP : Ir(phq)₂(acac) (8%, 30nm) / TpPyPB (25 nm) / LiF (1.5 nm) / Al (100 nm)

Device B: ITO / NPB (60 nm) / HATCN (5 nm) / NPB (60 nm) / BT-mCP : Ir(phq)₂(acac) (8%, 30nm) / TpPyPB (25 nm) / LiF (1.5 nm) / Al (100 nm)

Device C: ITO / NPB (60 nm) / HATCN (5 nm) / NPB (60 nm) / BT-PC : Ir(phq)₂(acac) (5%, 30nm) / TpPyPB (25 nm) / LiF (1.5 nm) / Al (100 nm)

All devices were prepared using thick HTL by using NPB (60 nm) / HATCN (5 nm) / NPB (60 nm) to reduce a leakage current level to obtain reasonable efficiency values. The energy diagram of the materials utilized for those devices is also depicted in Fig. 3(b).

Fig. 6(a) shows the current density – voltage (J - V) and luminance – voltage (L - V) characteristics of the fabricated red devices; the representative results are summarized in Table 2. At a given constant voltage of 5.0 V, current density values of 8.26, 8.29 and 9.49 mA/cm² were observed in the fabricated **Devices A, B,** and C, respectively. The reason why

BT-PC showed the greatest current density value could be due to the reasonable exciton formation inside the EML layer. In other words, the recombination zone may be formed close to the HTL / EML interface, because there is a huge difference in HOMO energy levels inbetween BT-PC and Ir(phq)₂acac. Nevertheless, the electron current could unproblematically be reached in this interface, as the electron barrier in-between BT-PC and TpPyPB is relatively small (~0.4 eV). This is somewhat different in the BT-mCP case. While the relatively shallow HOMO level of BT-mCP may result in an easier hole injection, the electron injection into BT-mCP is very difficult. Besides, a fairly low electron conductivity of BT-mCP may inhibit reasonable recombination of the hole and electron carriers. While CBP also exhibits large tapping behavior in-between HTL / EML interface because of the big difference of HOMO energy levels in-between CBP and dopant, they also showed moderate electron injection barrier (~ 0.5 eV). Our expectations from the calculation of relative current density and experiment results are somewhat different. Specifically, we expected that the device prepared with BT-mCP would show a better efficiency behavior than with CBP. However, the results suggest that the two show similar efficiency values. This means that the real energetic situation in-between host and dopant materials in EML could lead to the emergence of very complicated device properties. Nevertheless, as expected (see Fig. 4(b)), BT-PC have emerged as good candidates for excellent host materials for red PHOLEDs.

Fig. 7 shows normalized EL spectra at the brightness of 1000 cd/m^2 . All devices radiate the peak wavelength of Ir(phq)₂acac (603nm, 604nm, 600nm for **Devices A, B,** and **C**, respectively.

At a given constant luminance of 1000 cd/m², the current and power efficiencies were 13.6 cd/A and 8.7 lm/W for the **Device A**, 13.7 cd/A and 8.70 lm/W for the **Device B**, 19.1 cd/A and 13.2 lm/W for the **Device C**, respectively. These efficiency data correspond to 9.72, 10.3 and 12.8 % external quantum efficiencies of **Devices A**, **B** and **C**, respectively. The maximum current and power efficiencies were 13.6 cd/A and 13.4 lm/W for the **Device A**, 19.5 cd/A and 20.4 lm/W for the **Device B**, 23.6 cd/A and 24.7 lm/W for the **Device C**, respectively. All of detail device characteristics are summarized in Table 2. Our expectations

from the calculation of relative current density and experiment results have somewhat difference. In other words, we expected that the device prepared with BT-mCP could show better efficiency behavior than that with CBP, while they showed similar efficiency values. This means that the real energetic situation in between host and dopant materials in EML could cause very complicated device properties. Nevertheless, BT-PC has emerged as good candidates for excellent host materials for red PHOLEDs as we expected from Fig. 6 (b).

