



# Enhanced efficiency in nondoped, blue organic light-emitting diodes utilizing simultaneously local excitation and two charge-transfer exciton from benzimidazole-based donor–acceptor molecules



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## ABSTRACT

The simultaneous utilization of all charge-transfer excitons and local excitons is the pathway to obtain the high efficiency fluorescent organic light-emitting diodes (FOLEDs). Here, a twisted intramolecular charge transfer state (TICT-state), a planar intramolecular charge transfer state (ICT-state), and a locally excited state (LE-state) are demonstrated to enhance the occurrence of singlet excitons in the fluorescent emitters, which are based on benzimidazole and triphenylamine donor–acceptor derivatives. The synthesis, photophysics and electroluminescent (EL) performance are studied systematically. The fluorescence emitters (TPABBBI and TPABBI) with the special TICT and ICT characteristics realize the electron–hole (e–h) recombination via intramolecular conversion from charge-transfer excitons to radiative singlet exciton. The devices based on them show high efficiency (5.1 cd/A, 5.77 lm/W, 5.66% of EQE<sub>m</sub> for TPABBBI and 3.56 cd/A, 3.11 lm/W, 4.23% for TPABBI), low efficiency roll-off at high luminance and stable blue emission.

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## 1. Introduction

Organic light-emitting diodes (OLEDs) have attracted extensively attention for their potential applications in both full-color display [1] and solid-state lighting [2]. In the past decades, much effort has been paid to the development highly performance and full-color OLEDs, nearly 100% internal electroluminescence (EL) quantum efficiency ( $\eta_{\text{int}}$ ) has been achieved by employing transition metal-centered phosphorescent emitters such as iridium (III) and platinum (II) complexes, which can harvest both singlet and triplet excitons by fast intersystem crossing (ISC) for phosphorescent emission [3–5]. However, the efficiency and stability of blue electroluminescent emitters are still lacking compared to the reported green and red emitters. Moreover, a severe efficiency roll-off at high current densities is observed in these devices owing to the triplet-polaron or triplet–triplet exciton annihilation (TTA) [6].

In view of this, OLEDs incorporating fluorescent emitters should be given considerable concern due to their remarkably high reliability and stability. However, the  $\eta_{\text{int}}$  of fluorescent OLEDs (FOLEDs) is limited 25% because of the spin statistical limit of 1:3 for the singlet to triplet excitation ratio under electrical excitation [7].

Hence, it still remains a challenge to develop efficient luminescent materials to generate high performance fluorescent OLEDs. Recent works pointed to a significant role of intermediate charge transfer (CT) state to form radiative exciton or used radiative CT excitation immediately for improving the efficiency of FOLED [8]. Segal et al. demonstrated a device to improve the  $\eta_{\text{int}}$  of Alq<sub>3</sub> from 25% to 84% by adding a mixing layer to change interaction of CT states [9]. Very recently, Adachi and co-workers put forward a promising viable mechanism to realize higher efficiency OLEDs by using the high reverse intersystem crossing efficiency of the intermolecular CT state between electron-donating and electron-accepting molecules [10–12]. Ma et al. [13] reported a twisting donor–acceptor fluorescent molecule that utilized energy of the CT-state and locally excited state to obtain high-efficiency electroluminescence with a maximum external quantum efficiency >5.0%, corresponding to the  $\eta_{\text{int}}$  >25%. Although the CT-state and locally excited state models have been widespread acceptance and appear to be conclusion of the results. However, there are still some points that arise leading to doubt or contrary the interpretation. For example, both the twisted angle necessary and excited-state CT equilibria are not quite clear [14]. Herein, we choose benzimidazole containing triphenylamine unit as emitters to realized radiative exciton with high yield by intermediate CT-State in the exciton formation process, and gained some new insights into the CT-States in the two novel pretwisted D-A system. Commonly, imidazole-based donor–

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acceptor molecules are made up an imidazole and arylamine units. In these molecules, their N-substituted benzene rings were highly twisted about the imidazole plane [15]. It can be expected to help suppress fluorescence quenching caused by aggregation in the solid state. Moreover, their donor units also twisted with the imidazole plane with different dihedral angles. These would reduce the extent of conjugation in the molecules and thus the amount of charge transfer from the donor (arylamine) to the acceptor (imidazole) [15]. In addition, a large difference in the dipole moment between the ground states and excited states have been demonstrated [13]. These features lead to the emergence of dual or multiple fluorescence from two excited singlet states of imidazole-based donor–acceptor molecules, including LE-states and intramolecular charge transfer states [16].

In this study, we report the synthesis, characterization, photo-physical properties, and EL performances of benzimidazole containing triphenylamine donor–acceptor derivatives (TPABBBI and TPABBI). 1,2-diphenyl-1H-benzo[d]imidazole (BBI) is also synthesized for the control experiments. The synthetic routes of them are shown in Scheme 1. In these molecules, the triphenylamine moieties are attached to benzimidazole to enhance the hole-transport ability. By comparing with the BBI, TPABBBI and TPABBI exhibit the particular photophysical properties due to the presence of torsional motion in these molecules. The photoluminescent (PL) of TPABBBI and TPABBI arises from a LE- and two CT-states in solution, while the PL of them should be mainly considered as the contribution of LE-state in film state. The nondoped EL devices using the emitters (TPABBBI and TPABBI) show good performance and the  $\eta_{\text{int}}$  of them are over the limit of 25%, which can be attributed to generate the newborn local excitons and CT excitons. We estimate the maximum occurrence of singlet generation fraction is up to 75% in these devices. Our results open a pathway for obtaining high efficiency OLEDs.

