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High thermal stability fluorene-based hole-injecting material for organic light-emitting devices

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ABSTRACT

Novel N^1,N^3,N^5-tris(9,9-diphenyl-9H-fluroen-2-yl)-N^1,N^3,N^5-triphenylbenzene-1,3,5-triamine (TFADB) was synthesized and characterized as a hole-injecting material (HIM) for organic light-emitting devices (OLEDs). By incorporating fluorene group TFADB shows a high glass-transition temperature T_g > 168 °C, indicative of excellent thermal stability. TFADB-based devices exhibited the highest performance in terms of the maximum current efficiency (6.0 cd/A), maximum power efficiency (4.0 lm/W), which is improved than that of the standard device based on 4-4′-4″Tris(N-(naphthalene-2-yl)-N-phenyl-amino)triphenylamine (2T-NATA) (5.2 cd/A, 3.6 lm/W). This material could be a promising hole-injecting material, especially for the high temperature applications of OLEDs and other organic electronic devices.

1. Introduction

In recent years, organic light-emitting diodes (OLEDs) have attracted much scientific and commercial interest due to their potential applications in full-color, flat-panel displays and space illumination [1–3]. The past two decades have seen great progress in both device fabrication techniques and materials development [4–7]. For high-performance OLEDs devices, charge injection and transport from both anode and cathode must be balanced off by excitons formed in light emission layer [8,9].

To today, traditional hole injecting materials such as poly(3,4-ethylenedioxythiophene):poly(styrene-4-sulfonate)(PEDOT:PSS) [10–12], 4-4′-4″tris(N-(naphthalene-2-yl)-N-phenyl-amino)triphenylamine (2T-NATA) [13], have been the most widely used because their good performance. However, the thermal stability of these materials do not meet requirement of practical applications. Numerous efforts have been devoted to synthesizing new HIMs with better thermal stability [14].

Fluorene compounds with inherent rigid structures have been attracting attention as organic functional materials because of their special physical and chemical properties, such as high glass transition temperatures, good solubility and their amorphous nature, which make them very promising as an approach for optic electric materials [15,16].

In this work, we designed and synthesized a new compound N^1,N^3,N^5-tris(9,9-diphenyl-9H-fluroen-2-yl)-N^1,N^3,N^5-triphenylbenzene-1,3,5-triamine (TFADB), in which the fluorene moieties were covalently incorporated to the 1,3,5-tris(diphenylamino)benzene (TDAB) core to achieve high-Tg active materials. The compounds were found to form easily stable amorphous films by either vacuum deposition or spin-coating and to function as HIM in OLEDs. The TFADB-based device shows remarkably enhanced performance, over the corresponding 2T-NATA device. The performance of the device indicates that HIM TFADB has potential applications for full-color display.

2. Experimental procedure

The manipulation involving air-sensitive reagents was performed under an inert atmosphere of dry nitrogen. The absorption spectra were obtained using a Hitachi UV 3010 spectrophotometer. The photoluminescence (PL) spectra were collected by a Horiba Jobin Yvon Fluoromax-4 spectrophotometer. Glass transition temperatures (T_g) were determined with a differential scanning calorimeter (DSC, TA instruments DSC200PC) at a heating rate of 10 °C min^{-1} under a N_2 atmosphere. Cyclic voltammetry was performed using a Princeton Applied Research model 273A potentiostat at a scan rate of 100 mV s^{-1}. The HOMO and LUMO values were estimated by using the following general equation:

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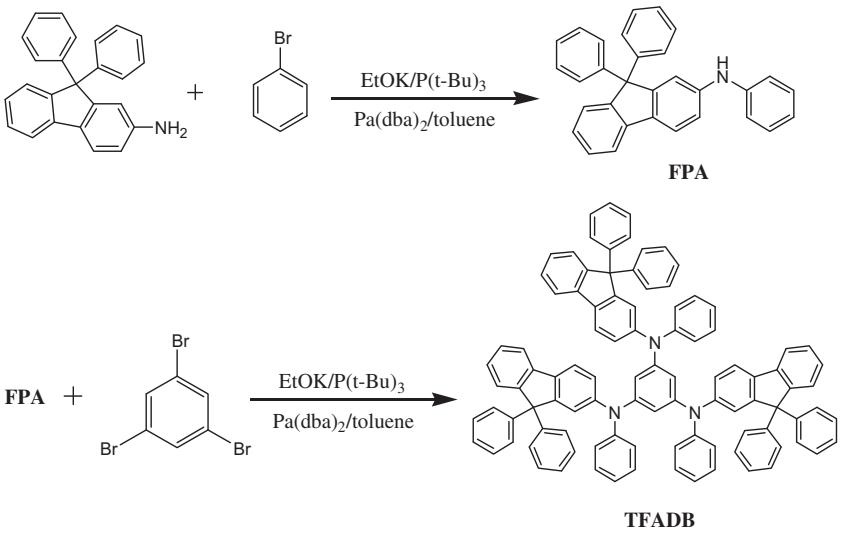

Fig. 1. Synthetic scheme of TFADB.

