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Efficient blue organic light-emitting diodes based on triphenylimidazole substituted anthracene derivatives

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ABSTRACT

A series of new blue emissive materials based on the conjugates of highly fluorescent diaryl anthracene and electron-transporting triphenylimidazole moieties: 2-(4-(anthracen-9-yl)phenyl)-1,4,5-triphenyl-1*H*-imidazole (**ACBI**), 2-(4-(10-(naphthalen-1-yl)anthracen-9-yl)phenyl)-1,4,5-triphenyl-1*H*-imidazole (**1-NaCBI**), 2-(4-(10-(naphthalen-2-yl)anthracen-9-yl)phenyl)-1,4,5-triphenyl-1*H*-imidazole (**2-NaCBI**) were designed and synthesized successfully. These materials exhibit good film-forming properties and excellent thermal stabilities. Meanwhile, the decreased π -conjugation in these compounds compared with phenanthroimidazole derivatives leads to obvious hypsochromic shift. To explore the electroluminescence properties of these materials, typical three-layer organic light-emitting devices were fabricated. With respect to the three layer device **2** using **1-NaCBI** as the emitting layer, its maximum current efficiency reaches 3.06 cd A⁻¹ with Commission Internationale del'Eclairage (CIE) coordinates of (0.149, 0.092). More interestingly, sky blue doped device **5** based on **1-NaCBI** achieved a maximum current efficiency of 15.53 cd A⁻¹ and a maximum external quantum efficiency of 8.15%, high EQE has been proved to be induced by the up-conversion of a triplet excited state.

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1. Introduction

In the past decade, organic light-emitting diodes (OLEDs) have attracted much scientific and commercial interest because of their potential application in full-color displays and large-area, flexible, light-weight light sources [1]. Full-color displays require red, green, and blue emissions of relatively equal stability, efficiency, and color purity. Specifically, highly efficient blue electroluminescent devices with Commission Internationale del'Eclairage (CIE) *y*-coordinate value <0.10, can not only effectively reduce the power consumption of a full-color OLED but

http://dx.doi.org/10.1016/j.orgel.2015.02.018 1566-1199/© 2015 Elsevier B.V. All rights reserved. be utilized to generate light of other colors by energy cascade to lower energy fluorescent to realize white light. Red and green phosphorescent electroluminescent devices with high efficiencies, long lifetimes, and proper CIE coordinates have been well developed. However, blue phosphorescent devices are still the bottleneck for the high CIE coordinates (*y*-coordinate value >0.30), high cost and short device lifetime [2]. To address the problem, a continuous effort has been contributed to develop highly efficient blue-light emitters with good color purity and high efficiency [3].

Anthracene derivatives have been studied extensively as blue-light-emitting materials in OLEDs because of their excellent photoluminescence (PL) and electroluminescence (EL) properties [4]. For example, Li' group [5] have synthesized some fluorene derivatives with naphthylanthracene







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endcaps and achieved device efficiency of 2.10 lm W^{-1} , color coordinates (0.16, 0.09). Shu's group [6] have developed 2-tert-butyl-9,10-bis[4'-(diphenylphosphoryl)phenyl]anthracene (POAn) with a maximum luminance efficiency of 2.9 cd A^{-1} , CIE coordinates of (0.15, 0.07). On the other hand, phenanthroimidazole derivatives have attracted great attention as electroluminescent materials because of their high thermal stability and efficient electron transporting ability. Huang's group [7] exploited bis(phenanthroimidazolyl)biphenyl derivatives as excellent non-doped blue emitting materials with optimized device efficiency of 7.3 Im W^{-1} , CIE coordinates of (0.15, 0.14). Using phenanthroimidazole as a building block for luminescent materials, Ma's group [8] fabricated pure blue devices with luminance efficiency of 6.87 cd A⁻¹, CIE coordinates of (0.15, 0.21) and a turn on voltage of 2.8 V. The impressive device performances of 2.63 cd A^{-1} CIE (0.15, 0.09) and 5.66 cd A⁻¹, (0.15, 0.11) based on donor-linkeracceptor structural deep-blue emitting phenanthroimidazole derivatives have been reported by Tong and Ma's group, respectively [9]. Very recently, an promising device performance with EOE of 7.8% and current efficiency of 10.4 cd A⁻¹ has been reported based on an excellent blue dopant PPIE containing n-type imidazole moiety [10]. In the subsequent research, the high EQE is proved to be induced by the triplet-triplet annihilation (TTA). In spite of their successful performance in a given aspect, satisfactory blue luminescent materials are still rare.

