Simple Bipolar Hosts with High Glass Transition Temperatures Based on 1,8-**Disubstituted Carbazole for Efficient Blue and Green Electrophosphorescent** Devices with "Ideal" Turn-on Voltage

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Abstract: Two hybrids based on 1,8-disubstituted carbazole, 1,8-OXDCz and 1,8-mBICz, have been designed and synthesized through a facile process. The incorporation of oxadiazole or Nphenylbenzimidazole moieties at the 1,8-positions of carbazole greatly improves its morphological stability, giving glass transition temperatures (T_{σ}) as high as 138 and 154 °C, respectively. Blue phosphorescent organic light-emitting devices (PhOLEDs) with 1,8-mBICz exhibit almost the same performance as a similarly structured device based on the mCP host, and green PhOLEDs employing the new

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host material 1,8-OXDCz exhibit an ideal turn-on voltage (2.5 V at 1.58 cdm⁻²), a maximum current efficiency $(\eta_{c,max})$ of 73.9 cd A⁻¹, and a power efficiency ($\eta_{p,max}$) of 89.7 lm W⁻¹. These results are among the best performances of [Ir(ppy)₃]-based devices with simple device configurations.

Introduction

The host-guest system has been used widely in phosphorescent organic light-emitting devices (PhOLEDs) since the triplet emitter of heavy-metal complexes (PtOEP) was first doped in a host matrix by Baldo and Forrest to reduce concentration quenching and triplet-triplet annihilation.^[1] A suitable host material for separation of the triplet emitters is vital for the achievement of efficient electrophosphorescence. Recently, large numbers of carbazole-based host materials have been developed, such as the widely utilized hole-transporting host 4,4'-bis (9-carbazolyl)-2,2'-biphenyl (CBP),^[2] 2,7-bis(N-carbazolyl)-N-phenyl carbazole (BCC-27),^[3] and the bipolar host material bis-4-(N-carbazolyl)phenylphosphine oxide (BCPO),^[4] 2,5-bis[2-(9H-carbazol-9-yl)phenyl]-1,3,4-oxadiazole (o-CzOXD).^[5] However, host mate-

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rials satisfying the requirements for practical applications are still rare, and further study is needed.

As we know, carbazole has a high triplet energy of 2.95 eV^[6] and an excellent hole-transporting ability.^[7] In addition, the simple structure of the carbazole unit offers many options for the introduction of building blocks into the carbazole core through a facile chemical approach. Of the reported carbazole-based host materials, most focused on 2,7-, 3,6-, or N-position functionalization. Recently, some 1,8-disubstituted carbazole derivatives were reported as fluorescent probes^[8] or to demonstrate the relationship between the rigidity of the structure and the linking positions.^[9,10] However, 1,8-disubstituted carbazole derivatives used as host materials for PhOLEDs have not yet been reported. According to the electron distribution rules of carbazole, the 1,8-positions of carbazole are electron-deficient; this will reduce the conjugation between carbazole and the other conjugated moieties, leading to a relatively high triplet energy level. Note that the relatively high spatial hindrance of 1,8-position derivatives will enhance their glass transition temperatures. Generally, the introduction of one or more 1,3,4-oxadiazole and N-phenylbenzimidazole groups to the corresponding carbazole/oxadiazole or carbazole/benzimidazole hybrids will impart a greater electron-transporting capability to the carbazole derivatives, coupled with increased conductivity.^[5,11] Herein, we present the synthesis and photophysical properties of a series of novel carbazole derivatives: 1,8-disubstituted carbazole/oxadiazole (1,8-OXDCz) and carbazole/benzimidazole (1.8-mBICz) hybrids. The PhOLEDs with $[Ir(ppy)_3]$ doped in 1.8-OXDCz exhibit a maximum power efficiency of 89.7 $\text{Im } \text{W}^{-1}$ and an external

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Scheme 1. Molecular structures and synthesis of **1,8-OXDCz** and **1,8-mBICz**. Reagents and conditions: a) Br_2 , AcOH, 90°C, 3.5 h, 85%; b) NaH, CH₃I, DMF, 18 h, 96%; c) [Pd(PPh₃)₄], 2-phenyl-5-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1,3,4-oxadiazole, $K_2CO_3(2M)$, toluene, ethanol, 90°C, 24 h, 78%; d) [Pd(PPh₃)₄], 1-phenyl-2-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1*H*-benzo[d]imidazole, $K_2CO_3(2M)$, toluene, ethanol, 90°C, 24 h, 74%.

quantum efficiency (EQE) of 20.3%; the turn-on voltage is even lower than 2.5 V. These are among the best reported results for simple carbazole-based devices.^[11,12] The results demonstrate that 1,8-disubstituted-carbazole-based bipolar host materials could be a promising class of phosphorescent host materials for PhOLEDs.

