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journal homepage: [www.elsevier.com/locate/jiec](http://www.elsevier.com/locate/jiec)1 Effect of interconnection position of bicarbazole-triazine type bipolar  
2 host materials on the photophysical and device performances

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## ABSTRACT

Organic compounds prepared from 1- position activated 9-phenylcarbazole interconnected with diphenyltriazine functionalized carbazole were examined as bipolar host materials of phosphorescent and thermally activated delayed fluorescent organic light-emitting diodes. Interconnection position of the 9-phenylcarbazole was 1- position, and that of diphenyltriazine functionalized carbazole was changed from 1- position to 4- position. Main influence of the interconnection position was current density of the device and 2- or 3- position interconnection increased current density of the devices. All host materials derived from the 1- position activated 9-phenylcarbazole performed well as the host of phosphorescent and thermally activated delayed fluorescent organic light-emitting diodes.

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## 5 Introduction

6 Host materials of organic light-emitting diodes (OLEDs) play a  
7 key role of assisting light emission of emitters by transporting  
8 carriers to the emitters (charge trapping) or transferring emission  
9 energy to emitters (energy transfer) [1–4]. Although no photon is  
10 directly generated by the host materials, the host material is as  
11 important as the emitters because carrier balance and exciton  
12 formation are governed by the host material. Many works  
13 reporting host materials touched those functions of host in the  
14 emitting layer [5–8].

15 In many publications, bipolar host materials were of main  
16 interest to researchers based on the knowledge that bipolar  
17 character is essential for carrier balance, efficient exciton generation,  
18 and carrier injection [9–14]. Many bipolar host materials were  
19 published in the literature as exemplified in several review papers  
20 and many of them were compatible with emitters [15,16]. General  
21 chemical structure of the reported bipolar host materials was a  
22 donor–acceptor backbone structure, and the engineering of the  
23 donor and acceptor moieties offered various compounds which  
24 have the energy level, carrier mobility, and emission energy  
25 required for the host materials [17]. One of the donor–acceptor  
26 type building blocks is carbazole–triazine type backbone structure  
27 which takes advantage of hole transport character of carbazole and

28 electron transport character of triazine. Fundamentally, the  
29 carbazole–triazine building block is ideal as the core structure  
30 of the bipolar host materials because of good carrier injection,  
31 carrier transport and chemical stability [18–21]. Several modifica-  
32 tion methods of the carbazole–triazine core were suggested and  
33 one example is to add an extra carbazole unit for intense hole  
34 carrying property and thermal stability. A few compounds were  
35 reported as the derivatives of the carbazole modified carbazole–  
36 triazine core and they showed satisfactory material and device  
37 results as the hosts of green phosphorescent OLEDs (PhOLEDs)  
38 [22–24]. It was reported that the properties of material and device  
39 performances were changed by engineering the substitution  
40 position of diphenyltriazine to carbazole unit by different  
41 geometrical structure and highest occupied molecular orbital  
42 (HOMO)/lowest unoccupied molecular orbital (LUMO) distribu-  
43 tion. However, chemical structure of the hosts was not diversified  
44 and systematic exploration of the effect of chemical structure on  
45 the material and device parameters has not been reported.

46 Herein, we explain our systematic investigation of four  
47 carbazole modified carbazole–triazine type hosts prepared from  
48 1- position activated 9-phenylcarbazole interconnected with  
49 diphenyltriazine functionalized carbazole. The change of the  
50 interconnect position between 1-position activated 9-phenyl-  
51 carbazole and carbazole–triazine core mostly affected carrier  
52 transport properties of the host materials. The interconnection of  
53 the carbazole unit via 2- or 3- position was advantageous for good  
54 carrier transport properties and high carrier density in the  
55 emitting layer. The synthesized host materials performed as the

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host materials in the green phosphorescent and thermally activated delayed fluorescent (TADF) devices.

## Experimental

### General information

Sodium tert-butoxide (NaO(*t*-bu)), tri-*tert*-butylphosphine (P(*t*-bu)<sub>3</sub>), tris(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) (P&H Tech Co.), 1-bromo-9-phenyl-9H-carbazole, 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole, 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole, and 2-chloro-4,6-diphenyl-1,3,5-triazine (JH Trade.) were used as received. Sodium hydroxide (NaOH), toluene, and tetrahydrofuran (THF) (Duksan Sci. Co.) were also used as received.

Basic analysis of the materials was similar to the analytical procedure in other works [25–27]. Nuclear magnetic resonance (NMR) spectra were obtained by Varian (<sup>1</sup>H NMR: 400 MHz), Avance-500 (<sup>13</sup>C NMR: 125 MHz). Ultraviolet–visible (UV–vis) absorption spectra were obtained by a Shimadzu UV-2501PC and fluorescence spectra were obtained by Hitachi F-7000. Low temperature PL measurement of the synthesized materials was carried out at 77 K using a dilute solution of materials in tetrahydrofuran. The mass spectra were obtained by a Waters Xevo TQ-S spectrometer in API mode. The HOMO energy levels were measured with a cyclic voltammetry (CV). CV measurement of organic materials was carried out in acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M concentration. Pt was counter electrode and Ag was used as the reference electrode. Ferrocene was used as the standard material for the CV measurement.

