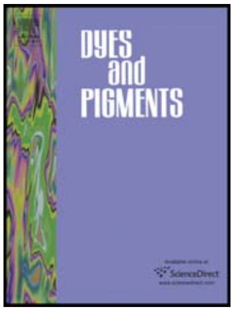

A Novel Carbazole Derivative Containing Dimesitylboron Units: Synthesis, Photophysical, Aggregation Induced Emission and Electroluminescent Properties

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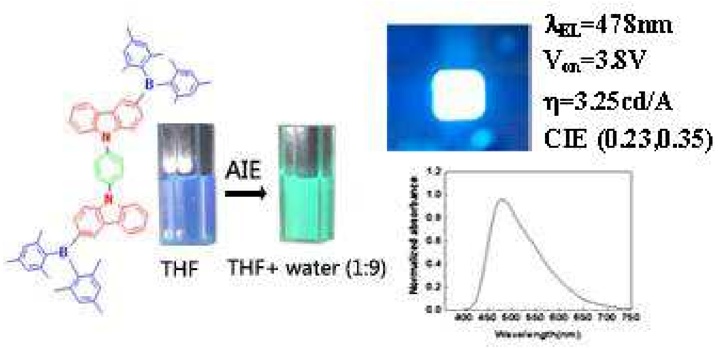

A novel carbazole derivative containing dimesitylboron groups with aggregation induced emission properties was synthesized and utilized as a highly efficient blue light-emitting material in OLEDs.

A Novel Carbazole Derivative Containing Dimesitylboron Units: Synthesis, Photophysical, Aggregation Induced Emission and Electroluminescent Properties

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ABSTRACT

A novel carbazole derivative containing dimesitylboron groups, 3-dimesitylboryl-9-(4-(3-dimesitylborylcarbazolyl)phenyl)carbazole has been successfully synthesized by introducing two dimesitylboron groups (two electron-acceptors) to 3-position and 3’-position of 1, 4-bis(carbazolyl)benzene (an electron-donor), respectively. The structure of the compound was fully characterized by elemental analysis, mass spectrometry and proton nuclear magnetic resonance spectroscopy methods. The electrochemical and photophysical properties of the compound were studied by electrochemical methods, UV-vis absorption spectroscopy and fluorescence spectroscopy. Our results show that the compound exhibits excellent thermal stability (T_d =190 ◦C) and electrochemical stability as well as aggregation induced emission properties. The multi-layered organic light-emitting diodes device was fabricated by using the compound as non-doped emitter. The device shows good electroluminescent performances with the same blue emission color (λ=478 nm) at different voltages, a turn-on voltage of 3.8 V, a maximum luminance of 2784 cd/m^2 and a maximum luminance efficiency of 3.25 cd/A.

Keywords: Carbazole; Dimesitylboron; Aggregation Induced Emission Properties; Photophysical Properties; Photoluminescent Properties; Electroluminescent Properties

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention owing to their potential applications in the future flat-panel displays and solid lighting resources since Tang's work in the late 1980s [1, 2]. In order to improve the efficiency of OLEDs, great efforts have been devoted to develop high-performance materials with desirable properties. At present, many types of high-performance materials have been produced [3-5]. Among them, carbazole and its derivatives are the most fashionable ones.

Carbazole is a significant heterocyclic compound with a nitrogen atom as an electron donor. A large number of carbazole derivatives have been generated through chemical modification because carbazole can be easily functionalized at 3-, 6-, 9-positions and covalently linked to other molecular groups [6-11]. Carbazole and its derivatives have high thermal stability and excellent photophysical properties [12-16]. Thus, they are often utilized as organic photoelectronic functional materials [17-20].

Studies of carbazole and its derivatives have further development in recent years. S. Grigalevicius and co-workers synthesized and characterized Phenyl or naphthyl-substituted carbazole derivatives. They prepared the devices using these compounds as hole-transporting layers. The devices exhibited good overall performance [21]. P. Y. Stakhira and co-workers synthesized and characterized a series of triphenylamine-substituted carbazoles. These materials showed excellent hole-transporting properties [22]. Lee and co-workers synthesized two carbazole-pyrene based fluorophores. These compounds showed excellent hole-transporting properties [23]. Park and co-workers synthesized a novel series of new carbazole derivatives, which were excellent deep-blue emitting materials [24]. Zeng and co-workers synthesized a series of starburst carbazole derivatives, and used these compounds as emitting materials to fabricate the non-doped OLED devices [25]. V. Promarak and co-workers synthesized a series of pyrene-functionalized carbazole derivatives. They fabricated double-layer and multi-layer devices using these materials as non-doped emitters. The devices they prepared exhibited good device performance [26]. R.-H. Lee and co-workers synthesized a series of carbazole derivatives. They fabricated the non-doped devices using these compounds as light-emitting layer. The devices exhibited excellent electroluminescent performance [27].

Triarylboron compounds have attracted a great deal of attention due to their intriguing electronic and photophysical properties [28, 29]. These excellent properties derive from the p-π conjugation between the vacant p-orbital on the boron centre with the π-orbital of the π-conjugated molecular system [30-34]. At present, many triarylboron compounds have been synthesized and used in materials chemistry as nonlinear optical materials and charge-transport and emissive materials in OLEDs and so on [35-43].

