Two novel indolo[3,2-b]carbazole derivatives containing dimesitylboron moieties: synthesis, photoluminescent and electroluminescent properties

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Abstract

Two novel indolo[3,2-b]carbazole derivatives, 5,11-di(4'-dimesitylboronphenyl)indolo[3,2-b]carbazole (**DDBICZ**) and 2,8-dimesitylboron-5,11-di(4'-dimesitylboronphenyl) indolo[3,2-b]carbazole

(**DDDBICZ**) were synthesized by introducing two dimesitylboron groups and/or four dimesitylboron groups (as electron-acceptors) to the indolo[3,2-b]carbazole moiety (as electron-donor). The structures of these two compounds were fully characterized by elemental analysis, mass spectrometry and proton nuclear magnetic resonance spectroscopy methods. Their thermal properties were studied by thermogravimetric analysis and differential scanning calorimetry. Their electrochemical and photophysical properties were studied by electrochemical methods, UV-vis absorption spectroscopy and fluorescence spectroscopy. The charge-transporting properties of **DDBICZ** and **DDDBICZ** were studied by fabricating single carrier devices using them as charge-transporting layers. The results reveal that **DDBICZ** and **DDDBICZ** have high thermal stability (the decomposition temperature of **DDBICZ** = 201 ◦C and the decomposition temperature of **DDDBICZ**=210◦C) and good electrochemical and electron-transporting properties. Moreover, in order to examine the electroluminescent properties of **DDBICZ** and **DDDBICZ**, **Device A** and **Device B** fabricated by using them as light-emitting layer, respectively. The turn-on voltage, maximum luminance and maximum luminance efficiency of **Device A** are 6.1 V, 5634 cd/m^2 and 2.96 cd/A, whereas those of **Device B** are 3.6 V, 1363 cd/m^2 and 2.88 cd/A.

***Keywords*:** Indolo[3,2-b]carbazole, Dimesitylboron, Synthesis, Photoluminescent Properties, Electroluminescent Properties

1. Introduction

Since the seminal work on organic light-emitting diodes (OLEDs) by Tang and VanSlyke [1], organic electroluminescent(EL) devices have gained enormous attention owing to their promising applications in solid-state lighting and full-color flat-panel display [2–7]. With the purpose of improving the efficiency and stability of the OLEDs, many efforts have been made to develop various novel organic materials with desirable properties [8-10]. Among these high-performance materials, indolo[3,2-b]carbazole (ICZ) derivatives and boron-containing π-conjugated compounds are the popular ones due to their excellent performance in EL devices.

Indolo[3,2-b]carbazole (ICZ) derivatives have received much attention due to their large planar and rigid conjugated structures together with the remarkable photophysical properties, so these compounds have received much attention. Many ICZ derivatives with outstanding properties such as better morphological stability and thermal durability as well as desirable charge-injecting and transporting properties have been reported during the past decades. Ong and his co-workers reported a series of ICZ derivatives, which could be served as excellent hole-transporting materials and organic thin-film transistor (OTFT) materials [11-14]. Tao et al. designed and synthesized several ICZ derivatives, which can be used as excellent luminescence and hole-transporting materials in the OLEDs [15-17]. Pierre-Luc et al. synthesized some new materials based on the ICZ framework, which were particularly suitable for organic field-effect transistors (OFETs) [18, 19]. J.V. Grazulevicius and his co-workers developed various *N*, *N*-diarylated ICZ and these compounds can be served as hole-transporting materials for OLEDs [20-24]. Recently, Chen et al. reported two new ICZ derivatives with multifunctionality, which were employed as deep-blue emitters, hole-transporting materials and hosts to fabricate organic light-emitting devices [25].

Boron-containing π-conjugated compounds have emerged for decades. They have high fluorescence quantum yields owing to the overlap between the vacant p-orbital of the boron center and the conjugated moieties [26-34], which make these compounds a promising class of candidate for optoelectronic materials. Generally, for the applications of organoboron compounds in optoelectronic materials and devices, the boron center must resist nucleophilic attack and hydrolysis. Researchers have readily achieved this by functionalizing the boron center with bulky aryl substituents [35]. Thus, triarylboron compounds containing a dimesitylboron group and/or several dimesitylboron groups have been successfully developed as materials for nonlinear optics [36, 37] and anion sensing [38-47] and utilized as emitting and/or electron-transporting materials for OLEDs [48-57]. Shirota and co-workers first reported the use of triarylboranes in OLEDs . They designed and synthesized a series of emitting materials with desired bipolar character containing a dimesitylboron group [50, 51]. Inspired by the work done by Shirota's group, Wang and co-workers synthesized various donor-acceptor type triarylboranes blue emitting materials, including compounds based on BNPB [54, 55], DPA and AZAIN systems [58, 53]. They evaluated the performances of those compounds by fabricating EL devices.

Their results shown that BNPB-2 can act as either a bifunctional electron-transporting and blue-emitting material in a simple double-layer EL device or a trifunctional electron-transporting, hole-transporting and blue-emitting material in a triple-layer EL device [54], BNPB-5 can act as an excellent hole-transporting material in OLEDs [28], BDPA-2 and BDPA-3 can be used as both blue-emitting and electron-transporting materials in OLEDs [53]. In addition, they investigated the use of triarylboron-containing metal complexes as phosphorescent materials in OLEDs [59-63]. Besides Wang and co-workers, many other research groups have devoted great effort in the exploration of triarylboranes compounds in the use of OLEDs. Among them, Lambert and co-workers synthesized a series of amino-substituted triarylboranes (TABs) and investigated their electrochemical and photophysical properties [64]. Later, they synthesized polymers based on the carbazole-substituted TABs mentioned above [65]. They found that the 3, 6-linked polycarbazole is a promising candidate for the application in OLEDs. Despite all those effort made by different groups, the field of boron-containing optoelectronic materials still remains largely unexplored.

As mentioned above, compounds containing ICZ moiety and/or dimesitylboron moiety are attractive materials for the organic electroluminescent (EL) devices due to their efficient luminescence and transport performance. Thus we became interested in incorporating ICZ moiety and dimesitylboron moiety into a single molecule to obtain novel materials with excellent luminescent, hole-transporting and electron-transporting properties.

In this paper, two new ICZ derivatives, 5,11-di(4'-dimesitylboronphenyl)-indolo[3,2-b]carbazole (**DDBICZ**) and 2,8-dimesitylboron-5,11-di(4'-dimesitylboronphenyl) indolo[3,2-b]carbazole (**DDDBICZ**), were synthesized by introducing dimesitylboron groups to the ICZ moiety. The synthetic route is presented in Scheme 1. To the best of our knowledge, these compounds have never been reported before. The structures of **DDBICZ** and **DDDBICZ** were characterized by ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. The thermal, electrochemical, photoluminescent properties were determined by thermogravimetric analysis combined with electrochemistry, UV-vis absorption spectroscopy and fluorescence spectroscopy. Furthermore, the electroluminescent properties were characterized by the devices fabricated using these compounds.

