



# Tunable crystal packing for enhanced electroluminescent properties based on novel thiazole derivatives with different connecting positions of carbazole



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## ABSTRACT

Two novel deep-blue fluorescent compounds, namely, 2-(4-(9-phenyl-9H-carbazol-3-yl)phenyl)benzo [d]thiazole (BCzBTZ) and 2-(4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)benzo [d]thiazole (CzBBTZ) were designed, synthesized and characterized. It is particularly intriguing to compare their crystal packing of BCzBTZ and CzBBTZ, both of them construct with the same heterocyclic units and linker. Their crystal packing can be effectively regulated by changing the connecting position of carbazole. Their thermal stabilities, optical and electrochemical properties were studied systematically and exhibited ideal performance for electroluminescent emitters. The device based on BCzBTZ as emitter shows deep-blue emission with the CIE (x, y) of (0.15, 0.08), which is close to the blue standard (0.14, 0.08) of National Television System Committee (NTSC). The maximal external quantum efficiency is 1.4% and current efficiency is 1.39 cd/A with low efficiency roll-off.

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## 1. Introduction

Heterocyclic compounds have been attracting extensive research interest for organic light-emitting diodes (OLEDs), organic solar cells (OSCs), and organic field-effect transistors (OFETs) due to their semiconducting features [1,2]. For OLEDs, the balance of carries play an important role to achieve high device performance [3]. To solve this issue, some effective strategies have been demonstrated including the fabrication of multilayer devices and development of novel bipolar molecules [4–6]. Regarding the promising potential of bipolar structures for low-cost OLEDs, it is highly desirable to design and synthesize novel multifunctional materials with different heterocyclic units.

In the past decades, numerous multifunctional materials have

been developed and some of them show excellent performance, including triarylamine-imidazole, triarylboron-bis(diphenylamino) carbazole, phenoxazine-quinoline, carbazole-1,3,4-diaryloxadiazole, triarylamine-1,3,4-diaryloxadiazole, and so on, especially for the derivatives of triarylamine-imidazole with hybridized local and charge-transfer characteristics [7–14]. By scanning these heterocyclic structures, thiazole, a well-known molecule in the azole family by replacing a carbon with nitrogen atom of thiophene, has been studied and exhibit modest electron-deficient properties, indicating a good candidate for constructing functional emitters. However, to the best of our knowledge, the research on thiazole and its derivatives for electroluminescence is still limited [15]. On the other hand, molecular packing in film or solid state greatly affects their charge transport properties and fluorescent quantum yield. Generally, the transport of carries is mainly depended on their electronic couplings and the reorganization energies [16]. The electronic coupling is strongly based on their molecular packing modes [17]. Therefore, tunable molecular packing or crystal packing are desired to obtain effective electroluminescent materials.

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Herein, a couple of benzothiazole derivatives, 2-(4-(9-phenyl-9H-carbazol-3-yl)-phenyl)benzo[d]thiazole (BCzBTZ) and 2-(4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)benzo[d]thiazole (CzBBTZ), was designed and synthesized with a strong electron-donating carbazole (Cz) and electron-accepting thiazole units as shown in Scheme 1. Both of them construct with the same heterocyclic units and linker and only the connecting position of Cz is changed. It is particularly intriguing to compare their crystal packing of BCzBTZ and CzBBTZ. Their crystal packing modes are effectively regulated. The thermal stabilities, optical and electrochemical properties were studied systematically and exhibited ideal performance for electroluminescence emitters. The electroluminescent device based on BCzBTZ as emitter shows deep-blue emission with the CIE(x, y) of (0.15, 0.08), which is close to the blue standard (0.14, 0.08) of NTSC. The maximal external quantum efficiency is 1.4% and current efficiency is 1.39 cd/A. Furthermore, at the high luminescence, the device still indicated good performance with relatively low efficiency roll-off.

## 2. Experimental

### 2.1. Chemicals and instruments

The reagents and starting materials, including 2-(4-bromophenyl)benzo[d]thiazole, bis(pinacolato)diboron, 3-bromo-9-phenyl-9H-carbazole and 9-(4-bromophenyl)-9H-carbazole, were purchased from local suppliers or TCI and used without further purification.  $^1\text{H}$  NMR spectra was measured on a Bruker DRX-400 spectrometer. Thermogravimetric analysis (TGA) were performed on a TA Q500 instrument. Their optical properties (UV–vis and fluorescent emission) were done on a Shimadzu UV-2550 and Shimadzu RF-5301PC spectrophotometers. Cyclic voltammetry (CV) measurements were performed on a CHI 660D electrochemical workstation using a Pt wire as the counter electrode, glass-carbon as the working electrode, and a Hg/HgCl electrode as the reference electrode in a dichloromethane solution containing 0.1 M of tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Single-crystal XRD data was collected on Bruker SMART 1000 CCD diffractometer collection. The empirical absorption correction was applied by using the SADABS program [18]. Single crystals of them were solved using direct method, and refined by full-matrix least-squares on  $F^2$  [19].

