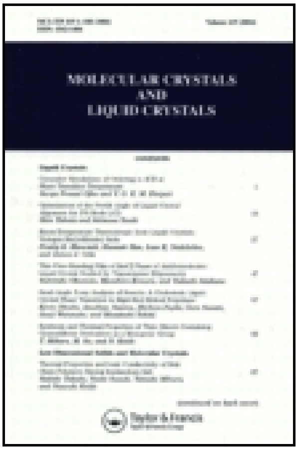

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Synthesis and Hole-Injection Property of Phenothiazinyl Derivative Containing Triphenylamine Moiety in OLED Device

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Synthesis and Hole-Injection Property of Phenothiazinyl Derivative Containing Triphenylamine Moiety in OLED Device

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We report the synthesis of a new conjugated compounds, tris-{4-[10-(4-tert-butylphenyl)-10H-phenothiazin-3-yl]phenyl}amine[TPPPA]. TPPPA showed UV-visible absorption maximum value of 352 nm and photoluminescence (PL) maximum value of 455 nm. It was found that TPPPA could be applied to HIL material by HOMO level calculation from cyclic voltammetry data. Organic light-emitting diodes (OLEDs) device with configuration of ITO/TPPPA(60 nm)/NPB(15 nm)/Alq$_3$ *(70 nm)/LiF(1 nm)/Al(200 nm) exhibited a current efficiency 2.85cd/A and power efficiency of 1.18 lm/W at 10 mA/cm*^{2} *current density.*

Keywords: electroluminescent; Hole Injection Layer (HIL); OLEDs; phenothiazine; Star-burst

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].

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Recently, a star-burst amine 4,4′,4″-tris{N,(3-methylphenyl)-N-phenylamino}-triphenylamine (m-MTDATA), 4,4',4"-tris{N,-(2-naphthyl)-N-phenylamino}-triphenylamine(2-TNATA) [3] and copper phthalocyanine (CuPc) [4] compound 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 [5]. In principle, all organic layers forming the EL devices had better have glass-transition temperature (T_g) as high as they can. The individual layer that has low T_g is likely to limit the thermal stability of the OLED.

In this article, we synthesized a new HIL material by using phenothiazinly and triphenylamine moieties, tris-{4-[10-(4-tert-butyl-phenyl)-10H-phenothiazin-3-yl]phenyl}amine [TPPPA].

Electro-optical properties of this material were characterized by cyclic voltammetry (CV), UV-visible and photoluminescence (PL) spectra. Moreover, multilayer EL device was fabricated using this material as a hole injection material.

EXPERIMENTAL

Synthesis

10-(4-t-Butyl-phenyl)-10H-phenothiazine (2)

Phenothiazine (1)(15 g, 75 mmol), *t*-BuONa (21.35 g, 225 mmol), $Pd_2(dba)_3$ (0.2 g, 2.25 mmol) were added to dried toluene solvent (500 ml), then $(t\text{-Bu})_3P$ and 1-bromo-4-*t*-butyl-benzen (14.5 ml, 82.5 mmol) were added into the reaction mixture. The mixture was heated to 110°C for 1 hr under nitrogen. After the reaction mixture cooled, it was then acidified with 1N HCl solution, and extracted with $CHCl_3$. The organic layer was dried by anhydrous $MgSO_4$ and filtered. The solution was evaporated. The residue was dissolved in $CHCl_3$ and added to methanol. The precipitate was filtered and washed with methanol. The dark blue residue was purified by column chromatography with $CHCl_3$: n-hexane (1:1) eluent to afford white solid(2) (23 g, 93%).

^{1}H NMR(300 MHz, $CDCl_3$): δ(ppm) 1.41(s, 9H), 6.20(d, 2H), 6.78(t, 2H), 6.84(t, 2H), 6.99(d, 2H), 7.27(d, 2H), 7.60(d, 2H), Fab$^+$-Mass m/e:330.

3-Bromo-10-(4-t-butyl-phenyl)-10H-phenothiazine (3)

10-(4-*t*-Butyl-phenyl)-10H-phenothiazine(2) (15 g, 45 mmol), NBS (7.9 g, 44 mmol) were added to 300 ml of $CHCl_3$ solution. The mixture was stirred at room temperature for 1 hr. The product was isolated by silicagel column chromatography using n-hexane as the eluent to afford white solid(3) (10 g, 54%).

