Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: http://www.elsevier.com/locate/dyepig

Phosphorescent OLEDs with extremely low efficiency roll-off enabled via rationally designed benzimidazole-based bipolar hosts

Tian Zhang ^a, Jingsheng Miao ^a, Muhammad Umair Ali ^{a,b}, Ming Shi ^a, Yaowu He ^a, Tianchen Fu ^a, Hong Meng ^{a,*}

^a School of Advanced Materials, Peking University Shenzhen Graduate School, Peking University, Shenzhen 518055, PR China
^b Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

Keywords: High efficiency Low efficiency roll-off Bipolar host PhOLEDs

ABSTRACT

Phosphorescent organic light-emitting diodes (PhOLEDs) have manifested enormous potential for display and lighting applications because of their high internal and external quantum efficiencies, nevertheless, severe efficiency roll-off at high luminance remains a major bottleneck in their large-scale commercialization. Herein, two new bipolar host compounds, **DCbz-Ph-Bz** and **DDPA-Ph-Bz**, based on carbazole/diphenylamine as the donor and benzimidazole as the acceptor, are successfully obtained. By employing these materials as hosts, extremely low efficiency roll-off PhOLEDs without sacrificing the efficiency are realized. Especially, green PhOLED based on **DDPA-Ph-Bz** as the host and GD001 as the dopant demonstrated a low turn-on voltage of 2.6 V, a peak current efficiency (CE) of 62.2 cd/A and a maximum luminance of 39,370 cd/m². Importantly, our green device exhibited a very low efficiency roll-off as the peak external quantum efficiency (EQE) of 18.3% at 1000 cd/m² was still retained at 17.6% even at a high luminance of 10,000 cd/m². Likewise, red PhOLED with **DCbz-Ph-Bz** as the host and RD001 as the dopant displayed a high maximum EQE of 20.1% and a CE of 24.5 cd/A. High efficiency with low efficiency roll-off in our devices reveals the potential of bipolar molecules as excellent hosts to achieve high-performance PhOLEDs.

1. Introduction

Organic light-emitting diodes (OLEDs) demonstrate exceptional potential for display and lighting applications on account of their excellent characteristics, including good color quality, low power consumption and easy fabrication of large area devices [1]. In particular, phosphorescent OLEDs (PhOLEDs) exhibit superior performance and have been widely used in smart phones. However, despite the enormous progress made so far, several challenges and issues still exist in currently commercialized PhOLEDs, such as their low efficiency, short lifetime, complicated fabrication and so on [2-4]. Usually, OLEDs work stably at low luminance ranging between 100 and 400 cd/m² [5], which is below the requirements of general illumination purposes (i.e. 5000 cd/m^2 to 10,000 cd/m^2). While, their efficiency tends to decrease as the luminance increases, especially at high luminance, which is called efficiency roll-off [5,6]. Efficiency roll-off in PhOLEDs is generally induced by various factors, such as triplet-triplet annihilation (TTA) between the emitters and triplet-polaron annihilation (TPA). In order to avoid TTA and TPA, emitters should be mixed in a host matrix, which plays an important part in achieving PhOLEDs with high efficiency and low efficiency roll-off.

The choice of suitable host is a key to attain PhOLEDs with high efficiency as hosts are responsible for balancing the charge transport and confinement of electron-hole pairs within the emitting layer (EML) [7–9]. As reported to date, three kinds of hosts are considered to realize efficient PhOLEDs, including monopolar hosts, bipolar hosts and co-hosts. Conventional monopolar hosts, such as mCP and CBP generally show severe efficiency roll-off because of their unipolar charge-transporting ability which results in narrow recombination area in the EML. Although, co-hosts can result in balanced carrier mobility, they increase the complexity of the devices. Whereas, in case of bipolar hosts, electron donor and acceptor units are linked together in a single small molecule, which not only make the electric flux high and balanced but also simplify the device structure and hence, the fabrication. Owing to these characteristics, bipolar hosts have gained considerable attention in PhOLEDs fabrication. For instance, Cheng's group reported a highly

https://doi.org/10.1016/j.dyepig.2020.108477

Received 11 December 2019; Received in revised form 16 March 2020; Accepted 23 April 2020 Available online 28 April 2020 0143-7208/© 2020 Elsevier Ltd. All rights reserved.







^{*} Corresponding author. *E-mail address:* menghong@pku.edu.cn (H. Meng).



