Thesis for the Degree of Master of Engineering

Design, Synthesis and Photovoltaic Properties of Novel Conjugated Copolymers with Fluorinated Quinoxaline for OPVs

by

Yeongkwon Kang

Department of Industrial chemistry

The Graduate School

Pukyong National University

February 2016

Design, Synthesis and Photovoltaic Properties of Novel Conjugated Copolymers with Fluorinated Quinoxaline for OPVs

(유기태양전지를 위한 플로로기를 치환한 퀴녹살린을
포함한 새로운 공액고분자의 설계와
합성과 특성)

Advisor: Prof. Youngeup Jin

by
Yeongkwon Kang

A thesis submitted in partial fulfillment of the requirements
for the degree of

Master of Engineering

in Department of Industrial Chemistry, The Graduate School,
Pukyong National University
February 2016

Design, Synthesis and Photovoltaic Properties of Novel Conjugated Copolymers with Fluorinated Quinoxaline for OPVs

A dissertation

by

Yeongkwon Kang

Approved by:

(SeongSoo Park)

(GunDae Lee)

(Youngeup Jin)

February 26, 2016

Contents

List of Figures

List of Tables

List of Schemes

유기태양전지를 위한 플로로기를 치환한 퀴녹살린을 포함한 새로운 공액고분자의 설계와 합성과 특성

강영권

부경대학교 대학원 공업화학과

요 약

지하자원이 점점 고갈됨에 따라 세계 각국에서는 대체 에너지에 대해 관심을 가지고 있다. 그 중 태양 에너지를 이용한 태양전지 같은 경우에는 원자재 값이 들지 않는 장점 때문에 많은 연구가 진행되고 있다. 실리콘을 사용해서 만든 무기태양전지 같은 경우 에너지 변환 효율이 뛰어나지만 가격이 비싸다는 단점을 가지고 있는 반면 유기 태양 전지 같은 경우 저가격 대면적 생산이 가능하고, 유연성을 가질 수 있는 장점을 가지고 있어 가장 각광 받고 있는 분야이다. 최근 연구에 의하면 Bulkheterojunction(BHJ) 고분자 태양전지 같은 경우 10% 이상의 효율을 가지고 있다는 것이 보도되었다. 높은 효율을 내기 위해서는 고분자의 빛의 흡수량을 늘리는 것이 중요하고 이는 고분자가 좁은 밴드갭을 가지고 있어야 한다. 그리하여 본 연구에서는 좁은 밴드갭을 만들기 위해 Electron-acceptor로써 Quinoxaline 유도체를 사용 하였고 이에 치환기로 Fluorine을 0개, 1개 그리고 2개를 도입했다. 또한 Solubility를 높이기 위해 2개의 dodecyl기를 도입했다. 또한 분자 내 전하이동을 높이기 위해 Electron-donor로써 Thiophene 시리즈와 Fluorene과의 D-A Alternating 구조로 합성해 새로운 고분자를 만들었다. 이로 인해 고분자를 이용한 유기태양전지에서 Fluorine을 치환한 Quinoxaline과 Thiophene 그리고 Fluorene의 역할에 대해서 연구를 진행 하였다.

Chapter I. Introduction

I-1.The Background of Polymer solar cells (PSCs)

Solar cells based on organic materials have been considered as one of the most successful approaches to solve these global energy issues. Compared with polymer solar cells, inorganic based solar cells have been widely investigated because of their high energy conversion efficiency. Nonetheless, production cost of inorganic solar cells has blocked their wide spread commercialization. There were many advantages of organic photovoltaic cells, in comparison with inorganic solar cells, such as light weight, flexibility and low cost according to application of solution process.

The most widely used device structures of polymer solar cells (PSCs) involves the concept of bulk heterojunctions (BHJs). BHJs solar cells were composed of conjugated polymer as donor and fullerene derivative as acceptor by blending between transparent indium tin oxide (ITO) and metal electrode. These solar cells achieved impressive progress of power conversion efficiencies (PCEs) over 10%. Commonly, the energy conversion of PSCs device from light energy to electrical energy experienced four fundamental steps: 1) photoexcitation and exciton formation, 2) excitons diffusion to the interface of the p-n junction, 3) exciton dissociation, 4) charge transport and collection. The PSCs are required several properties to increase PCE. First, introducing donor-acceptor (D-A) alternating structure can increase intramolecular charge transfer (ICT). Second, the polymers should have low band gap to absorb long range wavelength and should have a good hole-mobility for effective charge collection. Third, enhancing planarity of polymer backbone increases π-π interaction. Finally, some additives can improve phase separation of active layer in BHJ devices. These factors affect the characteristics of PSCs and determine PCEs of the devices, and the PCE of BHJ solar cells has been steadily increasing.

Figure I-1. Representative materials of PSCs.

I-2. Operating Principles of PSCs

The process of PSCs from light absorption to energy conversion can be schematically described by the following step. The general operating principle in the BHJ solar cells is shown in Figure (I-2). The first step is absorption of a photon leading to the formation of an excited state, that is, the exciton creation. These excitons diffuse to the interface of donor acceptor (D-A) where exciton dissociation occurs via an electron-transfer process. The ideal exciton diffusion length in a PSCs is around 10-20nm. If excitons do not reach the donor-acceptor interface, this excitons recombine and the absorbed energy is dissipated without generating photocurrent. The completely separated free charge carriers transport to the respective electrodes in the counter direction with the aid of the internal electric field, which in turn generates the photocurrent and photovoltage.

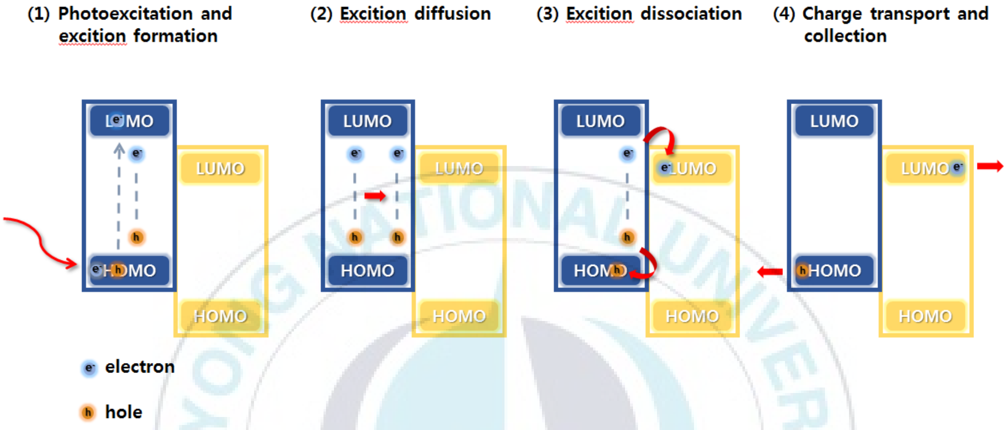


Figure I-2. Working mechanism for donor-acceptor heterojunction solar cells.

I-3. Device Structures of PSCs

I-3-1. Single layer Polymer Solar Cells

Single-layer OSCs are the simplest form. An organic photovoltaic cells consist of a single polymer layer sandwiched two different electrode, typically a layer of ITO with high work function and a layer of low work function metal such as aluminum. OSCs based on conjugated polymers were used in this type of photovoltaic cell. This device used polyacetylene as the organic layer and sandwiched Al and graphite. The reported open circuit voltage and a charge collection efficiency are 0.3V and 0.3%, respectively.

I-3-2. Bilayer Devices

Bilayer cells contain n-type and p-type semiconductors between the conductive electrodes.[1-10] An organic solar cells based two layer were first realized by C. W. Tang in 1985. The reported PCE was 1% under simulated AM^2 conditions. The layer with higher electron affinity and ionization potential is the electron acceptor, and the other layer is the electron donor. This structure is also called a bilayer heterojunction device. The $PC_{60}BM$ is good acceptor because of high electron affinity. A double layer cell based on C_{60}/MEH-PPV had a relatively high fill factor of 0.48 and a PCE of 0.04% under monochromatic illumination. Bilayer device using PPV/C_{60} cells displayed a monochromatic external quantum efficiency of 9%, a power conversion efficiency of 1% and a fill factor of 0.48.

