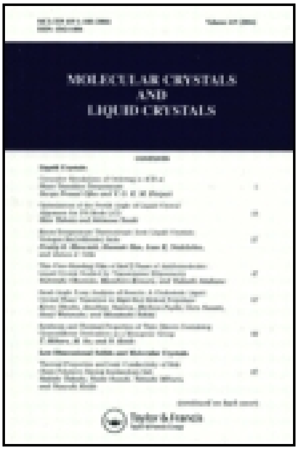

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Organic Light-Emitting Devices Consisting of N-Triarylamine-Based Hole Injecting/Transporting Materials

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Organic Light-Emitting Devices Consisting of *N*-Triarylamine-Based Hole Injecting/Transporting Materials

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A series of N-triarylamine-based derivatives such as 4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α-NPD), 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) were synthesized and characterized. Specially, 1-TNAPB was synthesized with high yield in 1 hr. The hole injecting/transporting properties of these materials were investigated by using double-layered organic light-emitting diodes (OLEDs) with the configuration of ITO/N-triarylamine/Alq_3*/LiF/Al, in which *Alq_3* was used as an emitting and electron transporting layer. A comparative study on EL performance of OLEDs fabricated with N-triarylamines as the hole injecting/transporting layer revealed that better results were observed in OLED with m-MTDAPB and α-NPD, respectively. OLED with m-MTDAPB (20 nm thickness) showed maximum luminescence of 15,970 cd/*m^2* at 10 V and turn-on voltage of 4 V. On the other hand, α-NPD (50 nm thickness) exhibited maximum luminescence of 17,650 cd/*m^2* at 17 V and turn-on voltage of 7 V.*

Keywords: hole injection; hole transport; *N*-triarylamine; OLED

INTRODUCTION

Organic light-emitting diodes (OLEDs) are promising for the next generation of flat panel display [1]. Typically, OLEDs are fabricated

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Address correspondence to Prof. Jae-Yong Ham, Department of Chemical Engineering, Daegu University, Gyeongsan, Gyeongbuk 712-714, Korea. E-mail: hjy6494@daegu.ac.kr using organic thin films derived either from vapor deposited small molecules or spin cast polymers. It is well known that the charge injection and transport can be facilitated by sandwiching the emissive layer between a hole injection/transporting layer (HIL/HTL) above the anode and an electron injection/transporting layer (EIL/ETL) under the cathode. The use of multilayer structure with appropriate HTL and ETL can not only lower the driving voltage but also balance the charge transporting, hence improving the performance of the devices with long lifetime and high quantum efficiency [2,3].

It has been known that there are three key requirements for hole injecting/transporting materials for use in OLEDs. These materials must have good hole injection efficiency from a certain anode, demonstrate high hole mobility, and possess suitable band gap offsets between an anode and an emitting layer within OLEDs [4,5]. Varying the chemical structure of materials can influence hole injecting/transporting capabilities in OLEDs. One of the most common classes of these materials is the arylamines, exhibiting extremely high hole mobility. The other one is carbazole that has interesting optical and electronic properties. OLEDs based on carbazole derivatives have been investigated, where carbazole derivatives are often used as hole transporting layer, utilizing the high hole mobility [6,7].

In this paper, we report the synthesis of a series of *N*-triarylamine derivatives such as 4,4′-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (α-NPD), 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). We chose *N*-triarylamine group as a building block because of its well-known hole transporting property, feasibility on modifying chemical structure, and wide application in OLEDs. Physical, thermal, optical and electrochemical properties of these compounds were measured, and their application as a hole injecting/transporting layer in OLEDs was presented.

