Thesis for the Degree of Master of Engineering

Interface Materials and Their Applications of the Organic Opto-Electronic Devices

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(유기 광전자 소자에 사용되는 층간 소재의 합성 및 적용)

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요 약

본 연구는 소자의 성능을 향상 시키기 위한 정공 및 전자 주입/전달 소재의 합성 및 합성한 소재들의 적용에 대한 연구논문이다. Triphenlyamine (TPA)는 뛰어난 전자 제공물질로 알려져 있으며, 정공 주입/전달 층으로 많이 연구 된다. 또한 열경화가 가능한 물질은 열경화시 뛰어난 용제 저항성과 전기 화학적 안정성을 가지고 있기 때문에 정공 주입/전달 물질로 적합하다. 용재 저항성을 부여하기 위해 TPA 에 열경화가 가능한 vinyl 기를 포함시킨 oligomer 형태의 물질을 합성했다. 열적 거동을 알아보기 위하여 시차 주사 열량측정법 (differential scanning calorimetry, DSC)으로 분석하였으며, 열경화 온도를 180 °C 로 정하였다. UV-Vis spectroscopy 및 순환 전압 전류법 (cyclic voltammetry, CV) 를 이용하여 우수한 내용매성을 가지는 것을 확인하였으며, 호모(highest occupied molecular orbital (HOMO)) 에너지 준위가 -5.09 eV 이며 정공 주입소재로 적합함을 확인했다. 합성한 TPA oligomer 를 유기 발광 소자의 정공 수송/주입층으로 사용하였을 때, 사용하지 않은 소자보다 발광효율 및 소자의 성능이 향상됨을 확인했다.

또한 알킬기 말단에 quaternary ammonium salt 를 가진 water/alcohol soluble π-conjugated polymer 를 전자 주입/전달 층으로 사용하면 금속 음전극의 일함수가 작아져 유기 광전자 소자의 효율을 향상시킨다는 연구결과가 있다. 하지만 polymer 는 합성의 재현성 및 제조 공정이 복잡하다는 단점이 있다. 따라서 polymer 보다 합성 재현성이 높고 제조공정이 쉬운 oligomer 형태의 water/alcohol soluble π-conjugated

물질을 합성했다. 합성한 oligomer 는 물 또는 알코올에 잘 용해 되며, 유기용매에 대한 내용매성을 가진다. 자외선 광전자 분광법 (ultraviolet photoelectron spectroscopy, UPS)으로 water/alcohol soluble π-conjugated oligomer 가 금속전극의 일함수를 감소 시키는 것을 확인했다.

물과 알코올에 잘 용해되는 polyvionogen 을 유기 태양전지 소자의 전자 주입/전달 층으로 적용했다. Polyviologen 의 counter anion (CA) (bromide (Br^-), tosylate (OTs^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), tetraphenlyborate (BPh_4^-))의 종류에 따른 유기 태양전지 소자의 성능변화를 확인하였다. Polyviologen 유도체들을 X 선 광전자 분광법(X-ray Photoelectron Spectroscopy, XPS)으로 분석한 결과 CA 의 교환을 확인 하였다. UPS 으로 금속전극(Al)의 일함수의 감소를 확인했다. Polyviologen 의 CA 에 따라 소자의 성능이 변화되는 것을 확인했다. BPh_4^-를 가진 polyviologen 이 전자 수송/전달 층으로 사용된 유기 태양전지 소자의 contact property 가 가장 좋은 것을 확인했고, photo conversion efficiency (PCE)가 가장 좋은 것을 확인했다.

Chapter I. Introduction

I-1. Introduction to the organic opto-electronic device

Recently, the opto-electronic devices have attracted attention as advanced technology. The opto-electronic devices are made of organic materials with the optical and electronic transporting properties. Such materials produce light or generate electricity. The opto-electronic device with materials that produce light is a light emitting diode (LED) and the opto-electronic device with materials that generate electricity is solar cells. The opto-electronic devices with the inorganic materials are in general use. Because, the optical and electrical efficiency of the optoelectronic devices with organic materials is lower than that with inorganic materials. But the opto-electronic devices with the organic materials have been studies. The organic opto-electronic devices have flexibility and make the process easier. And the organic materials are cheaper than the inorganic materials [1,2].

In general, the opto-electronic organic materials consist of π-conjugated system. Examples of π-conjugated material are polythiophene (PT) and its derivatives like poly(3-hexylthiophene) (P3HT)[3-5], derivatives of poly(phenylenevinylene)[6-8], pentacene[9], derivatives of polyfluorene[10-13], fullerenes and their derivates like PCBM[14-17] and C_{70} [18,19].

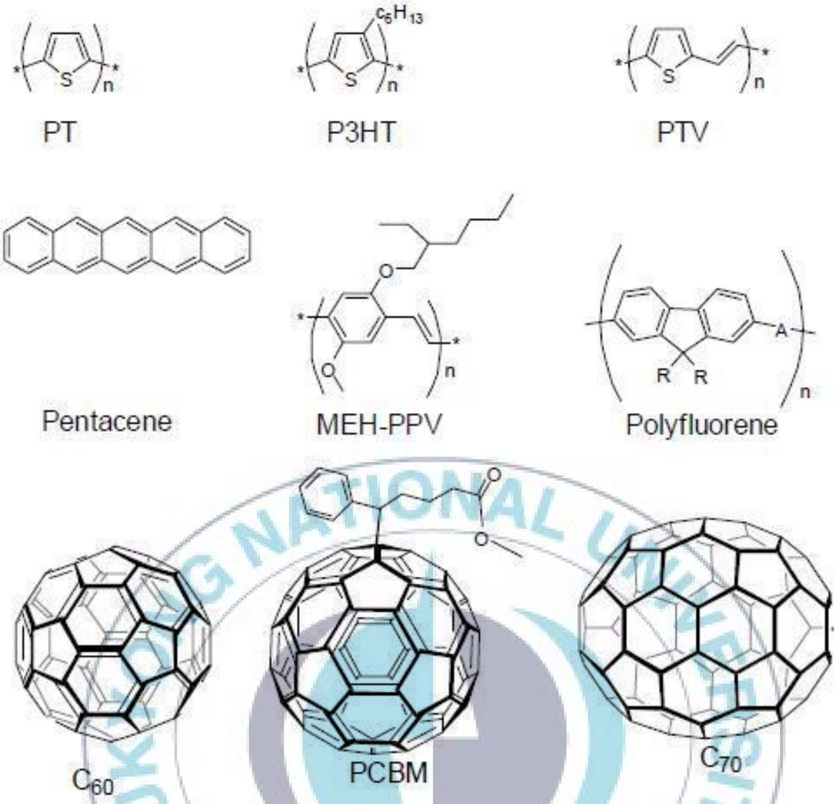


Figure I-1. Examples of π-conjugated materials.

I-2. The architectures and the operating principle of organic opto-electronic device

The opto-electronic device with organic device consists of single or multiple layers of organic films, sandwiched between a glass substrate coated with indium-tin oxide (ITO), and low work function metal. Generally, the active layer consists of a organic light-emitting / photovoltaic layer and charge transporting materials.

I-2-1. The operating principle of an organic light emitting diode (OLED)

In an OLED, when a driving voltage is applied both electrode, electrons are injected from the cathode into the lowest unoccupied molecular orbital (LUMO) of the organic light-emitting layer, while the anode injects holes into the highest occupied molecular orbital (HOMO) of the organic light-emitting layer. Electrons and holes that have been moved to the organic light-emitting layer recombine to form of an “exciton” capable of relaxing from its excited state to the ground state by emission of light [20].

I-2-2. The operating principle of an organic solar cell (OSC)

The working operation of the OSC is a reverse phenomenon of that of the OLED. In generally, when the light absorption, a donor generates the exciton. The exciton flows until it reaches the donor : acceptor interface. Subsequently, the exciton separates electrons and holes in interface of the donor : acceptor. Electrons transport to the anode, while holes transport to the cathode. The electricity is generated the combination of electrons and holes from the electrode [21,22].

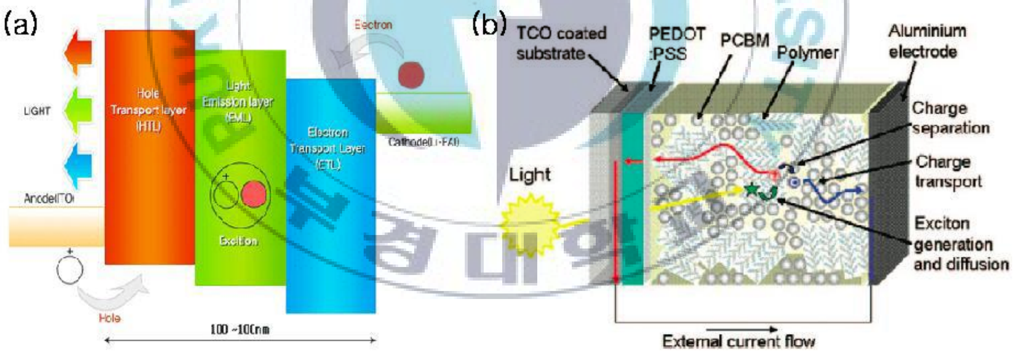


Figure I-2. Principle of OLED and OSC.

I-3. Buffer layer

The organic opto-electronic devices are constructed by sandwiching single layer or multi-layer. The characteristic of the interface between the organic layer and the electrodes are important factor for the efficiency of the organic opto-electronic devices. The understanding of the interface between the organic layer and the electrodes should lead to improved efficiency of organic opto-electronic devices [23].

The electrode buffer layers are divided by anode buffer layer (ABL) and cathode buffer layer (CBL). The holes flow to the anode electrode or the organic light-emitting layer via the ABL, while the electrons flow to the cathode or the organic light-emitting layer electrode via the CBL.

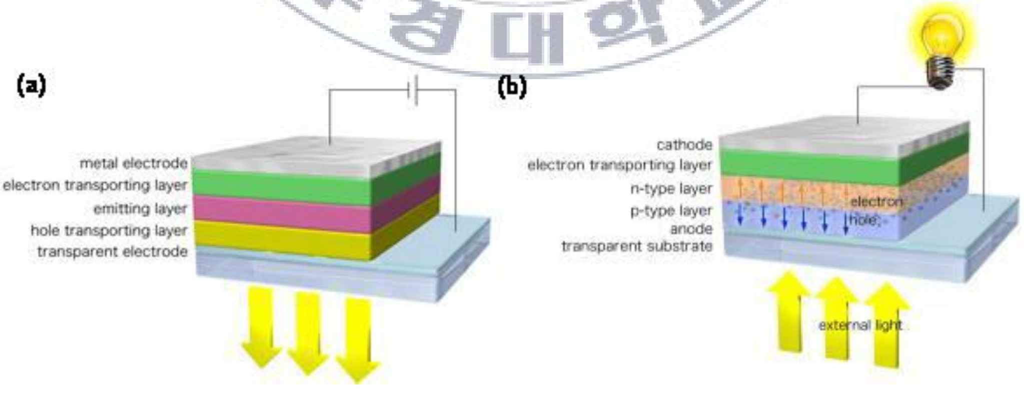


Figure I-3. Structure of (a) OLED and (b) OSC.

I-3-1. Anode buffer layer (ABL)

The role of an ABL is the enhancement of the anode electrode efficiency in collecting and withdrawing holes. The anode layer (ITO) is able to collect and withdraw both holes and electrons. So, the following characteristics are required in ABL.

1. it has to provide an ohmic contact with the donor material;
2. it has to transport holes efficiently;
3. it has to select holes, thus it has to block electrons
4. it has to stability and transparency [24]

I-3-1-1. Poly(3,4-ethylenedioxithiophene):poly(styrene sulfonic acid)

Scientists at the Bayer AG announced poly (3, 4 - ethylenedioxythiophene) (PEDOT). Conductivity of PEDOT was very high. At first, PEDOT was found to be an insoluble polymer. The solubility problem was subsequently circumvented by using a water-soluble polyelectrolyte, poly (styrene sulfonic acid) (PSS) in 1988 [25]. This is synthetic yields a water-soluble polyelectrolyte with a good film properties, hole mobility, high transparency. But, there have several disadvantages as ABL. PEDOT:PSS is high acidity and degrade ITO layer [26]. Furthermore, that has poor hole transporting ability for most of the blue- and green-emitting material. To solve this problem, it needs to study for new materials [27]

I-3-1-2. Cross-linkable materials

One of the alternatives is to develop cross-linkable materials for ABL. Cross-linkable materials have solvent resistance after cross-linking. Two cross-linkable material groups, one is thermally cross-linkable materials which are cross-linked as heat. And other is photo cross-linkable materials which are cross-liked as Ultraviolet radiation (UV)[27,28].

The thermal cross-linkable materials is initially announced by Scott et al. as hole injection polymer [29]. Also Alex K. Y. Jen et al. announce perfluorocyclobutane (PFCB) or vinyl as hole injection materials [30, 31]. And the photo cross-linkable materials are reported to Oskar Nuyken et al. by triarylamine derivatives with oxetane functionality [32, 33].

I-3-2. Cathode buffer layer (CBL)

The role of a CBL is the enhancement of the cathode electrode efficiency in collecting and withdrawing electrons. And it is essential in opto-electronic device to include a low work function as cathode such as Mg, Li, Ca, Al... But they are very sensitive to air. The following characteristics are required in CBL :

1. it has to provide an ohmic contact with the acceptor material;
2. it has to transport electrons efficiently;
3. it has to select electrons, thus it has to block holes
4. it has to control the work function of the cathode [23,24].

I-3-2-1. Lithium fluoride (LiF)

The LiF is the most famously used CBL in opto-electronic devices. And the LiF was initially used in the OLED [34-37]. The CBL of the LiF has been protected the active layer during the evaporation of the metal layer. Also, the LiF is controlling the work function of the metal cathode, because a LIF layer can be formed on a dipole [38].

But, the LiF is not an useful CBL in the opto-electronic device. Because the LiF layer must be very thin by the methods of the vacuum evaporation. The use of the vacuum evaporation is difficult to commercialize [39].

I-3-2-2. Water/alcohol soluble material

The water/alcohol soluble materials have been studied as the alternative materials to the LiF. These materials include the ionic side chains which provide good solubility in polar solvents and excellent electron-injecting abilities. The ionic side chains can form an interfacial dipole to improve electron injection from Al and to control the work function of the metal cathode. And High-efficiency blue-, green-, and white-emitting OLEDs could be achieved by using water/alcohol soluble materials [40].

I-3-2-3. Polyviologen (PV)

The viologen (4,4′-bipyridinium) is well known as an organic electrochromic polymers. The viologen of various salt forms has the stability of the environment and good the electron transporting ability. They are an interesting and unique class of organic redox-active material with a characteristic, high known oxidative/reductive negative potential [41].

Chapter II. Synthesis and characterization of thermally cross-linkable trimer based on triphenylamine

II-1. Introduction

Organic opto-electronic devices are affected by the characteristics of the ABL. Thus, the ABL should have the properties such as good hole mobility, organic solvent resistance, not affect other layers and thermal, chemical, mechanical stability.

PEDOT:PSS has been used for opto-electronic devices as ABL. Because PEDOT:PSS has a good film properties, hole mobility, high transparency. But PEDOT:PSS is high acidity and degrade ITO layer [26].

One of the alternatives is to develop cross-linkable materials for ABL. Cross-linkable material with triphenylamine (TPA) derivatives are well known very strong electron donor. And these materials showed good hole injection properties [44]. In addition, thermally cured polymer revealed very good solvent resistance and was electrochemically very stable [44, 45]. Also, thermal cross-linking temperature was up to 220 ^{o}C, which was pretty high. In order to overcome these disadvantages, we introduce vinyl group on TPA trimer.

II-2. Experimental

II-2-1. Materials and synthesis

II-2-1-1. Materials

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 were used as received unless otherwise described.

