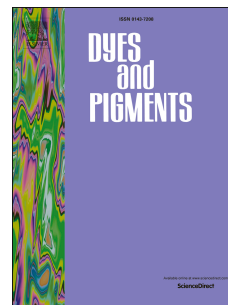


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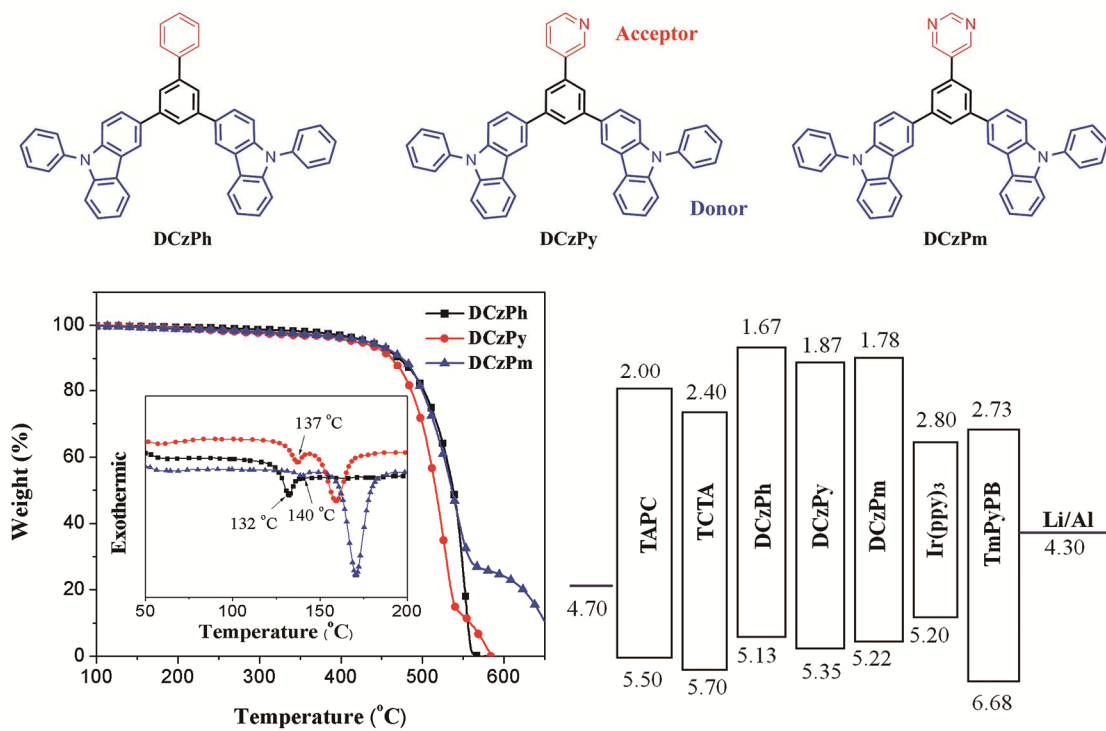
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Graphical abstract



Abstract

Three host materials, **DCzPh**, **DCzPy** and **DCzPm**, were developed for phosphorescent organic light emitting devices (PhOLEDs). These three compounds exhibit high triplet energy level ($E_T > 2.7$ eV), suitable glass transition temperatures ($T_g > 130$ °C), appropriate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, and balanced charge-transporting properties. Green PhOLEDs were fabricated by utilizing these three materials as hosts and the efficiencies were satisfactory. Device G3 based on DCzPm exhibited high efficiency with the maximum external quantum efficiency (EQE) of 17.2%, and even at the brightness of 1000 cd m^{-2} , the EQE reached 17.1%, demonstrating its low efficiency roll-off. The above results indicate that these host materials possess great commercial potential in OLED applications.

Keywords

Green phosphorescent organic light-emitting diodes; Carbazole derivatives; High thermal stability; Host materials;

1. Introduction

In the past few decades, PhOLEDs have received huge attention because of their application potential in high-resolution and flexible displays. [1-4] Compared with traditional fluorescent OLED, PhOLEDs are more favored due to their 100% theoretical internal quantum efficiencies (IQEs), [2,5-6] which is because phosphorescent emitter can utilize both singlet and triplet excitons via the heavy-atom effect. To achieve better performance, PhOLEDs usually adopt host-guest system for the emitting layer (EML). [7-10] The host-guest system can reduce unfavorable factors such as triplet-triplet annihilation (TTA) and concentration quenching. An ideal host material should have a high triplet energy level (E_T) to ensure that the energy can be transferred from host to the emitter. Besides, host materials should have appropriate HOMO/LUMO levels to improve carrier injection into the EML. [8,11-12] More importantly, to achieve charge-balances in the EML, host materials must possess a bipolar nature. Bipolar host materials composed of hole-transporting unit and electron-transporting unit can balance the hole and electron transport in the EML and realize better electroluminescence (EL) performance as well as lower efficiency roll-off. [13-14] Thus, the development of high-performance bipolar host materials is significantly important for PhOLEDs.