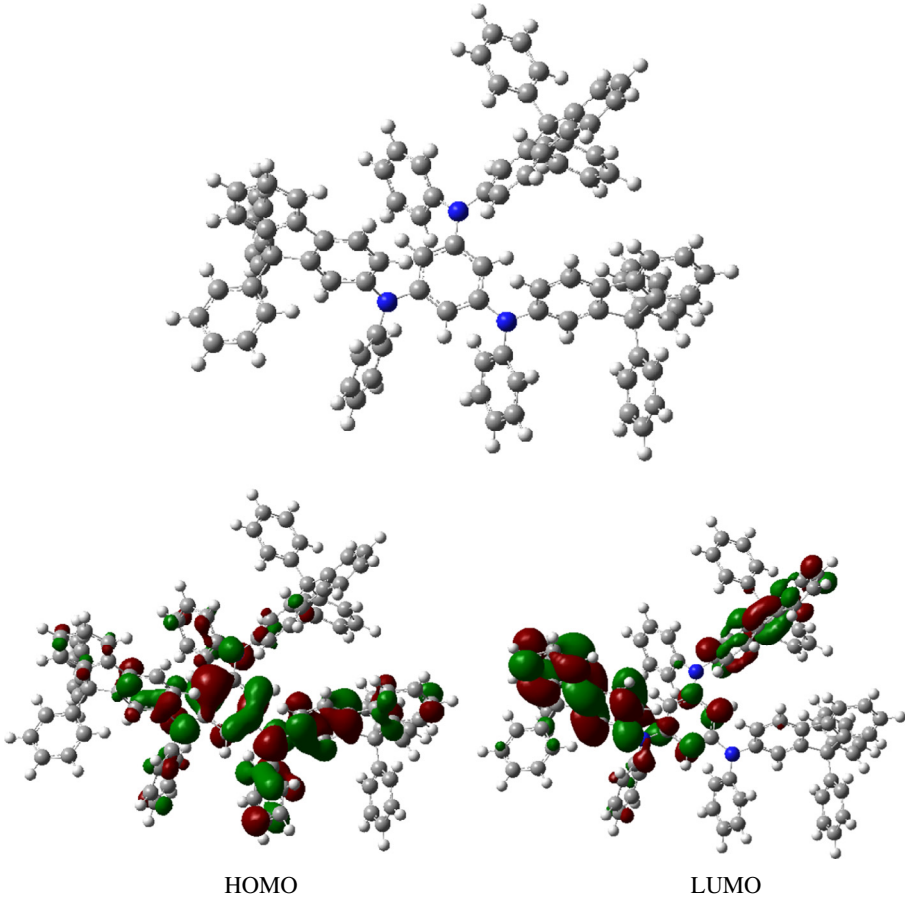

Fig. 2. The optimized geometries and the molecular orbital surfaces of the HOMOs and LUMOs for the TFADB obtained at the B3LYP/6-31G level.

$E_{HOMO} = -(qE_{ox} + 4.8)$ eV; $E_{LUMO} = E_{HOMO} + E_g^{opt}$, which were calculated with the internal standard ferrocene value of −4.8 eV with respect to the vacuum level.

2.1. (9,9-Diphenyl-9H-fluoren-2-yl)-phenyl-amine(FPA)

9,9-Diphenyl-9H-fluoren-2-ylamine (1.8 g, 5.4 mmol), bromobenzene (0.8 g, 5 mmol), potassium t-butoxide (0.84 g, 7.5 mmol), butylphosphine (0.2 ml, 0.01 mmol), tris(dibenzylideneacetone)dipalladium (0.3 g, 0.325 mmol) were added to dry Toluene (30 ml) under nitrogen. The resultant mixture was refluxed for 4 h, quenched using ice-water, extracted with chloroform, and purified by column chromatography with an eluent of ethyl acetate:petrol ether = 1:10. FPA was obtained as a beige solid (1.82 g, 76%). ^{1}H NMR (DMSO, 400 MHz): δ7.26 (m, 4H), 7.56(m, 5H), 7.686–7.874 (m, 8H), 7.94(d, 2H), 8.01(s, 3H). Anal calcd for $C_{31}H_{23}N$: C, 90.95; H, 5.62; N, 3.42. Found: C, 90.91; H, 5.58; N, 3.41.