Scheme 1 the synthetic route of **DDBICZ** and **DDDBICZ**.

2. Experimental

2.1. Synthesis of compounds

The synthesis of compounds cyclohexane-1,4-dione-diphenyl-hydrazone (**1**), cyclohexane-1, 4-dione-bis (p-bromophenyl)-hydrazone (**2**), indolo[3,2-b]carbazole (**3**) and 2,8-dibromoindolo[3,2-b]carbazole (**4**) were performed according to or slightly modified literature procedures [66].

2.1.1 Synthesis of cyclohexane-1, 4-dione-diphenyl hydrazone (Compound 1)

To a solution of 1,4-cyclohexanedione (5 g, 44.5 mmol) in absolute EtOH (100 mL) was added 90 ml absolute ethyl alcohol and 0.1 ml Acetic Acid. The reaction mixture was stirred for 20 min, and then 10.73 ml phenylhydrazine was added dropwise. The reaction mixture was heated to 35 °C and kept at the same temperature for 30 min and then cooled. A precipitate was slowly filtered off, washed carefully with water and dried to give cyclohexane-1, 4-dione-diphenyl hydrazone (7.13, 54.9%) as a yellow powder.

2.1.2 Synthesis of cyclohexane-1, 4-dione-bis(p-bromophenyl)-hydrazone (Compound 2).

1, 4-cyclohexanedione (5.62 g, 50 mmol) was dissolved in absolute ethanol (EtOH) (100 mL) and was added with stirring to a mixture of powdered 4-bromophenylhydrazine hydrochloride (22.4 g, 100 mmol), sodium acetate (8.2 g, 100 mmol) and absolute ethanol (200 mL) at room temperature. The mixture was quickly heated to 50 °C, and then, the temperature was cooled to 0 °C. A precipitate was filtered off, washed carefully with water to give **2** (yield 59%).

2.1.3. Synthesis of indolo[3,2-b]carbazole (Compound 3)

Cyclohexane-1, 4-dione-bisphenyl hydrazone (10 g, 0.036 mmol) was added portionwise to a mixture of AcOH and H_2SO_4 (4:1, 50ml) with stirring at 10 °C. Thereafter, the mixture was heated to 30 °C and kept for 30 min. Afterwards, the temperature was increased slowly to 60-70 °C and the mixture changed colour from bright raspberry to grey-green. After half an hour, the reaction mixture was refluxed another 30min with the colour changing to yellow. Then the mixture was allowed to cool to room temperature and a precipitate was slowly filtered off and was washed carefully with water and EtOH, and dried to give the target compound (5.74 g, 62.3%) as a yellow solid.

2.1.4. Synthesis of 2, 8-dibromoindolo[3,2-b]carbazole (Compound 4)

Compound **2** (10 g, 22 mmol) was added into a mixture of AcOH (130 mL) and H_2SO_4 (32 mL) at 0 °C and stirred for 5 min. The mixture was heated up to 30 °C and kept stirring for 1 h. Afterward, the mixture was further risen up to 60–70 °C and stirred for another 1 h. Then it was cooled down to room temperature and poured into an ice water with stirring. The greenish solid was filtered off and washed with water and EtOH to neutral pH. Finally, dried and pure 2, 8-dibromoindolo [3,2-b]carbazole (Compound **4**) (4.88 g, yield 52.8%) was achieved. Mp > 300 °C. ^{1}H NMR (600 MHz DMSO-d_6) δ (ppm): 11.14 (2H, s, and N–H), and 7.1– 8.24 (8H, m, and Ar–H).

2.1.5. Synthesis of 5, 11-di(4'-bromophenyl)indolo[3,2-b]carbazole (Compound 5)

Indolo[3,2-b]carbazole (2.563 g, 10 mmol) and 1-bromo-4-iodobenzene (8.487 g, 30 mmol) were dissolved in 80 ml of dry DMF under a nitrogen atmosphere. Then powdered potassium carbonate (11.040 g, 80 mmol), Cu (2.921 g, 46 mmol) and 18-crown-6 (1.056g, 4 mmol) were added into it. The mixture was stirred for 30 min at room temperature and then heated up slowly to 150 °C and kept for 48 h.

Afterwards, the reaction mixture was cooled down to room temperature and poured into an ice water with stirring 1 h. The precipitate was collected and recrystallized with EtOH and dried finally. The residue was purified by flash chromatography on silica gel (CH_2Cl_2/hexane) to afford compound **5**. Yield: 50%. Mp: > 300 °C. ^{1}H NMR (600 MHz $CDCl_3$) δ (ppm): 8.118 (2H, d, J = 7.8), 8.033-7.992 (3H, m, J = 7.2), 7.805 (3H, d, J = 8.4), 7.575 (3H, d, J = 8.4), 7.359-7.384 (5H, m , J = 9.0), 7.273 (1H, d, J = 7.2), 6.981 (1H, s).

2.1.6 Synthesis of 2, 8-dibromo-5,11-di(4'-bromophenyl)Indolo[3,2-b]carbazole (Compound 6)

To a solution of 2, 8-dibromoindolo[3,2-b]carbazole (2.76 g, 6.7 mmol) in anhydrous DMF (80 mL) in the round-bottomed flask, 1-bromo-4-iodobenzene (5.64 g, 20 mmol) was added under a nitrogen atmosphere. Then powdered potassium carbonate (7.36 g, 53 mmol), CuI (0.38 g, 2 mmol) and 18-crown-6 (0.704 g, 2.7 mmol) were added into it. The mixture was heated up slowly to 170 °C after stirred for 30 min at room temperature and kept for 48 h. Then, the reaction mixture was cooled down to room temperature and poured into an ice water with stirring 1 h. The precipitate was collected and recrystallized with EtOH and dried. The crude product was purified by flash chromatography on silica gel (CH_2Cl_2/hexane) to afford compound **6**. Yield: 28.7%. Mp: > 300 °C. ^{1}H NMR (600 MHz $CDCl_3$) δ (ppm): 8.674 (1H, s), 8.375-8.363 (2H, t, *J* = 4.2), 8.074 (1H, d, *J* = 7.8), 7.918 (2H, d, *J* = 7.8), 7.714 (4H, t, *J* =7.8), 7.606-7.513(3H, m, *J* =7.8), 7.349 (2H, d, *J* = 9.0), 7.240 (1H, d, *J* = 9.0).