II-2-1-2. Synthesis

II-2-1-2-1. Synthesis of (4-butyl-phenyl)-diphenyl-amine (1)

A mixture of iodobenzene (41.8 mL, 375 mmol), 4-butyl-phenylamine (22.4 g, 150 mmol), copper powder (28.6 g, 450 mmol), potassium carbonate (62.19 g, 450 mmol) and 18-crown-6 (1.98 g, 7.49 mmol) in 1,2-ichlorobenzene (DCB) was stirred at 170 ^{o}C for 72 h under nitrogen (N_2) atmosphere. After the reaction mixture was cooled down to room temperature (RT), excess of K2CO$_3$ and Cu are removed by the filtration. A portion of 100 mL of water was added into the filtrate and then extracted three times of with a portion of 100 mL of MC. The combined organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) then the solvent was removed using a rotary evaporator. The crude liquid was purified by flash column chromatography on silica gel using *n*-hexane. The yield of the colorless liquid product was 24.15 g (53.4%). Anal. Calcd. For $C_{22}H_{23}N$: C, 87.66; H, 7.69; N, 4.65. Found: C, 87.73; H, 7.76; N, 4.51. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.16~7.12 (m, 4H), 7.04~6.69 (m, 8H) 6.92~6.88 (t, *J*=4.0 Hz, 2H), 2.55~2.51 (t, *J*=8.0 Hz, 2H), 1.61~1.53 (m, 2H), 1.39~1.30 (m, 2H), 0.93~0.89 (t, *J*=4.0 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 149.11, 146.16, 138.70, 130.26, 130.18, 130.04, 125.78, 124.76, 123.30, 36.14, 34.77, 23.52, 15.12.

II-2-1-2-2. Synthesis of bis-(4-bromo-phenyl)-(4-butyl-phenyl)-amine (2)

A portion of 16.18 g (90.93 mmol) of *N*-bromosuccinimide (NBS) was added dropwise to a solution of compound 1(10.96 g, 36.37 mmol) in 30 mL of *N*,*N'*-dimethylformamide (DMF) under the N_2 atmosphere at 5 ^oC. The reaction mixture was stirred at RT for 5 h. A portion of 100 mL of water was added into the reaction mixture then extracted three times with a portion of 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 on silica gel using *n*-hexane. The yield of the colorless liquid product was 15.65 g (93.7%). Anal. Calcd. For $C_{22}H_{21}Br_2N$: C, 57.54; H, 4.61; Br, 34.80; N, 3.05. Found: C, 57.18; H, 4.59; N, 3.08. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30~7.27 (dd, J_1=12 Hz, J_2=4.0 Hz, 4H), 7.07~7.05 (d, *J*=8 Hz, 2H), 6.96 ~6.88 (m, 6H), 2.57~2.54 (t, *J*=8.0 Hz, 2H), 1.62~1.54 (m, 2H), 1.40~1.31 (m, 2H), 0.94~0.91 (t, *J*=4.0 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.78, 145.47, 139.94, 133.31, 130.61, 126.10, 126.06, 116.07, 36.16, 34.71, 23.52, 15.11.

II-2-1-2-3. Synthesis of (4-butyl-phenyl)-bis-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]amine (3)

A mixture of compound 2 (2.02 g, 6.66 mmol), potassium acetate (2.56 g, 26.68 mmol), bis(pinacolato)diborane (3.55 g, 13.99 mmol) and Pd(dppf)Cl_2 (0.163 g, 0.20 mmol) in 20 mL of DMF was stirred at 60 ^{o}C for 24 h under the N_2 atmosphere at 60 ^{o}C. The reaction mixture was cooled down to RT and a portion of 100 mL of water added into the reaction mixture and then extracted three times with a portion of 50 mL of EA. The combined organic layer washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator. The crude product was purified by column chromatography on silica gel using *n*-hexane/EA. The yield of the white solid product was 1.54 g (42.9%). Anal. Calcd. For $C_{34}H_{45}B_2NO_4$: C, 73.80; H, 8.20; B, 3.91; N, 2.53; O, 11.57. Found: C, 73.76 H, 8.17; N, 2.64; O, 11.61. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.07~7.05 (d, *J* =8 Hz, 4H), 7.08~7.00 (m, 8H), 2.59~2.55 (t, *J*=8.0 Hz, 2H), 1.63~1.58 (m, 2H), 1.39~1.35 (m, 2H), 1.32 (s, 24H), 0.94~0.91 (t, *J*=4.0 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 172.02, 151.33, 145.55, 136.89, 130.40, 126.89, 126.45, 84.65, 36.18, 34.65, 25.92, 23.50, 15.05.

II-2-1-2-4. Synthesis of 4-[(4-bromo-phenyl)-(4-butyl-phenyl)-amino]-benzaldehyde (4)

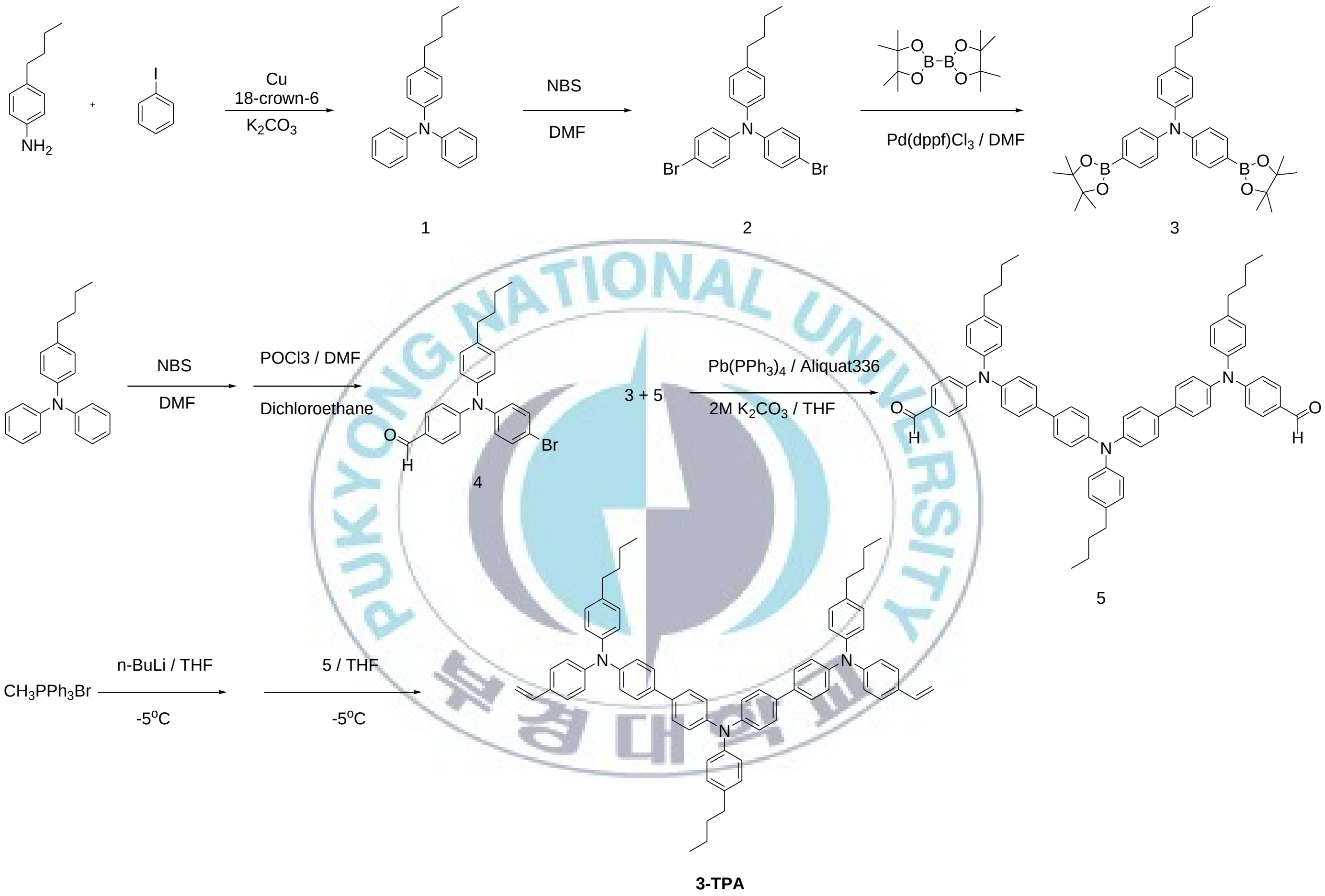
A portion of 2.36 g (13.28 mmol) of NBS was added dropwise to a solution of compound 1 (3.64 g, 12.07 mmol) in 10 mL of DMF under the N_2 atmosphere at 5 ^{o}C and stirred for 30 min. The reaction mixture was heated up to RT and stirred for additional 5 h. A portion of 100 mL of water was added into 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 using a rotary evaporator. The crude product will be mixture of dibrominated and monobrominated. This mixture was used for next reaction without purification. A portion of 0.70 mL (13.60 mmol) of DMF was added dropwise to phosphous oxy chloride (1.27 mL, 13.60 mmol). The reaction mixture was stirred for 30 min at 0 ^{o}C. This reaction mixture was added to a solution of unpurified mono- and di-brominated (4-butyl-phenyl)-diphenyl-amine (4.32 g) in 20 mL of dichloroethane. Then reaction mixture was stirred at 80 ^{o}C for 24 h. The reaction mixture was cooled down to RT and a portion of 100 mL of water added into the reaction mixture and then extracted three times with a portion of 100 mL of MC. The combined organic layer was washed with aqueous sodium carbonate (10 wt%) and then dried over anhydrous $MgSO_4$. And the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography on silica gel using MC/*n*-hexane. The yield of yellow liquid product was 4.40 g (89.4%). Anal. Calcd. For $C_{23}H_{22}BrNO$: C, 67.65; H, 5.43; Br, 19.57;. N, 3.43; O, 3.92. Found: C, 67.61; H, 5.47; N, 3.45 ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.78 (s, 1H), 7.73~7.70 (dd, J_1=12 Hz, J_2=4Hz, 2H), 7.55~7.52 (m, 2H), 7.24~7.22 (d, *J*=8 Hz, 2H), 7.10~7.07 (m, 5H), 6.91~6.89 (d, *J*=8 Hz, 2H), 2.59~2.55 (t, *J*=8.0 Hz, 2H), 1.59~1.52 (m, 2H), 1.36~1.27 (m, 2H), 0.92~0.88 (t, *J*=4.0 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.39, 145.06, 146.45, 144.28, 141.59, 133.73, 132.35, 130.87, 130.36, 128.30, 127.44, 120.45, 118.53, 36.17, 34.56, 23.44, 14.99.

II-2-1-2-5. Synthesis of (4-Butyl-phenyl)-bis-[4-((4-formyl-phenyl)-(4-butyl-phenyl)-phenyl-amine)-phenyl]-amine (5)

A mixture of compound 3 (0.58 g, 1.05 mmol), compound 4 (0.95 g 2.31 mmol), tetrakis(triphenyl-phosphine)palladium ($Pd(PPh_3)_4$) (0.036 mg, 0.032 mmol), and aliquat 336 in 10 mL of 1:1 (by volume) mixed solvent of degassed THF and 2.0 M K_2CO_3 was stirred under the N_2 atmosphere at 80 ^oC for 24 h. The reaction mixture was cooled down to RT and a portion of 100 mL of water added into the reaction mixture and then extracted three times with a portion of 100 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$ and then the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography on silica gel using *n*-hexane/EA. The yield of yellow solid product was 0.34 g (34.1%). Anal. Calcd. For $C_{68}H_{65}N_3O_2$: C, 85.41; H, 6.85; N, 4.39; O, 3.35. Found: C, 85.36; H, 6.92; N, 4.38; O, 3.34. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.80 (s, 2H), 7.70~7.67 (d, *J*=12 Hz, 6H), 7.54~7.52 (d, *J*=8 Hz, 6H), 7.26~7.04 (m, 24H), 2.63~2.59 (t, *J*=8 Hz, 6H), 1.66~1.58 (m, 6H), 1.43~1.33 (m, 6H), 0.97~0.93 (t, *J*=8 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.69, 154.64, 146.14, 144.74, 141.62, 138.27, 132.63, 131.17, 131.05, 130.10, 128.80, 128.25, 127.80, 127.39, 123.48, 120.35, 119.96, 110.02, 36.45, 34.87, 30.99, 23.83, 23.73, 23.70, 15.35, 15.30.

II-2-1-2-6. Synthesis of (4-butyl-phenyl)-bis-[4-((4-vinyl-phenyl)-(4-butyl-phenyl)-phenyl-amine)-phenyl]-amine (3-TPA)

A portion of 0.11 mL of *n*-BuLi (2.5 M in *n*-hexane, 0.27 mmol) was added dropwise into a slurry of methyl triphenylphosphonium bromide (0.11 g, 0.31 mmol) in 10 mL of THF under N_2 atmosphere at -20 ^{o}C and then the reaction mixture was stirred for 30 min. A solution of compound 5 (0.10 g 0.10 mmol) in 10 mL of THF was added into the reaction mixture at -20 ^{o}C. Then the reaction mixture was stirred at 40 ^{o}C for additional 24 h. The reaction mixture was cooled down to RT and then a portion of 100 mL of water added into the reaction mixture. This reaction mixture was extracted three times with a portion of 100 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$ then the solvent was removed using a rotary evaporator. The crude product was purified by flash column chromatography using EA/*n*-hexane. The yield of yellowish green solid product was 0.053 g (52.8%). Anal. Calcd. For $C_{70}H_{69}N_3$: C, 88.28; H, 7.30; N, 4.41. Found: C, 88.27; H, 7.31; N, 4.39. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.62~7.03 (m, 30H), 6.69~6.62 (dd, J_1=28 Hz, J_2=8 Hz, 2H), 5.65~5.61 (d, *J*=16 Hz, 2H), 5.65~5.61 (d, *J*=12 Hz, 2H), 2.60~2.56 (t, *J*=8.0 Hz, 4H) 1.64~1.57 (m, 4H) 1.40~1.26 (m, 17H), 0.96~0.90 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.53, 146.62, 144.95, 138.16, 136.26, 134.60, 129.37, 129.86, 129.26, 127.22, 127.09, 127.01, 125.17, 124.94, 124.86, 123.88, 123.65, 123.29, 111.95, 35.08, 33.67, 31.93, 29.70, 29.37, 22.69, 22.65, 22.44, 14.13, 13.99.



Scheme II-1. Synthesis of thermally linkable **3-TPA**.

II-2-2. Device fabrication

ITO-coated glass substrates were cleaned with deionized water, acetone, methanol, 2-propanol in the ultrasonic bath. A solution of compound **3-TPA** (10 mg/mL in chlorobenzene) layer was spin-coated as a CBL onto the ITO. Before spin coating, compound **3-TPA** solution was filtered through 0.20 μm PTFE syringe filter. After spin coating, the thin film was heated up to 180 ^{o}C for 2 h. The green emitting emissive polymer (PF9B) were dissolved in toluene and filtered through 0.20 μm PTFE syringe filter before spin coating. The typical thickness of emissive layer was 60 nm. Al was evaporated as cathode onto the surface of the emissive polymer film by thermal evaporation technique at 2.0×10^{-6} torr. The typical active area of the devices was 13 mm^2.

II-2-3. Measurements

Synthesized compounds were characterized by ^{1}H NMR and ^{13}C NMR spectra, which were obtained with a JEOL JNM ECP-400 spectrometer. The elemental and MASS analysis of synthesized compounds was carried out on a Elementar Vario macro/micro elemental analyzer and Shimadzu GC-MS QP-5050A spectrometer. Differential scanning calorimetry (DSC) was measured by a Mettler Toledo (DSC 1, STARe system) under nitrogen atmosphere at a scan rate of 10

^{o}C/min. UV-visible spectrum of the oligomers were recorded using a JASCO V-530 UV/vis spectrophotometer. Cyclic voltammetry was performed by a CompactStat-Plus (Ivium technology) Scanning Potentiostat with a three electrode cell in a solution of Bu_4NPF_6 (0.1 M) in freshly distilled MC at a scan rate of 100 mV/s. Pt coil and ITO coated glass were used as the counter and working electrode, respectively. A Ag/Ag+ electrode was used as the reference electrode. Prior to each measurement, the cell was deoxygenated with nitrogen. The current density-voltagebrightness (*J-V-B*) characteristics were measured using a source meter (KEITHLEY 2400) and a luminometer (Minolta LS110).

