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Molecular design of host materials for stable blue phosphorescent organic light-emitting diodes

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Stable host materials based on dibenzothiophene and 9-phenylcarbazole were synthesized to elongate the life span of blue phosphorescent organic light-emitting diodes (PHOLEDs). Three host materials with the 9-phenylcarbazole moiety directly linked with dibenzothiophene moiety via 1, 3, and 4- positions of 9-phenylcarbazole were compared in terms of lifetime and efficiency of the blue PHOLEDs. The connection between dibenzothiophene and 9-phenylcarbazole through 3- position of carbazole was an effective way of improving the lifetime of the blue PHOLEDs more than twice and the molecular structure was well correlated with the lifetime of the blue PHOLEDs.

1. Introduction

The development of blue phosphorescent organic light-emitting diodes (PHOLEDs) [1,2] is of great importance due to strong demand for high efficiency blue devices which can substitute common low efficiency blue fluorescent devices. However, the blue PHOLEDs [3–8] have a critical problem of short lifetime [9] because of lack of stable high triplet energy host and charge transport materials which can confine triplet excitons and prolong the lifetime of the blue PHOLEDs.

There have been many papers reporting high efficiency blue PHOLEDs [9–12] by preparing various high triplet energy host and charge transport materials [13–21], but there have been only several works investigating the lifetime of blue PHOLEDs [22]. There have been mainly two approaches to improve the lifetime of the blue PHOLEDs. One approach was to engineer the device structure and device fabrication condition in order to extend the lifetime of the blue PHOLEDs. A graded doping structure in the emitting layer could control recombination zone in the emitting layer and more than doubled the lifetime of pristine blue PHOLEDs with a uniform doping structure. In other work, a high vacuum condition was found to be useful to improve the lifetime by removing impurities which degrade the device performances of OLEDs.

The other approach for long lifetime blue PHOLEDs was to develop stable high triplet energy organic materials for stable operation of the devices. An acridine and carbazole derived high triplet energy hole transport material could enhance the quantum efficiency and lifetime of blue PHOLEDs with a phenylimidazole ligand based Ir triplet emitter [23,24]. Other than the hole transport material, a few Ir based triplet emitters were proven to induce stable driving of the blue PHOLEDs by doping in 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP) [25]. However, no host material with better lifetime than mCBP was reported. Therefore, it is essential to develop high triplet energy host materials which can show better lifetime than mCBP.

In this work, three high triplet energy host materials, 2,8-bis(9-phenyl-9*H*-carbazol-1-yl)dibenzo[*b*,*d*]thiophene (1Cz-DBT), 2,8-bis(9-phenyl-9*H*-carbazol-3-yl)dibenzo[*b*,*d*]thiophene (3Cz-DBT) and 2,8-bis(9-phenyl-9*H*-carbazol-4-yl)dibenzo[*b*,*d*]thiophene (4Cz-DBT), were developed as the host materials of blue PHOLEDs in order to increase the lifetime of blue PHOLEDs. The substitution position of 9-phenylcarbazole to 2,8-dibenzothiophene was correlated with the lifetime of the blue PHOLEDs doped with a tris [1-(2,4-diisopropyldibenzo[b,d]furan-3-yl)-2-phenylimidazole] ($Ir(dbi)_3$) emitter. It was revealed that 3Cz-DBT is better than other

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host materials to improve the lifetime of the blue PHOLEDs. A lifetime of 303 h up to 70% of initial luminance at an initial luminance of 1000 cd/m^2 was demonstrated in the 3Cz-DBT device and it was longer than that of mCBP device. This work is the first demonstration of high triplet energy host materials which can exhibit longer lifetime than mCBP.

2. Experimental

2.1. General information

Palladium(II) acetate (Pd(OAc)$_2$), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos), [1,1′-bis(diphenylphosphino) ferrocene]dichloropalladium(II) (Pd(dppf)Cl$_2$) and tetrakis(-triphenylphosphine)palladium(0) ((Pd(PPh$_3$)$_4$) were purchased from P&H tech Co. 1-Bromo-9*H*-carbazole, 4-chloro-9*H*-carbazole, sodium sulfate and iodobenzene were supplied from Sigma Aldrich Co. Copper, 9-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole and 9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole were supplied from Sun fine global Co. was used without further purification. Sodium hydroxide, potassium carbonate, tetrahydrofuran, ethanol and toluene were products of Duksan Sci. Co.

2.2. Synthesis

2.2.1. 2,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo [b,d]thiophene

2,8-Dibromodibenzo[*b,d*]thiophene (3.0 g, 8.8 mmol), bis(pinacolato)diboron (6.7 g, 26.3 mmol), potassium acetate (4.3 g, 44.0 mmol) and Pd(dppf)Cl$_2$ (0.72 g, 0.88 mmol) were put into 1,4-dioxane (100 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 4 h. The reaction mixture was celite filtered, diluted with ethyl acetate, and washed with water. The organic layer was dried over anhydrous MgSO$_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/n-hexane. The product was obtained as white powder (2.5 g, Yield 65%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 8.56 (s, 2H), 8.03 (d, 2H, J = 8.0H$_Z$), 7.75 (d, 2H, J = 8.4H$_Z$), 1.33 (s, 24H).