In view of the above-mentioned situation, the molecular design and synthesis of novel compounds need to be further developed by the structural modification, aiming to improve the properties and establish the relationship between structures and properties. In this paper, a novel carbazole derivative containing dimesitylboron groups, 3-dimesitylboryl-9-(4-(3-dimesitylborylcarbazolyl)phenyl)carbazole(**DDCPC**), was synthesized by introducing two dimesitylboron groups (two electron-acceptors) to 3-position and 3'-position of 1, 4- bis(carbazolyl)benzene (an electron-donor), respectively. The synthetic details are illustrated in Scheme 1. The structure of this compound was characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR and MS. The thermal, electrochemical and photophysical properties of **DDCPC** are also reported. Finally, **DDCPC** has been successfully applied to electroluminescent device.

2. Experimental section

2.1 Materials and General Methods

All reagents were used as received from commercial sources without further purification unless otherwise stated. Solvents were freshly distilled according to the standard procedures. All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques. Melting points were determined on an X-5 melting point detector. NMR spectra were measured on a Bruker 600 MHz spectromenter. Thermo gravimetric analysis were performed with a TGA 2050 thermo gravimetric analyzer under nitrogen atmosphere with a heating rate of 10 °C/min from room temperature to 600 °C. Elemental analyses were performed with an Element Analysis System. Mass spectra were recorded with the LC-MS system consisted of a Waters 1525 pump and a Micromass ZQ4000 single quadrupole mass spectrometer detector. Cyclic voltammetry was acquired on a CHI-600C electrochemical analyzer. The measurements were performed with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum-disk auxiliary electrode and an Ag/AgCl reference electrode. The scan rate was 50 mV/s. UV–vis absorption spectra were obtained from a Shimadzu UV-2450 absorption spectrophotometer. Fluorescence spectra were taken on a Shimadzu RF-5301PC fluorescence spectrometer. Fluorescence quantum yields were determined using a standard actinometry method; quinine sulphate was used in the actinometer with a known fluorescence quantum yield of 0.55 in 0.1 M sulfuric acid (excited at 350 nm). FE-SEM images were studied by a JEOL JSM-67010F field emission scanning electron microscope. TEM images were studied by a Hitachi H-8100 transmission electron microscopy. All measurements were performed at room temperature.

2.2 Device fabrication and testing

The multilayer OLEDs were fabricated by vacuum-deposition method. Organic layers were fabricated by high-vacuum (5×10^{-4} Pa) thermal evaporation onto a glass (3 cm×3 cm) substrate precoated with an ITO layer. N, N-bis (naphthalen)-N, N-bis (phenyl)-benzidine (NPB) was used as the HTL, 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) was used as the electron-blocking layer, **DDCPC** was used as the emitting layer, 4,7-diphenyl-1,10-phenanthroline(Bphen) was used as the electron-transport layer(ETL) and LiF/Al was evaporated as cathode. All organic layers were sequentially deposited. Thermal deposition rates for organic materials, LiF and Al were 0.5 Å/s, 0.5 Å/s and 1 Å/s, respectively. The active area of the devices is 9 mm^2. The electroluminescent spectra were measured on a Hitachi MPF-4 fluorescence spectrometer. The voltage–current density (V–J) characteristics of OLEDs were recorded on 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.

2.3 Synthesis of DDCPC

2.3.1 3-bromo-9-(4-(3-bromocarbazolyl)phenyl)carbazole (Compound 1)

A mixture of 3-bromocarbazole (1.934 g, 7.86 mmol), 1, 4-diiodobenzene (1.235 g, 3.74 mmol), 18-crown-6 (0.264 g, 1 mmol), K_2CO_3 (4.145 g, 30 mmol) and CuI (0.427 g, 2.24 mmol) was dissolved in DMPU. The reaction mixture was heated to 170 °C for 18 h under a nitrogen atmosphere and then poured into water (600 mL) to obtain the precipitate. The precipitate was filtered and washed with ethanol (100 mL). The crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexane) to afford the pure white solid (1.191 g, 56% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.25 (d, *J* = 1.9 Hz, 4H), 7.82 (s, 2H), 7.58 (dd, *J* = 8.7, 1.9 Hz, 4H), 7.42 (d, *J* = 8.6Hz, 4H).7.34(s, 4H).

2.3.2.

