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<Graphical Abstract>

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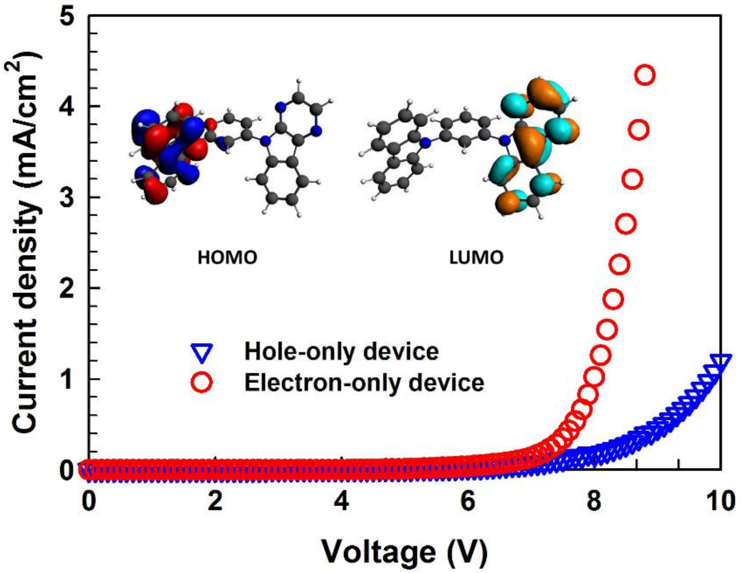

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Synthesis and Blue Phosphorescent Device Performances of a New Bipolar Host Material Containing Pyrazino[2,3-b]indole Moiety

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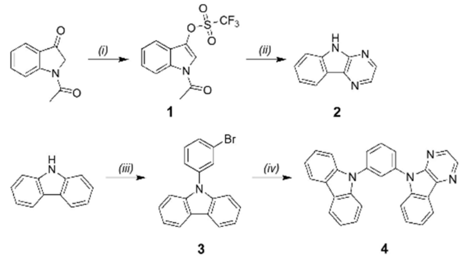
A new bipolar host material (CzPhPz) consisted of 5*H*-pyrazino[2,3-b]indole unit was synthesized and its photophysical properties and device performances were investigated. It showed good electron transport properties with a high triplet energy of 2.83 eV. CzPhPz was effective as the host material for FIrpic-based blue PHOLED with a high quantum efficiency of 15.0 %.

For more than ten years, the progress of device performances of phosphorescent organic light emitting devices (PHOLEDs) has drawn tremendous attention because of their high quantum efficiency as well as their potential applications in full-color flat-panel displays and solid-state lighting applications.[1]
In research field for PHOLEDs, a host material plays a crucial role in determining the device performances (*e.g.*, external quantum efficiency, current efficiency, and lifetime through charge balance and efficiency energy transfer). Thus, designing host materials with these features remains a challenge for materials scientists. One of the most widely used building blocks for host materials in blue PHOLEDs is a carbazole moiety having excellent hole-transporting property and large triplet energy.[2] Meanwhile, the carbazole structure showed poor electron-accepting property. To surmount this constraint, many host materials possessing bipolar properties for PHOLEDs have been developed. In order to construct bipolarity in the carbazole-based host material designs, a large number of moieties capable of electron-accepting such as pyridine, triazole, triazine, phenanthroline, oxadiazole, benzimidazole, phosphine oxide, and phosphine sulfide, were incorporated to be a bipolar host materials.[3]
As another electron acceptor, pyridoindole having high triplet energy and better electron-accepting properties than carbazole has developed as a building block to improve the poor electron-accepting properties of the carbazole-based host materials.[4] Several research groups have used the pyridoindole derivatives as the host materials for blue PHOLEDs and white tandem PHOLEDs to enhance their quantum efficiency.[5] The pyridoindole moiety could enhance the quantum efficiency of blue PHOLEDs because of balanced charge density by electron accepting character of the pyridoindole moiety. Therefore, the incorporation of six-membered heterocycle in the indole moiety was an effective approach for good charge balance in the emitting layer. However, only a few six-membered heterocycle modified indole moieties have been reported and most of them were pyridine modified indole moieties. In particular, no six-membered heterocycles with two nitrogen atoms were combined with indole to develop electron accepting moieties of bipolar host materials.
In this work, a heterocycle with two nitrogen atoms, 5*H*-pyrazino[2,3-b]indole, was designed and synthesized as electron-acceptor unit of carbazole-based host material due to its high electron affinity attributed to symmetric unsaturated imine nitrogen (C=N) structures.[6] Here, we demonstrate a new carbazole-based bipolar host material containing pyrazino[2,3-b]indole unit, 5-(3-(9*H*-carbazol-9-yl)phenyl)-5*H*-pyrazino[2,3-b]indole (CzPhPz), for the purposes of improving device performances and photophysical properties.
The design of 5*H*-Pyrazino[2,3-*b*]indole is based on an concept that the introduction of two nitrogen atoms in the six-membered ring combined with a indole moiety would improve the electron accepting properties compared with a well-known carbazole moiety. The two sp^2 nitrogen atoms make 5*H*-pyrazino[2,3-*b*]indole electron deficient and allow it to accept electrons easily. Since the 5*H*-pyrazino[2,3-*b*]indole moiety can possess electron accepting and transport properties, the conjugated connection of the electron deficient 5*H*-pyrazino[2,3-*b*]indole and electron rich 9-phenylcarbazole may produce bipolar host materials.



