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# PAPER

# New carbazole-based host material for low-voltage and highly efficient red phosphorescent organic light-emitting diodes<sup>†</sup>‡

Jeonghun Kwak,<sup>a</sup> Yi-Yeol Lyu,<sup>b</sup> Hyunkoo Lee,<sup>c</sup> Bonggoo Choi,<sup>d</sup> Kookheon Char<sup>\*e</sup> and Changhee Lee<sup>\*c</sup>

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A new carbazole-based host material for red emitters, **BBTC**, was designed, synthesized and characterized with the phosphorescent organic light-emitting diodes (PHOLEDs). With the molecular design strategy of maintaining the large triplet energy and a good hole transporting ability of carbazole while increasing the morphological and electrochemical stability, the C3 and C6 positions of carbazole are blocked with biphenyl groups and the C9 position is terminated with a terphenyl group. Red PHOLEDs employing a conventional dopant material, bis(1-phenylisoquinoline)(acetylacetonate) iridium(III) ((piq)<sub>2</sub>Ir(acac)), in the emissive layer showed nearly 100% internal quantum efficiency (corresponding to the external quantum efficiency of 19.3%) with reduced efficiency roll-off. We attribute these results to the good electron–hole balance resulting from the good hole mobility of **BBTC** and low hole injection barrier from the hole transport layer to **BBTC** host in the emission layer. In addition, owing to its good hole transporting property, it can be utilized as a hole transport layer in organic light-emitting devices enabling low voltage operation of the devices.

# Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have been intensively investigated because their internal quantum efficiency can be increased up to 100% in principle, corresponding to an external quantum efficiency of about 20%.<sup>1</sup> Owing to their high efficiency, PHOLEDs are some of the most noticeable candidates for full-color, large-area flat-panel displays and solid-state lightings.<sup>2,3</sup> However, efficiency roll-off at high current densities or high operating voltages due to triplet exciton–triplet exciton annihilation (TTA) or triplet exciton– polaron quenching (TPQ) are significant issues of PHOLEDs.<sup>4,5</sup> Improving the charge carrier balance and broadening the recombination zone using double-emission layers or mixed host structure of electron- and hole-transporting materials can reduce the efficiency roll-off phenomenon.<sup>6-8</sup> These approaches, however, often require detailed optimization of various layers such as carrier injection and transport layers, emissive layers, and electron/hole/exciton blocking layers, resulting in a complicated device structure. Thus, it is desirable to develop suitable host materials for PHOLEDs that have high carrier mobility, higher triplet energy ( $E_{\rm T}$ ) and appropriate energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in order to align the energy levels with proximal layers and obtain high device performances.

Various organic compounds especially carbazole derivatives have been synthesized recently to satisfy these properties for PHOLEDs. They usually have a good carrier transporting ability to be used as a hole transporting material,9 and high triplet energy suitable for the host materials of red,<sup>10,11</sup> green,<sup>11,12</sup> and even blue PHOLEDs.13,14 For example, 4,4'-N,N'-dicarbazolebiphenyl (CBP) is a representative carbazole derivative as a host for red and green phosphorescent emitters, which has a high triplet energy  $(E_{\rm T} \approx 2.56 \text{ eV})^{15}$  and ambipolar conducting properties. When we adopt CBP for PHOLEDs, however, high driving voltage was required due to the large energy barrier between CBP and the adjacent transporting layers because CBP has low HOMO energy level (6.0 eV).<sup>16</sup> Since many of the carbazole-based organic materials have low glass transition temperatures ( $T_g$ ) (e.g., CBP: 62 °C,<sup>17</sup> 1,3-bis(carbazol-9-yl) benzene (mCP): 55 °C18), the morphological and device stabilities were poor when we utilized those materials. In addition, CBP film can easily crystallize,<sup>16</sup> causing short operational lifetime in PHOLEDs. In order to enhance the thermal properties, a lot of carbazole derivatives have been newly synthesized so far such as

<sup>&</sup>lt;sup>a</sup>Department of Electronic Engineering, Dong-A University, Busan, 604-714, Republic of Korea

<sup>&</sup>lt;sup>b</sup>Unitech Co., Ltd., Ansan-city, Gyeonggi-do, 425-100, Republic of Korea <sup>c</sup>School of Electrical and Computer Engineering, Inter-University Semiconductor Research Center, Seoul National University, Seoul, 151-744, Republic of Korea. E-mail: chlee7@snu.ac.kr; Fax: +82-2-877-6668 <sup>d</sup>Department of Chemical and Biomolecular Engineering, Electronic Material Lab, Yonsei University, Seoul, 120-749, Republic of Korea <sup>e</sup>School of Chemical and Biological Engineering, Intelligent Hybrids Research Center, Seoul National University, Seoul, 151-744, Republic of Korea. E-mail: khchar@snu.ac.kr

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 ‡ J. Kwak and Y.-Y. Lyu contributed equally to this work.

