Molecular Topology Tuning of Bipolar Host Materials Composed of Fluorene-Bridged Benzimidazole and Carbazole for Highly Efficient Electrophosphorescence

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Dedicated to Professor Scott E. Denmark on the occasion of his 60th birthday

Abstract: Two new molecules, CzFCBI and CzFNBI, have been tailor-made to serve as bipolar host materials to realize high-efficiency electrophosphorescent devices. The molecular design is configured with carbazole as the holetransporting block and N-phenylbenzimidazole as the electron-transporting block hybridized through the saturated bridge center (C9) and meta-conjugation site (C3) of fluorene, respectively. With structural topology tuning of the connecting manner between N-phenylbenzimidazole and the fluorene core, the resulting physical properties can be subtly modulated. Bipolar host CzFCBI with a C connectivity between phenylbenzimidazole and the fluorene bridge exhibited extended π conjuga-

Introduction

Phosphorescent organic light-emitting devices (PhOLEDs) have currently attracted intensive research activities in both academia and industry because of their potential applications in full-color flat-panel displays and solid-state light-ing.^[1] To achieve 100% internal quantum efficiency in PhOLEDs, heavy-metal-centered phosphorescent emitters must typically be homogeneously dispersed into an appropriate host material to suppress detrimental processes, such

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tion; therefore, a low triplet energy of 2.52 eV was observed, which is insufficient to confine blue phosphorescence. However, the monochromatic devices indicate that the matched energy-level alignment allows **CzFCBI** to outperform its N-connected counterpart **CzFNBI** while employing other long-wavelength-emitting phosphorescent guests. In contrast, the high triplet energy (2.72 eV) of **CzFNBI** imparted by the N connectivity ensures its utilization as a universal bipolar host for

Keywords: bipolar hosts • electrophosphorescence • luminescence • organic light-emitting devices • photochemistry blue-to-red phosphors. With a common device configuration, CzFNBI has been utilized to achieve highly efficient and low-roll-off devices with external quantum efficiency as high as 14% blue, 17.8% green, 16.6% yellowish-green, 19.5% yellow, and 18.6% red. In addition, by combining yellowish-green with a sky-blue emitter and a red emitter, a CzFNBI-hosted single-emittinglayer all-phosphor three-color-based white electrophosphorescent device was successfully achieved with high efficiencies (18.4%) $36.3 \text{ cd } \text{A}^{-1}$. 28.3 lm W⁻¹) and highly stable chromaticity (CIE x = 0.43 - 0.46 and CIE y =0.43) at an applied voltage of 8 to 12 V, and a high color-rendering index of 91.6.

as concentration quenching through triplet-triplet annihilation.^[2] Therefore, the development of suitable host materials also plays an important role in PhOLED-related research. Regardless of the various emitting colors, to obtain high efficiency in PhOLEDs the host material should have 1) appropriate highest occupied/lowest unoccupied molecular orbital (HOMO/LUMO) energy levels matching with the adjacent layers for efficient charge injection; 2) good and balanced charge-transporting properties to lead to efficient charge recombination occurring on the phosphorescent emitter; 3) a triplet energy $(E_{\rm T})$ higher than that of the phosphorescent emitter to prevent reverse energy transfer from guest to host, and effective confinement of the triplet excitons on the guest emitter;^[3] and 4) high thermal and morphological stability for the thin-film stability of the emitting layer. In this regard, bipolar host materials incorporating hole- and electron-transporting moieties provide the necessary physical characteristics required for these purposes.^[4]

For more cost-effective production, a particular challenge will be the development of universal bipolar hosts suitable for blue, green, and red phosphorescent emitters with a common device configuration. Furthermore, the blue host

Chem. Eur. J. 2013, 19, 10563-10572

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needs a higher $E_{\rm T}$ (\geq 2.70 eV) than that of blue phosphorescent emitters.^[5] To preserve such a high $E_{\rm T}$, the bipolar hosts usually comprise large-bandgap hole- and electron-transporting building blocks. However, such a molecular configuration may lead to ill-matched HOMO/LUMO levels relative to those of neighboring functional layers, which leads to high operation voltage and thus low efficiency. Therefore, an essential compromise between the triplet energy $E_{\rm T}$ and HOMO/LUMO levels of the bipolar host materials is inevitable for designing universal host materials. With judicious selection of molecular building blocks, universal bipolar host materials suitable for high-efficiency red/green/blue (RGB) and even white OLEDs (WOLEDs) using a common device structure can be reasonably achieved. For designing bipolar hosts, carbazole is commonly used as the hole-transporting (HT) component, since carbazole-based materials have been widely used in PhOLEDs because of their high triplet energy and HT properties.^[6] On the other hand, benzimidazole is an important component that is utilized widely as a functional group for facilitating the injection and transport of electrons.^[6g,7] We have previously achieved an interesting universal bipolar host, CNBzIm, which incorporates two electron-transporting (ET) N-phenylbenzimidazole units onto the C3 and C6 positions of HT N-phenylcarbazole.^[8] CNBzIm has been used to realize a high-efficiency RGB device and a two-color, all-phosphor single-emitting-layer WOLED. Another important issue for designing bipolar host materials is the molecular structural feature linking the HT and ET blocks. In this regard, a saturated spacer has been successfully utilized for blocking the direct electronic coupling between the HT and ET blocks, thus allowing the resultant bipolar host to have a high $E_{\rm T}$. One excellent example was recently reported by Yang et al., in which a silicon-bridged bipolar compound, p-BISiTPA, which combines

triphenylamine and benzimidazole moieties, exhibited a high $E_{\rm T}$ of 2.69 eV and a glass transition temperature $T_{\rm g}$ of 102 °C.^[9] Devices with *p*-BISiTPA as the host gave external quantum efficiencies (EQEs) as high as 16.1% for blue, 22.7% for green, 20.5% for orange, and 19.1% for all-phosphor twocolor-based WOLEDs employing a common device structure.