In our previous work, some hybrid bipolar phosphorescent hosts for green and orange OLEDs have been synthesized by conjugating carbazole moiety to the rigid skeleton of 1,2-diphenyl-1H-phenanthro[9,10-d]imidazole [11]. We also developed some asymmetric phenanthroimidazole C2-phenyl or N1-phenyl position substituted anthracene derivatives for efficient blue OLEDs [12]. The introduction of anthracene moieties can effectively increase the electron injection and transport ability and also finely adjust the ionization potentials (Ip) of the compounds, resulting in reduced hole injection barrier and balanced recombination ability. In this paper, we introduced the bulky non-planar triphenylimidazole instead of phenanthroimidazole moiety to obtain deeper blue fluorescent materials. As expected, these new materials show excellent thermal stabilities, proper HOMO levels and excellent EL performances with low onset voltages. Three layer device 2 using 1-NaCBI as the emitting layer, achieved a maximum current efficiency of 3.06 cd A⁻¹ with Commission Internationale del'Eclairage (CIE) coordinates of (0.149, 0.092). In addition, device 5 based on doping BUBD-1 in 1-NaCBI, the maximum current efficiency reaches 15.53 cd A^{-1} with maximum external quantum efficiency of 8.3%. The high EQE has been proved to be induced by the up-conversion of a triplet excited state.

2. Experimental section

2.1. Material and methods

All reagents and solvents were used as purchased from Aldrich without further purification. Most of experiment methods were according to our published results [11,12].

¹H NMR spectra were recorded on a Bruker-AF301 at 400 MHz. Mass spectra were carried out on an Agilent MALDI-TOF. Elemental analyzes of carbon, hydrogen, and nitrogen were performed on an Elementar (Vario Micro cube) analyzer. Fluorescence spectra and transient fluorescence decay lifetimes were obtained on Edinburgh instruments (FLSP920 spectrometers) and UV-Vis absorption spectra were measured using a Shimadzu UV-Vis-NIR Spectrophotometer (UV-3600). The differential scanning calorimetry (DSC) analyzes were performed under a nitrogen atmosphere at a heating rate of 10 °C/min using a PE Instruments DSC 2920. Thermogravimetric analyzes (TGA) were undertaken using a PerkinElmer Instruments (Pyris1 TGA) under nitrogen atmosphere at a heating rate of 10 °C/min. Atomic force microscopies (AFMs) were measured using Shimadzu (SPM9700). To measure the photoluminescence (PL) quantum yields ($\Phi_{\rm F}$), degassed solutions of the compounds in CH₂Cl₂ were prepared. The concentration was adjusted so that the absorbance of the solution would be between 0.05 and 0.1. The excitation was performed at 330 nm and 9,10-diphenylanthracene (DPA) in cyclohexane ($\Phi = 0.9$ in cyclohexane) was used as a standard [13]. Cyclic voltammetry (CV) measurements were carried out in a conventional three electrode cell using a Pt button working electrode of 2 mm in diameter, a platinum wire counter electrode, and a Ag/AgNO₃ (0.1 M) reference electrode on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. Oxidations of all compounds were performed in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as supporting electrolyte. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram and calibrated to the ferrocene/ferrocenium (Fc|Fc⁺) redox couple. DFT calculations were performed to characterize the 3D geometries and the frontier molecular orbital energy levels of ACBI, 1-NaCBI and 2-NaCBI at the B3LYP/6-31G* level by using the ADF2009.01 program.

