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Enhanced efficiency in nondoped, blue organic light-emitting diodes utilizing simultaneously local excition 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_m for TPABBBI and 3.56 cd/A, 3.11 lm/W, 4.23% for TPABBI), low efficiency rolloff 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 (η_{int}) has been achieve 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 η_{int} of fluorescent OLEDs (FOLEDs) is limited 25% because of the spin statistical limit of 1:3 for the singlet to triplet excition 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 excition immediately for improving the efficiency of FOLED [8]. Segal et al. demonstrated a device to improve the η_{int} of Alq₃ 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 η_{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, photophysical 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 η_{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
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Гhe р	hysical	properties	of TPABBI,	and 1	PABBBI.
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Comp	$T_m/T_g/T_d$ (°C)	E ^{ox} onset	<i>E</i> ^{red} _{onset} HOMO (eV)		LUMO (eV)	Energy gap (eV)	
		v	v	Optical/ calculated	Optical/ calculated	Optical/ calculated	
TPABBI TPABBBI	212/-/401 257/-/410	0.89 0.86	-1.97 -1.88	-5.25/-5.17 -5.22/-5.17	-2.39/-1.50 -2.48/-1.61	2.84/3.67 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 π -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° and



Scheme 1. The synthetic route of TPABBBI and TPABBI.



Fig. 1. a) TGA thermograms of TPABBI and TPABBBI. b) DSC trance of TPABBI and TPABBBI.

38° for TPABBI and TPABBBI, respectively. Hence, these benzimidazole derivatives are pretwisted D-A molecules. In HOMO, most of π -electrons located on the triphenylamine moieties and linkers, while in LUMO, the π -electrons delocalized on the whole



Fig. 2. Electrochemical properties of TPABBI, and TPABBBI.

molecules. Subsequently, we also optimized the geometric structures of them with different twisting angles between the triphenylamine moieties and benzimidazole planes from 0° to 90°. Interestingly, when the twisting angle is up to 90°, all of them have almost complete separation of the HOMO and LUMO at benzimidazole and triphenylamine moieties. The complete separation is preferable for efficient CT transition of HOMO (donor) \rightarrow LUMO (acceptor). However, all of them in such a 90° twisting conformations are unstable, because their energies are ≈ 0.1 eV higher than that of them at the most stable states. Based on DFT total-energy analysis, it can be found both the HOMO and the LUMO partially delocalize to the whole molecules, instead of a fully separated (or localized) HOMO and LUMO.

2.3. Optical properties

The absorption spectra of TPABBI and TPABBBI in solution and the photoluminescence spectra in solution and film are given in Fig. 4 and Table 2. By comparing with the BBI, the absorption spectra of TPABBI and TPABBBI appear another peck at ~360 nm, indicating strong electron coupling between the benzimidazole moiety (A) and triphenylamine (D) unit. Furthermore, the absorption spectra of them appear to be markedly alike because of the presence of the same electronic transitions. As shown in Fig. 4, the fluorescence spectra of TPABBI and TPABBBI reveal a single-band emission, which gradually red-shift relative to BBI. This shows that excited-state energy levels of these compounds from BBI to TPABBBI are reduced, in other words, there is a gradual increase in charge-separation degree or dipole moment.

The fluorescence spectra of TPABBI and TPABBBI in various polarity solvents were recorded and are shown in Fig. 5 and Table 2. With increase of the solvent polarity gradually from petroleum ether to acetonitrile, the fluorescence spectra of them exhibit a larger red-shifted, broader shape and longer fluorescence lifetime (τ) (in Fig. 6). Obviously, a large difference in the dipole moment between the excited state and the ground state, the CT state with a large polarity is usually stabilized in polar solvents, and the change is consistent with a variety of the excited state from the LE-state to an excited state with the strong CT character [18]. The dipole moment (μ_e) of the fluorescence maxima (v_f) against the solvent parameter Δf (shown in Fig. 7 and Table 2) and the values of them are 24.2 D for TPABBBI and 24.6 D for TPABBI according to the equation of Lippert–Mataga, respectively. [18]

