

Novel host materials based on phenanthroimidazole derivatives for highly efficient green phosphorescent OLEDs



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ABSTRACT

Two novel host materials, 2-(4,4''-di(9H-carbazol-9-yl)-[1,1':3',1''-terphenyl]-5'-yl)-1-(4-(trifluoromethyl)phenyl)-1H-phenanthro[9,10-d]imidazole (DCzBPI) and N4,N4,N4'',N4''-tetraphenyl-5'-(1-(4-(trifluoromethyl)phenyl))-1H-phenanthro[9,10-d] (DTPABPI), were designed and synthesized. The electroluminescence (EL) characteristics by using them as host materials were investigated. Results were found both of them showed good performance, especially for DCzBPI. The maximal external quantum efficiency is up to 21.2% and the brightness is up to 63,610 cd/m² with current efficiency of 53.8 cd A⁻¹.

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1. Introduction

Host materials in phosphorescent organic light-emitting diodes (PhOLEDs) have drawn intensive attention owing to their capability to prevent triplet–triplet annihilation and concentration quenching effect [1–3]. During the past decade, much effort has been made to develop highly efficient host materials, and some significant advances have been reported [4–11]. For example, external quantum efficiencies of over 15%, even approaching 30% have been accessible in red, green, and blue (RGB) PhOLEDs by using different host materials. Most of them for hosts are the derivatives of including triphenylamine [12], carbazole [13], fluorene [14]. However, these units are predominantly hole transporters, and a key requirement for an efficient host material is balanced carriers in hosts and emitters. In view of this, the strategy to design and synthesis of hosts with both hole- and electron-transporting properties have been attracting extensive interests. Many relevant studies have been extensively applied for phosphorescent emitters [15–17]. Ge et al. reported triphenylamine/imidazole derivatives as host materials for green phosphorescent OLEDs in 2008 [18]. Subsequently, Ma et al. synthesized a carbazole/oxadiazole hybrid

molecule as host materials, the maximum external quantum efficiency (EQE) was up to 20.2% for green and 18.5% for deep red electrophorescence [19]. Recently, Padmaperuma et al. demonstrated a host containing diphenylamine unit for blue PhOLEDs with EQE of 17.1% [20]. The strategy incorporating p-type and n-type units into a single molecule has been extensively applied to design host materials [11,21]. Nevertheless, the intramolecular donor–acceptor interaction lowers the triplet energy levels of the materials, which can lead to reverse energy transfer and result in undesirable efficiency decline in PhOLEDs [22]. Therefore, design of host materials with high triplet energy levels and balanced hole- and electron-transporting properties is still a huge challenge.

In this paper, we designed and synthesized two novel hosts integrating electron-donating arylamine and electron-accepting phenanthroimidazole moieties. In the molecules, the arylamine and phenanthroimidazole moieties are extended to different planes in order to decrease the interaction of donor and acceptor units. Both of them show high triplet energy levels. Electroluminescence (EL) characteristics were investigated and found to be good candidates for green PhOLEDs host materials.

2. Experimental

2.1. Materials and characterization

Phenanthrene-9,10-dione, 3,5-dibromobenzaldehyde, 4-(trifluoromethyl)aniline, (4-(diphenylamino)phenyl)boronic

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acid were purchased from Tokyo Chemical Industry Co., Ltd. 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole was synthesized followed the method reported literature [15]. All other reagents were used as received from commercial sources, unless otherwise stated. ^1H and ^{13}C NMR spectra were determined in CDCl_3 with a Bruker DRX 400 or 100 MHz spectrometer. Chemical shifts (δ) were given relative to tetramethylsilane (TMS). Elemental analyses were recorded with a Perkin-Elmer 2400 analyzer. UV–vis absorption and steady-state photoluminescence (PL) spectra of the derivatives in dichloromethane solutions were measured with HITACHI U3010 and Perkin-Elmer Lambda 950 spectrophotometers. The room-temperature (RT) lifetime measurements were determined on a FSP920-combined time-resolved and steady-state fluorescence spectrometer (Edinburgh Instruments) equipped with a F900 microsecond flash lamp. Differential scanning calorimetry (Mettler Toledo DSC I) was calibrated with an indium standard and employed to characterize the glass-transition temperature (T_g) at $10^\circ\text{C min}^{-1}$ under nitrogen flushing. Thermogravimetric analyses (TGA) were carried out using a Perkin-Elmer thermogravimeter (model TGA7) under a dry nitrogen gas flow at a heating rate of $10^\circ\text{C min}^{-1}$. The voltammetric characterization of the redox process was performed with a computer-controlled CHI 600C Electrochemical Workstation using a Pt disk working electrode of 0.01 cm^2 , a Pt wire counter electrode, and a Ag/AgCl reference electrode in a conventional three-electrode cell containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte with a scan rate of 100 mV/s. The procedure was performed in dry dichloromethane solutions for oxidation process or dry N,N-dimethylformamide solutions for reduction process at room temperature and a nitrogen atmosphere was maintained over the solution during measurements.