Herein, we utilized fluorene as a bridge to make two bipolar host materials (**CzFCBI** and **CzFNBI**, Scheme 1) with carbazole as the HT block and *N*-phenylbenzimidazole as the ET block attached to the saturated bridge center (C9) and *meta*-conjugation site (C3) of fluorene, respectively. In this molecular design, the electronic

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coupling between the HT and ET moieties can be effectively blocked, and the limited extension of molecular conjugation by a meta substitution can be anticipated to retain a reasonably high $E_{\rm T}$. In addition, the rigidity of fluorene will ensure the resulting bipolar hosts exhibit a sufficiently high T_{s} , hence giving a morphologically stable emitting layer. Through the structural topology tuning of the manner of connectivity between N-phenylbenzimidazole and the fluorene core, the physical properties of the bipolar hosts can be subtly modulated, to give the new host **CzFNBI** with an $E_{\rm T}$ of 2.72 eV and suitable energy levels to realize PhOLEDs with low roll-off and high EQE for blue (14%, [FIr(pic)]; pic=picolinic acid), green $(17.8\%, [Ir(acac)(PPy)_2]; acac =$ acetylacetonate, Py = pyridine), yellowish green (16.6%, [Ir- $(acac)(m-tpm)_2$; m-tpm = meta-tolylpyrimidine), yellow $(19.5\%, [Ir(acac)(bt)_2]; bt=2$ -phenyl benzothiazolate), and red $(18.6\%, [Os(bpftz)_2(PPhMe_2)_2]; bpftz = 3-(trifluoro$ methyl)-5-(4-tert-butylpyridyl)-1,2,4-triazolate), respectively (see below for details of complexes). In contrast, a slightly extended π conjugation of the C-connected counterpart **CzFCBI** gives a lower $E_{\rm T}$ of 2.52 eV, which is unable to confine blue phosphor emission, but superior EQEs were reached for green (20%), yellowish green (18%), yellow (19.4%), and red (18.1%). More importantly, CzFNBI was utilized to realize a high-efficiency (18.4%, 36.3 cd A^{-1} , 28.3 lm W⁻¹) single-emitting-layer WOLED showing three evenly separated RGB emission peaks with highly stable chromaticity (CIE x = 0.43 - 0.46 and CIE y = 0.43) at applied voltages of 8 to 12 V, and a high color-rendering index (CRI) of 91.6. This result represents one of the best examples of efficient all-phosphor three-color-based WOLEDs.[10] We attributed the high color stabilities to the broad charge recombination zone in the emitting layer incorporated with this novel bipolar host.



Scheme 1. Synthesis and chemical structures of CzFCBI and CzFNBI.

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Results and Discussion

Scheme 1 illustrates our synthetic route to new bipolar hosts **CzFCBI** and **CzFNBI**. The starting material, 3-(3-bromo-9*para*-tolyl-9*H*-fluoren-9-yl)-9-phenyl-9*H*-carbazole (1), was prepared according to our previously reported procedure.^[10c] The Suzuki coupling reaction of 1 and boronic esters 2^[11] and 3 in the presence of a palladium(0) catalyst gave **CzFCBI** and **CzFNBI** in 74 and 70% yield, respectively. **CzFCBI** and **CzFNBI** have been fully characterized with ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis (see the Experimental Section).

Figure 1 depicts the room-temperature UV/Vis absorption and photoluminescence (PL) spectra of **CzFCBI** and **CzFNBI** in dilute solution (CH₂Cl₂). The photophysical data



Figure 1. Room-temperature absorption (Abs) and photoluminescence (PL) spectra of **CzFCBI** and **CzFNBI** in CH_2Cl_2 and the corresponding phosphorescence (Phos) spectra recorded in EtOH at 77 K.

are summarized in Table 1. Both **CzFCBI** and **CzFNBI** show an absorption peak at approximately 300 nm, which can be assigned to the π - π * transition of the carbazole moiety. An evident absorption peak centered at 320 nm of **CzFCBI** is attributed to the π - π * transition of the extended π conjugation from fluorene to the benzimidazole unit. In contrast, **CzFNBI** shows an absorption peak around 270 nm, which indicates the disruption of π conjugation between fluorene and the benzimidazole unit due to the distorted N-bridged linkage.^[6c,7a,d,9a,b] The redshifted emission spectrum of **CzFCBI** with λ_{max} centered at 388 nm as compared to 357 nm for **CzFNBI** agrees with our assumption of the extended π conjugation in **CzFCBI** through the C connection of benzimidazole to fluorene. The phosphorescence spectra

Table 1. Physical properties of CzFCBI and CzFNBI.

of **CzFCBI** and **CzFNBI** were measured in EtOH at 77 K and the triplet energy levels were estimated from the highest-energy vibronic sub-band of the phosphorescence spectra. The high-energy phosphorescence emission peak of **CzFCBI** is at 492 nm, corresponding to a triplet energy (E_T) of 2.52 eV. In contrast, **CzFNBI** exhibits a higher E_T of 2.72 eV. The high E_T of **CzFNBI** again confirms the disruption of π conjugation from C3-substituted fluorene to the Nbridged benzimidazole moiety. Based on this observation, **CzFCBI** can be a useful host material for green-to-red triplet emitters, whereas **CzFNBI** can be utilized in RGB and white PhOLEDs.

