Thesis for the Degree of Master of Engineering

Improvement of efficiency of polymer light-emitting diodes and polymer solar cells through the interfacial engineering

By

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February 2012

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(계면 공학을 통한 고분자발광소자 및
고분자태양전지의 효율 향상)

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by
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계면 공학을 통한 고분자발광소자 및 고분자태양전지의 효율 향상

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요 약

본 논문은 층간 소재의 개발을 통해 고분자 발광 소자와 고분자 태양 전지의 효율을 향상시키기 위한 연구 결과이다. 고분자 발광 소자 및 고분자 태양전지는 양극/정공 주입 및 수송층/발광층 (고분자 발광 소자) 또는 활성층 (고분자 태양전지)/전자 주입 및 수송층/음극의 구조를 가진다. 일반적으로 많이 사용되는 정공 주입 및 수송 물질인 poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)의 경우, pH 2 정도의 강한 산성을 띄고 있어 소자의 수명과 효율에 좋지 않은 영향을 끼친다고 보고되었다. 이를 개선하기 위해 중성을 띄며, 전자 주개 성능이 우수한 높은 호모 (highest occupied molecular orbital, HOMO)에너지 준위를 가지는 phenothiazine (PT) oligomer 에 열경화가 가능한 methacrylate (MA), vinylbenezene (VB), vinyl (V)기를 도입하였다. 열경화 조건을 differential scanning calorimetry (DSC)를 통해 조사하였으며, UV-Vis spectrum 을 통해 우수한 내용매성을 가지는 것을 확인하였다. 또한 순환 전압 전류법 (cyclic voltammetry, CV)으로 호모에너지 준위를 조사하였다. MA 기를 가지는 PT oligomer 의 호모에너지 준위는 열경화 과정이 끝나면 -4.9eV 에서 -5.6 eV 정도의 낮은 에너지로 변하는 것을 확인하였다. 이는 MA 의 carbonyl 기에 전자가 트랩 (trap)되면서 나타나는 현상으로 예상된다. 합성한 열경화가 가능한 oligomer 를 정공 주입 및 수송층으로 사용한 결과, 고분자 발광 소자는 사용하지 않은 소자보다 최대 발광효율이 85~250% 향상됨을 확인할 수 있었다.

또한 알킬기 말단에 quaternary ammonium salt 를 도입하여 물 또는 알코올에 용해되며, 유기용매에 대한 내용매성을 가지는 물질을 합성하였다. 이런 물질들은 주로 전자 주입 및 수송층으로 5nm 이하의 두께로 코팅하면 quaternary ammonium salt 의 쌍극자의 배열을 통해 음극의 일 함수를 조절할 수 있다고 알려져 있다. 합성된 수용성 물질을 전자 주입 및 수송층으로 이용하여 전구조의 고분자 태양 전지와 고분자 발광 소자를 제작하였다. 고분자 태양 전지의 경우, 전자 수송층을 도입함으로써 약 20% 정도의 효율 향상을

보였고, 고분자 발광 소자의 최대 발광 효율은 10~70% 향상되었다. 이는 쌍극자의 배열로 인해 알루미늄 (aluminum, Al)의 일 함수가 작아져 전자의 이동이 향상된 결과로 예상된다.

Chapter I. Introduction

I-1. Background of Polymer Light Emitting Diodes and Polymer Solar Cells

Electroluminescence (EL) may be defined as the non-thermal generation of light upon the application of an electric field to a substrate. Since EL in conjugated polymers was first reported on poly(*p*-phenylene vinylene) (PPV) in 1990 [1], the considerable effort has been devoted to developing conjugated materials as the emissive units in polymer light-emitting device (PLED) for usage in display applications. The advantage of the PLED display is that it can work without a backlight due to emitting light by itself. Thus, PLED can display deep black levels and be thinner and lighter than liquid crystal display (LCD). In low ambient light conditions such as dark rooms, screen of PLED can achieve a higher contrast ratio than LCD. Another advantage is low cost due to solution process. And PLED can be fabricated on flexible plastic substrates. However, the disadvantages are short lifetime, low efficiency of blue PLED, color balance issues and so on.

Also, harvesting energy from sunlight directly using photovoltaic technology is considered as being one of the most important ways to address growing global energy needs using a renewable resource. Polymer solar cell (PSC) is one of alternative for producing clean and renewable energy due to that it can be fabricated onto large areas of lightweight flexible substrates by solution processing at a low cost. [2-3] First organic solar cell (OSC) was reported by C. W. Tang in 1986. The structure of OSC was bi-layer using CuPc and perylene derivates and the efficient of the device was about 1%. Since then, N. S. Sariciftci discovered photo-induced charge transfer (PICT) in device using a belnd of poly(*p*-phenylenevinylene) (PPV) and fullerene (C_{60}) derivative as a photo-active layer, they found that polymer/fullerene blend was effective material for photo-induced charge generation system in PSC. [4]

I-2. Device Structures and Operating Principles

The architectures of PLEDs and PSCs are almost same. The devices have anode/hole injection or transporting layer/emissive (PLEDs) or active (PSCs) layer/electron injection or transporting layer/cathode. But the current flow in PLEDs and PSCs is the opposite direction. In other words, light was made by electric energy in PLEDs; however, electric energy was made by solar energy in PSCs.

1-2-1. Polymer Light Emitting Diodes

Basically, PLEDs are made by placing several thin emissive polymer films between a transparent ITO electrode and a low work function metal electrode. To get high efficiency, charge (hole and electron) injection or transporting layer as a buffer layer between the electrode and the emissive layer was introduced in PLEDs. When the electric field is applied to the device, the anode injects holes into the emissive layer via the hole injection or transporting layer (HIL/HTL), while the cathode injects electrons into the emissive layer via the electron injection or transporting layer (EIL/ETL). The injected hole and electron are recombined in the emissive layer, then they emit light.

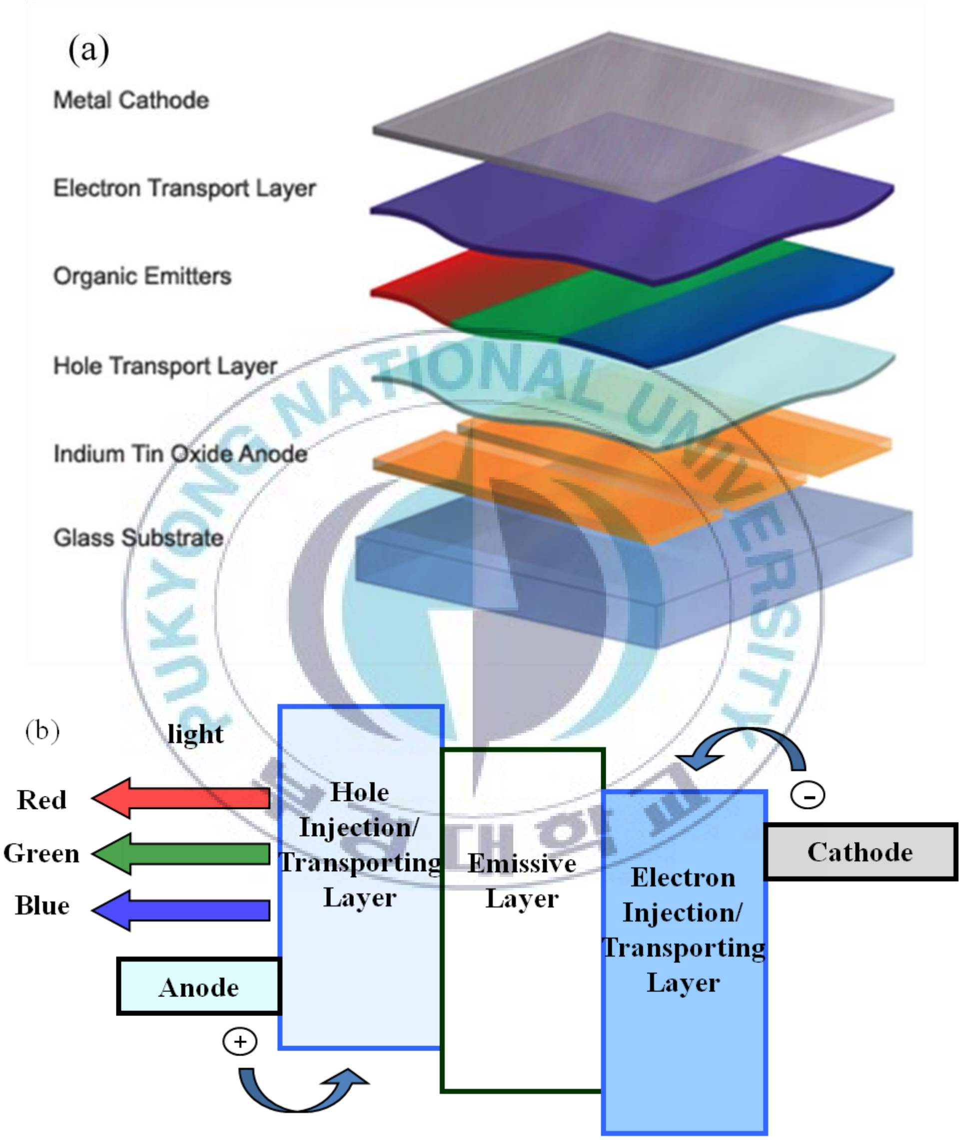


Figure I-1. (a) Device structure and (b) energy level diagram of PLED.

1-2-2. Polymer Solar Cells

Basically, PSCs are made by placing a blend of π-conjugated polymer (donor, D) and fullerene (acceptor, A) derivatives between a transparent anode and a metal cathode. The process of conversion of light into electricity of PSCs can be schematically described by the following steps: (1) Photo exitation of the donor to generate an electron-hole pair, which is called exciton. (2) Exciton diffusion to the donor-acceptor (D-A) interface. A distance longer than the maximum diffusion length (~ 20 nm) of exciton will lead to relaxation of the exciton. (3) Exciton dissociation at the D-A interface. (4) Charge transportation and collection at electrodes. [3]

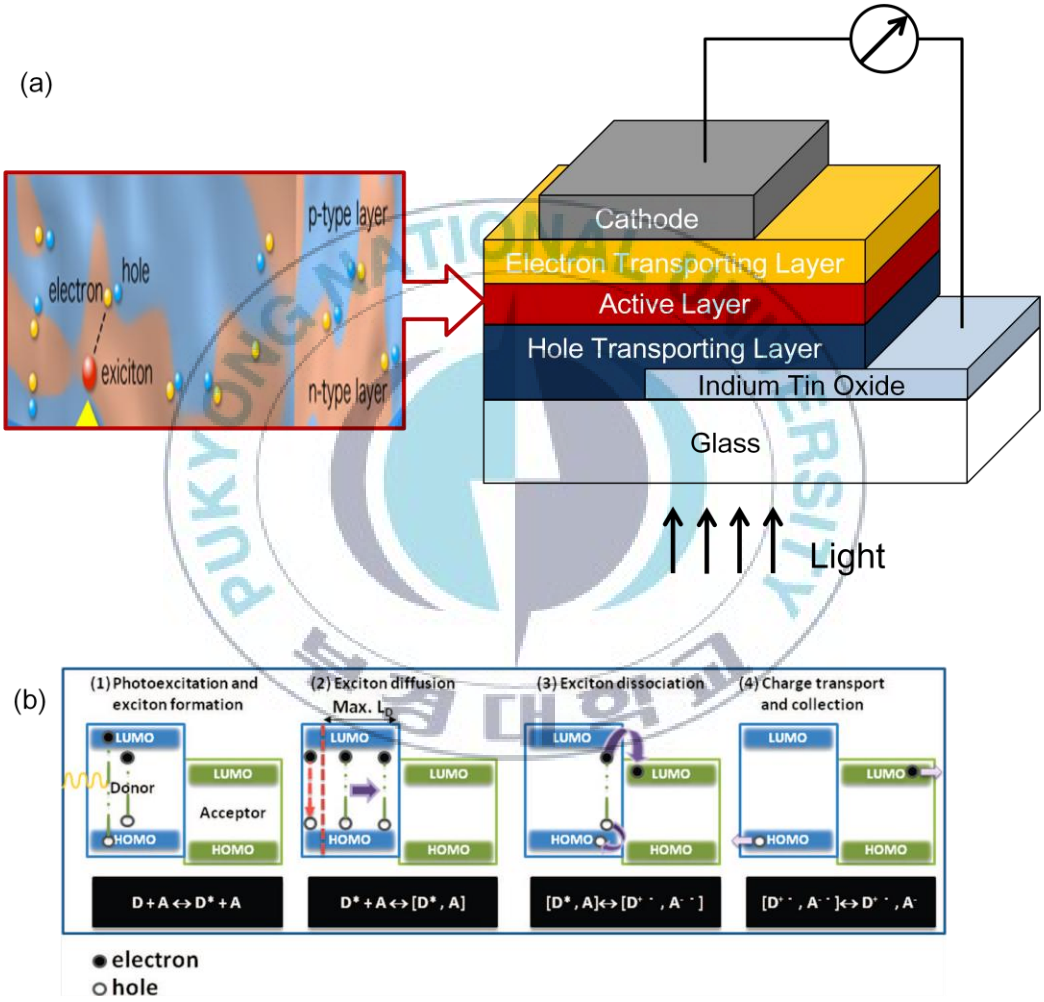


Figure I-2. (a) Device structure of PSC with a bulk hetero-junction configuration, and (b) the operating principle of bulk hetero-junction type PSC.

I-3. Buffer Layer

The initial structure of PLEDs and PSCs, emissive or active layer was sandwiched between an anode and a cathode. But, study for structure has kept researching to improve the efficiency, lifetime, and brightness because the efficiency and lifetime of devices depend on charge balance between the electrode and the emissive polymer layer in PLEDs. Also to get high efficiency in PSCs, the dissociated hole and electron from exciton in active layer are transporting from active layer to electrode effectively. Thus, both PLEDs and PSCs need to introduce the buffer layer called charge injection or transporting layer between the electrode and the emissive or active layer. The buffer layer between the anode and the emissive or active layer acts injection and transport of holes, called the hole injection or transporting layer (HIL/HTL). Also, the buffer layer between the cathode and the emissive or active layer acts injection and transport of electrons, we called the electron injection/transporting layer (EIL/ETL).

I-3-1. Hole Injection/Transporting Layer

The HIL/HTL between the anode and the emissive or active layer should be introduced because hole injection barrier between the anode and the emissive or active layer is relatively high. Requirements for the HIL/HTL is that it should have good hole injection/transporting capability and thermal, chemical, mechanical stability. Also it has good organic solvent resistance because device fabrications are solution process. And HOMO energy level of the HIL/HTL is lying between the anode and the emissive layer.

For example, polyaniline (PANI) doped acid was introduced on ITO to enhance hole collection, device with PANI was improved the efficiency and lifetime than those of device without PANI. [5-6] Also when poly(3,4-ethylenedioxythiophene) doped poly(styrenesulfonate) (PEDOT:PSS) was introduced as HIL, the efficiency of the device was dramatically improved. [7-8] In case of doped conductive polymers such as PANI and PEDOT:PSS, those have high hole mobility and conductivity. Also those have outstanding feature that it can form uniform film.

However, it is demonstrated that PEDOT:PSS well known hole injection materials on ITO is unstable, with indium contaminating the polymer, thus degrading the performance of devices because of their acidic nature. [9] To solve this problem, it needs to study for new structure and materials.

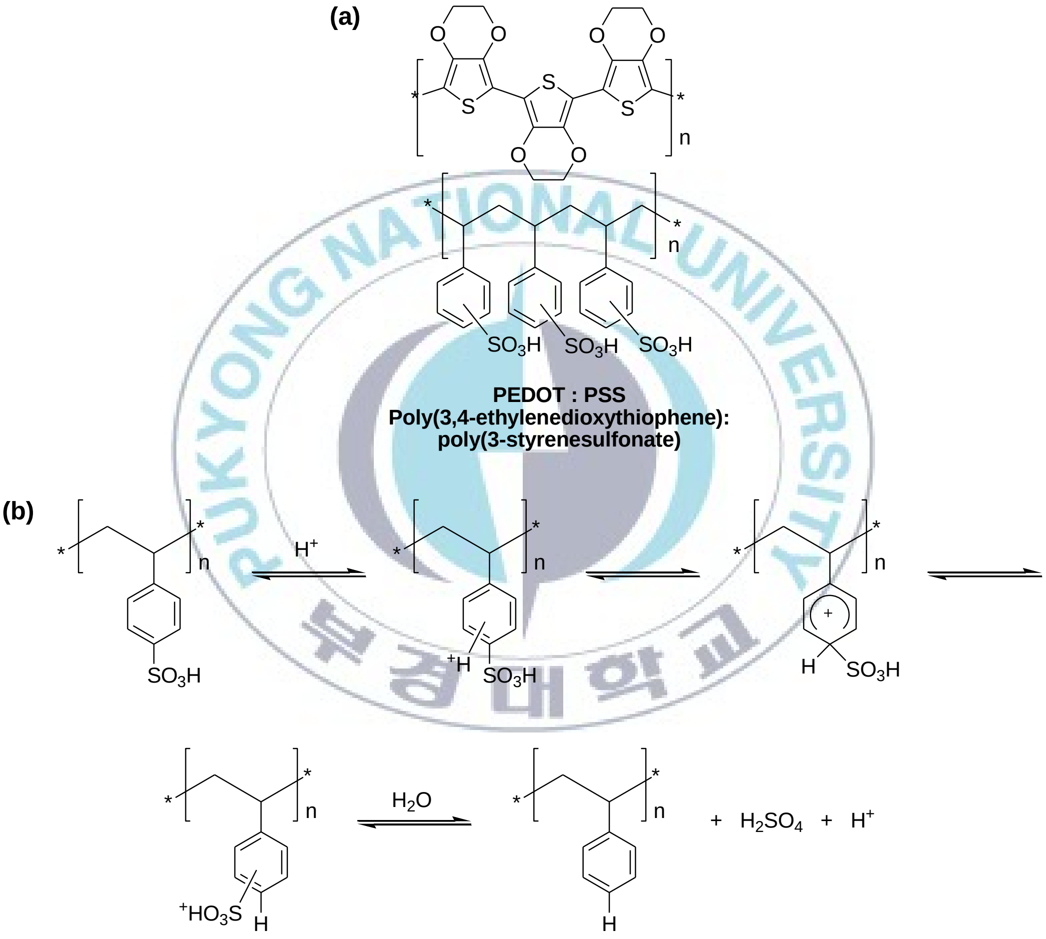


Figure I-3. (a) Chemical structure and (b) degradation mechanism of PEDOT:PSS based device.

I-3-1-1. Cross-linkable Materials

One of the methods, it can introduce the cross-linkable unit to meet requirements. The cross-linkable material kept soluble during the fabrication of the device. After cross-linking, this layer was insoluble for organic solvent such as toluene, chloroform, chlorobenzene, and dichlorobenzene (DCB), which are the common solvents used for making the emissive or active layer. Methods of cross-linking process are thermal or photo cross-linking.

In case of the thermal cross-linking, Scott et al. reported hole injection polymer introduced aryl amine as thermally cross-linkable unit. [10] Also new hole injection materials introduced perfluorocyclobutane (PFCB) [11] or vinyl [12-13] were reported by Alex K. –Y. Jen et al.. The advantage of thermally cross-linkable materials is that those don’t produce byproducts during the polymerization because those don’t require initiator or catalyst. And those have high solvent resistance.

