Naphthyl or pyrenyl substituted 2-phenylcarbazoles as hole transporting materials for organic light-emitting diodes

Chih-Hao Chang [a, *], Gintare Krucaite [b], Dain Lo [a], Yun-Lan Chen [a], Chu-Chun Su [a], Tzu-Chun Lin [a], Juozas Vidas Grazulevicius [b], Laura Peciulyte [b], Saulius Grigalevicius [b, **]

[a] Department of Photonics Engineering, Yuan Ze University, Chung-Li, 32003, Taiwan
[b] Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu Plentas 19, LT50254, Kaunas, Lithuania

ARTICLE INFO

ABSTRACT

A new series of 9-hexylcarbazole-based hole transporting materials (HTM) with naphthyl or pyrenyl substitutions were synthesized and characterized. The respective glass transition temperatures of the new HTM were estimated to be 58 and 61 °C, which can provide morphologically-stable films for electroluminescence (EL) applications. The pyrenyl substituted analogue possesses an adequate ionization potential and triplet energy gap of 5.54 eV and 2.48 eV, respectively, which makes it a suitable HTM for use in red phosphorescent organic light-emitting diodes (OLEDs). In contrast, the ionization potential of the naphthyl substituted analogues was estimated to be 5.72 eV, thus the p-type conducting dopant should be introduced for device fabrication. The respective peak efficiencies of the naphthyl and pyrenyl based OLEDs with the p-type dopant were recorded at 15.4% (26.0 cd/A and 24.2 lm/W) and 17.3% (26.1 cd/A and 19.1 lm/W), demonstrating their high potential for EL applications.

1. Introduction

Organic light-emitting diode (OLED) displays are emerging as the mainstream of next-generation display applications due to their superior performance and flexibility. Phosphorescent OLEDs (PhOLEDs) have attracted significant attention because of their use of both singlet and triplet excitons, making 100% internal quantum efficiency possible. In general, achieving high level internal quantum efficiency depends on several factors, including high quantum yield emitters, exothermic energy transfer from host to emitter, balanced carrier transport, and effective exciton confinement [1]. The bottleneck to further progress is blue PhOLEDs, and material R&D efforts are focused on carrier transport and host materials with wide energy gaps. In contrast, considerably less attention has been paid to materials with lower energy gaps. Actually, considerable exertion is needed in the development of red PhOLEDs to further improve performance, because the lower gap of red phosphors usually induces serious carrier trapping, leading to higher operation voltages and carrier imbalance [2]. Accordingly, it is desirable to exploit new transport materials to create red PhOLEDs with reduced power consumption and improved efficiency.

Hole transport materials (HTMs) for PhOLEDs have several requirements including high triplet energy for triplet exciton confinement, adequate energy levels of the highest occupied molecular orbital (HOMO) for effective hole injection, and high hole mobility [3]. Recalling the developing progress of HTMs, hole transport capability has been recognized in various moieties, including benzidine, amine, carbazole and fluorene [4–9]. For instance, N,N′-bis(3-methylphenyl)-N,N′-bis(phenyl)-benzidine (TPD) and N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB) are the most famous HTMs in the early stage, and belong to the benzidine family [4,5]. An amine-based HTM, 4,4′,4″-tris(N-3-methylphenyl-N-phenyl-amino)triphenylamine (m-MTDATA), is an another successful example [10]. Furthermore, 4,4′,4″-tris(carbazol-9-yl)triphenylamine (TCTA) is commonly used as the hole transport layer (HTL) or the host for emitters, and consists of carbazole and amine moieties [11]. In the molecular design aspect, the carbazole moiety has several commendable properties including easy modification, chemical stability, and large triplet energy [12]. Our group has considerable experience in synthesizing HTMs using carbazole-containing designs and their

* Corresponding author.
** Corresponding author.
E-mail address: chc@saturn.yzu.edu.tw (C.-H. Chang).

electroluminescent (EL) applications. In 2007, we developed a series of carbazole-based aromatic amines with oxetanyl groups, which demonstrated adequate ionization potential and the charge mobility [13]. Moreover, 3,6-di(9-carbazolyl)-9-(2-ethylhexyl) carbazole (TCz1) was synthesized with a nonplanar structure to construct a morphologically stable film for emitters [14]. OLEDs using TCz1 and FIrpic as the host-guest system achieved a maximum external quantum efficiency of 15%. In 2014, our group also synthesized a series of 3,6-diaryl substituted 9-alkylcarbazoles as hole transporting materials for OLEDs [15]. The Ir(ppy)$_3$-based OLEDs using 3,6-diphenyl-9-ethylcarbazole as the hole transporting layer demonstrated a peak current efficiency of 22.5 cd/A. Recently, we reported on the synthesis and characterization of a new series of electro-active carbazole-based compounds which are thermally stable with glass transition temperatures up to 93 °C [16]. In addition, red PhOLEDs with 3-[bis(9-ethylcarbazol-3-yl)methyl]-9-hexylcarbazole exhibited superior performance with a peak efficiency of 8.4% and a low turn-on voltage of 3.5 V.