I-3-3. Bulk Heterojunction Polymer Solar Cells

Bulk heterojunctions polymer solar cells have an absorption layer consisting of a nanoscale blend of electron donor (D) and electron acceptor (A) materials. The layer consisting of wide D-A interfacial area results in a higher likelyhood for the short-lived excitons to reach an interface and dissociate. Bulk heterojunctions polymer solar cells are manufactured by forming a solution containing the two parts, casting and then permitting the two phases to separate. The donor part and acceptor part will self-assemble into an interpenetrating network linking the two electrodes.

A bulk heterojunction polymer solar cells are composed of polymer as donor and fullerene derivative as acceptor. The morphology of nanoscale at bulk heterojunctions polymer solar cells tends to be difficult to control. After the catch of a photon, electrons transfer to the acceptor domains then are moved through the device and collected by one electrode, and holes transfer in the opposite direction and collected at the other side. If the dispersion of donor and acceptor is too fine, it will result in poor charge transfer through the layer. [11]

The polymer solar cells based on bulk heterojunction devices are much more sensitive to the nanostructure morphology in the blend. The bulk heterojunctions devices can be accomplished by co-deposition of donor and acceptor pigments[12] or solution casting of either polymer/polymer,[13,14] polymer/molecule,[17] or molecule/molecule[15,16] donor-acceptor blends.[17]

Heterojunction photovoltaic cells using MEH-PPV and a methano-functionalized C_{60} derivative displayed a monochromataic quantum efficiency of 29% and a power conversion efficiency of 2.9%. Replacing MEH-PPV with P3HT produced a quantum yield of 45% under a 10 V reverse bias.[18,19]

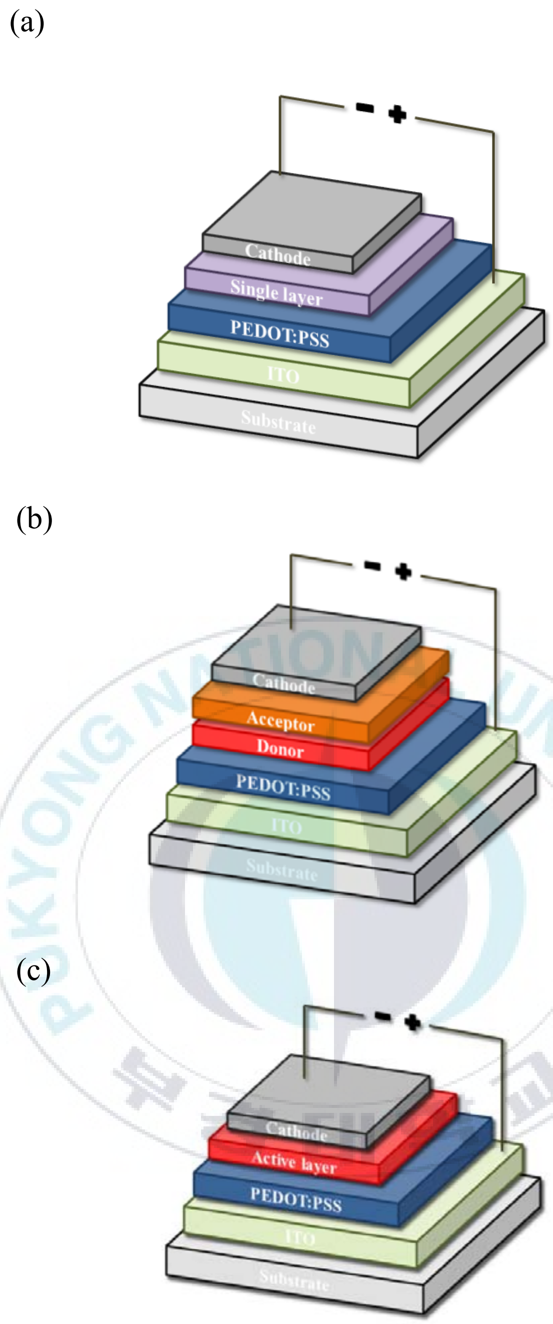


Figure I-3. Structures of (a) single-layer device (b) bilayer device and (c) bulk hetero junction device.

I-4. Parameters of PSCs

In PSCs, the power conversion efficiency (PCE) is decided by an open-circuit voltage (V_{oc}), a short-circuit current (J_{sc}), and fill factor (FF). The efficiency of a PSC is given by $\eta = V_{oc} \times J_{sc} \times FF$. The explanation about parameters is indicated in Figure I-4.

I-4-1. Open-Circuit Voltage (V_{oc})

The open-circuit voltage (V_{oc}) is the maximum voltage available from a solar cell, and this occurs at zero current. V_{oc} is related to the difference between the highest occupied molecular orbital (HOMO) energy level of a donor and the lowest unoccupied molecular orbital (LUMO) energy level of an acceptor.[17] So the polymer design is one of the key factors for improving V_{oc} of the PSCs. Designing an alternated copolymer backbone is the most common methods to obtain improved intra-molecular charge transfer. In this reason, using the polymers with low-lying HOMO levels could achieve higher V_{oc}. However, if HOMO level of donor polymer is very low that would not be effective. The reason for that is because commonly a minimum energy difference of ~0.3 eV between the LUMO energy levels of the acceptor and the donor polymer is required to forward effective exciton dissociation and charge separation. Continually lowering the HOMO level of the donor polymer would expand the band gap of the donor polymer, declining the light absorbing ability of the donor polymer. Also the V_{oc} of the organic solar cells is influenced by work function of the electrodes.[18]

I-4-2. Short-Circuit Current Density (J_{sc})

The Short-Circuit Current Density (J_{sc}) is the current available from a solar cell, and this occurs at zero voltage. And the J_{sc} commonly depend on the morphology of the active layer, charge transport, intermolecular interaction, hole/electron mobility and molecular chain packing. Therefore, In order to increase J_{sc}, active layer should make by highly crystalline morphology and tune the band gap at low.[19,20,21] Since fullerene derivative has a low absorption in the visible and near-IR region therefore the donor polymer is key factor to achieve high light absorption.

Because approximately 70% of the sunlight energy is focused on the wavelength range from 380 to 900 nm, the most ideal donor polymer should have a broad and strong absorption spectra.[19] The polymer band gap of 1.4 ~ 1.5 eV is required because of this reason.

A polymer having narrow band gap can absorb more sunlight energy, which would increase the J_{sc}; but, continuously lowering the band gap necessarily results in high HOMO level of the donor polymer. The low band gap polymer increase J_{sc}, however reduces V_{oc}.

I-4-3. Fill Factor (FF)

And the FF is defined as ratio between the maximum obtainable power and the product of J_{sc} and V_{oc}. This FF is influenced by many factors, such as charge carrier mobility and balance, interface recombination, film morphology and miscibility among the donor and acceptor. In respect to material development, planarity of backbone, intermolecular interaction, molecular packing and crystallinity are also important. Side-chain can tune π-stacking, polymer crystallinity and material miscibility, by controlling steric hindrance of polymer backbone. This being so, side-chain selection is important for achieving high FF.

.

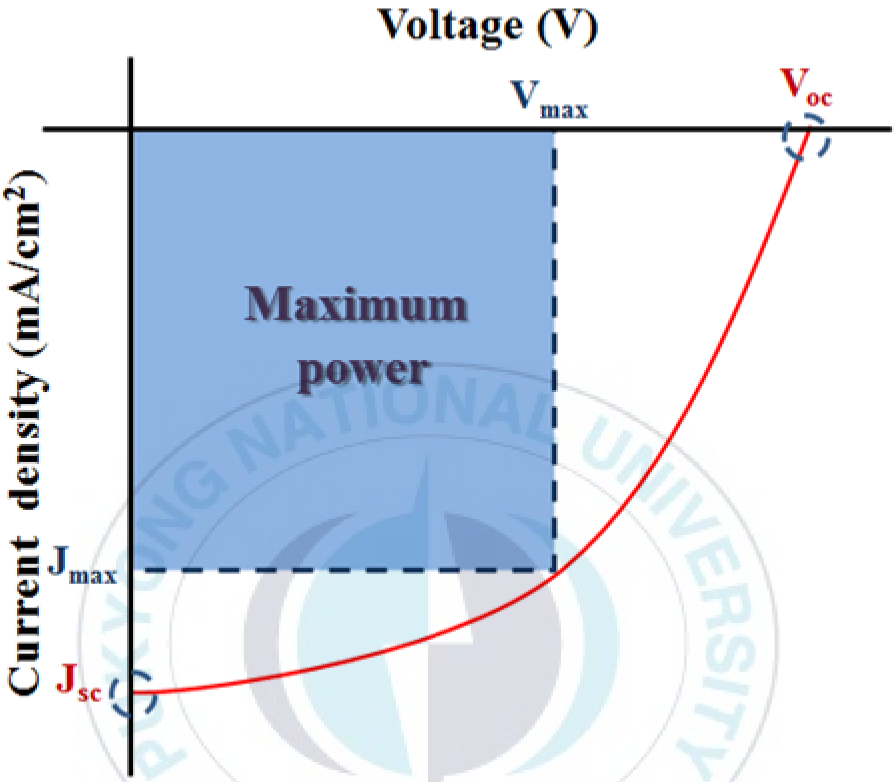


Figure I-4. Graph of an open-circuit voltage (V_{oc}), a short-circuit current (J_{sc}), and fill factor (FF).

