

ARTICLE

High Brightness Blue Luminescent Material with Hole-Transporting Ability of 9-(pyren-1-yl)-9H-Carbazole

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A novel bifunctional blue-light material, 9-(pyren-1-yl)-9H-carbazole (CzPy), has been synthesized and its structure is identified by electron ionization mass spectrometry, ¹H NMR, and element analysis. The absorption, photoluminescence spectra and thermal properties were studied, results showed that CzPy was stable under ambient conditions with a blue-light emission (461 nm). Additionally, its electroluminescence properties were characterized with four different devices. Results indicated a maximum luminous efficiency reached 1.56 cd/A and maximum luminance up to 3526 cd/m² at 10 V with commission international De L' Eclairage coordinates of (0.20, 0.24) when it was used as emitter. Furthermore, CzPy also indicated hole-transporting ability.

Key words: Blue-light emission, 9-(pyren-1-yl)-9H-carbazole, Electroluminescence

I. INTRODUCTION

Blue-light materials have been extensively attracting researchers' interest owing to their potential application in full color display, multiphoton fluorescence imaging, and organic light-emitting diodes (OLED) [1–10]. Commonly, they show lower efficiencies and brightness than the green and red materials because of their large band-gap energies. The carriers are very difficult to be injected into the molecules. However, the blue-light materials are essential for construction of white-light devices, especially in host-dopant system. Design and synthesis of highly effective materials with intensely blue fluorescence are thought as an important strategy to obtain white-light OLEDs. Usually, two primary ways were used to improve efficiencies and brightness of devices [11, 12]. As far as device structures are concerned, carrier transfer and combination can be enhanced and balanced by choosing some suitable materials [13–15], but the cost of OLEDs will be bound to be increased as the intricately fabricated processes. Recently some new approaches to design and synthesize novel molecules with multifunctional properties were discussed [16, 17], which can be synchronously used as charge transfer materials and emitter. Unfortunately, some of these molecules showed low efficiency and brightness. Furthermore, one of the huge chal-

lenges in developing multifunctional blue-light materials is the prevention of the emission from red-shifting because the large π -conjugation would bring about a huge red-shifting effect.

Carbazole and their derivatives are extensively used to generate short-wavelength absorption or emission due to their weak π -conjugation [18]. Additionally, most of them are capable of exhibiting multifunctional properties including emission and hole-transporting abilities [19]. Moreover, pyrene and their derivatives are also widely used as probes in recognized DNA labels [20] owing to their strong π electron delocalization energy and efficient fluorescence property. Recently, pyrene and their derivatives have been also used in OLEDs as dopants to obtain high brightness and efficiency devices [21, 22]. However, the blends of host materials and dopant have a tendency to show phase separation over time, which leads to instability in the performance of devices [23].

In this work we designed and synthesized a multifunctional molecule containing carbazole and pyrene by chemical bond, which has been demonstrated hole-transporting and luminescent properties. Synthetic route and chemical structures are shown in Fig.1. Its electroluminescence (EL) performances were studied by constructing devices, and results showed the molecule indeed possesses good hole-transporting ability and highly efficient blue-light emission.