3-dimesitylboryl-9-(4-(3-dimesitylborylcarbazolyl)phenyl)carbazole(DDCPC)

1 (1 g, 1.79 mmol) was dissolved in anhydrous THF (50 mL) under a nitrogen atmosphere and was cooled to -78 °C. Then *n*-butyllithium (2 mL, 4.47 mmol) was added. Subsequently, the reaction mixture was left to room temperature for an hour and then cooled again to -78 °C. Dimesitylboron fluoride (1.2 g, 4.47 mmol) in THF (20 mL) was dropwisely added over 30 min, and the reaction mixture was warmed slowly to room temperature. Then it was stirred for 12 h before being quenched with water (30 mL). The THF was removed under a reduced pressure and the residue was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to obtain the crude product. The crude product was purified by silica-gel column chromatography (CH_2Cl_2/hexane). Yellow solid of **DDCPC** was obtained in 27.5% yield (0.44 g). Mp: 170 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 (s, 4H), 7.84 (s, 4H), 7.59 (d, *J* = 8.1 Hz, 4H), 7.48 (d, *J* = 8.1 Hz, 4H), 6.72 (m, 10H), 2.27 (s, 12H), 2.02 (s, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 143.87, 141.83, 141.39, 139.50, 131.32, 131.20, 131.10, 129.08, 123.53, 123.25, 112.67, 25.20, and 24.09. MS (*m*/*z*): 904.43 (M^+); Anal. Calcd for $C_{66}H_{62}B_2N_2$: C, 87.61%; H, 6.91%; N, 3.10%; and Found: C, 86.64%; H, 6.84%; N, 3.08%.

3. Results and discussion

3.1 Synthesis and Characterization

In this work, the synthesis of 3-dimesitylboryl-9-(4-(3-dimesitylborylcarbazolyl)phenyl)carbazole (**DDCPC**) was discussed. At first, compound **1** was synthesized via the modified Ullmann reaction. Then, the final product **DDCPC** was obtained by reacting compound **1** with *n*-BuLi, followed by the addition of dimesitylboron fluoride. The chemical structure of compound **1** was confirmed by ^{1}H NMR whereas **DDCPC** was confirmed by ^{1}H NMR, ^{13}C NMR and MS. The ^{1}H NMR spectrum of **DDCPC** displays downfield peaks at 7.00-8.48 ppm which are assigned to the characteristic peaks of carbazole moieties protons. The downfield peaks at 6.59-6.89 ppm and the upfield peaks at 2.09 and 2.37 are assigned to dimesitylboron moieties protons. The ^{13}C NMR, MS and elemental analysis are consistent with the desirable structure. Further details are given in the experimental section. **DDCPC** is soluble in many common organic solvents such as CH_2Cl_2, chloroform, DMF, THF, toluene and DMSO. The thermal property of **DDCPC** was investigated by thermogravimetric analysis under a nitrogen atmosphere. There is only a 5% weight loss at temperature higher than 190°C (Table 1), indicating that **DDCPC** has good thermal stability and should be adequate for most optoelectronic device applications.

3.2. Theoretical Calculation

Theoretical calculations can provide a reasonable qualitative indication of the excitation and emission properties of a compound [44]. The molecular structure of **DDCPC** contains one 1,4-bis(carbazolyl)benzene unit as the core, two dimesitylboron units as the terminals. Its geometry at ground state was optimized at DFT/B3LYP/6-31G (d, p) level using the polarized continuum model (PCM). The results show that two carbazole moieties are of planar structures and two mesityl groups form propeller-like conformations originated from their trigonal boron centers. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **DDCPC** (Fig. 1) were also investigated at DFT/B3LYP/6-31G (d, p) level using the polarized continuum model (PCM). The HOMO of **DDCPC** is localized mainly in the carbazole while the LUMO is in the dimesitylboron units. Thus, the electronic transition from the ground state to the first excited state mainly involves intramolecular charge transfer (ICT) from the carbazole (electron-donor) to the dimesitylboron groups (electron-acceptors). The calculated HOMO and LUMO energy levels are -5.12 and -1.68 eV, respectively. The HOMO-LUMO energy gap is 3.44 eV (Table 1). The calculated HOMO and LUMO levels are higher than the experimental ones and the calculated HOMO-LUMO energy gap is *ca.* 0.20 eV larger than that of the optical energy band gap obtained from UV-vis absorption measurement.

3.3. Photophysical Properties

The UV-vis absorption spectra of **DDCPC** in various solvents (1.0×10^{-5} M) are shown in Fig. 2. The absorption data of **DDCPC** in THF are displayed in Table 1. **DDCPC** exhibits one absorption band at 280-320 nm corresponding to the π-π* electronic transitions. The low-energy broad band at 320-380 nm is assigned to ICT from the carbazole core to dimesitylboron terminals and shows almost identical maxima absorption in the different solvents, meaning the slightly solvent-dependence [45]. The result indicates that solvent polarity does not affect the structural and electronic characteristics of the ground state of **DDCPC** significantly. Moreover, the optical energy band gap calculated from the absorption band edges of the UV-vis absorption spectra is approximately 3.24 eV.

Fig. 3 depicts the fluorescence spectra of **DDCPC** in various solvents (1.0×10^{-5} M). The fluorescence data in THF is summarized in Table 1. The absorption spectrum of **DDCPC** shows slight solvatochromism effect whereas the fluorescence emission shows a significant solvatochromism effect. With the polarity increasing of the solvents, a bathochromic shift of 44 nm ranging from 368 nm (in hexane) to 412 nm (in DMSO) was observed. Such a distinct solvatochromism indicates that intramolecular charge transfer from the carbazole core to two dimesitylboron terminals takes place during the excitation process. The fluorescence quantum yield (Φ) of **DDCPC** in various solvents were measured by using quinine bisulfate in 0.1 M sulfuric acid as the standard [46]. The fluorescence quantum yield data in THF solvent is summarized in Table 1. The solid fluorescence spectrum of **DDCPC** was obtained by measuring its solid film. The spectrum is shown in Electronic Supplementary Information (Fig. S1). The spectrum shows the emission maximum of **DDCPC** is at 480 nm in the solid film state, demonstrating that it can emit blue light. The photoluminescent properties of **DDCPC** in solutions and solid film state indicate it could be used as an excellent optoelectronic material with blue light emission in OLEDs.

