

## Research Article

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# Synthesis and optical characterization of bipod carbazole derivatives

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**Abstract:** In this study, some new biscarbazole derivatives were synthesized for the purpose of being used in OLED technologies and related areas. The following compounds: {1,2-bis(2-(3,6-diphenyl-9H-carbazole-9-yl)ethoxy)ethane (**C-1**), bis[2-(2-(3,6-diphenyl-9H-carbazole-9-yl)ethoxy)ethyl]ether (**C-2**), bis[2-(2-(3,6-di(naphthalene-1-yl)-9H-carbazol-9-yl)ethoxy)ethyl]ether (**C-3**) and bis[2-(2-(3,6-di(naphthalene-2-yl)-9H-carbazol-9-yl)ethoxy)ethyl]ether (**C-4**) were synthesized by Suzuki-Miyaura Cross Coupling reactions. The structural properties of the synthesized compounds were characterized by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and LC-MS. The maximum product yields of 81.6% were obtained for **C-4** biscarbazole derivatives. The optical properties were studied using UV-visible and temperature/excitation power density dependent photoluminescence (PL) techniques. The emissions were observed at green and yellow-red color spectral bands. By applying Gaussian fitting to the measured spectra, the superposition of the broad peaks was deconvoluted into two peaks. The origin of emissions was attributed to  $\pi$ - $\pi^*$  transition in aromatic compounds caused by intramolecular charge transfer from host carbazole to these compounds.

**Keywords:** Bipod Carbazole, Suzuki-Miyaura Cross Coupling, Optical Characterization, Photoluminescence, OLED

## List of abbreviations

OLED	:	Organic Light Emitting Diodes
FT-IR	:	Fourier Transform Infrared Spectroscopy
<sup>1</sup> H-NMR	:	Proton Nuclear Magnetic Resonance
<sup>13</sup> C-NMR	:	Carbon Nuclear Magnetic Resonance
TBAI	:	Tetrabutylammonium iodide
$\delta$	:	Chemical Shift
M <sup>+</sup>	:	Molecular Ion Peak

## Introduction

Biscarbazoles as luminescent materials which include two aromatic heterocyclic organic compounds have been designed and synthesized for exploring some applications. These include organic light-emitting diodes (OLEDs) [1–3], organic photovoltaic and electronic devices [4–10], studying biochemical activities [11–18] and fundamental points of view [19,20]. Such molecules are especially suited to implementation in OLED technologies because of the electron donation of nitrogen on the carbazole ring. The efficient charge transfer from host carbazoles to connected molecules is provided by a strong  $\pi$ -electron conjugation. Carbazoles have been used as host matrices in highly efficient blue, green, or red electro-phosphorescent devices [6–8,16,21]. They also have good thermal properties and structural stability, allowing them to be used as a hole transport layer in OLED technology [22–30]. Carbazole/thioxanthene-S, S'-dioxide (EBCz-ThX) bipolar molecules synthesized by electron accepting and electron donating groups with a solvent-free green chemistry method were presented as blue phosphorescent light emitting devices [31]. A green light with a peak maximum at 550 nm under an applied external voltage was reported from a diode based on 2,4-dicarbazolylquinoline [32]. Multi-carbazole derivatives with twisted and zigzag-shape structures were synthesized and used as sensitizers for dye-sensitized solar cells [33].

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To identify the potential use of newly synthesized molecules in various applications, their photophysical and electrochemical properties need to be investigated. As an example, Slodek et al. reported a strong dependence of optical properties on the number of carbazole units and length of alkyl chain on said carbazole units in the molecule, as well as the position of substitution of carbazole for a donor-acceptor (D-A) system based on 2,4-dicarbazolyl-substituted quinolines. The low-temperature PL spectra were characterized by the spin-allowed fluorescence (400 nm) and spin-forbidden phosphorescence (490–527 nm) bands [34]. The synthesis and optical characterization of a salicylaldimine difluoroboron complex with tert-butyl group was carried out by Zhang and co-workers. The maximal emission peak of the synthesized compound in THF at 514 nm was ascribed to intramolecular charge transfer (ICT) emission. The peak positions of fluorescence emissions were blue and red-shifted to 506 and 522 nm for crystal structure and ground powder respectively [32]. Complex yellow (centered at ~574 nm) and red (centered at ~704 nm) colors were observed, with the relative intensities dependent on functional groups in PL spectra, for novel carbazole derivatives synthesized using a condensation reaction between carbazole amines and aromatic aldehydes [35].

