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Comparison of Bipolar Hosts and Mixed-Hosts as Host Structures for Deep-Blue Phosphorescent Organic Light Emitting Diodes

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In recent years, phosphorescent organic light-emitting diodes (PHOLEDs) are being actively studied because of the high quantum efficiency of PHOLEDs. Theoretically, PHOLEDs can show up to four times higher quantum efficiency than fluorescent organic light-emitting diodes by harvesting triplet excitons. There have been several studies reporting theoretical maximum external quantum efficiency over 20 % in red, green, and blue PHOLEDs.[1–7]

It is important to balance charge carriers and to confine triplet excitons in the emitting layer to obtain high quantum efficiency in PHOLEDs. One effective way of balancing and confining charge carriers was to adopt a mixed-host emitting structure in the emitting layer.[8–12] The mixed-host structure is made up of hole-transport-type and electron-transport-type host materials. The hole-transport-type host material provides a path for hole injection and transport, whilst the electron-transport-type host material is a path for electron injection and transport. Therefore, both holes and electrons can be effectively injected and transported using the mixed-host structure. Several mixed-host emitting structures were reported to be effective for improving the driving voltage, quantum efficiency, and efficiency roll-off of red, green, and blue PHOLEDs.[8–12] However, using the mixed-host emitting structure is complicated because two host materials and one dopant material should be deposited at the same time. Therefore, it is better to use one bipolar host material with hole-transport and electron-transport units in the molecular structure.[13–19] However, there has been no study correlating the device performances of the PHOLED with the host structure.

Herein, we report the use of three dibenzofuran-type host materials with different functional groups, and the device performances of the single bipolar host device and mixed-host device were compared. A dibenzofuran-core-based hole-transport-type host, electron-transport-type host and bipolar host with both hole transport and electron transport functional groups were used. We demonstrated that the single biplolar host device shows comparable device performance to mixed-host device in the deep-blue PHOLEDs. A high external quantum efficiency close to 20 % was achieved both in the single bipolar host and mixed-host devices.

Three host materials with a dibenzofuran core structure were used to compare bipolar single-host and mixed-host structures in deep-blue PHOLEDs because the dibenzofuran core has a high triplet energy of 3.14 eV.[20] A dibenzofuran-based host with two carbazole units, 2,8-di(9H-carbazol-9-yl)dibenzo[b,d]furan (DFCz), was used as the hole-transport-type host material as the carbazole unit has good hole-transport properties.[21] A dibenzofuran-type host with two diphenylphosphine oxide units, 2,8-bis(diphenylphosphoryl)-dibenzo[b,d]furan (DFPO), was utilized as an electron-transport-type host material as the diphenylphosphine oxide unit shows strong electron-transport properties.[22] A bipolar host with the dibenzofuran core, 9-(8-(diphenylphosphoryl)-dibenzo[b,d]furan-2-yl)-9H-carbazole (DFCzPO), was developed as the bipolar host material with one carbazole unit and one diphenylphosphine oxide unit. The hole-transport carbazole and electron-transport diphenylphosphine oxide groups were combined in the molecular structure to obtain bipolar charge transport properties. The syntheses of the DFCz and DFPO have been reported before and the synthesis of the DFCzPO is shown in Scheme 1.[21,22]

Photophysical properties of the DFCzPO host material were analyzed using UV/Vis and photoluminescence (PL) spectroscopy. Figure 1 shows UV/Vis and PL spectra of the

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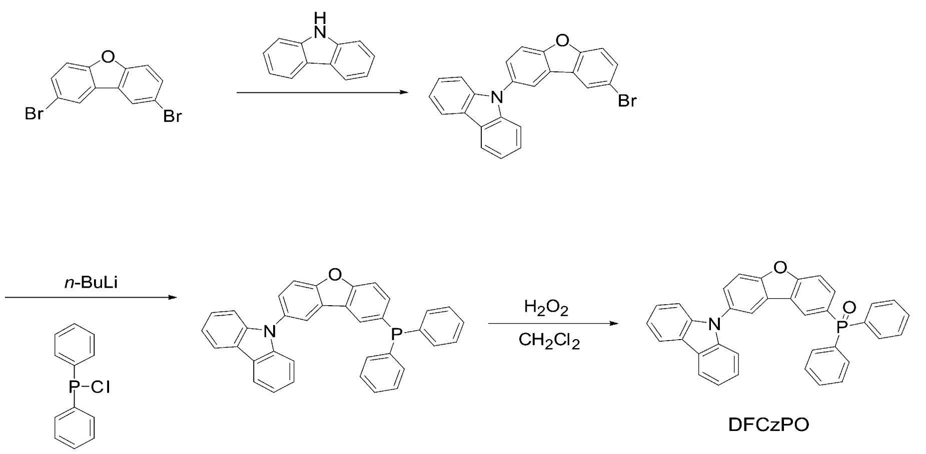

Scheme 1. Synthesis of the host material.

