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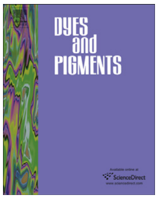

Review

High thermal-stability benzocarbazole derivatives as bipolar host materials for phosphorescent organic light-emitting diodes

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ABSTRACT

Two novel host materials based on 5- and 9-substituted benzocarbazole have been developed for application in phosphorescent organic light-emitting diodes. Both host materials exhibit excellent thermal stability with high decomposition temperatures of ca.515 °C, while the 9-substituted benzocarbazole derivative exhibits a high glass transition temperature of 181 °C. Additionally, the electroluminescence characteristics of green phosphorescent organic light-emitting diodes made with two new host materials were also evaluated. The devices exhibited an electroluminescent emission peak at 528 nm with CIE coordinates of (0.31, 0.64) and possessed low turn-on voltages of <2.84 V.

1. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have attracted worldwide attention for application in flat panel displays and area lighting. The heavy-metal complexes employed allows harvesting of both singlet and triplet excitons for realizing 100% internal quantum efficiency in the PHOLEDs [1]. To prevent efficiency roll-off induced by concentration quenching and triple–triple annihilation, the heavy-metal phosphors are usually doped in a host matrix [2,3]. Thus, the choice of host materials is crucial to realize high efficiency PHOLEDs. In general, the following host material properties are a prerequisite for achieving efficient PHOLEDs: i) the triplet energy level (E_T) should be higher than the dopant to prevent the energy transfer from guest to host [4]; ii) the hole–electron mobility is balanced to confine the excitons within the emitting layer [5,6]; iii) a high glass transition temperature (T_g) to enhance thermal and morphological stability during device operation that could extend the operational lifetime of the device [7,8].

In recent years, tremendous efforts have been devoted to developing the host materials with desired characteristics [9–11]. Among them, the carbazole-based materials are widely used as a host in the PHOLEDs to improve the device efficiency [12–14]. For example, the carbazole-based material 4,4′-bis(*N*-carbazolyl)-1,10-biphenyl (CBP) with a high triplet energy level and excellent hole transporting property is commonly used as the host material for green and red PHOLEDs [15–18]. However, the glass transition temperature of CBP is low (62 °C), which would shorten the device lifetime due to the crystallization at a low dopant concentration [19].

To increase the glass transition temperature, two novel host materials 9-(dibenzo[*b,d*]thiophen-4-yl)-7-(4-(1-phenyl-1*H*-benzo[*d*]imidazole-2-yl)phenyl)-7*H*-benzo[*c*]carbazole (**DYNS**) and 5-(dibenzo[*b,d*]thiophen-4-yl)-7-(4-(1-phenyl-1*H*- benzo[*d*]imidazole-2-yl)phenyl)-7*H*-benzo[*c*]carbazole (**DYSN**) which contain a benzocarbazole core were designed and synthesized. In addition, the introduction of dibenzothiophene on the 5- or 9- position of

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benzocarbazole core was expected to enhance the molecular distortion and reduce the intramolecular charge transfer for increasing their triplet energy levels and thermal stability. Furthermore, we also imported a commonly used electron-deficient moiety benzimidazole to modify the bipolar charge transport property of the new compounds.

2. Experimental

2.1. Materials and measurement

Chemicals and solvents used in the process were reagent grades and purchased from J & K Chemical Co. and Aladdin Chemical Co. without further purification. Tetrahydrofuran (THF) was disposed by primary procedures. All reactions and manipulations were carried out under N_2 atmosphere. Silica gel (300–400 mesh) column chromatography was used as the stationary phase in the column. 2-(4-bromophenyl)-1-phenyl-1*H*-benzo [*d*] imidazole was synthesized following the method reported in the literature [20,21].

The ^1H and ^{13}C NMR spectra were measured using a Bruker AM 400 spectrometer. Mass spectra were obtained on a Waters LCT Premier XE spectrometer. The IR spectra were recorded in the range 4000–600 cm^{-1} using the potassium bromide disk for solid samples by the FTIR instrument. The ultraviolet–visible (UV–Vis) absorption spectra of the samples were characterized using a Varian Cary 500 spectrophotometer. Photoluminescence (PL) measurements were conducted by a Varian-Cary fluorescence spectrophotometer at room temperature. The cyclic voltammetry experiments were performed by a Versastat II electrochemical workstation (Princeton applied research) using a conventional three-electrode configuration with a glassy carbon working electrode, a Pt wire counter electrode, and a regular calomel reference electrode in saturated KCl solution, 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane solution as the supporting electrolyte with a scan rate of 100 mV/s. The $E_{1/2}$ values were determined by $(E_{\mathrm{pa}} + E_{\mathrm{pc}})/2$ using Ferrocene as an external standard, where E_{pa} and E_{pc} were the anodic and catholic peak potentials, respectively. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere using a NETZSCH STA 409 PC/PG instrument with a heating scan rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out using a TGA instrument under a nitrogen atmosphere with a heating scan rate of 10 °C/min.