Although carbazoles have been synthesized with substitutions in all positions (on benzene rings and nitrogen) [36], substitutions on 3- and 6- positions are very common [30, 32–35]. Various methods with several steps have been used for substitution on the aromatic rings [36, 39]. The most common and successfully used method is the Suzuki-Miyaura Cross Coupling Reaction [42–48]. The selection of groups expected to substitute on the desired positions is very important due to their crucial effect on the optical properties of the final product.

This study includes the synthesis and characterization of novel biscarbazole derivatives which were obtained by connection of two carbazole molecules through their nitrogen positions and substitution of phenyl,  $\alpha$ -naphthyl and  $\beta$ -naphthyl on their 3- and 6- positions using the Suzuki-Miyaura Cross Coupling Reaction. The formation of synthesized molecules was determined by infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), mass spectrometry (MS) and microanalysis methods. Their optical properties were studied using UV-Vis spectroscopy and temperature/excitation power density dependent photoluminescence (PL).

## Materials and methods

### General

All starting materials were purchased from Merck, Sigma-Aldrich and Fluka Co., and were used after further analytical purifications using silica gel column chromatography. FT-IR spectra were taken using Perkin Elmer BX2 FTIR Spectrometer. Both  $^1\text{H-NMR}$  (400 MHz) and  $^{13}\text{C-NMR}$  (100 MHz) spectra were obtained in  $\text{CDCl}_3$  using an Agilent Tech. 400 NMR Spectrometer. LC-MS spectra were recorded on an Agilent Technologies-1260 Infinity (LC) 6130 Quadropole (MS) Mass Spectrometer using acetonitrile as the solvent. Microanalyses were performed with a Thermo Scientific Flash 2000 elemental analyzer. The absorption spectra were recorded using a Perkin-Elmer Lambda 25 UV-Vis Spectrometer. The temperature and excitation power density dependent photoluminescence measurements were performed in the temperature range of 20–300 K and excitation power densities between 2.6–330  $\text{mW}/\text{cm}^2$ . A frequency tripled Nd:YLFQ-switched pulse laser at 349 nm was used for the excitation. The luminescence was collected by suitable lenses and then dispersed with a 500 mm spectrometer using 1200 line/mm grating and detected by Intensified Charge Coupled Device (ICCD) camera.

### Experimental

#### Synthesis of 3,6-dibromocarbazole (B)

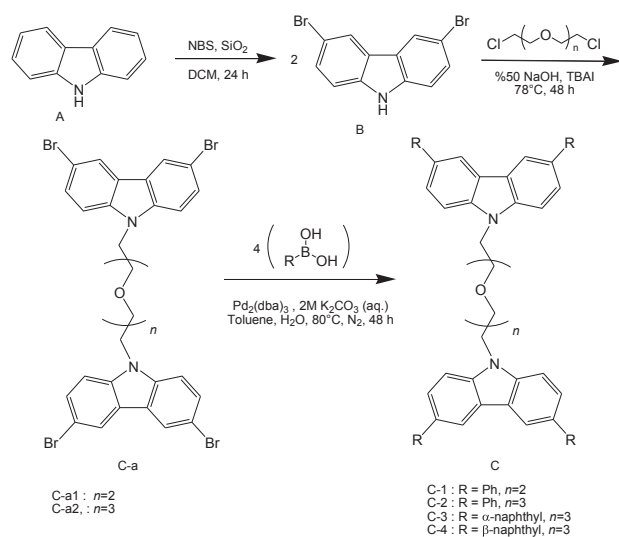
Carbazole (A) (5 mmol, 0.835 g) was firstly dissolved in 100 ml of dichloromethane.  $\text{SiO}_2$  (20 g) was then added and stirred. A solution which contained NBS (10 mmol, 1.78 g) dissolved in 150 ml of dichloromethane was added dropwise to the carbazole mixture, and was continuously stirred at room temperature for 24 hours in a dark environment [45]. The entire mixture was then filtered and the residue was washed with dichloromethane (3 x 30 ml). The combined organic fractions were rinsed with water (200 ml) and, after the phases were separated, the organic layer was collected. The solvent was evaporated after which a light green powder was obtained (1.176 g, yield: 72%). FT-IR ( $\nu$   $\text{cm}^{-1}$ ): 3403 (N-H stretch), 3071 (aromatic C-H stretch), 1598 (aromatic C=C stretch), 1459 (carbazole ring stretch), 1127 (C-N bend), 802 (C-Br bend), 739 and 686 (aromatic C-H out-of-plane bend)