3.4 Aggregation Induced Emission (AIE) Properties

The aggregation induced emission (AIE) behavior was investigated by monitoring the change in PL intensity with the addition of water ratio in a THF–water solvent mixture. Here, THF acts as the solvent and water acts as the non-solvent [47]. There is a dramatic change of the fluorescence spectra of **DDCPC** from the THF solution to the THF–water mixture (Fig.4). With the increasing proportion of water, the emission intensity and wavelength show a slight decrease and red shift, respectively, due to the increasing polarity of the system. When the water content is higher than 50vol%, nano-particles begin to form and the purple emission band centered at 402 nm gradually “turns-off’’, along with the blue emission band at 493 nm rapidly “turning-on’’, which suggests that molecules begin to aggregate in the solvent mixture with this composition. The nano-particles of **DDCPC** were prepared by the precipitation method in the absence of surfactants. **DDCPC** must aggregate into nano-particles in the THF–water mixture because water is a non-solvent for **DDCPC** in THF. The shape of nano-particles was investigated by FE-SEM and TEM. Fig. 5 shows FE-SEM images of nano-particles from THF-water (1: 9) mixture solution onto a conductive tape substrate, which shows a large number of discrete nano-particles. Besides, nano-particles with a diameter of about 30-80 nm are clearly observed by TEM images (the inset of Fig.5), which are in good agreement with those shown in the FE-SEM images. In addition, to date such a ratiometric fluorescence change with a large red-shift of 90 nm in an ICT compound has rarely been reported. Furthermore, this AIE active molecule can be used as luminescent materials in OLEDs.

3.5 Electrochemical Properties

The electrochemical properties of **DDCPC** were investigated by cyclic voltammetry (CV) with Ag/AgCl as the reference electrode. The measurement was conducted in 1.0×10^{-3} M **DDCPC** in acetonitrile containing 0.10 M tetrabutylammonium perchlorate as the supporting electrolyte under a nitrogen atmosphere. The cyclic voltammogram (CV) of **DDCPC** is shown in Fig. S2 (ESI). The CV curves remain unchanged under multiple successive potential scans, indicating its excellent stability against electrochemical oxidation. 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 [48]. The E_{ox} is 0.85 eV and the HOMO energy level of **DDCPC** is -5.25 eV. The energy band gap (E_g) was estimated to be 3.24 eV by the absorption edges of the UV-vis spectra. The LUMO energy level of **DDCPC** is -2.01 eV, which was calculated from the HOMO energy level and E_g ($E_{LUMO} = E_{HOMO} + E_g$). The results are summarized in Table 1. The HOMO energy level of **DDCPC** is lower than the work functions of indium tin oxide (ITO) electrodes, implying its potential application as hole- transporting materials in OLEDs [49].

3.6 Electroluminescent property

In order to demonstrate the potential application of **DDCPC** as luminescent material in device, the multi-layer device (**Device M)** with the structure of indium tin oxide (ITO) / N,N’-di-1-naphthyl-N,N’-diphenylbenzidine (NPB) (40 nm) / 4,4’-bis(N-carbazol-yl)-1,10-biphenyl (CBP) (10 nm) / **DDCPC** (20 nm) /4,7-diphenyl-1,10-phenanthroline (Bphen) (40 nm) / LiF (1 nm) / Al (180 nm) was fabricated by vacuum deposition, wherein NPB and Bphen were used as the hole-transporting layer and the electron-transporting layer, respectively; CBP and **DDCPC** served as the electron-blocking layer and the emitting layer, respectively. The multi-layer device (**Device M)** emits an excellent blue light (λ=478 nm) with CIE coordinates (0.23, 0.35). The EL spectra of the device keep unchanged when the driving voltage increases from 3.6 to 14 V and the EL spectra are identical to its PL spectrum of thin film. The multi-layer device (**Device M)** exhibits good performance with a turn-on voltage of 3.8 V, a maximum luminance of 2784 cd m^{-2} and a maximum luminescent efficiency of 3.25 cd/A (Table 2). The current density–voltage–luminance curve and luminance efficiency-current density curve of the device are shown in Fig. 6 and Fig.7, respectively. It should be pointed out that the electroluminescent performances were obtained in a non-optimized test device under ordinary laboratory conditions. The device performances may be further improved by an optimization of the layer thicknesses and processing conditions. Studies on the improvement of the device performances are currently underway.

