Synthesis, characterization and electroluminescence of two highly-twisted non-doped blue light-emitting materials

Xiaojie Gong [a], Yipeng Pan [a], Xiang Xie [b], Tong Tong [a], Runfeng Chen [b], Deqing Gao [a, *]

[a] Key Laboratory of Flexible Electronics & Institute of Advanced Materials, Jiangsu National Synergistic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing, Jiangsu, 211816, PR China
[b] Key Laboratory for Organic Electronics & Information Displays and Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing, Jiangsu, 210003, PR China

ARTICLE INFO

ABSTRACT

Two pyrene derivatives, substituted with 2-methylnaphthalene units on 1,3-position and 1,6-position of pyrene backbones, were designed and synthesized. DFT calculation confirmed that the two molecules were highly twisted and the dihedral angles between pyrene backbone and naphthalene unit were over 80°, being attributed to the steric hindrance of ortho-methyl group and the substitution position of pyrene itself. As a result, the intermolecular aggregation was greatly inhibited in the solid state, being beneficial for suppressing the fluorescence quenching. By analyzing the optical and thermal properties, it was found that the π-π conjugation extension could be adjusted and a balance for high fluorescent efficiency and avoiding quenching at the same time could be reached, which may guide the molecular design in the future. The electroluminescence properties of the non-doped devices were enhanced with the double hole-transporting layers by optimizing the energy level matching. The stable blue EL emission, with the Commission Internationaled'Eclairage ($CIE_{x,y}$) color coordinates of (0.15, 0.13) and (0.15, 0.11) at 7, 8, 9 and 10 V respectively, was obtained.

1. Introduction

Organic light-emitting devices (OLED) have been developed rapidly since first reported by Tang et al. [1] and have been broadly applied in the flat-panel displays due to their advantages of low drive voltage, high luminance and high efficiency. Full-color displays require the use of red, green, and blue emitters. Nowadays red and green emission can be provided by highly efficient phosphorescent transition metal complexes while blue emission to this day often stems from fluorescent materials due to their better long-time stability [2]. It is still difficult to develop the color-pure and high-efficient blue emitters due to their intrinsic wide band gap, which means that the efficient hole/electron injection was hard to be achieved at a moderate drive voltage. It also has to be taken into account to avoid the possibility of exciton energy transfer from the emission layer to neighboring materials [3].

Among various blue emitting materials, pyrene is a potentially good candidate for OLED applications due to its native deep blue

fluorescence and high photoluminescence quantum yield, excellent thermal stability and high charge-carrier mobility [4,5]. However, in the solid state the planar pyrene molecule shows a strong tendency to aggregate and form excimers which generally quench light emission and undermine the device performance, so pyrene itself is not suitable for the use in OLED [6]. There are two ways to disrupt the aggregation. One way is to adopt the host-guest system in the fabrication of the device [3,7]. However, the host-guest system usually faces some challenges like phase separation upon heating, complexity and the high cost of mass production in the doping process [8,9]. Another way is to construct the hindered structures, such as polypyrene [10], pyrene-core dendrimers [11,12], tetraarylpyrene [13], pyrene-fluorene [14], and pyrene-carbazole [3] systems. The undesirable π-π stacking in the solid state was greatly inhibited in these kinds of derivatives [11,15–17]. The non-doped devices based on these derivatives showed high efficiency and pure blue emission. Methyl, one of the simplest substituent groups, has been widely used to make a highly twisted structure between two adjacent aromatic rings [18,19].

Generally, we designed the chromophores which can be processed from solution or by vacuum-deposition techniques and can be easily prepared on a gram scale. In this study, we chose

2-methylnaphthalene as the bulky aromatic substituent due to its low cost, highly selectivity to be brominated, its coplanar structure and the hindrance which was induced by the ortho-position substituted methyl group. The molecular backbones were 1,6-position substituted pyrene and 1,3-position substituted 7-*tert*-butylpyrene, considering their weak stacking in the solid state [20,21]. In result, the two molecules were expected to show bulky and rigid non-coplanar structures and greatly inhibited π-π stacking in the solid state. They were expected to show pure and high efficient blue emission in the OLED devices.