### 2.2. Synthesis

#### 2.2.1. Synthesis of 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzo[d]thiazole

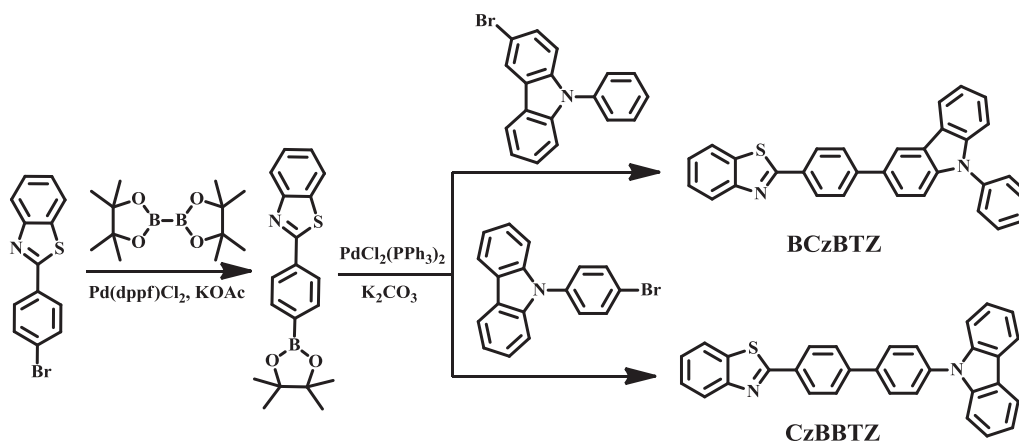
A mixture of 2-(4-bromophenyl)benzo[d]thiazole (5.80 g, 20 mmol), bis(pinacolato)diboron (7.62 g, 30 mmol),  $\text{PdCl}_2(\text{dppf})$  (150 mg, 0.2 mmol) and KOAc (8.00 g, 81 mmol) suspended in 70 mL of 1,4-dioxane under the protection of argon was stirred at 87 °C for 4 h. After cooling, the mixture was forced through a short pad of silica with dichloromethane (DCM). The solvent was removed under reduced pressure and the crude product was absorbed onto silica. Chromatography on silica gel with gradient elution and a white solid was got (6.40 g, yield: 95%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm] 8.05–8.10 (m, 3H), 7.87–7.95 (m, 3H), 7.48 (t, 1H,  $J = 7.54$  Hz), 7.37 (t, 1H,  $J = 7.40$  Hz), 1.24 (s, 12H).

#### 2.2.2. Synthesis of 2-(4-(9-phenyl-9H-carbazol-3-yl)phenyl)benzo[d]thiazole (BCzBTZ)

2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzo[d]thiazole (1.69 g, 5 mmol), 3-bromo-9-phenyl-9H-carbazole (1.61 g, 5 mmol) and  $\text{PdCl}_2(\text{PPh}_3)_2$  (100 mg, 0.14 mmol) were added to a 250 mL flask with 40 mL toluene, 20 mL 2M  $\text{K}_2\text{CO}_3$  and 20 mL ethanol. The mixture was heated to 100 °C and stirred for 24 h. After cooling, the mixture was extracted with DCM, organic layer was collected and dried with  $\text{MgSO}_4$ . The solvent was removed and purified by chromatography on silica gel with gradient elution. 1.63 g white solid was obtained with yield of 72%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm] 8.43 (s, 1H), 8.20–8.24 (m, 3H), 8.11 (d, 1H,  $J = 8.24$  Hz), 7.93 (d, 1H,  $J = 7.95$  Hz), 7.86 (d, 2H,  $J = 8.30$  Hz), 7.72 (d, 1H,  $J = 8.67$  Hz), 7.57–7.66 (m, 4H), 7.44–7.54 (m, 3H), 7.37–7.45 (m, 3H), 7.30–7.35 (m, 1H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 154.0, 144.7, 141.4, 140.8, 137.5, 134.9, 132.1, 131.5, 130.0, 128.1, 127.7, 127.6, 127.1, 126.4, 126.3, 125.3, 125.2, 124.0, 123.4, 123.1, 121.6, 120.4, 120.3, 118.9, 110.2, 110.0. Anal. Calcd for  $\text{C}_{31}\text{H}_{20}\text{N}_2\text{S}$ : C, 82.27; H, 4.45; N, 6.19; S, 7.09; found: C, 82.20; H, 4.49; N, 6.25; S, 7.06. ESI-MS ( $m/z$ ): 452.99 ( $\text{M}^+$ ). FTIR (KBr,  $\text{cm}^{-1}$ ) 3039 (C–H), 1625 (C=N), 1596, 1502, 1473, 1453 (C=C), 1233 (C–N), 965 (C–S).

#### 2.2.3. Synthesis of 2-(4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)benzo[d]thiazole (CzBBTZ)

The synthesis of CzBBTZ is carried out in the same procedure as BCzBTZ. Yied = 75%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm] 8.24–8.28 (m, 2H), 8.20 (d, 2H,  $J = 7.79$  Hz), 8.15 (d, 1H,  $J = 7.99$  Hz), 7.97 (d, 1H,  $J = 7.84$  Hz), 7.89–7.73 (m, 2H), 7.83–7.87 (m, 2H), 7.69–7.73 (m, 2H), 7.41–7.58 (m, 6H), 7.32–7.37 (m, 2H).  $^{13}\text{C}$  NMR (400 MHz,



Scheme 1. Synthesis and structures of target compounds.

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