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## Rational design of host materials for phosphorescent organic light-emitting diodes by modifying the 1-position of carbazole<sup>†</sup>

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A novel carbazole moiety with bromine at the 1-position of carbazole was synthesized and four carbazole compounds derived from the 1-position modified carbazole were developed as the host materials for phosphorescent organic light-emitting diodes. The 1-position modified carbazole was coupled with another carbazole to prepare bicarbazole intermediates, which were substituted with 4,6-diphenyl-triazine to yield four bicarbazole derivatives modified with the electron deficient diphenyltriazine unit. The triplet host materials showed high quantum efficiency above 20% and low driving voltage below 5.0 V at 1000 cd m<sup>-2</sup> in green phosphorescent organic light-emitting diodes.

Carbazole derivatives have been widely developed as the host materials for phosphorescent organic light-emitting diodes (OLEDs) because of several merits of the carbazole moiety such as good hole transport properties, high triplet energy, and thermal stability. In particular, high triplet energy of the carbazole moiety expanded the application of carbazole as the core structure of triplet host materials.<sup>1-7</sup> Another merit of carbazole is diverse modification at different positions of carbazole. Typically, the 9-position of carbazole was coupled to various functional units by coupling reaction mediated by transition metal based catalysts. The coupling of carbazole via the 9-position produced well-known triplet host materials such as 1,3-bis(N-carbazolyl)benzene (mCP) and 4,4'-bis(N-carbazolyl)-1,1'-biphenyl.8-12 The electrophilic substitution of carbazole produced various carbazole derivatives with functional groups at 3- and 6-positions. Many host materials were prepared by substituting electron rich and electron poor moieties at the 3-position of carbazole using a simple synthetic procedure.<sup>13-16</sup> Modification of carbazole via the 2-position of carbazole was also an effective way of designing triplet host materials although the triplet energy of the host materials was lowered by the 2-position substitution.<sup>17-20</sup> Another way of developing carbazole compounds

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In this work, 1-bromo-9*H*-carbazole was synthesized as the core structure of triplet host materials and four compounds derived from the 1-bromo-9*H*-carbazole moiety were developed. The 1-bromo-9*H*-carbazole moiety was coupled with a boronic ester of 9-phenylcarbazole at different substitution positions followed by coupling with 2-chloro-4,6-diphenyl-1,3,5-triazine to produce four bicarbazole compounds. The four host materials derived from the 1-position modified carbazole moiety showed high quantum efficiency above 20% in green phosphorescent OLEDs. It was demonstrated that the 1-position modification of carbazole is a good way of securing high triplet energy, thermal stability, high quantum efficiency and high power efficiency in the host materials.

The four host materials derived from 1-bromo-9*H*-carbazole, 9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9*H*,9'*H*-1,1'-bicarbazole (1-PCz-1-TCz), 9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9*H*,9'*H*-1,2'-bicarbazole (2-PCz-1-TCz), 9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9*H*,9'*H*-1,3'-bicarbazole (3-PCz-1-TCz) and 9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9'-phenyl-9*H*,9'*H*-1,4'-bicarbazole (4-PCz-1-TCz) have a bicarbazole backbone structure at different interconnect positions as a donor unit and diphenyltriazine as an acceptor unit to impart bipolar charge transport properties. The 1-position modified carbazole moiety was connected with 9-phenylcarbazole *via* 1-, 2-, 3-, and 4-positions followed by modification with diphenyltriazine to investigate the effect of linking position on the photophysical properties and device performances of the host materials. It is expected that the 1-position modification can increase the triplet energy by distorting the molecular structure.

All compounds synthesized in this work were derived from 1-bromo-9*H*-carbazole prepared from (2-bromophenyl)hydrazine hydrochloride and cyclohexanone at a synthetic yield of 56% after purification because the 1-position halogenated carbazole

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moiety cannot be synthesized by direct halogenation. The 1-bromo-9*H*-carbazole was reacted with bis(pinacolato)diboron to couple the 1-position modified carbazole moiety with other carbazole moieties with a functional group at different positions of carbazole. Four bicarbazole intermediates were produced by a Suzuki coupling reaction using a Pd catalyst and were modified with 2-chloro-4,6diphenyl-1,3,5-triazine to synthesize final compounds. The synthetic scheme of the host materials is shown in Scheme 1.

Fig. 1 shows the HOMO and LUMO distribution of the four host materials. The LUMO distribution was similar in all host materials and was localized on the diphenyltriazine moiety in all host materials due to the electron deficiency of the triazine unit. The HOMO of the host materials was dominated by the electron rich bicarbazole moiety and was dispersed over the bicarbazole moiety. Therefore, the HOMO and the LUMO were separated and all host materials showed bipolar charge transport properties.

The HOMO was dominated by the electron rich bicarbazole moiety, but the HOMO distribution within the bicarbazole backbone structure was rather localized on the 9-phenylcarbazole unit because electron deficient diphenyltriazine moiety was coupled to the other carbazole unit through the N of carbazole.