2.2. Device fabrication and measurement

The EL devices were fabricated by vacuum thermal evaporation technology according to the methods modified from our previous approach [11,12]. Before the deposition of an organic layer, the clear ITO substrates were treated with oxygen plasma for 5 min. The deposition rate of organic compounds was 0.9-1.1 Å s⁻¹. Finally, a cathode composed of cesium pivalate (2 nm) and aluminum (100 nm) was sequentially deposited onto the substrate in the vacuum of 10^{-5} Torr. The *L*–*V*–*J* curves of the devices were measured with a Keithley 2400 Source meter and PR655. All measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

3.1. Synthesis

The structures and synthetic routes of the three well-defined compounds are shown in Scheme 1. Anthracen-9-yl-



Scheme 1. Synthetic routes for ACBI, 1-NaCBI and 2-NaCBI. Reagents and conditions: (i) CH₃COONH₄, CH₃COOH, reflux; (ii) toluene, K₂CO₃, ethanol, aryl boric acid, Pd(PPh₃)₄, reflux.

Table 1							
The optical,	photophysical	and thermal	properties of a	ACBI,	1-NaCBI,	and 2-N	aCBI.

Compound	HOMO/LUMO (eV) ^a	HOMO/LUMO (eV) ^b	$\Phi_{\rm F}$	$E_{\rm g}({\rm eV})$	$E_{\mathrm{ox}}\left(V\right)$	PL (nm)		Abs (nm)	$T_g/T_m/T_d~(^\circ C)$
						Solution (FWHMs)	Film (FWHMs)		
ACBI 1-NaCBI 2-NaCBI	-5.54/-2.47 -5.56/-2.56 -5.53/-2.55	-5.18/-2.06 -5.17/-2.23 -5.14/-2.28	0.70 0.65 0.56	3.07 3.00 2.98	0.88 0.90 0.87	420 (57) 428 (54) 434 (53)	443 (76) 439 (57) 445 (51)	350, 368, 388 358, 377, 398 359, 378, 398	123/282/402 165/NA/412 161/336/420
2-MaCDI	-5.55/-2.55	-5.14/-2.20	0.50	2.50	0.07	4J4 (JJ)	445 (51)	555, 578, 558	101/330/420

^a Determined from the onset of oxidation potentials and the E_g = HOMO-LUMO.

^b Values from DFT calculation.

boronic acid, 9-(1-naphthyl)anthracene-10-boronic acid, and 9-(2-naphthyl)anthracene-10-boronic acid were synthesized according to the literature [14]. The intermediate 2-(4-bromophenyl)-1,4,5-triphenyl-1H-imidazole was synthesized in high yield [15]. The target products were prepared through the palladium-catalyzed Suzuki coupling reactions between the intermediate and the corresponding aryl boronic acid, then purified by column chromatography on silica gel using petroleum ether-dichloromethane as the eluent. Repeated temperature-gradient vacuum sublimation are required for further purification of these materials used in OLEDs. All the new compounds were fully characterized by ¹H and ¹³C NMR, mass spectrometry, and elemental analysis. The detailed procedure, ¹H, ¹³C NMR and MS spectra for preparation of compounds are summarized in Supporting Information.

3.2. Thermal properties

The thermal properties of the three compounds were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere, and the related data are listed in Table 1. Compounds **ACBI**, **1-NaCBI** and **2-NaCBI** exhibit good thermal stability with decomposition temperatures (T_d , 5% weight loss) at 402, 412 and 420 °C, respectively. As shown in Fig. 1, Obvious glass transition temperatures (T_g) are observed at 123, 165, 161 °C for **ACBI**, **1-NaCBI** and **2-NaCBI** show endothermic melting transition temperatures (T_m) at 282

and 336 °C, respectively. From **ACBI** to **2-NaCBI**, the enhancement of T_g can be attributed to the increase of efficient molecular weight. High T_g and T_d values indicate that these compounds are stable and have the potential to be fabricated into devices by vacuum thermal evaporation technology, which is highly desirable for high performance OLED applications.

