Bipolar Molecule as an Excellent Hole-Transporter for Organic-Light Emitting Devices

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A new bipolar molecule containing hole-transporting and electron-transporting moieties has been synthesized and characterized. The compound, 4,4′,4″-tris(8-quinoline)-triphenylamine (TQTPA) exhibited good thermal stability and luminescence properties. A single-layer TQTPA light-emitting device shows sky blue emission with a low turn-on voltage of 2.8 V, a maximum brightness greater than 7500 cd/m^2 at 10 V, and a maximum current efficiency of 1.6 cd/A. Bipolar transport properties of TQTPA were investigated via the hole-only and electron-only devices. Using the bipolar molecule as a hole-transporter, a typical bilayer device with a configuration of ITO/TQTPA (60 nm)/Alq$_3$ (50 nm)/LiF (0.5 nm)/MgAg yields a maximum current efficiency of 5.6 cd/A (with Alq$_3$ emission), which is much better (50% higher) than that of the prototypical NPB-based device (3.8 cd/A) with a similar device structure.

Introduction

Since the first application of a multilayer thin-film structure in organic light-emitting devices (OLEDs) by Tang et al., OLEDs have attracted a great deal of attention because of its wide applications in full-color flat-panel displays and solid-state lightings.[1,2] Maintaining a balance between electron and hole currents in OLEDs is an important factor for achieving high device efficiency.[3] Various strategies have been developed to meet the requirement of charge balance, which includes the employment of multilayered structures and the introduction of bipolar or multifunctional molecules.[4−7] Bipolar molecules with both hole- and electron-transporting properties have attracted much interest in OLEDs for the new possible device configurations they offer. For example, simply structured devices with double layers or even a single organic layer can be achieved using bipolar molecules.[6−11] It is well-recognized that the mobility of holes in most hole-transporting materials (HTMs) is much higher than that of electrons in typical electron transporting materials (ETMs).[2,12] Consequently, holes from the anode tend to transport easily to the ETM and even further to the cathode without recombining efficiently with electrons in the emitting layer. This will largely decrease the current efficiency of the devices.[3] The use of a material with a hole drift mobility lower than NPB as HTM could lead to better charge balance and higher charge recombination efficiency.[13−15]

In this paper, we report the synthesis and characterization of a novel bipolar molecule, 4,4′,4″-tris(8-quinoline)-triphenylamine (TQTPA). The compound exhibits good thermal stability with a glass transition temperature (T_g) of 130 °C. The combination of the hole-transporting triphenylamine moiety and the electron-transporting quinoline moiety in TQTPA gives it bipolar charge transport property. An efficient blue-emitting device based on a single layer of TQTPA has been achieved with a turn-on voltage of 2.8 V, a maximum brightness greater than 7500 cd/m^2 at 10 V, and

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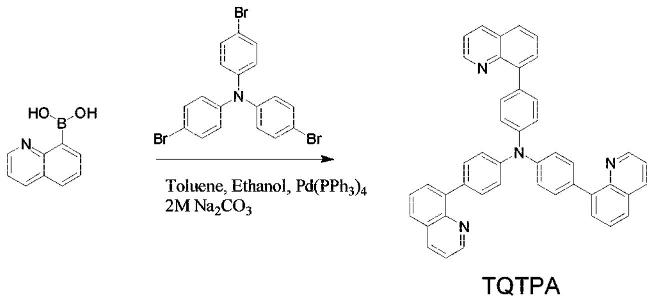

Figure 1. Molecular structure and the synthetic route of TQTPA.

a maximum current efficiency of 1.6 cd/A. Bipolar transport properties of TQTPA were investigated via its hole-only and electron-only devices. By using the bipolar molecule as hole-transporting material in a typical two-layer configuration of ITO/TQTPA (60 nm)/Alq_3 (50 nm)/LiF (0.5 nm)/MgAg, the device gave green emission with a maximum luminescence efficiency of 5.6 cd/A and 4.0 lm/W. The performance is much higher (50% higher) than that of the prototypical NPB-based device (3.8 cd/A) with a similar device structure.

Experimental Details

Material Synthesis. The compound (TQTPA) was synthesized according to the procedures shown in Figure 1 using a Suzuki coupling reaction. All solvents used in the reaction were purified by routine procedures. Other reagents in the scheme were used as received from commercial sources.