2.2. Synthesis of compounds DCzBPI and DTPABPI

2.2.1. Preparation of 2-(3,5-dibromophenyl)-1-(4-(trifluoromethyl)phenyl)-1H-phenanthro[9,10-d]imidazole (Br_2BPI)

A mixture of 4-(trifluoromethyl)aniline (16.11 g, 100 mmol), phenanthrene-9,10-dione (4.16 g, 20 mmol), 3,5-dibromobenzaldehyde (5.27 g, 20 mmol), ammonium acetate (6.55 g, 85 mmol), and acetic acid (200 mL) was heated for 12 h under argon in an oil bath maintained at 125°C . After cooling and filtering, the residue was purified by column chromatography (dichloromethane/petroleum ether 60–90°C, 1/1, v/v) on silica gel to yield a white powder. Yield, 45.6%; ^1H NMR (400 MHz, CDCl_3): δ 8.85 (d, 1H, $J=8.08$ Hz), 8.81 (d, 1H, $J=8.22$ Hz), 8.73 (d, 1H, $J=8.21$ Hz), 7.97 (d, 2H, $J=8.31$ Hz), 7.79 (t, 1H, $J=8.14$ Hz), 7.73–7.65 (m, 4H), 7.60–7.56 (m, 3H), 7.38–7.32 (m, 1H), 7.18 (d, 1H, $J=8.44$ Hz).

2.2.2. N4,N4,N4'',N4''-tetraphenyl-5'-(1-(4-(trifluoromethyl)phenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)-[1,1':3',1''-terphenyl]-4,4''-diamine (DTPABPI)

To a suspended solution of Br_2BPI (1.19 g, 2.0 mmol), 4-(diphenylamino) phenylboronic acid (1.45 g, 5 mmol), and bis(triphenylphosphine) palladium(II) chloride (0.25 g, 0.20 mmol) in toluene (100 mL) was added sodium carbonate aqueous solution (2 M, 5 mL) under argon. The reaction mixture was refluxed for 24 h and then water (50 mL) added. The crude compound was extracted into dichloromethane. After removing solvent under reduced pressure, the residue was purified by column chromatography (dichloromethane/petroleum ether 60–90°C, 7/3, v/v) on silica gel to yield a white powder. Yield, 32.2%. The crude product was further sublimated before characterization. ^1H NMR (400 MHz, CDCl_3): δ 8.91 (d, 1H, $J=7.43$ Hz), 8.80 (d, 1H, $J=8.17$ Hz), 8.73

(d, 1H, $J=7.43$ Hz), 7.92 (d, 2H, $J=7.40$ Hz), 7.75–7.55 (m, 8H), 7.31–7.06 (m, 31H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.7, 147.6, 142.4, 141.3, 137.8, 134.2, 132.1, 131.8, 130.7, 130.0, 129.6, 129.5, 129.3, 128.4, 127.8, 127.5, 127.4, 127.3, 127.1, 126.5, 126.2, 125.9, 125.7, 125.2, 124.9, 124.5, 124.4, 123.8, 123.1, 123.0, 122.9, 122.7, 122.2, 120.7. Anal. Calcd for $\text{C}_{64}\text{H}_{43}\text{F}_3\text{N}_4$: C, 83.10; H, 4.69; N, 6.06. Found: C, 82.88; H, 4.67; N, 5.99.

2.2.3. 2-(4,4''-di(9H-carbazol-9-yl)-[1,1':3',1''-terphenyl]-5'-yl)-1-(4-(trifluoromethyl)phenyl)-1H-phenanthro[9,10-d]imidazole (DCzBPI)