In this work, three bipolar host materials, 3,5-bis(9-phenyl-9*H*-carbazol-3-yl)-1,1'-biphenyl (**DCzPh**), 3,3'-(5-(pyridin-3-yl)-1,3-phenylene)bis(9-phenyl-9*H*-carbazole) (**DCzPy**) and 3,3'-(5-(pyrimidin-5-yl)-1,3-phenylene)bis(9-phenyl-9*H*-carbazole) (**DCzPm**) were designed and synthesized. The carbazole moiety was chosen as the hole-transporting unit, because of its high triplet energy level and good hole-transporting ability. [15-17] Biphenyl, phenylpyridine and phenylpyrimidine were selected as electron-transporting units, respectively. [18] Carbazole was linked to the electron-transporting units at its 3-site C atom, this link mode is beneficial for hole transporting. [19-20] These three compounds exhibit high triplet energy levels (all higher than 2.7 eV), good thermal stability, and appropriate HOMO/LUMO energy levels. Green PhOLEDs based on the above three hosts exhibit excellent

performance, for example, for device G3 hosted by DCzPm, the turn-on voltage is 3.1V, and the maximum EQE can achieve as high as 17.2%. At the brightness of 1000 cd m⁻², EQE of G3 can still reach 17.1%, which is almost the same as the maximum value.

2. Experimental

2.1. Materials and measurements

All reagents used in this work were of analytical grade and obtained via commercial source without further purification. The silica gel used in the column purification was 200 to 300 mesh.

¹H and ¹³C NMR spectra were characterized on a Bruker AM-400 spectrometer. Mass spectra were analyzed using a Waters LCT Premier XE spectrometer. Elemental analysis was measured by Vario EL. The ultraviolet-visible (UV-Vis) spectra were measured on a Nicolet CARY-100 spectrophotometer. Photoluminescence (PL) spectra were carried out on a Varian Cary fluorescence spectrophotometer. The electrochemical property was investigated on a VersaSTAT II workstation using 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte in dichloromethane. Differential scanning calorimetry (DSC) analysis was measured on a NETZSCH STA 409 PC/PG instrument.

2.2. Synthesis

2.2.1. Synthesis of (9-phenyl-9*H*-carbazol-3-yl)boronic acid

3-Bromo-9-phenyl-9*H*-carbazole (10.0 g, 31 mmol) was dissolved in anhydrous tetrahydrofuran (80 mL) at -78 °C and *n*-BuLi (23 mL, 2.0 M in *n*-hexane, 36.8 mmol) was added dropwise under N₂ protection and stirred for 3 h. Afterwards, triisopropyl borate (8.8 g, 46.8 mmol) was added dropwise and maintained for 0.5 h before warming to ambient temperature slowly to stir overnight before pouring into aq. HCl (2M, 80 mL) and extraction with DCM twice. Removal of the dried Na₂SO₄ solvent and recrystallisation with DCM and *n*-hexane (v/v = 1/1) to deliver solid (7.2g, yield 80%). ¹H NMR (CDCl₃, 400 MHz, δ): 9.12 (s, 1H), 8.37 (d, 2H), 7.60-7.66 (m, 4H),

7.52 (m, 2H), 7.45 (m, 2H), 7.39 (m, 1H).

2.2.2. Synthesis of 3,3'-(5-chloro-1,3-phenylene)bis(9-phenyl-9H-carbazole) (**DCzCl**)
(9-phenyl-9H-carbazol-3-yl)boronic acid (7.0 g, 24.4 mmol), 1,3-dibromo-5-chlorobenzene (3.0 g, 11.1 mmol) and K₂CO₃ (4.7 g, 34.0 mmol) were charged to THF (30 mL) and deionized water (15mL), Pd(PPh₃)₄ (0.06 g, 0.52 mmol) was charged after bubbling with N₂ for 15 min. Reflux the mixture under N₂ protection for 6 h, cooled down and pour into mL H₂O (100 mL) and filter. The crude solid was purified by recrystallization using THF/methanol (v/v = 1/2) to deliver 3.9 g solid (60%). ¹H NMR (400 MHz, CDCl₃, δ): 8.45-8.46 (m, 2H), 8.25 (d, *J* = 7.6 Hz, 2H), 7.94-7.95 (m, 1H), 7.62-7.76 (m, 12H), 7.46-7.52 (m, 8H), 7.33-7.38 (m, 2H).