4,4′,4″-Tris(8-quinoline)-triphenylamine (TQTPA). 4,4′,4″-Tris-bromo-triphenylamine (5 mmol), 8-quinoline boronic acid (17 mmol), Pd $(PPh_3)_4$ (0.5 mmol), aqueous Na_2CO_3 (2.0M, 15 mL), ethanol (10 mL), and toluene (30 mL) were mixed in a flask. The mixture was degassed and the reaction was refluxed for 24 h under nitrogen. After being cooled, the solvent was evaporated under a vacuum and the product was extracted with dichloromethane (CH_2Cl_2). The CH_2Cl_2 solution was washed with water and dried with $MgSO_4$. Evaporation of the solvent, followed by column chromatography on silica gel (petroleum ethoer/CH_2Cl_2) yielded a pale yellow powder. Yield: 85%. Mp: 275 °C. Ms: *m/z* 627 (M^+). ^{1}HNMR ($CDCl_3$, 300 MHz): δ 7.42−7.46 (m, 9H), 7.59−7.64 (t, 3H), 7.69−7.74 (m, 6H), 7.79−7.83 (m, 6H), 8.20−8.24 (m, 3H), 8.99−9.01 (m, 3H). Anal. Calcd for $C_{45}H_{30}N_4$: C, 86.24; H, 4.82; N, 8.94. Found: C, 86.67; H, 4.80; N, 8.75.

Measurements and OLED Fabrication. Absorption and fluorescence spectra were recorded using a Perkin-Elmer Lambda 2S UV−vis spectrophotometer and a Perkin-Elmer LS50B Luminescence spectrophotometer, respectively. Glass transition temperatures (T_g) were determined with a differential scanning calorimeter (DSC, TA instruments 2910MDSC) at a heating rate of 5 °C min^{-1}. Decomposition temperature (T_d) was obtained from TGA measurements using a TA instruments Q50 TGA with a heating rate of 20 °C/min. The highest occupied molecular orbital (HOMO) values were measured directly using ultraviolet photoelectron spectroscopy (UPS), while the lowest unoccupied molecular orbital (LUMO) values were estimated by subtracting from the HOMO values the lowest energy absorption edges of the UV absorption spectra.

OLEDs were fabricated by vacuum deposition on ITO glass substrates with a sheet resistance of 30 Ω/square. Before deposition, the ITO substrate was carefully cleaned, dried in an oven at 120°C for 1 h, and finally treated with UV-ozone and loaded into a deposition chamber. The devices were fabricated by evaporating organic layers onto the ITO substrate sequentially at an evaporation rate of 2−4 Å/s and a vacuum better than 5 × 10^{-6} mbar. The Mg:Ag alloy cathode was prepared by coevaporation of Mg and Ag at a volume ratio of 10:1. EL spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer and the current−voltage−luminescence characteristics with a computer-controlled Keithley 236 Source-Meter under ambient condition.

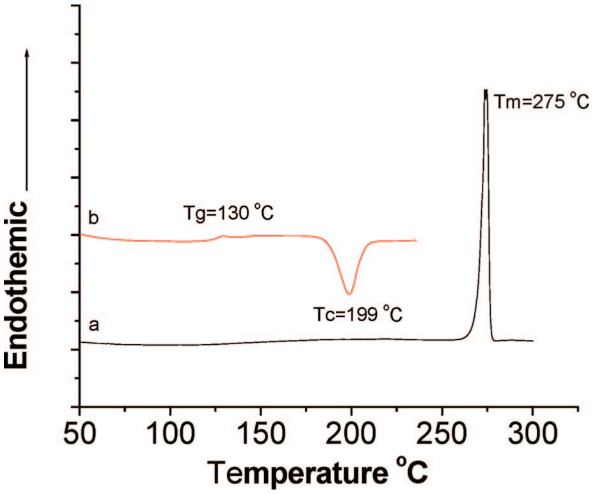

Figure 2. DSC curves of TQTPA. (a) first run, (b) second run.