And in case of the photo cross-linking, Oskar Nuyken et al. reported photo cross-linkable triarylamine derivatives with oxetane functionality. During the device processing, a solution of the cross-linkable material mixed with small amounts of a photosensitive cationic initiator is spin-coated on the substrate and cross-linked by UV irradiation. [14-15]

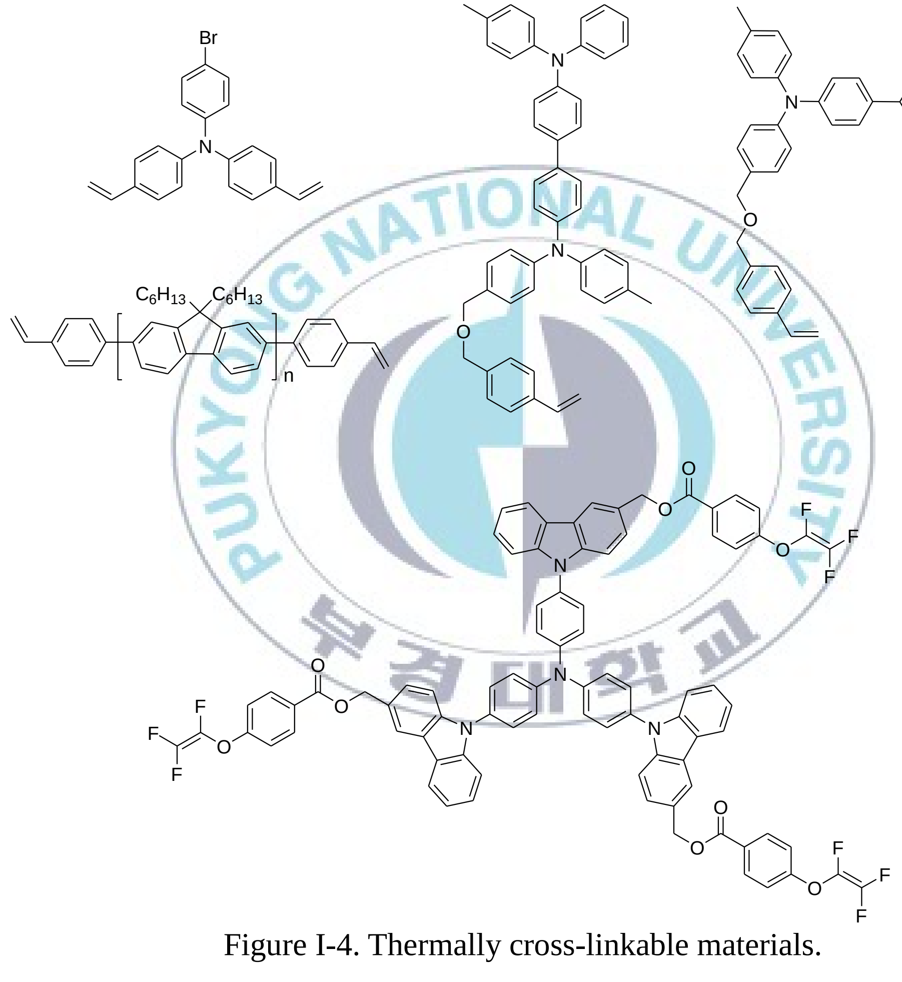


Figure I-4. Thermally cross-linkable materials.

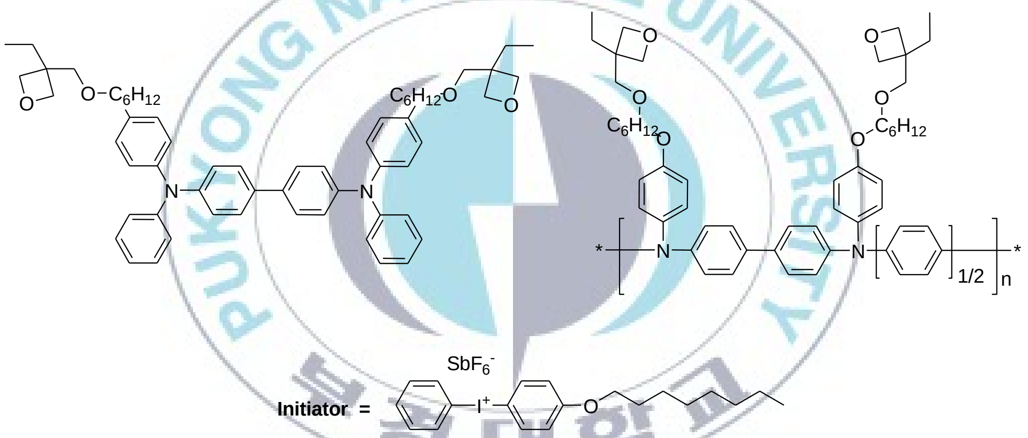


Figure I-5. Photo cross-linkable materials.

I-3-1-2. Self-Assembled Monolayer

Self-assembled monolayer (SAM) is the ordered molecular aggregates that form a monolayer of the material on a surface. Bond between the surface and the functional group of the molecule is covalent bond, which is very strong. After reacting, SAM has good solvent resistance. Marks et al. reported that hole injection ability of PLEDs applied SAM-based anode modification was improved. [16-17]

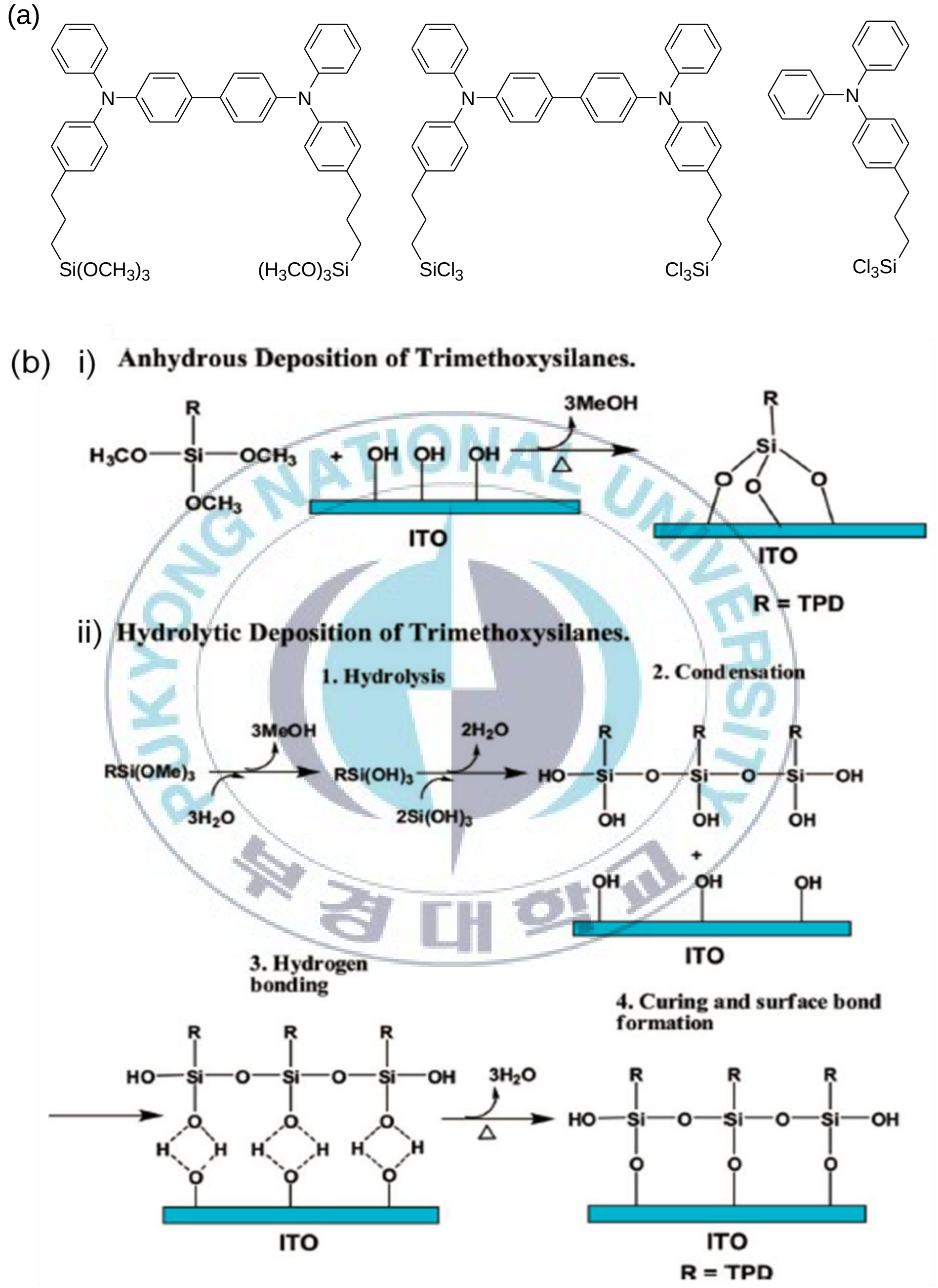


Figure I-6. (a) Hole injection materials based on silane derivatives, (b) the reaction mechanisms of ITO surface modification by HIL.

I-3-2. Electron Injection/Transporting Layer

In the past few years, efforts on improving the performance of PLEDs and BHJ solar cells have been mainly focused on fundamental issues such as an improved understanding of device physics, optimization of morphologies by advanced processing methods, and development of high-performance materials.

For practical applications of PSCs, the efficiency of PSCs needs to be over 10%, and those have to have good environmental stability, especially. To achieve these goals, other issues such as optimization of electrical contact at different interfaces in PSCs and the development of new device structures are equally important. [18] One of the methods, modification of electrodes has been commonly employed to improve the contact between the emissive or active layer and the cathode.

I-3-2-1. Lithium Fluoride

It is hard to increase open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) simultaneously in PSCs, because larger photocurrents require a low bandgap absorber for maximum overlap with the solar spectrum, but a high bandgap absorber is needed to enhance V_{oc}. It is common to use a thin layer of LiF between the active layer and the cathode to improve the V_{oc} in PSCs. The role of the submonolayer of LiF has been suggested to be that of protecting the organic layer during the metal deposition, modifying the work function of the cathode, and introducing a dipole at the cathode interface, affecting charge injection. [19]

However, LiF is not an ideal EIL/ETL in PSCs. Because the LiF layer must be very thin which is hard to achieve. And vapor deposition of LiF in a vacuum is not well-suited for commercialization. [20]

I-3-2-2. Water-soluble Materials

Water soluble polymer could also have good candidates for the interfacial layer materials in PLEDs or PSCs because they can prevent damage to the underlying the organic soluble emissive or active layer, and solution processing capabilities. These polymers also possess either ionic or polar groups that can reduce the work-function of the cathode through favorable interface dipoles. [20-21]

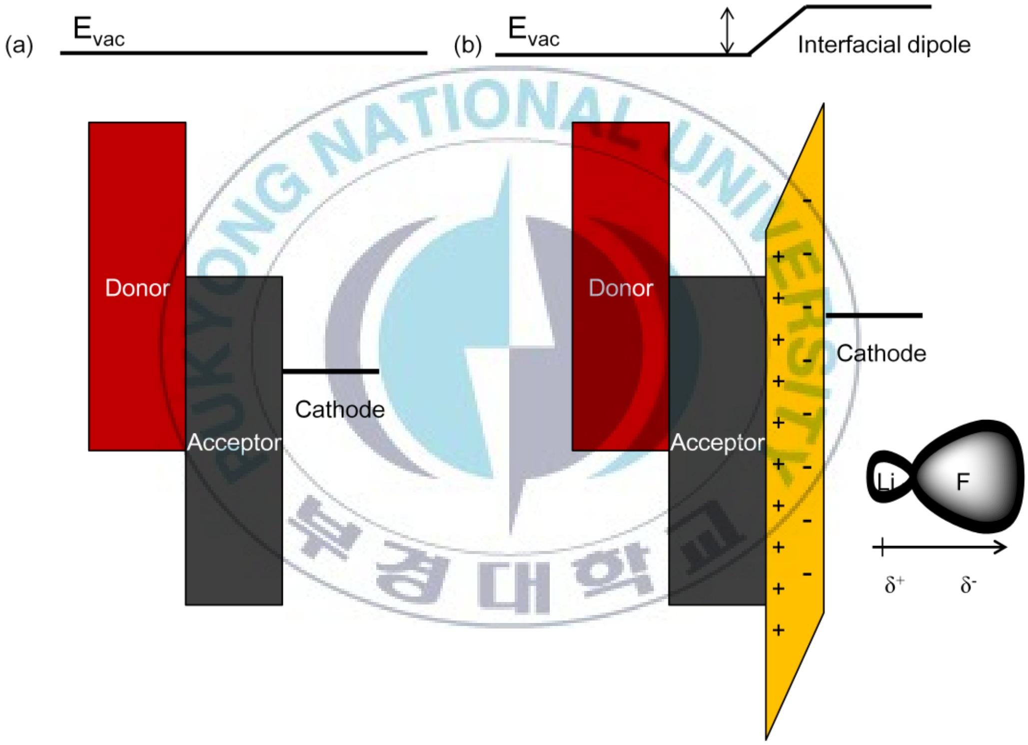


Figure I-7. Schematic illustration of energy level diagram of the device with (a) metal-only cathode, and (b) LiF/metal cathode.

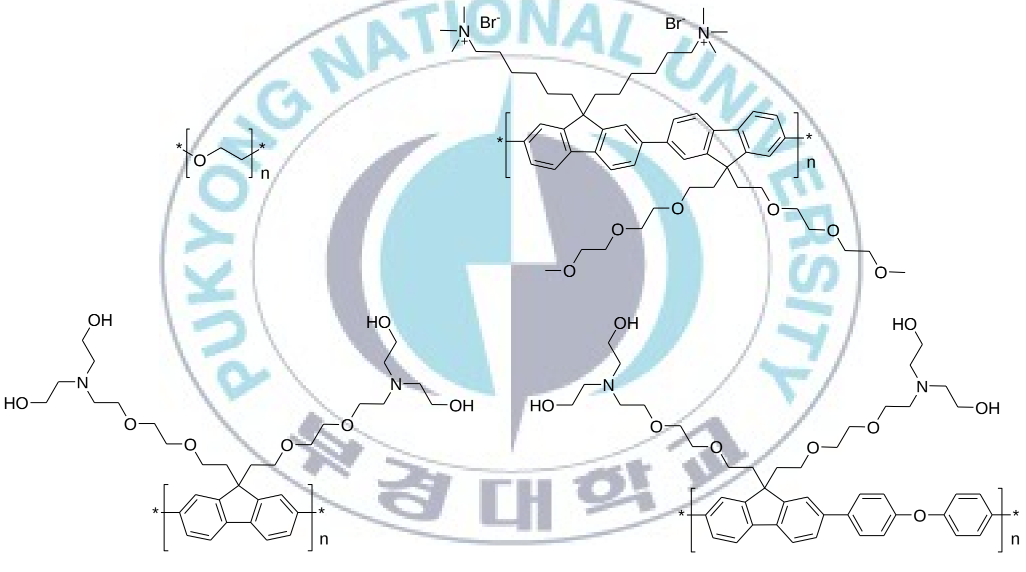


Figure I-8. ETL based on water or alcohol-soluble materials.

Chapter II. Synthesis and Characterization of *in-situ* Thermally Cross-linkable Hole Injection Materials Based on Oligo-phenothiazine

II-1. Introduction

Conjugated polymers have been studied in polymer light-emitting diodes (PLEDs) [1], polymer solar cells (PSCs) [2-4], thin film transistors (TFTs), and electro chromic devices (ECDs). Among these, PLEDs and PSCs have been tremendously focused because of easiness of process. To get the high efficiency of devices, multi-layer structured devices are fabricated with charge (hole and electron) injection and transporting layer. The charge (hole and electron) injection and transporting processes are crucial factors for improving the performances of PLEDs and PSCs. In order to fabricate multi-layer structured device, the hole injection/transporting layer (HIL/HTL) should have good organic solvent resistance to coat the successive layer. Recently, *in-situ* thermally polymerizable hole injection materials based on triarylamine, alkylphenothiazine, alkylcarbazole have been studied. That devices based on hole injection materials exhibited excellent performances was reported.

Poly(10-hexyl-10*H*-hexylphenothiazin-3,7-diyl) is well known very strong electron donor and has high-lying ionization potential so that it can be used as hole injection material. We synthesized *in-situ* thermally polymerizable oligomers. The purification and reproducibility in the synthesis of oligomers such as trimer, pentamer or hyper-branched oligomer are much easier than those of analogues' polymers. Here, we report the synthesis, physical, and device properties of oligophenothiazine with *in-situ* thermally polymerizable methacrylate (MA), vinyl benzene (VB) or vinyl (V).

II-2. Experimental Section

II-2-1. Materials and Synthesis

Tetrahydrofuran (THF) was distilled over sodium/benzophenone. Methylene chloride (MC) was distilled over calcium hydride (CaH_2). All other chemicals were purchased from Sigma-Aldrich Co, Tokyo Chemical Industry (TCI) or Alfa Aesar (A Johnson Matthey Company) and used as received unless otherwise described.

II-2-1-1. 10-Butyl-10*H*-phenothiazine (1)

A portion of 100 mg of benzyltriethylammonium chloride and 100 mL of 50 wt.% aqueous NaOH were added to a solution of 30.0 g (0.150 mol) of 10*H*-phenothiazine (PT) in 100 mL of dimethyl sulfoxide (DMSO). The reaction mixture was stirred for 30 min. A portion of 28.8 g (0.210 mol) of 1-bromobutane was added to the reaction mixture and then stirred for 12 hours at room temperature. The reaction mixture was neutralized with aqueous HCl (35 wt.%) and extracted three times with 100 mL of ethyl acetate (EA). The combined organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$). And the solvent was removed by using a rotary evaporator. The crude liquid product was purified by flash column chromatography using n-hexane. The yield of light yellow liquid was 36.2 g (94.3%). MS: [M^+], *m/z* 255. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.18~7.14 (m, 4H), 6.94~6.86 (m, 4H), 3.88~3.84 (t, *J* = 7.3 Hz, 2H), 1.84~1.77 (m, 3H), 1.52~1.42 (m, 2H), 0.97~0.94 (t, *J* = 7.3 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 145.10, 127.20, 126.99, 124.68, 122.12, 115.22, 46.79, 28.78, 20.00, 13.72. Anal. Calcd. for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48; S, 12.56. Found: C, 75.92; H, 6.62; N, 5.58; S, 12.67.

II-2-1-2. 3,7-Dibromo-10-butyl-10*H*-phenothiazine (2)

A potion of 58.6 g (0.330 mol) of *N*-bromosuccinimide (NBS) in 100 mL of N,N'-dimethylformamide (DMF) was added dropwise to a solution of compound **1** (35.0 g, 0.140 mol) in 50 mL of DMF under the nitrogen (N_2) atmosphere at 5 ^{o}C then stirred for 30 min. The reaction mixture was stirred for 5 hours at room temperature. A potion of 200 mL of water was added into the reaction mixture then extracted three times with 100 mL of EA. The combined organic layer was washed with aqueous sodium bisulfite (10 wt.%) and then dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography using n-hexane. The yield of yellow liquid was 45.1 g (79.7%). MS: [M^+], *m/z* 413. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.24~7.21 (m, 4H), 6.69~6.67 (d, *J* = 8.8 Hz, 2H), 3.77~3.74 (t, *J* = 6.9 Hz, 2H), 1.76~1.69 (m, 2H), 1.47~1.37 (m, 2H), 0.94~0.90 (t, *J* = 7.3 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 143.91, 129.95, 129.49, 126.21, 116.49, 114.57, 47.08, 28.55, 19.93, 13.71. Anal. Calcd. for $C_{16}H_{15}Br_2NS$: C, 46.51; H, 3.66; Br, 38.68; N, 3.39; S, 7.76. Found: C, 45.39; H, 3.624; N, 3.447; S, 7.624.

II-2-1-3. 2-(4-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (3)

A portion of 20.8 mL (52.0 mmol) of n-butyl lithium (2.50 M in hexane) was added dropwise to a solution of 1-bromo-4-methoxy-benzene (7.50 g, 40.1 mmol) in 150 mL of THF under the N_2 atmosphere at -78 ^{o}C. The reaction mixture was stirred for 2 hours at -78 ^{o}C. A portion of 10.0 g (53.9 mol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added into the reaction mixture at -78 ^{o}C. Then, the resulting mixture was allowed to warm up to room temperature and stirred for 12 hours. A portion of 100 mL of water was slowly added to the reaction mixture and extracted three times with 100 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography using MC/n-hexane (7/3). The yield of yellow liquid was 8.67 g (92.6%). MS: [M^+], *m/z* 234. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.77~7.74 (d, *J* = 8.8 Hz, 2H), 6.91~6.88 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 12H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 161.96, 136.33, 113.06, 83.23, 54.71, 24.63. Anal. Calcd. for $C_{13}H_{19}BO_3$: C, 66.70; H, 8.18; B, 4.62; O, 20.50. Found: C, 66.57; H, 8.28.

II-2-1-4. General procedure of the Suzuki coupling reaction

A mixture of aryl bromide, aryl boronic ester, 3.0 mol% of tetrakis(triphenylphosphine) palladium [Pd(PPh_3)$_4$], and several drops of aliquat. 336 in degassed 1:1 (by volume) mixed solvent of THF and 2M K_2CO_3 aqueous was stirred for 12 hours at 75 ^oC under the N_2 atmosphere. A portion of water was added to the reaction mixture and then extracted several times with EA. The combined organic layer dried over anhydrous $MgSO_4$. The solvent was removed by the evaporation under reduced pressure.