2.2.3. Synthesis of 3,5-bis(9-phenyl-9H-carbazol-3-yl)-1,1'-biphenyl (**DCzPh**)

Charge **DCzCl** (1.0 g, 1.68 mmol), phenylboronic acid (0.22 g, 1.80 mmol) and K₂CO₃ (0.7 g, 5.06 mmol) into THF (12 mL) and deionized water (6 mL), then Pd(OAc)₂ (0.02 g, 0.09 mmol) and X-phos (0.04 g, 0.08 mmol) were charged after bubbling with N₂ for 15 min. Reflux the mixture for 12 h under protection of N₂, cool down to ambient temperature, pour into H₂O (50 mL) and filter. The crude product was refined by recrystallization using THF/methanol (v/v = 1/1.5) to deliver solid (0.68 g, yield 63%). ¹H NMR (400 MHz, CDCl₃, δ): 8.53 (d, *J* = 1.2 Hz, 2H), 8.26 (d, *J* = 8.0 Hz, 2H), 8.06-8.07 (m, 1H), 7.94 (d, *J* = 1.6 Hz, 2H), 7.82-7.85 (m, 4H), 7.63-7.70 (m, 8H), 7.43-7.58 (m, 11H), 7.33-7.38 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 143.14, 142.44, 141.60, 141.40, 140.53, 137.67, 133.54, 129.96, 128.88, 127.57, 127.51, 127.11, 126.20, 125.70, 125.62, 124.78, 123.97, 123.49, 120.48, 120.14, 119.10, 110.12, 109.96. HRMS (ESI, *m/z*): [M+H]⁺ calcd for C₄₈H₃₃N₂, 637.2638, found, 637.2647. Elemental analysis calcd for C₄₈H₃₂N₂: C, 90.54; H, 5.07; N, 4.40. Found: C, 90.93; H, 4.43; N, 4.14.

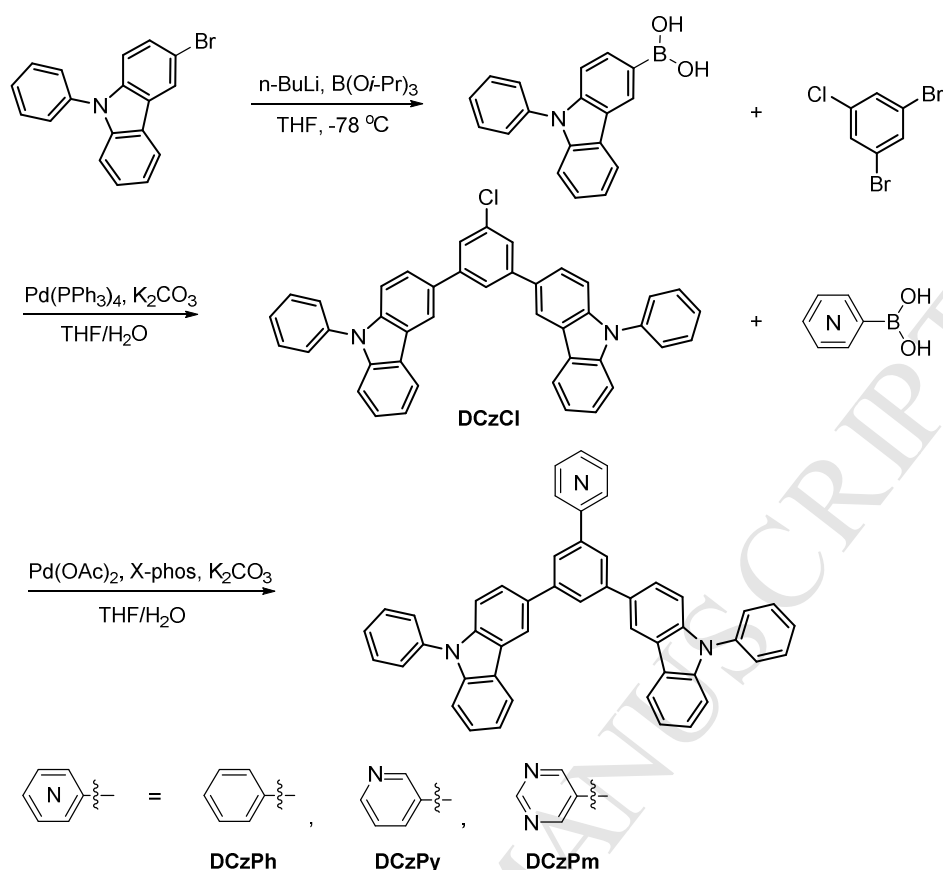
2.2.4. Synthesis of 3,3'-(5-(pyridin-3-yl)-1,3-phenylene)bis(9-phenyl-9H-carbazole) (**DCzPy**)

Charge **DCzCl** (1.0 g, 1.68 mmol), pyridin-3-ylboronic acid (0.23 g, 1.87 mmol) and

0.7 g K_2CO_3 (5.06 mmol) into THF (12 mL) and deionized water (6 mL), then $Pd(OAc)_2$ (0.02 g, 0.09 mmol) and X-phos (0.04 g, 0.08 mmol) were charged after bubbling with N_2 for 15 min. Reflux the mixture for 12 h under protection of N_2 , cool down to ambient temperature, pour into water and filter. The crude solid was purified by recrystallization using THF/methanol (v/v = 1/1.5) to deliver solid (0.62 g, yield 58%). 1H NMR (400 MHz, $CDCl_3$, δ): 9.00 (s, 1H), 8.60 (s, 1H), 8.43 (d, $J = 1.2$ Hz, 2H), 8.17 (d, $J = 7.6$ Hz, 2H), 8.00-8.03 (m, 2H), 7.82 (d, $J = 1.2$ Hz, 2H), 7.72-7.75 (m, 2H), 7.37-7.60 (m, 17H), 7.24-7.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.70, 148.66, 143.54, 141.44, 140.63, 139.04, 137.61, 137.06, 134.73, 133.12, 129.99, 127.64, 127.12, 126.38, 126.30, 125.63, 124.63, 124.03, 123.67, 123.43, 120.50, 120.21, 119.10, 110.22, 110.01. HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{47}H_{32}N_3$, 638.2591, found, 638.2598. Elemental analysis calcd for $C_{47}H_{31}N_3$: C, 88.51; H, 4.90; N, 6.59. Found: C, 88.37; H, 4.45; N, 6.71.

