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Two spiro[fluorene-9,8′-indolo[3,2,1-de]acridine] derivatives as host materials for green phosphorescent organic light-emitting diodes

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A R T I C L E   I N F O

A B S T R A C T

Two host materials based on spiro[fluorene-9,8′-indolo[3,2,1-de]acridine] derivatives were designed and synthesized by introducing the benzofuran/benzothiophene unit to the spiro [fluorene-9,8′-indolo[3,2,1-de]acridine] unit. The two host materials exhibited high triplet energy level (> 2.65 eV) and the benzofuran-substituted derivative presented suitable glass transition temperature (> 130 °C). Their electrochemical and photophysical properties were also determined. The green phosphorescent organic light-emitting diodes based on the two host materials obtained electroluminescence performances with external quantum efficiencies of 14.3 ± 0.1% and 11.9 ± 0.1%, respectively.

1. Introduction

In the past two decades, an enormous number of research findings have been devoted to study the organic light-emitting diodes (OLEDs) for their practical application in full color flat panel displays and low-cost solid-state lighting sources. Under electrical excitation, the ratio of singlet and triplet excitons is approximately 1:3, which makes the efficiency of fluorescent OLEDs under 25% with the emission solely from singlet exciton. In 1998, Forrest and Thompson reported highly efficient phosphorescent organic light-emitting diodes (PHOLEDs) with the heavy-metal phosphors as the emission layer, which boosted the theoretical internal quantum efficiency from 25% to 100% by utilizing both singlet and triplet excitons [1]. Typical PHOLEDs often adopts host-guest strategy by dispersing the heavy metal-containing complex homogeneously into a host matrix to avoid efficiency roll-off induced by the concentration quenching and triple-triple annihilation [2–3]. In this regard, the design of host materials with great performance is of equal importance to the phosphors to achieve high efficiency.

As an ideal host material, one important design principle is that those compounds should obtain a higher triplet energy level (E_T) than the dopant, which would be benefit to prevent the back energy transfer from the dopant to host [4]. On the other hand, suitable frontier molecular level, great thermal/morphological stability and balanced carrier mobility should also be taken into consideration in the molecule design [5–8]. One straightforward strategy to achieve eligible host

material is to use the building block such as the spiro-based heteroaromatic compounds [9–12]. Among these organic molecules, carbazole-based materials, such as 4,4′-bis(N-carbazolyl)-1,10-biphenyl (CBP), have attracted exceptional attention as their excellent properties [13–18]. However, those carbazole-based materials ineluctable inherited the drawback of CBP with a low glass transition temperature. To cover this shortage, tremendous efforts have been devoted to. For example, Yang et al. reported a host material BCBP, which exhibited a high glass transition temperature (173 °C) and 13.7% of external quantum efficiency (EQE) for green PHOLEDs [19]. Liao et al. developed two fused N-phenylcarbazole ring host materials, which achieved high E_T (> 2.70 eV) and excellent electroluminescence (EL) properties with the maximum current efficiencies (CE) of 33.9 cd/A and 40.8 cd/A [20].

Enlighten from the previous work, the indoloacridine derivatives with good hole-transporting ability and high triplet energy could be used as donor. Meanwhile, benzofuran/benzothiophene moieties with good thermal stability could be a candidate as an electron acceptor. We develop a sp^3 C as a bridge to connect the donor group and accept moiety to increase their steric conformation and then the triplet energy level tuned, owning to their unique conformation with two mutually perpendicular chromophores [21]. In this article, two spiro-based heteroaromatic compounds spiro[fluoreno[4,3-b]benzofuran-7,8′-indolo[3,2,1-de] acridine] (CZO) and spiro[benzo[b]fluoreno[3,4-d]thiophene-7,8′-indolo[3,2,1-de]acridine] (CZS) were designed and

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synthesized by installing the benzofuran/benzothiophene unit to the indoloacridine moiety via a spiro structure as bridge [22–23]. To further evaluate the EL performances of those host materials, the PHOLED devices using the Ir(ppy)$_3$ as triple emitter were fabricated. Both two materials exhibited low efficiency roll-off with the external quantum efficiencies of 14.3% at 1000 cd/m^2 and 10.7% at 10000 cd/m^2 for **CZO**, 11.9% at 1000 cd/m^2 and 10.5% at 10000 cd/m^2 for **CZS**.

