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# Efficient red phosphorescent OLEDs employing carbazole-based materials as the emitting host

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ABSTRACT

We report on the synthesis and characterization of a new series of electro-active carbazole-based compounds. The derivatives are thermally stable amorphous materials with glass transition temperatures in the range of 54–93 °C. Electron photoemission spectra of thin layers of the materials show ionization potential in the range of 5.4–5.5 eV. The carbazole-based derivatives are fully characterized and their spectroscopic properties are determined by absorption and photoluminescence. All developed materials and commonly-used tris(4-carbazoyl-9-ylphenyl)amine (TCTA) were used as hosts in red phosphorescent organic light-emitting diodes (OLEDs) for comparison. Results indicate that a device with 3-[bis(9-ethylcarbazol-3-yl)methyl]-9-hexylcarbazole exhibited superior performance with peak efficiencies of 8.4%, 5.3 cd/A and 5.5 lm/W.

## 1. Introduction

Applications for organic light-emitting devices (OLED) displays are expanding rapidly due to their superior performance and flexibility as compared with liquid crystal display. Furthermore, phosphorescent OLEDs (PhOLEDs) have attracted research attention because of their intrinsically higher efficiencies as compared to fluorescent OLEDs [1]. To achieve theoretical efficiency levels, the triplet energy should be confined on the phosphorescent dopant without endothermic energy transfer to the host material. Thus, multiple-layer configurations have been widely developed to enhance device efficiency of PhOLEDs, especially in blue and green devices. In contrast, red phosphorescent materials with lower triplet energy gaps allow for simplified device architectures [2]. However, the lower gap of red phosphors usually induces serious carrier trapping, resulting in higher operation voltages. Accordingly, realizing red PhOLEDs with low power consumption and high performance requires the development of new host materials.

To guarantee exothermic energy transfer, the triplet energy of host materials must be higher than that of the dopant [3]. In addition, a host material with a bulky structure is desirable to favor a spatially-dispersed triplet exciton, which could reduce the incidence of triplet–triplet annihilation (TTA) [4]. The carbazole moiety possesses several commendable properties, including chemical stability, easy modification, large triplet energy etc. [5] Consequently, many successful host or hole transport materials adopted carbazole-containing designs. For instance, in 2007 our group synthesized and characterized carbazole-based aromatic amines with oxetanyl functional groups. The adequate ionization potentials (4.9–5.0 eV) and the charge mobility demonstrated the suitability of these carbazole-based compounds for use in organic electronics [6]. At the same time, we also synthesized a carbazole-based material, 3,6-di(9-carbazolyl)-9-(2-ethylhexyl) carbazole (TCz1), which possesses structurally rigid moieties and a nonplanar molecular configuration, resulting in a morphologically-stable molecule with a wide triplet energy gap [7]. Sky blue PhOLEDs with a TCz1 host were demonstrated with efficiencies of up to 15%, 31 cd/A, and 28 lm/W. In 2011, Chang et al. developed a bipolar carbazole-based material 9-(4,6-diphenyl-1,3,5-triazin-2-yl)-9′-phenyl-3,3'-bicarbazole (CzT) comprising a dicarbazole donor linked to an electron deficient 1,3,5-triazine acceptor [8]. Sufficient triplet energy ($E_T = 2.67$ eV) together

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with promising physical properties and morphological stability ($T_g = 134$ °C) make CzT a potential host material for yellowish-green and red phosphorescent dopants. The yellowish-green OLEDs demonstrated high performance, with maximum efficiencies of 20.0%, 75.7 cd/A and 71.3 lm/W achieved in trilayer device architectures. In 2012, Curiel et al. reported the successful use of a series of carbazolo[4,3-c]carbazoles as hole transporting and emitting host materials in red PhOLEDs [9]. Different N-substituents attached to the carbazolo[4,3-c]carbazole skeleton were used to condition the charge transporting properties. The disparate transport capabilities of these materials provide advantages including flexibility for adjusting the carrier balance in the device architecture design. Recently, our group also synthesized a series of phenyl, naphthyl or biphenyl disubstituted 9-alkylcarbazoles for hole transporting materials [10]. These derivatives show high thermal stability and form amorphous layers with glass transition temperatures of 50–62 °C. A green PhOLEDs using 3,6-diphenyl-9-ethylcarbazole as hole transporting layer demonstrated a maximum current efficiency of 22.5%. In this paper, we describe a series of carbazole-based derivatives for use as emitting hosts. The red PhOLEDs with 3-[bis(9-ethylcarbazol-3-yl)methyl]-9-hexylcarbazole (**3**) as host material exhibited superior performance with peak efficiencies of 8.4% and a low turn-on voltage of 3.5 V.