## 2. Results and discussions

### 2.1. Thermal and electrochemical properties

The thermal properties of TPABBBI and TPABBI were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. Results are shown in Table 1 and Fig. 1. The decomposition temperatures ( $T_d$ ,

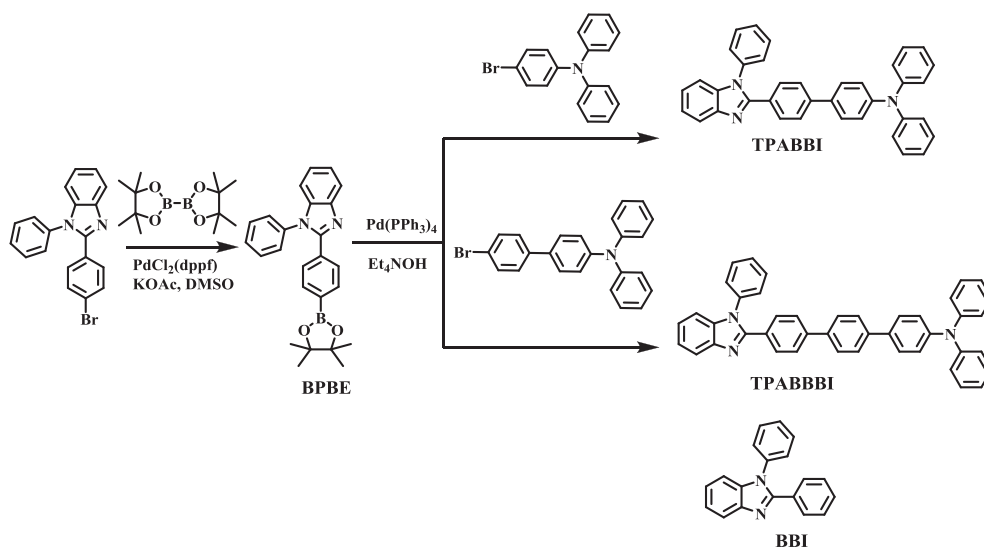
**Table 1**  
The physical properties of TPABBI, and TPABBBI.

Comp	$T_m/T_g/T_d$ (°C)	$E_{\text{onset}}$		HOMO (eV)	LUMO (eV)	Energy gap (eV)
		$E_{\text{onset}}^{\text{ox}}$	$E_{\text{onset}}^{\text{red}}$			
		V	V	Optical/ calculated	Optical/ calculated	Optical/ calculated
TPABBI	212/-/401	0.89	-1.97	-5.25/-5.17	-2.39/-1.50	2.84/3.67
TPABBBI	257/-/410	0.86	-1.88	-5.22/-5.17	-2.48/-1.61	2.74/3.56

corresponding to 5% weight loss) of them are 401 and 410 °C for TPABBI, and TPABBBI, respectively. No obvious glass transition temperatures ( $T_g$ ) are observed for them, while endothermic melting transition temperatures ( $T_m$ ) appear obviously at 212 and 257 °C for TPABBI and TPABBBI, respectively. Such high  $T_m$  and  $T_d$  values indicate that these molecules are stable and have the potential to be fabricated into devices by vacuum thermal evaporation technology. Their highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) energy levels are deduced by the results of cyclic voltammetry (CV) with three electrodes system as shown in Fig. 2. The HOMO and LUMO energy levels of TPABBI, and TPABBBI are estimated to be -5.25, -2.39, and -5.22, -2.48 eV with regard to ferrocene (-4.36 eV [17]), respectively. Obviously, the HOMO levels of these materials are elevated significantly compared to that of TPBi (HOMO level of -6.2 eV), revealing an enhanced hole injection ability. Likewise, the levels of them are at the range of -2.39 eV to -2.48 eV, which are close to that of TPBi (LUMO level of -2.7 eV), showing that the electron injection abilities of them are similar with the TPBi.

### 2.2. Theoretical calculations

To understand electronic structures of these compounds, the molecular configuration and frontier molecular orbitals were optimized using DFT at the B3LYP/6-31G(d,p) level in the Gaussian 03 software. In the optimized configurations of TPABBI and TPABBBI as shown in Fig. 3, a large dihedral angle ( $\sim 70^\circ$ ) between the N-substituted benzene and benzimidazole planes, this might prevent intramolecular extending of  $\pi$ -electron and suppress molecular packing in the solid state effectively. In addition, these molecules also show the dihedral angles between the triphenylamine moieties and benzimidazole planes with the twisting angle of  $36^\circ$  and



**Scheme 1.** The synthetic route of TPABBBI and TPABBI.

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