$$\nu_f = \frac{2\mu_e \left(\mu_e - \mu_g\right)}{4\pi\epsilon_0 h c a^3} \Delta f + C \tag{1}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{0.5(n^2 - 1)}{2n^2 + 1}$$
(2)

$$a = \left(\frac{3M}{4N\pi d}\right)^{\frac{1}{3}} \tag{3}$$

where μ_g is the ground-state dipole moment, *a* is the solvent cavity (Onsager) radius, which was derived from Avogadro's number (*N*), molecular weight (*M*), and density (*d* = 1), and ε , ε_0 , and *n* are the solvent dielectric constant, vacuum permittivity, and solvent refractive index, respectively. The value of μ_g was calculated at the B3LYP 6-31G* level with Gaussian 03.

Obviously, the large dipole moments of TPABBI and TPABBBI are one of evidences for the formation of the twisted intramolecular charge transfer state (TICT state) [19]. In order to confirm deeply the TICT state and LE-state, we studied the temperature dependent



Fig. 3. Optimized geometries and molecular orbital amplitude lots of HOMO and LUMO energy levels of TPABBI and TPABBBI at different twisting angles.



Fig. 4. Normalized UV and PL spectra of BBI, TPABBI, and TPABBBI.

Table 2

Detailed parameters of photophysical properties of TPABBI and TPABBBI.

relationships of their fluorescence spectra as shown in Fig. 8. Obviously, the fluorescent intensities of TPABBI and TPABBBI reduce and lead to a broad and red-shifted spectrum, which can be attribute to three main factors, (1) decreasing of temperature causes a higher solvent polarity [20], improving the stability of TICT-state and dominating a broad featureless and red-shifted TICT emission; (2) decreasing the fluctuation of surrounding medium (solvent molecules) at low temperature, emission from the LE-state starts to compete with the solvent reorganization time, then both LE and TICT emission are observed simultaneously; (3) the twisted equilibrium conformation of the TICT state results in low fluorescence transition moments, because the TICT-state always adjusts the dihedral angle between the two planes by the torsional relaxation to accommodate with the change of the surrounding medium polarity.

Comp.	Solvent	ε	n	Δf	$V_{\rm max}^{\rm em}~{ m cm}^{-1}$	$\varPhi_{f}\%$	λ_{em} (FWHM) nm	$\lambda_{abs} \ nm$	τ ns
TPABBI	Petroleum ether	1.8	1.417	0.0734	24752	64	404(43)	353	
	Hexane	1.9	1.375	0.0944	24691	68	405(44)	354	_
	Cyclohexane	2.02	1.426	0.1004	24510	65	408(45)	353	_
	Toluene	2.38	1.497	0.1264	23529	78	425(51)	354	_
	Chloroform	4.81	1.446	0.2534	22075	88	453(70)	355	_
	Ethyl acetate	6.02	1.372	0.2924	21978	93	455(72)	354	_
	Tetrahydrofuran	7.58	1.407	0.3146	21882	83	457(68)	355	2.8
	Methylene chloride	8.93	1.424	0.3189	20920	80	478(80)	355	3.5
	Acetonitrile	37.5	1.344	0.2929	19881	45	503(100)	353	3.9
TPABBBI	Film	_	_	_	22222	84	450(61)	353	3.4
	Petroleum ether	1.8	1.417	0.0734	25000	52	400(43)	352	_
	Hexane	1.9	1.375	0.0944	24938	56	401(44)	354	_
	Cyclohexane	2.02	1.426	0.1004	24876	54	402(46)	353	_
	Toluene	2.38	1.497	0.1264	23810	66	420(50)	354	_
	Chloroform	4.81	1.446	0.2534	22727	72	440(61)	352	_
	Ethyl acetate	6.02	1.372	0.2924	22573	81	443(63)	355	_
	Tetrahydrofuran	7.58	1.407	0.3146	22321	71	448(61)	354	3.5
	Methylene chloride	8.93	1.424	0.3189	21008	63	476(85)	355	1.9
	Acetonitrile	37.5	1.344	0.2929	19841	36	504(72)	353	4.5
	Film	_	_	_	23310	68	429(55)	352	1.8



Fig. 5. Fluorescence spectra of TPABBI and TPABBBI in various polarity solvents.

