Phenyl-Naphthyl Amine Effect of New Phenothiazine Derivatives with High Tg for Hole Injection and Hole Transporting Materials

Soo-Kang Kim[1], Ji-Hoon Lee[2], and Jong-Wook Park[1*]

[1]Department of Chemistry, The Catholic University of Korea, Pucheon, 420-743, Korea
TEL:82-2-2164-4821, e-mail: hahapark@catholic.ac.kr

[2]Department of Polymer Science and Engineering, Chungju National University, Chungju, 380-702, Korea

Keywords : OLED, Phenothiazine, High Tg, HIL, HTL

Abstract

We synthesized a new HIL and HTL materials by using phenothiazinly moiety, 1,4-diphenothiazyl-benzene [DPtzB], 3',7',3'',7''-tetrakis(N-phenyl-2-naphthylamine)-1,4-diphenothiazyl-benzene[PNA-DPtzB]. Synthesized materials exhibited high Tg in the range of 175 – 202℃. These values are much better than commonly used hole transporting materials (2-TNATA and NPB). The OLED device that used DPtzB as a HIL showed the highest efficiency of 4.31cd/A at 10mA/cm^2.

1. Introduction

Organic light-emitting diodes (OLEDs) have been the subject of intensive investigation in the past few years because of their potential application as emissive elements for flat panel displays[1,2]. Generally, multi-layered devices consisting of charge transport and emitting layers exhibit higher EL efficiency than a single-layer device. This is because multi-layered devices balance hole and electron carrier and then the exciton occurs in the middle of emitting layer.

Although considerable research efforts by using charge carrier material layer have been carried out to enhance the performance suitable for practical use, a lot of problems to solve still remain. For example, there are still needs for the device lifetime, the luminous efficiency, and the operation stability, etc[3].

Recently, star-burst amines 4,4',4''-tris{N,(3-methyl phenyl)-N-phenylamino}-triphenylamine(m-MTDATA)[4], 4,4',4''-tris{N,-(2-naphthyl)-N-phenylamino} –triphenyl amine(2-TNATA)[4] or copper phthalocyanine (CuPc)[5] acting the role of the hole injection layer (HIL) in OLED device, have been inserted between the hole transport layer(HTL) and the transparent anode[typically an indium tin oxide(ITO)] to improve device performance. Unfortunately CuPc absorbs slightly blue and red light, it can't be used in full color display. m-MTDATA has disadvantage of low T_g and recrystallization or melting of amorphous organic materials causes to device degradation[6]. Likewise, the most commonly used hole transporting material, 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl(NPB)[7], has disadvantage of low T_g.

The durability of multilayer devices strongly depends on the thermal and morphological stability of materials in each layer. Amorphous materials possessing high glass transition temperature (T_g) should have better opportunity for retaining the film morphology during device operation[8,9]. Thus, a high T_g material is always desirable[10,11]. Crystallization or melting phenomena of amorphous organic materials caused by Joule heating are considered as common causes of device degradation. Many efforts have been devoted to synthesis for high Tg hole injection and transporting layer materials[12].

In this paper, we synthesized a new HIL and HTL materials by using phenothiazinly moiety, 1,4-diphenothiazyl-benzene [DPtzB][13], 3',7',3",7"-tetrakis(N-phenyl-2-naphthyl amine)-1,4-diphenothiazyl-benzene [PNA-DPtzB]. PNA-DPtzB includes four groups of N-phenyl-2-naphthyl amine at 3',7',3" and 7" positions compared to DPtzB in order to check the its effect to DPtzB. Thermal, electrochemical, and optical properties of these materials were characterized by differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA), cyclic voltammetry (CV), UV-visible and photoluminescence (PL) spectroscopies. Moreover, multilayer EL devices were fabricated using these materials as hole injection materials or hole transporting materials.