2.2. Synthesis

2.2.1. Synthesis of 1-(4-bromo-2-nitrophenyl) naphthalene (1–1)

A mixture of naphthalen-1-ylboronic acid (3.44 g, 20 mmol), 1,4-dibromo-2-nitrobenzene (6.13 g, 22 mmol) in tetrahydrofuran (100 mL) and 2 M K_2CO_3 (100 mL) was added into a round bottom flask and bubbled with argon whilst stirring for 15 min. $Pd(PPh_3)_4$ (0.46 g, 0.4 mmol) was added to the mixture, and the resulting mixture was refluxed for 5 h under argon atmosphere. The reaction mixture was cooled down to room temperature, poured into H_2O and then extracted with dichloromethane three times. The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the crude product was purified by SiO_2 column chromatography, affording a white solid (3.33 g, 51%). IR (KBr, disk) ν 3058.26, 1529.69, 1348.88, 800.66, 776.71 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.23 (d, J = 1.7 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.84 (dd, J = 8.2, 1.9 Hz, 1H), 7.51 (td, J = 7.9, 3.4 Hz, 2H), 7.42 (d, J = 3.7 Hz, 2H), 7.38 (d, J = 8.2 Hz, 1H), 7.32 (d, J = 7.0 Hz, 1H). HRMS (ESI, m/z): $[M+K]^+$ calcd for: $C_{16}H_{10}BrNO_2$, 365.9526, found, 365.9521.

2.2.2. Synthesis of 9-bromo-7H-benzo[c]carbazole (1–2)

A mixture of 1-(4-bromo-2-nitrophenyl) naphthalene **1–1** (3.27 g, 10 mmol) and triphenylphosphine (5.25 g, 20 mmol) in 1,2-dichlorobenzene 20 mL was added into a round bottom flask, then heated to reflux for 5 h. After cooling to room temperature, the mixture was filtered under vacuum and washed with dichloromethane three times. The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the crude product was purified by SiO_2 column chromatography, affording the yellow solid (1.53 g, 52%). IR (KBr, disk) ν 3404.88, 3061.90, 1584.84, 1529.22, 1467.48, 1433.99 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.69 (d, *J* = 8.4 Hz, 1H), 8.47 (s, 1H), 8.41 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.76–7.68 (m, 2H), 7.63 (d, J = 8.8 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H). HRMS (ESI, m/z): $[M-H]^+$ calcd for: $C_{16}H_9NS$, 293.9918, found, 293.9920.

2.2.3. Synthsis of 9-(dibenzo[b,d]thiophen-4-yl)-7H-benzo[c]carbazole (1–3)

A mixture of 9-bromo-7*H*-benzo[*c*]carbazole **1–2** (1.16 g, 4 mmol), dibenzo [*b,d*] thiophen-4-ylboronic acid (1.00 g, 4.4 mmol) in tetrahydrofuran (20 mL) and 2 M K_2CO_3 (20 mL) was added into a round bottom flask and bubbled with argon stirring for 15 min. $Pd(PPh_3)_4$ (0.092 g, 0.08 mmol) was added to the mixture, and the reaction was refluxed for 5 h under argon atmosphere. The reaction mixture was cooled down to room temperature, poured into H_2O and then extracted with dichloromethane three times. The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the crude product was purified by SiO_2 column chromatography, affording an orange solid (1.20 g, 75%). IR (KBr, disk) ν 3402.79, 3061.27, 1440.63, 1382.53 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.86 (d, *J* = 8.4 Hz, 1H), 8.71 (d, *J* = 8.4 Hz, 1H), 8.57 (s, 1H), 8.24 (dd, *J* = 8.8, 6.4 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.92 (t, *J* = 7.2 Hz, 1H), 7.88 (dd, *J* = 6.0, 2.4 Hz, 1H), 7.84–7.75 (m, 2H), 7.71–7.62 (m, 3H), 7.58–7.48 (m, 3H). HRMS (ESI, m/z): $[M-H]^+$ calcd for: $C_{28}H_{16}NS$, 398.1003, found, 398.1007.

2.2.4. Synthesis of 9-(dibenzo[b,d]thiophen-4-yl)-7-(4-(1-phenyl-1H-benzo[d] imidazole-2-yl)phenyl)-7H-benzo[c]carbazole (DYNS)

A mixture of 9-(dibenzo[*b,d*]thiophen-4-yl)-7*H*-benzo[*c*]carbazole **1–3** (0.099 g, 0.25 mmol), 2-(4-bromophenyl)-1-phenyl-1*H*-benzo[*d*]imidazole (0.13 g, 0.375 mmol) in *m*-xylene (20 mL) and potassium tert-butoxide (0.034 g, 0.3 mmol) were added into a round bottom flask and bubbled with argon stirring for 15 min. $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol) and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos, 8.8 mg, 0.025 mmol) were added to the mixture, and the reaction was refluxed overnight under argon atmosphere. After cooling down to room temperature, the reaction mixture was extracted with dichloromethane three times, and the organic layer was dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the crude product was purified by SiO_2 column chromatography, affording a white solid (0.10 g, 60%). IR (KBr, disk) ν 3051.22, 1602.70, 1586.50, 1450.61, 1434.95, 744.64, 699.88 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, δ): 8.94 (dd, *J* = 16.0, 8.4 Hz, 2H), 8.50–8.38 (m, 2H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.92–7.77 (m, 8H), 7.73–7.62 (m, 3H), 7.62–7.50 (m, 7H), 7.43 (d, *J* = 4.0 Hz, 1H), 7.38–7.27 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO, δ): 150.92, 142.58, 139.36, 138.46, 138.33, 137.53, 137.16, 137.07, 136.62, 136.40, 136.31, 136.00, 135.30, 130.91, 130.03, 129.39, 129.34, 129.27, 128.99, 128.89, 128.25, 127.69, 127.54, 127.42, 127.28, 127.12, 125.79, 124.96, 123.76, 123.62, 123.26, 123.07, 122.99, 122.92, 122.74, 122.31, 121.28, 121.12, 119.50, 114.81, 111.57, 110.54,