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# **Highly Efficient New Hole Injection Materials for Organic** Light Emitting Diodes Base on Phenothiazine Derivatives

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New hole injection materials for OLED based on phenothiazine were synthesized, and the electrooptical properties of synthesized materials were examined by through UV-Vis. and photoluminescence spectroscopy as well as cyclic voltammetry. 1-NDD-t-BPBP and 2-NDD-t-BPBP showed Ta of 180 and 177 °C. These are higher than that (110 °C) of 2-TNATA, commercial HIL material. As for the HOMO level of the synthesized materials, 1-NDD-t-BPBP and 2-NDD-t-BPBP were 4.99 and 5.02 eV, indicating well-matched values between HOMO (4.8 eV) of ITO and HOMO (5.4 eV) of NPB, HTL material. In addition, judging from the fact that the synthesized materials both barely showed any absorption in the range of over 450 nm, the synthesized materials could be effectively used as an HIL material. The synthesized materials were used as the HIL in OLED device, yielding luminance efficiencies of 4.51 cd/A (1-NDD-t-BPBP) and 4.44 cd/A (2-NDD-t-BPBP). These results indicated that 1-NDD-t-BPBP shows more excellent luminance efficiency which is about 11% improved over 2-TNATA a commercial HIL material.

Keywords: Phenothiazine, OLED, Hole Transporting Material, HIL Material.

# **1. INTRODUCTION**

Organic light emitting diodes (OLEDs) are optoelectronic devices based on the photoluminescent properties of  $\pi$ conjugated organic materials. It is useful for lighting applications and next-generation flat panel displays.<sup>1,2</sup> In particular, as for OLED device using small molecule, multi-layer device can be produced through deposition method, so it can implement high efficiency than polymer OLED. In general, layers comprising multi-layering system in low molecule OLED device are broadly composed of hole injection/transport, emitting and electron injection/transporting layers. Therefore, development of material with characteristics optimized for each layer can be one of the most important objectives of the development.

Good hole injection layer (HIL) materials used in OLEDs have the following common properties: (1) highest occupied molecular orbital (HOMO) level should be between ITO and hole transfer layer (HTL); (2) the less the absorption of red, blue, green (RGB) emission coming out of emitting layer (EML) is, the better; (3) the higher  $T_{o}$ , the better it is for the endurance of device degradation by Joule heat occurring while driving device in device stability standpoint.<sup>3-6</sup> Recently, star-bust amine 4,4',4"-Tris (N-(naphthalen-2-yl)-N-phenyl-amino) triphenylamine

4,4',4"-Tris(N-3-methylphenyl-N-phenyl-(2-TNATA), amino)triphenylamine (m-MTDATA) or copper phthalocyanine (CuPc) compound acting the role of the hole injection layer, was inserted between the hole transport layer and the transparent anode to improve device durability. Unfortunately, CuPc absorbs slightly blue and red light, it can't use fabrication of full color display. And m-MTDATA has disadvantage of low glass-transition temperatures  $(T_{o})$ . Crystallization or melting of amorphous organic materials cause by Joule heat or short-circuit current due to pinholes in thin films are considered common causes of device degradation. In principle, all the organic layers forming the EL devices should have  $T_o$  as high as possible. The individual layer that the lowest  $T_{g}$  is likely to limit the thermal stability of the OLED.<sup>3,7</sup>

Therefore, in this study, new hole injection materials based on dimeric phenothiazine derivatives were synthesized as alternative to solve the above problem. Phenothiazine have been mainly developed as *p*-type material or ambipolar materials that can transport hole and/or electron in organic photovoltaic (OPV) device and organic thin-film transistor (OTFT) field of optoelectronic field.<sup>8-11</sup> Therefore, in order to strengthen the transfer of electron to basic moiety of phenothiazine fundamentally with hole transfer characteristics and to induce amorphous molecule condition and proper HOMO energy level, bulky aromatic

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1-NDD-t-BPBP

2-NDD-t-BPBP

Scheme 1. Chemical structure of new phenothiazine materials.

amine group was substituted. Two new HIL materials 1-NDD-*t*-BPBP and 2-NDD-*t*-BPBP were synthesized as shown in Scheme 1.

The synthesized compounds based on dimeric phenothiazine were compared on the electro-optical and thermal properties through UV-visible (UV-vis), photoluminescence (PL), cyclic voltammetry (CV), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis. Furthermore, the hole injection layer properties of phenothiazine derivatives synthesized through electroluminescence (EL) device experiment were compared and analyzed with the commercial HIL material 2-TNATA as reference.