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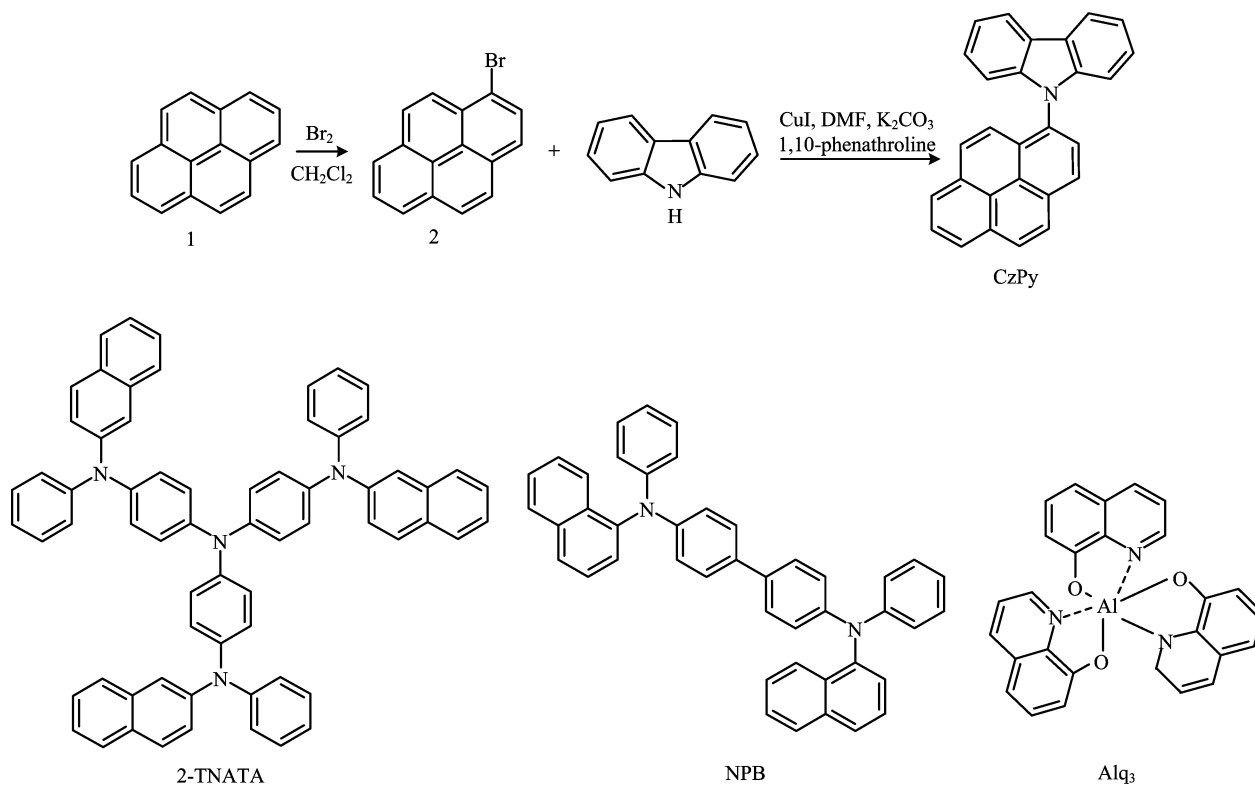


FIG. 1 The synthetic route of CzPy and the molecular structures used in device fabrications. 2-TNATA: *N*-(naphthalene-2-yl)-*N'*, *N'*-bis(naphthalene-2-yl-(phenyl)amino)phenyl)-*N*-phenyl- benzene-1,4-diamine, NPB: *N*, *N'*-bis(naphthyl)-*N*, *N'*-diphenyl-1,1'-biphenyl-4,4'-diamine, and Alq_3 : *tris*-8-hydroxyquinolato-aluminum.

II. EXPERIMENTS

A. General

Carbazole and pyrene were purchased from Tokyo Chemical Industry Co. Ltd (TCI). Cuprous iodide (CuI), potassium carbonate (K_2CO_3) and 1,10-phenanthroline were obtained from Guangzhou Chemical Reagent Company. The solvents were dried using standard procedures. All other reagents used were received from commercial sources, unless otherwise stated. Melting points were determined using an Electro-thermal IA 900 apparatus and the thermometer was uncorrected. ^1H NMR spectra were determined in CDCl_3 with a Bruker DRX 400 MHz spectrometer. Chemical shifts δ were given relative to tetramethylsilane (TMS). The coupling constants J were reported in Hz. Elemental analyses were recorded with a Perkin-Elmer 2400 analyzer. Electron ionization mass spectrometry (EI-MS) spectra were performed with a FINNIGAN Trace DSQ mass spectrometer at 70 eV using a direct inlet system. UV visible spectra and photoluminescence spectra were measured with a Shimadzu UV-2550 and HITACHI 2003 spectrophotometer, respectively. The experiment was monitored by thin-layer chromatography (TLC). Column chromatography was carried out on silica gel (100–200 mesh).