2.2.2. 1-Bromo-9-phenyl-9H-carbazole

1-Bromo-9*H*-carbazole (20.0 g, 81.3 mmol), iodobenzene (49.7 g, 243.8 mmol), copper (2.6 g, 40.6 mmol), K$_2$CO$_3$ (33.6 g, 243.8 mmol) and Na$_2$SO$_4$ (34.6 g, 243.8 mmol) were vacuum dried for 1 h, and nitrobenzene (500 ml) was added to the mixture under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h. The mixture was evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/n-hexane. The product was obtained as oil. (20.8 g, Yield 79%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 8.27 (d, 1H, J = 7.6 Hz), 8.24 (d, 1H, J = 7.2 H$_Z$), 7.60–7.55 (m, 4H), 7.45 (d, 2H, J = 8.0 Hz), 7.39 (t, 1H, J = 7.6 Hz), 7.28 (t, 1H, J = 7.2 Hz), 7.17 (t, 1H, J = 7.6 Hz), 6.97 (d, 1H, J = 8.0 Hz). MS (API+) m/z: 323.8 [(M + H)$^+$].

2.2.3. 2,8-Bis(9-phenyl-9H-carbazol-1-yl)dibenzo[b,d]thiophene (1Cz-DBT)

1-Bromo-9-phenyl-9*H*-carbazole (1.0 g, 2.8 mmol), 2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]thiophene (0.4 g, 0.93 mmol), NaOH (0.15 g, 3.7 mmol) and Pd(PPh$_3$)$_4$ (0.1 g, 0.1 mmol) were put into a round-bottomed flask with THF (50 ml) and water (30 ml) under a nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h. The reaction mixture was diluted with methylene chloride and washed with water. The organic layer was dried over anhydrous MgSO$_4$ and evaporated in vacuo to give the crude product. The crude product was purified by recrystallization using toluene. The product was obtained as white powder.

Yield 73% (0.45 g), T$_g$ 145 °C, ^{1}H NMR (400 MHz, DMSO): δ 8.83–8.29 (m, 4H), 7.94 (s, 2H), 7.53–7.36 (m, 8H), 7.29 (t, 2H, J = 7.2 Hz), 7.19–7.11 (m, 8H), 6.97–6.85 (m, 6H), MS (FAB) m/z 666.83 [(M + H)$^+$].

2.2.4. 2,8-bis(9-phenyl-9H-carbazol-3-yl)dibenzo[b,d]thiophene (3Cz-DBT)

Synthetic process and reaction materials of 3Cz-DBT was the same as that of 1Cz-DBT except for starting material of 9-phenyl-3-(4,4,5,5-tetrameth-yl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole.

Yield 83% (1.3 g), T$_g$ 150 °C, 1H NMR (400 MHz, DMSO): δ 9.00 (s, 2H), 8.81 (s, 2H), 8.42–8.40 (d, 2H, J = 7.6 H$_Z$), 8.16–8.14 (d, 2H, J = 8 H$_Z$), 8.01–7.99 (d, 4H, J = 8.8 H$_Z$), 7.75–7.67 (m, 8H), 7.59–7.56 (t, 2H, J = 7.2 H$_Z$), 7.53–7.41 (m, 6H), 7.36–7.32 (t, 2H, J = 7.2 H$_Z$), ^{13}C NMR (100 MH$_Z$, DMSO): δ 140.65, 139.67, 137.69, 137.44, 136.79, 135.95, 132.21, 130.13, 127.65, 126.56, 126.38, 126.10, 125.55, 123.42, 123.33, 122.90, 120.76, 120.09, 118.86, 109.93, 109.67, MS (FAB) m/z 666.83 [(M + H)$^+$].

2.2.5. 4-Chloro-9-phenyl-9H-carbazole

4-Chloro-9*H*-carbazole (5.0 g, 24.9 mmol), iodobenzene (15.2 g, 74.7 mmol), copper (0.32 g, 5.0 mmol), K$_2$CO$_3$ (6.9 g, 49.8 mmol) and Na$_2$SO$_4$ (7.1 g, 49.8 mmol) were dissolved in nitrobenzene (100 ml) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h. The mixture evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/n-hexane. The product was obtained as white powder. (4.5 g, Yield 65%).

^{1}H NMR (400 MH$_Z$, DMSO): δ 8.53 (d, 1H, J = 8.0H$_Z$), 7.67 (m, 2H), 7.56 (m, 3H), 7.48 (t, 1H, J = 8.4H$_Z$), 7.40 (m, 1H), 7.33 (m, 3H), 7.28 (d, 1H, J = 8.0H$_Z$). MS (API+) m/z: 277.1 [(M + H)$^+$].

2.2.6. 2,8-bis(9-phenyl-9H-carbazol-4-yl)dibenzo[b,d]thiophene (4Cz-DBT)

2,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo [*b,d*]thiophene (0.72 g, 1.65 mmol), 4-chloro-9-phenyl-9*H*-carbazole (0.92 g, 3.3 mmol), XPhos (0.16 g, 0.33 mmol), K$_2$CO$_3$ (0.91 g, 3.7 mmol) and Pd(OAc)$_2$ (0.04 g, 0.17 mmol) were dissolved in toluene (30 ml), ethanol (10 ml) and water (10 ml) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 4 h. The reaction mixture was diluted with methylene chloride and washed with water. The organic layer was dried over anhydrous MgSO$_4$ and evaporated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel using ethyl acetate/n-hexane. The product was obtained as white powder.