Results and Discussion

Synthesis: The new hosts were synthesized according to the synthetic route shown in Scheme 1. Starting from commercially available 3,6-di-tert-butyl-9H-carbazole, 1,8-dibromo-3,6-di-tert-butyl-9H-carbazole 1 was prepared by the traditional bromination reaction; the key precursor 1,8-dibromo-3,6-di-tert-butyl-9-methyl-9H-carbazole 2 was obtained by treatment of compound 1 with sodium hydrogen for 0.5 h and subsequent methylation with iodomethane. The Suzuki coupling reaction between compound 2 and 2-phenyl-5-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1,3,4oxadiazole or 1-phenyl-2-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1*H*-benzo[*d*]imidazole gave rise to the final products 1,8-OXDCz and 1,8-mBICz, respectively. The detailed procedures and characterization of the new compounds are described in the Experimental Section. The pure compounds 1,8-OXDCz and 1,8-mBICz are white powders, and exhibit excellent solubility in common solvents such as THF, CH₂Cl₂, and toluene for the incorporation of two tertbutyl groups. The structures of 1,8-OXDCz and 1,8-mBICz were determined by atmospheric-pressure chemical ionization mass spectrometry (APCI-MS), ¹H NMR and ¹³C NMR spectroscopy, and elemental analyses.

Thermal properties: The good thermal stabilities of **1,8-OXDCz** and **1,8-mBICz** are indicated by their high decomposition temperatures (T_d , corresponding to 5% weight loss, see Figure 1) of 416 and 433 °C, respectively. The glass tran-



Figure 1. TGA thermograms of **1,8-OXDCz** and **1,8-mBICz** recorded at a heating rate of 10 °Cmin⁻¹. Inset: DSC thermograms of **1,8-OXDCz** and **1,8-mBICz** recorded at a heating rate of 10 °Cmin⁻¹.

sition temperatures (T_g) were observed at 138 and 154°C, respectively, through differential scanning calorimetry (DSC); these values are higher than those of the carbazole analogues such as CBP (62°C) and mCP (60°C).^[6] The high T_g values of these host materials may be attributed mainly to the two *tert*-butyl groups on the 3,6-positions of the carbazole, which can suppress intermolecular aggregation and improve the film morphology. The relatively high T_g and T_d values mean that these compounds avoid phase separation upon heating and have the potential for use in high-performance devices fabricated by vacuum thermal evaporation technology.

Photophysical properties: The absorption and fluorescence properties of **1,8-OXDCz** and **1,8-mBICz** were tested in both solution and thin film form (Figure 2 a). The absorption peak at 287 nm is attributed to the $n-\pi^*$ transitions of the carbazole, and the absorption maximum peak at about

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Figure 2. a) Absorption and emission spectra of **1,8-OXDCz** and **1,8-mBICz** in toluene solution or as thin films at room temperature. b) Phosphorescence spectra of **1,8-OXDCz** and **1,8-mBICz** in 2-methyl tetrahydrofuran at 77 K.

