N^1,N^1,N^3,N^3-tetra([1,1′-biphenyl]-4-yl)-N^5,N^5-diphenylbenzene-1,3,5-triamine: Synthesis, optical properties and application in OLED devices as efficient hole transporting material

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A B S T R A C T

A hole-transporting material, N^1,N^1,N^3,N^3-tetra([1,1′-biphenyl]-4-yl)-N^5,N^5-diphenylbenzene-1,3,5-triamine (**TDAB-BP**), was synthesized by di([1,1′-biphenyl]-4-yl)amine and 3,5-dichloro-N,N-diphenylaniline via Buchwald—Hartwig coupling reaction. The material exhibit high hole mobility, excellent thermal and morphological stability. TDAB-based OLED device exhibited the highest performance in terms of the maximum current efficiency (9.34 cd/A), maximum power efficiency (5.89 lm/W), and maximum external quantum efficiency (6.61%), which is significantly improved than that of the standard device based on 4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl (NPB) (7.12 cd/A, 4.90 lm/W and 5.31%). Furthermore, **TDAB-BP** shows a higher decomposition temperature (T_d) of 505 °C than that of NPB (418 °C). This material could be a promising hole-transporting material, especially for the high-temperature applications of OLEDs and other organic electronic devices.

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention due to their great potential applications in both full-color display and solid state lightings [1–5]. Since the pioneering work of small-molecular OLEDs by Tang et al. [1] and polymeric OLEDs by Friend et al. [2], much effort has been paid to the development of highly efficient electroluminescent materials with good stabilities and film-forming properties [6–11]. Although considerable progress has been achieved in both material development and device fabrication techniques in the past decades [12]. It still remains a challenge to develop efficient materials to generate high performance fluorescent OLEDs. Previous works pointed to a significant role that maintaining the charge balance in an OLED structure is an important issue for improving its performance. Thus, one of the key challenges in the development of high-performance OLEDs is the rational design of a hole transporting material (HTM)

with high efficiency of hole injection and adequate hole mobility. By far, triphenylamine (TPA) derivatives have been the most widely used as hole transporting materials because of their excellent hole mobilities [13–17].

Generally, based on the high efficiency of hole injection and adequate hole mobility, it is also critical to enhance the thermal and morphological stability of the HTMs in OLEDs. So HTMs with high glass-transition temperature (T_g) is one of the essential requirements to realize high-stability OLEDs. Shirota et al. and Schmidt et al. reported several families of high T_g starburst aromatic amines as efficient HTMs in OLED fabrications, which exhibit good thermal and morphological stability [18–21]. For example, Shirota and co-workers synthesized a series of dendrimer-like amines with high hole mobility, which suppressed crystallization formation and improved the morphological stability of deposited films during the device operation. Furthermore, as charge-transporting layer in OLEDs, the materials should have high optical transparency that allows the passage of light emitted from the device to ensure a high light collecting efficiency [22]. Therefore, morphologically stable amorphous HTMs that exhibit moderate hole mobility to match the electron mobility of electron-transporting material (ETM), high

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optical transparency to visible light, and good film-forming property, are desired in realizing highly efficient and stable OLEDs. Among these, 1,3,5-tris(diphenylamino)benzene (TDAB) and its derivatives have gained increasing interest due to their significant advantages for HTMs, such as high hole mobility, low ionization potentials and high optical transparency [23].

In this work, we report a facile synthesis of a TDAB derivative (**TDAB-BP**, as shown in Scheme 1) [24] and its application as an HTM in a blue light-emitting OLED device. Compared to 4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl (NPB), **TDAB-BP** exhibits higher highest occupied molecular orbital (HOMO) energy level, and the TDAB-based device shows remarkably enhanced performance, over the corresponding NPB device. The hole mobility of the **TDAB-BP** was investigated by a hole-only device for comparison, which is nearly one order of magnitude higher than that of NPB. Furthermore, the T_d of **TDAB-BP** is much higher than that of NPB, suggesting it can be an alternative material to NPB especially in OLEDs and other devices for high-temperature operations. High efficiency has been achieved for blue light-emitting OLED device based on **TDAB-BP**. The mechanisms for enhancement in efficiency are also discussed. The performance of the device indicates that HTM **TDAB-BP** has potential applications for full-color display.

2. Experimental

2.1. Materials and methods

All the reagents and solvents used for the synthesis of **TDAB-BP** were purchased from Aldrich and Energy Chemical Company and used without further purification. Silica gel (200–300 mesh) used for chromatography was purchased from Sinopharm Chemical Reagent Co. Ltd. Host and guest materials and NPB for OLED device fabrication were purchased and purified by train sublimation.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer at 400 MHz, with tetramethylsilane (TMS) as internal standard. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario El III elemental analyzer. UV–Vis spectra were recorded using an HP-8453 UV/Vis/near-IR spectrophotometer (Agilent) with a 1 cm quartz cell. Photoluminescence (PL) spectra were carried out on a LS-55 spectrofluorometer (Perkin-Elmer). Thermal transitions were measured on DSC-60 and TG 209-F3 under a nitrogen atmosphere at a heating rate of 10 °C/min. HOMO energy was determined with a photoelectron emission yield spectrometer (Riken Keiki AC-2).