Scheme 1. Synthetic routes of DCbz-Ph-Bz and DDPA-Ph-Bz.i) t-BuOK, DMSO, 120 °C, 40 min ii) PdCl₂(dppf), KOAc, 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane), 1,4-dioxane, 90 °C,12 h iii) t-BuNa, tris(dibenzylideneacetone)dipalladium, anhydrous toluene, 90 °C, 2.5 h iv) Pd(PPh₃)₄, 2 M K₂CO₃, toluene/ ethanol, 110 °C, 24 h.

efficient universal bipolar host, BCPO, which consists of carbazole and phosphine oxide moieties [10]. D. Ma et al. integrated mCP with benzimidazole moiety on different positions of *N*-phenyl [11], and applied the resulting materials as universal phosphorescent hosts in OLEDs which demonstrated substantially low efficiency roll-off at high luminance. Among their reported hosts, the devices based on o-mCPBI showed the best characteristics with EQEs of over 20% for white, red, green, blue and yellow PhOLEDs. Sue et al. linked TP and carbazole to synthesize bipolar host for TADF and green PhOLEDs [12], which revealed exceptional capability to attain high efficiency with low roll-off. TP26DCbz-Ph-Bz2-host based PhOLEDs developed in their work exhibited the maximum EQE of 25.6%, which was maintained at 25.2% even at a high luminance of 5000 cd/m².

In this work, we successfully developed two new bipolar hosts, 9,9'-(4'-(1-phenyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-3,5-diyl)bis (9H-carbazole) (DCbz-Ph-Bz) and N3,N3,N5,N5-tetraphenyl-4'-(1phenyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-3,5-diamine (DDPA-Ph-Bz), using benzimidazole as the acceptor moiety and carbazole/diphenylamine (DPA) as the donor unit. Carbazole and DPA are selected because of their attractive hole mobilities [13], and benzimidazole unit is employed as acceptor for its high electron injection and transport capability [14]. By linking the two moieties with a size-appropriate biphenyl π -conjugated bridge, we mainly focused on exploring the effect of benzimidazole-based compounds as bipolar hosts in PhOLEDs. As expected, both of our synthesized compounds exhibited suitable energy levels, high triplet energies (E_T), good thermal stability and considerable glass transition temperature (Tg). In order to explore the potential of these compounds as hosts, we fabricated green and red PhOLEDs, and achieved impressive electroluminescence (EL) performance. Especially, DDPA-Ph-Bz hosted green PhOLEDs demonstrated quite low efficiency roll-off as the EQE was retained at 18.3% and 17.7% at corresponding luminance of 1000 and 10,000 cd/m², respectively. Red PhOLEDs containing DCbz-Ph-Bz as host showed a high EQE of 20.1% with corresponding power efficiency (PE) of 28.5 lm/W and CE of 24.5 cd A⁻¹. It is worth mentioning that the efficiency roll-off in our devices (3.3%) at 10,000 cd/m^2 is the best value ever reported for bipolar host-based green PhOLEDs (see Table S1). Our results demonstrate that the development of benzimidazole-based bipolar hosts is an effective way to acquire high-efficiency PhOLEDs with low efficiency roll-off.

2. Experimental section

2.1. General information

¹H NMR and ¹³C NMR spectra were acquired on a Bruker Avance 300

NMR spectrometer. Thermal gravimetric analysis (TGA) was conducted using a TA Instruments Thermogravimetric Analyzer, TA2950 at a heating rate of 10 °C/min under nitrogen flow rate of 50 cm³/min. Differential scanning calorimetry (DSC) experiments were performed using a TA Instruments Q1000 DSC at a heating or cooling rate of 5 °C/ min under nitrogen flow. UV-Vis absorption spectra of vacuum deposited thin films were recorded by PerkinElmer Lambda 750 Spectrometer. The fluorescence spectra were obtained with a Hitachi F-7000 Spectrometer at room temperature and the phosphorescence spectra were measured with a Hitachi F-7000 Spectrometer at 77 K in toluene. Cyclic voltammetry (CV) measurements were conducted using a Gamry Interface 1000 Potentiostat Electrochemical Work Station in DMF solution containing 0.1 M/L tetra-nbutylammonium (TBAPF₆). A glassy carbon electrode, a working electrode, a Pt wire counter electrode and an Ag wire reference electrode were employed for the CV measurements along with ferrocene/ferrocenium (Fc/Fc⁺) as the internal reference. Theoretical calculations were performed using PBE0 functional.

2.2. PhOLED fabrication and characterizations

Pre-cleaned ITOs with a sheet resistance of $12 \Omega/\Box$ were used as the substrates. First, the substrates were transferred into a vacuum chamber (Super-SPECTROS 200, Kurt J. Lesker) to deposit the organic layers with a base pressure of $<10^{-6}$ Torr. Then, the device fabrication was completed via thermal deposition of Liq (2.5 nm) followed by capping the underlayers with Al metal (100 nm) as the cathode. The CIE coordinates and current density–voltage–luminance (J–V–L) curves of the fabricated PhOLEDs were measured using a luminance clorimeter (BM7A, TOPCON, Inc.), and the EL spectra of the devices were recorded with a spectroradiometer (PR-788, Photo Research, Inc.).

