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Synthesis of Pyrimidine-cored Host Materials Bearing Phenylcarbazole for Efficient Yellow Phosphorescent Devices: Effect of Linkage Position

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Two isomeric host materials were synthesized and their photophysical properties and device performances were investigated. In particular, para-substituted pPDPC exhibited the most intense efficiency regardless of the low triplet energy compared to that of meta-substituted mPDPC. EQE of the pPDPC device reached as high as 22.3% with a yellow color coordinate of (0.49, 0.50).

During the past decade, the development of organic light emitting devices (OLEDs) has drawn tremendous attention due to their unique features including large area, flexibility, fast response, high efficiency, lifespan, manufacturing cost, driving voltage, high brightness, etc. in full-color flat-panel displays and solid-state lighting applications.¹⁻⁴ To fabricate a high efficiency OLED, phosphorescent material based devices have been used because they can harvest both singlet and triplet excitons for light emission, providing the opportunity to accomplish internal electroluminescence (EL) quantum efficiency of close to 100%.⁵ From molecular design perspective in PHOLEDs, a host material plays a key role in determining the device performance, such as external quantum efficiency, current efficiency, and lifetime through charge balance and energy transfer. As we know, the host material reported in 1998 was the CBP (4,4'-bis(N-carbazolyl)-2,2'-biphenyl) molecule which consists of two carbazole moieties and a biphenyl group and its concise synthetic route makes it widely used in PHOLED research field.² Although numerous host materials have been developed to date, the carbazole derivatives are still the most favorable building units in design of the most effective host materials for PHOLEDs, because the derivatives can be readily modified to fulfill the requirements for designing a good host, e.g. high triplet energy level, good thermal stability, appropriate transport mobility and matched HOMO and LUMO levels.⁶ Unfortunately, the lack of electron transporting property in carbazole derivatives usually requires the attachment of electron withdrawing group to balance the carrier transport.⁷ Therefore, we selected pyrimidine moiety as the electron acceptor due to the more electron-deficient nature.8

Since the yellow PHOLED can be used as a lighting source for lithography labs, traffic lights, and signal lights, it can also be a major color component for displays such as RGBY-TV. In this



carbazole) (mPDPC), comprised of pyrimidine moiety and two *N*-phenylcarbazole units and could be quite simply prepared. By altering the linking positions such as para- or meta-position, the effect of their isomeric molecular structures on the device performances was evaluated.



Scheme 1. Reagents and conditions: (i) dihalobenzene, CuI, K_2CO_3 , 18-Crown-6, DMF, 130°C, 24hrs; (ii) KOAc, Pd(dppf)Cl₂, 1,4-dioxane, reflux, 12hrs; (iii) K_2CO_3 , Pd(PPh₃)₄, toluene, reflux, 36hrs.

Scheme 1 showed the synthetic route toward isomeric host materials, pPDPC and mPDPC. Synthesis of the host materials began with commercially available 9*H*-carbazole, which was *N*-arylated with 1,4-dibromobenzene or 3-bromoiodobenzene using Ullmann coupling reaction to give **1** (47%) and **2** (36%) that were subsequently treated with *bis*(pinacolato)diboron under Pd catalyzed condition (Miyaura borylation reaction) to form the desired

intermediates, **3** (68%) and **4** (62%). These transformations were supported by the new singlet peaks for **3** and **4** at 1.44 and 1.37 ppm (- CH_3) in the ¹H NMR spectra, respectively. The intermediates were coupled with 5-bromo-2-iodopyrimidine by Suzuki-Miyaura coupling reaction under basic condition to form the desired pPDPC (37%) and mPDPC (39%). The desired host materials were fully characterized by ¹H NMR, ¹³C NMR, and mass spectrometry. The detailed synthetic procedures and structural characterizations were presented in the electronic supplementary information.

