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PAPER

# Carbazole-benzimidazole hybrid bipolar host materials for highly efficient green and blue phosphorescent OLEDs<sup>†</sup>

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In this study, we synthesized a series of bipolar hosts (**CbzCBI**, **mCPCBI**, **CbzNBI**, and **mCPNBI**) containing hole-transporting carbazole and electron-transporting benzimidazole moieties and then examined the morphological, thermal, and photophysical properties and carrier mobilities of these bipolar host materials. Altering the linking topology (C- or N-connectivity of the benzimidazole) changed the effective conjugation length and led to different excited-state solvent relaxation behavior. The N-connected compounds (**CbzNBI**, **mCPNBI**) possessed higher triplet energies ( $E_T$ ) than those of their C-connected analogues (**CbzCBI**, **mCPCBI**) by 0.23 eV. The higher values of  $E_T$  of **CbzNBI** and **mCPNBI** endowed them with the ability to confine triplet excitons on the blue-emitting guest. A blue PhOLED device incorporating **mCPNBI** achieved a maximum external quantum efficiency, current efficiency, and power efficiency of 16.3%, 35.7 cd A<sup>-1</sup>, and 23.3 lm W<sup>-1</sup>, respectively; confirming the suitability of using N-connected bipolar hosts for the blue phosphor. The donor/acceptor interactions of the C-connected analogue resulted in a lower triplet energy, making it a suitable bipolar host for green phosphors. A green-phosphorescent device incorporating **CbzCBI** as the host doped with (PBi)<sub>2</sub>Ir(acac) achieved a maximum external quantum efficiency, and power efficiency of 20.1%, 70.4 cd A<sup>-1</sup>, and 63.2 lm W<sup>-1</sup>, respectively.

# 1. Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) have attracted much attention because they can achieve 100% internal quantum efficiency when they incorporate triplet emitters.<sup>1</sup> To reduce concentration quenching (triplet–triplet annihilation) of PhOLEDs, phosphorescent metal-complex emitters are usually doped into a suitable host material.<sup>2</sup> To ensure exothermic energy transfer and well-confined triplet exciton formation on the dopant, the triplet energy ( $E_T$ ) of the host material must be higher than that of the dopant. For efficient PhOLEDs, host materials typically require good energy level match-ups with the neighboring functional layers.<sup>3</sup> In addition, host materials with good carrier transporting properties are required to increase the opportunity of electron and hole recombination within the emitting layer.<sup>4</sup> Recent research trends have drifted to the

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development of host materials possessing bipolar properties. Tailor-made bipolar host materials can be obtained through judicious selection of functional sub-structures featuring linked hole-transporting (donor) and electron-transporting (acceptor) moieties; the resulting emitting layer can, therefore, achieve balanced charge fluxes, resulting in high device performance.<sup>5</sup> In this regard, many classes of bipolar host materials have been prepared with various combinations of hole- and electrontransporting moieties. For example, carbazoles and arylamines are frequently used as hole-transporting moieties because they possess attractive hole mobilities ( $\mu_h$  ca. 10<sup>-3</sup> to 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup>  $s^{-1}$ ;<sup>8</sup> typical electron-transporting materials feature molecular structures based on oxadiazole, triazine, phenanthroline, and benzimidazole units.5b,6,7 Benzimidazole groups are used widely as functional groups that facilitate electron injection and transport.<sup>5e,7,8</sup> Recently, Ma and Yang et al. reported a series of host materials, incorporating benzimidazole/carbazole hybrids, for green phosphors; the maximum external quantum efficiency, current efficiency, and power efficiency obtained from these devices were 18.7%, 70.2 cd A<sup>-1</sup>, and 73.4 lm W<sup>-1</sup>, respectively.9 Anzenbacher et al. used the same p/n-type [1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene/carbazole and diphenylamine] moieties in their design of bipolar host materials for green PhOLEDs, achieving a maximum external quantum efficiency, current efficiency, and power efficiency of 14%, 48.2 cd A<sup>-1</sup>, and 46.0 lm W<sup>-1</sup>, respectively.<sup>10</sup> Carbazoles are widely used key

