**Organic Light-Emitting Diodes** 



# High Efficiency Deep-Blue Phosphorescent Organic Light-Emitting Diodes with CIE x, y ( $\leq 0.15$ ) and Low Efficiency Roll-Off by Employing a High Triplet Energy Bipolar Host Material

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Recently, bipolar host materials are the most promising candidates for achieving high performance phosphorescent organic light-emitting diodes (PHOLEDs) in order to maximize recombination efficiency. However, the development of host material with high triplet energy ( $E_{T}$ ) is still a great challenge to date to overcome the limitations associated with the present PHOLEDs. Herein, a highly efficient donor- $\pi$ -acceptor (D- $\pi$ -A) type bipolar host (4'-(9H-carbazol-9-yl)-2,2'-dimethyl-[1,1'-biphenyl]-4-yl)diphenylphosphine oxide (m-CBPPO) comprising of carbazole, 2,2'-dimethylbiphenyl and diphenylphosphoryl as D- $\pi$ -A unit, respectively, is developed. Interestingly, a high  $E_{T}$  of 3.02 eV is observed for *m*-CBPPO due to highly twisted conformation. Furthermore, the new host material is incorporated in PHOLEDs as emissive layer with a new carbene type Ir(cb)<sub>3</sub> material as a deep-blue emitter. The optimized devices show an excellent external quantum efficiency (EQE) of 24.8% with a notable Commission internationale de l'éclairage (x, y)  $\leq$  0.15, (0.136, 0.138) and high electroluminescence performance with extremely low efficiency roll-off. Overall, the above EQE is the highest reported for deep-blue PHOLEDs with very low efficiency roll-off and also indicate the importance of appropriate host for the development of high performance deep-blue PHOLEDs.

## 1. Introduction

Extensive research has been carried out in recent years to enhance the performance of display and lighting devices for

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commercial applications using phosphorescent organic light-emitting diodes (PHOLEDs).<sup>[1-5]</sup> Among the three primary colors, there is a huge inhibition for commercialization owing to low efficient deep-blue emitting devices, which in particular is crucial to reduce the power consumption in lighting applications.<sup>[6-9]</sup> Deep-blue PHOLED devices<sup>[9–12]</sup> with high efficiency, excellent color purity, long lifetime, and high photoluminescence quantum yield (PLQY) is still at large due to their wide band gap  $(E_{o})$  and high triplet energy  $(E_{\rm T})$  of dopants. It has been proven that, phosphorescence emitters have longer excited state lifetime, triplet-triplet annihilation, triplet-polaron quenching, and self-quenching at high concentration, which results in low electroluminescence (EL) performance.<sup>[10-14]</sup> Therefore, phosphorescence triplet emitter doped with high  $E_{\rm T}$  host material would certainly be suitable for deep-blue PHOLED device fabrication to prevent back energy

transfer from dopant to host along with the suppressed emission quenching.

The most commonly used hosts for deep-blue PHOLEDs are N,N'-dicarbazolyl-3,5-benzene (mCP) and materials with tetra aryl-based silane because of their high  $E_{\rm T}$  (2.9–3.36 eV). Nevertheless, they result in insufficient charge balance and exciton confinement in the emitting layer imparting poor device performance due to higher lowest unoccupied molecular orbital energy (LUMO) level of –2.4 eV for mCP and deeper highest occupied molecular orbital energy (HOMO) level of –7.0 eV for silane-based host materials.<sup>[15–19]</sup> Recently, thermally activated delayed fluorescence (TADF)-based organic molecules as hosts have attracted great attention owing to their potential of achieving 100% internal quantum efficiency.<sup>[20,21]</sup> In particular, Lin et al. reported an impressive external quantum efficiency (EQE) of 31.8% with Commission International de l'Eclairage (CIE) 1931 coordinates of (0.16, 0.36) using TADF host with blue Ir(III) complexes.<sup>[21]</sup>

The national television system committee (NTSC) color coordinate system for standard blue CIE (x, y) is (0.14, 0.08),



which is highly pursued despite being hard to achieve the NTSC standard with high efficiencies.<sup>[22]</sup> Generally, deep-blue PHOLEDs with CIE "y" value  $\leq 0.15$  are likely preferred since they reduce the power consumption while used in display devices. Unfortunately, most of them often suffer from inferior color chromaticity with CIEy higher than 0.15.<sup>[6,12,23-31]</sup> However, it still remains a great challenge to achieve both CIE (x, y) color coordinates  $\leq 0.15$  for deep-blue PHOLEDs with high efficiency<sup>[22]</sup> and there are only a very few reports with notable EQE with CIE  $(x, y) \le 0.15$ . For instance, Lee and co-workers reported deep-blue PHOLEDs with  $EQE_{max}$  and CIE of 8.4% and (0.14, 0.11), respectively. Also, Lee et al. reported a high EQE<sub>max</sub> of 18.4% with CIE (0.14, 0.15).<sup>[8,14,32]</sup> Quite recently, Forrest and co-workers successfully demonstrated deep-blue PHOLEDs using carbene-based emitter with diphenyl-4-triphenylsilylphenylphosphine oxide (TSPO1) as a host material. EQE<sub>max</sub> of 10.1%  $\pm$  0.2% was accomplished for fac-Ir(pmb)<sub>3</sub> with CIE of (0.16, 0.09) and  $14.4 \pm 0.4\%$  for mer-Ir(pmb)<sub>3</sub> with a CIE of (0.16, 0.15).<sup>[33]</sup>

