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Conjugated copolymer, poly[N-(2-ethylhexyl)phenothiazine-alt-6-phenyl phenanthridine] [poly(PZ-PTI)], with azomethine linkage was synthesized by Schiff-base reaction. This new conjugated copolymer exhibited improved solubility in common organic solvents due to the presence of alkyl side chains on phenothiazine rings as well as polar azomethine groups in main chains. Single-layered PLED made with poly(PZ-PTI) as an emitting layer exhibited EL (emission) at 572 nm (yellow; color coordinates of $x = 0.51$, $y = 0.48$). Double-layered PLED fabricated with the synthesized polymer as an emitting layer and Alq₃ as an electron transporting layer exhibited enhanced EL emission and efficiency compared to that of single-layered PLED. With increasing the thickness of Alq₃ layer in double-layered PLED the emission peak gradually shifted to the single-layered PLED made with only Alq₃ as an emitting layer, confirming good hole transporting behaviour of the synthesized conjugated copolymer.

Keywords: azomethine, hole transporting, phenothiazine, phenyl phenanthridine, polymer light emitting diode

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INTRODUCTION

A number of conjugated polymers have been synthesized and investigated for utilizing as light emitting layers since R. H. Friend [1] reported electroluminescence devices fabricated with poly(*p*-phenylene vinylene) (PPV). It has been shown so far that many polymeric electronic materials have an advantage on processing method in that polymers are usually spin-coated from solution. However, PPV must be vacuum-deposited in a low molecular precursor with subsequent thermal conversion due to its insolubility in organic solvents. The dialkoxy substitution on PPV, for example MEH-PPV, has been utilized to impart the solubility of PPV derivatives in common organic solvents and to tune their electro-optic properties. Another class of conjugated polymers is based on heterocyclic conjugated polymers such as polythiophene, polypyridine and polypyridine vinylene. Substitution in case of polythiophene at the 3-position also serves to provide the solution processability in the fabrication of PLED and modified electro-optic characteristics of the final PLED. It has been reported that with electron-deficient aromatic groups of heterocyclic conjugated polymers, they tend to act as electron transporting layers in PLEDs in comparison to their PPV analogs.

Polyazomethine-type conjugated polymers containing $-\text{C}=\text{N}-$ repeating units prepared by the reaction of aromatic dialdehydes and aromatic diamine have been suggested as an alternative for light-emitting layers in PLEDs. Weaver *et al.* [2] fabricated organic PLED with chemical vapor deposited polyazomethine films and reported that the polyazomethine having a large ionization potential acted as a hole-blocking electron transporting layer. Fisher *et al.* [3] prepared a thin film of oligoazomethine via successive deposition of aromatic diamine and dialdehyde monomers under high vacuum conditions and showed electron transporting capability of the oligoazomethine layer in PLEDs. It has been revealed, however, that polyazomethine itself is difficult to dissolve in organic solvent and thus require vapor deposition technique to make thin films.

In this work, we present the synthesis of conjugated alternating copolymer that can be used for the fabrication of PLEDs by spin-coating, and then the electro-optic properties of PLEDs. The conjugated alternating copolymer containing both phenothiazine moiety and azomethine linkage in the main chain was synthesized via Schiff-base reaction [4,5]. Long alkyl group on phenothiazine ring and polar azomethine unit in the main chain were introduced, respectively, in order to impart higher solubility of the copolymer in organic solvents. Single- and double-layered PLEDs were fabricated by spin-coating the conjugated

copolymer as a light-emitting layer on ITO glass and their electroluminescent properties such as emission color and efficiency were studied from the viewpoint of polymer structure.