Additionally, the formation of a TICT state would generate a significant charge separation between the D–A pair, which is a nearly electronically decoupled D–A pair with forbidden radiative transition to the ground state, thus a small TICT fluorescence quantum yield is expected. Hence, the changes of fluorescence quantum yields (Φ_f) of TPABBI and TPABBBI should be the other evidences (Table 2). By comparison of the changes of Φ_f in the various polarity solvents of TPABBI and TPABBBI, we can found Φ_f improves firstly and then decreases quickly by the increase of the polarities of the solvents. Obviously, the decrease process is attributed to the appearing TICT state in these molecules, while the increase of Φ_f may be produced by another CT process.

To understand the conformational change of the ICT state, we selected two solvents, glycerol with high viscosity and high polarity $(\varepsilon, 42.5)$ and ethanol with low viscosity and relatively low polarity $(\varepsilon, 24.5)$ for binary solvents. The fluorescence spectra of TPABBI and TPABBBI were measured in ethanol-glycerol (E-G) solvent mixtures, the ratio of E:G ranging from 100 : 0 to 10 : 90 as shown in Fig. 9. The fluorescence spectrum of TPABBI and TPABBBI in neat ethanol is characterized by a single long-band emission with a peak at 469 and 478 nm, respectively. With increasing the proportion of glycerol, the LE emission appears and rises by comparing with the PL of them in hexane. The long-band peaks of them shift to 478 nm for TPABBI and 499 nm for TPABBBI. Then a new peak appears at \sim 435 nm in the PL of TPABBI and TPABBBI. When E:G is 5:95, there are only the LE-emission peaks. Besides the LE state, there are two CT states of TPABBI and TPABBBI in the binary solvents. The emission peak from 469 to 498 nm may be assigned to the TICT-state emission. The peak at ~430 nm may be assigned to the ICT-state



Fig. 6. The fluorescence decay profiles of TPABBI and TPABBBI at room temperature, excitation wavelength = 360 nm.

emission. With increasing the proportion of glycerol, the increase in solvent polarity results in initial red-shifts of the TICT-emission peak, and the increase in solution viscosity would suppress the formations of the TICT state and then the ICT state, because conformational transitions in the formation of the excited states



Fig. 7. Solvent polarity (Δf) dependence of the fluorescence maxima of TPABBI and TPABBBI.



Fig. 8. The PL spectra of TPABBI and TPABBBI in dichloromethane measured at different temperatures.

(TICT and ICT) are limited in high-viscosity solutions. Obviously, the formation of TICT state is suppressed more easily than the ICT state.

In the above processes, there are two kinds of effects, one is from polarity when increasing initially the proportion of glycerol, and another is from viscosity at high levels of glycerol. In fluorescence spectra of them in binary solvents, there are isoemissive points, 435 nm for TPABBBI and 430 nm for TPABBI, which can be interpreted in terms of two emission species with a parent-daughter relationship as a proof for conversion from the TICT state to the ICT state. In addition, the LE-states of TPABBI and TPABBBI are electronically excited to come into being the vertical nonpolar singlet excited state. Then, the LE-state relaxes to the lowest singlet LEstate (¹LE₁) by the geometry relaxation that needs a torsional motion. After then, LE emission will be observed. When the compounds are surrounded by the polar solvents, their LE-states will vanish. The large geometry relaxation happens to form orthogonal configuration that facilitates electron transfer from one unit to the other and forms TICT-state. At last, the TICT emission can be observed after a large variation of torsion angle. Therefore, upon photoexcitation, it seems that there is a mother-daughter relationship from the TICT-state to ICT-state to LE-state [18].

