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Synthesis and Electroluminescent Properties of Phenothiazyl Derivatives Having Aromatic Moieties

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We report the synthesis and electroluminescent properties of new aromatic compounds as hole-transporting materials based on phenothiazine, such as 1,4-diphenothiazyl-benzene [DPtzB], 1,4-diphenothiazyl-xylene [DPtzX] and 9,10-diphenothiazyl-anthracene [DPtzA]. DPtzB thin film exhibited photoluminescence (PL) maximum emission peak and emission shoulder at 450 and 475 nm, and maximum emission at 447 nm without emission shoulder was found in DPtzX thin film. When DPtzA was excited by incident light of 359 nm, DPtzA showed strong PL emission at 417 nm and weak emission at 600 nm. Luminance efficiencies of DPtzB, DPtzX and DPtzA-based electroluminescence (EL) devices were 3.57, 3.46 and 0.47 cd/A, and power efficiencies of DPtzB, DPtzX and DPtzA-based EL devices were 48, 1.26 and 0.20 lm/W.

Keywords: electroluminescence; hole-transporting layer; phenothiazine

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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 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].

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 [4]. Thus, a high T_g material is always desirable [5]. The most commonly used hole transporting material, 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl(NPB), has disadvantage of low T_g . 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 T_g hole transporting layer (HTL) materials [6,7].

In this paper, we synthesized a new HTL materials by using phenothiazyl moiety, 1,4-diphenothiazyl-benzene [DPtzB], 1,4-diphenothiazyl-xylene [DPtzX] and 9,10-diphenothiazyl-anthracene [DPtzA]. Optical properties of these materials were characterized by UV-visible and photoluminescence (PL) spectra. Moreover, multilayered EL devices were fabricated using these materials as hole- transporting materials.

EXPERIMENTAL

General Methods

^1H -NMR spectra were recorded on a Bruker, 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 temperatures (T_m), glass-transition temperatures (T_g) and degradation temperatures (T_d) 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 150 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/AgNO₃ reference electrode. Ferrocene was used for potential calibration (all reported potentials are reference against ferrocene/ferrocenium, FOC) and for reversibility criteria.

For EL device DPtzB, DPtzX, DPtzA were vacuum-deposited on top of ITO(1200 Å/30 ohm) under 10⁻⁶ torr, the rate of deposition being 1 Å/sec to give an emitting area of 9 mm² 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.

Synthesis

1,4-Diphenothiazyl-Benzene [DPtzB]

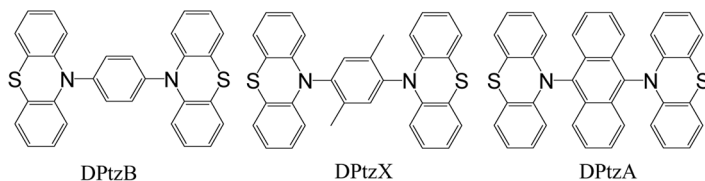
1,4-dibromo-benzene (1 g, 4.15 mmol), Phenothiazine (1.8 g, 9.13 mmol), *t*-BuONa (2.56 g, 24.9 mmol), Pd₂(dba)₃ (0.153 g, 0.25 mmol) were added to dried toluene solvent (150 ml), then (*t*-Bu)₃P and were added into the reaction mixture. The mixture was heated to 110°C for 1 hr under nitrogen. After the reaction mixture cooled, it was then acidified with 1N HCl solution, and extracted with CHCl₃. The organic layer was dried by anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered and washed with methanol. The dark blue residue was purified by column chromatography with CHCl₃:n-hexane (1:1) eluent to afford white solid (1.85 g, 94.4%).

¹H NMR(500 MHz, CDCl₃): δ(ppm) 7.49(s, 4H), 7.12(d, 4H), 7.10(t, 4H), 6.91(t, 4H), 6.52(d, 4H) Fab⁺-Mass *m/e*: 472.

1,4-Diphenothiazyl-Xylene [DPtzX]

DPtzX was obtained by using 2,5-dibromo-*p*-xylene (1 g, 3.8 mmol) and phenothiazine (1.6 g, 8.3 mmol) for the C-N coupling reaction. (1.74 g, 91.6%).

