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Novel hole transport materials based on triarylamine/naphtho[2,1-*b*] benzofunan for efficient green electroluminescent device

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ABSTRACT

Two hole transport materials, N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(naphtho[2,1-*b*]benzofuran-6-yl)phenyl)-9H-fluoren-2-amine (DFA) and N-(9,9-dimethyl-9H-fluoren-2-yl)-9,9-dimethyl-7-(naphtho[2,1-*b*]benzofuran-6-yl)-N-phenyl-9H-fluoren-2-amine (TFA) were designed, synthesized and fully characterized. The photophysical and thermal properties of these two compounds were investigated by UV–vis absorption spectra, photoluminescence spectra, thermogravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC), which indicated that DFA and TFA would be efficient hole transport materials due to their proper HOMO energy levels and excellent thermal stability. Then, green OLEDs with DFA and TFA as hole transport layer, respectively, were fabricated, NPB-based OLEDs was also prepared for comparison. It turned out that DFA- and TFA-based devices exhibited higher efficiencies than that of NPB-based device, and TFA-based device showed the best performances with current efficiency, power efficiency and external quantum efficiency of 41.68 cd/A, 32.04 lm/W and 12.04%, respectively.

1. Introduction

Organic light- emitting diodes(OLEDs) have caused extensive and strong attention since the first efficient OLED presented by the research group of Tang,[1] which is mainly attributed to their properties of small volume, fast response, high luminous efficiency and large view angle, etc.[2–5] The initial OLED was called single-layer device due to the simple constitution of anode, emitting layer and cathode. With the rapid development of scientific research, the construction of OLED has been improved. To date, organic light-emitting devices are generally fabricated of anode, hole transport layer(HTL), emitting layer, electron transport layer(ETL) and cathode. The improved OLEDs can achieve higher carrier injection efficiencies than single-layer device.[6,7] Novel OLEDs have become vital segment of flat panel displays and lighting equipment.[8–12] In the past decades, great development has been achieved in OLED materials and devices, however there are some crucial problems to be solved.[13–16]

Hole transport materials are one of the key factor for high efficient organic light-emitting diodes, which play the roles of hole transporter and electron blocker between hole injection layer and emitting layer. The proper highest occupied molecular orbital(HOMO) energy level, good thermal stability and excellent film-forming property are necessary for a satisfied hole transport material.[17–21] Triarylamine type compounds are ideal hole transport materials for OLEDs, which possess high thermal stability, appropriate HOMO energy level and good solubility.[22–25] N,N'-bis-(3-methylphenyl)-N,N'-bis-phenyl-benzidine(TPD) and N,N'-di(naphthalen-1-yl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine (NPB) are among the most familiar hole transport materials due to their excellent hole-transport property, although their poor thermal stability is an obvious defect of them.[26–28] For this reason, new

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hole transport materials need to be explored.

In this work, two triarylamine-based hole transport materials, N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(naphtho[2,1-b] benzofuran-6-yl)phenyl)-9H-fluoren-2-amine(DFA) and N-(9,9 dimethyl-9H-fluoren-2-yl)-9,9-dimethyl-7-(naphtho[2,1-b] benzofuran-6-yl)-N-phenyl-9H-fluoren-2-amine(TFA) were designed and synthesized. According to literature,[29] benzofuran moiety is an ideal electron acceptor with excellent stability, while dibenzo[*b*,*d*]furan moiety can decrease the oxidation potential and increase the number of delocalized electrons, thus enhancing the HOMO energy level and facilitating the transport of hole excitons. Thus, we guessed that the addition of benzene ring on dibenzofuran moiety can increase the molecular weight, which can improve the thermal stabilities and amorphous state of compounds, thereby realizing excellent device performance of the corresponding OLEDs. Based on the above considerations, the naphtho[2,1-*b*]benzofuran was introduced to the structure of these three compounds, which can boost the molecular planarity and thermal stability. To verify the hole transport capacity of these two triarylamine compounds, OLED devices using DFA and TFA as hole transport materials were fabricated, and evaluated by comparing with NPB based device in the same structure.

