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The Effect of the Substitution Position of Dibenzofuran on the Photophysical and Charge-Transport Properties of Host Materials for Phosphorescent Organic Light-Emitting Diodes

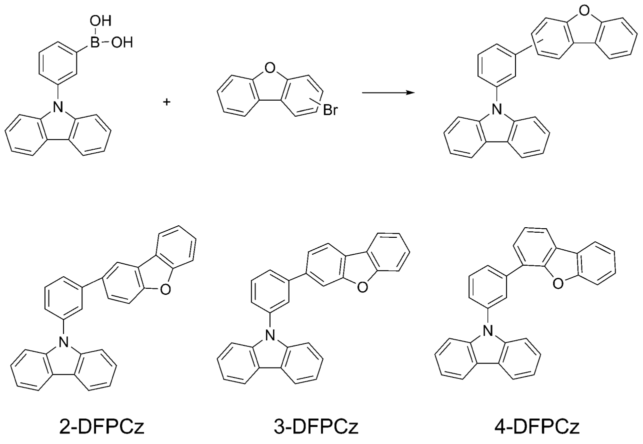
Chil Won Lee,[a] Jeong-A Seo,[b] Myoung-Seon Gong,[b] and Jun Yeob Lee*[a]

Dibenzofuran has been used as a high-triplet-energy core structure of organic materials for phosphorescent organic light-emitting diodes (PHOLEDs) because of its high triplet energy of 3.14 eV.[1–4] As it has strong electron-withdrawing oxygen linkage in the molecular structure, and has been used as a core structure of electron-transport materials or electron-transport-type host materials.

The dibenzofuran core has been modified at the 2- or 4-position to synthesize various derivatives for use in PHOLEDs. The 2-position of dibenzofuran was modified simply by bromination using N-butylsuccinimide or bromine,[4] while the 4-position of dibenzofuran was substituted with functional groups by direct lithiation owing to the electron-withdrawing character of oxygen in dibenzofuran.[3] Several high-triplet-energy host materials have been developed by using this method. However, the 3-position of dibenzofuran could not be directly functionalized, and no organic material with substituent at the 3-position of dibenzofuran has been reported for use in PHOLEDs. Therefore, no systematic investigation about the relationship between the substitution position of dibenzofuran and device performances of PHOLEDs has been carried out. The synthesis of a dibenzofuran derivative with a substituent at the 3-position may thus enable the systematic study of the effect of substitution position of dibenzofuran on material characteristics and device performance.

Herein, we synthesized high-triplet-energy host materials based on dibenzofuran and phenylcarbazole derived from a dibenzofuran intermediate with a substituent at 2-, 3- and 4-positions, and the relationship between the substitution position of dibenzofuran and material properties of host materials was systematically investigated. Furthermore, the device performances of green and blue PHOLEDs doped with phosphorescent dopants were also compared. It was shown that substitution at the 3-position of dibenzofuran is useful to lower the driving voltage, while substitution at the 2-position is effective in achieving a high triplet energy and high quantum efficiency.

Three host materials, 9-(3-(dibenzo[b,d]furan-2-yl)phenyl)-9H-carbazole (2-DFPCz), 9-(3-(dibenzo[b,d]furan-3-yl)-phenyl)-9H-carbazole (3-DFPCz) and 9-(3-(dibenzo-[b,d]furan-4-yl)phenyl)-9H-carbazole (4-DFPCz) were synthesized by a Suzuki coupling reaction of brominated dibenzofuran with 3-(9H-carbazol-9-yl)phenylboronic acid. Brominated benzofuran and carbazole intermediates were prepared according to a previously reported procedure.[5–8] 2-DFPCz was also synthesized by a previously reported procedure.[9] The synthesis of the three host materials is shown in Scheme 1 (a detailed synthetic method is described in the Supporting Information).



Scheme 1. Overview of the synthesis of 2-DFPCz, 3-DFPCz, and 4-DFPCz.