3.3. Morphology properties

Since good film-forming properties of light emitting materials are crucial for the total performance of the devices, the surface morphologies of vacuum-deposited thin films of the three new compounds, ACBI, 1-NaCBI and 2-NaCBI, were studied by atomic force microscopy (AFM). For a direct comparison, we prepared both unannealed films and thermally annealed samples films at 120 °C for 2 h under an N₂ atmosphere. As shown in Fig. 2, the unannealed film samples exhibit a root-mean-square (RMS) roughness of 0.816, 0.706 and 0.667 nm for ACBI, 1-NaCBI and 2-NaCBI, respectively. The annealed film exhibits a smooth surface morphology with a root-mean-square (RMS) roughness of 0.477, 0.575 and 0.373 nm for ACBI, 1-NaCBI and 2-NaCBI, respectively. The small RMS difference between unannealed and annealed film samples suggests their excellent thermal and amorphous stability, which indicates that attaching triphenyl-1*H*-imidazole moiety to anthracence's 9-position may influence the arrangement of the molecules in the thin films and makes them desirable for good performance OLEDs. After annealing,



Fig. 1. (a) DSC curves of ACBI, 1-NaCBI and 2-NaCBI; (b) TGA curves of ACBI, 1-NaCBI and 2-NaCBI.



Fig. 2. AFM topographic images of the three compounds ACBI, 1-NaCBI and 2-NaCBI in unannealed and annealed films.

the roughness of the three films become a little smaller, it can be induced by the very slightly rearrangement of molecular morphology.

3.4. Theoretical calculations

The three-dimensional geometries and the frontier molecular orbital energy levels of these compounds were calculated using density functional theory. It was obvious that the planarities of those phenanthroimidazole-substituted anthracene derivatives were broken by the bulky and non-planar triphenylimidazole moiety. The resulted HOMO and LUMO distribution are depicted in Table 1. As shown in Fig. 3, the spatial distributions of electron densities of HOMO and LUMO for all the three compounds are mostly localized on the anthracene units, it implies that the absorption and emission process may mainly be attributed to the π - π ^{*} transition centered at the anthracene moiety, which is the same with the compound ACPI, 1-NaCPI and 2-NaCPI [12]. The HOMO level of ACBI, 1-NaCBI and 2-NaCBI locate at -5.18, -5.17 and -5.14 eV, respectively. As a comparison with **ACBI**, the HOMO levels for 1-NaCBI and 2-NaCBI increase in a value of about 0.01-0.04 eV for the elongation of π -conjugation when introducing naphthyl group on the 9-position of anthracene of **ACBI**. Also the energy levels of HOMO is about 0.08–0.12 eV higher than those of the phenanthroimidazole-substituted anthracene derivatives [12].

3.5. Photophysical properties

Fig. 4(a) shows the UV–Vis spectra of compounds ACBI, 1-NaCBI and 2-NaCBI at room temperature in a CH₂Cl₂ solution. And Fig. 4(b) shows the fluorescence spectra of compounds ACBI, 1-NaCBI and 2-NaCBI at room temperature for solutions in CH₂Cl₂ and solid film. The related photophysical properties are summarized in Table 1. All of these compounds have similarly structured absorption spectra in the range of 340–425 nm in CH₂Cl₂, which are assigned to the π - π ^{*} transition of the characteristic vibrational structures of anthracene groups [12]. The 10 nm red shift for 1-NaCBI and 2-NaCBI compared to ACBI was observed and attributed to the increased π -conjugation. And upon excitation at 330 nm, the maximum emission wavelengths of ACBI, 1-NaCBI and 2-NaCBI in CH₂Cl₂ were observed at 420, 428 and 434 nm, respectively. Compared with ACPI, 1-NaCPI and 2-NaCPI, hypsochromic shifts of 3-7 nm were attributed to the decreased conjugation by the bulky and nonplanar triphenylimidazole moiety. The maximum



Fig. 3. Three-dimensional structures and calculated HOMO and LUMO density maps of ACBI, 1-NaCBI and 2-NaCBI.