The thermal stabilities of the pPDPC and mPDPC were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. The glass transition temperatures of pPDPC and mPDPC were clearly observed at 128 °C and 119 °C, respectively. In addition, the decomposition temperatures at which initial 5 wt.-% loss of mass were 437 °C (pPDPC) and 440 °C (mPDPC). The molecular configurations of two isomeric host materials should provide them with high thermal stability. As results, these host materials should construct homogeneous and stable amorphous films upon thermal evaporation. Also, they should be suitable to use as PHOLED component for long lifetime. (See Fig. S3 and S4 in ESI[†])

In order to gain insight into the electronic structures of the pPDPC and mPDPC hosts, their theoretical molecular orbital distributions were calculated with the Gaussian program at the B3LYP/6-31G(d) level, using the density function theory (DFT) for the geometry optimizations. As shown in the Fig. 1, the highest occupied molecular orbitals (HOMOs) of both host materials were mostly dispersed on the electron-rich unit of carbazole moiety. In contrast, their lowest unoccupied molecular orbitals (LUMOs) were localized on the electron-deficient unit of pyrimidine together with two phenyl moieties. The clear separation of the HOMO and LUMO suggested that the HOMO-LUMO excitation would shift the electron density distribution from the donor carbazole moiety to the acceptor pyrimidine moiety, leading to a polarized excited state. It is more important, such separation of HOMO and LUMO can provides hole-and electron-transporting channel respectively.

mPDPC

pPDPC



Fig. 2 presented the UV/vis absorption, photoluminescence (PL), and low-temperature PL emission spectra of the synthesized host materials in dilute solution. The relatively weak peaks at around 340 nm which appeared in absorption spectra of all these materials can be attributed to the $n-\pi^*$ transitions of extended conjugation of the carbazole moiety. And the absorption peaks below 290 nm could be assigned to $\pi-\pi^*$ transitions of carbazole moiety.⁹ The optical bandgaps of pPDPC and mPDPC were calculated from the absorption edges of the UV/vis spectra. The calculated optical bandgaps from the data acquired for pPDPC and mPDPC were 3.14 and 3.54 eV, which corresponded to absorption edges of 396 and

350 nm, respectively. The bandgap discrepancy of the isomeric host materials should be induced by more extended conjugation length of para-substituted pPDPC compared to meta-substituted mPDPC. The solution PL emissions of pPDPC and mPDPC were observed at 427 and 441 nm, respectively. The narrow bandgap of pPDPC contributed to the small red-shift (14 nm) of the PL emission peak compared to that of mPDPC. The first phosphorescent emission peak of low temperature (77K) PL emission spectra for the pPDPC and mPDPC were observed at 428 and 441 nm, which corresponded to their triplet energies of 2.40 and 2.50 eV, respectively. The triplet energy of mPDPC was higher than that of pPDPC due to effective breaking of conjugation through meta-substitution of the mPDPC. Because the triplet energies of the host materials were higher than the estimated value for iridium(III) bis(4-phenylthieno[3,2c]pyridinato-N,C2')acetylacetonate (PO-01) ($E_T = 2.20 \text{ eV}$),¹⁰ they were sufficient to be used as host materials in PO-01 based vellow PHOLEDs. As reported previously, the higher triplet energy of the host material would facilitate energy transfer from the host to the dopant in host-guest system.¹¹ Accordingly, the two isomeric host materials can be effective in the phosphorescent devices because energy transfer from the dopant to the host is prevented, and thus, triplet excitons in the guest are effectively confined to the emission zone



Fig. 2 UV/vis absorption and PL spectra of pPDPC and mPDPC.

The cyclic voltammetry (CV) of the host materials was measured in CH_3CN to study the energy levels of the host materials. The HOMO levels of pPDPC and mPDPC were calculated from the electrochemical oxidation onset potential peaks in cyclic voltammogram. During the first anodic scan, all the materials exhibited an irreversible oxidation peaks at around 1.75 eV. (See Fig. 5 in ESI[†]) These peak irreversibility indicated the short lifetime of the radical ions formed during the electrochemical processes. Their HOMO levels were calculated as -6.01 and -6.08 eV, respectively. The LUMO levels of them were -2.88 and -2.54 eV, calculated from the HOMO level and energy bandgaps determined from the UV/vis absorption threshold.

To understand the hole and electron density of host materials, holeand electron-only devices composed of pPDPC and mPDPC were fabricated as follow structures: ITO/PEDOT:PSS (60nm)/TAPC (20nm)/mCP (10nm)/ Host (25nm)/TAPC (5nm)/Al (hole); ITO/PEDOT:PSS (60nm)/TSPO1 (10nm)/Host (25nm)/TSPO1 (5nm)/TPBi (30nm)/LiF (0.15nm)/Al (electron). Fig. 3 showed the current density-voltage curves of hole- and electron-only devices bearing pPDPC and mPDPC. Considering the molecular structures of isomeric host materials, the hole current density of pPDPC and mPDPC was higher than their electron current density due to the carbazole unit. Furthermore, hole and electron current densities of

HOMO

LUMO

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pPDPC were higher than those of mPDPC, which indicates that pPDPC shows better performance than mPDPC, in terms of charge transportation. Generally, the hole and electron current densities reflect charge injection and charge transport properties. From the hole- and electron-only devices, carbazole unit should play a role of strong hole transporting unit and pyrimidine unit should work as a strong electron transporting unit, indicating the balance of hole and electron in the emitting layer.



