PAPER

A carbazole–phenylbenzimidazole hybrid bipolar universal host for high efficiency RGB and white PhOLEDs with high chromatic stability

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A novel bipolar molecule **CNBzIm** comprised of electron-donating carbazole and electron-accepting phenylbenzimidazole is designed, synthesized and characterized for RGB phosphorescent organic light emitting diodes (PhOLEDs). **CNBzIm** exhibits promising properties such as high triplet energy ($E_{\rm T} =$ 2.71 eV) due to disrupted π -conjugation, bipolar and balanced charge transport ability ($\mu_{\rm h} \approx \mu_{\rm e} \approx 10^{-5}$ cm² V⁻¹ s⁻¹), and high morphological stability ($T_{\rm g} = 185$ °C). PhOLEDs adopted **CNBzIm** as a host respectively doped with Os(bpftz)₂(PPh₂Me)₂, (PPy)₂Ir(acac) and FIrpic under the same device structure show excellent performance with external quantum efficiencies ($\eta_{\rm ext}$) as high as 19.1% for red, 17.8% for green, and 12.7% for blue. A two-color, all-phosphor and single-emitting-layer WOLED hosted by **CNBzIm** was achieved with a maximum $\eta_{\rm ext}$ of 15.7%, current efficiency (η_c) of 35 cd A⁻¹, and power efficiency (η_p) of 36.6 lm W⁻¹. Utilizing a bipolar host with balanced mobilities, WOLED can effectively broaden its recombination zone and show high color stability. The Commission Internationale de L'Eclairage (CIE) coordinates of the WOLED remain almost constant when the brightness goes from 1700 cd m⁻² (0.32, 0.41) to 49 900 cd m⁻² (0.31, 0.41).

Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) have become a subject of great research interest in recent years from both academy and industry owing to their potential applications in flat-panel displays and lighting sources.¹ It is essential to deliver a set of primary RGB emitters with sufficiently high luminous efficiency for full-color OLED display applications. Recently, the use of phosphorescent materials in which strong spin-orbit coupling leads to singlet-triplet state mixing has boosted the electroluminescence efficiency up to unity internal quantum efficiency. To date, green and red PhOLEDs with 100% internal quantum efficiency have been successfully achieved,² while efficient and stable blue PhOLEDs still remain challenging. On the other hand, white organic light-emitting diodes (WOLEDs) have drawn intensive interests because of their potential application in full-color flat-panel displays, backlights for LCDs, and solid-state lighting.3 White emission is generally achieved by mixing several materials that give rise to the three primary colors (blue, green, and red) or two complementary

colors by adopting either fluorophore/phosphor or all-phosphor systems. The fluorophore/phosphor system so-called hybrid WOLED combines a blue fluorophore with complementary phosphors,⁴ in which the blue fluorophore needs to have both high photoluminescent quantum yield and higher triplet energy $(E_{\rm T})$ than that of the complementary phosphors. In our previous work, we reported that benzimidazole/carbazole hybrid bipolar material (CPhBzIm) exhibits a blue fluorescent peak at 426 nm with excellent solid state photoluminescence quantum yield ($\Phi_{\rm PL} = 69\%$), and suitable triplet energy ($E_{\rm T} = 2.48$ eV), and bipolar charge transport ability.5 Hybrid WOLEDs can be reached by only one single emission layer made of the fluorescent blue emitter doped with very small amounts of yellow-green phosphorescent emitter. However, the limitation set by the intrinsic photophysical property of a fluorescent blue emitter, the WOLED, only exhibited a maximum η_{ext} of 7% (15.5 cd A⁻¹) and 12.8 lm W⁻¹.