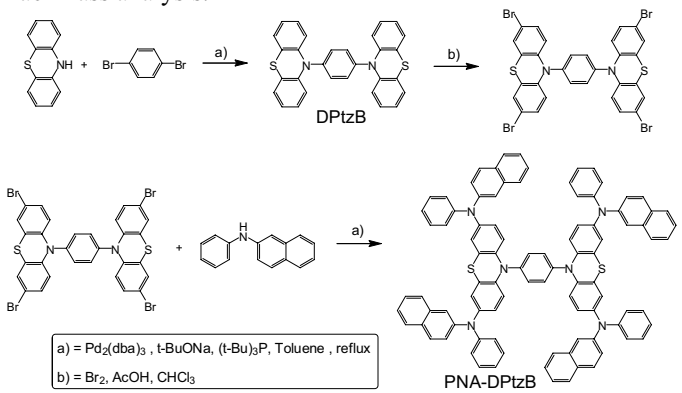
2. Experimental

EL devices were fabricated using 2-TNATA or synthesized materials as a hole injection layer, NPB or synthesized materials as a hole transporting layer, Alq_3 as electron transporting and emitting layer, LiF as electron injection layer, ITO(1200Å, 30ohm) as the anode and Al as the cathode; ITO/HIL(60nm)/HTL(15nm)/Alq_3 (70

nm)/LiF (1 nm)/Al (200 nm). The organic layer were vacuum-deposited using thermal evaporation at a vacuum base pressure of 10^{-6} torr, the rate of deposition being 1 Å/s to give an emitting area of $4mm^2$ and aluminum layer was continuously deposited with same vacuum condition. Current-voltage (I-V) characteristics of the fabricated EL devices were measured using Keithley 2400 electrometer. Light intensity was obtained by Minolta CS-100A.

3. Result and Discussion

New hole-transporting compounds, shown in Scheme 1, were synthesized through simple Pd-catalyzed C-N coupling reaction. These products were finally purified with silica-gel column chromatographic method to have highly pure powder and were identified by ^{1}H-NMR, and Fab-Mass analysis.



Scheme 1. Synthetic routes of DPtzB, PNA-DPtzB.

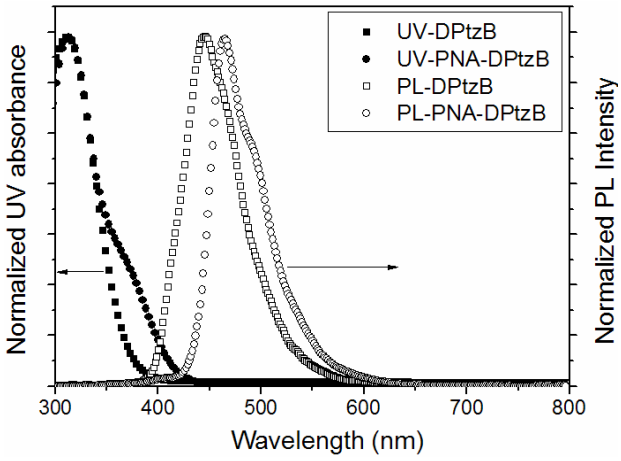


Figure 1. UV-visible absorption(solid) and PL emission(open) spectra of (a) DPtzB (squre) and (b) PNA-DPtzB(circle) solution in Toluene (1.0 * 10^{-4}M).

Figure 1 shows UV-Visible and PL spectra in the solution state of DPtzB and PNA-DPtzB. It was found that compared to DPtzB, UV_{onset} and PL_{max} values of PNA-DPtzB were red-shifted about 20nm and this is attributed to the fact that the conjugation length of PNA-DPtzB which four phenyl-naphthyl amine groups were added to DPtzB increased. When the full width at half maximum (FWHM) of PL spectrum was examined, it was identified that PNA-DPtzB was 57nm, becoming narrower than 64nm of DPtzB. This could be understood that when phenyl-naphthyl amine group is added, molecules become bulky, and this increases the inter-molecular distance, which reduces the inter-molecular π-π* interaction.

UV-visible and PL spectra measured in the film condition of two materials after vacuum deposition are illustrated in Figure 2. UV-visible and PL spectra in the film condition also showed that the spectrum of PNA-DPtzB was red-shifted. The optical data of two spectra are summarized in Table 1.

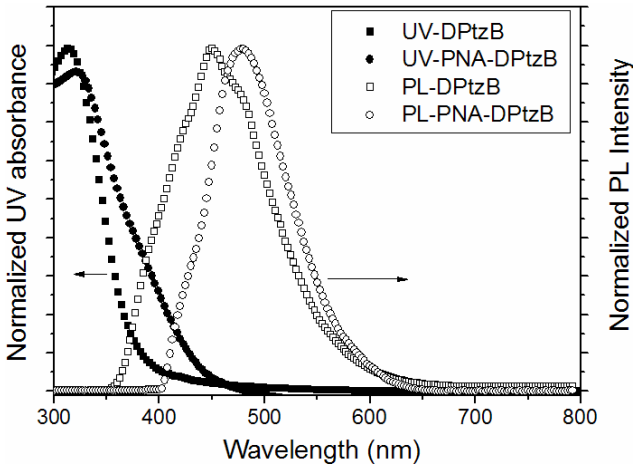


Figure 2. UV-visible absorption(solid) and PL emission(open) spectra of (a) DPtzB (squre) and (b) PNA-DPtzB(circle) films on glass.