Molecular simulation of the host materials was carried out to study the effect of substitution position on the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). A suite of the Gaussian 03 program and the nonlocal density functional of Becke's three parameters employing the Lee–Yang–Parr functional (B3LYP) with 6-31G* basis sets were used for the simula-

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[a] Prof. C. W. Lee, Prof. J. Y. Lee
Department of Polymer Science and Engineering
Dankook Univeristy, 126, Jukjeon-dong, Suji-gu
Yongin-si, Gyeonggi-do, 448-701 (Korea)
Fax: (+82) 31-8005-3585
E-mail: leej17@dankook.ac.kr

[b] J.-A. Seo, Prof. M.-S. Gong
Department of Nanobiomedical Science and
WCU Research Center of Nanobiomedical Science
Dankook University, Cheonan
Chungnam 330-714 (Korea)

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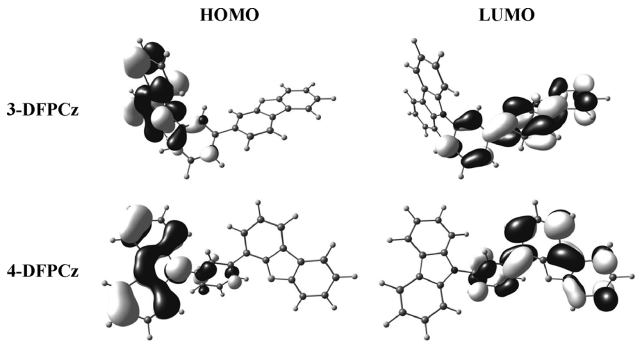

Figure 1. HOMO and LUMO distributions of 3-DFPCz and 4-DFPCz.

tion.[10] Figure 1 shows the HOMO and LUMO distribution of host materials. Phenylcarbazole plays a role of hole transport unit owing to the electron-donating character of the carbazole moiety,[11] while dibenzofuran acts as an electron-transport unit owing to the electron-withdrawing property of oxygen. Therefore, the HOMO was dispersed over carbazole unit, whereas the LUMO was localized on dibenzofuran unit. The HOMO distribution was similar, and there was little difference of simulated HOMO levels between host materials. However, the simulated LUMO level was different depending on the substitution position. The LUMO was distributed only on dibenzofuran in 2-DFPCz, as reported in other work[9] (Supporting Information), while the LUMO was extended to a phenyl unit of phenylcarbazole of 3-DFPCz and 4-DFPCz. The extension of the LUMO orbital stabilized the LUMO level of 3-DFPCz and 4-DFPCz. The simulated LUMO levels of 3-DFPCz and 4-DFPCz were −1.34 eV and −1.27 eV, respectively, compared with −1.09 eV of 2-DFPCz.

The HOMO level of the three host materials were measured by a surface analyzer using vacuum-deposited thin films. The HOMO levels of 2-DFPCz, 3-DFPCz and 4-DFPCz were −5.90 eV, −5.98 eV and −5.85 eV, respectively. The LUMO level was calculated from the HOMO level and the optical band gap from UV/Vis spectra of thermally evaporated thin films(Figure 2). LUMO levels of 2-DFPCz, 3-DFPCz and 4-DFPCz were −2.45 eV, −2.48 eV and −2.40 eV, respectively. Energy levels of host materials are summarized in Table 1.

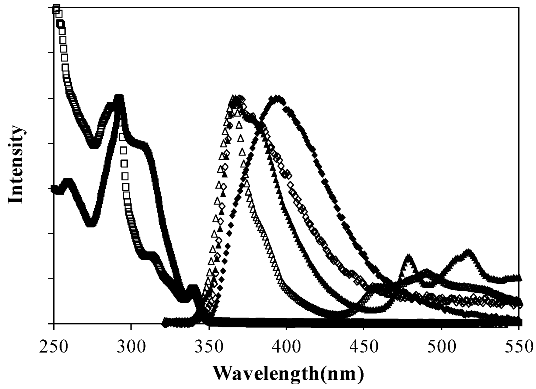

Figure 2. UV/Vis (■,□), solution photoluminescence (PL; ◆,◇) and low-temperature PL spectra (▲,△) of 3-DFPCz (filled symbols) and 4-DFPCz (open symbols).

Table 1. Energy levels of the host materials.

Material	HOMO [eV][a]	LUMO [eV][b]	Band gap [eV][c]	Triplet energy [eV][d]
2-DFPCz	−5.90	−2.45	3.45	2.89
3-DFPCz	−5.98	−2.48	3.50	2.59
4-DFPCz	−5.85	−2.40	3.45	2.79

[a] The HOMO was measured by a surface analyzer. [b] The LUMO was calculated from the difference between the HOMO and the band gap. [c] The band gap was calculated from the absorption edge of the UV/Vis spectra. [d] The triplet energy was calculated from the first emission peak position of the low-temperature PL spectra.

