N,N-Diphenylpyridin-4-amine as a Bipolar Core Structure of High-Triplet-Energy Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes

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High-triplet-energy bipolar host materials with both holetransport and electron-transport units in the molecular structure have been developed to improve the quantum efficiency of blue phosphorescent organic light-emitting diodes (PHOLEDs) through charge balance in the emitting layer.^[1-3] The use of the bipolar host materials enabled the fabrication of high-efficiency blue PHOLEDs with a quantum efficiency above 20 %.^[4-7]

Several chromophores have been used as the core structures of bipolar host materials. Fluorene was one bipolar core structure for host materials, and several derivatives of fluorene were synthesized as bipolar host materials for blue PHOLEDs.^[8-10] Modification of fluorene with hole- and electron-transport units yielded various bipolar host materials.^[10] Diphenylsilane was another common core structure for high-triplet-energy bipolar host materials. Diphenvlsilane could be easily modified with hole- and electron-transport moieties by nucleophilic substitution reactions.^[11] The other core structure which has been widely used is phenylcarbazole. As phenylcarbazole is a hole-transport core, it was modified with an electron-transport substituent for better electron-transport properties.[12-16] Phenylcarbazolebased bipolar host materials were effective as host materials for blue PHOLEDs.

Although many bipolar host materials have been studied for application in blue PHOLEDs, further development of the core structure and its derivatives is required to improve the device performances of blue PHOLEDs. Herein, *N*,*N*-diphenylpyridin-4-amine (DPPA) was developed as a hightriplet-energy bipolar core structure for blue host materials, and two derivatives of DPPA, 2,6-di(biphenyl-3-yl)-*N*,*N*-diphenylpyridin-4-amine (PyA-3BP) and 2,6-bis(3-(9H-carbazol-9-yl)phenyl)-*N*,*N*-diphenylpyridin-4-amine(PyA-PCz), were synthesized as host materials. It was demonstrated that PyA-3BP and PyA-PCz show bipolar charge-transport properties and high triplet energy for use in blue PHOLEDs.

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Supporting information for this article, including synthetic procedures

and details of characterization and device fabrication, is available on the WWW under http://dx.doi.org/10.1002/asia.201200463.

DPPA was designed as a bipolar core structure with high triplet energy. DPPA has a molecular structure with an electron-donating diphenylamine unit attached to an electrondeficient pyridine unit. As DPPA has the electron-deficient pyridine and electron-donating amine moieties, it can play the role of a bipolar core structure. Moreover, it can exhibit high triplet energy.

The synthetic route for DPPA-based host materials is shown in Scheme 1. The halogenated DPPA core was prepared by the reaction between 4-amino-2,6-dichloropyridine and bromobenzene using palladium catalyst. The halogenated DPPA was treated with boronic acid of biphenyl and phenylcarbazole to produce PyA-BP and PyA-PCz.



Scheme 1. Synthesis of PyA-BP and PyA-PCz.

Molecular simulation of DPPA was carried out to understand its basic material properties. The Gaussian 03 program suite and the nonlocal density functional of Becke's 3-parameters employing Lee–Yang–Parr functional (B3LYP) with 6-31G* basis sets were used for the simulation.^[17] Figure 1 shows simulated highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) levels and HOMO/LUMO orbital distribution of DPPA. Molecular simulation results for DPPA were compared with that of a common triphenylamine (TPA). The simulated HOMO/LUMO level of DPPA was -5.38/-0.59 eV compared with -4.95/-0.30 eV of TPA. Both HOMO and

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Figure 1. HOMO and LUMO distributions of TPA and DPPA.

LUMO levels of DPPA were stabilized by replacing one phenyl unit with a pyridine unit due to electron deficiency of the pyridine unit. This finding indicates that DPPA shows better electron-transport properties than DPA owing to the electron-withdrawing character of the pyridine unit. Therefore, the DPPA core is more suitable as a bipolar core structure for bipolar host materials. Additionally, the simulated triplet energy of DPPA was higher than that of TPA by 0.08 eV, implying that DPPA can be effective as a high-triplet-energy core for blue host materials. The HOMO distribution of DPPA was similar to that of TPA, but the LUMO distribution was different because of electron deficiency of the pyridine unit. The LUMO distribution was rather localized on the pyridine unit in DPPA, while it was uniform in TPA.