4. Conclusions

In summary, a novel acceptor-π-donor-π-acceptor type compound, 3-dimesitylboryl-9-(4-(3-dimesitylborylcarbazolyl)phenyl)carbazole(**DDCPC**), has been successfully synthesized and characterized by elemental analysis, NMR, MS and thermogravimetric analysis. The electrochemical and photophysical properties of **DDCPC** were studied by combination of experimental and theoretical methods. Our results show that **DDCPC** exhibits excellent thermal stability (T_d =190 ◦C) and electrochemical stability as well as aggregation induced emission (AIE) properties. Furthermore, the multi-layer electroluminescent device using **DDCPC** as light-emitting layer is fabricated. The multi-layer device (**Device M)** emits an excellent blue light (λ=478 nm) with CIE coordinates (0.23, 0.35) and shows good electroluminescent performances with a turn-on voltage of 3.8 V, a maximum luminance efficiency of 3.25 cd A^{-1} and a maximum luminance of 2784 cd m^{-2}. All results indicate **DDCPC** is a promising material for the construction of efficient non-doped blue OLEDs.

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Appendix A. Electronic Supplementary Information

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Captions for Table, Figures and Scheme

Table 1. Physical properties of compound **DDCPC**

Table 2. Electroluminescent characteristics of **Device M**

Fig. 1. HOMO and LUMO diagrams of **DDCPC**

Fig. 2. UV-vis absorption spectra of DDCPC in different solvents**.**

Fig. 3. Fluorescence emission spectra of **DDCPC** in different solvents. The excitation wavelength is 350 nm.

Fig. 4. Fluorescence spectra of **DDCPC** (5 mM) in the THF–water mixture with different fractions of water (fw). Excited at 350 nm.

Fig. 5. FE-SEM and TEM (the inset) images of the nanoparticles prepared in the THF–water(1: 9) mixture.

Fig. 6. Current density–voltage–luminance curves of the **Device M**

Fig. 7. Current density-luminance efficiency curve of the device

Scheme 1 Synthetic routes of **DDCPC**.

Table 1. Physical properties of compound **DDCPC**

Com.	λ_{abs}[a] (nm)	λ_{em}[a] (nm)	λ_{em}[b] (nm)	Φ[c]	T_d[d] (°C)	HOMO/ LUMO[e] (eV)	E_g[f] (eV)	HOMO/ LUMO[g] (eV)	E_g[g] (eV)
DDCPC	**293/348**	**383**	**480**	**0.22**	**190**	**-5.25/-2.01**	**3.24**	**-5.12/-1.68**	**3.44**

[a] Measured in THF. [b] Measured in film. [c] Measured in THF with quinine sulfate as a standard. [d] Obtained from TGA. [e] Obtained from CV in CH_3CN/n-Bu_4NClO_4 and estimated from HOMO= -(4.44+E^{ox}_{onset}); LUMO=HOMO+E_g. [f] Calculated from the absorption edge, E_g=1240/λ_{onset}. [g] Obtained from DFT calculation.

Table 2. Electroluminescent characteristics of **Device M**

Device	λ_{EL} (nm)	V_{ON} (V)	L_{max} (cd m^{-2})	$\eta_{L,max}$ (cd A^{-1})
Device M	**478**	**3.8**	**2784**	**3.25**

V_{on} = turn-on voltage at 1 cd m^{-2}, L_{max} = maximum luminance, $\eta_{L,max}$ = maximum luminance efficiency