In this study, a new series of 9-hexylcarbazole-based materials with naphthyl or pyrenyl substitutions were synthesized and characterized. Our previous study found that introducing a hexyl moiety in a molecule could increase the spatial hindrance of the carbazole moiety and thus could be used for the preparation of thin amorphous layers with adequate morphology on substrates [16]. However, the extended conjugation in the molecules will result in a narrower energy gap. As such, the energy gaps of the new HTMs could be tailored for red phosphorescent emitters by trying different substitutions. Following comprehensive studies of photophysics and thermal properties, we examined these novel HTMs in the fabrication of red PhOLEDs. A maximum efficiency of 17.3%, a luminance efficiency of 26.1 cd/A, and a power efficiency of 19.1 lm/W were obtained for the compound possessing pyrenyl substitution (i.e. **5**), compared with 15.4%, 26.0 cd/A, and 24.2 lm/W obtained by OLEDs with compound **4** (c.f. naphthyl substitution). Moreover, devices with both **4** and **5** were recorded to have respective turn on voltages of 3.2 V and 4.5 V. The high efficiencies and low operation voltages of these red PhOLEDs suggest great potential for these 9-hexylcarbazole-based HTMs in EL applications.

2. Experimental

2.1. Materials and synthesis

9H-Carbazole-2-boronic acid pinacol ester (**1**). 1,4-dibromobenzene, 1-bromohexane, 1-naphtalene boronic acid, pyrene-1-boronic acid, bis(triphenylphosphine)palladium (II) dichloride (Pd(PPh$_3$)$_2$Cl$_2$), potassium hydroxide were purchased from Aldrich and used as received.

2-(4-Bromophenyl)-9H-carbazole (**2**). 9H-carbazole-2-boronic acid pinacol ester (1 g, 3.4 mmol), 1,4-dibromobenzene (1.04 g, 4.4 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.095 g, 0.013 mmol) and powdered potassium hydroxide (0.95 g, 16.9 mmol) were stirred in THF (15 mL) containing degassed water (1.5 mL) at 80 °C under nitrogen for 3 h. After TLC control, the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethyl acetate. The combined extract was dried over anhydrous Na$_2$SO$_4$. The crude product was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (vol. ratio 1:4) as an eluent. Yield: 0.75 g of white amorphous material.

MS (APCI$^+$, 20 V): 322.02 ([M+H], 100%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 11.10 (s, 1H, Ar), 7.92 (d, 1H, J = 4.8 Hz, Ar), 7.87 (d, 1H, J = 4.4 Hz, Ar), 7.47–7.40 (m, 5H, Ar), 7.19 (dd, 1H, J_1 = 1.2 Hz, J_2 = 4.8 Hz, Ar), 7.16–7.13 (m, 1H, Ar), 6.99–6.90 (m, 1H, Ar), 1.82 (s, 1H, N-<u>H</u>). ^{13}C NMR spectrum (CDCl$_3$, δ, ppm): 207.11, 140.06, 131.86,

129.06, 128.78, 127.51, 126.08, 120.71, 120.44, 119.74, 118.91, 110,67, 109.1, 108.91. FTIR (KBr, cm^{-1}): 3418, 3059, 1626, 1606, 1557, 1491, 1457, 1440, 1366, 1326, 1249, 1235, 1154, 1117, 1004, 934, 860, 767, 746, 676. Elemental analysis for C$_{18}$H$_{12}$Br N % Calc.: C 67.10, H 3.75, N 4.35; % Found: C 67.09, H 3.77, N 4.32.

2-(4-Bromophenyl)-9-hexylcarbazole (**3**) was obtained by a standard alkylation reaction of 2-(4-bromophenyl)-9H-carbazole (**2**) using 1-bromohexane as the alkylation reagent and KOH as the base [17].

MS (APCI$^+$, 20 V): 406.19 ([M+H], 100%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.09 (d, 1H, J = 8.0 Hz, Ar), 8.05 (d, 1H, J = 7.6 Hz, Ar), 7.78 (s, 2H, Ar), 7.57 (d, 1H, J = 0.8 Hz, Ar), 7.47 (dd, 1H, J_1 = 1.6 Hz, J_2 = 8.0 Hz, Ar), 7.42–7.32 (m, 3H, Ar), 7.19–7.15 (m, 2H, Ar), 4.29 (t, 2H, J = 7.2 Hz, N<u>CH$_2$</u>(CH$_2$)$_4$CH$_3$), 1.88–1.79 (m, 2H, NCH$_2$<u>CH$_2$</u>(CH$_2$)$_3$CH$_3$), 1.40–1.16 (m, 6H, NCH$_2$CH$_2$(<u>CH$_2$</u>)$_3$ CH$_3$), 0.80 (t, 3H, J = 7.2 Hz, NC(H$_2$)$_5$<u>CH$_3$</u>). ^{13}C NMR spectrum (CDCl$_3$, δ, ppm): 141.0, 138.63, 131.83, 129.17, 127.96, 125.65, 122.63, 122.18, 120.62, 120.39, 118.91, 118.41, 108.70, 107.09, 43.11, 31.61, 28.99, 27.03, 22.57, 14.03. FTIR (KBr, cm^{-1}): 2921, 2855, 1599, 1454, 1355, 1326, 1231, 1155, 1125, 919, 806, 740, 721. Elemental analysis for C$_{24}$H$_{24}$Br N % Calc.: C 70.94, H 5.95, N 3.45; % Found: C 70.91, H 5.98, N 3.42.