EXPERIMENTAL

Materials

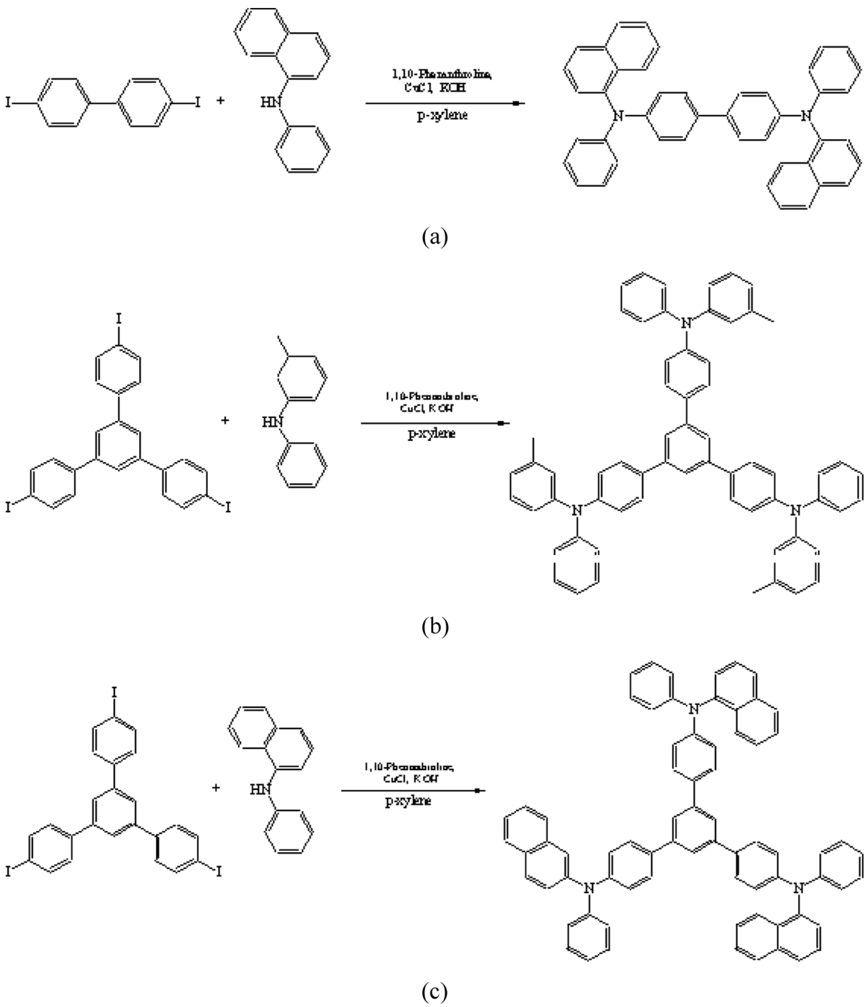
N-phenyl-1-naphthylamine, 4,4′-diiodobiphenyl, 1,10-phenanthroline, 3-methyldiphenylamine, and 1,3,5-tris(p-iodiphenyl)benzene were purchased from Aldrich Chemical Co. Tri(8-hydroxyquinolate)aluminum (Alq_3) and lithium fluoride (LiF) were obtained from Tokyo Kasei Co. Aluminum was purchased from CERAC, USA. Indium-tin oxide (ITO) coated glass with a sheet resistance of 50Ω/n was obtained from Sin'an SNP Co.

Synthesis

α-NPD and *m*-MTDAPB were prepared by using Ullmann condensation reaction, as shown in Scheme 1.

1,3,5-Tris[4-{1-naphthyl(phenyl)amino}phenyl]benzene (1-TNAPB)

Into a three neck round bottomed flask was added a mixture of *N*-phenyl-1-naphthylamine (19.2 g, 8.8×10^{-2} Mole), 1,3,5-tris(p-iodiphenyl)



SCHEME 1 Synthetic route to (a) α-NPD, (b) *m*-MTDAPB, and (c) 1-TNAPB.

benzene (10.0 g, 1.5×10^{-2} mole), 1,10-phenanthroline (2.0 g, 1.1×10^{-2} mole), CuCl (1.2 g, 1.2×10^{-2} mole) in 30 mL of *p*-xylene. Temperature was increased to 100°C, followed by addition of KOH (16.02 g, 28.6×10^{-2} mole). The mixture was refluxed with stirring for 1 h. After reaction, the mixture was cooled down to room temperature, and then 50 mL of toluene was poured into the mixture. The mixture was filtered after stirring, followed by recrystallization from chloroform/methanol. The product was purified by sublimation with high vacuum (Yield = 75.6%).

Characterization

Differential scanning calorimetry (DSC) was performed with a 2010 DSC (TA Instruments) using a heating scan rate of 10°C/min in the temperature range from 30°C to 350°C. UV-Visible absorption spectra were taken with Shimadzu UV-2100. 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 8092 A Digital Multimeter and luminance meter (Minolta LS-100).