To realize high-efficiency WOLEDs, the more promising alternative approach is to use all phosphor system that enable an internal efficiency as high as 100%.⁶ Nevertheless, there are challenges of using all phosphor WOLEDs, particularly difficult to find highly efficient and stable blue host materials for significantly reducing efficiency roll-off at the practical luminance. In addition, the adaptation of two or multiple emitting layer (EML) structures typically will result in higher complexity of device fabrication, higher operation voltages and thus lower power efficiency.⁷ Alternatively, the full-phosphor approach of WOLEDs can be achieved by using only a single emitter layer

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composed of a universal host doped with different color dopants simultaneously. This approach could pave the way towards relatively simple and more cost-effective fabrication processes for WOLED with comparable output efficiencies. Along this line, universal host materials for phosphorescent devices recently caught great attention. For example, Shu et al. reported fluorene/ triarylamine hybrid hole-transport-type host material, tris[4-(9phenylfluoren-9-vl)phenyllamine (TFTPA), with a high triplet energy $(E_{\rm T})$ of 2.89 eV and a high glass transition temperature (T_{s}) of 186 °C.⁸ Devices with TFTPA as host show external quantum efficiencies (η_{ext}) as high as 12.3% for blue, 11.8% for green and 9.2% for red. Cheng et al. reported a hole transporting host material, 2,6,14-tris-(diphenylamino)triptycene (TATP), exhibiting a remarkably high $E_{\rm T}$ of 2.94 eV and a $T_{\rm g}$ of 178 °C.⁹ TATP can be employed as a general host for blue, green and red electrophosphorescence devices providing η_{ext} of 7.8%, 11.5% and 9.8%, respectively. Furthermore, Cheng and Chou reported that a bipolar host material bis-(4-(N-carbazolyl)phenyl)phenylphosphine oxide (BCPO) containing a phenylphosphine oxide and two carbazole groups shows a high $E_{\rm T}$ of 3.01 eV and a $T_{\rm g}$ of 137 °C.¹⁰ BCPO can be applied as a universal host to blue, green and red phosphorescent devices using simple device architectures, giving extremely high η_{ext} of 23.5%, 21.6% and 17%, respectively. Yang et al. reported a silicon-bridged compound p-BISiTPA combining p-type triphenylamine and n-type benzimidazole moiety, giving a high $E_{\rm T}$ of 2.69 eV, a $T_{\rm g}$ of 102 °C and bipolar transporting features.¹¹ Devices with p-BISiTPA as host show excellent performance, with η_{ext} as high as 16.1% for blue, 22.7% for green, 20.5% for orange and 19.1% for WOLED. In addition, Kido et al. developed a bipolar host material 26DCzPPy by combining carbazole and pyridine into a single molecule, exhibiting high $T_{\rm g}$ (102 °C) and triplet energy ($E_{\rm T}$ = 2.71 eV).¹² Excellent RGB phosphorescent devices employing 26DCzPPy as host with η_{ext} as high as 24.3% for blue, 26.9% for green, 12.6% for red were achieved at a brightness of 100 cd m⁻². Based on this reported literature, an ideal universal host should have (i) high triplet energy suitable for blue, green and red phosphors, preventing from a reverse energy transfer, (ii) appropriate HOMO/LUMO levels relative to neighboring functional layers, allowing smooth charge carriers injection into the emitting layer, and (iii) bipolar transporting characteristics, rendering a broad exciton-formation zone and consequently reducing the efficiency roll-off. In this report, we modified the efficient green host CPhBzIm by changing the linking topology from a C- into a N-bridge connecting the electron-accepting Nphenylbenzimidazole to the electron-donating carbazole core. This molecular design leads to a new benzimidazole/carbazole hybrid compound, 3,6-bis(N-phenylbenzimidazol)-9-phenylcarbazole (CNBzIm, Scheme 1) with reduced π -conjugation and thus an increased triplet energy ($E_{\rm T} = 2.71$ eV); meanwhile, the whole molecule would maintain suitable frontier orbitals energy, bipolar charge transport ($\mu_h \approx \mu_e \approx 10^{-5} \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) and sufficient morphological stability ($T_g = 185$ °C). PhOLEDs employing CNBzIm as a host doped with various phosphors under the same device structure show excellent performance, with external quantum efficiencies as high as 12.7% for blue, 17.8% for green, 19.1% for red. A two-color, all-phosphor and single-emitting-layer WOLED hosted by CNBzIm was also achieved with a maximum η_{ext} of 15.7%, current efficiency (η_c) 35