In order to achieve balanced charge transportation and high efficiency of deep-blue phosphorescent triplet emitter in the host matrix, doping concentration (≥5 wt%) is vital in order to reduce concentration quenching. However, most of the PHOLEDs employ unipolar host materials, which results in moderate charge transportation and inferior recombination efficiency. To overcome this issue, hosts with bipolar nature<sup>[33–38]</sup> with high  $E_{\rm T}$  are more desirable.<sup>[33,40]</sup> Until now, the most successful strategy for the development of bipolar host material is to combine the donor (D) and acceptor (A) units in order to achieve a broad recombination zone and balanced charge in emitting layer (EML), which could result in the high performance, that is highly sought after.<sup>[40]</sup> Inspired from above research, herein, we developed a D- $\pi$ -A based host material *m*-CBPPO by combining the carbazole (Cz), 2,2'-dimethylbiphenyl and diphenylphosphine oxide (Ph<sub>2</sub>P=O) as D,  $\pi$  and A. respectively. Cz in m-CBPPO acts as a good hole transport unit due to their shallow HOMO level and rigid frame work whereas, the Ph<sub>2</sub>P=O behaves as electron transporting group and are linked to both end sides of the 2,2'-dimethylbiphenyl system. The hindered molecular structure of Ph<sub>2</sub>P=O prevents the crystallization and molecular motion, thus being a suitable building block for bipolar type high  $E_{\rm T}$  host material. Besides, the electron withdrawing nature of Ph2P=O assists to maintain the charge balance and enhance the recombination efficiency in EML.<sup>[40]</sup> The incorporation of 2,2'-dimethylbiphenyl as  $\pi$ -conjugated bridge in the host material *m*-CBPPO leads to steric hindrance as well as increase in the twist angle, which are the important factors for high  $E_{\rm T}$  of 3.02 eV.<sup>[21]</sup> To this end, we presume that high  $E_{T}$  for *m*-CBPPO is because of their electronic interaction between D and A units are depressed by the steric hindrance of two methyl groups in the core structure.

Herein, we fabricated deep-blue PHOLEDs with a carbene ligand-based [[5-(1,1-dimethylethyl)-3-phenyl-1H-imidazo[4,5-b]pyrazin-1-yl-2(3H)-ylidene]-1,2-phenylene]bis[[6-(1,1-dimethylethyl)-3-phenyl-1H-imidazo[4,5-b]pyrazin-1-yl-2(3H)-ylidene]-1,2-phenylene]iridium, Ir(cb)<sub>3</sub> and *m*-CBPPO as dopant and host, respectively. The optimized devices with *m*-CBPPO as host showed an impressive EQE<sub>max</sub> of 24.8% with a notable CIE (0.136, 0.138). Further, we investigated the origin of high EQE





**Figure 1.** Comparison on the CIE ( $x+y \le 0.33$ ) with EQE<sub>max</sub> (see refs. [1–9] in Table S1, Supporting Information).

and suppressed efficiency roll-off at different phosphor concentrations (5–15%) using bipolar type *m*-CBPPO host material. The unbiased hole and electron transport along with the suitable singlet and triplet energies that are favored for exothermic energy transfer from *m*-CBPPO to  $Ir(cb)_3$ , ensures high EQE without compromising the color purity.

To the best of our knowledge, this is the highest reported EQE for deep-blue emitting phosphors with CIE (x, y)  $\leq$  0.15 using bipolar host so far (see **Figure 1**; Table S1, Supporting Information).

#### 2. Results and Discussion

The synthetic route of *m*-CBPPO is shown in **Scheme 1**. The host material was synthesized by Suzuki-coupling reaction and purified using column chromatography. In addition, *m*-CBPPO was sublimed via high vacuum train sublimation to achieve high purity. The molecular structure of *m*-CBPPO was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Figures S1 and S2, Supporting Information). The basic photophysical and electrochemical properties of *m*-CBPPO were summarized in **Table 1**.

The UV–vis absorption spectra of *m*-CBPPO shown in Figure S3 of the Supporting Information with strong absorption peak at 293 nm, which could be assigned to  $\pi$ – $\pi$ \* transition of Cz unit. Whereas the two weak absorption peaks at 328 and 341 nm were assigned as characteristic peak of Cz-centered n– $\pi$ \* transition. Due to steric hindrance of 2,2′-dimethylbiphenyl system, there was no CT absorption peak observed at longer wavelength region in the UV–vis absorption spectra.<sup>[12,17,21,41]</sup> The estimated optical  $E_g$  of *m*-CBPPO was 3.5 eV (Table 1). The emission spectra of *m*-CBPPO showed clear vibrionic features with an emission peak at 350 nm. The emission spectra of *m*-CBPPO in various solvents were measured at room temperature and are shown in Figure S4 of the Supporting Information. It was clearly revealed that the intramolecular charge transfer was almost suppressed in the molecule, *m*-CBPPO. This could be attributed to







Scheme 1. Synthetic scheme of *m*-CBPPO.

the effective breakdown of  $\pi$ -conjugation, which further leads to the steric hindrance at center of the biphenyl system.<sup>[42,43]</sup> The  $E_{\rm T}$  was calculated from the first emission peak of the low temperature photoluminescence (PL) spectra at 77 K and singlet energy was calculated from low temperature fluorescent spectra at 77 K, shown in Figure S3 of the Supporting Information.

