Dyes and Pigments 128 (2016) 84–88

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Molecular design of modifying 4-position of dibenzofuran for high temperature stability and high efficiency

Yirang Im, Jun Yeob Lee*

School of Chemical and Engineering, Sunkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 16419, Republic of Korea

ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form
8 January 2016
Accepted 18 January 2016
Available online 25 January 2016

Keywords:
Dibenzofuran
Thermal stability
Pyridoindole
Blue device
Phosphorescent
Triplet energy

ABSTRACT

A molecular design modifying 4- position of dibenzofuran with a pyridoindole moiety for high temperature stability and high efficiency was examined as an approach to develop host materials for blue phosphorescent organic light-emitting diodes. The simple pyridoindole modification of 4- position of carbazole substituted dibenzofuran lead to high glass transition temperature above 130 °C in addition to high quantum efficiency in the blue phosphorescent device.

1. Introduction

The development of blue phosphorescent organic light-emitting diodes (PHOLEDs) is a critical issue in the field of organic light-emitting diodes (OLEDs) because blue PHOLEDs can solve the problem of high power consumption of OLED panels [1–3]. It was proven that the blue PHOLEDs would increase the current efficiency of blue device experimentally by more than three times, which motivated researchers to search and develop better blue PHOLEDs by material and device design [4–8].

Although it is essential to find and apply an optimized device structure, optimized host and dopant materials are even more important to reach the device performance level satisfying the specification of blue PHOLEDs. One of key parameters to be considered is thermal stability of the devices which is related with glass transition temperature (T_g) of host materials. High T_g above 120 °C is needed to satisfy the high temperature criteria of the OLED devices. Therefore, thermally stable host materials should be employed in the emitting layer of blue PHOLEDs [8–11]. Other than the temperature stability, the host material should have a design to reach high efficiency by balancing carriers [12–15].

In this work, a molecular design to increase the T_g of the host materials was approached by modification of 4- position of dibenzofuran with a pyridoindole moiety. The 4- position modification approach using the pyridoindole moiety increased the T_g of the carbazole substituted dibenzofuran host materials above 130 °C and allowed bipolar charge transport characteristics. Moreover, the quantum efficiency (QE) values of the blue PHOLEDs having the high T_g host material were as high as 19.1% and 22.7% by doping phenylpyridine type and phenylimidazole type blue triplet emitters.

2. Experimental section

2.1. General information

General analysis method of the synthesized compounds is described in previous work [16,17]. 9*H*-Carbazole (Cz), periodic acid, copper iodide (CuI), trans-1,2-diaminocyclohexane (1,2-TCH), and *n*-butyl lithium (*n*-BuLi) (Aldrich Chem. Co.), dibenzofuran and diiodoethane (TCI. Co.), 9*H*-pyrido[2,3-*b*]indole (α-carboline, α-Cb) (P&H tech Co.), sulfuric acid (H_2SO_4), acetic acid, potassium phosphate (K_3PO_4), and 1,4-dioxane (Duksan Sci. Co.), iodine (I_2) (Samchun Chem. Co.) were also used as received.

2.2. Synthesis

2-Iododibenzofuran (**1**), 9-(dibenzofuran-2-yl)-9*H*-carbazole (**2**), 9-(4-iododibenzofuran-2-yl)-9*H*-carbazole (**3**), 2,8-diiododibenzo[*b*,*d*]furan (**4**), 2,8-di(9*H*-carbazol-9-yl)dibenzo[*b*,*d*]

---

* Corresponding author. Tel./fax: +82 31 299 4716.
E-mail address: leej17@skku.edu (J.Y. Lee).

http://dx.doi.org/10.1016/j.dyepig.2016.01.018

furan (**5**), 9-(2-(9*H*-carbazol-9-yl)dibenzo[*b*,*d*]furan-4-yl)-9*H*-pyrido[2,3-*b*]indole (**CzDBFCb**), 9,9′-(4-iododibenzo[*b*,*d*]furan-2,8-diyl)bis(9*H*-carbazole) (**6**), and 9-(2,8-di(9*H*-carbazol-9-yl)dibenzo[*b*,*d*]furan-4-yl)-9*H*-pyrido[2,3-*b*]indole (**BCzDBFCb**) are synthesized according to previous literature [16,17].