2. Experimental

2.1. General information

Chemicals and solvents used in the process were reagents grades and purchased from J & K Chemical Co. and Aladdin Chemical Co. without further purification. Tetrahydrofuran (THF) was purified by distillation over sodium under N$_2$ atmosphere prior to use. In addition, the boronic acid pinacol ester (**3** and **4**) were obtained from Shanghai Taoe chemical technology Co., Ltd. All reactions and manipulations were carried out under N$_2$ atmosphere. All materials were purified further by vacuum sublimation prior to fabrication of OLED devices.

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM 400 spectrometer with tetramethylsilane as the internal standard. High-resolution mass spectra (HRMS) were measured on a Waters LCT Premier XE spectrometer. The infrared radiation (IR) spectra were recorded in the range 4000–600 cm^{-1} using the potassium bromide disk for solid samples by the Fourier transform infrared spectroscopy instrument. The ultraviolet-visible (UV–vis) absorption spectra were obtained on a Varian Cary 500 spectrophotometer. Photoluminescence (PL) spectra were recorded on room temperature by Varian-Cary fluorescence spectrophotometer. The cyclic voltammetry experiments were performed by a Versastat II electrochemical work station (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. The oxidation and reduction potentials were measured in solution tetrahydrofuran containing of 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte at a scan rate of 100 mV/s. The differential scanning calorimetry (DSC) analysis was performed on a DSC Q2000 V24.11 Build 124 instrument with a heating scan rate of 5 °C/min from 0 °C to 250 °C under nitrogen atmosphere. Thermo gravimetric analysis (TGA) was carried out on the TGA instrument by measuring weight loss of samples with a heating scan rate of 10 °C/min from 50 °C to 800 °C under nitrogen.

2.2. Preparation of materials

2.2.1. Synthesis of 7H-fluoreno[4,3-b]benzofuran-7-one

A mixture of methyl 2-bromobenzoate (2.16 g, 10 mmol), dibenzo [b,d]furan-4-ylboronic acid (2.34 g, 11 mmol) and 2 M K$_2$CO$_3$ (10 mL) in tetrahydrofuran (40 mL) was bubbled with argon with stirring for 30 min. Tetrakis(triphenylphosphine)palladium (0.108 g, 0.092 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$_2$O and then extracted with dichloromethane for three times. The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the crude product was recrystallization by ethyl alcohol, affording yellow solid methyl 2-(dibenzo[b,d]furan-4-yl)benzoate (2.84 g, 9.4 mmol, 94.04%). Then, to a round flask added methyl 2-(dibenzo [b,d]furan-4-yl)benzoate (1.51 g, 5 mmol) and 15 mL PPA (polyphosphoric acid), and then the mixture was heated to 140 °C and stirred by electric mechanical agitator for 4 h. After cooling to ambient temperature, 70 mL water was dropwise slowly into the mixture under 0 °C. After 1 h, the mixture was filtered under vacuum and washed with ethyl alcohol (3 × 20 mL). The solid was dried under vacuum for 20 h,

affording the yellow procedure (1.04 g, 3.9 mmol, 77.20%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (dd, J = 7.2, 4.0 Hz, 2H), 7.85 (d, J = 7.6 Hz, 1H), 7.73–7.65 (m, 3H), 7.57 (tdd, J = 8.4, 4.0, 1.2 Hz, 2H), 7.44–7.38 (m, 1H), 7.34 (td, J = 7.6, 0.8 Hz, 1H).