Yield 69% (0.76 g), T$_g$ 162 °C, ^{1}H NMR (400 MH$_Z$, DMSO): δ 8.69 (s, 2H), 8.32–8.30 (d, 2H, J = 8.4 H$_Z$), 7.84–7.82 (d, 2H, J = 8.4 H$_Z$), 7.73–7.69 (t. 4H, J = 7.8 H$_Z$), 7.62–7.56 (m, 6H), 7.52–7.48 (t, 2H, J = 7.8 H$_Z$), 7.44–7.42 (d, 2H, J = 8 H$_Z$), 7.36–7.29 (m, 6H), 7.25–7.23 (d, 2H, J = 7.8 H$_Z$), 7.02–6.98 (t, 2H, J = 8.2), ^{13}C NMR (100 MHz, DMSO): δ 140.74, 140.60, 138.50, 137.31, 136.81, 136.62, 135.43, 130.14, 128.13, 127.93, 127.11, 125.95, 123.16, 122.43, 122.04, 121.79, 121.42, 119.89, 119.57, 109.49, 108.68, MS (FAB) m/z 666.83 [(M + H)$^+$].

2.3. Device fabrication and measurements

Blue PHOLEDs were fabricated using the sublimed 1Cz-DBT, 3Cz-DBT and 4Cz-DBT. Device stack structure was indium tin oxide

(ITO, 120 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (60 nm)/4,4′-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC) (30 nm)/host:Ir(dbi)$_3$ (25 nm, 10%)/diphenyl-4-triphenylsilylphenyl-phosphine oxide (TSPO1) (5 nm)/2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBI) (30 nm)/LiF (1 nm)/Al (200 nm). Hole only device had a device structure of ITO (120 nm)/PEDOT:PSS (60 nm)/TAPC (30 nm)/1Cz-DBT or 3Cz-DBT or 4Cz-DBT (25 nm)/TAPC (5 nm)/Al (200 nm). Electron only device had a device structure of ITO (120 nm)/PEDOT:PSS (60 nm)/TSPO1 (10 nm)/1Cz-DBT or 3Cz-DBT or 4Cz-DBT (25 nm)/TSPO1 (5 nm)/TPBI (30 nm)/Al (200 nm). Lifetime device of blue PHOLEDs had a structure of ITO (120 nm)/N,N′-diphenyl-N,N′-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine (DNTPD) (60 nm)/N,N,N′N′-tetra[(1,10-biphenyl)-4-yl]-(1,10-biphenyl)-4,4′-diamine (BPBPA) (30 nm)/host:Ir(dbi)$_3$ (30 nm, 10%)/tris(8-hydroxyquinolinato)aluminium (Alq$_3$) (35 nm)/LiF (1 nm)/Al (200 nm). Device performances were characterized by scanning a voltage at a step of 0.5 V from 0 V. Current density and luminance were gathered using Keithley 2400 source measurement unit CS1000 spectroradiometer.

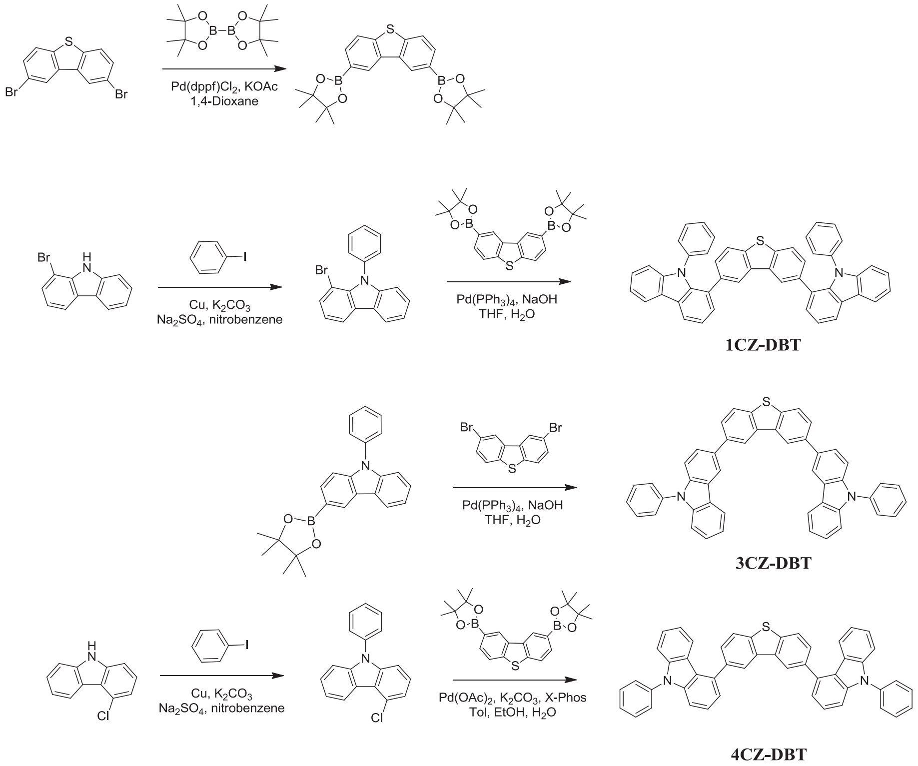
3. Results and discussion

Commonly, host materials of blue PHOLEDs such as mCBP and 1,3-bis(N-carbazolyl)benzene (mCP) were derived from carbazole because the carbazole moiety has a high triplet energy (≥~3.0 eV) and good hole carrying properties. In particular, mCBP is the most widely used high triplet energy host material for blue PHOLEDs due to long-term stability. However, the mCBP host material cannot increase the lifetime of blue PHOLEDs further and other host materials are required for better lifetime in the blue PHOLEDs.