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building blocks for hole-transporting-type host materials because they possess high triplet energies and excellent holetransport properties.<sup>11</sup> For example, the most commonly used carbazole-based material, 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP), possessing a triplet energy  $(E_{\rm T})$  of 2.56 eV, has been used prominently as a host for green and red phosphorescent emitters.<sup>12-18</sup> A structurally modified variant of this host material, 1.3-bis(9-carbazolvl)benzene (mCP), behaves as a superior phosphorescent host because of its higher triplet energy ( $E_{\rm T} = 2.9$ eV).<sup>15b</sup> Although CBP and mCP possess appropriate triplet energies, their relatively low thermal and morphological stabilities [e.g., glass transition temperatures  $(T_g)$  of 62 and 60 °C, respectively],14,15a,19 and low electron drift mobilities20,21 hinder their applications as host materials in OLEDs. In this study, we combined versatile carbazole core units (N-phenylcarbazole and mCP) with an electron-deficient benzimidazole moiety to prepare new bipolar materials, applying a concise strategy to manipulate the physical properties of the bipolar host materials by changing the linking topology (C- or N-connectivity of the benzimidazole unit). We investigated the thermal, photophysical, electrochemical, and carrier-transport properties of the host materials with respect to their molecular structures. These bipolar host materials have potential practical use as hosts for highly efficient green and blue PhOLED devices.

### 2. Results and discussion

#### 2.1 Synthesis

Scheme 1 presents the synthetic routes that we followed to prepare the bipolar host materials CbzCBI, CbzNBI, mCPCBI, and mCPNBI. We obtained CbzCBI and CbzNBI in 67% and 62% yields, respectively, through Negishi couplings of the organozinc intermediate 3, prepared through lithium/bromine exchange of 2-bromo-N-phenylcarbazole (2) followed by treatment with zinc(II) chloride, with the brominated diphenylbenzimidazole derivatives  $4^{5c}$  and  $5^{5c}$  respectively. During the preparation of this manuscript, CBzCBI used to serve as the green host is reported by Park et al.<sup>22</sup> We isolated mCPCBI and mCPNBI in 54% and 45% yields, respectively, after Negishi and Suzuki couplings, respectively. We obtained (in 84% yield) the key intermediate for both of these products, 1-(3-bromocarbazolyl)-3-carbazolylbenzene (7), through treatment of 1,3-dicarbazolylbenzene (6) with N-bromosuccinimide (NBS). The organozinc intermediate 8 (boronic ester 9) used for the Negishi (Suzuki) coupling was prepared through treatment of 7 sequentially with *n*-BuLi and zinc(II) chloride (isopropyl pinacol borate).

#### 2.2 Thermal analysis

We used differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to characterize the thermal properties of **CbzCBI**, **CbzNBI**, **mCPCBI**, and **mCPNBI** (Table 1). The mCP-linked compounds (**mCPCBI**, **mCPNBI**) exhibit much higher decomposition temperatures ( $T_d$ , corresponding to 5% weight loss; 432–435 °C) and glass transition temperatures ( $T_g =$ 151 °C) relative to those of the *N*-phenylcarbazole-based analogues (**CbzCBI**, **CbzNBI**), consistent with their greater molecular weights. Interestingly, the glass transition



Scheme 1 Synthetic routes toward bipolar host materials, CbzCBI, CbzNBI, mCPCBI, and mCPNBI and their chemical structures.

temperatures of the carbazole–benzimidazole hybridized bipolar hosts having the same molecular weight (**CbzCBI** and **CbzNBI**; **mCPCBI** and **mCPNBI**) were identical, regardless of the linking topology (C- or N-connectivity of the benzimidazole unit to the carbazole moiety). In contrast, the C-linked species (**CbzCBI**, **mCPCBI**) possessed slightly higher thermal stabilities than those of their N-connected counterparts (**CbzNBI**, **mCPNBI**). A high glass transition temperature is desirable for a host material to be used in a PhOLED because it suppresses the formation of aggregates and prevents morphological changes of the amorphous organic layer upon heating.<sup>23</sup> The high values of  $T_g$  and  $T_d$ for these compounds imply that they are capable of enduring not only vacuum thermal sublimation—a general requirement for PhOLED fabrication—but also the inevitable joule heating that would occur during device operation.