Fig. 4. (a) Normalized absorption spectra of solutions in dichloromethane and (b) normalized photoluminescence spectra of solutions in dichloromethane and solid films for ACBI, 1-NaCBI and 2-NaCBI.

emission peaks of ACBI, 1-NaCBI and 2-NaCBI thin films are red-shifted by 23, 19, and 19 nm compared with those of solutions in CH₂Cl₂, respectively, which are slightly lower than the corresponding values of 29, 24 and 20 nm for ACPI, 1-NaCPI and 2-NaCPI, respectively [12]. In addition, the FWHMs of 1-NaCBI and 2-NaCBI are much shorter than ACBI. These features in film state are reasonable for decreased aggregation by greater steric hindrance of 1-naphthalene moiety and non-plannarity property of triphenylimidazole moiety. Using 9,10-diphenylanthracene as a standard, the PL quantum yields ($\Phi_{\rm F}$) were determined as high as 0.70, 0.65 and 0.56, for ACBI, 1-NaCBI and 2-NaCBI, respectively. The high PL quantum yield along with good film-forming property and excellent thermal stability indicate those compounds are excellent candidates as efficient emitting materials in OLEDs.

3.6. Electrochemical properties

To further evaluating the feasibility of those new materials for optoelectronic applications, the electrochemical behaviors of **ACBI**, **1-NaCBI** and **2-NaCBI** were examined by cyclic voltammetry (Fig. 5). The onset oxidation peaks (E_{ox}) for **ACBI**, **1-NaCBI** and **2-NaCBI** are 0.88, 0.90, and 0.87 eV versus the Ag/Ag⁺ redox couple, respectively. And the HOMO levels were calculated to be -5.54, -5.56 and -5.53 eV for **ACBI**, **1-NaCBI** and **2-NaCBI**, respectively (Table 1) by the method $-(E_{ox} + 4.66)$ eV calibrated to the Ag/Ag⁺ redox couple. The HOMO levels for **ACBI**, **1-NaCBI** and **2-NaCBI** are higher than that of **ACPI**, **1-NaCBI** and **2-NaCPI** and **2-NaCPI** are higher than that of **ACPI**, **1-NaCPI** and **2-NaCPI**, respectively [12]. It could be rationalized that the decreased conjugation might reduce the oxidation potentials of the molecule and increase the HOMO energy



Fig. 5. The CV measurement of ACBI, 1-NaCBI and 2-NaCBI.

level. This trend is in good agreement with the calculated values and confirms the above hypothesis. Higher HOMO levels reduce the energy barriers between hole transport and emitting layers and will facilitate hole injection into the emission layer.

3.7. Electroluminescence

To evaluate the EL performances of **ACBI**, **1-NaCBI** and **2-NaCBI** as blue emitters, devices with three layers: anode/ HTL/emitter/ETL/cathode were fabricated. In these devices, indium tin oxide (ITO) was used as the anode, 4,4',4"-tris[*N*-(1-naphthyl)-*N*-phenylamino]triphenylamine (2-TNATA) was selected as the hole-injection layer, 4,4-bis[N-(1-naphthyl)-N-phenyl-l-amino]biphenyl (NPB) was used as the hole transporting layer (HTL), 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBI) was used as the electron transporting layer [16]. The relative HOMO/LUMO energy levels of the materials are illustrated in Scheme 2, and detailed structures and key performance of these devices are summarized in Table 2.