II-2-1-5. 3-Bromo-10-butyl-7-(4-methoxy-phenyl)-10*H*-phenothiazine (4)

Compound **4** was synthesized by the general procedure of the Suzuki coupling reaction between 39.4 g (95.4 mmol) of compound **2** and 3.72 g (15.9 mmol) of compound **3**. The crude product was purified by flash column chromatography using MC/n-hexane (3/7). The yield of yellow solid was 4.40 g (62.7%). MS: [M^+], *m/z* 441. mp: 88.9 ^oC. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.57~7.55 (d, J = 8.8 Hz, 2H), 7.46~7.44 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 7.39~7.38 (d, J = 1.8 Hz, 1H), 7.36~7.34 (m, 2H), 7.08~7.06 (d, J = 2.5 Hz, 1H), 6.99~6.95 (m, 3H), 3.88~3.85 (t, J = 7.0 Hz, 2H), 3.78 (s, 3H), 1.39~1.62 (m, 2H), 1.44~1.35 (m, 2H), 0.90~0.86 (t, J = 7.0 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.89, 144.32, 143.50, 135.42, 132.34, 129.82, 129.58, 127.48, 126.74, 125.61, 125.41, 124.36, 116.39, 115.60, 114.29, 114.15, 55.30, 47.15, 28.76, 20.08, 13.79. Anal. Calcd. for $C_{23}H_{22}BrNOS$: C, 62.73; H, 5.04; Br, 18.14; N, 3.18; O, 3.63; S, 7.28. Found: C, 62.91; H, 5.143; N, 3.220; S, 7.184.

II-2-1-6. 10-Butyl-3-(4-methoxy-phenyl)-7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-10*H*-phenothiazine (5)

A portion of 4.23 mL (10.7 mmol) of n-butyl lithium (2.50 M in hexane) was added dropwise to a solution of compound **4** (3.22 g, 7.83 mmol) in 100 mL of THF under the N_2 atmosphere at -78 ^{o}C. The reaction mixture was stirred for 2 hours at -78 ^{o}C. A portion of 2.07 g (11.1 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added into the reaction mixture at -78 ^{o}C. Then, the resulting mixture was allowed to warm up to room temperature and stirred for 12 hours. A portion of 100 mL water was added slowly to the reaction mixture and then the reaction mixture was extracted three times with 100 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography using EA/n-hexane (2/8) and recrystallization using methanol/MC. The yield of yellow solid was 2.63 g (67.8%). MS: [M^+], *m/z* 487. mp: 119.5 ^{o}C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm):

δ 7.59~7.53 (d, *J* = 9.2 Hz, 2H), 7.50~7.48 (m, 2H), 7.37~7.34 (d, *J* = 5.5 Hz, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.06~6.97 (m, 4H), 3.91~3.88 (t, *J* = 7.0 Hz, 2H), 3.78 (s, 3H), 1.71~1.64 (m, 2H), 1.42~1.35 (m, 2H), 1.27 (s, 12H), 0.89~0.86 (t, *J* = 7.3 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 159.04, 147.82, 143.48, 135.44, 133.86, 133.51, 132.66, 128.18, 127.11, 126.02, 125.25, 124.89, 123.67, 115.88, 114.82, 114.63, 83.82, 56.03, 54.83, 47.26, 28.23, 25.51, 20.25, 13.97. Anal. Calcd. for $C_{29}H_{34}BNO_3S$: C, 71.45; H, 7.03; B, 2.22; N, 2.87; O, 9.85; S, 6.58. Found: C, 71.93; H, 7.116; N, 2.94; S, 6.68.

II-2-1-7. 7-[4-methoxy-phenyl]-{7'-[4-methoxy-phenyl]-10-butyl-10*H*-phenothiazine-3-yl}-10,10'-dibutyl-10*H*,10'*H*-3,3'-biphenothiazine (6)

Compound **6** was synthesized by the general procedure of the Suzuki coupling reaction between 829 mg (2.00 mmol) of compound **2** and 1.95 g (4.00 mmol) of compound **5**. The crude product was purified by recrystallization using methanol/MC. The yield of yellow solid was 1.79 g (91.5%). MS (MALDI-TOF): $[M\text{-}H]^+$, *m/z* 973.2. mp: 122.4 ^{o}C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.58~7.56 (d, *J* = 8.4 Hz, 4H), 7.48~7.40 (m, 12H), 7.06~7.04 (m, 6H), 6.99~6.97 (d, *J* = 8.4 Hz, 4H), 3.93~3.89 (t, *J* = 6.9 Hz, 6H), 3.78 (s, 6H), 1.74~1.67 (m, 6H), 1.47~1.38 (m, 6H), 0.92~0.88 (t, *J* = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 159.78, 144.93, 144.83, 144.60, 135.99, 135.12, 135.07, 133.48, 128.39, 126.36, 126.29, 126.13, 126.01, 125.65, 125.59, 125.56, 120.00, 116.32, 115.10, 56.22, 48.07, 29.86, 21.11, 14.78. Anal. Calcd. for $C_{62}H_{59}N_3O_2S_3$: C, 76.43; H, 6.10; N, 4.31; O, 3.28; S, 9.87. Found: C, 76.13; H, 6.191; N, 4.38; S, 9.74.

II-2-1-8. 7-[4-hydroxy-phenyl]-{7’-[4-hydroxy-phenyl]-10-butyl-10*H*-phenothiazine-3-yl}-10,10’-dibutyl-10*H*,10’*H*-3,3’-biphenothiazine (7)

A portion of 7.00 mL (7.00 mmol) of boron tribromide (BBr_3) (1 M in MC) was added dropwise to a solution of compound **6** (1.70 g, 1.75 mmol) in 50 mL of MC under the N_2 atmosphere at 4 ^{o}C. The reaction mixture was allowed to warm up to 35 ^{o}C and then stirred for 5 hours. A portion of 100 mL of water was added to the reaction mixture and extracted three times with 50 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography using EA and recrystallization using n-hexane/MC. The yield of yellow solid was 1.20 g (72.3%). MS (MALDI-TOF): $[M-H]^+$, *m/z* 945. mp: 145.4 ^{o}C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 9.48 (s, 2H), 7.47~7.38 (m, 16H), 7.05~7.03 (d, J = 8.0 Hz, 6H), 6.82~6.80 (d, J = 8.5 Hz, 4H), 3.90~3.88 (t, J = 6.6 Hz, 6H), 1.74~1.67 (m, 6H), 1.47~1.38 (m, 6H), 0.92~0.88 (t, J = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, THF-d_8, ppm): δ 157.95, 153.26, 140.22, 140.01, 139.47, 131.55, 130.19, 130.04, 127.02, 123.20, 121.02, 120.93, 120.82, 120.76, 120.67, 111.57, 42.74, 24.98, 15.99, 9.37. Anal. Calcd. for $C_{60}H_{55}N_3O_2S_3$: C, 76.15; H, 5.86; N, 4.44; O, 3.38; S, 10.17. Found: C, 76.31; H, 5.854; N, 4.495; S, 10.28.

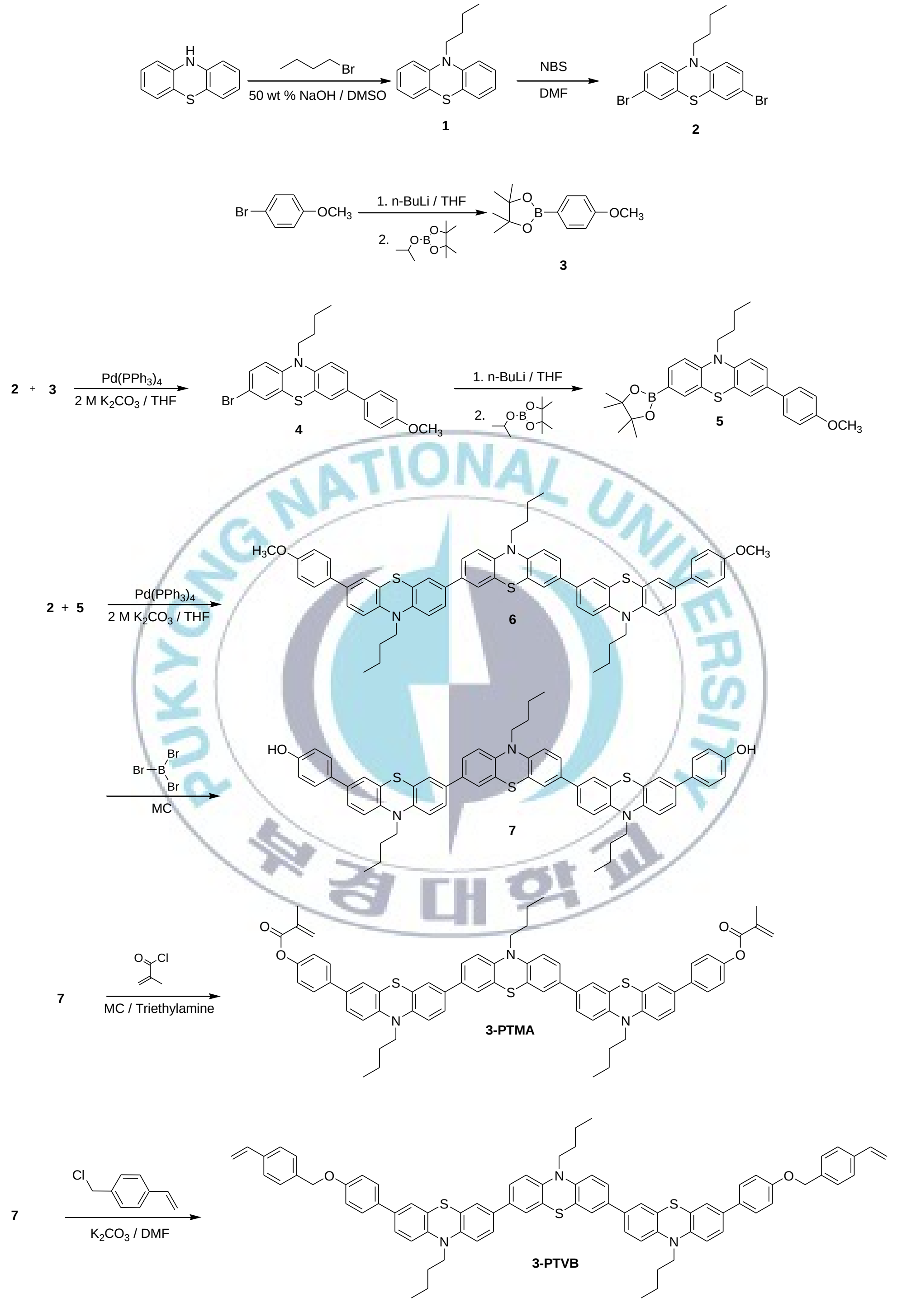
II-2-1-9. 7-[4-(2-methyl-acryloyloxy)-phenyl]-{7'-[4-methyl-acryloyloxy]-phenyl]-10-butyl-10*H*-phenothiazine-3-yl}-10,10'-dibutyl-10*H*,10'*H*-3,3'-biphenothiazine (3-PTMA)

A portion of triethylamine (160 mg, 1.60 mmol) and 2-metha-acryloyl chloride (170 mg, 1.60 mmol) were added dropwise to a portion of compound **7** (300 mg, 0.320 mmol) in degassed MC (20 mL) under the N_2 atmosphere at 0 ^oC. The reaction mixture was allowed to warm up to room temperature and then stirred for 2 hours. A portion of 100 mL of water was added to the reaction mixture and extracted three times with 50 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by recrystallization using methanol/MC. The yield of yellow solid is 0.33 g (95.4%). MS (MALDI-TOF): $[M-H]^+$, *m/z* 1080.9. mp: 101.6 ^oC. ^1H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.59~7.51 (m, 4H), 7.40~7.29 (m, 12H), 7.22~7.15 (m, 4H), 6.96~6.87 (m, 6H), 6.38~6.37 (d, *J* = 0.8 Hz, 2H), 5.78~5.77 (d, *J* = 1.5 Hz, 2H), 3.90~3.87 (t, *J* = 6.2

Hz, 6H), 2.07 (s, 6H), 1.90~1.78 (m, 6H), 1.55~1.43 (m, 6H), 1.00~0.96 (t, *J* = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 171.37, 165.90, 150.06, 137.65, 136.60, 135.86, 127.44, 127.30, 125.90, 125.24, 121.85, 121.51, 115.45, 103.97, 81.16, 47.21, 30.74, 25.55, 24.69, 20.19, 18.40, 18.20, 13.85. Anal. Calcd. for $C_{68}H_{63}N_3O_4S_3$: C, 75.45; H, 5.87; N, 3.88; O, 5.91; S, 8.89. Found: C, 75.75; H, 5.789; N, 3.711; S, 8.810.

II-2-1-10. 7-[4-(4-vinyl-benzyloxy)-phenyl]-{7'-[4-(4-vinyl-benzyloxy)-phenyl]-10-butyl-10*H*-phenothiazine-3-yl}-10,10'-dibutyl-10*H*,10'*H*-3,3'-biphenothiazine (3-PTVB)

A solution of 4-vinyl benzyl chloride (64.0 mg, 0.420 mmol) was added dropwise to a portion of compound **7** (150 mg, 0.170 mmol) and potassium carbonate (580 mg, 0.420 mmol) in DMF (20 mL) under the N_2 atmosphere at 40 ^{o}C. After stirring for 12 hours, a portion of 50 mL of water was added to the reaction mixture and extracted three times with 50 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by recrystallization using methanol/MC. The yield of yellow solid is 87.1% (0.17 g). MS (MALDI-TOF): $[M-H]^+$, m/z 1176.8. mp: 211.3 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.43~7.42 (b, 14H), 7.33~7.31 (b, 10H), 7.01~7.00 (d, *J* = 8.8 Hz, 4H), 6.88 (b, 4H), 6.77~6.70 (dd, J_1 = 17.6 Hz, J_2 = 11.0 Hz, 2H), 5.79~5.75 (dd, J_1 = 17.6 Hz, J_2 = 0.7 Hz, 2H), 5.28~5.25 (dd, J_1 = 11.0 Hz, J_2 = 0.7 Hz, 2H), 5.08 (s, 4H), 3.90~3.87 (t, J = 6.9 Hz, 6H), 1.86~1.79 (m, 6H), 1.54~1.45 (m, 6H), 0.99~0.95 (t, J = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.05, 144.06, 143.98, 143.79, 137.33, 136.52, 136.43, 135.10, 134.29, 134.24, 132.91, 127.66, 127.52, 126.43, 125.45, 125.23, 125.16, 115.62, 115.40, 115.15, 114.08, 69.85, 47.21, 29.69, 28.98, 20.20, 13.84. Anal. Calcd. for $C_{78}H_{71}N_3O_2S_3$: C, 79.49; H, 6.07; N, 3.57; O, 2.71; S, 8.16. Found: C, 77.31; H, 4.044; N, 6.337; S, 10.41.



Scheme II-1. Synthesis of thermally cross-linkable 3-PTMA and 3-PTVB.

II-2-1-11. 7-Bromo-10,10'-dibutyl-7'-(4-methoxy-phenyl)-10*H*,10'*H*-[3,3']biphenothiazinyl (8)

Compound **8** was synthesized by the general procedure of the Suzuki coupling reaction between 1.07 g (2.6 mmol) of compound **2** and 1.27 g (2.6 mmol) of compound **5**. The crude product was purified by flash column chromatography using MC/n-hexane (3/7) and recrystallization using methanol/MC. The yield of yellow solid is 1.37 g (75.4%). MS (MALDI-TOF): $[M-H]^+$, *m/z* 693.9. mp: 164.7 °C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.57~7.55 (d, *J* = 8.8 Hz, 2H), 7.45~7.39 (m, 6H), 7.22~7.14 (m, 2H), 7.05~6.90 (m, 6H), 3.91~3.86 (m, 4H), 3.78 (s, 3H), 1.73~1.63 (m, 4H), 1.46~1.35 (m, 4H), 0.91~0.86 (m, 6H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.84, 144.16, 143.66, 129.80, 129.51, 127.43, 126.64, 125.39, 125.16, 125.03, 124.35, 116.36, 115.55, 115.34, 114.28, 114.14, 55.25, 47.11, 28.73, 20.14, 20.04, 13.82, 13.75. Anal. Calcd. for $C_{39}H_{37}BrN_2OS_2$: C, 67.52; H, 5.38; Br, 11.52; N, 4.04; O, 2.31; S, 9.24. Found: C, 67.30; H, 5.239; N, 4.345; S, 9.204.

II-2-1-12. 10,10'-Dibutyl-7'-(4-methoxy-phenyl)-7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-10*H*,10'*H*-[3,3']biphenothiazinyl (9)

A portion of 0.90 mL (2.24 mmol) of n-butyl lithium (2.50 M in hexane) was added dropwise to a solution of compound **8** (1.30 g, 1.90 mmol) in 50 mL of THF under the N_2 atmosphere at -78 ^{o}C. The reaction mixture was stirred for 2 hours at -78 ^{o}C. A portion of 0.460 g (2.47 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added into the reaction mixture at -78 ^{o}C. Then, the resulting mixture was allowed to warm up to room temperature and stirred for 12 hours. A portion of 50 mL of water was slowly added to the reaction mixture and extracted three times with 50 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography using EA/n-hexane (3/7) and then recrystallization using methanol/MC. The yield of yellow solid is 0.900 g (64.2%). MS (MALDI-TOF): $[M-H]^+$, *m/z* 740. mp: 123.9 ^{o}C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.57~7.55 (d, *J* = 8.8 Hz, 2H), 7.49~7.39 (m, 7H), 7.34~7.32 (d, *J* = 1.5 Hz, 1H), 7.07~7.03 (m, 3H), 6.99~6.97 (m, 3H), 3.92~3.89 (t, *J* = 6.6 Hz, 4H), 3.82 (s, 3H), 1.74~1.64 (m, 4H), 1.47~1.37 (m, 4H), 1.26 (s, 12H), 0.92~0.86 (m, 6H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.83, 147.54, 144.10, 143.68, 143.54, 135.75, 134.39, 134.13, 133.76, 132.55, 127.44, 125.40, 125.36, 125.18, 125.10, 125.02, 123.43, 115.49, 115.35, 114.53, 114.15, 83.62, 55.27, 47.11, 28.91, 28.83, 24.78, 20.15, 20.06, 13.82, 13.77. Anal. Calcd. for $C_{45}H_{49}BN_2O_3S_2$: C, 72.96; H, 6.67; B, 1.46; N, 3.78; O, 6.48; S, 8.66. Found: C, 72.10; H, 6.574; N, 3.724; S, 8.94.

II-2-1-13. 3,6-bis-[10,10'-dibutyl-7'-(4-methoxy-phenyl)-10*H*,10*H*'-[3,3']biphenothiazinyl]-10-hexyl-10*H*-phenothiazine (10)

Compound **10** was synthesized by the general procedure of Suzuki coupling reaction between 0.326 g (0.79 mmol) of 2,7-dibromo-10-hexyl-10*H*-phenothiazine[22] and 1.17 g (1.58 mmol) of compound **9**. The crude product was purified by column chromatography using EA/n-hexane (2/8). The yield of yellow solid is 1.04 g (87.0%). MS (MALDI-TOF): [M-H]$^+$, *m/z* 1508.3. mp: 154.2 °C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.58~7.56 (d, J = 8.8 Hz, 4H), 7.48~7.40 (m, 20H), 7.07~7.05 (m, 10H), 7.00~6.98 (d, J = 8.8 Hz, 4H), 3.93~3.90 (t, J = 5.8 Hz, 10H), 3.78 (s, 6H), 1.75~1.67 (m, 10H), 1.46~1.40 (m, 14H), 0.92~0.89 (t, J = 7.3 Hz, 15H),^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 160.15, 145.28, 145.18, 144.96, 136.34, 135.45, 133.83, 128.76, 126.73, 126.65, 126.50, 126.37, 126.00, 125.94, 116.70, 115.48, 56.59, 48.80, 48.44, 32.78, 30.23, 28.11, 27.97, 23.93, 21.50, 15.37, 15.19. Anal. Calcd. for $C_{96}H_{93}N_5O_2S_5$: C, 76.40; H, 6.21; N, 4.64; O, 2.12; S, 10.62. Found: C, 76.33; H, 6.661; N, 4.803; S, 10.53.