2.3. Materials synthesis

(i) DCbz-Ph-Bz

Synthesis routes for **DCbz-Ph-Bz** and **DCbz-Ph-Bz** are presented in Scheme 1. For the synthesis of **DCbz-Ph-Bz**, compound 4 (10.8 mmol), 2-(4-bromophenyl)-1-phenyl-1H-benzo[d]imidazole (9.8 mmol), ethanol (40 mL) and toluene (150 mL) were added into a 350 mL flask followed by the addition of aqueous potassium carbonate (2 M). After that, nitrogen was purged into the mixture for 20 min, and a small quantity of Pd(PPh₃)₄ was added as the catalyst. Afterwards, the mixture was left for reaction at 110 °C for 20 h. After the temperature of the mixture droped to room temperature, it was poured into methanol (350 mL). Water and methanol were used to wash the precipitates which were obtained though filtration. At last, the raw product was dried under



Fig. 1. (a) TGA and (b) DSC curves of DCbz-Ph-Bz and DDPA-Ph-Bz.

vacuum and further purified via sublimation for four times. ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.27 (d, *J* = 7.6 Hz, 4H), 8.12 (d, *J* = 1.8 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.86 (t, *J* = 1.8 Hz, 1H), 7.81 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.70–7.54 (m, 9H), 7.52–7.45 (m, 6H), 7.37–7.25 (m, 6H), 7.19 (dd, *J* = 7.0, 1.6 Hz, 1H). MS (+ESI, *m*/*z*) (M + H)⁺ calculated for 677.2661, found 677.2702.

5-chloro-N¹,N¹,N³,N³-tetraphenylbenzene-1,3-diamine (7).

The compounds, 1,3-dibromo-5-chlorobenzene (2.70 g,10 mmol) and diphenylamine (3.55 g, 21 mmol), t-BuNa(2.98 g, 31 mmol) along with 35 mL anhydrous toluene were poured into a 350 mL flask. Later, nitrogen was purged into the mixture for 20 min, and dichlorobis[di-tertbutyl(4-diMethylaMinophenyl) phosphine]palladium(II) (Pd (AMPHOS)₂Cl₂) (0.07 g, 0.1 mmol) was added. Afterwards, the reaction was kept at 90 °C for 3 h. Then, after cooling, some water was poured into the flask, and chloroform was used to extract the organic phase, which was then treated with anhydrous MgSO4. To remove the solvent, residual was purified through column chromatography using dichloromethane (DCM)/petroleum at 1:9 (v:v) as the eluent. Finally, the intermediate product in the form of white solid was obtained (Yield: 73%). ¹H NMR (400 MHz, CDCl₃): δ 7.24–7.17 (m, 8H), 7.05 (dt, J = 8.8, 1.7 Hz, 8H), 7.02–6.96 (m, 4H), 6.65 (t, J = 2.0 Hz, 1H), 6.57 (d, J = 2.0 Hz, 2H). ^{13}C NMR (400 MHz, CDCl_3) δ 149.50, 147.05, 135.24, 129.41, 124.78, 123.53, 116.69, 115.90. HRMS(APCI): m/z calculated for $C_{30}H_{24}ClN_2$ [M+H]⁺ 447.1628, found 447.1621.

 N^1 , N^1 , N^3 , N^3 -tetraphenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,3-diamine (8).

A mixture of anhydrous 1,4-dioxane (35 mL), 7 (2.23 g, 5 mmol), tris (dibenzylideneacetone)dipalladium (0.10 g, 0.1 mmol), 2-di-tert-butylphosphino-2',4',6'-trIIsopropylbiphenyl (0.08 g, 0.2 mmol), bis(pinacolato)diboron (1.40 g, 5.5 mmol) and potassium acetate (1.47 g, 15 mmol) was refluxed at 90 °C in a nitrogen atmosphere for 12 h. When the temperature dropped to 25 °C, the mixture was treated with saturated sodium chloride solution and chloroform sequentially. After separating out the organic layers, the mixture was further treated with anhydrous MgSO₄. To remove the solvent, the solid was purified through column chromatography with petroleum ether acted as the eluent and a white powder was obtained (Yield: 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.23–7.16 (m, 10H), 7.07–7.01 (m, 8H), 6.94 (dd, J = 10.5, 4.2 Hz, 5H), 1.27 (s, 12H). $^{13}\mathrm{C}$ NMR (400 MHz, CDCl_3) δ 148.37, 147.77, 129.20, 126.08, 125.17, 123.77, 122.44, 83.96, 67.24, 24.94. HRMS(APCI): m/z calculated for $C_{36}H_{36}BN_2O_2$ [M+H]⁺ 539.2870, found 539.2872.

(ii) DDPA-Ph-Bz

The synthesis method for **DDPA-Ph-Bz** was the same as that for **DCbz-Ph-Bz** (except using compound 8 instead of compound 4) and the material was attained with a yield of 56.8%. ¹H NMR (300 MHz,

DMSO- d_6): δ 7.77 (d, J = 7.1 Hz, 1H), 7.60–7.45 (m, 5H), 7.39 (dd, J = 7.6, 1.7 Hz, 2H), 7.35–7.20 (m, 12H), 7.16 (d, J = 7.3 Hz, 1H), 7.05–6.96 (m, 12H), 6.75 (d, J = 1.9 Hz, 2H), 6.61 (d, J = 1.7 Hz, 1H). MS (+ESI, m/z) (M + H)⁺ calculated for 681.2974, found 681.3013.