II-3. Results and discussion

II-3-1. Thermal analysis of 3-TPA

To investigate thermal behavior and find out thermal cross-linking temperature of **3-TPA**, we performed differential scanning calorimetry (DSC). Figure II-1 shows the DSC thermogram of **3-TPA**, which exhibits two endothermic processes in the first heating scan. The endothermic process at 122 ^{o}C corresponds to melting behavior of **3-TPA** and the other at 218 ^{o}C seems to be thermal cross-linking behavior. In the second scan, thermogram does not show any peak, which means **3-TPA** is perfectly thermally cross-linked at the first heating scan. From the DSC thermogram, we confirm that thermal cross-linking occurs at abroad temperature range between 180~250 ^{o}C.

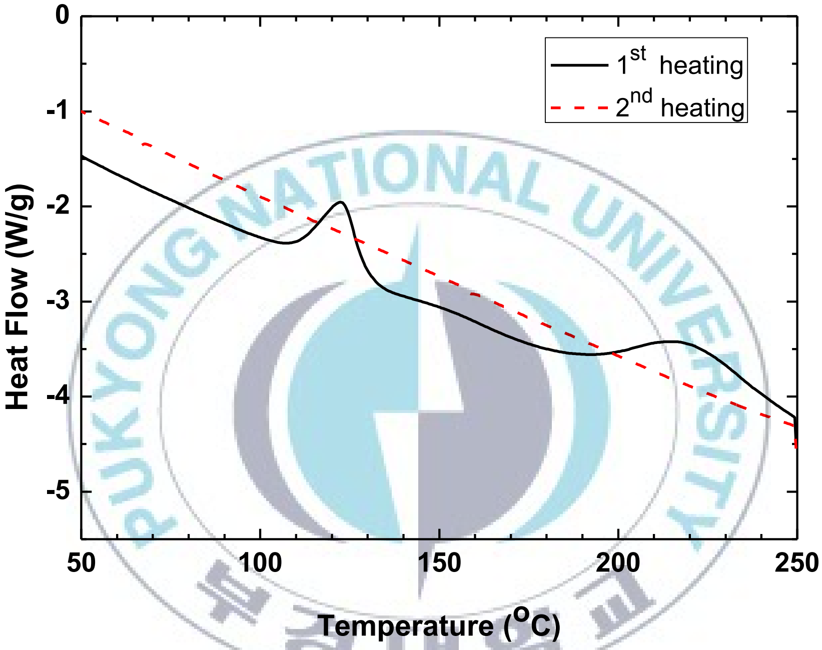


Figure II-1. DSC thermogram of **3-TPA**.

II-3-2. Optical properties of 3-TPA

The chemical structure of before and after cured of **3-TPA** was confirmed by the FTIR spectra. Thin film for FT-IR measurements was prepared by the drop casting of **3-TPA** solution in chloroform (10 mg/mL) onto the silicon wafer. Thermal cross-linking was performed at 180 ^{o}C for 1 h. Figure II-2-(a) shows FTIR spectrum of **3-TPA** film and thermally cured **3-TPA** film. To compare the peak intensities, the FTIR spectra are normalized with the absorbance at 2925 cm^{-1}, which corresponds to C(sp^3)-H stretching vibration of *n*-butyl substituent. The absorption peaks at 989 and 899 cm^{-1} of **3-TPA** film correspond to out-of-plane bending motion of vinyl group (C=C). The absorption peaks at 989 and 899 cm^{-1} in the cured **3-TPA** film are almost disappeared, indicating that thermal curing occurs at 180 ^{o}C. As shown in Figure II-2-(b), the absorbance of thermally cured and washed thermally cured **3-TPA** are almost same, indicating that thermally cured film is very good solvent resistance. The absorbance of cured **3-TPA** is lower than that of uncured **3-TPA** film. This is presumably due to that the packing density of the molecules in cured **3-TPA** is bigger than that of pristine film.

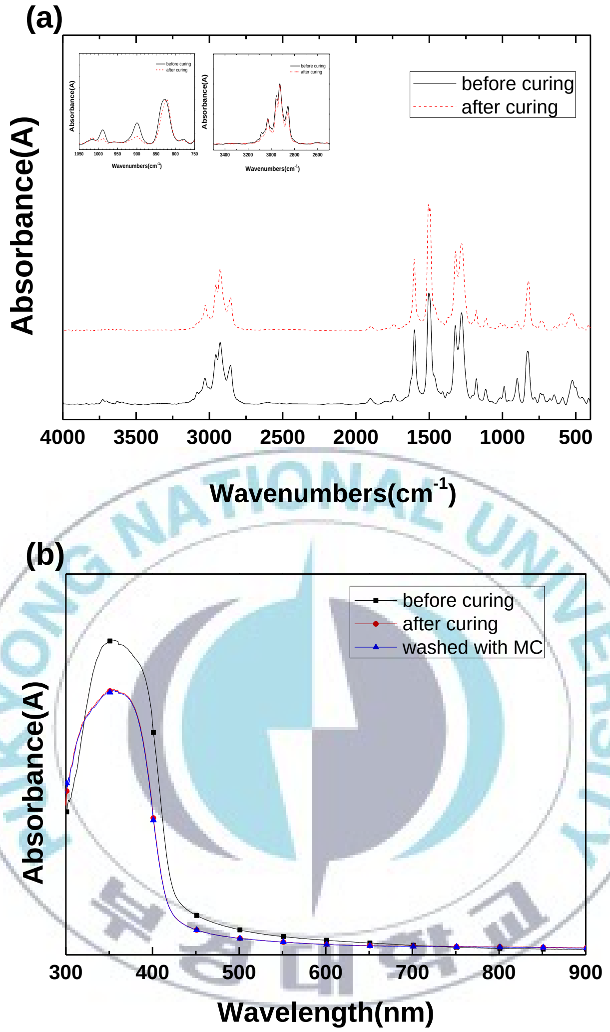


Figure II-2. (a) FTIR spectra of **3-TPA** film and thermally cured **3-TPA**film and (b) UV-Vis spectra of **3-TPA**, thermally cured **3-TPA**, and thermally cured **3-TPA** film after wash with methylene chloride.

II-3-3. Electrochemical properties of 3-TPA

Cyclic voltammetry (CV) is used to investigate the redox behavior of organic electronic materials and to access the energy levels. The CV measurements were conducted in 0.1 M Bu_4NPF_6 in freshly distilled in MC at a scan rate of 100 mV/s. Figure II-3 shows cyclic voltammograms of thermally cured **3-TPA** on ITO-coated glass. Thermally cured **3-TPA** film on ITO shows two reversible redox processes. Cured **3-TPA** shows oxidation peaks at 0.48 and 0.69 V *vs*. Fc/Fc^+. The change significantly upon repeated redox scans in 0.1 M Bu_4NPF_6 in MC. This indicates that cured **3-TPA** exhibits good electrochemical stability and solvent resistance. The highest occupied molecular orbital (HOMO) energy levels were estimated from the oxidation onset potential by the energy level of ferrocene is -4.8 eV. The HOMO energy level of cured **3-TPA** is -5.09 eV, which is very similar to that of PEDOT:PSS. The lowest unoccupied molecular orbital (LUMO) energy level of **3-TPA** estimated from the HOMO level and optical band gap is -2.10 eV. From the energy level data, cured **3-TPA** film would be good hole transportring and electron blocking layer.

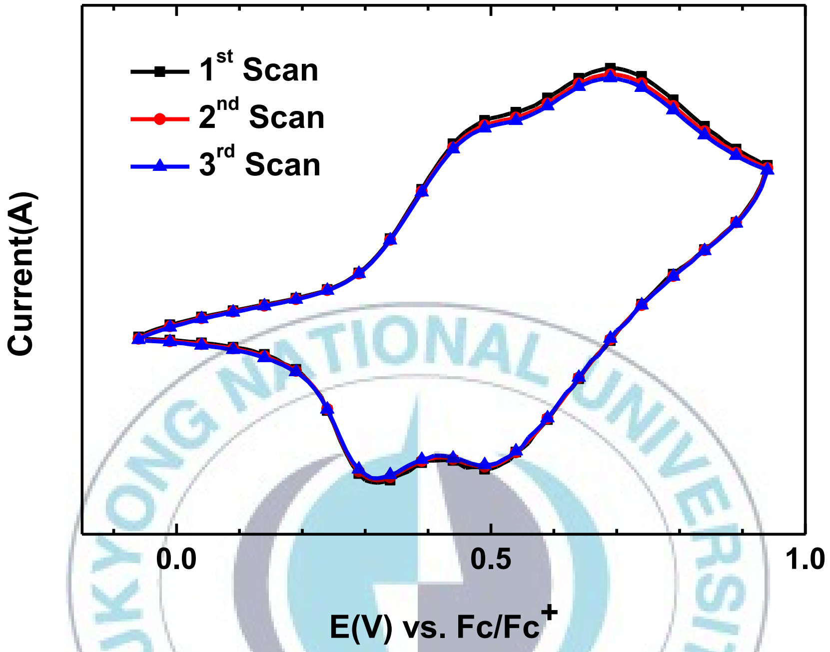


Figure II-3. Cyclic voltammograms of the thermally cured **3-TPA**.

Table II-1. Electrochemical properties of **3-TPA**.

	HOMO (eV)	**LUMO (eV)** [a]	**E_{gap} (eV)** [b]
3-TPA	-5.09	-2.13	2.96

[a] : Estimated from the HOMO energy level and band gap energy

[b] : Optical band gap

II-3-4. Hole transporting properties of 3-TPA

In order to investigate performances of cured **3-TPA** as a hole injection/transporting layer, PLEDs with a structure of ITO/cured **3-TPA**/PF9B/Al are fabricated. Also, we fabricate the device without **3-TPA** to compare characteristics of cured **3-TPA**. Figure show current density (*J*) and brightness (*B*) as a function of applied voltage (V) of devices. The PLED performance data are summarized in Table II-2 . The turn on voltage (defined by the voltage was required to give a luminescent of 1 cd/m^2) of device without cured **3-TPA** is 15.5 V, which is bigger than those of the devices with cured **3-TPA** as a buffer layer. The turn on voltage of PLED with **3-TPA** coated by 3000 rpm is 12.5 V, which is smaller than those of the devices with **3-TPA** coated by 4000, 5000 rpm (12 V for **3-TPA** coated by 4000 rpm and 13 V for **3-TPA** coated by 5000 rpm). This indicates that cured **3-TPA** has hole injection properties. The luminance efficiency and maximum brightness of the device with cured **3-TPA** film exhibit much higher than that of the device without **3-TPA** (Figure II-4), indicating that 3-TPA film has hole transporting property as well. As shown in Figure II-4 and Table II-2 , the device with **3-TPA** coated by 4000 rpm shows best performances with a maximum efficiency of 1.29 cd/A and a maximum brightness of 2,500 cd/m^2

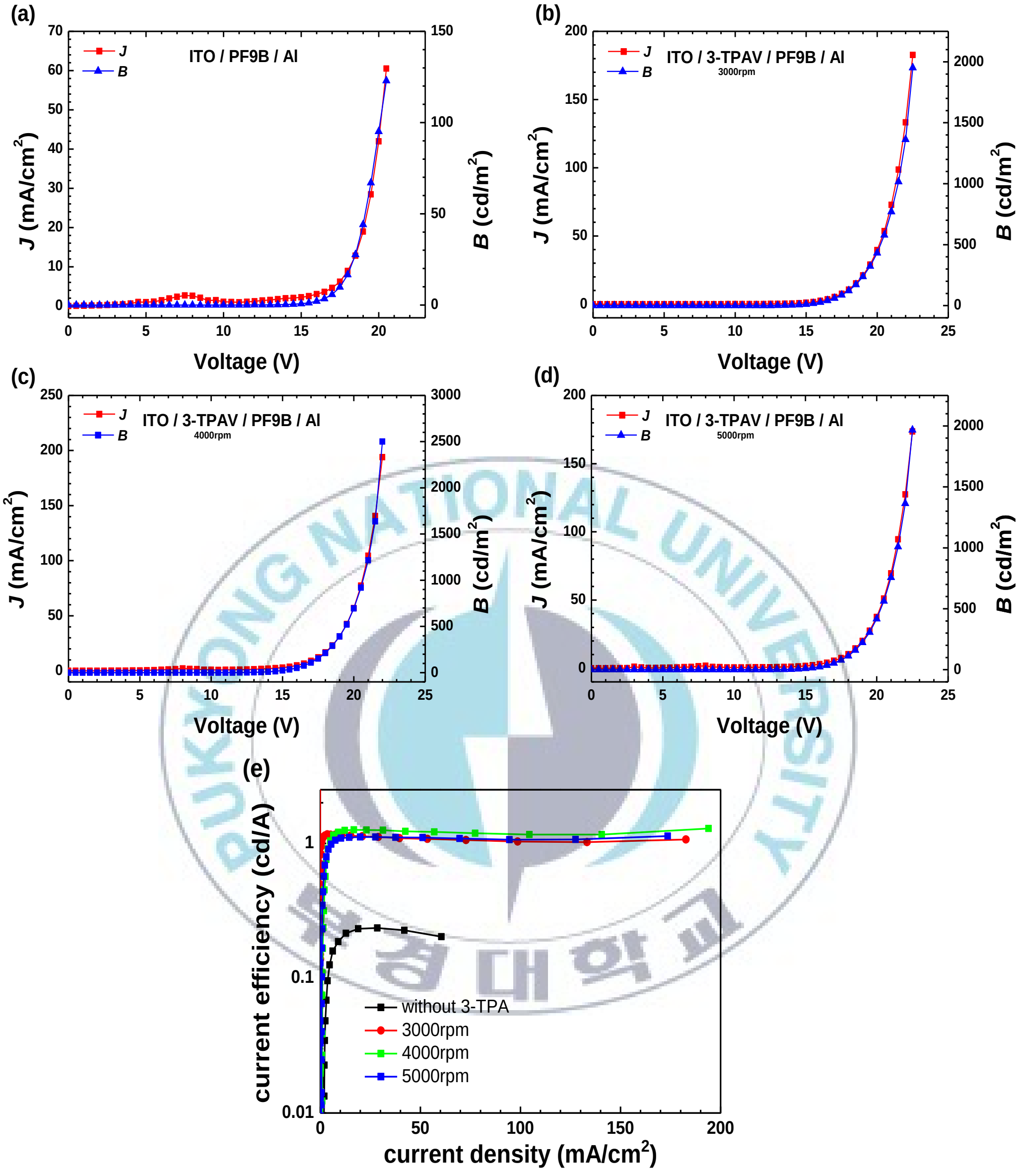


Figure II-4. *J*-V-L curves of PLEDs with/without **3-TPA** (a) without **3-TPA,** (b) coated by 3000 rpm, (c) coated by 4000 rpm, (d) coated by 5000 rpm (e) luminance efficiency *vs.* current density curves of the devices.

Table II-2. Device performances of PLEDs based on thermally cross-linked **3-TPA**.

	V_{on}[a] (V)	PE_{max} (cd/A)	PE_{100}[b] (cd/A)	B_{max} (cd/m^2)
Without ABL	15.5	0.24 @ 28.4 mA/cm^2	0.203	496
With 3-TPA (3000rpm)	12.5	1.07 @ 183 mA/cm^2	1.15	1979
With 3-TPA (4000rpm)	12.0	1.29 @ 194 mA/cm^2	1.20	2500
With 3-TPA (5000rpm)	13	1.13 @ 174 mA/cm^2	1.09	1966

[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 π-conjugated trimer (3-TPA) based on 4-butyl-triphenylamine with vinyl group as thermally crosslinkable unit. Thermally cured 3-TPA film is safe to coat the successive layer by the solution process. In addition, cured 3-TPA is electrochemically very stable. The luminance efficiency and maximum brightness of PLED with cured 3-TPA as a buffer layer exhibited higher values than those of the device without 3-TPA. Among devices, PLED with 3-TPA coated by 4000 rpm showed best performances. From the results, cured 3-TPA film is potential materials for hole injection and transporting layer.