2.2.5. Synthesis of 3,3'-(5-(pyrimidin-5-yl)-1,3-phenylene)bis(9-phenyl-9H-carbazole) (DCzPm)

Charge **DCzCl** (1.0 g, 1.68 mmol), pyrimidin-5-ylboronic acid (0.23 g, 1.86 mmol) and 0.7 g K_2CO_3 (5.06 mmol) into THF (12 mL) and water (6 mL), then $Pd(OAc)_2$ (0.02 g, 0.09 mmol) and X-phos (0.04 g, 0.08 mmol) were charged after bubbling with N_2 for 15 min. Reflux the mixture for 10 h under N_2 protection, cool down to ambient temperature, pour into H_2O (50 mL) and filter. The crude product was refined by recrystallization using THF/methanol (v/v = 1/1) to deliver solid (0.65 g, yield 61%). 1H NMR (400 MHz, $CDCl_3$, δ): 9.28 (s, 1H), 9.16 (s, 2H), 8.49 (d, $J = 1.6$ Hz, 2H), 8.24 (d, $J = 7.6$ Hz, 2H), 8.14-8.15 (m, 1H), 7.87 (d, $J = 1.6$ Hz, 2H), 7.77-7.81 (m, 2H), 7.60-7.67 (m, 8H), 7.48-7.55 (m, 4H), 7.43-7.46 (m, 4H), 7.31-7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.69, 155.24, 143.96, 141.47, 140.72, 137.55, 135.46, 134.81, 132.70, 130.01, 127.69, 127.19, 127.12, 126.37, 125.54, 124.32, 124.07, 123.36, 120.49, 120.26, 119.10, 110.30, 110.05. HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{46}H_{31}N_4$, 639.2543, found, 639.2548. Elemental analysis calcd for $C_{46}H_{30}N_4$: C, 86.49; H, 4.73; N, 8.77. Found: C, 86.87; H, 4.52; N, 8.37.



Scheme 1. Synthetic routes for **DCzPh**, **DCzPy** and **DCzPm**.

3. Results and discussion

3.1. Synthesis and characterization

As presented in Scheme 1, the key intermediate **DCzCl** was synthesized between (9-phenyl-9H-carbazol-3-yl)boronic acid and 1,3-dibromo-5-chlorobenzene, and the titled molecules were coupled between **DCzCl** and corresponding arylboronic acid. All three compounds were obtained in satisfactory yield, and their structures were fully characterized by ^1H , ^{13}C NMR and mass spectrometry (HRMS).

3.2. Thermal properties

Good thermostability is beneficial to prolong the operation lifetime of OLEDs. Consequently, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were adopted to evaluate the thermal properties of **DCzPh**, **DCzPy** and **DCzPm**. Seen from Fig. 1 and Table 1, the glass-transition temperature (T_g) of **DCzPh**, **DCzPy** and **DCzPm** were 132, 137 and 140 $^\circ\text{C}$, respectively, while the thermal decomposition temperatures (T_d) were 434, 418 and 433 $^\circ\text{C}$, respectively,

demonstrating excellent thermostability of all these newly designed molecules.

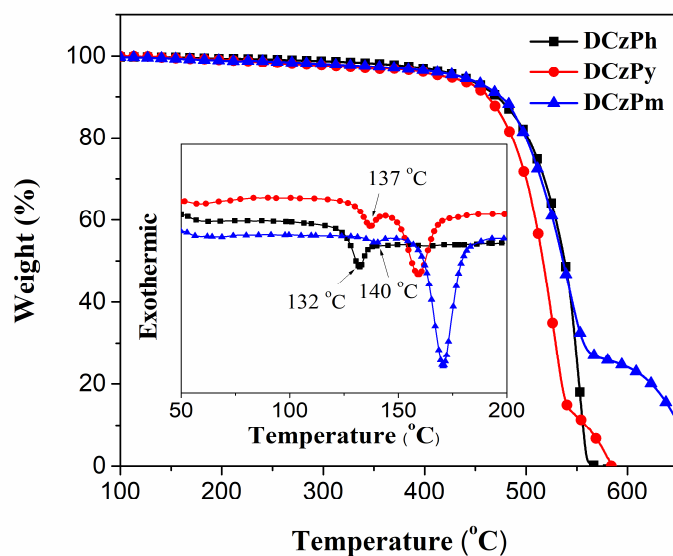


Fig. 1. Thermal properties of DCzPh, DCzPy and DCzPm.