Fig. 7 shows normalized EL spectra at a brightness of 1000 cd/m^2 . All devices radiate the peak wavelength of Ir(phq)₂acac (603nm, 604nm, 600nm for the **Devices A**, **B** and **C**, respectively.)

3. Conclusion

In this study, we verified the effect of novel bipolar host materials for red PHOLEDs. Although materials with benzothiophene moieties were expected to have high hole transporting ability, they manifested reasonable electron carrier characteristics. Our red PHOLED devices showed fairly good current efficiency and EQE values, as their relative charge density is close to unity. Finally, 46% of the efficiency improvement had been achieved by using newly synthesized BT-PC as red host

4. Experimental

4.1. Instruments

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer and chemical shifts were referenced to chloroform (7.26 ppm). UV-Vis spectra were recorded with a HEWLETT PACKARD 8453 UV-Vis spectrophotometer. Photoluminescence Spectrometer was used PERKIN ELMER LS 50B model. The molecular mass value of the compound was analyzed by Synapt G2 HDMS quadrupole time-of-flight (TOF) mass spectrometer equipped with an electrospray ion source (Waters, Milford, MA, USA). The instrument was calibrated using NaF solution. The sample was dissolved in 100 %

MeOH and introduced by direct infusion at a flow rate of 20 µl/min into the ion source operating in positive mode. All spectra were acquired at a range of 50 to 1500 m/z. Leucine enkephalin was used as the lock mass for the exact mass measurement correction. Thermal properties were measured by differential scanning calorimetry (DSC) under nitrogen atmosphere using a (TA instruments) and thermogravimetric analysis (TGA) using TGA-1000 (SINCO). Cyclic voltammetry were measured by a Autolab/PGSTAT 2 model at room temperature in a solution of tetra-*n*-butylammonium hexafluorophospate(n-Bu₄NPF₆)(0.1 N) in acetonitrile under nitrogen gas protection at a scan rate of 100 or 50 mV/s. The working electrode was Pt disk type and reference electrode was Ag/0.1M AgNO₃.

4.2. Synthesis of new host materials

4.2.1. Synthesis of 9-(4-bromophenyl)-9H-carbazole (1)

9H-carbazole (5.0 g, 29.9 mmol), 1-bromo-4-iodobenzene (8.88 g, 31.4 mmol), copper(I) iodide (0.86 g, 4.5 mmol), potassium phosphate (27.5 g, 125.6 mmol) and trans-1,2-diaminocyclohexane (1.1 ml, 9.0 mmol) in 200 ml of anhydrous toluene was stirred at 120 °C for 48 h under nitrogen atmosphere. After the reaction had finished, the mixture was washed three times with distilled water and extracted with chloroform. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using *n*-hexanetetrahydrofuran (5:1) eluent to afford (1) a white powder, yield 65%. ¹H-NMR (CDCl₃, 400 MHz) 8.16-8.14 (d, J = 7.6 Hz, 2H), 7.75-7.73 (d, J = 8.4 Hz, 2H), 7.48-7.45 (d, J = 8.4 Hz, 2H), 7.43-7.37 (m, 4H), 7.34-7.29 (t, J = 8 Hz, 2H) ppm.

4.2.2. Synthesis of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole(2)

n-Butyllithium (26 mL, 41.59 mmol) was added to a solution of 9-(4-bromophenyl)-9Hcarbazole (6.7 g, 20.79 mmol) in anhydrous tetrahydrofuran (70 mL) at -78 °C under nitrogen atmosphere. The mixture was stirred for 30 minutes at the same temperature. And then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21.2 mL, 103.97 mmol) was added dropwise to the reaction mixture and stirred for 12 h at room temperature. The reaction mixture was poured into water and extracted with chloroform. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using toluene eluent to afford (2) a white powder, yield 54%. ¹H-NMR (CDCl₃, 400 MHz) 8.17-7.15 (d, J = 8 Hz, 2H), 8.10-8.08 (d, J = 8 Hz, 2H), 7.64-7.62 (d, J = 8.4 Hz, 2H), 7.49-7.47 (d, J = 8 Hz, 2H), 7.45-7.41 (t, J = 6.8 Hz, 2H), 7.33-7.29 (t, J = 6.8 Hz, 2H), 1.43 (s, 12H) ppm.