B. Synthesis of compound 2

The synthesis of compound 2 (Fig.1) was based on the literature [20]. 3.232 g Br_2 (4.4 mmol) was dissolved in 15 mL CH_2Cl_2 and dropped 1.015 g pyrene (5 mmol) in CH_2Cl_2 at the 0°C , stirred over night. After the reaction finished, the solution was washed with NaHSO_3 (1 mol/L) and adjusted pH to 8, then the solution was extracted with CH_2Cl_2 and dried with anhydrous magnesium sulfate, and purified by recrystillization. Yield 1.052 g, 84.9%. EI-MS: 283.1 (M^+ , 96%), 281 (M^+ , 99%), which is the same as the literature [20].

C. Synthesis of CzPy

0.955 g carbazole (5.5 mmol), 1.408 g 1-bromopyrene (5 mmol), 0.113 g CuI (0.29 mmol), 1.375 g potassium carbonate and 0.11 g 1,10-phenanthroline (0.58 mmol) were dissolved in 10 mL dimethylformamide (DMF) using an overhead stirrer under nitrogen atmosphere. The mixture was refluxed for 48 h. After the reaction finished, the mixture was added 50 mL water to and stirred about 10 min, then extracted with dichloromethane (DCM) (3×50 mL) using tap funnel. The product was purified by column chromatography using DCM and petroleum ether as eluent. The white powder was ob-

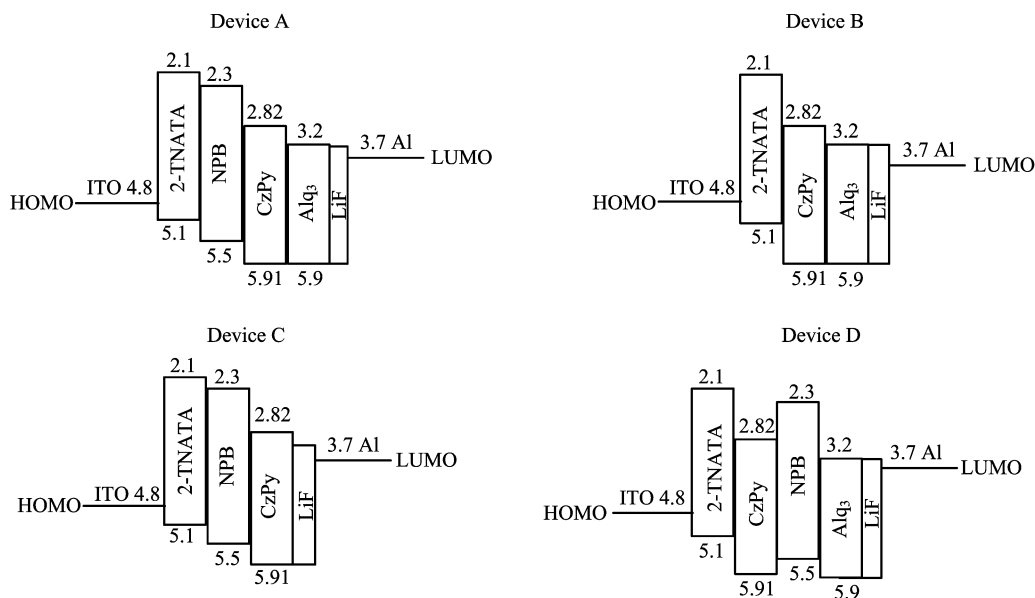


FIG. 2 The devices structures and energy diagrams of the devices.

tained with 91% yield. EI-MS: 368.1 (M^++1 , 43%), 367.2 (M^+ , 100%). ^1H NMR (CDCl_3): 8.35 (d, 1H, $J=8.0$ Hz), 8.28–8.24 (m, 3H), 8.21–8.18 (m, 3H), 8.10 (d, 1H, $J=8.0$ Hz), 8.06 (t, 1H, $J=7.8$ Hz), 7.94 (d, 1H, $J=9.6$ Hz), 7.55 (d, 1H, $J=8.4$ Hz), 7.36–7.31 (m, 4H), 7.04–7.02 (m, 2H). Calculated elemental analysis for CzPy: C, 91.52; H, 4.66; N, 3.81. Found: C, 91.44; H, 4.55; N, 4.01.