EXPERIMENTAL

Monomer Synthesis

Synthesis of aromatic dialdehyde monomer, *N*-(2-ethylhexyl)-3,6-diformylphenothiazine (DFPZ) containing phenothiazine moiety is shown in Figure 1. *N*-(2-Ethylhexyl)phenothiazine (EHPZ) was prepared in the first synthetic step [6,7]. Phenothiazine (6 g, 0.03 mol) was added to a suspension of sodium hydroxide (7.2 g, 0.18 mol) in 60 ml of dimethyl sulfoxide (DMSO) which was prepared by vigorous stirring for 0.5 hr under nitrogen atmosphere. After stirring for 1 hr 2-ethylhexylbromide (5.8 g, 0.03 mol) was added. The reaction was carried out for 3 hr at room temperature. The resulting mixture was concentrated under reduced pressure utilizing a rotary evaporator, and then extracted with water and dichloromethane. The collected organic layer was concentrated and purified using silicagel column (eluent; *n*-hexane:petroleum ether = 2:1). After evaporating the eluent EHPZ was obtained as liquid in 73% yield. $^1\text{H-NMR}$ (CDCl_3), δ : 6.87, 7.12 (*m*, 8H, Ar-H), 3.70 (*m*, 2H, $>\text{N}-\text{CH}_2-$), 1.93 (*t*, 1H, $>\text{CH}-$), 1.22–1.44 (*m*, 9H, $-\text{CH}_2-$), 0.83–0.87 (*m*, 6H, $-\text{CH}_3$), IR (KBr), cm^{-1} : 3064 (Ar CH), 2926 (aliphatic CH), 2857 ($>\text{N}-\text{CH}_2-$), 1593, 1485 (Ar C=C).

DFPZ was synthesized with Vilsmeier-Haack formylation in the second step [8]. Phosphoryl chloride (122.7 g, 0.8 mol) was added

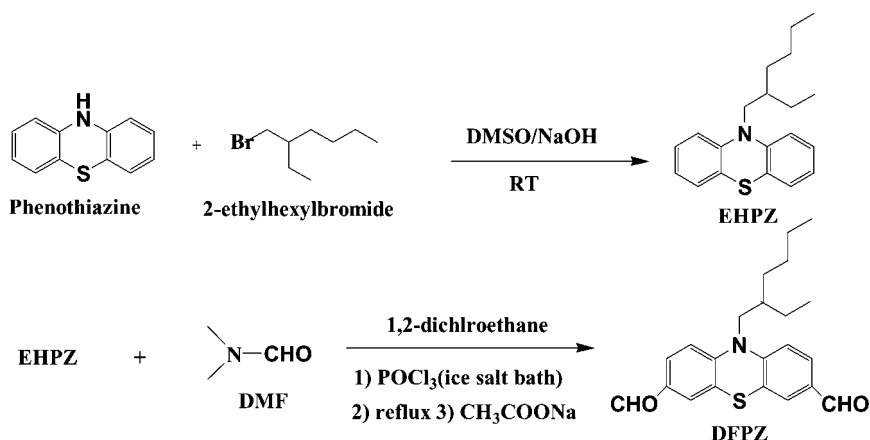


FIGURE 1 Synthesis of dialdehyde compound as a monomer.

dropwise over a period of 0.5 hr to a mixture solution of EHPZ (12.36 g, 0.04 mol) and *N,N*-dimethylformamide (DMF) (58.5 g, 0.8 mol) in 1,2-dichloroethane (15 ml) in an ice bath. The solution was then heated to reflux temperature. After refluxing for 72 hr, the solution was cooled to room temperature. The solution was poured into a 33 wt% sodium acetate (27.8 g) aqueous solution, and stirred for 4 hr to complete the hydrolysis. The resulting mixture was concentrated under reduced pressure, and poured into acetone. Insoluble salts in acetone were filtered off, and the filtrate was concentrated. The residue was extracted with water and dichloromethane, and the collected organic layer was concentrated. After purification by silicagel column (eluent; *n*-hexane: petroleum ether = 2:1) and evaporation of eluent, DFPZ was obtained as liquid in 69% yield. $^1\text{H-NMR}$ (CDCl_3), δ : 9.73 (*m*, 2H, aldehydic hydrogen), 6.88, 7.56 (*m*, 6H, Ar H), 3.73 (*t*, 2H, $>\text{N-CH}_2-$), 1.17–1.85 (*m*, 9H, $-\text{CH}_2-$, $>\text{CH-}$), 0.76–0.82 (*m*, 6H, $-\text{CH}_3$), IR (KBr), cm^{-1} : 3048 (Ar CH; weak signal), 2927 (aliphatic CH), 2857 ($>\text{N-CH}_2-$), 2724 (aldehydic hydrogen), 1688 (C=O), 1600, 1465 (Ar C=C).