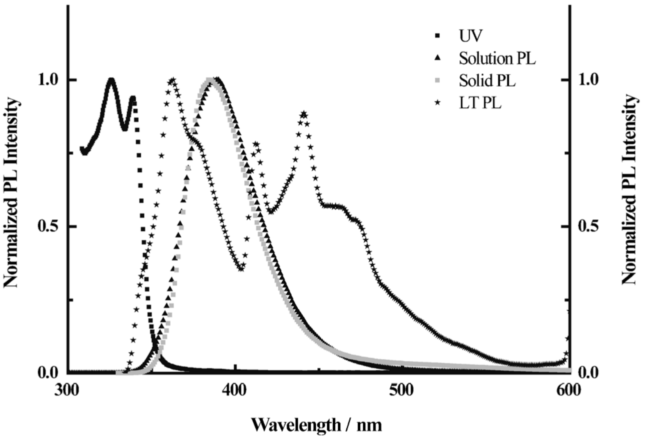

Figure 1. UV/Vis, solution PL, solid PL, and low-temperature PL spectra of DFCzPO.

DFCzPO. DFCzPO showed UV/Vis absorption peaks at 325 nm and 339 nm which are assigned to the absorption of carbazole units. The absorption of the dibenzofuran core was observed below 300 nm. The band-gap of DFCzPO was calculated from the edge of the UV/Vis absorption spectra to be 3.52 eV. The band-gap was similar to that of the DFCz (3.51 eV) with the carbazole unit because of extended conjugation of the dibenzofuran core through the carbazole unit. A PL emission peak of the DFCzPO was observed at 384 nm. The triplet energy of the DFCzPO was measured from the low-temperature PL emission spectra and the triplet energy of the DFCzPO was 3.00 eV. The DFCzPO showed high triplet energy (over 2.90 eV) and is suitable as the host material for deep-blue PHOLEDs.

Molecular simulation was carried out to study the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) distribution of the DFCzPO. Density functional theory calculation of the compounds was carried out using the Gaussian 09 program and the nonlocal density functional of Becke's 3-parameters employing Lee–Yang–Parr functional (B3LYP) with 6-31G* basis sets. Figure 2 shows the HOMO and LUMO distribution of the DFCzPO. The HOMO of the DFCzPO was localized on the carbazole unit, whilst the LUMO was localized on the dibenzofuran unit. As the carbazole group has electron-donating character, the HOMO was concentrated on the carbazole unit. The electron-withdrawing character of the diphenylphosphine oxide induced the localization of the LUMO on the dibenzofuran. The simulated HOMO and LUMO levels of the DFCzPO were 5.41 eV and 1.39 eV, respectively.

The HOMO level of the DFCzPO was measured using cyclic voltammetry (CV). The HOMO level of the DFCzPO was determined from the oxidation curve of the CV spectra (6.08 eV). The HOMO level of the DFCzPO was similar to that of the DFCz (6.09 eV) and was much-lower than that of the DFPO (6.68 eV). As expected from molecular orbital distribution simulations, the DFCzPO showed a similar HOMO level to DFCz. The LUMO level was calculated from the HOMO level and band-gap of the DFCzPO, and was 2.56 eV.

As the DFCzPO was designed as the bipolar-type host material, the charge-transport properties of the DFCzPO were compared with those of hole-transport-type DFCz and electron-transport-type DFPO. Figure 3 shows the hole-only and electron-only current-density data of the DFCzPO host material. The device structure of hole-only device was indium tin oxide (ITO)/*N*,*N*′-diphenyl-*N*,*N*′-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine (DNTPD, 60 nm)/*N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB, 5 nm)/*N*,*N*′-dicarbazolyl-3,5-benzene (mCP, 10 nm)/DFCzPO, or DFCz (30 nm)/DNTPD (5 nm)/Al and the device structure of the electron-only device was ITO/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 5 nm)/DFCzPO or DFPO (30 nm)/TSPO1 (25 nm)/LiF/Al. The hole-current density of the DFCzPO was compared with that of the hole-transport-type DFCz, whilst the electron-current density of the DFCzPO was compared with that of the DFPO. The bipolar-type DFCzPO showed a little higher hole-current density than the DFCz and comparable electron-current density to the DFPO. This result confirms that the DFCzPO shows bipolar charge-transport properties

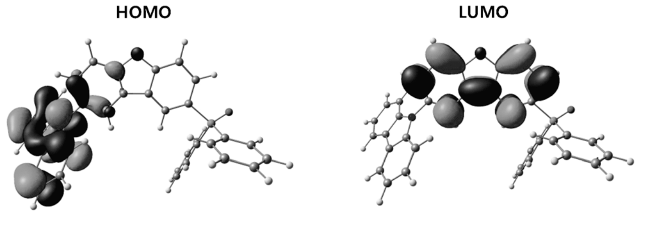

Figure 2. HOMO and LUMO distribution of DFCzPO.

