



# Pyridine/Isoquinoline-Carbazole Containing Bipolar Host Materials for Green Phosphorescent Organic Light-Emitting Diodes

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We demonstrated the electroluminescent properties of bipolar host materials such as 9-(3-(6-methylpyridin-2-yl)phenyl)-9H-carbazole (**Czmpy**), 9-(6-phenylpyridin-2-yl)-9H-carbazole (**Czppy**), and 9-(3-(isoquinolin-1-yl)phenyl)-9H-carbazole (**Czpiq**). Particularly, by using host (**Czpiq**) and dopant (bis[2-(1,1',2',1''-terphen-3-yl)pyridinato-C,N]iridium(III) (**tphpy**)<sub>2</sub>Ir(acac)) as the emitting layer, a green phosphorescent OLED was fabricated, showing a maximum luminance of 12780 cd/m<sup>2</sup> at 10 V, maximum luminous efficiency of 45.0 cd/A, power efficiency of 47.1 lm/W, maximum external quantum efficiency of 12.3%, and CIE x, y coordinates of (0.34, 0.58) at 8 V.

**Keywords:** OLEDs, Green Phosphorescence, Bipolar Host, Pyridine/Isoquinoline-Carbazole Containing Materials.

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## 1. INTRODUCTION

Organic light-emitting diodes (OLEDs) are being investigated widely for their potential applications in full-color flat-panel displays.<sup>1,2</sup> Forrest and Thompson's groups have developed transition metal complexes, which emit phosphorescence from their triplet states, realizing nearly 100% internal quantum efficiencies of electroluminescence.<sup>3-6</sup> For efficient phosphorescent OLEDs (PHOLEDs), the heavy-metal guest materials are doped into charge-transporting host materials. Recently, bipolar molecules have attracted much interest in this field, since a balanced density of charge could be achieved by simultaneously supplying the electron and hole to electroluminescent (EL) materials, resulting in high efficiency and excellent device stability.<sup>7-11</sup>

In this paper, we report a molecular design strategy of combining the carbazole with the good hole-transporting ability and pyridine or isoquinoline with high electron affinity and high triplet energy to yield the bipolar host material 9-(3-(6-methylpyridin-2-yl)phenyl)-9H-carbazole (**Czmpy**), 9-(6-phenylpyridin-2-yl)-9H-carbazole (**Czppy**), and 9-(3-(isoquinolin-1-yl)phenyl)-9H-carbazole (**Czpiq**). As will be seen below, by using these materials as host materials, efficient green PHOLEDs were demonstrated.

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## 2. EXPERIMENTAL DETAILS

### 2.1. Synthesis and Characterization

9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole<sup>9</sup> and 2-bromo-6-phenylpyridine<sup>12</sup> were prepared by a previously-reported method. Low resolution mass spectra were measured using a Jeol JMS-600 spectrometer in EI mode. Elemental Analysis was done using an EA1108 Elemental analyzer (Fisons Instrument). UV-vis absorption spectra were measured on a Shimadzu UV-1650PC spectrometer. Photoluminescence (PL) spectra were measured on an Aminco-Bowman series 2 luminescence spectrometer. The UV-vis and PL spectra of phosphorescent host materials were measured in a 10<sup>-5</sup> M dilute CH<sub>2</sub>Cl<sub>2</sub> solution. The energy levels were measured with a low-energy photo-electron spectrometer (Riken-Keiki, AC-2). Thermal properties were measured using thermogravimetric analysis (TGA) (DTA-TGA, TA-4000) and differential scanning calorimeter (DSC) (Mettler Toledo; DSC 822) under N<sub>2</sub> at a heating rate of 10 °C/min and cooling rate of 10 °C/min.

