High T_g Fluorene-based Hole-transporting Materials for Organic Light-emitting Diodes

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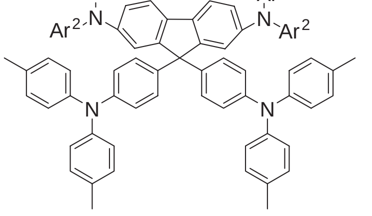
A new series of fluorene-based hole-transporting materials, 9,9-bis[4-(di-*p*-tolylamino)phenyl]-2,7-bis(diphenylamino)fluorene (**1**), 9,9-bis[4-(di-*p*-tolylamino)phenyl]-2,7-bis(di-*p*-tolylamino)fluorene (**2**), 9,9-bis[4-(di-*p*-tolylamino)phenyl]-2,7-bis-(2-naphthylphenylamino)fluorene (**3**), and 9,9-bis[4-(di-*p*-tolylamino)phenyl]-2,7-bis(9-carbazolyl)fluorene (**4**), was prepared and employed in the fabrication of organic light-emitting devices (OLEDs). These materials were designed to have bulky triarylamine moieties at the C-9 position, which provides them with excellent thermal stability and high glass-transition temperatures ($T_g = 139$–$171\,^\circ C$). **1** and **3** are comparable to 1,4-bis(1-naphthylphenylamino)biphenyl (NPB) in terms of device performance (maximum luminence and current efficiency) in a standard hole-transporting layer (HTL)/tris(8-hydroxyquinolino)aluminum (Alq_3) double-layer device, but are superior to NPB in terms of higher glass-transition temperatures ($T_g =$ 139 and 145 °C, respectively), while **2** shows higher luminance and current efficiency as well as T_g (140 °C) than those of NPB (100 °C).

Organic light-emitting diodes (OLEDs) have attracted much attention because of their promising application in full-color flat-panel displays in recent years[1,2] since the initial work by Tang et al.[3] For practical applications, high efficiency and good durability are particularly important among the device performances. The morphological changes caused by the Joule heating during the operation, especially in the hole-transporting layer (HTL),[4,5] seem to be one reason of degradation[6,7] which reduce the stability of OLEDs. Therefore, thermally and morphologically stable organic hole-transporting materials (HTMs) are required to realize the practical application of OLEDs. Many endeavors[8–13] have been made to develop new HTMs with high stabilities. For this reason, a new series of 9,9-bis(triarylamine)-substituted fluorene-based triaryldiamines (**1**–**4**) with excellent thermal and morphological stabilities have been synthesized (Scheme 1),[14] and the use of these triaryldiamines as HTMs in OLEDs are studied.

Glass-transition temperatures (T_g), melting temperatures (T_m), and crystallization temperatures (T_c) concerning new triaryldiamines determined by differential scanning calorimetry (DSC) are summarized in Table 1. Obviously, T_g values (139–171 °C) of compounds **1**–**4** are higher than that of 1,4-bis(1-naphthylphenylamino)biphenyl (NPB, $T_g = 100\,^\circ C$)[11] widely used as HTM in OLEDs. Meanwhile, TGA measurements for **1**–**4** revealed that no decomposition was found within 400 °C.



1: $Ar^1 = Ar^2 =$ Ph
2: $Ar^1 = Ar^2 =$ p-Tol
3: $Ar^1 =$ Ph, $Ar^2 =$ 2 -Np
4: Ar^1, $Ar^2 =$ carbazolyl

Scheme 1. Triaryldiamines **1**–**4**.

The highest occupied molecular orbital (HOMO) energy levels of **1**–**4** were determined by cyclic voltammetry (CV) in a supporting electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in THF using ferrocene as the internal standard. The HOMO–LUMO (lowest unoccupied molecular orbital) band gap was calculated from the absorption edge of the absorption spectrum of a thin film on quartz substrate. The LUMO energy levels were calculated by subtraction of the optical band gap from the HOMO energy levels. The results are also listed in Table 1.

Double-layer device I–IV with a configuration of indium-tin-oxide (ITO) (30 Ω)/triaryldiamines **1**–**4** (50 nm)/Alq_3 (45 nm)/Al (100 nm), in which **1**–**4** were used as HTMs and Alq_3 used as electron-transporting material (ETM) and emitter. A standard device with the same configuration using NPB as HTM was also prepared under identical conditions for comparison.