D. Devices fabrication

The indium tin oxides (ITO) coated glass substrate was firstly immersed sequentially in ultrasonic bath of acetone, alcohol and deionized water for 10 min, respectively, and then dried in an oven. The resistance of a sheet ITO was $50 \Omega/\square$. The devices were fabricated in a multi-source organic molecule gas deposition system. There were different materials in every source, and the temperature of every source can be controlled independently. The different organic material layer was deposited onto the ITO-coated glass substrate according to the designed structure, LiF buffer layer and Al were deposited as a co-cathode under a pressure of 0.5 mPa. Electroluminescent spectra and CIE coordination of these devices were measured by a PR655 spectra scan spectrometer. The luminance-current-voltage characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer through a Keithly model 2400 programmable voltage-current source. The layer thickness of the deposited materials was monitored *in situ* using a model FTM-V oscillating quartz thickness monitor made in Shanghai, China. All the measurements were carried out at room temperature under ambient

TABLE I Thermal and photophysical properties of CzPy (λ in nm)*.

Solvent	$\lambda_{\text{max}}^{\text{abs}}$ (intensity)	$\lambda_{\text{max}}^{\text{PL}}$ (intensity)	Φ_{F}
THF ^a	340 (3.1)	456 (760)	0.83
Toluene	339 (1.6)	456 (450)	0.49
CH_2Cl_2	340 (2.1)	456 (550)	0.60
Acetone	340 (2.7)	456 (650)	0.71

* $\lambda_{\text{max}}^{\text{abs}}$, $\lambda_{\text{max}}^{\text{PL}}$, and Φ_{F} are maximal absorption wavelength, maximal photoluminescent wavelength, and fluorescence spectra, respectively.

conditions. The constructed devices were as shown in Fig.2.

III. RESULTS AND DISCUSSION

A. Thermal and photophysical properties

The thermal properties of CzPy, were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass-transition temperatures T_g and thermal decomposition temperatures T_d of CzPy were about 82 and 297 °C, respectively, which indicated that CzPy was stable under ambient condition. And the energies of HOMO and LUMO are 2.82 and 5.91 eV, respectively.

The UV absorption and photoluminescent (PL) data for CzPy were summarized in Table I and Fig.3. The maximal absorption peak appears at 340 nm, attributed to the absorption from pyrene moiety by comparing the absorptive peaks with that of carbazole (290

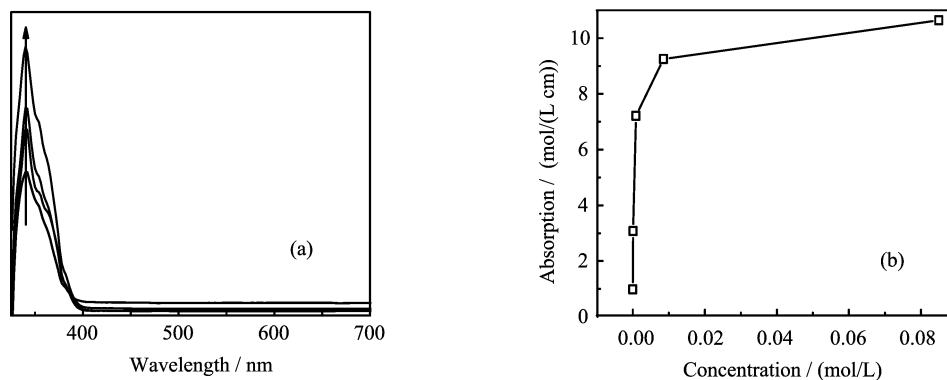


FIG. 3 (a) The UV spectra of 85 $\mu\text{mol/L}$ CzPy in different solvents (toluene, CH_2Cl_2 , acetone, and THF in arrow direction) and (b) concentration-dependence of CzPy.