II-2-1-14. 3,6-bis-[10,10’-dibutyl-7’-(4-hydroxy-phenyl)-10*H*,10*H*’-[3,3’]biphenothiazinyl]-10-hexyl-10*H*-phenothiazine (11)

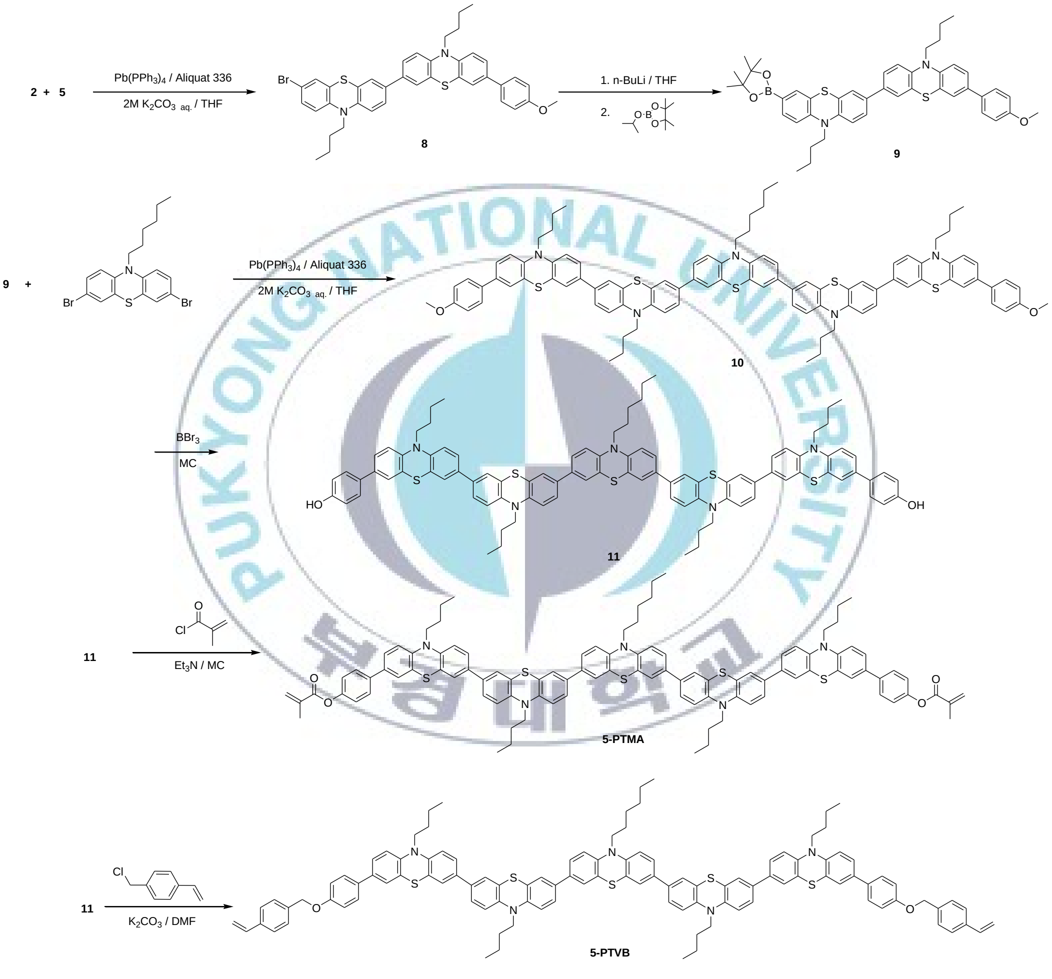
A portion of 2.00 mL (2.00 mmol) of BBr_3 (1 M in MC) was added dropwise to a solution of compound **10** (700 mg, 0.460 mmol) in 50 mL of MC under the N_2 atmosphere at 4 ^{o}C. The reaction mixture was allowed to warm up to 35 ^{o}C and then stirred for 5 hours. A portion of 100 mL of water was added to the reaction mixture and extracted three times with 50 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography using EA and recrystallization using n-hexane/MC. The yield of yellow solid is 0.520 g (77.2%). MS (MALDI-TOF): $[M\text{-}H]^+$, *m/z* 1479.8. mp: 163.1 ^{o}C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 9.49 (s, 2H), 7.51~7.41 (m, 24H), 7.05~7.03 (m, 10H), 6.82~6.79 (m, 4H), 3.90 (s, 10H), 1.71~1.68 (m, 10H), 1.45~1.39 (m, 14H), 0.91~0.81 (m, 15H), ^{13}C-NMR (100 MHz, THF-d_8, ppm): δ 158.07, 145.08, 144.88, 144.34, 136.44, 135.07, 135.02, 134.92, 131.87, 127.99, 125.91, 125.82, 125.69, 125.60, 125.53, 116.34, 47.94, 47.56, 32.39, 29.84, 27.70, 27.37, 23.45, 20.80, 14.33, 14.13. Anal. Calcd. for $C_{94}H_{89}N_5O_2S_5$: C, 76.23; H, 6.06; N, 4.73; O, 2.16; S, 10.82. Found: C, 76.87; H, 6.104; N, 4.791; S, 10.16.

II-2-1-15. 3,6-bis-[10,10’-dibutyl-7’-[(4-methyl-acryloyloxy)-phenyl]-10*H*,10*H*’-[3,3’]biphenothiazinyl]-10-hexyl-10*H*-phenothiazine (5-PTMA)

A portion of triethylamine (1.70 mg, 0.170 mmol) and 2-metha-acryloyl chloride (1.80 mg, 0.170 mmol) were added dropwise to a portion of compound **10** (60.0 mg, 0.042 mmol) in MC (20 mL) under the N_2 atmosphere at 0 ^{o}C. The reaction mixture was allowed to warm up to room temperature and then stirred for 2 hours. A portion of 100 mL of water was added to the reaction mixture and extracted three times with 50 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography using MC/n-hexane (6/4). The yield of yellow solid is 57.0 mg (85.0%). MS (MALDI-TOF): $[M\text{-}H]^{+}$, *m/z* 1615.3. mp: 116.6 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.70~7.68 (d, *J* = 8.8 Hz, 4H), 7.53~7.43 (m, 20H), 7.23~7.21 (d, *J* = 8.4 Hz, 4H), 7.11~7.04 (m, 10H), 6.29~6.25 (d, *J* = 8.0 Hz, 2H), 6.02~5.91 (d, *J* = 1.1 Hz, 2H), 3.94~3.91 (t, *J* = 6.2 Hz, 10H), 2.01 (s, 6H), 1.78~1.64 (m, 10H), 1.46~1.39 (m, 14H), 0.92 ~0.89 (t, *J* = 7.6 Hz, 15H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 165.89, 150.03, 143.87, 137.65, 135.85, 134.56, 134.38, 127.49, 127.42, 127.27, 125.87, 125.74, 125.22, 125.14, 124.79, 124.68, 121.83, 121.49, 115.41, 103.95, 81.14, 47.19, 31.45, 28.94, 26.65, 24.68, 22.59, 20.17, 18.38, 18.17, 13.99, 12.82. Anal. Calcd. for $C_{102}H_{97}N_5O_4S_5$: C, 75.75; H, 6.05; N, 4.33; O, 3.96; S, 9.91. Found: C, 77.29; H, 6.001; N, 4.272; S, 9.99.

II-2-1-16. 3,6-bis-{10,10'-dibutyl-7'-[4-(4-vinyl-venzyloxy)-phenyl]-10*H*,10*H*'-[3,3']biphenothiazinyl}-10-hexyl-10*H*-phenothiazine (5-PTVB)

A solution of 4-vinyl benzyl chloride (32.0 mg, 0.210 mmol) was added dropwise to a portion of compound **11** (100 mg, 0.070 mmol) and potassium carbonate (290 mg, 0.210 mmol) in DMF (20 mL) under the N_2 atmosphere at 40 ^{o}C. After stirring for 12 hours, a portion of 50 mL of water was added to the reaction mixture and extracted three times with EA. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by recrystallization using methanol/MC. The yield of yellow solid is 71.8% (86.0 mg). MS (MALDI-TOF): $[M-H]^+$, m/z 1712.3. mp: 131.2 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.45~7.41 (m, 14H), 7.31 (b, 20H), 7.02~7.00 (d, J = 8.8 Hz, 6H), 6.89 (b, 6H), 6.73 (dd, J_1 = 17.6 Hz, J_2 = 11.0 Hz, 2H), 5.79~5.74 (dd, J_1 = 17.6 Hz, J_2 = 1.1 Hz, 2H), 5.27~5.25 (dd, J_1 = 11.0 Hz, J_2 = 0.7 Hz, 2H), 5.08 (s, 4H), 3.91~3.88 (t, J = 6.9 Hz, 10H), 1.87~1.79 (m, 10H), 1.52~1.47 (m, 14H), 0.99~0.95 (t, J = 7.4 Hz, 15H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.04, 144.02, 143.94, 143.75, 137.31, 136.51, 136.43, 135.05, 134.23, 132.87, 127.65, 127.50, 126.41, 125.44, 125.22, 125.13, 124.76, 124.70, 115.40, 115.14, 114.07, 69.82, 47.55, 47.19, 31.47, 28.96, 26.83, 26.67, 22.60, 20.19, 14.01, 13.84. Anal. Calcd. for $C_{112}H_{105}N_5O_2S_5$: C, 78.51; H, 6.18; N, 4.09; O, 1.87; S, 9.36. Found: C, 80.06; H, 4.577; N, 6.066; S, 10.36.



Scheme II-2. Synthesis of thermally cross-linkable 5-PTMA and 5-PTVB.

II-2-1-17. 1,3,5-tris-[{10-Butyl-3-(4-methoxy-phenyl)-7-yl-10*H*-phenothiazine}]-benzene (12)

Compound **6** was synthesized by the general procedure of the Suzuki coupling reaction between 0.378 g (1.20 mmol) of 1,3,5-tribromobenzene and 1.93 g (3.96 mmol) of compound **5**. The crude product was purified by flash column chromatography using EA/n-hexane (2/8). The yield of yellow solid is 1.15 g (82.8%). MS (MALDI-TOF): $[M-H]^+$, m/z 1155.4. mp: 274.4 ^oC. ^1H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.61(s, 3H), 7.48~7.45 (m, 12H), 7.34~7.32 (m, 6H), 6.96~6.90 (m, 12H), 3.93~3.90 (t, J = 5.8 Hz, 6H), 3.84 (s, 9H), 1.90~1.82 (m, 6H), 1.56~1.48 (m, 6H), 1.00~0.96 (t, J = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.92, 143.73, 141.01, 135.50, 132.60, 157.54, 126.08, 125.48, 123.51, 115.48, 114.18, 47.37, 29.68, 29.21, 20.21, 13.86. Anal. Calcd. for $C_{75}H_{69}N_3O_3S_3$: C, 77.89; H, 6.01; N, 3.63; S, 8.32. Found: C, 77.79; H, 6.11; N, 3.73; S, 8.29.

II-2-1-18. 1,3,5-tris-[{10-Butyl-3-(4-hydroxy-phenyl)-7-yl-10*H*-phenothiazine}]-benzene (13)

A portion of 6.16 mL (6.16 mmol) of BBr_3 (1 M in MC) was added dropwise to a solution of compound **6** (1.02 g, 0.878 mmol) in 50 mL of MC under the N_2 atmosphere at 4 ^{o}C. The reaction mixture was allowed to warm up to 35 ^{o}C and then stirred for 5 hours. A portion of 100 mL of water was added to the reaction mixture and extracted three times with 50 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography using EA/MC/n-hexane (1/2/7). The yield of yellow solid is 0.860 g (87.9%). MS (MALDI-TOF): $[M-H]^+$, m/z 1113.5. mp: 229.3 ^{o}C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 9.49 (s, 3H), 7.78 (s, 3H), 7.71~7.69 (d, J = 7.3 Hz, 6H), 7.46~7.40 (m, 9H), 7.11~7.06 (m, 6H), 6.83~6.81 (d, J = 8.8 Hz, 6H), 3.96~3.92 (t, J = 6.9 Hz, 6H), 1.77~1.70 (m, 6H), 1.49~1.42 (m, 6H), 0.93~0. 90 (t, J = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, THF-d_8, ppm): δ 158.07, 145.57, 144.31, 141.92, 136.47, 136.03, 131.79, 127.97, 126.79, 126.43, 125.95, 125.83, 125.70, 125.58, 123.85, 120.00, 116.38, 116.32, 47.54, 29.82, 20.78, 14.13. Anal. Calcd. for $C_{72}H_{63}N_3O_3S_3$: C, 77.59; H, 5.70; N, 3.77; S, 8.63. Found: C, 77.67; H, 5.61; N, 3.87; S, 8.73.

II-2-1-19. 1,3,5-tris-[{10-Butyl-3-(4-(2-methyl-acryloyloxy)-phenyl)-7-yl-10H-phenothiazine}]-benzene (tris-PTMA)

A portion of triethylamine (0.160 g, 1.70 mmol) and 2-metha-acryloyl chloride (0.180 g, 1.70 mmol) were added dropwise to a portion of compound **7** (0.300 g, 0.262 mmol) in MC (20 mL) under the N_2 atmosphere at 0 ^{o}C. The reaction mixture was allowed to warm up to room temperature and then stirred for 2 hours. A portion of 100 mL of water was added to the reaction mixture and extracted three times with 50 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by recrystallization using n-hexane/MC. The yield of yellow solid is 0.260 g (75.3%). MS (MALDI-TOF): $[M-H]^+$, m/z 1317.4. mp: 139.2 ^{o}C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.80 (s, 3H), 7.73~7.69 (m, 14H), 7.53~7.52 (d, *J* = 8.4 Hz, 3H), 7.49~7.48 (d, *J* = 1.1 Hz, 3H), 7.24~7.22 (d, *J* = 8.4 Hz, 4H), 7.14~7.12 (d, *J* = 8.7 Hz, 6H), 6.29 (s, 3H), 5.91 (s, 3H), 3.99~3.96 (t, *J* = 6.9 Hz, 6H), 2.02 (s, 9H), 1.77~1.70 (m, 6H), 1.49~1.43 (m, 6H), 0.95~0.91 (t, *J* = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 166.13, 150.28, 144.69, 144.53, 141.28, 137.87, 136.08, 135.55, 134.89, 127.73, 127.66, 127.50, 126.33, 126.12, 125.98, 125.04, 123.67, 122.08, 121.73, 115.73, 104.16, 81.36, 47.48, 29.17, 20.42, 18.61, 14.07. Anal. Calcd. for $C_{84}H_{75}N_3O_6S_3$: C, 76.51; H, 5.73; N, 3.19; S, 7.29. Found: C, 76.41; H, 5.61; N, 3.29; S, 7.21.

Scheme II-3. Synthesis of thermally cross-linkable tris-PTMA.

II-2-1-20. 3-bromo-10-butyl-10*H*-phenothiazine (14)

A potion of 3.88 g (21.8 mmol) of NBS in 20 mL of DMF was added dropwise to a solution of compound **1** (4.64 g, 18.2 mmol) in 20 mL of DMF under the N_2 atmosphere at 5 ^{o}C then stirred for 30 min. The reaction mixture was stirred for 5 hours at room temperature. A potion of 100 mL of water was added into the reaction mixture then extracted three times with 100 mL of EA. The combined organic layer was washed with aqueous sodium bisulfite (10 wt.%) and then dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography using n-hexane. The yield of yellow liquid was 5.65 g (92.8%). MS: [M^+], m/z 335. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.17~7.13 (d, *J* = 9.5 Hz, 2H), 7.11~7.04 (m, 2H), 6.88~6.77 (m, 2H), 6.61~6.58 (d, *J* = 8.4 Hz, 1H), 3.73~3.70 (t, *J* = 7.1 Hz, 2H), 1.73~1.65 (m, 2H), 1.41~1.35 (m, 2H), 0.90~0.86 (t, *J* = 7.3 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 146.61, 130.97, 130.70, 128.63, 128.61, 128.33, 125.28, 123.79, 120.00, 117.66, 116.69, 115.52, 48.28, 30.00, 21.29, 15.01. Anal. Calcd. for $C_{16}H_{16}BrNS$: C, 57.49; H, 4.82; Br, 23.90; N, 4.19; S, 9.59. Found: C, 57.39; H, 4.624; N, 3.947; S, 9.624.

II-2-1-21. 10-butyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine (15)

A portion of 4.78 mL (11.9 mmol) of n-butyl lithium (2.50 M in hexane) was added dropwise to a solution of compound **14** (2.15 g, 5.20 mmol) in 50 mL of THF under the N_2 atmosphere at -78 ^{o}C. The reaction mixture was stirred for 2 hours at -78 ^{o}C. A portion of 2.32 g (12.5 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added into the reaction mixture. Then, the resulting mixture was allowed to warm up to room temperature and stirred for 12 hours. A portion of 100 mL water was added slowly to the reaction mixture and then extracted three times with 100 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography using MC/n-hexane (5/5) and recrystallization using n-hexane. The yield of light yellow solid was 2.07 g (78.4%). MS: [M^+], *m/z* 507. mp: 132.7 ^{o}C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.57~7.54 (dd, J_1 = 17.5 Hz, J_2 = 1.4 Hz, 2H), 7.52~7.51 (d, *J* = 1.5 Hz, 2H), 6.81~6.79 (d, *J* = 8.0 Hz, 2H), 3.87~3.83 (t, *J* = 7.3 Hz, 2H), 1.79~1.71 (m, 2H), 1.45~1.38 (m, 2H), 1.31 (s, 24H), 0.93~0.89 (t, *J* = 7.3 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 147.44, 134.18, 133.91, 124.15, 119.09, 114.88, 83.83, 47.28, 28.98, 24.99, 20.18, 13.94. Anal. Calcd. for

$C_{28}H_{39}B_2NO_4S$: C, 66.29; H, 7.75; B, 4.26; N, 2.76; O, 12.62; S, 6.32. Found: C, 66.10; H, 7.574; N, 2.724; S, 6.94.

II-2-1-22. 10-butyl-3,7-bis(10-butyl-10*H*-phenothiazin-3-yl)-10*H*-phenothiazine (16)

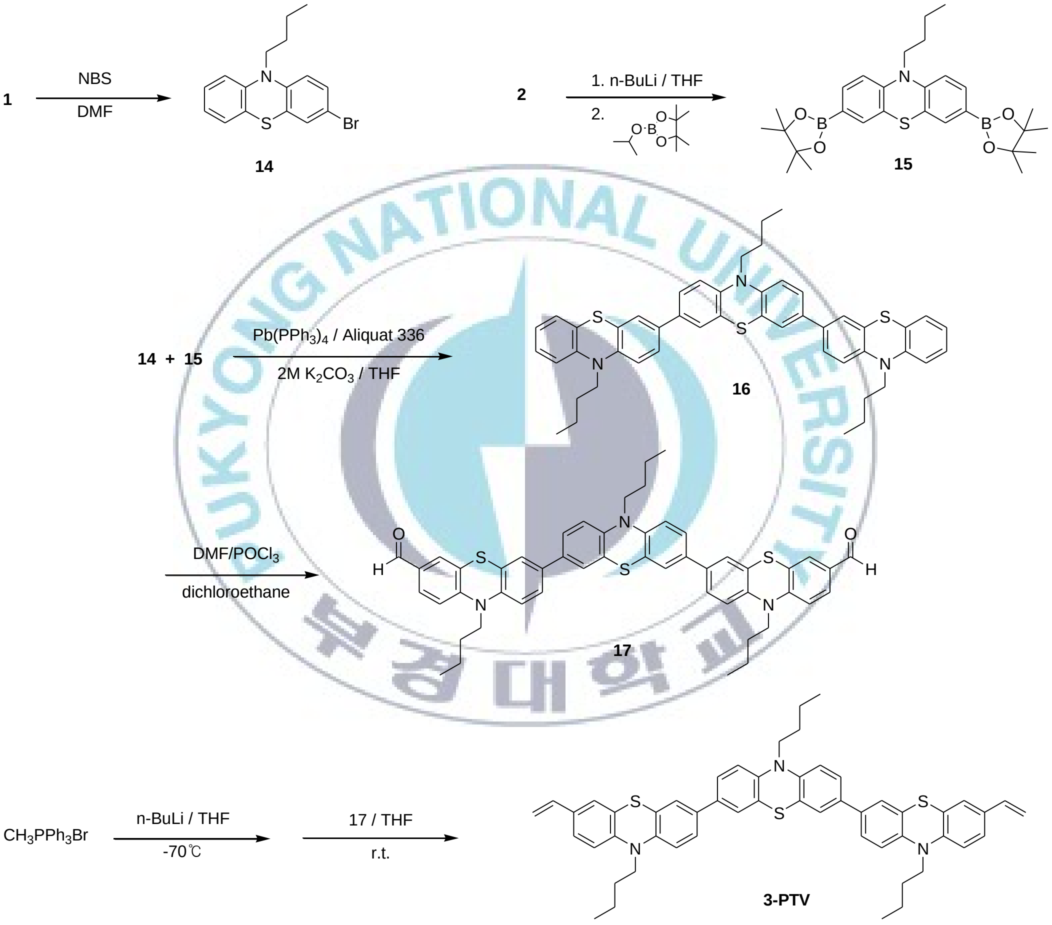
Compound **16** was synthesized by the general procedure of the Suzuki coupling reaction between 2.07 g (6.2 mmol) of compound **14** and 1.52 g (3.0 mmol) of compound **15**. The crude product was purified by flash column chromatography using MC/n-hexane (2/8). The yield of yellow solid is 1.74 g (76.1%). MS: [M^+], m/z 761. mp: 114.5 ^{o}C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.47~7.44 (d, *J* = 8.6 Hz, 4H), 7.41 (s, 4H), 7.22~7.15 (m, 4H), 7.06~7.02 (m, 6H), 6.96~6.92 (t, *J* = 7.3 Hz, 2H), 3.90~3.87 (t, *J* = 6.9 Hz, 6H), 1.71~1.64 (m, 6H), 1.44~1.38 (m, 6H), 0.90~0.86 (t, *J* = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 145.23, 144.33, 144.06, 134.38, 134.34, 127.59, 127.38, 125.37, 125.32, 125.30, 125.28, 125.24, 124.82, 124.55, 122.47, 115.62, 115.55, 115.45, 47.31, 47.25, 29.11, 29.08, 24.96, 20.34, 14.08, 14.02. Anal. Calcd. for $C_{48}H_{47}N_3S_3$: C, 75.65; H, 6.22; N, 5.51; S, 12.62. Found: C, 75.92; H, 6.62; N, 5.084; S, 12.57.