### Synthesis

**9-Phenyl-9H,9'H-1,2'-bicarbazole (1)** 1-Bromo-9-phenyl-9H-carbazole (1.56 g, 4.84 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1.7 g, 5.80 mmol), NaOH (0.58 g, 14.5 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.28 g, 0.24 mmol) were dissolved in a mixed solvent of THF (40 ml) and water (20 ml) under a nitrogen bubbling. The reaction mixture was continuously stirred for 3 h under reflux condition and then was cooled down to room temperature. At room temperature, it was diluted with ethyl acetate and washed with water using a separator funnel. The ethyl acetate layer was separated and was dried using anhydrous MgSO<sub>4</sub>. Evaporation of ethyl acetate after filtering off MgSO<sub>4</sub> produced a crude product which was purified by column chromatography on silica gel using an ethyl acetate/*n*-hexane eluent. Purified product was obtained as a white powder (1.8 g, Yield 91%).

<sup>1</sup>H NMR (400 MHz, DMSO): δ 10.95 (s, 1H), 8.28 (d, 2H, J = 7.2 Hz), 7.97 (d, 1H, J = 8.0 Hz), 7.67 (d, 1H, J = 8.0 Hz), 7.39 (m, 4H), 7.30 (m, 2H), 7.17 (d, 1H, J = 8.0 Hz), 7.14 (s, 1H), 7.08 (m, 3H), 6.95 (t, 2H, J = 7.6 Hz), 6.85 (d, 1H, J = 7.6 Hz), 6.78 (t, 1H, J = 6.8 Hz).

**9'-(4,6-Diphenyl-1,3,5-triazin-2-yl)-9-phenyl-9H,9'H-1,2'-bicarbazole (PCz2TCz)** 9-Phenyl-9H,9'H-1,2'-bicarbazole (1.8 g, 4.42 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (1.8 g, 6.63 mmol), NaO(*t*-bu) (1.3 g, 13.2 mmol), P(*t*-bu)<sub>3</sub> (50%) (0.18 g, 0.44 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub> (0.20 g, 0.22 mmol) were dissolved in toluene (40 ml) under a nitrogen flow. After refluxing the reaction mixture for 2 h, it was diluted with dichloromethane at room temperature followed by washing with water. The dichloromethane layer was separated, dried using anhydrous MgSO<sub>4</sub>, and evaporated in vacuo. A crude product was obtained, purified by column chromatography on silica gel using an ethyl acetate/*n*-hexane eluent, and sublimed under vacuum. A white powder was obtained as a final product (1.4 g, Yield 52%).

<sup>1</sup>H NMR (400 MHz, DMSO): δ 9.08 (d, 1H, J = 8.0 Hz), 9.03 (s, 1H), 8.55 (d, 4H, J = 8.0 Hz), 8.38 (d, 2H, J = 7.6 Hz), 8.16 (d, 1H, J = 7.6 Hz), 7.93 (d, 1H, J = 8.0 Hz), 7.64 (t, 1H, J = 7.6 Hz), 7.60 (m, 3H), 7.50 (t, 1H, J = 7.6 Hz), 7.44 (t, 1H, J = 7.6 Hz), 7.34 (m, 7H), 7.15 (m, 1H), 6.98 (d, 2H, J = 7.2 Hz), 6.84 (m, 2H), 6.73 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 172.45, 165.18, 142.62, 139.50, 138.79, 138.60, 138.43, 138.33, 136.27, 132.83, 129.21, 128.90, 128.30, 127.66, 127.55, 126.92, 126.86, 126.45, 126.30, 125.52, 124.93, 124.43, 123.60, 123.45, 120.46, 120.31, 120.25, 119.81, 119.75, 119.61, 118.61, 118.24, 110.61. MS (API+) m/z: 640.9 [(M+H)<sup>+</sup>]

**9-Phenyl-9H,9'H-1,3'-bicarbazole (2)** Synthetic method of 2 was the same as that of 1 except the 1-bromo-9-phenyl-9H-carbazole (2.7 g, 8.38 mmol) and 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (3.0 g, 10.1 mmol) starting materials. A beige powder was obtained as a product (2.0 g, Yield 59%).

