Organic Electronics xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Multi-triphenylamine–functionalized dithienylbenzothiadiazoles as hole-transporting non-doped red emitters for efficient simple solution processed pure red organic light-emitting diodes

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ARTICLE INFO

Article history:
Received 9 February 2015
Received in revised form 4 March 2015
Accepted 5 March 2015
Available online xxxx

Keywords:
Triphenylamine
Dithienylbenzothiadiazoles
Hole-transporting red emitter
Solution process
Organic light-emitting diode

ABSTRACT

To achieve high efficiency solution processed red OLED, a series of new triphenylamine–functionalized dithienylbenzothiadiazoles, namely **TB**, **T3TB** and **T4TB**, as non-doped solution-processed hole-transporting red emitters were synthesized and characterized. Particularly, **T3TB** having five triphenylamine units substituted on the dithienylbenzothiadiazole core exhibited a good red emission with high T_g amorphous and good film-forming properties. A simple structured non-doped red OLED (ITO/PEDOT:PSS/**T3TB**(spin coating)/BCP/LiF–Al) with an efficiency (η) of 6.25 cd A^{-1} at 4.1 mA cm^{-2} (PE = 5.17 lm W^{-1}), a low turn-on voltage (3.0 V) and a pure red emission (λ_{EL} = 656 nm, CIE (x,y) = 0.67,0.33) was attained.

1. Introduction

The last decade has seen tremendous scientific interest and progress in organic light-emitting diodes (OLEDs) in order to realize high efficiency devices due to their practical applications in both large area flat-panel displays and solid-state lighting [1]. Current research in the field is mainly focus on cost reduction of the whole processes [2]. Regarding material development, new emitting materials that offer the advantages of easy synthesis and purification, cheap solution processing, simple device structure and superior device performance are of interest [2]. Among the three-primary color light-emitting materials and devices, the performance of red one still lag behind in terms of both efficiency and color purity [3]. More efforts are needed to achieve promising red-emitting materials and devices. A series of red fluorescent dyes has been recently reviewed by Chen [4]. According to their structural characteristics, they are summarized as pyran-containing compounds [5–7], push–pull red emitters [3,6–10], polyacenes red emitters [11,12], and metal chelates [13,14]. Most of them are usually polar or have flat molecular structures, which are prone to aggregation in the solid state owing to dipole–dipole interaction or intermolecular π–π stacking. As a consequence, they are usually used as the dopant in guest–host system. In such system, a careful control of the dopant concentration is very vital since incomplete energy transfer processes from the host will result in a combined guest–host emission leading to a broader emission. There are some materials that have a bulky structure and are successfully used as solution processed non-doped red emitters in OLEDs [15–19]. Nevertheless, it is still necessary to develop solution processed non doped red-emitting materials with pure red emission, high emission efficiency and good thermal stability.

Owing to its stronger electron-withdrawing ability and relatively high oxidation potential, benzothiadiazole is regarded as one of the most effective building blocks used in the chemistry of optoelectronic materials [20–22]. Push–pull systems containing dithienylbenzothiadiazole units first investigated by Roncali [23] have shown very interesting properties for electro-optical applications [24] such as organic photovoltaics [25–29] and electroluminescent devices [30–32]. Number of dithienylbenzothiadiazole-based small molecules and polymers have been developed

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http://dx.doi.org/10.1016/j.orgel.2015.03.009
1566-1199/

and their performances as dopant and non-doped red emitters in OLED were examined [16,33–38]. Recently, our groups reported a group of dithienylbenzothiadiazoles end-capped with carbazole dendrons for non-doped red OLEDs fabricated by solution technique [39,40]. A red light-emitting device with CIE coordinates and high luminance efficiency of (0.66, 0.33) and 3.97 cd A^{-1} was achieved, respectively [40]. In this work, we present the design of new solution processed non-doped red emitters based on the emissive dithienylbenzothiadiazole core aiming to improve the performance of the material. Our strategy for the new red-emitting materials involves multiple substitutions of this core with bulky electron donating triphenylamine (TPA) units in different manners which could be sufficient for tuning the emission to pure red and for reducing luminance quenching by aggregation of the planar conjugated core as well as improving the hole transporting capability, thermal stability and solubility of the molecule. TPA is a typical donor and has been used most widely as a building block for hole-transport materials [41,42]. With this approach, we notice a significant improvement in thermal and morphological properties of the material and the performance of red OLED compared to the parent compound. Herein, we report a synthesis, physical properties, and a study on OLED fabrication and performance of three triphenylamine–functionalized dithienylbenzothiadiazoles (Scheme 1).

2. Experimental section

2.1. Materials and methods

Solvents were purified and dried using standard protocols. All column chromatography was performed with the use of silica gel Merck Silica gel 60 (0.0630–0.200 mm). ^{1}H and ^{13}C NMR spectra were recorded using 300/500 MHz spectrometers. UV–vis spectra were measured on a UV Lambda 25 spectrometer. Photoluminescence spectra and fluorescence quantum yields (Φ_F) were determined with a LS 50B luminescence spectrometer. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on a DSC823e and TG-DTA 8120 thermal analyzers, respectively, operated at a heating rate of 10 °C min^{-1} under N_2 atmosphere. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were recorded on a PGSTAT 12 equipped with platinum counter electrode, glassy carbon working electrode and Ag/AgCl reference electrode. The substrates are dissolved 1 mM in CH_2Cl_2 solution containing 0.1 M Bu_4NPF_6 as a supporting electrolyte. High-resolution mass spectrometry (HRMS) analysis was performed on Autoflex II Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) mass spectrometer (BIFEX). The elemental analysis was measured on a CHNS-932/O VTF-900 analyzer. The atomic force microscopy (AFM) analysis was performed on a XE 100.

