



# Synthesis, characterization and electroluminescence of carbazole-benzimidazole hybrids with thiophene/phenyl linker



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## ABSTRACT

New organic luminescent materials containing carbazole and benzimidazole chromophores were synthesized by tethering them together using thiophene or phenyl spacer. Both 3,6- and 2,7-disubstitutions were explored. The functional properties of the new materials were analyzed by photophysical, electrochemical, thermal and electroluminescence properties. The thiophene containing dyes showed red-shifted absorption and emission profiles than that of the phenyl analogs due to effective electronic delocalization in the former. Also, the thiophene-based dyes exhibited low oxidation potentials than that of the phenyl analogs attributable to electron richness. Electroluminescence devices were fabricated using these dyes as emitting layer or dopant in a multi-layered configuration. The devices containing thiophene-based dyes showed relatively low turn-on voltage in the neat devices due to the favorable alignment of energy levels, which facilitated balanced charge transport. A thiophene-based dye exhibited better performance in the series with external quantum efficiency as high as 1.5%.

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## 1. Introduction

Organic dyes containing conjugated chromophores have drawn flurry of interest due to their beneficial applications in organic electronics [1–3]. Among the organic electronic devices, organic light-emitting diode (OLED) received immense attention by synthetic chemists as it offered ways to optimize the function of materials by tethering diverse chromophores by simple chemical modifications [4,5]. OLEDs dominate in lightings and full-color display applications due to its low power consumption. In the last few decades, enormous amount of research was directed to improve the performance and color purity of OLED device by subtle variation of materials used in the fabrication [6,7]. Several new concepts based on fluorescence [8], phosphorescence [9,10] and thermally activated delayed fluorescence (TADF) [11], have been exemplified. Though the phosphorescent OLEDs (PHOLED) give exceptional efficiency, they suffer due to high production cost and cumbersome fabrication procedures. Though PHOLEDs possess longer lifetime, they possess comparable or lower lifetime than fluorescence OLEDs [12]. On the other hand, TADF is the newly

tested promising strategy to achieve high efficiency through conversion of triplet to singlet excitons" [11]. Recently, Fukagawa and co-workers reported the new strategy of use of TADF material as host for PHOLED to realize low turn-on voltage and high efficiency at low dopant concentration with increased device lifetime [13].

Generally, to obtain a high performance OLED the emissive material should have balanced charge transport character, high fluorescence quantum yield, high thermal stability and amorphous morphology. The functional properties of the organic materials can be tuned by connecting donor and acceptor *via* a linker of appropriate choice, using different connecting topology and changing the number of either donor or acceptor groups [14–16]. Usually, the donor and acceptor were connected through phenyl linker because it provides different positional linkage *via ortho-, meta- and para-*substitution and even multiple substitution on all the atoms [17]. Moreover, fluorene [18], oligofluorene [19], acetylenes [20,21], oligothiophenes [22], etc., were used as linker in the design of dipolar compounds. Simple thiophene as linker showed good semiconducting properties [23–26], and gave low turn-on voltage than the phenyl counterparts.

Carbazole inherently possesses hole-transporting ability and suitable triplet energy and offers efficient functionalization possibilities at different nuclear positions. So, it has been exploited in the construction of hole-transporting [27,28], fluorescent [29] and

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TADF [30] emissive and host materials [31]. Similarly, benzimidazole has been largely treated as acceptor in the OLED materials [32–34]. Jabbour and co-workers reported carbazole-benzimidazole dipolar dyes connected with phenyl linker for deep-blue FOLED and achieved EQE of 4.1% [35]. Wong and co-workers have reported carbazole-benzimidazole hybrids for use in blue FOLED with maximum EQE of 3.0% [36]. Lu and co-workers have reported carbazole/phenanthroimidazole based bipolar dyes for non-doped deep blue FOLED with maximum EQE of 3.02% [37]. Kim and co-workers reported triphenylamine-benzimidazole hybrids for non-doped FOLED and demonstrated EQE as high as 4.67% [38]. Though, carbazole donor and benzimidazole acceptor connected through phenyl linker with different positions have been studied intensively by several groups for different types of OLED applications their thiophene analogs remained elusive.

In this work, we report new materials (Fig. 1) featuring donor-acceptor<sub>2</sub> system with carbazole as donor and benzimidazole as acceptor and linked through thiophene linker *via* different positions such as 3,6- and 2,7- of carbazole and their functional properties. For comparison the phenyl-linked derivatives were also prepared. To study the effect of benzimidazole on functional properties a mono-benzimidazole dye possessing donor-acceptor configuration was also synthesized and characterized. Among the dyes the dye **T3** showed better device performance of external quantum efficiency ( $\eta_{\text{exe}}$ ) of 1.5%, power efficiency ( $\eta_{\text{p}}$ ) of 6.8 lm/W and current efficiency ( $\eta_{\text{c}}$ ) of 0.7 cd/A at 100 cd/m<sup>2</sup> with low turn-on voltage.