¹H NMR(500 MHz, CDCl₃): δ(ppm) 7.45(s, 2H), 6.99(d, 4H), 6.89(t, 4H), 6.81(t, 4H), 6.13(d, 4H), 2.45(s, 6H) Fab⁺-Mass *m/e*: 500.



SCHEME 1 Chemical structure of new hole-transporting materials.

9,10-Diphenothiazyl-anthracene [DPtzA]

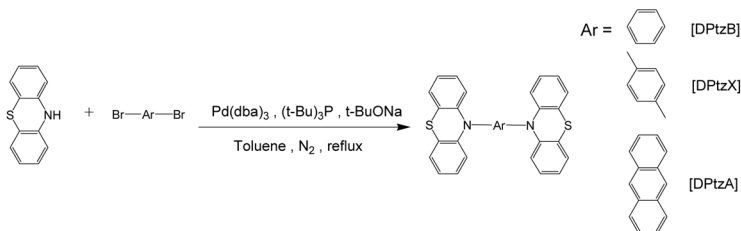
DPtzA was obtained by using 9,10-dibromo-anthracene (1g, 2.9 mmol) and phenothiazine (1.30 g, 6.55 mmol) for the C-N coupling reaction. (1.5 g, 90.4%).

^1H NMR(500 MHz, CDCl_3): δ (ppm) 8.43(d, 4H), 7.535(d, 4H), 7.09(d, 4H), 6.80(t, 4H), 6.69(t, 4H), 5.84(d, 4H) Fab^+ -Mass m/e : 572.

RESULT AND DISCUSSION

New hole-transporting compounds, shown in Scheme 1, were synthesized through simple Pd-catalyzed C-N coupling reaction to get high reaction yield(90 ~ 95%) Scheme 2. These products were finally purified with column and recrystallization method to have highly pure powder and were identified by ^1H -NMR, and Fab-Mass analysis.

Figure 1 shows UV-visible and photoluminescence spectra of DPtzB and DPtzX thin film on glass substrate. The maximum absorption of DPtzB and DPtzX appeared at around 314 and 324 nm, which are explained by electron donating effect of methyl group in DPtzX. Photoluminescence (PL) spectra of synthesized compounds were determined by using the excitation of the maximum absorption wavelength. DPtzB thin film exhibited PL maximum emission peak and emission shoulder at 450 and 475 nm, and PL maximum emission at 447 nm without emission shoulder was found in DPtzX thin film. This result



SCHEME 2 Synthetic routes of DPtzB, DPtzX and DPtzA.

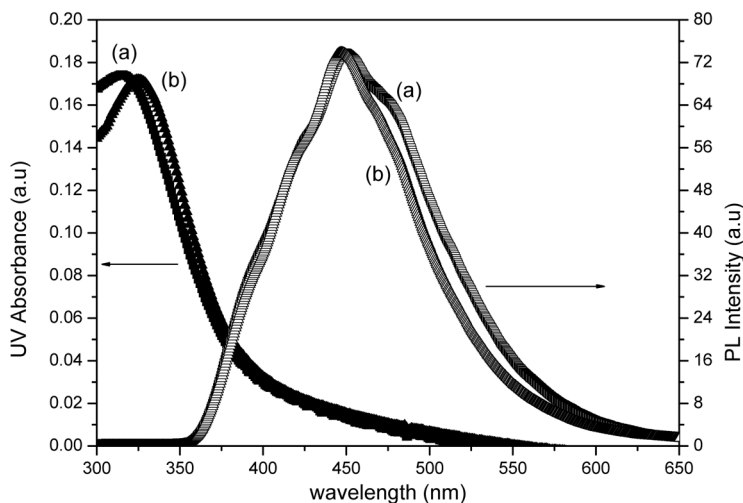


FIGURE 1 UV-visible absorption (solid) and PL emission spectra (open) of (a) DPtzB and (b) DPtzX thin films.

offers that a bulky xylene linkage of DPtzX reduces intermolecular interaction at excited state.