The thermal properties were investigated using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure S5, Supporting Information). The thermal decomposition temperature ( $T_d$ ) of *m*-CBPPO found to be 315 °C measured corresponding to 5% weight loss. It is substantial to have high glass transition temperature ( $T_g$ ) (>100 °C) for host materials to improve the operational stability of the OLED devices. We also measured the  $T_g$  of new *m*-CBPPO host, which was above 100 °C. The obtained value was relatively higher when compared to the  $T_g$  of conventional host materials mCP, 4,4'-bis(9-carbazolyl)-biphenyl and 4,4'-bis(9-carbazolyl)-2,2'-dimethylbiphenyl (55, 62, and 94 °C, respectively).<sup>[41,44,45]</sup> The systematic design strategy of *m*-CBPPO allowed us to achieve a high  $T_d$  and  $T_g$ . Furthermore,

the high  $T_{\rm g}$  and  $T_{\rm d}$  values feature a good surface morphology and high thermal stability, which is a prerequisite for vacuum deposition in OLED device fabrication. The HOMO energy level of *m*-CBPPO was estimated by cyclic voltammetry (Figure S6, Supporting Information). The calculated HOMO of m-CBPPO is -5.68 eV and the LUMO is -2.18 eV (estimated from addition of  $E_{g}$  and HOMO). Figure 2a, shows the HOMO and LUMO distributions of m-CBPPO calculated from DFT using Gaussian 09 program. Ground state geometry optimization was performed using B3LYP exchange-correlation functional with 6-31G(d) basis set. HOMO was distributed on Cz, while LUMO on the Ph<sub>2</sub>P=O. This clearly implies the spatial separation of the HOMO and LUMO. To achieve a high  $E_{T}$ , decoupling of the electron accepting and electron donating unit in bipolar host materials is important. In m-CBPPO, this was accomplished by the 87.6° twist between the two phenyl rings in the biphenyl unit by two methyl groups in 2- and 2'-position of the biphenyl.<sup>[46]</sup>

The *m*-CBPPO host was designed to afford bipolar charge transport character using Cz and Ph<sub>2</sub>P=O functional moieties.

 Table 1. Photophysical, thermal, and electrochemical properties of *m*-CBPPO.

Compound	$\lambda_{\mathrm{abs}}{}^{\mathrm{a})}$ [nm]	$\lambda_{ m em}{}^{ m b)}$ [nm]	$\lambda_{ m em}{}^{ m c)}$ [nm]	$\lambda_{ m phos}{}^{ m d)}$ [nm]	$E_{\rm S}/E_{\rm T}^{\rm e)}$ [eV]	HOMO/LUMO <sup>f)</sup> [eV]	$E_{g}^{g}$ [eV]	$T_{\rm g}/T_{\rm d}^{\rm h)}$ [°C]
т-СВРРО	293, 328, 341	350, 362	348, 363	410, 437, 459	3.56/3.02	-5.68/-2.18	3.5	101/315

<sup>a)</sup>Measured in 2-MeTHF at  $1 \times 10^{-5}$  M solution at 298 K; <sup>b)</sup>Measured in 2-MeTHF at  $1 \times 10^{-5}$  M solution at 298 K; <sup>c)</sup>Measured in 2-MeTHF at  $1 \times 10^{-5}$  M solution at 77K; <sup>d)</sup>Measured in 2-MeTHF at  $1 \times 10^{-5}$  M solution at 77 K. <sup>e)</sup>Singlet and triplet energies were measured at first emission peak form the fluorescence and phosphorescence spectra at 77 K; <sup>f)</sup>HOMO calculated from onset oxidation potentials using CV and LUMO Calculated from  $E_g$  (optical); <sup>g)</sup>Optical band gap  $E_g$  was measured at onset of U–vis absorption spectra; <sup>h)</sup>Thermal data were estimated from DSC and TGA.





Figure 2. a) HOMO and LUMO orbital distribution by molecular simulation results, b) current density-electric field calculated from single carrier devices, c) energy level diagram of PHOLEDs using *m*-CBPPO as host, and d) molecular structure of the deep-blue emitter used.