Devices I–IV have almost the same emission peaks with the NPB standard device from Alq_3 (Figure 1), suggesting that the charge recombination is localized in the Alq_3 layer and triaryldiamines **1**–**4** act as hole transporter without causing exciplex for-

Table 1. Thermal and electrochemical properties of **1**–**4**

Compound	T_g /°C	T_m /°C	T_c /°C	E_{HOME} /eV	E_{LUMO} /eV	E_{GAP} /eV
1	139	281	187	5.1	2.0	3.1
2	140	267	196	5.0	2.0	3.0
3	145	259	227	5.1	2.1	3.0
4	171	371	221	5.3	1.9	3.4

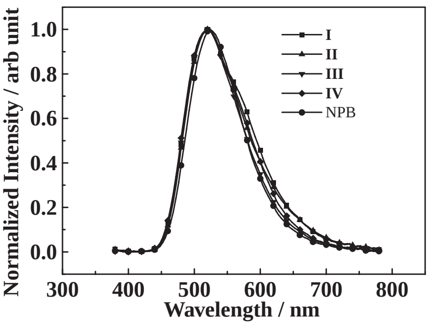


Figure 1. Normalized EL spectra of ITO/HTL/Alq_3/Al devices.

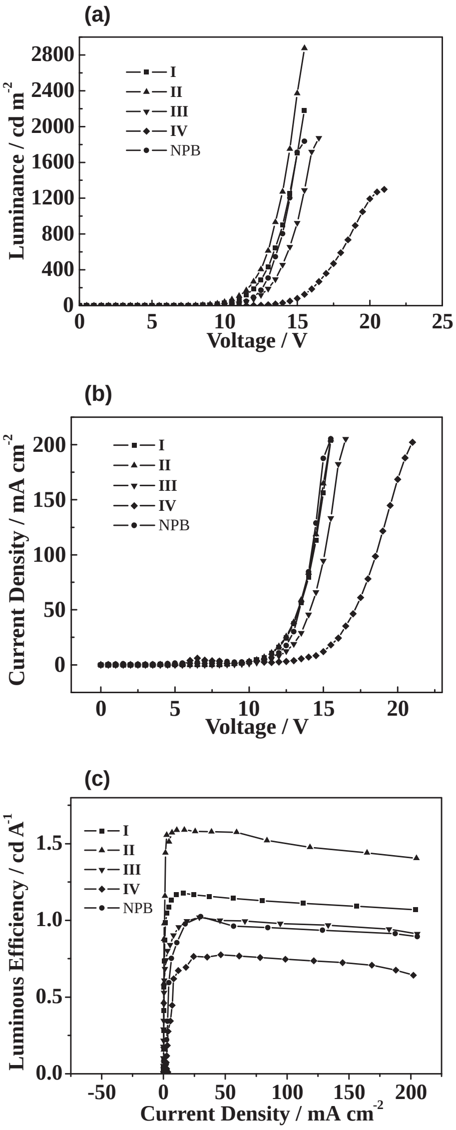


Figure 2. (a) Luminance–voltage, (b) current density–voltage, and (c) current efficiency–current density characteristics of ITO/HTL/Alq$_3$/Al devices.

mation at the interface with Alq$_3$. This could be attributed to the proper HOMO energy levels of **1**–**4**, which is favorable for hole injection from ITO to HTL and then to the Alq$_3$ layer.

Figure 2 shows the luminance–voltage (L–V), current–voltage (*I*–*V*) characteristics, and the current efficiency of the devices. The current density and luminance of devices I and III are comparable to those of NPB standard device, while device II are superior to NPB standard device in terms of higher luminance. Device I has a slightly higher brightness of 2180 cd/m^2 at 15.5 V than NPB standard device (1840 cd/m^2, 15.5 V), while device II has a luminance of 2870 cd/m^2 at 15.5 V, which is 55 percent higher than that of NPB device.

The current efficiency–current density characteristics (Figure 2c) indicated that device I has a slightly higher current efficiency (maximum, 1.17 cd/A, 290 cd/m^2) than that of NPB device (1.01 cd/A, 310 cd/m^2), while device II was obviously higher (1.59 cd/A, 270 cd/m^2). This suggest that new triaryldiamine **1** is at least as good as NPB when used as HTM in OLEDs but expected to be thermally more stable based on its higher T_g value, while **2** has both higher performance in double-layer HTL/Alq$_3$ devices and better stability than NPB.

In conclusion, these new materials were comparable to NPB when used in OLEDs as HTMs (except for **4**) in terms of luminence and current efficiency, while **2** shows obviously higher luminance and current efficiency than NPB. Because of their higher T_g than NPB, they are expected to be potential candidates for application as HTMs in OLEDs. Since the device configuration has not been optimized in the present work, further improvement can be expected by fine-tuning of device structures.

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14 Synthesis and characterization data of these new compounds are available from Supporting Information.

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