DPtzA thin film exhibited maximum UV-visible absorption value at 400 nm and very weak absorption at 456 nm. When DPtzA was excited by incident light of 359 nm, DPtzA showed strong PL emission at 417 nm and weak emission at 600 nm (Fig. 2). As the concentration of DPtzA solution was diluted, solution PL peak of DPtzA under the excitation of 376 nm appeared only at 425 nm and the longer wavelength emission peak of 624 nm disappeared due to dilution effect (Fig. 2 (c)). As a result, we can estimate that the longer wavelength emission of 624 nm from DPtzA might be originated from the intermolecular aggregation both in ground and excited state.

As we mentioned the importance of thermal property in introduction part, we checked thermal property by TGA and DSC experiment. As shown in Table 1, each compound showed its own melting temperature (T_m) and initial thermal degradation temperature (T_d). The order of T_d and T_m was DPtzA, DPtzB and DPtzX, and this order could be related with bulkiness and flatness of chemical structures. DPtzA and DPtzB also showed high glass transition temperature (T_g) of 207°C and 202°C. When we consider T_g of NPB as 96°C [8], these are high values in OLED materials.

The energy band gaps and HOMO, LUMO level of DPtzB, DPtzX and DPtzA were estimated by cyclic voltammograms (CV) and the

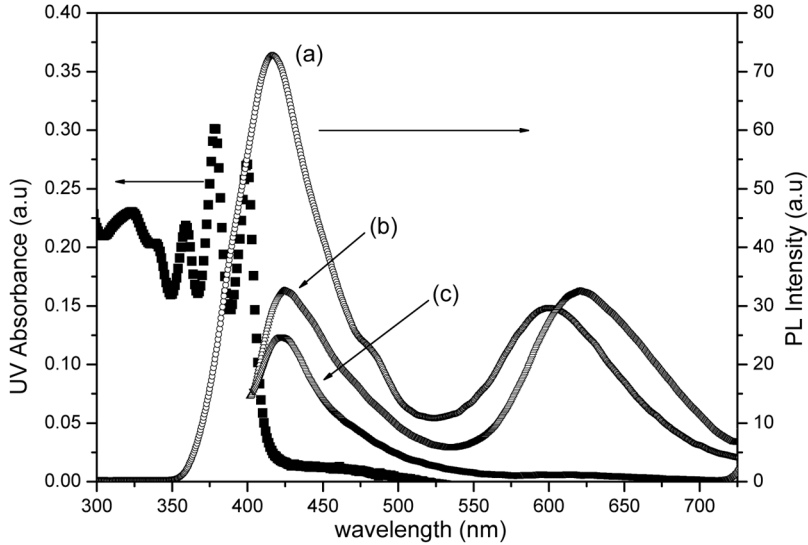


FIGURE 2 UV-visible absorption (solid) and PL emission spectra of (a) DPTzA thin film, (b) 8.74×10^{-4} M DPTzA solution in CHCl_3 and (c) 8.53×10^{-7} M DPTzA solution in CHCl_3 .

analysis of absorption edge with a plot of $(h\nu)$ vs. $(\alpha h\nu)^2$, where α , h , and ν are absorbance, Plank’s constant, and the frequency of light and summarized in Table 1. As you see in Table 1, energy band gap of DPTzA is slightly decreased from 3.4 eV to 3.0 eV because of longer conjugation length of anthracene. LUMO level of DPTzA as 2.2 eV is located at upper level than DPTzB and DPTzX’s. It accounts that there is electron blocking effect between DPTzA layer and Alq_3 both as emitter and electron transporting layer in EL device. Based on aggregation effect of only DPTzA in UV and PL data, we could get another bandgap value of aggregated form in DPTzA. We asterisked the mark with the value in Table 1.

TABLE 1 Thermal and Electrical Properties of DPTzB, DPTzX and DPTzA

	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$T_d(^{\circ}\text{C})$	HOMO (eV)	LUMO (eV)	E_g (eV)
DPTzB	202	259	362	5.12	1.73	3.39
DPTzX	–	178	329	5.12	1.76	3.36
DPTzA	207	324	408	5.25	2.21 (2.85)*	3.04 (2.40)*

*Calculated from aggregation feature of DptzA.