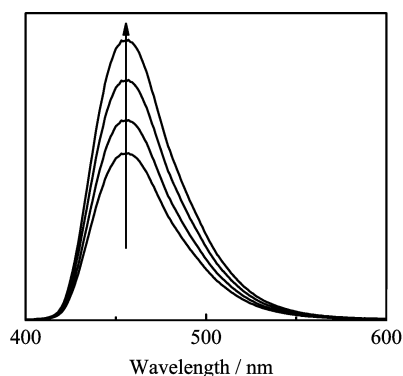


FIG. 4 The fluorescent spectra of 48 $\mu\text{mol/L}$ CzPy in four different solvents (THF, acetone, CH_2Cl_2 , and toluene in arrow direction).

and 336 nm pyrene). It can be found the energy was transferred from pyrene to carbazole. Then, the solvent effect and concentration dependence of CzPy were also analyzed based on the PL data shown in Fig.4. The results indicated little solvatochromic effect with different polar solvents. Furthermore, molecular aggregation phenomena of CzPy also were studied using THF as solvent with different concentrations. The plot of absorption values at 340 nm *vs.* concentration was shown in Fig.3(b). The apparent deviation from Beer's law indicates that the CzPy is not homogeneously dispersed in the solvent when the concentration increases to 8.5 mmol/L. It can be seen aggregated phenomena appear in high concentration (>8.5 mmol/L). Meanwhile, in Fig.3, absorptive intensity is increased as a function of the increasing polarity of solvents, which showed that the absorptive intensity of CzPy depends strongly on the molecular structures, hyperchromic and intermolecular excited states.

The PL spectra gave a maximum emission peak centered at about 456 nm using 340 nm to excite the CzPy, exhibiting blue-light emission (Fig.4). In comparison of the absorption, CzPy showed about 110 nm Stock

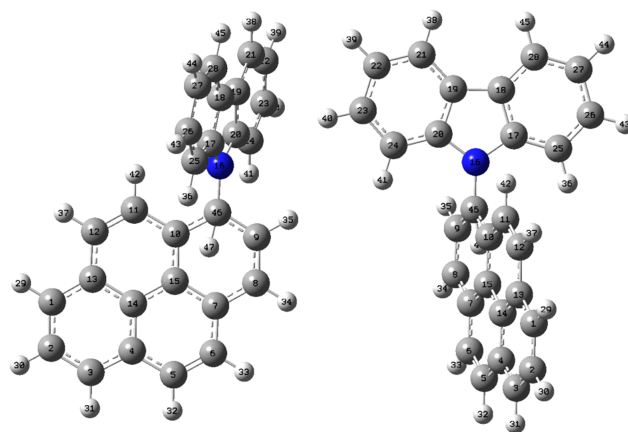


FIG. 5 The ground-state geometry structure of CzPy (gray ball: C, blue ball: N, white ball: H) in x (left) and z (right) arrow direction. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

shifts. It can be concluded the PL and photoabsorption are not in mirror image. Usually, pyrene had two luminescent peaks located at 370 nm (monomer) and 480 nm (dimer). On the other hand, the emission of CzPy showed peak at 456 nm which is close to the emission of dimer pyrene. Therefore, the energy was transferred from pyrene to carbazole in the molecule by analyzing the luminescent properties. The solvatochromic effect of solvents was also studied and the maximum peak didn't change with the polarity of solvents, which was in agreement with the analysis of absorption. Similarly, the intensity of fluorescence increased with the increasing polarity of solvents. In addition, we also estimated fluorescence quantum yield by the integrating sphere method with reference to the absorption and fluorescence spectra of Rhodamine B ($\Phi_F=0.95$), the fluorescent quantum yields of CzPy were 0.83, 0.71, 0.6, and 0.49 in THF, acetone, CH_2Cl_2 , and toluene, respectively.

In order to investigate the solvent effect in future depth, its geometries, electronic and emission spectra

TABLE II Electronic and emission spectra of CzPy with different solvent at the B3LYP/6-31G(d,p) optimized geometries.

Solvent	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$	$\lambda^{\text{ex}}/\text{nm}$	f	Excitation energy/eV	Main configuration	ν
THF	338.6	—	0.28	3.67	HOMO→LUMO+1	0.61
	—	441.4	0.52	2.82	LUMO→HOMO	0.68
Toluene	340.6	—	0.12	3.65	HOMO→LUMO	0.59
	—	443.1	0.38	2.805	LUMO→HOMO-1	0.71
CH ₂ Cl ₂	339.3	—	0.16	3.66	HOMO→LUMO	0.59
	—	442.4	0.84	2.81	LUMO→HOMO-1	0.77
Acetone	340.7	—	0.53	3.65	HOMO→LUMO	0.66
	—	442.9	0.17	2.806	LUMO→HOMO-1	0.68

* λ^{ex} is excited wavelength, f is oscillator strength.