*Synthesis of 9-(3-(6-methylpyridin-2-yl)phenyl)-9H-carbazole (**Czmpy**).* 9-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (1.29 g, 2.90 mol), 2-bromo-6-methylpyridine (0.5 g, 3.49 mol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 mol), aqueous K<sub>2</sub>CO<sub>3</sub> (2.0 M, 29.1 mol), Aliquat 336, and toluene were mixed in a flask. The mixture was

refluxed for 4 h. After the reaction finished, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried with anhydrous  $\text{MgSO}_4$  and filtered with silica gel. The solution was then evaporated. **Czmpmpy** was obtained as a white solid (0.76 g, 78%) after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{EtOH}$ .  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (t,  $J = 7.7$  Hz, 2H), 8.08 (d,  $J = 7.8$  Hz, 1H), 7.70–7.51 (m, 5H), 7.46–7.37 (m, 4H), 7.31–7.26 (m, 2H), 7.09 (d,  $J = 7.5$  Hz, 1H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.9, 156.1, 142.1, 141.2, 138.4, 137.3, 130.5, 127.6, 126.3, 126.2, 126.1, 123.6, 122.4, 120.6, 120.2, 118.0, 110.1. FT-IR [ATR]:  $\nu = 3015, 2970, 1366, 1092, 1033$   $\text{cm}^{-1}$ . MS(EI<sup>+</sup>)  $m/z$  334 (M<sup>+</sup>). Anal. calcd for  $\text{C}_{24}\text{H}_{18}\text{N}_2$ : C 86.20, H 5.43, N 8.38 found: C 85.56, H 5.44, N 8.32.

**Synthesis of 9-(6-phenylpyridin-2-yl)-9H-carbazole (Czppy).** 2-Bromo-6-phenylpyridine (0.80 g, 3.42 mmol), carbazole (0.69 g, 4.10 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.16 g, 0.17 mmol),  $\text{P}(t\text{-Bu})_3$  (0.01 g, 0.0342 mmol), and  $\text{NaOt-Bu}$  (0.62 g, 6.40 mmol) were dissolved in anhydrous toluene (20 mL). The mixture was heated to reflux with stirring at 120 °C for 18 h. After cooling to room temperature, the solvent was removed and the residue was purified by column chromatography eluting with 5–20% ethyl acetate/hexane. **Czppy** was obtained as a white solid (0.57 g, 52%).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15–8.11 (m, 4H), 7.94 (d,  $J = 8.4$  Hz, 3H), 7.73–7.70 (m, 1H), 7.54–7.41 (m, 6H), 7.35–7.30 (m, 2H).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.3, 151.8, 139.9, 139.4, 138.7, 129.7, 129.1, 127.1, 126.4, 124.6, 121.2, 120.4, 117.5, 117.3, 111.7. FT-IR [ATR]:  $\nu = 3015, 1738, 1366, 1092, 1055, 1032$   $\text{cm}^{-1}$ . MS(EI<sup>+</sup>)  $m/z$  320 (M<sup>+</sup>). Anal. calcd for  $\text{C}_{23}\text{H}_{16}\text{N}_2$ : C 86.22, H 5.03, N 8.74 found: C 85.86, H 5.03, N 8.76.

**Synthesis of 9-(3-(isoquinolin-1-yl)phenyl)-9H-carbazole (Czpiq).** White solid with a yield of 0.88 g (76%).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.62 (d,  $J = 5.72$  Hz, 1H), 8.19–8.12 (m, 3H), 7.89 (d,  $J = 11.7$  Hz, 1H), 7.85–7.78 (m, 2H), 7.74 (d,  $J = 7.48$  Hz, 1H), 7.71–7.64 (m, 3H), 7.57–7.51 (m, 3H), 7.43–7.38 (m, 2H), 7.29–7.25 (m, 2H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.8, 158.0, 142.6, 141.8, 141.1, 138.0, 137.2, 130.5, 130.3, 129.2, 128.8, 127.8, 127.4, 127.3, 126.9, 126.3, 123.7, 120.7, 120.6, 120.3, 110.1. FT-IR [ATR]:  $\nu = 3015, 1366, 1092, 1055, 1032$   $\text{cm}^{-1}$ ; MS (EI,  $m/z$ ) 370 (M<sup>+</sup>). Anal. Calcd for  $\text{C}_{27}\text{H}_{18}\text{N}_2$ : C 87.54, H 4.90, N 7.56; found: C 87.02, H 4.84, N 7.57.