3. Results and discussion

3.1. Synthesis and characterization

The chemical structures and synthetic routes of the target pruducts, DCbz-Ph-Bz and DDPA-Ph-Bz can be found in Scheme 1. The intermediate compound 4 was obtained by adopting a previously reported method [1]. The target compounds, DCbz-Ph-Bz and DDPA-Ph-Bz were attained via palladium catalyzed Suzuki-Miyaura coupling reaction of compounds 4 and 8 with 2-(4-bromophenyl)-1-phenyl-1H-benzo[d] imidazole, respectively. Both of the final products were further purified through column chromatography and then processed via temperature-gradient vacuum sublimation before employing in PhO-LEDs. The material's purity was further confirmed through nuclear magnetic resonance (NMR) and high-resolution mass spectrometery (HRMS). The Experimental Section and Supporting Information contain the details of synthetic procedures and characterization results.

3.2. Thermal properties

TGA and DSC were used to evaluate the thermal properties of the newly developed materials. As can be observed from the obtained curves (Fig. 1), both materials indicate great thermal stability: the decomposition temperatures (T_d) that refers to the 5% weight loss are estimated to be 508 °C and 456 °C, while clear T_g values are measured to be 156 °C and 113 °C, respectively for DCbz-Ph-Bz and DDPA-Ph-Bz. DCbz-Ph-Bz has higher T_d and T_g values with lower molecular weight compared with DDPA-Ph-Bz, which is caused by the carbazole group. Carbazole is a well-known chemically and morphologically stable building block. Also, its good coplanrity can increase the molecular rigidity and reduce torsion resistance. Both of our materials exhibit substantially higher T_d and T_g than those for previously reported compounds, such as for mCP [15] or similar benzimidazole compounds (o-mCPBI, m-mCPBI, p-mCPBI) [11]. Overall, the improved thermal properties are beneficial for PhO-LEDs as they ensure the formation of stable amorphous thin films and maintain high operational stability.

3.3. Photophysical properties

The UV–*vis* absorption and photoluminescence (PL) spectra (at 25 °C) of thin films, as well as PL spectra (at 77 K) in toluene of **DCbz-Ph-Bz**



Fig. 2. (a) Absorption and fluorescence spectra of DCbz-Ph-Bz (black lines) and DDPA-Ph-Bz (red lines) films and (b) corresponding phosphorescence spectra in toluene at 77 K. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table	1		
-------	---	--	--

Physical properties of **DCbz-Ph-Bz** and **DDPA-Ph-Bz**.

Compound	λ_{abs} [nm]	λ_{PL} [nm]	HOMO ^a [eV]	LUMO [eV]	Egb [eV]	S ₁ [eV]	T ₁ ^c [eV]	$\triangle E_{st}$ [eV]	T_d^d [°C]	T_g^d [°C]
DCbz-Ph-Bz	317, 326, 340	404	-5.60	$-2.21 \\ -2.53$	3.39	3.42	2.80	0.62	508	156
DDPA-Ph-Bz	313	435	-5.50		2.97	3.10	2.83	0.27	456	114

^a Deduced from CV. ^bElectrochemical band-gaps calculated according to the absorption spectra of films using $\Delta E_g = 1240 / \lambda_{onset}$.

^c Measured in toluene at 77 K ^dMeasured by TGA and DSC.

and DDPA-Ph-Bz are displayed in Fig. 2, and the obtained values are summarized in Table 1. Both of the molecules possess similar absorption spectra since they contain nearly identical molecular skeleton and functional groups. The absorption peaks for DCbz-Ph-Bz and DDPA-Ph-Bz are observed at around 317 and 313 nm, respectively, which could have resulted from the $\pi \rightarrow \pi^*$ transition corresponding to the benzimidazole group and adjacent benzene ring. While in the absorption spectra of DCbz-Ph-Bz, other absorption peaks can be seen at 324 nm and 340 nm, corresponding to the $n \rightarrow \pi^*$ electron transitions of the carbazole unit [9]. PL emission peaks of these materials are found at 404 nm and 435 nm in the form of neat films, while at 419 nm and 461 nm in dilute DCM solution for DCbz-Ph-Bz and DDPA-Ph-Bz, respectively. As can be observed in the PL spectra, the corresponding peaks of both of these materials in the form of neat films are blue-shifted by 15-26 nm compared with those in DCM, possibly due to the different dielectric surroundings. Compared with DDPA-Ph-Bz, DCbz-Ph-Bz has short emission wavelength, which is attributed to its improved non-planarity between the middle biphenyl unit. As a result, the twisted biphenyl core limits π -conjugation length, as shown in Fig. 2. The dihedral angle is 37.0° for DCbz-Ph-Bz and 35.8° for DDPA-Ph-Bz as calculated by density functional theory (DFT). According to the onset of absorption and emission wavelengths of the spectra in the form of films, the optical energy gap (E_{σ}) /singlet energy (S_1) values are estimated to be 3.39/3.42 eV and 2.97/3.10 eV for DCbz-Ph-Bz and DDPA-Ph-Bz, respectively, revealing well-matched S1 and Eg values. Based on the onset of phosphorescence spectra [16], E_T values are evaluated to be 2.80 and 2.83 eV for DCbz-Ph-Bz and DDPA-Ph-Bz, respectively. Though, these materials have different singlet energies, their triplet energies are almost the same. The similar triplet energies can be explained by the low E_T values of the benzimidazole group, since phosphorescence is derived from the triplet emission of the benzimidazole with the lowest E_T values; both of these materials behave analogously. Considering CbzNBI, Mcpnbi [17] and CbPr-3, Bim-4 [18] for example, the PL spectra of DCbz-Ph-Bz and DDPA-Ph-Bz is consistent with the phosphorescent emission of benzimidazole derivatives. The ET values of DCbz-Ph-Bz and DDPA-Ph-Bz are sufficiently high, making them suitable to adopt as hosts for