Non-doped devices **1–4** were fabricated with typical configuration as follows: ITO/2-TNATA(60 nm)/NPB (10 nm)/emitting layer (30 nm)/TPBI (10 nm)/(CH₃)₃ CCOOCs (1 nm)/Al (100 nm). The current density–voltage–luminance (*I–V–L*) and current density–current efficiency characteristics are shown in Fig. 6. Simple devices **1–4** utilizing compounds **ACBI**, **1-NaCBI**, **2-NaCBI** and reference 2-methyl-9,10-bis(naphthalen-2-yl)anthracene (MADN) as



Scheme 2. Energy-level diagram of the materials used in the devices.

host exhibit a maximum brightness of 9007, 6372, 11,520 and 5831 cd m⁻², luminous efficiency of 2.94, 3.06, 4.49 and $3.03 \text{ cd } \text{A}^{-1}$, low threshold voltage of 2.92, 2.63, 2.62 and 3.62 V, respectively (see Table 2). Compared with the high turn-on voltage of MADN and previous reported phenanthroimidazole-substituted anthracene derivatives [12], the lower turn on voltages of the devices based on the three compounds can be attributed to the matched HOMO levels of the hole-transporting layer and the emissive layer. The EL spectra of 1, 2 and 3 show blue light emission with peaks at 460, 448 and 452 nm, respectively (Fig. 7(a)). Narrow EL peaks in the ACBI, 1-NaCBI and 2-NaCBI devices with FWHMs of 71, 58 and 61 nm, respectively, are observed. At a current density of 20 mA $\rm cm^{-2}$, the CIE coordinates of devices 1, 2 and 3 are (0.152, 0.137), (0.149, 0.092) and (0.161, 0.150), respectively (see Table 2). Although ACBI exhibits the shortest emission in solution, aggregation induces bathochromic shift in EL spectrum. Compared with ACPI, 1-NaCPI and 2-NaCPI with almost the same device structure, ACBI, 1-NaCBI and 2-NaCBI exhibit lower CIE_v. The results demonstrated that the introduction of bulky and non-planar triphenylimidazole moiety with decreased π -conjugation is beneficial for achieving deeper blue emitting material. Moreover, device 2 using 1-NaCBI as emitting layers shows the shortest emission peak, the narrowest FWHMs and the lowest value of CIE_v, which is consistent with its PL of solid thin film. Take the widely used deep blue fluorescent material MADN as reference, the device performance of 1-NaCBI is superior in turn-on voltage and efficiency based on the same device structure.

Inspired by the impressive device performance of the non-doped device 2, we further explore the possibility of using this new blue emissive material as host in doped sky blue device. For this purpose, we fabricated device 5 utilizing 1-NaCBI as the host and a sky blue fluorescent material BUBD-1 as the dopant with the following structure: ITO/2-TNATA(60 nm)/NPB (10 nm)/emitting layer (30 nm):3% BUBD-1/TPBI (10 nm)/(CH₃)₃CCOOCs (1 nm)/ Al (100 nm). The detailed device performances and EL emission characteristics are summarized in Table 2. Apparently, the EL spectrum of device 5 shows a similar blue light emission to the emitter BUBD-1 [17] with peaks at 472 and 496 nm and CIE of (0.151, 0.299) at a current density of 20 mA cm⁻² (see Fig. 7(b)), indicating an efficient energy transfer from the host to the dopant. As described in Fig. 8, device 5 shows a maximum brightness of 10,570 cd m⁻², luminous efficiency of 15.53 cd A⁻¹, and maximum external quantum efficiency (EQE) of 8.15 %. The efficiency of device 5 using 1-NaCBI as the host is much better than the published literature values [12,17]. Devices 6 and 7 with 2-NaCBI and ACBI as the host were also fabricated, which exhibit a maximum external guantum efficiency of 6.75% and 5.89%, respectively. The typical emission from BUBD-1 means that the energy transfer from the hosts to the dopant is complete.

