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Synthesis and properties of a thiophene-substituted diaza[7]helicene for application as a blue emitter in organic light-emitting diodes

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Introduction

It is well known that three kinds of RGB (red, green, blue) emitting materials are required to meet demands of a full-color display and white solid-state lighting. The red and green emitters have a good development while the suitable blue-light-emitting materials are still needed to develop and are ongoing towards commercialization.¹⁻⁶

Helicenes have a twisted and non-coplanar screw-shaped configuration, which can effectively prevent close-packing effect and decrease excited-state quenching. What's more, their highly twisted geometry could shorten the π -system. This characteristic makes helicenes to be utilized in Blue-Emitting OLEDs.^{7,8}

The group thiophene enhances the molecular fluorescence, which is called fluorescence auxochrome. Thiophene has a conjugated structure and the capability to donate electrons. Therefore, it increases the conjugated system HOMO energy level and enhances the ability to donate π electrons. At the same time, the energy gap between HOMO and LUMO energy levels is decreased, reducing the energy required for electrons from the ground state to the excited state transition and facilitating the corresponding transition. Easier electron transition is conducive to the generation of fluorescence. Thiophene can occur electrophilic substitution reaction on α or β position. As a functional group attached to the core rings, it has been widely used in organic photovoltaic materials,^{9,10}

ABSTRACT

Carbazole-based diaza[7]helicene substituted by thiophene groups, 2,12-dithiophene-5,15-dihexyl-5,15-diaza[7]helicene (6), was synthesized successfully and confirmed by ¹H NMR, ¹³C NMR, High Resolution Mass Spectrometry, Time of Flight Mass Spectrometry. Compound 6 exhibited good solubility and excellent thermal stability with no melting point and a high decomposition temperature of 453.64 °C. A doped device with a structure of ITO/NPB (50 nm)/CBP: 10% 6 (30 nm)/Bphen (20 nm)/Mg:Ag (150 nm)/Ag (50 nm) emitted the blue light at 460 nm with Commission Internationale de LEclairage (CIE) coordinate of (0.176, 0.26). The maximum brightness and external quantum efficiency (EQE) were 2306 cd m⁻² and 0.41%, respectively.

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materials,¹¹ biomedicine,¹² light-emitting materials on OLEDs,¹³⁻ ¹⁵ and so on.

A carbazole-based diaza[7]-helicene, 2,12-dihexyl-2,12diaza[7]helicene (Compound 7) exhibited excellent thermal stability with a high decomposition temperature (T_d) of 372.1 °C and a high glass transition temperature (T_g) up to 203.0 °C, which is beneficial to the stability of device performance at high temperature. However, the imbalanced charge injection of OLED based on compound 7 brought damage to the performance since the electron-injection barrier between ETL and EML was 0.93 eV while the potential barrier of the hole-injection between HTL and EML was 0.37 eV.⁷ It is well known that balanced charge injection have a positive effect on the OLED performance. Thiophene is an electron-rich ring group and can be used to increase the intermolecular force as a substituent attached to the helicene core and facilitate charge transfer. Therefore, in this paper, we introduced thiophene into the helicene to decrease the electron-injection barrier and optimize the fluorescent properties. 2,12-dithiophene-5,15-dihexyl-diaza[7]helicene(6), was designed and synthesized through Suzuki reaction, Mcmurry reaction and photocyclization reaction. Compound 6 exhibited good solubility and excellent thermal stability with a high T_d of 453.64 °C. In differential scanning calorimetry measurement, the heating temperature rose from room temperature to 600 °C and the melting point had not appeared. This suggested that compound 6 was amorphous material, which was also proved in the fact that it is difficult to grow single crystals. A doped device with a

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structure of ITO/NPB (50 nm)/CBP: 10% **6** (30 nm)/Bphen (20 nm)/Mg:Ag (150 nm)/Ag (50 nm) emitted blue light at 460 nm with Commission Internationale de LEclairage (CIE) coordinates of (0.176,0.26). The maximum luminance efficiency and brightness were 0.70 cd A^{-1} (0.15 Lm W^{-1}) and 2306 cd m^{-2} and EQE was 0.41%. Compared with diaza[7]-helicene-based OLED, compound **6**-based OLED exhibited better electroluminescent properties. The way to modify the existing helicenes through the substitution reactions opens a new door to taking advantage of helicenes as light emitters in OLEDs.