Fig. 3. CV curves of DCbz-Ph-Bz and DDPA-Ph-Bz in dilute DCM.

phosphorescent emitters.

3.4. Electrochemical properties

To understand the electrochemical behavior of these newly developed materials, CV analysis was performed and the obtained results are depicted in Fig. 3. According to the onsets of the oxidation, the HOMOs of **DCbz-Ph-Bz** and **DDPA-Ph-Bz** are estimated to be -5.60 and -5.50eV, respectively, and the corresponding LUMOs are -2.21 eV and -2.53eV, as calculated from the HOMO levels and E_g values obtained from the absorption spectra. **DCbz-Ph-Bz** exhibits irreversible oxidation curves like most of the carbazole derivatives since their radical cations are unstable [19]. The almost same HOMOs indicate that the donor



Fig. 4. HOMO–LUMO levels, energy gaps and frontier-molecular-orbital distribution of DCbz-Ph-Bz (Left) and DDPA-Ph-Bz (Right).

electronic units have similar oxidation potential, and between the donor and acceptor units, there is an interaction which results in similar HOMOs of both of these compounds. In addition, they exhibit deep LUMOs, potentially due to the increased electron-withdrawing benzoimidazole units, that could improve the electron-injection to the EML in

PhOLEDs.

3.5. Theoretical calculations

To further explore the structure-property relationship of these materials at the molecular level, density functional theory(DFT) calculations were performed. The HOMO–LUMO levels, energy gaps and frontier-molecular-orbital distributions estimated via PBE0 calculations are presented in Fig. 4 which revealed that **DCbz-Ph-Bz** and **DDPA-Ph-Bz** show similar orbital distributions. Their HOMOs are scattered among DPA or carbazole which are the electron-donating groups, while their LUMOs are located in the benzimidazole due to the electron affinity of nitrogen. The separated HOMOs and LUMOs suggest that holes and electrons can be efficiently transported by these molecules, which could improve the device performance. Moreover, there is a little overlap at the benzene rings between carbazole or DPA, and an appropriate overlap between LUMO and HOMO offers an effective intramolecular charge transfer (ICT) transition emission and a higher E_T .

3.6. Single carrier devices

To investigate the charge-transporting performance of the synthesized compounds, single carrier devices were developed. The hole-only devices with a structure of ITO/NPB (10 nm)/Host (80 nm)/NPB (10 nm)/Al (100 nm), and the electron-only devices with a configuration of ITO/TPBI (10 nm)/Host (80 nm)/TPBI (10 nm)/Liq (2.5 nm)/Al (100 nm) were fabricated. To block electron injection from anode to the EML,



Fig. 5. Current density versus voltage (J-V) characteristics of the hole-only and electron-only devices for (a) DCbz-Ph-Bz and (b) DDPA-Ph-Bz, (c) Absorption spectra of GD001 and RD001, and fluorescence spectra of DCbz-Ph-Bz and DDPA-Ph-Bz films.



Fig. 6. Energy-level diagram of the fabricated PhOLEDs and the molecular structures of constituent materials.

we used NPB as an electron-blocking layer in hole-only devices. While, in case of electron-only devices, TPBI palys a part in transporting the electrons and blocking the holes. As can be seen in Fig. 5a and b, it is clear that the current densities are quite low which indicates that the charge-transporting property of these hosts is poor. The low current desnities in these single carrier devices is ascribed to the twisted molecular conformation of hosts which resulted in an inapproperiate molecular stacking order in the neat films. As mentioned above, the dihedral angle of the two middle benzene rings in case of DCbz-Ph-Bz is bigger than that of DDPA-Ph-Bz. Bigger dihedral angle suggests weaker coplanar configuration and less ordered molecular arrangement, which undoubtedly contributes to rough or poor charge transportation, leading to lower charge-transporting property of DCbz-Ph-Bz. Nevertheless, the charge-transporting characteristics of the hosts are well-balanced; the low but balanced charge-transporting property of the hosts could enlarge the recombination area of the EML and reduce the efficiency roll-off. Compared with the hole-only devices, the corresponding electron-only devices show slightly higher current densities, indicating that both of the materials are bipolar hosts.