The phosphorescent spectra of TPABBI and TPABBBI at 77 K and the corresponding LE spectra of them are shown in Fig. 10. The fluorescence of them are mainly attributed to the contribution of nonrelaxed LE-state in low polar solvent, suggesting the TICT emission will becomes insignificant due to the limit of the torsional motion and environment fluctuation, while the phosphorescent



Fig. 9. Fluorescence spectra of TPABBI and TPABBI in various ethanol-glycerol binary mixtures (100:0–5:95, v/v) at room temperature.

emissions are from the properties of their triplet levels, Obviously, the energy levels of ³LE-states from TPABBI and TPABBBI are higher than that of the ¹LE-states states (0.6 eV for TPABBI and 0.45 eV for TPABBI). Hence, the principal components of the LE-states are formed when electrons in the π orbital of the benzimidazole or triphenylamine ring are excited to the π^* orbital. The other



Fig. 10. The phosphorescent spectra and corresponding LE spectra of TPABBI and TPABBBI.

component is the CT-state that involves the excitation of electrons from the triphenylamine or linkers (donor) to the benzimidazole group (acceptor). The LE-state of them should be a mixed state containing the $\pi\pi^*$ state and some partial CT-states.

2.4. Electroluminescent properties

The OLEDs were fabricated to evaluate the EL performances of TPABBI and TPABBBI, the construction of devices is ITO/MoO₃ (10 nm)/NPB (80 nm)/TCTA (5 nm)/TPABBI or TPABBBI (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm), where indium tin oxide (ITO) is used as the anode, MoO₃ as hole-injecting layer, N,N'-di-1-naphthyl-N,N'-diphenylbenzidine (NPB) as hole-transporting layer, 4,4',4"-tri(N-carbazolyl)-triphenylamine (TCTA) as electron-blocking layer, 1,3,5-tri(phenyl-2-benzimidazolyl)benzene (TPBi) as electron- transporting and hole- blocking layer, and LiF used as the electron injecting layer. The relative energy levels of the materials employed in the devices are illustrated in Scheme 2.

Comparing the EL and PL spectra of them, they show the similar results. Obviously, the EL spectra are identical with the PL spectra, suggesting the electron and hole (e–h) recombination in the emitting layers, and both EL and PL originate from the same radiative decay process of singlet excitons. The maximum emission peaks of device based on TPABBI and TPABBBI are located at 440 nm and 460 nm with the FWHM of 60–62 nm, respectively. The EL spectra of TPABBI and TPABBBI show little changes by increasing voltages of devices. When the driving voltage is at 8 V, the CIE coordinates (x, y) of TPABBI- and TPABBI-based on devices are found to be (0.151, 0.113) for TPABBI and (0.156, 0.132) for TPABBI, respectively.

The current density-voltage-Brightness (I-V-B) characteristics of these devices are shown in Fig. 11, and the main performance parameters of them are summarized in Table 3. As shown in Fig. 11, the devices based TPABBI and TPABBBI show similar profiles of current density-voltage owing to the same HOMO and LUMO levels. The brightness-efficiencies relationships are shown in Fig. 12. Obviously, the efficiency of the device based on TPABBBI is much higher than that of the device based on TPABBI, may be because of the different fluorescence quantum yields, charge-transfer excitons and carries recombination natures of TPABBBI and TPABBI. In this regard, we also fabricated hole-only and electron-only devices with the structures of ITO/MoO₃ (10 nm)/NPB (80 nm)/TCTA (5 nm)/ TPABBI or TPABBBI (20 nm)/TPBI (40 nm)/MoO₃ (40 nm)/Al (100 nm), and ITO/TPBI (40 nm)/NPB (80 nm)/TCTA (5 nm)/TPABBI or TPABBBI (20 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). The current density versus voltage curves of the devices are shown in



Scheme 2. Energy level diagrams for devices.