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. For the device with the configuration of ITO/HTL/Alq_3 (40 nm)/LiF (2 nm)/Al (140 nm), HTL material such as α-NPD, *m*-MTDAPB, or 1-TNAPB was first vacuum deposited, and then an emissive layer of Alq_3 was 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

The *N*-triarylamine derivatives such as α-NPD, *m*-MTDAPB, and 1-TNAPB (Scheme 1) required for the present study were successfully synthesized generally by using Cu-catalyzed Ullmann reaction of an arylhalide and an arylamine. α-NPD was synthesized by the reaction of 4,4′-diiodobiphenyl and *N*-phenyl-1-naphthylamine, and *m*-MTDAPB and 1-TNAPB were prepared by the reaction of 1,3,5-tris(*p*-iodiphenyl)benzene and the corresponding arylamines, respectively. Synthesized *N*-triarylamine derivatives were sublimed twice prior to use.

Table 1 summarized their thermal, optical and electrochemical properties of these compounds. These compounds are amorphous in nature with obvious glass transition temperature (T_g). It was observed that 1-TNAPB had higher T_g than α-NPD and *m*-MTDAPB, showing 100.4°C for α-NPD, 107.7°C for *m*-MTDAPB, and 149.4°C for 1-TNAPB, respectively.

UV-Visible absorption spectra of these compounds diluted in chloroform are presented in Figure 1. Similar UV-Visible absorption maximum ($\lambda_{max,UV}$) corresponding to maximum π-π^* transition was measured at 341 nm for α-NPD and 343 nm for *m*-MTDAPB. However, 1-TNAPB showed $\lambda_{max,UV}$ at 331 nm. With the excitation at their $\lambda_{max,UV}$, PL emission peaks of these compounds are shown in Figure 2. Maximum PL emission ($\lambda_{max,PL}$) values were observed at 443 nm for α-NPD, 405 nm for *m*-MTDAPB, and 447 nm for 1-TNAPB, respectively.

Band gap energies of these compounds were estimated from UV-Visible absorption and PL emission spectra, and electrochemical properties of these compounds were also listed in Table 1. Similar band gap energies around 3.07 ~ 3.13 eV were measured in α-NPD and 1-TNAPB, whereas *m*-MTDAPB exhibited higher band gap energy of 3.32 eV. HOMO energy levels from ionization potential values were measured by a RIKEN Keiki AC-2 instrument. These compounds showed HOMO energy levels of −5.39 ~ −5.60 eV, which might be matched to the work function (~ −4.8 eV) of ITO anode when they were employed as hole injecting/transporting layers in OLEDs.

Double-layered OLEDs with the configuration of ITO/*N*-triarylamine/Alq_3 (40 nm)/LiF (2 nm)/Al (140 nm) were fabricated, where synthesized *N*-triarylamine derivatives were used as the hole injecting/transporting layer, and Alq_3 worked as the emitting layer. Figure 3

TABLE 1 Summary on Thermal, Photoluminescent and Electrochemical Properties of HTL Materials

HTL	HOMO (eV)	LUMO (eV)	Band gap (eV)	$\lambda_{max,\ UV}$ (nm)	$\lambda_{max,\ PL}$ (nm)	T_g (°C)
α-NPD	−5.60	−2.47	3.13	341	443	100.4
m-MTDAPB	−5.39	−2.07	3.32	343	405	107.7
1-TNAPB	−5.53	−2.46	3.07	331	447	149.4

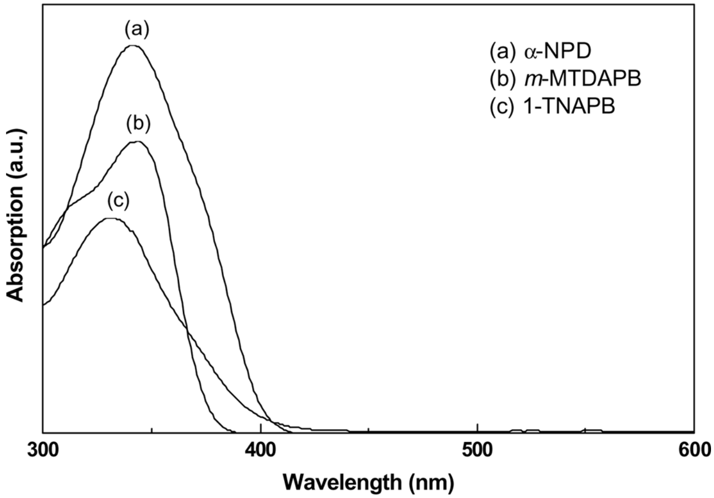


FIGURE 1 UV-Visible absorption spectra of α-NPD, *m*-MTDAPB, and 1-TNAPB.