I-4-4. Requirements for Materials in PSCs

As described above, it would be important to obtain a high value of fill factor, external quantum efficiency and optimized nanostructure morphology. If PSCs based on polymer:PCBM have a fill factor of 0.65, external quantum efficiency of 65% and an enhanced nanoscale structure that is indicated a PCE of 10%. An ideal material of polymer has narrow band gap of 1.5 eV and proper HOMO energy level around -5.4 eV. In order to realize the ideal PSCs, several conditions are required. (1) Excellent solubility due to the influence on the chain, (2) high molecular weight and good PDI ratio, (3) HOMO energy level and LUMO energy level should indicate around -5.4 eV and -3.9 eV, respectively, (4) high hole mobility, (5) improved morphology system and (6) long-time stability.

I-5. Strategies to Synthesize Conjugated Polymers for High Performance.

I-5-1. Donor-Acceptor (D-A) Alternating Structure

Organic photovoltaic cells based on donor-acceptor (D-A) alternating conjugated polymers were extensively developed. Recently, polymer solar cells used D-A alternating conjugated polymer reported PCE over 11%. The repeating unit of D−A polymers comprises of an electron-rich as donor and an electron-deficient as acceptor moiety. It is fairly easy to construct narrow bandgap polymers with tunable energy levels via the donor−acceptor (D−A) approach. This molecular prototype commonly leads to linear structure with a rigid backbone, which requires cautiously optimized side chains to approach proper intermolecular interactions that will ensure process ability and charge transport properties. This strategy was first proposed in 1993.[22,23] The internal charge transfer (ICT) intrinsic with the D−A alternating structure leads to more advantageous double bond feature between repeating units. The principle of band gap and energy level control by ICT interaction in D-A structure can be explained without difficulty by molecular orbital theory. (As shown in Figure I-5) The D-A conjugated polymer backbone adopts a more planar configuration to forward the π-electrons delocalization along the conjugated backbone, leading to a smaller band gap. One distinctive characteristic of the D-A conjugated polymer is that the HOMO and LUMO energy levels are mainly localized on the donor moiety and the acceptor moiety, respectively. Therefore, this feature leads to many advantages such as low band gap and proper energy levels.[24] For instance, the narrower band gap can be obtained by copolymerizing a more electron-rich donor moiety and a more electron-deficient acceptor moiety, while the HOMO and LUMO levels can also be adjusted by varying the electron donating ability of the donor moiety and the electron affinity of the acceptor moiety.[24]

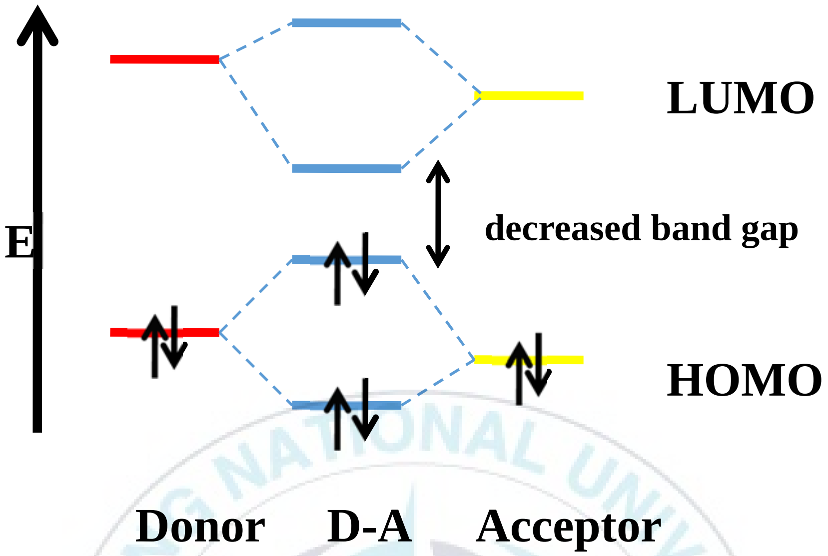


Figure I-5. Molecular orbital interactions of donor and acceptor units, resulting in a narrowing of the band gap in D-A conjugated copolymers.

I-5-1-1. Selection of Donor Unit in Conjugated Polymer

The fluorene (FL) unit is a typical rigid and planar polycyclic aromatic structure, which displays good thermal, optical and optoelectronic performances. Moreover, possible dialkylation at 9-position and selective bromination at the 2,7-positions of fluorene permit versatile molecular manipulation to accomplish excellent solubility and extended conjugation via archetypal Suzuki or Stille cross-coupling reactions.[26] Fluorene and its derivatives have been widely investigated for their application Organic electro luminescence(OLED) due to balanced carrier transporting properties, high photoluminescent quantum efficiency and facile color tenability.[27] In photovoltaic utilization, fluorene block has been introduced as weak donor block with electron-deficient unit, such as quinoxaline (QX), benzothiadiazole (BT), diketopyrrolopyrrole (DPP), etc., for constructing narrow bandgap conjugated copolymers.

In recent reports, thieno[3,2–*b*]thiophene (TT) unit was widely used to substitute thiophene for narrow the band gap of conjugated polymers and large absorption spectra to catching more photons.[28,29] Synchronously, fused thieno[3,2–*b*]thiophene units with more coplanar structure promote a more delocalized HOMO distribution along the main backbone, which lead to an improved intermolecular charge–carrier hopping.[30,31] This result predicts that thieno[3,2–*b*]thiophene is a promising donor for D–A type polymer solar cells.

Thiophene is a material which is used advantageously in polymer solar cells.

Polythiophene as donor at D-A alternating structure is expected to reduce the HOMO energy level, resulting in a higher stability of the polymers against photooxidation and oxidation.[32,33] V_{oc} of polythiophene will be higher than thiophene, because V_{oc} is related to the difference between the HOMO energy level of a donor and LUMO energy level of an acceptor.

I-5-1-2. Selection of Acceptor Unit in Conjugated Polymer

Recently, the most commonly used monomer as acceptor unit is the 2,1,3-benzothiadiazole (BT) due to its commercial availability and strong electron-accepting ability. BT as acceptor unit has been popular electron accepting building block for achieving low-band-gap conjugated polymers. In addition, these two nitrogen(N) atoms in the thiadiazole ring could perhaps form hydrogen bonding with neighbouring units (e.g., the hydrogen atom on the thiophene ring), leading to improved planarity of backbone. Because of these advantages, many polymers using a BT have indicated low band gaps and excellent photovoltaic performance. Quinoxaline(Qx) is also a typical electron-deficient unit with strong electronegativity because of the two nitrogen atoms in it.[34,35,36,37,38] The electron-withdrawing ability of Qx is slightly weaker than that of BT, which would lead to a little larger band gaps for the resulting polymers. As the alkyl groups are introduced to Qx, solubility of the polymers improves. One of the significant merit of quinoxaline is that the low-lying HOMO levels can be maintained for the resulting polymers, which will be beneficial for not only the chemical stability of the polymer but also for achieving a high V_{oc}. The introduction of fluoro group onto Qx has been proven to be an efficient method to reduce HOMO and LUMO levels.[39] Composing one thienyl group on both sides of the Qx, it becomes 5,8-di(thiophen-2-yl)quinoxaline (DTQx), which has a few more merit in distinction with the fundamental Qx unit. Introduction of side chain such as thiophene reduce steric hindrance between the Qx unit and donor unit and improve the hole mobility of polymer.[40,41]