Chapter III. π-Conjugated oligomers as cathode buffer Layer

III -1. Introduction

In recent years, the water-soluble materials have been studied as cathode buffer layer (CBL) in multi-layer structured opto-electronic devices, because their polar groups can modify the work function of cathode through favorable interface dipoles. Besides, it was presented that the water-soluble materials with electron-rich unit have good electron transporting ability as CBL compared to these with electron-deficient unit. And oligomer is better synthetic reproducibility and solubility than those of polymer. Therefore, the water-soluble oligomers with good solubility and electron-rich unit based on carbazole, phenothiazine and fluorene derivatives were synthesized, characterized and used to fabricate OSCs as CBL.

III-2. Experimental

III-2-1. Materials and synthesis

III-2-1-1. Materials

Tetrahydrofuran (THF) was distilled over sodium/benzophenone. 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-2-1-2. Synthesis

III-2-1-2-1. Synthesis of (6-bromo-hexyl)-9*H*-carbazole (1)

A solution of aqueous potassium hydroxide (KOH, 20 mL, 35 wt.%) was added to a portion of 9*H*-carbazole (1.02 g, 6.10 mmol) in 1,6-dibromo-hexane (8.75 g, 36.6 mmol). Then reaction mixture was stirred for 48 hours at 80 ^{o}C. The water was added and the mixture was allowed to cool to room temperature (R.T.), and that was washed with aqueous hydrochloric acid (HCl, 35 wt.%). The washed mixture was extracted with 50 mL of dichloromethane (MC) and the combined organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$). The solvent was removed by using a rotary evaporator. After, distilling the 1,6-dibromo-hexane in the mixture, the crude product was purified by column chromatography on silica gel using MC/n-hexane (Hex). The yield of the white solid was 1.53 g

(76.0%). MS: [M$^+$], *m/z* 329. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.13~8.11 (d, J = 8.00 Hz, 2H), 7.49~7.45 (m, 2H), 7.41~7.39 (d, J = 8.00 Hz, 2H), 7.26~7.22 (m, 2H), 4.31~4.29 (t, J = 4.00 Hz, 2H), 3.37~3.33 (t, J = 8.00 Hz, 2H), 1.92~1.77 (m, 4H), 1.52~1.34 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 140.33, 125.57, 120.32, 118.73, 108.55, 42.78, 33.68, 32.51, 28.76, 27.87, 26.40. Anal. Calcd. for. $C_{18}H_{20}BrN$: C, 65.46; H, 6.10; Br, 24.19; N, 4.24. Found: C, 65.38; H, 6.38; Br, 24.11; N, 4.13

III-2-1-2-2. Synthesis of 3,6-dibromo-9-(6-bromo-hexyl)-9*H*-carbazole (2)

A portion of *N*-bromosuccinimide (NBS, 1.18 g, 6.64 mmol) in 10 mL of N,N-dimethylformamide (DMF) was added dropwise to a solution of compound 1 (1.00 g, 3.02 mmol) in 20 mL of DMF under nitrogen atmosphere (N_2) at 5 ^{o}C then stirred for 30 min. The reaction mixture was stirred for 3 hours at R.T. The reaction mixture was washed with aqueous sodium bicarbonatand then extracted with ethyl acetate (EA). The extracted organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography on silica gel using MC/Hex. The yield of the white solid was 1.07 g (73.1%). MS: [M$^+$] *m/z* 487. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.13~8.11 (d, J = 8.00 Hz, 2H), 7.51~7.49(dd, J_1 = 8.00 Hz, J_2 = 1.60 Hz, 2H), 7.19~7.17 (d, J = 8.00 Hz, 2H), 4.16~4.13 (t, J = 4.00 Hz, 2H), 3.33~3.31 (t, *J* = 4.00 Hz, 2H), 1.82~1.73 (m, 4H), 1.46~1.25 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 139.09, 128.93, 123.30, 123.14, 110.90, 110.21, 42.97, 33.60, 32.40, 28.60, 27.73, 26.27. Anal. Calcd. for $C_{18}H_{18}Br_3N$: C, 44.30; H, 3.72; Br, 49.12; N, 2.87. Found: C, 41.98; H, 3.99; N, 2.68

III-2-1-2-3. Synthesis of 9-(6-bromo-hexyl)-3,6-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9*H*-carbazole (3)

A mixture of compound 2 (1.50 g, 3.07 mmol), potassium acetate (KOAc, 1.77 g, 7.68 mmol), bis(pinacolato)diborane (1.95 g, 7.68 mmol) and Pd(dppf)Cl_2 (100 mg, 0.122 mmol) were mixed together in flask. After degassing, the mixture was stirred in 20 mL of DMF under N_2 at 70 ℃ for 24 hours. The water was added and the mixture was allowed to cool to R.T. The cooled mixture was extracted with EA. The extracted organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography on silica gel using Hex/EA. The yield of the white solid was 1.35 g (75.5%). MS: [M^+], *m/z* 584. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ, 8.63 (s, 2H), 7.88~7.85 (d, *J* = 12.0 Hz, 2H), 734~7.32 (d, *J* = 8.00 Hz, 2H), 4.27~4.24 (t, *J* = 8.00 Hz, 2H) 3.96~3.93 (t, *J* = 4.00 Hz, 2H), 1.96 (s, 4H), 1.22 (s, 24H), 0.900~0.840 (m, 4H) ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 139.09, 128.93, 123.30, 123.14, 110.91, 110.21, 42.97, 33.60, 32.40, 28.60, 27.73, 26.27.

Anal. Calcd. for $C_{18}H_{18}Br_3N$: C, 44.30; H, 3.72; Br, 49.12; N, 2.87. Found: C, 44.01; H, 3.67; N, 2.95

III-2-1-2-4. Synthesis of 3,6-dibromo-9-hexyl-9*H*-carbazole (4)

A portion of NBS (1.95 g, 11.0 mmol) in 10 mL of DMF was added dropwise to a solution of 9-hexyl-9*H*-carbazole (1.25 g, 5.00 mmol) in 20 mL of DMF under N_2 at 5 ^{o}C then stirred for 30 min. The reaction mixture was stirred for 3 hours at R.T. The reaction mixture was washed with aqueous sodium bicarbonate then extracted with EA then extracted organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography on silica gel using MC/Hex. The yield of the white solid was 1.53 g (74.8%). MS: [M^+], *m/z* 409.00. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.14~8.13 (d, J = 8.00 Hz, 2H), 7.56~7.53 (dd, J_1 = 8.00 Hz, J_2 = 4.00 Hz, 2H), 7.27~7.25 (d, J = 8.00 Hz, 2H), 4.25~4.21 (t, J = 8.00 Hz, 2H), 1.85~1.78 (m, 2H), 1.32~1.25 (m, 6H), 0.87~0.83 (t, J = 8.00 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 130.09, 124.34, 120.00, 113.01, 111.47, 101.92, 44.44, 32.57, 29.90, 27.96, 23.57, 15.05. Anal. Calcd. for. $C_{18}H_{19}Br_2N$: C, 52.84; H, 4.68; Br, 39.06; N, 3.42. Found: C, 52.61; H, 4.86; N, 3.28

III-2-1-2-5. Synthesis of 9-hexyl-3,6-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9*H*-carbazole (5)

A mixture of compound 4 (1.45 g, 3.57 mmol), potassium acetate (KOAc, 2.06 g, 21.4 mmol), bis(pinacolato)diborane (1.99 g, 7.86 mmol) and Pd(dppf)Cl_2 (174 mg, 0.216 mmol) were mixed together in flask. After degassing, the mixture was stirred in 30 mL of DMF under N_2 at 70 ℃ for 24 hours. The water was added and the mixture was allowed to cool to R.T. The cooled mixture was extracted with EA. The extracted organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography on silica gel using Hex/EA. The yield of yellow solid was 0.975 g (54.3%). MS: [M^+], *m/z* 503.00 ^oC ^1H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.68 (s, 2H), 7.92-7.90 (d, J = 8.00 Hz, 2H), 7.39-7.37 (d, J = 8.00 Hz, 2H), 4.30-4.26 (t, J = 8.00 Hz, 2H), 1.89-1.80 (m, 2H), 1.39 (s, 24H), 1.28-1.23 (m, 6H), 0.860-0.820 (t, J = 8.00 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 142.61, 131.31, 127.99, 122.76, 108.08, 83.46, 43.05, 31.51, 28.83, 26.82, 24.29, 22.45, 13.95. Anal. Calcd. for. $C_{30}H_{43}B_2NO_4$: C, 71.59; H, 8.61; B, 4.30; N, 2.78; O, 12.72. Found. C, 71.36; H, 8.77; N, 2.91; O, 12.48.

III-2-1-2-6. Synthesis of 10-hexyl-3,7-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-10*H*-phenothiazine (6)

A portion of 4.78 mL (11.0 mmol) of n-butyl lithium (2.30 M in hexane) was added dropwise to a solution of 3,7-dibromo-10-hexyl-10*H*-phenothiazine (2.20 g, 5.00 mmol) in 50 mL of THF under N_2 at -70 ^{o}C. The reaction mixture was stirred for 1 hour. A portion of 4.81 mL (12.0 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added into the reaction mixture. Then, the reaction mixture was allowed to warm up to R.T. and stirred for 12 hours. The water was added to the reaction mixture then extracted three times with 50 mL of diethyl ether. The extracted organic layer yer 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/Hex. The yield of the white solid was 1.98 g (74.0%). MS: [M^+], *m/z* 535. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (d, J = 4.10 Hz, 2H), , 7.51 (s, 2H), 6.80 (d, J = 4.00 Hz, 2H), 3.84 (t, 2H), 1.76 (m, 2H), 1.40 (m, 2H), 1.31 (s, 24H), 0.85 (t, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 133.9, 114.6, 83.7, 50.3, 31.3, 26.4, 24.7, 22.4, 13.83. Anal. Calcd. for $C_{30}H_{43}B_2NO_4S$: C, 67.31; H, 8.10; B, 4.04; N, 2.62; O, 11.95; S, 5.99. Found. C, 67.20; H, 8.15; N, 2.73; S, 5.87.

III-2-1-2-7. Synthesis of 10-(4-bromo-butyl)-10*H*-phenothiazine (7)

A portion of benzyltriethylammonium chloride (50.0 mg) and aqueous sodium hydroxide (NaOH, 30 mL, 50 wt.%) were added to a solution of 10*H*-phenothiazine (5.00 g, 25.1 mmol) in 30 mL of dimethyl sulfoxide (DMSO). The reaction mixture was stirring for 30 min. After, 1,4-dibromobutane (53.9 g, 0.25 mol) was added to the reaction mixture then stirred for 12 hours at R.T. The reaction mixture was washed with aqueous HCl (35 wt.%). The washed mixture was extracted three times with 100 mL of MC. The extracted organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator. After, the 1,4-dibromobutane in the mixture was distilled. The crude product was purified by column chromatography on silica gel using MC/Hex. The yield of light yellow liquid was 58.4% (4.90 g). MS: $[M^+]$, *m/z* 335.00 ^{1}H-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 = 7.00 Hz, 2H), 3.43~3.40 (t, J = 6.20 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-2-1-2-8. Synthesis of 3,7-dibromo-10-(4-bromobutyl)-10*H*-phenothiazine (8)

A portion of NBS (1.64 g, 9.21 mmol) in 10 mL of DMF was added dropwise to a solution of compound 1 (1.40 g, 4.19 mmol) in 20 mL of DMF under N_2 at 5 ^{o}C then stirred for 30 min. The reaction mixture was stirred for 5 hours at R.T. The reaction mixture was washed with aqueous sodium bicarbonate then extracted with EA. The extracted organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography using Hex. 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* = 8.80 Hz, 2H), 3.77~3.74 (t, *J* = 6.90 Hz, 2H), 1.76~1.69 (m, 2H), 1.47~1.37 (m, 2H), 0.94~0.90 (t, *J* = 7.30 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.

III-2-1-2-9. Synthesis of 10-(4-bromo-butyl)-3,7-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-10*H*-phenothiazine (9)

A mixture of compound 8 (0.770 g, 1.57 mmol), KOAc (1.59 g, 6.30 mmol), bis(pinacolato)diborane (0.92 g, 9.40 mmol) and Pd(dppf)Cl_2 (77.0 mg, 0.084 mmol) were mixed together in flask. After degassing, the mixture was stirred in 30 mL of DMF under N_2 at 60 ℃ for 24 hours. The water was added and the mixture was allowed to cool to R.T. The cooled mixture was extracted with EA. The extracted organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography on silica gel using Hex/EA. The yield of yellow solid was 0.43 g (46.7%). MS: [M^+], *m/z* 586. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.58~7.55 (dd, J_1 = 8.10 Hz, J_2 = 1.40 Hz, 2H), 7.54~7.53 (d, J = 1.40 Hz, 2H), 6.82~6.80 (d, J = 8.1 Hz, 2H), 4.06~4.02 (t, J = 6.60 Hz, 2H), 3.93~3.89 (t, J = 7.00 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-2-1-2-10. Synthesis of 2-bromo-9,9-bis(6-bromohexyl)-9*H*-fluorene (10)

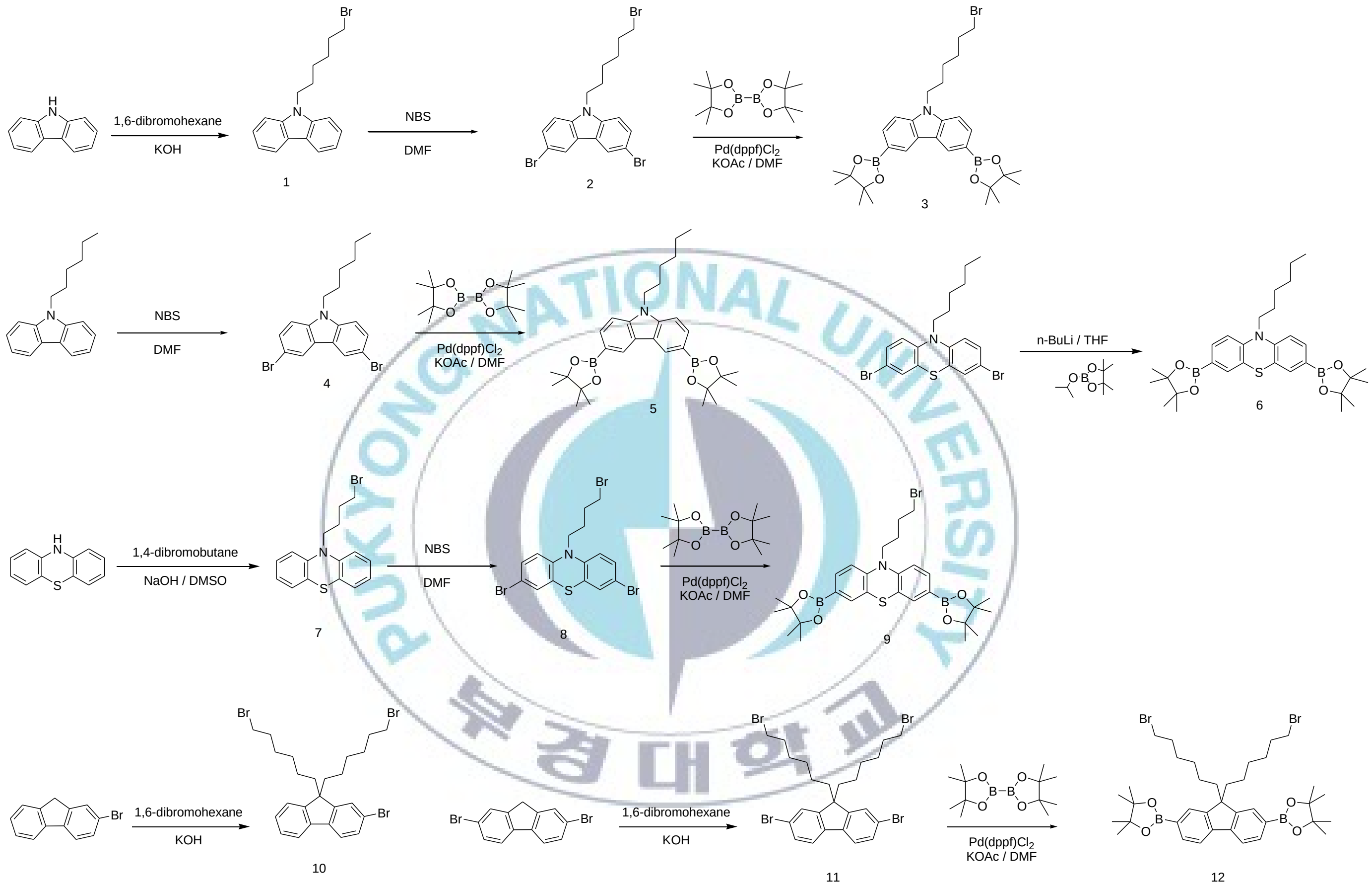
A solution of aqueous KOH (40 mL, 45 wt.%) was added to a portion of bromo-9*H*-fluorene (4.90 g, 20.0 mmol) in 1,6-dibromo-hexane (97.6 g, 400 mmol). Then reaction mixture was stirred for 4 hours at 80 ^{o}C. The water was added and the mixture was allowed to cool to R.T., and that was washed with aqueous HCl (35 wt.%). The washed mixture was extracted with 100 mL of MC. The extracted organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator. After, distilling the 1,6-dibromo-hexane in the mixture, the crude product was purified by column chromatography on silica gel using MC/ Hex. The yield of light yellow liquid was 89.7% (10.2 g). MS[M^+], m/z 570.00 ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.66~7.65 (t, J = 3.70 Hz, 1H), 7.56~7.53 (d, J = 8.80 Hz, 1H), 7.45~7.43 (m, 2H), 7.33~7.31 (m, 3H), 3.28~3.24 (t, J = 6.60 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-2-1-2-11. Synthesis of 2,7-dibromo-9,9-bis(6-bromohexyl)-9*H*-fluorene (11)