The triplet host materials developed in this work were derived from dibenzothiophene and 9-phenylcarbazole for high triplet energy and chemical stability of the molecular structure. As both the dibenzothiophene and 9-phenylcarbazole moieties have high triplet energy above 3.0 eV, the dibenzothiophene and 9-phenylcarbazole derivatives can possess triplet energy high enough for use as a host material of blue PHOLEDs [26–28]. Additionally, the dibenzothiophene and carbazole moieties have a fully aromatic molecular structure and can be chemically stable. Therefore, three host materials were designed using the dibenzothiophene and 9-phenylcarbazole moieties just by changing substitution position of 9-phenylcarbazole. Three compounds with 1-, 3- and 4- position modified 9-phenylcarbazole were prepared, but a host material with 2- position modified 9-phenylcarbazole was not synthesized because of low triplet energy from molecular orbital calculation.

All three host materials were synthesized by Suzuki coupling reaction between functionalized dibenzothiophene at 2- and 8-positions and functionalized 9-phenylcarbazole at 1-, 3- or 4- positions of 9-phenylcarbazole. All compounds were purified by column chromatography followed by vacuum train sublimation before material characterization and device fabrication. Synthetic scheme of the host materials is presented in Scheme 1.

Molecular orbital calculation of the host materials were performed using a density functional theory method implemented in Gaussian 09 program with a B3LYP 6-31G basis set and the HOMO/LUMO distribution of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT is shown in Fig. 1. It was discovered that the HOMO of 1Cz-DBT and 4Cz-DBT was rather localized on the carbazole moiety, while the HOMO of 3Cz-DBT was broadly spread on carbazole and dibenzothiophene moieties. The different HOMO distribution of the three host materials is related with geometrical structure of the host materials in Fig. 2. Calculated dihedral angles of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT from optimized geometrical structure were 56, 38 and 54°, respectively. The large dihedral angle of 1Cz-DBT and 4Cz-DBT disconnected the dibenzothiophene and 9-phenylcarbazole



Scheme 1. Synthetic scheme of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT.

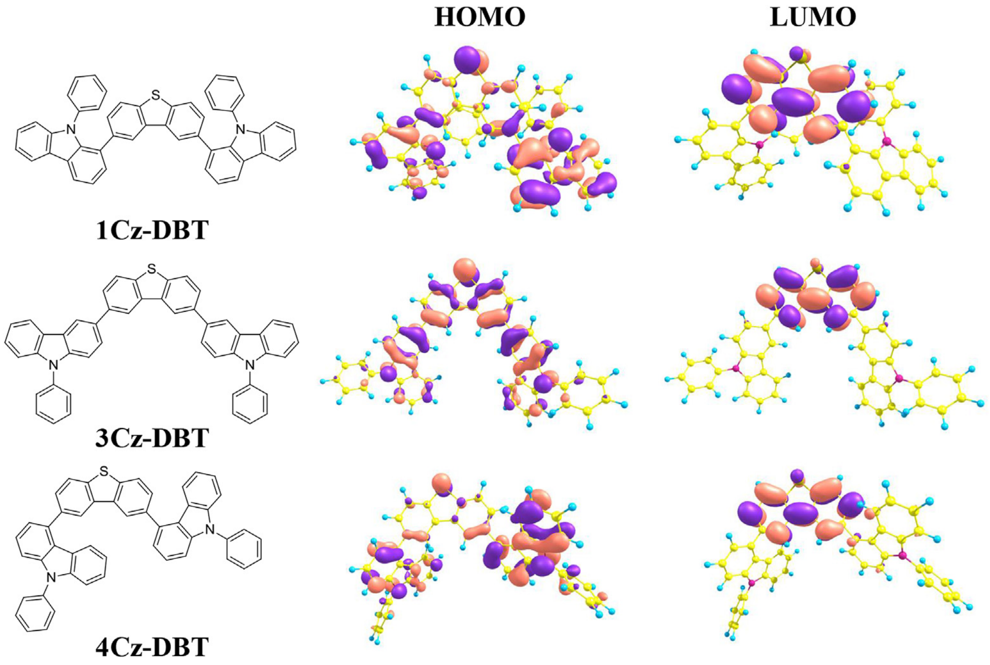


Fig. 1. HOMO and LUMO distribution of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT.

moieties electronically and the HOMO was found mostly in the strong electron donating carbazole moiety. On the other hand, small dihedral angle of 3Cz-DBT enabled electronic communication between dibenzothiophene and 9-phenylcarbazole, which resulted in wide dispersion of the HOMO on the dibenzothiophene and 9-phenylcarbazole. In the case of LUMO, the LUMO was locally observed in the dibenzothiophene moiety in all host materials because of relatively strong electron deficiency of the dibenzothiophene moiety compared to 9-phenylcarbazole moiety. In spite of small dihedral angle of 3Cz-DBT, the LUMO was not dispersed over the 9-phenylcarbazole moiety because 3- position of 9-phenylcarbazole is a node of the LUMO.

Photophysical properties of the host materials were examined by ultraviolet–visible (UV–vis), photoluminescence (PL) and low temperature PL analysis. Normalized UV–vis absorption, solution and low temperature PL spectra are presented in Fig. 3. UV–vis absorption spectra of 1Cz-DBT and 4Cz-DBT were similar and reflected $\pi-\pi^*$ absorption of dibenzothiophene and 9-phenylcarbazole moieties independently. However, 3Cz-DBT showed strong $\pi-\pi^*$ absorption of conjugated dibenzothiophene and 9-phenylcarbazole moieties. The conjugation between the two moieties through small dihedral angle affected the UV–vis absorption of 3Cz-DBT. Solution PL emission of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT in tetrahydrofuran was similarly detected at 371 nm, 378 nm and 379 nm, respectively. The first phosphorescent emission peak at 77 k was observed at 474 nm, 470 nm and 475 nm. Therefore, triplet energies of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT were 2.61 eV, 2.64 eV, and 2.61 eV, respectively.