Fig. 1 Compound 6, compound 7 and thiophene

Results and discussion

The synthetic process for compound **6** was showed in Scheme 1. Compound **1** was synthesised by using phase transfer catalyst. The hexyl could increase the solubleness of compound **6**. Then, compound **1** with DMF and POCl₃ underwent Vilsmeier-Hack reaction to afford compound **2**, and NBS reacted with compound **2** to obtain compound **3**. Using Suzuki reaction, compound **3** reacted with 2-thiophene boric acid to achieve compound **4**. Compound **5** was synthesised by utilizing Mcmurry reaction. Finally, under the high pressure mercury lamp's illumination, the 2,12-dithiophene-5,15-dihexyl-diaza[7]helicene(**6**) was achieved. These compounds were verified by ¹H NMR, ¹³C NMR, High Resolution Mass Spectrometry, Time of Flight Mass Spectrometry. Experimental section including materials and instruments, device fabrication and measurement, and synthesis was in the supplementary data.



Scheme 1. Synthesis of compound 6.

Simple and convenient synthetic process and satisfactory product yields made $\mathbf{6}$ to be gained on a large scale. Particularly, compound $\mathbf{6}$ was achieved in a short reaction time (about 20 min) and high productivity (71%), which gave an efficient and convenient strategy to us to synthesize helicene derivative or modify helicene. Compound $\mathbf{6}$ had good solubleness in common organic solvents, because of its hexyl substituents. The non-

coplanar spiral structure also had a significant contribution. Such good solubility not only overcame the formidable insolubility problem of long helicenes, which typically form highly rigid and annulated structures,¹⁶ but also made it possible for us to afford homogeneous films¹⁷ and the fabrication of devices in solution.^{18,19}

The thermal properties of compound **6** were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under N₂. As shown in Fig. 2, the TGA was measured from room temperature to 600 °C. There was a weight loss of 7.045% within 100 and 276.92 °C, which was similar to that of the compound **7**.⁷ We speculated that this was caused by the solvent absorbed in the clathrate.⁷ Decomposition temperature (T_d) was about 453.64 °C, which was higher than that of compound **7** because of the higher molecular weight.²⁰ High T_d could meet requirements of the fabricating device. The DSC was also measured from room temperature to 600 °C. No melting point was found, which indicated that compound **6** might be amorphous.



Fig. 2 TG and DSC curves of compound 6 recorded under nitrogen at heating rates of 10° C min⁻¹.

The optical properties of compound 6 were investigated by UV-vis spectra and fluorescence-emission spectra in different solvent and film state. As shown in Fig. 3, we measured the UVvis and fluorescene-emission in dichloromethane, tetrahydrofuran, ethyl acetate, trichloromethane, N.N-dimethyl formamide. The test concentration was 10^{-5} mol L⁻¹. In the UV-vis spectra, compound 6 had an absorption maximum peak at 310 nm, a secondary maximum peak at 347 nm, two shoulders at 368 and 376 nm, and some small peaks at nearby 420 nm, 441 nm in dichloromethane. When the polarity of solvents changed, a very small red-shift or blue-shift phenomenon occurred. This indicated that the compound 6 had a good solvent independence of UV/Vis absorption spectra. In the film state, there was about 5 nm redshifted in absorption spectrum compared with those in solvents and a new peak at 325 nm appeared. Furthermore, the main peaks were broadened than those in the dilute solutions.²¹ These phenomena could be explained by the formation of weak Jaggregated molecules 22,23 in the ground state of the thin film. In the fluorescence emission measurement, the excitation wavelength was 310 nm. Compound 6 emitted blue light with the peaks at 456 and 490 nm. The shape of film spectrum was similar to those in solvents. There was a red-shift of about 2 nm in the emission of the thin film, which indicated that the screw and noncoplanar molecular structure and a long hexyl substitution attached to the helical core could effectively decrease close-

packing in the solid state. Compared with the compound $7,^7$ there was a red-shift of ca. 10 nm in absorption and emission spectrum of compound 6 due to the π -conjugation increase. Thiophene is an electron-rich group and the delocalization of the π -electron system along the backbone is extended by introducing thiophene groups into the helical core. Therefore, the HOMO-LUMO energy gap was decreased²⁴ and the fluorescence quantum yield was increased.²⁵⁻²⁹ Based on the UV absorption edge at 471 nm, the band gap was calculated to be 2.32 eV, which was lower than that of compound 7 (2.79 eV). The fluorescence quantum yields of compound **6** in different solvents were also measured with 10^{-5} M Quinine sulfate aqueous solution used as a reference, whose values were from 13% to 32% (summarized in Table 1). The value up to 32% in ethyl acetate was the best, which increased by more than two-fold compared with fluorescence quantum yields from 9% to 10% of the compound 7.