## 2. Experimental section

### 2.1. General methods

All the chemicals were purchased from readily available commercial sources and used as such without further purification. All solvents were dried by standard procedures prior to use. All reactions were performed under inert atmosphere. Column chromatography purifications were performed with silica gel (230–400 mesh) as a stationary phase in a column with 40.0 cm length and 3.0 cm diameter. All the spectroscopic measurements were performed at room temperature using freshly distilled spectroscopic grade solvents. The IR spectra were recorded with a Perkin-Elmer spectrometer by using KBr pellets. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker NMR spectrometer operating at 500.13 and 125.77 MHz, respectively. Deuterated chloroform

(CDCl<sub>3</sub>) were used as solvent and the chemical shifts were calibrated from the residual peaks at  $\delta$  7.26 ppm for <sup>1</sup>H; 77.0 ppm for <sup>13</sup>C NMR, respectively. UV–Vis spectra were recorded in quartz cuvettes using a Cary UV–300 spectrophotometer. Emission spectra were recorded using Shimadzu spectrofluorimeter. Drop-cast thin films on quartz plates were prepared from toluene solution and used to measure solid state photoluminescence. Absolute fluorescence quantum yield ( $\pm 3\%$  accuracy) was measured in Edinburgh FLS980 fluorescence spectrometer equipped with an integrating sphere. The TGA analyses were performed on a PerkinElmer Pyris Diamond Analyzer using nitrogen as carrier gas and at a heat rate of 10 °C min<sup>-1</sup>. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed with BASi Epsilon electrochemical analyzer using a glassy carbon working electrode, a non-aqueous Ag/AgNO<sub>3</sub> reference electrode and platinum as a counter electrode. DCM solutions of the compounds with tetrabutylammonium perchlorate used as supporting electrolyte (0.1 M) and ferrocene as internal standard to calibrate the redox potentials were used in the measurements. The high resolution mass spectra were obtained from a HRMS ESI mass spectrometer (Bruker Daltonics) in the positive ion mode. Elemental analyses data were collected from vario EL III microanalyser for carbon, hydrogen and nitrogen.

### 2.2. Synthesis

#### 2.2.1. 4,4'-(9-butyl-9H-carbazole-3,6-diyl)dibenzaldehyde (**4**)

A mixture of 3,6-dibromo-9-butyl-9H-carbazole **3** (1.00 g, 2.62 mmol), 4-formylphenylboronic acid (0.87 g, 5.77 mmol), K<sub>2</sub>CO<sub>3</sub> (2.17 g, 15.72 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (178 mg) and 30 mL of THF/water mixture (3/1) was refluxed. After 20 h, it was allowed to cool to room temperature and extracted with chloroform and washed with brine solution. The combined organic layer was dried over anhydrous sodium sulfate, evaporated, adsorbed on silica and purified by column chromatography using chloroform as eluent. Greenish yellow solid; yield 0.85 g (49%); mp 185 °C; IR (KBr): 1594 cm<sup>-1</sup> ( $\nu_{\text{C=O}}$ ); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.13 MHz):  $\delta$  0.99 (t,  $J = 7.5$  Hz, 3H), 1.43–1.48 (m, 2H), 1.93 (q,  $J = 7.5$  Hz, 2H), 4.39 (t,  $J = 7.5$  Hz, 2H), 7.54 (d,  $J = 8.5$  Hz, 2H), 7.80 (dd,  $J = 8.0$  Hz, 2.0 Hz, 2H), 7.90 (d,  $J = 8.0$  Hz, 4H), 7.99 (d,  $J = 8.5$  Hz, 4H), 8.45 (d,  $J = 2.0$  Hz, 2H), 10.08 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz):  $\delta$  13.9, 20.6, 31.2, 43.2, 190.5, 119.4, 123.5, 125.6, 127.5, 130.4, 131.0, 134.6, 141.1, 147.9, 191.9 ppm; HRMS calcd for C<sub>30</sub>H<sub>25</sub>NO<sub>2</sub> [M+Na]<sup>+</sup>  $m/z$  454.1783, found 454.1794; Found: C, 83.5; H, 5.6; N, 3.3%;

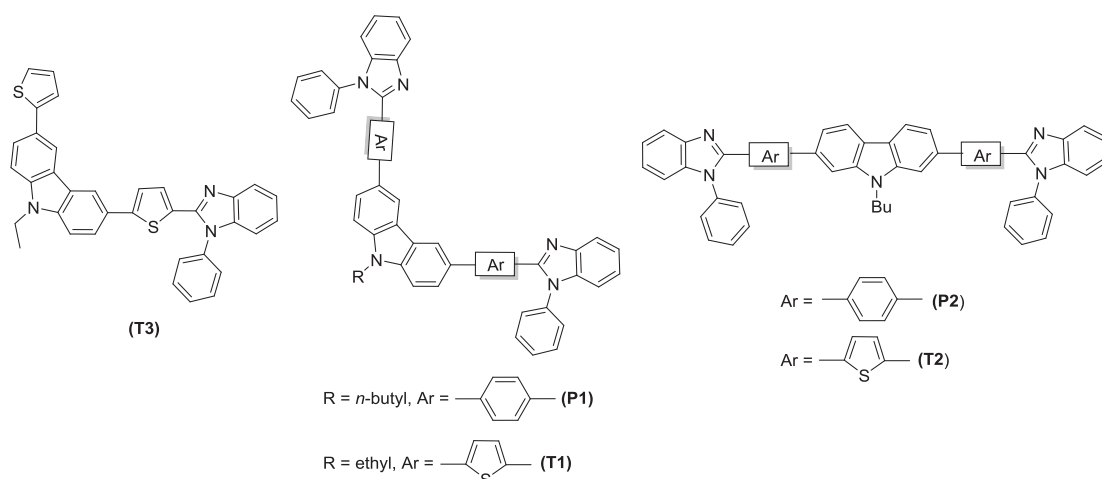


Fig. 1. Structures of dyes.

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