2.2.1. *9-(2-(9H-carbazol-9-yl)dibenzo[b,d]furan-4-yl)-9H-pyrido[2,3-b]indole (**CzDBFCb**)*

Compound **3** (0.72 g, 1.57 mmol), α-carboline (0.37 g, 2.19 mmol), K_3PO_4 (0.83 g, 3.91 mmol) and CuI (0.21 g, 1.09 mmol) were dissolved in 1,4-dioxane. After nitrogen bubbling, 1,2-TCH (0.13 ml, 1.09 mmol) was added to the solution. The mixture was refluxed overnight under nitrogen atmosphere and then cooled down to room temperature. The mixture was filtered and the solution was extracted with methylene chloride and distilled water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated using a rotary evaporator. The product was purified by column chromatography using methylene chloride/*n*-hexane as an eluent. A white powder was obtained by vacuum train sublimation (0.28 g, yield: 36%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, 1H, $J = 6.4$ Hz), 8.46 (d, 1H, $J = 9.2$ Hz), 8.31 (d, 1H, $J = 2.0$ Hz), 8.21–8.18 (m, 3H), 8.04 (d, 1H, $J = 8.0$ Hz), 8.00 (d, 1H, $J = 2.0$ Hz), 7.70 (s, 2H), 7.55–7.29 (m, 11H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.08, 152.17, 150.42, 146.77, 141.35, 139.99, 133.39, 128.62, 128.49, 127.89, 127.30, 126.26, 126.14, 126.63, 124.00, 123.63, 123.59, 121.89, 121.44, 121.33, 121.23, 120.52, 120.29, 119.05, 116.98, 116.79, 112.48, 111.08, 110.05. MS (FAB) *m*/*z* 500 $[(M + H)^+]$. Elemental Analysis (calculated for $C_{35}H_{21}N_3O$): C, 84.15; H, 4.24; N, 8.41; O, 3.20. Found: C, 84.22; H, 4.24; N, 8.46; O, 3.27.

2.2.2. *9-(2,8-Di(9H-carbazol-9-yl)dibenzo[b,d]furan-4-yl)-9H-pyrido[2,3-b]indole (**BCzDBFCb**)*

Compound **6** (1 g, 1.60 mmol), α-carboline (0.32 g, 1.92 mmol), K_3PO_4 (0.68 g, 3.20 mmol) and CuI (0.15 g, 0.80 mmol) were dissolved in 1,4-dioxane. After nitrogen bubbling, 1,2-TCH (0.10 ml, 0.80 mmol) was added to the solution. The mixture was refluxed overnight under nitrogen atmosphere and then cooled down to room temperature. The mixture was filtered, diluted with methylene chloride, and washed with distilled water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated using a rotary evaporator. The product was purified by column chromatography using methylene chloride/*n*-hexane as an eluent. A white powder was obtained by vacuum train sublimation (0.31 g, yield: 29%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, 1H, $J = 6.4$ Hz), 8.48 (d, 1H, $J = 9.2$ Hz), 8.30 (d, 1H, $J = 2.4$ Hz), 8.23–8.15 (m, 7H), 8.07 (d, 1H, $J = 2.0$ Hz), 7.70 (m, 4H), 7.56 (t, 1H, $J = 7.8$ Hz), 7.50–7.29 (m, 12H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.84, 152.10, 151.11, 146.78, 141.55, 141.20, 139.87, 133.82, 133.56, 128.69, 127.93, 127.37, 126.79, 126.30, 126.20, 125.52, 123.62, 123.45, 121.46, 121.32, 120.52, 120.39, 120.30, 120.17, 119.19, 116.99, 116.91, 113.75, 110.94, 109.90, 109.64. MS (FAB) *m*/*z* 665 $[(M + H)^+]$. Elemental Analysis (calculated for $C_{47}H_{28}N_4O$): C, 84.92; H, 4.25; N, 8.43; O, 2.41. Found: C, 84.93; H, 4.24; N, 8.43; O, 2.42.