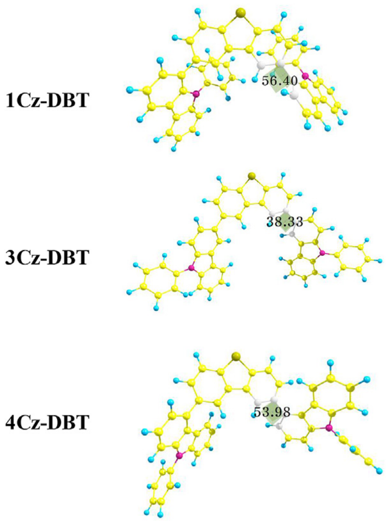


Fig. 2. Geometrical structure of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT.

Characteristics of oxidation and reduction aspects of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT were estimated using cyclic voltammetry scan. Separate oxidation and reduction scan data of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT are shown in Fig. 4. Ionization potential and electron affinity of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT were −6.06 eV/−2.45 eV, −5.90 eV/−2.58 eV and −6.08 eV/−2.77 eV, respectively. The ionization potential of 3Cz-DBT was shallower than that of other hosts because of the HOMO expansion through 3- position of carbazole. In the case of 1Cz-DBT and 4Cz-DBT, the HOMO isolation by large dihedral angle deepened the HOMO level.

Using differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA), we estimated the glass transition temperature (T_g) and thermal decomposition temperature (T_d) as the thermal properties of the host materials according to substitution positions (1-, 3-, 4- position). DSC and TGA curves of host materials are shown in Fig. 5. The T_gs of host materials were observed at 145 °C, 150 °C, and 162 °C from second heating scan data of DSC measurement. T_d at 5% weight loss was detected at 403 °C, 452 °C and 417 °C in the TGA thermogram. All host materials exhibited high T_g above 140 °C and high T_d above 400 °C, which indicates that the dibenzothiophene and 9-phenylcarbazole based host materials are thermally stable and may potentially enable stable operation of blue PHOLEDs. Thermal, photophysical and electrochemical analysis results of the host materials are summarized in Table 1.

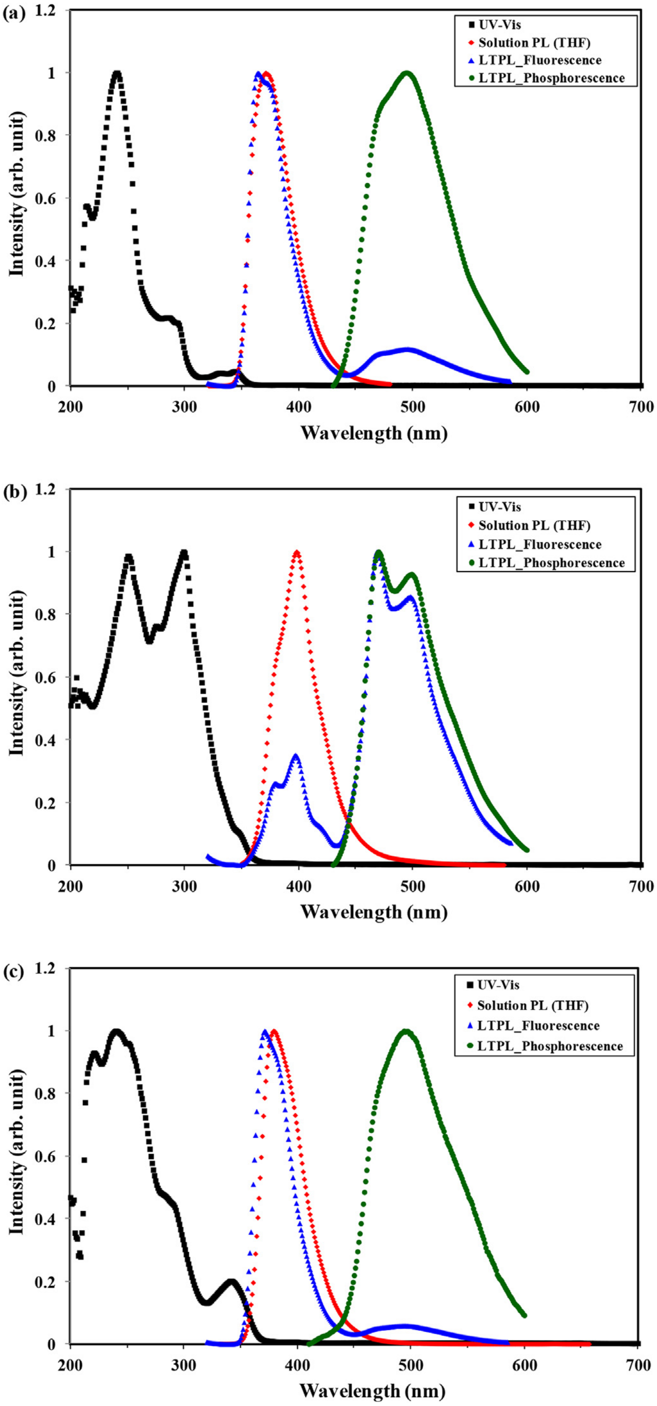


Fig. 3. UV–vis, solution PL and low temperature PL spectra of tetrahydrofuran solution of 1Cz-DBT (a), 3Cz-DBT (b) and 4Cz-DBT (c).

