



Indenocarbazole based bipolar host materials for highly efficient yellow phosphorescent organic light emitting diodes



Gyeong Heon Kim^a, Raju Lampande^a, Byoung Yeop Kang^a, Hyeong Woo Bae^a,
Ju Young Lee^a, Jang Hyuk Kwon^{a,*}, Jung Hwan Park^{b,**}

^a Department of Information Display, Kyung Hee University, 26, Kyungheedaero, Dongdaemun-gu, Seoul, 130-701, Republic of Korea

^b Duksan Neolux Co., Ltd., 21-32, Ssukgol-gil, Ipjang-myeon, Seobuk-gu, Cheonan-si, Chungcheongnam-do, 331-821, Republic of Korea

ARTICLE INFO

Article history:

Received 3 November 2015

Received in revised form

29 December 2015

Accepted 2 January 2016

Available online 16 January 2016

Keywords:

Bipolar host

Indenocarbazole

Phosphorescence

Organic light-emitting diodes

Triplet energy

ABSTRACT

We report bipolar host materials with robust indenocarbazole and biphenyl moiety as hole-electron-transporting unit for phosphorescent yellow organic light-emitting diodes (OLEDs). New host materials demonstrated an excellent morphological stability with high glass transition temperature of 207 °C. Simultaneously, it also revealed appropriate triplet energy of about 2.6 eV for ideal triplet energy transfer to yellow phosphorescent dopant. A phosphorescent yellow OLED with new host ICBP1 (and ICBP2) and conventional yellow dopant iridium(III)bis(4-(4-t-butylphenyl)thieno[3,2-c]pyridinato-N,C2')acetylacetonate (Ir(tptpy)₂acac) shows a low driving voltage of 3.4 (and 3.6 V) at 1000 cd/m², and maximum external quantum efficiency as high as 26.4%. Such efficient performance of phosphorescent yellow OLEDs is attributed to a good charge balance and high electron transport properties of host materials.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of organic electroluminescent devices, several research papers have been investigated for the high performance of phosphorescent organic light emitting diodes (OLEDs). Phosphorescent materials can harvest both singlet and triplet excitons, which helps to achieve theoretical 100% internal quantum efficiency of OLED devices. The favorable attributes of OLEDs are low manufacturing cost, easy fabrication process, flexibility, high brightness, fast response time, wide viewing angle and good lifetime yield etc. for the solid state lighting [1,2]. Although, several studies have been reported towards highly effectual host, proficient interfacial layers and optimized architectures but still the intrinsic limits of OLED upto their theoretical limit have not been reached yet [3]. Therefore, further scientific efforts are needed in the direction of new material design for host with suitable triplet energy, charge transport and injection layers to reach the theoretical limit of OLED performance.

Phosphorescent yellow and blue host materials are crucial

component in modern two stacks tandem white organic light emitting diodes for solid state lighting applications [4]. Additionally, phosphorescent yellow materials are getting important components to have high color rendering index in modern proper multiple peak white OLED for lighting applications [5]. To get a high performance of white OLEDs, efficient phosphorescent yellow host is equally important due to their great potential. Therefore, to determine high quantum efficiency and current/power efficiency of yellow devices, development of new host materials containing new hole and electron moieties with suitable bipolar characteristics, large triplet energy and high charge carrier mobility as well as efficient hole and electron transport layers are needed. Another performance decisive factor is the charge balance, which plays a vital role in determining the external quantum efficiency and current/power efficiencies of OLEDs [6]. Proper charge balance not only widens the recombination zone in the emissive layer (EML) but also leads to a high performance with minimization of triplet–triplet annihilation [7]. To achieve a proper charge balance in the EML, bipolar characteristics of host materials are very crucial for efficient hole and electron movement. The strong bipolar characteristics can be attained by using appropriate hole and electron transport moiety in the host materials. Furthermore, proper charge balance in the emissive layer can also be achieved by tuning the energy levels of host and dopant system [8]. This helps to reduce

* Corresponding author.

** Corresponding author.

E-mail addresses: jhkwn@khu.ac.kr (J.H. Kwon), jhpark@dshn.co.kr (J.H. Park).

the charge trapping emission by dopant molecules and provides a complete energy transfer from host to dopant molecule.