4.2.3. Synthesis of 2,3-dibromobenzo[b]thiophene (3)

Benzo[b]thiophene (10 g, 74.5 mmol) was dissolved in 250 ml of chloroform. The resulting solution was cooled down to 0°C and bromine (7.87 ml, 152.8 mmol) was added. The mixture was stirred for 12 h. The reaction mixture was poured into water and extracted with chloroform. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to afford (3) as a white solid, yield 90%. ¹H-NMR (CDCl₃, 400 MHz) 7.76-7.74 (d, J = 8.8 Hz, 1H), 7.73-7.71 (d, J = 8 Hz, 1H), 7.41-7.36 (t, J = 8 Hz, 1H) ppm.

4.2.4. Synthesis of 2,3-diphenylbenzo[b]thiophene (4)

2,3-dibromobenzo[b]thiophene (6.3 g, 21.6 mmol), phenylboronic acid (5.5 g, 45.3 mmol), tetrakis(triphenylphosphine)palladium(0) (0.6 g, 0.5 mmol), and 1.0 M Na₂CO₃ (86 ml) in 220 ml of toluene was stirred at 130 °C for 48 h under nitrogen atmosphere. After the

reaction had finished, the mixture was washed three times with distilled water and extracted with chloroform. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using *n*-hexane-toluene (5:1) eluent to afford (4) a white powder, yield 80%. ¹H-NMR (CDCl₃, 400 MHz) 7.90-7.88 (dd, J = 6.4 Hz, 1H), 7.62-7.59 (dd, J = 7.6 Hz, 1H), 7.41-7.32 (m, 10H), 7.25-7.24 (d, J = 2 Hz, 2H) ppm.

4.2.5. Synthesis of 5-bromo-2,3-diphenylbenzo[b]thiophene (5)

2,3-diphenylbenzo[b]thiophene (6.1 g, 21.3 mmol) was dissolved in 70 ml of chloroform. The resulting solution was cooled down to 0 °C and bromine (1.1 ml, 21.9 mmol) was added. The mixture was stirred for 12 h. The reaction mixture was poured into water and extracted with chloroform. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The crude product purified by recrystallization in acetone to afford (5) as a white solid, yield 70%. ¹H-NMR (CDCl₃, 400 MHz) 8.01 (s, 1H), 7.43 (s, 2H), 7.41-7.39 (d, J = 7.2 Hz, 3H), 7.31-7.29 (m, 5H), 7.25-7.24 (d, J = 3.6 Hz, 2H) ppm.

4.2.6. Synthesis of 9,9'-(5-bromo-1,3-phenylene)bis(9H-carbazole) (6)

1,3,5-Tribromobenzene (5 g, 15.9 mmol), 9H-carbazole (5.31 g, 31.8 mmol), copper(I) iodide (0.91 g, 4.7 mmol), potassium phosphate (41.71 g, 190.6 mmol) and trans-1,2-diaminocyclohexane (1.2 ml, 9.5 mmol) in 160 ml of anhydrous toluene was stirred at 120 °C for 48 h under nitrogen atmosphere. After the reaction had finished, the mixture was washed three times with distilled water and extracted with chloroform. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using *n*-hexane-

tetrahydrofuran (5:1) eluent to afford (6) a white powder, yield 27%. ¹H-NMR (CDCl3, 400 MHz) 8.16-8.14 (d, J = 7.6 Hz, 4H), 7.87 (s, 2H), 7.8 (s, 1H), 7.57-7.54 (d, J = 8.4 Hz, 4H), 7.49-7.45 (t, J = 7.2 Hz, 4H), 7.36-7.32 (t, J = 7.6 Hz, 4H) ppm.