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## 2. EXPERIMENTAL DETAILS

#### **2.1. General Method**

<sup>1</sup>H-NMR spectra were recorded using Bruker Advance 300 and 500 instruments, fast atom bombardment (FAB) mass spectra were recorded using a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained using an HP 8453 UV-VIS-NIR spectrometer. A Perkin-Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo-luminescence (PL) spectroscopy. The melting temperatures  $(T_m)$ , glass-transition temperatures  $(T_o)$ , crystallization temperatures  $(T_c)$ , and degradation temperatures  $(T_d)$  of the compounds were measured by DSC under a nitrogen atmosphere using a DSC2910 (TA Instruments), and TGA was performed using an SDP-TGA2960 (TA Instruments). The redox potentials of the compounds were determined by CV using an AUTOLAB/PG-STAT128N model system with a scan rate of 100 mV/s. The working electrode was formed by depositing the synthesized materials onto ITO substrates, Ag/AgNO<sub>3</sub> in acetonitrile (AN) as reference electrode, Pt wire as counter electrode, and 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile as the electrolyte. All potentials are quoted versus the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple as the internal standard. The band gap was estimated from the tailing edges of UV-vis. spectra. From the oxidation potential, HOMO

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energy level was derived by assuming that the energy level of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) is 4.8 eV. Finally, their LUMO energy level was derived from HOMO energy level and the band gap. OLED devices were fabricated with the following structure: ITO/2-TNATA or synthesized material (60 nm)/NPB (15 nm)/Alq3 (70 nm)/LiF (1 nm)/Al (200 nm), where 2-TNATA and the synthesized material formed the HILs, N,N'-bis(naphthalen-1yl)-N,N'-bis(phenyl)benzidine (NPB) formed the HTL, 8-hydroxyquinoline aluminum (Alq3) formed the EML and electron transport layer (ETL), lithium fluoride (LiF) formed the electron injection layer (EIL), ITO formed the anode, and Al formed the cathode. The organic layer was vacuum-deposited by thermal evaporation at a vacuum base pressure of  $10^{-6}$  Torr and a rate of deposition of 1/s to give an emitting area of 4 mm<sup>2</sup>; the Al layer was continuously deposited under the same vacuum conditions. The current–voltage (I-V) characteristics of the fabricated OLED devices were obtained using a Keithley 2400 electrometer. Light intensity and electroluminescence (EL) was measured using a Minolta CS-1000A. The operational stability of the devices was measured with encapsulation in glove box.

#### 2.2. General Syntheses of New Materials

These synthesized materials by Suzuki aryl-aryl coupling reaction using Pd catalyst. A typical synthetic procedure was as follows: To 7,7'-Dibromo-10,10'-bis-(4-tertbutyl-phenyl)-10H,10'H-[3,3']biphenothiazinyl (0.32 g, 0.4 mmol) and N1-(naphthalen-1-yl)-N4,N4-diphenylbenzene-1,4-diamine or N1-(naphthalen-2-yl)-N4,N4-diphenylbenzene-1,4-diamine (0.34 g, 0.9 mmol) and in a 250 mL round-bottomed flask under a nitrogen atmosphere were added Pd<sub>2</sub>(dba)<sub>3</sub> (0.02 g, 0.02 mmol), Sodium tertbutoxide (0.25 g, 2.6 mmol), Tri-t-butylphosphine (1 ml) and xylene. The temperature was increased to 140 °C. Stirring was continued at this temperature and the reaction was monitored by TLC. When the reaction was complete, extraction of the product was performed with water and toluene. The organic extract was dried with  $MgSO_4$ added, and then filtered the solvent removed in vacuo. The resulting crude mixture was passed through a short-column of silica with THF as the eluent and then recrystallized from THF to obtain as a yellow solid.