2,2'-bis(4-carbazolyl-phenyl)-1,1'-biphenyl (BCBP),<sup>19</sup> 2,6-bis(3-(carbazol-9-yl)phenyl) pyridine (26DCzPPy) and 3,5-bis(3-(carbazol-9-yl)phenyl) pyridine (35DCzPPy)<sup>20</sup> with improved performances.

In this study, we report a novel carbazole derivative, 3,6-bisbiphenyl-4-yl-9-[1,1',4',1'']terphenyl-4-yl-9*H*-carbazole (**BBTC**), which possesses high  $T_g$  and good hole transporting property. Red PHOLEDs using this material as a host exhibited nearly 100% internal quantum efficiency. We also demonstrated PHO-LEDs using **BBTC** as the hole transporting layer in this work.

# **Results and discussion**

# Design and synthesis

The chemical structure and synthetic routes of the targeted compound, BBTC, are shown in Scheme 1. With the molecular design strategy of maintaining the large triplet energy and a good hole transporting ability of carbazole while increasing the morphological and electrochemical stability, the C3 and C6 positions of carbazole are blocked with biphenyl groups and the C9 position is terminated with terphenyl group. Compound 1 was synthesized from 1,4-dibromobenzene and 9-H carbazole through copper-catalyzed Ullmann condensations. Bromination of compound 1 with N-bromosuccinimide (NBS) leads to the terbromo compound 2 in reasonable yield (61%). Subsequently, Suzuki coupling reactions of 3,6-dibromo-9-(4-bromophenyl)-9H-carbazole with 4-biphenylboronic acid, in the presence of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> and 2 M K<sub>2</sub>CO<sub>3</sub>, yielded the **BBTC**, which was purified by multiple sublimation in a tube furnace to give the final product and then characterized by elemental analysis (EA), <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectrometry. The detailed data are shown in the Experimental section.

# Thermal properties

The thermal properties of **BBTC** are investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Fig. 1(a), TGA indicates that **BBTC** exhibits a high decomposition temperature ( $T_d$ , which corresponds to a 5% weight loss) of 482 °C. The melting temperature ( $T_m$ ) was observed at 270 °C with DSC in the first heating scan, and the glass-transition temperature ( $T_g$ ) was measured at 148 °C in the second, third, and fourth heating scans, which are depicted in Fig. 1(b). The values of  $T_d$  and  $T_g$  are very high among the reported carbazole derivative compounds as host materials,<sup>10-14</sup>



Fig. 1 (a) TGA and (b) DSC curves of BBTC.

which means that **BBTC** has excellent thermal and morphological stabilities. Thus, **BBTC** can form homogeneous and amorphous thin film through thermal evaporation for the high performance PHOLEDs.

#### **Optical properties**

Fig. 2 plots the optical absorption and photoluminescence (PL) spectra at room temperature (293 K) and the phosphorescence spectrum at 77 K of **BBTC** dissolved in toluene, normalized at the peak of each spectrum. The PL spectrum shows deep blue emission with vibronic peaks at 375, 393 and 414 nm. The optical absorption peak is at 315 nm and the energy gap is estimated at 3.35 eV from the absorption edge at around 370 nm. The phosphorescence spectrum of **BBTC** at 77 K shows the highest energy peak at 495 nm, which corresponds to the triplet energy level of 2.51 eV. In general, red phosphorescent dopants such as  $[Ir(piq)_3]$  (piq = 1-phenylisoquinolinato) or  $[(piq)_2Ir(acac)]$  (acac = ace-tylacetonate) have the triplet energy level of about 2.0 eV,<sup>22</sup>



**Fig. 2** The optical absorption (dashed line), the PL spectrum (solid line) at room temperature (293 K) and the phosphorescent (Ph) spectrum at 77 K of **BBTC** dissolved in toluene in normalized values.