Fig. 11. The current density-voltage-luminance (J-V-L) of TPABBBI and TPABBI.

Fig. 13. Obviously, a slight difference between the hole and electron current densities based on TPABBI and TPABBBI devices are found. This indicated the efficient carries reconstruction and recombination can be formed in the layer of TPABBI or TPABBBI. Additionally, with the same voltage, the current densities of TPABBBI are better than that of TPABBI. It can also be explained from another aspect why the performance of TPABBBI is better than that of TPABBI. It is worthwhile to note that the EQE of the TPABBBI- and TPABBI-based devices only show a little decrease at high current densities, indicating TPABBBI and TPABBI are promising candidates for OLED emitters.

2.5. Discussions about local excition and two kinds of chargetransfer excitons

Noteworthy, the external quantum efficiencies (EQE) (η_{ext}) of these FOLEDs are 4.23% for TPABBI and 5.66% for TPABBBI. Naturally, the EQE is relative on the light out-coupling efficiency (η_{Ph}) and internal quantum efficiency (η_{int}) with the formula of $\eta_{\text{ext}} = \Phi_f \times \eta_{\text{int}} \times \eta_{\text{Ph}}$, where the η_{Ph} is 20% by measuring the glass substrate with an index of refraction n = 1.5, Φ_f is the fluorescent quantum yield of the emitters, and the η_{int} is limited to 0.25. Ideally, when the values of their Φ_f were assumed to be 100%, the maximal of η_{ext} is calculated to only be 4.2% for TPABBBI and 3.4% for TPABBI, respectively, which is significantly lower than the values of 5.66% and 4.23%. However, the TTA does not play a role in the high EQEs of these devices because the brightness increases linearly with the increase of the current density at low current injection and less than linearly at higher current injection [21]. Therefore, the improved EL performance is related to the intrinsic factors of TPABBBI and TPABBI, which can capture e-h pair enthusiastically and convert it into the emissive exciton efficiently.

In order to analyze deeply the appeared results, we proposed two assumptions demonstrated as follows, (1) The benzimidazole and triphenylamine moieties in TPABBI and TPABBBI keep orthogonal structure in solid film, thus the two moieties have the independent electronic configuration in ground state; (2) the e–h capture is predominantly intramolecular. In these OLED devices,

Table 3	
The Electroluminescence characteristics of TPABBI, and TPABBBI.	

Emitter	CIE(x, y)	LE _{max} (cd/A)	PE _{max} (lm/W)	EQE (%)	L _{max} (cd/m ²)	Devices performance at 100 cd m^{-2}		
						LE (cd/A)	PE (lm/W)	EQE (%)
TPABBI TPABBBI	0.15,0.11 0.15,0.13	3.56 5.1	3.11 5.77	4.23 5.66	7895 20680	3.27 5.09	2.72 4.26	4.19 5.62



Fig. 12. The brightness-efficiencies curves of TPABBBI and TPABBI.

electron and hole encounter and capture each other with Coulomb interaction to form bound e-h pair [22], which results in the neutral excitons or charge transfer (CT) states [23]. The bound e-h pair is often localized on a molecule or single conjugated segment due to relatively low dielectric constant of organic molecule [24]. For TPABBI and TPABBBI, two channels might bring about the bound e-h pair. When the e-h pair localizes at single conjugated segments (benzimidazole planes of TPABBI and TPABBBI) (Fig. 14), then forms neutral, tightly bound local exciton (LE). This exciton has large exciton binding energy owing to the result of both the Coulomb interaction and image potential [25]. Commonly, the random recombination of carries will produce only one singlet local exciton (¹LE) for every three triplet local excitons (³LE) in this process. Moreover, the electron and hole of a bound e-h pair may reside on benzimidazole and triphenylamine moiety of one molecule respectively, and then give rise to a loosely bound TICT exciton (TICTE). For this exciton, the electron and hole are stabilized by a twist in the molecule of up to 90°. Since the electron and hole wave function are orthogonal in perpendicular conformation, the two electrons of TICTE are neither parallel ($\downarrow \downarrow$ or $\uparrow \uparrow$) nor antiparallel $(\uparrow\downarrow)$, just remain nearly perpendicular to each other. The TICT state that will undergo geometry relaxation of the TPA and BBI moieties by a slight torsion, results in a mixing state of singlet CT-state (¹CTstate) and triplet CT-state (³CT-state). Furthermore, it is possible that the transition of ${}^{1}CT \leftrightarrow {}^{3}CT$ is allowed due to the small energy splitting between them [26]. Additionally, the e-h pair may be held