2.3. *Device fabrication and measurements*

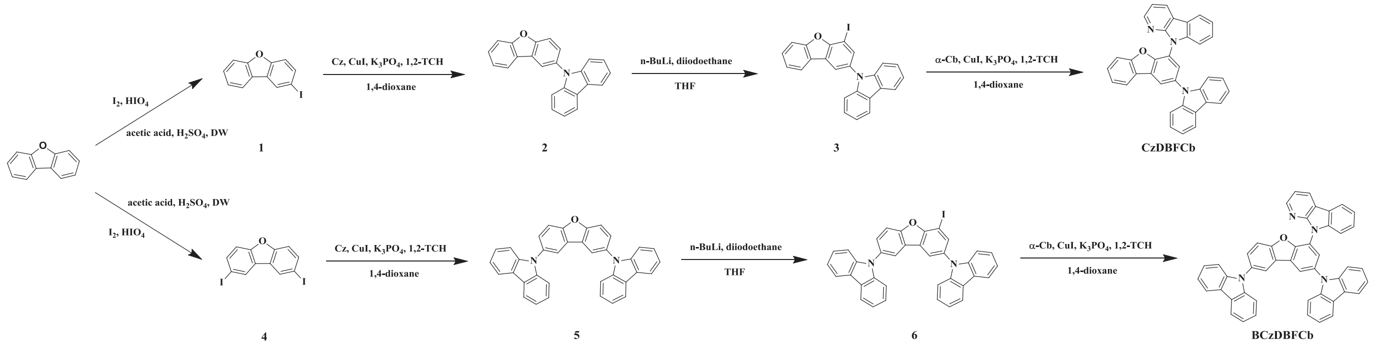
The device structure of blue PHOLEDs was indium tin oxide (ITO, 50 nm)/polyethylene-3,4-dioxythiophene:poly-styrenesulfonate (PEDOT:PSS) (60 nm)/1, 1′-bis(di-4-tolylaminophenyl)cyclohexane (TAPC) (20 nm)/N,N-dicarbazolyl-3,5-benzene (mCP) (10 nm)/**CzDBFCb** or **BCzDBFCb**: iridium (III) bis[2-(4,6-difluorophenyl)-pyridinato-N,C2]picolinate (FIrpic) (25 nm, 5%)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSP01) (35 nm)/LiF (1 nm)/Al (100 nm). Single carrier device fabrication and device characterization were performed according to the method reported in the literature [18].

3. Results and discussion

A dibenzofuran core has been known to be activated at 2- position by halogenation and 4- position by lithiation [19–22]. The 2-position or 4- position activation followed by substitution with hole or electron transport moieties produced hole or electron or bipolar type compounds. Hole transport type substituent was mostly carbazole and electron transport type substituent was typically diphenylphosphine oxide. However, the diphenylphosphine oxide derived host materials have an issue of poor stability because of low dissociation energy of C-P bond [23,24]. Therefore, a molecular design route to stabilize the molecular structure, to obtain bipolar charge carrying property, and to secure high temperature stability is needed. The molecular stability and bipolar charge transport character requirements can be met by using a pyridoindole moiety and the high temperature stability can be satisfied by substituting the pyridoindole moiety at 4- position of dibenzofuran as reported in other articles [10,22,25,26]. Based on this concept, two compounds, **CzDBFCb** and **BCzDBFCb**, were designed, simulated, synthesized, characterized, and evaluated as the host materials of blue PHOLEDs.

Reaction scheme of **CzDBFCb** and **BCzDBFCb** is shown in Scheme 1. Carbazole substituted dibenzofuran intermediates were prepared and they were lithiated, iodinated, and coupled with a pyridoindole moiety via 9-position of pyridoindole. Wet and dry purification by column chromatography and sublimation provided highly pure **CzDBFCb** and **BCzDBFCb**.

In the case of the host materials, photophysical properties such as photoluminescence (PL) emission spectrum and triplet energy need to be characterized as they are directly related with light emission of dopant materials. Fluorescence and phosphorescence



Scheme 1. Synthetic scheme of **CzDBFCb** and **BCzDBFCb**.