Over the past few years, very limited studies have been reported on developing new phosphorescent host materials for yellow OLED devices. The 4,4'-bis-9-carbazolyl-2,2'-biphenyl (CBP) has been one of the widely used phosphorescent yellow host material, which consist of robust carbazole moiety and biphenyl group [9]. The CBP has good triplet energy but shows a relatively low glass transition temperature (T_g , 62 °C) value, which could results in poor thermal stability of the device. Additionally, it also has a high LUMO energy value, which may directly effects on the electron injection properties from transport layer and form improper charge balance at the emissive layer, results in average device performance [10]. Therefore, to improve the performance of OLEDs, narrow bandgap host materials with their good charge injection properties from the charge transport are required. Recently, Hwang et al. reported a phenylcarbazole and pyrimidine based phosphorescent host material with a bandgap of 3.13 eV. They showed a maximum current efficiency of 68.3 cd/A and EQE of 22.3% for yellow OLED device [11]. Similarly, Yang et al. also designed and synthesized a phenanthroimidazole/carbazole based hybrid bipolar host materials for phosphorescent yellow devices and which has a bandgap of 3.11 eV and high T_g value in the range of 113–243 °C. They demonstrated a maximum EQE and current efficiency of 19.3% and 57.2 cd/A for the 2-(4-(9H-carbazol-9-yl)phenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole and (fbi)₂Ir(acac) host dopant combination [6]. In our previous report, we demonstrated a maximum current efficiency of 84.4 cd/A for the Bepp₂: iridium(III)bis(4-(4-t-butylphenyl)thieno[3,2-c]pyridinato-N,C2')acetylacetonate (Ir(tptpy)₂acac) host dopant system [12]. Recently, we reported series of new green host materials with indenocarbazole as hole transporting moiety, and exhibited an excellent OLED device performances [7]. Encouraging from these results, we developed host materials using indenocarbazole moiety to further enhance the yellow OLED performances in terms of efficiency and lifetime.

In this work, we modified the carbazole based CBP compound by adding efficient indolocarbazole moiety with dimethyl group at inner and outer position of the compound to decrease the band gap and to improve the charge balance property as well as thermal stability of the new bipolar host materials. The new compound was successfully synthesized and used as a host for phosphorescent yellow OLEDs. The photo-physical, electro-chemical and thermal characteristics of new materials were successfully examined by using UV–vis absorption, photoluminescence (PL), cyclic voltammetry (CV), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) respectively.

2. Experimental section

2.1. Synthesis

2.1.1. 9,9-Dimethyl-2-(2-nitrophenyl)-9H-fluorene (1)

2-(9,9-dimethyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (150 g, 468.41 mmol), 1-bromo-2-nitrobenzene (89.89 g, 444.99 mmol), tetrakis(triphenylphosphine)palladium(0) (27.07 g, 23.42 mmol) and potassium carbonate (2.2 M, 640 mL, 1405.24 mmol) with tetrahydrofuran (2200 mL) and water(500 mL) solvents were refluxed for 4 h in 5 L round bottom flask. The solution was extracted with dichloromethane, and dried over anhydrous MgSO₄. After removal of solvent under reduced pressure, final residue was purified by column chromatography (eluent = dichloromethane/hexane, 1:3) to get the pale yellow solid of 9,9-dimethyl-2-(2-nitrophenyl)-9H-fluorene (yield: 147.7 g, 84%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.88–7.85 (m, 1H), 7.79–7.74 (m, 2H), 7.66–7.61 (m, 1H), 7.55–7.42 (m, 3H), 7.39–7.30

(m, 4H), 7.37–7.25 (m, 6H), 1.51 (s, 6H).

2.1.2. 12,12-Dimethyl-11,12-dihydroindeno[2,1-a]carbazole (2) and 11,11-dimethyl-5,11-dihydroindeno[1,2-b]carbazole (3)