^{1}H NMR(300 MHz, $CDCl_3$): δ(ppm) 1.40(s, 9H), 6.01(d, 1H), 6.16(d, 1H), 6.77 $\sim$ 6.85(m, 2H), 6.90(d, 1H), 6.97(d, 1H), 7.09(s, 1H), 7.27(d, 2H), 7.60(d, 2H), Fab$^+$-Mass m/e:410.

10-(4-t-Butyl-phenyl)-3-(4,4,5,5-tetramethyl)-1,3,2dioxaborolan-2-yl)-10Hphenothiazine(4)

3-Bromo-10-(4-*t*-butyl-phenyl)-10H-phenothiazine (6 g, 14.6 mmol) was dissolved in 200 ml of dry THF solution and stirred at -78°C, then 1.6 M n-BuLi 15 ml was added. And then isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6 ml, 30 mmol) was added to the reaction mixture after 30 min. After the reaction finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried by anhydrous $MgSO_4$ and filtered. The product was isolated by silicagel column chromatography using ethyl acetate:n-hexane (1:19) as the eluent to afford yellowish green solid(4) (4 g, 60%).

^{1}H NMR(300 MHz, $CDCl_3$): δ(ppm) 1.10(s, 12H), 1.30(s, 9H), 6.13(d, 2H), 6.79(m, 2H), 6.94(d, 1H), 7.22 $\sim$ 7.28(t, 3H), 7.40 (s, 1H), 7.60(d, 2H), Fab$^+$-Mass m/e:457.

Tris-{4-[10-(4-tert-butyl-phenyl)-10H-phenothiazin-3-yl]phenyl}amine[TPPPA]

10-(4-*t*-Butyl-phenyl)-3-(4,4,5,5-tetramethyl)-1,3,2dioxaborolan-2-yl)-10H-phenothiazine(4) (4 g, 8.75 mmol), tris(4-bromophenyl)-amine(5) (1.1 g, 2.23 mmol), $Pd(OAc)_2$ (0.5 g, 2.1 mmol) and (tris-*o*-tolyl)$_3$P (0.7 g, 2.2 mmol) were added to DME (300 ml) solution, then the prepared K_2CO_3 solution, which was dissolved in DME and H_2O (1:1, 100 ml) solvent, was added to reaction mixture. The organic layer was concentrated and then poured into acetone to give crude solid. The obtained solid was purified by column chromatography with $CHCl_3$: n-hexane (1:1) eluent to afford yellow solid (TPPPA) (2 g, 72%).

^{1}H NMR(500 MHz, Acetone): δ(ppm) 1.42(s, 27H), 6.21(d, 3H0, 6.25(d, 3H), 6.85(t, 3H), 6.91(t, 3H), 7.05(d, 3H), 7.13(d, 6H), 7.18(d, 3H), 7.32(s, 3H), 7.38(d, 6H), 7.53(d, 6H), 7.75(d, 6H), Fab$^+$-Mass m/e:1233.

Characterization

^{1}H NMR spectra were recorded on a Brucker, Advance DPX-300. Fast atom bombardment (FAB) mass spectra were recorded on a

JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were measured by a HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50(Xenon flash tube) was used for photo- and electro-luminescence spectroscopy. Melting point (T_m), grass-transition temperatures (T_g), and crystallization temperatures (T_c) of respective compounds were measured by differential scanning calorimetry (DSC) under nitrogen atmosphere using a DSC2910 (TA instrument) and thermogravimetric analysis (TGA) using SDP-TGA2960 (TA instrument). Redox potential of the compounds were determined by cyclic voltammetry (CV) using an EG&G 362 electrochemical workstation with a scanning rate of $50 \sim 200\,\mathrm{mV/s}$. The compound of interest was dissolved in N,N-Dimethylformamide (DMF) with 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte. We used a platinum working electrode and a saturated $Ag/AgNO_3$ referenced electrode. Ferrocene was used for potential calibration (all reported potentials are referenced against ferrocene/ferrocenium, FOC) and for reversibility criteria.