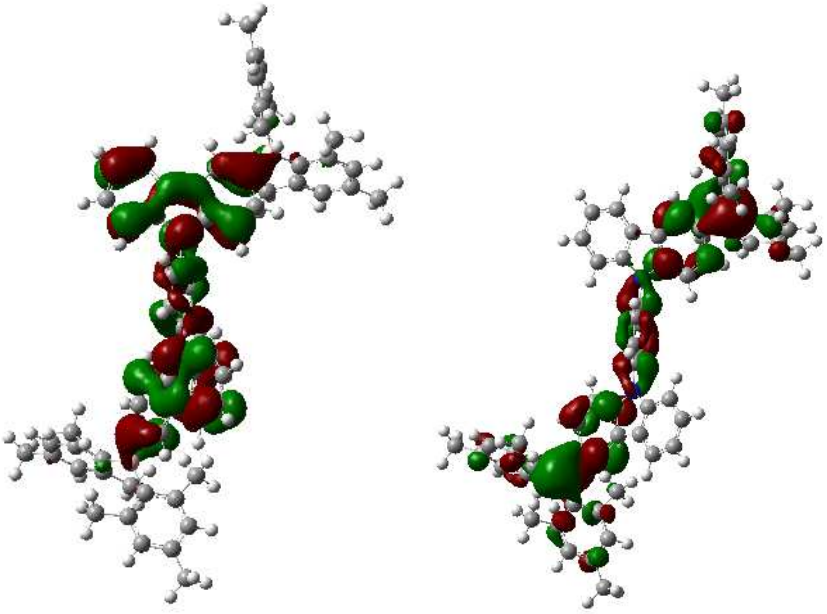


Fig. 1. HOMO and LUMO diagrams of **DDCPC**

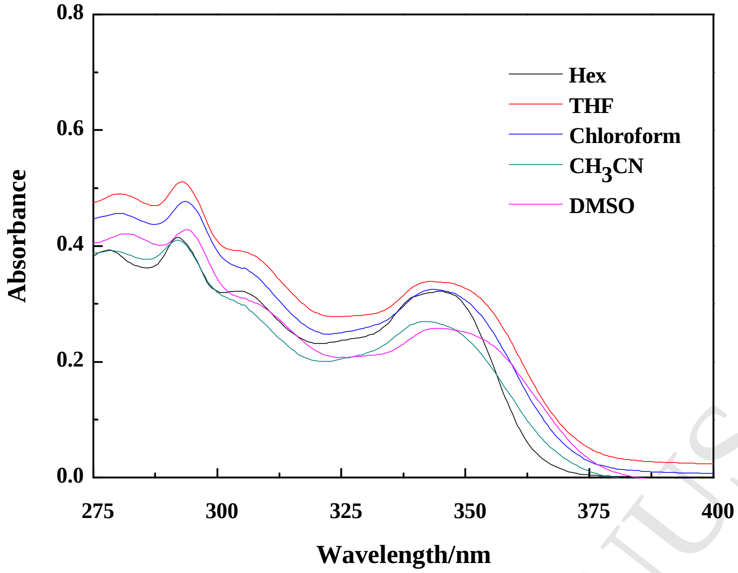


Fig.2. UV–vis spectra of **DDCPC** in different polar solvents.

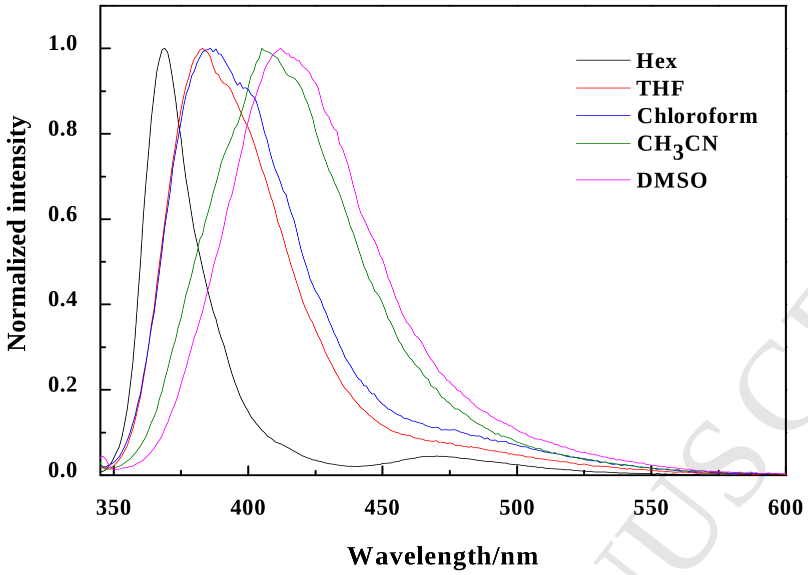


Fig. 3. Fluorescence emission spectra of **DDCPC** in different solvents. The excitation wavelength is 350 nm

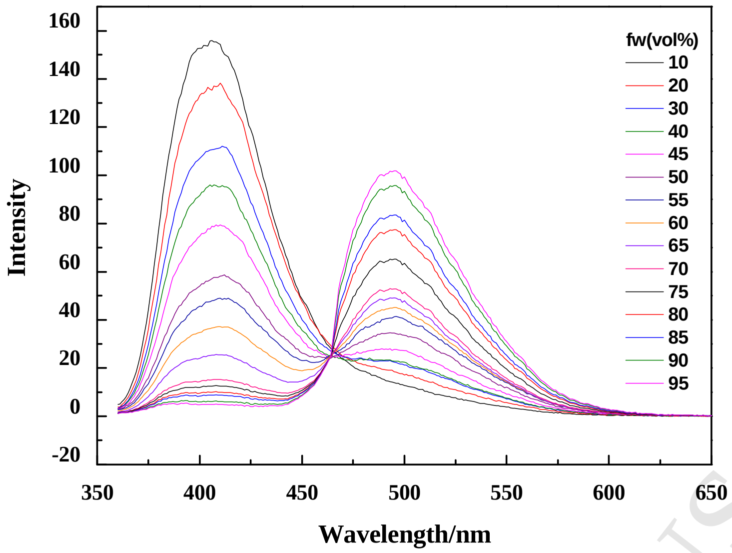


Fig. 4. Fluorescence spectra of **DDCPC** (5 mM) in the THF–water mixture with different fractions of water (fw). Excited at 350 nm.

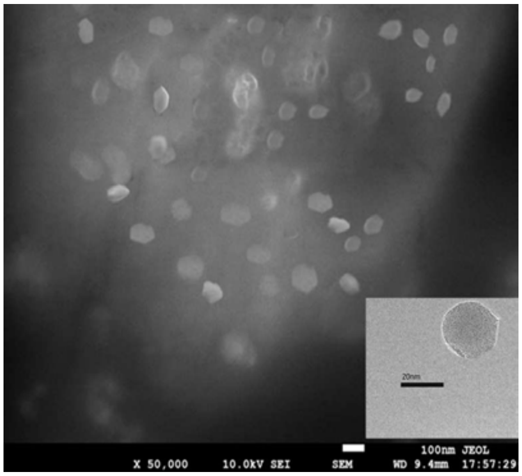


Fig. 5 FE-SEM and TEM (the inset) images of the nanoparticles prepared in the THF–water(1: 9) mixture.