2.1.7. Synthesis of 5,11-di(4'-dimesitylboronphenyl)indolo[3,2-b]carbazole(DDBICZ)

Compound **5** (0.846 g, 1.5 mmol) was suspended in anhydrous THF (60 mL) under a nitrogen atmosphere and the solution was cooled to -78 °C with stirring. To this solution, butyllithium (1.7 mL, 2.2 M in hexanes) was injected and the resulting solution was stirred for 30 min at this temperature. Afterwards, the reaction solution was raised to room temperature and kept so for 6 h. Then the solution was cooled to -78 °C again, and dimesitylboron fluoride (1.005 g, 3.75 mmol) was quickly added into the stirred reaction mixture under a nitrogen atmosphere. The mixture was allowed to warm to room temperature with stirring 48 h. Afterwards, the solvent was removed. The residue was diluted with CH_2Cl_2 and the organic layer was collected. The combined organic phase was evaporated in vacuo and the residue was washed carefully with Et_2O and EtOH, filtered off and dried to get the crude product, and the crude product was purified by flash chromatography on silica gel (CH_2Cl_2/hexane) to obtain **DDBICZ** (0.464 g, 34%) as light yellow solid. ^{1}H NMR (600 MHz $CDCl_3$) δ (ppm): 8.146 (4H, dd, J = 19.8, 22.2), 7.815 (4H, d, J = 7.8), 7.700 (4H, d, J = 4.2), 7.527 (2H, d, J = 4.2), 7.415 (4H, t, J = 7.2), 6.892 (8H, s), 2.345 (12H, s), 2.150 (24H, s). ^{13}C NMR (600 MHz $CDCl_3$) δ (ppm): 144.612, 144.521, 144.480, 143.787, 141.773, 141.081, 139.551, 132.900, 132.793, 130.239, 130.018, 129.050, 128.983, 128.904, 128.800, 126.797, 126.672, 123.211, 123.159, 123.107, 122.707, 122.657, 122.611, 122.100, 112.690, 112.644, 103.106, 102.973, 102.888, 26.454, 24.119.

MS(m/z):904.6(M+). Anal. Calcd. for $C_{66}H_{62}B_2N_2$: C, 87.61%; H, 6.91%; N, 3.10%. Found: C, 87.69%; H, 6.87%; N, 3.14%.

2.1.8 Synthesis of 2, 8-dimesitylboron-5, 11-di(4'-dimesitylboronphenyl)indolo[3,2-b]carbazole] (DDDBICZ)

Compound 6 (0.5 g, 0.69 mmol) was dissolved in anhydrous THF (60 mL) under a nitrogen atmosphere and the resulting solution was cooled to -78 °C with stirring. Then, n-butyllithium (5.3 mL, 1.3 M in hexanes) was added to the stirred solution at this temperature. After 30 min, the reaction solution was raised to room temperature and kept so for 6 h. Then, the solution was cooled to -78 °C again, and dimesitylboron fluoride (2.22 g, 8.28 mmol) was quickly added into the stirred reaction mixture under a nitrogen atmosphere. The mixture was allowed to warm to room temperature with stirring 48 h. Afterwards, the solvent was evaporated and the residue was extracted with water and CH_2Cl_2. The organic layer was collected and evaporated in vacuo, and then the residue was washed carefully with Et_2O and EtOH, filtered off and dried to get the crude product. Finally, the crude product was purified by flash chromatography on silica gel (CH_2Cl_2/hexane) to obtain **DDDBICZ** (0.268 g, 28%) as light yellow solid. ^1H NMR (600 MHz DMSO) δ (ppm): 8.335 (2H, s), 8.068 (2H, s), 7.802 (4H, d, J = 7.8), 7.651 (4H, d, J = 8.4), 7.589 (2H, d, J = 8.4), 7.368 (2H, d, J =8.4), 6.874 (8H, s), 6.842 (8H, s), 2.346 (12H, s), 2.327 (12H, s), 2.104 (24H, s), 2.049 (24H, s) ^{13}C NMR (600 MHz DMSO) δ (ppm): 145.15, 144.533, 143.847, 143.795, 143.725, 141.759, 141.227, 141.045, 140.184, 138.772, 133.096, 132.766, 131.982, 131.213, 131.035, 130.427, 129.231, 127.019, 126.571, 112.056, 103.872, 32.563, 28.493, 26.489, 26.405, 24.095. MS(m/z): 1401.5(M+). Anal. Calcd. for $C_{102}H_{104}B_4N_2$: C, 87.43%; H, 7.48% ; N, 2.00%. Found: C, 87.37%; H, 7.51% ; N, 2.05%.

2.2 Measurement and characterization

Melting points were determined on an X-5 melting point detector. All NMR spectra were measured on a Bruker 600 MHz spectrometer. Thermogravimetric analysis (TGA) was performed on a TGA 2050 thermogravimetric analyser under N_2 atmosphere with a heating rate of 10 °C/ min from room temperature to 750 °C. Differential scanning calorimetry (DSC) was performed on a Q2000 DSC differential Scanning Calorimeter under N_2 atmosphere with a heating rate of 10 °C/ min from room temperature to 250 °C. Elemental analyses were performed on an Element Analysis System. Mass spectra were recorded with a LC-MS system consisted of a Waters 1525 pump and a Micromass ZQ4000 single quadrupole mass spectrometer detector. Cyclic voltammetry (CV) was performed on a CHI-600C electrochemical analyser. The CV measurements were carried out with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum-disk auxiliary electrode and a Ag/AgCl reference electrode, and the scan speed was 50 mV/s. UV-vis absorption spectrum was acquired on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were obtained on a Hitachi F-4500 spectrofluorometer. Fluorescence quantum yield was determined by using quinine sulfate as the reference. All measurements were performed at room temperature.

2.3 Device fabrication and testing

The multilayer OLEDs were fabricated by the vacuum-deposition method. Organic layers were deposited by high-vacuum (5×10^{-4} Pa) thermal evaporation onto a glass (3 cm×4 cm) substrate pre-coated with an indium tin oxide (ITO) layer. *N*,*N*-bis(naphthyl)-*N*,*N*-bis(phenyl)benzidine(NPB), 4,4′-cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)benzenamine] (TAPC) , **DDBICZ/ DDDBICZ**, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 4,7-diphenyl-1,10-phenanthroline (BPhen) and LiF/Al were used as the hole-transporting layer, electron-blocking layer, emitting layer, hole-blocking layer, electron-transporting layer and cathode, respectively. All organic layers were sequentially deposited. Thermal deposition rates for organic materials, LiF and Al were 0.5, 0.5 and 1 Å/s, respectively. The active area of the devices was 12 mm^2. The electroluminescent spectra were measured on a Hitachi MPF-4 spectrofluorometer. The voltage-current density (V-J) characteristics of OLEDs were recorded on a Keithley 2400 Source Meter. The characterization of brightness-current-voltage (B-I-V) were measured with a 3645 DC power supply combined with a 1980A spot photometer and were recorded simultaneously. All measurements were done at room temperature in ambient conditions.