2. Experimental

2.1. General information

Pyrene, 2-methylnaphthalene, *n*-butyllithium, 2-isopropoxy-4,4,5,5-tetramethyl −1,3,2-dioxaborolane and tetrakis (triphenylphosphine)-palladium(0) (Pd(PPh₃)₄) were purchased from Energy Chemical. Bromine, potassium acetate, HOAc, anhydrous MgSO₄ and sodium carbonate were purchased from Sinopharm Chemical Reagent. They were used without any further purification. Anhydrous THF was freshly distilled after treated with sodium and benzophenone. Dry CHCl₃ and CH₂Cl₂ were obtained by distilling the corresponding solvent previously treated with CaH₂.

The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on Bruker AMX 400 spectrometer in CDCl₃. The NMR spectra are available in Supporting Information. UV/Vis spectra were recorded on Shimadzu UV-1750. Fluorescence spectra were recorded on Hitachi F-4600. Fluorescence quantum yields (Φ_f) were measured through the integrated sphere method on the Edinburgh FLS-920 Instruments. Cyclic voltammetry (CV) experiments were performed with a CHI-621B electrochemical analyzer. All measurements were carried out at room temperature with a conventional three electrode configuration consisting of a platinum working electrode, an auxiliary electrode and a non-aqueous Ag/AgCl reference electrode. The solvent was degassed dry CHCl₃ in CV measurement. The supporting electrolyte was 0.1 mol/L tetrabutylammonium hexafluorophosphate. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA7 thermal analyzer at a heating rate of 10 °C/min under dry nitrogen flow. Differential scanning calorimetry (DSC) measurement was performed on NETZSCH DSC214 Polyma instrument under a heating rate of 10 °C/min and a nitrogen flow rate of 20 cm³/min.

2.2. Synthesis

2.2.1. 1-Bromo-2-methylnaphthalene

According to the literature [22], a solution of Br₂ (0.40 mL, 7.8 mmol) in acetic acid (2 mL) was added dropwise to a solution of 2-methylnaphthalene (1.01 g, 7.10 mmol) and anhydrous KOAc (0.75 g, 7.8 mmol) in AcOH (2 mL). After stirred for 15 min, CH₂Cl₂ (20 mL) was added to the mixture. The solution was washed with saturated NaHCO₃ aqueous solution (30 mL) and H₂O (20 mL). After extraction, the organic phase was dried over anhydrous MgSO₄, filtrated and concentrated in vacuum. The product was obtained as yellow oil (1.43 g, 92% in yield). It was used in the next reaction without any purification. ^{1}H NMR (300 MHz, CDCl₃, 298 K) δ: 8.30 (d, 1H, J = 9 Hz), 7.80 (d, 1H, J = 6 Hz), 7.72 (d, 1H, J = 6 Hz), 7.58 (m, 1H), 7.46 (t, 1H, J = 6 Hz), 7.36 (d, 1H, J = 6 Hz), 2.64 (s, 3H).

2.2.2. 4,4,5,5-Tetramethyl-2-(2-methyl-1-naphthyl)-1,3,2-dioxaborolane

n-Butyllithium (8.8 mL of a 2.5 M solution in hexane, 22 mmol) was added dropwise into a solution of 1-bromo-2-methylnaphthalene (4.42 g, 20 mmol) in dry THF (50 mL) at −78 °C under an atmosphere of N₂ over 30 min. The mixture was stirred at −78 °C for 2 h, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.57 mL, 22 mmol) was injected into the reaction mixture. After stirred at room temperature overnight, the reaction mixture was poured into water and extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed by vacuum evaporation. The purification with column chromatography (silica gel, ethyl acetate/petroleum ether = 1/20, v/v) gave the product as white solid (4.30 g, 80% in yield). ^{1}H NMR (300 MHz, CDCl₃, 298 K) δ: 8.11 (d, 1H, J = 6 Hz), 7.73 (m, 2H), 7.40 (m, 2H), 7.25 (s, 1H), 2.62 (s, 3H), 1.48 (s, 12H).