Table 1 Properties of DCzPh, DCzPy and DCzPm.

Compound	λ_{\max} abs (nm) ($\epsilon/M^{-1}\text{cm}^{-1}$) ^a	λ_{\max} em (nm)	Q.Y. (%) ^b	Stokes Shift (cm^{-1})	E_g (eV) ^c	HOMO (eV) ^d	LUMO (eV) ^d	E_T (eV) ^e	T_g (°C) ^f	T_d (°C) ^g
DCzPh	296 (7791)	378	11.32	7382	3.41	-5.13	-1.67	2.74	132	434
DCzPy	297 (8608)	380	10.45	7355	3.43	-5.33	-1.87	2.72	137	418
DCzPm	295 (6505)	394	10.68	8518	3.38	-5.22	-1.78	2.75	140	433

^a Determined in dichloromethane solution (10^{-5} M), ϵ = molar extinction coefficient.

^b Emission quantum yield, measured in the dichloromethane solution using an integrated sphere.

^c Estimated from absorption spectrum onset ($E_g^{\text{opt}} = 1241/\lambda_{\text{onset}}$).

^d Estimated from CV curve and the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$.

^e Estimated from phosphorescence spectrum at 77 K.

^f Measured from the DSC.

^g Measured from the TGA.

3.3. Photophysical properties

Initially, the photophysical properties of the titled materials were investigated by the absorption and fluorescence spectra, and the results were displayed in Fig. 2a. It can be seen that they exhibit similar maximum absorption bands at around 296 nm, which

could be ascribed to the intramolecular charge transfer (ICT) effect from the electron-rich phenylcarbazole to the electron-deficient pyridine or pyrimidine unit.[21-22] The band gaps (E_g) of **DCzPh**, **DCzPy** and **DCzPm** estimated by absorption edge were 3.41, 3.43 and 3.38 eV, respectively. Besides, these three compounds show a single emission band with maximum peaks positioned at 378, 380 and 394 nm, respectively, and the slightly red-shift of emission peaks was caused by the increasing electrophilic property of electron accepting moiety which enhanced the ICT effect.

Additionally, the triplet levels (E_T) of **DCzPh**, **DCzPy** and **DCzPm** were calculated to be 2.74, 2.72 and 2.75 eV, respectively, by analyzing the low temperature phosphorescent spectrum at 77 K, which qualify them to be hosts in the green and red PhOLEDs.

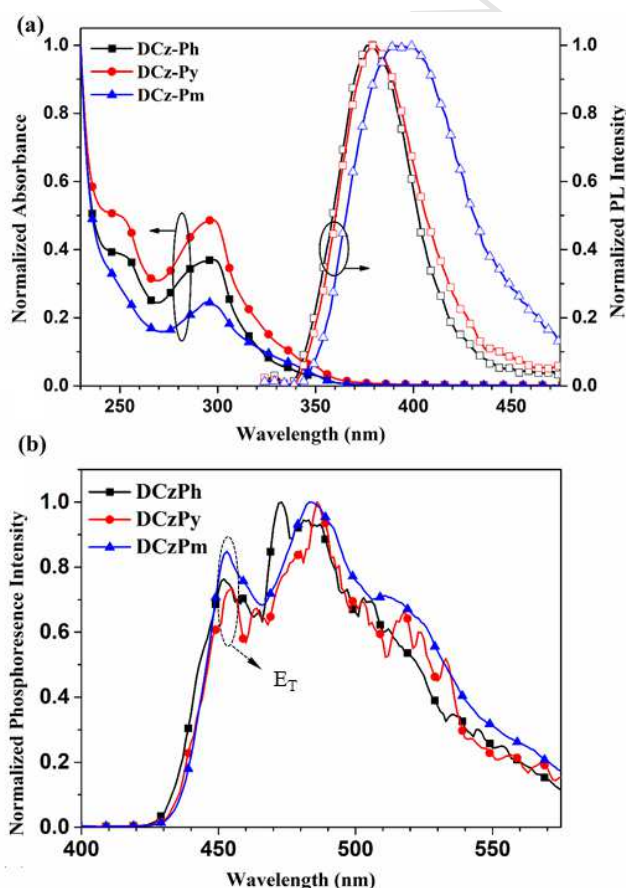


Fig. 2. (a) UV-Vis absorption and room temperature emission spectra of **DCzPh**, **DCzPy** and **DCzPm** in DCM at 10^{-5} M. (b) The corresponding phosphorescence spectra recorded in 2-methyltetrahydrofuran at 77 K.