Fig. 3 Current density-voltage curves of hole- and electron-only devices for pPDPC and mPDPC.

Since the isomeric host materials showed the suitable HOMO/LUMO levels for good hole and electron injection and enough triplet energy for energy transfer to yellow emitting PO-01, they were examined as the host materials for the yellow PHOLEDs. Fig. 4 showed the current density-voltage-luminance curves of the yellow PHOLEDs with two different structural isomers as host materials. The yellow-emitting PO-01 dopant was optimized at a doping concentration of 5 wt.-% and the device performances were compared. The current density in the pPDPC device was higher than that in the mPDPC device, as predicted by hole- and electron-only device data. The luminance showed the same tendency as the current density.



Fig. 4 Current density-voltage-luminance curves of pPDPC and mPDPC yellow PHOLEDs.

We investigated the device performances based on two structural isomeric hosts and also compared them with commercial available host, 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP), based yellow PHOLED. Quantum efficiency-luminance curves of the yellow PHOLEDs based on pPDPC, mPDPC and CBP were depicted in Fig. 5. The quantum efficiency of pPDPC yellow device was better than

those of the mPDPC- and CBP-based yellow devices. The maximum quantum efficiency of the pPDPC, mPDPC and CBP devices were 22.3, 19.7 and 18.8%, while the quantum efficiencies at 1000 cd/m^2 of pPDPC, mPDPC and CBP devices were 19.2, 15.8 and 16.1%, respectively. These results imply that the design concept for constructing new bipolar hosts is adequate to improve the efficiency of PHOLEDs. The much higher quantum efficiency of pPDPC device could be explained by the efficient energy transfer, balanced charge density and exciton confinement in the emitting layer. The higher quantum efficiency of the pPDPC device is due to better charge balance as can be proved by the hole and electron current density of the hole and electron only devices. In addition to that, the maximum current efficiency of pPDPC yellow was 68.3 cd/A, and the maximum power efficiency was 47.5 lm/W as best value most of all. (See Fig. S6 and S7 in ESI⁺)



Fig. 5 Quantum efficiency-luminance curves of yellow PHOLEDs based on pPDPC, mPDPC and CBP.

The electroluminescence (EL) spectra of the yellow PHOLEDs were shown in Fig. 6. As shown in Fig. 6, the yellow emission spectra were observed with a maximum emission peak around 558 nm and vibrational shoulder peak around 590 nm of typical PO-01 based devices. Only these two emission peaks implied that complete energy transfer from the hosts (pPDPC, mPDPC and CBP) to the PO-01 dopant and charge confinement were occurred inside the emitting layer. Consequently, high quantum efficiencies were achieved in the yellow PHOLED with pPDPC and mPDPC host materials. The color coordinate of the yellow PHOLEDs were (CIE_{x,y}= 0.49, 0.50) for pPDPC device, (CIE_{x,y}= 0.50, 0.50) for mPDPC device and (CIE_{x,y}= 0.50, 0.50) for CBP device, respectively.



Fig. 6 EL spectra of yellow PHOLEDs based on pPDPC, mPDPC and CBP.

In conclusion, two structural isomers comprised of pyrimidine and phenylcarbazole moieties were synthesized as new bipolar host materials for yellow PHOLED, successfully. All the compounds could be afforded by a facile synthetic route. Although relatively low triplet energy was obtained in pPDPC incorporating a pyrimidine on phenylcarbazole with para-position, it exhibited better charge transport properties compared to those of mPDPC. These phenomena led to increasing the maximum quantum efficiency, current efficiency and power efficiency. Using the employed PO-01 based yellow device structures, the maximum quantum efficiency, current efficiency and power efficiency of the pPDPC device were as high as 22.3%, 68.3 cd/A and 47.5 lm/W, respectively. This newly designed host materials should be useful for the future development of host materials for yellow PHOLEDs as well as white PHOLEDs.

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Notes and references

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