A solution of aqueous KOH (40 mL, 45 wt.%) was added to a portion 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 °C. The water was added and the mixture was allowed to cool to R.T., and that was washed with aqueous HCl (35 wt.%). The washed mixture was extracted with 100 mL of MC. The extracted organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$). The solvent was removed by using a rotary evaporator. After, distilling the 1,6-dibromo-hexane in the mixture, the crude product was purified by column chromatography on silica gel using MC/Hex. 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-2-1-2-12. Synthesis of 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 (12)

A mixture of compound 11 (2.95 g, 4.54 mmol), KOAc (2.67 g, 27.2 mmol), bis(pinacolato)diborane (4.15 g, 27.2 mmol) and Pd(dppf)Cl_2 (222 mg, 0.274 mmol) were mixed together in flask. After degassing, the mixture was stirred in DMF (20 mL) under N_2 at 60 ℃ for 24 hours. The water was added and the mixture was allowed to cool to R.T. The cooled mixture was extracted with EA. The extracted organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography on silica gel using Hex/EA and recrystallization using Hex. The yield of white solid was 1.78 g (53.2%). MS: [M^+], *m/z* 744. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.83~7.81 (d, *J* = 7.70 Hz, 2H), 7.74~7.72 (m, 4H), 3.92~3.89 (t, *J* = 6.90 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.



Scheme III-1. Synthesis of water/alcohole soluble monomer.

III-2-1-2-13. 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 80 ^oC under the N_2. The water was added and the mixture was allowed to cool R.T. The cooled mixture was extracted with EA. The extracted organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by using a rotary evaporator

III-2-1-2-13-1. Synthesis of 3,7-bis[9,9-bis(6-bromohexyl)-9*H*-fluoren-2-yl]-10-(4-bromo-butyl)-10*H*-phenothiazine (13)

A mixture of compound 9 (200 mg, 0.342 mmol), compound 10 (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. The water was added and the mixture was allowed to cool to R.T. The cooled mixture was extracted with EA. The extracted organic layer was dried over anhydrous $MgSO_4$. And the solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography on silica gel using

MC/Hex. The yield of light yellow liquid was 212 mg (47.2%). ^{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 = 8.40 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 = 7.00 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-2-1-2-13-2. Synthesis of 3,6-bis-[9,9-bis-(6-bromo-hexyl)-9*H*-fluoren-2-yl]-9-(6-bromo-hexyl)-9*H*-carbazole (14)

Compound 14 was synthesized by the general procedure of the Suzuki coupling reaction between 0.116 g (0.200 mmol) of compound 3 and 0.239 g (0.420 mmol) of compound 10. The crude product was purified by column chromatography on silica gel using Hex/EA. The yield of light yellow liquid was 108 mg (41.3%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.82~7.76 (m, 12H), 7.51~7.44 (m, 2H), 7.37~7.28 (m, 6H), 4.40~4.36 (t, J = 8.00 Hz, 2H), 4.04~4.02 (t, J = 4.00 Hz, 2H), 3.27~3.24 (t, *J* = 4.00 Hz, 8H), 2.01~1.98 (m, 8H), 1.70~1.61 (m, 10H), 1.46~1.40 (m, 4H), 1.28~1.05 (m, 18H), 0.79~0.62 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 141.03, 140.35, 139.63, 132.92, 128.75, 127.28, 126.90, 126.19, 125.54, 123.57, 122.75, 121.44, 120.00, 119.68, 118.98, 109.04, 64.34, 55.04, 40.32, 33.95, 32.61, 29.06, 28.47, 27.75, 26.99, 25.83, 23.55, 20.97. Anal. Calcd. for $C_{68}H_{80}Br_5N$; C, 62.30; H, 6.15; Br, 30.48; N, 1.07. Found: C, 61.92; H, 6.62; N, 1.08.

III-2-1-2-13-3. Synthesis of 9,9,9',9',9'',9''-hexakis-(6-bromo-hexyl)-9*H*,9'*H*,9''*H*-[2,3';6',2'']-terfluorene (15)

Compound 15 was synthesized by the general procedure of the Suzuki coupling reaction between 0.102g (0.134 mmol) of compound 9 and 0.229 g (0.402 mmol) of compound 10. The crude product was purified by column chromatography on silica gel using Hex/EA. The yield of light yellow liquid was 63.4 mg (32.1%) . ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.82~7.77 (m, 4H), 7.74~7.72 (d, *J* = 8.00 Hz, 2H), 7.68~7.61 (m, 8H), 7.35~7.29 (m, 6H), 3.93~3.90 (t, *J* = 4.00 Hz, 4H), 3.27~3.94 (t, *J* = 4.00 Hz, 8H), 2.12~2.02 (m, 10H), 1.68~1.61 (m, 10H), 1.45~1.42 (m, 4H), 1.23~1.05 (m, 28H), 0.73~0.63 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 171.10, 151.49, 151.13, 150.55, 140.41, 126.96, 126.24, 126.13, 122.53, 121.24, 121.16, 120.07, 119.81, 64.45, 55.26, 55.07, 40.42, 40.21, 33.91, 32.57, 29.72, 29.01, 28.53, 27.71, 25.65, 23.87, 23.56, 20. Anal. Calcd. for $C_{75}H_{92}Br_6$; C, 61.16; H, 6.30; Br, 32.55. Found: C, 60.96; H, 6.72.

III-2-1-2-13-4. Synthesis of 3,7-bis-[9,9-bis-(6-bromo-hexyl)-9*H*-fluoren-2-yl]-10-hexyl-10*H*-phenothiazine (16)

Compound 16 was synthesized by the general procedure of the Suzuki coupling reaction between 0.107 g (0.200 mmol) of compound 9 and 0.239 g (0.420 mmol) of compound 10. The crude product was purified by column chromatography on silica gel using Hex/EA. The yield of light yellow liquid was 107 mg (42.7%) . ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.73~7.69 (m, 6H), 7.63~7.46 (m, 12H), 7.35~7.32 (m, 2H), 3.94~3.91 (t, J = 6.00 Hz, 2H), 3.28~3.24 (t, J = 8.00 Hz, 5H), 2.01~1.84 (m, 8H), 1.66~1.49 (m, 10H), 1.42~1.33 (m, 6H), 1.20~1.05 (m, 16H), 0.91~0.88 (t, J = 6.00 Hz, 3H), 0.72~0.62(m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 141.99, 138.22, 137.39, 136.73, 136.59, 135.67, 134.15, 125.24, 119.83, 116.38, 115.63, 113.95, 110.14, 109.01, 55.01, 54.41, 49.59, 32.94, 32.63, 29.04, 27.75, 25.40, 23.53, 23.15, 22.06, 21.42. Anal. Calcd. for $C_{68}H_{81}Br_4NS$; C, 64.61; H, 6.46; Br, 25.28; N, 1.11; S, 2.54. Found: C, 64.52; H, 6.18;; N, 1.41; S, 2.37

III-2-1-2-13-5. Synthesis of 3,6-bis-[9,9-bis-(6-bromo-hexyl)-9*H*-fluoren-2-yl]-9-hexyl-9*H*-carbazole (17)

Compound 17 was synthesized by the general procedure of the Suzuki coupling reaction between 0.106 g (0.200 mmol) of compound 5 and 0.239 g (0.420 mmol) of compound 10. The crude product was purified by column chromatography on silica gel using Hex/EA. The yield of light yellow liquid was 96.0 mg (39.2%). ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 8.49~8.48 (d, J = 4.00 Hz, 2H), 7.87~7.80 (m, 4H), 7.76~7.74 (m, 4H), 7.69 (s, 2H), 7.54~7.51 (d, J = 12.0 Hz, 2H), 7.38~7.25 (m, 6H), 4.40~4.37 (t, J = 8.00 Hz, 2H), 3.29~3.25 (t, J = 8.00 Hz, 8H), 2.12~1.91 (m, 10H), 1.70~1.62 (m, 8H), 1.36~1.18 (m, 16H), 1.14~1.07 (m, 8H), 0.91~0.88 (t, J = 4.00 Hz, 3H) 0.80~0.63 (m, 6H). ^{13}C-NMR (100 MHz, CDCl$_3$, ppm): δ 152.13, 151.57, 142.18, 142.10, 141.49, 140.70, 133.92, 127.99, 127.28, 123.85, 122.54, 121.09, 120.77, 110.19, 56.13, 41.42, 35.04, 33.71, 32.70, 30.15, 28.84, 28.09, 24.65, 23.64, 15.12 Anal. Calcd. for $C_{68}H_{81}Br_4N$; C, 66.29; H, 6.63; Br, 25.94; N, 1.14. Found: C, 66.31; H, 6.96;; N, 1.02.

III-2-1-2-14. Synthesis of 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 (FPiF)

A portion of 0.5 mL of trimethylamine in ethanol (33 wt.%) was added to a solution of compound 13 (50.0 mg, 0.038 mmol) in 5 mL of THF. Then reaction mixture was stirred for at R.T. for 2 days. Then the solvent was removed. ^{1}H-NMR (400 MHz, CD$_3$OH, ppm): δ 7.72~7.58 (m, 6H), 7.51~7.19 (m, 12H), 7.00~6.98 (m, 2H), 2.95(s, 45H), 2.06~1.76 (m, 14H), 1.45~1.22 (m, 18H), 1.57~0.83(m, 16H), 0.54 (m, 8H),. Anal. Calcd. for $C_{81}H_{121}Br_5N_6S$; C, C, 60.41; H, 7.57; Br, 24.81; N, 5.22; S, 1.99. Found: C, 60.73; H, 7.48; N, 5.15; S, 1.84

III-2-1-2-15. Synthesis of 3,6-bis-[9,9-bis-(6-(*N*,*N*,*N*-trimetylammonium)-hexyl)-9*H*-fluoren-2-yl]-9-(6-(*N*,*N*,*N*-trimetylammonium)-hexyl)-9*H*-carbazole (FCiF)

A portion of 0.5 mL of trimethylamine in ethanol (33 wt.%) was added to a solution of compound 14 (50.0 mg, 0.038 mmol) in 5 mL of THF. Then reaction mixture was stirred for at R.T. for 2 days. Then the solvent was removed. ^{1}H-NMR (400 MHz, CD$_3$OH, ppm): δ 8.06~8.04 (d, J = 8.00 Hz, 2H), 7.89~7.66 (m, 14H), 7.25~7.18 (m, 4H), 2.91 (s, 45H), 1.97~1.93 (m, 2H), 1.67~1.22 (m, 26H), 0.89~0.64 (m, 24H), 0.29 (s, 8H). Anal. Calcd. for $C_{83}H_{125}Br_5N_6$; C, 62.06; H, 7.84; Br, 24.87; N, 5.23. Found: C, 62.13; H, 7.58; N, 5.17.

III-2-1-2-16. Synthesis of 9,9,9',9',9'',9''-bexakis-(6-(*N*,*N*,*N*-trimetylammonium)-hexyl)-9H,9'H,9''H-[2,3';6',2'']terfluorene (FFiF)

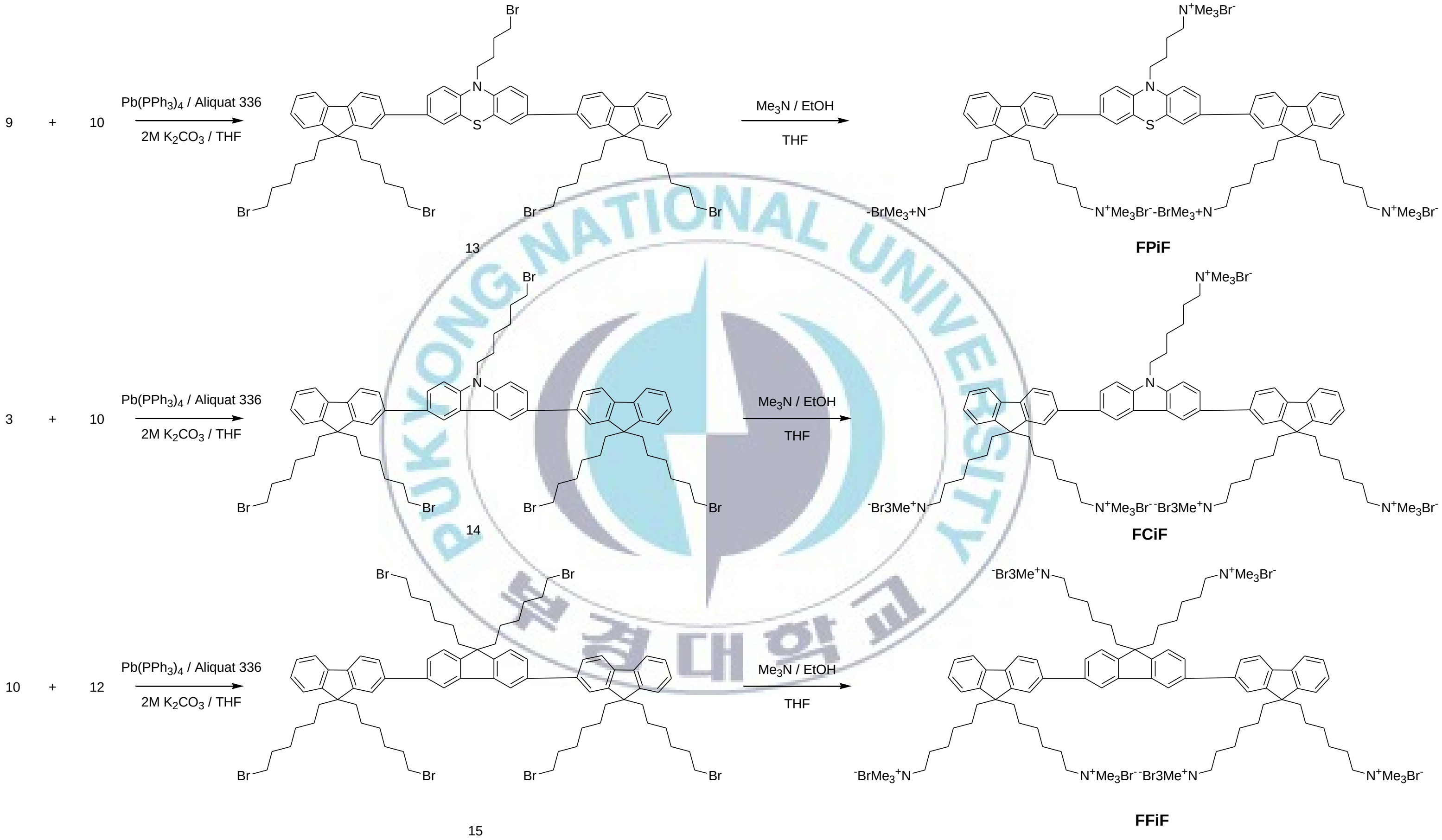
A portion of 0.5 mL of trimethylamine in ethanol (33 wt.%) was added to a solution of compound 15 (50.0 mg, 0.033 mmol) in 5 mL of THF. Then reaction mixture was stirred for at R.T. for 2 days. Then the solvent was removed. ^{1}H-NMR (400 MHz, CD_3OH, ppm): δ 7.88~7.80 (m, 4H), 7.74~7.67 (m, 10H), 7.42~7.30 (m, 6H), 3.01 (s, 54H), 2.11~2.09 (br, 12H), 1.51 (br, 10H), 1.34~1.23 (br, 10H), 1.23~0.69 (m, 28H), 0.67~0.60 (m, 12H). Anal. Calcd. for $C_{93}H_{146}Br_6N_6$; C, 61.12; H, 8.05; Br, 26.23; N, 4.60. Found: C, 61.81; H, 7.85; N, 4.32.