362 nm may be due to the intermolecular or intramolecular interactions resulting from the higher degree of conjugation, as the benzene units are linked at the 1,8-positions. The emission maxima in toluene solution are centered at about 394 and 385 nm, respectively, and the emission maximum in the film are redshifted by just 16 and 22 nm, respectively, suggesting that the two tert-butyl groups suppress intermolecular aggregation effectively.^[13] On the basis of the absorption edges of 1,8-OXDCz and 1,8-mBICz in toluene, the corresponding optical energy gaps (E_s) were calculated to be 3.27 and 3.26 eV, respectively. Figure 2b depicts the phosphorescence spectra of 1,8-OXDCz and 1,8-mBICz measured in a frozen 2-methyltetrahydrofuran matrix at 77 K. The triplet energies $(E_{\rm T})$ were about 2.6 and 2.7 eV, respectively, by the highest-energy vibronic sub-band of the phosphorescence spectrum, which suggests that $E_{\rm T}$ of **1,8-mBICz** is high enough for blue or green emitters such as FIrpic (2.65 eV) and $[Ir(ppy)_3]$ (2.4 eV),^[14] and that **1,8-OXDCz** could be applied as a host for green phosphorescent emitters. Note that when phenylbenzimidazole was attached to the 3,6-position of carbazole, E_T was only 2.48 eV.^[15] The relatively high E_T of **1,8-mBICz** also verified our design principle that 1,8-disubstitued carbazole derivatives possess higher E_T values than the corresponding 3,6-disubstitued carbazole derivatives.

Electrochemical properties: For evaluation of the HOMO/ LUMO energy levels, the electrochemical properties of **1,8mBICz** and **1,8-OXDCz** were probed by cyclic voltammetry (CV). Both compounds exhibited reversible oxidation peaks (Figure 3); the respective electrochemical data are summa-



Figure 3. Cyclic voltammograms of 1,8-mBICz and 1,8-OXDCz in CH_2Cl_2 solution.

rized in Table 1. The oxidation potentials of **1,8-mBICz** and **1,8-OXDCz** were found at 0.88 V and 0.90 V versus Ag/Ag⁺, respectively. The HOMO levels of **1,8-mBICz** and **1,8-OXDCz** were estimated to be approximately -5.58 and -5.60 eV, respectively, according to the equation $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}}+4.7) \text{ eV}.^{[16]}$ The corresponding LUMO levels were calculated from the HOMO values, and the energy gaps (3.27 and 3.26 eV), and were found to be approximately -2.31 and -2.34 eV, respectively. Moreover, the HOMO-level values were all significantly higher than that of the CBP host (-6.0 eV), implying lower hole-injection barriers from the hole-transporting layer to the emissive layer compared with CBP.^[17]

Theoretical calculations: Quantum chemical calculations performed using the DFT/B3LYP/6-31G (d,p) method re-

Table 1. Optical, photophysical, and thermal properties of 1,8-mBICz and 1,8-OXDCz.

	$\lambda_{abs,ma}$ Sol ^[a]	_x [nm] Film	$\lambda_{ m em,max}$ Sol ^[a]	[nm] Film	$E_{\rm g}[{\rm eV}]^{\rm [b]}$	HOMO/LUMO [eV] ^[c]		HOMO/LUMO [eV] ^[d]		$E_{\mathrm{T}} \mathrm{[eV]}^{\mathrm{[e]}}$	$T_{\rm g}/T_{\rm d} \ [^{\rm o}{\rm C}]^{\rm [f]}$		
1,8-mBICz	362/299	363/302	385	407	3.27	-5.58	-2.31	-5.34	-2.46	2.7	154/433		
1,8-OXDCz	365/281	362/288	394	410	3.26	-5.60	-2.34	-5.30	-2.45	2.6	138/416		

[a] Measured in toluene solution. [b] Calculated from the edge of the absorbance of the solution. [c] Measured from the CV. [d] Calculated from DFT. [e] Measured in 2-MeTHF at 77 K. [f] Measured from DSC and TGA.

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Figure 4. Spatial distributions of the HOMO and LUMO levels for 1,8-mBICz and 1,8-OXDCz.

vealed that the molecules exhibit non-coplanar conformations (Figure 4). In particular, the 1,8-disubstituted carbazole twists nearly perpendicularly to the adjacent two oxadiazole or benzimidazole moieties because of the steric repulsion between them. Such special structural characteristics can influence their electronic and physical properties. The HOMO and LUMO orbitals of **1,8-mBICz** and **1,8-OXDCz** are delocalized over the electron-acceptor (oxadiazole and benzimidazole) and electron-donor (carbazole) units, respectively. The separation of the HOMO and LUMO orbitals is beneficial for efficient charge-carrier transport and the prevention of reverse energy transfer.^[18] The calculated HOMO/LUMO values are -5.35/-2.46 eV and -5.30/-2.45 eV, respectively, which also correlate well with the experimental data.