Fig. 3 UV-vis and fluorescence-emission normalized spectra of compound 6 at different solvent and film.

Table 1. The maximum absorption wavelength, maximum

 emission wavelength and corresponding fluorescence

 quantum yield of compound 6 at different solvent.

Solvent	λ_{\max}^{a} [a](nm)	λ_{\max}^{e} [b](nm)	$\Phi_{f}[c](\%)$
Dichloromethane	310	456	23
Tetrahydrofuran	308	453	17
Ethyl acetate	306	452	32
Trichloromethane	307	456	13
N,N- Dimethylformamide	309	456	19
a) a	······································		

^a λ_{\max}^{a} maximum absorption wavelength.

^b λ_{\max}^{e} maximum emission wavelength excited at 313 nm.

 $^{\rm c}$ $\Phi_{\rm f}$ $\,$ PL quantum yields calculated using a quinine sulfates in 0.1 mol L-1 $\rm H_2SO_{4\cdot}$.

The electrochemical properties were identified by cyclic voltammetry under N₂. A three-electrode cell with a Pt working electrode, a glassy carbon assistant electrode, a saturated Ag/AgCl reference electrode was utilized. The potential of a saturated Ag/AgCl reference electrode in the purified dichloromethane (0.1 M tetrabutylammonium perchlorate) was calibrated by using ferrocene (Fc/Fc⁺) redox system.³⁰ In this measurement, the half-wave potential of Fc/Fc⁺ was 0.65 eV versus Ag/AgCl.

Fig. 4 was the curve of electrochemical properties. The oxidation peaks were at 1.03 V and 1.98 V, and its onset oxidation potential was determined to be 0.80 V. According to the equation HOMO = $-[E_{onset(ox)}-E_{1/2,Fc/Fc+}+4.8] \text{ eV}$,³¹ the HOMO energy level was calculated to be -4.95 eV. Correspondingly, the LUMO energy level was located at -2.63 eV.



Fig. 4 CV of compound 6 in CH_2Cl_2 (0.1 mol L^{-1} Bu₄NClO₄) at a scanning rate of 200 mV s⁻¹.

Electroluminescence properties of compound **6** were examined by using the configuration of ITO/NPB (50 nm)/Emitter (30 nm)/Bphen (20 nm)/Mg:Ag (150 nm)/Ag (50 nm). Layers of the device **A** based on compound **6** were fabricated by vacuum evaporation. The device configuration and the energy diagram were shown in Fig. 5. The EL properties of compound **6** and **7** were summarized in Table 2.



Fig. 5 (a) The configuration of device **A**: ITO/NPB (50 nm)/Emitter (30 nm)/Bphen (20 nm)/Mg:Ag (150 nm)/Ag (50 nm). (b) Energy-level diagram of device **A** (relative to the vacuum energy level).



Fig. 6 The normalized emission spectra of compound 6 in dichloromethane, thin-film and device A.

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Fig. 6 depicted EL spectrum of device A at the driving voltage of 8 V and PL spectra of compound 6 in dichlormethane and solid state film. Device A emitted blue light with two peaks at 460 and 488 nm with the CIE coordinate of (0.176, 0.260). The maximum peak of the device had a slight red-shift of about 4 nm compared to that at 456 nm in dichloromethane. EL spectrum of device A was almost consistent with the PL spectra of compound 6 in thin-film and dichlormethane (Fig. 6). This suggested that the EL of device A originated from compound 6 and compound 6 in the emitting layer was maintained in a good amorphous state. According to the energy level diagram presented in Fig. 5, there were energy barriers of 0.73 eV for ITO/NPB junction and 0.77 eV for the NPB/CBP junction. Since HOMO energy level of compound 6 was higher than those of NPB and CBP, holeaccumulation occurred at the interface between NPB and the emitting layer. The electron-injection barriers ranged from 0.4 eV to 0.8 eV. Similarly, the electrons appeared at the interface of the blue-emitting layer and Bphen layer. These injection barriers were responsible for the slightly high turn-on voltage of 5.2 V (Table 2).