The photophysical properties of the three host materials were analyzed using UV/Vis and photoluminescence (PL) spectroscopy. UV/Vis spectra were obtained from vacuum-deposited thin films of the host materials. Figure 2 shows UV/Vis and PL spectra of the host materials, which exhibited typical UV/Vis absorption of phenylcarbazole and dibenzofuran. The optical band gap was calculated from the absorption edge of UV/Vis spectra. 2-DFPCz, 3-DFPCz and 4-DFPCz showed optical band gaps of 3.45 eV, 3.50 eV and 3.45 eV, respectively. There was little difference of optical band gaps between three host materials in solid state. Triplet energies calculated from peak position of the first emission peak of low-temperature PL spectra were 2.89 eV, 2.59 eV and 2.79 eV, for 2-DFPCz, 3-DFPCz and 4-DFPCz, respectively. The triplet energy was low in 3-DFPCz because of extended conjugation through the *para*-substituted phenyl group. In the case of 2-DFPCz and 4-DFPCz, *meta* substitution of the phenyl group suppressed the extension of conjugation, leading to a high triplet energy. In particular, 2-substitution was effective in raising the triplet energy of host materials. The triplet energy of the host materials was rather low compared with other dibenzofuran derivatives with diphenylphosphine oxide owing to the phenyl linkage and carbazole unit.

Hole-only and electron-only devices of three host materials were fabricated to study the effect of substitution position on the hole and electron transport properties of the host materials. Figure 3 shows current-density–voltage curves of hole- and electron-only devices. The hole current density of hole-only devices was similar in all three devices, while the electron current density of electron-only devices was high in 3-DFPCz and 4-DFPCz. This can be explained by the HOMO and LUMO distribution of host materials. There was little difference of HOMO distribution between host materials, leading to similar hole transport properties in all three host materials. However, the LUMO distribution was different depending on the substitution position of dibenzofuran. 3-DFPCz and 4-DFPCz with a widely dispersed LUMO showed high electron current density, but 2-DFPCz with a localized LUMO distribution exhibited low electron current density. The dominant electron transport mechanism

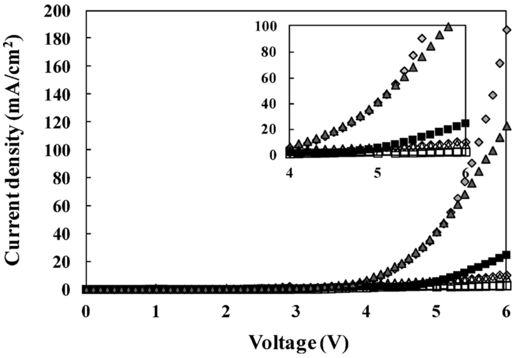

Figure 3. Current-density–voltage curves of hole-only (open symbols) and electron-only devices (filled symbols): 2-DFPCz (■,□), 3-DFPCz (◆,◇), 4-DFPCz (▲,△).

in host materials is electron hopping between host molecules, which is dependent on orbital overlap between molecules. The orbital overlap is efficient in 3-DFPCz and 4-DFPCz owing to extended dispersion of the LUMO, resulting in high electron current density.

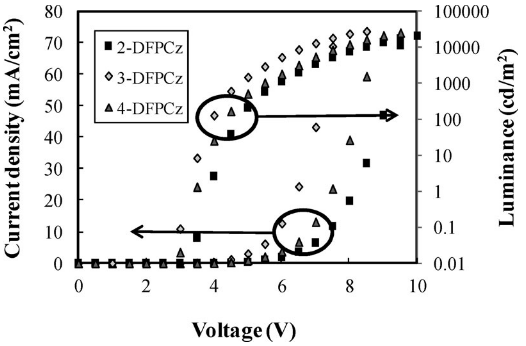

Figure 4. Current-density–voltage–luminance curves of green PHOLEDs.