A mixture of **1** (56 g, 459.78 mmol) and triphenylphosphine (301.49 g, 1149.44 mmol) was dried in vacuum and filled with nitrogen gas in 5 L round bottom flask. 1,2-Dichlorobenzene (2200 mL) was added to dissolve the mixture and refluxed for 12 h in nitrogen atmosphere. After solvent removal with distillation, the residue was divided by column chromatography (eluent = CH₂Cl₂/hexane, 1:7) to 12,12-dimethyl-11,12-dihydroindeno[2,1-a]carbazole and 11,11-dimethyl-5,11-dihydroindeno[1,2-b]carbazole, respectively. Two residues were recrystallized with CH₂Cl₂/hexane and obtained white solid of 12,12-dimethyl-11,12-dihydroindeno[2,1-a]carbazole and 11,11-dimethyl-5,11-dihydroindeno[1,2-b]carbazole, respectively (yield: 12,12-dimethyl-11,12-dihydroindeno[2,1-a]carbazole 42.5 g, 11,11-dimethyl-5,11-dihydroindeno[1,2-b]carbazole 37.5 g, 73%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm) (12,12-dimethyl-11,12-dihydroindeno[2,1-a]carbazole) 8.14–8.10 (m, 3H), 7.85–7.83 (m, 1H), 7.71–7.69 (d, J = 8.0 Hz, 1H), 7.55–7.50 (m, 2H), 7.48–7.29 (m, 4H), 1.73 (s, 6H) (11,11-dimethyl-5,11-dihydroindeno[1,2-b]carbazole) 8.11–8.06 (m, 2H), 7.75–7.70 (m, 1H), 7.67 (s, 1H), 7.49–7.44 (m, 1H), 7.40–7.32 (m, 5H), 7.26–7.22 (m, 1H), 1.60 (s, 6H). ¹³C NMR (CDCl₃, 500 MHz) δ (ppm) 153.3, 140.3, 140.1, 137.4, 135.3, 134.2, 127.2, 126.8, 125.7, 123.9, 123.5, 122.2, 120.3, 120.0, 119.8, 117.4, 112.3, 110.7, 46.7, 25.7.

2.1.3. 11-(4-bromophenyl)-12,12-dimethyl-11,12-dihydroindeno[2,1-a]carbazole (4)

A mixture of **2** (30 g, 105.87 mmol), 1-bromo-4-iodobenzene (89.85 g, 317.61 mmol), copper powder (7.40 g, 116.46 mmol), potassium carbonate (14.63 g, 105.87 mmol) and 18-crown-6 (2.80 g, 10.59 mmol) was refluxed for 24 h in nitrogen atmosphere in 2 L round bottom flask. After reaction, the residue was divided by column chromatography (eluent = CH₂Cl₂/hexane, 1:3). And the residue was recrystallized using CH₂Cl₂/hexane (yield: 31.5 g, 68%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 8.19–8.17 (d, J = 8.1 Hz, 1H), 8.13–8.10 (d, J = 7.2 Hz, 1H), 7.96–7.93 (d, J = 8.4 Hz, 1H), 7.80–7.73 (m, 3H), 7.43–7.40 (d, J = 8.4 Hz, 1H), 7.37–7.25 (m, 6H), 6.81–6.78 (d, J = 7.2 Hz, 1H), 1.19 (s, 6H). ¹³C NMR (CDCl₃, 500 MHz) δ (ppm) 154.4, 144.44, 144.42, 139.5, 139.3, 138.9, 133.2, 133.0, 132.9, 127.0, 126.9, 125.9, 125.2, 123.8, 122.0, 120.4, 119.7, 119.5, 119.4, 113.2, 110.7, 110.6, 48.0, 26.5.

2.1.4. 12,12-Dimethyl-11-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-11,12-dihydroindeno[2,1-a]carbazole (5)

A mixture of **4** (20.0 g, 45.62 mmol), 4,4,4',4',5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (12.74 g, 50.19 mmol), [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (1.12 g, 1.37 mmol) and Potassium acetate (13.43 g, 136.87 mmol) was dried and filled with nitrogen gas in 1 L round bottom flask. DMF (230 mL) was added to dissolve the mixture and refluxed for 3 h in nitrogen atmosphere. After reaction, the solution was extracted with ethyl acetate and dried over anhydrous MgSO₄. The dried solution was filtered. And finally the solution was purified with column chromatography (eluent = ethyl acetate/hexane, 1:3) and recrystallized with CH₂Cl₂/hexane to get white solid (yield: 13.7 g, 62%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 8.21–8.19 (d, J = 7.9 Hz, 1H), 8.14–8.11 (m, 1H), 8.08–8.05 (d, J = 8.3 Hz, 2H), 7.81–7.76 (m, 2H), 7.57–7.54 (d, J = 8.2 Hz, 1H), 7.37–7.25 (m, 5H), 6.80–6.78 (m, 1H), 1.45 (s, 12H), 1.18 (s, 6H). ¹³C NMR (CDCl₃, 500 MHz) δ (ppm) 154.6, 144.6, 144.0, 139.6, 139.3, 135.94, 135.91, 130.6, 126.8, 126.7, 125.7, 125.1, 123.7, 121.9, 120.1, 119.5, 119.3, 119.3, 112.9, 110.8, 84.2, 48.0, 26.3, 24.9.

Download English Version:

<https://daneshyari.com/en/article/1267024>

Download Persian Version:

<https://daneshyari.com/article/1267024>

[Daneshyari.com](https://daneshyari.com)