### General Procedure-I for synthesis of bromine substituted bis-carbazoles

3,6-dibromocarbazole (**B**) (2.0 equivalent), 1,2-bis(2-chloroethoxy)ethane (1.0 equivalent), TBAI and 50% NaOH solution (10 ml) were added in 100 ml flask and refluxed while it was stirring at 78 °C for 48 hours [49]. After the reaction was complete, the mixture was cooled down to room temperature. The mixture was then filtered with dichloromethane (3x30 ml) and washed in water (200 ml). Organic phase was obtained after separating the layers and drying over Na<sub>2</sub>SO<sub>4</sub>. The solution was evaporated and the oily solid product was obtained by recrystallizing from a mixture of chloroform/*n*-hexane (1:1) (see Figure 1).

### Synthesis of 1,2-bis(2-(3,6-dibromo-9H-carbazole-9-yl)ethoxy)ethane (**C-a1**)

Synthesized using General Procedure-I with 3,6-dibromocarbazole (3 mmol, 0.970 g), 1,2-bis(2-chloroethoxy)ethane (1.5 mmol, 0.24 ml), TBAI (0.36 g) to give the oily solid product (0.585 g, 46.7%). FT-IR (γ cm<sup>-1</sup>): 3071 (Aromatic C-H stretch), 2956 and 2871 (symmetric and asymmetric aliphatic C-H stretch), 1624-1546 (carbazole ring stretch), 1471 (asymmetric aliphatic C-H bend), 1435 (carbazole ring stretch), 1290 (symmetric aliphatic C-H bend), 1108 (C-O-C asymmetric bend), 1058 (N-C bend), 1031 (C-O-C symmetric bend), 1017 (aliphatic C-H out-of-plane bending), 797 (C-Br bend), 750 and 648 (Aromatic C-H out-of-plane symmetric bending).



**Figure 1** Synthesis of the original bipod carbazole derivatives (**C-1**, **C-2**, **C-3**, **C-4**)

### Synthesis of Bis[2-(2-(3,6-dibromo-9H-carbazole-9-yl)ethoxy)ethyl]ether (**C-a2**)

Synthesized using General Procedure-I with 3,6-dibromocarbazole (2.8 mmol, 0.91 g), bis[2-(2-chloroethoxy)ethyl] ether (1.38 mmol, 0.27 ml), TBAI (0.50 g) to give the oily solid product (0.424 g, 37.5%). FT-IR (γ cm<sup>-1</sup>): 3062 (aromatic C-H stretch), 2956 and 2871 (aliphatic asymmetric and symmetric stretch), 1471 (aliphatic asymmetric C-H bend), 1435 (carbazole ring stretch), 1290 (aliphatic C-H, in-plane, symmetric bending), 1108 (C-O-C asymmetric bend), 1057 (N-C bend), 1033 (C-O-C symmetric bend), 1017 (C-H, aliphatic out-of-plane bending), 798 (C-Br bend), 737 and 648 (aromatic C-H out-of-plane, symmetric bending).

### General Procedure-II for synthesis of bipod carbazole derivatives

Brominated carbazoles (**C-a1** or **C-a2**) (3.33 equivalent), PhB(OH)<sub>2</sub> (13.33 equivalent) and Pd<sub>2</sub>(dba)<sub>3</sub> (1.0 equivalent) were placed in 100 ml flask. K<sub>2</sub>CO<sub>3</sub> (aq., 2M), toluene and two drops of Aliquot 336 were quickly added. The mixture degassed with nitrogen was stirred at 80°C for 48 hours in a nitrogen atmosphere. The reaction was complete and allowed to cool to room temperature. It was then filtered in dichloromethane (3 x 30 ml) and washed with water (200 ml). Organic phase was obtained after separating the layers and drying over Na<sub>2</sub>SO<sub>4</sub>. The solution was evaporated and recrystallized from ethanol.

