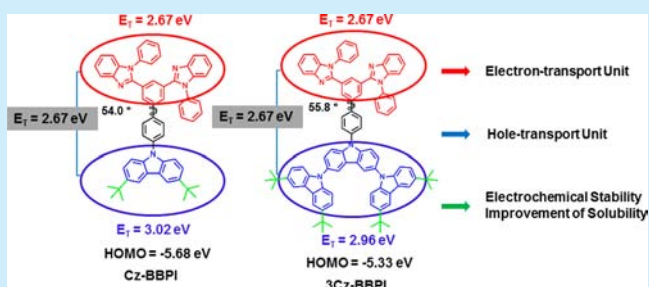


Ideal Bipolar Host Materials with Bis-benzimidazole Unit for Highly Efficient Solution-Processed Green Electrophosphorescent Devices

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Supporting Information

ABSTRACT: An ideal host material with high triplet energy, suitable HOMO energy level, excellent thermal and electrochemical stability, and bipolar charge carrier transport ability was synthesized. A high external quantum efficiency of 13.7% and a luminance efficiency of 48.2 cd A⁻¹ with low efficiency roll-off were achieved in solution-processed green electrophosphorescent devices.



Phosphorescent organic light-emitting diodes (PhOLEDs) employing triplet emitters doped into a host material have attracted significant attention because of their high efficiencies as a result of the utilization of singlet and triplet excitons for emission.¹ While vacuum deposited PhOLEDs with very high efficiencies have been demonstrated, solution-based PhOLEDs are economically highly desired to low-cost and large-area lighting devices.² To suppress severe concentration quenching and triplet-triplet annihilation, the triplet emitter is usually dispersed into an appropriate host. Thus, promotion of host materials is the key to highly efficient PhOLEDs. An ideal host material for solution-processed PhOLEDs should satisfy the following requirements: (1) high triplet energy, (2) good charge carrier transport property, (3) appropriate high occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, (4) high solubility and film-forming ability. To date, a large number of solution-processed PhOLEDs with poly(*N*-vinylcarbazole) (PVK) as the host material have been reported.³ It is known that PVK-based devices usually have relatively high operational voltages owing to its low HOMO level and a large barrier with the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer.⁴ For purposes of balancing charge fluxes in the emitting layer (EML), a large amount of electron-transporting material must be admixed with PVK to improve electron transporting, such as 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) and 1,3-bis[4-*tert*-butylphenyl-1,3,4-oxadiazolyl]phenylene (OXD-7), which may lead to phase separation.^{2b} Considering the high purity and structural uniformity features of small molecules, solution-processed PhOLEDs using small molecules as the host material may serve as an approach to resolving such a problem. However, due to poor film morphology and high crystallization tendency, the widely used small-molecule-based host materials (such as

mCP and CBP) for vacuum deposition are almost unsuitable for the solution process.