Scheme 1 Synthetic pathways of CNBzIm and molecular structure of CPhBzIm.

cd A⁻¹ and power efficiency (η_p) of 36.6 lm W⁻¹. This WOLED shows high color stability ascribed to a broad charge recombination zone in the emitting layer incorporating with this superior bipolar host. The Commission Internationale de L'Eclairage (CIE) coordinates of WOLED remain almost constant when the brightness goes from 1700 cd m⁻² (0.32, 0.41) to 49 900 cd m⁻² (0.31, 0.41).

Results and discussion

Scheme 1 depicts the synthetic routes for the bipolar host material CNBzIm. The synthesis of 1-(4'-bromophenyl)-2phenyl-1*H*-benzoimidazole $(1)^{13}$ was carried out by reacting N-(4-bromophenyl)-o-phenylenediamine with benzaldehyde in acetic acid under refluxing condition gave a yield of 70%. CNBzIm was obtained in 74% yield when benzimidazole derivative 1 was treated with carbazole-based diboronic ester 214 in the presence of a catalytic amount of Pd(PPh₃)₄. CNBzIm was well characterized with ¹H NMR, ¹³C NMR, mass and elemental analysis. CNBzIm exhibits high thermal stability with a decomposition temperature (T_d , corresponding to 5% weight loss) of 405 °C by the thermogravimetric analysis (TGA). The glass transition temperature ($T_g = 185 \,^{\circ}$ C) of CNBzIm was determined by differential scanning calorimetry (DSC). We could use vacuum deposition to prepare homogeneous, stable amorphous thin films. The similar thermal stability as compared to that of counterpart molecule CPhBzIm is presumably the result of the same molecular weight (Table 1). CNBzIm exhibits excellent thermal and morphological stability, which could reduce the possibility of phase separation upon heating, thus can potentially prolong the device operational lifetime.

Fig. 1 displays the room-temperature absorption and photoluminescence (PL) spectra of **CNBzIm** recorded from a dilute dichloromethane solution and as a neat film on a quartz substrate. A remarkable blue-shift (*ca.* 20 nm) in the spectra of **CNBzIm** as compared with those obtained from **CPhBzIm** indicating the efficient disruption of the π -conjugation between the *N*-phenylbenzimidazole peripherals and 3,6-diarylcarbazole

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	$T_{\rm g}/^{\circ}{\rm C}$	$T_{\rm d}/^{\circ}{\rm C}$	$E_{1/2}^{\text{OX}a}/E_{1/2}^{\text{REV}b}/\text{V}$	HOMO/LUMO/Eg ^c /eV	$E_{\rm T}/{\rm eV}$	λ_{abs}/nm [sol./film]	λ _{PL} /nm [sol./film]			
CNBzIm CPhBzIm	185 170	405 480	1.27/-2.13 1.24/-2.06	-5.57/-2.2/3.37 -5.49/-2.37/3.12	2.71 2.48	300/304 317/322	391/398 412/426			

^{*a*} Oxidative CV was performed in 1.0 mM CH₂Cl₂ containing 0.1 M TBAF₆. ^{*b*} Reductive CV was performed in 1.0 mM THF containing 0.1 M TBAP. ^{*c*} Determined through AC2 measurements; LUMO = HOMO + E_g ; the value of E_g was calculated from the absorption onset of the solid film.



Table 1 Physical properties of CNBzIm and CPhBzIm

Fig. 1 Room-temperature UV-Vis absorption and PL spectra of CNBzIm in dilute CH_2Cl_2 solution (dotted lines) and in neat film (solid lines); Phosphorescence spectra of CNBzIm and CPhBzIm in EtOH solution (symbol lines) at 77 K.

core. Fig. 1 also depicts the phosphorescence spectra of **CNBzIm** and **CPhBzIm** in EtOH solution at 77 K. The highest energy 0–0 phosphorescent emission of **CNBzIm** located at 457 nm was used to calculate the triplet energy ($E_{\rm T} = 2.71$ eV), which is higher than that of **CPhBzIm** ($E_{\rm T} = 2.48$ eV).