2.2.3. 1,6-Dibromopyrene

A solution of bromine (2.0 mL) in dichloromethane (50 mL) was added dropwise to a solution of pyrene (4.0 g) in dichloromethane (70 mL) at room temperature over 2 h. The reaction mixture was then stirred overnight at room temperature. The white precipitate was collected by filtration. 1,6-Dibromopyrene was obtained by recrystallization from toluene for several times as needle like crystals with the yield of 35%. ^{1}H NMR (CDCl₃, 300 MHz, 298 K) δ: 8.48 (d, 2H, J = 9 Hz), 8.27 (d, 2H, J = 9 Hz), 8.12 (d, 2H, J = 9 Hz), 8.06 (d, 2H, J = 9 Hz).

2.2.4. 2-(tert-Butyl)pyrene

According to the literature [23], anhydrous AlCl₃ (3.62 g, 27.2 mmol) was added in one portion to a stirred solution of pyrene (5 g, 24.7 mmol) and 2-chloro-2-methylpropane (3.23 mL, 29.7 mmol) in anhydrous CH₂Cl₂ (40 mL) at 0 °C. The resulting mixture was stirred for 3 h at room temperature and poured into a large excess of ice/water. The mixture was extracted with CH₂Cl₂ and the organic phase was dried over anhydrous MgSO₄. After filtration the solvent was removed by vacuum evaporation. The purification with column chromatography (silica gel, petroleum ether) and then recrystallization from hexane gave 2-*tert*-butyl-pyrene (4.5 g) in the yield of 71% as silver-colored plates. ^{1}H NMR (CDCl₃, 300 MHz, 298 K) δ: 8.23 (s, 2H), 8.16 (d, 2H, J = 9 Hz), 8.06 (m, 4H), 7.97 (t, 1H, J = 9 Hz), 1.60 (s, 9 H).

2.2.5. 1,3-Dibromo-7-tert-butylpyrene

According to the literature [24], a solution of Br₂ (2 mL, 38.7 mmol) in anhydrous CH₂Cl₂ (200 mL) was slowly added to a degassed solution of 2-*tert*-butylpyrene (5 g, 19.4 mmol) in anhydrous CH₂Cl₂ (100 mL) at −78 °C under N₂. The resulting mixture was allowed to slowly warm up to room temperature and stirred overnight. The white precipitate was collected by filtration and washed by ethanol. The solid was used in the next reaction without any further purification.

2.2.6. 1,6-Bis(2-methylnaphthalen-1-yl)pyrene (**1**)

The mixture of 1,6-dibromopyrene (0.36 g, 1 mmol), 4,4,5,5-tetramethyl-2-(2-methyl-1-naphthyl)-1,3,2-dioxaborolane (0.81 g, 3 mmol), one drop of methyl trioctyl ammonium chloride, toluene (25 mL) and 2 M Na₂CO₃ aqueous solution (5 mL) was bubbled with N₂ for 20 min. Then Pd(PPh₃)₄ (46 mg, 0.04 mmol) was added. The mixture was heated at 90 °C for 24 h. The mixture was cooled to room temperature and extracted by CH₂Cl₂. The combined organic phase was dried over anhydrous MgSO₄ and evaporated. The crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether = 1/10, v/v) and then recrystallization from CH₂Cl₂/CH₃OH to get the product as white solid (245 mg, 50%). ^{1}H NMR (CDCl₃, 300 MHz, 298 K) δ: 8.27 (d, 2H, J = 6 Hz), 7.90 (m, 8H), 7.57 (m, 4H), 7.42 (t, 4H, J = 6 Hz), 7.20 (m, 2H), 7.14 (m, 2H), 2.18 (s, 6H). ^{13}C NMR (CDCl₃, 75 MHz, 298 K) δ: 136.6, 135.3, 134.8, 133.8, 132.1, 130.7, 130.1, 128.7, 128.5, 127.9, 127.8,