#### 2.3 Photophysical properties

Fig. 1 displays UV-Vis absorption and photoluminescence (PL) spectra (recorded at room temperature) of these compounds in

	$T_g/^{\circ}C$	$T_{\rm m}/^{\circ}{\rm C}$	$T_{\rm d}/^{\circ}{\rm C}$	$E^{\text{ox}}/\text{V}^a$	$E_{1/2}^{\mathrm{red}}/\mathrm{V}^a$	$\lambda_{abs}/nm$ , sol. <sup><i>a</i></sup> /film	$\lambda_{\rm PL}/\rm nm,  sol.^{\it b}/\rm film$	$E_{\rm T}/{\rm eV}$	(HOMO <sup>c</sup> /LUMO/E <sub>g</sub> )/eV
CbzCBI	117	286	371	1.21	-2.00	304, 327/309, 332	402/425	2.49	-5.52/-2.32/3.2
CbzNBI	117	n.d.	351	1.31	-2.15	295, 525/297, 551 297/300 292/296	352/390	2.30	-5.62/-2.22/3.4
mCPNBI	151	n.d.	432	1.28	-2.17	292/296	360/392	2.73	-5.8/-2.36/3.44

Table 1 Physical properties of CbzCBI, mCPCBI, CbzNBI, and mCPNBI

<sup>*a*</sup> On-set potential. <sup>*b*</sup> In CH<sub>2</sub>Cl<sub>2</sub>, PL spectra were obtained by the excitation at the absorption maxima in solution. <sup>*c*</sup> Determined by AC-2 measurements. LUMO = HOMO +  $E_g$ . The value of  $E_g$  was calculated from the absorption onset of the solid film. <sup>*d*</sup> Not detected.

various solutions and in the form of solid thin films, as well as their phosphorescence spectra in EtOH at 77 K; Table 1 summarizes the data. The absorption, fluorescence, and phosphorescence maxima depended on the *N*-phenylbenzimidazole linking topology (C- or N-connectivity) to the carbazolyl moiety. Remarkable red-shifts appeared in the spectra of C-connected compounds (CbzCBI, mCPCBI) relative to those of their N-connected counterparts (CbzNBI, mCPNBI).

For example, the absorption spectrum of CbzCBI displays an additional broad peak centered at 327 nm, whereas its N-linked counterpart CbzNBI provided a peak centered at 297 nm. We ascribe this long wavelength  $\pi$ - $\pi^*$  electronic transition of **CbzCBI** to the extended  $\pi$  conjugation resulting from Cconnection between the N-phenylbenzimidazole acceptor and the carbazole donor. We assign the absorption peak centered near 300 nm to the  $\pi$ - $\pi$ \* electronic transition of the donor moiety (N-phenylcarbazole). The signals in the PL spectra of these four compounds in the form of neat films were red-shifted by 20-30 nm relative to those in CH<sub>2</sub>Cl<sub>2</sub> solution, presumably because of different dielectric surroundings in the solid state. Fig. 1 also displays the UV and PL spectra of CbzCBI, mCPCBI, CbzNBI, and mCPNBI in various organic solvents. The absorption spectra of these four compounds in cyclohexane, toluene, CH2Cl2, and MeCN are nearly identical. Such solvent-independent absorption spectra suggest that the Franck-Condon excited