presents the OLED structure with energy levels of each layer. Table 2 summarizes data on the device performance. When voltages were applied on the electrodes, devices emitted bright green light at 530 nm, indicating Alq_3 layer was the exiton formation layer. CIE

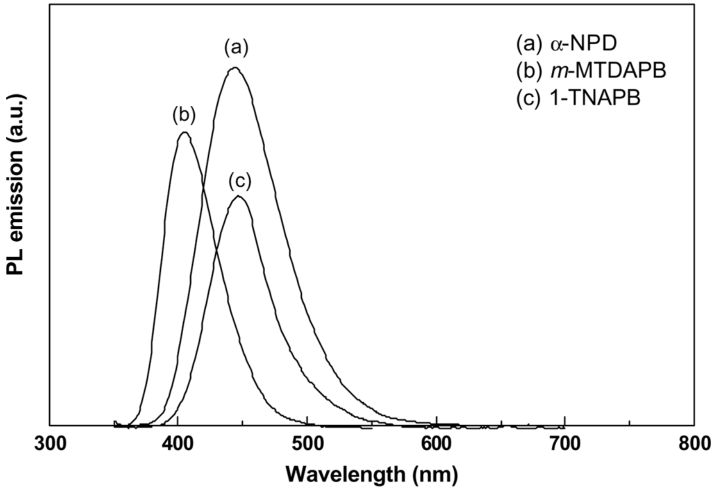


FIGURE 2 Photoluminescence emission spectra of α-NPD, *m*-MTDAPB, and 1-TNAPB.

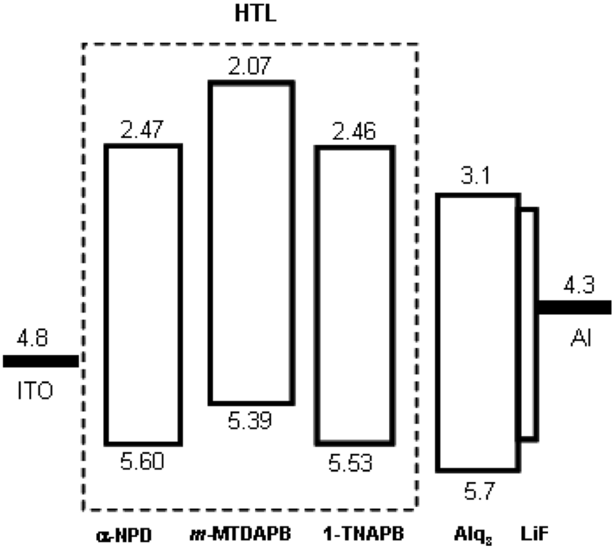


FIGURE 3 OLED structure with the configuration of ITO/*N*-triarylamine/ Alq_3 (40 nm)/LiF (2 nm)/Al (140 nm).

coordinates of double-layered OLEDs were compared with those of standard R, G, B, and W colors established by NTSC [8,9]. Based on these color coordinates and Kelly's map in CIE 1931 chromaticity diagram [10], it appeared all double-layered OLEDs illuminated green (CIE coordinates of $x = 0.312 \sim 0.345$ and $y = 0.535 \sim 0.556$) color.

Figure 4 presents luminescence vs. voltage curves of three OLEDs with different thickness of the hole injecting/transporting *N*-triarylamine layer. Their luminescence increased generally with

TABLE 2 Device Performance of the OLEDs with the configuration of ITO/ HTL/Alq_3/LiF/Al

HTL materials	Thickness of HTL (nm)	Turn-on voltage (V)	Max. luminescence (cd/m^2) at voltage	Color coordinate (x,y)
α-NPD	30	3.0	6,710 (at 15.0 V)	0.332,0.556
	50	7.0	17,650 (at 17.0 V)	0.331,0.553
m-MTDAPB	20	4.0	15,970 (at 10.0 V)	0.337,0.551
	30	3.0	13,210 (at 11.0 V)	0.345,0.547
	50	4.0	2,880 (at 12.0 V)	0.328,0.535
1-TNAPB	10	4.5	248 (at 8.5 V)	0.312,0.550
	30	5.0	643 (at 10.5 V)	0.330,0.556