Polymerization

Schiff-base reaction was used to prepare the conjugated copolymer, poly[*N*-(2-ethylhexyl)phenothiazine-*alt*-6-phenyl phenanthridine] [poly (PZ-PTI)], which contains phenothiazine, phenanthridine and azo-methine moieties in the main chain, as shown in Figure 2 [4,9]. 3,8-Diamino-6-phenyl-phenanthridine (2.85 g, 0.01 mol) was added dropwise to a mixture solution of DFPZ (3.67 g, 0.01 mol) in benzene (60 ml) at room temperature under nitrogen atmosphere. The solution was then heated to reflux temperature. After reaction, the resulting mixture was concentrated under reduced pressure, and then washed with methanol and water. After filtration and vacuum drying at 50°C for 48 hr the poly(PZ-PTI) was obtained as orange color powder. Yield = 62%, IR (KBr), cm^{-1} : 3027 (Ar CH), 2923 (aliphatic CH), 2855 ($>\text{N-CH}_2-$), 1621, 1471 ($-\text{N}=\text{C-}$), 1574, 1496 (Ar C=C).

Polymer LED Device Fabrication

Single-layered PLED was assembled with using the synthesized conjugated poly(PZ-PTI) as an emitting layer. Indium-tin oxide (ITO) coated glass with a sheet resistance of $30\ \Omega/\square$ was cut into $2.0 \times 2.0\ \text{cm}^2$, and electrode area was prepared by photo-etching technique. It was cleaned successively with acetone, methanol, and mixture of isopropyl alcohol and water (1:1 by vol.) in an ultrasonic bath. Filtered solutions of

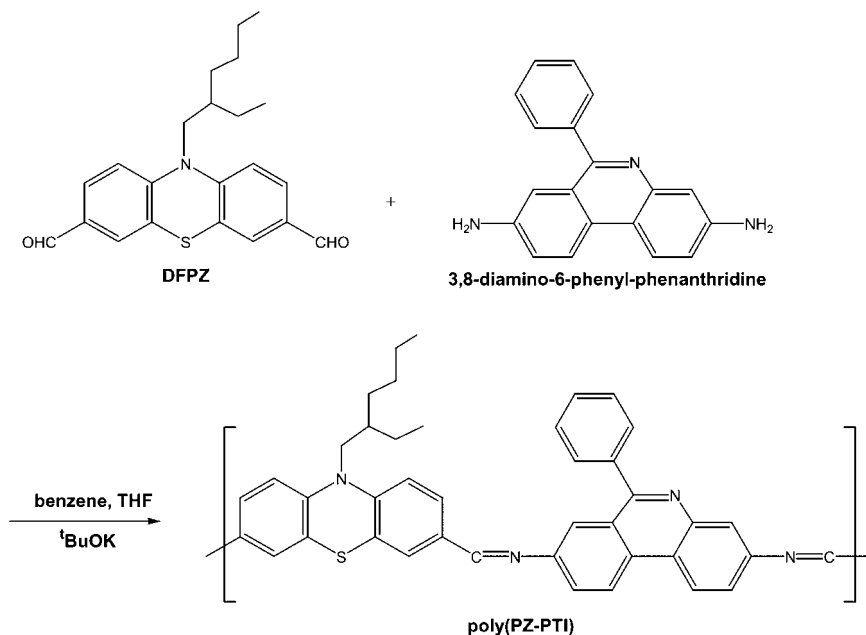


FIGURE 2 Synthesis of conjugated polymer poly(PZ-PTI).

conjugated poly(PZ-PTI) in benzene were cast on patterned ITO glass by spin coating and the solvent was evaporated to give emitting layers with thickness about 600 Å measured by scanning probe microscope (Nanoscope Multimode SPM & Bio Scope). Thin Mg film with about 4000 Å thickness was deposited as cathode (approximately 0.4 cm²) by E-beam method at a rate of 20 Å/sec on top of the emitting layer.