4.2.7. Synthesis of 2-(2,3-diphenylbenzo[b]thiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (7)

5-Bromo-2,3-diphenylbenzo[b]thiophene (10 g, 27.4 mmol), bis(pinacolato) diborate (8.3 g, 32.8 mmol), [1,10-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.4 g, 0.5 mmol), and potassium acetate (13.6 g, 136.9 mmol) were dissolved in anhydrous 1,4-dioxane (120 ml) and refluxed under nitrogen for 24 h. After the reaction had finished, the mixture was washed three times with distilled water and extracted with chloroform. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using *n*-hexane-toluene (1:1) eluent to afford (7) a white powder, yield 70%. ¹H-NMR (CDCl₃, 400 MHz) 7.36 (s, 1H), 7.75-7.73 (d, J = 8 Hz, 1H), 7.59-7.57 (d, J = 8 Hz, 1H), 7.43-7.36 (m, 3H), 7.34-7.31 (m, 4H), 7.25-7.23 (m, 3H), 1.38 (s, 12H) ppm.

4.2.8. Synthesis of 9-(4-(2,3-diphenylbenzo[b]thiophen-5-yl)phenyl)-9H-carbazole (BT-PC)

2-(2,3-Diphenylbenzo[b]thiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 g, 2.74 mmol), 9-(4-bromophenyl)-9H-carbazole (0.86 g, 2.67 mmol), tetrakis(triphenylphosphine)palladium(0) (0.14 g, 0.12 mmol), and 1.0 M Na₂CO₃ (9.7 ml) in 50 ml of toluene was stirred at 130 °C for 48 h under nitrogen atmosphere. After the reaction had finished, the mixture was washed three times with distilled water and extracted with chloroform. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The crude product was purified by silica gel column

chromatography using *n*-hexane-tetrahydrofuran (3:1). The final product was obtained as a white powder after purification by vacuum sublimation at a synthetic yield of 63%. ¹H-NMR (CDCl₃, 400 MHz) 8.20 (s, 1H), 8.18-8.16 (d, J = 7.6 Hz, 2H), 7.92-7.90 (d, J = 6.4 Hz, 2H), 7.73-7.71 (d, J = 8 Hz, 1H), 7.69-7.67 (d, J = 8.8 Hz, 3H), 7.52-7.50 (d, J = 8 Hz, 2H), 7.46-7.27 (m, 14H) ppm; ¹³C-NMR (CDCl₃, 400 MHz) 138.6, 138.1, 138.0, 137.8, 137.4, 134.6, 133.2, 131.9, 130.9, 128.2, 127.4, 126.5, 126.4, 126.2, 125.6, 125.3, 125.2, 123.8, 121.8, 121.5, 121.2, 118.2, 118.1, 117.8, 107.6 ppm. HRMS (ESI, m/z): $[M+H]^+$ calcd for C₃₈H₂₆NS, 528.1786; found, 528.1777. Anal. calcd for C₃₈H₂₅NS: C 86.49, H 4.78; found: C 86.43, H 4.79 %.