2-(4-(1-Naphthyl)phenyl)-9-hexylcarbazole (**4**). 2-(4-Bromophenyl)-9-hexylcarbazole (0.27 g, 0.66 mmol), 1-naphtalene boronic acid (0.17 g, 0.98 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.018 g, 0.025 mmol) and powdered potassium hydroxide (0.18 g, 3.2 mmol) were stirred in tetrahydrofuran (THF) (7 mL) containing degassed water (0.8 mL) at 80 °C under nitrogen for 24 h. After thin layer chromatography (TLC) control, the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethyl acetate. The combined extract was dried over anhydrous Na$_2$SO$_4$. The crude product was purified by silica gel column chromatography using a mixture of toluene and hexane (vol. ratio 1:50) as an eluent. Yield: 0.2 g of white crystals. M.p.: 121–122 °C.

MS (APCI$^+$, 20 V): 454.25 ([M+H], 100%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.17 (d, 1H, J = 8.0 Hz, Ar), 8.11 (d, 1H, J = 7.6 Hz, Ar), 8.03 (d, 1H, J = 7.2 Hz, Ar), 7.94–7.82 (m, 4H, Ar), 7.67 (d, 1H, J = 0.8 Hz, Ar) 7.65–7.60 (m, 2H, Ar), 7.58–7.39 (m, 7H, Ar), 7.29–7.19 (m, 1H, Ar), 4.34 (t, 2H, J = 7.2 Hz, N<u>CH$_2$</u>(CH$_2$)$_4$CH$_3$), 1.94–1.85 (m, 2H, NCH$_2$<u>CH$_2$</u>(CH$_2$)$_3$CH$_3$), 1.47–1.38 (m, 2H, N(CH$_2$)$_2$ <u>CH$_2$</u>(CH$_2$)$_2$ CH$_3$), 1.37–1.22 (m, 4H, N(CH$_2$)$_2$CH$_2$(<u>CH$_2$</u>)$_2$CH$_3$), 0.86 (tr, 3H, J = 7.2 Hz, N(CH$_2$)$_5$<u>CH$_3$</u>). ^{13}C NMR spectrum (CDCl$_3$, δ, ppm): 141.0, 138.63, 131.83, 129.17, 127.96, 125.65, 122.63, 122.18, 120.62, 120.39, 118.91, 118.41, 108.70, 107.09, 43.11, 31.61, 28.99, 27.03, 22.57, 14.03. FTIR (KBr, cm^{-1}): 3045, 2942, 2862, 1626, 1597, 1505, 1491, 1476, 1441, 1096. Elemental analysis for C$_{34}$H$_{31}$N % Calc.: C 90.02, H 6.89, N 3.09; % Found: C 90.01, H 6.91, N 3.06.

2-(4-(Pyren-1-yl)phenyl)-9-hexylcarbazole (**5**). 2-(4-Bromophenyl)-9-hexylcarbazole (0.4 g, 0.98 mmol), pyrene-1-boronic acid (0.36 g, 1.46 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.027 g, 0.038 mmol) and powdered potassium hydroxide (0.27 g, 4.8 mmol) were stirred in THF (10 mL) containing degassed water (1 mL) at 80 °C under nitrogen for 24 h. After TLC control, the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethyl acetate. The combined extract was dried over anhydrous Na$_2$SO$_4$. The crude product was purified by silica gel column chromatography using a mixture of toluene and hexane (vol. ratio 1:50) as an eluent. Yield: 0.36 g of yellow crystals. M.p.: 129–130 °C.

MS (APCI$^+$, 20 V): 528.26 ([M+H], 100%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.36 (d, 1H, J = 9.2 Hz, Ar), 8.29 (d, 1H, J = 8.0 Hz, Ar), 8.27–8.03 (m, 9H, Ar), 7.98 (d, 2H, J = 8.4 Hz, Ar), 7.81 (d, 2H, J = 8.4 Hz, Ar), 7.76 (d, 1H, J = 0.8 Hz, Ar), 7.65 (dd, 1H, J_1 = 0.8 Hz, J_2 = 8.0 Hz, Ar), 7.56–7.48 (m, 2H, Ar), 7.33–7.27 (m, 1H, Ar), 4.41 (t, 2H, J = 7.2 Hz, N<u>CH$_2$</u>(CH$_2$)$_4$CH$_3$), 2.03–1.91 (m, 2H,