Bipolar transporting characteristics: For a better understanding of the effect of the structural change on the energy levels and the carrier-injection and transport abilities, holeonly and electron-only devices of these bipolar host materials were fabricated.^[4] The configuration of the hole-only device was ITO/NPB (10 nm)/Host (30 nm)/NPB (10 nm)/A1 (100 nm), and that of the electron-only device was ITO/BCP (10 nm)/Host (30 nm)/BCP (10 nm)/LiF (1 nm)/A1 (100 nm). NPB (*N*,*N*^r-bis-(1-naphthyl)-*N*,*N*^r-diphenyl-1,10-biphenyl-4,4^r-diamine) and BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) layers were used to prevent electron and hole injection from the cathode and anode, respectively.^[19] As shown in Figure 5, the hole-only device gives a slightly

Figure 5. Current density versus voltage characteristics of the hole-only and electron-only devices.

of the hole-only device of **1,8-mBICz** is higher than that of the **1,8-OXDCz** device, which may be ascribed to the stronger electron-withdrawing ability of oxadiazole. The results also demonstrate that electron injection from the cathode into the host **1,8-mBICz** is more difficult than into **1,8-OXDCz**, which means the device based on **1,8-OXDCz** may exhibit a better performance.

Electrophosphorescent OLED characterization: Compounds 1,8-mBICz and 1,8-OXDCz were also examined in terms of their use as host materials for phosphorescent devices. Because the triplet energy level of **1,8-mBICz** is higher than that of FIrpic (E_T =2.65 eV), Device A was fabricated using FIrpic as the dopant, with the device structure ITO/MoO₃ (10 nm)/NPB (40 nm)/mCP (5 nm)/1,8-mBICz: 6 wt % FIrpic (20 nm)/TmPyPB (40 nm)/LiF(1 nm)/Al (100 nm). In this device, 1,4-bis[(1-naphthyl-phenyl)amino]biphenyl (NPB) acts as a hole-transporting material, and mCP acts as both a hole-transporting material and an exciton blocker $(E_{\rm T}, 2.9 \,{\rm eV})$ to prevent diffusion of the excitons to the NPB layer. 3,3'-{5'-[3-(pyridine-3-yl)phenyl]-(1,1':3',1"-terphenyl)-3,3"-diyl}dipyridine (TmPyPB) acts as both the electrontransporting and hole-blocking layer. The device performance is summarized in Table 2. As shown in Figure 6a, Device A exhibits a maximum external quantum efficiency and power efficiency of 11.6% and 27.0 lm W^{-1} , respectively. The EL spectra are the same as the emission of FIrpic (see Figure 6b), suggesting that the triplet energy of **1,8-mBICz** is high enough to transfer energy to the dopant FIrpic. The relatively poor performance of Device A may be induced by reverse energy transfer; nevertheless, the performance is comparable with that of the blue device based on mCP.^[20]

lower current density than the electron-only device for the compound **1,8-OXDCz**, but for **1,8-mBICz**, the current density of the hole-only device is higher than that of the electron-only device. However, both devices exhibit bipolar properties. The current density

Table 2. Electroluminescence characteristics of the devices.

Device	Host	$V_{ m on} \ [{ m V}]^{[a]}$	$L_{\max} [cd m^{-2}]^{[b]}$ (V at L_{\max} , [V])	$\eta_{ m c}^{[m c]}$ [cd A ⁻¹]	$\eta_{\mathrm{p}}^{\mathrm{[d]}} \ [\mathrm{lm}\mathrm{W}^{-1}]$	EQE ^[e] [%]	CIE $x, y^{[f]}$
A	1,8-mBICz	3.0	9565 (12.3)	27.6	27.0	11.6	0.15, 0.31
В	1,8-mBICz	2.7	38440 (9.5)	64.0	70.0	17.5	0.30, 0.63
С	1,8-OXDCz	2.5	37920 (10.3)	73.9	89.7	20.3	0.30, 0.63

[a] Turn-on voltage (V) at a luminance of 1.58 cdm⁻². [b] Maximum brightness of the device. [c] Maximum current efficiency. [d] Maximum power efficiency. [e] Maximum external quantum efficiency. [f] CIE coordinates.