### Synthesis of 1,2-bis(2-(3,6-diphenyl-9H-carbazole-9-yl)ethoxy)ethane (**C-1**)

**C-1** was obtained from 1,2-bis(2-(3,6-dibromo-9H-carbazole-9-yl)ethoxy)ethane (**C-a1**) (0.2 mmol, 0.15 g), PhB(OH)<sub>2</sub> (0.8 mmol, 0.098 g) and Pd<sub>2</sub>(dba)<sub>3</sub> (0.06 mmol, 0.055 g) and K<sub>2</sub>CO<sub>3</sub> (aq., 2M, 3 ml), toluene (6 ml) following the General Procedure-II. The yellow, slightly oily solid product was achieved by recrystallization from ethanol (0.020 g, 13.5%). FT-IR (γ cm<sup>-1</sup>): 3058 and 3024 (aromatic C-H stretch), 2926 and 2871 (C-H, symmetric and asymmetric stretch), 1599 (Aromatic C=C stretch), 1470 (C-H, aliphatic, in-plane, asymmetric bend), 1449 (carbazole ring stretch), 1340 (aliphatic C-H bend, in-plane, symmetric), 1135 (C-O-C asymmetric bend), 1111 (aliphatic C-H, out-of-plane bending), 1067 (C-N bend), 1018 (C-O-C symmetric bend), 748 and 702

(aromatic C-H, out-of-plane, symmetric bending).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 3.475 (2H, s), 3.832 (2H, t), 4.429 (2H, t), 7.526 (1H, d), 8.107 (1H, m), 7.612 (1H, m), 7.612 (1H, d), 7.406 (1H, s), 7.412 (1H, d), 7.390 (1H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 69.323, 70.527, 58.602, 130.514, 123.191-110.632, 143.323, 139.551, 128.380, 128.959, 129.081. Anal. Calc. for  $\text{C}_{54}\text{H}_{44}\text{N}_2\text{O}_2$  (MW=752.34): C, 86.14; H, 5.89; N, 3.72. Found: C, 86.00; H, 5.81; N, 3.77%. LC-MS ( $m/z$ ): 753.30 ( $\text{M}^+$ ,  $\text{CH}_3\text{CN}$ , Error % = 0.128).

### Synthesis of Bis[2-(2-(3,6-diphenyl-9H-carbazole-9-yl)ethoxy)ethyl]ether(C-2)

**C-2** was obtained from bis[2-(2-(3,6-dibromo-9H-carbazole-9-yl)ethoxy)ethyl]ether (C-a2) (0.2 mmol, 0.16 g),  $\text{PhB}(\text{OH})_2$  (0.8 mmol, 0.098 g) and  $\text{Pd}_2(\text{dba})_3$  (0.06 mmol, 0.055 g) and  $\text{K}_2\text{CO}_3$ (aq., 2M, 3 ml), toluene (6 ml) following the General Procedure-II. The yellow-green, slightly oily solid was recrystallized from ethanol (0.127 g, 80.3%). FT-IR ( $\gamma\text{cm}^{-1}$ ): 3055 (aromatic C-H stretch), 2924 and 2855 (aliphatic C-H, symmetric and asymmetric stretch), 1596 (aromatic C=C stretch), 1470 (aliphatic C-H bend, asymmetric), 1448 (carbazole ring stretch), 1343 (aliphatic C-H bend, symmetric), 1139 (C-O-C asymmetric bend), 1112 (aliphatic C-H bend, out-of-plane), 1055 (C-N bend), 1018 (C-O-C symmetric bend), 740 and 701 (aromatic C-H bend, out-of-plane, symmetric).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 3.472 (4H, s), 3.810 (2H, t), 4.291 (2H, t), 7.619 (1H, d), 8.074 (1H, d), 8.089-8.106 (1H, d), 8.040 (1H, d), 7.601 (1H, s), 7.401 (1H, s), 7.417 (1H, d), 7.333 (1H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 70.535, 69.301, 70.901, 60.644, 131.885, 110.831, 123.434, 143.323, 123.945, 123.023, 139.521, 128.395, 128.974, 127.237. Anal. Calc. for  $\text{C}_{56}\text{H}_{48}\text{N}_2\text{O}_3$  (MW=796.37): C, 84.39; H, 6.07; N, 3.51. Found: C, 84.36; H, 6.01; N, 3.55%. LC-MS ( $m/z$ ): 796.40 ( $\text{M}^+$ ,  $\text{CH}_3\text{CN}$ , Error % = 0.004).