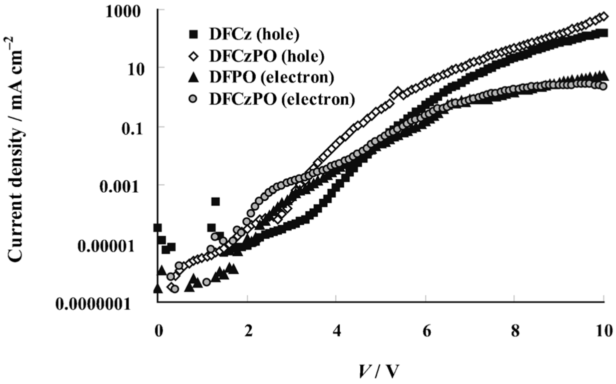

Figure 3. Hole only and electron only device data of DFCzPO.

owing to the hole-transport carbazole and electron-transport diphenylphosphine oxide groups. Considering that the mixed-host device shows the hole-transport properties of the hole-transport-type host and electron-transport properties of the electron-transport-type host, the bipolar DFCzPO host is comparable to the mixed-host in terms of hole- and electron-transport properties.

As all three host materials showed high triplet energies of over 2.90 eV, a deep-blue-emitting dopant, FCNIrpic, was doped in the single bipolar host and the mixed host. Two deep-blue PHOLEDs with a single bipolar host or a mixed host were fabricated to compare the device performances of the two different host systems. DFCz, DFPO, and DFCzPO were tested as the host materials for blue PHOLEDs. The device structure of the blue PHOLEDs was ITO (150 nm)/DNTPD (60 nm)/NPB (5 nm)/mCP (10 nm)/DFCz:DFPO (50:50) or DFCzPO:bis((3,5-difluoro-4-cyanophenyl)pyridine) iridium picolinate (FCNIrpic) (30 nm, 3%)/TSPO1 (20 nm)/LiF(1 nm)/Al(200 nm). The doping concentration of the FCNIrpic was 3% in all devices. In the mixed-host device, the hole-transport-type DFCz and electron-transport-type DFPO were mixed and the relative ratio of the DFCz to DFPO was 50:50. Figure 4 shows the current-density-voltage–luminance curves of the single-host and mixed-host devices. The single-host and the mixed-host devices showed similar current density and luminance over all voltages investigated although the current density and luminance were a little higher in the single-host device than in the mixed-host device at high voltage. This result indicates that the single bipolar host is similar to the mixed host in terms of charge density and exciton formation. The current density is generally determined by the hole and electron density in the device. More hole and electron injection into the emitting layer usually increases the current density. Therefore, the similar current density of the single-host device and the mixed-host device implies similar charge-injection ability of the two different host systems. The basic concept of the mixed-host structure is to inject holes and electrons through a hole-transport-type DFCz host and an electron-transport-type DFPO host, respectively. The problem of poor electron transport of the DFCz host and poor hole transport of DFPO host can be solved by mixing two host materials. The single-host material, DFCzPO, possesses the hole-transport carbazole unit in the DFCz and the electron-transport diphenylphosphine oxide unit in the DFPO. Therefore, it can have both hole-transport and electron-transport properties. The charge transport must be comparable in both cases because the hole-transport and electron-transport groups are the same in the single host and the mixed host, as shown in the molecular orbital diagram.

Quantum-efficiency–luminance curves of the single-host and mixed-host devices are shown in Figure 5. The quantum efficiency of the two devices showed little difference over the measured luminance range although the quantum efficiency of the single-host device was a little higher than that of the mixed-host device. The maximum quantum efficiency and quantum efficiency at 1,000 cd m^{-2} of the single-host device were 21.4% and 17.5%, respectively, whilst those of the mixed-host device were 20.3% and 16.7%, respectively. A high quantum efficiency of over 20% was achieved both in the single-host and mixed-host devices. The high quantum efficiency of the two devices originated from the balanced charge density in the emitting layer. In the mixed-host device, both holes and electrons were effectively injected from the charge-transport layer through the hole-transport-type DFCz and electron-transport-type DFPO host materi-

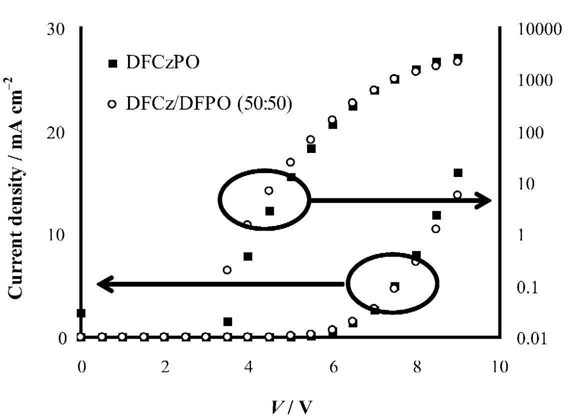

Figure 4. Current density/voltage/luminance curves of DFCzPO and DFCz/DFPO (50:50) mixed-host devices.