We used cyclic voltammetry to probe the electrochemical properties of **CzFCBI** and **CzFNBI**, as shown in Figure 2. These compounds have similar oxidation behavior with one irreversible oxidation peak (onset at ca. 1.27 V vs. Ag/AgCl)



Figure 2. Cyclic voltammograms of **CzFCBI** and **CzFNBI**. The oxidation potential was measured in CH_2Cl_2 with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte and reduction cyclic voltammetry was performed in DMF with 0.1 M TBAP as the supporting electrolyte.

of the forward scan and a new peak appears at 0.98 V of the backward scan. This result agrees with the typical signature of a C3 and/or C6 unprotected carbazole moiety.^[12] Notably, the more π -conjugated chromophore in **CzFCBI** leads to a reversible reduction potential $(E_{1_{2}}^{\text{red}})$ at -1.88 V (vs. Ag/AgCl). In contrast, the higher reduction potential of **CzFNBI** is irreversible, which is a characteristic feature of N-connected benzimidazole-containing materials.^[6c,7a,d,9a,b] For the practical applications of **CzFCBI** and **CzFNBI** in their solid films, we determined the HOMO energy level of **CzFCBI** and **CzFNBI** to be -5.60 and -5.80 eV, respectively, by using a Riken AC-2 photoemission spectrometer. From the equation LUMO = HOMO + ΔE_g , in which ΔE_g is the optical bandgap determined from the absorption thresh-

	Т _g [°С]	T _d [⁰C]	$E^{\mathrm{ox}[\mathrm{a}]}_{rac{1/2}{2}} \left[\mathrm{V} ight]$	$E^{\mathrm{red}[\mathrm{a}]}_{rac{1/2}{2}} \left[\mathrm{V} ight]$	HOMO ^[b] [eV]	LUMO ^[c] [eV]	$\Delta E_{g}^{[c]}$ [eV]	E_{T} [eV]	$\lambda_{ m abs}$ [nm] sol./film	λ _{PL} [nm] sol./film
CzFCBI	175	415	1.30	-1.88	-5.6	-2.21	3.39	2.52	300, 320/301, 321	370, 388/397
CzFNBI	181	441	1.27	-2.22	-5.8	-2.17	3.63	2.72	270, 298/271, 300	357, 373/361, 381

[a] Determined from onset oxidation/reduction potential (vs. Ag/AgCl). [b] HOMO determined by using photoelectron spectroscopy (AC-2). [c] LUMO=HOMO+ E_g , in which E_g was calculated from the absorption onset of the solution.

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old, we estimated the LUMO energy level of CzFCBI and CzFNBI to be -2.21 and -2.17 eV, respectively.

To acquire the carrier mobility of **CzFCBI** and **CzFNBI**, we first attempted to use a conventional time-of-flight (TOF) transient-photocurrent technique. However, the transient-photocurrent signals were too weak due to the weak absorption at 337 nm used for excitation. Instead, we introduced an ambipolar terfluorene $(T3)^{[13]}$ as the charge-generation layer for TOF measurements^[14] (see the Experimental Section). Figure 3a and b display typical room-temperature



Figure 3. Representative TOF transients for a) **CzFCBI** ($E=4.2 \times 10^5 \text{ V cm}^{-1}$) and b) **CzFNBI** ($E=4.1 \times 10^5 \text{ V cm}^{-1}$). Inset: Double-logarithmic plot. c) Hole mobilities of **CzFCBI** and **CzFNBI** plotted with respect to $E^{i_{\pm}}$.

TOF transient photocurrents under an applied electric field. 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. Figure 3c shows that the field dependence of the hole mobility follows the nearly universal Poole–Frenkel relationship, and the values are in the range of 2.3×10^{-6} to 1.8×10^{-5} cm²V⁻¹s⁻¹ for **CzFCBI** at fields varying from 1.6×10^5 to 4.2×10^5 V cm⁻¹ and 6.9×10^{-6} to 2.8×10^{-5} cm²V⁻¹s⁻¹ for **CzFNBI** at fields varying from 6.5×10^5 to 1.1×10^6 V cm⁻¹. Unfortunately, the electron transition of V cm⁻¹ to the transite of V

sient-photocurrent signals were still too weak and cannot be used to determine the electron mobility.

To verify the bipolar transport character of **CzFCBI** and **CzFNBI**, we then fabricated hole-only devices having the structure of indium tin oxide (ITO)/N,N'-diphenyl-N,N'-bis[1-naphthyl-(1,1'-biphenyl)]-4,4'-diamine (NPB) (10 nm)/ test (30 nm)/NPB (10 nm)/LiF/Al and electron-only devices having the configuration of ITO/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (10 nm)/test (30 nm)/BCP (10 nm)/LiF/Al. The introduction of NPB and BCP layers is to prevent electron and hole injection from the cathode and anode, respectively. The current density versus voltage curves shown in Figure 4 indicate the bipolar charge-transport nature, in



Figure 4. Current-density-voltage (I-V) characteristics of carrier-only devices: hole-only device [ITO/NPB (10 nm)/test (30 nm)/NPB (10 nm)/ LiF/Al] and electron-only device [ITO/BCP (10 nm)/test (30 nm)/BCP (10 nm)/LiF/Al].