As DPPA showed potential as a core structure of hightriplet-energy bipolar host materials, it was modified with biphenyl and phenylcarbazole moieties. Two biphenyl or phenylcarbazole moieties were attached to the 2- and 6-positions of pyridine. Both units were substituted through meta linkage to obtain high triplet energy. Biphenyl was introduced as a bipolar substituent, while phenylcarbazole was used as a hole-transport substituent. Two host materials were synthesized by Suzuki coupling reaction of 2,6-dichloro-*N*,*N*-diphenylpyridin-4-amine with boronic acid of biphenyl or phenylcarbazole.

Photophysical properties of PyA-BP and PyA-PCz were analyzed using ultraviolet-visible (UV/Vis) and photoluminescence (PL) spectroscopy. PyA-BP exhibited a broad absorption peak between 230 and 350 nm, which is assigned to π - π * transition of the DPPA core (Figure 2). In the case of PyA-PCz, phenylcarbazole absorption peaks at 325 and 339 nm were also observed in addition to the broad absorption peak of DPPA. Optical bandgaps were calculated from the edge of UV/Vis absorption peak, which were 3.46 and 3.52 eV for PyA-BP and PyA-PCz, respectively. Solution PL emission of PyA-BP and PyA-PCz was observed at 414 and 421 nm, respectively. Low-temperature PL measurement was carried out in liquid nitrogen to measure triplet energy of host materials. The triplet energy calculated from the first phosphorescence emission peak was 2.76 eV for both compounds. The triplet energy of the two compounds is deter-



Figure 2. UV/Vis, solution PL, and low-temperature PL spectra of a) PyA-BP and b) PyA-PCz. UV/Vis and solution PL spectra were measured in tetrahydrofuran. Low-temperature PL was measured in liquid nitrogen.

mined by the central phenyl-pyridine-phenyl structure as this is the unit with the lowest triplet energy in the molecular structure. The two compounds had the same phenyl-pyridine-phenyl structure, resulting in the same triplet energy.

The HOMO levels of PyA-BP and PyA-PCz were measured using a surface analyzer, and the LUMO level was calculated from the HOMO and the bandgap from UV/Vis absorption measurement. HOMO/LUMO levels of PyA-BP and PyA-PCz were -5.76/-2.28 eV and -5.81/-2.29 eV, respectively.

HOMO and LUMO simulation of PyA-BP and PyA-PCz was carried out to study the effect of different substituents on the molecular orbital distribution. The HOMO and LUMO distribution of PyA-BP and PyA-PCz is shown in Figure 3. The HOMO of PyA-BP was localized on the DPPA core due to the strong electron-donating character of the diphenylamine unit, but the HOMO of PyA-PCz was dispersed over the phenylcarbazole unit. This result indicates that hole transport of PyA-BP is dominated by the DPPA core, while that of PyA-PCz is dependent on phenylcarbazole. The LUMO was localized on the pyridine and

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Figure 3. HOMO and LUMO distribution of PyA-BP and PyA-PCz.

phenyl units, and the LUMO distribution was similar in both host materials due to the electron-accepting properties of pyridine.

Hole-only and electron-only devices were fabricated to compare hole and electron current density of the two host materials. Figure 4 shows current-density-voltage curves of



Figure 4. Hole-only device (a) and electron-only device (b) data of PyA-BP and PyA-PCz.

hole- and electron-only devices of PyA-BP and PyA-PCz. Hole current density was high in PyA-PCz, while electron current density was similar in the two host materials. The hole and electron current density is generally decided by an energy barrier for charge injection and by charge-transport properties. Considering the energy barrier for charge injection, there are no energy barriers for hole injection and sim-



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Figure 5. Energy-level diagram of the blue-light-emitting PHOLED. $N^1,N^{1'}$ -(biphenyl-4,4'-diyl)bis(N^1 -phenyl- N^4,N^4 -di-mtolylbenzene-1,4-diamine (DNTPD), N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB), 1,3-bis(carbazol-9-yl)benzene (mCP), diphenylphosphine oxide-4-(triphenylsilyl) (TSPO1).

ilar energy barriers for electron injection in the two host materials. The energy-level diagram is shown in Figure 5. Therefore, the high hole current density of PyA-PCz implies that PyA-PCz has better hole-transport properties than PyA-BP, which can be explained by the molecular-orbital distributions of PyA-BP and PyA-PCz. The HOMO of PyA-PCz was localized on hole-transporting phenylcarbazole, while that of PyA-BP was dispersed over the bipolar DPPA core. As phenylcarbazole is more suitable as a hole-transport unit than bipolar DPPA, better hole-transport properties were observed in PyA-PCz. The LUMO distribution was similar in the two host materials, resulting in similar electron density in electron-only devices. In terms of bipolar charge-transport properties, PyA-PCz was better than PyA-BP. Although electron current density was higher than hole current density, the difference of hole and electron current density was small in PyA-PCz.