Scheme 1 Synthesis procedure of BBTC.

indicating that **BBTC** can be a suitable host material for red phosphorescent emitters. The HOMO energy level of **BBTC** was 5.68 eV, which can reduce the hole injection barrier from the hole transporting layer (HTL) to **BBTC**, compared with commercial host materials such as CBP (6.0 eV). The LUMO energy level which was calculated by the difference between the HOMO level and optical energy band gap was 2.33 eV.

## **Electroluminescence properties**

To investigate the characteristics of **BBTC** as a host material for red phosphorescent emitters, we fabricated PHOLEDs with the device structure of ITO/MoO<sub>3</sub> (10 nm)/4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α-NPD, 50 nm)/BBTC doped with [Ir (piq)<sub>3</sub>] or [(piq)<sub>2</sub>Ir(acac)] (8 wt%, 30 nm)/BCP (10 nm)/Bebg<sub>2</sub> (40 nm)/LiF (0.5 nm)/Al (100 nm), as can be seen in Fig. 3. Two different red phosphorescent dopants, [Ir(piq)<sub>3</sub>] for device A and [(piq)<sub>2</sub>Ir(acac)] for device B, were co-evaporated to examine the performance of **BBTC** as a host with a concentration of 8 wt% in **BBTC**. We employed MoO<sub>3</sub> as a hole injecting layer,  $\alpha$ -NPD as a HTL, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as an efficient hole blocking layer, and bis(10-hydroxybenzo[h])quinolinato)beryllium (Bebq<sub>2</sub>) as an electron transporting layer (ETL). Since the electron mobility of Bebg<sub>2</sub> is about one order of magnitude higher than that of tris(8-hydroxyquinoline) aluminium (Alq<sub>3</sub>),<sup>21</sup> we can lower the operating voltage as well as enhance the hole-electron balance.

The current density (J)-voltage (V) characteristics, and the efficiency curves of devices A and B are shown in Fig. 4(a) and (b), respectively. The device with  $[Ir(pig)_3]$  dopant (device A) showed a maximum brightness of 49 370 cd m<sup>-2</sup> at 15.4 V, a maximum external quantum efficiency ( $\eta_{\text{FOE}}$ ) of 11.8%, corresponding to the current efficiency ( $\eta_{CE}$ ) of 10.9 cd A<sup>-1</sup>. Meanwhile, the device B using [(piq)<sub>2</sub>Ir(acac)] as a dopant exhibited much higher performances: the maximum external quantum efficiency of 19.3% and current efficiency of 16.4 cd  $A^{-1}$ at the luminance of 98 cd m<sup>-2</sup>, and the maximum luminance of 82 625 cd m<sup>-2</sup> at 14.3 V. Both efficiencies and maximum luminance are excellent performances among recently reported red PHOLEDs.<sup>22-25</sup> This device also showed low efficiency roll-off at high current densities. The current efficiencies at 1000 cd m<sup>-2</sup> and at 10 000 cd m<sup>-2</sup> were still high as 15.9 cd A<sup>-1</sup> ( $\eta_{EOE} = 18.7\%$ ) and 13.1 cd  $A^{-1}$  ( $\eta_{EQE} = 15.4\%$ ), respectively, compared with the efficiencies of 16.4 cd A<sup>-1</sup> ( $\eta_{EOE} = 19.3\%$ ) at 100 cd m<sup>-2</sup>. The high efficiency and reduced efficiency roll-off for the device using



**Fig. 3** Energy level diagram of the materials and the chemical structures of the phosphorescent dyes.



**Fig. 4** (a) Current density–voltage–luminance curves and (b) the external quantum efficiency and current efficiency curves of the devices A–C.

**BBTC** as a host layer can be attributed to the facilitated hole injection owing to the high HOMO energy level of **BBTC** compared with the conventional host materials (e.g. CBP) and the suppression of the triplet exciton quenching processes (TTA and TPO) through the enhanced and balanced electron and hole injection by using the materials possessing high electron and hole mobility (the hole transport characteristics of **BBTC** is described in the following paragraph and in Fig. S1<sup>†</sup>). The turn-on voltage (corresponding to the voltage at the luminance of >1 cd m<sup>-2</sup>) of the device B was 2.9 V, which is lower than the device A by 0.3 V, and the driving voltage at 1000 cd  $m^{-2}$  for the device B was 7.0 V, while the device A showed the same brightness at 8.7 V. The current density of device B is also higher than device A at the same voltage. We attribute these phenomena to the difference of charge trap depth between two dopants, [(piq)<sub>2</sub>Ir(acac)] and [Ir (piq)<sub>3</sub>]. As depicted in Fig. 3, [(piq)<sub>2</sub>Ir(acac)] has 0.38 eV higher HOMO level and 0.47 eV lower LUMO level than the BBTC host. In contrast, [Ir(piq)<sub>3</sub>] has much larger energy gaps, 0.48 eV higher and 0.67 eV lower than the HOMO and LUMO levels of BBTC, respectively, which indicates that [Ir(piq)<sub>3</sub>] makes deeper traps in **BBTC** to both holes and electrons, causing the higher turn-on and operating voltages.