Green PHOLEDs were fabricated to evaluate three materials as host materials of PHOLEDs. A device consisting of indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene) : polystyrenesulfonate (PEDOT:PSS) (60 nm)/4,4′-(cyclohexane-1,1-diyl)bis(N-phenyl-*N*-p-tolylaniline) (TAPC, 30 nm)/host : *fac*-tris(2-phenylpyridine) iridium (Ir(ppy)$_3$) (30 nm, 3 %)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 25 nm)/LiF (1 nm)/Al (200 nm) was used. Figure 4 shows current-density–voltage curves of green PHOLEDs. The current density of 3-DFPCz and 4-DFPCz devices was higher than that of 2-DFPCz device, as can be expected from hole-only and electron-only device data. The high electron current density of 3-DFPCz and 4-DFPCz increased the whole current density of the devices. The higher current density of 3-DFPCz than that of 4-DFPCz is due to the high electron current density of 3-DFPCz. Luminance followed the same trend as the current density. The driving voltage at 1,000 cd m^{-2} was 5.9 V, 4.7 V and 5.5 V for 2-DFPCz, 3-DFPCz and 4-DFPCz, respectively. 3-DFPCz showed the lowest driving voltage owing to the high current density.

Figure 5 shows quantum-efficiency–luminance curves of green PHOLEDs. The quantum efficiency of green PHOLEDs was high in 2-DFPCz, while 3-DFPCz and 4-DFPCz showed a lower quantum efficiency than 2-DFPCz. The maximum quantum efficiency of 2-DFPCz was 21.2 % compared with 16.9 % and 17.4 % of 3-DFPCz and 4-DFPCz. The high quantum efficiency of 2-DFPCz can be explained by the hole and electron current density in the emitting layer. It is well known that charge balance in the emitting layer is critical to the quantum efficiency of green PHOLEDs. In the case of 3-DFPCz and 4-DFPCz, a high electron current density relative to hole current density has a negative effect on the charge balance in the emitting layer. The high hole current density was reduced in 2-DFPCz, improving the charge balance in the emitting layer. Although the driving voltage was high in 2-DFPCz owing to low electron current density, the quantum efficiency was enhanced owing to a better charge balance in the emitting layer.

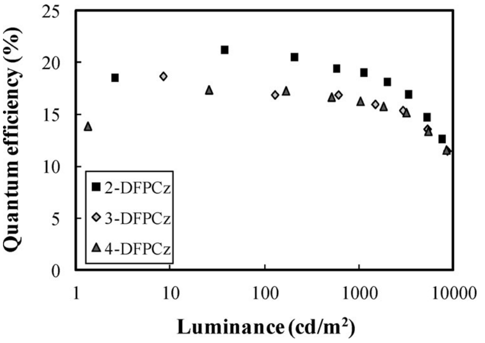

Figure 5. Quantum-efficiency–luminance curves of green PHOLEDs.

As the triplet energies of 2-DFPCz and 4-DFPCz were high enough for energy transfer to a blue emitting phosphorescent dopant, blue PHOLEDs were fabricated using the three host materials. The device for the blue PHOLED consisted of ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (30 nm)/host : iridium (III) bis(4,6-(difluorophenyl)-pyridinato-N,C′) picolinate (FIrpic) (30 nm, 3 %)/TSPO1 (25 nm)/LiF (1 nm)/Al (200 nm). Figure 6 shows current-density–voltage-lumi-

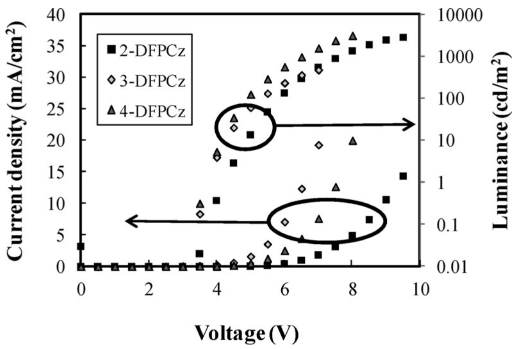

Figure 6. Current-density–voltage–luminance curves of blue PHOLEDs.

nance curves of blue PHOLEDs. The current density of blue PHOLEDs showed a similar tendency to that of green PHOLEDs. However, the luminance behavior of blue PHOLEDs was different from that of green PHOLEDs. The luminance of 3-DFPCz was low despite the high current density, which is related with the triplet energy of 3-DFPCz. The triplet energy of 3-DFPCz was 2.59 eV, which was lower than that of FIrpic dopant (2.65 eV). Therefore, energy transfer from host to FIrpic is not efficient, and triplet excitons of FIrpic are quenched by 3-DFPCz, leading to low luminance in the 3-DFPCz device.