Double-layered PLED was also fabricated with Alq₃ as an additional electron transporting layer between an emitting layer and a metal electrode. After spin coating and drying of poly(PZ-PTI) emitting layer, vacuum deposition of Alq₃ was performed on top of emitting layer at a rate of 3–5 Å/sec yielding 200 Å thickness. The Mg metal was deposited on Alq₃ thin film to give ITO/poly(PZ-PTI)/Alq₃/Mg type double-layered PLEDs.

Characterization and Measurement

¹H-NMR and FT-IR spectra of synthesized compounds were taken on a Varian Unity Plus 300 and Jasco FT/IR-620 spectrometer, respectively. Molecular weight of conjugated copolymer was measured by using Waters gel permeation chromatography (GPC) equipped with

a 410 differential refractometer, 510 HPLC pump, and Styragel HR 5E column using tetrahydrofuran (THF) as an eluent against polystyrene standards at room temperature. UV-visible absorption spectra of the copolymers were obtained by Shimadzu UV-2100. Electroluminescence spectra and color coordinates were measured by using Spectroscan PR 704 (Photoresearch Inc.). Current and luminance vs. voltage profiles were obtained by using a dc power supply connected with Model 8092A Digital Multimeter (Hyun Chang Product Co. Ltd) and luminance meter (Minolta LS-100) equipped with close-up lens (No. 110, Φ 40.5 mm) at room temperature, respectively.

RESULTS AND DISCUSSION

Results on the solubility of poly(PZ-PTI) synthesized are listed in Table 1. It appeared that the poly(PZ-PTI) was soluble in organic solvents such as THF, DMF, 1,1,2,2-tetrachloroethane, benzene and *N*-methyl-2-pyrrolidone at room temperature. Improved solubility of the poly(PZ-PTI) has been suggested to originate from relatively long bulky alkyl substitution in the phenothiazine units and polar azo-methine linkages in the main chain. PLED devices therefore could be easily fabricated by spin-coating process using poly(PZ-PTI) as a light-emitting layer. The molecular weight and molecular weight distribution of the synthesized conjugated copolymer determined by GPC were calculated to be $\overline{M}_n = 4,700$ g/mol and $\overline{M}_w/\overline{M}_n = 1.15$.

In Table 2, electro-optical properties were summarized in terms of maximum π - π^* transition ($\lambda_{\max,UV}$) and HOMO-LUMO band gap energy ($\lambda_{\text{edg},UV}$) from UV-visible spectrum, and emission maximum ($\lambda_{\max,EL}$) from EL spectrum. The $\lambda_{\max,UV}$ and the $\lambda_{\text{edg},UV}$ of the poly(PZ-PTI) were observed at 414 nm (2.99 eV) and 514 nm (2.41 eV), respectively. The $\lambda_{\max,EL}$ of single-layered PLED consisted of ITO/poly(PZ-PTI)/Mg was recorded at 572 nm (2.17 eV).

Figure 3 shows the luminance vs. voltage profile of single-layered (ITO/poly(PZ-PTI)/Mg) and double-layered (ITO/poly(PZ-PTI)/Alq₃/

TABLE 1 Solubility Properties of Conjugated Copolymer

Solvnet	CHCl ₃	CH ₂ Cl ₂	Benzene	THF	DMF	DMSO	TCE	NMP
Solubility	Δ	O	O	O	O	Δ	O	O

O: soluble, Δ : swelling; CHCl₃: chloroform, CH₂Cl₂: dichloromethane, THF: tetrahydrofuran, DMF: *N,N*-dimethylformamide, DMSO: dimethylsulfoxide, TCE: 1,1,2,2-tetrachloroethane, NMP: *N*-methyl-2-pyrrolidone.