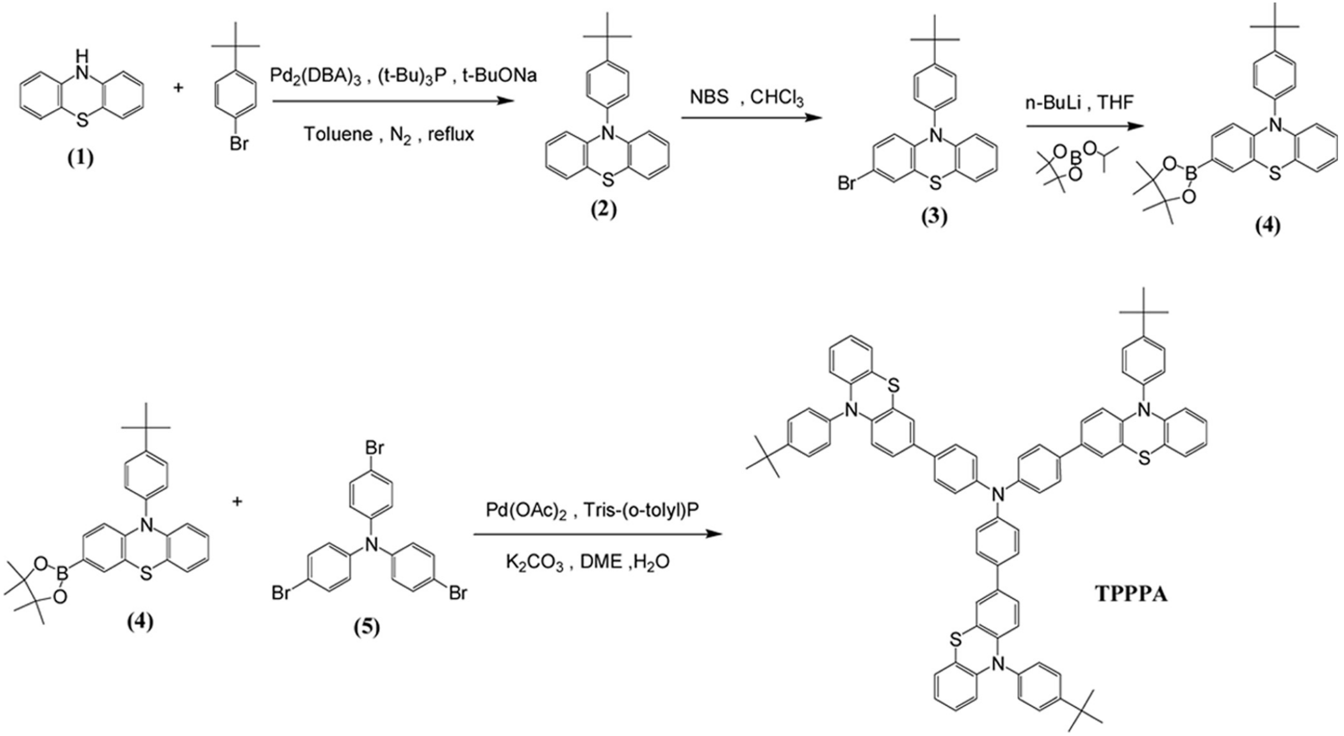
EL devices were fabricated using TPPPA as a hole injection layer, NPB as a hole transporting layer, Alq_3 as electron transporting and emitting layer, LiF as electron injection layer, ITO(1200 Å, 30 ohm) as the anode and Al as the cathode; ITO/TPPPA (60 nm)/NPB (15 nm)/Alq3 (70 nm)/LiF (1 nm)/Al (200 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 $9\,\mathrm{mm}^2$ 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-1000.

RESULTS AND DISCUSSION

In material synthesis (Scheme 1), we have placed triphenylamine moiety, which is very useful for hole injection property, into core site of molecule and have attached tri-molecules of phenothiazine group to triphenylamine as star-burst type. We also used tertiary butyl group in order to decrease packing effect and light absorption at visible light region. Phenothiazine group has been previously reported as hole injection layer by our group [6].

TPPPA was finally purified with column method to have highly pure powder and were identified NMR, Fab^+-MS.



SCHEME 1 Synthetic route of TPPPA.

