## COMMUNICATION

## Modified N, N'-Dicarbazolyl-3, 5-benzene as a High Triplet Energy Host Material for Deep-Blue Phosphorescent Organic Light-Emitting Diodes

Yong Joo Cho and Jun Yeob Lee<sup>\*[a]</sup>

It is important to balance holes and electrons in the emitting layer to obtain high quantum efficiency in phosphorescent organic light-emitting diodes (PHOLEDs). The hole and electron balance can be improved by using bipolar host materials that can transport both holes and electrons.<sup>[1-14]</sup> Therefore, there has been much effort to develop bipolar host materials for high efficiency PHOLEDs.

Various bipolar host materials have been synthesized for applications in red-, green-, and blue PHOLEDs. Both holeand electron-transport units were introduced in the molecular structure to balance holes and electrons in the emitting layer.<sup>[1–14]</sup> Aromatic amine and carbazole groups have typically been used as the hole-transport units, whereas oxadiazole, pyridine, and imidazole have been introduced as the electron-transport units. In general, bipolar host materials showed high quantum efficiency due to an improved charge balance in the emitting layer.

The bipolar host materials have also been developed for deep-blue PHOLEDs.<sup>[8,9,14]</sup> The bipolar host materials for deep-blue PHOLEDs should possess high triplet energy as well as bipolar charge-transport properties. Phenylcarbazole,<sup>[8,9]</sup> tetraphenylsilane,<sup>[11]</sup> and triazine<sup>[10]</sup> core structures were combined with other charge-transport units to obtain bipolar charge-transport properties. Conjugation of the molecular structure was minimized to obtain high triplet energy, and both hole- and electron-transport units were introduced for bipolar charge-transport properties. Several high triplet energy host materials were found to be effective as host materials for deep-blue PHOLEDs.<sup>[8,9,14]</sup> The separation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was not complete in these materials; the development of bipolar host materials with a separated HOMO and LUMO is required to reduce both the driving voltage and the bandgap.

In this work, a high triplet energy bipolar host material based on the N,N'-dicarbazolyl-3,5-benzene (mCP) core, (3,5-di(9*H*-carbazole-9-yl)phenyl)diphenylphosphine oxide (DCPPO), was developed as the host material for deep-blue

PHOLEDs. It was designed as the host material with an isolated HOMO and LUMO in the molecular structure. The HOMO was the localized hole-transport carbazole unit, whereas the LUMO was the localized electron-transport diphenylphosphine-oxide-modified phenyl unit. DCPPO was evaluated as the host material for deep-blue PHOLEDs and demonstrated a high quantum efficiency of 22.4% with a color coordinate of (0.14,0.17).

DCPPO has a backbone structure of common mCP with a diphenylphosphine oxide moiety attached to the mCP backbone. mCP has been known to have strong hole-transport and poor electron-transport properties due to the carbazole group. Therefore, the mCP was modified with a strong electron-transporting diphenylphosphine oxide group. The diphenylphosphine oxide was introduced in the phenyl core of the mCP to isolate the HOMO and LUMO; the carbazole is a hole-transport unit and the diphenvlphosphine-oxidemodified phenyl is an electron-transport unit. As the HOMO and LUMO can be localized on the hole- and electron-transport units, it is easy to obtain bipolar charge-transport properties. The introduction of the diphenylphosphine oxide group may improve the electron-transport properties of the DCPPO and charge balance in the emitting layer. In addition, the stability of the material under continuous operation can also be improved.

DCPPO could be effectively synthesized from the brominated mCP intermediate, which was prepared by treating the starting material 1,3,5-tribromobenzene with 9*H*-carbazole (Scheme 1). The intermediate was then phosphorylated



Scheme 1. Synthesis of DCPPO.

Chem. Eur. J. 2011, 17, 11415-11418

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY CONLINE LIBRARY

- 11415

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

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201101095.

with chlorodiphenylphosphine, yielding DCPPO after oxidation with hydrogen peroxide. A detailed synthetic procedure is described in the Supporting Information.

A molecular simulation of the DCPPO was carried out using density functional theory calculations to study the HOMO and LUMO distribution. Figure 1 shows the



Figure 1. HOMO and LUMO distribution of DCPPO.

HOMO/LUMO distribution and simulated HOMO/LUMO levels of DCPPO. The HOMO of the DCPPO was localized on the carbazole group of DCPPO, whereas the LUMO was dispersed over the phenyl unit connected to the carbazole group. The carbazole is an electron-donating unit, which induced the localization of the HOMO level. The localization of the LUMO in the phenyl unit is due to the electron-withdrawing diphenylphosphine oxide group, which makes the phenyl unit electron-deficient. The HOMO was localized on the hole-transport carbazole unit and the LUMO was localized on the diphenylphosphine-oxide-modified phenyl unit. Although a few bipolar host materials with carbazole and diphenylphosphine oxide groups were reported, the LUMO was distributed over the hole-transport carbazole units.<sup>[8,9,14]</sup> However, the LUMO of the DCPPO was distributed only over the diphenylphosphine-oxide-modified phenyl unit, without any dispersion of the LUMO over the carbazole unit. Therefore, the bipolar charge-transport properties can be obtained in the DCPPO. The simulated HOMO and LUMO levels of the DCPPO were 5.44 and 1.18 eV, respectively.