3.4. Electrochemical properties and theoretical calculation

The suitability of energy levels between different functional layers is critical to the performance of OLEDs devices. Therefore, cyclic voltammetry (CV) was adopted to evaluate the electrochemical properties of the titled compounds and the pertinent data are depicted in Table 1 and Fig. 3. The HOMO levels could be estimated with the first oxidizing potentials through the following equation: $E_{\text{HOMO}} = -E_{\text{ox}} - 4.4$ eV. Afterwards, the LUMO levels can be determined by E_{HOMO} and E_{g} . As a consequence, the HOMO/LUMO levels of **DCzPh**, **DCzPy** and **DCzPm** were calculated to be $-5.13/-1.67$ eV, $-5.33/-1.87$ eV and $-5.22/-1.78$ eV, respectively.[23]

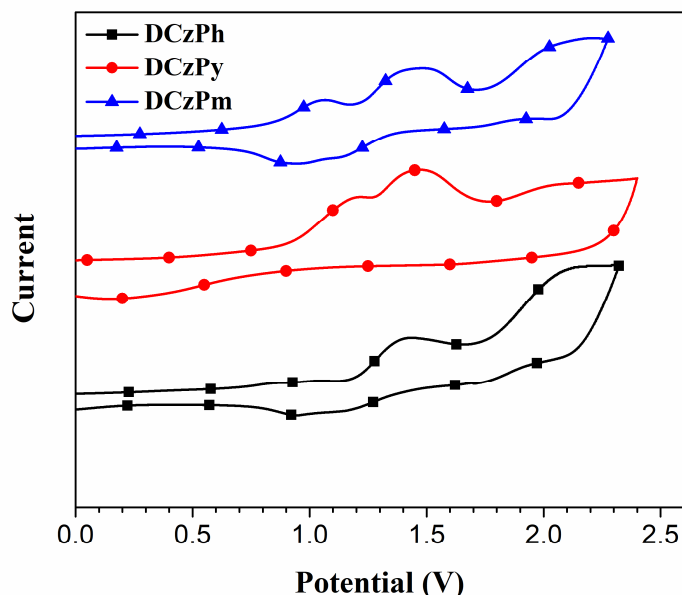
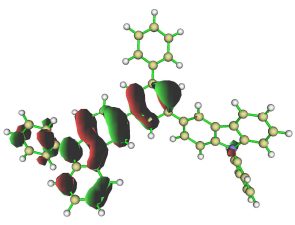
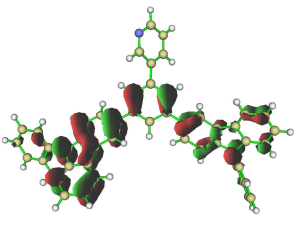
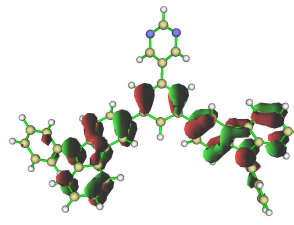
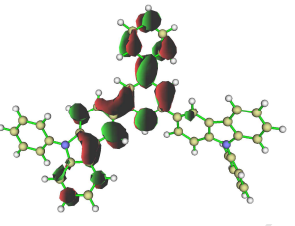
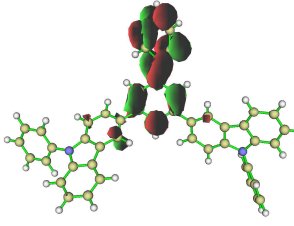
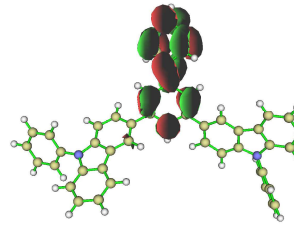


Fig. 3. Cyclic voltammograms of **DCzPh**, **DCzPy** and **DCzPm** in DCM solution with 0.1 mol L^{-1} TBAPF₆ electrolyte, scanning rate: 100 mV/s.

To get an in-depth into the electronic structures of these compounds, density functional theory (DFT) computations for **DCzPh**, **DCzPy** and **DCzPm** were implemented at B3LYP/6-31G* level.[24] It can be learnt from Table 2 that the HOMO of **DCzPh** is mostly situated at one of the carbazole moieties and the core phenyl, and the LUMO lies on the biphenyl and slightly extended to carbazole unit. Meanwhile, the HOMOs of **DCzPy** and **DCzPm** are mostly dispersed on the biscarbazole moieties and the core phenyl group, while the LUMOs are totally located on the core phenyl and pyridine/pyrimidine moieties. Compared to **DCzPh**, **DCzPy**

and **DCzPm** exhibit more separated HOMO/LUMO distributions, which could be ascribed to the enhanced ICT effect that improved their charge carriers transporting property. Besides, the HOMO/LUMO energy levels of **DCzPh**, **DCzPy** and **DCzPm** were calculated to be $-5.38/-1.44$ eV, $-5.53/-1.25$ eV and $-5.61/-1.47$ eV, respectively.

Table 2. Calculated molecular orbits and HOMO/LUMO energy levels of **DCzPh**, **DCzPy** and **DCzPm**.

	DCzPh	DCzPy	DCzPm
HOMO			
	-5.38 eV	-5.53 eV	-5.61 eV
LUMO			
	-1.44 eV	-1.25 eV	-1.47 eV

3.5 EL performance

To directly assess the EL performance of **DCzPh**, **DCzPy** and **DCzPm**, these materials were fabricated in green PhOLEDs. The device structure is ITO/ TAPC (40 nm)/ TCTA (5 nm)/Ir(ppy)₃-host (20 nm)/ TmPyPB (50 nm)/LiF (0.6 nm)/Al (80 nm). Herein, a classical green phosphorescent Ir-complex (Ir(ppy)₃) was selected as the emitter, and the common doping concentration of 8% was chosen. TAPC and TCTA were used as the hole-transporting layer (HTL), meanwhile, TCTA also acts as electron-blocking layer (EBL). TmPyPB was used as the electron transporting layer (ETL).[13] Fig. 4 shows the device structure details and the chemical structures of organic molecules in each layer.