It is worth noting that the maximum EQE of all doped devices are above the classical estimate for the maximum EQE of fluorescent OLEDs without enhanced optical out coupling [18], especially for the device **5**. Two possible mechanisms for the up-conversion of a triplet excited state

Та	ble 2			
EL	performance	of	devices	1-7.

Device	$V_{\rm on}({\rm V})^{\rm a}$	Lmax (voltage) (cd m ⁻²) (V) ^b	$\eta_P (\mathrm{Im}\mathrm{W}^{-1})^{\mathrm{c}}/^{\mathrm{d}}$	$\eta_C (\mathrm{cd}\mathrm{A}^{-1})^\mathrm{e}/^\mathrm{f}$	$\eta_{\mathrm{ext}} (\%)^{\mathrm{g}/\mathrm{h}}$	L (voltage) (cd m ⁻²) (V) ⁱ	λ_{em} (FWHM) $(nm)^j$	$CIE (x,y)^k$
1 2 3 4 5 6	2.80 2.63 2.62 3.62 2.61 2.70	9007 (9.00) 6372 (9.50) 11,520 (7.75) 5831 (9.90) 10,570 (13.50) 15,640 (11.5)	1.70 (2.11) 1.94 (2.52) 2.91 (3.88) 1.32 (1.88) 3.88 (7.41) 4.57 (7.21)	2.90 (2.94) 3.03 (3.06) 4.30 (4.49) 2.59 (3.03) 12.78 (15.53) 12.37 (12.58)	2.59 (2.66) 3.49 (3.50) 3.54 (3.55) 3.15 (3.67) 7.92 (8.15) 6.66 (6.74)	594 (5.33) 620 (4.89) 910 (4.79) 514 (6.23) 2592 (10.33) 2322 (8.50)	460 (71) 448 (58) 452 (61) 456 (66) 472 (57) 468 (53)	(0.152, 0.137) (0.149, 0.092) (0.161, 0.150) (0.144, 0.092) (0.151, 0.299) (0.162, 0.274)
7	4.70	18,170 (15.00)	2.59 (4.79)	9.91 (11.41)	5.15 (5.89)	1878 (12.00)	468 (55)	(0.158, 0.296)

^a V_{on} : turn-on voltage.

^b Lmax: maximum luminance. Voltage: voltage at the maximum luminance.

^c η_P : power efficiency measured at 20 mA cm⁻².

^d Maximum power efficiency.

^e η_C : current efficiency measured at 20 mA cm⁻².

f Maximum current efficiency.

^g η_{ext} : external quantum efficiency measured at 20 mA cm⁻².

^h Maximum external quantum efficiency.

ⁱ L: luminance measured at 20 mA cm⁻². Voltage: voltage at the luminance.

^j V: FWHM: full width at half maximum at 20 mA cm⁻².

^k λ_{em} : CIE at 20 mA cm⁻².



Fig. 6. (a) Voltage-current density-luminance (V-J-L) characteristics and (b) efficiency curves for blue devices 1-4.



Fig. 7. (a) EL spectra of devices 1-4 and (b) EL spectrum of device 5.

 (T_1) into a singlet excited state (S_1) have already been proposed to improve EQE of fluorescent OLEDs. One is triplettriplet annihilation (TTA) and the other is thermally activated delayed fluorescence (TADF) [19]. For TADF, the up-conversion of exciton occurs through reverse intersystem crossing (RISC) process, thus small ΔE_{ST} is an essential factor. Yet to achieve small ΔE_{ST} , a small overlap between HOMO and LUMO is considered to be necessary. Here, we tried to test the triplet energy level of these compounds in 77 K, but failed. It should be noted that the ΔE_{ST} of all



Fig. 8. (a) Voltage-current density-luminance (V-J-L) characteristics and (b) efficiencies curves for devices 5, 6 and 7.