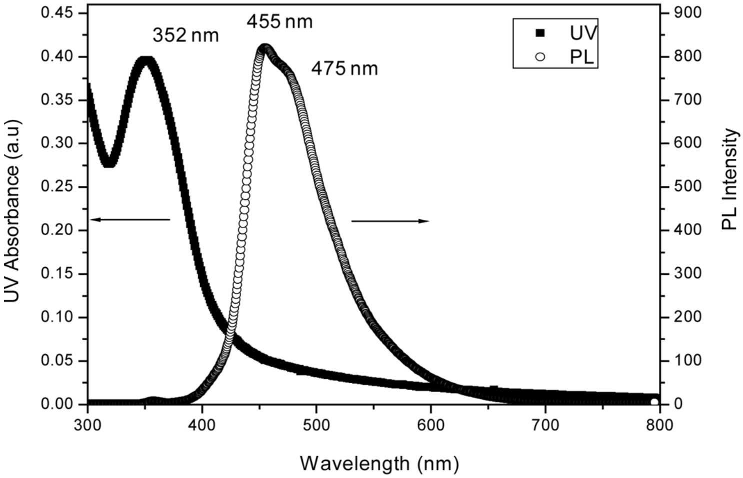


FIGURE 1 UV-Visible(■) and PL(○) spectra of TPPPA.

Figure 1 shows UV-visible absorption and PL spectra of TPPPA. UV-visible absorption maximum value was 352 nm and edge value was 401 nm, therefore this compound could be applied to HIL layer due to no absorption at visible light region. PL maximum values were shown at 455 nm and 475 nm.

Thermal property of TPPPA was determined by DSC and TGA experiment. As shown in Table 1, TPPPA exhibited glass transition temperatures of 130°C, which is relatively higher than conventional commercialized hole injection materials such as m-MTDATA ($T_g = 75°C$) and 2-TNATA ($T_g = 110°C$) [3]. We believe that TPPPA has better property for retaining the film morphology during device operation due to its high glass transition and recrystallization temperature [5]. TPPPA showed its own melting temperature as $T_m = 212°C$ and initial thermal degradation temperature of $T_d = 402°C$ under the nitrogen atmosphere.

To investigate electrochemical kinetic behavior, the measured cyclic voltammograms of TPPPA with the various scan rate (50 mV/s ~ 200 mV/s)

TABLE 1 Optical, Electrochemical and Thermal Property of TPPPA

UV_{onset} (nm)	UV_{max} (nm)	PL_{max} (nm)	T_g (°C)	T_m (°C)	T_d (°C)	HOMO (eV)	LUMO (eV)	Eg (eV)
401	352	455	130	212	402	5.08	1.99	3.09

are shown Figure 2. The peak potentials are gradually shift to higher potentials as the scan rate is increased.

The redox current value gradually increased as the scan rate increased. This result suggest that the electrochemical process of TPPPA is reproducible in the potential range of $-0.7 \sim 0.7\,\text{V}$ vs. Ag/Ag^{+}.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows: [7]

$$i_{p,a} = k\ v^{x} \tag{1}$$

$$\log i_{p,a} = \log k + x \log v \tag{2}$$

where $i_{p,a}$ = oxidation peak current density, v = scan rate, k = proportional constant, and x = exponent of scan rate.

Assuming that electrode kinetics satisfies Eq. (1), the electrochemical redox reaction on the electrode is controlled by either the electron transfer process, where x = 1, or the reactant diffusion process, where x = 0.5 [7].

The oxidation current density of TPPPA versus the scan rate is approximately linear relationship in the range of $50 \sim 200\,\text{mV/sec}$. The exponent of scan rate, x, value of TPPPA is found to be 0.40.

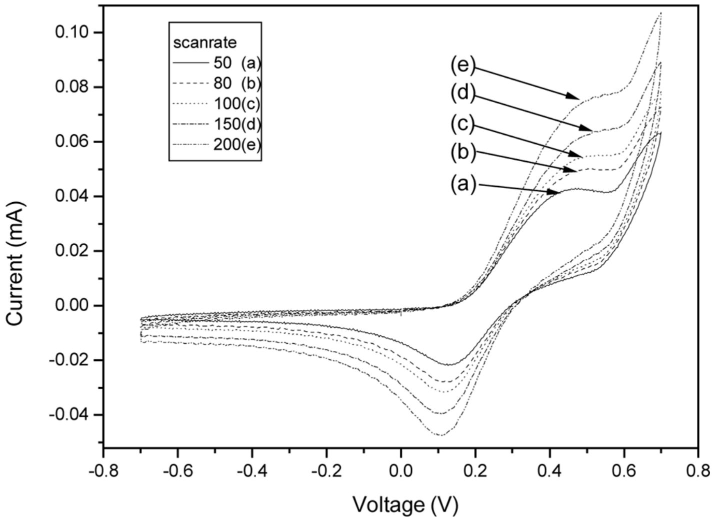


FIGURE 2 Cyclic voltammograms of TPPPA with various scan rate (0.1 M $(n\text{-}Bu)_4NBF_4$/DMF). (a) 50 mV/sec, (b) 80 mV/sec, (c) 100 mV/sec, (d) 150 mV/sec, sec, (e) 200 mV/sec.

