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High-T_g *N*-Triarylamine Derivatives as a Hole Injecting Layer in Organic Light-Emitting Diodes

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N-triarylamines, m-MTDAPB and 1-TNAPB, with high glass transition temperature and hole affinity were evaluated as a hole injection layer (HIL) in organic light-emitting diodes (OLEDs) with the configuration of ITO/N-triarylamine/α-NPD (HTL)/Alq_3 (EML)/LiF/Al. The performance of N-triarylamines as HIL in OLEDs was investigated in terms of turn-on voltage, luminescence, color purity, etc. Better EL performance was observed in OLED with m-MTDAPB as HIL, showing turn-on voltage of 6 V and maximum luminescence of 2,976 cd/m^2 at 13.5 V. This might be attributed to well-matched HOMO energy offsets at the interfaces of anode/HIL/HTL layers in OLED with the configuration of ITO/m-MTDAPB/α-NPD (HTL)/Alq_3 (EML)/LiF/Al, compared to OLED with 1-TNAPB as HIL.

Keywords: hole injecting layer; OLED; starburst; *N*-triarylamine

INTRODUCTION

Organic light-emitting diodes (OLEDs) hold the potential to make affordable full color large flat panel displays on low cost [1,2]. The past two decades have seen great progress in both device fabrication techniques and materials development [3]. However, further improvement in both the efficiency and durability of OLEDs is still necessary.

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It has been generally accepted [4] that it is essential to balance the hole and electron injected into the emitting layer (EML) of the OLEDs to improve the electrolumineescence efficiency and life time. Since electron transporting materials with higher electron transport mobility are not available at present to match the existing hole transporting materials, optimization of the OLEDs using hole injecting and transporting materials with moderate hole mobility to match the present electron transporting materials would be an alternative way to balance the hole and electron into the EML. In addition, all the organic layers forming the OLEDs should have glass transition temperature (T_g) as high as possible, since the individual layer that has low T_g is likely to limit the thermal stability of the OLEDs.

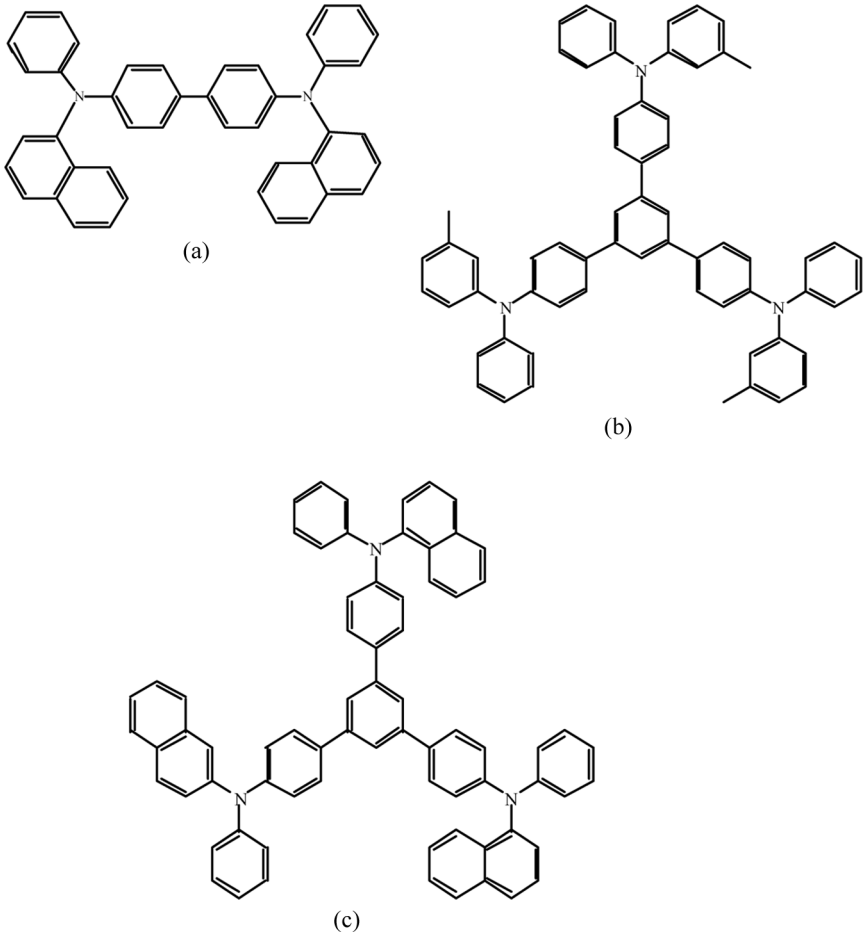
To improve hole injection from the anode (e.g., ITO) into an organic layer, i.e., hole transporting layer (HTL) or EML, is a challenge for designing efficient OLEDs. The use of a hole injecting layer (HIL) placed between the anode and the hole transporting layer (HTL) is commonly adopted in order to increase hole injection. Materials for the use as HIL will be characterized by HOMO level in between the work function of ITO and HOMO level of HTM. Copper phthalocyanine (CuPc) with good thermal property has been the most commonly used HIL to enhance hole injection [5,6]. However, the use of CuPc was sometimes limited due to its absorption behavior in the range of visible region.