The theoretical calculations for HOMO/LUMO orbitals of **CNBzIm** were performed by density functional theory (DFT) using B3LYP with 6-31 + G(d,p) basis set. Fig. 2 shows the HOMO of **CNBzIm** which is distributed over the carbazole and

phenylene rings connected to C3 and C6 positions with major contribution from central carbazole moiety. On the other hand, LUMO is mainly populated on carbazole and phenylene ring connected to C3 position of carbazole core with minor contribution from benzimidazole, implying that π -conjugation between peripheral N-phenylbenzimidazole and carbazole core is largely disrupted. The spatial distribution of CNBzIm frontier orbitals is largely different from those of **CPhBzIm**, in which the N-phenylbenzimidazole blocks made a significant contribution for both HOMO and LUMO.5 These results indicate that the manipulation of the spatial distributions of frontier orbitals, energy levels, and triplet energies of benzimidazole/carbazole hybrid bipolar materials can be easily achieved by a facile strategy of altering the linking topologies (C- versus N-connection) between peripheral benzimidazole and central carbazole. The triplet energy of **CNBzIm** ($E_{\rm T} = 2.71$ eV) is sufficiently higher than that of blue phosphor bis[4,6-(difluorophenyl)-pyridinato-N,C21 picolinate (FIrpic, 2.62 eV)15 and other long-wavelength phosphorescent dopants implying effective confinement of the triplet excitons on the guest and prevention of back energy transfer from the guest to the host are feasible.

The electrochemical properties of **CNBzIm** were investigated by cyclic voltammetry (CV) as shown in Fig. 3. We observed one reversible oxidation potential at 1.27 V and one quasi-reversible reduction potential at -2.13 V (*versus* Ag/AgCl). Obviously, there is no typical electropolymerization of carbazole upon electrochemical oxidation since the electroactive sites (C3 and C6) of carbazole were blocked with benzimidazole groups. The HOMO energy level (-5.57 eV) of **CNBzIm** was estimated by atmospheric photoelectron spectroscopy, and the LUMO energy level (-2.2 eV) was calculated by subtraction of the optical energy gap (3.37 eV) from the HOMO value. The electrochemical results and HOMO/LUMO energy levels of **CNBzIm** are slightly different from those of **CPhBzIm** (Table 1), indicating that the



Fig. 2 Frontier molecular orbitals HOMO (top) and LUMO (bottom) of CNBzIm calculated with DFT on a B3LYP/6-31 + G(d,p).



Fig. 3 Cyclic voltammogram of CNBzIm.

electron-accepting *N*-phenylbenzimidazole peripherals have weaker electronic communications toward the carbazole core upon using N-connectivity, which is in good agreement with the results obtained by theoretical calculations.

To evaluate the bipolar character of **CNBzIm**, we used the time-of-flight (TOF) transient-photocurrent technique at room temperature to determine the carrier mobilities.¹⁶ Fig. 4(a) and (b) show the representative TOF transient for holes and electrons of **CNBzIm**.

The transient photocurrent signals were slightly dispersive, suggesting the presence of carrier traps. 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. The carrier mobilities of **CNBzIm** were determined by using the equation $\mu = d^2/Vt_{\rm T}$, where *d* is the sample thickness and *V* is the applied voltage. The hole mobility ($\mu_{\rm h}$) of **CNBzIm** lies in the range from 4.3×10^{-6} to 1.2×10^{-5} cm² V⁻¹ s⁻¹ for fields varying from 3.4×10^5 to 5.6×10^5 V cm⁻¹; the electron mobility (μ_e) lies