Results and Discussion

The chemical structure and synthetic route of 4,4′,4″-tris(8-quinoline)-triphenylamine (TQTPA) are shown in Figure 1. 4,4′,4″-tris-bromo-triphenylamine and 8-quinoline boronic acid are commercially obtained and the final product TQTPA can be easily obtained by using one step Suzuki coupling reaction.[16] TQTPA was isolated and purified by column chromatography on silica gel; recrystallized from chloroform and ethanol with good yields (yields: 85%) and high purity. The molecular structure of TQTPA was confirmed with ^{1}H nuclear magnetic resonance (HNMR), mass spectrometry (MS), and element analysis.

The thermal properties of TQTPA were characterized by TGA and DSC measurements. TQTPA is thermally stable up to 420 °C as shown by its high decomposition temperatures (T_d) in the TGA measurements. DSC scan results of TQTPA are shown in Figure 2. The sample melted at 275 °C to give an isotropic liquid in the first run of the DSC measurement. Upon cooling, the isotropic liquid changed into a glassy state. As the glassy sample was reheated for the second run, a glass transition was observed at 130 °C, which is defined as the glass transition temperature (T_g) of TQTPA. Upon further heating beyond T_g, an exothermal crystallization was observed at 199 °C. The T_g of TQTPA is much higher than that of the commonly used hole-transporting material (e.g., 98 °C for NPB).[2]

Figure 3 shows the absorption and fluorescence spectra of the compound in dilute *n*-hexane solution and in film. The absorption spectrum has two major bands. The band from 350 to 400 nm can be attributed to transitions in the three quinoline groups, whereas the absorption bands at 240−300 nm should come from the n−π* transition of

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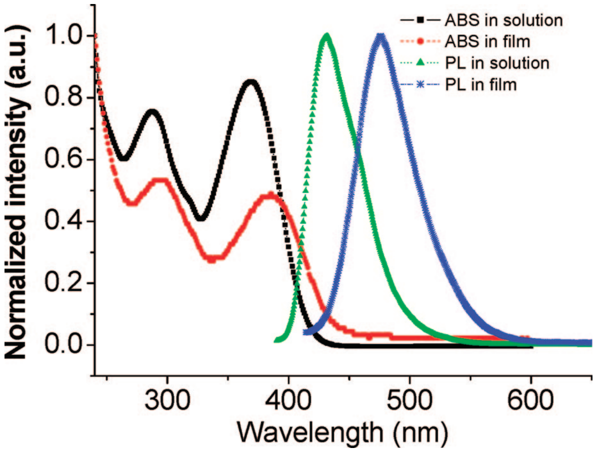

Figure 3. Absorption and fluorescence spectra of TQTPA in solution and in film.

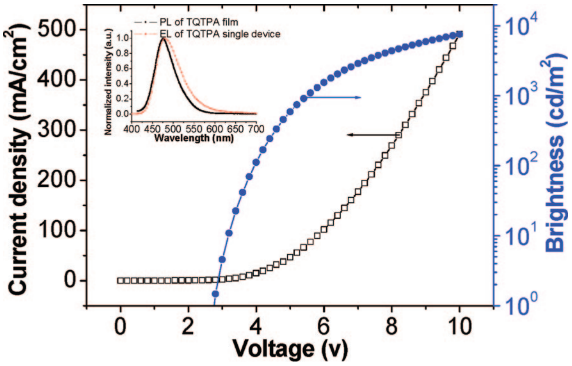

Figure 4. Current density−voltage and brightness−voltage characteristics of TQTPA-based single-layer device: ITO /TQTPA (100 nm)/LiF (0.5 nm)/ Mg:Ag. The inset is the EL spectrum of the single-layer device and the PL of TQTPA film.

triphenylamine moiety. The compound exhibits blue emission with a maximum peak at 431 nm in solution and 476 nm in film, respectively. Other than red-shifts due to intermolecular interactions in solid, the profiles of both absorption and photoluminescence (PL) spectra of the compound in films are almost identical to those in solution.

The incorporation of the hole-transporting triphenylamine moiety and the electron-transporting quinoline moiety in TQTPA is expected to lead to bipolar charge transporting property for both holes and electrons. Moreover, similar to most other triphenylamine compounds, TQTPA has a HOMO (5.3 eV) close to the work function of oxygen plasma-treated ITO and thus allows efficient hole injection. On the other hand, the incorporation of the quinoline moiety can potentially lead to efficient electron injection and electron transport. Thus, TQTPA can potentially be used as a multifunctional emitter in a single-layer OLED.