To a solution of Br_2BPI (0.953 g, 1.6 mmol), 5 (1.35 g, 3.68 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.11 g, 0.10 mmol) in toluene (100 mL) was added Et_4NOH (3.7 mL of a 20% aqueous solution) under argon. The reaction mixture was refluxed for 24 h and then water (50 mL) added. The crude compound was extracted into dichloromethane. After removing solvent under reduced pressure, the residue was purified by column chromatography (dichloromethane/petroleum ether 60–90°C, 9/1, v/v) on silica gel to yield a white powder. Yield, 31.5%. The crude product was further sublimated before characterization. ^1H NMR (400 MHz, CDCl_3): δ 8.98 (d, 1H, $J=8.21$ Hz), 8.84 (d, 1H, $J=8.20$ Hz), 8.76 (d, 1H, $J=8.21$ Hz), 8.18 (d, 4H, $J=7.82$ Hz), 8.05 (d, 2H, $J=8.21$ Hz), 7.97 (s, H), 7.79 (t, 1H, $J=8.14$ Hz), 7.86–7.79 (m, 5H), 7.73–7.67 (m, 4H), 7.59 (t, 1H, $J=7.78$ Hz), 7.51–7.44 (m, 8H), 7.39–7.30 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 150.1, 142.4, 141.3, 140.8, 139.3, 137.9, 137.6, 132.4, 132.1, 131.2, 130.1, 129.6, 128.6, 128.5, 128.0, 127.6, 127.5, 127.4, 127.3, 127.1, 126.7, 127.6, 126.1, 125.4, 125.0, 124.5, 123.6, 132.3, 123.0, 122.6, 122.3, 120.8, 120.4, 120.2, 109.8. Anal. Calcd for $\text{C}_{64}\text{H}_{43}\text{F}_3\text{N}_4$: C, 83.46; H, 4.27; N, 6.08. Found: C, 83.01; H, 4.30; N, 5.99.

2.3. Fabrication of OLEDs

The EL devices were fabricated by vacuum deposition of the materials at 10^{-6} Torr onto Indium-tin oxide (ITO) coated glass with a sheet resistance of $10\ \Omega/\text{square}$. The patterned ITO coated glass substrates were precleaned carefully and treated with UV/O_3 plasma. Then, tris(4-(9H-carbazol-9-yl)phenyl)amine (TCTA), 4,4'-N,N'-dicarbazole-biphenyl (CBP), emissive layer, and 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) were sequentially evaporated on the substrate. The doping concentration of $\text{Ir}(\text{ppy})_3$ was controlled $\sim 6\%$. The cathode was deposited with LiF and Al. The current–voltage (I – V) characteristics were measured by a Keithley 2400 source measurement unit. The EL spectra, luminance characteristics were measured by using a PR-705 Spectroscan spectrometer.

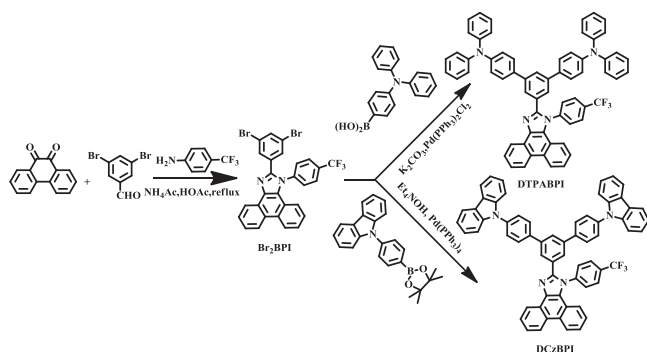
2.4. Theoretical calculations

The predications of DCzBPI and DTPABPI were carried on the huge computer origin 2000 server center using Gaussian03 program package, their ground-state structures and electronic properties were calculated by B3LYP/6–31G (d,p). Their molecular orbitals were analyzed using the GaussView 3.0 program.

3. Results and discussions

3.1. Synthesis and characterization

The synthetic routes and molecular structures of DCzBPI and DTPABPI are depicted in the Scheme 1. The electron-accepting phenanthroimidazole moiety and electron-donating carbazole or diphenylamine moiety were introduced to one molecule. In the design of DCzBPI and DTPABPI, some phenyl ring units are introduced between the phenanthroimidazole and the arylamine groups to extend the π -conjugation length and adjust the HOMO



Scheme 1. The synthetic routes to DTPABPI and DCzBPI.

and LUMO energy levels. The important intermediate for the synthesis of DCzBPI and DTPABPI was Br₂BPI, which was synthesized by refluxing phenanthrene-9,10-dione, 3,5-dibromobenzaldehyde and 4-(trifluoromethyl)aniline and ammonium acetate in acetic acid. Then, the DCzBPI and DTPABPI were easily obtained via Suzuki couplings of Br₂BPI and (4-(diphenylamino)phenyl)boronic acid or 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-yl)phenyl)-9H-carbazole. The chemical structures of all the compounds are fully characterized by ¹H NMR, ¹³C NMR spectra, and elemental analysis.