Fig. 4 Typical transient photocurrent signals for **CNBzIm** (3.2 μ m thick) at $E = 5.6 \times 10^5$ V cm⁻¹: (a) hole; (b) electron. Insets are the double logarithmic plots of (a) and (b). (c) Electron and hole mobilities *versus* $E^{1/2}$, compared with **CPhBzIm**.

in the range from 1.1×10^{-5} to 3.2×10^{-5} cm² V⁻¹ s⁻¹ for fields varying from 5.6×10^5 to 7.2×10^5 V cm⁻¹. Fig. 4(c) shows the carrier mobilities of **CNBzIm** and **CPhBzIm** plotted as a function of the square root of the electric field. Apparently, *N*-phenylbenzimidazole linking topologies, *i.e.* C- or N-connection, with the carbazolyl moiety do not have a pronounced effect on the hole transporting ability but play a crucial role on electrontransporting ability. The electron mobility of **CPhBzIm** is two times of magnitude higher than that of **CNBzIm**. However, the bipolar host **CNBzIm** had relatively balanced hole and electron transporting ability as compared with that of **CPhBzIm**, which will be highly beneficial for charge carrier balance in the emitting layer to generate broader recombination zones.

In view of the high triplet energy ($E_{\rm T} = 2.71 \, {\rm eV}$) of **CNBzIm**, the application of it as host material for RGB electrophosphorescent devices was investigated by a simple three-layer configuration: indium tin oxide (ITO)/poly(3.4-ethylenedioxythiophene) : poly (styrene sulfonate) (PEDOT : PSS) (30 nm)/DTAF (25 nm)/ emitter (25 nm)/TPBI (50 nm)/LiF (0.5 nm)/Al (100 nm). To illustrate our concept, three phosphorescent dyes, osmium(II) bis[3-(trifluoromethyl)-5-(4-tert-butylpyridyl)-1,2,4-triazolate] diphenylmethylphosphine [Os(bpftz)₂(PPh₂Me)₂] for red emission.17 bis(2-phenylpyridinato)iridium(III) acetvlacetonate [(PPy)₂Ir(acac)] for green emission,¹⁸ and Iridium(III)[bis(4,6difluorophenyl)-pyridinato- $N, C^{2\prime}$ picolinate (FIrpic) for blue emission, are exploited (Scheme 2). The hole-transporting material 1,1-bis[(di-4-tolylamino)phenyl]-9,9'-fluorene (DTAF), with a high triplet level ($E_T = 2.87 \text{ eV}$) and wide bandgap ($E_g = 3.47 \text{ eV}$) that can efficiently confine the triplet energy of phosphors, is selected as the hole-transporting layer (HTL).^{5,19} To further confine the holes or generated excitons within the emissive region, 1,3,5-tris(*N*-phenylbenzimidizol-2-yl)benzene (TPBI)²⁰ with a high-energy gap is selected as the electron-transporting layer (ETL). PEDOT : PSS and LiF served as hole- and electroninjecting layer, respectively.

Fig. 5 shows the current density–voltage–brightness (*J*–*V*–*L*) characteristics, EL efficiencies, and spectra of RGB devices using **CNBzIm** doped with 10% Os(bpftz)₂(PPh₂Me)₂ (red, R), 10% (PPy)₂Ir(acac) (green, G), and 12% FIrpic (blue, B), respectively. The device performances are summarized in Table 2. All devices displayed low turn-on voltage at 2.5 V. The blue emission device B reveals a maximum brightness of 36 400 cd m⁻² at 12 V (900 mA cm⁻²) with the CIE coordinates of (0.17, 0.39). The maximum external quantum efficiency (η_{ext}) and power efficiency (η_{p}) were 12.7% (29 cd A⁻¹) and 30.5 lm W⁻¹, respectively.

These values are moderate among FIrpic-based OLEDs presumably because the $E_{\rm T}$ of **CNBzIm** is not sufficiently high enough relative to FIrpic for blocking the thermally activated



Scheme 2 Chemical structures of the heavy metal complex used in this study.