In this paper, we report high-T_g *N*-triarylamine derivatives, i.e., 1,3,5-tris[4-{3-methylphenyl(phenyl)amino}phenyl]benzene (*m*-MTDAPB) and 1,3,5-tris[4-{1-naphthyl(phenyl)amino}phenyl]benzene (1-TNAPB), and their application as HIL in OLEDs with a configuration of ITO/HIL/α-NPD/Alq_3/LiF/Al, where α-NPD and Alq_3 were used as HTL and EML, respectively.

EXPERIMENTAL

Materials

Tri(8-hydroxyquinolate)aluminum (Alq_3) and lithium fluoride (LiF) were obtained from Tokyo Kasei Co. Aluminum was purchased from CERAC, USA. Indium-tin oxide (ITO) coated glass with a sheet resistance of 50 Ω/sq was obtained from Sin'an SNP Co. *N*-Triarylamine derivatives such as *m*-MTDAPB, 1-TNAPB, and *N*,*N*′-di(1-napthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (α-NPD) were successfully synthesized via Ullmann condensation [7]. (Scheme 1). Synthesized *N*-triarylamine derivatives were sublimed twice prior to use.



SCHEME 1 Chemical structures of (a) α-NPD, (b) *m*-MTDAPB, and (c) 1-TNAPB.

Characterization

Differential scanning calorimeter (DSC, Model 2010 DSC, TA Instrument) was performed using a heating scan rate of 10°C/min in the temperature range from 30°C to 350°C. A nitrogen flow of 50 mL/min was maintained through the sample holder assembly during all runs and the sample size was about 5–10 mg. Each sample was first scanned from 30°C to 350°C, and then cooled down fast until 30°C. The melting temperature (T_m) and the glass transition temperature (T_g) of samples were taken as the peak temperature of the melting

endotherm and as the midpoint of the specific heat jumps, respectively, in the second heating scan. The crystallization temperature (T_c) of samples was taken as the peak temperature of the exotherm in the second heating scan. UV-visible absorption spectra were taken with Shimadzu UV-2100. The photoluminescence (PL) spectra excited by He-Cd laser at 325 nm were monitored by Optical Multichannel Analyzer (Laser Photonics, OMA system). The ionization potential (IP) was measured by a photoelectron spectroscopy (Riken Keiki AC-2). Electroluminescence (EL) spectra were measured by using Spectroscan PR 704 (Photoresearch Inc). Current-luminescence-voltage (*I-V-L*) profiles of devices were obtained by using dc power supply connected Model 8092A Digital Multimeter and luminance meter (Minolta LS-100). Transient fluorescent decay (Model: Fluo Time 200, PicoQuant) was measured, and data of fluorescent life time was fitted with the program (Fluo Time 4.0, PicoQuant).

Fabrication of OLEDs

ITO coated glass was cut into 5.0 cm × 5.0 cm, and electrode area was prepared by photo-etching technique. It was sequentially cleaned in an ultrasonic bath of acetone, methanol, and mixture of isopropyl alcohol and water solution. OLEDs were fabricated with a configuration of ITO/HIL/α-NPD (50 nm)/Alq_3 (40 nm)/LiF (2 nm)/Al (140 nm), where α-NPD as a hole transporting layer (HTL) and Alq_3 as an emitting layer were used. For the devices, a hole injecting layer (HIL) material such a *m*-MTDAPB or 1-TNAPB was first vacuum deposited, and then HIL of α-NPD and an emissive layer of Alq_3 were deposited sequentially. Finally LiF and Al were successively deposited under pressure $<10^{-6}$ torr. The active area of the OLEDs was 2 mm × 2 mm.