3.2. Photophysical properties

Fig. 1 shows the absorption and fluorescent spectra of compounds DTPABPI and DCzBPI in dilute CH₂Cl₂ solution. As can be seen in Fig. 1a, DTPABPI and DCzBPI exhibit similar absorption bands at a wavelength of 250 nm, which is attributed to the π – π^* transition of their common benzene ring [23]. The longer wavelength absorption bands are located at range of 325–350 nm. For the fluorescent spectra of DTPABPI and DCzBPI, they emit blue fluorescence peaking at 393 nm for DCzBPI and 433 nm for DTPABPI. Additionally, it is worth noting that the PL spectrum of DTPABPI is more red-shifted compared with DCzBPI. It can be attributed to the stronger electron-donating character of diphenylamino groups in DTPABPI, which renders a more evident intramolecular charged transfer (ICT) behavior. Their phosphorescence spectra were measured in dilute CH₂Cl₂ solution at 77 K (Fig. 1b), the triplet energy levels were estimated from the highest-energy vibronic sub-band of the phosphorescence spectra. All of them show high triplet energy levels (3.04 eV for DTPABPI, and 3.09 eV for DCzBPI). The high triplet energy levels, facilitating to inhibit the reverse energy transfer from the phosphorescent emitter back to the host, can be contributed to the fluorine-substituted moieties [21,24].

3.3. Thermal properties

The thermal properties of DCzBPI and DTPABPI were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as shown in Fig. 2 and Table 1. The two compounds exhibit high thermal decomposition temperatures (*T_d* corresponding to 5% weight loss) in the range of 498–526 °C. Their glass-transition temperature (*T_g*) is 145 °C for DTPABPI and 191 °C

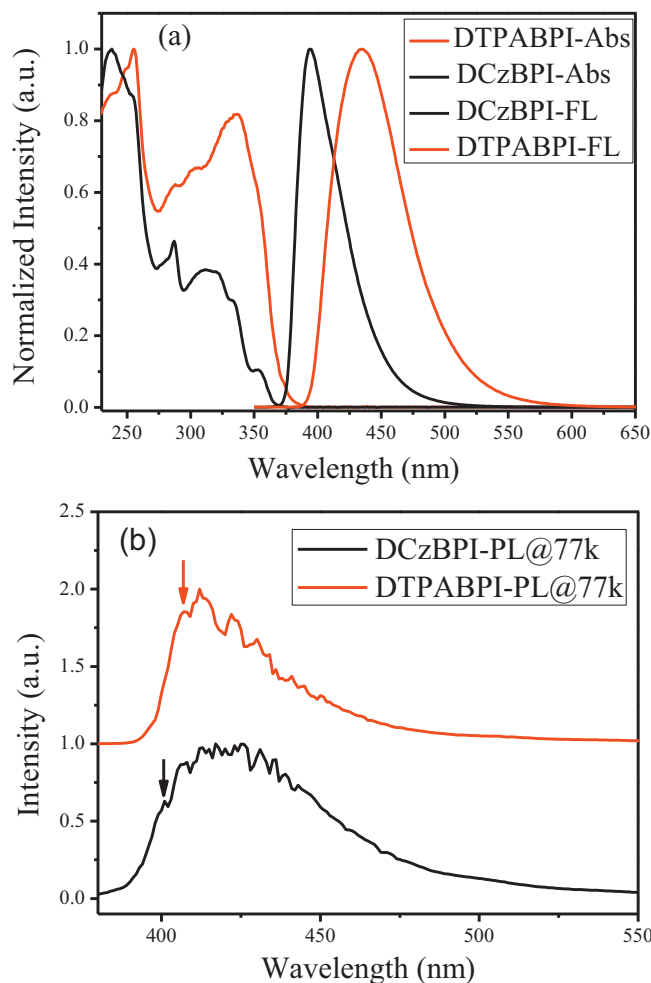


Fig. 1. UV absorption and PL spectra of DTPABPI and DCzBPI.

for DCzBPI. Obviously, their *T_g* is higher than those of widely used host materials such as CBP (62 °C) and 1,3-di(9H-carbazol-9-yl)benzene (mCP) (60 °C) [25], which indicates the introduction of phenanthroimidazole moieties enhances their morphological stability. On the other hand, the *T_g* of DCzBPI is higher than that of DTPABPI, which can be attributed to the excellent molecular rigidity of carbazole moieties [26].