reported anthracene derivatives was very large. Meanwhile, to achieve small ΔE_{ST} , a small overlap between HOMO and LUMO is considered to be necessary [20]. However, a well overlap between HOMO and LUMO of ACBI, 1-NaCBI and 2-NaCBI shown above excludes the assumption (see Fig. 3). In addition, transient fluorescence decay lifetime excited at 330 nm in a film of 1-NaCBI (3% doped) was also measured. The fluorescence emission displays a dual-exponential decay with τ_1 of 0.759 ns and τ_2 of 2.488 ns, respectively (Fig. 9(a)). The short decay lifetime indicates that the singlet excitons involved in emission are not generated through TADF process, otherwise a us tail should be observed in the decay curve. On the other hand, transient electroluminescence response of the 3% doping blue emitting device 5 is shown in Fig. 9(b). The EL intensity rapidly decreased in the sub-microseconds at the end of the excitation pulse. It is clear that the TTA occurs in the electroluminescence process. After TTA, the energy of new produced singlet excitons were transferred to BUBD-1. The energy transfer process of devices have been demonstrated in Scheme 3. The ratio of the delayed component depicted in Fig. 9(b) show a nonmonotonic transformation, which was increased with the excitation pulse voltage from 5.8 V to 6.5 V and then decreased with more higher driving voltage. These results can be explained by the two competitive processes in electroluminescence. At the low current density, the contribution from



Scheme 3. The process of TTA and energy transfer.

the TTA process dominates the delayed fluorescence. While with the increasing operating voltage, the initially balanced charge injection will be changed, and the surplus charge will react with the triplet exciton and triplet-charge annihilation (TCA) process will be unfavorable for delayed fluorescence emission through TTA [21]. The regular is also in accordance with the efficiency roll-off curve.

In order to further investigate the high EQE of device **5**, we also fabricated electron and hole only device with the following structure: ITO/LiF (1 nm)/TPBi (40 nm)/**1-NaCBI** (30 nm):0–3% BUBD-1/TPBi (40 nm)/LiF (1 nm)/Al



Fig. 9. (a) Transient fluorescence decay lifetime of doping film in 1-NaCBI; (b) transient electroluminescence decay lifetime of device 5 with various excitation pulse voltages.



Fig. 10. (a) Voltage-current density characteristics for electron-only devices and (b) hole-only devices.

(100 nm) and ITO/MOO₃ (10 nm)/NPB (10 nm)/**1-NaCBI** (30 nm):0–3% BUBD-1/NPB (40 nm)/ MoO₃ (10 nm)/Al (100 nm). For the electron-only devices (see Fig. 10(a)), no obvious current density change was observed between doped and undoped device. However, dramatic decrease in current density exhibited from doped device to undoped device for hole-only devices. It can be attributed to the hole capture of BUBD-1. The large energy level offset between HOMO of NPB and BUBD-1 would trap charge carriers and thus reduce current density. On one hand, moderate trap effect of the dopant further balances the charge in emission layer and increases the efficiency. On the other hand, regrettably, the more trapped holes will lead to singlet (or triplet)-charge annihilation and induce the efficiency roll-off when the current density is increased.

4. Conclusions

In summary, three new robust blue fluorescence materials were developed based on anthracene and triphenylimidazole moieties. These compounds with good film-forming, excellent thermal properties and appropriate energy levels exhibit strong blue emission for solid thin film and EL device. The decreased π -conjugation in these compounds compared with phenanthroimidazole derivatives leads to obvious hypsochromic shift With respect to the three layers device **2** using **1-NaCBI** as the emitting layer, its maximum current efficiency reaches 3.06 cd A⁻¹ with Commission Internationale del'Eclairage (CIE) coordinates of (0.149, 0.092). In addition, device **5** based on doping BUBD-1 in **1-NaCPI**, maximum current efficiency reaches 15.53 cd A⁻¹ with maximum external quantum efficiency 8.15%, which can be attributed to TTA.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.orgel.2015.02.018.

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