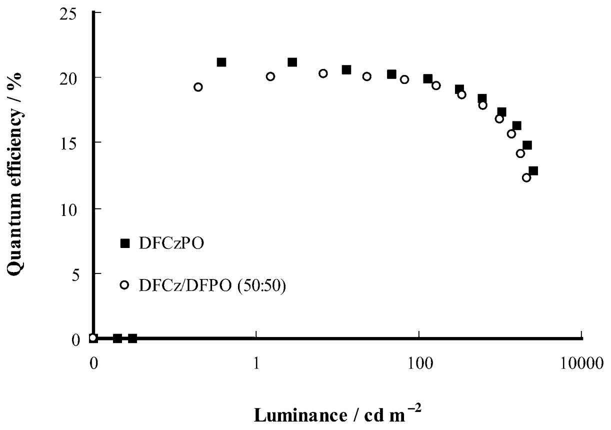

Figure 5. Quantum efficiency/luminance curves of DFCzPO and DFCz/DFPO (50:50) mixed-host devices.

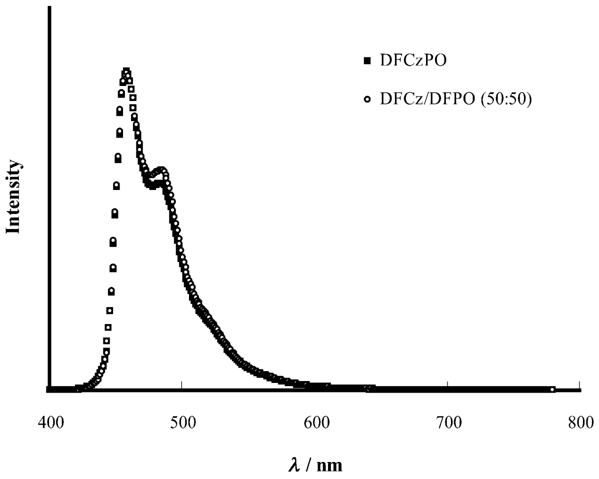

Figure 6. Electroluminescence spectra of DFCzPO and DFCz/DFPO (50:50) mixed-host devices.

als, resulting in balanced hole- and electron density in the emitting layer. Similarly, both holes and electrons were effectively injected and transported through the hole-transport carbazole and electron-transport diphenylphosphine oxide units, leading to charge balance in the emitting layer. Therefore, both the single bipolar host and the mixed-host worked comparably in the deep-blue PHOLEDs. The maximum current efficiency and current efficiency at 1000 cd m^{-2} of the DFCzPO device were 26.4 cd A^{-1} and 21.5 cd A^{-1}, respectively. The maximum power efficiency and power efficiency at 1000 cd m^{-2} of the DFCzPO device were 22.6 Lm W^{-1} and 10.0 Lm W^{-1}, respectively.

Electroluminescence (EL) spectra of the single-host and mixed-host devices are also shown in Figure 6. Similar EL spectra were observed in the two devices with a maximum emission peak at 457 nm and a shoulder peak at 478 nm. The color coordinate of the single-host and mixed-host devices was (0.14,0.18), corresponding to the deep-blue emission color. No extra peak originated from charge transport layer was observed in the EL spectra of two devices, thus indicating an effective charge confinement inside the emitting layer.

In conclusion, the design and synthesis of hole transport, electron transport, and bipolar host materials revealed that a single bipolar host can show the same device performances as the mixed-host device. The current density, luminance, and quantum efficiency were similar in the deep-blue PHOLEDs with the single bipolar host and mixed host. A high quantum efficiency over 20 % was achieved both in the single-bipolar host and mixed-host devices. This approach proved that a well-designed single bipolar host is comparable to mixed host and can be useful in the future development of bipolar host materials for deep-blue PHOLEDs.

Experimental Section

Detailed synthetic procedure and characterization of DFCzPO are described in supporting information. All device fabrication process is presented in the Supporting Information.

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Keywords: bipolar compounds · high efficiency · host-guest systems · OLEDs · phosphorescence

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