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Figure 6. Blue electrophosphorescence properties of Device A with **1,8-mBICz** as the host. a) EQE–J–PE curves of Device A; b) EL spectra of Device A.

For further evaluation of the performances of 1,8-mBICz and 1,8-OXDCz as host materials, green PhOLEDs were fabricated with the following configuration: ITO/MoO₃ (10 nm)/NPB (80 nm)/TCTA (5 nm)/host: 9 wt % [Ir(ppy)₃] (20 nm)/TmPyPB (40 nm)/LiF(1 nm)/Al (100 nm) (1,8mBICz for Device B; 1,8-OXDCz for Device C). 1,4-bis[(1naphthylphenyl)amino]biphenyl (NPB) was used as the hole-transporting material, TmPyPB was used as both the electron-transporting and hole-blocking layer, and MoO₃ and LiF served as the hole- and electron-injecting layers, respectively.^[21] In the two devices, TCTA was chosen as the exciton blocker to prevent the diffusion of excitons to the hole-transporting layer. TCTA has been proven to be an efficient exciton blocker for green and red phosphorescence devices.^[22] In addition, the phosphor [Ir(ppy)₃] doped in 1,8-OXDCz was used as the emitting layer, with the doping level of [Ir(ppy)₃] optimized at 9%. The current densityvoltage-luminance (J-V-L) characteristics, efficiency-current density $(J-\eta)$ characteristics, and EL spectra of the devices are shown in Figure 7, and the key parameters are summarized in Table 2.

Both the **1,8-mBICz**- and **1,8-OXDCz**-based devices have low turn-on voltages of 2.7 and 2.5 V, respectively, at a brightness of 1.58 cdm^{-2} . Considering that the triplet energy of $[\text{Ir}(\text{ppy})_3]$ is about 2.42 eV,^[17] the turn-on voltage value of Device C has already reached the limit of $[\text{Ir}(\text{ppy})_3]$ -based green PhOLEDs; this could be attributed to the bipolar



Figure 7. Green electrophosphorescence properties of Devices B and C: a) *J*–*V*–*L* curves; b) EQE–J–PE curves; c) EL spectra.

properties of the host and the suitable HOMO and LUMO energy levels of **1,8-OXDCz** with the adjacent layers. Schematic energy level diagrams of the devices are shown in Figure 8. The small energy barriers show that carrier injection from TCTA into **1,8-mBICz** or **1,8-OXDCz** is easy. Fur-



Figure 8. Energy levels of the materials used in Devices B and C.

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thermore, there are energy barriers of approximately 1.1 eV between the EML and TmPyPB interfaces. This means that the carriers can be confined efficiently in the EML, which will result in high exciton formation efficiencies even at high current densities. Both devices show very high and stable efficiencies. Device C has a maximum current efficiency of 73.9 cd A^{-1} , a maximum power efficiency of 89.7 lm W^{-1} , and a maximum luminance of 37920 cdm⁻² at a low driving voltage of 10.3 V. On the other hand, the efficiency of Device B based on 1,8-mBICz is slightly lower than that of Device C, with a maximum current efficiency of $64 \text{ cd } A^{-1}$ and a maximum power efficiency of 70.0 lm W⁻¹. These results can be understood by considering the hole- and electrontransporting properties of these bipolar compounds and their HOMO/LUMO spatial distributions. More balanced carriers in the 1,8-OXDCz-based device could lead to a higher utilization ratio of the charge carriers. The low turnon voltage and high power efficiency are attractive in comparison with that of the $[Ir(ppy)_3]$ -based PhOLEDs.

Conclusion

In summary, we have synthesized two novel bipolar 1,8-disubstituted carbazole derivatives, 1,8-mBICz and 1,8-OXDCz, containing two benzimidazole or oxadiazole units as the electron-transporting groups. Excellent photophysical and thermal properties mean that these compounds are good candidates for high-performance blue and green PhO-LEDs. Blue PhOLEDs with 1,8-mBICz exhibit similar performances to similarly structured devices based on the traditional mCP host. The PhOLEDs with the 1,8-OXDCz as the host and $[Ir(ppy)_3]$ as the dopant exhibit a maximum brightness of 37920 cdm^{-2} and a maximum power efficiency of 89.7 $\text{Im } \text{W}^{-1}$, with a turn-on voltage as low as 2.5 eV. The good performance of the 1,8-OXDCz-based PhOLEDs is among the best reported results for [Ir(ppy)₃]-based green PhOLEDs, indicating their great potential for further commercial application.