Fig. 1 Room-temperature absorption and PL spectra of CbzCBI, mCPCBI, CbzNBI, and mCPNBI in various solutions and in neat films, as well as phosphorescence (Phos) spectra recorded from their EtOH solutions at 77 K.

states are subjected to rather small changes in dipole moment with respect to the ground states.<sup>24</sup> The corresponding PL spectra, however, revealed pronounced solvent-dependent emission signals, especially for the C-linked bipolar molecules CbzCBI and mCPCBI. The different levels of dependence of the emission spectra of CbzCBI and mCPCBI on the solvent polarity relative to those of CbzNBI and mCPNBI imply different behaviors of the excited states in these two sets of bipolar molecules. In the compounds featuring carbazole moieties linked to the N-phenylbenzimidazole acceptor via C-connections, the emission spectral shift was proportional to the solvent polarity. suggesting a mechanism involving rapid photo-induced electron transfer (PET) within the bipolar molecule.<sup>25</sup> The PET process would lead to a large change in the dipole moment in the excited state, rendering the excited state highly sensitive to the dielectric environment, thereby providing fluorescence solvatochromism. On the other hand, the spectra of the N-connected analogues CbzNBI and mCPNBI featured broad emission peaks near 450 nm, rather than red-shifting of the emission maxima, upon increasing the solvent polarity. This solvent relaxation process involving two emitting species is consistent with a reversible excited-state two-step reaction, in which the emission is contributed from the locally (Frank-Condon) excited (LE) and charge transfer (CT) emissions. The overlapped LE and CT emissions are probably due to weak orbital interactions between the donor and acceptor units in the N-connected bipolar molecules, resulting in lower electron transfer rate constants. Notably, the triplet energies  $(E_{\rm T})$  of **CbzCBI** and **mCPCBI** (2.49 and 2.50 eV, respectively), determined from the highest energy vibronic sub-band of the phosphorescence spectra, were significantly lower than those of CbzNBI and mCPNBI (2.72 and 2.73 eV, respectively). The values of  $E_{\rm T}$  of CbzCBI and mCPCBI are sufficiently high for them to host the green phosphorescent bis(2-phenylpyridinato)iridium(III) acetylacetonate emitter [(PPy)<sub>2</sub>Ir(acac)], which exhibits a value of  $E_{\rm T}$  of 2.3 eV.<sup>25</sup> We suspected that CbzNBI and mCPNBI, with their high values of  $E_{\rm T}$ , might serve as hosts for the blue emitter bis[4,6-(diffuorophenyl)-pyridinato- $N, C^{2'}$ ]picolinate (FIrpic), which has a value of  $E_{\rm T}$  of 2.62 eV.<sup>26</sup>

#### 2.4 Crystal structure

We obtained crystals of **CbzCBI** suitable for X-ray diffraction analysis, through slow evaporation of the solvent from a CHCl<sub>3</sub>/ hexane solution. The crystal data were summarized in Table S1 (ESI†). In the crystals, two **CbzCBI** molecules were found to pair up with opposite orientations due to the donor/acceptor interactions. There are two sets of face-to-face packings, one is



Fig. 2 Selected molecular packing in the unit cell and molecular structure of **CbzCBI**. Selected dihedral angles: C(16)-C(17)-C(20)-C(21), 37.6°; N(1)-C(13)-C(14)-C(15), 28.7°.

between the phenylene rings bridging carbazole and benzimidazole with a closest point-to-point distance of *ca.* 3.65 Å, another one is between the *N*-phenyl groups of benzimidazole with a closest point-to-point distance of *ca.* 3.75 Å, suggesting negligible intermolecular  $\pi$ - $\pi$  interactions (Fig. 2). This large intermolecular separation resulted from the molecule's twisted conformation; the dihedral angles of the carbazole/phenylene linker and phenylene linker/benzimidazole units of 37.6° and 28.7°, respectively, render the molecule rather bulky. A lack of intermolecular interactions in the solid state would benefit the formation of an amorphous thin film by vacuum deposition.