4.2.9. Synthesis of 9,9'-(5-(triphenylen-2-yl)-1,3-phenylene)bis(9H-carbazole) (BT-mCP)

9,9'-(5-Bromo-1,3-phenylene)bis(9H-carbazole) (1.1)2.26 mmol), 2-(2,3g, diphenylbenzo[b]thiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.96 g, 2.33 mmol), tetrakis(triphenylphosphine)palladium(0) (0.08 g, 0.07 mmol), and 1.0 M Na₂CO₃ (4.8 ml) in 30 ml of toluene was stirred at 130 °C for 48 h under nitrogen atmosphere. After the reaction had finished, the mixture was washed three times with distilled water and extracted with chloroform. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduce pressure. The crude product was purified by silica gel column chromatography using n-hexane-tetrahydrofuran (5:1). The final product was obtained as a white powder after purification by vacuum sublimation at a synthetic yield of 58%. ¹H-NMR (DMSO-d₆, 400 MHz) 8.71 (s, 1H), 7.30-8.28 (d, J = 8 Hz, 4H), 8.21 (s, 1H), 7.98-7.95 (d, J = 8.8 Hz, 1H), 7.88 (s, 1H), 7.70-7.68 (d, J = 8.4 Hz, 4H), 7.57-7.54 (d, J = 8.8 Hz, 1H), 7.52-7.46 (m, 6H), 7.44-7.42 (d, J = 6.8 Hz, 1H), 7.35-7.31 (m, 11H) ppm; 13 C-NMR (CDCl₃, 400 MHz) 144.6, 141, 140.6, 139.9, 139.8, 135.7, 135.2, 134, 133.1, 130.4, 129.6, 128.9, 128.5, 128, 127.7, 126.3, 124.5, 124, 123.9, 123.7, 120.7, 120.6, 120.5, 109.8 ppm. HRMS (ESI,

m/z): [M+H]+ calcd for C50H33NS, 693.2364; found, 693.2342. Anal. calcd for C50H32NS: C 86.67, H 4.66; found: C 86.60, H 4.67 %.

4.3. Fabrication of PHOLEDs

4.3.1 Materials : NPB / HATCN / NPB as a hole injection layer, Ir(phq)₂acac as a red dopant, TpPyPB as a hole blocking layer, and ETL, LiF, LiQ as an electron injection layer and Al as a cathode were purchased from commercial suppliers and were used without purification.

4.3.2 Device Fabrication: To fabricate OLED devices, clean glass substrates pre-coated with a 150-nm-thick ITO layer with a sheet resistance of ~12 Ω /sq were used. Line patterns of ITO were formed on glass by photolithography process. The ITO glass was cleaned by sonification in an isopropylalcohol and acetone, rinsed in deionized water, and finally irradiated in a UV-ozone chamber. All organic materials were deposited by the vacuum evaporation technique under a pressure of ~1x10⁻⁷ Torr. The deposition rate of organic layers was about 0.5 Å/s. Deposition rates of LiF and Al were 0.1 Å/s and 3 Å/s, respectively.

4.3.3 Measurements: The current density-voltage (*J-V*) and luminance-voltage (*L-V*) data of OLEDs were measured by Keithley 2635A and Minolta CS-100A, respectively. The OLED area was 4 mm² for all the samples studied in this work. Electroluminescence (EL) spectra and CIE coordinate were obtained using a Minolta CS-2000A spectroradiometer.

Acknowledgments

Prof. M. C. Suh was supported by the Industrial Strategic Technology Development Program (Grant No. 10042590). Prof. J.-H. Lee was supported by a grant from Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the

Ministry of Education, Science and Technology (Grant No. NRF-2010-0012463). We would like to thank Dr. Young Hye Kim (KBSI) for the ESI MS analysis.

References

- Lee NJ, Jeon JH, In IS, Lee JH, Suh MC. Triphenylene containing host materials with high thermal stability for green phosphorescent organic light emitting diode. Dyes Pigments 2014;101:221-228.
- [2] Lee HK, Ahn H, Lee CH. Device characteristics of blue phosphorescent organic light-emitting diodes depending on the electron transport materials. Journal of information display 2011;12:219.
- [3] Kim SY, Jang JS, and Lee JY. High efficiency phosphorescent organic light-emitting diodes using carbazole-type triplet exciton blocking layer. Appl Phys Lett 2007;90:223505.
- [4] Krummacher BC, Choong VE, Mathai MK, Choulis SA, Franky. Highly efficient white organic light-emitting diode. Appl Phys Lett 2006;88:113506.
- [5] King KA, Spellane PJ, Watts RJ. Excited-state properties of a triply orthometalated iridium(III) complex. American Chemical Society 1985;107:1431.
- [6] Kim SY, Jeong WI, Mayr C, Park YS, Kim KH, Lee JH, Moon CK, Brütting W, and Kim JJ. Organic Light-Emitting Diodes with 30% External Quantum Efficiency Based on a Horizontally Oriented Emitter. Advanced Functional Materials 2013;23:3896–3900.
- [7] Suh MC, Shin HY, Cha SJ. Highly efficient green phosphorescent organic light emitting diodes with simple structure. Organic Electronics 14; 2013: 2198-2203
- [8] Lee NJ, Lee DH, Kim DW, Lee JH, Cho SH, Jeon WS, Kwon JH, Suh MC. Highly efficient soluble materials for blue phosphorescent organic light emitting diode. Dyes and Pigments 95; 2012: 221-228.
- [9] Chen HF, Yang SJ, Tsai ZH, Hung WY, Wang TC and Wong KT. 1,3,5-Triazine derivatives as new electron transport –type host materials for highly efficient green phosphorescent OLEDs. Journal of Material Chemistry 2009;19:8112-8.