To gain insight into the charge carrier transport property of *m*-CBPPO, we fabricated the single carrier devices and their current density-voltage (I-V) curve is shown in Figure 2b. The single carrier device results confirmed the bipolarity nature of the *m*-CBPPO host from the similar hole and electron carrier mobilities. The hole and electron mobilities of the host were  $3.8 \times 10^{-6}$  and  $1.4 \times 10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. Thus, *m*-CBPPO is effective in balancing the both types of carriers in EML, which resulted in a balanced charge transportation. We presume that bipolar charge transport properties of *m*-CBPPO are a key factor in achieving high quantum efficiency of the deep-blue PHOLEDs. As intended in the molecular design, the spatially separated Cz and Ph<sub>2</sub>P=O units allowed the bipolarity in host material. Further investigation was carried out to compare the carrier mobility with the commercial deepblue host TSPO1. From the analysis, m-CBPPO was found to occupy superior carrier mobility (both hole and electron) than that of TSPO1 (Figure S7, Supporting Information). The *m*-CBPPO host satisfied all requirements of the host for deep-blue phosphorescent emitter such as high  $E_{\rm T}$  over 2.9 eV, bipolarity and suitable HOMO/LUMO for carrier injection from transporting layers. Following, deep-blue PHOLEDs were fabricated with deep-blue emitting Ir(cb)<sub>3</sub> as a phosphorescent emitter and the energy level diagram is shown in Figure 2c. The Ir(cb)<sub>3</sub> was synthesized according to the method described in the literature and the emitter structure is shown in Figure 2d.<sup>[47]</sup> Interestingly, the Ir(cb)<sub>3</sub> emitter bearing bulky tert-butyl group in the pyrazine unit results in suppressing the intermolecular interaction induced quenching process which could be attributed to steric hindrance of tert-butyl moiety. The HOMO and LUMO levels of Ir(cb)<sub>3</sub> were found to be -5.9 and -2.9 eV, respectively, which were calculated from CV measurement (Figure S8, Supporting Information). Deep HOMO and LUMO levels were observed in the Ir(cb)<sub>3</sub> emitter by the electron deficiency of the heteroaromatic structure in the carbene-based ligand. The PL emission of Ir(cb)<sub>3</sub> was observed at a peak wavelength of 456 nm using a toluene solution, indicating the deep blue emission property of the Ir(cb)<sub>3</sub> (Figure S9, Supporting Information). Also, the full-width at half maximum (FWHM) of PL measured for Ir(cb)<sub>3</sub> was 46 nm. PLQY of the Ir(cb)<sub>3</sub> in a polystyrene matrix at a doping concentration of 1% was 88%. Excited state

lifetime of Ir(cb)<sub>3</sub> was 0.41 µs from transient PL measurement (Figure S10, Supporting Information). High PLQY and fast phosphorescent decay were observed, which is advantageous to obtain high EQE and suppressed triplet exciton quenching by triplet-triplet annihilation or triplet-polaron annihilation. The  $T_d$  at 5% weight loss was 404 °C from TGA, implying good thermal stability of the emitter (Figure S11, Supporting Information). The  $T_g$  could not be determined because of the inflection point during heating scan of DSC measurement was not detected. Therefore, the Ir(cb)<sub>3</sub> would be a high efficiency phosphorescent emitter with a deep blue emission color.

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Devices with *m*-CBPPO as host and  $Ir(cb)_3$  as dopant were fabricated to evaluate the performance of *m*-CBPPO as deep-blue host. PHOLEDs were fabricated with a device architecture ITO/poly(3,4-ethylenedioxythiophene):poly of (styrenesulfonate) (PEDOT:PSS) (60 nm)/TAPC (20 nm)/ mCP (10 nm)/m-CBPPO:Ir(cb)<sub>3</sub> (25 nm)/TSPO1 (5 nm)/TPBi (20 nm)/LiF/Al, with varying Ir(cb)<sub>3</sub> concentrations (5-15%). J-V, luminance-voltage, EQE-luminance, and EL spectra of the deep-blue PHOLEDs are presented in Figure 3 and their performances are summarized in Table 2. Furthermore, to understand the PL and EL property in detail, it is necessary to characterize the photophysical behavior. Figure S12 of the Supporting Information shows the PL spectra of Ir(cb)<sub>3</sub> (15 wt%) films doped in TSPO1 and *m*-CBPPO. From the PL results, it is clear that no substantial spectral changes were observed when compared to EL. Thus, it should be noted that the EL spectra are independent of driving voltage, which would be expected if there were no significant shifts in the location of the recombination zone. The current density of the PHOLEDs was slightly decreased at 10% doping concentration, but it increased again at 15% doping concentration. This might be due to the large energy barrier for electron injection of 0.77 eV between *m*-CBPPO and Ir(cb)<sub>3</sub> as shown in energy level diagram in Figure 2c resulting in a weak carrier trapping effect of Ir(cb)<sub>3</sub> emitter. The luminance was also affected by the current density and the maximum luminance of the device was over 10 000 cd  $m^{-2}$ , which is a considerably high luminance in the deep-blue PHOLEDs.

The EQEs of the deep-blue PHOLEDs were almost the same in the different doping concentration range examined (Figure 3c). Maximum EQE was 24.8% and the EQEs at







Figure 3. a) Current density-voltage-luminance characteristics, b) current efficiency and power efficiency versus luminance curves, c) EQE-luminance curves, and d) EL spectra of devices with *m*-CBPPO as host with varying dopant concentrations (5–15%).

