



# Novel fluorescent blue-emitting materials based on anthracene-fluorene hybrids with triphenylsilane group for organic light-emitting diodes



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## ARTICLE INFO

### Article history:

Received 3 July 2014

Received in revised form

30 October 2014

Accepted 3 November 2014

Available online 10 November 2014

### Keywords:

Blue OLED

Triphenylsilane

Suzuki-coupling reaction

Anthracene

Fluorescence

OLED emitters

## ABSTRACT

This paper reports the synthesis and electroluminescence properties of new blue-emitting materials based on anthracene-fluorene derivatives with triphenylsilane groups for organic light-emitting diodes. To study the electroluminescence properties, OLEDs were fabricated in the following sequence: ITO/4,4-Bis(*N*-(1-naphthyl)-*N*-phenylamino)biphenyl (50 nm)/newly designed blue materials (30 nm)/4,4-bis(*N*-(1-naphthyl)-*N*-phenylamino)biphenyl (30 nm)/8-Hydroxyquinolinolato-lithium (2 nm)/Al (100 nm). All devices exhibited blue electroluminescence. In particular, the device using 10-(9,9-dimethyl-2-(triphenylsilyl)-9*H*-fluoren-7-yl)-9-(4-(triphenylsilyl)phenyl) anthracene as the emitting material exhibited the deepest blue-emission with CIE coordinates of ( $x = 0.15$ ,  $y = 0.09$ ). Also, the device using (9,9-dimethyl-2-(10-(10-phenylanthracen-9-yl)anthracen-9-yl)-9*H*-fluoren-7-yl)triphenylsilane exhibited high luminous, power and quantum efficiencies of 2.53 cd/A, 1.94 lm/W and 1.72% at 20 mA/cm<sup>2</sup>, respectively.

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## 1. Introduction

Since the first report on organic light-emitting diodes (OLEDs) by C.W. Tang in 1987 [1], the use of OLEDs has rapidly grown because of their extensive potential applications in full-color flat-panel displays and lighting sources. In recent OLED studies, researchers have mainly focused on developing new emitting materials with excellent emission efficiency and stability, which is the key point in OLED development for full-color displays [2,3]. Although many fluorescent blue emitters have been reported, such as anthracene [4], phenylene [5], pyrene [6], fluorene [7] and aromatic hydrocarbons [8], further developments are required in terms of efficiency and color purity, compared to red and green emitters [9].

Anthracene derivatives have been widely used as blue-emitting materials in OLEDs due to their excellent photoluminescence (PL) and electroluminescence (EL) characteristics, as well as good thermal properties [10]. Furthermore, various anthracene

derivatives including bulky substituents at the anthracene 9- and 10- position have been investigated. The bulky substituents provide steric hindrance, which prevents intermolecular interactions and thus reduces the self-quenching effect, thereby improving the EL performance [11,12]. Fluorene also offers several advantages such as excellent fluorescent properties, good morphological and thermal stability with high purity [13].

In this report, we present the synthesis and EL properties of anthracene-fluorene derivatives **1–4** containing triphenylsilane moieties. The introduction of triphenylsilane moieties into the anthracene-fluorene emitting cores provides a non-coplanar structure, which effectively inhibits molecular aggregation and excimer formation in the solid state [14]. In materials **1–4**, four different emitting cores are used to study the effect of structural variations on the EL performance of OLED devices using them as the emitting materials.

## 2. Experimental details

### 2.1. Synthesis and characterization

All reactions were performed under nitrogen. Solvents were carefully dried and distilled from appropriate drying agents prior to

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use. Commercially available reagents were used without further purification unless otherwise stated.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on a Bruker Avance III 500 MHz NMR spectrometer FT-IR spectra were recorded using a Bruker VERTEX70 FT-IR spectrometer. Low and high-resolution mass spectra were measured using a Jeol JMS-AX505WA spectrometer in APCI mode, and a JMS-T100TD (AccuTOF-TLC) spectrometer in positive-ion mode, respectively. Elemental analysis (EA) was measured using an EA 1108 spectrometer.