II-2-1-23. 10-butyl-3,7-bis(10-butyl-7'-formyl-10*H*-phenothiazin-3-yl)-10*H*-phenothiazine (17)

A portion of 2.16 g (29.5 mmol) of DMF was added dropwise to a portion of phosphorus oxychloride (4.52 g, 29.5 mmol). The reaction mixture was stirred for 30 minutes at 0 °C. The mixture was added to a solution of compound **5** (1.50 g, 1.97 mmol) in 50 mL of dichloroethane. Then reaction mixture was stirred for 12 hours at 90 °C. A potion of 200 mL of water was added into the reaction mixture then extracted three times with 100 mL of MC. The combined organic layer was washed with aqueous sodium carbonate (10 wt.%) and then dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using MC/n-hexane (1/1). The yield of yellow solid was 1.49 g (92.7%). mp: 114.3 °C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 9.80 (s, 2H), 7.65~7.65 (d, J = 8.5 Hz, 2H), 7.60 (s, 2H), 7.32~7.26 (m, 8H), 6.92~6.90 (d, J = 8.5 Hz, 6H), 3.93~3.89 (t, J = 6.6 Hz, 6H), 1.86~1.79 (m, 6H), 1.52~1.46 (m, 6H), 0.99~0.95 (t, J = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 190.08, 150.49, 144.22, 142.27, 135.48, 133.89, 131.06, 130.31, 128.44, 125.53, 125.40, 125.23, 124.80, 124.55, 124.16, 122.73, 116.19, 115.59, 114.77, 47.82, 47.32, 29.02, 28.85, 20.30, 20.17, 13.98, 13.89. Anal. Calcd. for $C_{50}H_{47}N_3O_2S_3$: C, 73.40; H, 5.79; N, 5.14; O, 3.91; S, 11.76. Found: C, 74.39; H, 5.624; N, 4.947; S, 11.624.

II-2-1-24. 10-butyl-3,7-bis(10-butyl-7'-vinyl-10*H*-phenothiazin-3-yl)-10*H*-phenothiazine (3-PTV)

A portion of 0.37 mL (0.912 mmol) of n-butyl lithium (2.50 M in hexane) was added dropwise to a solution of methyltriphenyl-phosphoniumbromide (0.393 g, 1.10 mmol) in 20 mL of THF under the N_2 atmosphere at -4 ^{o}C for 30 minutes. A solution of compound **6** (300 mg, 0.367 mmol) in 5mL of THF was added into reaction mixture. Then reaction mixture was stirred for 12 hours at 40 ^{o}C. A potion of 100 mL of water was added into the reaction mixture then extracted three times with 100 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by flash column chromatography using MC/n-hexane (1/1). The yield of yellow solid was 0.236 g (78.9%). mp: 98.9 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.29~7.27 (d, J = 7.0 Hz, 4H), 7.20~7.15 (m, 4H), 6.88~6.84 (m, 4H), 6.80~6.78 (d, J = 8.4 Hz, 2H), 6.62~6.55 (dd, J_1 = 17.6 Hz, J_2 = 1.1 Hz, 2H), 5.63~5.58 (d, J = 17.6 Hz, 2H), 5.14~5.11 (d, J = 11.4 Hz, 2H), 3.86~3.82 (t, J = 6.9 Hz, 6H), 1.83~1.75 (m, 6H), 1.50~1.43 (m, 6H), 0.96~0.93 (t, J = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 144.63, 143.98, 135.63, 134.38, 134.34, 132.22, 125.57, 125.34, 125.32, 125.26, 125.21, 124.97, 124.82, 124.79, 124.52, 115.57, 115.19, 112.26, 46.34, 47.31, 29.05, 29.02, 20.31, 20.27, 13.97, 13.94. Anal. Calcd. for $C_{52}H_{51}N_3S_3$: C, 76.71; H, 6.31; N, 5.16; S, 11.82. Found: C, 76.92; H, 6.62; N, 5.084; S, 11.77.



Scheme II-4. Synthesis of thermally cross-linkable 3-PTV.

II-2-2. Fabrication of Device

ITO-coated glass substrates were cleaned with deionized water, acetone, methanol, 2-propanol in ultrasonic bath. A solution of 3-PTMA (5 mg/mL in dichloroethane), 5-PTMA, 3-PTVB, 5-PTVB (5 mg/mL in chloroform:chlorobenzene (1:1 by volume)), tris-PTMA, 3-PTV layer (5 mg/mL in dichloroethane) was spin-coated onto the ITO (sheet resistance = 15 Ω/sq). After spin coating, the thin film of 3-PTMA, 5-PTMA, tris-PTMA or 3-PTV was heated up to 220 ^{o}C for 2 hours in the glove box. Whereas the thin film of 3-PTVB or 5-PTVB was heated up to 185 ^{o}C for 2 hours in the glove box. The typical thickness of films was less than 10 nm. The green emitting polymer (PF9B) [23] was dissolved in toluene (15 mg/mL) and filtered through a 0.20-μm of PTFE syringe filter before spin coating. The typical thickness of emissive layer was 60 nm. A 1000 nm-thick Al was evaporated as cathode onto the surface of the emissive polymer (PF9B) film by thermal evaporation technique at 2.0 x 10^{-6} torr. The typical emissive area of the devices was 6 mm^2.

Table II-1. Thermally cross-linking condition of oligomers.

	Concentration (mg/mL)	Solvent	Temp. (^{o}C)	Time (hr)
3-PTMA	5	dichloroethane	220	2
3-PTVB	5	chloroform:chlorobenzene (1:1 by volume)	185	2
5-PTMA	5	chloroform:chlorobenzene (1:1 by volume)	220	2
5-PTVB	5	chloroform:chlorobenzene (1:1 by volume)	185	2
tris-PTMA	5	dichloroethane	220	2
3-PTV	5	dichloroethane	220	2

II-2-3. Measurement

Synthesized compounds were characterized by ^{1}H-NMR and ^{13}C-NMR spectrum, which were obtained with a JEOL JNM ECP-400 spectrometer. The elemental and MASS analyses of synthesized compounds were carried out an Elementar Vario macro/micro elemental analyzer, Shimadzu GC-MS QP-5050A spectrometer, and a Perkin-Elmer Voyager-DE PRO. The thermo gravimetric analysis (TGA) was carried out under the N_2 atmosphere at a heating rate of 10 ^{o}C/min with a Perkin-Elmer TGA 7 thermal analyzer. The differential scanning calorimetry (DSC) was measured by a Perkin Elmer (Pyris 1, Diamond) under the N_2 atmosphere at a scan rate of 10 ^{o}C/min. The UV-Vis spectrum was recorded using a JASCO V-530 UV-Vis Spectrophotometer. The cyclic voltammetry (CV) was performed by a EG&G 362 Scanning Potentiostat with a three electrode cell in a solution of Bu_4NPF_6 (0.1 M) in freshly distilled methylene chloride at a scan rate of 100 mV/s. Pt wires were used as the counter and working electrode and a Ag/Ag$^+$ electrode was used as the reference electrode. Prior to each measurement, the cell was deoxygenated with the N_2. The current density-voltage-brightness (*J*-V-B) characteristics were measured using a source meter (KEITHLEY 2400) and a luminometer (Minolta LS110). The thickness of films was measured by Alpha-Step IQ surface profiler (KLA-Tencor Co.).

II-3. Results and Discussion

II-3-1. Synthesis of Oligomers

We introduce *n*-butyl substituent on PT to improve solubility. We adapted well-known palladium-catalyzed Suzuki coupling reaction between brominated PT and borylated PT to extend length of π-conjugation. All the compounds were well characterized by elemental analysis, MASS, ^{1}H-NMR, and ^{13}C-NMR.

II-3-2. Thermal Analysis of Oligomers

Figure II-1 shows the TGA thermogram of synthesized oligomers. Those are quite thermally stable because the point 5%-weight loss in TGA thermogram of 3-PTMA which has the lowest thermal stability of them is 270 ^{o}C. Also, we confirm that degradation temperature of oligomers with methacrylate unit is lower than others, because ester group of methacrylate unit is easy to be broken by heat. And among them, 3-PTVB shows the best thermal stability.

In order to investigate thermal properties of oligomers, we performed the DSC. As shown in Figure II-2, all of them show that glass transition temperature (T_g) in the second heating scan is higher than that in the first heating scan, because the network polymers are formed after cross-linking. From the DSC thermograms, we confirm that T_g of pentamer is higher than that of trimer, because chain length of pentamer is longer than that of trimer. Also in Figure II-2, oligomers with methacrylate unit, 3-PTMA, 5-PTMA, and tris-PTMA, show endothermic process in the region of about 160 – 210 ^{o}C. And oligomers with vinylbenzene unit, 3-PTVB and 5-PTVB, didn’t discover region of cross-linking. Because it seems to be overlap melting point. Also 3-PTV with vinyl unit shows endothermic process in the region of about 170 – 150 ^{o}C. We found that thermally cross-linking temperature is depended on cross-linking unit. And in second heating scan, we can’t observe endothermic process around cross-linking temperature in first heating scan, indicating that thermally cross-linking reaction is completed in the first heating.

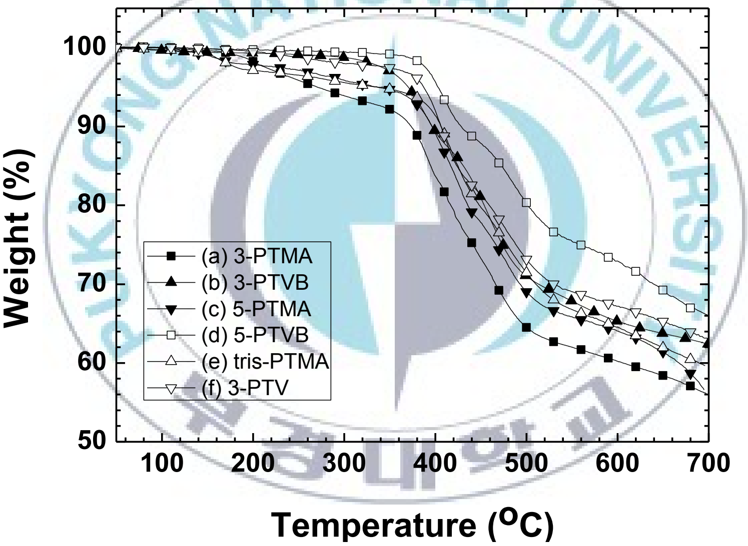


Figure II-1. TGA thermogram of (a) 3-PTMA, (b) 3-PTVB, (c) 5-PTMA, (d) 5-PTVB, (e) tris-PTMA, and (f) 3-PTV.

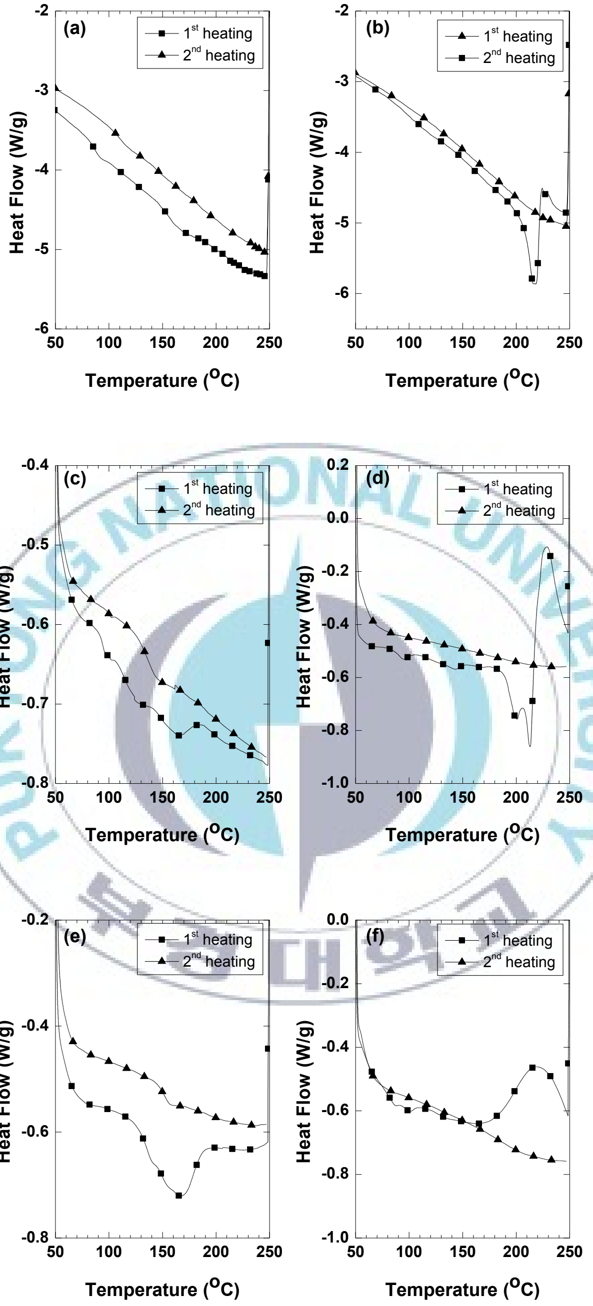


Figure II-2. DSC thermogram of (a) 3-PTMA, (b) 3-PTVB, (c) 5-PTMA, (d) 5-PTVB, (e) tris-PTMA, and (f) 3-PTV (rectangle: first heating, triangle: second heating).

II-3-3. Optical Properties of Oligomers

Thermal cross-linking of oligomers with methacrylate unit or vinyl unit was performed at 220 ^{o}C for 2 hours. And oligomers with vinylbenzene were polymerized at 185 ^{o}C for 2hours. In order to complete the cross-linking reaction, we performed thermal cross-linking at higher temperature than the temperature of endothermic process from the DSC thermogram. Figure II-3 shows the UV-Vis spectra of oligomers. In order to investigate organic solvent resistance of oligomers, we compared with UV-Vis spectra of film coated oligomer before cross-linking, after cross-linking, and washed with organic solvent, methylene chloride (MC). The absorbance of thermally cross-linked film (triangle) and film washed with MC (diamond) was almost same as the absorbance of pristine film coated oligomer before cross-linking (rectangle). From the UV-Vis spectra, indicating that thermally cross-linked oligomers have good organic solvent resistance. Also, all of oligomers have almost same shapes, and wavelength of maximum absorbance at about 340 nm, due to same backbone and similar to π-conjugated length.

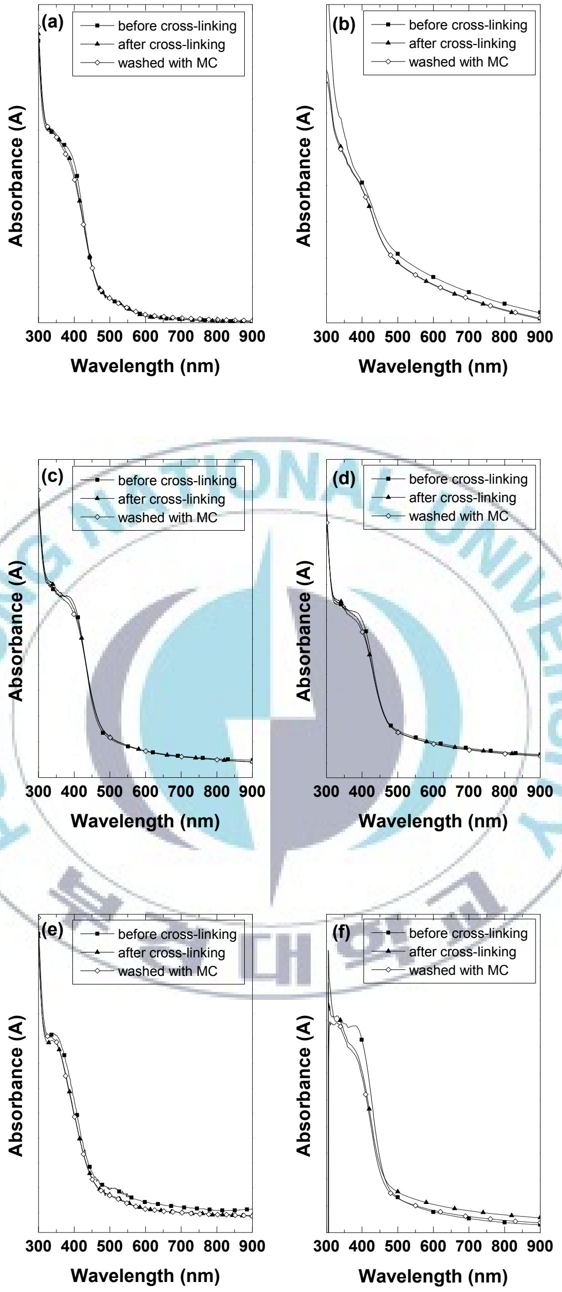


Figure II-3. UV-Vis spectra of (a) 3-PTMA, (b) 3-PTVB, (c) 5-PTMA, (d) 5-PTVB, (e) tris-PTMA, and (f) 3-PTV (rectangle: before cross-linking, triangle: after cross-linking, diamond: after washing with methylene chloride).

II-3-4. Electrochemical Properties of Oligomers

The CV is used to investigate the redox behavior of organic electronic materials and to access the energy levels. The highest occupied molecular orbital (HOMO) energy levels were estimated from the oxidation onset potential by the energy level of ferrocene as -4.8 eV. Figure II-4 shows the CV of thermally cross-linked films of oligomers on ITO and oligomers in MC solution. Thermally cross-linked 3-PTMA, 3-PTVB, and 5-PTMA film on ITO show quasi-reversible behavior. And almost of oligomers based on PT have two oxidation peaks because PT is very strong electron donor.

First cross-linked oligomers with methacylate unit, cross-linked 3-PTMA film, 5-PTMA film, and tris-PTMA film show two oxidation peaks at 0.94 and 1.15 V, 1.04 and 1.28 V, 0.89 and 1.21 V vs. Fc/Fc$^+$, respectively. The magnitude of cathodic and anodic peak current does not change significantly upon repeated redox scans in 0.1 M Bu_4NPF_6 in MC, indicating that all of cross-linked oligomers exhibit good electrochemical stability and solvent resistance. The HOMO energy level of oligomers was figured out from the oxidation onset potential of the first scan of the CV. The HOMO energy levels of cross-linked oligomers with methacrylate unit, cross-linked 3-PTMA film, 5-PTMA film, and tris-PTMA film are -5.58, -5.54, and -5.54 eV, respectively. These HOMO energy levels are far lower than the value of poly(hexylphenothiazine) and thermally cross-linked poly(alkylphenothiazine), these HOMO energy level is -4.9 ~ -5.0 eV. As shown in Figure II-4, oxidation onset potential of 3-PTMA, 5-PTMA, and tris-PTMA are 0.1, 0.11, and 0.11 V vs. Fc/Fc^+, respectively. The estimated HOMO energy level of 3-PTMA, 5-PTMA, and tris-PTMA are -4.90, -4.91, and -4.91 eV, respectively. In the cross-linked film, the molecules are closely packed. Therefore, an oxidized electron from PT unit in the oxidation process would be trapped in carbonyl group with high electron affinity because the molecules are closely packed.

Whereas, in the CV of cross-linked film of 3-PTVB, two oxidation peaks were shown at 0.41 and 0.60 V vs. Fc/Fc^+. And, in the CV of cross-linked film of 5-PTVB, and 3-PTV shows oxidation peaks at 0.40 and 0.71 V, 0.62 V vs. Fc/Fc^+, respectively. The HOMO energy level of cross-linked 3-PTVB film was figured out -4.98 eV from same method, which is very similar to that of cross-linked 5-PTVB film (-4.86 eV) and 3-PTV film (-4.88 eV). Those are very similar to that of 3-PTVB (-5.04 eV), 5-PTVB (-4.94 eV), and 3-PTV (-4.83 eV). In other word, the HOMO energy levels of 3-PTVB, 5-PTVB, and 3-PTV don’t change during the thermally cross-linking process. Also, as shown in Figure II-4, almost of oligomers have good electrochemical stability and solvent resistance, too. There is energy diagram of oligomers at Figure II-5.