2.4. Theoretical calculations

The ground-state geometries of **DDBICZ** and **DDDBICZ** were optimized at B3LYP level with 6-31G (d, p) basis set [67-69]. Their vibration frequencies and frontier molecular orbital characteristics were analysed on the optimized structure at the same level. Solvent effect was also taken into account by using the polarised continuum model [70, 71]. All calculations were carried out with the Gaussian 03 program package [72] and performed in the Supercomputing Centre of Computer Network Information Centre of the Chinese Academy of Sciences.

3. Results and Discussion

3.1 Synthesis

As shown in Scheme 1, the syntheses of indolo[3,2-b]carbazole derivatives comprising dimesitylboron moieties were carried out by a multi-step synthetic route. Firstly, compound **1** was synthesized via the reaction of 1, 4-cyclohexanedione with phenylhydrazine. Then compound **3** was prepared by the Fischer reaction of compound **1** in a mixture of acetic acid and sulfuric acid at 65 °C in high yield. Secondly, the intermediate compound **5** was prepared by reacting of indolo[3,2-b]carbazole with 1-bromo-4-iodobenzene in the presence of Cu, 18-crown-6 and potassium carbonate at 170 °C with 50% yield. Finally, **DDBICZ** was synthesized by compound **5** reacting with n-BuLi and dimesitylboron fluoride at −78 °C with 34% yield. The synthetic route of **DDDBICZ** was similar to that of **DDBICZ**. **DDDBICZ** was obtained with 28% yield. **DDBICZ** and **DDDBICZ** were characterized by ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. The ^{1}H NMR spectra of **DDBICZ** and **DDDBICZ** displayed downfield peaks at 7.00-8.48 ppm, which were assigned to the protons of 5, 11-diphenylindolo[3,2-b]carbazole moiety. The downfield peaks at 6.59-6.89 ppm and the upfield peaks at 2.09 and 2.37 ppm were assigned to the protons of dimesitylboron moieties. The ^{13}C NMR, mass spectrum and elemental analysis were consistent with the desired structures. Further details are given in the experimental section. **DDBICZ** and **DDDBICZ** are soluble in many common organic solvents such as dichloromethane, chloroform, DMF, THF, toluene and DMSO.

3.2 Thermal properties

The thermal property of **DDBICZ** and **DDDBICZ** was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under under a nitrogen atmosphere. The TGA and DSC curves of **DDBICZ** and **DDDBICZ** are shown in Fig. 1 and Fig. 2, respectively. The decomposition temperatures (T_d) were observed for **DDBICZ** ($T_{d\,=}$ 201 °C) and **DDDBICZ** ($T_{d\,=}$ 210 °C) by TGA analyses. The glass transition temperatures (T_g) were observed for **DDBICZ** ($T_{g\,=}$ 145 °C) and **DDDBICZ** ($T_{g\,=}$ 162 °C) by DSC analyses. These data are also collected in Table 1. The high T_d and T_g of **DDBICZ** and **DDDBICZ** can be attributed to their large molecular mass, rigid indolo[3,2-b]carbazole cores and non-planar dimesitylboron peripheries. Our results indicate that these two compounds have excellent thermal properties which should be adequate for most optoelectronic device applications.

Fig. 1. TGA curves of **DDBICZ and DDDBICZ**

Fig. 2. DSC curves of **DDBICZ and DDDBICZ**

3.3 Theoretical calculation

Theoretical calculations can provide a reasonable qualitative indication of the excitation and emission properties of a compound [73]. The ground-state geometries of **DDBICZ** and **DDDBICZ** were optimized at B3LYP level with 6-31G (d, p) basis set. The vibration frequencies and the frontier molecular orbital characteristics were analyzed on the optimized structures at the same level. The molecular structure of **DDBICZ** contains a 5, 11-diphenylindolo[3, 2-b]carbazole unit as core and two dimesitylboron groups as the terminals. As shown in Fig 3, the indolo[3,2-b]carbazole moiety is of planar structure, the two phenyl present a twisted structure relative to this plane and the two mesityl groups form propeller-like conformations originated from the trigonal boron center. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **DDBICZ** were also calculated at DFT/B3LYP/6-31G (d, p) level using the polarized continuum model for geometry optimization. Coordinates of **DDBICZ** are collected in **Table S1**. **Table S1** is dded in the Electronic Supporting Information (ESI). The HOMO of **DDBICZ** is localized mainly in the indolo[3,2-b]carbazole moiety, while the LUMO is localized in the dimesitylborylphenyl moiety (Fig. 1a). The molecular structure of **DDDBICZ** contains a 5, 11-diphenylindolo[3,2-b]carbazole unit as the core and four dimesitylboron groups as the terminals. The geometry of **DDDBICZ** at ground state was optimized using the same method. Coordinates of **DDDBICZ** are collected in **Table S2**(ESI). Fig. 1b shows that the geometry of **DDDBICZ** is similar with **DDBICZ** and the distribution of HOMO and the LUMO of **DDDBICZ** are similar to those of **DDBICZ**, respectively. Generally, holes and electrons in OLEDs are transferred through the individual HOMO and LUMO levels [74]. Fig. 1a and Fig. 1b show that **DDBICZ** and **DDDBICZ** exhibit almost complete separation of LUMO and HOMO, which is essential for the efficient hole and electron transport [75]. The calculated HOMO, LUMO energy levels and their energy gap of **DDBICZ** are -5.20, -1.97 and 3.23 eV (Table 1), while those of **DDDBICZ** are -5.34, -2.02 eV and 3.32 eV (Table 1), respectively. The theoretical HOMO and LUMO levels of **DDBICZ** and **DDDBICZ** are higher than the experimental ones, the HOMO-LUMO energy gaps of **DDBICZ** and **DDDBICZ** in theory is *ca.* 0.34 eV and 0.36 larger than those of the optical energy band obtained from UV-vis absorption measurement, respectively.

Fig. 3. HOMO and LUMO diagrams of **DDBICZ** and **DDDBICZ**.