2.2. Synthesis

The designed synthetic route for the HTM **TDAB-BP** is depicted in Scheme 2.
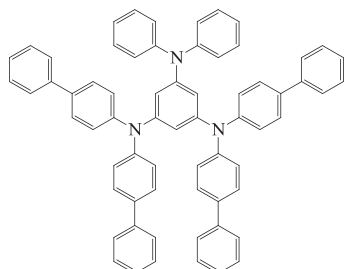
Scheme 1. Structure of **TDAB-BP**.
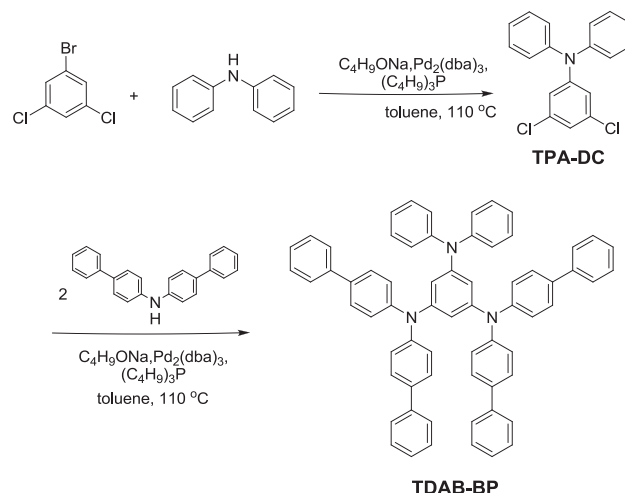
Scheme 2. Synthetic procedure of **TDAB-BP**.

2.2.1. Synthesis of 3,5-dichloro-N,N-diphenylaniline (TPA-DC)

A solution of diphenylamine (3.38 g, 20 mmol), 1-bromo-3,5-dichlorobenzene (6.8 g, 30 mmol), Pd$_2$(dba)$_3$ (0.28 g, 0.3 mmol), (C$_4$H$_9$)$_3$P (1.3 mL, 5 mmol) and C$_4$H$_9$ONa (2.9 g, 30 mmol) in toluene (200 mL) was heated to reflux under argon for 3 h. After being cooled to room temperature, the solvent was then removed by rotary evaporation. Silica gel column chromatography (petroleum ether) gives a pale yellow solid (4.14 g, 66.1%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.42–7.38 (m, 4H), 7.22–7.14 (m, 6H), 7.08 (s, 1H), 6.72 (s, 2H). ^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm): 149.9, 145.6, 134.5, 130.0, 125.7, 125.1, 119.9, 118.1 (Figs. S1 and S2).

2.2.2. Synthesis of N^1,N^1,N^3,N^3-tetra([1,1′-biphenyl]-4-yl)-N^5,N^5-diphenylbenzene-1,3,5-triamine (TDAB-BP)

A solution of di([1,1′-biphenyl]-4-yl)amine (11.2 g, 35 mmol), 3,5-dichloro-N,N-diphenylaniline (4.70 g, 15 mmol), Pd$_2$(dba)$_3$ (0.35 g, 0.38 mmol), (C$_4$H$_9$)$_3$P (8 mmol, 2 mL) and C$_4$H$_9$ONa (46 mmol, 4.4 g) in toluene (200 mL) was heated to reflux under argon for overnight. After being cooled to room temperature, the precipitate was filtered, washed with ethanol (200 mL), and dried in vacuum. Silica gel column chromatography (petroleum ether: ethyl acetate = 3:1) affords a white solid (10.55 g, 79.6%). m.p. 284–285 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.41 (d, J = 8.1 Hz, 8H), 7.39 (d, J = 8.4 Hz, 8H), 7.37–7.35 (t, J = 7.6 Hz, 8H), 7.30–7.29 (t, J = 7.3 Hz, 4H), 7.22–7.15 (m, 12H), 7.08 (d, J = 8.2 Hz, 4H), 6.94–6.92 (t, J = 7.3 Hz, 2H), 6.54 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm): 149.2, 148.8, 147.3, 146.4, 140.7, 135.5, 129.1, 128.8, 127.8, 126.8, 126.7, 124.1, 124.0, 122.8, 114.6, 114.5 (Figs. S3 and S4); Elemental analysis for C$_{66}$H$_{49}$N$_3$% Calc.: C 89.66, H 5.59, N 4.75; % found: C 89.61, H 5.58, N 4.78.

2.3. OLED device fabrication and measurements

An OLED device was fabricated with a configuration of ITO (150 nm)/HTMs (90 nm)/NNA: MPC 5wt% (30 nm)/Be(Bq)$_2$ (20 nm)/ LiF (0.8 nm)/Al (80 nm) as shown in Fig. 1, together with the molecular structures of the organic materials used. In device A, TDAB-BP was used as the HTM, NNA: MPC (20:1 by weight) as emitting material, Be(Bq)$_2$ as ETM and LiF as electronic injection material (EIM). In device B, NPB was used as HTM to replace TDAB-BP. Where N^6,N^6,N^{12},N^{12}-tetrakis(3,4-dimethylphenyl)chrysene-6,12-diamine (MPC) was used as guest material. 9-(naphthalen-1-yl)-10-(naphthalen-2-yl)anthracene (NNA) was used as host material. It is noted that the compound NNA exhibits bipolar properties, its electronic