#### 2.5 Electrochemical properties

We used cyclic voltammetry (CV) to probe the electrochemical properties of the bipolar compounds CbzCBI, CbzNBI, mCPCBI, and mCPNBI, with tetra(n-butyl)ammonium hexafluorophosphate (TBAPF<sub>6</sub>) in  $CH_2Cl_2$  and tetra(n-butyl)ammonium perchlorate (TBAP) in DMF as supporting electrolytes for the oxidation and reduction scans, respectively. Table 1 summarizes the measured redox potentials. The irreversible oxidations during the first CV scan of the four bipolar molecules were due to the dimerization or electropolymerization of the carbazole units at the C3 and/or C6 positions. The oxidation onsets of CbzCBI, CbzNBI, mCPCBI, and mCPNBI occurred at 1.21, 1.31, 1.24, and 1.28 V (vs. AgCl), respectively (Fig. 3). Once again, these values closely correlate to the degree of  $\pi$ -conjugation, in which the higher degree of  $\pi$ -conjugation in the C-connected bipolar molecules CbzCBI and mCPCBI impart lower oxidation potentials. In the reduction scans, C-connected



Fig. 3 Cyclic voltammograms of CbzCBI, CbzNBI, mCPCBI, and mCPNBI; 0.1 M TBAP (reduction) in DMF and 0.1 M TBAPF<sub>6</sub> (oxidation) in CH<sub>2</sub>Cl<sub>2</sub> were used as supporting electrolytes. A glassy carbon electrode was used as the working electrode; scan rate: 100 mV s<sup>-1</sup>.

molecules CbzCBI and mCPCBI exhibited quasi-reversible reduction waves, arising from their N-phenylbenzimidazole segments, in which slightly extended  $\pi$ -conjugations as N-phenylbenzimidazole connected to the C3 of carbazole are expected. Obviously, the reduction on-sets of CbzNBI and mCPNBI are at higher potentials as compared to those of C-connected counterparts, suggesting the electron distributions on their lowest unoccupied molecular orbitals (LUMOs) are solely localized on the N-phenylbenzimidazole moieties. Because of the lack of reversibility of the oxidation scans, we determined the energy levels of highest occupied molecular orbitals (HOMOs) using photoelectron yield spectroscopy (Riken AC-2); we calculated the LUMO energy levels from the HOMO energy levels using the equation LUMO = HOMO +  $E_g$ , where  $E_g$  is the optical band gap determined from the onset wavelength of the absorption band. Table 1 summarizes the calculated HOMO and LUMO energies. The lower energy gaps of CbzCBI, mCPCBI as compare to their counterparts CbzNBI, mCPNBI are accounted for their shallow HOMO and lower LUMO energy levels.

#### 2.6 Charge carrier mobility

To further understand the charge-carrier transport properties of CbzCBI, mCPCBI, CbzNBI, and mCPNBI, we used the time-offlight (TOF) technique<sup>27</sup> to evaluate the carrier mobilities. Fig. 4 (a) displays representative TOF transient for holes of CbzCBI. The transit time,  $t_{\rm T}$ , can be evaluated from the intersection point of two asymptotes in the double-logarithmic representation of the TOF transient. It is then used to determine the carrier mobilities, according to the equation  $\mu = d^2/Vt_T$ , where d is the sample thickness and V is the applied voltage. Fig. 4(b) reveals that the field dependence of the hole mobility follows the nearly universal Poole-Frenkel relationship, with values in the range from 3  $\times$  10^{-5} to 8  $\times$  10^{-6} cm² V^{-1} s^{-1}. In contrast, the TOF transient for electrons exhibited strong dispersive photocurrents, which could not be used to determine the electron mobility. For the other three compounds, the transient photocurrent signals were too weak for us to evaluate their mobilities using the TOF technique.