TABLE 2 Electro-Optical Properties of the Conjugated poly(PZ-PTI) Copolymer

Conjugated polymers	$\lambda_{\max,UV}$ (nm/eV)	$\lambda_{\text{edg},UV}^a$ (nm/eV)	$\lambda_{\max,EL}$ (nm/eV)
Poly(PZ-PTI)	414/2.99	514/2.41	572/2.17

^aCalculated from the onset point of UV-visible absorption spectrum.

Mg and ITO/Poly(*N*-vinylcarbazole) (PVK)/poly(PZ-PTI)/Mg PLEDs. Double-layered PLED with Alq₃ as an electron transporting layer exhibited both enhanced emission intensity (168 cd/cm² at 21 V) and efficiency compared to the single-layered PLED (7.9 cd/cm² at 19 V). Turn-on voltage of single-layered PLED was higher than that of double-layered PLED including Alq₃ electron transporting layer. These results indicated that energy barrier at the interface between poly(PZ-PTI) and Mg cathode in single-layered PLED is higher than that at Alq₃/Mg interface in the double-layered PLED. Luminance and efficiency of double-layered PLED made with PVK known as a hole transporting layer, however, were lower than those of single-layered PLED. In addition, the luminance maximum of ITO/PVK/poly(PZ-PTI)/Mg

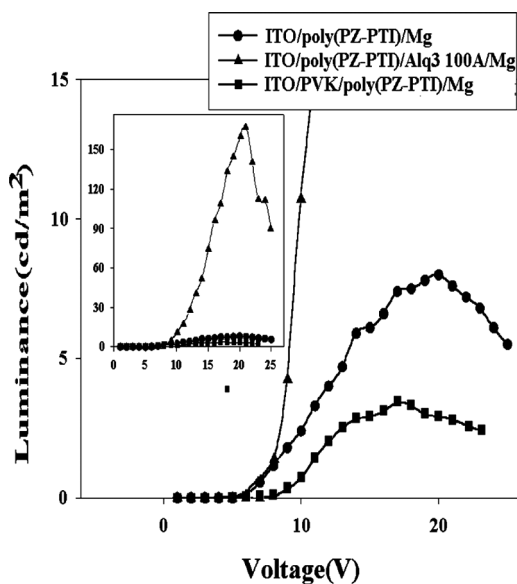
**FIGURE 3** Luminance versus voltage profile of single and double layer PLED fabricated with poly(PZ-PTI) as light emitting layer.

TABLE 3 Color Coordinates of Single and Double Layered PLEDs

Device no.	Structure of PLED	Color coordinates (x, y)	Emission color
(1)	ITO/poly(PZ-PTI)/Mg	0.51, 0.48	Yellow
(2)	ITO/poly(PZ-PTI)/Alq3(100 Å)/Mg	0.49, 0.50	Greenish yellow
(3)	ITO/poly(PZ-PTI)/Alq3(200 Å)/Mg	0.42, 0.53	Greenish yellow
(4)	ITO/poly(PZ-PTI)/Alq3(400 Å)/Mg	0.39, 0.54	Yellow green
(5)	ITO/Alq3(300 Å)/Mg	0.35, 0.53	Yellowish green

devices was lower than that of ITO/poly(PZ-PTI)/Mg device. From these results, it could be concluded that conjugated poly(PZ-PTI) synthesized had good hole transporting property under the induced electric field. This may be due to the presence of alkyl substituted phenothiazine units in the polymer since the aromatic amines are well known to be as a hole transporting layer in the EL devices [10].