Scheme 1. Synthetic scheme of **CzPhPz**.

First of all, synthesis of the strong electron-acceptor unit, 5*H*-Pyrazino[2,3-*b*]indole, (Scheme 1) began with commercially available 1-acetyl-1*H*-indol-3(2*H*)-one, which reacted under LDA/-78 °C/ *N*-phenyl-*bis*(trifluoromethanesulfonimide) condition to give

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triflate **1** (77%) that was subsequently treated with ethylenediamine in the presence of Pd(PPh_3)$_4$ in DMF to form the desired 5*H*-Pyrazino[2,3-*b*]indole **2** (70%). This transformation was supported (^{1}H and ^{13}C NMR) by the appearance of peaks at 8.40, 8.48 ppm and 141.6, 141.8 ppm (protons and carbons of C2 and C3 position), respectively. Synthesis of 5-(3-(9*H*-carbazol-9-yl)phenyl)-5*H*-pyrazino[2,3-b]indole (CzPhPz; **4**) began with commercially available 9*H*-carbazole, which was *N*-arylated with 1,3-dibromobenzene using Ullmann coupling reaction to give **3** (47%) that was subsequently treated with 5*H*-Pyrazino[2,3-*b*]indole to form the desired host material, CzPhPz (33%). The synthesis of the expected host materials was confirmed by ^{1}H and ^{13}C NMR, mass data. (See Fig. S1 and S2 in ESI†)

To compare the electronic character of building blocks used in this study, the molecular simulation of the carbazole and pyrazino indole moieties were carried out. (See in Fig. S3 and Table S1 in ESI†) As shown in Fig. S3, the LUMO distribution of pyrazino indole was more dispersed than that of the carbazole unit. This means that the LUMO of pyrazino indole is stabilized compared to that of carbazole unit due to electron withdrawing character of symmetric unsaturated imine nitrogen (C=N) structures in the heterocycle. Furthermore, the increased intramolecular charge transfer (ICT) characters of pyrazino indole unit make the energy of HOMO and LUMO stabilized and the energy gaps between HOMO and LUMO decrease, which would make the photoluminescence spectrum red shifted. (See in Fig. S4 in ESI†) It can be presumed from the molecular simulation results that the electron accepting properties of pyrazino indole moiety is better than that of carbazole moiety.

The thermal properties of CzPhPz were investigated by means of DSC under a nitrogen atmosphere. The glass transition temperature (T_g) of the host material was obtained from the second heating scan of the cooled glassy sample after the first up to their melting temperature (T_m). Its T_g and T_m were found to be 83 ^{o}C and 188 ^{o}C, respectively. (See in Fig. S5 in ESI†) The T_g is higher than that of the *N,N'*-dicarbazolyl-3,5-benzene (55 ^{o}C)[7] due to an enhanced intermolecular interaction between electron-rich carbazole and electron-deficient heteroaromatic moiety. It is even higher than T_g of 9-(3-(9*H*-carbazol-9-yl)phenyl)-9*H*-pyrido[2,3-b]indole (75 ^{o}C) with pyridine instead of pyrazine.[5(c)] One additional nitrogen of pyrazine strengthens the intermolecular interaction and increases the T_g of the host material.