**Fig. 4** (a) Representative TOF transients for **CbzCBI** (thickness: 1.1  $\mu$ m;  $E = 5.4 \times 10^5$  V cm<sup>-1</sup>). Inset: double-logarithmic plot. (b) The hole mobility of **CbzCBI** plotted with respect to  $E^{1/2}$ .



**Fig. 5** Current density–voltage (I-V) characteristics of (a) hole- and (b) electron-only devices.

Next, we fabricated carrier-only devices to investigate the effect of the compounds on the transport characteristics. We prepared hole-only single-carrier devices, having the device structure indium tin oxide (ITO)/ $\alpha$ -NPD (20 nm)/compounds (60 nm)/ $\alpha$ -NPD (20 nm)/LiF/Al, to evaluate the hole transport behavior of **CbzCBI**, mCPCBI, CbzNBI, and mCPNBI (Fig. 5 (a)).

With its high-lying LUMO, we used  $\alpha$ -NPD to limit the electron carrier. The lowest turn-on voltage was that provided by the

device incorporating **CbzCBI**, indicating that the most favorable hole-transport occurred in the **CbzCBI** thin film, probably because preferential molecular alignment in the solid state created suitable transport channel for holes. To assess the electron transport properties, we fabricated electron-only devices having the device structure ITO/BCP (30 nm)/compounds (60 nm)/TPBI (20 nm)/LiF/Al (Fig. 5(b)). Here, BCP served as the hole-blocking layer to impede the hole current in the devices. The similar turn-on voltages for the devices featuring each of the four compounds suggest that they have comparable electrontransport abilities, presumably because of their similar electrontransport structures.

# 2.7 OLED characteristics

In view of the favorable triplet energy gaps of **CbzCBI** (2.49 eV) and mCPCBI (2.50 eV), we selected bis(2-phenylpyridinato) iridium(III) acetylacetonate (PPy)<sub>2</sub>Ir(acac)<sup>25</sup> and bis(2,N-diphenylbenzimidazolito) iridium(III) acetylacetonate (PBi)<sub>2</sub>Ir(acac)<sup>28</sup> (see Scheme 2 for structures) as green emitters for electrophosphorescent devices having the configuration ITO/polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) nm)/9,9-di[4-(di-p-tolyl)aminophenyl]fluorene (30)(DTAF) (40 nm)/host:dopant 8 wt% (30 nm)/1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene (TPBI) (30 nm)/LiF/Al. Here, we used the conducting polymer PEDOT:PSS as the hole injection layer (HIL) and bulky DTAF as the hole transporting layer (HTL) to facilitate hole transport, due to its good hole injection and transporting capability with limited intermolecular interactions in the solid state.<sup>29</sup> We expected the low HOMO/LUMO energy levels of TPBI<sup>30</sup> to benefit hole blocking and facilitate electron injection and transport. LiF and Al served as the electroninjection layer and cathode, respectively. Table 2 summarizes the EL characteristics of these PhOLEDs.

Fig. 6 presents the current density-voltage-luminance (I-V-L)characteristics, device efficiencies, and EL spectra of the devices incorporating CbzCBI and mCPCBI doped with green phosphors (devices A1, A2, B1, and B2). These devices exhibited turnon voltages of 2.0-2.5 V (defined as the voltage at which EL became detectable), high external quantum efficiencies (17.8-20.1%, 66.9-70.4 cd A<sup>-1</sup>), high power efficiencies (59.3-67 lm  $W^{-1}$ ), and maximum brightnesses of 125 700–152 000 cd m<sup>-2</sup>. In the series of devices A and B, the turn-on voltages of the devices incorporating CbzCBI (which featured a lower injection barrier for holes at the DTAF-CbzCBI interface) as host were slightly lower (ca. 2 V) than those of the devices incorporating mCPCBI. Furthermore, the CbzCBI-based devices required lower driving voltages (4.7-4.9 V at a practical brightness of 1000 cd m<sup>-2</sup>) than those of the corresponding mCPCBI-based devices, consistent with our results obtained using the hole-only single-carrier



Scheme 2 Structures of the heavy metal complexes used in this study.