III-2-1-2-17. Synthesis of 3,7-bis[9,9-bis(6-(*N*,*N*,*N*-trimetylammonium)-hexyl)-9*H*-fluoren-2-yl]-10-hexyl-10*H*-phenothiazine pentabromide (FPF)

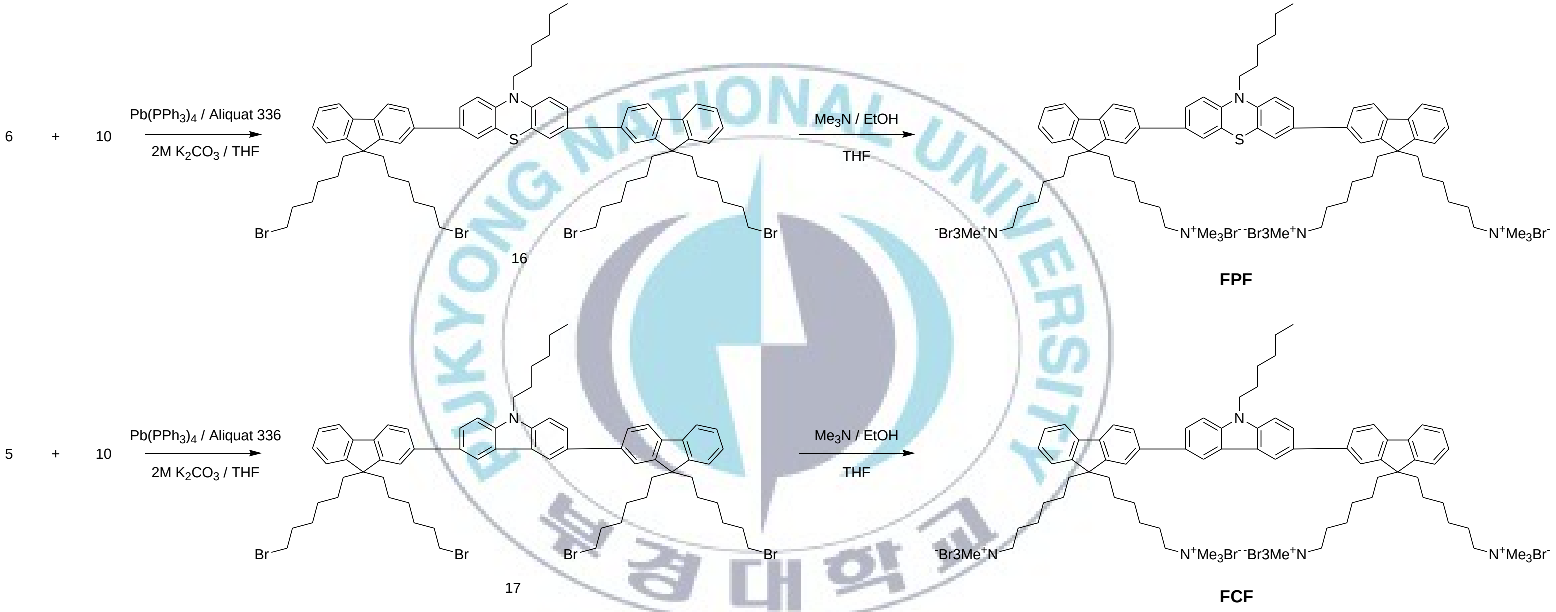
A portion of 0.5 mL of trimethylamine in ethanol (33 wt.%) was added to a solution of compound 16 (50.0 mg, 0.039 mmol) in 5 mL of THF. Then reaction mixture was stirred for at R.T. for 2 days. Then the solvent was removed. NMR (400 MHz, CD_3OH, ppm): δ 7.71~7.58 (m, 6H), 7.51~7.24 (m, 13H), 7.00~6.98 (d, J = 8.00 Hz, 1H), 2.96 (s, 36H), 2.12~1.96 (m, 6H), 1.78~1.74 (m, 1H), 1.49~0.83 (m, 46H), 0.58 (s, 8H). Anal. Calcd. for $C_{81}H_{121}Br_5N_6S$; C, 60.41; H, 7.57; Br, 24.81; N, 5.22; S, 1.99. Found: C, 60.73; H, 7.48; N, 5.15; S, 1.84

III-2-1-2-18. Synthesis of 3,6-bis-[9,9-bis-(6-(*N*,*N*,*N*-trimetylammonium)-hexyl)-9*H*-fluoren-2-yl]-9-hexyl-9*H*-carbazole (FCF)

A portion of 0.5 mL of trimethylamine in ethanol (33 wt.%) was added to a solution of compound 17 (50.0 mg, 0.040 mmol) in 5 mL of THF. Then reaction mixture was stirred for at R.T. for 2 days. Then the solvent was removed. ^{1}H-NMR (400 MHz, CD_3OH, ppm): δ 8.06~8.04 (d, J = 8.00 Hz, 2H), 7.89~7.87 (d, J = 8.00 Hz, 4H), 7.79~7.66 (m, 6H), 7.26~7.22 (m, 6H), 2.91 (s, 36H), 1.99~1.93 (m, 2H), 1.80~1.22 (m, 30H), 0.89~0.64 (m, 23H), 0.29 (s, 6H). Anal. Calcd. for $C_{80}H_{117}Br_4N_5$; C, 65.43; H, 8.03; Br, 21.77; N, 4.77. Found: C, 65.21; H, 7.97; N, 4.51.



Scheme III-2. Synthesis of water/alcohole soluble oligomer (**FPiF, FCiF, FFiF**).



Scheme III-3. Synthesis of water/alcohole soluble oligomer (**FPF, FCF**).

III-2-2. Device fabrication

ITO-coated on glass substrates were cleaned with deionized water, acetone, methanol, iso-propanol in ultrasonic bath. First, OSCs were fabricated through the conventional process. A layer 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 = 13 Ω/sq) which was pre-treated by UV/O_3 for 300 0sec. 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 CBL was spin-coated from the solution in ethanol (1 mg/ml) onto active layer at 4000 rpm for 60 s. A 100 nm-thick layer of Al was vacuum deposited as a cathode through shadow mask onto the top of the CBL films at 2 x 10^{-6} Torr. The typical active area of the devices was 13 mm^2.

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 work function measurements were carried out using a UPS with a He I source (hm = 21.2 eV) at a pressure of 1×10^{-8} Torr (Thermo Electron Co., Multilab 2000). 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.

III-3. Results and discussion

III-3-1. Ultraviolet photoelectron spectroscopy (UPS)

Oligomers with salt will be able to form dipole. Thus, it will modify the work function of the metal electrode. We performed Ultraviolet photoelectron spectroscopy (UPS) and investigated the effect of the thin layer of oligomer on the work function of metal cathode. The work function of Al with a thin layer of oligomers is decreased. Therefore, a Schottky barrier of active layer/cathode in

OSC with water/alcohol soluble oligomer as CBL will be smaller than that without water/alcohol soluble oligomer as CBL.

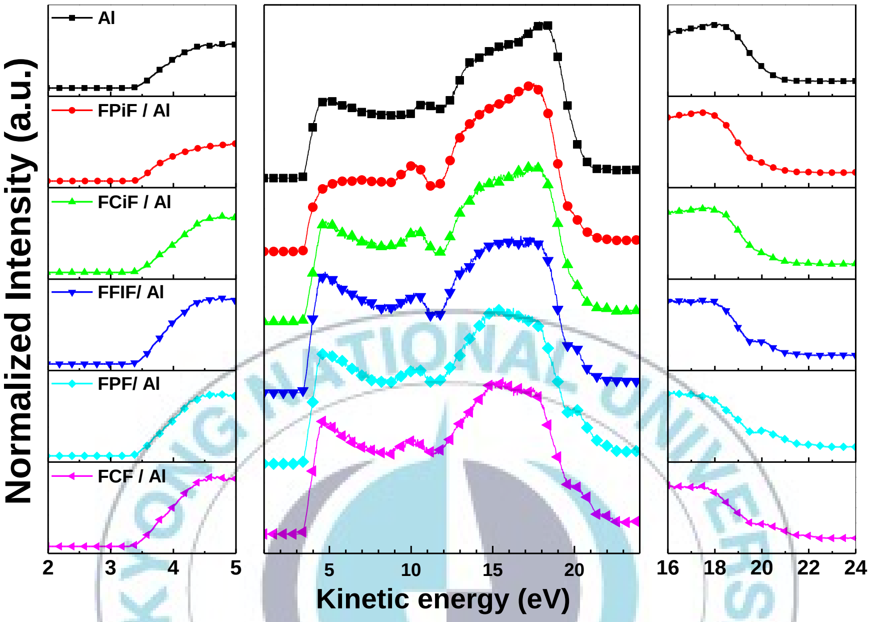


Figure III-1. UPS spectra of Al and water/alcohol soluble oligomers coated Al.

Table III-1. UPS properties of Al and water/alcohol soluble oligomers coated Al.

	Al	**FPiF/Al**	**FCiF/Al**	**FFiF/Al**	**FPF/Al**	**FCF/Al**
E_C[a]	3.39	3.40	3.42	3.40	3.41	3.39
E_F[b]	20.41	20.93	20.94	20.92	20.95	20.96
Φ[c]	4.18	3.67	3.68	3.68	3.66	3.63

[a] : Cut off [b] : Fermi edge [c] : Work founction

III-3-2. Photovoltaic properties

OSCs were fabricated using water/alcohole soluble oligomer as CBL. The current density (*J*) – voltage (V) characteristics of OSCs measured under AM 1.5 G simulated illumination with an intensity of 100 mW/cm^2 and shown in Figure III-2. The OSC with **FPiF** showed an open circuit voltage (V$_{oc}$) of 0.58 V, a short circuit current (J_{sc}) of –8.024 mA/cm^2, a fill factor (FF) of 59.4%, and a power conversion efficiency (PCE) of 2.81%. The device with **FCiF** gave a V$_{oc}$ of 0.58 V, a J_{sc} of -8.76 mA/cm^2, a FF of 55.6%, and a PCE of 2.82%. The device using **FFiF** gave a V$_{oc}$ of 0.59 V, a J_{sc} of -8.90 mA/cm^2, a FF of 57.8%, and a PCE of 3.04%. The device using **FPF** gave a V$_{oc}$ of 0.59 V, a J_{sc} of -9.19 mA/cm^2, a FF of 61.2%, and a PCE of 3.37%. The device using **FCF** gave a V$_{oc}$ of 0.59 V, a J_{sc} of -8.92 mA/cm^2, a FF of 60.7%, and a PCE of 3.25%.

The performances of the device with oligomers as CBL showed better performances than those of the device without oligomers. This is due to the contact properties between the active layer and the metal cathode are enhanced. We calculate the series resistnace (R$_s$) and paralell resistance (R$_p$) of the OSC to investigate the contact property between the active layer and the metal cathode. The contact property is strongly related to the R$_s$ and R$_p$ values. The R$_s$ and R$_p$ values are calculated the current density– voltage curve of OSCs under the dark condition (Figure III-2 (b)). The R$_s$ values of the OSC with **FPiF**, **FCiF**, **FFiF**,

FPF and **FCF** are 2.68, 2.36, 1.98, 1.76, and 1.59 Ω cm^2. The R_s value of the device without CBL is 3.02 Ω cm^2. The R_s valses of OSC without oligomer are lower than that with oligomers. Therfore, the contact properties of the OSC with oligomers as CBL is improved by introducing the thin layer of oligomers as CBL.

The PCE of OSCs with **FCF** and **FPF** are higher than those of the device with the other oligomers. The contact property at the cathode interface may be related to the chemical structure of oligomers. The side chain on the core unit of **FCF** and **FPF** (carbazole or phenthiazine) doesn't have quaternary ammonim salt whereas the side chain on the core unit of the other oligomers has quarternary ammonium salt. According to the literature [42], the spontaneous organization of conjugated polyelectrolytes (CPE) take places during the spin coating process. Ionic components of the CPE are accumulated at the top of the CPE surface due to the ionic groups rejected the hydrophobic semiconducting polymer layer. S. H. Oh et al. [43] reported that Polyfluorene (PF)-based CPE with both quaternary ammonium bromide side group and ethylene oxide side group on the 9-position of fluorene ring (PF-oxy-F) induces very large interfacial dipoles at the cathode interface. Also, the conformation of main chain may affect the performances of the device. For **FCF** and **FPF**, zig-zag orientation may preferred conformation because of a large rotational energy barrier. Hydrophibic alkyl side chain without quarternary ammonium salt will be oriented to the surface of active layer. Therefore, the device with **FCF** and **FPF** as CBL showed the best performances among the devices.

The R_s values of OSC with **FPF** and **FCF** are 1.76, 1.59 Ω cm^2, which are lower than the R_s values of OSC with **FPiF** and **FCiF**. From the results, we confirm that the PCEs of the device with **FPF** and **FCF** are better than those the device with **FPiF**, **FCiF**, **FFiF**. In contrary, the contact property at the cathode interface of the device with **FPiF** and **FCiF** is poorer than those of the device with **FCF** and **FPF** because the alkyl chain on the core unit of **FPiF** and **FCiF** has quarternay ammonium salt. In addition, The perpormance of OSC with **FFiF** is better than that of the device with **FPiF** and **FCiF**. This is presumably due to that the the arrangement of salt of **FFiF** is totally reversed orientation. The FF of OSC with oligomers with phenothiazine is higher than that with other oligomer.