Fig. 13. Current density versus voltage characteristics of the hole-only and electrononly devices for TPABBBI and TPABBI.

on benzimidazole moiety and the linkers (benzene and biphenyl) of one molecule respectively, which will appear a bound ICT exciton (ICTE). In this process, the electron and hole are stabilized at the special dihedral angles. Similarly, The ICT state also produces a mixing state of singlet CT-state (¹CT-state) and triplet CT-state (³CTstate), and the transition of ¹CT \leftrightarrow ³CT is also allowed. Thus, three type excitons will appear in TPABBBI- and TPABBI-based device, LE, ICT, and TICT, comprising ¹LE-state, ³LE-state, ¹CT-state and ³CTstate. However, the efficient radiative decay pathway mainly centers on ¹LE-state, while the radiationless transitions might take place in other states (³LE-state, ¹CT-state, ³CT-state) owing to the presence of the spin-forbidden and space-forbidden [27].

The CT-states containing TICT and ICT that lie energetically between the free carrier continuum and the final states, can be regarded as the immediate precursor to the final, strongly bound states (singlet states or triplet states) [28]. The formation rate of the triplet exciton is considerably smaller than that of the singlet exciton due to a consequence of more ionic nature and smaller binding energy of the singlet exciton [29]. For TPABBI and TPABBBI, the same results are found that the formation rate of ³LE is much smaller formation rate of ¹LE. In addition, the donor and acceptor groups in TPABBI and TPABBBI are linked by benzene or biphenyl and having nearly similar π systems. The TICT- and ICT-states are one of spin-orbit, charge-transfer intersystem crossing mechanism (SOCT-ISC). This SOCT-ISC system from CT-state may take place via a spin-orbit mechanism to produce the neutral LE-state involved in the spin flip that is coupled to a significant change in orbital angular momentum [30]. Moreover, the SOCT–ISC rate is enhanced with an approximately perpendicular orientation between the donor and acceptor. For the TPABBI and TPABBBI, the electron transferring happens between the donor and acceptor in the CT-states to form neutral LE due to the delocalization of the electron wave function in the imidazole and triphenylamine or linkers units (Fig. 15). Therefore, it is possible that the transitions are responsible for the newborn ¹LE from CTE, e.g., ¹CT \rightarrow ¹LE and ${}^{3}\text{CT} \rightarrow {}^{1}\text{CT} \rightarrow {}^{1}\text{LE}.$

According to the above discussions, we put forward two hypotheses, (1) mixing equal proportions of LE, ICT, and TICT; (2) ideally, converting all of the ICT and TICT to ¹LE. A maximum generation rate of ¹LE can be estimated, e.g., $1/3 \times 1/4(^{1}LE) + 1/3(TICT) + 1/3(ICT) = 75\%$. The result is agreed with experimental data for the TPABBI- and TPABBI-based devices. Our results deduce that increasing TICT and ICT in the EL device can increase efficiently the ¹LE, because it is a significantly intermediate state in the newborn ¹LE formation. Significantly, the EQE of the TPABBI and TPABBI-based devices at high current densities (Fig. 13). This suggests that TPABBI and TPABBI are the promising candidates for blue emitters.