Experimental Section

Materials and measurements: All the reagents and solvents used for the synthesis were purchased from Aldrich and were used without further purification. All reactions were performed under a dry nitrogen atmosphere. ¹H NMR and ¹³C NMR spectra were measured on a Bruker-AF301 AT 400 MHz spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on an Elementar (Vario Micro cube) analyzer. Mass spectra were obtained on an Agilent (1100 LC/MSD Trap) instrument using ACPI ionization. UV/Vis absorption spectra were recorded on a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600). Photoluminescence (PL) spectra were recorded on Edinburgh instruments (FLSP920 spectrometers). Differential scanning calorimetry (DSC) was performed on a PE Instruments DSC 2920 unit at a heating rate of 10°Cmin⁻¹ from 30 to 300°C under nitrogen. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken using a PerkinElmer Instruments (Pyris1 TGA) apparatus. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of $10 \,^{\circ}$ Cmin⁻¹ from 30 to 700 °C. Cyclic voltammetry measurements were recorded for a conventional three-electrode cell using a Pt carbon working electrode of 2 mm in diameter, a platinum wire counter electrode, and an Ag/AgNO₃ (0.1 M) reference electrode on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. Reduction CVs of all compounds were obtained in dichloromethane containing 0.1 M tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte. All solutions were purged with a nitrogen stream for 10 min before measurement.

Computational details: The geometrical and electronic properties were analyzed with the Amsterdam Density Functional (ADF) 2009.01 program package. The calculation was optimized by means of the B3LYP (Becke three-parameters hybrid functional with Lee–Yang–Perdew correlation functionals)^[23] with the 6–31G(d) atomic basis set. Then, the electronic structures were calculated at the τ -HCTHhyb/6–311++G(d,p) level.^[24] Molecular orbitals were visualized using ADFview.

Device fabrication: The hole-injection material MoO₃, hole-transporting material 1,4-bis[(1-naphthyl- phenyl)amino]biphenyl (NPB), electron/exciton-blocking material TCTA, and electron-transporting material 3,3'-[5'-[3-(pyridine-3-yl)phenyl]-(1,1':3',1''-terphenyl)-3,3''-diyl}dipyridine

(TmPyPB) were commercially available. Commercial indium tin oxide (ITO)-coated glass with a sheet resistance of 20 Ω per square was used as the substrates. Before device fabrication, the ITO glass substrates were precleaned carefully and treated with oxygen plasma for 2 min. MoO₃ was deposited first on the ITO substrate, followed by NPB, mCP or TCTA, the emissive layer, and TmPyPB. Finally, a cathode composed of lithium fluoride and aluminum was deposited sequentially onto the substrate under a vacuum of 10⁻⁶ Torr. The current density—voltage–brightness (*J*–*V*–*L*) curves of the devices were measured with a Keithley 2400 Source meter equipped with a calibrated silicon photodiode. The EL spectra were measured with a PR655 spectrometer. The EQE values were calculated according to previously reported methods.^[25]

Synthesis: 1,3,4-oxidazole and *N*-phenylbenzimidazole boronic esters were prepared by the procedure reported in the literature.^[26] *N*-methyl-1,8-dibromo-3,6-ditetrabutyl-carbazole was synthesized according to the literature method.^[8] The Suzuki coupling reaction was conducted under a nitrogen atmosphere, avoiding light exposure.