A single-layer TQTPA device was fabricated with a configuration of ITO/TQTPA (100 nm)/LiF (0.5 nm)/ Mg: Ag (200nm). $I-V-L$ characteristics of the device are shown in Figure 4. The inset of Figure 4 shows the EL and PL spectra of the device and TQTPA film, respectively. The device shows a sky blue emission with a maximum EL peak at 481 nm and CIE coordinates of ($x = 0.17$, $y = 0.32$). It can be seen that the PL and the EL spectra are almost identical, indicating that the EL of the device can be attributed to the emission from the singlet excited-state of TQTPA. The turn-on voltage (defined as the driving voltage required to give a brightness of 1 cd/m^2) of the device is only 2.8 V and the device achieves a maximum brightness of over 7500 cd/m^2 at 10 V. The maximum efficiency of the single-layer device is 1.6 cd/A (0.8 lm/W).

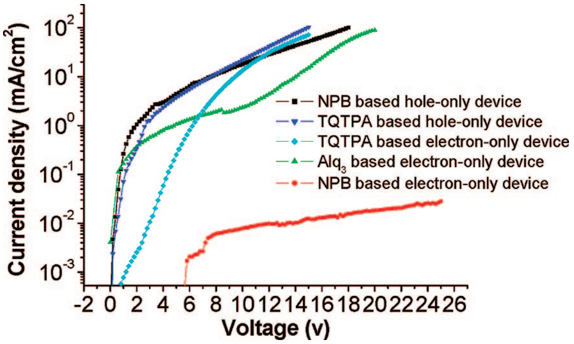

Figure 5. $I-V$ characteristics of the hole-only devices and electron-only devices.

The good performance of the single-layer device shows that TQTPA may have bipolar charge transport abilities. For further confirmation, hole-only and electron-only devices were fabricated and characterized. For the hole-only devices, the organic layer with a thickness of 100 nm was sandwiched between the ITO anode and Ag cathode.[17−19] Both electrodes have a work function close to the HOMO level of the organic materials to prevent the electron injection from the Ag cathode. For comparison, NPB-based hole-only device with a similar device structure was also fabricated in the same conditions. Figure 5 shows the $I-V$ characteristics of the hole-only devices. The hole-injection properties from ITO to both organic materials are almost identical for TQTPA and NPB. This is consistent with their similar HOMO energy positions. The hole current in TQTPA-based hole-only device is lower than that in NPB-based hole-only device at applied voltages lower than 8 V, which implies lower hole transport of TQTPA than NPB. The electron-only device with a configuration of ITO/Mg:Ag (25 nm)/TQTPA (100 nm)/Mg: Ag (100 nm) was fabricated to investigate the electron injection and transport ability of TQTPA.[20] NPB- and Alq_3-based electron-only devices were also fabricated with the same structure and their $I-V$ curves are shown in Figure 5 for comparison. It can be seen that the electron injection property into Alq_3 is better than into TQTPA due to the lower LUMO level of Alq_3 (Alq_3, 3.1 eV, TQTPA, 2.6 eV). The electron current of TQTPA-based electron-only device is higher than that of the Alq_3 and the NPB electron-only devices at applied voltages higher than 6 V, which suggests better electron transport of TQTPA than Alq_3 and NPB. The above results confirm that TQTPA has good bipolar charge transport properties.

The results thus suggest TQTPA may serve as a better hole-transporting material (HTM) because of a lower hole drift mobility than NPB, which leads to better charge balance.

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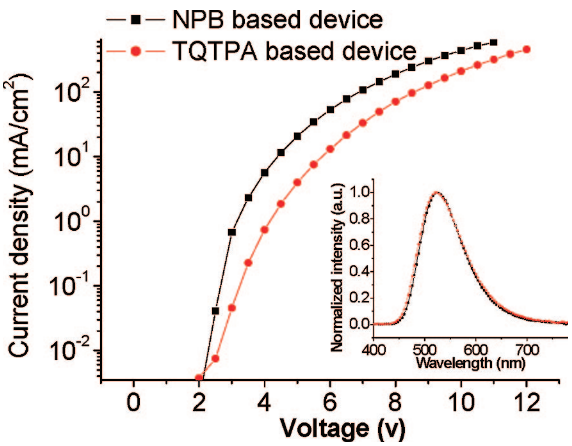

Figure 6. Current density−voltage characteristics of the two two-layer devices. The inset is the EL spectra of the two devices.