Table 2 EL performance of devices incorporating various hosts and emitters

Device	Host:dopant <sup>a</sup>	$V_{\rm on}{}^c/{\rm V}$	<i>L</i> = 1000 nit (V, %)	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$I_{\rm max}/{\rm mA~cm^{-2}}$	$\eta_{\text{ext}} \max (\%, \text{cd } \mathbf{A}^{-1})$	$\eta_{\rm p}$ max/lm W <sup>-1</sup>	CIE1931 ( <i>x</i> , <i>y</i> )		
A1	CbzCBI:PPy2Iracac	2.0	4.7, 17.7	152 000 (9.5 V)	1800	17.8, 67.6	59.3	0.33, 0.64		
A2	CbzCBI:PBi <sub>2</sub> Iracac	2.0	4.9, 19.1	150 000 (9.5 V)	2100	20.1, 70.4	63.2	0.38, 0.60		
B1	mCPCBI:PPy2Iracac	2.5	5.2, 17.5	138 000 (10.5 V)	1250	17.9, 66.9	67	0.34, 0.63		
B2	mCPCBI:PBi <sub>2</sub> Iracac	2.5	5.7, 19.5	125 700 (11.5 V)	1780	19.6, 67.8	63.5	0.38, 0.59		
C3	CbzNBI:FIrpic <sup>b</sup>	2.5	7, 13	38 500 (14 V)	680	13.5, 28.7	25.8	0.16, 0.36		
D3	mCPNBI:FIrpic <sup>b</sup>	3.5	8.1, 15.8	47 200 (14.5 V)	1310	16.3, 35.7	23.3	0.17, 0.37		
<sup>d</sup> Davies configuration: ITO/DEDOT (20 nm)/DTAE (40 nm)/host:donant 8 utl/ (20 nm)/TPDI (20 nm)/LiE/A1 <sup>b</sup> Davies configuration: ITO/DEDOT										

<sup>*a*</sup> Device configuration: ITO/PEDOT (30 nm)/DTAF (40 nm)/host:dopant 8 wt% (30 nm)/TPBI (30 nm)/LiF/Al. <sup>*b*</sup> Device configuration: ITO/PEDOT (30 nm)/DTAF (40 nm)/host:FIrpic 12 wt% (30 nm)/TAZ (30 nm)/LiF/Al. <sup>*c*</sup> Turn-on voltage at which emission became detectable (10<sup>-2</sup> cd m<sup>-2</sup>).



Fig. 6 (a) I-V-L characteristics, (b) plots of EL efficiency *versus* brightness, and (c) EL spectra for devices incorporating **CbzCBI** and **mCPCBI** doped with green phosphors.

devices (Fig. 5(a)). In devices A1 and A2, we employed CbzCBI as the host for  $(PPy)_2Ir(acac)$  and  $(PBi)_2Ir(acac)$ , respectively.

The (PBi)<sub>2</sub>Ir(acac)-based device **A2** exhibited maximum efficiencies (20.1%, 70.4 cd A<sup>-1</sup>, 63.2 ml W<sup>-1</sup>) that were superior to those of the (PPy)<sub>2</sub>Ir(acac)-based device **A1** (17.8%, 67.6 cd A<sup>-1</sup>, 59.3 ml W<sup>-1</sup>). The maximum external quantum efficiency ( $\eta_{ext}$ ) of 20.1% was equal to the theoretical limit (20%) for a PhOLED. When the brightness reached 1000 cd m<sup>-2</sup>, the value of  $\eta_{ext}$ remained high (19.1%; retaining >95% of the external quantum efficiency), suggesting that balanced injection and transport of holes and electrons in the device occurred even at high current densities. Therefore, the use of a bipolar host material can provide balanced charge fluxes within the emitting layer, rendering devices exhibiting only a limited external quantum efficiency roll-off. When compared with devices **A1** and **A2**, devices **B1** and **B2** with **mCPCBI** as the host, we achieved similar device efficiencies (Fig. 6 (b)). Next, we doped the host materials with higher triplet energy gaps, **CBzNBI** (2.72 eV) and **mCPNBI** (2.73 eV), with a commercially available triplet blue emitter, bis(4,6-difluorophenylpyridinato-*N*,*C*<sup>2</sup>) picolinatoiridium(III) (FIrpic),<sup>26</sup> to prepare devices **C3** and **D3** with the configuration ITO/PEDOT:PSS (30 nm)/DTAF (40 nm)/host:dopant 12 wt% (30 nm)/3-(4-biphenyly)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ, 30 nm)/LiF/AI.