To evaluate the hole transporting characteristics of the **BBTC**, we fabricated and compared the hole-only devices of **BBTC** with a typical hole transporting materials, *i.e.*,  $\alpha$ -NPD and CBP, in the structures of ITO/MoO<sub>3</sub> (10 nm)/organic semiconductor (100 nm)/MoO<sub>3</sub> (10 nm)/Al (100 nm). As shown in Fig. S1 in ESI†, **BBTC** conducted higher current (two times or more) than  $\alpha$ -NPD or CBP. Considering the hole mobilities of  $\alpha$ -NPD

 $(7.64 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})^{26}$  and CBP  $(1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ ,<sup>27</sup> the hole mobility of **BBTC** may be similar with or higher than CBP or  $\alpha$ -NPD. All these results explain that **BBTC** can be used in the HTL with high hole mobility as well as the phosphorescent host.

In order to utilize these good hole transporting properties of **BBTC**, we substituted  $\alpha$ -NPD with **BBTC** in the device B. The device structure is ITO/MoO<sub>3</sub> (10 nm)/BBTC (50 nm)/BBTC: [(piq)<sub>2</sub>Ir(acac)] (8 wt%, 30 nm)/BCP (10 nm)/Bebg<sub>2</sub> (40 nm)/LiF (0.5 nm)/Al (100 nm) (device C). The J-V characteristics and efficiency curves of device C is also plotted in Fig. 4(a) and (b), respectively. The device C showed a maximum current efficiency of 14.1 cd A<sup>-1</sup> ( $\eta_{\text{EOE}} = 16.4\%$ ), which is a bit lower than that of device B, but its power efficiency (12 lm W<sup>-1</sup>) is still comparable to that of device B (13 lm  $W^{-1}$ ). The higher hole conducting property of BBTC compared to α-NPD causes excess hole injection and transport into the emissive layer. This deteriorates the electron-hole balance, resulting in slightly lower efficiencies in the device C. Nevertheless, in device C, turn-on voltage and the driving voltage at 1000 cd m<sup>-2</sup> are improved as 2.8 V and 5.9 V, respectively. It is an encouraging fact that **BBTC** lowers the operating voltages by 1.1 V at 1000 cd m<sup>-2</sup> as compared to device B (α-NPD as the HTL). Therefore, BBTC can be a good hole transporting material. The performances of devices A-C are summarized in Table 1.

Considering these results, **BBTC** has various advantages as the host material for red phosphorescent emitters and as the HTL: as a host, it is a very efficient host material for red phosphorescent emitters, and also has a small hole injection barrier from HTL compared to common host materials like CBP (HOMO: 6.0 eV). As the HTL, it lowers operating voltage owing to superior hole transporting property. Comparing with  $\alpha$ -NPD, rather low HOMO energy (5.68 eV) facilitates hole injection into wide band gap host materials which usually have HOMO levels from 6.0 eV (CBP) to 7.1 eV (*p*-bis(triphenylsilyl)benzene; UGH2).<sup>28</sup> Therefore, **BBTC** can contribute to lowering the operating voltages, increasing the efficiencies, and simplifying the device structures as both the HTL and host layer, which are all important issues in this field.

# Conclusions

In summary, a new carbazole derivative, **BBTC**, which shows great properties as the host and hole transporting material in PHOLED, was synthesized and investigated. Red PHOLEDs employing [(piq)<sub>2</sub>Ir(acac)] doped **BBTC** in the emissive layer showed nearly 100% internal quantum efficiency ( $\eta_{EQE} = 19.3\%$ ) with reduced efficiency roll-off. The driving voltage was also

Table 1The performances of devices A–C.