- [10] Jeon WS, Park TJ, Kim SY, Pode R, Jang J. Low roll-off efficiency green phosphorescent organic light-emitting devices with simple double emissive layer structure. Applied Physics Letter 2008;93:063303.
- [11]Yook KS and Lee JY. Organic Materials for Deep Blue Phosphorescent Organic Light-Emitting Diodes. Advanced Materials 2012; 24: 3169–3190
- [12] Lee CW and Lee JY. Above 30% External Quantum Efficiency in Blue Phosphorescent Organic Light-Emitting Diodes Using Pyrido[2,3-b] indole Derivatives as Host Materials. Advanced Materials 2013; 25: 5450–5454
- [13] Lee CW and Lee JY. High Quantum Efficiency in Solution and Vacuum Processed Blue Phosphorescent Organic Light Emitting Diodes Using a Novel Benzofuropyridine-Based Bipolar Host Material. Advanced Materials. 2013; 25; 596–600
- [14] Campaigne, E. Comprehensive Heterocyclic Chemistry (Eds.: A. R. Katritzky, C. W. Rees). Pergamon Press, Oxford, 1984;4:863 934.
- [15] Russell, RK. Press, JB. Comprehensive Heterocyclic Chemistry II, (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon Press, Oxford, 1996;2:679 729.
- [16] Kim MS, Choi BK, Lee TW, Shin D, Kang SK, Kim JM, Tamura S, and Noh T. A stable blue host material for organic light-emitting diodes. Applied Physics Letters 2007;91:251111-1–251111-3.
- [17] Bren VA, Dubonosov AD, Minkin VI, Tsukanov AV, Gribanova TN, Shepelenko, EN, Revinsky YV and Rybalkin VP. Photochromic crown-containing molecular switches of chemosensor activity. Journal of Physical Organic Chemistry 2007;20: 917–928.
- [18] Zander M. On the photoluminescence of thiophene benzologues. Z. Naturforsch., A, Phys. Phys. Chem., Kosmophys 1985;40A(5):497-502.
- [19] Montalti M, Credi A, Prodi L and Gandolfi MT. Handbook of Photochemistry 3rd Ed. 2006;205.