All calculations were performed by Gaussian 09 code and the solvent effect of CH_2Cl_2 was taken into account by C-PCM model [43]. The energy calculations and geometry optimizations were done by B3LYP/6-31G(d,p) method. The ground to excited state excitation energies were calculated by TD-B3LYP/6-31G(d,p) in CH_2Cl_2.

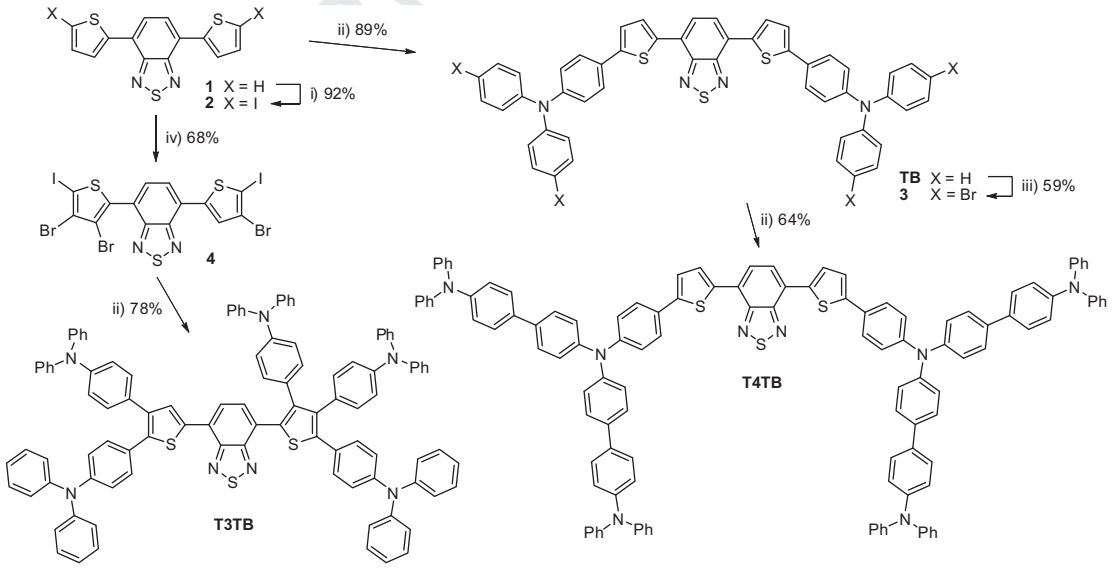
2.2. Synthesis

2.2.1. Synthesis of compound 2

Compound **1** (0.25 g, 8.22 mmol) was dissolved in THF (10 ml) and acetic acid (10 ml), and the resulting solution was cooled to 0 °C. NIS (0.39 g, 1.75 mmol) in THF (5 ml) was added slowly. The reaction mixture was stirred at room temperature for 2 h followed by the addition of CH_2Cl_2 (20 ml). The organic phase was washed with $NaHCO_3$ solution (50 ml), water (50 ml), brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered and the solvent was removed to dryness. The product was obtained by silica gel chromatography eluting with a mixture of CH_2Cl_2 and hexane (1:4) as orange solids (0.42 g, 92%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (2H, s), 7.27 (2H, d, J = 3.9 Hz), 7.35 (2H, d, J = 3.9 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.05, 137.78, 128.48, 125.28 ppm; MALDI-TOF (m/z) calcd for $C_{14}H_6I_2N_2S_3$: 551.7782; found 551.2311 (M^+).

2.2.2. Synthesis of compound 3

To a solution of **TB** (0.25 g, 0.32 mmol) in THF (15 ml) was added with NBS (0.45 g, 2.56 mmol) in small portions. The mixture was stirred at room temperature for 1 h. Water (10 ml) and CH_2Cl_2 (30 ml) were added. The organic phase was washed with water (50 ml × 2), brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, and the solvent was removed to dryness. The pure product was obtained by silica gel chromatography eluting with a mixture



Scheme 1. Synthesis of dithienylbenzothiadiazole derivatives. Reagents and conditions: (i) NIS, THF; (ii) 4-(diphenylamino)phenylboronic acid, $Pd(PPh_3)_4$, 2M Na_2CO_3 (aq), THF, heat; (iii) NBS, THF; (iv) Br_2, CH_2Cl_2.

Please cite this article in press as: A. Thangthong et al., Multi-triphenylamine–functionalized dithienylbenzothiadiazoles as hole-transporting non-doped red emitters for efficient simple solution processed pure red organic light-emitting diodes, Org. Electron. (2015), http://dx.doi.org/10.1016/j.orgel.2015.03.009