which the electron current density is slightly higher than the hole current density in both **CzFCBI** and **CzFNBI**. The electron current density of **CzFCBI** is higher than that of **CzFNBI**, whereas the hole current density of **CzFCBI** is lower than that of **CzFNBI**. The hole currents clearly follow the results observed by TOF measurements. The results from single-carrier devices indicate that the electron-transport behavior is better and the hole-transport property is worse on altering the linking topology from C to N connectivity of the benzimidazole unit, which is consistent with our previous report of indolocarbazole–benzimidazole hybridized materials (TICCBI and TICNBI).^[15]

To evaluate the utilization of CzFCBI and CzFNBI as host materials for different dopants (from blue to red), we blue [bis(4,6-difluorophenyl)pyridinatoselected *N*,*C*²]picolinate iridium(III) ([FIr(pic)]),^[16] green bis(2phenylpyridinato)iridium(III) acetylacetonate ([Ir(acac)-(PPy)₂]),^[17] yellow-green bis(*meta*-tolylpyrimidine)iridium-(III) acetylacetonate ([Ir(acac)(m-tpm)₂]),^[10c] yellow bis(2phenylbenzothiazolato)(acetylacetonato)iridium(III) ([Ir-(acac)(bt)₂]),^[5b] and red bis[3-(trifluoromethyl)-5-(4-tertbutylpyridyl)-1,2,4-triazolate]dimethylphenylphosphine osmium(II) ([Os(bpftz)₂(PPhMe₂)₂], OS1)^[18] as dopants (Scheme 2). To improve the hole injection from the anode, poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonic acid) (PEDOT/PSS) was spun onto the precleaned ITO substrate to form a 30 nm thick polymer buffer layer. Two hole-transport layers (HTLs), which consisted of a 20 nm thick layer



Scheme 2. Molecular structures of the dopants used in this study and an energy level diagram of the device.

of 9,9-di[4-(di-*para*-tolyl)aminophenyl]fluorine (DTAF)^[6g,19] and a 5 nm thick layer of 4,4',4"-tri(*N*-carbazolyl)triphenylamine (TCTA)^[20] were implemented. It is notable that TCTA, with E_T =2.76 eV and HOMO/LUMO levels of 5.7/ 2.4 eV, also served as a triplet blocker to confine the excitons in the emissive layer (EML, Scheme 2). Moreover, a 25 nm thick emissive layer consisted of 10 wt% of phosphors doped into the host material. Finally, a 50 nm thick layer of diphenylbis[4-(pyridin-3-yl)phenyl]silane (DPPS)^[21] was used as the electron-transport layer (ETL), for which DPPS (E_T : 2.7 eV, HOMO/LUMO: 6.5/2.5 eV) could be more effective in blocking the excitons within the emissive layer. A cathode consisting of a 0.5 nm thick layer of LiF and a 100 nm thick layer of Al was deposited through a shadow mask.

Figures 5 and 6 depict the current density-voltage-luminance (J-V-L) characteristics, device efficiencies, and electroluminescence (EL) spectra of the devices incorporating **CzFCBI** and **CzFNBI** host materials, respectively. Table 2 summarizes the EL data obtained. In the blue emission device, the **CzFNBI**-based device B2 displayed a maximum brightness (L_{max}) as high as 43500 cdm⁻² at 13 V (630 mA cm⁻²), achieving a maximum EQE (η_{ext}) of 14.0% corresponding to a current efficiency (η_c) of 32.7 cd A⁻¹ and power efficiency (η_p) of 30 lm W⁻¹. In contrast, **CzFCBI**,



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Figure 5. a) Current-density-voltage-luminance (J-V-L) characteristics, b) external quantum (η_{ext}) and power efficiencies (η_p) as a function of brightness, and c) EL spectra of devices with **CzFCBI** as host.

which possesses a relatively low triplet energy ($E_{\rm T}$ = 2.52 eV) that leads to inefficient confinement of emissive excitons, gives poor device performance (device B1). To further verify the exciton-confinement behavior of the host, the transient PL decay characteristics of 10 wt % [FIr(pic)]doped CzFCBI and CzFNBI were investigated; the results are shown in Figure 7. The CzFCBI/[FIr(pic)] film exhibits two-component decay, that is, a fast decay process and a slow decay process. The latter can be attributed to thermally activated triplet-triplet energy transfer between the host and the guest, such as in the [FIr(pic)]/CBP system (CBP= N,N'-dicarbazolyl-4,4'-biphenyl).^[22] It may induce triplet exciton quenching on CzFCBI/[FIr(pic)]-based blue PhOLEDs and then a relatively poor device performance. However, the emission of the [FIr(pic)]-doped CzFNBI film displays a clear single exponential decay with a lifetime of 1.73 µs and no slow decay process. This can be understood from the relatively high triplet energy level of 2.72 eV (CzFNBI), which successfully suppresses triplet energy back-transfer and con-

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Figure 6. a) Current-density-voltage-luminance (J-V-L) characteristics, b) external quantum (η_{ext}) and power efficiencies (η_p) as a function of brightness, and c) EL spectra of devices with **CzFNBI** as host.

fines the [FIr(pic)] excitons in the emissive layer, thus leading to highly efficient blue PhOLEDs.