- [20] Bonesi SM and Erra-Balsells R. Electronic spectroscopy of carbazole an N- and Csubstituted carbazoles in homogeneous media and in solid matrix. J Lumin. 2001;93: 51-74.
- [21] Bonesi SM. and Erra-Balsells R. Electronic spectroscopy of carbazole an N- and Csubstituted chlorocarbazoles in homogeneous media and in solid matrix. J Lumin 2002;97: 83-101.
- [22] Barbarella G, Favaretto L, Zanelli A, Gigli G, Mazzeo M, Anni M, Bongini A. V-Shaped Thiophene-Based Oligomers with Improved Electroluminescence Properties. Advanced Functional Materials 2005;15:664-670.
- [23] Zhou Y, Wang L, Wang J, Pei J, Cao Y. Highly Sensitive, Air-Stable Photodetectors Based on Single Organic Sub-micrometer Ribbons Self-Assembled through Solution Processing. Advanced Materials 2008;20:3745-3749.
- [24] Tsuji H, Yokoi Y, Mitsui C, Ilies L, Sato Y, Nakamura E. Tetraaryl-Substituted Benzo[1,2-b:4,5-b']dipyrroles: Synthesis, Properties, and Applications to Hole-Injection Materials in OLED Devices. Chemistry - An Asian Journal 2009;4:655-657.
- [25] Matsushima T, Kinoshita Y, Murata H. Formation of ohmic hole injection by inserting an ultrathin layer of molybdenum trioxide between indium tin oxide and organic hole transporting layers. Applied Physics Letter 2007;91:253504.
- [26] Matsushima T, Murata H. Observation of space-charge-limited current due to charge generation at interface of molybdenum dioxide and organic layer. Applied Physics Letter 2009;95:203306.
- [27] Matsushima T, Jin GH, Kanai Y, Yokota T, Kitada S, Kishi T, et al. Interfacial charge transfer and charge generation in organic electronic devices. Organic Electronics 2011;12:520-8.
- [28] Liu Z, Salata OV, Male N. Improved electron injection in organic LED with lithium quinolate/aluminium cathode. Synthetic Metals 2002;128:211e4.

FIGURE CAPTIONS

Scheme 1. Synthesis scheme of novel red host materials

Fig. 1. Geometries of two host materials having benzothiophene.

Fig. 2. (a) UV-visible absorption and photoluminescence spectra (at 298 and 77K),(b) DSC and TGA analyses of red host materials

Fig. 3. Energy band diagrams of used materials in this work.

Fig. 4. (a) Hole current characteristics of HOD A~C and electron current characteristics of EOD A ~C. (b) Relative charge density in host materials. (J(hole) / J(electron))

Fig. 5. Schematic diagram of device architecture and molecular structure used in this study.

Fig. 6. (a) J - V - L characteristics of fabricated red devices. (b) Luminance vs current efficiency and power efficiency characteristics of fabricated red PHOLEDs.

Fig. 7. The normalized EL spectra at a brightness of 1000 cd/m^2 of fabricated red devices.

Compound	λ _{abs} [nm]	λ_{pl} . [nm]		T_1	T_1	НОМО	LUMO	Ea	Ta	Tm	Ta
		Solution	Film	- (eV) (Exp)	(eV) (Cal)	[eV] (CV)	[eV]	[eV]	[נו ר	[[־] ֺֺֺ֢֢֢֢֢֢֢֢֢֢֢֢֘֕֕֕֕׀	[[¯] Ĉ ["]]
BT-mCP	245, 293, 326, 340	393	404	2.26	2.25	- 5.66	- 2.18	3.48	150	255	430
BT-PC	244, 294, 330	398	416	2.26	2.27	- 5.96	- 2.57	3.39	110	258	393

1 able. 1. Summary of physical properties of new nost ma

Table 2. Summary of device performance of all fabricated PHOLED devices.

Device	Turn-on voltage [V] ^[a]	Driving voltage [V] ^[b]	Current Efficiency [cd/A] ^{[b][c]}	Power Efficiency [cd/A] ^{[b][c]}	EQE [%] ^[b]	CIE (x , y) ^[b]
Device A	2.58	4.90	13.6 (13.6)	8.70 (13.4)	9.72	(0.620, 0.379)
Device B	2.53	4.90	13.7 (19.5)	8.70 (20.4)	10.3	(0.624, 0.374)
Device C	2.54	4.49	19.1 (23.6)	13.2 (24.7)	12.8	(0.626, 0.381)

^[a] Measured at 1 cd m⁻²

^[b] Measured at 1000 cd m⁻²

^[c] The values in parentheses mark the maximum efficiency











R







Research Highlight

> Highly efficient phosphorescent red OLED devices with newly synthesized materials. > Application of benzothiophene moieties for good charge transportation. > Effect of relative charge density on phosphorescent red OLED devices. > OLED devices with balanced charge carrier density. > Thermostable OLED host material.

A ALANA