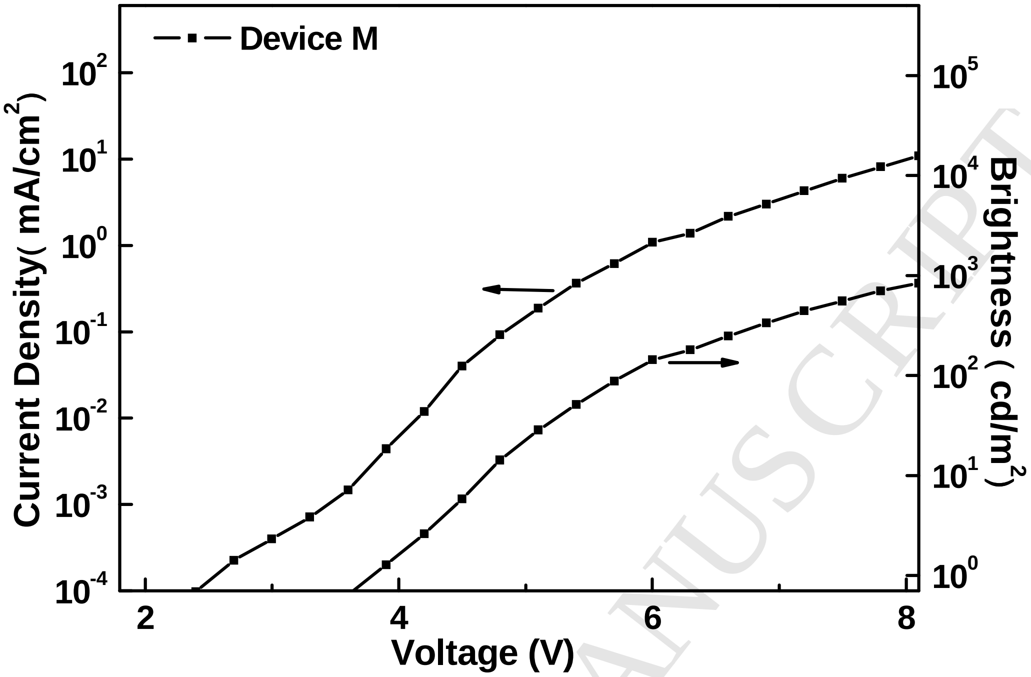


Fig. 6. Current density–voltage–luminance curves of the **Device M**

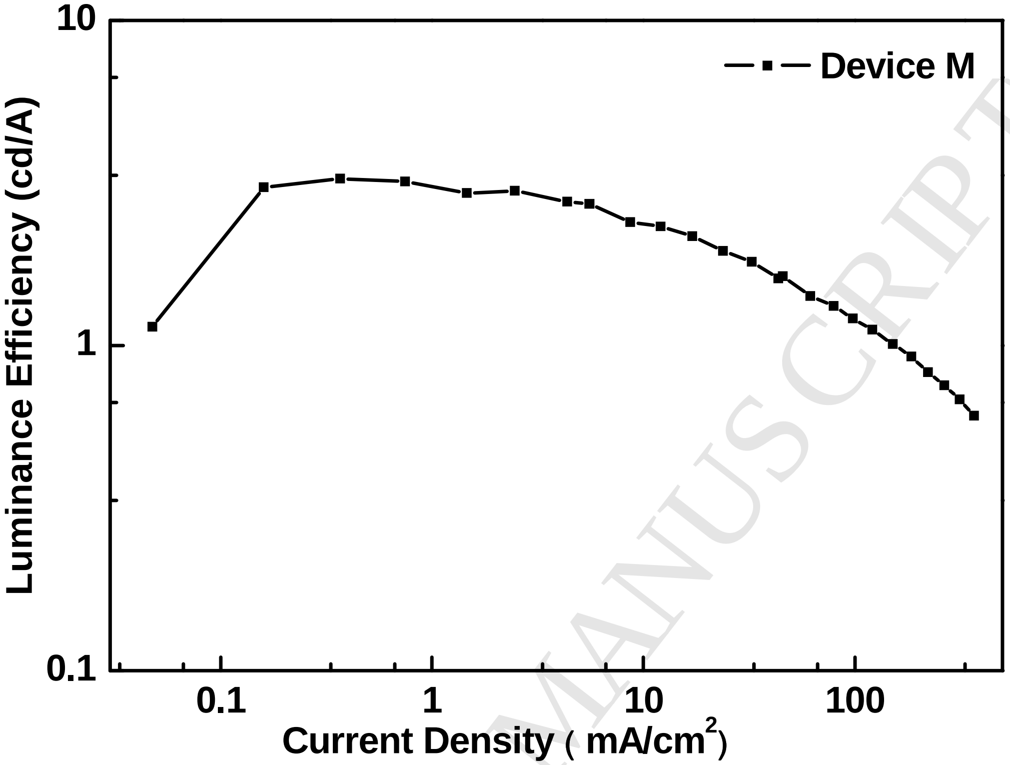
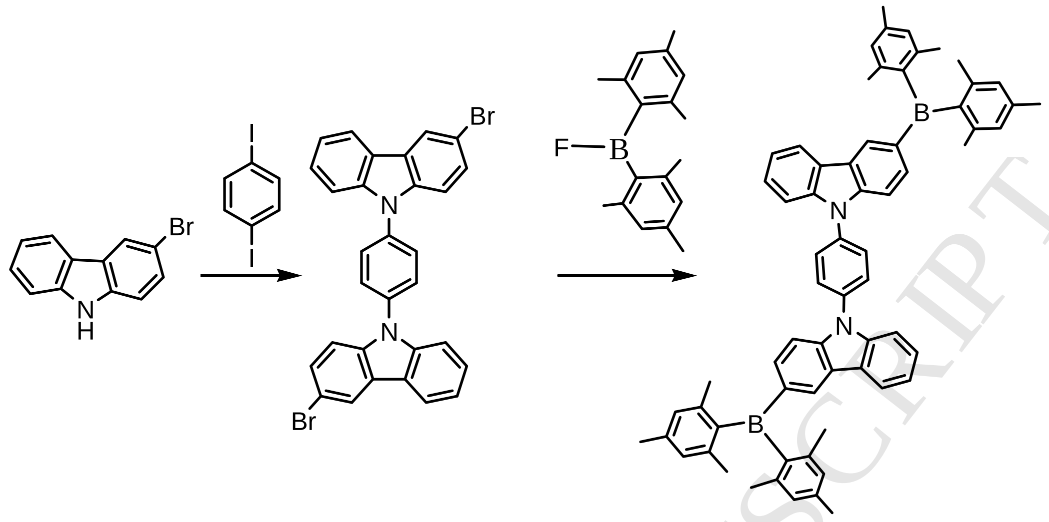


