



# Investigation of novel carbazole-functionalized coumarin derivatives as organic luminescent materials



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## ABSTRACT

Four new carbazole-based coumarin derivatives comprising a carbazole core and one or two coumarin chromophores, 7-(diethylamino)-3-(4-(9-(*p*-tolyl)-9*H*-carbazol-3-yl)phenyl)coumarin (**Cz-Ph-C**) and 3,3'-((9-(*p*-tolyl)-9*H*-carbazole-3,6-diyl)bis(4,4'-phenyl))bis(7-(diethylamino)coumarin) (**Cz-2(Ph-C)**), 7-(diethylamino)-3-(5-(9-(*p*-tolyl)-9*H*-carbazol-3-yl)thiophen-2-yl)coumarin (**Cz-Th-C**) and 3,3'-((9-(*p*-tolyl)-9*H*-carbazole-3,6-diyl)bis(thiophene-5,2-diyl))bis(7-(diethylamino)coumarin) (**Cz-2(Th-C)**), were successfully synthesized as the emissive materials for organic light-emitting devices. The photophysical, electrochemical properties and thermal stabilities of the compounds were systematically investigated. The results showed that these coumarin-carbazole hybrids exhibited excellent thermal stabilities and high photoluminescence quantum efficiencies in dichloromethane solutions, and they emitted strong green emissions. The vacuum-processed doped devices with a configuration of ITO/TAPC (20 nm)/TBADN: Coumarin-carbazole hybrid (*x* wt%, 30 nm)/TPBi (50 nm)/LiQ (2 nm)/Al (150 nm) was fabricated, in which the devices based on **Cz-Ph-C** exhibited the best electroluminescence performance with a maximum brightness of 12910 cd/m<sup>2</sup> and a maximum luminous efficiencies of 7.39 cd/A and a maximum external quantum efficiency (EQE) of 3.36%.

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## 1. Introduction

Coumarin and its derivatives caused considerable attentions for decades because of their wide range of applications in biological, chemical, physical and medical fields. Numerous natural and synthetic coumarin derivatives not only display excellent biological and medical activities [1,2], but also exhibit unique fluorescence properties that make them using for several photonic applications, from laser dyes to sensors and light-emitting devices [3–12]. The photophysical properties of coumarin derivatives, such as absorption and emission wavelength, and photoluminescence quantum yield (PLQY), strongly depend on the nature and the position of substituents [13–15]. Generally, for coumarins with an electron-donating group in position 7 and/or an electron-withdrawing group at position 3 would enhance their optical behavior due to the resonance and inductive effects (i.e. push-pull effect), and the push-pull effect is stronger, the resonance and inductive effects will

be more pronounced. For example, the presence of electron-donating group at the 7-position and/or electron-withdrawing substituent at the 3-position not only results in a large red shift in coumarin UV–vis absorption spectra but it also increases the light absorption efficiency of coumarins. The accurate prediction of photophysical properties of coumarins is a very important criterion for designing more efficient coumarin dyes for laser and optoelectronic applications.

Since 3-(2-benzothiazolyl)-7-diethylaminocoumarin (coumarin 540) as an efficient fluorescent emitter had been used in the fabrication of organic light-emitting diodes (OLEDs) [10], the coumarin derivatives have been extensively investigated as the emitters in OLEDs [11–13,16–20]. However, most of coumarin derivatives are easy to crystallize and usually have relatively low glass transition temperature which will impact on the thermal stability of the devices, and they are easily suffered from concentration quenching at highly concentrated solution or in solid state due to interaction and aggregation with its neighboring molecules. Therefore, the coumarin derivatives are usually used as disperse dyes in polymer matrices or in host materials to fabricate OLEDs, and the doping concentration of the coumarin derivatives is very

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low. From the perspective of application, developing highly efficient fluorescent coumarin-based materials at highly concentrated solution or in solid state are in high demand. Generally, incorporation of bulky groups as well as nonplanar molecular moieties at the coumarin framework would prevent orderly molecular packing, and can reduce the fluorescence quenching resulting from molecular interactions and aggregation.

The carbazole core is known to be a very efficient donor and can cause the coumarin core in achieving the red-shift emission by pushing electrons in the chromophoric system, and the introduction of coumarin units on carbazole core to form the coumarin-carbazole hybrid material can improve the molar extinction coefficient of the dye [21]. In addition, the carbazole derivatives have excellent hole transporting ability, luminescence efficiency, thermal stability, versatile structural derivatization and unique ability to form amorphous film [22]. Thus, the coumarin-carbazole hybrids are expected to be the ideal luminescent materials.

In previous studies we have reported the synthesis, crystal structures and photo- and electro-luminescent properties of various coumarin derivatives [18–20,23–25]. As part of our continuous research interests in the synthesis and luminescent evaluation of coumarin-based materials, in this paper we concern the synthesis, photophysical and electrochemical properties, and thermal stabilities of four new coumarin-carbazole hybrids, in which one or two coumarin units were introduced carbazole core through an aromatic spacer (Fig. 1). Investigation of the doped OLED device fabrication and performance using these coumarin-carbazole hybrids as emitting materials is also reported.

## 2. Experimental

### 2.1. Materials and methods

Carbazole and *p*-Iodotoluene were purchased from Shanghai Zhongqin Chemical Reagent Co. Ltd (China). 4-(*N,N'*-diethylamino) salicylaldehyde, 4-bromophenylacetonitrile, 2-thiopheneacetonitrile, tetrabutyl ammonium bromide (TBAB), bis(pinacolato) diboron, tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>), 4-iodotoluene and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (PdCl<sub>2</sub>(dppf)) were obtained from Energy Chemical (China). *N*-bromobutanamide (NBS), piperidine and 1,10-phenanthroline were bought from Tianjing Chemical Reagent Co. Ltd (China). All the other chemicals were analytical grade reagent. All of the organic solvents used in this study were dried over appropriate drying agents and freshly distilled prior in the related reaction.