2.2.2. Synthesis of 7H-benzo[b]fluoreno[3,4-d]thiophen-7-one

A mixture of methyl 2-bromobenzoate (2.16 g, 10 mmol), dibenzo [b,d]thiophen-4-ylboronic acid (2.5 g, 11 mmol) and 2 M K$_2$CO$_3$ (10 mL) in tetrahydrofuran (40 mL) was bubbled with argon with stirring for 30 min. Tetrakis(triphenylphosphine)palladium (0.108 g, 0.092 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$_2$O and then extracted with dichloromethane for three times. The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the crude product was recrystallization by ethyl alcohol, affording yellow solid methyl 2-(dibenzo[b,d]thiophen-4-yl)benzoate (3.0 g, 9.4 mmol, 94.34%). Then, to a round flask added 2-(dibenzo [b,d]thiophen-4-yl)benzoate (1.59 g, 5 mmol) and 15 mL PPA (polyphosphoric acid), and then the mixture was heated to 140 °C and stirred by an electric mechanical agitator for 4 h. After cooling to ambient temperature, 70 mL water was dropwise slowly into the mixture stirring under 0 °C. After 1 h, the mixture was filtered under vacuum and washed with ethyl alcohol (3 × 20 mL). The solid was dried under vacuum for 20 h, affording the yellow procedure (1.03 g, 3.6 mmol, 72.03%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.16 (dd, J = 7.6, 0.8 Hz, 2H), 7.50 (td, J = 8.0, 1.6 Hz, 1H), 7.45–7.37 (m, 3H), 7.32–7.27 (m, 2H), 7.07 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H).

2.2.3. Synthesis of spiro[fluoreno[4,3-b]benzofuran-7,8′-indolo[3,2,1-de] acridine] (CZO)

A mixture of 9-(2-bromophenyl)-9H-carbazole (1.61 g, 5 mmol) in the THF (40 mL) was treated with the n-BuLi (2 mL, 2.5 M, 5 mmol) under argon at −78 °C for 30 min. Then, 7H-fluoreno[4,3-b]benzofuran-7-one (1.35 g, 5 mmol) dissolved in 40 mL THF was added dropwise. The mixture was stirred for 30 min under argon at −78 °C, and allowed to warm to the room temperature. After 12 h, the organic layer was washed with water and extracted with dichloromethane for three times. The combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the alcohol product was obtained. Then the alcohol was added without further purification to a mixture of 5 mL concentrated aqueous HCl and acetic acid 50 mL. The mixture was heated to reflux and stirred for 2 h. The reaction mixture was cooled down to room temperature, poured into H$_2$O and then extracted with dichloromethane for 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 column chromatography on silica gel. The solid was dried under vacuum for 20 h, affording the white procedure (1.03 g, 2.1 mmol, 42.04%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (d, J = 7.6 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.26 (dd, J = 8.4, 0.8 Hz, 1H), 8.20 (dd, J = 7.6, 0.8 Hz, 1H), 7.93 (dd, J = 7.6, 0.8 Hz, 1H), 7.88 (dd, J = 7.6, 0.8 Hz, 1H), 7.74 (dd, J = 8.0, 4.4 Hz, 2H), 7.64 (ddd, J = 8.4, 7.6, 1.2 Hz, 1H), 7.54–7.46 (m, 2H), 7.44–7.39 (m, 1H), 7.39–7.31 (m, 2H), 7.24–7.18 (m, 2H), 7.16–7.11 (m, 1H), 7.06 (dd, J = 9.6, 5.6 Hz, 1H), 6.87–6.79 (m, 1H), 6.66 (dd, J = 8.0, 1.6 Hz, 1H), 6.55 (dd, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 156.92, 155.71, 155.22, 150.51, 138.56, 137.06, 136.73, 129.44, 129.15, 128.46, 127.13, 126.69, 126.40, 125.49, 124.44, 123.92, 123.54, 123.04, 122.69, 121.19, 120.66, 120.29, 118.20, 114.48, 113.73, 111.95, 57.71. IR (KBr, disk) ν 3060.15, 2925.56, 1676.69, 1631.58, 1594.74, 1394.74, 1226.31, 785.71 cm^{-1}. HRMS (ESI, m/z): [M + H]$^+$ calcd for: C$_{37}$H$_{21}$NO 496.1701, found, 496.1704.