#### 2.1.1. 10-(9,9-Dimethyl-2-(triphenylsilyl)-9H-fluoren-7-yl)-9-(4-(triphenylsilyl)phenyl)anthracene (1)

4,4,5,5-tetramethyl-2-(4-(triphenylsilyl)phenyl)-1,3,2-dioxaborolane (0.39 g, 0.84 mmol) and (2-(10-bromoanthracen-9-yl)-9,9-dimethyl-9H-fluoren-7-yl)triphenylsilane (0.5 g, 0.7 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.032 g, 0.028 mmol), aqueous 2.0 M  $\text{K}_2\text{CO}_3$  (3.5 ml, 7.0 mmol), Aliquat 336 (0.028 ml, 0.07 mmol), and toluene (8 ml) were mixed in a flask. The mixture was refluxed for 4 h at 120 °C. After the reaction had finished, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried with anhydrous  $\text{MgSO}_4$  and filtered with silica gel. The solution was then evaporated. The crude product was purified by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  (Yield: 0.3 g, 44%).  $V_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 3016, 2965, 1739, 1437, 1367, 1218, 1099, 900;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ ): 7.97 (d,  $J = 7.5$  Hz, 1H), 7.86–7.82 (m, 3H), 7.79–7.72 (m, 2H), 7.74–7.71 (m, 8H), 7.62–7.63 (m, 6H), 7.61 (d,  $J = 7.5$  Hz, 1H), 7.56 (s, 1H), 7.51–7.45 (m, 15H), 7.43–7.40 (m, 7H), 7.37–7.34 (m, 4H), 1.50 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ ): 140.53, 140.52, 138.48, 137.68, 136.90, 136.61, 136.54, 136.48, 136.41, 135.52, 134.59, 134.28, 130.89, 130.46, 130.21, 130.02, 129.85, 129.75, 129.62, 128.08, 128.02, 127.92, 127.05, 127.02, 125.86, 125.10, 125.06, 123.64, 120.21, 120.01, 119.68, 119.60, 47.11, 27.19; HRMS:  $[\text{M}^+]$  calculated for  $\text{C}_{71}\text{H}_{54}\text{Si}_2$ , 962.3764, found: 962.3761; APCI-MS ( $m/z$ ): 962  $[\text{M}^+]$ ; Anal. Calcd: C, 88.52; H, 5.65. Found: C, 87.41; H, 5.82.

#### 2.1.2. 10-(9,9-Dimethyl-2-(triphenylsilyl)-9H-fluoren-7-yl)-9-(10-(9,9-dimethyl-2-(triphenylsilyl)-9H-fluoren-7-yl)anthracen-9-yl)anthracene (2)

4,4,5,5-tetramethyl-2-(9,9-dimethyl-2-(triphenylsilyl)-9H-fluoren-7-yl)-1,3,2-dioxaborolane (0.5 g, 0.86 mmol) and 10-bromo-9-(10-bromoanthracen-9-yl)anthracene (0.2 g, 0.4 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.036 g, 0.03 mmol), aqueous 2.0 M  $\text{K}_2\text{CO}_3$  (2 ml, 3.92 mmol), Aliquat 336 (0.018 ml, 0.039 mmol), and toluene (5 ml) were mixed in a flask. The mixture was refluxed for 4 h at 120 °C. After the reaction had finished, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried with anhydrous  $\text{MgSO}_4$  and filtered with silica gel. The solution was then evaporated. The crude product was purified by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  (Yield: 0.31 g, 63%).  $V_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 3016, 2965, 1739, 1437, 1366, 1218, 1102, 900;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ ): 8.05 (d,  $J = 7.5$  Hz, 2H), 7.93–7.86 (m, 6H), 7.76–7.62 (m, 21H), 7.49–7.41 (m, 17H), 7.37–7.34 (m, 5H), 7.30–7.27 (m, 3H), 7.21–7.16 (m, 4H), 1.57 (s, 12H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ ): 154.39, 153.25, 140.54, 138.48, 138.38, 136.50, 135.57, 134.60, 133.44, 133.12, 131.47, 130.51, 130.37, 130.24, 129.64, 127.94, 127.34, 127.20, 126.05, 125.60, 125.54, 125.32, 125.28, 120.29, 119.65, 47.18, 27.24; HRMS:  $[\text{M}^+]$  calculated for  $\text{C}_{94}\text{H}_{70}\text{Si}_2$ , 1254.5016, found: 1254.5011; APCI-MS ( $m/z$ ): 1254  $[\text{M}^+]$ ; Anal. Calcd: C, 89.91; H, 5.62. Found: C, 88.76; H, 5.73.

#### 2.1.3. (9,9-Dimethyl-2-(10-(10-phenylanthracen-9-yl)anthracen-9-yl)-9H-fluoren-7-yl)triphenylsilane (3)

phenylboronic acid (0.68 g, 0.56 mmol) and (2-(10-(10-bromoanthracen-9-yl)anthracen-9-yl)-9,9-dimethyl-9H-fluoren-7-yl)triphenylsilane (0.33 g, 0.37 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.017 g,

