



Thermally activated delayed fluorescence materials based on benzophenone derivative as emitter for efficient solution-processed non-doped green OLED



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ABSTRACT

A series of thermally activated delayed fluorescence materials based on benzophenone derivatives have been synthesized by Ullmann coupling reaction. The optical, electrochemical and thermal properties of benzophenone derivatives were systematically characterized. In comparison with the reported thermally activated delayed fluorescence materials based on benzophenone derivatives, bis-[4-[3,6-bis(3,6-di-*tert*-butyl-carbazol-9-yl)carbazol]-9-yl-phenyl]-methanone exhibited better solubility and smaller energy gap between the singlet and triplet excited states (0.08 eV). The solution-processed non-doped green OLED using this novel material as an emitter exhibited a low turn-on voltage of 4.5 V, a maximum current efficiency of 9.2 cd A⁻¹, a high external quantum efficiency of 4.3%, and a maximum luminance of 4200 cd m⁻².

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1. Introduction

Recently, thermally activated delayed fluorescence (TADF) materials based on small organic molecules have received increasing attention attributing to the promise to substitute the phosphors based on rare metals such as Ir(III), Pt(III), or Os(II) for low-cost and high-efficiency OLEDs [1–8]. For a TADF molecule as emitter to realize high-efficiency in OLEDs, small energy gap between their singlet and triplet excited states (ΔE_{ST}) and high photoluminescence efficiency (Φ_{PL}) are necessary [6]. Although various TADF materials based on cyanobenzene [1,9], triazine [5–7,10–15], sulfone [3,16–23], benzophenone [24], anthraquinone [25], heptazine [26], trifluoromethyl benzene [27], oxadiazole and triazole [28] as emitters or hosts have been designed and applied to high-efficiency OLEDs, rational design of TADF materials with small

ΔE_{ST} and high Φ_{PL} is still a great challenge [4].

With the developments of OLED technologies, trends are focusing on the predigestion of fabrication process and optimization of device structure of OLEDs to reduce the cost of larger area displays [29]. Solution-processed and non-doped OLEDs have attracted more and more attention [30,31]. Very recently, Lee et al. reported solution-processed OLEDs using TADF materials as emitters [9]. In which, TADF material 4CzIPN was modified with a methyl or *tert*-butyl group to improve the solubility and applied to solution-processed OLEDs with high-efficiency. Duan et al. demonstrate that *tert*-butyl units of sterically shielded TADF emitters could not only improve the solubility but also their stability [32]. Yamamoto et al. reported solution-processed non-doped green OLEDs based on TADF materials carbazole dendrimers. OLEDs using these dendrimers as spin-coated emitting layers realized external quantum efficiencies (EQEs) of up to 3.4% [11]. However, only a few TADF materials are suitable for solution-processed non-doped OLEDs, and keep room for improvement.

In 2014, Adachi et al. reported TADF materials composed of

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electron-transporting benzophenone and hole-transporting carbazole or bicarbazole (Cz2BP and CC2BP) doped host material bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) as emitter layer for vacuum-deposited blue TADF OLEDs [24]. According to the results based on time-dependent density functional theory (TD-DFT) calculations, Cz2BP and CC2BP have small ΔE_{ST} values of 0.32 and 0.10 eV, respectively. In this work, carbazole and bicarbazole are substituted by 3,6-di-*tert*-butyl-carbazole (**t-BuCz2BP**, Scheme 1) and 3,6-bis-(3,6-di-*tert*-butylcarbazol-9-yl)-carbazole (**t-BuTCz2BP**, Scheme 1) to improve the solubility for solution-processed OLEDs. According to TD-DFT calculations, **t-BuCz2BP** and **t-BuTCz2BP** possess small ΔE_{ST} values of 0.28 and 0.05 eV, respectively. **t-BuTCz2BP** exhibited high thermal stability and moderate Φ_{PL} (0.652, oxygen free). The solution-processed non-doped green OLED using **t-BuTCz2BP** as emitter exhibited a low turn-on voltage of 4.5 V, a maximum current efficiency of 9.2 cd A⁻¹, a high EQE of 4.3%, and a maximum luminance of 4200 cd m⁻².

