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# Synthesis and device properties of carbazole/benzimidazole-based host materials



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# ABSTRACT

We report two bipolar host materials bearing hole-transport benzofurocarbazole/indenocarbazole cores and an electron-transport benzimidazole moiety for red phosphorescence organic light emitting devices (PhOLEDs). The two novel host materials exhibited excellent physical properties with high thermal stabilities, appropriate HOMO-LUMO energy levels and balanced charge transport. Both of them were applied to fabricate red PhOLEDs as promising host materials, and 7,7-dimethyl-5-(4'-(1-phenyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)-5,7-dihydroindeno[2,1-b]carbazole (**ICBI**) based device demonstrated outstanding electroluminescence performance with the maximum current efficiency, power efficiency and external quantum efficiency of 33.0 cd/A, 13.9 lm/W and 18.9%, respectively.

# Introduction

Phosphorescent organic light-emitting devices (PhOLEDs), as a revolutionary technology for display industry, could hopefully replace the dominant liquid crystal displays (LCDs) market in the future, due to their unique advantages such as active and large area emitting, high luminous efficiency, long operational lifetimes and low power consumption.<sup>1–7</sup> Theoretically, phosphorescence dyes can harvest both singlet and triplet excitons with nearly 100% of internal quantum efficiency by spin-orbit coupling. Although high performance PhOLEDs have been studied extensively, there are still some problems which limit its potential applications, such as efficiency roll-off induced by concentration quenching and triplettriplet annihilation (TTA).<sup>8</sup> In general, furnishing balanced carrier transporting characteristics for effective exciton recombination to the host materials should be a valid way to improve the electroluminescence (EL) performance of PhOLEDs. Besides, the triplet energy level  $(E_T)$  of the host materials should be higher than the dopant to avoid reverse energy transfer from the guest to the host. In addition, the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the host materials are required to match to those of the neighboring materials, to benefit the hole/electron injection and to relieve the TTA processes.9-12

trial communities have been made to develop efficient red phosphorescent host materials based on polycyclic heteroaromatic hydrocarbons (PHHs).<sup>14–18</sup> Among these PHHs molecules, carbazole is a widely used molecular fragment because of its several commendable properties, including rigid molecular structure, small conjugated system, high triplet energy level and chemical stability. All of the above merits make carbazole-based compounds as promising hole-transport materials in organic light emitting devices (OLEDs).<sup>19–21</sup> Meanwhile, benzimidazole derivatives with electron-transporting ability have also been successfully used in host materials due to its high electron mobility, good thermal stability and relatively high triplet energy level. 13,22-24 Ting and his co-workers reported two novel donor-acceptor bipolar host materials by incorporating electron-accepting benzimidazole and electron-donating indolo[3,2-b]carbazole units into one molecule, which achieved a maximum external quantum efficiency, current efficiency, and power efficiency of 22%, 28 cd/A and 22.1 lm/W, respectively, with CIE coordinates of (0.65, 0.35).<sup>25</sup> Mondal and his co-workers developed two bipolar host materials composed of electron-donating carbazole linked to the sp<sup>3</sup>-hybridized C bridge of fluorene and electron-accepting benzimidazole grafted onto the C3 position of fluorene, which exhibited a high glass transition temperature of 181 °C and triplet energy of 2.72 eV. The red PhOLEDs doped with Os(bpftz)<sub>2</sub>(PPhMe<sub>2</sub>)<sub>2</sub> demonstrated maximum efficiencies (EQE) of 18.6% (18.6 cd/A and 13 lm/W).<sup>26</sup> In

In recent years, several efforts from both academic and indus-







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spite of these reports, it is still a challenge to design and synthesize ideal host materials for red PhOLEDs with high performance.