I-6. General Method for Synthesis of Conjugated Polymers

I-6-1.Stille Coupling Reaction

The Stille coupling is an all-purpose carbon-carbon bond forming reaction between stannanes and halides or pseudohalides. This coupling reaction uses palladium as catalyst. The mechanism of the Stille coupling reaction is one of the most widely studied pathways for coupling reactions.[42] This figure is basic catalytic cycle. This mechanism entail oxidative addition of a palladium catalyst (1) and to halide or pseudohalide (2), transmetalation of (3) with an organo-tin reagent (4), and reductive elimination of (5) to yield the coupled product (7) and the regenerated palladium catalyst (1).[43]

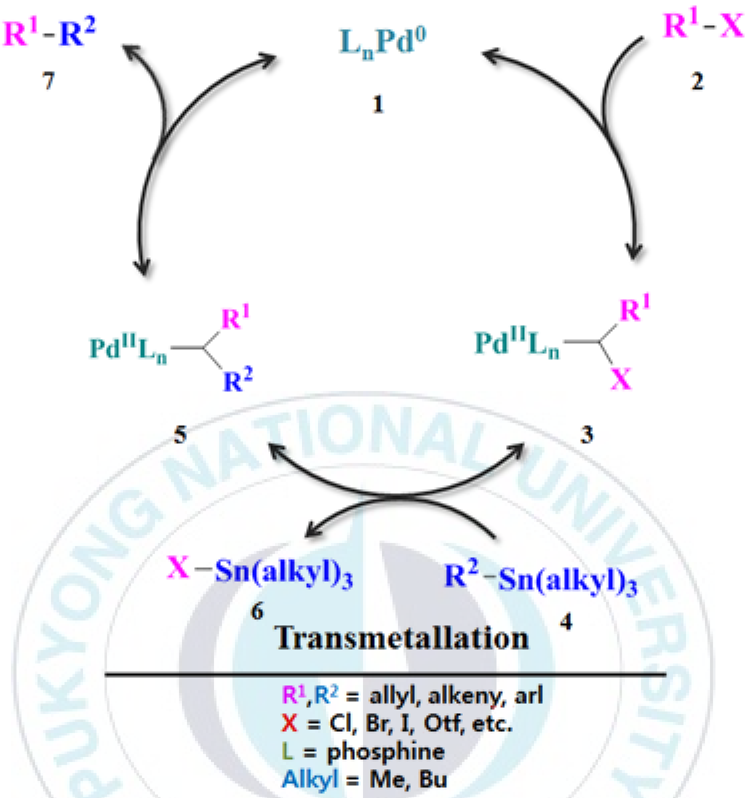
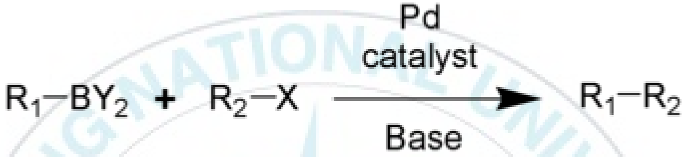


Figure I-6. Stille coupling reaction mechanism.

I-6-2. Suzuki Coupling Reaction

The coupling of aryl halides with organoboron specie is one of the most critical palladium-catalyzed cross-coupling reactions. Advantages of Suzuki reaction are mild reaction condition, tolerance of activative functional group, insensitivity to moisture and low toxicity. The scheme for the Suzuki reaction is indicated below. The material forms a carbon-carbon single bond by coupling between an organoboron species (R1-BY2) and a halide (R2-X) using a palladium catalyst and a base.



$$R_1{-}BY_2 + R_2{-}X \xrightarrow[\text{Base}]{\text{Pd catalyst}} R_1{-}R_2$$

The mechanism of the Suzuki reaction is shown below. This mechanism entails the oxidative addition of halide (2) to palladium cat. to construct the organo-palladium species (3). Reaction with base gives middle (4), which via transmetalation with the boron-ate compound (6) construct the organo-palladium species (8). The desired product (9) is formed via reductive elimination and palladium catalyst regenerate.

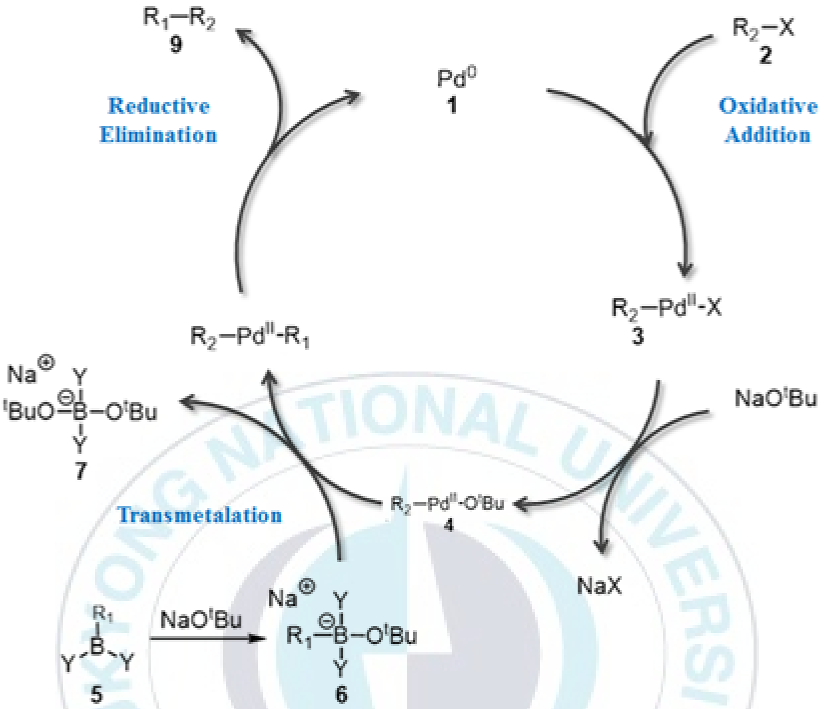


Figure I-7. Suzuki coupling reaction mechanism.

Chapter II. Experimental

II-1. Materials and Instruments

All reagents needed for the experiment were purchased from the Aldrich, TCI or Alfa. Flash column chromatography used Merck silica gel 60 (particle size 230-400 mesh ASTM) as stationary phase and ethyl acetate / hexane / methylene chloride as mobile phase. Analytical ^{1}H and ^{13}C NMR spectra were obtained using a JEOL JNM ECP-400 spectrometer. $CDCl_3$ and DMSO-d_6 with TMS (tetramethylsilane) were used as the internal standard. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV254. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) or fast atom bombardment (FAB) conditions in the Pukyong National University (Busan, Korea). Elemental analyses (EA) were performed by Flash EA 1112 Series. The UV-vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer. The CV was performed with a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6;0.10 *M*) in acetonitrile at a scan rate of 100 mV/s at room temperature. Pt wire and $Ag/AgNO_3$ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the $Ag/AgNO_3$ reference electrode (calibrated by the FC/FC^{+} redox system) was 4.80 eV below the vacuum level. HOMO levels were calculated according to the empirical formula (E_{HOMO}= - ([E_{onset}]$_{ox}$ + Fc/Fc+ redox potential eV). For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. The solution of the PEDOT:PSS in aqueous isopropyl alcohol was spin-coated on the surface-treated ITO substrate and dried on a hot plate for 30 min at 110 °C. On top of the PEDOT:PSS layer, the film of photoactive layer was obtained by spin casting o-dichlorobenzene solution blended with polymer and PCBM. The film was dried in vacuum, and aluminum electrodes were deposited on the top of the small molecule films through a mask by vacuum evaporation at pressures below 10^{-7}Torr, yielding active areas of 4 mm^2.