## 2.2. Device Fabrication and Characterization

OLEDs using green-light-emitting molecules were fabricated by vacuum ( $5 \times 10^{-7}$  torr) thermal evaporation onto precleaned ITO coated glass substrates. The structure was as follows: ITO/N,N'-diphenyl-N,N'-(1-naphthyl)-(1,1'-phenyl)-4,4'-diamine (NPB)

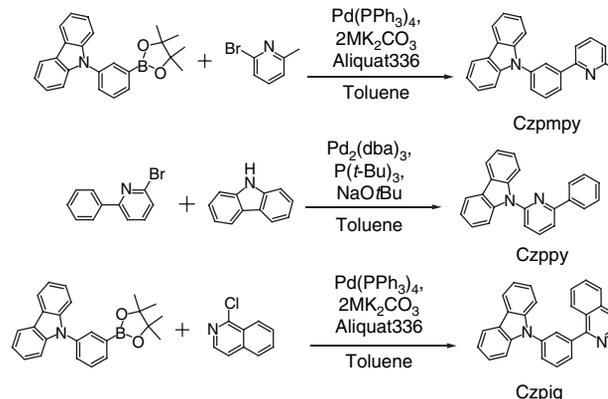
(50 nm)/4,4',4''-tris(N-carbazole)triphenylamine (TCTA) (10 nm)/Phosphorescent host materials: Green dopant material (tphpy)<sub>2</sub>Ir(acac)<sup>13</sup> (30 nm, 8%)/4,7-diphenyl-1,10-phenanthroline (Bphen) (30 nm)/lithium quinolate (Liq) (2 nm)/Al (100 nm). The current density (J), luminance (L), luminous efficiency (LE), and CIE chromaticity coordinates of the OLEDs were measured with a Keithly 2400, Chroma meter CS-1000A. Electroluminescence was measured using a Roper Scientific Pro 300i.

## 3. RESULTS AND DISCUSSION

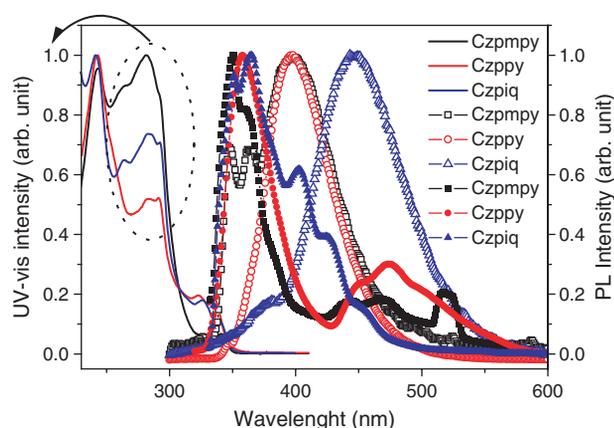
The syntheses of the phosphorescent host materials are outlined in Scheme 1. Suzuki cross-coupling of 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole with the corresponding halide afforded **Czmpmpy** and **Czpiq** in moderated yields. **Czppy** was prepared by the Buchwald-Hartwig cross-coupling with 2-bromo-6-phenylpyridine and carbazole in 52% yield.

The ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectra of **Czmpmpy**, **Czppy**, and **Czpiq** in dichloromethane are shown in Figure 1 (see Table I). The maximum absorption peaks were located at 282, 243, and 241 nm for **Czmpmpy**, **Czppy**, and **Czpiq**, respectively. The PL spectra of **Czmpmpy**, **Czppy**, **Czpiq** were 394, 392, and 444 nm in dichloromethane, respectively. The band gap of **Czmpmpy** (3.70 eV), **Czppy** (3.67 eV), **Czpiq** (3.59 eV) were broader than that (3.5 eV) of the CBP. The phosphorescence of **Czmpmpy**, **Czppy**, and **Czpiq** were also measured at 77 K (in 2-methyltetrahydrofuran). From the highest-energy 0–0 phosphorescence emissions, we estimate that their values of  $E_T$  are 2.64, 2.62, and 2.89 eV, respectively. These values are higher than that of CBP ( $E_T = 2.56$  eV) and (tphpy)<sub>2</sub>Ir(acac) ( $E_T = 2.23$  eV), which indicates that **Czpiq** may be an appropriate host materials for green, red, and even blue phosphorescent emitters.

Figure 2 displays the device structure and relative HOMO/LUMO energy level of the materials used in study. The HOMO energy levels of **Czmpmpy**, **Czppy**, and **Czpiq**, measured using a photoelectron spectrometer (Riken-Keiki



Scheme 1. Synthesis of **Czmpmpy**, **Czppy**, and **Czpiq**.

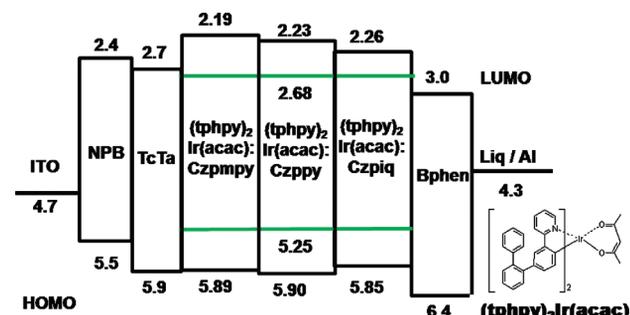


**Fig. 1.** UV-Vis absorption ( $\text{CH}_2\text{Cl}_2$ , room temperature, solid line), fluorescence spectra ( $\text{CH}_2\text{Cl}_2$ , room temperature, opened symbols), and phosphorescence spectra of (2-MeTHF, 77 K, closed symbols) for **Czpmpy**, **Czppy**, and **Czpiq**.

AC-2), were  $-5.89$ ,  $-5.90$ , and  $-5.85$  eV, respectively. Compared to the HOMO energy level of **Czpiq**, **Czpmpy** and **Czppy** showed lower HOMO energy levels of  $0.04$  and  $0.05$  eV, respectively. The LUMO energy levels were calculated at  $-2.19$ ,  $-2.23$ , and  $-2.26$  eV for **Czpmpy**, **Czppy**, and **Czpiq**. The LUMO energy level was decreased by directly connecting carbazole with the pyridine moieties. In addition, compared to LUMO energy level of **Czpmpy**, **Czpiq** showed lower LUMO energy level of  $0.07$  eV due to difference in electron affinity.

The thermal stability of **Czpmpy**, **Czppy**, and **Czpiq** are shown by the decomposition temperature ( $T_d$ , corresponding to 5% weight loss) of  $271$ ,  $292$ , and  $287$  °C by TGA. The glass transition temperature ( $T_g$ ) were observed at  $90$ ,  $98$ , and  $84$  °C for **Czpmpy**, **Czppy**, and **Czpiq**, which is much higher than that of CBP ( $62$  °C). We found that **Czppy**, with its direct connecting carbazole with pyridine moieties, exhibited higher value of  $T_d$  and  $T_g$  than **Czpmpy** and **Czpiq** with benzene ring.