The power efficiency, current efficiency and current density–voltage–luminance (J–V–L) characteristics of device **A** were shown in Fig. 7. Introducing thiophene into compound **7** resulted in the decrease of the LUMO energy level and the increase of the HOMO energy level relative to those of compound **7**. Therefore, the band gap was reduced and corresponding spectra were red-shifted. The device achieved maximum brightness of 2302 cd m⁻², maximum current efficiency of 0.70 cd A⁻¹, maximum power efficiency of 0.15 lm W⁻¹. The maximum external quantum efficiency of 0.41% was almost twice as much as that of device **1** based on compound **7**.

The maximum external quantum efficiency of the device was attributed to the following factors: 1) Fluorescence quantum yields of compound **6** in solvents were increased. 2) Introducing thiophene into compound **7** decreased the electronic injection barrier of device **A**, whose value was 1.2 eV. In contrast, that of the device **1** based on compound **7** was 1.43 eV. 3) The ability of hole transport and injection by introduction thiophene into compound **7** was superior to that of the device **1**. These results manifested that introduction thiophene into compound **7** could

improve the PL and EL performance, especially fluorescence quantum yield and the external quantum efficiency.



Fig.7(a) The power efficiency and current efficiency of device A.



Fig.7(b) The Current density (J)-voltage (V)-brightness (B) curve of device A.

Table 2. The properties of devices based on compound 6 and compound 7.

Device V	onset ^a [V]	$\boldsymbol{B}_{\max}^{b}$ [cd m ⁻²]	$\boldsymbol{\eta}_{c, \max}^{c} [cd A^{-1}]$	$\eta_{\mathrm{p,max}}^{\mathrm{d}}$ [lm W ⁻¹]	CIE ^e [x,y]	$\lambda_{\max}^{e} [nm]$	η _{ext, max} ^f [%]
A based on 6	5.2	2302	0.70	0.15	(0.176,0.260)	460	0.41
1 based on 7^7	5.3	2365	0.22	0.09	(0.150,0.100)	446	0.23

^a V_{onset} : The turn-on voltage was measured at the brightness of 1 cd m⁻².

 ${}^{b}B_{max}$: The maximum brightness was measured at 18 V and 14.6 V, respectively.

^cη_{c. max}: The maximum current efficiency was measured at 14.6 V and 11.8V, respectively.

 ${}^{d}\eta_{p, max}$: The maximum power efficiency was measured at 14.6 V and 7.1 V, respectively.

eThe CIE coordinate and emission peak was measured at 10 V and 8 V, respectively.

^fη_{ext, max}: The external quantum efficiency was calculated by using relevant current efficiency.

Conclusion

A thiophene modified carbazole-based diaza[7]helicene, namely, 2,12-dithiophene-5,15-dihexyl-diaza[7]helicene(6), was synthesised by a photochemical synthesis and characterized by ¹H NMR, ¹³C NMR, HRMS, MS (MALDI-TOF). Its thermal, photophysical, electrochemical, and electroluminescent properties were investigated. The study indicated that the compound 6 owned good solubility and high thermal stability and exhibited better photophysical, electrochemical, and electroluminescent properties compared with the compound 7 and showed that the introduced thiophene could optimize the structure and improve the performance and have the potential to use in other organic light-emitting material. An OLED that included compound 6 as the guest emitter with the configuration ITO/NPB (50 nm)/Emitter (30 nm)/Bphen (20 nm)/Mg:Ag (150 nm)/Ag (50 nm) emitted blue light at 460 and 488 nm with the CIE coordinate of (0.176, 0.260). The device achieved maximum brightness of 2302 cd m⁻², maximum current efficiency of 0.70 cd A⁻¹, maximum power efficiency of 0.15 lm W⁻¹, the maximum external quantum efficiency of 0.41%. It was worth noting that introducing thiophene into diaza[7]helicene could improve the PL and EL performance, especially fluorescence quantum yield and the external quantum efficiency, whose values were nearly a two-fold increase.

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Supplementary data

Supplementary data (experimental section, and ¹H NMR, ¹³C NMR, HRMS, MALDI-TOF spectra of compounds **1-6**) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/

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Highlights

- A synthetic route to a thiophene-• substituted diaza[7]helicene was demonstrated.
- Fluorescence quantum yield up to 32% • of this compound in acetidin was
- Accepted