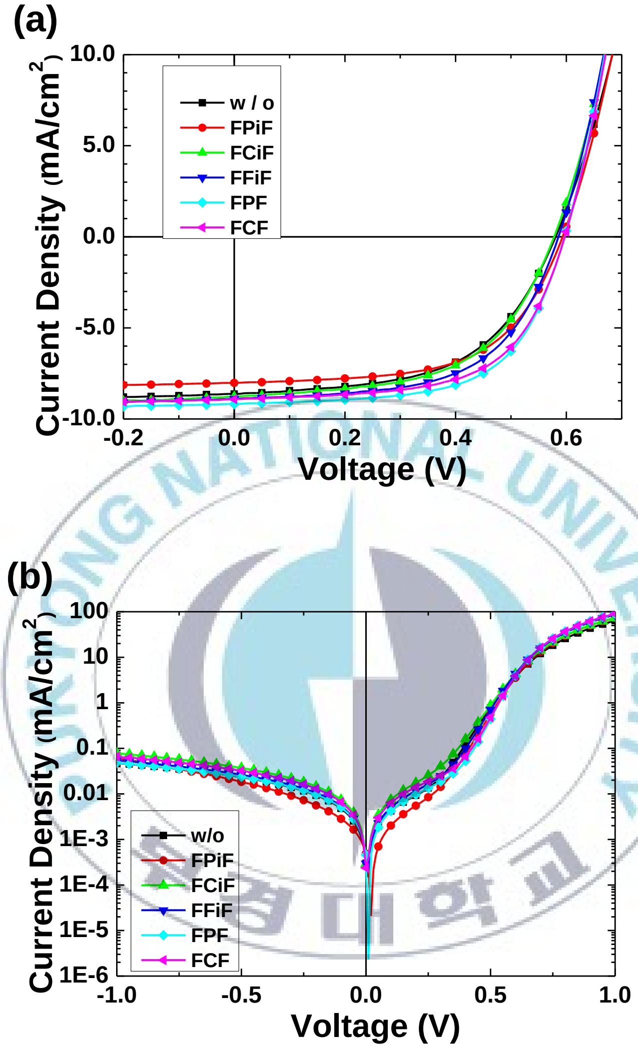


Figure III-2. Current density–voltage curves of water/alcohol soluble oligomers (a) under AM 1.5Gsimulated illumination with an intensity of 100 mW/cm^2 and (b) under the dark condition.

Table III-2. The best photovoltaic parameters and the averages for photovoltaic parameters of each device are given in parentheses with mean variation.

	V_{oc}	**J_{sc}**	**FF**	**PCE**	**R_s(Ω•cm^2)[a]**	**R_p(kΩ•cm^2)[a]**
w/o CBL	0.58	-8.63 (-8.31±0.34)	57.1 (55.8±1.76)	2.76 (2.70±0.13)	3.02	21.4
With FPiF	0.58	-8.02 (-8.16±0.15)	59.4 (57.0±1.02)	2.81 (2.73±0.06)	2.68	19.8
With FCiF	0.58	-8.76 (-8.27±0.30)	55.6 (55.6±0.88)	2.82 (2.67±0.08)	2.36	13.0
With FFiF	0.59	-8.90 (-8.41±0.25)	57.8 (57.9±1.37)	3.04 (2.87±0.10)	1.98	18.7
With FPF	0.59	-9.19 (-8.67±0.21)	61.2 (59.2±2.11)	3.37 (3.05±0.19)	1.76	21.2
With FCF	0.59	-8.92 (-8.87±0.16)	60.7 (59.1±1.00)	3.25 (3.11±0.11)	1.59	15.5

[a] : series resistnace (estimated from the devices with best PCE value).

[b] : paralell resistance (estimated from the devices with best PCE value).

III-4. Conclusions

UPS studies showed that the work function of Al is reduced by thin layer of water/alcohol soluble oligomers, and the R_s values of OSC with oligomers is lower than that without oligomer. Therefore, the contact properties of OSC with oligomers are better than that without oligomer. In addition, the OSC with **FCF** and **FPF** as CBL is showed the good contact property, because the R_s of OSC with **FCF** and **FPF** as CBL are smaller than that with **FPiF**, **FCiF**, and **FFiF**. And the R_s value of OSC with **FFiF** is better than that with **FPiF** and **FCiF**.

Chapter IV. Effect of counter anion of polyviologen on the photovoltaic properties.

IV-1. Introduction

Polyviologen (PV) derivatives are well known materials for improving the performances of solar cells by the formation of favorable interface dipole at the cathode interface. In this research, we investigate the effect of counter anion (CA) of polyviologen on the photovoltaic properties.

IV-2. Experimental

IV-2-1. Materials and synthesis

IV-2-1-1. Materials

All chemicals were purchased from Sigma-Aldrich Co or Alfa Aesar (A Johnson Matthey Company) and used as received unless otherwise described.

IV-2-1-2. Synthesis

IV-2-1-2-1. Synthesis of poly (1,1’-didodecyl-4,4’-bipyridinium dibromide) (PV12-Br)

A mixture of 4-dibromododecane (0.980 g, 3.00 mmol) and 4,4’- bipyridyl (0.470 g, 3.00 mmol) in 3 mL of N,N-dimethylformamide (DMF) was stirred at 140 ^{o}C for 12 hours. The reaction mixture was cooled to room temperature (R.T.), and solid particles in the reaction mixture was collected by filtration and washed with 50 mL of n-hexane and 50 mL of dichloromethane (MC). The residues were dried under the vacuum. The yield of yellowish brown solid was 86.8% (1.26 g). ^{1}H NMR (400 MHz, CD_3OH, ppm): δ 9.15~9.12 (Br, 4H), 8.59~8.56 (Br, 4H), 4.77~4.72 (Br, N^+-CH_2-, 4H), 2.15~2.06 (Br, -CH_2-, 4H), 1.42~1.26(Br, -CH_2-, 16H). ^{13}C NMR (100 MHz, CD_3OH, ppm): δ 151.12, 146.61, 128.18, 63.46, 31.80, 29.78, 29.67, 29.28, 26.47. Anal. Calcd. For $C_{22}H_{33}Br_2N_2$: C, 54.45; H, 6.85; N, 5.77; Br, 32.93. Found: C, 56.93; H, 7.45; N, 5.31.

IV-2-1-2-2. General procedure of the anion exchange reaction

A portion of 0.260 mmol of reactant containing the desired anion in 5 mL diionized water (DI water) was added dropwise to a solution of **PV12-Br** 61.0 mg

(0.130 mmol in repeat units) in 5 mL of DI water. The reaction mixture was stirred at R.T. for 24 hours. The particles in the reaction mixture were collected by filtration and washed with 50 mL of DI water. Residues were dried under the vacuum.

IV-2-1-2-2-1. Synthesis of poly (1,1’-didodecyl-4,4’-bipyridinium ditetra-fluoroborate) (PV12-BF_4)

PV12-BF_4 was anion-exchanged by the general procedure between 61.0 mg (0.130 mmol) and 29.0 mg (0.260 mmol) of a sodium tetrafluoroborate. The yield was 60.0 mg (90.1%). ^{1}H NMR (400 MHz, DMSO, ppm): δ 9.38 (Br, 4H), 8.78 (Br, 4H), 4.67 (Br, N^+-CH_2-, 4H), 1.98 (Br, -CH_2-, 4H), 1.32~1.28 (Br, -CH_2-, 16H). Anal. Calcd. For $C_{22}H_{33}B_2F_8N_2$: C, 52.94; H, 6.66; B, 4.33; F, 30.45; N, 5.61. Found: C, 53.21; H, 6.73; N, 5.48.

IV-2-1-2-2-2. Synthesis of poly (1,1’-didodecyl-4,4’-bipyridinium dihexa-fluorophosphate) (PV12-PF_6)

PV12-PF_6 was anion-exchanged by the general procedure between 61.0 mg (0.130 mmol) and 43.0 mg (0.260 mmol) of a ammonium hexafluorophosphate. The yield was 73.0 mg (89.2%). ^{1}H NMR (400 MHz, DMSO, ppm): δ 9.37~9.35

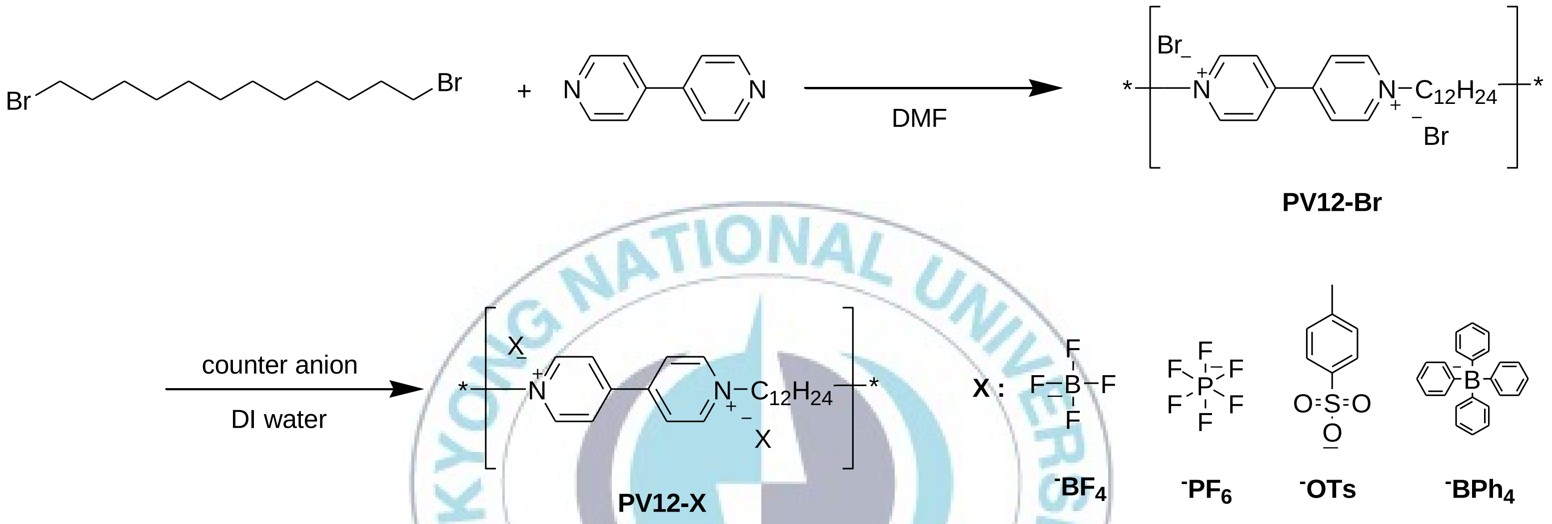
(Br, 4H), 8.77~8.75 (Br, 4H), 4.66 (Br, N^+-CH_2-, 4H), 1.97 (Br, -CH_2-, 4H), 1.32~1.27(Br, -CH_2-, 16H). Anal. Calcd. For $C_{22}H_{33}F_{12}N_2P_2$: C, 42.93; H, 5.40; F, 37.04; N, 4.55; P, 10.07. Found: C, 43.15; H, 5.28; 4; N, 4.73.

IV-2-1-2-2-3. Synthesis of poly (1,1'-didodecyl-4,4'-bipyridinium di-p-toluenesulfonate) (PV12-OTs)

PV12-OTs was anion-exchanged by the general procedure between 61.0 mg (0.130 mmol) and 51.0 mg (0.260 mmol) of a sodium p-toluenesulfonate. The yield was 87.0 mg (93.1%). ^{1}H NMR (400 MHz, CD_3OH, ppm): δ 9.23~9.22 (Br, 4H), 8.64~8.62 (Br, 4H), 7.64~7.65 (d, J = 4.0 Hz, 2H), 7.21~7.19 (d, J = 4.0 Hz, 2H), 4.72~4.69 (Br, N^+-CH_2-, 4H), 2.34 (s, 3H), 2.06 (Br, -CH_2-, 4H), 1.40~1.32 (Br, -CH_2-, 16H). Anal. Calcd. For $C_{36}H_{47}N_2O_6S_2$: C, 64.74; H, 7.09; N, 4.19; O, 14.37; S, 9.60. Found: C, 65.34; H, 7.31; N, 3.99; O, 13.69; S, 9.76.

IV-2-1-2-2-4. Synthesis of poly (1,1'-didodecyl-4,4'-bipyridinium ditetra-phenylborate) (PV12-BPh_4)

PV12-BPh_4 was anion-exchanged by the general procedure between 61.0 mg (0.130 mmol) and 90.0 mg (0.260 mmol) of a sodium tetraphenylborate. The yield was 113 mg (88.4%). ^{1}H NMR (400 MHz, DMSO, ppm): δ 9.32~9.27 (Br, 4H), 8.65~8.60 (Br, 4H), 7.17 (Br, 8H), 6.93~6.89 (t, *J* = 8.0 Hz, 8H), 6.79~6.75 (t, *J* = 8.0 Hz, 4H), 4.60 (Br, $N^{+-}CH_2$-, 4H), 1.92 (Br, -CH_2-, 4H), 1.29~1.24 (Br, -CH_2-, 16H). Anal. Calcd. For $C_{70}H_{73}B_2N_2$: C, 87.22; H, 7.63; B, 2.24; N, 2.91. Found: C, 87.51; H, 7.33; N, 3.02



Scheme IV. Synthesis of PV12 derivatives.

IV-2-2. Device fabrication

Device fabrication of chapter IV is followed by method of device fabrication (III-2-2) in Chapter III. The PV12 derivatives as CBL were spin-coated from the solution in MeOH / DMSO (1 mg/ml).

IV-2-3. Measurements

Measurements of chapter IV is followed by method of measurements (III-2-3) in Chapter III, and Elemental analysis of PV12 derivatives was performed using (THERMO VG SCIENTIFIC (UK), MultiLab2000) X-ray photoelectron spectroscopy (XPS) and recorded using Al Kα X-ray line (15 kV, 300 W).

IV-3. Results and discussion

IV-3-1. XPS elemental analysis

Anion exchange reaction of PV12 was confirmed by XPS elemental analysis (Figure IV-1 (a)). We are confirmed that the Br (3p, 3d) peak disappears. Br has been displaced to the other anion (OTs, BF_4, PF_6, BPh_4) (Figure IV-1 (b)).

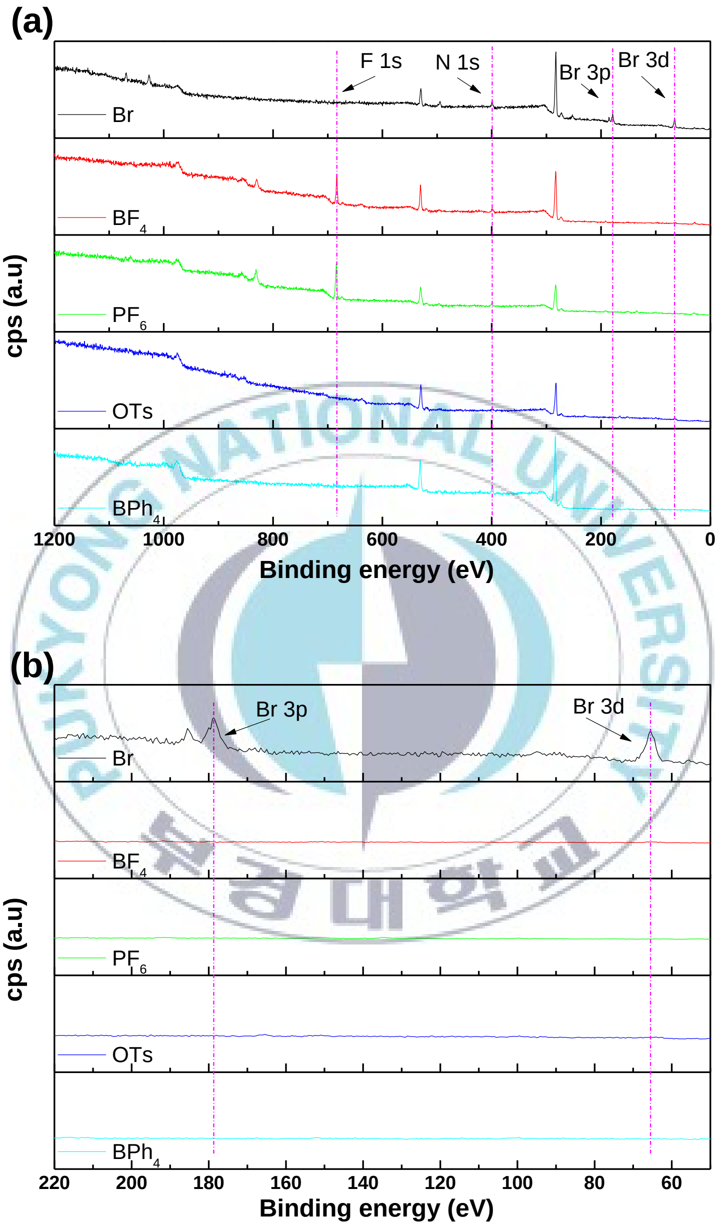


Figure IV-1. (a) Overall spectrum of PV12 derivatives and (b) elemental Analysis of PV12 derivatives bromine.