Besides blue PhOLEDs, **CzFCBI** and **CzFNBI** were also applied with different dopants (from green to red). All of the devices in this study exhibited a low turn-on voltage of 2.5 V (defined as the voltage at which EL became detecta-

Table 2.	EL	performances	of	devices.	[a]
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Figure 7. Transient PL decay of **CzFCBI** and **CzFNBI**/10 wt % [FIr(pic)] under excitation by a nitrogen laser ($\lambda = 337$ nm, 10 Hz, 700 ps pulses).

ble), similar operating voltage (5.5-6.5 V), and rather low efficiency roll-off at a brightness of 1000 cd m⁻² with different dopants. In green phosphorescent devices with [Ir(acac)-(PPy)₂] as dopant, the device G1 using CzFCBI as host showed a L_{max} of 108500 cd m⁻² at 13.5 V (930 mA cm⁻²), and a maximum $\eta_{\rm ext}$ of 20% corresponding to an $\eta_{\rm c}$ of 74.4 cd A^{-1} and an η_p of 75 lm W^{-1} , whereas device G2 using **CzFNBI** as host achieved a L_{max} of 149600 cd m⁻² at 13 V (920 mA cm⁻²), and a maximum η_{ext} of 17.8% corresponding to an η_c of 64.1 cd A⁻¹ and an η_p of 46 lm W⁻¹. This can be attributed to the more suitable energy-level alignments of CzFCBI, which facilitate efficient hole injection to the emitting layer. The same trend can also be observed for devices with different long-wavelength-emitting dopants and CzFCBI as host. Furthermore, yellowish-green (YG) PhO-LEDs were fabricated by using $[Ir(acac)(m-tpm)_2]$ as dopant with an EL wavelength (λ_{EL}) of 547 nm; device YG1 hosted by CzFCBI exhibited a relatively higher efficiency (18%, $62.9\ cd\ A^{-1},\ and\ 62.6\ lm\ W^{-1})$ than device YG2 hosted by **CzFNBI** (16.6%, 57.5 cd A^{-1} , and 42.5 lm W^{-1}). With this YG dopant, a broadband white spectrum with a uniform emission intensity covering the whole visible spectrum can be realized in a relatively simple three-emitter system.

Next, the yellow-emitting OLEDs were fabricated by using $[Ir(acac)(bt)_2]$ as dopant. Excellent performance of yellow electrophosphorescence can be achieved for devices Y1 (19.4%, 48.7 cd A⁻¹, and 47.6 lm W⁻¹) and Y2 (19.5%,

Device	$V_{\rm on}^{[b]}$	L_{\max}	I _{max}	η_{ext}	η_{c}	$\eta_{\rm p}$	At 1000 $[cd m^{-2}]$, [c]	CIE
	[V]	$[cd m^{-2}]([V])$	$[mA cm^{-2}]$	[%]	$[\operatorname{cd} A^{-1}]$	$[\operatorname{lm} W^{-1}]$	V [%]	[x,y]
B1	3.0	1200 (16)	590	4.0	8.5	5.3	15.0, 0.1	0.24,0.40
G1	2.5	108 500 (13.5)	930	20.0	74.4	75	5.5, 18.6	0.32,0.63
YG1	2.5	1176000 (13)	1000	18.0	62.9	62.6	5.9, 17.1	0.43,0.56
Y1	2.5	135100 (12)	1170	19.4	48.7	47.6	5.8, 19.0	0.52,0.48
R1	2.5	31 800 (12.5)	1000	18.1	18.2	17	6.5, 16.6	0.66,0.34
B2	2.5	43 500 (13)	630	14.0	32.7	30	6.6, 13.0	0.19,0.40
G2	2.5	149600 (13)	920	17.8	64.1	46	5.5, 17.4	0.32,0.63
YG2	2.5	109500 (13)	800	16.6	57.5	42.5	6.0, 16.3	0.43,0.55
Y2	2.5	116100 (13.5)	950	19.5	48.1	36.5	6.5, 18.9	0.53,0.47
R2	2.5	29400 (13)	820	18.6	18.6	13	6.5, 17.4	0.65,0.34
W2	2.5	47 500 (17)	480	18.4	36.3	28.3	9.5, 14.7	0.46,0.43

[a] The notation 1 and 2 indicates the devices fabricated with host materials of **CzFCBI** and **CzFNBI**, respectively. [b] Turn-on voltage at which emission became detectable. [c] η_{ext} and driving voltage of device at 1000 cd m⁻².

1	05	68	4

48.1 cd A⁻¹, and 36.5 lm W⁻¹). Remarkably, device Y1 shows rather low efficiency roll-off at a brightness of 1000 cd m⁻², whereas the recorded η_{ext} is still maintained as high as 19%. These values are comparable to those of the best yellow PhOLEDs in the literature, [6g, 10a, 23] and may serve as the potential emitting element for generating white emission in combination with a complementary blue phosphor.^[24] Finally, we demonstrated red-emitting OLEDs by using the emitter [Os(bpftz)₂(PPhMe₂)₂], OS1 (devices R1 and R2). Both devices also exhibited high performance. For instance, device R1 exhibited a L_{max} of 31 800 cd m⁻² at 12.5 V and respectable EL efficiencies (18.1%, 18.2 cd A^{-1} , and 17 lm W^{-1}), whereas device R2 exhibited a $L_{\rm max}$ of 29400 cd m⁻² at 13 V and good EL efficiencies (18.6%, $18.6 \text{ cd } \text{A}^{-1}$, and 13 lm W^{-1}). Besides device B1, all devices displayed relatively pure emission and there are no residual emissions from the host and/or adjacent layers, as shown in Figures 5c and 6c, thus indicating that the EL originates solely from the dopant and with complete energy transfer from host to dopant. More importantly, excellent RGB EL performances were obtained from CzFNBI-hosted devices with different phosphors using a common device architecture. On reaching a brightness of 1000 cdm⁻², the devices have similar driving voltages (6.0–6.6 V) whereas the $\eta_{\rm ext}$ still remains at 13 % for blue, 16.3% for yellowish-green, and 17.6% for red, which make them very attractive for commercial applications in full-color displays.