3.4 Photophysical properties

Fig. 4a shows the absorption spectra of **DDBICZ** in various solvents (1.0×10^{-5} M). The absorption spectra data are summarized in Table 1. As depicted in Fig. 4a, **DDBICZ** exhibits two major absorption bands at 290-350 and 350-429 nm, respectively. The absorption peak maximum (λ_{abs}) of 337 nm corresponds to the *π*-*π** electronic transition of indolo[3,2-b]carbazole skeleton and the λ_{abs} of 398 nm assigns to intramolecular charge transfer (ICT) from the indolo[3,2-b]carbazole core to dimesitylboron terminals. Fig. 4b shows the absorption spectra of **DDDBICZ** in various solvents (1.0×10^{-5} M). The absorption spectra data are also summarized in Table 1. As shown in Fig. 4b, the absorption spectra of **DDDBICZ** are similar with those of **DDBICZ** in various solvents. The optical energy band gap of **DDBICZ** calculated from the absorption band edge of the absorption spectrum is approximately 2.89 eV, while that of **DDDBICZ** is approximately 2.96 eV. The normalized fluorescence spectra of **DDBICZ** in various solvents (1.0×10^{-5} M) are shown in Fig. 5a and the data are also collected in Table 1. As shown in Fig. 5a, **DDBICZ** exhibits a strong fluorescence emission bands at 390-670 nm in various solvents. The emission peak maximums (λ_{em}) exhibit a red-shifted of 115 nm ranging from 425 nm (in hexane) to 540 nm (in DMSO) with the increasing polarity of the solvents, which is assigned to *π*–*π** transition of the intramolecular charge transfer (ICT) from the indolo[3,2-b]carbazole core to the dimesitylboron terminals in the excitation process. The fluorescence spectra of **DDDBICZ** show similar characteristics with those of **DDBICZ** in various solvents (Fig. 5b). The emission bands are located at 390 nm~660 nm with a red-shifted of 95 nm ranging from 423 nm (in hexane) to 518 nm (in DMSO). The fluorescence quantum yields (Φ) of **DDBICZ** and **DDDBICZ** in several solvents (1.0×10^{-6} M) were measured by using quinine bisulfate in 0.10 M sulfuric acid as the reference [76] and collected in Table 1. As shown in Table 1,

DDBICZ and **DDDBICZ** have relatively high fluorescence quantum yields, revealing their potential application as excellent optoelectronic materials in the optical field.

Fig. 4. the UV-vis absorption spectra of **DDBICZ** and **DDDBICZ** in several solvents.

Fig. 5. the normalized fluorescence spectra of **DDBICZ** and **DDDBICZ** in several solvents.

3.5 Electrochemical properties

The electrochemical properties of **DDBICZ** and **DDDBICZ** were studied by cyclic voltammetry (CV) with Ag/AgCl as the reference electrode. The measurement was conducted in 1.0 mM **DDBICZ** and/or **DDDBICZ** in acetonitrile containing 0.10 M tetrabutylammonium perchlorate as the supporting electrolyte under N_2 atmosphere. The CVs of **DDBICZ** are displayed in Fig. 6a. As shown in Fig. 6a, a reversible oxidation peak and one reversible reduction peak are observed within the entire electrochemical window of acetonitrile. The reversible oxidation peak around +1.12 V is assigned to the oxidation of indolo[3,2-b]carbazole, whereas the reversible reduction peak around -1.23V is attributed to the electron injection into the vacant *p*-orbital of dimesitylboron. The CVs of **DDDBICZ** are displayed in Fig. 6b. As shown in Fig. 6b, its reversible oxidation and reduction peak is at +1.18V and -1.25V, respectively. The electrochemical behaviors of **DDDBICZ** are similar with those of **DDBICZ**. The HOMO energy level can be calculated with the empirical equation: HOMO = – (E_{ox} + 4.40) eV, where E_{ox} is the onset oxidation potential [77]. The E_{ox} of **DDBICZ** is 0.87 and the HOMO energy level of **DDBICZ** is -5.27 eV. The E_g is estimated to be 2.89 eV by the absorption edge of the absorption spectrum of **DDBICZ**. The LUMO energy level of **DDBICZ** is thus -2.38 eV which is calculated from the HOMO energy level and E_g. The HOMO, LUMO and E_g of **DDBICZ** are very close to the theoretical values (Table 1). Similar with **DDBICZ**, the HOMO, LUMO and E_g of **DDDBICZ** are also very close to the theoretical values (Table 1). The LUMO levels of **DDBICZ** and **DDDBICZ** are as low as those of two common electron-transporting materials, 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (2.39 eV) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (**BCP**) (2.44 eV), indicating that these two compounds have small barrier of electron transport and can be use as effective electron-transporting materials for OLEDs [78]. Furthermore, the CV curves of the compounds remained unchanged under multiple successive potential scans, indicating the compounds have excelent redox properties [79].

Fig. 6 the cyclic voltammogram curves of **DDBICZ and DDDBICZ**

3.6 Charge-transporting properties

In order to further demonstrate the charge-transporting properties of **DDBICZ** and **DDDBICZ**, several single carrier devices were prepared. First, two hole-only devices, ITO/TAPC (8 nm)/ **DDBICZ** (30 nm)/TAPC (8 nm)/Al and ITO/TAPC (8 nm)/ **DDDBICZ** (30 nm)/TAPC (8 nm)/Al, were prepared to examine the hole-transporting capability of **DDBICZ** and **DDDBICZ**, respectively. In which TAPC was used to block the electron from the cathode because of its high LUMO level. Then, another two electron-only devices, ITO/BCP (8 nm)/ **DDBICZ** (30 nm)/BCP (8 nm)/LiF (1 nm)/Al and ITO/BCP (8 nm)/ **DDDBICZ** (30 nm)/BCP (8 nm)/LiF (1 nm)/Al, were prepared to examine the electron-transporting capability of **DDBICZ** and **DDDBICZ**, respectively. In which BCP was used to block the hole from the anode because of its low HOMO level. Fig. 7 depicts the current-characteristics of the four devices as a function of the average electric field. Both devices fabricated by using **DDBICZ** can conduct rather significant currents, suggesting **DDBICZ** has hole- and electron-transporting capabilities. Under the same average electric field, the electron-only device conducts higher currents than the hole-only device, indicating that **DDBICZ** may possess stronger electron-transporting ability in spite of its bipolar capability (Fig. 7a). The devices based on **DDDBICZ** have similar performance with the devices fabricated by using **DDBICZ (Fig. 7b).** Our results are in good agreement with the results obtained by Lin et al.[80]. Thus, these two compounds are promising candidate as electron-transporting materials.

Fig. 7. The current characteristics as a function of the average electric field for hole-only and electron-only devices.