Fig. 7. Current density-luminance efficiency curve of the device



Scheme 1 Synthetic routes of **DDCPC**.

Highlights

►We synthesized a novel carbazole derivative containing dimesitylboron groups (**DDCPC**). ► **DDCPC** exhibits aggregation induced emission (AIE) properties and excellent thermal stability. ► Efficient OLEDs fabricated with **DDCPC** show pure blue emission and good electroluminescent performances.

A Novel Carbazole Derivative Containing Dimesitylboron Units: Synthesis, Photophysical, Aggregation Induced Emission and Electroluminescent Properties

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Electronic Supplementary Information (ESI)

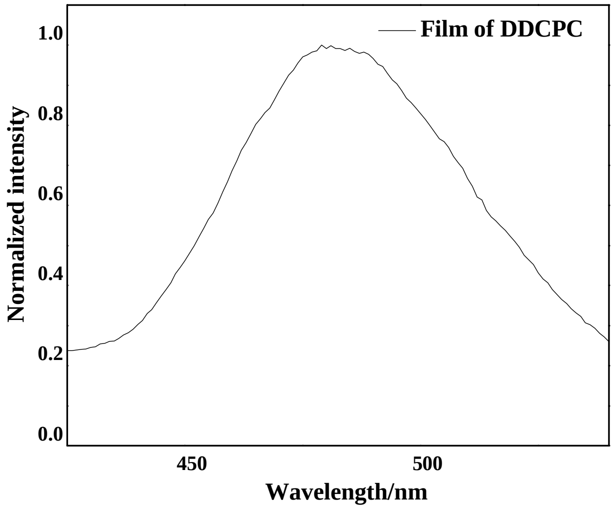

Fig. S1 the solid fluorescence spectrum of **DDCPC**

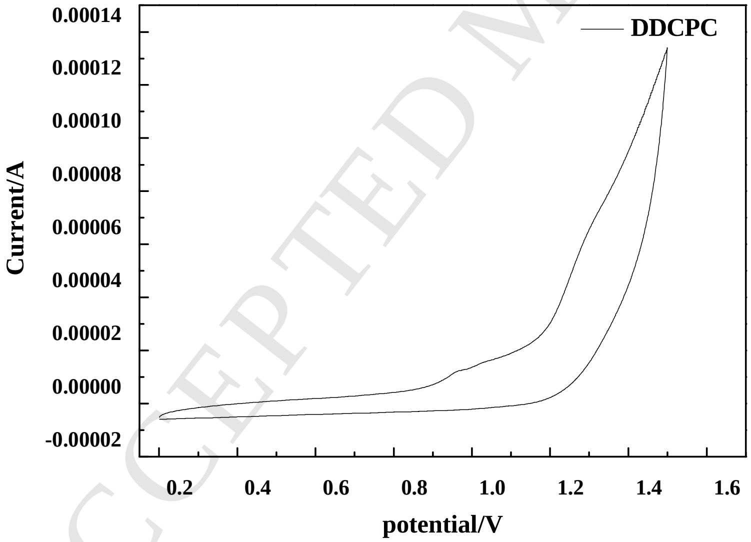

Fig. S2 cyclic voltammograms of **DDCPC**