The excellent performance of the CzFNBI-based monochromatic PhOLED prompted us to explore its application in WOLEDs. The WOLED (device W2) adopted a similar architecture to the aforementioned monochromatic devices except for the EML [CzFNBI/10% [FIr(pic)] (5 nm)/ **CzFNBI**:10% [Ir(acac)(*m*-tpm)₂] (5 nm)/**CzFNBI**/10% OS1 (5 nm)/CzFNBI/10% [FIr(pic)] (10 nm)]. Herein, we fabricated WOLEDs by distributing the primary color emitters with a B-G-R-B configuration in the EML, which can reduce structural heterogeneity and facilitate charge injection and transport between different emissive centers. With this strategy, device W2 exhibits rather high efficiency together with superior color rendition, particularly the impressive color stability. Figure 8 shows the J-V-L characteristics, EQE, and power efficiency versus brightness. The EL characteristics of the white device are also summarized in Table 2. Device W2 displayed a turn-on voltage of 2.5 V, which is the same as that for the monochromatic devices, a $L_{\rm max}$ of 47500 cd m⁻² at 17 V (480 mA cm⁻²), and a maximum η_{ext} of 18.4%, corresponding to an η_c of 36.8 cd A⁻¹ and an η_p of 28.3 lm W⁻¹. The EL spectra of this white device have clearly distinguished red, yellowish-green, and blue emissions to cover wavelengths from 450 to 800 nm as shown in Figure 8c. Moreover, the CRI is calculated to reach as high as (89.9-91.6) with low color temperatures (2820-3052 K) close to incandescent lamps. On increasing the driving voltage from 8 to 12 V, the variation of the Commission Internationale de L'Eclairage (CIE) coordinates is rather small, CIE x = 0.46 - 0.45 and CIE y = 0.41, thereby revealing superior device chromatic stability. The concomitant

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Figure 8. a) Current-density-voltage-luminance (J-V-L) characteristics, b) external quantum (η_{ext}) and power efficiencies (η_p) as a function of brightness, and c) EL spectra at various voltages of white device W2.

high efficiency (η_{ext} of 18.4%) and CRI value (91.6) are impressive in device W2, which is superior to most currently known all-phosphor three-color-based WOLEDs.^[10]

Conclusion

Two bipolar host materials (CzFCBI and CzFNBI), composed of electron-donating carbazole linked to the sp³-hybridized C bridge of fluorene and electron-accepting benzimidazole grafted onto the C3 position of fluorene, have been synthesized and characterized. The designated molecular configuration effectively decouples the direct electronic interactions between donor and acceptor subunits to give high triplet energy. These new materials show promising properties, such as high T_{g} values, suitable energy levels, and bipolar charge transport, thus rendering them good candidates for realizing highly efficient electrophosphorescent devices. More importantly, the physical properties can be subtly modified through the connecting pathways between the fluorene and benzimidazole units. Molecule CzFCBI exhibited a lower triplet energy (2.52 eV) due to the extended π conjugation relative to that of the counterpart CzFNBI, which led to an insufficient confinement of blue phosphorescence.

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However, the well-matched energy levels allow CzFCBI to serve as a common host for green-to-red PhOLEDs with excellent EQEs as high as 18.1-20%. In contrast, CzFNBI exhibited a high $E_{\rm T}$ of 2.72 eV, was successfully utilized as a universal bipolar host for various monochromic RGB PhO-LEDs, and achieved high EQEs of 14-19.5% with a common device configuration. In addition, white PhOLEDs with evenly separated RGB peaks were achieved by employing CzFNBI as host. The WOLEDs exhibited a high CRI of 91.6, high efficiencies $(18.4\%, 36.3 \text{ cd } \text{A}^{-1},$ 28.3 lm W⁻¹), and highly stable chromaticity (CIE x =0.43–0.46 and CIE y=0.43) at an applied voltage of 8 to 12 V. Notably, all devices exhibit low-efficiency roll-off at high luminance, which can be attributed to the matched energy levels between the emitting layer and neighboring layers for efficient charge-carrier injection, and balanced charge fluxes for a broader recombination zone within the emitting layer. These results clearly indicate the potential of using tailor-made bipolar universal hosts for the realization of efficient RGB and white PhOLEDs.

Experimental Section

Material characterization: ¹H and ¹³C NMR spectra were recorded in CDCl3 by using a Varian (Unity Plus 400) spectrometer at 400 and 100 MHz, respectively. Low- and high-resolution mass spectra were recorded with a JEOL SX-102A spectrometer in fast atom bombardment (FAB) mode. Elemental analyses were performed on a Perkin-Elmer CHN-2400 or Elementar Vario EL-III analyzer. UV/Vis absorption spectra were recorded on a JASCO V-670 instrument. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) analyses were performed on a TA Instruments DSC-2920 MDSC V2.6A low-temperature differential scanning calorimeter at a heating rate of 10°Cmin⁻¹ from 0 to 350°C under nitrogen. Thermogravimetric analysis (TGA) was undertaken with a TGA Q500 instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their 5% weight loss on heating at a rate of 10°Cmin⁻¹ from 0 to 800°C. Transient PL decays were measured under excitation by a pulsed nitrogen laser ($\lambda = 337$ nm, 10 Hz, 700 ps pulses) combined with a photomultiplier tube (R928, Hamamatsu) and a synchronous oscilloscope (500 MHz resolution).