Fig. 1 shows spatial distributions of the HOMO and LUMO of the CzPhPz that calculated with the Gaussian 03 program at the B3LYP/6-31G(d) level, using the density function theory (DFT) for the geometry optimizations. Triplet energy was calculated as the energy difference between the first excited triplet state and the ground singlet state. The calculated HOMO energy of CzPhPz was estimated to be -5.45 eV, and the LUMO energy was -1.65 eV. We also calculated the triplet energy level to be 2.94 eV using the same basis set, suggesting an effective triplet exciton confinement of phosphorescent blue emitters in CzPhPz. As shown in Fig. 1, the HOMO of CzPhPz was localized on the carbazole unit, while the LUMO of CzPhPz was dispersed over the pyrazino indole unit. The HOMO and LUMO of CzPhPz were separated due to the hole transport character of carbazole and electron transport character of pyrazino indole unit.

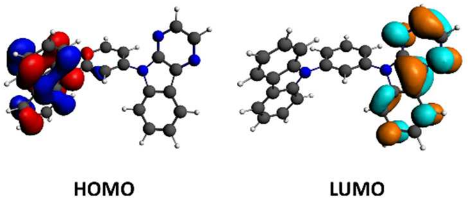

Fig. 1 HOMO and LUMO distribution of CzPhPz.

Fig. S6 shows UV/vis absorption and solution photoluminescence (PL) spectra of CzPhPz in various solvents under room temperature. The UV/vis absorption spectra in 1,3-Dioxane, CH_2Cl_2, and DMSO solvents are almost irrespective of solvent polarity. It implies that the Franck-Condon excited-state is subject to a rather small dipolar change with respect to the ground state. However, the peaks in the solution PL spectra moved significantly to longer wavelength according to increasing the solvent polarity. This phenomenon should be explained by a mechanism involving rapid photoinduced electron transfer between the carbazole donor and the pyrazino indole acceptor units, resulting in a large change in the dipole moment in the excited state; a subsequent solvent relaxation process leads to the solvent polarity-dependent emission.[8] Plotting the emission peak frequencies of CzPhPz in various organic solvents as a function of solvent polarities, we obtained almost linear relationship together with a slope as steep as -4179 cm^{-1}, consistent with our assignment of a charge-transfer emission (see Fig. S7 in ESI†).

Photophysical properties of CzPhPz was estimated by using UV/vis and PL spectrometer. UV/vis absorption, solution PL and low temperature PL emission spectra of CzPhPz are shown in Fig. 2. The UV/vis absorption spectrum of CzPhPz shows strong absorption peaks corresponding to π–π* absorption of the carbazole linked pyrazino indole backbone appeared below 300 nm. Also, the host material exhibits weak absorption bands between 310 nm and 370 nm assigned to n–π* transition of the carbazole and pyrazino indole moiety.[9] The triplet energy of CzPhPz was 2.83 eV, which could be calculated from the first phosphorescent emission peak of low temperature (77 K) PL spectrum at 438 nm. The triplet energy was high enough to use the host material as a blue phosphorescent dopant. The triplet energy of the *bis*[2-(4,6-difluorophenyl)pyridinato-C^2,*N*](picolinato)iridium(III) (FIrpic) dopant is 2.62 eV[10] and effective energy transfer from synthesized host material to FIrpic dopant is expected.

On the basis of the evaluated electrochemical oxidation onset potential, the HOMO level of CzPhPz was estimated as -6.20 eV. Its LUMO level was -2.94 eV, calculated from the HOMO level and energy bandgap determined from the UV/vis absorption threshold.

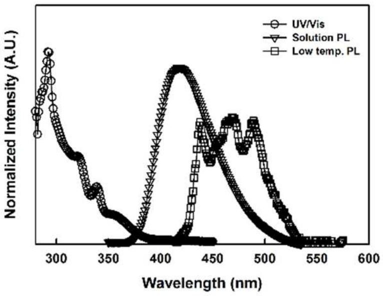

Fig. 2 UV/vis, solution PL and low temp. PL spectra of CzPhPz (emission was excited at 340 nm).

CzPhPz-based hole- and electron-only devices were fabricated to compare the hole and electron density in the host material. Fig. 3 shows the current density-voltage curves of hole- and electron-only devices bearing CzPhPz. The electron current density of CzPhPz was much higher than the hole current density, suggesting electron transport character of the CzPhPz host material. Strong electron deficiency of pyrazine unit of 5*H*-pyrazino[2,3-*b*]indole moiety contributed to the electron transport character of CzPhPz. Although CzPhPz was developed as a bipolar host material, electron transport character was stronger than hole transport character.