3.4. Calculations

To investigate the compounds relationship between structures and properties, their ground-state structures and electronic properties were predicated using B3LYP/6-31G (d,p) level as shown in Fig. 3. The density of HOMO orbitals are mainly populated on the electron-donating arylamine moieties, while the LUMO orbitals are mainly located on electron-accepting phenanthroimidazole moiety. The density of HOMO and LUMO orbitals exhibits almost complete separation, which is preferable for efficient hole- and electron-transporting properties [18,27].

Table 1
Physical data of DTPABPI and DCzBPI.

Compound	<i>T_g</i> (°C)	<i>T_d</i> (°C)	λ_{abs} (nm)	$\lambda_{\text{em,max}}$ (nm)	<i>E_T</i> (eV)	HOMO/LUMO _{exp} (eV)	HOMO/LUMO _{cal} (eV)
DTPABPI	145	498	336	433	3.04	5.48/2.73	4.92/1.44
DCzBPI	191	526	315	393	3.09	5.46/2.87	5.33/1.58

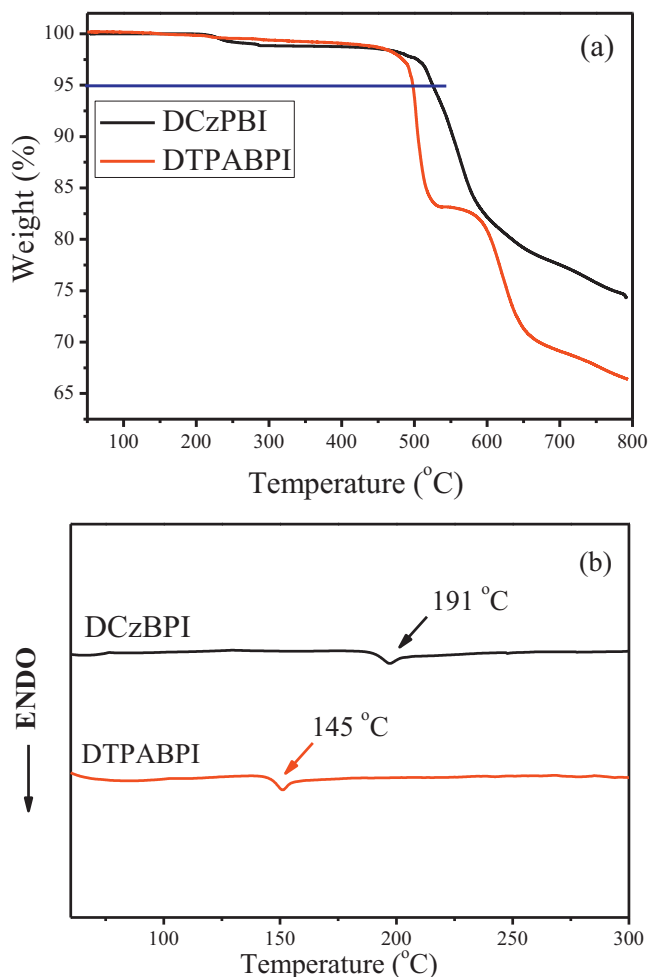


Fig. 2. (a) TGA thermograms of DTPABPI and DCzBPI recorded at a heating rate of $10^{\circ}\text{C min}^{-1}$, and (b) DSC traces of DCzBPI and DTPABPI recorded at a heating rate of $10^{\circ}\text{C min}^{-1}$.

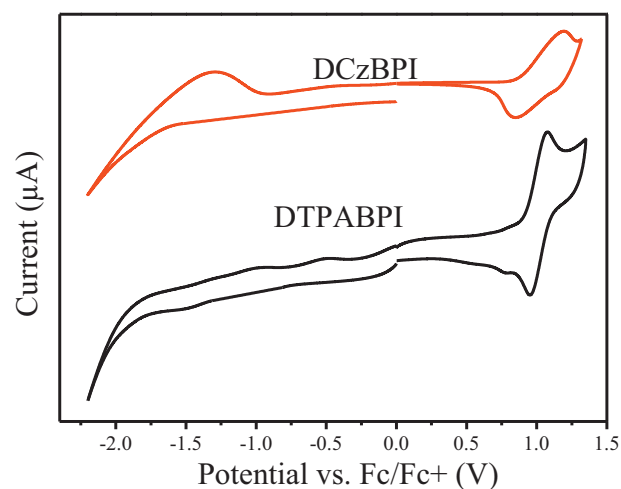


Fig. 4. Cyclic voltammograms of compounds DCzBPI and DTPABPI in CH_2Cl_2 .