0.015 mol), aqueous 2.0 M  $\text{Na}_2\text{CO}_3$  (1.9 ml, 3.37 mmol), ethanol (1.9 ml) and toluene (3.8 ml) were mixed in a flask. The mixture was refluxed for 4 h at 120 °C. After the reaction had finished, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried with anhydrous  $\text{MgSO}_4$  and filtered with silica gel. The solution was then evaporated. The crude product was purified by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  (Yield: 0.29 g, 87%).  $V_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 3013, 2968, 1739, 1438, 1366, 1218, 1049, 900;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ ): 7.91 (d,  $J = 8.5$  Hz, 2H), 7.83 (d,  $J = 8.5$  Hz, 3H), 7.67–7.61 (m, 15H), 7.47 (d,  $J = 7.0$  Hz, 3H), 7.44–7.41 (m, 8H), 7.37–7.33 (m, 6H), 7.21–7.16 (m, 5H), 1.57 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ ): 154.39, 153.26, 140.55, 139.11, 138.49, 138.45, 136.51, 136.47, 136.45, 134.61, 131.58, 131.50, 131.47, 131.41, 130.55, 130.51, 130.36, 130.23, 130.14, 129.64, 129.58, 128.80, 128.61, 128.50, 127.94, 127.60, 127.47, 127.29, 127.19, 127.13, 127.06, 125.62, 125.58, 125.29, 125.24, 120.29, 119.65, 47.18, 27.22; HRMS:  $[\text{M}^+]$  calculated for  $\text{C}_{67}\text{H}_{48}\text{Si}$ , 880.3525, found: 880.3519; APCI-MS ( $m/z$ ): 880  $[\text{M}^+]$ ; Anal. Calcd: C, 91.32; H, 5.49. Found: C, 90.48; H, 5.52.

#### 2.1.4. (9,9-Dimethyl-2-(10-(4-(10-phenylanthracen-9-yl)phenyl)anthracen-9-yl)-9H-fluoren-7-yl)triphenylsilane (4)

4,4,5,5-tetramethyl-2-(4-(10-phenylanthracen-9-yl)phenyl)-1,3,2-dioxaborolane (0.35 g, 0.77 mol) and (2-(10-bromoanthracen-9-yl)-9,9-dimethyl-9H-fluoren-7-yl)triphenylsilane (0.5 g, 0.7 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.032 g, 0.028 mmol), aqueous 2.0 M  $\text{K}_2\text{CO}_3$  (3.5 ml, 7.0 mol), Aliquat 336 (0.032 ml, 0.07 mmol), and toluene (8 ml) were mixed in a flask. The mixture was refluxed for 4 h at 120 °C. After the reaction had finished, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried with anhydrous  $\text{MgSO}_4$  and filtered with silica gel. The solution was then evaporated. The crude product was purified by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  (Yield: 0.3 g, 44%).  $V_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 3015, 2966, 1739, 1437, 1367, 1218, 1060, 900;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ ): 8.00 (dd,  $J = 8.0$ , 3 Hz, 2H), 7.88–7.85 (m, 3H), 7.78–7.42 (m, 7H), 7.67–7.62 (m, 10H), 7.56–7.46 (m, 11H), 7.44–7.41 (m, 10H), 1.54 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\delta$ ): 154.37, 153.23, 140.54, 139.14, 138.53, 138.38, 138.31, 137.82, 137.37, 136.92, 136.50, 135.55, 134.60, 133.09, 131.48, 131.40, 130.49, 130.27, 130.16, 130.13, 130.07, 130.5, 129.63, 128.48, 127.93, 127.56, 127.20, 127.16, 127.08, 127.04, 127.00, 125.91, 125.29, 125.20, 125.15, 120.26, 119.63, 47.15, 27.22; HRMS:  $[\text{M}^+]$  calculated for  $\text{C}_{73}\text{H}_{52}\text{Si}$ , 956.3838, found: 956.3831; APCI-MS ( $m/z$ ): 956  $[\text{M}^+]$ ; Anal. Calcd: C, 91.59; H, 5.48. Found: C, 90.63; H, 5.35.

## 2.2. Physical measurements

The UV–Vis absorption and PL spectra of the newly designed materials were measured in dichloromethane ( $10^{-5}$  M) using Shimadzu UV-1650PC and Aminco Browman series 2 luminescence spectrometers. The fluorescence quantum yields of the emitting materials were determined in dichloromethane at 293 K against 9,10-diphenylanthracene (DPA) as a reference ( $\Phi_{\text{DPA}} = 0.90$ ). The highest occupied molecular orbital (HOMO) energy levels were measured with a low-energy photoelectron spectrometer (Riken-Keiki, AC-2). The energy band gaps were determined from the intersection of the absorption and PL spectra. The lowest unoccupied molecular orbital (LUMO) energy levels were calculated by subtracting the corresponding optical band gap energies from the HOMO energy values.

## 2.3. OLED fabrication and measurement

For OLED fabrication, indium–tin–oxide (ITO) thin films coated on glass substrates, with a sheet resistivity of 30  $\Omega/\text{square}$  and thickness of 1800 Å were used. The ITO-coated glass was cleaned in

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