### Synthesis of Bis[2-(2-(3,6-di(naphthalene-1-yl)-9H-carbazol-9-yl)ethoxy)ethyl]ether(C-3)

**C-3** was obtained from bis[2-(2-(3,6-dibromo-9H-carbazole-9-yl)ethoxy)ethyl]ether (C-a2) (0.04 mmol, 0.032 g), naphthalene-1-boronic acid (0.16 mmol, 0.028 g) and  $\text{Pd}_2(\text{dba})_3$  (0.0012 mmol, 0.001 g) were placed in a 100 ml flask, then quickly  $\text{K}_2\text{CO}_3$  (aq., 2M, 6 ml), toluene (12 ml) following the General Procedure-II. The light-brown, slightly oily solid was recrystallized from ethanol (0.024 g, 61.3%). FT-IR ( $\gamma\text{cm}^{-1}$ ): 3062 and 3026 (aromatic C-H stretch), 2923 and 2854 (aliphatic C-H stretch, asymmetric and symmetric), 1656, 1579 and 1496 (aromatic C=C

stretch, naphthalene), 1600 (carbazole C=C stretch), 1467 (aliphatic C-H bend, asymmetric), 1454 (carbazole ring stretch), 1291 (aliphatic C-H bend, symmetric), 1120 (C-O-C asymmetric bend), 1075 (aliphatic C-H bend, out-of-plane), 1057 (C-N bend), 1030 (C-O-C symmetric bend), 801 and 780 (aromatic symmetric C-H bending on  $\alpha$ -substituted naphthalene, out-of-plane), 757 and 698 (aromatic symmetric carbazole bend, out-of-plane).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 3.388 (4H, s), 3.498 (2H, t), 3.635 (2H, t), 7.262 (1H, d), 7.590 (1H, d), 7.608 (1H, d), 7.539 (1H, d), 7.281 (1H, s), 8.060 (1H, m), 7.222-7.135 (2H, m), 7.467 (1H, m), 7.498 (1H, m), 7.377 (1H, d), 7.940 (1H, d).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 74.010-72.125, 61.406, 133.150, 125.332, 125.759, 141.253, 126.505, 125.926, 138.408, 132.807, 128.106, 127.854, 133.485, 128.185, 127.786. Anal. Calc. for  $\text{C}_{72}\text{H}_{56}\text{N}_2\text{O}_3$  (MW=996.43): C, 86.72; H, 5.66; N, 2.81. Found: C, 86.68; H, 5.60; N, 2.90. LC-MS ( $m/z$ ): 996.43 ( $\text{M}^+$ ,  $\text{CH}_3\text{CN}$ , Error % = 0.003).

### Synthesis of Bis[2-(2-(3,6-di(naphthalene-2-yl)-9H-carbazol-9-yl)ethoxy)ethyl]ether(C-4)

**C-4** was obtained from bis[2-(2-(3,6-dibromo-9H-carbazole-9-yl)ethoxy)ethyl]ether (C-a2) (0.06 mmol, 0.048 g), 2-naphthylboronic acid (0.24 mmol, 0.041 g) and  $\text{Pd}_2(\text{dba})_3$  (0.0018 mmol, 0.0016 g) were placed in a 100 ml flask, then quickly  $\text{K}_2\text{CO}_3$  (aq., 2M, 9 ml), toluene (18 ml) following the General Procedure-II. The light-brown, slightly oily solid was recrystallized from ethanol (0.048 g, 81.6%). FT-IR ( $\gamma\text{cm}^{-1}$ ): 3054 and 3022 (aromatic C-H stretch), 2923 and 2854 (symmetric and asymmetric aliphatic C-H stretch), 1624, 1569 and 1494 (aromatic C=C stretch, naphthalene), 1594 (carbazole C=C stretch), 1467 (aliphatic C-H bend, asymmetric), 1454 (cbz ring stretch), 1290 (C-H aliphatic, in-plane, symmetric), 1131 (C-O-C asymmetric bend), 1076 (aliphatic C-H bend, out-of-plane), 1031 (C-O-C symmetric stretch), 811 and 737 (aromatic symmetric C-H bend on  $\beta$ -substituted naphthalene, out-of-plane), 748 and 699 (aromatic symmetric C-H bend on carbazole benzene, out-of-plane).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 3.287 (4H, s), 3.725 (2H, t), 4.379 (2H, t), 7.218 (1H, d), 7.927 (1H, s), 7.900 (1H, d), 8.122-8.059 (1H, d), 7.258 (1H, s), 7.514 (2H, m), 7.279 (2H, s), 7.952 (1H, d), 7.361 (1H, d).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 70.548, 70.650, 125.332, 125.759, 61.434, 133.757, 125.718, 126.099, 143.210, 126.381, 126.030, 138.398, 127.684, 133.510, 128.537, 132.675, 128.233. Anal. Calc. for  $\text{C}_{72}\text{H}_{56}\text{N}_2\text{O}_3$  (MW=996.43): C, 86.72; H, 5.66; N, 2.81. Found: C, 86.65; H, 5.63; N, 2.85. LC-MS ( $m/z$ ): 996.43 ( $\text{M}^+$ ,  $\text{CH}_3\text{CN}$ , Error % = 0.003).