UV-visible and PL spectra measured in the film condition of two materials after vacuum deposition are illustrated in Figure 2. UV-visible and PL spectra in the film condition also showed that the spectrum of PNA-DPtzB was red-shifted. The optical data of two spectra are summarized in Table 1.

Table 1. Optical properties of DPtzB and PNA-DPtzB.

	Solution (10^{-4}M Toluene)				Film on glass			
	UV_{onset} (nm)	UV_{max} (nm)	PL_{max} (nm)	FWHM (nm)	UV_{onset} (nm)	UV_{max} (nm)	PL_{max} (nm)	FWHM (nm)
DPtzB	379	312	445	64	365	314	450	115
PNA-DPtzB	400	312	466	57	412	321	479	91

TGA and DSC were measured to identify thermal properties of synthesized materials. Glass transition temperature (T_g), melting temperature (T_m) and initial thermal degradation temperature (T_d) of the materials are summarized in Table 2. DPtzB and PNA-DPtzB show very high T_g with 202℃ and 175℃, respectively. These vaules

are much higher than 96℃[7] and 110℃[4] the T_g values of the reference materials, NPB and 2-TNATA, and it is expected to more stably exist when the device is operating. T_m value of DPtzB was 259℃. Although temperature is increased up to T_d of 470℃ in PNA-DPtzB, it is not found T_m of PNA-DPtzB even at the third scan. We believe that PNA-DPtzB is not easily crystallized material. T_d, temperature when degradation of materials begins were found to be more than 300℃ in all cases.

CV was measured to identify HOMO values of synthesized materials. Even when cycles are scanned for more than 50 times or so, CV result appeared stable. By using band-gap identified with UV_{onset} and HOMO value measured through CV, LUMO level was confirmed, and they are summarized in Table 2.

Table 2. Electical and thermal properties of DPtzB and PNA-DPtzB.

	HOMO (eV)	LUMO (eV)	Eg (eV)	T_g (℃)	T_m (℃)	T_d (℃)
DPtzB	5.12	1.73	3.39	202	259	362
PNA-DPtzB	4.82	1.88	2.94	175	-	474

The HOMO value of DPtzB was 5.12eV, which is similar with the HOMO value of 2-TNATA, 5.1eV[4]. PNA-DPtzB substituted with phenyl-naphthyl amine had the HOMO value of 4.82eV, which was higher than DPtzB by 0.2eV, and this is because the increase of amine group makes electrons inside the molecule abundant, allowing oxidation to be easier.

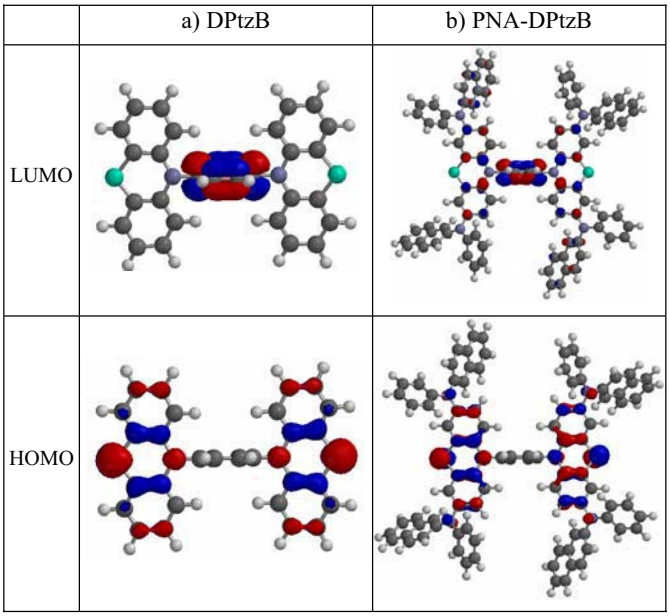


Figure 3. HOMOs and LUMOs of a) DPtzB and b) PNA-DPtzB calculated at Semi-Empirical with a AM-1 basis set using Spartan'04.