The photophysical properties of the DCPPO were analyzed by using UV/Vis and PL measurements. Figure 2 shows the UV/Vis, solution PL, solid PL, and low temperature (T) PL spectra of DCPPO. The DCPPO showed the absorption of the carbazole unit above 300 nm and phenyl unit connected to the carbazole below 300 nm. The absorption edge of the UV/Vis spectrum was 347 nm, which corresponded to the bandgap at 3.57 eV. The solution and solid PL emissions of the DCPPO were observed at 391 nm and there was little difference in the peak position between the solution and solid PL. The triplet energy of the DCPPO was 2.99 eV, which could be calculated from the first phosphorescent emission peak of low temperature PL spectrum at 414 nm. The triplet energy of the DCPPO was high enough to use the host material as a deep-blue phosphorescent dopant. The triplet energy of the bis((3,5-difluoro-4-cyano-



Figure 2. UV/Vis absorption ( $\bullet$ ) and PL spectra ( $\bullet$ =solution PL;  $\bullet$ = solid PL;  $\bullet$ =Low *T* PL) of DCPPO.

phenyl)pyridine) iridium picolinate (FCNIrpic) dopant is 2.74 eV and effective energy transfer from DCPPO host to FCNIrpic dopant is expected. In addition, the DCPPO showed a high glass transition temperature of 107 °C compared with 55 °C for the mCP.<sup>[15]</sup> The glass transition temperature was greatly increased because of the diphenylphosphine oxide unit.

The HOMO of the DCPPO was measured using cyclic voltametry (CV) and was 6.13 eV from the onset of the oxidation curve of CV (see the Supporting Information, Figure S1). The LUMO (2.56 eV) was calculated from the HOMO and bandgap (3.57 eV). Compared with the HOMO/LUMO levels of the common mCP host material. the LUMO level was lowered due the electron-withdrawing diphenylphosphine oxide group and the HOMO was similar. Therefore, the DCPPO can show similar hole-injection properties to mCP and better electron-injection properties than mCP, indicating bipolar charge-transport properties. An electron-only device of DCPPO was fabricated to confirm the electron-injection and -transport properties of DCPPO and was compared with a common mCP host. Figure 3 shows the hole- and electron current density of DCPPO and mCP. The electron current density of the DCPPO was higher than that of the mCP, indicating better electron-injection and -transport properties of the DCPPO. The diphenylphosphine oxide group improved the electron current density of the DCPPO device. The hole-only device



Figure 3. Hole- and electron current density of DCPPO ( $\blacksquare$ =electron;  $\triangle$ =hole) and mCP ( $\diamond$ =electron;  $\bigcirc$ =hole).

1	1	4	-1	6	-

## COMMUNICATION

data of the DCPPO was also added and it can be shown that the hole- and electron current density of the DCPPO is similar, indicating bipolar charge-transport properties of the DCPPO.

The device performances of deep-blue PHOLEDs with the DCPPO host were investigated by changing the doping concentration of the deep-blue-emitting FCNIrpic dopant. The doping concentration of the DCPPO was changed from 1 to 15%. The chemical structure and energy level diagram of the device are shown in Figure 4. A detailed fabrication



Figure 4. Chemical structure of materials and energy-level diagram of the blue device.

process for the deep-blue PHOLEDs is described in the Supporting Information. Figure 5 shows the current density-voltage and luminance-voltage curves of deep-blue PHO-LEDs with the DCPPO host. The current density was reduced according to the increase of the doping concentration and increased above 10%. The decrease of the current density below 10% doping concentration is caused by the charge-trapping effect of the FCNIrpic dopant, whereas the increase of the current density above 10% is due to the charge-hopping effect at a high doping concentration. The luminance followed a similar relationship as the current density, although the luminance at a 3% doping concentration of the device.

Figure 6 shows the quantum efficiency–luminance curves of the DCPPO devices. The quantum efficiency of the deepblue PHOLEDs was optimized at 3 % doping concentration. The maximum quantum efficiency of the deep-blue PHO-



Figure 5. a) Current density-voltage curves and b) luminance-voltage curves of DCPPO devices.



Figure 6. Quantum efficiency-luminance curves of DCPPO devices.