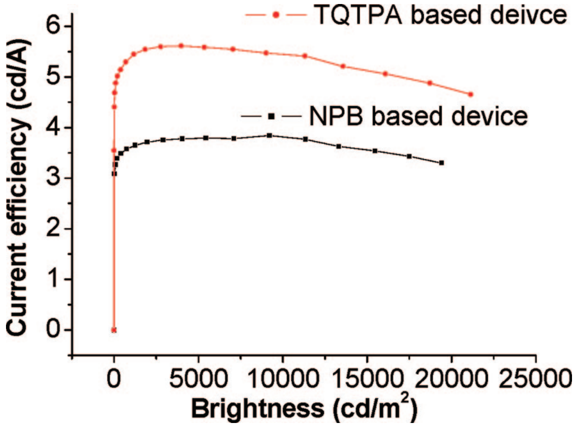

Figure 7. Current efficiency vs brightness of the two two-layer devices.

This feasibility is checked by fabricating a typical two-layer device with a structure of ITO/TQTPA (60 nm)/Alq_3 (50 nm)/LiF (0.5 nm)/MgAg. For comparison, a typical and widely used hole transporter NPB has been chosen and a conventional ITO/ NPB (60 nm)/Alq_3 (50nm)/LiF (0.5 nm)/ MgAg device was fabricated at the same conditions. Figure 6 shows the current density−voltage characteristics of the two devices. It clearly reveals that the current density of the TQTPA-based device is much lower than that of the NPB-based device at all voltages. The EL spectra of the two devices (inset of Figure 6) show identical Alq_3 emission centered at 524 nm. This confirms that TQTPA works as an HTM as NPB does in the two-layer device.

Figure 7 shows the current efficiency of the two devices. The NPB-based device gives a maximum current efficiency of 3.8 cd/A, whereas the maximum current efficiency of TQTPA-based device is 5.6 cd/A, which is nearly 50% higher than NPB-based device. The maximum power efficiency of the TQTPA-based device is 4.0 lm/W, which is again higher than that (3.0 lm/W) of the NPB-based device. Because the two devices have the same structure except for the different hole-transporting layer, the significant performance enhancement in the TQTPA-based device should be attributed to a better hole injection and/or a slower hole transport. Because of the similar HOMO levels of TQTPA (5.3 eV) and NPB (5.4 eV), the hole injection barrier at the ITO/TQTPA and ITO/NPB contacts are expected to be similar. Thus, a slower hole mobility in TQTPA than NPB is likely to be the main factor, which leads to a better balance in charge recombination in the Alq_3 layer and thus a higher efficiency. The lower hole mobility of TQTPA might be due to the fact that there is only one electron-donor moiety in the molecule.[13,14,19] Moreover, although the incorporation of the electron-transporting quinoline moiety into the molecule leads to the bipolar property of TQTPA, it could also decrease the hole mobility.[10]

Conclusion

In summary, a bipolar molecule, TQTPA, containing hole-transporting and electron-transporting moieties has been synthesized and characterized. This compound exhibited desirable thermal stability and luminescence property. A single-layer TQTPA-based OLED gave sky blue emission with a maximum brightness over 7500 cd/m^2 at 10 V, and a current efficiency of 1.6 cd/A. The bipolar transport properties of TQTPA were investigated via its hole-only and electron-only devices. Moreover, a typical two-layer device using TQTPA as hole-transporting material achieved a maximum current efficiency of 5.6 cd/A, which is significantly better than that of a similarly structured NPB-based device. In sight of its simple synthesis, its better thermal stability (T_g = 130 °C) than that of NPB (T_g = 98 °C), and the much better performance of TQTPA-based device, TQTPA holds good potential for replacing NPB for applications as a hole-transporting material.

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