RESULTS AND DISCUSSION

Two different types of high-T_g *N*-triarylamines, *m*-MTDAPB and 1-TNAPB, were prepared by using Cu-catalyzed Ullmann reaction, [8,9], and were applied to study their application to HIL in OLEDs. These compounds were sublimed twice prior to use. DSC thermograms of *N*-triarylamine such as α-NPD, *m*-MTDAPB and 1-TNAPB are presented in Figure 1. Since the samples were quenched from 350°C after first heating scan, the samples could be amorphous state. So, it was possible to observe T_g, T_c, and T_m at second heating scan, in some cases. Similar thermal properties were observed in *m*-MTDAPB and α-NPD. Specially, T_gs were measured to be 100.4°C for α-NPD and 107.7°C for *m*-MTDAPB, which were higher T_g than 63°C of commonly

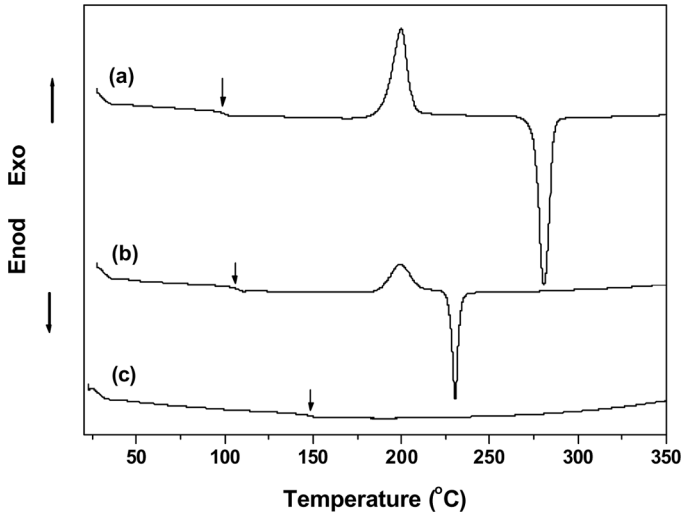


FIGURE 1 DSC thermograms of (a) α-NPD, (b) *m*-MTDAPB, and (c) 1-TNAPB.

used TPD. 1-TNAPB also showed the highest T_g of 149.4°C among them, however, T_m and T_c could not be detected using DSC.

UV-Visible absorption and PL emission spectra of *m*-MTDAPB and 1-TNAPB are shown in Figure 2. UV-Visible absorption maxima

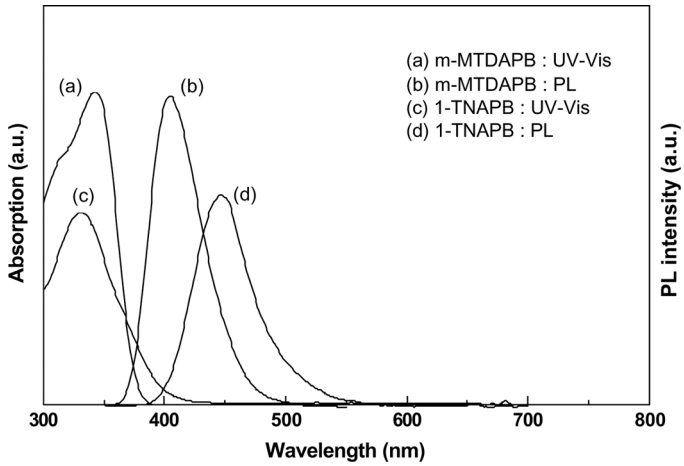


FIGURE 2 UV-Visible absorption and PL emission spectra of *m*-MTDAPB and 1-TNAPB.

TABLE 1 Characteristics of HIL Materials, *m*-MTDAPB and 1-TNAPB.

Materials	T_g (°C)	T_m (°C)	$\lambda_{max,UV}$ (nm)	$\lambda_{max,PL}$ (nm)	HOMO (eV)	LUMO (eV)	Band gap (eV)
m-MTDAPB	107.7	230.6	343	405	−5.39	−2.07	3.32
1-TNAPB	149.4	—	331	447	−5.53	−2.46	3.07

($\lambda_{max,UV}$) were measured to be 343 nm for *m*-MTDAPB and 341 nm for 1-TNAPB, respectively. With the excitation at their $\lambda_{max,UV}$, PL emission peak of 1-TNAPB ($\lambda_{max,PL} = 447$ nm) was red shifted, compared to *m*-MTDAPB ($\lambda_{max,PL} = 405$ nm).