# 2.3. Synthesis of 10,10'-bis(4-tert-butylphenyl)-N7,N7'-di(naphthalen-1-yl)-N7,N7'-di (phenyl-*p*-diphenylamine-yl)-10H, 10'H-3,3'-biphenoxazine-7,7'-Diamine (1-NDD-*t*-BPBP)

The yield was 30%. <sup>1</sup>H-NMR (300 MHz, THF-d8):  $\delta$  (ppm) 1.39(s, 18 H), 6.02(d, 2 H), 6.17(d, 2 H), 6.48(d, 2 H), 6.75(s, 2 H), 6.82(d, 4 H), 6.87(m, 8 H), 6.89(d, 2 H), 6.94(d, 8 H), 7.00(s, 2 H), 7.08(t, 8 H), 7.14(d, 6 H), 7.36(t, 2 H), 7.42(m, 4 H), 7.61(d, 4 H), 7.74(d, 2 H), 7.86(d, 2 H), 7.95(d, 2 H), HRMS: m/z 1428.5889 (M<sup>+</sup>, calcd 1428.5886). Anal. Calcd for C100H80N6S2: C, 84.00; H, 5.64; N, 5.88; S, 4.49 Found: C, 83.06; H, 5.64; N, 5.82; S; 4.43.

## 2.4. Synthesis of 10,10'-bis(4-tert-butylphenyl)-N7,N7'-di(naphthalen-2-yl)-N7,N7'-di (phenyl-*p*-diphenylamine-yl)-10H,10'H-3,3'-biphenoxazine-7,7'-Diamine (2-NDD-*t*-BPBP)

The yield was 41%. <sup>1</sup>H-NMR (300 MHz, CDCl3): $\delta$  (ppm) 1.39(*s*, 18 H), 6.14(*d*, 2 H), 6.18(*d*, 2 H), 6.62(*d*, 2 H),

6.85(s, 2 H), 6.97(m, 14 H), 7.05(d, 8 H), 7.14(s, 2 H), 7.18(m, 10 H), 7.25(t, 2 H), 7.30(d, 2 H), 7.35(d, 6 H), 7.58(d, 2 H), 7.68(m, 8 H), HRMS: m/z 1428.5890 (M<sup>+</sup>, calcd 1428.5886). Anal. Calcd for C100H80N6S2: C, 84.00; H, 5.64; N, 5.88; S, 4.49 Found: C, 84.13; H, 5.69; N, 5.85; S; 4.50.

### 3. RESULTS AND DISCUSSION

New 1-NDD-*t*-BPBP and 2-NDD-*t*-BPBP which are based on the dimeric phenothiazine moieties were synthesized by through C–C and C–N coupling reaction using palladiumcatalyst as shown in Scheme 2. The synthesized material was purified on a silica column and recrystallized to yield a pure solid material. The chemical structure of the synthetic material was confirmed by NMR, elementary analysis and FAB-MS analysis.

As a result of TGA and DSC, 1-NDD-*t*-BPBP and 2-NDD-*t*-BPBP showed  $T_g$  of 180 and 177 °C. These are higher than that (110 °C) of 2-TNATA, commercial HIL material. It is expected that the device using the synthesized materials would be longer life-time under the Joule heating due to the high  $T_g$  compared to 2-TNATA.<sup>7</sup>

Figure 1 and Table I show the summarized results of the UV-vis., PL spectrum and CV of the synthesized materials in solution and film state.





Scheme 2. Synthetic route of new hole injection materials.

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**Figure 1.** (a) UV-Visible absorption and PL spectra in THF solution (b) in film state: UV-Visible absorption of 1-NDD-*t*-BPBP (square), 2-NDD-*t*-BPBP (circle).

As for the maximum values of UV-vis absorption spectrum of the synthesized materials in solution state, 1-NDD*t*-BPBP and 2-NDD-*t*-BPBP were respectively 303 and 316 nm, and the values of PL spectrum were 474 and 479 nm.

On the other side, UV-Vis. maximum values of 1-NDD*t*-BPBP and 2-NDD-*t*-BPBP are 306 and 316 nm in film state. The UV-vis. spectra and the absorption edges of these materials displayed virtually no changes on going from the solution to the film state. Additionally, because the synthesized materials in the film state showed almost no absorption at wavelengths longer than 450 nm, the synthesized materials are appropriate HIL materials due to their transparency properties.

CV was performed over the range -1.50 to 1.50 V. The four compounds displayed normal reversible oxidation and

Table I. Optical properties of synthesized materials.

	Solution <sup>a</sup>		Film on glass				
Compound	UV <sub>max</sub>	PL <sub>max</sub>	UV <sub>max</sub>	PL <sub>max</sub>	HO	LU	Band
	(nm)	(nm)	(nm)	(nm)	MO	MO	gap
1-NDD- <i>t</i> -BPBP	303	474	306	513	4.99	1.82	3.17
2-NDD- <i>t</i> -BPBP	316	479	316	465	5.01	1.82	3.19

Note: <sup>a</sup>Tetrahydrofuran (THF) solution  $(1 \times 10^{-5} \text{ M})$ .