7-(*N,N'*-diethylamino)-3-(4-bromophenyl)coumarin was synthesized as previously described [26a]. 7-(*N,N'*-diethylamino)-3-

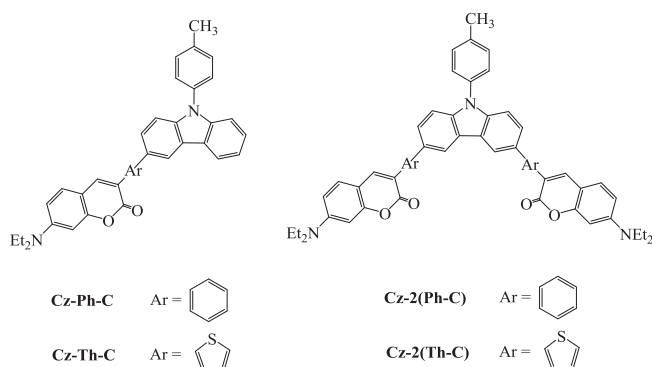


Fig. 1. Chemical structures of the synthesized coumarin-carbazole hybrids.

(thiophen-2-yl)coumarin and 3-(5-bromothiophen-2-yl)-7-(diethylamino)coumarin were prepared according to the procedure described in literature [26b]. 9-(*p*-Tolyl)-9H-carbazole, 3-Bromo-9-(*p*-tolyl)-9H-carbazole (**III**) and 3,6-Dibromo-9-(*p*-tolyl)-9H-carbazole (**IV**) were obtained as the procedure described in literature [26c].

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian Mercury Plus 400 MHz and Agilent Technologies DDZ 600 MHz. IR spectra (400–4000 cm<sup>-1</sup>) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. Mass spectra were recorded using a Thermo Scientific Orbitrap Elite mass spectrometer. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris system. UV–vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Cyclic voltammetry (CHI Instruments 760 B) was performed with a 0.10 mol/L solution of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in dichloromethane, with the analyte present in a concentration of 10<sup>-3</sup> mol/L and employing a scan rate of 50 mV/s at room temperature. A glassy carbon electrode was used as the working electrode, while a Pt wire and an Ag/Ag<sup>+</sup> electrode were used as the counter electrode and reference electrode, respectively. The photoluminescence quantum yield was measured by an absolute method using the Edinburgh Instruments FLS920 integrating sphere excited at 380 nm with the Xe lamp at room temperature. The photoluminescence decay lifetime was measured by a time-correlated single photon counting spectrometer using Edinburgh Instruments FLS920 with a microsecond flashlamp as the excitation source (repetition rate 90 Hz) at room temperature.

### 2.2. Synthesis and characterization of the coumarin-carbazole hybrids

#### 2.2.1. 7-(Diethylamino)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)coumarin (**I**)

The suspension of 7-(*N,N'*-diethylamino)-3-(4-bromophenyl) coumarin (5.0 g, 13.43 mmol), bis(pinacolato)diboron (5.48 g, 21.56 mmol), potassium acetate (2.11 g, 21.50 mmol) and Pd(dppf) Cl<sub>2</sub> (0.34 g, 0.48 mmol) in absolute 1,4-dioxane (100 mL) was placed in a three-necked flask. The mixture was heated up to 95 °C and stirred for 24 h under N<sub>2</sub>. After solvent was evaporated under vacuum, the mixture was dissolved in dichloromethane, washed with water (3 × 50 mL). The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated in vacuum. The crude was purified by chromatography on silica gel using EtOAc/CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:8:30, v/v/v) to form yellow solid (yield 74%). m.p.: 212–214 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.85 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.73 (s, 2H, Ar-H), 7.71 (s, 1H, Ar-H), 7.32 (d, *J* = 8.8 Hz, 1H, Ar-H), 6.59 (dd, *J* = 8.8, 2.1 Hz, 1H, Ar-H), 6.53 (s, 1H, Ar-H), 3.43 (q, *J* = 7.0 Hz, 4H, CH<sub>2</sub>), 1.35 (s, 12H, CH<sub>3</sub>), 1.22 (t, *J* = 7.0 Hz, 6H, CH<sub>3</sub>). Anal. Calcd. for C<sub>25</sub>H<sub>30</sub>BNO<sub>4</sub> (%): C 71.61, H 7.21, N 3.34. Found (%): C 71.53, H 7.29, N 3.30.

#### 2.2.2. 7-(Diethylamino)-3-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)coumarin (**II**)

The preparation of the compound **II** was similar to that described for the compound **I**, which was obtained from 3-(5-bromothiophen-2-yl)-7-(diethylamino)coumarin (3.0 g, 7.93 mmol), bis(pinacolato) diboron (3.23 g, 12.73 mmol). The crude was purified by chromatography on silica gel using ethyl acetate/dichloromethane/petroleum ether (1:1:5, v/v/v) to form reddish brown solid (yield 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.93 (s, 1H, Ar-H), 7.76 (d, *J* = 3.7 Hz, 1H, Ar-H), 7.59 (d, *J* = 4.0 Hz, 1H, Ar-H), 7.32 (s, 1H, Ar-H), 6.60 (d, *J* = 8.8 Hz, 1H, Ar-H), 6.53 (d, *J* = 2.4 Hz, 1H, Ar-H), 3.44 (q, *J* = 7.2 Hz, 4H, -CH<sub>2</sub>-), 1.35 (s, 12H, -CH<sub>3</sub>), 1.22 (t, *J* = 7.2 Hz, 6H, -CH<sub>3</sub>).

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