IV-3-2. UPS study

We performed UPS and investigated the effect of the thin layer of PV12 derivatives on the work function of metal cathode (Al) (Figure IV-2). The work functions were estimated from cut-off energy (E_c) and Fermi edge (E_f), which are summarized in Table IV-1. The work function of Al is 4.13 eV. The work function of Al with thin layer of **PV12-Br** is 4.03 eV, **OTs** is 4.06 eV, **BF$_4$** is 4.04 eV, **PF$_6$** is 4.07 eV **BPh$_4$** is 4.06 eV (Table IV-1). The work function of Al with thin layer of PV12 derivatives decreased. Therefore, PV12 derivatives with the ion will be able to form dipole, and a Schottky barrier of active layer/cathode in PV12 derivatives as CBL will be smaller than that without PV12 derivatives as CBL. Thus, it will modify the work function of the metal electrode.

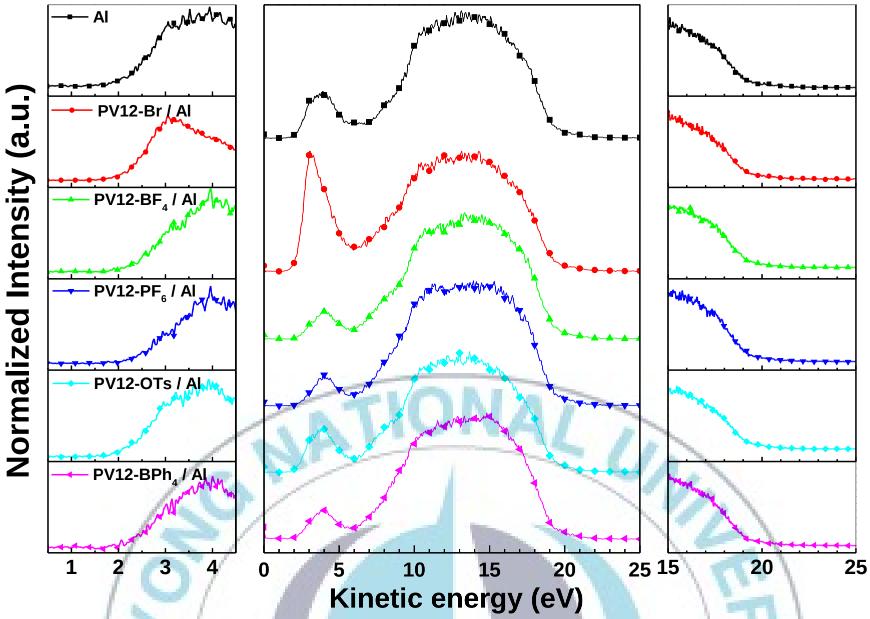


Figure IV-2. UPS spectra of Al and PV12 derivatives coated Al.

Table IV-1. UPS properties of Al and PV12 derivatives coated Al.

	Al	Br/Al	BF$_4$/Al	PF$_6$/Al	OTs/Al	BPh$_4$/Al
E_c^a	2.09	2.09	2.15	2.13	2.09	2.11
E_f^b	19.16	19.26	19.31	19.26	19.23	19.25
ϕ^c	4.13	4.03	4.04	4.07	4.06	4.06

[a]: Cut off [b] : Fermi edge [c]: Work founction

IV-3. OSCs properties of PV12 derivative

OSCs were fabricated using PV12 derivative as CBL. The current density (*J*) – voltage (V) characteristics of OSCs measured under AM 1.5 G simulated illumination with an intensity of 100 mW/cm^2 and shown in Figure IV-3.

The OSC using **PV12-Br** showed a turn-on voltage (V_{oc}) of 0.64 V, a short circuit current (J_{sc}) of -10.55 mA/cm^2, a fill factor (FF) of 50.49%, and a power conversion efficiency (PCE) of 3.41%. The device using **PV12-BF$_4$** gave a V_{oc} of 0.64 V, a J_{sc} of -11.08 mA/cm^2, a FF of 51.82%, and a PCE of 3.67%. The device using **PV12-PF$_6$** gave a V_{oc} of 0.64 V, a J_{sc} of -11.11 mA/cm^2, a FF of 50.42%, and a PCE of 3.59%. The device using **PV12-OTs** gave a V_{oc} of 0.64 V, a J_{sc} of -10.92 mA/cm^2, a FF of 51.38%, and a PCE of 3.61%. The device using **PV12-BPh$_4$** gave a V_{oc} of 0.64 V, a J_{sc} of -11.28 mA/cm^2, a FF of 53.0%, and a PCE of 3.82%. The device without the CBL shows that the V_{oc}, J_{sc}, FF value and PCE are 0.59 V, -10.66 mA/cm^2, 43.88%, and 2.74%, respectively.

It is confirmed by the UPS that PV12 derivatives will be able to form interface dipole. The work function of Al with thin layer of PV12 derivatives is decreased. Therefore, the V_{oc} of OSC with PV12 derivatives is higher than that without PV12 derivatives, and the enhancement of the V_{oc} of the device with PV12 derivatives may be related to the counter ion in PV12 derivatives.

The J_{sc} of OSC with PV derivatives depended on the CA, and the J_{sc} is related to the contact property. We calculate the series resistnace (R_s) and paralell resistance (R_p) of the OSC to investigate the contact property between the active layer and the cathode. The contact property is strongly related to the R_s and R_p values. The R_s and R_p values are calculated the current density– voltage curve of OSCs under the dark condition (Figure IV-3 (b)). The R_s values of the device based on **PV12-Br**, **PV12-BF$_4$**, **PV12-PF$_6$**, **PV12-OTs** and **PV12-BPh$_4$** are 3.06, 2.77, 2.72, 2.86, and 3.66 Ω cm^2. The R_s value of the device without CBL is 5.09 Ω cm^2. The R_s value of the device is decrease by PV12 derivatives. The R_p values of the device based on **PV12-Br**, **PV12-BF$_4$**, **PV12-PF$_6$**, **PV12-OTs** and **PV12-BPh$_4$** are 21.7, 23.9, 16.8, 22.9 and 24.2 kΩ cm^2. The R_p value of the device without CBL is 18.3 kΩ cm^2. The R_p values of the device are changed by CA. The R_p value of the device with **PV12-BPh$_4$** is the highest. Therefore, the Ohmic contact between the active layer and the cathode of device with PV12 derivatives is better than that without PV12 derivatives. And the change of the J_{sc} of the device with PV12 derivatives is related to the different CA, because the contact property between the active layer and the Al in the OSC with PV12 derivatives presumably due to the types of CA.

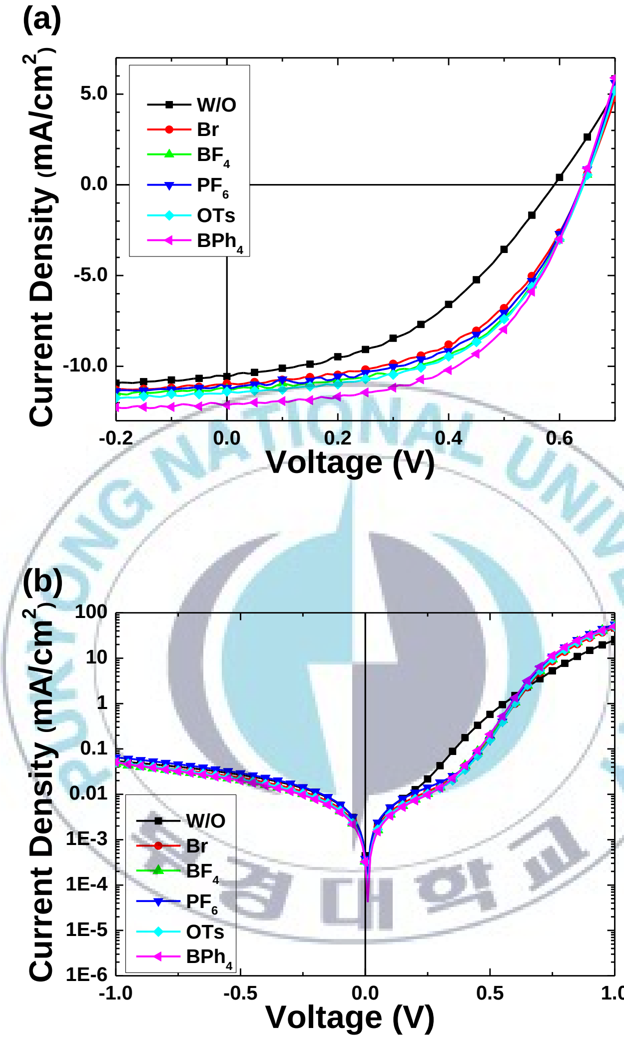


Figure IV-3. Current density–voltage curves of PV12 derivatives (a) under AM 1.5Gsimulated illumination with an intensity of 100 mW/cm^2 and (b) under the dark condition.

Table IV-2. The best photovoltaic parameters and efficiencies of OSCs with PV12 derivatives. The averages for photovoltaic parameters of each device are given in parentheses with mean variation.

	V_{oc} (V)	**J_{sc} (mA/cm^2)**	**FF (%)**	**PCE (%)**	**R_s(Ω•cm^2)^a**	**R_p(kΩ•cm^2)^a**
w/o CBL	0.59	-10.9 (-10.7±0.23)	44.2 (43.9±1.22)	2.85 (2.74±0.12)	5.09	18.3
With PV12-Br	0.64	-11.0 (-10.6± 0.25)	51.6 (50.5 ± 1.39)	3.62 (3.41 ± 0.13)	3.06	21.7
With PV12-BF_4	0.64	-11.2 (-11.1 ± 0.28)	53.7 (51.8± 2.08)	3.86 (3.67 ± 0.13)	2.77	23.9
With PV12-PF_6	0.64	-11.1 (-11.1 ± 0.03)	52.1 (50.4 ±1.15)	3.73 (3.59 ± 0.10)	2.72	16.8
With PV12-OTs	0.64	-11.4 (-10.9 ± 0.37)	53.5 (51.4 ± 1.86)	3.90 (3.61 ± 0.14)	2.82	22.9
With PV12-BPh_4	0.64	-12.1 (-11.3 ± 0.43)	53.9 (53.0 ± 0.8)	4.19 (3.82 ± 0.13)	3.66	24.2

[a] : series resistnace (estimated from the devices with best PCE value).

[b] : paralell resistance (estimated from the devices with best PCE value).

IV-4. Conclusions

PV12 derivatives were used as the CBL with Al cathodes. The work function of Al is reduced by the formation of interfacial dipole. The J_{sc} of OSC with PV12 derivatives will be strongly affected by the CA, because R_p is influenced by type of CA in PV12 derivatives. The contact property of OSC with **PV12-BPh$_4$** is the best in OSC with PV12 derivatives. Therefore, the performances of OSC with **PV12-BPh$_4$** are highest in OSC with PV12 derivatives

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감사의 글

논문이 나올 때까지 많은 일이 있었습니다. 좋고 즐거운 일도 있었습니다. 하지만 반대로 힘들고 싫은 일도 있었지만 저를 믿어주고, 이끌어주며, 곁에서 지켜 봐주신 분들이 있으셨기에 논문을 완성 할 수 있었던 것 같습니다.

우선 지난 2년 동안 저를 한결같이 뒷받침 해주신 어머니께 감사의 말 전합니다. 이 논문을 완성 할 수 있었던 것은 어머니께서 믿어 주셨기 때문에 가능했던 것이라 생각 합니다. 아직 많이 부족하지만 앞으로 더 멀리 나갈 수 있도록 지지 해 주시고 믿어 주실 것이기에 그 믿음에 보답하도록 노력하겠습니다.

이래저래 많은 조언을 해줬던 형. 아직 형보다 어리고 더 모르기 때문에 이것저것 걱정이 많이 되어서 조언을 많이 해주고 내가 이루고자 했던 목표를 이룰 수 있도록 도와 줬기에 무사히 석사 과정을 마칠 수 있었다고 생각합니다.

지도 교수님인 김주현 교수님. 이 논문은 교수님께서 저를 이끌어 주셨기에 완성할 수 있었습니다. 가장 힘든 시기여서 많이 방황도 했고, 아는 것이 적어 손봐야 할 곳이 많은 저를 받아 주셔서 감사합니다. 또한, 항상 걱정만 끼쳐 드렸기에 죄송했으며, 그때마다 해주신 말씀 절대 잊지 않으며 살아가겠습니다. 앞으로 많은 일이 있겠지만 좋은 소식으로 교수님께 찾아 뵐 수 있도록 노력하겠습니다.

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지가 되어서 고마웠고, 동기로서 재대로 도움을 주지 못한 것 같아서 미안했다. 둘 다 힘내서 좋은 곳으로 가도록 노력하자. 종현이는 아직 많이 남았고 힘든 것도 많이 있을 거지만 너라면 잘 견딜 수 있을 거야. 그리고 준환이하고, 경은이 선배로서 동기로서 잘 대해주라. 한번씩 심하게 아픈 경은아. 내년엔 아프지 말고, 건강하게 보내고, 좀 더 잘 가르쳐 줬어야 하는데 그러지 못한 것 같다. 하지만 힘내고 성과는 꼭 나올 거야. 지금 실험실 서열로 막내인 준환아. 앞으로 하고 싶은 것 보다 해야 하는 것에 집중해야 할거야. 해야 할 것이 많아서 힘들겠지만, 잘 이겨내고, 이겨내면 분명 많은 도움이 될 거야.

신웅 형님. 비록 많은 말은 나누었던 것은 아니었지만 형님께서 해주셨던 말이 저로 하여금 많은 생각을 가지게 하였습니다. 그래서 정말 감사하다는 말 드리고 싶습니다. 정배 형님, 갑자기 전화해도 잘 받아주시고, 힘내라 말해주셔서 감사했습니다. 상준 형님, 형님 기대 만큼 못해서 실망도 많이 하셨을 건데, 그런 내색 한번도 내비치시지 않고 한결 같이 대해주셔서 감사했습니다. 아직까지도 어색한 혜리 누나. 다음에는 안 어색하도록 노력 할게요, 그리고 준휘 형하고, 대성이 형 늘 힘내라 해주고 아무것도 몰랐던 1년차 때 많이 도와 주셔서 고마웠습니다.

동철, 경완, 창엽, 병수야. 자주는 못 만났지만 만날 때 마다 늘 좋았었고, 각자 다른 학교에서 열심히 하고 있었기 때문에 더 만나기가 힘들었던 것이라 생각한다. 앞으로 더 보기 힘들 수도 있지만 종종 연락할게. 서로 힘들 때 힘이 되도록 노력하자. 동인아. 너한테는 고맙다는 말밖에 할게 없구나. 서로 술을 잘 안 먹었지만 많은 말을 나누었고 그 말을 통해서 힘을 많이 얻었던 것 같다. 지윤, 효진, 은우. 정말 대책 없는 우리지만, 서로 힘이 되고, 도움이 되었으면 한다. 솔직히 말해서 이런 말 하는 자체가 낯간지럽네. 대학동기들인 원중, 현정, 유선. 내가 가장 마지막으로 취업 전선에 나가게 되네. 취업하고 나면 꼭 한턱 살게

그 때까지 종종 만나고 연락하고 지내자. 그리고 민호, 도길, 동욱, 혜리, 지현아. 자주 연락은 안 했지만 늘 생각하고 있다. 함께 모일 때도 개인 사정으로 잘 참석 못했지만, 다음부턴 잘 참석 하도록 할게.

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