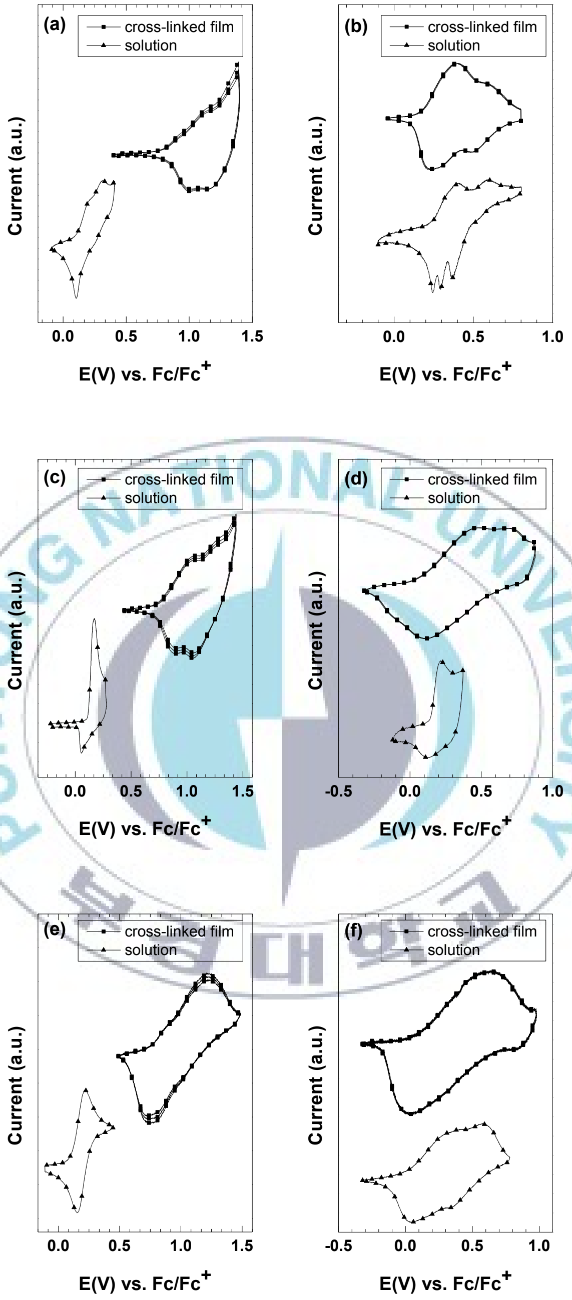


Figure II-4. Cyclic voltammograms of (a) 3-PTMA, (b) 3-PTVB, (c) 5-PTMA, (d) 5-PTVB, (e) tris-PTMA, and (f) 3-PTV (rectangle: thermally cross-linked film on ITO, triangle: solution of oligomers in methylene chloride).

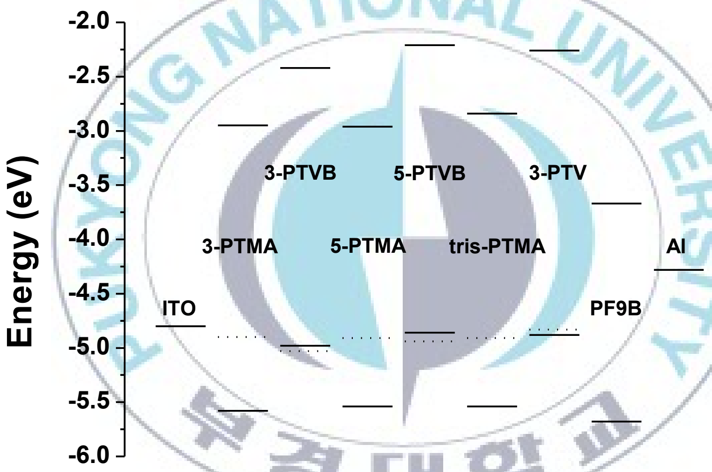


Figure II-5. Energy level diagram of oligomers (solid line: thermally cross-linked film, dot line: oligomer solution).

Table II-2. Optical and electrochemical properties of oligomers based on HIL.

	UV_{max} (nm)	E_{gap} (eV)[a]	$E_{ox,peak}$ (V)	E_{onset} (V), HOMO (eV)[b]	LUMO (eV)[c]	T_d (°C)[d]	T_g (°C)	T_c (°C)[g]
Cross-linked 3-PTMA	340	2.65	0.94, 1.15	0.78, -5.58	-2.95	-	-	-
Cross-linked 3-PTVB	340	2.64	0.41, 0.60	0.18, -4.98	-2.42	-	-	-
Cross-linked 5-PTMA	340	2.64	1.04, 1.28	0.74, -5.54	-2.96	-	-	-
Cross-linked 5-PTVB	340	2.67	0.40, 0.71	0.06, - 4.86	-2.21	-	-	-
Cross-linked tris-PTMA	345	2.68	0.89, 1.21	0.74, -5.54	-2.84	-	-	-
Cross-linked 3-PTV	340	2.63	0.62	0.08, -4.88	-2.26	-	-	-
3-PTMA	340	2.65	0.21, 0.31	0.10, -4.90	-	270	91.2[e] 113.4[f]	185
3-PTVB	340	2.64	0.40, 0.59	0.24, -5.04	-	403	113	-
5-PTMA	340	2.64	0.17	0.11, -4.91	-	336	127.3[e] 149.8[f]	185
5-PTVB	340	2.76	0.22	0.14, -4.94	-	370	95.3[e] 143[e]	-
tris-PTMA	345	2.72	0.21	0.11, - 4.91	-	336	140.0[e] 158.7[f]	192
3-PTV	340	2.67	0.30, 0.57	0.03, -4.83	-	387		220

[a] optical band gap

[b] Estimated from the oxidation onset potential by the energy level of ferrocene as -4.8 eV.

[c] Estimated from the HOMO energy level and optical band gap energy.

[d] the point of 5%-weight loss

[e] glass transition temperature in the first heating

[f] glass transition temperature in the second heating

[g] thermally cross-linking temperature in the first heating

II-3-5. Electroluminescent Properties of Oligomers

In order to investigate hole injection and transporting properties of cross-linked oligomers, we fabricated double layer structured devices, ITO/cross-linked oligomers (~10 nm)/PF9B (60 nm)/Al (100nm). Figure II-7 shows current density (*J*) and brightness (*B*) as a function of applied voltage (V) of devices. The performances of devices are summarized in Table II-2. The *J*-V curves of the devices show typical rectification properties. The turn-on voltage (defined by the voltage was required to give a luminescent of 1 cd/m^2) of devices using cross-linked oligomers as the HIL except tris-PTMA was lower than that of the devices without the HIL. The maximum brightness and maximum efficiency of all of devices were dramatically improved than those of the device without the HIL.

Generally, the charge mobility of the materials with longer effective π-conjugated length shows better charge mobility. In case of oligomers with methacrylate unit, turn-on voltage of tris-PTMA, 3-PTMA, and 5-PTMA (in the order of increasing π-conjugated length) is 10.5, 8.7, and 7.5 V, respectively. Also, the turn-on voltage of the device based on 5-PTVB (7.3 V) is lower than that of 3-PTVB (7.5 V). We confirm that devices based on HIL with long π-conjugated length exhibits better hole injection ability.

Also, we found that HOMO energy level of the HIL is crucial factor to improve performances of device such as efficiency and brightness. In case of the trimer, the maximum efficiency and brightness of device using 3-PTMA (0.685 cd/A, 1979 cd/m^2) are lower than those of the device using 3-PTVB (1.004 cd/A, 2906 cd/m^2). For the pentamer, similar features are observed. The maximum efficiency and brightness of the device using 5-PTMA or 5-PTVB are 0.760 cd/A, 2251 cd/m^2 and 1.074 cd/A, 3165 cd/m^2, respectively. Hole injection materials need to have the HOMO energy level between the ITO and the emissive layer to improve hole injection ability. But, the HOMO energy level of oligomers with methacrylate unit is about -5.6 eV. It isn't suitable for the HIL because the work-function of ITO is -4.8 eV and the HOMO energy level of PF9B is -5.68 eV. [23] Therefore, performances of the device using oligomers with appropriate HOMO energy level such as 3-PTVB, 5-PTVB, and 3-PTV are higher than those of the device using oligomers with methacrylate unit.

After thermally cross-linking, tris-PTMA may have amorphous property so that the Joule heat generation of the device based on tris-PTMA would be less that of the devices based on the others. Although the HOMO energy level of tris-PTMA is -.5.54 eV and short π-conjugated length, the efficiency and brightness of device using tris-PTMA are higher than those of device using oligomers with similar HOMO energy level. This is presumably due to that the stability of the device is improved during the operating. The efficiency and brightness of the device using 3-PTV shows best performances (1.326 cd/A, 6043 cd/m^2). All of the devices based on *in-situ* thermally cross-linked oligomers show good hole injection and transporting properties.

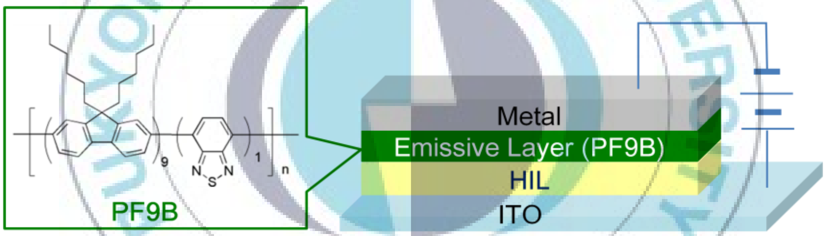


Figure II-6. Device structure of PLED.

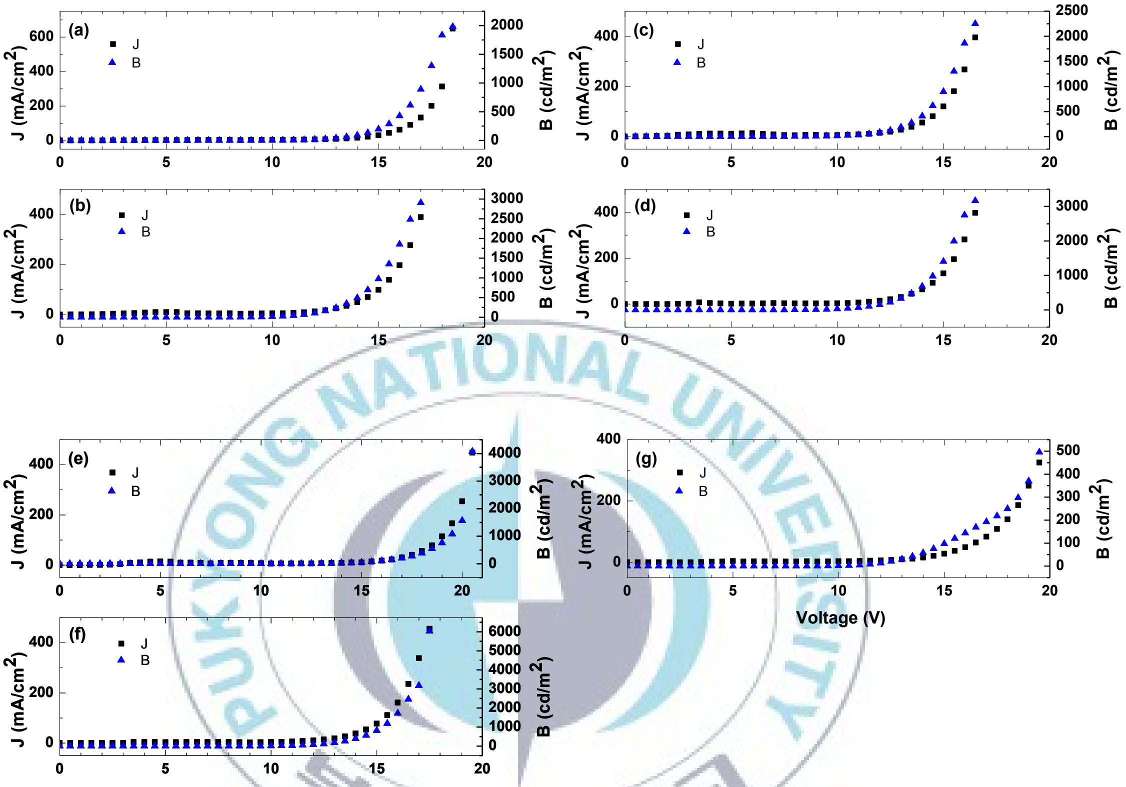


Figure II-7. *J*-V-L curves of PLEDs with the HIL using (a) 3-PTMA, (b) 3-PTVB, (c) 5-PTMA, (d) 5-PTVB, (e) tris-PTMA, (f) 3-PTV, and (g) without HIL (rectangle: current density, triangle: brightness).

Table II-3. Device performances of PLEDs based on thermally cross-linked oligomers.

	V_{on} (V)[a]	LE_{100} (cd/A)[b]	LE_{max} (cd/A)[c]	B_{max} (cd/m^2)
3-PTMA	8.7	0.591 @ 14.1 V	0.685 @ 16.0 V	1979 @ 18.5 V
3-PTVB	7.4	0.823 @ 11.8 V	1.004 @ 12.0 V	2906 @ 17.0 V
5-PTMA	7.5	0.609 @ 12.2 V	0.760 @ 14.5 V	2251 @ 16.5 V
5-PTVB	7.3	0.973 @ 11.5 V	1.074 @ 13.5 V	3165 @ 16.5 V
tris-PTMA	10.5	0.618 @ 16.0 V	0.909 @ 20.5 V	4071 @ 20.5 V
3-PTV	8.5	0.825 @12.5 V	1.326 @ 17.5 V	6043 @ 17.5 V
without HIL	9.5	0.348 @ 15.0 V	0.372 @ 14.0 V	496 @ 15.0 V

[a] defined by the voltage was required to give a luminescent of 1cd/m^2.
[b] luminance efficiency at 100 cd/m^2.
[c] maximum luminescence efficiency.

II-4. Conclusions

We synthesized new π-conjugated oligomers based on 10*H*-alkylphenothiazine with thermally cross-linkable unit such as methacrylate (MA), vinylbenzene (VB), and vinyl (V) unit by the well known palladium catalyzed the Suzuki coupling reaction. From the UV-Vis spectrum, *in-situ* thermally cross-linked oligomers are suitable for successive layer coating by the solution process. Also, we confirm that cross-linked oligomers have electrochemical stability. The maximum efficiency and brightness of the devices with thermally cross-linked oligomers as the HIL are dramatically improved than those of the device without the HIL due to reduced hole-injection barrier and high hole mobility.

Chapter III. Synthesis and Characterization of Water-soluble Materials as Buffer Layer for Polymer Light-emitting Diodes and Polymer Solar Cells Based on Phenothiazine and Fluorene

III-1. Introduction

To get high efficiency, devices should have the balanced charge injection and transporting properties. In order to achieve balanced charge injection/transporting property, the buffer layers such as HIL/HTL and EIL/ETL are introduced between an emissive layer or active layer and an anode or cathode. And to fabricate multi-layer structured polymer light emitting diodes (PLEDs) or polymer solar cells (PSCs), charge injection or transporting materials should have organic solvent resistance for successive layer coating. The lithium fluoride (LiF) is commonly used as the electron injection/transporting layer (EIL/ETL) to improve the performance of devices. The role of the sub-monolayer of the LiF has been suggested to be that of protecting the organic layer during the metal deposition, modifying the work-function of the cathode. [19] Although these advantages, the LiF isn’t suitable material for commercialization of devices due to vapor deposition under the high vacuum. Recently, the use of metal oxides, such as TiO_x and ZnO, as an efficient buffer layer led to significantly improved cell efficiency, and PSCs with SAM-modified ZnO showed dramatically enhanced efficiency. [20]

Also, water-soluble materials could be promising candidates as efficient interfacial layer materials because they are possible to process as solution. Water-soluble materials between the emissive or active layer and the cathode are known that performances of the device are improved than those of the devices without water-soluble materials.

We synthesized water-soluble polymer and oligomer based on phenothiazine and fluorene as the EIL/ETL. Here, we report the synthesis and optical, electrochemical and devices properties of water-soluble materials.

III-2. Experimental Section

III-2-1. Materials and Synthesis

Tetrahydrofuran (THF) was distilled over sodium/benzophenone. Methylene chloride (MC) was distilled over CaH_2. All other chemicals were purchased from Sigma-Aldrich Co, Tokyo Chemical Industry (TCI) or Alfa Aesar (A Johnson Matthey Company) and used as received unless otherwise described.

III-2-1-1. 10-(4-bromobutyl)-10*H*-phenothiazine (1)

A portion of benzyltriethylammonium chloride (50 mg) and 30 mL of 50 wt.% aqueous NaOH were added to a solution of 10*H*-phenothiazine (5.00 g, 25.1 mmol) in 30 mL of dimethyl sulfoxide (DMSO). After stirring for 30 min, 1,4-dibromobutane (54.0 g, 250 mmol) was added to the reaction mixture then stirred for 12 hours at room temperature. The reaction mixture was neutralized with aqueous HCl (35 wt.%) and extracted three times with 100 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. Excess of 1,4-dibromobutane was recovered by the vacuum distillation. The crude liquid product was purified by flash column chromatography using MC/n-hexane (1/9 by volume). The yield of light yellow liquid was 58.4% (4.90 g). MS: $[M^+]$, m/z 335. ^1H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.17~7.09 (m, 4H), 6.90~6.86 (m, 4H), 3.89~3.85 (t, J = 7.0 Hz, 2H), 3.43~3.40 (t, J = 6.2 Hz, 2H), 1.99~1.96 (m, 4H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 145.04, 127.50, 127.18, 125.34, 125.52, 115.45, 46.04, 33.49, 29.80, 25.16. Anal. Calcd. for $C_{16}H_{16}BrNS$: C, 57.49; H, 4.82; Br, 23.90; N, 4.19; S, 9.59. Found: C, 56.92; H, 4.92; N, 4.084; S, 9.77.

III-2-1-2. 3,7-dibromo-10-(4-bromobutyl)-10*H*-phenothiazine (2)

A potion of 1.64 g (9.21 mmol) of *N*-bromosuccinimide (NBS) in 10 mL of N,N'-dimethylformamide (DMF) was added dropwise to a solution of compound **1** (1.40 g, 4.19 mmol) in 20 mL of DMF under the N_2 atmosphere at 5 ^oC then stirred for 30 min. The reaction mixture was stirred for 5 hours at room temperature. A potion of 100 mL of water was added into the reaction mixture then extracted three times with 100 mL of ethyl acetate (EA). The combined organic layer was washed with aqueous sodium bisulfite (10 wt.%) and then dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using n-hexane. The yield of yellow liquid was 1.30 g (62.87%). MS: [M^+], m/z 491. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.38~7.36 (m, 4H), 6.99~6.97 (d, *J* = 9.2 Hz, 2H), 3.88~3.85 (t, *J* = 6.9 Hz, 2H), 3.55~3.52 (t, *J* = 6.6 Hz, 2H), 1.93~1.86 (m, 2H), 1.79~1.74 (m, 2H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 144.29, 130.93, 129.70, 126.19, 118.28, 114.73, 46.36, 35.23, 30.09, 25.33. Anal. Calcd. for $C_{16}H_{14}Br_3NS$: C, 39.05; H, 2.87; Br, 48.72; N, 2.85; S, 6.52. Found: C, 40.39; H, 2.624; N, 2.947; S, 6.624.

III-2-1-3. 2,7-dibromo-9,9-bis(6-bromohexyl)-9*H*-fluorene (3)

A solution of 20 mL of 45 wt.% aqueous KOH was added to a solution of 2,7-dibromo-9*H*-fluorene (3.24 g, 10.0 mmol) in 1,6-dibromo-hexane (48.8 g, 200 mmol). Then reaction mixture was stirred for 4 hours at 80 ^{o}C. The reaction mixture was neutralized with aqueous HCl (35 wt.%) and extracted three times with 100 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. Excess of 1,6-dibromohexane was recovered by the vacuum distillation. The crude liquid product was purified by flash column chromatography using MC/n-hexane (1/9 by volume). The yield of light yellow liquid was 87.3% (5.67 g). MS: $[M^+]$, m/z 650. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.54~7.52 (d, *J* = 8.0 Hz, 2H), 7.48~7.44 (m, 4H), 3.32~3.28 (t, *J* = 7.0 Hz, 4H), 1.95~1.90 (m, 4H), 1.71~1.63 (m, 4H), 1.23~1.16 (m, 4H), 1.12~1.05 (m, 4H), 0.61~0.55 (m, 4H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 153.39, 140.26, 131.55, 127.33, 122.82, 122.48, 56.77, 41.24, 35.14, 33.85, 30.18, 28.98, 24.70. Anal. Calcd. for $C_{25}H_{30}Br_4$: C, 46.19; H, 4.65; Br, 49.16. Found: C, 46.71; H, 4.89.