Taking advantage of the carbazole and benzimidazole in the host, two host materials, namely, 7-(4'-(1-phenyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)-7H-benzofuro [2,3-b]carbazole (FCBI) and 7,7-dimethyl-5-(4'-(1-phenyl-1H-benzo[d]imidazol-2yl)-[1,1'-biphenyl]-4-yl)-5,7-dihydroindeno [2,1-b]carbazole (ICBI) were designed, synthesized and characterized. We introduced a Nphenylbenzimidazole moiety as the acceptor to facilitate electron transport, and a benzofurocarbazole or indenocarbazole group as the electron donor, which was supposed to have a balanced charge transport. Both the carbazole and benzimidazole units own excellent carrier transport abilities and high E<sub>T</sub> values. The two heteroaromatic moieties were connected onto the para-position of a biphenvl linker to interrupt the  $\pi$ -conjugation between donor and acceptor, which was expected to have an appropriate  $E_{T}$ . Experimental results showed that both materials exhibited excellent physical properties with high thermal stabilities and suitable triplet energy for red phosphorescent emitters.

# **Results and discussion**

#### Synthesis

The synthetic routes for the two compounds are shown in Scheme 1. The two key intermediate compounds, 7-(4-bro-mophenyl)-7*H*-benzofuro[2,3-*b*]carbazole (**3**) and 5-(4-bro-mophenyl)-7,7-dimethyl-5,7-dihydroindeno[2,1-*b*]carbazole (**4**), were synthesized by Ullmann coupling according to the methods reported in the literature with yields of 35.6% and 60.4%, respectively, while the target compounds of **FCBI** and **ICBI** were obtained by Suzuki coupling reaction of the two intermediate compounds and the (4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)boronic acid with yield of 91.7% and 85.7%, respectively.<sup>27.28</sup> The molecular



Scheme 1. Synthetic route to target molecules.

structures of two intermediates were confirmed by <sup>1</sup>H NMR. Additionally, the final compounds were purified by column chromatography and the molecular structures were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR and high-resolution mass spectrometry (HRMS).

## Photophysical properties

Fig. 1 displayed the UV-vis absorption, fluorescence emission and phosphorescence spectra of the two compounds in dichloromethane (DCM) solution (related data were presented in Table 1). FCBI and ICBI showed quite similar absorption peaks with only a 4 nm difference. The strong absorption peak at around 300 nm could be assigned to the  $\pi$ - $\pi^*$  transition of the compounds. whereas the additional absorption peak around 330 and 360 nm could be attributed to the weak intramolecular charge transfer (ICT) from donor to the acceptor moiety. The optical energy bandgaps  $(E_g)$  of the two compounds estimated from the tailing edge of the absorption spectra were determined to be 3.28 and 3.26 eV for FCBI and ICBI, respectively. The maximum PL emission wavelengths for FCBI and ICBI were observed at 427 and 460 nm, respectively. This big Stoke shift of ICBI means that ICBI molecular has more geometrical changes at excited state than FCBI molecular. Furthermore, the triplet energies  $(E_T)$  estimated from



**Fig. 1.** Normalized UV-vis absorption, fluorescence emission spectra in dilute solution (DCM) at room temperature and phosphorescence spectra in a frozen 2-methyltetrahydrofuran at 77 K of a) **FCBI** and b) **ICBI**.

Table 1	
Physical properties	of the compounds.

Compounds	Absorption $\lambda_{max}^{a}$ [nm]	Emission $\lambda_{max}^{a}$ [nm]	$E_{g}^{b}$ [eV]	$E_{\rm T}^{\rm c}$ [eV]	HOMO <sup>d</sup> [eV]	LUMO <sup>e</sup> [eV]	$T_{g}^{f}$ [°C]	$T_m^{\mathbf{g}} [^{\circ}\mathbf{C}]$	$T_d^h$ [°C]
FCBI	356	427	3.28	2.57	-5.47	-2.19	145	270	452
ICBI	360	460	3.26	2.48	-5.42	-2.16	156	210	449

 $^a\,$  Measured in dichloromethane at a concentration of  $1.0\times 10^{-5}\,M.$ 

<sup>b</sup> Estimated from onset of the absorption spectra ( $E_g = 1241/\lambda_{onset}$ ).

<sup>c</sup> Estimated from the phosphorescence spectrum in 2-methyl-tetrahydrofuran at 77 K.

<sup>d</sup> The HOMO energy level was determined from cyclic voltammetry ( $E_{HOMO} = -4.4 - E_{ox}$ ).

<sup>e</sup> The LUMO energy level was calculated by the equation:  $E_{LUMO} = E_{HOMO} + E_{g}$ .

<sup>f</sup> Measured by DSC.

<sup>g</sup> T<sub>m</sub>: melting temperature.