(a) 250



Fig. 5 (a) J-V-L characteristics, (b) plots of EL efficiency *versus* brightness and (c) EL spectra for RGB devices under the same device structure.

exciton diffusion completely. However, this is a worthy sacrifice to acquire a compromise among the E_{TS} of RGB phosphors.

Next we fabricated the green emission device G with the same configuration as device B except for using $(PPy)_2Ir(acac)$ as the dopant. The maximum brightness reaches 140 000 cd m⁻² at 10.5 V (1080 mA cm⁻²) with the CIE coordinates of (0.35, 0.62) for device G. The maximum values of η_{ext} and η_p were 17.8% (66.8



Fig. 6 (a) J-V-L characteristics and (b) plots of EL efficiency versus brightness for white devices under different HTLs.

cd A⁻¹) and 59.4 lm W⁻¹, respectively. Remarkably, the device shows rather low efficiency roll-off: at a brightness of 1000 cd m^{-2} , η_{ext} is still as high as 17.7%. The values are similar to our previously reported results using CPhBzIm doped with (PBi)2Ir (acac), in which the value of η_{ext} reached 19.2%.⁵ In addition, the red emission device R using Os(bpftz)₂(PPh₂Me)₂ as the dopant exhibits strong emission with the CIE coordinates of (0.61, 0.39). For device R, the maximum values of η_{ext} and η_{p} reach as high as 19.1% (33.8 cd A^{-1}) and 27 lm W^{-1} , respectively, with a maximum brightness of 43 800 cd m^{-2} at 11.5 V (1040 mA cm⁻²). The electroluminescence (EL) spectra consist only of a phosphor emission without any residual emission from the host and/or adjacent layers as shown in Fig. 5(c), even at high driving currents-an indication of complete energy and/or charge transfer from the CNBzIm host to the phosphors upon electrical excitation. The EL spectra and CIE coordinates for the devices exhibited no significant change on the variation of operating bias voltages. More importantly, the excellent performances of these RGB devices were obtained from the same device architecture

Table 2	EL	performances	of	devices
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Device	$V_{\rm on}{}^a/{\rm V}$	At 1000 nit ^b /V, %	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$I_{\rm max}/{ m mA~cm^{-2}}$	$\eta_{\mathrm{ext}}/\%$	$\eta_{\rm c}/{ m cd}~{ m A}^{-1}$	$\eta_{ m p}/{ m lm}~{ m W}^{-1}$
В	2.5	5.5, 9.8	36 400 (12 V)	900	12.7	29	30.5
G	2.5	4.3, 17.7	140 000 (10.5 V)	1080	17.8	66.8	59.4
R	2.5	5.2, 17.6	43 800 (11.5 V)	1040	19.1	33.8	27
W1	2.5	7.5, 12.4	49 900 (14 V)	1240	15.7	35	36.6
W2	2.5	5.2, 11.2	51 600 (13 V)	1600	15.4	34.3	33.7

^a Turn-on voltage at which emission became detectable. ^b The values of driving voltage and η_{ext} of device at 1000 cd m⁻².

incorporated with different phosphors. When the brightness reaches to 1000 cd m⁻², the devices have similar driving voltages (4.3–5.5 V) as well as the η_{ext} still remains 9.8% for blue, 17.7% for green, and 17.6% for red, which make them very attractive for commercial applications of full-color display.