3.5. Electrochemical properties

The electrochemical properties of DCzBPI and DTPABPI were investigated by the cyclic voltammetry (CV) method as shown in Fig. 4. During the anodic scan in dichloromethane, the two compounds exhibit one quasi-reversible, one-electron oxidation process, which can be assigned to the oxidation of the arylamine moiety. The HOMO energy levels were obtained from the onsets of the oxidation potentials with regard to the energy level of ferrocene (4.58 eV). The values of them are -5.46 eV for DTPABPI and -5.48 eV for DCzBPI, respectively. Then, the CV analysis gives the LUMO levels of -2.87 eV and -2.73 eV for DCzBPI and DTPABPI (Table 1). Obviously, the oxidation onset of DCzBPI is lower than that of DTPABPI.

3.6. Electroluminescent performance of PhOLEDs

Their Electroluminescent properties as host materials were studied by fabricating green devices with the configuration of

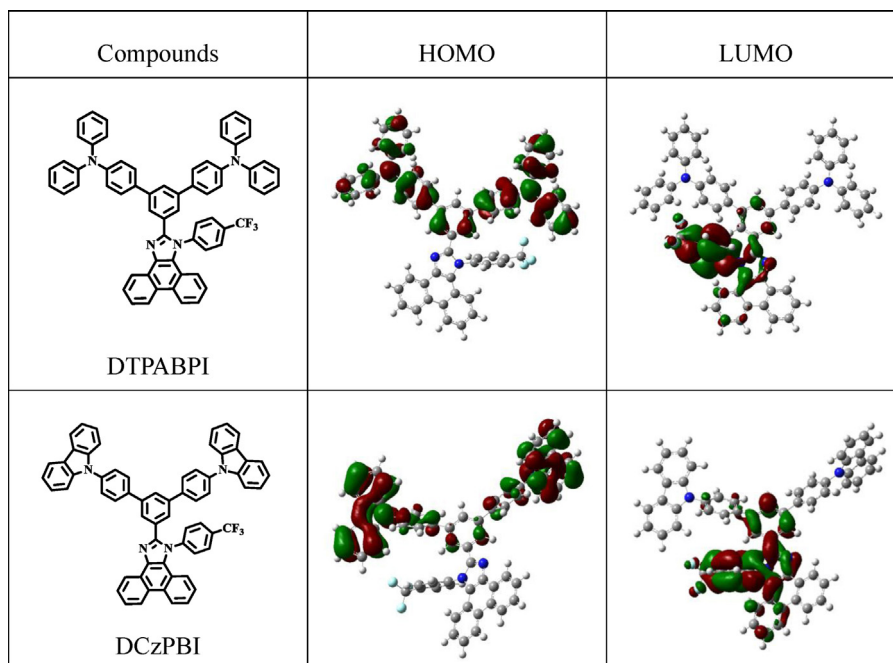


Fig. 3. Spatial distributions of HOMO and LUMO of DCzBPI and DTPABPI.

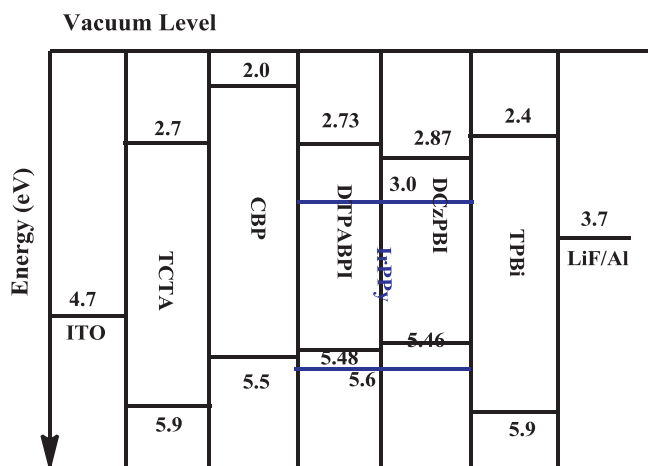


Fig. 5. Schematic energy diagram of LUMO/HOMO for DTPABPI and DCzBPI.

ITO/TCTA(20 nm)/CBP (24 nm)/DCzBPI or DTPABPI:Ir(PPy)₃ (20 nm 6%)/TPBi (30 nm)/LiF (1 nm)/Al (100 nm), where TCTA, CBP, TPBi were used as charge-transporting materials, LiF served as electron-injecting layer, Ir(PPy)₃ doped in host DCzBPI and DTPABPI was used as the emitting layer. The relative energy levels of these materials were depicted in Fig. 5. The EL spectra of these devices employing DCzBPI and DTPABPI exhibit the same peak at 512 nm with a shoulder at 542 nm as shown in Fig. 6, arising from the typical emission of the phosphor Ir(PPy)₃ [27].