3.7. PhOLEDs characterization

The excellent thermal stability, suitable energy levels, bipolar charge transport capability, and especially, extremely high E_T values of our newly developed benzimidazole-based materials motivated us to

evaluate their performance as hosts in PhOLEDs.

First, we fabricated green-emitting devices, G1 and G2, by utilizing DCbz-Ph-Bz and DDPA-Ph-Bz as green hosts for PhOLEDs with GD001 as the dopant in a device configuration of ITO/HATCN (5 nm)/LHT002 (30 nm)/LB002 (10 nm)/Host: Dopant (50 nm,10%)/LET003 (30 nm)/ Liq (2.5 nm)/Al (100 nm). The used materials, including LHT002, LEB002, LET003, LGD001 and LRD001 were synthesized according to previously reported methods [20-22]. The molecular structures of these organic materials and corresponding energy-levels diagram of the fabricated devices are depicted in Fig. 6. The key-paramters of green PhOLEDs can be seen in Table 2. The turn-on voltage, defined as the voltage at which a device achieves a luminance of 1 cd/m^2 , is quite low, i.e. 2.6 V for both of the devices. Such low turn-on voltage is ascribed to the well-matched energy-levels of the hosts with adjacent layers [23]. Device G1 using DCbz-Ph-Bz as the host rendered a maximum PE of 66.2 lm/W, the highest CE of 57.2 cd/A and a peak EQE of 16.1%. Device G2 hosted by DDPA-Ph-Bz exhibited superior performance with 44.4 lm/W, 62.2 cd/A and 18.9% as the maximum PE, CE and EQE values, respectively. As evident in Fig. 7, device G2 demonstrated a considerably higher maximum luminance of 39,370 cd/m^2 at 7 V than 12,890 cd/m^2 for G1, which could have resulted from different charge-transporting performance of the used host materials. DDPA-Ph-Bz has better carrier transport capability resulting in PhO-LEDs with higher current density and hence, higher luminance. Obviously, in case of green PhOLEDs, DDPA-Ph-Bz outperformed

Table	2
-------	---

Device	Host	V ^a _{on} [V]	CE ^b [cd/A]	PE ^c [lm/w]	EQE (%)		
					Maximum	@1000 cd/m ²	@10,000 cd/m ²
G1	DCbz-Ph-Bz	2.6	57.2	69.2	16.1	13.3	12.6
G2	DDPA-Ph-Bz	2.6	62.2	44.4	18.9	18.3	17.7
R1	DCbz-Ph-Bz	2.7	24.5	28.5	20.1	18.4	13.4
R2	DDPA-Ph-Bz	2.6	16.5	16.3	16.2	15.5	11.8

^aV_{on}, the turn-on voltage ^bThe maximum values of CE. ^cThe maximum values of PE.



Fig. 7. (a) Current density-voltage-luminance (J-V-L) characteristics, (b) CE-L-EQE curves, and (c) EL spectra of green PhOLEDs at 6 V. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

DCbz-Ph-Bz by demonstrating superior EQE possibly due to three potential reasons: (1) the slightly higher E_T of **DDPA-Ph-Bz** (2.83 eV) than that of the **DCbz-Ph-Bz** (2.80 eV), which could decrease the energy transfer loss between the host and dopant. Further, **DDPA-Ph-Bz**'s deeper S₁ of 3.10 eV is also beneficial on account of lower stress of the host in the process of light emission [24]. (2) **DDPA-Ph-Bz** has well-matched energy-levels, i.e. its HOMO is 5.5 eV, shallower than **DCbz-Ph-Bz**, which is good for hole transport. **DDPA-Ph-Bz**'s LUMO is 2.5 eV, which is the same as that of the adjacent electronic transport layer, resulting in reduced barrier for electron transfer. (3) **DDPA-Ph-Bz**'s higher charge-transporting property also plays an important role in superior device performance.

Interestingly, both of the devices revealed extremely low efficiency roll-off. In case of device G1, for example, the EQE was 13.3% at a luminance of 1000 cd/m² which still remained nearly unchanged at 12.6% when the luminance reached up to 10,000 cd/m^2 . Likewise, for device G2, the EQEs at 1000 and 10,000 cd/m^2 are observed to be 18.3% and 17.7%, respectively. The high EQEs with extremely low efficiency roll-off in these devices are ascribed to the two reasons, including: (1) balanced electron and hole transport characteristics of the constituent materials which effectively confined the electron-hole pairs in the EML, and (2) high E_T values of our newly developed hosts which could avoid reverse energy that transfers from the guest to the host. Furthermore, it is worth mentioning that green PhOLEDs with our newly developed compounds outperformed the counterpart adopting CBP, a commonly used host, both in terms of efficiency and the efficiency roll-off (see Fig. S5 and Table S1), thereby indicating superior potential of benzimidazole-based bipolar hosts over conventional materials.