Owing to the successful development of the high-efficiency RGB PhOLEDs, we shifted to fabricate a two-color WOLED (device W1) under the same device structure by utilizing 12 wt% FIrpic and 0.3 wt% Os(bpftz)₂(PPh₂Me)₂ co-doped into CNBzIm as a single-emitting layer. Fig. 6 shows the J-V-L characteristics and curves of external quantum efficiency and power efficiency versus brightness. The white emission device W1 reveals a low turn-on voltage of 2.5 V and a maximum brightness of 49 900 cd m⁻² at 1240 mA cm⁻² at 14 V. The maximum values of efficiencies (η_{ext} , η_{c} , and η_{p}) were 15.7%, 35 cd A⁻¹, and 36.6 lm W⁻¹, respectively. Even at a practical brightness of 1000 cd m⁻², the η_{ext} remained at 12.4%. Notably, this WOLED W1 possesses high color stability as shown in Fig. 7(a). When the brightness changes from 1700 to 49 900 cd m⁻² (which corresponds to an applied voltage of 6 to 12 V), the variation of the Commission Internationale de L'Eclairage (CIE) coordinates is rather small, CIE x = 0.31-0.32 and CIE y = 0.41, thus revealing superior device chromatic stability.

In general, WOLEDs suffer from low color stability (*i.e.*, the white spectra change with driving voltages), which is probably due to the shifting of the recombination zone.²¹ The stable white OLED device structure should be carefully tuned for better charge carrier balance, adjusted the recombination zone, and modulated energy transfer to achieve a balanced exciton distribution in emissive layer.^{7b} To gain further insight into the



Fig. 7 Electroluminescence spectra of the device with different HTLs: (a) W1(DTAF) and (b) W2(NPB/TCTA), measured at various brightness.

emission mechanism in the device W1, device W2 with different HTLs [4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB, 20 nm)/4,4',4"-tri(N-carbazolyl)triphenylamine (TCTA, 5 nm)] to replace DTAF in device W1 structure was also fabricated and tested. Fig. 7 displays the electroluminescence (EL) characteristics of white devices W1 and W2; the data are summarized in Table 2. The J-V characteristics reveal that the device W2 incorporating NPB/TCTA as HTL exhibits a lower driving voltage relative to device W1 incorporating DTAF as HTL. Compared with device W1, we note that device W2 gives a large efficiency roll-off problem (the η_{ext} decreases to 11.2% at 1000 cd m^{-2}) and a low color stability. The CIE coordinates (x, y)changed from (0.35, 0.40) at 720 cd m^{-2} to (0.31, 0.40) at 31 300 cd m^{-2} as shown in Fig. 7(b). This could be attributed to the recombination zone shifting in devices owing to the different charge transporting abilities of HTL. We can conclude that DTAF used as HTL can lead to a more balanced electron and hole recombination in the emissive layer, and play a crucial role in alleviating the efficiency roll-off problem and maintaining the chromatic stability of WOLEDs.

Conclusions

In summary, a new bipolar host molecule CNBzIm comprised of electron-donating carbazole core and electron-accepting N-phenylbenzimidazole peripherals has been synthesized and chemically characterized. CNBzIm adopted a N-connectivity to link benzimidazole and carbazole structures, rendering reduced π conjugation and thus a relatively high triplet energy state ($E_{\rm T} =$ 2.71 eV), balanced bipolar charge transport and sufficient morphological stability. Due to the promising physical properties, CNBzIm can be utilized as a universal host material for multicolor phosphors. We have successfully fabricated highefficiency RGB and white OLEDs incorporating various phosphors under the same device structure. The maximum external quantum efficiencies obtained for the R, G, B, and W devices are 12.7%, 17.8%, 19.1%, and 15.7%, respectively. Under this device structure, a WOLED can achieve a balanced exciton distribution in its emissive layer to generate high color stability and low efficiency roll-off. The CIE coordinates of the white device remain almost invariable when the brightness goes from 1700 cd m^{-2} (0.32, 0.41) to 49 900 cd m^{-2} (0.31, 0.41).