## Results

In this work 1,2-bis(2-(3,6-diphenyl-9*H*-carbazole-9-yl)ethoxy)ethane (**C-1**), bis[2-(2-(3,6-diphenyl-9*H*-carbazole-9-yl)ethoxy)ethyl]ether (**C-2**), bis[2-(2-(3,6-di(naphthalene-1-yl)-9*H*-carbazol-9-yl)ethoxy)ethyl]ether (**C-3**) and bis[2-(2-(3,6-di(naphthalene-2-yl)-9*H*-carbazol-9-yl)ethoxy)ethyl]ether (**C-4**) were synthesized. The syntheses of these compounds were started by brominating the 3- and 6- position of the carbazole ring. During this process, SiO<sub>2</sub> was used as an efficient-reusable catalyst [42]. Then, two molar equivalents of bromo carbazole were led to react with dichloroether derivatives via S<sub>N</sub>2 reaction. The oily solid product was obtained by recrystallizing the mixture of chloroform/*n*-hexane (1:1). Finally, the bromines were replaced by phenyl boronic acid,  $\alpha$ -naphthyl boronic acid and  $\beta$ -naphthyl boronic acid moieties via the Suzuki-Miyaura Cross Coupling Reaction. The oily solid products were re-crystallized from ethanol. The yields of **C-1**, **C-2**, **C-3** and **C-4** bipod carbazole derivatives were obtained as 13.5, 80.3, 61.3 and 81.6%, respectively.

In FT-IR spectra, the N-H stretch peak of secondary amines which is only seen in carbazole and 3,6-dibromocarbazole, disappeared due to the reaction between 3,6-dibromocarbazole and 1,2-bis(2-chloroethoxy)ethane. Therefore, the N-H stretch peak was not observed in FT-IR spectra of **C-a1**, **a2**, **1**, **2**, **3**, and **4**. The C-Br stretch peak was observed in 3,6-dibromocarbazole, **C-a1** and **C-a2** but not in **C-1**, **2**, **3**, and **4**. These results indicate that no Br atoms attached on carbazole were left. Br atoms were replaced by substitution of boron acid molecules via the Suzuki-Miyaura Cross Coupling reaction. Symmetric and asymmetric peaks of aliphatic C-H and C-O-C were observed in **C-a1**, **a2**, **1**, **2**, **3** and **4**, but not in carbazole or 3,6-dibromocarbazole. This indicates the presence of ether and aliphatic groups. As a result, the syntheses of intermediate and final products were confirmed with FT-IR data.

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra data also support successful synthesis of **C-1**, **C-2**, **C-3** and **C-4** (supplementary materials). For example, in <sup>1</sup>H-NMR spectra of **C-3** molecule, ether peaks labeled as 1, 2, and 3 were observed at  $\delta$  3.472-4.291 ppm and aromatic peaks at  $\delta$  7.619-8.106 ppm (supplementary materials). In <sup>13</sup>C-NMR spectra of the same molecule, ether peaks were observed at  $\delta$  60.644-70.901 ppm, and aromatic peaks at  $\delta$  110.831-143.323 ppm (supplementary materials).

The molecular ion peaks of **C-1**, **C-2**, **C-3**, and **C-4** were obtained from LC-MS spectra taken in dichloromethane. The spectra contain peaks of molecular ions and other

possible ions (supplementary materials). The results of microanalysis also support successful synthesis of compounds.

In UV-vis spectra, the absorption bands were observed in the range of 225-380 nm for all samples. This range is suitable for our PL measurement using 349 nm laser.

The PL spectra are shown in Figure 2 together with reference sample containing only carbazole for comparison. The reference sample has several relatively narrow peaks over the spectral range between 370 and 500 nm with the most intense peak situated at 420 nm.