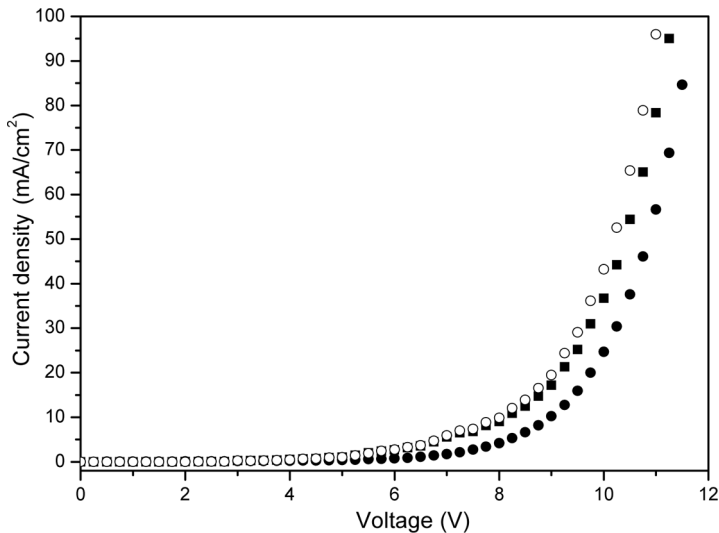


FIGURE 3 Current density-voltage characteristics of ITO/m-MTDATA (60 nm)/DPtzB(■) or DPtzX(●) or DPtzA(○)(15 nm)/Alq₃(70 nm)/LiF(1 nm)/Al device.

EL devices were fabricated in ITO/m-MTDATA(60 nm)/DPtzB or DPtzX or DPtzA(15 nm)/Alq₃(70 nm)/LiF(1 nm)/Al(200 nm) configuration for EL properties. Figure 3 shows typical current (I)-voltage (V) characteristics curve for proposed device configuration. All devices showed turn-on voltage of around 6 V and typical rectifying current behavior at above turn-on voltage.

All of these EL devices exhibited a green light emission at around 520 nm due to Alq₃ emission. EL properties of new hole-transporting layered devices are summarized in Table 2 at 10 mA/cm² current density.

TABLE 2 Performance Characteristics of Organic EL Device at 10 mA/cm²: ITO/m-MTDATA(60 nm)/DPtzB or DPtzX or DPtzA(15 nm)/Alq₃(70 nm)/LiF(1 nm)/Al(200 nm)

	EL _{max} (nm)	Voltage (V)	Luminance	Power	C.I.E. (x,y)
			Efficiency (cd/A)	Efficiency (lm/W)	
DPtzB	521	7.6	3.57	1.48	(0.344, 0.554)
DPtzX	521	8.6	3.46	1.26	(0.350, 0.549)
DPtzA	535	7.5	0.47	0.20	(0.424, 0.519)

Luminance efficiencies DPtzB, DPtzX and DPtzA-based EL devices were 3.57, 3.46 and 0.47 cd/A, and power efficiencies DPtzB, DPtzX and DPtzA-based EL devices were 1.48, 1.26 and 0.20 lm/W, respectively. The efficiency of DPtzA-based EL device appeared to be very lower than other's. It might be that some of electrons came from Alq₃ layer transport to the LUMO level of DPtzA. We are working on the related phenomena between morphology and device property. Further results of morphological aggregation effect will be reported.

CONCLUSION

New hole-transporting compounds were synthesized through simple Pd-catalyzed C-N coupling reaction to get high reaction yield. The maximum absorption of DPtzB and DPtzX appeared at around 314 and 324 nm. DPtzB thin film exhibited PL maximum emission peak and emission shoulder at 450 and 475 nm, and PL maximum emission at 447 nm without emission shoulder was found in DPtzX thin film. DPtzA thin film exhibited maximum UV-visible absorption value at 400 nm and very weak absorption at 456 nm. When DPtzA was excited by incident light of 359 nm, DPtzA showed strong PL emission at 417 nm and weak emission at 600 nm.

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