Fig. 7 shows the current density–luminance (*J*–*L*) characteristics for the devices, and the EL data are summarized in Table 2. The turn-on voltage (*V*_{on}, recorded at the luminance of 1 cd m^{−2}) significantly decreased from 3.4 V of DCzBPI to 2.8 V of DTPABPI. This is due to the fact that replacement of carbazole moiety with stronger electron-donating diphenylamine unit results in lower hole injection barrier from hole-transporting layer to host materials DTPABPI and DCzBPI. The maximal brightness of these devices is up to 63,610 cd m^{−2} for DCzBPI and 40,040 cd m^{−2} for DTPABPI, respectively.

The DCzBPI-based device achieves a maximum current efficiency (CE_{max}) of 53.8 cd A^{−1} and a maximum external quantum efficiency (EQE_{max}) of 21.2% (see Fig. 8 and Table 2), which are higher than that for DTPABPI (43.2 cd A^{−1}, 17.1%). Furthermore, The DCzBPI-based device can achieve current efficiency of 50.3 cd A^{−1} and external quantum efficiency of 19.9% at 100 cd m^{−2} (see Fig. 8 and Table 2), both of which are higher than that for

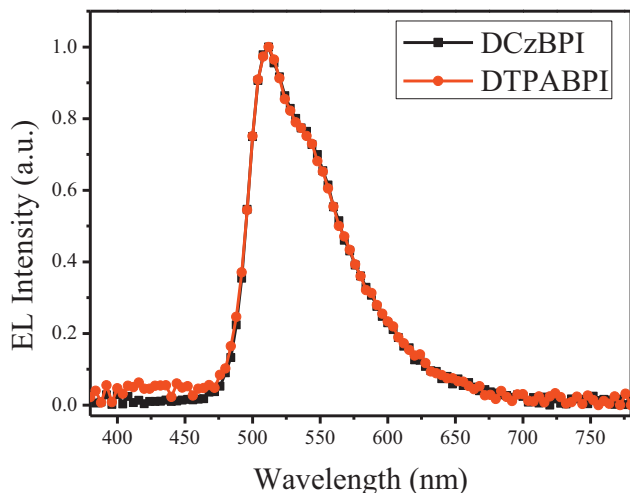


Fig. 6. Normalized EL spectra for the green PhOLEDs with different host materials.

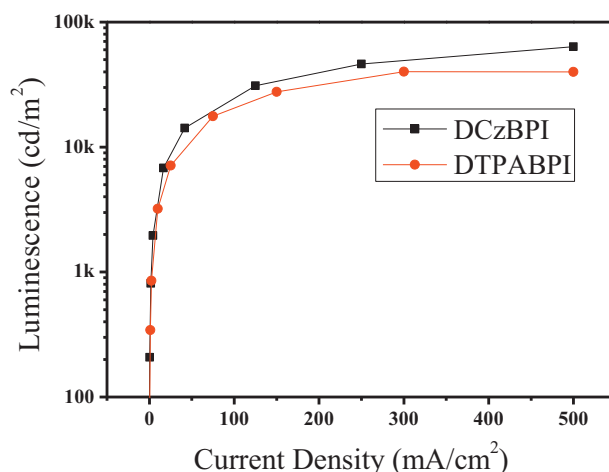


Fig. 7. Luminance at different current density for DTPABPI and DCzBPI based PhOLEDs.

DTPABPI (34.1 cd A^{−1}, 13.4%). In addition, The DCzBPI-based device shown better performance (48.2 cd m^{−2} for CE and 19.1% for EQE, respectively) at 1000 cd m^{−2}, compared to DTPABPI-based device (33.7 cd m^{−2} for CE and 13.3% for EQE, respectively). This can be attributed to the higher triplet energy level of DCzBPI (3.09 eV) compared with DTPABPI (3.04 eV), efficiently suppressing triplet energy back transfer from the guest to the host. Further optimization and detailed investigation on blue phosphorescent OLEDs, using DCzBPI and DTPABPI as host are currently under way.