The ground-state structure and electron state of HOMO and LUMO were calculated using by AM-1 method of Spartan'04 program[14,15].

Figure 3 shows electron distribution of HOMO and LUMO in DPtzB and PNA-DPtzB.

While the HOMO of DPtzB shows that electrons are mostly massed in phenothiazine, it was found that in the case of PNA-DPtzB, some electrons are partially distributed in the phenyl-naphthyl amine group. This demonstrates that the phenyl-naphthyl amine group, as an electron donating group, participates in the conjugation system of phenothiazine. This agrees with the reason why the maximum wavelengths in UV-Visible and PL spectra are red-shifted. Also, it was confirmed that since the HOMO electrons were distributed to total six sites of amine, not two sites in PNA-DPtzB, the oxidation was readily possible in terms of molecules. This also explains why the HOMO energy level of PNA-DPtzB increased more than that of DPtzB by 0.3 eV. Meanwhile, in the case of LUMO, while the electron distribution of DPtzB exists only in phenyl group, PNA-DPtzB was distributed throughout.

An OLED device was fabricated by using two synthesized materials as hole-injection layers. The structure of the fabricated device was ITO/ DPtzB or PNA-DPtzB(60nm)/ NPB(15nm)/ Alq_3(70nm)/ LiF(1nm)/ Al(200nm) (Device I or II). For objective comparison of performance, a standard device was also fabricated {ITO/ 2-TNATA(60nm)/ NPB(15nm)/ Alq_3(70nm)/ LiF(1nm)/ Al(200nm) (Device V)}. The J-V properties of the fabricated devices and the energy levels of the synthesized materials and other used EL materials are shown in Figure 4.

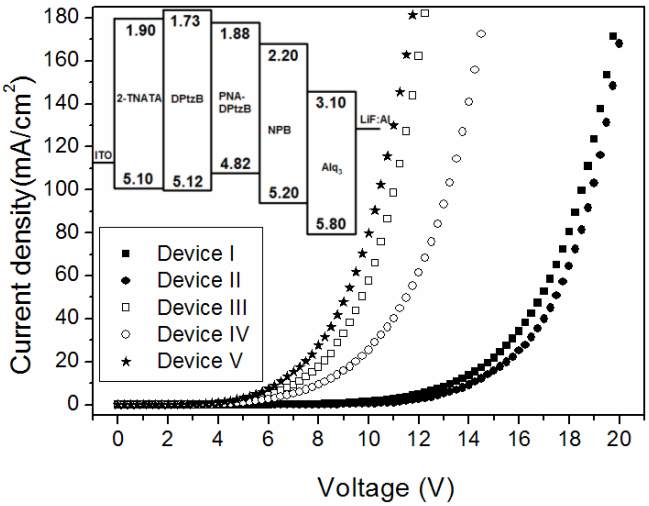


Figure 4. Energy diagram and current density-voltage characteristics of device I~V : ITO/ HIL(60nm) / HTL(15nm) / Alq_3(70nm) / LiF(1nm) / Al (200nm)

Device I):ITO/DPtzB/NPB/Alq_3/LiF/Al, II):ITO/PNA-DPtzB/NPB/Alq_3/LiF/Al, III):ITO/2-TNATA/DPtzB/Alq_3/LiF/Al, IV):ITO/2-TNATA/PNA-DPtzB/Alq_3/LiF/Al, V):ITO/2-TNATA/NPB/Alq_3/LiF/Al

Device I which used DPtzB had 4.31cd/A of luminance efficiency, showing more than 10% increase of efficiency compared to Device V which used the commercialized 2-TNATA. PNA-DPtzB had a similar result with 2-TNATA (see Table 3).

In order to evaluate hole transporting property of the synthesized materials, they were placed into HTL (Device III and IV). Efficiency of Device III was reduced slightly compared to that of Device V, and the efficiency of PNA-DPtzB device was sharply decreased to 0.33cd/A. Here, the HOMO level of PNA-DPtzB is as high as 4.82eV, causing mismatched HOMO interface levels between layers such as 2-TNATA and Alq_3. Therefore, in applying HTL with PNA-DPtzB, holes cannot smoothly reach to Alq_3, showing device efficiency as low as 0.33cd/A.