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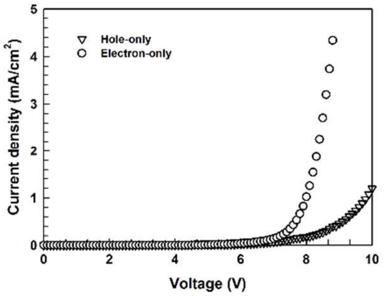

Fig. 3 Current density-voltage of hole- and electron-only devices made of CzPhPz.

The HOMO/LUMO and high triplet energy of CzPhPz enabled the fabrication of blue PHOLEDs using blue emitting FIrpic. The device performances of blue PHOLED with the CzPhPz host were investigated by changing the doping concentration of the blue-emitting FIrpic dopant from 5% to 30%. Fig. 4 shows the current density and luminance plots against driving voltage of blue PHOLEDs with the CzPhPz. As shown in Fig. 4, the current density was decreased as increasing the doping concentration. This decreasing tendency is caused by the charge-trapping effect of the FIrpic dopant. Electrons are mostly trapped by FIrpic and the current density was decreased by the electron trapping at high doping concentration. The luminance showed a similar trend as that of the current density.

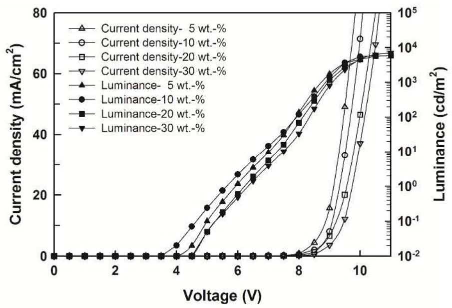

Fig. 4 Current density-voltage-luminance curves of CzPhPz device.

Quantum efficiency plots against luminance CzPhPz-based PHOLED devices are presented in Fig. 5. The quantum efficiency was calculated from the current density and luminance by assuming Lambertian distribution of light emission. The quantum efficiency was increased as increasing the doping concentration of host material and a maximum quantum efficiency of 15.0 % was obtained at 30% doping concentration. Moreover, the quantum efficiencies at 1000 cd/m^2 luminance was 11.2 %. The high quantum efficiency of the highly doped device can be explained by electron trapping of FIrpic dopant. In the single carrier device data, the CzPhPz host exhibited higher electron current density than hole current density. Therefore, holes and electrons balance in the emitting layer is improved by reducing the electron density in the emitting layer. As shown in the current density-voltage plots, the current density was decreased at high doping concentration by the decrease of electron density caused by electron trapping by FIrpic dopant. The reduction of electron density improves charge balance and upgrades the quantum efficiency of the highly doped CzPhPy devices.

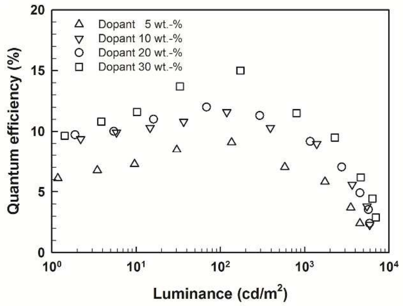

Fig. 5 Quantum efficiency-luminance curves of CzPhPz device.

Blue emission spectra with a maximum emission peak at 473 nm were obtained from the blue PHOLEDs. (Fig. 6) Only FIrpic emission peak was detected with no other emission from CzPhPz, implying exciton confinement and complete energy transfer from CzPhPz to FIrpic dopant. The color coordinates of the CzPhPz devices was presented in Table S2. Because of the intermolecular interaction between dopant materials, the slight red-shift of the color coordinate was occurred as increasing doping concentration.

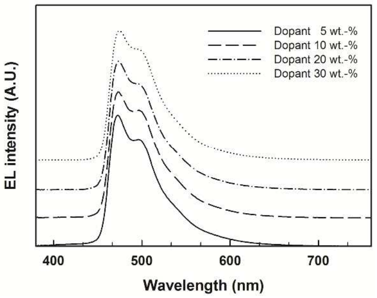

Fig. 6 Electroluminescence (EL) spectra of CzPhPz device.

In conclusion, CzPhPz with 5*H*-pyrazino[2,3-*b*]indole as an electron transport moiety was synthesized as the high triplet energy host material by coupling between 9-phenylcarbazole and 5*H*-pyrazino[2,3-*b*]indole. CzPhPz showed good electron transport properties and a high triplet energy of 2.83 eV. The application of the CzPhPz compound as the host material for blue triplet emitter produced a blue PHOLED with a high quantum efficiency of 15.0 %.

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Notes and references

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