Blue PHOLEDs were fabricated to evaluate PyA-BP and PyA-PCz as host materials for blue phosphorescent dopant materials. Figure 6 represents current-density-voltage-lumi-



Figure 6. Current-density-voltage-luminance curves of PyA-BP- and PyA-PCz-based blue PHOLEDs.

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nance curves of PyA-BP and PyA-PCz devices. The current density and luminance of the PyA-PCz device were higher than those of the PyA-BP device at the same driving voltage due to the better hole-transport properties of PyA-PCz (see Figure 4). The driving voltage of PyA-PCz device was lower than that of PyA-BP by 0.5 V.

Quantum-efficiency-luminance curves of PyA-BP and PyA-PCz devices are shown in Figure 7. Bis(3,5-difluoro-2-



Figure 7. Quantum-efficiency–luminance curves of PyA-BP- and PyA-PCz-based blue PHOLEDs.

(2-pyridyl)phenyl-(2-carboxypyridyl)iridium(III) (FIrpic) was doped as a blue phosphorescent dopant in the emitting layer. The quantum efficiency of the PyA-PCz device was higher than that of the PyA-BP device for the whole luminance range measured. Maximum quantum efficiency of the PyA-PCz device was 15.1%, and quantum efficiency at 1000 cd m^{-2} was 12.0%. The higher quantum efficiency of the PyA-PCz device can be explained by the balance of holes and electrons in the emitting layer. This can be confirmed by hole and electron density of the FIrpic-doped PyA-BP and PyA-PCz emitting layers (Figure 8). Hole current density of FIrpic-doped PyA-PCz was much higher than that of FIrpic-doped PyA-BP, while electron current density of both FIrpic-doped host materials was similar. Comparing relative hole and electron current density of the two host materials, PyA-PCz and PyA-BP showed relative ratio of about 2.0 and 0.25. Therefore, balance of holes and electrons in the FIrpic-doped emitting layer is better in PyA-PCz than in PyA-BP, resulting in high quantum efficiency in PyA-PCz. Device performances of PyA-BP and PyA-PCz are summarized in Table 1.

Table 1. Device performances of PyA-BP and PyA-PCz devices.

Material	Quantum effi-	Current effi-	Power effi-	Color coor-
	ciency [%]	ciency [cd A ⁻¹]	ciency [lm W ⁻¹]	dinate
PyA-BP	15.1, ^[a] 12.0 ^[b]	28.0, ^[a] 21.3 ^[b]	$21.6,^{[a]}, 9.4^{[b]}$ $17.7,^{[a]}, 7.6^{[b]}$	0.15, 0.33
PyA-PCz	14.5, ^[a] 10.5 ^[b]	25.6, ^[a] 18.1 ^[b]		0.15, 0.31

[a] Maximum efficiency. [b] Efficiency at 1000 cd m⁻².

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Figure 8. Hole-only device (a) and electron-only device (b) data of FIrpic-doped PyA-BP and PyA-PCz.



Figure 9. Electroluminescence (EL) spectra of PyA-BP- and PyA-PCzbased blue PHOLEDs.

Electroluminescence (EL) spectra of PyA-BP and PyA-PCz blue PHOLEDs are shown in Figure 9. Both devices

showed only an FIrpic emission peak, thus indicating effective energy transfer from host to FIrpic dopant material.

In conclusion, bipolar host materials based on the DPPA core were developed as high-triplet-energy host materials for blue PHOLEDs. High triplet energy above 2.70 eV and bipolar charge-transport

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properties were observed from DPPA-based host materials. Phenylcarbazole substitution yielded high quantum efficiency of 15.6% in blue PHOLEDs.

Keywords: bipolar hosts • electron transport • high efficiency • luminescence • organic materials

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Organic Materials

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N,N-Diphenylpyridin-4-amine as a Bipolar Core Structure of High-Triplet-Energy Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes





Got the blues: High-triplet-energy bipolar host materials based on a bipolar *N*,*N*-diphenylpyridin-4-amine (DPPA) core structure were developed for blue phosphorescent organic light-

PyA-PCz

emitting diodes (PHOLEDs). Two DPPA-based host materials (see picture) showed high triplet energy over 2.70 eV and a high quantum efficiency of 15.6%.

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