further fabricated red PhOLEDs, R1 and R2, in a device structure of ITO/ HATCN (5 nm)/LHT002 (20 nm)/LEB002 (10 nm)/Host: Dopant (30 nm, 3%)/LET003 (50 nm)/Liq (2.5 nm)/Al (100 nm), where RD001 is employed as the dopant while **DCbz-Ph-Bz** and **DDPA-Ph-Bz** are used as hosts, respectively. Both of the red PhOLEDs exhibited high efficiency, among which, the device R1 reached a higher maximum luminance of 14,140 cd/m² at 7 V, and maximum values of 24.5 cd/A, 28.5 lm/W, 20.1% as CE, PE and EQE, respectively, accompanied by CIE coordinates of (0.66, 0.33). While, the device R2 showed inferior performance as it could attain a maximum luminance of 12,800 cd/m² at 7 V (and maximum efficiencies of 16.5 cd/A and 16.3 lm/W, 12.7%) with CIE coordinates of (0.65, 0.34).

In case of red devices, the results are opposite to those acheived in case of green devices where **DCbz-Ph-Bz** exhibited better performance. This could be ascribed to the utilization of efficient energy transfer from host material to the phosphorescent dopant. The EL spectra of the green devices showed only the emission from green dopant, suggesting that the EL is resulted from sufficient exciton transformation from the host to the dopant. In red devices, as shown in Fig. 8 (c), there is another small peak in device R2's EL spectrum at 439 nm, which is the emission from **DDPA-Ph-Bz** itself, indicating that the energy transfer from the host to the dopant is incomplete. Moreover, **DDPA-Ph-Bz**'s PL and red dopant's absorption spectra do not overlap well with each other. Also, the dopant has wider absorption in **DCbz-Ph-Bz**'s emission range, so R2's efficiency is lower than that of the R1.

4. Conclusions

In summary, two new bipolar host compounds, DCbz-Ph-Bz and



Fig. 8. (a) J–V–L characteristics, (b) CE-L-EQE curves, and (c) EL spectra of red PhOLEDs at 6 V. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

DDPA-Ph-Bz, based on benzimidazole moiety, are successfully synthesized which demonstrated excellent performance in PhOLEDs. The application of benzimidazole unit to develop novel hosts resulted in materials with high thermal stability and well-balanced charge fluxes and high E_T values. PhOLEDs employing these materials as hosts showed decent characteristics and a low turn-on voltage of about 2.6 V with high efficiency. Importantly, PhOLEDs containing DDPA-Ph-Bz as green host showed extremely low efficiency roll-off at high luminance as the peak EQE of 18.9% at 2920 cd/m^2 was retained at 18.3% and 17.7% at corresponding luminance of 1000 and 10,000 cd/m^2 , respectively. In addition, red PhOLEDs with DCbz-Ph-Bz as the host exhibited a maximum CE of 24.5 cd/A and a peak EQE of 20.1%. These results reveal the potential of benzimidazole derivatives as hosts for red and green PhOLEDs with excellent performance. Our findings demonstrate that a host adopting benzimidazole unit could be an appropriate choice for the design of high efficiency PhOLEDs with low efficiency roll-off.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Tian Zhang: Conceptualization, Data curation, Formal analysis, Writing - original draft. Jingsheng Miao: Formal analysis. Muhammad Umair Ali: Writing - review & editing. Ming Shi: Methodology. Yaowu He: Investigation. Tianchen Fu: Software. Hong Meng: Funding acquisition, Project administration, Resources.

Acknowledgments

This work was financially supported by the Guangdong Key Research Project (No. 2019B010924003), the Shenzhen Engineering Laboratory (Shenzhen Development and Reform Commission [2018]1410), the Shenzhen Science and Technology Research Grant (JCYJ2018030 2153451987, JCYJ20190808182803805, JCYJ20170818085627721) and Shenzhen Peacock Plan (KQTD2014062714543296).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108477.

References

- [1] Wu C, Wu Z, Wang B, Li X, Zhao N, Hu J, et al. Versatile donor-π-acceptor-type Aggregation-enhanced emission active fluorophores as both highly efficient nondoped emitter and excellent host. ACS Appl Mater Interfaces 2017;9(38): 32946-56.
- [2] Wang F, Liu D, Li J, Ma M. Modulation of n-type units in bipolar host materials toward high-performance phosphorescent OLEDs. ACS Appl Mater Interfaces 2017; 9(43):37888–97.
- [3] Grimsdale AC, Leok Chan K, Martin RE, Jokisz PG, Holmes AB. Synthesis of lightemitting conjugated polymers for applications in electroluminescent devices. Chem Rev 2009;109(3). 897-1091.
- [4] Reineke S, Lindner F, Schwartz G, Seidler N, Walzer K, Lüssem B, et al. White organic light-emitting diodes with fluorescent tube efficiency. Nature 2009;459 (7244):234–8.
- [5] Murawski C, Leo K, Gather MC. Efficiency roll-off in organic light-emitting diodes. Adv Mater 2013;25(47):6801–27.
- [6] Liu B, Zhao J, Luo C, Lu F, Tao S, Tong Q. A novel bipolar phenanthroimidazole derivative host material for highly efficient green and orange-red phosphorescent OLEDs with low efficiency roll-off at high brightness. J Mater Chem C 2016;4(10): 2003–10.