Band gap energies of these compounds were calculated from the crosspoint of UV-Visible absorption and PL emission spectra, and HOMO energy levels from ionization potential values were measured by a RIKEN Keiki AC-2 instrument. Electrochemical properties of these compounds were summarized in Table 1. *m*-MTDAPB showed band gap energy of 3.32 eV and HOMO level of −5.39 eV, whereas 1-TNAPB exhibited band gap energy of 3.07 eV and HOMO level of −5.53 eV. It might be expected from the result of HOMO level that *m*-MTDAPB could be preferred as HIL, showing its HOMO (−5.39 eV) level in between the work function (∼−4.8 eV) of ITO anode and HOMO (−5.60 eV) level of α-NPD (HTL) in OLEDs. Figure 3 shows

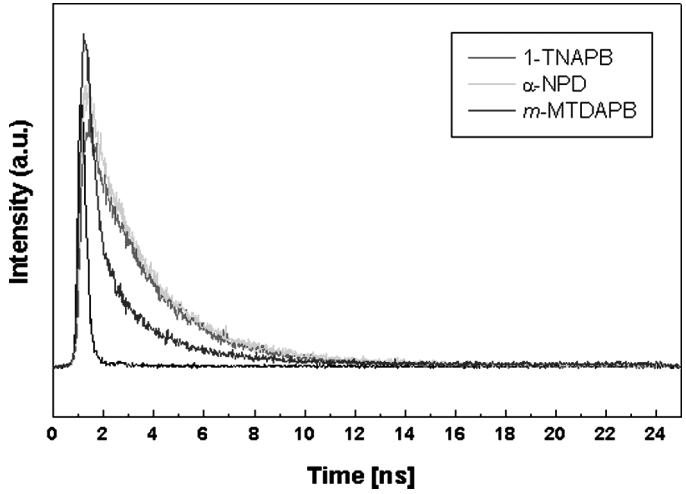


FIGURE 3 Transient photoluminescence decay characteristics of α-NPD, *m*-MTDAPB, and 1-TNAPB in chloroform solution at room temperature.

transient fluorescence decay curves of *N*-triarylamines. Fluorescence decay profiles of compounds were collected at their $\lambda_{max,PL}$, and then decay time was calculated to be 1.85 ns (α-NPD), 0.96 ns (*m*-MTDAPB), and 2.32 ns (1-TNAPB) [10,11].

The hole injecting property of *N*-triarylamines, *m*-MTDAPB and 1-TNAPB, was investigated by using OLEDs with the configuration of ITO/*N*-triarylamine/α-NPD/Alq_3 (40 nm)/LiF (2 nm)/Al (140 nm), where synthesized *N*-triarylamine derivatives were used as HIL, α-NPD as HTL, and Alq_3 as EML. Figure 4 presents schematic diagram of the OLED fabricated in this study. OLEDs emitted bright green luminescence when a positive voltage was applied to the electrode. As seen in Figure 5, maximum EL emission ($\lambda_{max,EL}$) value was measured to be 532 nm, which was in good agreement with PL emission of Alq_3.

Figure 6 presents luminescence vs. voltage curves for all OLEDs with varying the thickness of HIL/HTL. The performance of OLEDs was also summarized in Table 2. In Figure 6, OLED with *m*-MTDAPB (20 nm)/α-NPD (20 nm) as HIL/HTL exhibited turn-on voltage at 6.0 V and maximum luminescence of 2,976 cd/m^2 at 13.5 V. It appeared, however, that OLED with 1-TNAPB/α-NPD as HIL/HTL showed

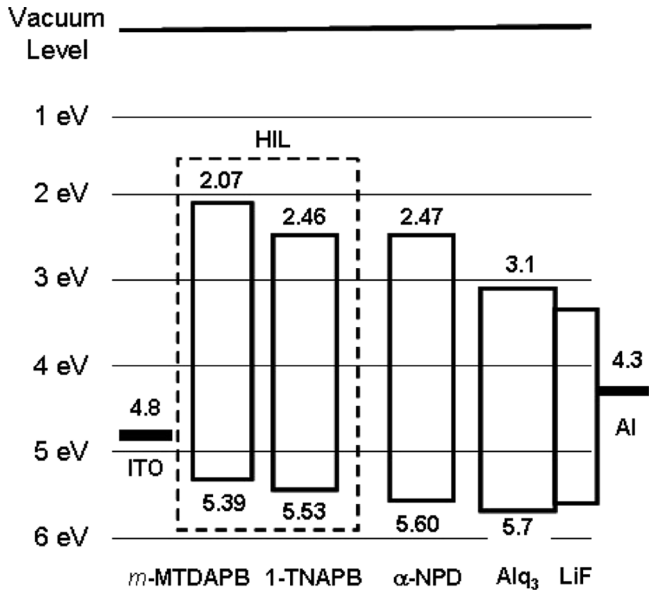


FIGURE 4 OLED structure with the configuration of ITO/HIL/α-NPD/Alq_3/LiF/Al.