100 and 1000 cd m<sup>-2</sup> were 24.3% and 22.2% for 15% doping concentration. Over 90% of the maximum EQE was observed even at a luminance of 1000 cd m<sup>-2</sup>, which is one of the best efficiency roll-off behaviors seen among the reported deepblue PHOLEDs. At a doping concentration of 5%, the EQEs at 100 and 1000 cd  $m^{-2}$  were 24.1% and 22.4%. For all different doping concentrations, significantly high EQE and very little efficiency roll-off were recorded because of the bipolar charge transport character of the m-CBPPO host and short triplet excited state lifetime of Ir(cb)<sub>3</sub>. In addition, the CIE color coordinates for devices with m-CBPPO as host was (0.136, 0.138) exhibiting an excellent deep-blue coordinate. By achieving excellent EQE of over 24% and CIE  $(x, y) \le 0.15$ , Ir(cb)<sub>3</sub> doped *m*-CBPPO devices exhibited ideal device performance that is expected of deep-blue PHOLEDs. The EL maximum of 462 nm without any vibrational shoulder peak and a narrow FWHM of 52 nm was observed from the EL spectrum showing high color purity. From the previous reports, [14,16,17,21] it is observed

that most blue-emitting Ir(III) complexes possess vibrational shoulder peak due to larger oscillator strength at longer wavelengths, resulting in a poor color purity in deep-blue PHOLEDs. From the observed EL spectra, there was no identifiable emission from the host *m*-CBPPO, suggesting the efficient energy transfer from *m*-CBPPO to Ir(cb)<sub>3</sub>.<sup>[48]</sup> The EL spectra were shifted to longer wavelength by 4 nm at 10% and 15% doping concentrations by intermolecular interaction between phosphorescent emitters. Additionally, to evaluate and compare the performance of *m*-CBPPO as deep-blue host, a commonly used deep-blue host, TSPO1, was used to fabricate PHOLEDs with the same device configuration. EQE<sub>max</sub> of the deep-blue PHOLEDs with TSPO1 host was 17.1%, which was much lower than that of the *m*-CBPPO device with 10% Ir(cb)<sub>3</sub> doping concentration (Figure S13, Supporting Information).

From the above results it is clear that *m*-CBPPO, with its high  $E_{\rm T}$ , excellent efficiency, color coordinates, and bipolar carrier properties, is an excellent choice and an exceptional

Host	Dopant conc. [%]	OV <sup>a)</sup> [V]	Luminance [cd m <sup>-2</sup> ]	EL [nm]	CIE [x, y]	EQE [%]			CE [cd A <sup>-1</sup> ]			PE [lm W <sup>-1</sup> ]		
						Max.	@200 cd m <sup>-2</sup>	@1000 cd m <sup>-2</sup>	Max.	@200 cd m <sup>-2</sup>	@1000 cd m <sup>-2</sup>	Max.	@200 cd m <sup>-2</sup>	@1000 cd m <sup>-2</sup>
т-СВРРО	5	3.4	6820	462	(0.13, 0.13)	24.7	23.8	22.4	28.5	26.0	24.0	25.6	16.9	12.9
	10	3.4	7312	466	(0.13, 0.15)	24.6	23.4	22.1	30.7	28.0	26.1	27.6	18.0	13.1
	15	3.2	10 188	466	(0.13, 0.16)	24.8	23.9	22.3	32.3	30.6	27.9	28.9	21.1	15.5
TSPO1	10	4.5	930	468	(0.14, 0.19)	17.1	13.5	-	18.3	19.8	-	26.3	8.8	-

 Table 2. Device performance of deep-blue PHOLEDs with different dopant concentrations.

<sup>a)</sup>Operation voltage (OV) at 1 cd m<sup>-2</sup>.

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candidate as host for deep-blue PHOLEDs. This strategy can be useful for further investigation and development of new bipolar type host materials.

## 3. Conclusion

In summary, we introduced a new host and dopant for deep-blue PHOLEDs using a unique molecular design with high Eт (4'-(9H-carbazol-9-yl)-2,2'-dimethyl-[1,1'biphenyl]-4-yl)diphenylphosphine oxide (*m*-CBPPO) and carbene-based deep-blue emitter [[5-(1,1-dimethylethyl)-3phenyl-1H-imidazo[4,5-b]pyrazin-1-yl-2(3H)-ylidene]-1,2-phenylene]bis[[6-(1,1-dimethylethyl)-3-phenyl-1H-imidazo[4,5-b] pyrazin-1-yl-2(3H)-ylidene]-1,2-phenylene]iridium Ir(cb)<sub>3</sub>, respectively. We achieved a maximum EQE of 24.8% with outstanding deep-blue CIE coordinate (0.136, 0.138) for the first time. This color coordinate describes some of the deepest blue emission ever achieved form PHOLEDs with considerably high EQEs. Furthermore, m-CBPPO exhibit balanced charge carrier transportation property, which results in extremely low efficiency roll-off in deep-blue PHOLEDs. It is worth mentioning that this is one of the deep-blue PHOLEDs reported with very low efficiency roll-off so far. Most importantly, m-CBPPO host show much better performance than that of commercial deepblue host material TSPO1. Our work will be helpful for further improve the performance of deep-blue PHOLEDs device especially with pure deep-blue CIE (x, y) color coordinate and low roll-off with considerably high EQE.