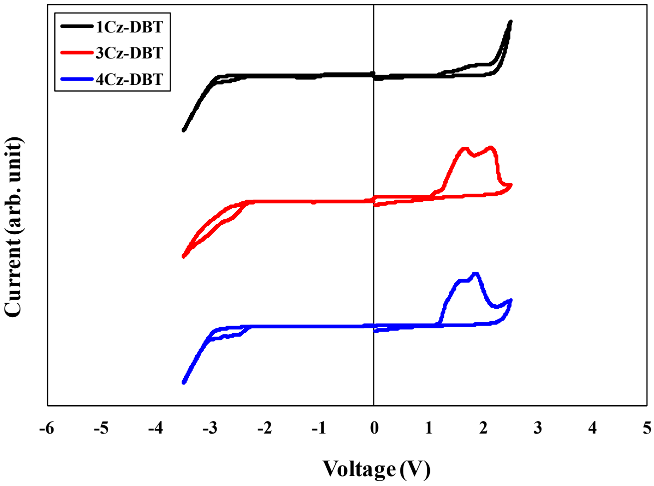


Fig. 4. CV curves for the oxidation and reduction of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT.

As the host materials were proven to satisfy the requirements of stable blue host materials such as high triplet energy, thermal stability and proper energy levels, blue PHOLEDs with the 1Cz-DBT, 3Cz-DBT and 4-Cz-DBT host materials doped with Ir(dbi)$_3$ were developed. Prior to device fabrication, hole and electron current densities of single carrier devices were compared. Fig. 6 shows current density-voltage characteristics of the single carrier devices. Overall, hole current density was much higher than electron current density because the host materials were designed as hole transport type host materials by combining dibenzothiophene and 9-phenylcarbazole. The single carrier device data verified that the host materials are hole transport type host materials. In addition, the carrier density was higher in the 3Cz-DBT and 4Cz-DBT devices than in the 1Cz-DBT device, which might be related with geometrical structure of the host materials. In the case of 1Cz-DBT, phenyl unit of 9-phenylcarbazole causes steric hindrance to the dibenzothiophene core and hinders charge hopping between molecules,

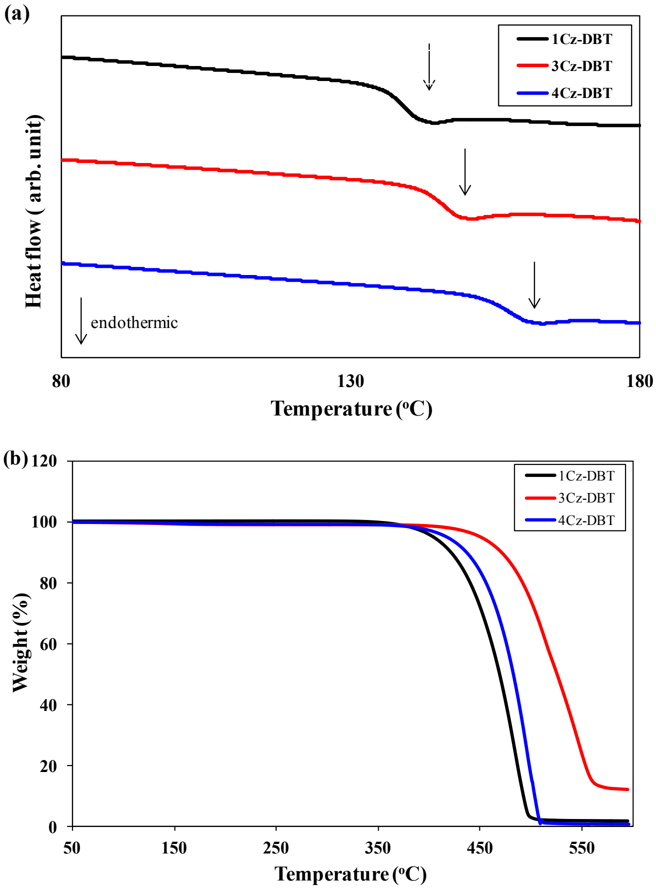


Fig. 5. DSC (a) and TGA (b) thermograms of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT at a heating rate of 10 °C/min under a nitrogen atmosphere.

Table 1
Photophysical and thermal properties of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT.

Material	Photophysical analysis						Thermal analysis	
	Absorption (nm)	Emission (nm)	HOMO (eV)	LUMO (eV)	Bandgap (eV)	Triplet energy (eV)	T_g (°C)	T_d (°C)
1Cz-DBT	240, 285 345, 356	372	−6.06	−2.45	3.61	2.61	145	403
3Cz-DBT	250, 299 346, 360	398	−5.89	−2.58	3.31	2.64	150	452
4Cz-DBT	240, 285 341, 365	379	−6.08	−2.77	3.31	2.61	162	417

which decreased the hole and electron current density at the same time.

The hole and electron current density of single carrier devices affected the current density of the blue PHOLEDs and the 3Cz-DBT and 4Cz-DBT devices showed higher current density than the 1Cz-DBT device as presented in Fig. 7. Driving voltages of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT devices at 1000 cd/m^2 were observed as 5.65 V, 4.62 V and 4.49 V and the luminance was also high in the 3Cz-DBT and 4Cz-DBT devices compared with 1Cz-DBT device. Turn-on voltage of the blue PHOLEDs was the same because there was no energy barrier for hole and electron injection from charge transport layers to emitting layer as shown in energy level diagram in Fig. 8.