Device	HTL	Dopant	$V_{\rm on}{}^a/{ m V}$	<i>V</i> <sub>1000</sub> <sup><i>b</i></sup> /V	$\eta_{\mathrm{EQE}}^{c}$ (%)	$\eta_{\mathrm{CE}}{}^{d}$ / cd $\mathrm{A}^{-1}$	$\eta_{\mathrm{PE}}^{e}$ / lm W <sup>-1</sup>
A	α-NPD	Ir(piq) <sub>3</sub>	3.2	8.7	11.8	10.9	7.2
B	α-NPD	(piq) <sub>2</sub> Ir(acac)	2.9	7.0	19.3	16.4	13.0
C	BBTC	(piq) <sub>2</sub> Ir(acac)	2.8	5.9	16.4	14.1	12.0

<sup>*a*</sup> Turn-on voltage defined as the lowest voltage at the luminance of >1 cd  $m^{-2}$ . <sup>*b*</sup> Driving voltage at 1000 cd  $m^{-2}$ . <sup>*c*</sup> The maximum external quantum efficiency. <sup>*d*</sup> The maximum current efficiency. <sup>*e*</sup> The maximum power efficiency.

lowered due to high hole mobility and low hole injection barrier from HTL to the **BBTC** host compared to the conventional host. These excellent performances are attributed to the suppression of the triplet exciton quenching processes through the enhanced electron and hole balance. In addition, **BBTC** possesses high hole mobility comparable with  $\alpha$ -NPD and CBP, so that **BBTC** can extend its role into HTL in PHOLEDs requiring high hole mobility and low energy barrier from/to the adjacent layers.

# **Experimental section**

#### Instrumentation

The  $^1H$  and  $^{13}C$  NMR spectra were recorded at 25  $^\circ C$  on a Bruker DPX-300 spectrometer. Mass spectra were recorded on a Shimadzu LCMS-IT-TOF. Elemental analysis was performed with a CE Instrument EA 1110 Elemental Analyzer. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2020 instrument with a heating rate of 10 °C min<sup>-1</sup> and a cooling rate of 20 °C min<sup>-1</sup>. Thermogravimetric analysis (TGA) was conducted on a TA Instruments TGA 2050 unit under a heating rate of 10 °C min<sup>-1</sup> and a N<sub>2</sub> flow rate of 90 ml min<sup>-1</sup>. UV-Visible spectra were measured with an HP 8453 spectrophotometer. Fluorescence spectra of BBTC in both solution and film were obtained at room temperature and phosphorescence spectrum of BBTC in a dilute 2-methyltetrahydrofuran solution was taken at 77 K using a Hitachi F-4500 fluorescence spectrometer. The HOMO energy levels were measured with an AC-2 photoelectron spectrometer (Riken Keiki Co.)

#### Synthesis

3,6-Bis-biphenyl-4-yl-9-[1,1',4',1'']terphenyl-4-yl-9*H*-carbazole (**BBTC**) was synthesized according to the procedure shown in Scheme 1. Unless stated otherwise, all the reagents were used as received from commercial sources. The solvents were dried using the standard procedure. All the reactions were performed under purified nitrogen atmosphere using the standard Schlenk technique.

**9-(4-Bromophenyl)-9H-carbazole** (1). 1,4-Dibromobenzene (24.00 g, 101.74 mmol), copper (0.30 g, 4.72 mmol) and potassium carbonate (20.00 g, 144.70 mmol) were added to a solution of 9-*H* carbazole (7.00 g, 41.86 mmol) in dry 1,2-dichlorobenzene (200 ml) under N<sub>2</sub> atmosphere. The solution was then heated under reflux for 24 h under N<sub>2</sub>. After the reaction mixture was cooled, the solvent was evaporated and the product was extracted with ethyl acetate. The organic extracts were washed with brine and H<sub>2</sub>O, and then dried over MgSO<sub>4</sub>. After the solvent was evaporated, the crude product was crystallized from ethyl acetate. Yield: 75% (10.10 g). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.21 (d, *J* = 7.5 Hz, 2H), 7.77–7.81 (m, 2H), 7.42–7.53 (m, 6H), 7.32–7.38 (m, 2H). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 141.2, 137.3, 133.6, 129.2, 126.6, 124.0, 121.3, 120.8, 120.7, 110.1. LCMS-IT-TOF [M]<sup>+</sup>: calcd 321.0153. Found: 321.0162.

