A Donor–Acceptor-type Host Material for Solution-processed Phosphorescent Organic Light-emitting Devices Showing High Efficiency

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The solution-processable host material, 3,3'-[bis(9-phenylcarbazol-3-yl)]benzophenone (BCzBP), containing donor-type phenylcarbazole units and an acceptor-type benzophenone unit was synthesized. BCzBP showed a high excited triplet energy level and a high photoluminescence quantum efficiency with tris[2-(4-tolyl)pyridine]iridium ([Ir(mppy)₃]) as a dopant, and a high glass-transition temperature. Solution-processed green phosphorescent OLEDs were fabricated with BCzBP. The device with BCzBP as a host showed comparable efficiencies to those of the corresponding device with 4,4'-bis(*N*-carbazolyl)biphenyl (CBP) as a host. At the same current density, the device with BCzBP showed a longer device lifetime than that with CBP, due to the high thermal stability and the bipolar nature of the host compound, BCzBP.

Solution-processed organic light-emitting devices (OLEDs) are considered essential for the next generation of low-cost and large-area flat-panel displays and lighting sources.^{1–6} Phosphorescent compounds are effective to improve the efficiency of the device, compared with fluorescent materials.^{7,8} However, it is rather difficult to achieve a long lifetime in phosphorescent OLEDs, and the solution process makes it more difficult.^{9,10} The host materials for solution-processed phosphorescent OLEDs require high energy level of excited triplet state (T₁) not to quench triplet exciton of the phosphorescent emitter, charge-transporting ability for low driving voltage, high glass-transition temperature (T_g) for long lifetime and less vulnerable to heat damage in OLEDs, bipolar property for electrochemical stability of cation radical and anion radical states, and good solubility in organic solvents for solution processability.^{11–14}

In this study, we report a unique molecular design of combining phenylcarbazol as electron-donor unit and benzophenone as electron-acceptor unit to give a novel bipolar host material of 3,3'-[bis(9-phenylcarbazol-3-yl)]benzophenone (BCzBP). The compound exhibited high T_1 and high T_g . Solution-processed green phosphorescent OLEDs using an emitter of tris[2-(4tolyl)phenylpyridine]iridium ([Ir(mppy)₃]) showed high external quantum efficiency (EQE) of 9.8% and a long half-lifetime of 365 h at a practical brightness of 1000 cd m⁻².

The bipolar host material, BCzBP was readily synthesized by the Pd(0)-catalyzed Suzuki–Miyaura cross-coupling reaction of two equivalents of 9-phenylcarbazole-3-boronic acid with 3,3'-dibromobenzophenone (Scheme 1). The chemical structure was identified by ¹H- and ¹³C NMR, mass spectrometry, and elemental analysis. The compound was thoroughly purified by train sublimation and the purity was higher than 99.9%, determined by high-performance liquid chromatography (HPLC) analysis. The thermal properties of BCzBP were investigated using thermal gravimetric analysis (TGA) and differential





Figure 1. Calculated spatial distributions (DFT, B3LYP/6-311G+(d,p)//B3LYP/6-31G(d), Gaussian 09) of HOMO and LUMO of BCzBP.

scanning calorimetry (DSC). The decomposition temperature (T_d , corresponding to 5% weight loss) was 487 °C, and T_g was 116 °C. The much higher T_d and T_g at 373 °C and 62 °C of 4,4'-bis(*N*-carbazolyl)biphenyl (CBP) is attributed to the high molecular weight of BCzBP.^{15,16} This high thermal stability is highly desirable for improving the lifetime of the OLEDs.

Density surfaces of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were calculated using density functional theory (DFT), shown in Figure 1. The HOMO is located on the electron-rich phenyl-carbazole unit, and its energy level is calculated at -5.61 eV. Conversely, the LUMO is located on the benzophenone unit, and its energy level is calculated at -2.00 eV. The T₁ of BCzBP is also calculated at -2.91 eV, using time-dependent DFT.