T. Zhang et al.

Dyes and Pigments 180 (2020) 108477

- [7] Holmes RJ, Forrest SR, Tung YJ, Kwong RC, Brown JJ, Garon S, et al. Blue organic electrophosphorescence using exothermic host–guest energy transfer. Appl Phys Lett 2003;82(15):2422–4.
- [8] Zhou G-J, Wong W-Y, Yao B, Xie Z, Wang L. Multifunctional metallophosphors with anti-triplet–triplet annihilation properties for solution-processable electroluminescent devices. J Mater Chem 2008;18(15):1799.
- [9] Huang J-J, Hung Y-H, Ting P-L, Tsai Y-N, Gao H-J, Chiu T-L, et al. Orthogonally substituted benzimidazole-carbazole benzene as universal hosts for phosphorescent organic light-emitting diodes. Org Lett 2016;18(4):672–5.
- [10] Chou H-H, Cheng C-H. A highly efficient universal bipolar host for blue, green, and red phosphorescent OLEDs. Adv Mater 2010;22(22):2468–71.
- [11] Zhao Y, Wu C, Qiu P, Li X, Wang Q, Chen J, et al. New benzimidazole-based bipolar hosts: highly efficient phosphorescent and thermally activated delayed fluorescent organic light-emitting diodes employing the same device structure. ACS Appl Mater Interfaces 2016;8(4):2635–43.
- [12] Song W, Chen Y, Xu Q, Mu H, Cao J, Huang J, et al. [1,2,4]Triazolo[1,5-a]pyridine-Based host materials for green phosphorescent and delayed-fluorescence OLEDs with low efficiency roll-off. ACS Appl Mater Interfaces 2018;10(29):24689–98.
- [13] Chen C-H, Huang W-S, Lai M-Y, Tsao W-C, Lin JT, Wu Y-H, et al. Versatile, benzimidazole/amine-based ambipolar compounds for electroluminescent applications: single-layer, blue, fluorescent OLEDs, hosts for single-layer, phosphorescent OLEDs. Adv Funct Mater 2009;19(16):2661–70.
- [14] Lai M-Y, Chen C-H, Huang W-S, Lin JT, Ke T-H, Chen L-Y, et al. Benzimidazole/ amine-based compounds capable of ambipolar transport for application in singlelayer blue-emitting OLEDs and as hosts for phosphorescent emitters. Angew Chem Int Ed 2008;47(3):581–5.

- [15] Lee TYH, Wang Q, Wallace JU, Chen SH. Temporal stability of blue phosphorescent organic light-emitting diodes affected by thermal annealing of emitting layers. J Mater Chem 2012;22(43):23175.
- [16] Su S-J, Takahashi Y, Chiba T, Takeda T, Kido J. Structure-property relationship of pyridine-containing triphenyl benzene electron-transport materials for highly efficient blue phosphorescent OLEDs. Adv Funct Mater 2009;19(8):1260–7.
- [17] Chen Y-M, Hung W-Y, You H-W, Chaskar A, Ting H-C, Chen H-F, et al. Carbazole–benzimidazole hybrid bipolar host materials for highly efficient green and blue phosphorescent OLEDs. J Mater Chem 2011;21(38):14971.
- [18] Yu E-S, Jung S-H, Chae M-Y, Jeon WS, Kulshreshtha C, Park J-S, et al. Phosphorescent blue organic light-emitting diodes with new bipolar host materials. J Nanosci Nanotechnol 2012;12(2):1361–4.
- [19] Sonntag M, Strohriegl P. Novel 2,7-linked carbazole trimers as model compounds for conjugated carbazole polymers. Chem Mater 2004;16(23):4736–42.
- [20] Amir P, Jonas K, Christian E, Tobias G, Aurelle L, Dominik J. Composition for organic electronic devices. Oct 18, 2018. Merck Patent, WO 2018/189134 A1.
- [21] Amir P, Jonas K, Jens E, Anja J, Christian E. Composition for organic electronic devices. Dec 05, 2019. Merck Patent, WO 2019/229011 A1.
- [22] Tasuku H, Tomohiro N. Organic electroluminescent element and electronic devices. Idemitsu Kosan Co., Ltd Patent; Jun 7, 2018. WO 2018/101492 A2.
- [23] Lyu Y-Y, Kwak J, Jeon WS, Byun Y, Lee HS, Kim D, et al. Highly efficient red phosphorescent OLEDs based on non-conjugated silicon-cored spirobifluorene derivative doped with Ir-complexes. Adv Funct Mater 2009;19(3):420–7.
- [24] Cho YJ, Yook KS, Lee JY. A universal host material for high external quantum efficiency close to 25% and long lifetime in green fluorescent and phosphorescent OLEDs. Adv Mater 2014;26(24):4050–5.