 $^{\rm h}$  T\_d: decomposition temperature at 5% weight loss.

the phosphorescence spectrum in 2-methyl-tetrahydrofuran at 77 K are 2.57 eV for **FCBI**, and 2.48 eV for **ICBI**. Therefore, high bandgaps with suitable triplet energy levels of the two compounds make them promising host materials for red PhOLEDs.

# Electrochemical properties

The electrochemical behaviors of the two compounds were determined by cyclic voltammetry (CV) using a Fc/Fc<sup>+</sup> couple as the internal reference. As shown in Fig. 2, the CV curves of host materials exhibited irreversible oxidation process in DCM solution, and the onset potentials were 1.07, 1.02 V (vs. Fc/Fc<sup>+</sup>) for **FCBI** and **ICBI**, respectively. Their HOMO levels, which were -5.47 eV for **FCBI** and -5.42 eV for **ICBI**, respectively, were determined from the onset potentials while ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was applied as the internal standard. Subsequently, based on the optical energy gaps and HOMO levels, their LUMO levels were deduced to be -2.19 eV for **FCBI** and -2.16 eV for **ICBI**.

# Thermal properties

Thermal stability of host materials plays a crucial role in the lifetime of PhOLEDs, because thermal degradation and microcrystalline of small organic molecules under high temperature could significantly influence the devices' stability.<sup>29</sup> Therefore, the thermal properties of the two compounds were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC) under nitrogen atmosphere. As shown in Fig. 3 and Table 1, the TGA measurement revealed their high



**Fig. 2.** Oxidation behaviors of the two compounds in CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M TBAPF<sub>6</sub> electrolytes, scanning rate: 100 mV/s.



Fig. 3. TGA and DSC (inset) traces of the two compounds.

thermal-decomposition temperatures (T<sub>d</sub>, corresponding to 5% weight loss) of 452 °C for **FCBI** and 449 °C for **ICBI**, respectively, which exhibit a good thermal stability. We also observed a well-defined melting peak of 270 °C for **FCBI** and 210 °C for **ICBI**. It was worth noting that two compounds showed similar endothermic glass transition temperature (T<sub>g</sub>) with 145 °C and 156 °C for **FCBI** and **ICBI**, which are higher than the widely-used CBP host material.<sup>30</sup> From the data above, we strongly believe that such excellent thermal stabilities of our host materials are beneficial to form stable films surface morphology.

#### Electroluminescence of PhOLEDs

To evaluate the properties of the two compounds as host materials, the device configuration of [ITO/TAPC (40 nm)/host: Ir(piq)<sub>2</sub>(acac) (20 nm, 5 wt%)/TmPyPB (50 nm)/LiF (0.6 nm)/Al (80 nm)] were fabricated. Here, the emitting layer (EMT) was composed of 5 wt% Ir(piq)<sub>2</sub>(acac) doped into the host materials. ITO and Al were used as the anode and composite cathode, respectively. LiF was employed as the electron injection layer (EIL), 4,4'-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline) (TAPC) served as hole-transporting laver (HTL) and electron-blocking laver (EBL), and 1.3.5-tril(3pyridyl)-phen-3-yl]benzene (TmPyPB) was employed as electrontransporting layer (ETL) and its low lying HOMO (6.68 eV) can also effectively block the holes. The device and the related HOMO and LUMO energy levels of these materials were shown in Fig. 4. In addition, the current density-voltage-luminance (I-V-L) characteristics, efficiencies and EL spectra for devices were shown in Fig. 5, and their key performances results were summarized in Table 2.



Fig. 4. The energy level diagram of the materials in devices.