The ionization potential (I_p) corresponding to the HOMO level of the BCzBP film was $-5.87 \,\text{eV}$, measured by photoelectron yield spectroscopy. The energy gap (E_g) was -3.32 eV, determined by the UV absorption edge of the film. The LUMO level was estimated at $-2.55 \,\mathrm{eV}$ from the difference of the $I_{\rm p}$ and the E_{g} . The photoluminescence (PL) spectrum of the film was measure at room temperature and low temperature at 5K (Figure 2). The fluorescence spectrum was obtained at room temperature with a maximum wavelength of 445 nm, while the low-temperature measurement showed a red-shifted phosphorescence spectrum. From the edge of the phosphorescence spectra, the T_1 level of BCzBP was estimated at -2.65 eV. This value is high enough to confine the triplet exciton of the green phosphorescence of $[Ir(mppy)_3]$ (-2.55 eV) in OLEDs. We measured the photoluminescence quantum yield (PLQY) of [Ir(mppy)₃] (12 wt %) doped in BCzBP or CBP film by selective



Figure 2. UV–vis absorption spectrum (circle) and PL spectrum (square) of the film of BCzBP, and phosphorescence spectrum (triangle) of the film of the BCzBP at 5 K.



Figure 3. (a) Current density–voltage characteristics and (b) EQE– current density characteristics of the devices using CBP and BCzBP.

excitation of $[Ir(mppy)_3]$ at 390 nm, where BCzBP and CBP have no absorption (Figure S1). The PLQY of $[Ir(mppy)_3]$ with BCzBP and CBP are 65% and 69%, respectively. These high PLQYs also support the efficient triplet exciton confinement of the hosts.

The OLEDs with a configuration of ITO (130 nm)/triphenylamine-containing polymer: 4-isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate (PPBI) (20 nm)/ poly(9,9-dioctylfluorene-*alt-N*-(4-butylphenyl)diphenylamine) (TFB) (20 nm)/CBP or BCzBP: 12 wt % [Ir(mppy)₃] (30 nm)/ bis(9,9-spirobifluoren-2-yl) ketone (SBFK) (10 nm)/1,4-di(1,10phenanthroline-3-yl)benzene (DPB): 25 wt % lithium quinolinolate (Liq) (40 nm)/Al (100 nm) were fabricated.¹⁷ The hole injection layer, hole-transporting layer, and emitting layer were solution-processed by the spin-coating method from the toluene and THF solution. The hole-blocking layer, electrontransporting layer, and cathode were deposited by evaporation in vacuum. The driving voltage of the device with BCzBP increased compared with that of the device with CBP, suggesting lower charge mobility in BCzBP than that in CBP (Figure 3a). However, BCzBP exhibited higher efficiencies than CBP (Figure 3b). At a luminance of 1000 cd m⁻², BCzBP showed an external quantum efficiency (EQE) of 9.8% and a current efficiency of $34 \text{ cd } \text{A}^{-1}$, while CBP showed efficiencies of 9.0% and $32 \text{ cd } A^{-1}$, respectively. The roll-off of the efficiencies was suppressed in the device with BCzBP. These higher efficiencies and less roll-off of the efficiencies are because of a wellbalanced ratio of holes and electrons in the emitting layer, derived from the bipolar property of BCzBP.



Figure 4. Lifetime characteristics of the devices using CBP and BCzBP, measured at 5 mA cm^{-2} .

Device stabilities were investigated under a 5 mA cm^{-2} driving condition. The initial luminances were 1700 and 1500 cd m⁻² for BCzBP and CBP, respectively. The device with BCzBP as a host showed much improved stability compared with CBP (Figure 4). The half lifetime was 89 h for CBP, on the other hand, it was 160 h for BCzBP. The longer lifetime of the device with BCzBP is considered to be resulted from its high thermal stability and bipolar nature.

In summary, we synthesized a thermally stable bipolar host, BCzBP, consisting of electron-donating phenylcarbazole units and an electron-accepting benzophenone unit. The T_g of BCzBP was much higher than that of usual CBP. The solution-processed green phosphorescence OLEDs showed higher efficiencies and longer lifetimes, compared with the device with CBP.

Supporting Information is available electronically on J-STAGE.

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