LEDs was 22.4% and the quantum efficiency at  $1000 \text{ cd m}^{-2}$  was 18.4%. This efficiency value is one of the best efficiency values reported in the literature. The maximum current efficiency was 27.1 cd A<sup>-1</sup> and the current efficiency at  $1000 \text{ cd m}^{-2}$  was 22.2 cd A<sup>-1</sup>. The high quantum and current efficiency of the DCPPO device can be explained by the efficient hole- and electron-injection from the charge-transport layer to the emitting layer. The HOMO level of the DCPPO was 6.13 eV, leading to only 0.03 eV HOMO level difference with the mCP hole-transport layer. The little energy barrier for hole injection improves the hole injection from the mCP layer to the DCPPO-emitting layer. The electron injection from the TSPO1 layer to the DCPPO-emitting layer is also efficient as there is no energy barrier for electron injection. Therefore, both holes and electrons can

www.chemeurj.org

- 11417

be efficiently injected from the charge-transport layer to the emitting layer, improving the quantum efficiency of the DCPPO device.

The electroluminescence (EL) spectra of the DCPPO device is shown in Figure 7. The DCPPO device with a 3% doping concentration exhibited a peak maximum at 458 nm



Figure 7. Electroluminescence spectra of DCPPO devices.

and shoulder peak at 477 nm. The peak maximum was slightly redshifted to 460 nm at high doping concentration due to intermolecular interaction. The color coordinate of the DCPPO device was (0.14,0.17) at 1 and 3% doping concentrations, whereas at 5 and 10% doping concentrations it was (0.14,0.18). The intermolecular interaction between dopant materials induced the redshift of the color coordinate at a high doping concentration.

In conclusion, a mCP-based material, DCPPO, was synthesized as the high triplet energy bipolar host material for deep-blue PHOLEDs. DCPPO showed a high triplet energy of 2.99 eV and was effective as the host material for deepblue PHOLEDs. A high quantum efficiency of 22.4% with a color coordinate of (0.14,0.17) was achieved in the deepblue PHOLEDs by using the DCPPO host material. This approach for the design of bipolar host materials can be useful for the future development of high triplet energy host materials for deep-blue PHOLEDs.

**Keywords:** bipolar host • cyclic voltammetry • density functional calculations • host–guest chemistry • high triplet energy • luminescence

- Y. Tao, Q. Wang, C. Yang, Q. Wang, Z. Zhang, T. Zou, J. Qin, D. Ma, Angew. Chem. 2008, 120, 8224–8227; Angew. Chem. Int. Ed. 2008, 47, 8104–8107.
- [2] Z. Q. Gao, M. Luo, X. H. Sun, H. L. Tam, M. S. Wong, B. X. Mi, P. F. Xia, K. W. Cheah, C. H. Chen, *Adv. Mater.* **2009**, *21*, 688–692.
- [3] M. M. Rothmann, S. Haneder, E. D. Como, C. Lennartz, C. Schildknecht, P. Strohriegl, *Chem. Mater.* 2010, 22, 2403–2410.
- [4] Y. Tao, Q. Wang, C. Yang, C. Zhong, J. Qin, D. Ma, Adv. Funct. Mater. 2010, 20, 2923–2929.
- [5] W. Y. Hung, L. C. Chi, W. J. Chen, Y. M. Chen, S. H. Chou, K. T. Wong, J. Mater. Chem. 2010, 20, 10113–10119.
- [6] S.-J. Su, H. Sasabe, T. Takeda, J. Kido, Chem. Mater. 2008, 20, 1691– 1693.
- [7] X. Cai, A. B. Padmaperuma, L. S. Sapochak, P. A. Vecchi, P. E. Burrows, *Appl. Phys. Lett.* **2008**, *92*, 083308.
- [8] S. O. Jeon, K. S. Yook, C. W. Joo, J. Y. Lee, Adv. Funct. Mater. 2009, 19, 3644–3649.
- [9] S. O. Jeon, K. S. Yook, C. W. Joo, J. Y. Lee, Adv. Mater. 2010, 22, 1872–1876.
- [10] K. Son, M. Yahiro, M.T. Imai, H. Yoshizaki, C. Adachi, *Chem. Mater.* 2008, 20, 4439–4446.
- [11] S. Gong, Y. Chen, C. Yang, C. Zhong, J. Qin, D. Ma, Adv. Mater. 2010, 22, 5370–5373.
- [12] J. Ding, Q. Wang, L. Zhao, D. Ma, L. Wang, X. Jing, F. Wang, J. Mater. Chem. 2010, 20, 8126–8133.
- [13] F. M. Hsu, C. H. Chien, P. I. Shih, C. F. Shu, Chem. Mater. 2009, 21, 1017–1022.
- [14] S. O. Jeon, S. E. Jang, H. S. Son, J. Y. Lee, Adv. Mater. 2011, 23, 1436–1441.
- [15] S. J. Yeh, M. F. Wu, C. T. Chen, Y. H. Song, Y. Chi, M. H. Ho, S. F. Hsu, C. H. Chen, Adv. Mater. 2005, 17, 285–289.

Received: April 11, 2011 Published online: August 29, 2011

11418 -