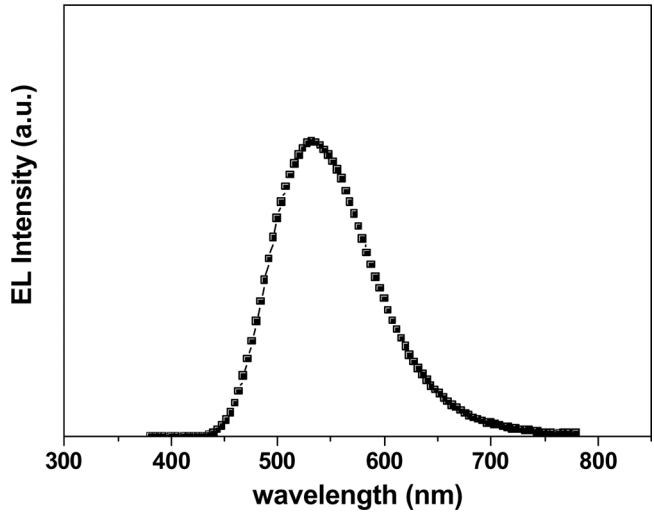


FIGURE 5 EL spectrum of OLEDs.

relatively low EL performance. The difference in EL performance of OLEDs might be originated from well-balanced HOMO level among layers in OLEDs. For OLED with the configuration of [ITO (−4.8 eV)/*m*-MTDAPB (−5.39 eV)/α-NPD (−5.60 eV)/Alq_3 (−5.70 eV)], hole injection/transfer from ITO through HIL/HTL to Alq_3 layer seems

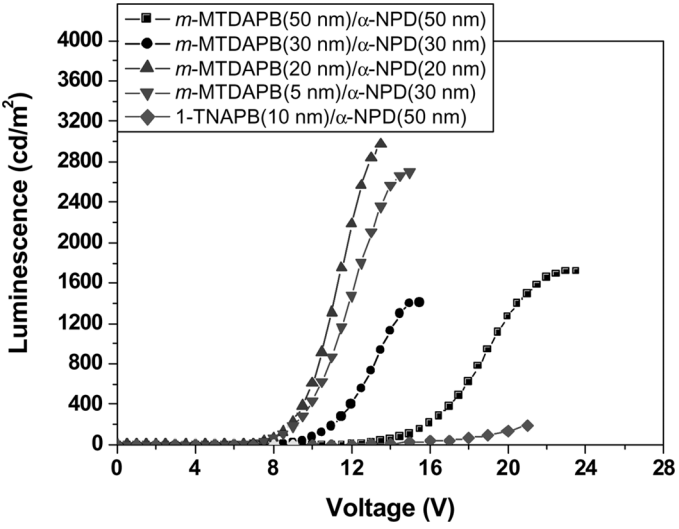


FIGURE 6 Luminescence vs. voltage curves of OLEDs.

TABLE 2 Characteristics of OLEDs with the Configuration of ITO/HIL/α-NPD/Alq_3/LiF/Al

HIL	Thickness (nm) HIL:α-NPD	Turn-on voltage (V)	Max. luminescence (cd/m^2)
m-MTDAPB	50:50	10.5	1,719 (at 23.5 V)
	30:30	7.5	1,407 (at 15.5 V)
	20:20	6.0	2,976 (at 13.5 V)
	5:30	5.5	2,700 (at 15.0 V)
1-TNAPB	10:50	12.0	188 (at 21.0 V)

to be feasible, due to HOMO level offsets of each layer placed in between neighboring layers. Considering higher energy barrier (0.73 eV) of ITO/1-TNAPB than that (0.59 eV) of ITO/*m*-MTDAPB, hole injection from ITO to 1-TNAPB seems to be relatively restricted in OLED with the configuration of [ITO (−4.8 eV)/1-TNAPB (−5.53 eV)/α-NPD (−5.60 eV)/Alq_3 (−5.70 eV)].

CONCLUSIONS

We report the application of two different types of high-T_g *N*-triarylamine derivatives, *m*-MTDAPB and 1-TNAPB, as a HIL in OLEDs with the configuration of ITO/*N*-triarylamine (HIL)/α-NPD (HTL)/Alq_3 (EML)/LiF/Al. From the result on electroluminescent properties measured with the same device structure, *m*-MTDAPB showed better hole injecting property in OLEDs, resulting in higher maximum luminescence at the same device structure. It appeared that well-matched HOMO energy offsets of ITO/*m*-MTDAPB/α-NPD layers could be responsible for higher hole injection from ITO through HIL to HTL, compared to relatively imbalanced HOMO energy offsets of ITO/1-TNAPB//α-NPD layers.

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