#### 4. Experimental Section

General Information: <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer in CDCl<sub>3</sub> using tetramethylsilane as an internal reference. The chemical shifts were reported in ppm relative to the singlet of CDCl<sub>3</sub> at 7.26 and 77 ppm for the <sup>1</sup>H and <sup>13</sup>C NMR, respectively. UV-vis and the emission spectra were recorded with a JASCO V-570 and Hitachi F-4500 fluorescence spectrophotometers at room temperature. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851e analyzer under N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup>. CV studies were carried out with a CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mV s<sup>-1</sup> in an anhydrous CH<sub>2</sub>Cl<sub>2</sub> solvent with 0.1 M TBACIO<sub>4</sub> as supporting electrolyte. A platinum wire was used as the counter electrode and an Ag/AgCI electrode was used as the reference electrode. The potentials were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc<sup>+</sup>).

Synthesis of 9-(4-bromo-3-methylphenyl)-9H-carbazole (1): 9H-Carbazole (0.3 g, 1.79 mmol),  $K_2CO_3$  (0.74 g, 5.38 mmol), Cu (0.34 g, 5.38 mmol), and 2-bromo-5-iodotoluene (0.58 g, 1.97 mmol) were mixed in dimethylformamide (10 mL) under  $N_2$  atmosphere. The reaction mixture was heated to 130 °C for 48 h. After completion of the reaction, cool the reaction mixture to room temperature and extracted with methylene chloride (MC), washed with brine solution, and dried over anhydrous  $Na_2SO_4$ . The solvent was distilled off, and the solid residue was purified by column chromatography on silica gel using ethyl acetate (EtOAc)/n-Hexane (1:9) eluent to afford 1 as a white solid. Yield: 70%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.13 (s, 2H), 7.77-7.74 (d, 1H), 7.40-7.27 (m, 8H), 2.51 (s, 3H).

Synthesis of 9-(3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)-9H-carbazole (2): n-BuLi (0.52 mL, 1.33 mmol) was added to the solution of 1 (0.3 g, 0.88 mmol) at -78 °C in dry THF. The mixture allowed to stirrer for 2 h at same temperature. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.24 g, 1.32 mmol) was added

and allow to stir at room temperature for 48 h. After completion of the reaction, the reaction mixture was quenched by the addition of water (50 mL). Finally, organic layer was extracted with MC, washed with brine solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was distilled off, and the solid residue was purified by column chromatography on silica gel using EtOAc/n-Hexane (1:9) eluent to afford 2 as a white solid. Yield: 50%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.18-8.07 (m, 3H), 7.45-7.34 (m, 8H), 2.71 (s, 3H), 1.44-1.33 (d, 12H).

Synthesis of (4-bromo-3-methylphenyl)diphenylphosphine oxide (3): 2-Bromo-5-iodotoluene (5 g, 16.83 mmol), diphenylphosphine oxide (3.4 g, 16.83 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.9 g, 0.84 mmol), triethylamine (1.7 g, 16.83 mmol), and toluene (30 mL) were dissolved in toluene under N<sub>2</sub> for 10 min and then the reaction mixture was stirred at 110 °C for 12 h. After completion of the reaction, the mixture was cooled to room temperature and water (50 mL) was added. The resulting mixture was extracted with MC (100 mL) and the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc/n-Hexane (5:5) to afford 3 as a white gray color solid. Yield: 75%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.58-7.41 (m, 13H) 2.35 (s, 3H).

Synthesis of (4'-(9H-carbazol-9-yl)-2,2'-dimethyl-[1,1'-biphenyl]-4-yl) diphenylphosphine oxide(m-CBPPO): A solution of 9-(3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (0.43 g, 1.13 mmol), 4-bromo-3-methylphenyl)diphenylphosphine oxide (0.35 g, 0.94 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.54 g, 0.47 mmol), and Na<sub>2</sub>CO<sub>3</sub> (0.18 g, 1.69 mmol) were mixed in degassed 1,2-dimethoxyethane (DME)/H<sub>2</sub>O (3:1) system and heated to 90 °C for 12 h. After completion of the reaction, the organic layer was extracted with MC, washed with brine solution and dried over anhydrous Na2SO4. The solvent was distilled off, and the solid residue was purified by column chromatography on silica gel using EtOAc/n-hexane (4:6) eluent to afford m-CBPPO as a white solid and further purified by high vacuum train sublimation afforded pure product Yield: 90%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ) 8.12 (d, 2H), 7.76 - 7.67 (m, 5H), 7.57 - 7.36 (m, 14H), 7.27 (d, 2H), 7.23 (d, 1H), 2.16 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 144.9, 144.8, 141.0, 139.8, 137.7, 137.2, 137.0, 136.8, 133.8, 133.7, 133.5, 133.5, 132.5, 132.4, 132.2, 132.1, 132.1, 131.1, 130.4, 129.7, 129.7, 129.5, 129.5, 128.8, 128.6, 128.5, 126.0, 124.4, 123.5, 120.5, 120.1, 110.0, 20.1.