II-2. Synthesis of donor monomer

II-2-1. Synthesis of Donor Monomers

II-2-1-1. Synthesis of 2,7-dibromofluorene (2)

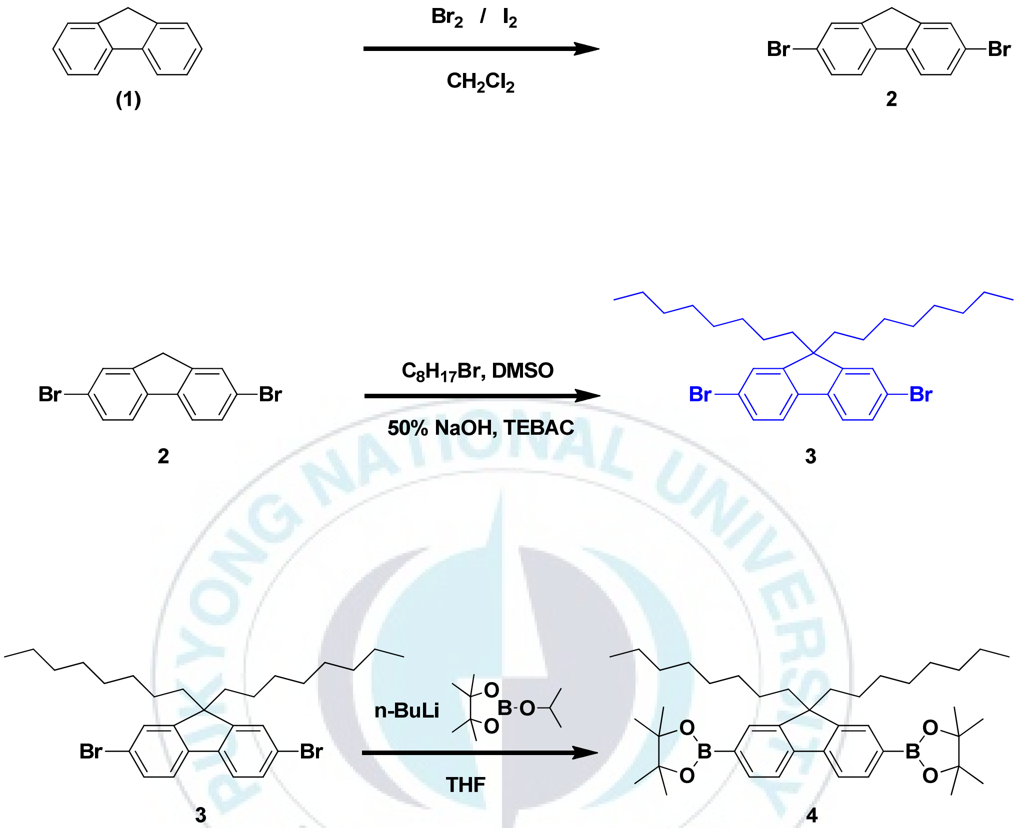
To a mixture of fluorene (10 g, 60.16mmol), iodine (0.016 g, 0.001 mol), and CH_2Cl_2 (100 mL), bromine (6.23 mL, 121.52mmol) diluted with CH_2Cl_2 (20 mL) was added dropwisely at 0 °C over a period of 1 h. After 12 h, a solution of sodium bisulfite (3.0 g) in water (20 mL) was added and the mixture was stirred for 30 min to become colorless. The organic phase was separated and washed with water (150 mL). The organic phase was dried over anhydrous $MgSO_4$ and CH_2Cl_2 was distilled off. The product slurry was filtered and the product was dried under vacuum. A white solid 15.28 g. ^1H NMR ($CDCl_3$, 500 MHz, δ): 7.62 (s, 2H), 7.58 (d, 2H), 7.48 (d, 2H), 3.83 (d, 2H).

II-2-1-2. Synthesis of 2,7-Dibromo-9,9'-dioctyl-9H-fluorene (3)

To a solution of 2,7-dibromofluorene (10 g, 30.86mmol) and tetrabutylammonium bromide (0.12 g, 0.52mmol) in DMSO (70 mL), octylbromide (13.72 g, 77.15mmol) was added. The mixture was stirred at 80 °C for 2 h and then poured into water (100 mL). The mixture was extracted two times with diethyl ether and the combined organic phases were washed with brine, water and dried over $MgSO_4$. Upon evaporating off the solvent the residue was purified via column chromatography with n-hexane as eluent to afford a white solid, which was recrystallized from ethanol at -20 °C to afford white crystals (90.6%). ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 7.52 (d, 2H), 7.46 (dd, 2H), 7.43 (d, 2H), 1.87-1.95 (m, 4H), 1.00-1.29 (m, 20H), 0.83 (t, 6H), 0.50-0.68 (m, 4H).

II-2-1-3. Synthesis of 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)-bis[4,4,5,5-tetramethyl-[1,3,2]dioxaborolane] (4)

A solution of 2,7-Dibromo-9,9'-dioctyl-9H-fluorene(3 g, 5.32mmol) in anhydrous THF (50 ml) was added to n-BuLi (1.6 M in hexane, 7.32 ml) at -78°C. The reaction mixture was stirred for 1 h before 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2.53 ml, 12.79mmol) was added in one portion. The mixture was warmed to room temperature, stirred overnight and poured into a large amount of water for extraction with methylene chloride. The organic extracts were washed with brine and dried over $MgSO_4$. Recrystallization of the crude product in methanol. white solid (yield: 3.11g, 90.94%). ^{1}H NMR ($CDCl_3$, 300MHz, δ): 0.50-0.60 (4 H, m), 0.81 (6 H, t) 0.96-1.23 (20 H, m), 1.39 (24 H, s), 1.95-2.05 (4 H, m), 7.72 (2H, d), 7.75 (2 H, s), 7.81 (2 H, dd).



Scheme 1. Synthetic route of donor monomer (FL).

II-2-1-4. Synthesis of 2,5-bis(trimethylstannyl)thiophene (6)

To a solution of 1 g (11.88 mmol) of thiophene in 40 mL of THF at -78 °C under argon was slowly added 27.95 mL (47.52 mmol) of 1.7M *t*-Butyllithium in THF. After 30 min at -78 °C, the reaction mixture was warmed to room temperature, stirred for 1 hr and cooled back to -78 °C. The reaction mixture was added 49.9 mL (49.9 mmol) of 1*M* trimethyltin chloride. After 30min at -78 °C, the reaction mixture was warmed to room temperature, stirred for overnight, treated with 20 ml of water. The reaction mixture was diluted with ether and washed with water. The combined organic phase was dried $MgSO_4$ after removal of the solvent under reduced pressure. The crude brown solid was recrystallized from ether/EtOH to give 1.02 g (28%) of compound **28** white solid. ^1H NMR ($CDCl_3$, 300MHz, δ): 7.37 (s, 2H), 0.34 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.39, 136.00, -9.02. HRMS (FAB^+, m/z) $[M]^+$ calcd for $C_{10}H_{20}SSn_2$ 411.9330, measured 411.9335.

II-2-1-5. Synthesis of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (8)

A solution of n-butyllithium (6.34mL, 15.84 mmol, 2.5 M in hexane) was added slowly to 2,2'-bithiophene (3 g, 18.04 mmol) in tetrahydrofuran (100 mL) at -78 °C. After addition, the mixture was stirred for 30 min at -78 °C, then warmed to 0 °C and stirred for 30 min. The mixture was cool to -78 °C again. Trimethyltin chloride solution (15.84 mL, 15.84 mmol, 1.0 M in hexane) was added to the mixture. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with addition of water (150 mL) and was extracted with diethyl ether for three times. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by recrystallization in ethanol to afford a grey solid (5.94 g, 66.94%). 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (6), yield 5.94 g, 66.94%. ^{1}H NMR (DMSO-d_6, 400MHz, δ): 7.33 (2H, d), 7.13 (2H, d), 0.35 (18H, s).

II-2-1-6. Synthesis of 2,5-Bis-trimethylstannyl-thieno[3,2-b]thiophene (10)

A solution of n-butyllithium (9.41 mL, 23.53 mmol, 2.5 M in hexane) was added slowly to thieno[3,2-b]thiophene (1.50 g, 10.70 mmol) in tetrahydrofuran (50 mL) at -78 °C. After addition, the mixture was stirred for 30 min at -78 °C, then warmed to 0 °C and stirred for 30 min. The mixture was cool to -78 °C again. Trimethyltin chloride solution (23.53 mL, 23.53 mmol, 1.0 M in hexane) was added to the mixture. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with addition of water (150 mL) and was extracted with diethyl ether for three times. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by recrystallization in ethanol to afford a white solid (3.10g, 58.73). ^{1}H NMR (DMSO-d_6, 400MHz, δ): 7.40 (2H, s), 0.35 (18H, s).

II-2-1-7. Synthesis of 2,5-Dibromothiophene (11)

A solution of n-bromosuccinimide (NBS) (8.46 g, 47.54mmol) in anhydrous DMF (60 mL) was slowly added dropwise in the dark to a solution of thiophene (2 g, 23.77 mmol) in anhydrous DMF (60 mL) at 0 °C. And the mixture was initially stirred at room temperature for 0.5 hr and then at 60°C for an additional overnight. The reaction was quenched with addition of water (150 mL) and was extracted with diethyl ether for three times. The combined organic phases were dried over anhydrous $MgSO_4$. Further purification was run by silica column with petroleum hexane to give an oily liquid. Yield: 5.21g (90.60%). ^{1}H NMR ($CDCl_3$, 300MHz, δ): 6.84 (s, 2H).