To evaluate **Czpmpy**, **Czppy**, and **Czpiq** as host materials in PHOLEDs, we have chosen the triplet green emitter  $(\text{tphpy})_2\text{Ir}(\text{acac})^{13}$  for the device fabrications. The device structure of ITO/NPB (50 nm)/TcTa (10 nm)/ Phosphorescent host materials: $(\text{tphpy})_2\text{Ir}(\text{acac})$  (30 nm, 8%)/Bphen



**Fig. 2.** Energy-level diagram of the materials used in devices.

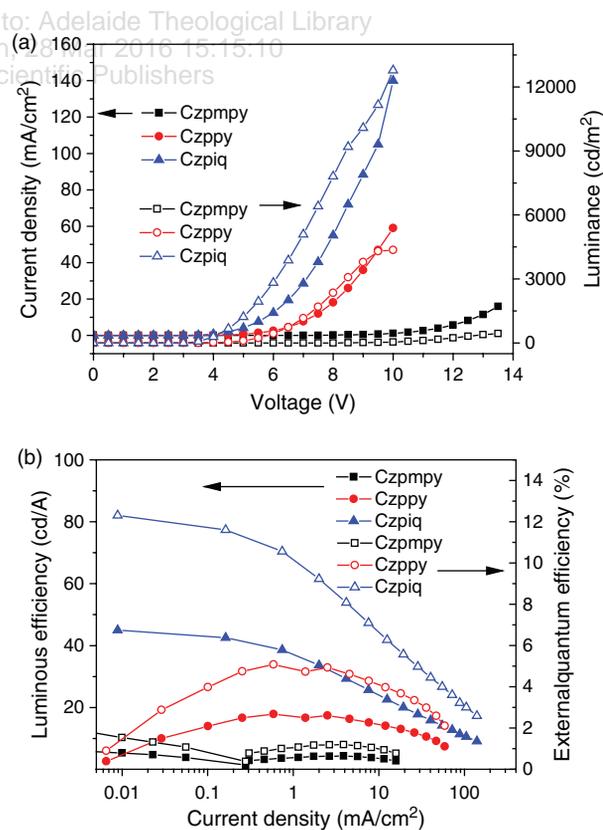
**Table I.** Optical properties of host materials (**Czpmpy**, **Czppy**, and **Czpiq**).

Compound	<b>Czpmpy</b>	<b>Czppy</b>	<b>Czpiq</b>
UV $\lambda_{\text{max}}$ [nm] <sup>a</sup>	282	243	241
PL $\lambda_{\text{max}}$ [nm] <sup>a</sup>	394	398	444
fwhm [nm] <sup>a</sup>	93	59	80
HOMO [eV] <sup>b</sup>	$-5.89$	$-5.90$	$-5.85$
LUMO [eV] <sup>b</sup>	$-2.19$	$-2.23$	$-2.26$
$E_g^b$ [eV]	3.70 eV	3.67 eV	3.59 eV
$E_T^c$ [eV]	2.64 eV	2.62 eV	2.89 eV
$T_d$ [°C]/ $T_g$ [°C]	271/90	292/98	287/84

<sup>a</sup>Measured in  $\text{CH}_2\text{Cl}_2$  solution. <sup>b</sup>Obtained from AC-2 and UV-vis absorption measurements. <sup>c</sup>Measured in 2-MeTHF solution at 77 K.

(30 nm)/Liq (2 nm)/Al (100 nm). NPB, Bphen and Liq were used as hole-transporting, electron-transporting and electron-injecting materials, respectively. TcTa was used as exciton-blocking materials to prevent exciton leakages from the emitting layer to NPB layer to improve the EL performances.

The current density–voltage–luminance (I–V–L) characteristics (a) and efficiency versus current density curves of devices examined in this work are shown in Figure 3. Table II summarizes the electroluminescence characteristics of the resulting devices.



**Fig. 3.** (a) I-V-L characteristics of devices and (b) luminous efficiency and external quantum efficiency versus current density relationship for PHOLEDs.