Device Fabrication and Measurements: The structure of the devices were as follows: PEDOT:PSS (60 nm)/4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC; 20 nm)/1,3-bis(N-carbazolyl) benzene (mCP; 10 nm)/m-CBPPO:Ir(cb)<sub>3</sub> (25 nm:5, 10, 15 wt%)/ diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1; 5 nm)/2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBi; 20 nm)/ LiF (1.5 nm)/Al (200 nm). The device structures of hole only and electron only devices were ITO/PEDOT:PSS (60 nm)/TAPC (20 nm)/ mCP (10 nm)/m-CBPPO (25 nm)/TAPC (5 nm)/Al (200 nm) and ITO/ TSPO1 (5 nm)/m-CBPPO (25 nm)/TSPO1 (5 nm)/TPBi (20 nm)/LiF (1.5 nm)/Al (200 nm), respectively. The devices were fabricated by thermal evaporation in a vacuum under a pressure of  $5 \times 10^{-7}$  Torr. The current density, voltage and luminance characteristics and EL spectrum analysis of the devices were conducted using the M6100 electrical analysis system by McScience and a CS2000 spectroradiometer by Konica Minolta.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

#### Keywords

bipolar hosts, deep-blue devices, high color purity CIE x, y ( $\leq 0.15$ ), high external quantum efficiency (EQE), low-roll off

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- M. Gross, D. C. Muller, H.-G. Nothofer, U. Scherf, D. Neher, C. Brauchle, K. Meerholz, *Nature* 2000, 405, 661.
- [2] L. S. Hung, C. H. Chen, Mat. Sci. Eng., R 2002, 39, 143.
- [3] J. Cui, Q. Huang, J. C. G. Veinot, H. Yan, Q. Wang, G. R. Hutchison, A. G. Richter, G. Evmenenko, P. Dutta, T. J. Marks, *Langmuir* 2002, 18, 9958.
- [4] S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, F. Sato, Appl. Phys. Lett. 2003, 83, 569.
- [5] M.-T. Lee, C.-H. Liao, C.-H. Tsai, C.-H. Chen, Adv. Mater. 2005, 17, 2493.
- [6] H.-J. Seo, K.-M. Yoo, M. Song, J. S. Park, S.-H. Jin, Y. I. Kim, J.-J. Kim, Org. Electron. 2010, 11, 564.
- [7] M. G. Helander, Z. B. Wang, J. Qiu, M. T. Greiner, D. P. Puzzo, Z. W. Liu, Z. H. Lu, *Science* 2011, 332, 944.
- [8] X. Yang, X. Xu, G. Zhou, J. Mater. Chem. C 2015, 3, 913.
- [9] S. Lee, S.-O. Kim, H. Shin, H.-J. Yun, K. Yang, S.-K. Kwon, J.-J. Kim, Y.-H. Kim, J. Am. Chem. Soc. 2013, 135, 14321.
- [10] J. Lee, C. Jeong, T. Batagoda, C. Coburn, M. E. Thompson, S. R. Forrest, *Nat. Commun.* **2017**, *8*, 15566.
- P. Erk, M. Bold, M. Egen, E. Fuchs, T. Geßner, K. Kahle, C. Lennartz,
   O. Molt, S. Nord, H. Reichelt, C. Schildknecht, H.-H. Johannes,
   W. Kowalsky, *Dig. Tech. Pap. Soc. Inf. Disp. Int. Symp.* 2006, 37, 131.
- [12] S. O. Jeon, S. E. Jang, H. S. Son, J. Y. Lee, Adv. Mater. 2011, 23, 1436.
- [13] Q. Wang, H. Aziz, ACS Appl. Mater. Interfaces 2013, 5, 8733.
- [14] Y.-C. Chiu, J.-Y. Hung, Y. Chi, C.-C. Chen, C.-H. Chang, C.-C. Wu, Y.-M. Cheng, Y.-C. Yu, G.-H. Lee, P.-T. Chou, Adv. Mater. 2009, 21, 2221.
- [15] M.-F. Wu, S.-J. Yeh, C.-T. Chen, H. Murayama, T. Tsuboi, W.-S. Li, I. Chao, S.-W. Liu, J.-K. Wang, Adv. Funct. Mater. 2007, 17, 1887.
- [16] M.-H. Tsai, H.-W. Lin, H.-C. Su, T.-H. Ke, C.-C. Wu, F.-C. Fang, Y.-L. Liao, K.-T. Wong, C.-I. Wu, *Adv. Mater.* **2006**, *18*, 1216.
- [17] S. O. Jeon, K. S. Yook, C. W. Joo, J. Y. Lee, Adv. Mater. 2010, 22, 1872.
- [18] R. J. Holmes, S. R. Forrest, Y.-J. Tung, R. C. Kwong, J. J. Brown, S. Garon, M. E. Thompson, *Appl. Phys. Lett.* **2003**, *82*, 2422.
- [19] R. J. Holmes, B. W. D'Andrade, S. R. Forrest, X. Ren, J. Li, M. E. Thompson, *Appl. Phys. Lett.* **2003**, *83*, 3818.
- [20] Y. J. Cho, S. K. Jeon, J. Y. Lee, Adv. Opt. Mater. 2016, 4, 688.