<sup>1</sup>H NMR (400 MHz, DMSO): δ 11.13 (s, 1H), 8.43 (d, 1H, J = 8.4 Hz), 8.32 (d, 1H, J = 7.2 Hz), 8.11 (t, 1H, J = 8.0 Hz), 7.77 (d, 1H, J = 8.4 Hz), 7.76 (d, 1H, J = 8.4 Hz), 7.63 (m, 4H), 7.45 (m, 6H), 7.33 (m, 2H), 7.23 (t, 1H, J = 7.6 Hz), 7.14 (t, 1H, J = 8.0 Hz). MS (API+) m/z: 409.9 [(M+H)<sup>+</sup>]

**9'-(4,6-Diphenyl-1,3,5-triazin-2-yl)-9-phenyl-9H,9'H-1,3'-bicarbazole (PCz3TCz)** Synthetic procedure of PCz3TCz was the same as that of PCz2TCz except for the 9-phenyl-9H,9'H-1,3'-bicarbazole (2.0 g, 4.91 mmol) reactant. Purification by column chromatography on silica gel using a dichloromethane/*n*-hexane eluent produced a white powder as a target material (1.9 g, Yield 61%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.15 (d, 1H, J = 8.0 Hz), 8.76 (m, 5H), 8.23 (t, 2H, J = 8.0 Hz), 7.86 (d, 1H, J = 8.0 Hz), 7.69 (s, 1H), 7.64 (m, 6H), 7.58 (m, 1H), 7.47 (d, 1H, J = 7.2 Hz), 7.41 (m, 3H), 7.33 (m, 2H), 7.28 (m, 1H), 7.10 (d, 2H, J = 7.6 Hz), 6.91 (t, 2H, J = 8.0 Hz), 6.70 (t, 1H, J = 7.6 Hz). <sup>13</sup>C NMR (125 MHz, DMSO): δ 171.78, 164.48, 141.87, 138.46, 138.03, 137.34, 136.68, 135.48, 133.61, 133.22, 129.18, 129.03, 128.77, 128.37, 127.96, 127.42, 127.18, 126.73, 126.36, 126.04, 125.91, 125.10, 124.38, 123.46, 122.63, 120.89, 120.41, 120.35, 120.23, 120.11, 119.57, 117.13, 116.18, 109.91. MS (API+) m/z: 640.8 [(M+H)<sup>+</sup>]

**9-phenyl-9H,9'H-1,4'-bicarbazole (3)** 1-Bromo-9-phenyl-9H-carbazole (1.5 g, 4.66 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1.64 g, 9.75 mmol) were used in the same synthetic procedure of 1. The product was obtained as a beige powder (1.45 g, Yield 76%).

<sup>1</sup>H NMR (400 MHz, DMSO): δ 11.00 (s, 1H), 8.39 (d, 1H, J = 6.4 Hz), 8.31 (d, 1H, J = 6.4 Hz), 7.42 (m, 3H), 7.34 (d, 1H, J = 8.0 Hz), 7.27 (m, 2H), 7.17 (t, 1H, J = 8.0 Hz), 7.12 (m, 2H), 6.82 (m, 4H), 6.62 (t, 1H, J = 8.0 Hz), 6.46 (d, 1H, J = 7.6 Hz), 6.38 (m, 1H), 5.96 (m, 1H).

**9'-(4,6-Diphenyl-1,3,5-triazin-2-yl)-9-phenyl-9H,9'H-1,4'-bicarbazole (PCz4TCz)** 9-Phenyl-9H,9'H-1,4'-bicarbazole (1.45 g, 3.56 mmol) was a reactant in the synthetic procedure of PCz2TCz. A white powder was obtained as a target product (1.3 g, Yield 56%).

<sup>1</sup>H NMR (400 MHz, DMSO): δ 8.99 (d, 1H, J = 7.2 Hz), 8.77 (d, 1H, J = 7.6 Hz), 8.69 (d, 4H, J = 7.6 Hz), 8.46 (d, 1H, J = 7.2 Hz), 8.34 (d, 1H, J = 7.6 Hz), 7.73 (m, 6H), 7.48 (m, 4H), 7.29 (m, 2H), 7.16 (d, 1H, J = 7.6 Hz), 6.94 (t, 1H, J = 7.6 Hz), 6.88 (m, 1H), 6.83 (d, 1H, J = 7.6 Hz), 6.79 (m, 1H), 6.74 (t, 1H, J = 7.2 Hz), 6.50 (d, 1H, J = 8.0 Hz), 6.42 (m, 1H), 6.05 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 172.59, 165.31, 142.69, 139.18, 138.86, 138.26, 137.15, 136.54, 133.81, 132.96, 129.34, 129.07, 128.42, 128.05, 127.87, 127.59, 127.29, 126.90, 126.57, 126.18, 125.71, 125.21, 124.48, 124.42, 123.26, 123.09, 121.88, 120.34, 120.23, 120.13, 120.07, 117.04, 116.24, 110.35. MS (API+) m/z: 640.9 [(M+H)<sup>+</sup>]

### Device fabrication and measurements

The phosphorescent devices were constructed on a 150 nm thick indium tin oxide (ITO) coated substrate which was cleaned

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