3.7 Electroluminescent properties

In order to evaluate **DDBICZ** and/or **DDDBICZ** as the potential luminescent materials for their application in OLEDs, Two multilayer organic electroluminescence (EL) devices with the configuration of ITO/NPB (50 nm)/ **DDBICZ** (50 nm)/ Bphen (20nm)/LiF(0.5 nm)/A1 (**Device A**) and ITO/NPB (50 nm)/ **DDDBICZ** (50 nm)/Bphen (20nm)/LiF(0.5 nm)/A1 (**Device B**) were fabricated, where NPB, and Bphen were used as the hole-transporting layer and the electron-transporting layer, respectively. The EL spectra of the **Device A** measured at different voltages are shown in Fig. S1 (ESI), which are in good agreement with those of **DDBICZ** films. (The PL spectra of **DDBICZ** films are displayed in Fig. S2) (ESI). The EL spectra of **Device A** exhibit the same pure blue emissions at different voltages with a maximum at 472nm and CIE coordinates of x=0.22 and y=0.32. The current density-voltage-luminance curves of the **Device A** are shown in Fig. 8a and the luminance efficiency-current density curve of the **Device A** is shown in Fig. 8b. The electroluminescent data of **Device A** are summarized in Table 2. As shown in Table 2, the turn-on voltage, maximum luminance and maximum luminance efficiency of the **Device A** are 6.1 V, 5634 cd/m^2 and 2.96 cd/A respectively. The EL spectra of the **Device B** measured at different voltages are shown in Fig. S3 (ESI), which are in good agreement with those of **DDDBICZ** films. (The PL spectra of **DDDBICZ** films are displayed in Fig. S4) (ESI). The EL spectra of **Device B** exhibit the same pure blue emissions at different voltages with a maximum at 464nm and CIE coordinates of x =0.16 and y = 0.19. The current density-voltage-luminance curves of the **Device B** are shown in Fig. 9a and luminance efficiency-current density curve of the **Device B** is shown in Fig. 9b. The electroluminescent data of **Device B** are also summarized in Table 2. As shown in Table 2, the turn-on voltage, maximum luminance and maximum luminance efficiency of **device B** are 3.6 V, 1363 cd/m^2 and 2.88 cd/A, respectively. Although the maximum luminance and luminance efficiency of the EL devices of **DDBICZ** and **DDDBICZ** might not be as high as in some of the blue EL devices reported before [28, 51, 53, 54, 81], these two novel compounds are promising for applications in OLEDs as emitting materials due to their excellent thermal, electrochemical and charge-transporting properties. In addition, these two materials can be utilized making white OLEDs devices by integrating with other materials, and we have obtained some preliminary results. The further large-scale application study of these two materials is currently in progress.

Fig. 8. current density-voltage-luminance curves and current density-luminance efficiency curve of **Device A**

Fig. 9. current density-voltage-luminance curves and current density-luminance efficiency curve of **Device B**

Table 1. Physical properties of compound **DDBICZ** and **DDDBICZ**

Table 2.. Electroluminescent characteristics of **Device A** and **B**

4. Conclusion

In summary, two novel indolo[3,2-b]carbazole derivatives, 5,11-di(4'-dimesitylboronphenyl)indolo[3,2-b]carbazole (**DDBICZ**) and 2,8-dimesitylboron-5,11-di(4'-dimesitylboronphenyl) indolo[3,2-b]carbazole (**DDDBICZ**) were synthesized by introducing two dimesitylboron groups and/or four dimesitylboron groups (as electron-acceptors) to indolo[3,2-b]carbazole moiety (as electron-donor). The structures of these two compounds were fully characterized by elemental analysis, mass spectrometry and proton nuclear magnetic resonance spectroscopy methods. Their thermal, electrochemical and photophysical properties were studied by thermogravimetric analysis combined with differential scanning calorimetry, electrochemistry, UV-vis absorption spectroscopy and fluorescence spectroscopy. The charge-transporting properties of **DDBICZ** and **DDDBICZ** were studied by fabricating single carrier devices using them as charge-transporting layers. The results reveal that **DDBICZ** and **DDDBICZ** have high thermal stability (the decomposition temperature of **DDBICZ** = 201 ◦C and the decomposition temperature of **DDDBICZ**=210◦C) and good electrochemical and electron-transporting properties. Moreover, in order to examine the electroluminescent properties of **DDBICZ** and **DDDBICZ**, **Device A** and **Device B** fabricated by using them as light-emitting layer, respectively. The turn-on voltage, maximum luminance and maximum luminance efficiency of **Device A** are 6.1 V, 5634 cd/m^2 and 2.96 cd/A, whereas those of **Device B** are 3.6 V, 2036 cd/m^2 and 2.88 cd/A. Our work demonstrates that **DDBICZ** and **DDDBICZ** are promising blue emitting materials with potential application in producing OLEDs devices.