1,8-Dibromo-3,6-di-tert-butyl-9H-carbazole (1): Bromine (0.92 g. 5.8 mmol) was added to a warm (90°C) solution of 3,6-di-tert-butyl-9Hcarbazole (0.81 g, 2.9 mmol) in glacial AcOH (100 mL). The mixture was stirred at 90°C under N2 for 3.5 h. After being cooled to room temperature, the reaction mixture was concentrated and dried. The solid obtained was washed with hexane, filtered, and dried to provide 1 as a white solid (1.07 g, 85%). ¹H NMR: (CDCl₃, 400 MHz): $\delta = 8.13$ (s, 1H), 7.97 (s, 2H), 7.63 (s, 2H), 1.44 ppm (s, 18H); MS (APCI): m/z: 436.1 [M+1]+. 1,8-Dibromo-3,6-di-tert-butyl-9-methyl-9H-carbazole (2): NaH (1.1 g, 4.5 mmol) was added slowly to a mixture of compound 1,8-dibromo-3,6di-tert-butyl-9H-carbazole (1) (1.30 g, 3.0 mmol) in anhydrous DMF (100 mL) solution. After 30 min, CH₃I (0.64 g, 4.5 mmol) was added. The mixture was stirred at room temperature for 18 h under nitrogen. The reaction was quenched with H2O and extracted with CH2Cl2. The organic fractions were dried under sodium sulfate and the solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (10% EtOAc in hexane as eluent) to give the title powder (1.30 g, 96%). ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ=7.94 (s, 1H), 7.64 (s, 1H), 4.42 (s, 3H), 1.45 ppm (s, 18H); MS(APCI): m/z: $450.3 [M+1]^+$

5,5'-[(3,6-Di-tert-butyl-9-methyl-9H-carbazole-1,8-diyl)bis(3,1-phenyl-

ene)]bis(2-phenyl-1,3,4-oxadiazole) (**1,8-OXDCz**): A mixture of **2** (0.45 g, 1.0 mmol), 2-phenyl-5-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-1,3,4-oxadiazole (0.84 g, 2.4 mmol), $[Pd(PPh_3)_4]$ (100 mg, 0.08 mmol), K₂CO₃ (2.0 M aqueous solution, 5.0 mL, 10.0 mmol), toluene (50 mL), and ethanol (25.0 mL) was stirred at 90 °C for 24 h. After being cooled to room temperature, dichloromethane was added to the reaction mixture. The organic phase was separated and washed with brine before being dried over anhydrous MgSO₄. The solvent was evaporated, and the solid residues were purified by column chromatography on silica gel with petroleum ether to afford the crude product as a white powder (0.57 g,

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78%). ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ =8.36 (s, 2H), 8.21–8.10 (m, 8H), 7.79–7.77 (d, *J*=7.6 Hz, 2H), 7.59–7.51 (m, 8H), 7.45 (s, 2H), 2.90 (s, 3H), 1.52 ppm (s, 18H); ¹³C NMR (100 MHz, CDCl₃, 25°C, TMS): δ =164.71, 164.53, 143.12, 141.95, 139.95, 132.70, 131.78, 129.11, 128.96, 127.61, 127.06, 126.96, 126.55, 125.45, 125.18, 124.47, 123.98, 123.95, 116.06, 38.17, 34.76, 32.04 ppm; MS (APCI): *m*/*z*: 734.5 [*M*+1]⁺; elemental analysis calcd (%) for C₄₉H₄₃N₅O₂: C 80.19, H 5.91, N 9.54, O 4.36; found: C 80.28, H 5.54, N 9.68, O 4.50.

3,6-Di-tert-butyl-9-methyl-1,8-bis[3-(1-phenyl-1 H-benzo[d]imidazole-2yl)phenyl]-9H-carbazole (1,8-mBICz): The synthesis procedure is similar to that for compound 1,8-OXDCz. Yield: 74%. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ =8.04 (s, 2 H), 7.89–7.87 (d, J=8.0 Hz, 2 H), 7.65 (s, 4 H), 7.51–7.39 (s, 10 H), 7.36–7.30 (m, 6 H), 7.29–7.25 (m, 4 H), 7.03 (s, 2 H), 2.70 (s, 3 H), 1.42 ppm (s, 18 H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ =152.32, 142.92, 142.44, 141.06, 139.56, 137.15, 136.89, 130.95, 130.08, 129.90, 128.77, 128.19, 128.01, 127.40, 126.42, 124.89, 124.67, 123.48, 123.11, 119.86, 115.39, 110.51, 37.61, 34.63, 32.00 ppm; MS (APCI): m/z: 830.5 [M+1]⁺; elemental analysis calcd (%) for C₅₉H₅₁N₅: C 85.37, H 6.19, N 8.44; found: C 85.44, H 6.04, N 8.52.

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1834 -