To further rationalize the better performance achieved by DCzBPI as compared to that of DTPABPI, transient PL decay measurements of Ir(PPy)₃/host co-deposited (~6%, by weight) film were studied (see Fig. 9). It is found that both of the phosphorescent counts are fitted with tri-exponential decay and the average phosphorescent lifetimes for the IrPPy/DCzBPI and IrPPy/DTPABPI co-deposited film are 1.86 μs and 0.91 μs, respectively. The phosphorescent lifetimes (~1.5 μs), can be assigned to the decay of IrPPy exciton [28,29]. The longer phosphorescent lifetime for the Ir(PPy)₃/DCzBPI (1.86 μs) than that for DTPABPI (0.91 μs) is attributed to more efficient energy transfer from the host to the guest and better confinement of triplet energy on the phosphor molecules in DCzBPI/Ir(PPy)₃ film, compared to DTPABPI/Ir(PPy)₃ film [28,30].

Although these values are moderate relative to the highest values reported for Ir(PPy)₃-based PhOLEDs, it provides a simple way to realize efficient green PhOLEDs.

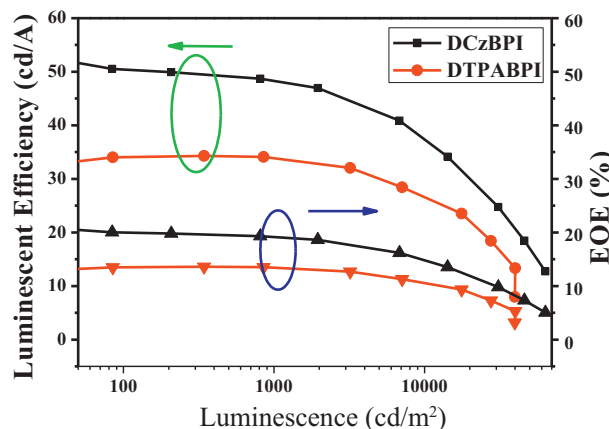


Fig. 8. The current efficiency and external quantum efficiency of DCzBPI and DTPABPI based PhOLEDs.

Table 2
Electroluminescent characteristics of the devices.

Host	V_{on} (V)	L_{max} (cd/m ²)	CE_{max} (cd A ⁻¹)	EQE_{max} (%)	@100 cd/m ²			@1000 cd/m ²		
					V (V)	CE (cd A ⁻¹)	EQE (%)	V (V)	CE (cd A ⁻¹)	EQE (%)
DTPABPI	2.8	40,040	43.2	17.1	3.7	34.1	13.4	4.7	33.7	13.3
DCzBPI	3.4	63,610	53.8	21.2	4.5	50.3	19.9	5.3	48.2	19.1

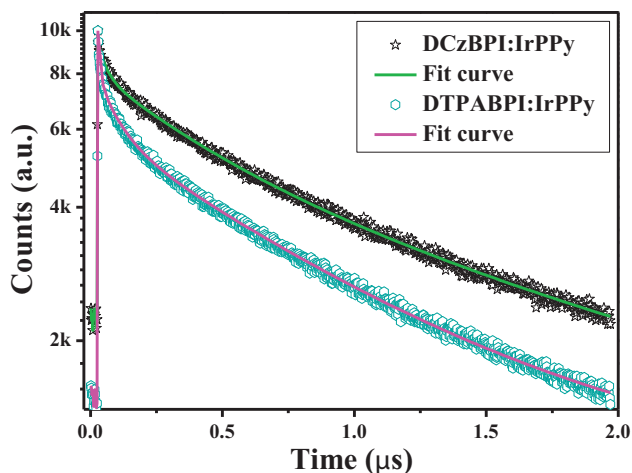


Fig. 9. Transient photoluminescence decay curves for IrPPy co-deposited film with DCzBPI and DTPABPI.

4. Conclusion

In summary, we have demonstrated two star-shaped host materials containing both electron donor and acceptor moieties. Both of them show high triplet energy levels (3.04 eV for DTPABPI, and 3.09 eV for DCzBPI). Their electrophosphorescence properties were investigated by using DCzBPI or DTPABPI as host materials. The devices hosted by DTPABPI achieve maximum external quantum efficiency of 17.1% and a maximum current efficiency of 43.2 cd A⁻¹. While the devices hosted by DCzBPI, the maximum external quantum efficiency is up to 21.2% with the CE_{max} of 53.8 cd A⁻¹. The maximal brightness of them is 63,610 cd m⁻² for DCzBPI and 40,040 cd m⁻² for DTPABPI, respectively. Our results provide a new avenue for designing highly efficient phosphorescence host materials for electroluminescent applications, in particular, for green electrophosphorescence OLEDs.

Acknowledgments

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