As revealed in Fig. 5 and Table 2, FCBI showed higher current density when compared to ICBI. This probably came from an effective charge transport in the emitting layer due to its high lying HOMO and low lying LUMO energy levels, which was favorable for the injection of the hole and electron from the adjacent HTL and ETL, respectively. However, ICBI displayed higher luminance in the same current density, which might be attributed to the more

balanced confinement of hole and electron in ICBI-based emitting layer. The current/power efficiency-luminance characteristics are shown in Fig. 5(b). The ICBI based device exhibited more efficient electroluminescence performance with the demonstrated respective current and power efficiency of 33.0 cd/A and 13.9 lm/W compared to those of 31.7 cd/A and 12.7 lm/W for FCBI. The high efficient performance is caused by its approximate LUMO energy levels with the TmPyPB, which is beneficial for electron transportation. As showed in Fig. 5(c), the maximum external quantum efficiency of 18.9% is achieved by ICBI, while 18.2% for FCBI. Both two compounds show high electroluminescence efficiency even at a high luminance, and only slight efficiency roll-off over a wide range of luminance is observed. Importantly, a high efficiency of 25.2 cd/A, 7.3 lm/W (14.7% EQE) even at 5000 cd/m<sup>2</sup> was also obtained for **ICBI**. From the EL spectra showed in Fig. 5(d), red light emissions with the respective emission peaks of 603 and 602 nm (the corresponding CIE coordinates of (0.62, 0.38) and (0.62, 0.38) at 8 V) for two compounds based device are proved. We believe that the electroluminescence performance could be further improved via the optimizing device configurations.

To further access the bipolar transporting characteristics of two compounds, hole and electron only devices were fabricated with the structure of [ITO/PEDOT:PSS (40 nm)/NPB (5 nm)/host (60 nm)/NPB (5 nm)/Al (80 nm)] for the hole, and [ITO/TmPyPB (5 nm)/host (60 nm)/TmPyPB (5 nm)/LiF (0.5 nm)/Al (80 nm)] for the electron. The I-V characteristics of the hole-only and electron-only devices were shown in Fig. 6. It was clear that both of two host materials exhibited good bipolar transporting ability for their smoothly rising current density of holes and electrons with the increase of voltage. Both **FCBI** and **ICBI** revealed relatively balanced hole and electron transport abilities, which might be



**Fig. 5.** (a) Current density-voltage (*I-V*) and luminance-current density (*L-I*) (inset) characteristics; (b) current and power efficiency; (c) external quantum efficiency (EQE) *versus* current density; (d) EL spectra at 8 V of red PhOLEDs.

#### Table 2 Characteristics of OLEDs with FCBI and ICBI host materials.

Device	Host	$L_{\rm max}^{\rm a}  [{\rm cd}/{\rm m}^2]$	$\eta_{c}^{b}$ [cd/A]	$\eta_{\rm p}^{\rm b}$ [lm/W]	$\eta_{\rm ext}^{\rm b}$ [%]	CIE <sub>(x,y)</sub> <sup>c</sup>
A	FCBI	17,377	31.7, 30.9, 24.5	12.7, 10.1, 7.2	18.2, 17.6, 13.9	(0.62, 0.38)
B	ICBI	12,942	33.0, 32.9, 25.2	13.9, 10.9, 7.3	18.9, 18.7, 14.7	(0.62, 0.38)

L<sub>max</sub>: maximum luminance.

Order of measured values: maximum, then at 1000 cd/m<sup>2</sup> and 5000 cd/m<sup>2</sup>.  $\eta_c$ : current efficiency.  $\eta_p$ : power efficiency.  $\eta_{ext}$ : external quantum efficiency.

Measured form the EL spectra at 8 V by inverting chromaticity coordinates on the CIE 1931 diagram.



Fig. 6. Current density-voltage curves of hole and electron only devices.

attributed to the introduction of donor-acceptor system. In general, such above mentioned carriers transport behavior was in good agreement with the red PhOLEDs EL performances.

### Conclusion

In summary, two carbazole/benzimidazole-based triplet host materials, FCBI and ICBI, were synthesized and characterized. The twisted connection of benzimidiazole with benzofurocarbazole or indenocarbazole rigid scaffold ensures good thermal stability with high T<sub>d</sub> of 452 °C and 449 °C, respectively. Both of the two compounds were demonstrated as suitable bipolar host materials with high performances in red PhOLED devices. The red PhOLEDs based on ICBI host material with the structure of ITO/TAPC/host: Ir(piq)<sub>2</sub>(acac) (5 wt%)/TmPyPB/LiF/Al showed

superior electroluminescence performance, with maximum current, power and external quantum efficiency of 33.0 cd/A, 13.9 lm/W and 18.9%, respectively. We believe that this work could shed light on promising commercial triplet bipolar host materials with rational connection of carbazole and benzimidiazole derivatives.

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