Cyclic voltammetry: The oxidation/reduction potentials of **CzFCBI** and **CzFNBI** were measured by cyclic voltammetry. The oxidation potential was determined in CH₂Cl₂ (1.0 mM) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte at a scan rate of 100 mV s⁻¹. The reduction potential was recorded in DMF (1.0 mM) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAClO₄) as a supporting electrolyte at a scan rate of 100 mV s⁻¹. A glassy carbon electrode and platinum wire were used as the working and counter electrodes, respectively. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple in CH₂Cl₂/TBAPF₆ occurred at E'_{o} = +0.47 V for oxidation and in DMF/TBAP occurred at E'_{o} = +0.51 V for reduction. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode.

Time-of-flight (TOF) mobility measurements: The terfluorene T3 was used as the charge-generation layer in the TOF transient-photocurrent technique. The TOF devices were configured as ITO glass/T3 $(0.2 \,\mu\text{m})$ /**CzFCBI** (1.69 μm) or **CzFNBI** (1.74 μm)/Ag (150 nm). The thicknesses of organic materials under test were set substantially larger than that of T3 so that the total transit time was larger than the time resolution of the electronic system and the transit time. The thickness of the organic film was monitored in situ with a quartz sensor and calibrated by a thin-

film thickness measurement (K-MAC ST2000). A pulsed nitrogen laser (337 nm) was used as the excitation light source through the transparent electrode (ITO) and induced photogeneration of a thin sheet of excess carriers. Under an applied dc bias, the transient photocurrent was swept across the bulk of the organic film toward the collection electrode (Ag), and then recorded with a digital storage oscilloscope. Depending on the polarity of the applied bias, selected carriers (holes or electrons) were swept across the sample with a transit time of $t_{\rm T}$. With the applied bias V and the sample thickness D, the applied electric field E is V/D, and the carrier mobility is then given by $\mu = D/(t_{\rm T}E) = D^2/(Vt_{\rm T})$, in which the carrier transit time $t_{\rm T}$ can be extracted from the intersection of two asymptotes to the tail and plateau sections in double-logarithmic plots.

OLED device fabrication: All chemicals were purified through vacuum sublimation prior to use. The OLEDs were fabricated through vacuum deposition of the materials at 10^{-6} Torr onto ITO-coated glass substrates having a sheet resistance of $15 \Omega \text{sq}^{-1}$. The ITO surface was cleaned ultrasonically—sequentially with acetone, methanol, and deionized water—and then with UV/ozone. The deposition rate of each organic material was approximately $1-2 \text{ Å s}^{-1}$. Subsequently, LiF was deposited at 0.1 Å s^{-1} and then capped with Al (ca. 5 Å s^{-1}) through shadow masking without breaking the vacuum. The *J*–*V*–*L* characteristics of the devices were measured simultaneously in a glovebox by using a Keithley 6430 source meter and a Keithley 6487 picoammeter equipped with a calibration Si photodiode. EL spectra were measured by using a photodiode array (Ocean Optics USB2000).

Synthesis: The starting material, 3-(3-bromo-9-para-tolyl-9H-fluoren-9-yl)-9-phenyl-9H-carbazole (1), was synthesized by following our literature procedure.^[10c]

9-Phenyl-3-{3-{4-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl]-9-para-

tolyl-9H-fluoren-9-yl]-9H-carbazole (CzFCBI): Compound 1 (3.0 g, 5.22 mmol), 1-phenyl-2-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1*H*-benzo[*d*]imidazole (2; 2.48 g, 6.26 mmol), [Pd(PPh₃)₄] (0.72 g, 0.62 mmol), and Na₂CO₃ (2.71 g, 25.58 mmol) were mixed in a flask. The vessel was then vacuum-evacuated and filled with argon. Dry THF (80 mL) and degassed H₂O (15 mL) were added to the reaction mixture, which was then heated at 85°C for 12 h under an argon atmosphere. After cooling, the solvent was evaporated under vacuum and the product was extracted with CH_2Cl_2 (100 mL×2). The organic solution was washed with water and dried with MgSO4. Evaporation of the solvent was followed by column chromatography on silica gel with CH2Cl2/ EtOAc (95:5) as eluent to give a white solid, CzFCBI (2.95 g, 74%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.00-7.93$ (m, 4H; ArH), 7.85 (d, J =7.6 Hz, 1H; ArH), 7.70 (d, J=8.4 Hz, 2H; ArH), 7.64 (d, J=8.8 Hz, 2H; ArH), 7.59-7.50 (m, 10H; ArH), 7.45-7.28 (m, 12H; ArH), 7.22-7.18 (m, 3H; ArH), 7.07 (d, J=8.0 Hz, 2H; ArH), 2.3 ppm (s, 3H; CH₃); ¹³C NMR (100 MHz, CDCl₃): $\delta = 152.34$, 152.03, 151.74, 143.38, 142.74, 142.26, 141.12, 140.82, 139.74, 139.71, 139.39, 137.67, 137.40, 137.24, 136.99, 136.25, 129.96, 129.86, 129.78, 128.98, 128.68, 128.50, 128.07, 127.98, 127.48, 127.41, 127.33, 127.00, 126.92, 126.80, 126.63, 126.52, 126.30, 125.86, 123.43, 123.27, 123.13, 123.10, 120.36, 120.22, 119.78, 119.72, 119.43, 118.71, 110.46, 109.70, 109.58, 65.09, 20.95 ppm; MS (FAB⁺): m/z (%): 765.3562 (61) [M⁺], 766.3483 (100) [MH⁺]; HRMS (FAB⁺): m/z calcd for C₅₇H₃₉N₃: 765.3144 [M]⁺; found: 765.3159; elemental analysis calcd (%) for C57H39N3: C 89.38, H 5.13, N 5.49; found: C 89.52, H 4.96, N 5.08.