Experimental

Synthesis

Synthesis of bipolar material CNBzIm. A mixture of 3,6-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-phenyl-9*H*-carbazole (3)¹⁴ (2.97 g, 6.0 mmol), 1-(4-bromophenyl)-2-phenyl-1*H*-benzo[*d*]imidazole (5.0 g, 14.3 mmol), Pd(PPh₃)₄ (0.35 g, 0.3 mmol), K₃PO₄ (24 mL, 2 M) and tri(*tert*-butyl)phosphine (12 mL, 0.05 M in toluene, 0.6 mmol) in 60 mL was refluxed for 2 days. The reaction mixture was cooled to room temperature, and extracted with CH₂Cl₂ (100 mL \times 2). The organic layer was washed with brine and dried over MgSO₄. The solution was concentrated in vacuum to obtain a residue which was purified by column chromatography on silica gel (SiO₂) using ethyl acetate/hexane (1 : 1) as eluent to give a white solid **CNBzIm** (3.46 g, 74%). Mp 346–347 °C; IR (KBr) ν 3044, 2921, 2850,

1597, 1496, 1479, 1380, 1277, 809, 741, 696; ¹H NMR (CDCl₃, 400 MHz) δ 8.49 (d, J = 1.6 Hz, 2H), 7.93 (d, J = 7.2 Hz, 2H), 7.86 (d, J = 8.4 Hz, 4H), 7.76 (dd, J = 1.6, 8.8 Hz, 2H), 7.70–7.64 (m, 8H), 7.56–7.53 (m, 3H), 7.43 (d, J = 8.4 Hz, 4H), 7.39–7.29 (m, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 152.2, 142.9, 141.8, 141.0, 137.1, 135.3, 132.0, 130.0, 129.9, 129.4, 129.3, 128.3, 128.2, 127.8, 127.6, 126.8, 125.5, 123.9, 123.2, 122.9, 119.8, 118.9, 110.4; MS (m/z, FAB+) 780 (2.15); HRMS (m/z, FAB+) Calcd for C₅₆H₃₇N₅ 779.3049, found 779.3052; Anal. Calcd. C, 86.24; H, 4.78; N, 8.98; found C, 86.50; H, 5.07; N, 9.12.

Photophysical measurements

Steady state spectroscopic measurements were conducted both in solution and solid films prepared by vacuum (2×10^{-6} Torr) deposition on a quartz plate (1.6×1.0 cm). Absorption spectra were recorded with a U2800A spectrophotometer (Hitachi). Fluorescence spectra at 300 K and phosphorescent spectra at 77 K were measured on a Hitachi F-4500 spectrophotometer upon exciting at the absorption maxima. The experimental values of HOMO levels were determined with a Riken AC-2 photoemission spectrometer (PES), and those of LUMO levels were estimated by subtracting the optical energy gap from the measured HOMO.

Cyclic voltammetry

The oxidation potential was determined by cyclic voltammetry (CV) in CH₂Cl₂ solution (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 THF solution (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. All potentials were recorded *versus* Ag/AgCl (saturated) as a reference electrode.

Time-of-flight (TOF) mobility measurements

Carrier-transport properties were studied in vapor-deposited glasses of CNBzIm by the time-of-flight (TOF) transient photocurrent technique. The samples for the TOF measurement were prepared by vacuum deposition using the structure: ITO glass/ CNBzIm (1.56 mm)/Al (150 nm), and then placed inside a cryostat and kept under vacuum. The thickness of organic film was monitored in situ with a quartz crystal sensor and calibrated by a thin film thickness measurement (K-MAC ST2000). A pulsed nitrogen laser was used as the excitation light source through the transparent electrode (ITO) 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 (Al), and then recorded with a digital storage oscilloscope. Depending on the polarity of the applied bias, selected carriers (holes or electrons) are 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 $\mu = D/(t_T E) = D^2/(V t_T)$, in which the carrier transit time, $t_{\rm T}$, can be extracted from the

intersection point of two asymptotes to the plateau and the tail sections in double-logarithmic plots.

OLED device fabrications

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 Ω sq⁻¹. The ITO surface was cleaned ultrasonically—sequentially with acetone, methanol, and deionized water—and then it was treated with UV-ozone. The deposition rate of each organic material was *ca*. 1–2 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 glove box using a Keithley 6430 source meter and a Keithley 6487 picoammeter equipped with a calibration Si-photodiode. EL spectra were measured using a photodiode array (OTO SD1200).

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