Fig. 7 (a) I-V-L characteristics, (b) plots of EL efficiency versus brightness, and (c) EL spectra for devices incorporating CbzNBI and mCPNBI doped with 12 wt% FIrpic.

This device structure is similar to that of device A, except for the presence of TAZ as the ETL. The triplet energies of DTAF (2.87 eV)<sup>29</sup> and TAZ (2.70 eV)<sup>31</sup> were sufficiently high to prevent any possible luminescence quenching by the carrier-transporting layers and to confine the triplet excitons in the EML. Fig. 7(a)displays the I-V-L characteristics of these blue light-emitting devices. The CBzNBI-based device C3 exhibited significantly lower turn-on and operation voltages than did the mCPNBIbased device D3. We attribute the enhanced device current to the facilitation of hole injection when using CBzNBI as the host material, as revealed by its relatively high HOMO energy level and hole transporting properties (Fig. 5(a)). Table 2 and Fig. 7(b) reveal that the mCPNBI-based device D3 exhibited maximum efficiencies (16.3%, 35.7 cd  $A^{-1}$ , 23.3 ml  $W^{-1}$ ) that were superior to those of the CBzNBI-based device C3 (13.5%, 28.7 cd  $A^{-1}$ , 25.8 ml  $W^{-1}$ ), presumably because **mCPNBI** possesses relatively poor hole injection and transport behavior, leading to a balanced hole and electron in the EML. These values are comparable to those that we reported previously for a device based on CzSi,11 confirming the suitability of using N-connected bipolar hosts for the blue phosphor.

## Conclusions

We have synthesized four bipolar hosts, CbzCBI, mCPCBI, CbzNBI, and mCPNBI, containing hole-transporting carbazole and electron-transporting benzimidazole moieties, for the realization of highly efficient green and blue electrophosphorescent devices. Different linking topologies between the benzimidazole group (C- or N-connectivity) and the carbazole donor resulted in different effective conjugation lengths and different excited-state solvent relaxation processes. Each of the bipolar hosts exhibited high morphological and thermal stability, suitable energy levels, and balanced electron/hole transporting characteristics, all of which are necessary for high-performance PhOLEDs. A greenphosphorescent device incorporating CbzCBI as host doped with (PBi)<sub>2</sub>Ir(acac) achieved a maximum external quantum efficiency, current efficiency, and power efficiency of 20.1%, 70.4 cd A<sup>-1</sup>, and 63.2 lm  $W^{-1}$ , respectively (device A2). The bipolar compounds featuring N-connected benzimidazole moieties (CbzNBI, mCPNBI) possessed the higher triplet energies required to host blue phosphors. A blue PhOLED device (device D3) incorporating mCPNBI as the host achieved a maximum external quantum efficiency, current efficiency, and power efficiency of 16.3%, 35.7 cd A<sup>-1</sup>, and 23.3 lm W<sup>-1</sup>, respectively. Our results suggest that varying the molecular linking topology is a possible strategy toward designing useful bipolar host materials; we hope that this approach will trigger the molecular design of novel host materials for highly efficient PhOLEDs.

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