**Table II.** EL performance characteristic of the devices **Czmpy**, **Czppy**, and **Czpiq**.

Devices	<b>Czmpy</b>	<b>Czppy</b>	<b>Czpiq</b>
EL <sub>max</sub> [nm]	531	526	529
V <sub>turn-on</sub> <sup>a</sup> [V]	7.0 V	3.5 V	3.0 V
L <sup>b</sup> [cd/m <sup>2</sup> ]	438 (10 V)	4362 (10 V)	12780 (10 V)
LE <sup>b</sup> [cd/A]	6.44 (5.0 V)	17.9 (5.0 V)	45.0 (3.0 V)
PE <sup>b</sup> [lm/W]	4.05 (5.0 V)	11.6 (4.5 V)	47.1 (3.0 V)
EQE <sup>b</sup> [%]	4.41 (5.0 V)	5.08 (5.0 V)	12.3 (3.0 V)
CIE <sup>c</sup> (x, y)	(0.34, 0.62)	(0.35, 0.61)	(0.34, 0.58)

<sup>a</sup>Turn-on voltage at 1 cd/m<sup>2</sup>. <sup>b</sup>Values in parentheses are the voltages at which the maximum value were obtained. <sup>c</sup>Commission Internationale d'Éclairage (CIE) coordinates at a 8 V.

Under a constant voltage of 6 V, the current density of **Czmpy**, **Czppy**, and **Czpiq** were found to be 0.02, 7.65, and 12.5 mA/cm<sup>2</sup>, respectively. As expected, the current flow with **Czpiq** was significantly improved because of the lower electron injection barrier and reduction of carrier trapping by the dopant materials. The turn-on voltage, defined as the bias required attaining a luminance of 1 cd/m<sup>2</sup>, is 7.0, 3.5, and 3.0 V for the **Czmpy**, **Czppy**, and **Czpiq**, respectively. Interestingly, the device using **Czpiq** as a host shows the much superior current density flow, and the lower operation driving voltage and turn-on voltage than those using **Czmpy** and **Czppy** as hosts. The luminous and external quantum efficiencies (EQE) achieved with bipolar host **Czpiq** (45.0 cd/A; 12.3% EQE) are higher than those obtain with **Czppy** (17.9 cd/A; 5.08% EQE) and **Czmpy** (6.44 cd/A; 4.41% EQE) as the host.

A green OLED using **Czpiq** as a host exhibited the improved EL performances, compared to that using **Czmpy** and **Czppy** as a host because **Czpiq** has the lower LUMO level and thus the improved electron injection property. This may be attributed to the more suitable energy-level matching for the host and the dopant in device using **Czpiq**. The green dopant (tphpy)<sub>2</sub>Ir(acac) has HOMO and LUMO levels of -5.25 and -2.68 eV, respectively.<sup>13</sup> Therefore, the HOMO and LUMO levels of (tphpy)<sub>2</sub>Ir(acac) fall within those of the **Czpiq** host, with shallow hole and electron trap depth of 0.60 and 0.42 eV, respectively, which leads to a more balanced charge trapping and recombination, and more efficient

energy transfer from **Czpiq** host to the dopant compared to devices of **Czmpy** and **Czppy**.

This study clearly demonstrated the simple molecular design strategy of combining carbazole and isoquinoline groups for bipolar host materials for the efficient PHOLEDs.

#### 4. CONCLUSION

We demonstrated a molecular design strategy of combining a carbazole as an electron donor and pyridine or isoquinoline as an electron acceptor to give the bipolar host materials for the efficient PHOLEDs. Particularly, a green PHOLED using **Czpiq** as a bipolar host material and (tphpy)<sub>2</sub>Ir(acac) as a dopant in the emitting layer showed the maximum luminous efficiency of 45.0 cd/A, power efficiency of 47.1 lm/W, the maximum external quantum efficiency of 12.3% and CIE x, y coordinates of (0.34, 0.58) at 8 V.

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Received: 13 November 2009. Accepted: 24 March 2010.