The photophysical properties of the four host materials are summarized in Table 1. The HOMO and the LUMO of the four host materials were analyzed by cyclic voltammetry (CV) measurements. Separate oxidation and reduction curves of the host materials are presented in Fig. S1 (ESI†). The oxidation potential of the host materials was similar in all host materials because the oxidation occurred in the carbazole unit of the backbone structure and there was also little difference in reduction potentials because the reduction occurred in the diphenyltriazine unit. The HOMO–LUMO levels of 1-PCz-1-TCz, 2-PCz-1-TCz, 3-PCz-1-TCz and 4-PCz-1-TCz were -6.06/-3.24, -6.05/-3.32, -6.00/-3.33 and -6.16/-3.32 eV, respectively, from the oxidation and reduction potentials.



Fig. 1 The HOMO and LUMO distribution of four host materials.

Table 1	Photophy	/sical pro	perties of	the for	our host	materials
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Material	HOMO <sup>a</sup> [eV]	LUMO <sup>a</sup> [eV]	$E_{g}^{a}$ [eV]	$E_{g}^{b}$ [eV]	Singlet energy [eV]
1-PCz-1-TCz	-6.06	-3.24	2.82	3.31	2.69
2-PCz-1-TCz	-6.05	-3.32	2.73	3.43	2.63
3-PCz-1-TCz	-6.00	-3.33	2.67	3.49	2.53
4-PCz-1-TCz	-6.16	-3.32	2.84	3.31	2.62

<sup>*a*</sup> The HOMO and the LUMO were measured by CV. <sup>*b*</sup> HOMO–LUMO gap measured from the UV-vis edge.

The HOMO–LUMO gaps of 1-PCz-1-TCz, 2-PCz-1-TCz, 3-PCz-1-TCz and 4-PCz-1-TCz were 2.82, 2.73, 2.67 and 2.84 eV, respectively. The HOMO–LUMO gap was relatively large in the 1-PCz-1-TCz and 4-PCz-1-TCz hosts due to the distortion of the bicarbazole backbone and diphenyltriazine units. The dihedral angles between two carbazole units were 61, 50, 49 and 55° for 1-PCz-1-TCz, 2-PCz-1-TCz, 3-PCz-1-TCz and 4-PCz-1-TCz from geometrical optimization of the molecular structure.

The thermal stability of the host materials was estimated from glass transition temperature ( $T_g$ ) obtained from differential scanning calorimeter measurements in Fig. S2 (ESI<sup>†</sup>).

 $T_{\rm g}$  values for 1-PCz-1-TCz, 2-PCz-1-TCz, 3-PCz-1-TCz and 4-PCz-1-TCz were 120, 128, 122 and 126 °C, respectively. All compounds synthesized using 1-position modified carbazole showed good thermal stability.

Photophysical analysis of the host materials was performed using UV-vis and PL measurements of the host materials. UV-vis absorption and solution PL emission spectra are presented in Fig. 2. UV-vis absorption spectra of the host materials were extended to 370 nm by  $n-\pi^*$  and  $\pi-\pi^*$  absorption of the bicarbazole backbone structure modified with diphenyltriazine. PL emission spectra of 1-PCz-1-TCz, 2-PCz-1-TCz, and 4-PCz-1-TCz were observed at 470 nm, but the PL spectrum of 3-PCz-1-TCz was shifted to



Fig. 2 UV-vis, solution PL and low temperature PL spectra of 1-PCz-1-Trz (a), 1-PCz-2-Trz (b), 1-PCz-3-Trz (c) and 1-PCz-4-Trz (d).

501 nm, which may be due to a small dihedral angle between carbazole and diphenyltriazine units. Dihedral angles of the host materials were in the order of 1-PCz-1-TCz ( $53.5^{\circ}$ ) > 2-PCz-1-TCz ( $51.9^{\circ}$ ) > 4-PCz-1-TCz ( $49.3^{\circ}$ ) > 3-PCz-1-TCz ( $26.8^{\circ}$ ). The small dihedral angle of 3-PCz-1-TCz expanded the conjugated structure and resulted in a small HOMO–LUMO gap and red shifted PL emission. Low temperature PL emission in liquid nitrogen was used to calculate the triplet energy of the host materials and the triplet energies of 1-PCz-1-TCz, 2-PCz-1-TCz, 3-PCz-1-TCz and 4-PCz-1-TCz were 2.69, 2.55, 2.63 and 2.66 eV, respectively. Transient PL measurement also confirmed the phosphorescence emission and excited state lifetime longer than 10 µs was observed for the host materials (Fig. S3, ESI†).