III-2-1-4. 2-(9,9-bis(6-bromohexyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

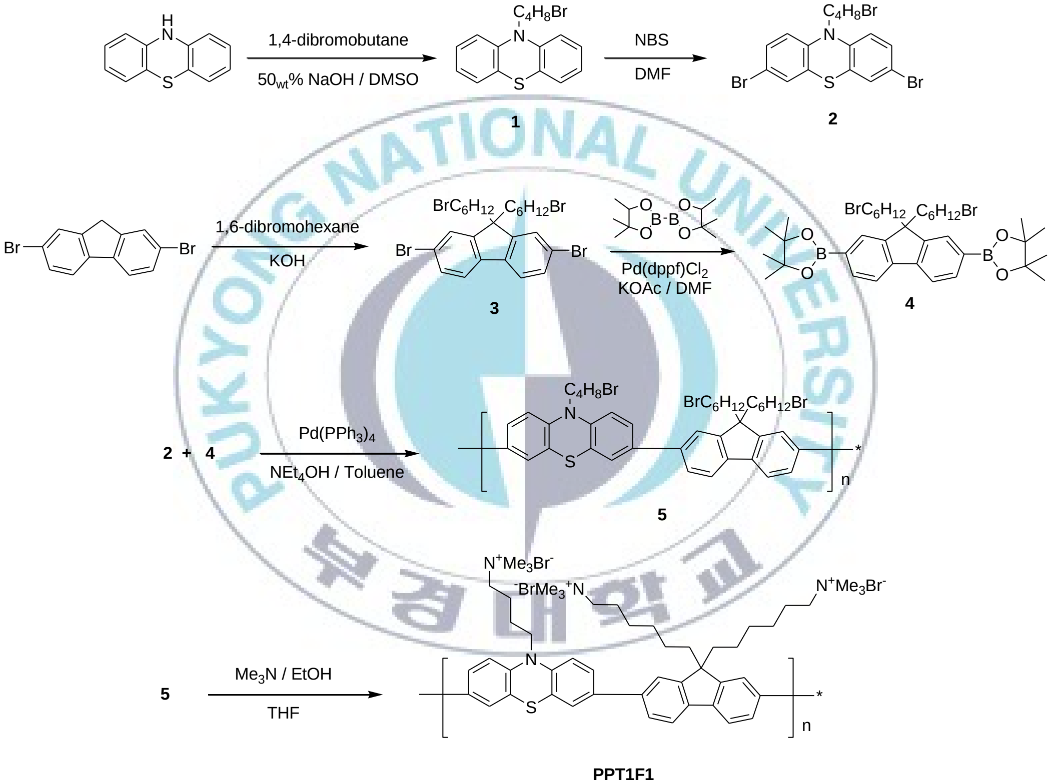
A mixture of 2.95g (4.54 mmol) of compound **3**, 4.15 g (27.2 mmol) of bis(pinacolato)diboron, 2.67 g, (27.2 mmol) of potassium acetate and 0.222 g (0.274 mmol) of Pd(dppf)Cl_2 in 30 mL of DMF was stirred at 60 ^{o}C for 24 hours under the N_2 atmosphere. The reaction mixture was cooled down to room temperature and 100 mL of water added into the reaction mixture and then extracted three times with 50 mL of EA. The combined organic layer washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator. The crude product was purified by the flash chromatography using EA/*n*-hexane (2/8 by volume) and recrystallization using n-hexane. The yield of white solid was 1.78 g (53.2%). mp: 108.7 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ7.83~7.81 (d, *J* = 7.7 Hz, 2H), 7.74~7.72 (m, 4H), 3.92~3.89 (t, *J* = 6.9 Hz, 4H), 2.03~1.99 (m, 8H), 1.39 (s, 24H), 1.06~1.04 (m, 8H), 0.57~0.50 (m, 4H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 171.15, 150.11, 143.84, 133.70, 128.68, 119.42, 83.72, 64.52, 55.02, 40.02, 29.50, 28.41, 25.51, 24.89, 23.42, 20.97. Anal. Calcd. for $C_{37}H_{54}B_2Br_2O_4$: C, 59.71; H, 7.31; B, 2.91; Br, 21.47; O, 8.60. Found: C, 59.11; H, 8.42.

III-2-1-5. Poly[10-(4-bromobutyl)-10*H*-phenothiazine-alt- 9,9-bis(6-bromohexyl)-9*H*-fluorene] (5)

A mixture of compound **2** (0.122 g, 0.250 mmol), compound **4** (0.184 g, 0.250 mmol) and 11.4 mg (0.010 mmol) of tetrakis(triphenylphosphine) palladium[Pd(PPh_3)$_4$] in 2 mL of degassed toluene was stirred for 2 hours at 110 ^{o}C under the N_2 atmosphere. At the end of polymerization, 30 mg (0.2 mmol) of phenylbronic acid was added as a monofuctional end-capping reagent. After being stirred the mixture for an hour, 40 mg (0.25 mmol) of bromobenzene was added to the reaction mixture and stirred for an hour. After cooling to room temperature, the reaction mixture was poured into 400 mL of methanol. The precipitate was filtered and dissolved 100 mL of chloroform. A solution of 100 mL of ammonia water (25 wt.%) was added to the solution and stirred for 12 hours to eliminate palladium catalyst. Then the combined organic layer was washed three times with 100 mL water and then dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator. After re-dissolving product in small amount of THF, the solution poured into 200 mL of methanol and precipitate was filtered. The resulting polymer was dried under the vacuum. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.76 (b, 4H), 7.55~7.50 (b, 6H), 6.99~6.98 (d, J = 7.7 Hz, 2H), 4.14~4.11 (t, J = 6.2 Hz, 2H), 3.94~3.91 (t, J = 6.6 Hz, 2H), 3.50~3.48 (b, 4H), 2.18~1.97 (b, 6H), 1.86~1.81 (m, 2), 1.47~1.33 (b, 8H), 1.11~1.05 (b, 4H), 0.72~0.67 (b, 4H).

III-2-1-6. Poly[10-(4-(*N*,*N*,*N*-trimetylammonium)-butyl)-10*H*-phenothiazine-alt- 9,9-bis(6-(*N*,*N*,*N*-trimethylammonium)-hexyl)-9*H*-fluorene] bromide (PPT1F1)

A solution of 0.5 mL of trimethylamine in ethanol (33 wt.%) was added to a solution of compound **5** (50.0 mg) in 5 mL of THF. Then reaction mixture was stirred for at room temperature for 2 days. Then the solvent was removed.



Scheme III-1. Synthesis of water-soluble polymer (PPT1F1)

III-2-1-7. 10-(4-bromobutyl)-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine (6)

A mixture of 77.0 mg (1.57 mmol) of compound **2**, 920 mg (9.4 mmol) of bis(pinacolato)diboron, 1.59 g (6.30 mmol) of potassium acetate and 77.0 mg (0.084 mmol) of Pd(dppf)Cl_2 in 30 mL of DMF was stirred at 60 ^{o}C for 24 hours under the N_2 atmosphere. The reaction mixture was cooled down to room temperature. And 100 mL of water added into the reaction mixture and then extracted three times with 50 mL of EA. The combined organic layer washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator. The crude product was purified by the flash chromatography using EA/*n*-hexane (2/8 by volume). The yield of yellow solid was 0.43 g (46.7%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.58~7.55 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 2H), 7.54~7.53 (d, J = 1.4 Hz, 2H), 6.82~6.80 (d, J = 8.1 Hz, 2H), 4.06~4.02 (t, J = 6.6 Hz, 2H), 3.93~3.89 (t, J = 7.0 Hz, 2H), 1.88~1.81 (m, 2H), 1.77~1.70 (m, 2H), 1.31 (s, 24H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 148.22, 135.11, 134.94, 125.48, 120.00, 115.88, 84.79, 65.01, 26.82, 25.88, 25.61, 47.82. Anal. Calcd. for $C_{28}H_{38}B_2BrNO_4S$: C, 57.37; H, 6.53; B, 3.69; Br, 13.63; N, 2.39; O, 10.92; S, 5.47. Found: C, 57.15; H, 6.42; N, 2.42; S, 5.58.

III-2-1-8. 2-bromo-9,9-bis(6-bromohexyl)-9*H*-fluorene (7)

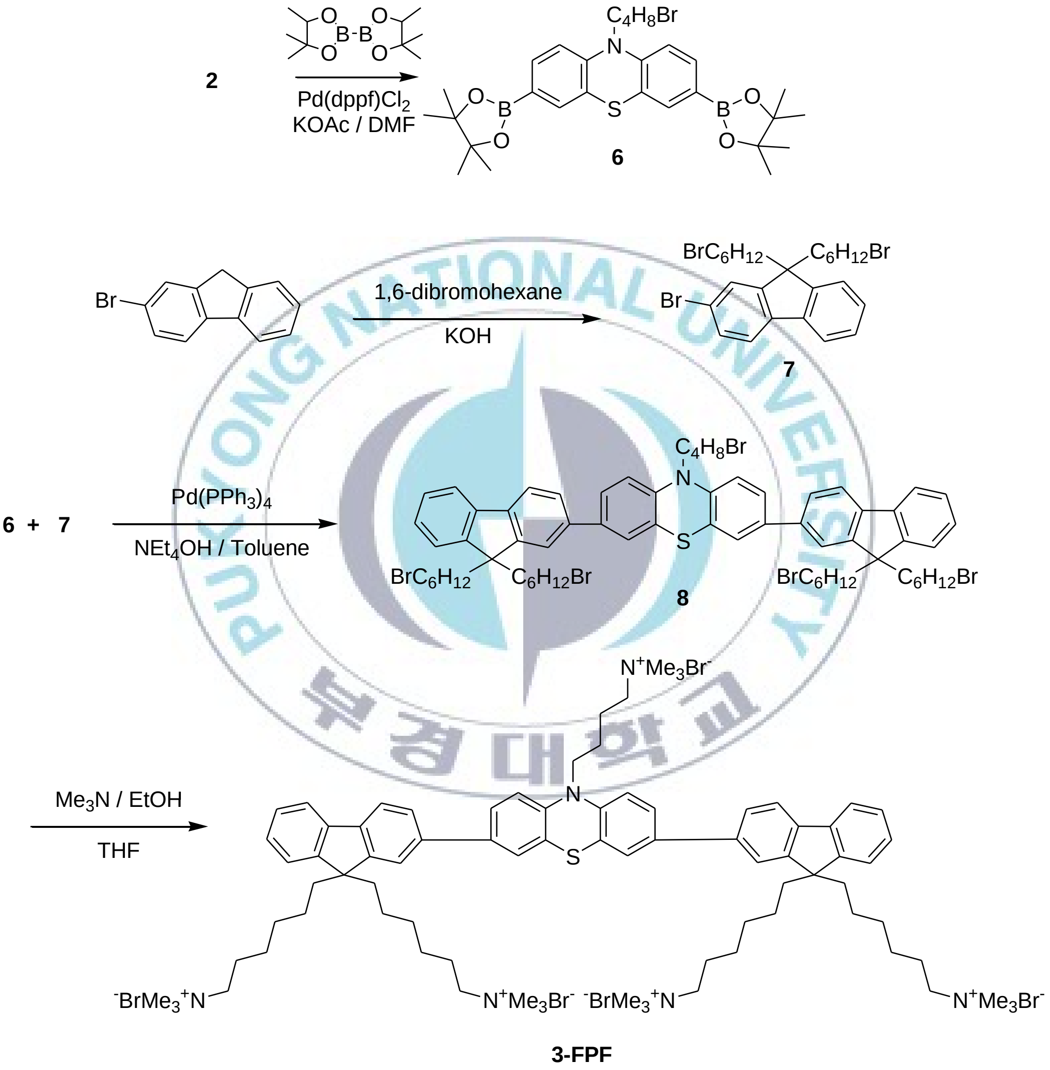
A solution of 40 mL of 45 wt.% aqueous KOH was added to a solution of 2-bromo-9*H*-fluorene (4.90 g, 20.0 mmol) in 1,6-dibromo-hexane (97.6 g, 400 mmol). Then reaction mixture was stirred for 4 hours at 80 ^{o}C. The reaction mixture was neutralized with aqueous HCl (35 wt.%) and extracted three times with 100 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator. Excess of 1,6-dibromohexane was recovered by the vacuum distillation. The crude liquid product was purified by flash column chromatography using MC/n-hexane (1/9 by volume). The yield of light yellow liquid was 89.7% (10.2 g). MS: [M^+], m/z 570. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.66~7.65 (t, *J* = 3.7 Hz, 1H), 7.56~7.53 (d, *J* = 8.8 Hz, 1H), 7.45~7.43 (m, 2H), 7.33~7.31 (m, 3H), 3.28~3.24 (t, *J* = 6.6 Hz, 4H), 1.97~1.91 (m, 4H), 1.67~1.60 (m, 4H), 1.21~1.14 (m, 4H), 1.09~1.02 (m, 4H), 0.63~0.55 (m, 4H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 153.77, 151.09, 141.32, 141.19, 131.23, 128.79, 128.28, 127.23, 123.98, 122.31, 122.24, 121.03, 56.42, 41.30, 35.12, 33.81, 30.18, 28.93, 24.67. Anal. Calcd. for $C_{25}H_{31}Br_2$: C, 52.57; H, 5.47; Br, 41.96. Found: C, 52.92; H, 5.52.

III-2-1-9. 3,7-bis[9,9-bis(6-bromohexyl)-9*H*-fluoren-2-yl]-10-(4-bromobutyl)-10*H*-phenothiazine (8)

A mixture of compound **6** (200 mg, 0.342 mmol), compound **7** (430 mg, 0.752 mmol), 3.0 mol% of tetrakis(triphenylphosphine) palladium[$Pd(PPh_3)_4$], and several drops of aliquat. 336 in 20 mL of degassed 1:1 (by volume) mixed solvent of THF and 2M K_2CO_3 aqueous was stirred for 12 hours at 75 ^oC under the N_2 atmosphere. A portion of 100 mL of water was added to the reaction mixture and then extracted three times of with 100 mL of EA. The combined organic layer dried over anhydrous $MgSO_4$. The solvent was removed by the evaporation under reduced pressure. The crude product was purified by flash column chromatography using MC/n-hexane (2/8 by volume). The yield of light yellow solid was 47.2% (212 mg). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.74~7.69 (m, 4H), 7.53~7.50 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 2H), 7.49~7.46 (m, 6H), 7.35~7.29 (m, 6H), 6.98~6.96 (d, J = 8.4 Hz, 2H), 4.13~4.10 (t, J = 6.2 Hz, 2H), 4.01~3.98 (t, J = 6.6 Hz, 2H), 3.28~3.24 (t, J = 7.0 Hz, 8H), 2.00~1.92 (m, 10H), 1.86~1.80(m, 8H), 1.67~1.61(m, 8H), 1.22~1.15 (m, 8H), 1.11~1.03 (m, 8H), 0.69~0.63(m, 8H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 152.17, 151.61, 145.21, 141.84, 141.31, 139.92, 137.25, 128.20, 128.04, 127.09, 126.52, 126.36, 123.88, 121.80, 121.14, 120.87, 119.98, 116.73, 65.08, 56.11, 41.36, 35.06, 33.73, 30.73, 30.15, 28.85, 24.66, 22.08. Anal. Calcd. for $C_{66}H_{76}Br_5NS$; C, 60.29; H, 5.83; Br, 30.38; N, 1.07; S, 2.44. Found: C, 61.92; H, 5.62; N, 1.084; S, 2.77.

III-2-1-10. 3,7-bis[9,9-bis(6-(*N*,*N*,*N*-trimetylammonium)-hexyl)-9*H*-fluoren-2-yl]-10-(4-*(N*,*N*,*N*-trimetylammonium)-butyl)-10*H*-phenothiazine pentabromide (3-FPF)

A solution of 0.5 mL of trimethylamine in ethanol (33 wt.%) was added to a solution of compound **8** (50.0 mg, 0.038 mmol) in 5 mL of THF. Then reaction mixture was stirred for at room temperature for 2 days. Then the solvent was removed. The yield of yellow solid was 94.1% (57.6 mg).



Scheme III-2. Synthesis of water-soluble trimer (3-FPF).

III-2-2. Fabrication of Devices

ITO-coated on glass substrates were cleaned with deionized water, acetone, methanol, 2-propanol in ultrasonic bath. First, PSCs were fabricated through the conventional process. A layer (~ 40 nm) of diluted poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P) with 2-propanol (PEDOT:2-propanol = 1:2 by volume) was spin-coated on pre-cleaned ITO substrate (sheet resistance = 15 Ω/sq) which was pre-treated by UV/O_3 for 120 sec. After being baked at 150 ^{o}C for 10 min under the air, active layer was spin-cast from the blend solution of P3HT/PCBM at 600 rpm for 40 s. The blend of 20 mg of P3HT and 20 mg of PCBM were dissolved in 1 mL of *o*-dichlorobenzene (DCB). The blended solution was stirred for 12 h at 60 ^{o}C in the glove box. Prior to spin coating, the blend solution was filtered through 0.20-μm of PTFE membrane filter. After drying active layer for 50 min under the air, the ETL was spin-coated from the solution in ethanol (1 mg/ml) onto active layer at 4000 rpm for 120 s. A typical thickness of the active layer was 200 nm and the ETL was less than 5 nm. A 100 nm-thick layer of Al was vacuum deposited as a cathode through shadow mask onto the top of the ETL films at 2 x 10^{-6} Torr. The typical active area of the devices was 12 mm^2.

For PLEDs, diluted PEDOT:PSS (P 4083) with 2-propanol (PEDOT:2-propanol = 1:1 by volume) was spin-coated on cleaned ITO glass substrate. After being baked at 150 ^{o}C for 10 min under the air, the emissive layer was spin-coated from the green emitting polymer (PF9B) solution. The 15 mg of PF9B was dissolved in 1 ml of toluene and filtered through a 0.20-μm of PTFE syringe filter before spin coating. And then, the ETL was spin-coated from the solution in ethanol (1 mg/ml) onto the emissive layer at 4000 rpm for 120 s. The typical thickness of the emissive layer and ETL were 60 nm, and less than 5 nm, respectively. A 100 nm-thick Al was evaporated onto the surface of the ETL film by thermal evaporation technique at 2.0 x 10^{-6} torr. The typical emissive area of the devices was 6 mm^2.

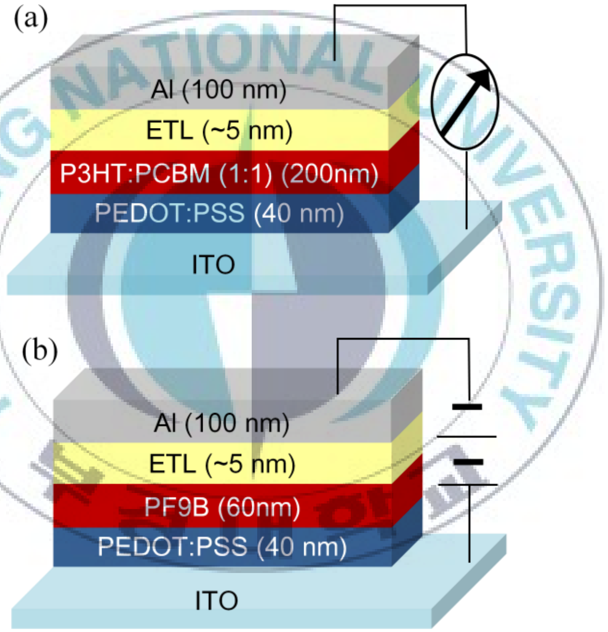


Figure III-1. The device structure of (a) conventional type PSC and (b) PLED.

III-2-3. Measurements

Synthesized compounds were characterized by ^{1}H-NMR and ^{13}C-NMR spectrum, which were obtained with a JEOL JNM ECP-400 spectrometer. The elemental and MASS analyses of synthesized compounds were carried out an Elementar Vario macro/micro elemental analyzer and Shimadzu GC-MS QP-5050A spectrometer. The UV-Vis spectrum was measured by using a JASCO V-530 UV-Vis Spectrophotometer. The cyclic voltammetry (CV) was performed by a EG&G 362 Scanning Potentiostat with a three electrode cell in a solution of Bu_4NPF_6 (0.1 M) in freshly distilled methylene chloride at a scan rate of 100 mV/s. Pt wires were used as the counter and working electrode and a Ag/Ag^+ electrode was used as the reference electrode. Prior to each measurement, the cell was deoxygenated with the N_2. The *J*–V measurements under the 1.0 sun (100 mW/cm^2) condition form a 150 W Xe lamp with AM 1.5G filter were performed using a KEITHLEY Model 2400 source-measure unit. A calibrated Si reference cell with a KG5 filter certified by National Institute of Advanced Industrial Science and Technology was used to confirm 1.0 sun condition. And the current density-voltage-brightness (*J*-V-B) characteristics were measured by using a source meter (KEITHLEY 2400) and a luminometer (Minolta LS110). The thickness of films was measured by an Alpha-Step IQ surface profiler (KLA-Tencor Co.).