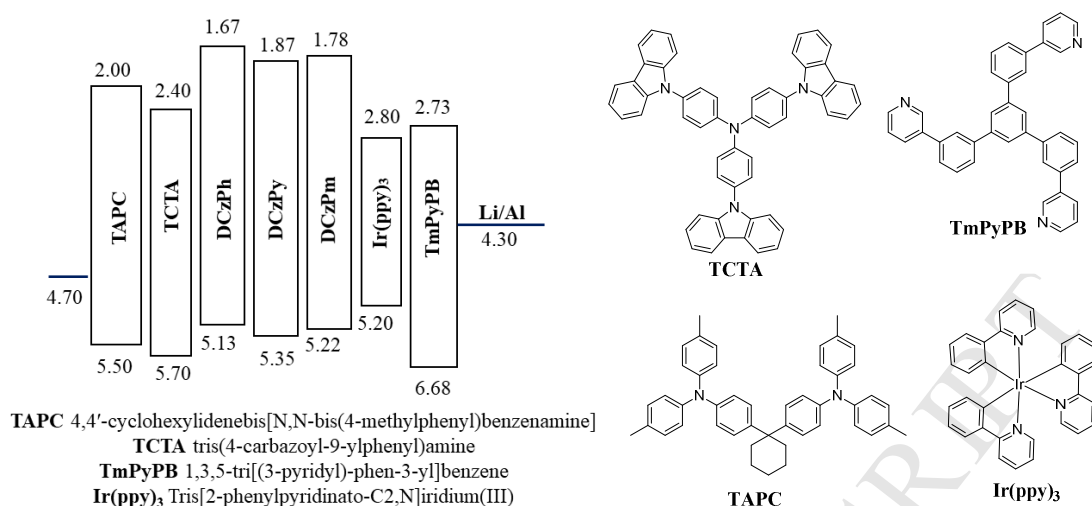


Fig. 4 The energy diagram of green PhOLED and the chemical structures of organic materials used in the PhOLEDs.

The EL performances of these three host materials are summarized in Table 3. The current density (J)–voltage (V)–luminance (L) curves are shown in Fig. 5a. All devices exhibit relatively low turn-on voltages (< 4 V), and the V_{on} of **D CzPm** based device G3 is the lowest among the three devices because of the suitable energy levels and bipolar charge transport properties. Fig. 5b exhibits the current efficiency (η_c) and the external quantum efficiency (EQE) versus J of G1, G2 and G3. Both the η_c and EQE of these three devices are satisfactory. Specifically speaking, Device G1 based on **DCzPh** exhibits the maximum EQE of 14.5% and maximum η_c of 49.1 cd A⁻¹, and the device G2 based on **DCzPy** exhibits higher maximum efficiencies with maximum EQE of 15.6% and maximum η_c of 52.6 cd A⁻¹. The performance of Device G3 is the best among these three devices with the maximum EQE of 17.2% and maximum η_c of 58.0 cd A⁻¹, respectively. It can be inferred from the above results that the maximum efficiencies of these devices are closely related to their turn-on voltages, as well as the electron-transporting units. The strong EL performance of pyrimidine-based host material **DCzPm** can be explained by its outstanding bipolar charge transport property. Moreover, as shown in Fig. 5c, all devices exhibit pure green emission originated from the Ir(ppy)₃. Besides, these three devices exhibit low efficiency roll-off, at the luminance of 1000 cd m⁻², the EQE of device G3 can still reach up to 17.1% with almost no change. Even at the extremely

high luminance of 5000 cd m^{-2} , the EQE still maintains at 16.9%. The ultralow efficiency roll-off merit can be explained by the balanced carrier-transport property of **DCzPm**, which broadens the exciton recombination region and reduces the density of triplet exciton, thus decreasing the annihilation of triplet excitons.