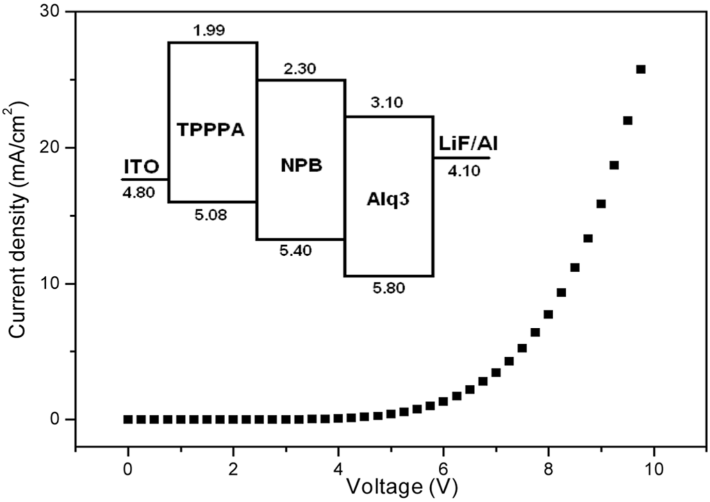


FIGURE 3 Energy diagram and current density-voltage characteristic of ITO/TPPPA/NPB/Alq$_3$/LiF/Al device.

HOMO, LUMO level and energy band gap were summarized in Table 1 and Figure 3. This electronic energy level showed that HOMO level of TPPPA is located between ITO work function and NPB HOMO level and is well matched with ITO and NPB layer. TPPPA LUMO level was located at high position of 1.99 eV and could be expected to block electron movement from EML layer to anode.

EL devices were fabricated in ITO/TPPPA (60 nm)/NPB (15 nm)/ Alq$_3$(70 nm)/LiF(1 nm)/Al(200 nm) configuration.

Figure 3 showed I-V characteristics of ITO/TPPPA (60 nm)/PB (15 nm)/Alq$_3$ (70 nm)/LiF (1 nm)/Al (200 nm) device and turn-on voltage of 5.5 V.

TABLE 2 Electroluminescent Properties of Multi-layered Device: ITO/ TPPPA (60 nm)/NPB (15 nm)/Alq$_3$ (70 nm)/LiF (1 nm)/Al (200 nm)

Current density (mA/cm^2)	Voltage (V)	EL$_{max}$ (nm)	Brightness (cd/m^2)	CIE (x, y)	Efficiency (cd/A)	Efficiency (lm/W)
10	7.6	515	285	(0.313, 0.524)	2.85	1.18
25	8.7	515	740	(0.313, 0.524)	2.96	1.07
50	9.8	515	1500	(0.312, 0.523)	3.00	0.96
100	10.8	515	2930	(0.313, 0.522)	2.93	0.85

We summarized EL performance in Table 2. The device showed high luminance efficiency of about 3 cd/A and power efficiency of about 1 lm/W. It also exhibited typical Alq_3 green emission of 515 nm and $x = 0.31$, $y = 0.52$ CIE value.

CONCLUSIONS

We synthesized new phenothiazyl derivatives containing triphenylamine moiety and applied this compound to OLED device as HIL material.

UV-visible absorption maximum value of TPPPA film was 352 nm and edge value was 401 nm, this compound could be applied to HIL layer due to proper HOMO level and no absorption at visible light region. PL maximum values were shown at 455 nm and 475 nm. TPPPA exhibited glass transition temperatures of 130°C, which is relatively higher than conventional commercialized hole injection materials such as m-MTDATA ($T_g = 75$°C) and 2-TNATA($T_g = 110$°C). The oxidation current density of TPPPA versus the scan rate is approximately linear relationship in the range of $50 \sim 200$ mV/sec. The exponent of scan rate, x, value of TPPPA is found to be 0.40. EL devices were fabricated in ITO/TPPPA (60 nm)/NPB(15 nm)/Alq_3(70 nm)/LiF(1 nm)/Al(200 nm) configurations. The device showed high luminance efficiency of about 3 cd/A and power efficiency of about 1 lm/W. It also exhibited typical Alq_3 green emission of 515 nm and $x = 0.31$, $y = 0.52$ CIE value.

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