II-2-1-8. Synthesis of tributyl(thiophen-2-yl)stannane(12)

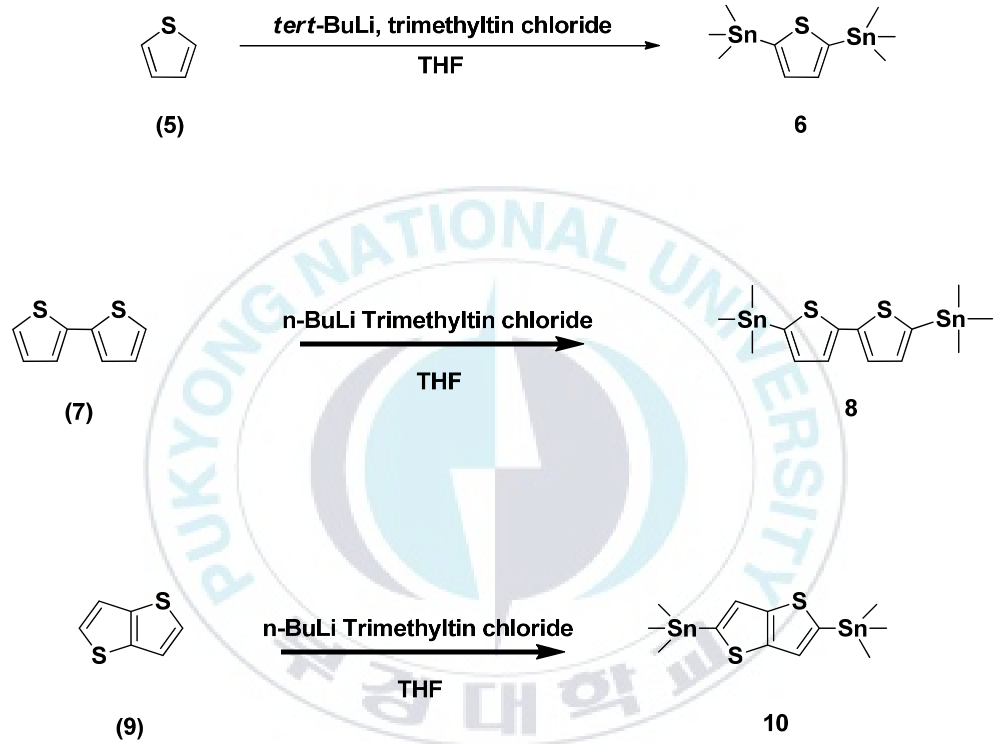
To a round bottom flask loaded with dry THF (30 mL), thiophene (5 ml, 63.57 mmol) was added and the mixture was cooled to -78 °C by acetone/dry ice bath. *n*-BuLi in hexane solution (1.6M, 26 mL) was added dropwise. After stirring at -78 °C for 1hr, tributyl tin chloride (12 ml, 42 mmol) was added dropwise and removed the dry ice bath immediately. After six more hours, the reaction was then terminated by adding saturated $NaHCO_3$ solution (100 ml) into the flask. the solvent was removed by rotary evaporation. The remaining oil was diluted with diethyl ether and washed with brine several times. The collected organic layer was dried over $MgSO_4$ and the organic solvent was removed by rotary evaporation. The collected orange oil was dried under vacuum for another 3h and used directly for the next step.

II-2-1-9. Synthesis of 2,2':5',2''-terthiophene (13)

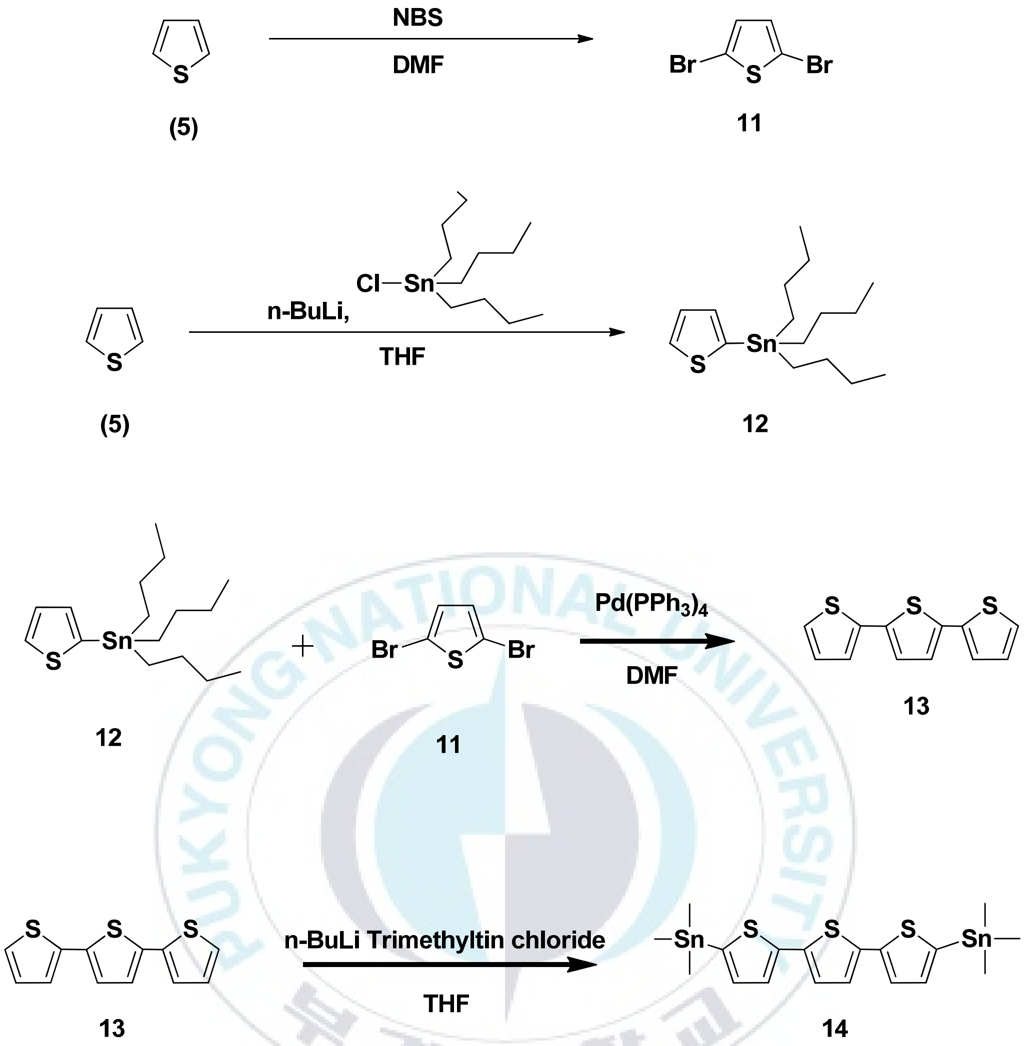
The solution of 2,5-dibromothiophene (2.94g, 12.15 mmol), 2-(tributylstannyl) thiophene (9.04g, 24.22 mmol) and tertrakis(triphenylphosphine)palladium(0) was dissolved in dimethylformamide (30ml). The mixture was stirred at 80 °C for overnight under argon atmosphere. The aqueous layers were extracted with diethylether, the combined extracts were washed with distilled water, dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. Recrystallization of the crude product in ethanol. Yellow solid (yield : 1.72g, 57.13%). ^{1}H NMR ($CDCl_3$, 300MHz, δ): 7.20 (dd, 2H), 7.15 (dd, 2H), 7.06 (s, 1H), 7.00 (dd, 2H).