QE data in Fig. 9 suggested that 1Cz-DBT is better than other host materials to improve the QE of the Ir(dbi)$_3$ doped blue PHOLEDs, and maximum QE of the 1Cz-DBT, 3Cz-DBT and 4Cz-DBT devices were 25.4%, 21.0% and 19.3%, respectively. Although the driving voltage of the 1Cz-DBT device was higher than that of 3Cz-DBT and 4Cz-DBT devices, high QE was observed in the 1Cz-DBT device possibly due to balanced hole and electron density in the emitting layer. Electroluminescence spectra in Fig. 10 verified that all host materials effectively induced Ir(dbi)$_3$ emission.

As the main objective of designing the host materials was to enhance the lifetime of the blue PHOLEDs, lifetime of the 1Cz-DBT, 3Cz-DBT and 4Cz-DBT devices was measured at a constant current mode as shown in Fig. 11. Initial luminance for lifetime measurement was 1000 cd/m^2. The operational lifetimes of the 1Cz-DBT, 3Cz-DBT and 4Cz-DBT devices were 50 h, 303 h and 133 h up to 70% of initial luminance, respectively. The lifetime of the 3Cz-DBT device was much longer than that of 1Cz-DBT and 4Cz-DBT devices, and was even longer than that of common 3,3-di(9H-carbazol-9-yl) biphenyl (mCBP) device. In our previous work, the mCBP device doped with Ir(dbi)$_3$ exhibited shorter lifetime at the same driving

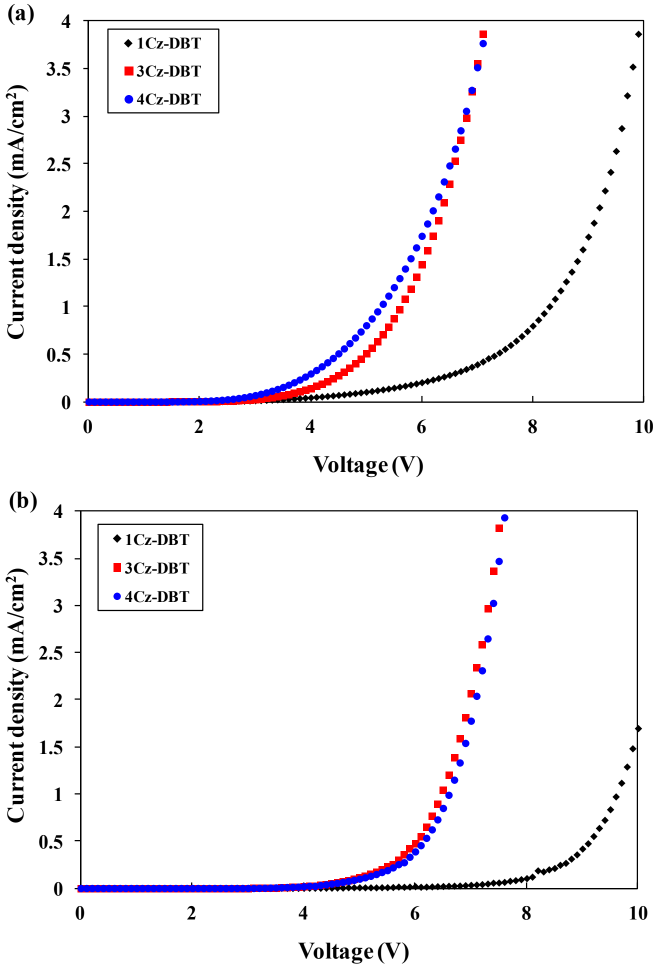


Fig. 6. Current density–voltage plots of hole (a) and electron (b) single carrier devices of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT.

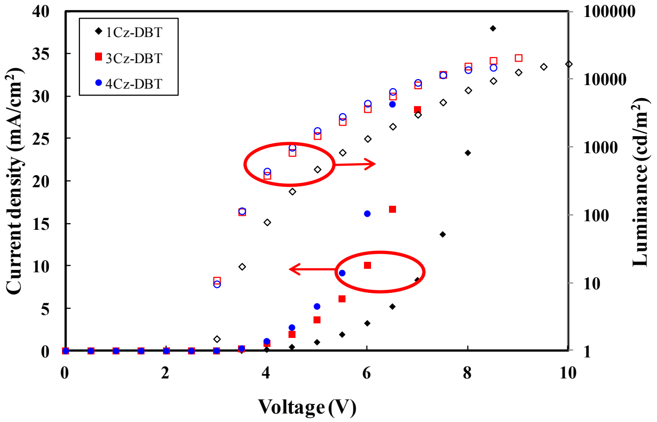


Fig. 7. Current density–voltage–luminance curves of the blue PHOLEDs with 1Cz-DBT, 3Cz-DBT and 4Cz-DBT.

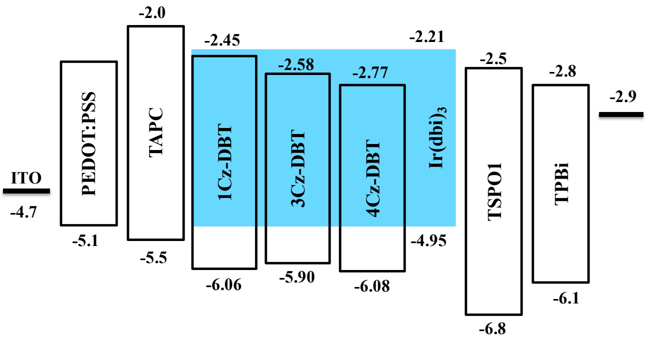


Fig. 8. Energy level diagram of the blue PHOLEDs with 1Cz-DBT, 3Cz-DBT and 4Cz-DBT.