## 2. Experimental

### 2.1. Materials and synthesis

9H-carbazole, 9-ethylcarbazole, 1-bromohexane, 4-fluorobenzaldehyde, phosphorus oxychloride ($POCl_3$) and triphenylamine were purchased from Aldrich and used as received. 9-Hexylcarbazole [11], 4-(9-carbazolyl)benzaldehyde (**1a**), 4-(diphenylamino)benzaldehyde (**2a**) [12] and 9-hexyl-3-formylcarbazole (**3a**) were synthesized according to the procedures outlined in the literature [13].

9-{4-[bis(9-hexylcarbazol-3-yl)methyl]phenyl}carbazole (**1**). 9-hexylcarbazole (1.2 g, 4.6 mmol) hydrochloric acid (10 ml, 35%) was slowly added to an acetic acid (16 ml) solution of 4-(9-carbazolyl)benzaldehyde (0.5 g, 1.85 mmol) under stirring and the mixture was refluxed for 3 h. The resulting solution was poured into $H_2O$ and filtered. The deposit was dissolved in methylene chloride and washed with $H_2O$ three times. The separated organic layer was dried over anhydrous $Na_2SO_4$. The crude product was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (vol. ratio 1:25) as an eluent, yielding 0.23 g. (30%) of a white amorphous solid.

$^1$H NMR spectrum (400 MHz, $CDCl_3$, δ, ppm): 8.13 (d, 2H, J = 8.0 Hz, Ar); 8.02 (d, 2H, J = 7.6 Hz, Ar); 7.96 (s, 2H, Ar); 7.51 -7.36 (m, 16H, Ar); 7.27 (t, 2H, J = 7.4 Hz, Ar); 7.17 (t, 2H, J = 7.4 Hz, Ar); 6.09 (s, 1H, CH); 4.29 (t, 4H, J = 7.4 Hz, $NCH_2$); 1.91–1.84 (m, 4H, $NCH_2CH_2$); 1.44–1.37 (m, 4H, $NCH_2CH_2CH_2$); 1.36–1.24 (m, 8H, $CH_2CH_2CH_3$); 0.86 (t, 6H, J = 7.0 Hz, $CH_3$).

$^{13}$C NMR spectrum (400 MHz, $CDCl_3$, δ, ppm): 14.1 ($CH_3$(2C)), 22.5 ($\underline{CH}_2CH_3$(2C)), 27.1 ($\underline{CH}_2CH_2CH_3$(2C)), 29.1 ($\underline{CH}_2CH_2CH_2CH_3$(2C)), 31.6 ($\underline{CH}_2CH_2N$(2C)), 43.3 ($\underline{CH}_2N$(2C)), 56.7 (CH); 108.7 (2C); 108.8 (2C); 110.0 (2C), 118,7 (2C), 119.9 (2C), 120.3 (2C), 120.5 (2C), 121.2 (2C), 122.7 (2C), 122.8 (2C), 123.4 (2C), 125.7 (2C), 125.9 (2C), 126.8 (2C), 127.6 (2C), 131.0 (2C), 134.0 (2C), 135.6 (C), 139.7 (2C), 140.2 (2C), 141.0 (2C), 145.0 (C).

MS (APCI+, 20 V, *m/z*): 757.43 ($[M + H]^+$, 100%).

Elemental analysis for $C_{55}H_{53}N_3$ % Calc.: C 87.38, H 7.07, N 5.56; % Found: C 87.36, H 7.11, N 5.54.

IR (KBr, $cm^{-1}$): 3048 (C–H, Ar); 2953, 2926, 2853 (C–H); 1626, 1598 (C=C Ar); 1483, 1479, 1467 (C=C, Ar and C–H); 1348, 1332, 1316 (C–N, Ar); 1230 (C–N); 798, 770, 747, 724, 627 (C–H Ar).

N-{[bis(9-hexylcarbazol-3-yl)methyl]phenyl}-N,N-diphenylamine (**2**). 9-hexylcarbazole (1.2 g, 4.6 mmol) hydrochloric acid (10 ml, 35%) was slowly added to an acetic acid (16 ml) solution of 4-(diphenylamino)benzaldehyde (0.5 g, 1.83 mmol) under stirring and the mixture was refluxed for 48 h. The resulting solution was poured into $H_2O$ and filtered. The deposit was dissolved in methylene chloride and washed with $H_2O$ three times. The separated organic layer was dried over anhydrous $Na_2SO_4$. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:25) as an eluent, yielding 0.4 g (30%) of a white amorphous solid.

$^1$H NMR spectrum (400 MHz, $CDCl_3$, δ, ppm): 8.00 (d, 2H, J = 7.6 Hz, Ar); 7.90 (s, 2H, Ar); 7.42–7.33 (m, 8H, Ar); 7.24–7.25 (m, 5H, Ar); 7.20 (t, 2H, J = 6.8 Hz, Ar); 7.18–7.09 (m, 6H, Ar); 7.02 (d, 2H, J = 8.4 Hz, Ar); 6.97 (t, 2H, J = 7.6 Hz, Ar); 5.91 (s, 1H, CH); 4.26 (t, 4H, J = 7.2 Hz, $NCH_2$); 1.89–1.82 (m, 4H, $NCH_2CH_2$); 1.41–1.36 (m, 4H, $NCH_2CH_2CH_2$); 1.34–1.25 (m, 8H, $CH_2CH_2CH_3$); 0.86 (t, 6H, J = 7.0 Hz, $CH_3$).