**3,6-Dibromo-9-(4-bromophenyl)-9H-carbazole (2).** Acetic acid (100 ml) was added to a solution of 9-(4-bromophenyl)-9H-carbazole (10.00 g, 31.15 mmol) in dry chloroform (100 ml). The mixture was stirred at room temperature for 1 h. After the mixture was cooled to

0 °C, *N*-bromosuccinimide (NBS) (11.60 g, 65.17 mmol) was added to the mixture. The solution was slowly warmed to room temperature and then stirred for 3 h. The reaction mixture was quenched with H<sub>2</sub>O, and extracted with chloroform. The organic extracts were washed with brine and H<sub>2</sub>O, and then dried over MgSO<sub>4</sub>. After the solvent was evaporated, the crude product was crystallized from toluene. Yield: 61% (9.10 g). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.21 (d, J = 1.8 Hz, 2H), 7.73–7.78 (m, 2H), 7.54 (d, J = 1.8 Hz, 1H), 7.51 (d, J = 1.8 Hz, 1H), 7.38–7.43 (m, 2H), 7.26 (d, J = 8.7 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 140.2, 136.4, 133.9, 130.0, 129.1, 124.6, 123.7, 122.1, 113.7, 112.0. LCMS-IT-TOF [M]<sup>+</sup>: calcd 476.8363. Found: 476.8373.

3,6-Bis-biphenyl-4-yl-9-[1,1',4',1"]terphenyl-4-yl-9H-carbazole (BBTC). 3,6-Dibromo-9-(4-bromophenyl)-9H-carbazole (1.00 g, 2.10 mmol) and 4-biphenylboronic acid (1.37 g, 6.92 mmol) were mixed in dry toluene. K<sub>2</sub>CO<sub>3</sub> (2.0 M, 12 ml) was added, and the mixture was stirred. The mixture was degassed and tetrakis (triphenylphosphine)palladium (0.36 g, 0.31 mmol) was added in one portion under N<sub>2</sub> atmosphere. The solution was then heated under reflux for 36 h under N2. After the reaction mixture was cooled, the solvent was evaporated and the product was extracted with chloroform. The organic extracts were washed with brine and H<sub>2</sub>O, and then dried over MgSO<sub>4</sub>. After the solvent was evaporated, the crude product was purified by column chromatography (eluent = hexane/chloroform; 8:2 v/v), the product was crystallized from chloroform/methanol. Yield: 62% (0.92 g). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.57 (d, J = 1.2 Hz, 2H), 7.98-8.01 (m, 2H), 7.85-7.92 (m, 7H), 7.78-7.83 (m, 9H), 7.73–7.76 (m, 6H), 7.67 (d, J = 8.7 Hz, 2H), 7.49–7.54 (m, 6H), 7.41-7.43 (m, 3H). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, δ): 141.4, 141.2, 141.0, 139.9, 133.5, 129.5, 129.4, 129.0, 128.1, 128.0, 127.8, 127.7, 127.5, 127.4, 126.1, 124.7, 119.2, 110.9. LCMS-IT-TOF [M]+: calcd 699.2926. Found: 699.2917. Anal. calcd for C54H37N: C, 92.67; H, 5.33; N, 2.00%. Found: C, 92.65; H, 5.38; N, 2.01%.

## Device fabrication and characterization

Phosphorescence organic light-emitting diodes were fabricated according to the following procedure: the ITO substrates were cleaned ultrasonically in organic solvents (isopropyl alcohol, acetone, and methanol), rinsed in deionized water, and dried in an oven at 120 °C for more than 30 minutes. Subsequently, MoO<sub>3</sub>,  $\alpha$ -NPD or **BBTC** as a hole transporting layer, **BBTC** doped with phosphorescent guest ([(piq)<sub>3</sub>Ir] or [(piq)<sub>2</sub>Ir(acac)]), BCP as a hole blocking layer, Bebq<sub>2</sub> as an electron transporting layer, LiF and Al electrodes were deposited on the substrates under the vacuum of about  $3 \times 10^{-6}$  Torr. The deposition rate was about 1–2 Å s<sup>-1</sup> for organic materials, and 4–6 Å s<sup>-1</sup> for Al electrodes. The active area of the devices, defined by the overlap of ITO and Al cathode, was 1.96 mm<sup>2</sup>. The current-voltageluminance characteristics were measured at room temperature using a Keithley 236 source-measure unit and a Keithley 2000 multimeter equipped with a calibrated Si photodiode and Konica-Minolta CS-1000 spectroradiometer, and the EL spectra were measured by a photomultiplier tube (PMT) through an ARC 275 monochromator. For the lifetime test (Fig. S2<sup>†</sup>), the devices were encapsulated with a cover glass and UV-epoxy resin.

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