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Figure 2. Cyclic voltammetry 0.1 M TBAP in acetonitrile; 1-NDD-*t*-BPBP (square), 2-NDD-*t*-BPBP (circle).

reduction waves as shown in Figure 2. The area corresponding to oxidation in the CV curve was larger than that for the reduction step, suggesting that these compounds favored the cationic state, consistent with a p-type material.

Based on these results, the HOMO and LUMO energy levels were calculated from the CV and optical band gap measurements (see Table I).<sup>12, 13</sup>

From the oxidation potential, the HOMO energy level was derived by assuming that the energy level of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) is 4.8 eV. The LUMO energy level was determined from the HOMO level and the optical band gap. The optical band gap was derived by analyzing the absorption edge with a plot of  $(h\nu)$  versus  $(\alpha h\nu)^2$ , where  $\alpha$ , h, and  $\nu$  are absorbance, Plank's constant, and the frequency of light.

The HOMO levels for the synthesized phenothiazine materials were 4.99 eV and 5.01 eV, intermediate between the HOMO of ITO (4.8 eV) and that of NPB (5.4 eV), the HTL material. Thus, the HOMO levels of the new materials were well-matched with the required HOMO level of HIL.

Based on the results above, OLED device was fabricated by using the synthesized material as HIL layer, and the EL characteristics were examined with device configuration of ITO/synthesized material or 2-TNATA (60 nm)/NPB

Table II. EL performances of synthesized material: ITO/Synthesizedmaterials or 2-TNATA (60 nm)/NPB (15 nm)/Alq3 (70 nm)/LiF(1 nm)/Al (200 nm) at 10 mA/cm².

Compounds	Operating voltage (V)	L. E. <sup><i>a</i></sup> (cd/A)	P. E. <sup>b</sup> (lm/W)	C.I.E $(x, y)$
1-NDD-t-BPBP	8.18	4.60	1.95	(0.35, 0.54)
2-NDD-t-BPBP	8.55	4.54	1.84	(0.35, 0.54)
2-TNATA	6.79	4.05	2.07	(0.34, 0.54)

Notes: a Luminance efficiency; b Power efficiency.



**Figure 3.** (a) *I–V–L* data, (b) Luminance and power efficiency of EL device: ITO/2-TNATA (triangle) or 1-NDD-*t*-BPBP (square) or 2-NDD-*t*-BPBP (circle) (60 nm)/NPB (15 nm)/Alq3 (70 nm)/LiF (1 nm)/Al (200 nm).

(15 nm)/Alq3 (70 nm)/LiF (1 nm)/Al (200 nm). The results are summarized in Table II and Figure 3.

In the case of power efficiency that considered operation voltage, 1-NDD-*t*-BPBP, 2-NDD-*t*-BPBP were 1.95 lm/W and 1.84 lm/W. These values are almost same as 2-TNATA's (about 2 lm/W) which is a commercial HIL material.

Also in luminance efficiency, 1-NDD-*t*-BPBP showed higher efficiency of 4.60 cd/A than 2-TNATA of about 4 cd/A at the same current density of 10 mA/cm<sup>2</sup>. In particular, it was shown that 1-NDD-*t*-BPBP shows a luminance efficiency about 12% improved compared to 2-TNATA, a commercial HIL material.

# 4. CONCLUSION

In this study, new hole injection materials for OLED based on phenothiazine were synthesized. The electro-optical properties of synthesized materials were examined by through UV-Vis., PL spectrum and CV.

As for the HOMO level of the synthesized materials, 1-NDD-*t*-BPBP and 2-NDD-*t*-BPBP were 4.99 and 5.01 eV, indicating well-matched values between HOMO (4.8 eV) of ITO and HOMO (5.4 eV) of NPB, HTL material.

In addition, judging from the fact that the synthesized materials both barely showed any absorption in the range of over 450 nm, the synthesized materials could be effectively used as an HIL material.

As a result of using the synthesized materials in OLED device as HIL, 1-NDD-*t*-BPBP of 4.60 cd/A was higher than 2-TNATA of about 4 cd/A. These results indicated that 1-NDD-*t*-BPBP shows more excellent luminance efficiency which is about 12% improved over 2-TNATA a commercial HIL material.

Moreover, it is expected that the device using the synthesized materials could be longer life-time under the Joule heating because of the high  $T_g$  compared to 2-TNATA.

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