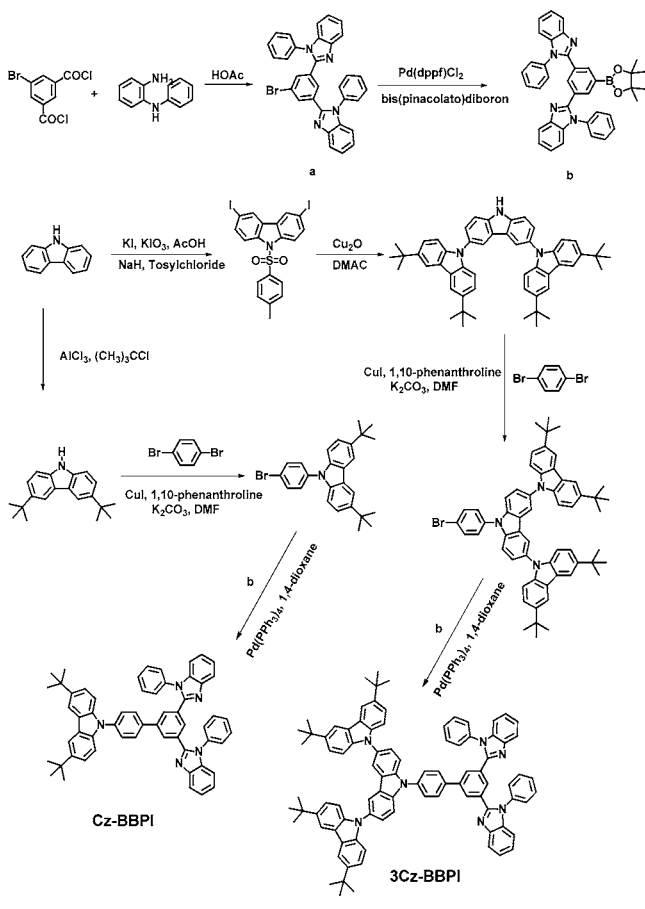
In this communication, we report two novel bipolar host materials, 9-(3',5'-bis(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)-3,6-ditert-butyl-9*H*-carbazole (Cz-BBPI) and 9-(3',5'-bis(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)-3,3'',6,6''-tetra-*tert*-butyl-9'*H*,9,3':6',9''-tercarbazole (3Cz-BBPI), which use carbazole units as the electron donor and benzimidazole units as the electron acceptor. As shown in Scheme 1, the newly synthesized compounds meet almost all the requirements of an ideal host material for solution-processed PhOLEDs. First, the twisted configuration and meta-position linkage mode keep the molecules at high triplet energy levels and enhance the thermal stability with high glass transition temperatures. Second, carbazole units and benzimidazole units are introduced to the molecular structure to achieve bipolar transporting, which can balance charge refluxes and broaden the recombination zone, thereby reducing the efficiency roll-off. In addition, the bipolar transport nature of host materials avoids the need of a mixed host system and prevents phase separation in EML. Third, *tert*-butyl groups improve the solubility and film-forming properties of compounds in common solvents and protect the electrochemically active sites of carbazole units, keeping hosts stable when they transport positive charge carriers in devices. Finally, the HOMO energy levels can be adjusted to approach the work function of PEDOT:PSS, facilitating the injection of holes to EML and reducing the turn-on voltage.

The synthetic routes are illustrated in Scheme 1. The reaction of 5-bromoisophthaloyl dichloride *N*-phenylbenzene-

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Scheme 1. Synthetic Routes toward Cz-BBPI and 3Cz-BBPI



1,2-diamine gave 2,2'-(5-bromo-1,3-phenylene)bis(1-phenyl-1H-benzo[*d*]imidazole) (a) in 60% yield, which then converted to the arborboronic ester of 2,2'-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-phenylene)bis(1-phenyl-1H-benzo[*d*]imidazole) (b) catalyzed by PdCl₂(dppf) in the presence of KOAc. 9-(4-Bromophenyl)-3,6-di-*tert*-butyl-9H-carbazole and 9-(4-bromophenyl)-3,6-bis(3,6-di-*tert*-butyl-carbazol-9-yl)-carbazole were prepared following the literature method.⁵ Finally, Cz-BBPI and 3Cz-BBPI can easily be synthesized by a Suzuki cross-coupling reaction with moderate yields. The structures of hosts are confirmed by ¹H NMR, ¹³C NMR, mass spectrometry, and elemental analysis, as described in the experimental section. As shown in Figure S9 in Supporting Information, Cz-BBPI and 3Cz-BBPI both exhibit excellent thermal stability at the decomposition temperatures (*T*_d, 5% weight loss) of 417 and 514 °C, with the glass transition temperatures (*T*_g) of 161 and 228 °C, respectively. With two extra carbazole units in the structure, 3Cz-BBPI showed much higher *T*_d and *T*_g values than Cz-BBPI. The thermal properties of Cz-BBPI and 3Cz-BBPI are substantially superior to those of analogous carbazole-based host materials, such as mCP and CBP.⁶ The high quality of spin-coated thin films of Cz-BBPI and 3Cz-BBPI doped with 8% Ir(mppy)₃ is investigated by AFM with the surface roughness of 0.56 and 0.32 nm, respectively. No phase separation or any aggregation is observed. The results demonstrate that these host materials are capable of forming uniform amorphous films, which are one of the key factors for highly efficient solution-processed PhOLEDs.

To understand the electronic states of host molecules, density functional theory (DFT) calculations are performed. The results reveal that the HOMO and LUMO electron density distributions of Cz-BBPI and 3Cz-BBPI are similar mainly on the electron-donating carbazole and the electron-accepting benzimidazole fragments. The separation of HOMO and LUMO is believed to benefit the charge transport properties. For Cz-BBPI, the HOMO is mainly concentrated in the 9-phenylcarbazole unit, while the HOMO of 3Cz-BBPI is distributed over the whole tricarbazole moiety. Thus, the calculated HOMO value of 3Cz-BBPI is 0.25 eV higher than that of Cz-BBPI, which better matches the work function of PEDOT:PSS for the injection of holes. As shown in Figure 1b,