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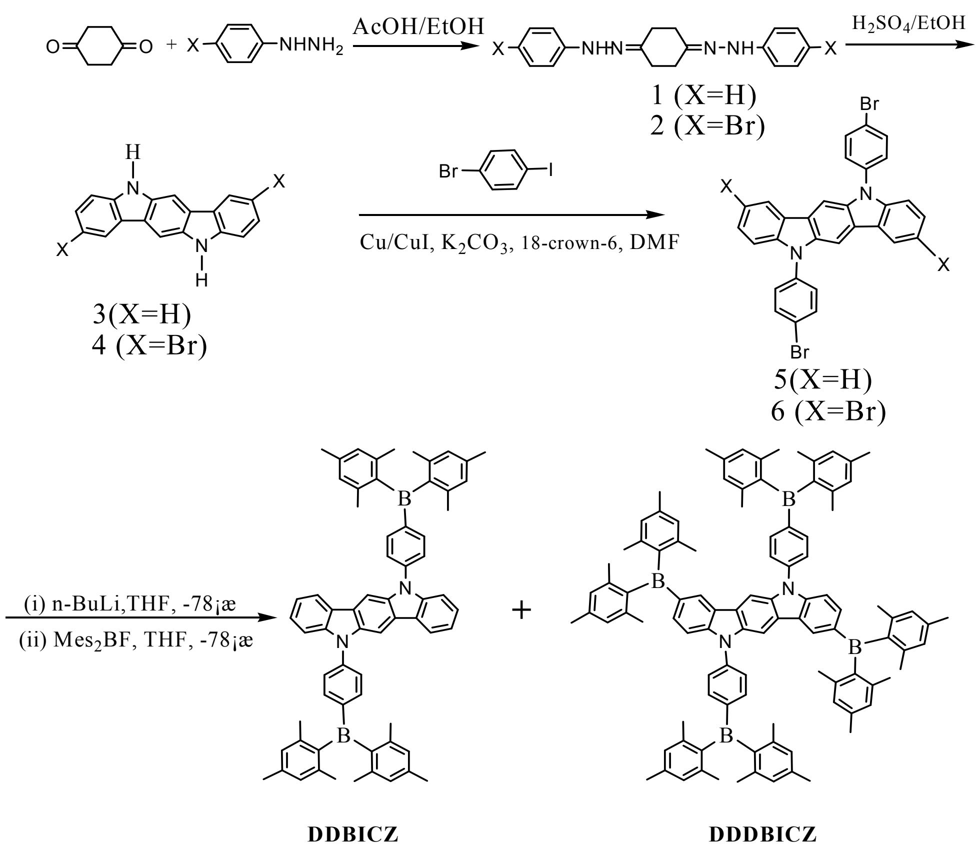
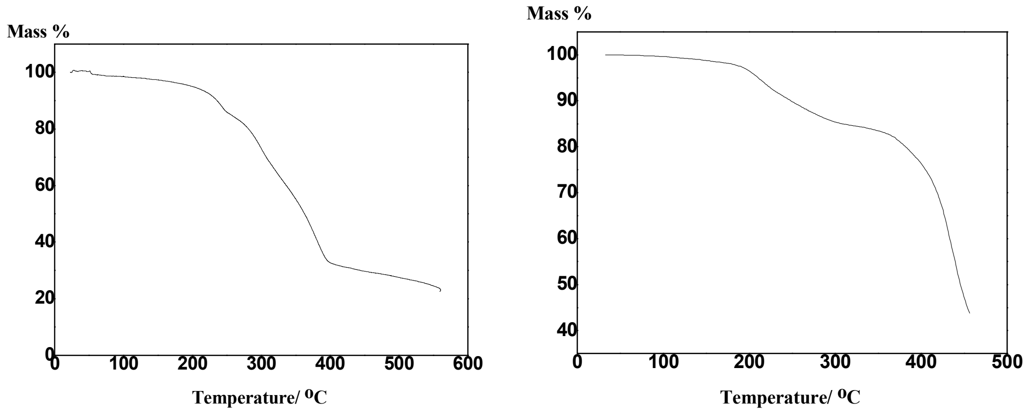
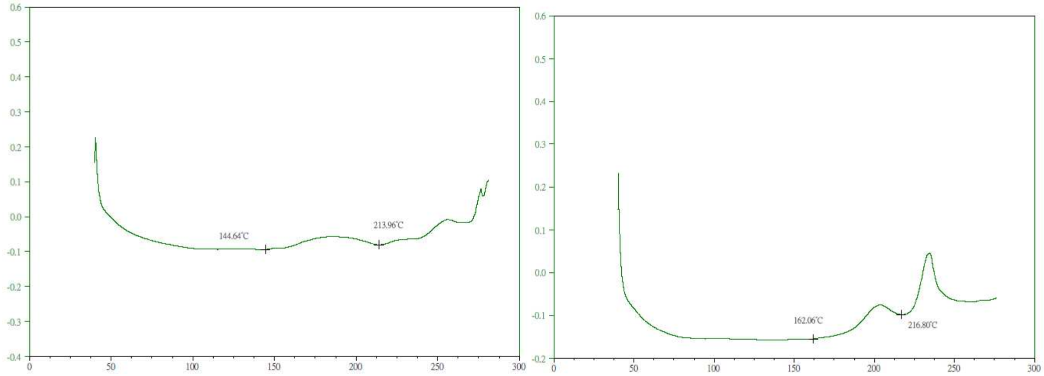


Scheme 1 the synthetic route of **DDBICZ** and **DDDBICZ**.



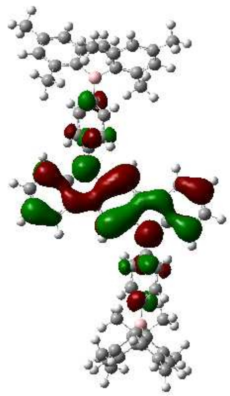
(a) TGA curve of **DDBICZ** (b) TGA curve of **DDDBICZ**

Fig. 1. TGA curves of **DDBICZ** and **DDDBICZ**

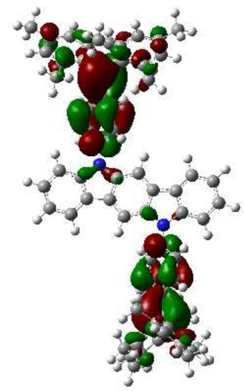


(a) DSC curve of **DDBICZ** (b) DSC curve of **DDDBICZ**

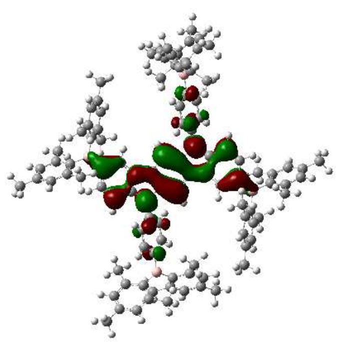
Fig. 2. DSC curves of **DDBICZ** and **DDDBICZ**



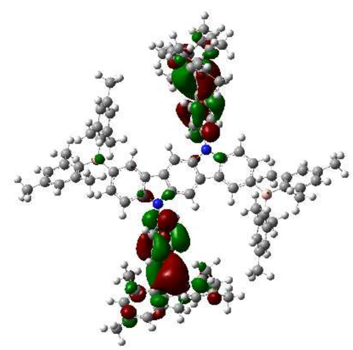
(a)HOMO of **DDBICZ**



(a) LUMO of **DDBICZ**

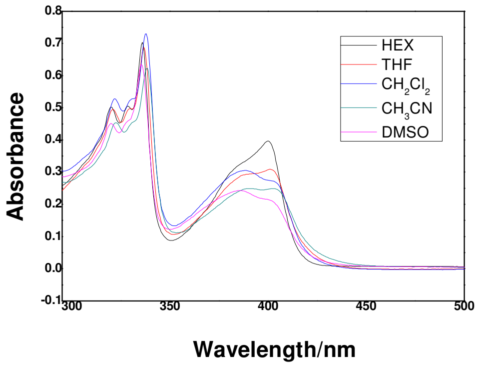


(b) HOMO of **DDDBICZ**

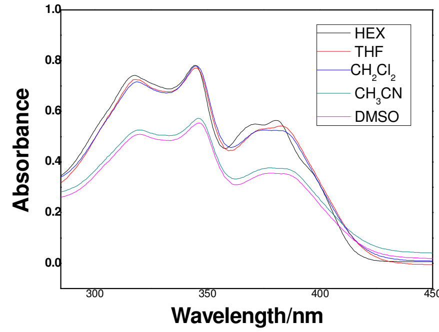


(b) LUMO of **DDDBICZ**

Fig. 3. HOMO and LUMO diagrams of **DDBICZ** and **DDDBICZ**



(a)

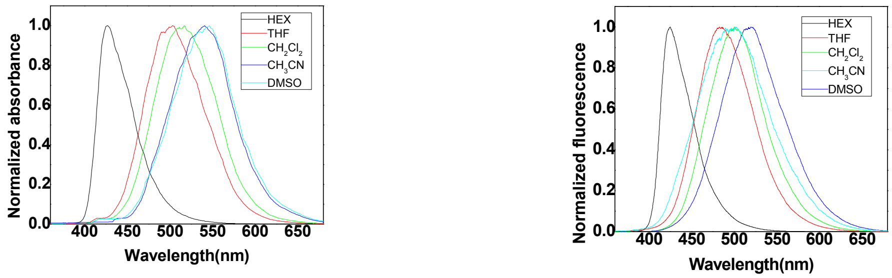


(b)

(a) the UV-vis absorption spectra of **DDBICZ** in several solvents.