In the work done by Zhang et al. [32], three absorption peaks located at 294, 354 and 379 nm were observed for salicylaldehyde difluoroboron complex with tert-butyl group. They were attributed to carbazole,  $\pi$ - $\pi^*$  and intramolecular charge transfer (ICT) transitions respectively. The emission peak of the synthesized compound in THF mixture present at 514 nm was ascribed to ICT emission. The peak positions of fluorescence emissions were blue and red-shifted to 506 and 522 nm for crystal structure and ground powder respectively. The optical properties of two 2,4-difluorenylquinoline derivatives with different lengths of alkyl chain at the fluorene unit (one with methyl and other with octyl chain) of donor-acceptor (D-A) type were reported by Slodek et al [50]. They observed bright emission in the blue spectral region at 406 nm, whereas the replacement of fluorine with carbazole unit resulted in a bathochromic shift of peak wavelength with emission bands at 425 and 530 nm.

Due to stronger  $\pi$ -conjugation and efficient intramolecular charge transfer from carbazole to aromatic

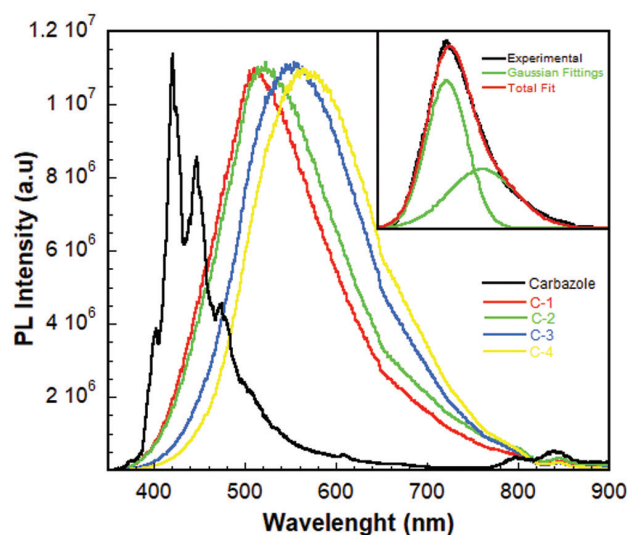


Figure 2 PL spectra for all samples at room temperature

compounds, the PL spectra of **C-1**, **C-2**, **C-3** and **C-4** depict completely different character compared to carbazole. As first seen, all spectra were dominated with a broad peak at about ~513, 523, 553, 565 nm for samples **C-1**, **C-2**, **C-3** and **C-4**, respectively. However, these peaks were decomposed into two peaks using Gauss fitting as shown in the inset.

Figures 3 and 4 show temperature dependent PL peak positions (the one at high energy side of spectrum) and normalized integrated intensities deduced from the Gauss fitting to the experimental data. From figures, the peak wavelengths and integrated intensities are approximately temperature independent for **C-1** and **C-2**. This is consistent with the spatial configuration of structures **C-1** and **C-2**, where the most stable formation is expected at the anti-position of the carbazole and benzene rings. Within the temperature range studied in PL measurement, no changes are expected for both structures. On the other hand, for the samples (**C-3** and **C-4**), in which the  $\alpha$ -naphthyl and  $\beta$ -naphthyl are attached to carbazole, the peak wavelengths and integrated intensities increase as the temperature increases. At low temperatures, the rotation around the sigma bond is weak and prefers to be at the most stable anti-position. As the temperature increases the rotation of the sigma bond is expected to increase. A resonance occurs when the electrons of p orbital of carbazole that do not participate in hybridization and p orbital of naphthyl group come to the same parallel plane. This provides a complete resonance on the molecule that causes redshift in the peak wavelength positions and increases in integrated intensities

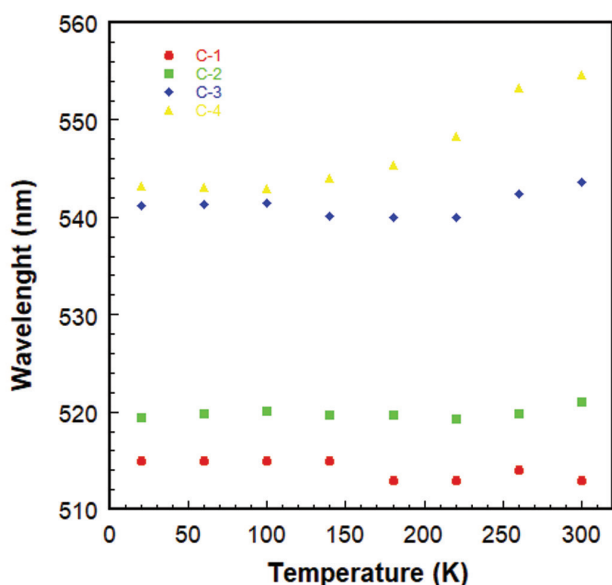


Figure 3 Temperature dependent peak positions

of PL spectra, as observed. The change of integrated intensity within a temperature range of 20-300 K for **C-3** is approximately three times, while for **C-4** it is about 2.3 times. This is probably due to the difference in stereo-electronic effect of compounds attached to the alpha and beta positions.