Quantum-efficiency–luminance curves of blue PHOLEDs are shown in Figure 7. A high quantum efficiency was obtained in the 2-DFPCz device because of balanced hole and electron density in the emitting layer. The maximum quantum efficiency of the 2-DFPCz blue device was 19.6 % and the quantum efficiency at 1,000 cd m^{-2} was 17.2 %. The quantum efficiency of 3-DFPCz and 4-DFPCz devices was lower than that of the 2-DFPCz device. In particular, the quantum efficiency of the 3-DFPCz device was very low owing to triplet exciton quenching by the low triplet energy of 3-DFPCz and poor energy transfer from host to dopant material. The poor energy transfer can be confirmed by PL spectra of the vacuum-deposited host:FIrpic film (Figure 8). The 2-DFPCz and 4-DFPCz films exhibited a strong FIrpic emission peak, but the 3-DFPCz film showed strong host emission peak at 354 nm owing to incomplete energy transfer, which lead to a substantial decrease of quantum efficiency in the 3-DFPCz device. The poor energy transfer is due to reduced overlap of PL emission of 3-DFPCz and FIrpic dopant in comparison with 2-DFPCz and 4-DFPCz because of a red-shift of PL emission in 3-DFPCz. Additionally, triplet exciton quenching of FIrpic by 3-DFPCz suppressed FIrpic emission.

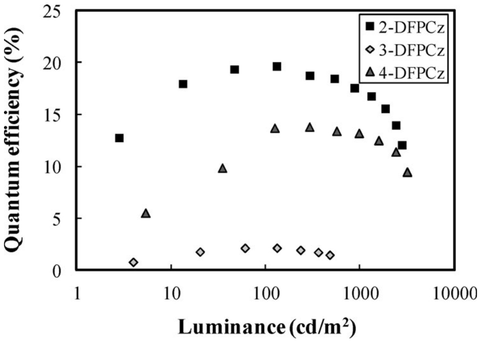

Figure 7. Quantum-efficiency–luminance curves of blue PHOLEDs.

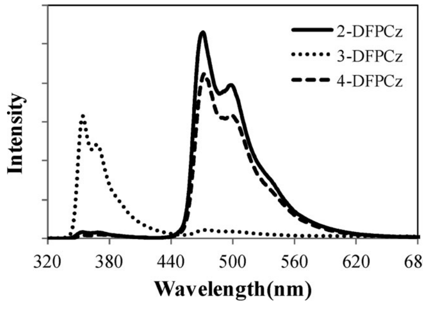

Figure 8. Photoluminescence spectra of FIrpic-doped host films.

Power-efficiency–luminance curves of three host materials are shown in Figure 9. Despite a high driving voltage of 2-DFPCz, the high quantum efficiency of 2-DFPCz resulted in a high power efficiency compared with the other host materials.

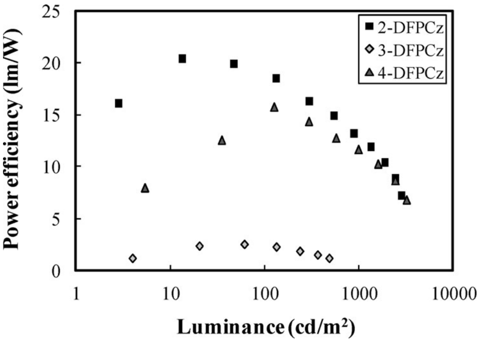

Figure 9. Power-efficiency–luminance curves of blue PHOLEDs.

In conclusion, the effect of substitution position of dibenzofuran on photophysical properties and device performances of host materials was systematically investigated by synthesizing three host materials with different substitution positions. Substitution of dibenzofuran from 3-position reduced triplet energy, but improved charge transport properties of the host materials. Substitution at the 4-position maintained the high triplet energy of dibenzofuran and also enhanced the charge-transport properties. Substitution at the 2-position had a negative effect on the charge-transport properties, but it retained the high triplet energy of the core. Therefore, this work has revealed that proper selection of substitution position can control the photophysical properties and device performances of host materials.

Keywords: charge transport · dibenzofurans · quantum efficiency · substituent effects · triplet energy

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