3. Conclusions

In conclusion, we have demonstrated a method to enhance the occurrence of singlet excitons in the fluorescent emitters by utilizing simultaneously a twisted intramolecular charge transfer state (TICT-state), a planar intramolecular charge transfer state (ICT-state), and a locally excited state (LE-state) based on benzimidazole donor—acceptor derivatives. The EL properties of them were investigated with the device structure of ITO/MoO₃/NPB/TCTA/TPABBI or TPABBBI/TPBi/LiF/Al. The devices based them present a stable and high efficiency blue emissions of 5.1 cd/A, 5.77 lm/W, 5.66% for TPABBBI and 3.56 cd/A, 3.11 lm/W, 4.23% for TPABBI. Interestingly, the devices show a significant characteristic of increasing the radiative exciton generation efficiency due to the influence of TICT-states and ICT states. Our results reveal that TPABBBI and TPABBI are good candidates to serve as highly-



Fig. 14. The formation process of exciton in EL device based on TPABBI and TPABBBI.



effective blue OLEDs. This opens an avenue for designing and synthesizing highly-efficient blue OLEDs by employing the emitters with the twisted $D-\pi$ -A and planar linkers.

4. Experimental

4.1. Materials and characterization

All starting materials were purchased from TCI, the reagents were obtained from J&K Chemical company and used without further purification. ¹H NMR and ¹³C NMR spectra were determined in CDCl₃ with a Bruker DRX 400 MHz spectrometer. Chemical shifts (δ) were given relative to tetramethylsilane (TMS). The coupling constants (*J*) were reported in Hz. Elemental analyses were recorded with a Perkin–Elmer 2400 analyzer. ESI-Ms spectra were performed with a FINNIGAN Trace DSQ mass spectrometer at 70 eV. Fluorescence emission spectra of these samples were measured with a FLSP920 spectrophotometer. Experiment course was monitored by TLC. Column chromatography was carried out on silica gel (100–200 mesh).

4.2. Synthesis

2-(4-bromophenyl)-1-phenyl-1H-benzo[d]imidazole, 4'bromo-N,N-diphenyl-[1,1'- biphenyl]-4-amine, and 1-phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)-1H-benzo [d]imidazole (BPPE) were synthesis following the methods of published papers [17].

4.2.1. General method for the synthesis of TPABBI and TPABBBI

BPBE (3.0 mmol), 4-bromo-N,N-diphenylanilineor 4'-bromo-N,N-diphenyl- [1,1'-biphenyl]-4-amine (3.5 mmol) and Pd(PPh₃)₄ (0.03 mmol) were suspended in toluene (12 mL) and Et₄NOH (6 mL of a 20% aqueous solution), the reaction was heated to reflux for 18 h. After cooled, the solution was extracted with CH_2Cl_2 (30 mL), washed with water (2 × 50 mL), dried by MgSO₄ and evaporated to dryness. After drying under vacuum, then, it was purified by ethyl acetate/petroleum ether (1:12) as an eluant to afford white solid.

N,N-diphenyl-4'-(1-phenyl-1H-benzo[d]imidazol-2-yl)-[1,1'biphenyl]-4-amine (TPABBI): yield: 1.05 g, 68%. ¹H NMR(CDCl₃, 400 MHz, ppm) δ : 7.94 (d, 1H, J = 8.4 Hz), 7.66 (d, 2H, J = 8.4 Hz), 7.54 (d, 5H, J = 8.0 Hz), 7.49 (d, 2H, J = 8.0 Hz), 7.38 (d, 3H, J = 7.64 Hz), 7.35–7.27 (m, 6H), 7.14 (d, 6H, J = 8.0 Hz), 7.06 (t, 2H, J = 7.6 Hz). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ : 152.2, 147.7, 147.5, 142.9, 141.5, 137.3, 137.1, 133.7, 130.0, 129.8, 129.3, 128.6, 128.1, 127.7, 127.5, 126.3, 124.6, 123.6, 123.4, 123.2, 123.1, 119.8, 110.5. ESI-MS (m/ z): 513.2 (M⁺). Anal. calcd for C₃₇H₂₇N₃: C, 86.52; H, 5.30; N, 8.18; Found: C, 86.54; H, 5.22; N, 8.23.