$^{13}$C NMR spectrum (400 MHz, $CDCl_3$, δ, ppm): 14.0 ($CH_3$(2C)), 22.5 ($\underline{CH}_2CH_3$(2C)), 27.0 ($\underline{CH}_2CH_2CH_3$(2C)), 29.0 ($\underline{CH}_2CH_2CH_2CH_3$(2C)), 31.5 ($\underline{CH}_2CH_2N$(2C)), 43.2 ($\underline{CH}_2N$(2C)), 56.5 (CH); 108.4 (2C); 108.6 (2C); 118.5 (2C), 120.4 (2C), 121.0 (2C), 122.5 (2C), 122.7 (2C), 122.8 (2C), 123.85 (C), 123.95 (2C), 124.05 (3C), 124.15 (C), 125.5 (2C), 127.5 (2C), 129.0 (3C), 130.0 (2C), 135.5 (2C), 139.2 (2C), 140.0 (C), 140.7 (2C), 140.7 (C), 148.0 (2C).

MS (APCI+, 20 V, *m/z*): 759.43 ($[M + H]^+$, 100%).

Elemental analysis for $C_{55}H_{55}N_3$ % Calc.: C 87.14, H 7.31, N 5.54; % Found: C 87.16, H 7.36, N 5.51.

IR (KBr, $cm^{-1}$): 3049 (C–H, Ar); 2953, 2926, 2853 (C–H); 1626, 1627, 1590 (C=C Ar); 1505, 1490, 1467 (C=C, Ar and C–H); 1328, 1276 (C–N, Ar); 1242 (C–N); 770, 746, 695 (C–H Ar).

3-[bis(9-ethylcarbazol-3-yl)methyl]-9-hexylcarbazole (**3**). 9-ethylcarbazole (5.6 g, 28.6 mmol) hydrochloric acid (60 ml, 35%) was slowly added to an acetic acid solution (90 ml) of 9-hexyl-3-formylcarbazole (3.2 g, 11.5 mmol) under stirring and the mixture was refluxed for 2 h. The resulting mixture was poured into $H_2O$ and filtered. The deposit was dissolved in methylene chloride and washed with $H_2O$ three times. The separated organic layer was dried over anhydrous $Na_2SO_4$. The crude product was purified by silica gel column chromatography using the mixture of chloroform and hexane (vol. ratio 1:6) as an eluent. yielding 1.8 g (25%) of white crystals. M.p.: 135 °C (DSC).

$^1$H NMR spectrum (400 MHz, $CDCl_3$, δ, ppm): 7.97–7.92 (m, 6H, Ar); 7.43 -7.30 (m, 12H, Ar); 7.12 (t, 3H, J = 7.2 Hz, Ar); 6.20 (s, 1H, CH); 4.33 (q, 4H, J = 7.0 Hz, $NCH_2CH_3$); 4.26 (t, 2H, J = 7.2 Hz, $NCH_2$); 1.90–1.80 (m, 2H, $NCH_2CH_2$); 1.42 (t, 6H, J = 7.2 Hz, $NCH_2CH_3$); 1.39–1.35 (m, 2H, $NCH_2CH_2CH_2$); 1.32–1.23 (m, 4H, $CH_2CH_2CH_3$); 0.85 (t, 3H, J = 7.2 Hz, $CH_3$).

$^{13}$C NMR spectrum (400 MHz, $CDCl_3$, δ, ppm): 13.95 ($\underline{CH}_3CH_2N$(2C)), 14.1 ($CH_3$), 22.5 ($\underline{CH}_2CH_3$), 27.0 ($\underline{CH}_2CH_2CH_3$), 29.0 ($\underline{CH}_2CH_2\ CH_2CH_3$), 31.5 ($\underline{CH}_2CH_2N$), 37.5 ($CH_3\underline{CH}_2N$(2C)), 43.3 ($\underline{CH}_2N$), 56.8 (CH); 108.2 (2C); 108.35 (2C); 108.4 (C), 108.45 (C), 118,5 (C), 118.6 (2C), 120.5 (C), 120.6 (2C), 121.2 (C), 121.3 (2C), 122.7 (C), 122.8 (2C), 122.9 (C), 123.0 (2C), 125.3 (C), 125.4 (2C), 127.7 (C), 127.8 (2C), 136.2 (C), 136.3 (2C), 138.6 (2C), 139.1 (C), 140.2 (2C), 140.7 (C).

MS (APCI+, 20 V, *m/z*): 652.37 ($[M + H]^+$, 100%).

Elemental analysis for $C_{47}H_{45}N_3$ % Calc.: C 86.60, H 6.96, N 6.45; % Found: C 86.57, H 6.99, N 6.41.