(b) the UV-vis absorption spectra of **DDDBICZ** in several solvents.

Fig. 4. the UV-vis absorption spectra of **DDBICZ** and **DDDBICZ** in several solvents.

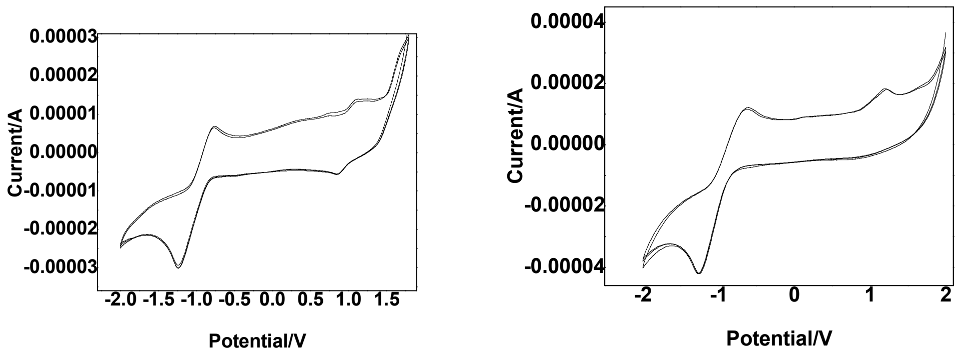


(a) (b)

(a) the normalized fluorescence spectra of **DDBICZ** in several solvents.

(b) the normalized fluorescence spectra of **DDDBICZ** in several solvents.

Fig. 5. the normalized fluorescence spectra of **DDBICZ** and **DDDBICZ** in several solvents.

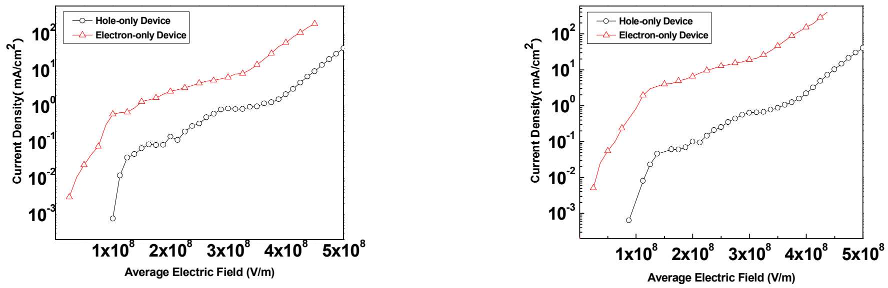


(a) **(b)**

(a) the cyclic voltammogram curves of **DDBICZ**

(b) the cyclic voltammogram curves of **DDDBICZ**

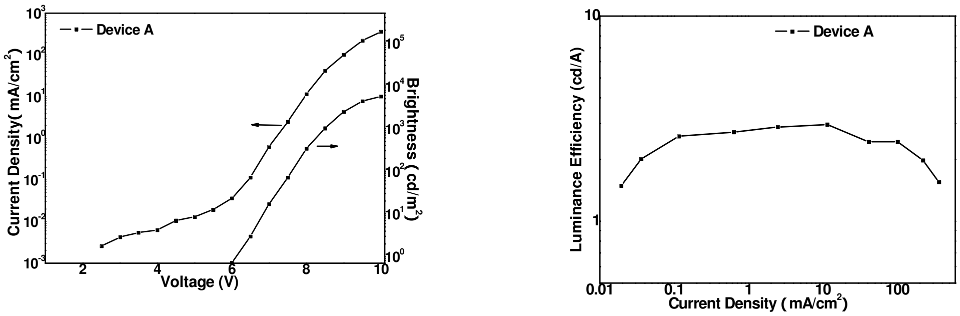
Fig. 6 the cyclic voltammogram curves of **DDBICZ and DDDBICZ**



(a) hole-only and electron-only devices of **DDBICZ**

(b) hole-only and electron-only devices of **DDDBICZ**

Fig. 7. The current characteristics as a function of the average electric field for hole-only and electron-only devices.

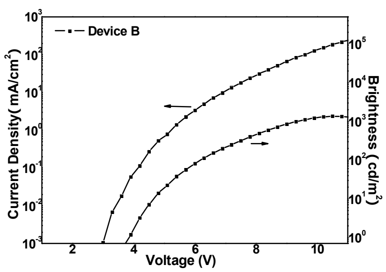


(a) (b)

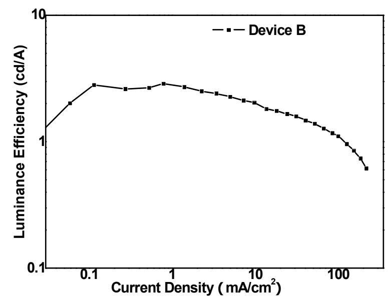
(a)current density-voltage-luminance curves

(b) current density-luminance efficiency curve

Fig. 8. current density-voltage-luminance curves and current density-luminance efficiency curve of **device A**



(a)



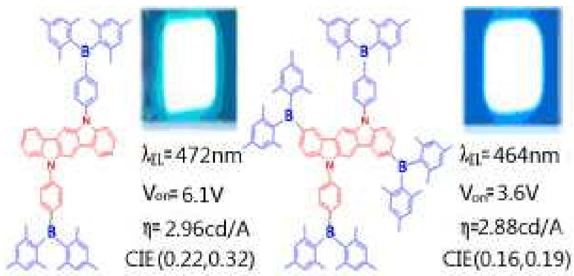
(b)

(a) current density-voltage-luminance curves

(b) current density-luminance efficiency curve

Fig. 9. current density-voltage-luminance curves and current density-luminance efficiency curve of **device B**

Graphical abstract



Highlights

The OLEDs devices using two novel indolo[3,2-b]carbazole derivatives containing dimesitylboron groups as electroluminescent material show reasonable good performance.