^a ν is rate of electric transition.

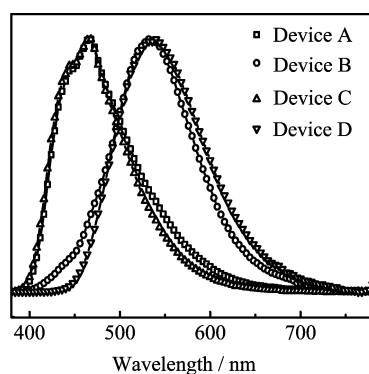


FIG. 6 Normalized EL spectra of devices A, B, C, and D.

were predicated by Gaussian 03 software using density functional theory (DFT). Figure 5 showed the stable ground-state geometries of CzPy. The carbazole moiety was vertical with the plane of pyrene moiety due to the steric hindrance in Fig.5. Then, its electronic spectra was studied by time-dependent DFT method with different solvents. Table II summarized the transition energies of electronic spectra, oscillator strength, configurations of the orbits and experimental results. Table II shows all of the electronic transitions are the $\pi \rightarrow \pi^*$ type and in agreement with the experimental results, and the solvent effect of absorption and emission was negligible according to the results of calculations, which was in good agreement with the observed results.

B. The device properties of CzPy

The normalized EL spectra of devices A, B, C, and D were shown in Fig.6. It was obvious that the devices A and C exhibited blue-light fluorescence with a peak at 463 nm, and the devices B and D gave yellowish-green emission at around 530 nm. Comparing the PL spectra with the EL spectra, it was clear that observed blue-light emission originated from the CzPy layer, and yellowish-green emission originated from the Alq₃ layer.

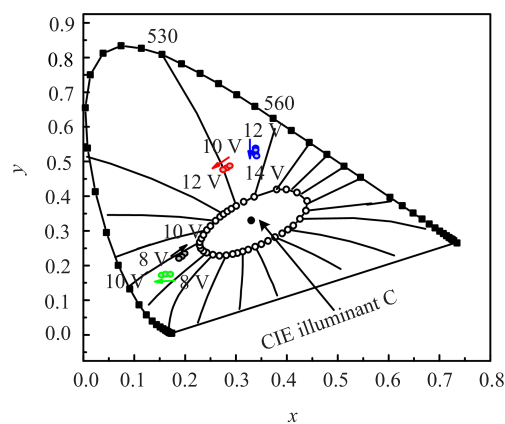


FIG. 7 The CIE coordinates of devices A(black), B(red), C(green), and D(blue) with different color circle. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

CIE coordinates of the four devices were shown in Fig.7. The changes of CIE coordinates of the four devices were small as a function of applied voltage.

The configuration and HOMO/LUMO energy alignment in EL devices for CzPy (devices A, B, C, and D) were also shown in Fig.2. For these devices, NPB was used as the hole-transporting layer, ITO glass is transparent anode, 2-TNATA was acted as hole-injecting material (HIM), Alq₃ was electron-transporting material or emitter in these devices, CzPy was HTL or EM in these devices, and lithium fluoride (LiF) was used as the buffer layer.

Luminescence-voltage and efficiency-voltage characteristics of devices A, B, C, and D were shown in Fig.8 and Fig.9. The turn-on voltages of the devices A and B were all below 5 V. On the other hand, the turn-on voltages of devices C and D are 6 and 8 V respectively. In device D, CzPy was sandwiched by hole-injection layer (2-TNATA) and hole-transport layer (NPB). The high threshold voltage of this device would be due to the mismatch of HOMOs of CzPy and NPB. By analyzing the energy diagrams of these devices, the barrier difference