N,N-diphenyl-4"-(1-phenyl-1H-benzo[d]imidazol-2-yl)-[1,1':4',1"-terphenyl]-4-amine (TPABBBI): yield: 1.53 g, 65%.¹H NMR(CDCl₃, 400 MHz, ppm) δ :7.92 (d, 1H, *J* = 8.4 Hz), 7.69–7.65 (m, 6H), 7.61–7.57 (m, 3H), 7.55–7.50 (m, 5H), 7.39–7.36 (m, 3H), 7.31–7.28 (m, 5H), 7.15 (d, 6H, *J* = 8.0 Hz), 7.04 (t, 2H, *J* = 7.6 Hz). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ : 152.1, 147.6, 147.4, 143.1, 141.5, 140.1, 138.4, 137.4, 137.1, 134.2, 129.9, 129.8, 129.3, 128.8, 128.6, 127.6, 127.5, 127.4, 127.0, 126.7, 124.5, 123.8, 123.4, 123.0, 119.8, 110.4. ESI-MS (*m/z*): 589.1 (M⁺); Anal. calcd for C₃₇H₂₇N₃: C, 87.58; H, 5.30; N, 7.13; Found: C, 87.62; H, 5.17; N, 7.24.

4.3. Devices fabrication

The ITO-coated glass substrate was first immersed sequentially in ultrasonic baths of acetone, alcohol and deionized water for 10 min, respectively, and then dried in an oven. The resistance of a sheet ITO is $10 \ \Omega/\Box$. The devices were fabricated in a multi-source organic molecule gas deposition system. Different organic materials were deposited on the ITO-coated glass substrate according to the designed structure. LiF buffer layer and Al were deposited as a co-cathode under a pressure of 5×10^{-4} Pa. Electroluminescent spectra and commission international De L' Eclairage(CIE) coordination of these devices were measured by a PR655 spectra scan spectrometer. The luminescent brightness (*L*)-current (*I*)-voltage (*V*) characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer through a Keithly model 2400 programmable voltage–current source. The layer thicknesses of the deposited materials were monitored in situ using a model FTM-V oscillating quartz thickness monitor made in Shanghai, China. All the measurements were carried out at room temperature under ambient conditions.

4.4. Computational details

The geometric and electronic structure of them were optimized by Density functional theory (DFT) level of theory with the threeparameter Becke-style hybrid functional (B3LYP). The HOMO and LUMO energy levels are predicated by 6-31G (d,p) basis set. All of calculations about the molecule have been performed on the huge computer origin 2000 server center using the Gaussian 03 program package [31]. The compositions of molecular orbits were analyzed using the GaussView 3.0 program.

4.5. Fluorescence, phosphorescence and lifetime measurements

The fluorescence and phosphorescence spectrum was recorded using a Hitachi F-4500 fluorescence spectrometer. Excitation and emission slit width were set at 10 nm and 10 nm, respectively. Compounds were dissolved in tetrahydrofuran with the concentration of $\sim 10^{-7}$ mol/L. For the phosphorescence, the solution was then inserted into a Dewar vessel containing liquid nitrogen (77 K). The liquid column in the quartz tube was solidified and appeared to be a transparent glass. The F-4500 phosphorescence accessory was used to measure phosphorescence spectra. The measurement was performed at 77 K using a chopper to remove shorter-lived singlet emissions.

The fluorescence lifetimes were measured by a time correlated single photon counting spectrometer from Edinburgh Instruments (FLS920) with a nanosecond hydrogen flash lamp as the excitation source (repetition rate 40 kHz) at room temperature. The instrument response (FWHM ca. 1 ns) was determined by measuring the light scattered by a Ludox suspension (solution) or solid film itself (film). The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using software package provided by Edinburgh Instruments.

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