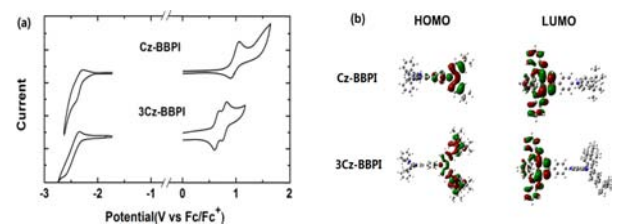


Figure 1. (a) Electrochemical properties of Cz-BBPI and 3Cz-BBPI. (b) Calculated HOMO and LUMO density maps for Cz-BBPI and 3Cz-BBPI.

the dihedral angles of the biphenyl unit in Cz-BBPI and 3Cz-BBPI are 54.0° and 55.8°, respectively. The highly twisted configurations of host molecules allow the separation of HOMO and LUMO, which is the key point for high triplet energies. The cyclic voltammetry is used to investigate electrochemical properties of host materials. Cz-BBPI and 3Cz-BBPI exhibit similar reversible oxidation and irreversible reduction processes, which arise from their electron-donating carbazole unit and electron-accepting benzimidazole unit. These behaviors indicate that Cz-BBPI and 3Cz-BBPI possess bipolar carrier transport characteristics, which are further confirmed by hole-only and electron-only devices. As shown in Figure S11 in Supporting Information, the hole current density of 3Cz-BBPI device is much higher than that of Cz-BBPI, while the electron current density of 3Cz-BBPI and Cz-BBPI are similar. There is a slight difference of the hole and electron current density in 3Cz-BBPI, which indicated the charge transport property of 3Cz-BBPI is more balanced. It is worth noting that the oxidation curves show no change during the repeated anodic scans, which can be attributed to the blocking of electrochemically active sites of carbazole units, improving the electrochemical stability of the host materials.⁷ On the basis of the onset potentials for oxidation and reduction, the HOMO and LUMO values of Cz-BBPI and 3Cz-BBPI are estimated to be -5.68, -2.51, -5.33, and -2.52 eV, respectively.

The newly synthesized host materials exhibit almost the same photophysical properties. The UV-vis absorption and photoluminescence (PL) spectra of Cz-BBPI and 3Cz-BBPI are shown in Figure 2. In the UV-vis spectra, the strong absorption bands observed around 296 nm for Cz-BBPI and 3Cz-BBPI can be assigned to the *n*- π^* transitions of the carbazole moiety, while the longer-wavelength weak absorption at around 347–353 nm could be attributed to the π - π^* transitions from the electron-donating carbazole moiety to the electron-accepting benzimidazole moiety.⁸ Cz-BBPI and 3Cz-BBPI show deep blue emission with peaks at 414 and 418 nm,

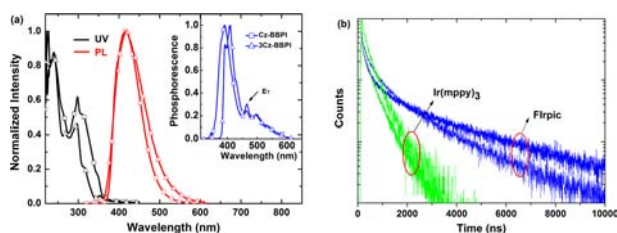


Figure 2. (a) Absorption and emission spectra in CH_2Cl_2 and phosphorescent spectra in 2-methyltetrahydrofuran at 77 K. (b) Transient photoluminescence decay curves of FIrpic and $\text{Ir}(\text{mppy})_3$ doped films monitored at 470 and 520 nm, respectively.

respectively. The triplet energies (E_T) of Cz-BBPI and 3Cz-BBPI determined by the phosphorescence spectra at 77 K are both 2.67 eV, which is higher than that of $\text{Ir}(\text{mppy})_3$ (2.40 eV) and FIrpic (2.62 eV), implying that they might be used as host materials for green and blue triplet emitters. To further confirm their exciton confinement property, transient photoluminescence decays of Cz-BBPI and 3Cz-BBPI films doped with 5% FIrpic and $\text{Ir}(\text{mppy})_3$ are measured. As shown in Figure 2b, the decay curves of FIrpic-doped films are multiexponential with long decay components, which demonstrate the exothermic back energy transfer from FIrpic to host materials, while $\text{Ir}(\text{mppy})_3$ -doped films exhibit monoexponential decay curves, indicating that the triplet energy transfer from $\text{Ir}(\text{mppy})_3$ to hosts are completely suppressed.⁹ The results indicate that the E_T 's of Cz-BBPI and 3Cz-BBPI are not high enough to confine the triplet excitons on FIrpic molecule and unsuitable to serve as the host for blue PhOLEDs.¹⁰ Thus, Cz-BBPI and 3Cz-BBPI are expected to be used as appropriate hosts for green PhOLEDs.