III-3. Results and Discussion

III-3-1. Synthesis and Characterization

We synthesized water-soluble π-conjugated polymer and oligomer based on phenothiazine and fluorene derivatives which have quaternary ammonium salt on the end of alkyl chain to dissolve in polar solvent such as water, methanol, and ethanol. We adapted the well-known palladium-catalyzed Suzuki coupling reaction to synthesize the polymer (PPT1F1) and oligomer (3-FPF). All the compounds were well characterized by elemental analysis, MASS, ^{1}H-NMR, and ^{13}C-NMR.

Generally, the polymer with long π-conjugated length exhibits good charge mobility. However, the polymer is hard to purify due to low solubility. And polymerization reaction lacks reproducibility because polymerization reaction is hard to control. Therefore, it is difficult to get identical product. To release this matter, we synthesized oligomer because the purification and reproducibility in the synthesis of oligomer are much easier than those of polymer. The contact angles of PPT1F1 and 3-FPF films on glass substrate were measured by using distilled water. The contact angles of PPT1F1 and 3-FPF are 49.7 ^{o}, and 31.2 ^{o}, respectively. As a result, indicating that PPT1F1 has more hydro-phobicity than that of 3-FPF. In other words, the solubility of 3-FPF in polar solvent such as water, methanol, and ethanol is higher than that of PPT1F1. This is because 3-FPF has more quaternary ammonium salts than those in the repeating unit of PPT1F1.

Table III-1. Optical and electrochemical properties of PPT1F1 and 3-FPF.

	UV_{max} (nm)	E_{gap} (eV)[a]	$E_{ox,peak}$ (V)	E_{onset} (V), HOMO (eV)[b]	LUMO (eV)[c]	Contact angle (^{o})[d]
PPT1F1	386	2.87	0.29, 0.87	0.27 -5.07	-2.2	49.7
3-FPF	350	2.98	0.33, 0.92	0.21 -5.01	-2.03	31.2

[a] optical band gap

[b] Estimated from the oxidation onset potential by the energy level of ferrocene as -4.8 eV

[c] Estimated from the HOMO energy level and optical band gap energy

[d] Estimated using distilled water

III-3-2. Optical and Electrochemical Properties

Figure III-2 shows UV-Vis spectra of the PPT1F1 and 3-FPF. The UV-Vis spectrum was measured by solution of material before going over the PPT1F1 or 3-FPF in MC. The maximum absorption of PPT1F1 appeared at 386 nm and the band gap figured out from the absorption edge is 3.21 eV. In case of the 3-FPF, it has optical band gap of 2.98 eV and shows the maximum absorption at 350 nm. As shown in Figure III-2, the maximum absorption of PPT1F1 was red-shifted about 35 nm than that of 3-FPF, because the π-conjugated length of PPT1F1 is longer than that of 3-FPF.

The CV is used to investigate the redox behavior of organic electronic materials and to access the energy levels. The highest occupied molecular orbital (HOMO) energy levels were estimated from the oxidation onset potential by the energy level of ferrocene as -4.8 eV. Figure III-3 shows CV of before going over the PPT1F1 and 3-FPF in MC solution. The PPT1F1 and 3-FPF show quasi-reversible behavior. The PPT1F1 shows two oxidation peaks at 0.29 and 0.87 V vs. Fc/Fc^+. And oxidation peaks of the PPT1F1 are shifted to lower potential compared with those of 3-FPF (0.33 and 0.99 V vs. Fc/Fc^+) due to that ratio of phenothiazine ring, which is known strong electron donor, in the repeating unit of PPT1F1 is higher than that of 3-FPF. The HOMO energy level of PPT1F1 and 3-FPF was -5.07 and -5.01 eV, respectively, which is figured out from the oxidation onset potential of the first scan of the CV. As shown in Figure III-3, the magnitude of cathodic and anodic peak current does not change significantly upon repeated redox scans, indicating that PPT1F1 and 3-FPF exhibit good electrochemical stability.

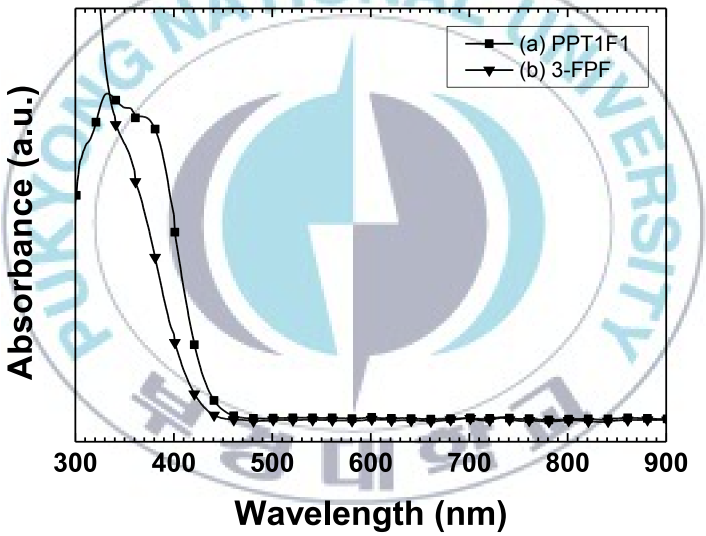


Figure III-2. UV-Vis spectrum of (a) PPT1F1 and (b) 3-FPF.

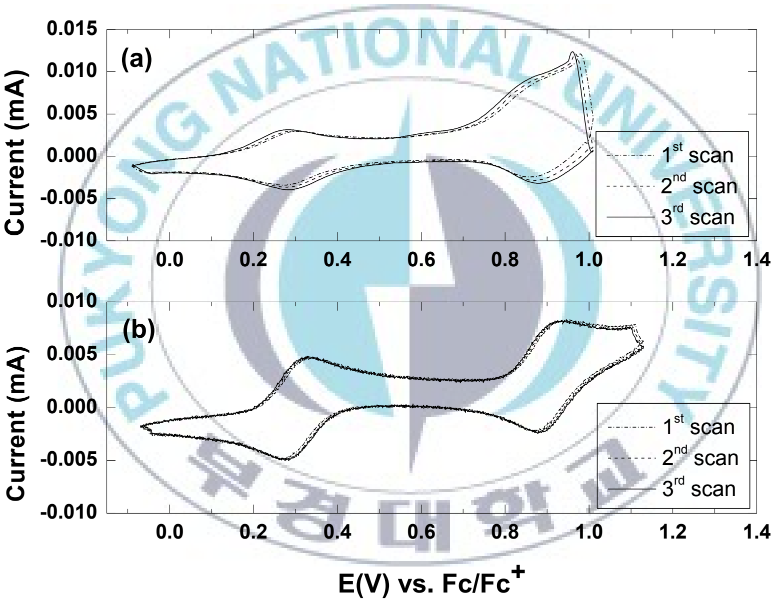


Figure III-3. Cyclic voltammograms of (a) PPT1F1 and (b) 3-FPF (solid line: first scan, dashed line: second scan, dash-dot line: third scan).

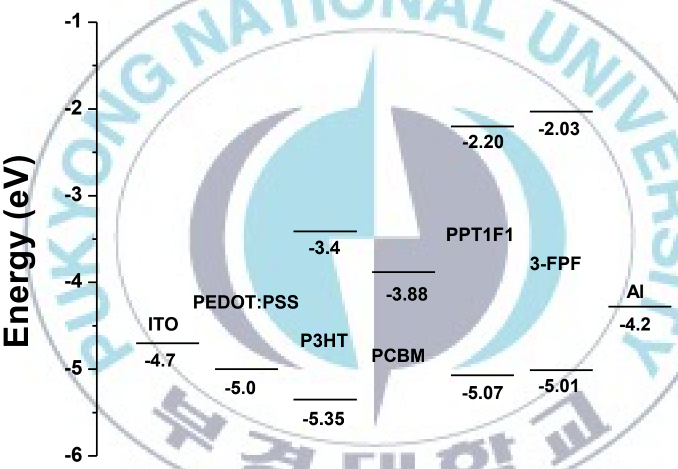


Figure III-4. Energy level diagram of PPT1F1 and 3-FPF.

III-3-3. Photovoltaic Properties of Conventional Type PSCs

PSCs were fabricated using PPT1F1 or 3-FPF as ETL. The current density (*J*) – voltage (V) characteristics of PSCs measured under AM 1.5 G simulated illumination with an intensity of 100 mW/cm^2 and shown in Figure III-5. The PSC using PPT1F1 showed a turn-on voltage (V_{oc}) of 0.61 V, a short circuit current (J_{sc}) of -9.01 mA/cm^2, a fill factor (FF) of 60.9%, and a power conversion efficiency (PCE) of 3.37%. The device using 3-FPF gave a V_{oc} of 0.60 V, a J_{sc} of -9.46 mA/cm^2, a FF of 56.8%, and a PCE of 3.22%. The device without the ETL shows that the V_{oc}, J_{sc}, FF value and PCE are 0.55 V, -8.25 mA/cm^2, 59.9%, and 2.72%, respectively. The performances of the devices based on water-soluble materials showed better performances than those of the device without water-soluble material as the ETL. And the series resistance (R_s) attributed to the bulk conductivity is calculated from the inverse slope near V_{oc} in Figure III-6 under the dark condition. The R_s of devices with PPT1F1 (2.18 Ω·cm^2) or 3-FPF (2.43 Ω·cm^2), and is lower than that of device without them, 4.96 Ω·cm^2. Because the PPT1F1 and 3-FPF induced an interfacial dipole pointing away from the metal surface in the device introduced water-soluble materials as the ETL. For the reasons, the work-function of Al is reduced.

The reduction of the work-function of Al could help electron transport from the active layer to the cathode. Also, the series resistance of PSCs with the ETL decreases this is due to that the ETL reduces the contact resistance between active layer and cathode.

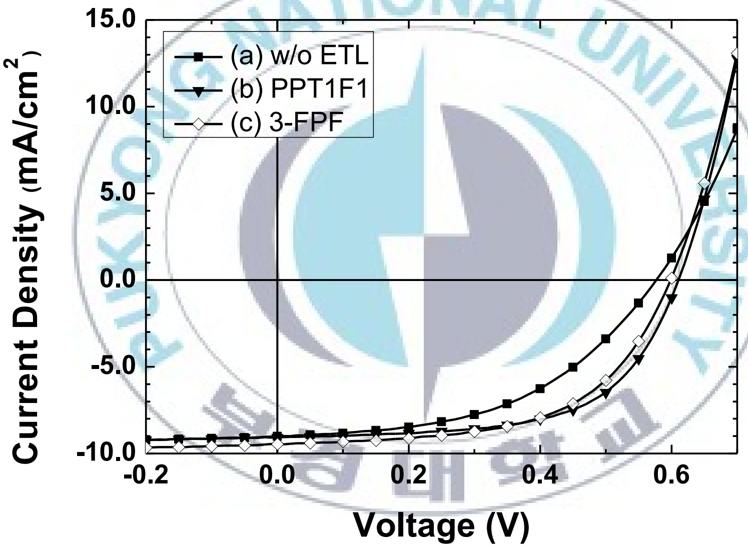


Figure III-5. *J*-V curves of conventional type PSCs (a) without ETL, (b) with PPT1F1, and (c) with 3-FPF under the illumination (100 mA/cm^2) of AM 1.5G and 1.0 sun condition.

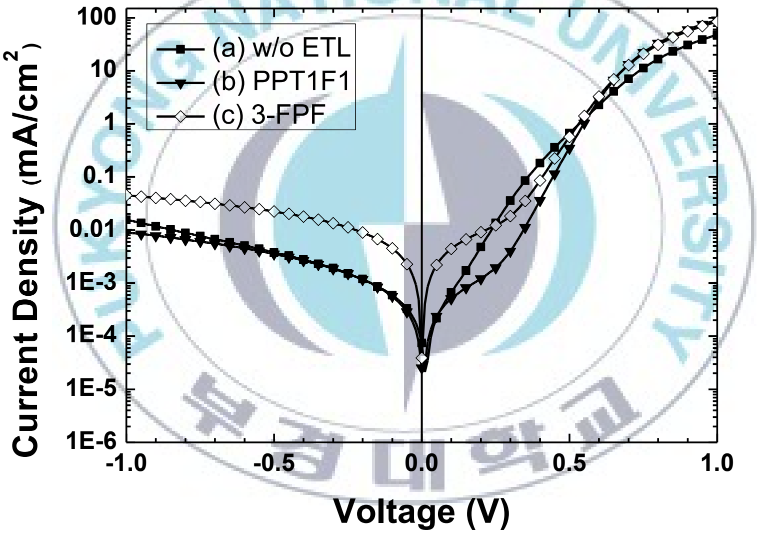


Figure III-6. *J*-V curves of conventional type PSCs (a) without ETL, (b) with PPT1F1, and (c) with 3-FPF under the dark condition.

Table III-2. Device performances of conventional type PSCs.

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)	R_s ($\Omega \cdot cm^2$)
w/o ETL	-8.25	0.55	59.9	2.72	4.96
with-PPT1F1	-9.01	0.61	60.9	3.37	2.18
with 3-FPF	-9.46	0.60	56.8	3.22	2.43

III-3-4. Electroluminescent Properties

In order to investigate electron injection properties of water-soluble materials, we fabricated double layer structured device, ITO/PEDOT:PSS (P 4083) (40 nm)/PF9B (60 nm)/water-soluble material (~10 nm)/Al (100nm). Figure III-8 shows current density (*J*) and brightness (*B*) as a function of applied voltage (V) of devices. The performances of devices are summarized in Table III-3. The turn-on voltage (defined by the voltage was required to give a luminescent of 1 cd/m^2) of device using PPT1F1 as the EIL was 5.6 V, and that of device using 3-FPF was almost same, 5.5 V. Also, we fabricated the device without the EIL. The turn-on voltage of device without the EIL was 7.5 V, which is slightly higher than that of the devices using water-soluble materials as the EIL. And the maximum efficiency and brightness of devices using PPT1F1 or 3-FPF were 2.05 cd/A, 4849 cd/m^2 and 3.27 cd/A, 8845 cd/m^2, respectively. The maximum efficiency and brightness of devices using water-soluble materials were dramatically improved than the device without the EIL (1.86 cd/A, 3374 cd/m^2) due to reduction of work-function of aluminum.

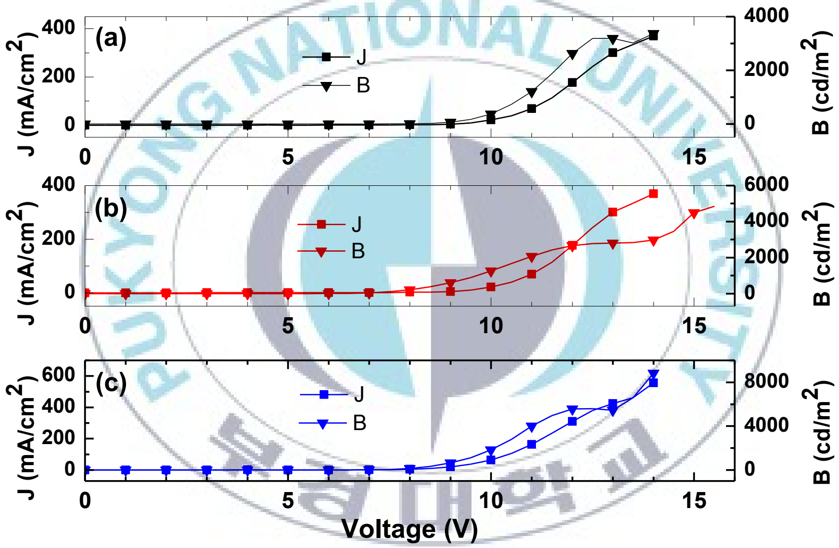


Figure III-8. *J*-V-L curves of PLEDs (a) without EIL, with the EIL using (b) PPT1F1, (c) 3-FPF (rectangle: current density, triangle: brightness).

Table III-3. Device performances of PLEDs.

	V_{on} (V)[a]	LE_{100} (cd/A)[b]	LE_{max} (cd/A)[c]	B_{max} (cd/m^2)
w/o EIL	7.5	1.51 @ 9.2 V	1.86 @ 10.5 V	3374 @ 14.5 V
with PPT1F1	5.6	2.05 @ 7.5 V	2.05 @ 7.5 V	4849 @ 15.5 V
with 3-FPF	5.5	2.87 @ 7.75 V	3.27 @ 8.5 V	8845 @ 8.5 V

[a] defined by the voltage was required to give a luminescent of 1cd/m^2.

[b] luminance efficiency at 100 cd/m^2.

[c] maximum luminescence efficiency.

III-4. Conclusion

We synthesized water-soluble polymer and oligomer based on phenothiazine and fluorene which have quaternary ammonium salt on the end of alkyl chain by well known palladium catalyzed the Suzuki reaction. From the UV-Vis spectrum, CV, water-soluble materials are suitable to use as the EIL/ETL by the solution process. Conventional type PSCs, inverted type PSCs and PLEDs based on water-soluble materials as the EIL/ETL were fabricated successfully. The PCE of device with water-soluble materials were dramatically improved than that of device without the ETL. The maximum efficiency and brightness of PLEDs with water-soluble materials as the EIL were much higher than those of device without the EIL, because the reduction of the work-function of Al could help electron inject or transport. And the contact resistance of between the active or emissive layer and the cathode should be reduced.

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감사의 글

항상 아껴주고 믿어주시는 사랑하는 엄마, 아빠
그리고 언니에게 감사의 마음을 전합니다.

대학원에 입학한 게 엊그제 같은데, 벌써 졸업을 한다는 생각을 하니 실감이 나지 않습니다. 항상 친절히 가르쳐주시고 늘 힘이 되어 주시는 김주현 교수님이 계셨기에 지금의 제가 있는 것 같습니다. 항상 딸이라 불러주시고, 교수님을 아빠라고 해주실 때, 그 한마디가 힘이 되고 그런 교수님을 만날 수 있었던 것을 큰 행운으로 생각합니다. 언제나 교수님의 가르침을 잊지 않고 교수님의 자랑스러운 제자가 되겠습니다. 또한 전공에 대한 많은 가르침을 주신 공업화학과 교수님들과 대학원을 잘 마치게끔 이끌어주신 고분자공학과의 민성기 교수님, 박찬영 교수님, 박상보 교수님, 이봉 교수님, 이원기 교수님, 유성일 교수님께도 감사의 마음을 전합니다.

그리고 우리 유기광전자재료연구실 식구들..!! 먼저, 우리 웅 선배. 지금은 선배랑 떨어져 있지만 늘 곁에 있는 것처럼 챙겨주시고 언제나 저보다 더 절 걱정해주시고 항상 고맙고 감사하게 생각해요. 공부 잘 끝내고 돌아와요 기다리고 있을께요. 그리고 혜리 언니. 같이 있었던 시간은 길지 않았지만 언니 덕분에 실험실 잘 적응 할 수 있었던 것 같아요. 상준 선배~ 선배의 권유로 실험실에 들어오게 되었는데 늘 고맙게 생각해요. 선배랑 있으면서 우리 정말 많이 싸웠었는데, 제가 그만큼 선배 좋아하는 거 아시죠?? 그리고 어디 가서도 살아 남을 수 있는 정배 선배~ 학교에도 자주자주 놀러 오세요. 졸업하고 나니깐 선배가 제일 보기 힘들어요. 또 저 멀리 네덜란드에서도 제 걱정하느라 잠도 못 주무신다는 선영 언니. 언니 한번 놀러 갈께요. 그리고 못된 성격 가진 날 만나서 고생 많이 한 준휘 선배. 선배가 있어서 다행이예요 늘 미안하고 고마워요. 멀리 창원에서도 실험실에 무슨 일 있으면 늘 바로 달려오는

대성선배~ 누가 못되게 굴면 다 데리고 와요 내가 혼내 주께!! 그리고 쿨 한 성격이 매력적인 trang 언니. 요즘은 좀 의사소통 되는 순욱이, 예은이. 예은아 네가 고생이 많다. 언니랑 한 올해 미션 알지? 우리 실험실 킬러들 종현이, 경은이. 너희는 동기니깐 그만 싸우고 서로 잘 챙겨줘. 선배들이랑 너희가 있어서 내가 지금 여기 있을 수 있는 것 같아. 언제나 고맙고 감사하게 생각해. 우리 대학원 동기들을 비롯하여, 바쁘다는 핑계로 자주 보지 못한 친구들 이제 자주자주 연락하고 지내자.

언제나 저를 응원해 주시고 아껴주시고 걱정해 주시는 모든 분들께 감사의 말을 전합니다.

2012 년 2 월

조 미 영 올림