2-Phenyl-1-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1Hbenzo[d]imidazole (3): A solution of 1-(4-bromophenyl)-2-phenyl-1Hbenzo[d]imidazole (6.0 g, 17.24 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'bis(1,3,2-dioxaborolane) (5.21 g, 20.51 mmol), KOAc (4.61 g, 47.23 mmol), and [Pd(dppf)Cl₂] (70 mg; dppf=1,1'-bis(diphenylphosphino)ferrocene) in anhydrous THF (120 mL) was deoxygenated by purging with argon and then the reaction mixture was heated at 85 °C under argon. After 12 h, the reaction mixture was cooled to room temperature. mixed with water (50 mL), and extracted with CH2Cl2 (3×100 mL). The combined organic extracts were dried over MgSO4 and concentrated under reduced pressure. The crude product was purified through column chromatography (n-hexane/EtOAc, 10:1) to give compound 3 (5.2 g, 76%) as a white solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.92$ (d, J =

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8.0 Hz, 2H; ArH), 7.88 (d, J=8.0 Hz, 1H; ArH), 7.56 (d, J=7.2 Hz, 2H; ArH), 7.35–7.24 (m, 8H; ArH), 1.36 ppm (s, 12H; 4×CH₃); ¹³C NMR (100 MHz, CDCl₃): δ =152.24, 142.81, 139.35, 136.92, 136.24, 129.70, 128.35, 126.55, 123.42, 123.09, 119.80, 110.45, 84.22, 24.90 ppm; MS (ES + TOF): m/z: 397 [MH⁺], 315 [MB(OH)₂+H⁺]; HRMS (TOF, ES⁺) m/z calcd for C₂₅H₂₆N₂O₂B: 397.2087 [MH⁺]; found: 397.2093.

9-Phenyl-3-{3-{4-(2-phenyl-1H-benzo[d]imidazol-1-yl)phenyl]-9-paratolyl-9H-fluoren-9-yl]-9H-carbazole (CzFNBI): Compound 1 (2.1 g, 3.65 mmol), compound **3** (1.74 g, 4.4 mmol), $[Pd(PPh_3)_4]$ (0.5 g, 0.43 mmol), and Na₂CO₃ (1.9 g, 18 mmol) were mixed in a flask. The vessel was then vacuum-evacuated and filled with argon. Dry THF (70 mL) and H₂O (10 mL) were added to the reaction mixture, which was then heated at 85 °C for 12 h under an argon atmosphere. After cooling, the solvent was evaporated under vacuum and the product was extracted with CH2Cl2. The CH2Cl2 solution was washed with water and dried with MgSO₄. Evaporation of the solvent was followed by column chromatography on silica gel with CH2Cl2/EtOAc (95:5) as eluent to give a white solid, **CzFNBI** (2.35 g, 70%). ¹H NMR (400 MHz, CDCl₃): $\delta =$ 8.11 (brs, 1H; ArH), 7.99–7.91 (m, 3H; ArH), 7.87–7.83 (m, 3H; ArH), 7.67-7.52 (m, 9H; ArH), 7.49-7.29 (m, 15H; ArH), 7.23-7.20 (m, 3H; ArH), 7.10 (d, J = 8.0 Hz, 2H; ArH), 2.33 ppm (s, 3H; CH₃); ¹³C NMR (100 MHz, CDCl₃): $\delta = 153.03$, 152.99, 152.43, 143.95, 143.91, 142.07, 141.89, 141.58, 140.51, 140.33, 139.94, 138.26, 138.12, 138.02, 137.17, 136.88, 130.94, 130.49, 130.13, 129.98, 129.64, 129.58, 129.12, 128.67, 128.61, 128.40, 128.19, 128.06, 127.55, 127.45, 127.25, 127.17, 126.94, 126.58, 123.86, 123.79, 123.42, 120.99, 120.81, 120.45, 120.30, 119.98, 119.54, 111.14, 110.40, 110.22, 65.84, 21.26 ppm; MS (FAB+LR): m/z (%): 523.1743 (21.29) [MPhCz⁺], 674.1599 (9.76) [MC₆H₄CH₄⁺], 766.2271 (63.99) [M⁺]; HRMS (FAB⁺): m/z calcd for C₅₇H₃₉N₃: 765.3144 $[M^+]$; found: 765.3142; elemental analysis calcd (%) for C₅₇H₃₉N₃: C 89.38, H 5.13, N 5.49; found: C 89.52, H 5.29, N 5.33.

Acknowledgements

We gratefully acknowledge financial support from the National Science Council of Taiwan (NSC 100-2112-M-019-002-MY3, 98-2119-M-002-007-MY3, 100-2119-M-007-010-MY3).

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Received: February 25, 2013 Revised: April 29, 2013 Published online: June 20, 2013