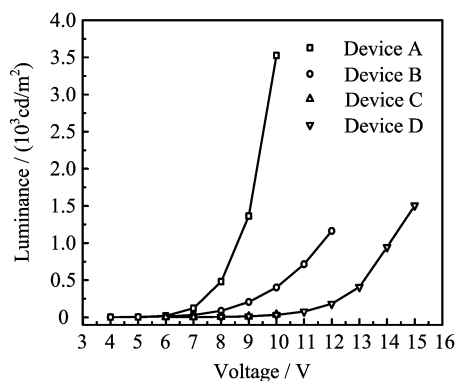


FIG. 8 Luminescence-voltage characteristics of four devices of devices A, B, C, and D.

was found between the interface of aluminum and CzPy in the configuration of device C, especially the energies of the lowest occupied molecular orbits (LUMO), which was about 0.9 eV between the CzPy layer and aluminum layer. In order to investigate the luminescent properties of CzPy, the structure of device A was designed. In the device, NPB acted as hole-transporting layer (HTL), Alq₃ was used as electron-transporting layer (ETL), and CzPy was used as blue-light emitter layers. In Fig.8, we can find the maximum luminance and maximum current efficiency of device A are 3526 cd/m² and 1.52 cd/A at 10 V. Compared with our results, we found that the luminescent brightness of CzPy was improved about two times than that of published results reported in Ref.[24]. Therefore, CzPy was an excellent blue-light material and the CIE was located at (0.20, 0.24).

For device B, the hole-transporting layer (NPB) was removed, CzPy would be used as the hole-transporting material and luminescent material, and its hole-transporting ability and luminescent property can be investigated. Likewise, the maximum brightness and maximum current efficiency of device B were 1162 cd/m² and 0.69 cd/A at 10 V, respectively. By comparing these results with the published papers [24], the brightness and efficiency were similar with them. In this results, CzPy was used not only as emitter, but also as hole-transporting layer.

In the device C, Alq₃ layer were removed in order to evaluate the electron-transporting ability and luminescent property of CzPy. The maximum luminance and maximum current efficiency decreased to 36 cd/m² and 0.02 cd/A at 10 V, indicated bad electro-transporting ability of CzPy.

In view of these results, we designed another structure of device D in order to investigate the hole-transporting ability of CzPy. In this device, CzPy was used as hole-transporting layer, NPB was used as emitter. It was found that the maximum luminance and maximum current efficiency of CzPy in device D were 945 cd/m² and 0.53 cd/A at 14 V, respectively. There-

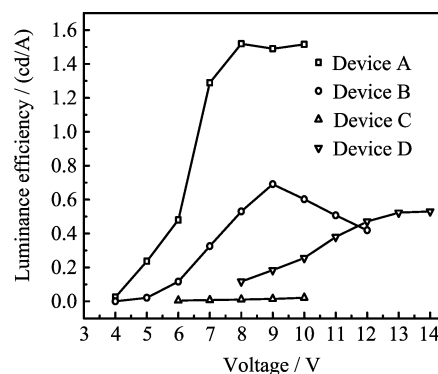


FIG. 9 Efficiency-voltage characteristics of devices A–D.

fore, CzPy was an excellent hole-transport material.

IV. CONCLUSION

We have demonstrated a novel bifunctional blue-light material 9-(pyren-1-yl)-9H-carbazole (CzPy) as blue-light material with hole-transporting ability, its luminescent property was characterized by four types of device structures: (A) ITO/2-TNATA (30 nm)/NPB (20 nm)/CzPy (30 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al, (B) ITO/2-TNATA (30 nm)/CzPy (50 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al, (C) ITO/2-TNATA (30 nm)/NPB (20 nm)/CzPy (50 nm)/LiF (0.5 nm)/Al, (D) ITO/2-TNATA (30 nm)/CzPy (30 nm)/NPB (20 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al. Results were found that CzPy was an excellent blue-light material with strong hole-transporting ability. In device A, the maximum brightness was up to 3526 cd/m² and maximum efficiency 1.56 cd/A, Interestingly, the maximum brightness arrived at 1162 cd/m² (at 10 V) with 0.69 cd/A at 10 V efficiency in device B, when the CzPy was acted as hole-transporting and fluorescent material.

V. ACKNOWLEDGMENTS

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