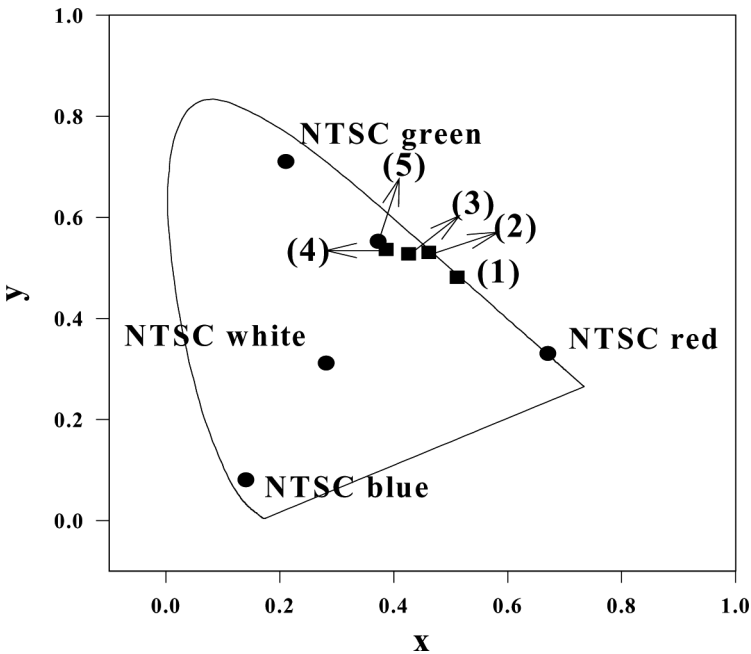


FIGURE 4 Effect of Alq₃ layer thickness in the color coordinates of PLEDs; (1) single-layered ITO/poly(PZ-PTI)/Mg, (2) double layered ITO/poly(PZ-PTI)/Alq₃(100 Å)/Mg, (3) double layered ITO/poly(PZ-PTI)/Alq₃(200 Å)/Mg, (4) double layered ITO/poly(PZ-PTI)/Alq₃(400 Å)/Mg, and (5) single-layered ITO/Alq₃(300 Å)/Mg.

Color coordinates and color name of single and double layered PLEDs with corresponding color name were summarized in Table 3. The emission color name could be determined from these color coordinates as measured by Spectroscan PR-704 (Photoresearch Inc.) and Kelly's map [11] in CIE (Commission Internationale de l'Eclairage) 1931 chromaticity diagram [12]. With increasing thickness of electron transporting Alq₃, emission color was changed from yellow to green. EL emission colors of double-layered (ITO/poly(PZ-PTI)/Alq₃/Mg) PLEDs with different thickness of Alq₃ were compared with those of standard red, green, blue, and white color established by NTSC (national television system committee) in Figure 4 [13]. As the thickness of Alq₃ layer increased, the emission color of double-layered (ITO/poly(PZ-PTI)/Alq₃/Mg) PLED exhibited gradual shift to that of the single-layered (ITO/Alq₃/Mg) PLED fabricated with only Alq₃ as an light-emitting layer. This result indicated that recombination of holes and electrons also took place in the Alq₃ layer with increasing the thickness of Alq₃ layer, since the Alq₃ layer could function both as an emitting layer and an electron transporting layer. This phenomenon further supported that the synthesized azomethine-type conjugated copolymer had a good hole transporting property, which has been suggested to originate from phenothiazine functional groups in the main chain.

CONCLUSIONS

Alternating conjugated copolymer containing phenothiazine and phenanthridine moiety, and azomethine ($-C=N-$) linkage in the main chain was synthesized by Schiff-base type reaction. The polymer exhibited good solubility in common organic solvents due to long alkyl substitution in the phenothiazine units and polar azomethine linkages in the main chain. Single and double-layered polymer light emitting diode (PLED) made with poly(PZ-PTI) as an emitting layer were fabricated by spin-coating on ITO (indium-tin oxide) glass and their electroluminescent properties were studied. Double-layered (ITO/poly(PZ-PTI)/Alq₃/Mg) PLED made with the synthesized polymer as an light-emitting layer and Alq₃ as an electron transporting layer exhibited enhanced EL emission and high efficiency compared to those of single-layered (ITO/poly(PZ-PTI)/Mg) PLED. As the thickness of the Alq₃ layer increased, the emission color of double-layered (ITO/poly(PZ-PTI)/Alq₃/Mg) PLEDs approached to that of single-layered (ITO/Alq₃/Mg) PLED indicating that the synthesized copolymer performed as good hole transporting layer.

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