I-2-1-10. Synthesis of 2,5''-Bis(trimethylsilyl)-5,2',5',2''-terthiophene (14)

To a solution of 2,5"-Dibromo-5,2',5',2"- terthiophene (2 g, 8.05 mmol) was dissolved in anhydrous THF (80 mL). The mixture was cooled to -78 °C and n-BuLi (7.08 mL, 2.5 M solution) was added dropwise. After the addition, the mixture was stirred at same temperature for 1 h. A solution of trimethyltin chloride (17.71 ml, 1 M) was added dropwise. After stirred overnight, the mixture was quenched with water. The aqueous layers were extracted with diethylether, the combined extracts were washed with distilled water, dried over anhydrous $MgSO_4$. the solvent was removed by rotary evaporation. Recrystallization of the crude product in ethanol. Yellow solid (yield: 2.60 g, 56.27 %). ^1H NMR ($CDCl_3$, 300MHz, δ): 7.39 (d, 2H), 7.21 (s, 2H), 7.16 (d, 2H), 0.36 (s, 1H).



Scheme 2. Synthetic route of donor monomer (2T and TT)



Scheme 3. Synthetic route of donor monomer (3T).

II-2-2. Synthesis of acceptor monomers

II-2-2-1. Synthesis of 2,3-difluoro-1,4-bis-(trimethylsilyl)benzene (16)

n-butyllithium (1.6 *M* in *n*-hexane, 120 mL, 192mmol) was added to a solution of di-isopropylamine (27 mL, 192mmol) in anhydrous THF (80 mL) at -78 °C. After stirring 30 min at -78 °C, 1,2-difluorobenzene (7.5 mL, 77mmol) and chlorotrimethylsilane (24 mL, 192mmol) were added to the solution at a rate which allowed the internal reaction temperature to remain below -50 °C. The solution was stirred at -78 °C for an additional 1 hr. 1 *M* H_2SO_4 solution (20 mL) was added and then extracted with diethyl ether (20 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to afford colorless needle-shaped crystals of compound **17** (19.0 g, 98%). ^{1}H NMR ($CDCl_3$, 300MHz, δ): 7.09 (s, 2H), 0.32 (s, 18H). LRMS (EI): m/z = 258 (M^+).

II-2-2-2. Synthesis of 1,4-dibromo2,3-difluoro-benzene (17)

To a neat bromine (5.3 mL, 103mmol) cooled to 0 °C was added portion wise solid 17 (8.9 g, 34.4mmol) while maintaining the internal temperature between 20 and 40 °C. The reaction mixture was stirred at 58 °C for 2 hr. After 1 hr of this period had elapsed, additional bromine (0.9 mL, 17.2mmol) was added. The reaction mixture was cooled to 0 °C and slowly poured into ice-cold saturated $NaHCO_3$ solution and extracted with diethyl ether (50 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to afford colorless liquid of compound **18** (9.2 g, 99%). ^{1}H NMR ($CDCl_3$, 300MHz, δ): 7.23 (m, 2H). LRMS (EI): m/z = 272 (M^+).

II-2-2-3. Synthesis of 1,4-dibromo-2,3-difiuoro-5,6-dinitro-benzene (18)

In a 500 mL flask, concentrated sulphuric acid (44 mL) was added and cooled to 0-5°C in an ice water bath. Fuming nitric acid (44 mL) and 2,3-difluoro-1,4-dibromo-benzene (8.8 g, 32.5mmol) were slowly added. Then, the flask was heated to 65°C for 14 hr. The mixture was then precipitated into ice water. The resulting yellow solid was filtered and purified by column with petroleum hexane/CH_2Cl_2 (4:1) to afford a white solid of compound **19** (3.4 g, 29%).

II-2-2-4. Synthesis of 3,6-dibromo-4,5-difluorobenzene-1,2-diamine (19)

To a solution of compound **19** (6.3 g, 17.5mmol) in ethanol (100 mL) and conc. HCl (60mL) was added $SnCl_2 \cdot 2H_2O$ (39.5 g, 175mmol) in several portions. The mixture was refluxed for 1 hr and stirred overnight at room temperature. Then, pH value of the mixture was adjusted to 8~9 by adding aqueous KOH solution. then the mixture was extracted with ethyl acetate three times. The combined organic phases were dried over anhydrous $MgSO_4$. Further purification was run by silica column with petroleum hexane/CH_2Cl_2 (1:1) to give a white-solid of compound **20** (4.6 g, 88%). ^{1}H NMR ($CDCl_3$, 300MHz, δ): 3.85 (s, 4H). ^{13}C NMR ($CDCl_3$, ppm):

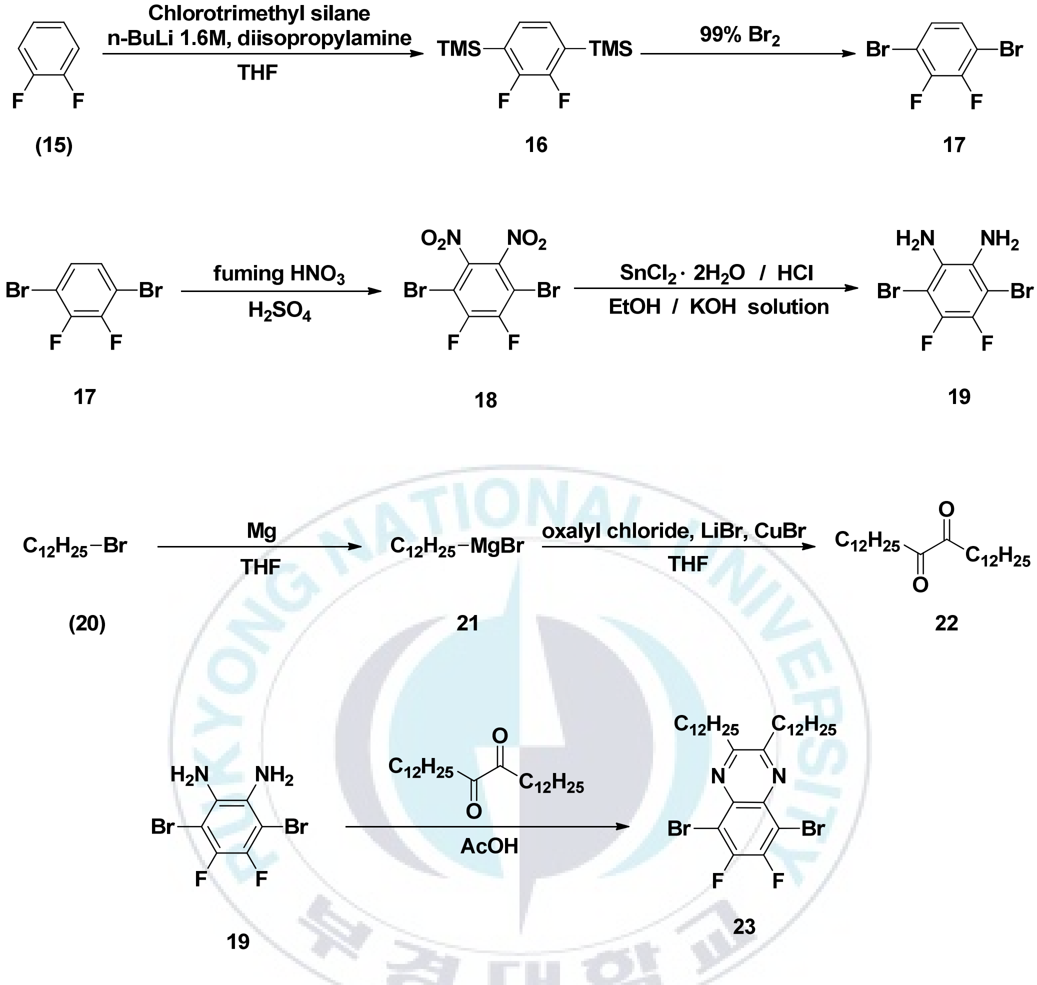
142.99 (d, J = 18.11 Hz), 141.06 (d, J = 17.65 Hz), 129.78, 98.39 (t). ^{19}F NMR ($CDCl_3$, ppm): -139.02. GC-MS (M^+, $C_6H_4Br_2F_2N_2$), cacld, 301.9; found: 302.