Table 3. Performance characteristics of organic EL device at 10mA/cm^2: ITO/ HIL(60nm)/ HTL(15nm)/ Alq_3(70nm)/ LiF(1nm)/ Al(200nm).

	HIL / HTL	EL_{max} (nm)	Luminance Efficiency (cd/A)	CIE (x,y)
I)	DPtzB / NPB	520	4.31	(0.333, 0.526)
II)	PNA-DPtzB / NPB	520	3.82	(0.333, 0.524)
III)	2-TNATA / DPtzB	521	3.15	(0.342, 0.524)
IV)	2-TNATA / PNA-DPtzB	524	0.33	(0.342, 0.524)
V)	2-TNATA / NPB	524	3.81	(0.342, 0.524)

All fabricated devices, however, showed green electroluminescence caused by Alq_3 at around 520nm. And it is expected that all synthesized materials could be applied as a hole injection layer and the case of DPtzB as a hole transporting layer.

4. Conclusion

We synthesized a new HIL and HTL materials by using phenothiazinly moiety, 1,4-diphenothiazyl-benzene [DPtzB] and 3',7',3",7"-tetrakis(N-phenyl-2-naphthyl amine)-1,4-diphenothiazyl-benzene[PNA-DPtzB].

In the case of PNA-DPtzB, the material synthesized by bringing four N-phenyl-2-naphthyl amines into the 3- and 7-positions compared to DPtzB, as N-phenyl-naphthyl amine group was induced, molecular oxidation became easier; and this agrees with the result of molecular modeling study. Also, it was found that Td was increased with regard to thermal property.

Synthesized materials also exhibited high Tg in the range of 175 – 202℃. These values are much higher than commonly used hole transporting materials (2-TNATA and NPB). The OLED device that used DPtzB as HIL showed the highest efficiency of 4.31cd/A at 10mA/cm^2.

5. Acknowledgment

This study was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Commerce, Industry and Energy, Republic of Korea.

6. Reference

[1] C. W. Tang and S. A. Van Slyke, *Appl. Phys. Lett.* 51, 913. (**1987**)

[2] S. K. Kim, Y. I. Park, I. N. Kang, J. H. Lee and J. W. Park, *J. Mater. Chem.* 17, 4670(**2007**)

[3] a) D. Kolosev and S. R. Forrest, *J. Appl. Phys*, 90, 3242 (**2001**) b) Y. I. Park, J. H. Son, J. S. Kang, S. K. Kim, J. H. Lee, J. W. Park, C*hem. Commun.*, DOI:10.1039/b718873k. (**2008**)

[4] Y. Shirota, Y. Kuwabara, D. Okuda, R. Okuda, H. Ogawa, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami and K. Imai, *J. Lumin.*, 72, 985. (**1997**)

[5] C.W. Tang, S.A.Van Slyke and C.H. Chen, *Appl. Phys. Lett.*, 69, 2160. (**1996**)

[6] Y. Kuwabara, H. Ogawa, H. Inada, N. Nona and Y. Shirota, *Adv. Mater.*, 6, 667 (**1994**)

[7] J. Li, D.Liu, Y. Li, C. S. Lee, H. L. Kwong and S. T. Lee, *Chem. Mater.*, 17, 1208 (**2005**)

[8] K. Danel and T. T. Lin, *Chem. Mater.*, 14, 3860 (**2002**)

[9] H. Aziz, Z. D. Popovic, *Chem. Mater.*, 16, 4522. (**2004**)

[10] S. Thayumanavan, S. Barlow and S. R. Marder, *Chem. Mater.* 9,3231 (**1997**)

[11] K. Katsuma and Y. Shirota, *Adv. Mater.*, 10, 223 (**1998**)

[12] S. K. Kim, C. J. Lee, I. N. Kang, J. H. Lee and J. W. Park, *Thin Solid Films*, 509, 132, (**2006**)

[13] S. K. Kim, C. J. Lee, I. N. Kang, J. W. Park, J. H. Lee, K. S. Kim, C. K. Choi and S. D. Lee, *Mol. Cryst. Liq. Cryst.*, 462, 135 (**2007**)

[14] *Spartan'04 for Windows*; Wavefunction, Inc.: Irvine, CA, 2003.

[15] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewant, *J. Am. Chem. Soc.*, 107, 3902, (**1985**)