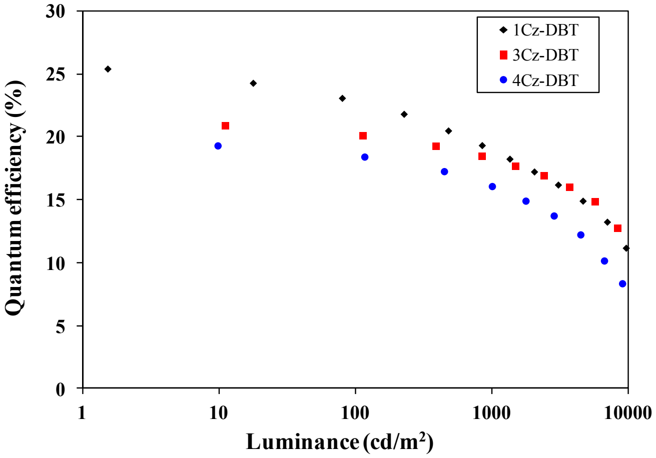


Fig. 9. Quantum efficiency plots of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT blue PHOLEDs against luminance.

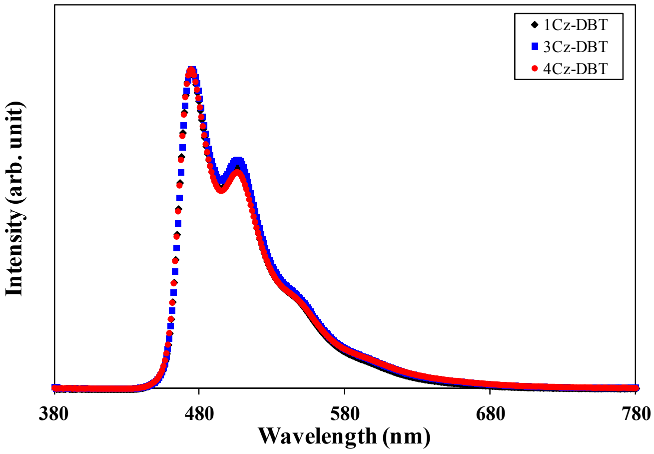


Fig. 10. EL spectra of 1Cz-DBT, 3Cz-DBT and 4Cz-DBT blue PHOLEDs at a luminance of 1000 cd/m^2.

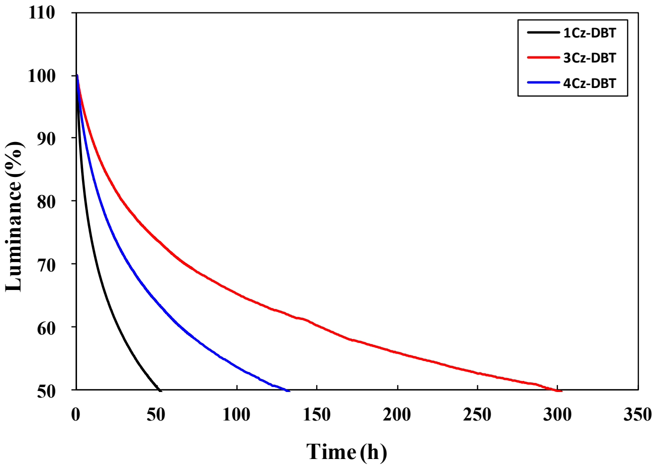


Fig. 11. Lifetime curves of 1Cz-DBT:Ir(dbi)$_3$, 3Cz-DBT:Ir(dbi)$_3$ and 4Cz-DBT:Ir(dbi)$_3$ devices. Lifetime was measured at an initial luminance of 1000 cd/m.^{2}.

condition [29,30]. Therefore, there was more than three times improvement of the operational lifetime of the blue PHOLEDs using the 3Cz-DBT host material. There can be several origins for the long lifetime of the 3Cz-DBT device, but the improved lifetime can be mainly explained by a stable molecular structure of the 3Cz-DBT host. The 3Cz-DBT host has a dibenzothiophene core and two 9-phenylcarbazole units which have an aromatic nature. The aromatic character of the two moieties can stabilize the molecular structure of 3Cz-DBT and elongate the lifetime. In particular, the small dihedral angle of 38.3° between dibenzothiophene and 9-phenylcarbazole extends the conjugation and strengthen the chemical bond between the two moieties. Therefore, long lifetime was observed in the 3Cz-DBT device. In addition, thermal stability of the 3Cz-DBT host confirmed from the thermal analysis data is another contributor to the long lifetime. The relatively short lifetime of the 1Cz-DBT and 4Cz-DBT devices is ascribed to large dihedral angle between dibenzothiophene and 9-phenylcarbazole in spite of good thermal stability.

4. Conclusions

Three host materials, 1Cz-DBT, 3Cz-DBT, and 4Cz-DBT, designed as stable host materials were used as the host materials of blue PHOLEDs and improved lifetime of the Ir(dbi)$_3$ doped blue PHOLEDs. In particular, the 3Cz-DBT host showed more than three times longer lifetime than a common mCBP host due to stable molecular structure. Therefore, the molecular design consisted of dibenzothiophene and 9-phenylcarbazole can be effective to elongate driving time of the blue PHOLEDs.

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