2. Experimental

2.1. General

All reactants and solvents were purchased from commercial sources and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker ARX300 NMR spectrometer with Si(CH₃)₄ as the internal standard. Elemental analysis was performed on an Elementar Vario EL CHN elemental analyzer. Mass spectra were obtained using a Thermo Electron Corporation Finnigan LTQ mass spectrometer. UV-vis absorption spectra and PL spectra were recorded with a spectrophotometer (Agilent 8453) and a fluorospectrophotometer (FluoroMax-3, Horiba), respectively. The transient photo-luminescence decay characteristics and time-resolved fluorescence

were recorded using a spectrofluorometer (Fluoromax-4, Horiba). Thermogravimetric analysis (TGA) was performed using a Netzsch simultaneous thermal analyzer (STA) system (STA 409 PC) under dry nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Glass transition temperature was recorded by differential scanning calorimetry (DSC) at a heating rate of °C min⁻¹ with a thermal analysis instrument (DSC 2910 modulated calorimeter). Cyclic

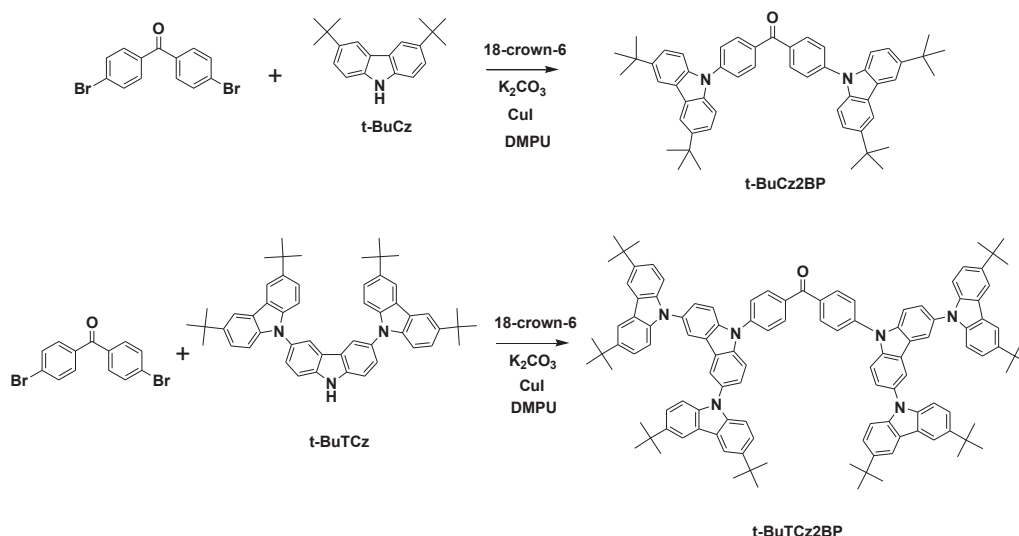
voltammetry (CV) measurements was performed on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer in CH₂Cl₂ solutions (10⁻³ M) at a scan rate of 100 mV s⁻¹ with a platinum plate as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene was selected as the internal standard. The solutions were bubbled with a constant argon flow for 10 min before measurements.

Density functional theory (DFT) calculations of these compounds were performed using the Gaussian 09 program package [33]. The calculations were optimized at the B3LYP/6-31G(d) level of theory. The molecular orbitals were visualized using Gaussview. To investigate the properties of the excited states of **t-BuCz2BP** and **t-BuTCz2BP**, we performed quantum chemical calculations of the low-lying excited states of **t-BuCz2BP** and **t-BuTCz2BP** using TD-DFT.

2.2. Synthesis

2.2.1 Synthesis of bis-[4-(3,6-di-*tert*-butyl-Carbazol-9-yl)-phenyl]-methanone (**t-BuCz2BP**)

To a solution of 4,4'-dibromobenzophenone (5.0 mmol), 3,6-di-*tert*-butyl-carbazole (18.0 mmol) and 18-crown-6 (0.50 mmol) in 10 mL of 1,3-di-methyltetrahydropyrimidin-2(1H)-one (DMPU) solution was added K₂CO₃ (30.0 mmol). The reaction mixture was then purged with nitrogen for 10 min before adding copper(I) iodide (0.50 mmol). The mixture was heated to 170 °C under nitrogen for 24 h. After the reaction finished, the resulting mixture was cooled to room temperature, poured into water, and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phase was washed with saturated aqueous NaCl solution (2 × 10 mL) and dried with anhydrous Na₂SO₄. After removal of the solvent by rotary evaporation, the residue was purified by silica gel column chromatography to afford **t-BuCz2BP** as a yellow solid. Yield: 68.08%. M.p. 144–146 °C. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.17–8.17 (d, 8H, *J* = 7.5 Hz), 7.80–7.88 (dd, 4H, *J* = 8.4 Hz), 7.56–7.49 (m, 8H), 1.49 (s, 36H). ¹³C NMR (300 MHz, CDCl₃) δ (ppm): 31.57, 34.37, 108.95, 116.18, 120.23, 123.48, 125.43, 125.82, 131.43, 134.86, 137.94, 138.15, 141.66, 142.01, 143.46, 194.11. MS (MALDI-TOF) [*m/z*]: Calcd for C₅₃H₅₆N₂O, 736.44; found, 736.22. Anal. Calcd. for C₅₃H₅₆N₂O (%): C, 83.37; H,



Scheme 1. Synthesis of **t-BuCz2BP** and **t-BuTCz2BP**.

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