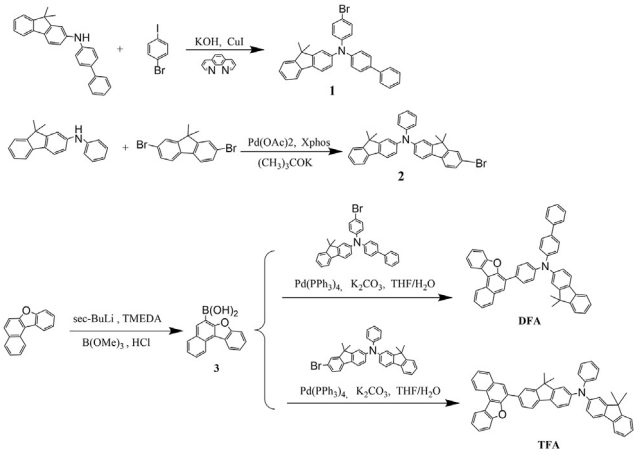
2. Result and discussion

2.1. Synthesis and characterization

The synthetic routes of the intermediates and target compounds were shown in Scheme 1. Firstly, the naphtho[2,1-*b*]benzofuran was treated with n-BuLi at −78 °C, followed by reaction with boric acid triisopropyl ester to give rise to the compound **3**. The intermediates **1** and **2** were synthesized by Buchwald–Hartwig and Ullmann reaction according to procedure as reported in literature. The target products were prepared by Suzuki coupling reaction, then purified by flash column chromatography and recrystallization method with yields of 68% and 92.53%, respectively. The molecule structures of these compounds were characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectrometry(HRMS).

2.2. Photophysical properties

The absorption and emission spectra of DFA and TFA were measured in tetrahydrofuran solution. As shown in Fig. 1 and Table 1, the stronger UV–Vis absorption peaks of DFA and TFA are similarly located at around 278 nm, which is attributed to the π-π*



Scheme 1. Synthetic routes of the compounds.

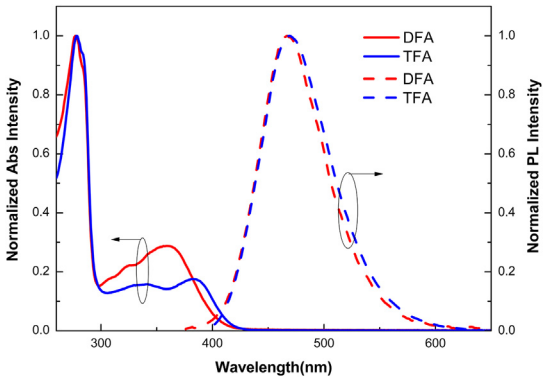


Fig. 1. Normalized UV–vis absorption and fluorescence emission spectra of the compounds in tetrahydrofuran solution at room temperature.

transitions of the conjugated aromatic segments, the weaker absorption peaks for DFA and TFA are respectively located at around 359 nm and 382 nm, which should be derived from the n-π* transitions for the extended conjugation of triarylamine and naphtho[2,1-*b*]benzofuran. The optical energy bandgaps (E_g) of these two compounds are calculated to be 3.05 eV and 3.01 eV, respectively, through calculation from the onset of the absorption spectra. The maximum PL emission peak was located at 467 nm and 469 nm for DFA and TFA, respectively. The mild red-shifted photoluminescence spectrum of TFA compared to that of DFA could be ascribed to the larger conjugation of TFA.

2.3. Thermal properties

The thermal properties of DFA and TFA were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC) under nitrogen atmosphere with a heating rate of 10 °C/min. As shown in Fig. 2a, the decomposition temperatures (T_d), which correspond to 5% weight loss, were measured to be 426 and 408 °C for DFA and TFA, respectively. Meanwhile, their corresponding glass transition temperatures (T_g) can be found from DSC curves (Fig. 2b), which were determined to be 122 and 129 °C for DFA and TFA, respectively. In addition, the whole DSC analysis of DFA and TFA are showed in Fig. S1 and Fig. S2, respectively, the first heating eliminated thermal history of these two materials, and the second heating revealed the original property of these two materials. Powder XRD did not reveal any sharp reflections (Fig. S3 and Fig. S4). Hence, XRD and the excellent thermal behaviors indicate that these two materials are amorphous and thermally stable. The decomposition (T_d) and glass transition (T_g) temperatures are summarized in Table 1.

2.4. Electrochemical properties

The electrochemical behaviors of these two compounds were investigated by cyclic voltammograms (CV) using a standard three-electrode electrochemical cell in an electrolyte solution (0.1M TBAPF6/DCM), with ferrocene as external reference. The CV curves of DFA and TFA were shown in Fig. 3, from which the highest occupied molecular orbital (HOMO) energy level of DFA and TFA were calculated to be −5.22eV and −5.19eV, respectively. The lowest unoccupied molecular orbital (LUMO) were then determined to be −2.17eV and −2.18eV, respectively, through the equation of $E_{LUMO} = E_{HOMO} + E_g$. The high HOMO energy levels imply that these two compounds would be ideal hole transport materials.