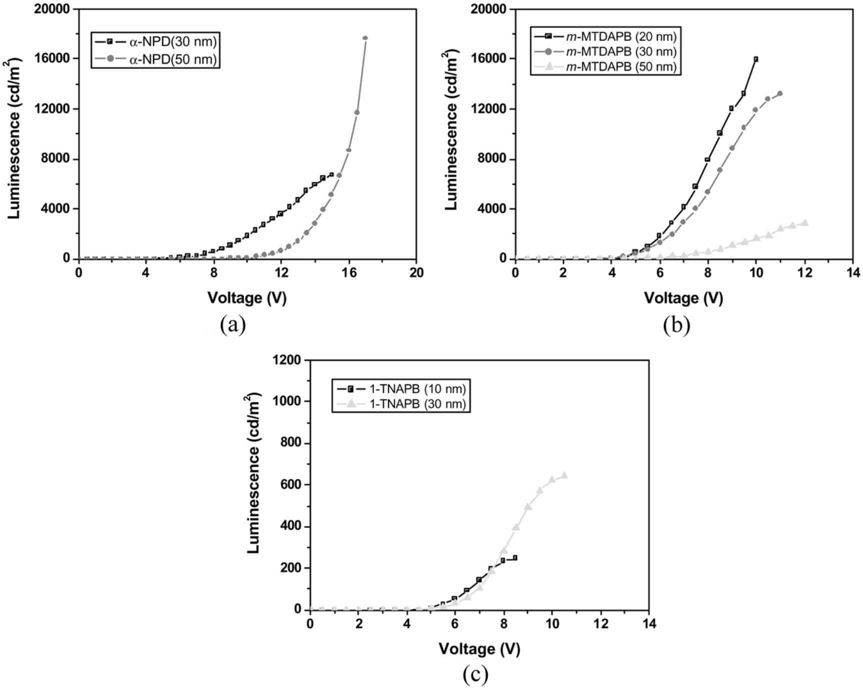


FIGURE 4 Luminescence vs. voltage curves of OLEDs with the following configuration: (a) ITO/α-NPD/Alq_3/LiF/Al, (b) ITO/*m*-MTDAPB/Alq_3/LiF/Al, Al, and (c) ITO/1-TNAPB/Alq_3/LiF/Al.

increasing the applied voltage. It appeared in Figures 4 (a) and (b), respectively, that OLED containing α-NPD with thickness of 50 nm showed turn-on voltage at 7.0 V and maximum luminescence of 17,650 cd/m^2 at 17.0 V, and OLED comprised of *m*-MTDAPB with thickness of 20 nm presented turn-on voltage at 4.0 V and maximum luminescence of 15,970 cd/m^2 at 10.0 V. As can be seen in Figure 4 (c), on the other hand, relatively lower performance was observed in OLED with 1-TNAPB (thickness of 30 nm), showing turn-on voltage at 5.0 V and maximum luminescence of 643 cd/m^2 at 10.5 V. In general, the device based on *m*-MTDAPB as the hole injecting/transport-ansporting layer showed better electroluminescent performance among OLEDs fabricated in this study. This result revealed that *m*-MTDAPB had suitable band gap offsets between ITO anode and the emitting Alq_3 layer within OLEDs, compared to other devices. In addition, high energy barrier (1.03 eV) between *m*-MTDAPB and

Alq_3 might also provide an additional contribution on preventing electron transfer from Alq_3 to *m*-MTDAPB.

CONCLUSIONS

Series of *N*-triarylamine-based derivatives such as α-NPD, *m*-MTDAPB and 1-TNAPB were synthesized and characterized. New synthetic procedure for 1-TNAPB was reported, providing improved yield within relatively short reaction time. Thermal, optical and electrochemical properties of these materials and their application to OLEDs were studied. Specially, the hole injecting/transporting properties of these materials were demonstrated well in the devices in which Alq_3 was used as an emitter and electron transporting layer. It appeared that optimized band gap offsets between ITO anode and the emitting Alq_3 layer within OLEDs was one of major factors for the use as the hole injecting/transporting layer.

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