Figure 5 shows the excitation power density dependent normalized integrated intensities for all samples. As seen from the figure integrated intensity increases with excitation power density as expected. At high excitation density, a small degree of saturation is realized.

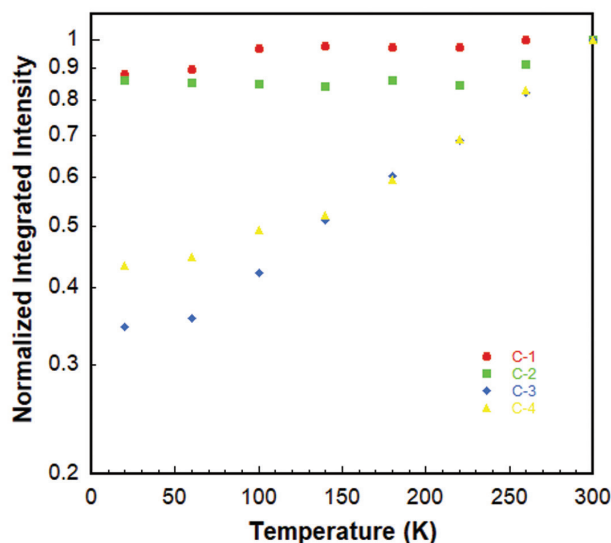


Figure 4 The normalized integrated intensity versus temperature for all samples

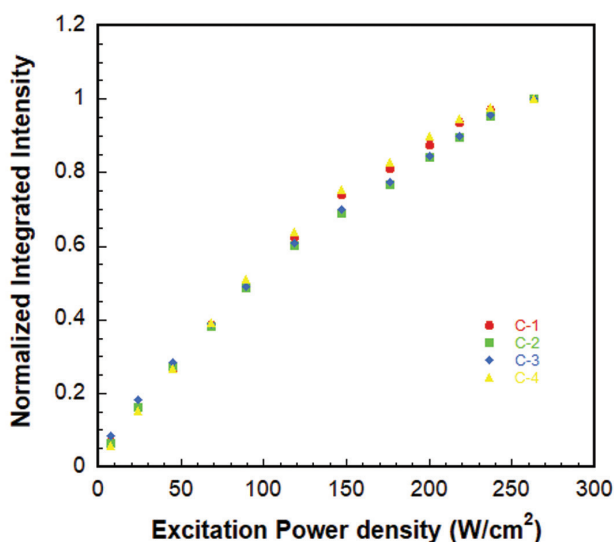


Figure 5 The normalized integrated intensity versus excitation density for all samples

## Conclusions

In this study, some original bipod carbazole derivatives named as **C-1**, **C-2**, **C-3** and **C-4** were successfully synthesized using a Suzuki-Miyaura Cross Coupling reaction between 1,2-bis-3,6-dibromo depot carbazole and aromatic boronic acids. The compounds **C-3** and **C-4** were obtained by substituting the  $\alpha$ - and  $\beta$ -naphthalene on 3- and 6- positions of carbazole for the first time. They were characterized by FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , LC-MS and elemental analysis methods, confirming their formations. The optical characterization was performed by using UV visible spectroscopy and temperature and excitation power density dependent PL measurements. Compared with a reference carbazole host material, two broad peaks were resolved by applying Gaussian fitting to PL spectra in the wavelength range of 510-520 (greenish) and 620-630 (reddish) for all samples. This demonstrates an efficient charge transfer to  $\pi$ -conjugated systems, dependent on associated functional groups. These newly synthesized bipod carbazole derivatives could be explored for organic light emitting diodes as an active emissive or hole transport layer. The emission wavelengths can be shifted as desired by optimizing or changing the functional groups. In order to test their use in such devices, they must be produced with appropriate layer and contact configurations in a device design.

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**Supplementary material:** All FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , LC-MS spectrums (Figures 1-5) for syntheses (C-1)–(C-4) are given in Supportive/Supplementary material.

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