As the triplet energy of the host materials was higher than that of green emitting tris[2-phenylpyridinato- $N, C^2$ ] iridium(III) (Ir(ppy)<sub>3</sub>) (2.40 eV), green phosphorescent OLEDs were developed by doping  $Ir(ppy)_3$  in the host materials. The green phosphorescent devices with the configuration of indium tin oxide/ poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (60 nm)/ 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (20 nm)/ 1,3-bis(N-carbazolyl)benzene (10 nm)/host:Ir(ppy)<sub>3</sub> (3%:25 nm)/ diphenylphosphineoxide-4-(triphenylsilyl)phenyl (5 nm)/1,3,5tris(1-phenyl-1H-benzimidazol-2-yl)benzene (30 nm)/LiF (1 nm)/ Al were fabricated to evaluate their host performances. Fig. 3a shows plots of current density and luminance against voltage for the green phosphorescent OLEDs. The current density of the devices was in the order of 4-PCz-1-TCz > 3-PCz-1-TCz > 2-PCz-1-TCz > 1-PCz-1-TCz and the luminance showed the same tendency. The driving voltage of the green phosphorescent OLEDs at 1000 cd  $m^{-2}$  was low in the 3-PCz-1-TCz and 4-PCz-1-TCz devices and could reach 4.6 V with a low turn-on voltage of 2.5 V. The high current density of the 3-PCz-1-TCz and 4-PCz-1-TCz devices can be correlated with electron current density of the devices as shown in single carrier current density-voltage curves in Fig. S4 (ESI<sup>+</sup>). As Ir(ppy)<sub>3</sub> is a strong hole trapping dopant due to a large HOMO gap in the host materials, the current density of the green device is dominated by electron current density rather than hole current density. Therefore, the order of current density was the same as that of electron current density. The low current density of the 1-PCz-1-TCz green device is due to low



**Fig. 3** Current density-voltage-luminance (a) and quantum efficiencyluminance (b) plots of green phosphorescent organic light-emitting diodes with 1-PCz-1-TCz, 2-PCz-1-TCz, 3-PCz-1-TCz and 4-PCz-1-TCz host materials. Ir(ppy)<sub>3</sub> was doped as a green triplet emitter.

hole and electron current densities of the single carrier devices, which is due to significant distortion of the molecular structure by steric hindrance.

The quantum efficiency of the green phosphorescent OLEDs is presented against luminance in Fig. 3b. The 2-PCz-1-TCz device showed higher quantum efficiency than other devices and the maximum quantum efficiency of the 2-PCz-1-TCz device was 24.5% at 2000 cd m<sup>-2</sup>. Other host materials showed a similar maximum quantum efficiency of about 20%. The high quantum efficiency of the 2-PCz-1-TCz device seems to be due to balanced charge density in the emitting layer by hole trapping effect of Ir(ppy)<sub>3</sub>. Although the hole current density was higher than the electron current density in the 2-PCz-1-TCz single carrier devices, hole trapping by Ir(ppy)<sub>3</sub> balanced holes and electrons in the emitting layer. Too high electron current density (3-PCz-1-TCz and 4-PCz-1-TCz) or too low electron current density (1-PCz-1-TCz) could not improve the charge balance further.

The performances of the 2-PCz-1-TCz device were further studied by changing the hole transport layer and the electron transport layer. A double layer of 4,4',4''-tris(*N*-carbazolyl)triphenylamine (TCTA)/mCP instead of mCP was selected as the hole transport layer for better hole injection and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene was an electron transport layer instead of the TSPO1/ TPBI double layer for better electron injection. The current density and luminance of the 2-PCz-1-TCz device were greatly increased by replacing the charge transport materials. The driving voltage at 1000 cd m<sup>-2</sup> was 3.8 V without any p- or n-type doping of charge transport materials. Maximum quantum efficiency and power efficiency of the 2-PCz-1-TCz device were 22.4% and 104 lm W<sup>-1</sup>,

Table 2 Device performances of the green devices

Material	Max. Q.E. (%)	QE (%) at 1000 nit	$\begin{array}{l} \text{Max PE} \\ \left( \text{lm } \text{W}^{-1} \right) \end{array}$	Color index at 1000 nit
1-PCz-1-TCz <sup>a</sup>	20.9	18.1	53.4	0.29, 0.62
2-PCz-1-TCz <sup>a</sup>	24.5	23.8	62.9	0.29, 0.62
3-PCz-1-TCz <sup>a</sup>	19.7	16.8	68.6	0.30, 0.62
4-PCz-1-TCz <sup>a</sup>	20.6	19.6	77.2	0.30, 0.62
2-PCz-1-TCz <sup>b</sup>	22.4	19.9	103.7	0.32, 0.63
<sup><i>a</i></sup> mCP hole tra	nsport layer	<sup>b</sup> TCTA/mCP	hole transpo	rt layer.

respectively. Device performances are summarized in Fig. S5 (ESI<sup>†</sup>) and Table 2.

In conclusion, four host materials derived from bicarbazole were synthesized by coupling the 1-position modified carbazole with the 1-, 2-, 3-, 4-modified carbazole. High quantum efficiency above 20% could be achieved using the host materials and 2-PCz-1-TCz showed the highest quantum efficiency of 24.5% in the green phosphorescent OLEDs. Additionally, optimization of the device structure could provide a high power efficiency of 104  $\text{Im W}^{-1}$  in the 2-PCz-1-TCz device.

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