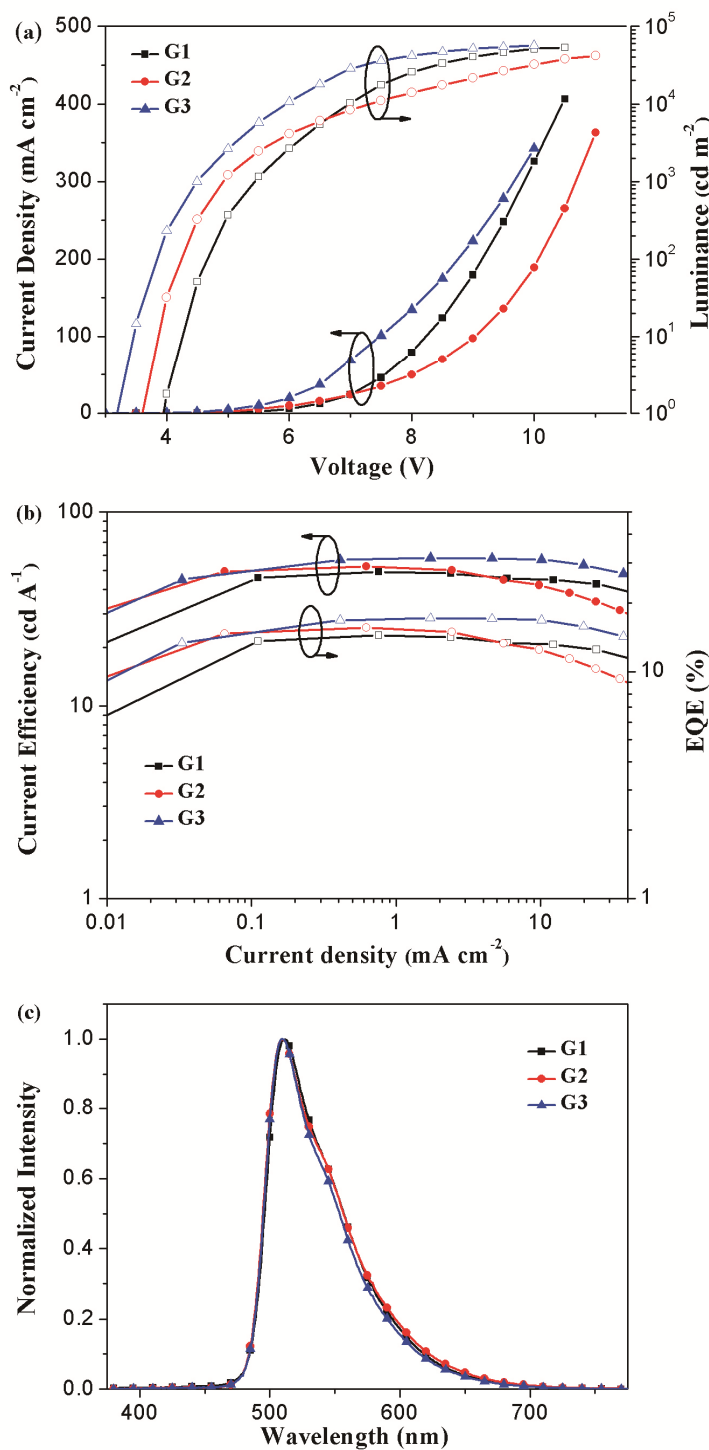


Fig.5. (a) Current density-voltage-luminance (J - V - L) characteristics of green PhOLEDs G1, G2 and G3; (b) η_c and η_{ext} versus current density of G1, G2 and G3; (c)

EL spectra of G1, G2 and G3 at 6 V.

Table 3. Electroluminescence performance of PhOLEDs

devices	hosts	$V_{on}(V)^a$	$L_{max}(cd\ m^{-2})^b$	$\eta_c (cd\ A^{-1})^c$	$\eta_p (lm\ W^{-1})^d$	EQE (%) ^e	CIE(x, y) ^f
G1	DCzPh	3.9	49832	49.1 48.9 45.3	32.1	14.5 14.2 13.3	0.28, 0.62
G2	DCzPy	3.5	28602	52.6 50.7 40.8	38.9	15.6 15.2 12.0	0.29, 0.62
G3	DCzPm	3.1	34280	58.0 58.0 56.7	45.6	17.2 17.1 16.9	0.28, 0.62

^a V_{on} , turn-on voltage, the voltage at luminance of $1\ cd\ m^{-2}$;

^b L_{max} , maximum luminance;

^c Current efficiency, order: maximum, at $1\ 000\ cd\ m^{-2}$, at $5\ 000\ cd\ m^{-2}$;

^d Maximum power efficiency;

^e External quantum efficiency, order: maximum, at $1\ 000\ cd\ m^{-2}$, at $5\ 000\ cd\ m^{-2}$;

^f CIE coordinates (x,y), measured at 6 V.

4. Conclusion

In summary, three novel host materials **DCzPh**, **DCzPy** and **DCzPm** were developed by utilizing carbazole as the electron-donating unit, biphenyl/phenylpyridine /phenylpyrimidine as the electron-acceptor units, respectively. These three compounds exhibit high triplet energy level, good thermal stability, suitable HOMO/LUMO energy levels and balanced charge-transporting properties. Green PhOLEDs based on these hosts were fabricated and characterized in detail to evaluate their EL performances. Notably, **DCzPm**-based device exhibited the best performance with the maximum EQE of 17.2%, and with negligible efficiency roll-off even at $1000\ cd\ m^{-2}$, demonstrating its great commercial application potential in OLEDs.

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Highlights

- Three bipolar host materials **DCzPh**, **DCzPy** and **DCzPm** were designed and synthesized.
- The above three hosts exhibit good thermal stability with $T_g > 130$ °C.
- **DCzPm**-based green PhOLED exhibits excellent performance with maximum EQE of 17.2%.