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- [21] C.-C. Lin, M.-J. Huang, M.-J. Chiu, M.-P. Huang, C.-C. Chang, C.-Y. Liao, K.-M. Chiang, Y.-J. Shiau, T.-Y. Chou, L.-K. Chu, H.-W. Lin, C.-H. Cheng, *Chem. Mater.* **2017**, *29*, 1527.
- [22] H. Fu, Y.-M. Cheng, P.-T. Chou, Y. Chi, Mater. Today 2011, 14, 472.
- [23] G. Sarada, W. Cho, A. Maheshwaran, V. G. Sree, H.-Y. Park, Y.-S. Gal, M. Song, S.-H. Jin, *Adv. Funct. Mater.* **2017**, *27*, 1701002.
- [24] C.-H. Yang, M. Mauro, F. Polo, S. Watanabe, I. Muenster, R. Fröhlich, L. D. Cola, *Chem. Mater.* **2012**, *24*, 3684.
- [25] Y. Takahira, E. Murotani, K. Fukuda, V. Vohra, H. Murata, J. Fluorine Chem. 2016, 181, 56.
- [26] J.-B. Kim, S.-H. Han, K. Yang, S.-K. Kwon, J.-J. Kim, Y.-H. Kim, Chem. Commun. 2015, 51, 58.
- [27] H. J. Park, J. N. Kim, H.-J. Yoo, K.-R. Wee, S. O. Kang, D. W. Cho, U. C. Yoon, J. Org. Chem. 2013, 78, 8054.
- [28] Y. J. Cho, J. Y. Lee, Chem. Eur. J. 2011, 17, 11415.
- [29] K.-Y. Lu, H.-H. Chou, C.-H. Hsieh, Y.-H. O. Yang, H.-R. Tsai, H.-Y. Tsai, L.-C. Hsu, C.-Y. Chen, I.-C. Chen, C.-H. Cheng, *Adv. Mater.* 2011, *23*, 4933.
- [30] C.-H. Hsieh, F.-I. Wu, C.-H. Fan, M.-J. Huang, K.-Y. Lu, P.-Y. Chou, Y.-H. O. Yang, S.-H. Wu, I.-C. Chen, S.-H. Chou, K.-T. Wong, C.-H. Cheng, *Chem. Eur. J.* 2011, *17*, 9180.
- [31] G. Sarada, A. Maheshwaran, W. Cho, T. Lee, S. H. Han, J. Y. Lee, S.-H. Jin, Dyes Pigm. 2018, 150, 1.
- [32] S. O. Jeon, K. S. Yook, C. W. Joo, J. Y. Lee, Adv. Funct. Mater. 2009, 19, 3644.
- [33] J. Lee, H.-F. Chen, T. Batagoda, C. Coburn, P. I. Djurovich, M. E. Thompson, S. R. Forrest, *Nat. Mater.* **2016**, *15*, 92.
- [34] Y. Wang, W. Song, Y. Chen, Y. Jiang, H. Mu, J. Huang, J. Su, Org. Electron. 2018, 61, 142.
- [35] X. Jing, L. Jiang, K. Sun, W. Tian, W. Jiang, New J. Chem. 2018, 42, 4081.
- [36] T. Yang, H. Xu, K. Wang, P. Tao, F. Wang, B. Zhao, H. Wang, B. Xu, Dyes Pigm. 2018, 153, 67.
- [37] C. Yao, C. Peng, Y. Yang, L. Li, M. Bo, J. Wang, J. Mater. Chem. C 2018, 6, 4912.
- [38] K. Guo, H. Wang, Z. Wang, C. Si, C. Peng, G. Chen, J. Zhang, G. Wang, B. Wei, Chem. Sci. 2017, 8, 1259.
- [39] Z. Wang, H. Wang, J. Zhu, P. Wu, B. Shen, D. Dou, B. Wei, ACS Appl. Mater. Interfaces 2017, 9, 21346.
- [40] K. S. Yook, J. Y. Lee, Chem. Rec. 2016, 16, 159.
- [41] P. Schrögel, A. Tomkevičiene, P. Strohriegl, S. T. Hoffmann, A. Köhler, C. Lennartz, J. Mater. Chem. 2011, 21, 2266.
- [42] F. Wang, D. Liu, J. Li, J. Photochem. Photobiol., A 2018, 355, 152.
- [43] G. Turkoglu, M. E. Cinar, T. Ozturk, *Molecules* **2017**, *22*, 1522.
- [44] Y. P. Jeon, K. S. Kim, K. K. Lee, I. K. Moon, D. C. Choo, J. Y. Lee, T. W. Kim, J. Mater. Chem. C 2015, 3, 6192.
- [45] M. Gantenbein, M. Hellstern, L. L. Pleux, M. Neuburger, M. Mayor, Chem. Mater. 2015, 27, 1772.
- [46] P. Strohriegl, D. Wagner, P. Schrögel, S. T. Hoffmann, A. Köhler, U. Heinemeyer, I. Münster, Proc. SPIE 2013, 8829, 882906.
- [47] P. Murer, K. Dormann, F. L. Benedito, G. Battagliarin, S. Metz, U. Heinemeyer, C. Lennartz, G. Wagenblast, S. Watanabe, T. Gessner, US Patent WO2015000955, 2015.
- [48] Q. Sun, L.-S. Cui, Y.-M. Xie, J.-J. Liang, Z.-Q. Jiang, L.-S. Liao, M.-K. Fung, Org. Electron. 2017, 48, 112.