To investigate the utility of Cz-BBPI and 3Cz-BBPI as host materials for solution-processed green PhOLEDs, devices with the configuration ITO/PEDOT:PSS/Hosts: $\text{Ir}(\text{mppy})_3$ (8 wt %)/TPBi/ Cs_2CO_3 /Al have been fabricated by spin coating method. The conducting polymer PEDOT:PSS was used as the hole injection layer, Cs_2CO_3 is used as the electron-injection layer, and TPBi serves as the hole/exciton blocking and electron transport layers simultaneously. According to the J - V curves, the introduction of two carbazole units leads to a slight increase in the current density, with a decrease of turn-on voltage (corresponding to 1 cd m^{-2}) of 5.4 and 4.5 V for Cz-BBPI and 3Cz-BBPI, respectively. As shown in Figure 3a, the

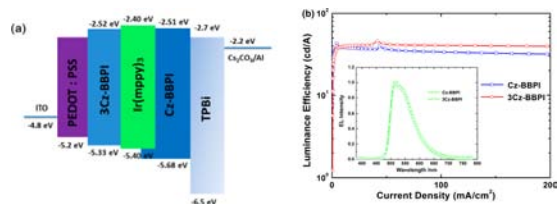


Figure 3. (a) Schematic energy-levels diagram of the devices. (b) Luminescence efficiency versus current density plots and EL spectra for the devices.

lower turn-on voltage of 3Cz-BBPI is mainly due to its high-lying HOMO level, which better matches the work function of the PEDOT:PSS layer and improves hole injection of the device. Furthermore, these devices exhibited excellent performance with a maximum luminance efficiency (LE) of 42.6 and 48.2 cd A^{-1} and a maximum external quantum efficiency of

12.1% and 13.7%, for Cz-BBPI and 3Cz-BBPI, respectively. The luminance efficiency of our devices is higher than the values reported previously with polymer and small molecule hosts.¹¹ For example, Ge et al.^{11a} reported triphenylamine-benzimidazole-based bipolar hosts for solution-processed green PhOLEDs with a turn on voltage of 6.9 V and the maximum LE value of 27.3 cd A^{-1} , and Li et al.^{11b} reported green PhOLEDs using carbazole-based dendritic as hosts with a turn on voltage of 4.5 V and the maximum LE value of 38.7 cd A^{-1} . The electroluminescence spectra of devices is green emission with the Commission Internationale de L'Eclairage coordinates of (0.34, 0.60), corresponding to the emission of $\text{Ir}(\text{mppy})_3$. No additional emission from the host materials is observed, which indicated efficient energy transfer from the hosts to the triplet emitter.

It is noteworthy that these devices exhibit rather low efficiency roll-off. Even though the LE values decrease gradually as the current density increases, the luminance efficiency is still 36.3 and 42.1 cd A^{-1} with a brightness of 1000 cd m^{-2} for Cz-BBPI and 3Cz-BBPI, respectively. The high efficiencies and low efficiency roll-off at high brightness for PhOLEDs can be mainly attributed to the use of the bipolar host materials, which balance charge fluxes and broaden the recombination region on the emitting layer. The improvement of hole and electron injection and excellent thermal and electrochemical stability also make considerable contributions to the device performance.

In summary, we have designed and synthesized two novel bipolar host materials Cz-BBPI and 3Cz-BBPI for solution-processed green PhOLEDs. These host materials satisfy the requirements of an ideal host material for solution-processed green PhOLEDs, because they have a high triplet energy level, excellent thermal and electrochemical stability, bipolar charge transport character, solubility and film-forming property, and appropriate HOMO energy level at the same time. When these new compounds are used as host materials, solution-processed green PhOLEDs with $\text{Ir}(\text{mppy})_3$ as a dopant show a maximum current efficiency of 48.2 cd A^{-1} and a maximum external quantum efficiency of 13.7%. The performance of Cz-BBPI- and 3Cz-BBPI-based devices are among the highest for solution-processed green PhOLEDs. Our work paves the way to designing ideal host materials for solution-processed PhOLEDs.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and characterization details of the new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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