II-2-2-5. Synthesis of hexacosane-13,14-dione (22)

A Grignard reagent was prepared by the dropwise addition of the respective 1-bromododecane (12.21 ml, 51 mmol) to a stirred suspension of magnesium (1.85 g, 76 mmol) in THF (30 mL). In a separate flask, LiBr (8.05 g, 93 mmol) in THF (150 mL) was added to a stirred suspension of CuBr (7.31 g, 51 mmol) in THF (150 mL) to form a pale green suspension. This mixture was then cooled to -78 °C via a pentane/liquid nitrogen bath. The Grignard reagent was slowly added to the LiBr/CuBr suspension by cannula such that the temperature of the reaction mixture did not exceed -75 °C. Oxalyl chloride (2 ml, 23 mmol) was then added slowly via syringe to maintain a temperature below -70 °C. The mixture was stirred at -78 for 60 min, allowed to warm to room temperature and quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer extracted repeatedly with ethyl acetate. The combined organic layers were dried with anhydrous Na_2SO_4, concentrated by rotary evaporation, and separated on a silica column using a 10:1 hexane/methylene chloride mixture. The compound **23** was obtained as a yellow solid (5.36g, 58%). ^{1}H NMR ($CDCl_3$, 400MHz, δ): 2.70 (t, 4H, J = 7.38 Hz), 1.54 (m, 4H, J = 7.12 Hz), 1.23 (m, 36H), 0.85 (t, 6H, J = 6.84 Hz)

II-2-2-6. Synthesis of 5,8-dibromo-6,7-difluoro-2,3-didodecylquinoxaline (23)

The compound **20** (2.2 g, 7.3 mmol) and compound **16** (3.48 g, 8.8 mmol) were dissolved in acetic acid (60 mL). The mixture was refluxed overnight. After cooling to room temperature, the resultant mixture was poured into water and extracted with ethylacetate. After dried over $MgSO_4$ and purified by silica column with petroleum hexane to give a white solid of compound **24** (3.67 g, 66%). ^{1}H NMR ($CDCl_3$, 400MHz, δ): 3.03 (t, 4H, J = 7.66 Hz), 1.88 (m, 4H, J = 7.52 Hz), 1.24-1.44 (m, 36H), 0.86 (t, 6H, J = 6.84 Hz). ^{13}C NMR ($CDCl_3$, 600MHz, ppm): 158.16, 150.43(d), 135.75, 109.19, 34.62, 31.92, 29.58(m), 27.66, 22.69, 14.12.



Scheme 4. Synthetic route of acceptor monomer (DFQx).

II-2-2-7. Synthesis of 2,5-dibromo-4-fluoro-nitrobenzene (25)

To a solution of 1,4-dibromo-2-fluorobenzene (5.0 g, 19.7 mmol) in dichloromethane (16 mL), trifluoroacetic acid (8 mL), and trifluoroacetic anhydride (16 mL) at 0 ℃ was added NH_4NO_3 (2 g, 25 mmol) and then the mixture was then stirred at room temperature overnight. After that, the mixture was poured into water and the aqueous solution was extracted with dichloromethane twice. The combined organic phase was dried over $MgSO_4$. After removing the solvent, the crude compound was purified by silica column to give off white solid (5.0 g, 85%). ^{1}H NMR ($CDCl_3$, 300MHz, δ): 8.21 (d, J = 6.36 Hz, 1H), 7.57 (d, J = 7.41 Hz, 1H). GC-MS (M+, $C_6H_2Br_2FNO_2$), calcd, 298.9; found: 299.

II-2-2-8. Synthesis of Synthesis of N-(2',5'-dibromo-4'-fluorophenyl)-2,2,2-trifluoroacetamide (27)

To a solution of compound **26** (5.0 g, 16.7 mmol) in ethanol (16 mL) and conc. HCl (14 mL) at 0 ℃ was added $SnCl_2$•$2H_2O$ (20 g, 88 mmol) in several portions. After addition, the mixture was heated to reflux for 45 min and then stirred at room temperature overnight. Aqueous KOH solution was added to adjust the pH value to ~9. Then, the mixture was extracted with dichloromethane three times. The combined organic phases were washed with water twice and dried over anhydrous $MgSO_4$. After removing the solvent, the crude product was dissolved into chloroform (250 mL). The trifluoroacetic anhydride (19 mL) was added into the mixture slowly and the resulting mixture was stirred at room temperature for 2 hours. The saturated aqueous $NaHCO_3$ was then added into the mixture, and the organic phase was separated and dried over $MgSO_4$. After removing solvent, the crude product was purified by silica column to give a yellow solid (4.1 g, 61%). ^1H NMR ($CDCl_3$, 300MHz, δ): 8.62 (d, J = 6.66 Hz, 1H), 8.31 (s, 1H), 7.45 (d, J = 7.32 Hz, 1H). GC-MS(M+, $C_8H_3Br_2F_2NO$), cacld, 364.9; found: 365.

II-2-2-9. Synthesis of N-(2',5'-dibromo-4'-fluoro-6'-nitrophenyl)-2,2,2-trifluoroacetamide(28)

To a solution of conc. H_2SO_4 (40 mL) and HNO_3 (20 mL) was added compound **28** (3.8 g, 9.3 mmol) very slowly at -10 ℃. The mixture was stirred at this temperature for 2 hours and then poured into ice. The resulting solid was recovered and purified by a short flash column using dichloromethane to give a white solid (3.6 g, 85%). ^1H NMR ($CDCl_3$, 300MHz, δ): 7.84 (s, 1H), 7.71 (d, J = 7.11 Hz, 1H).GC-MS(M+, $C_8H_2Br_2F_4N_2O_3$), cacld, 409.9; found: 410.

II-2-2-10. Synthesis of 2,5-dibromo-4-fluoro-6-nitroaniline (29)

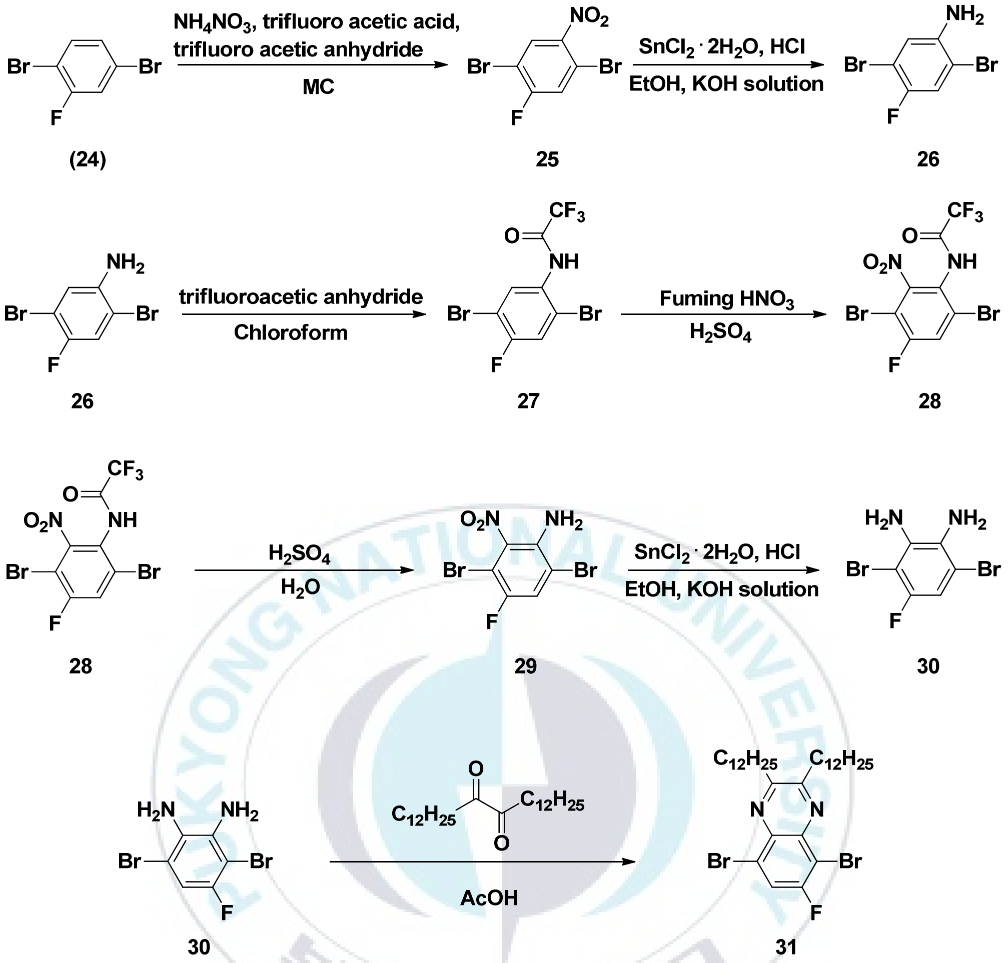
In a 100-mL single neck flask, the mixture solution of compound **29** (2 g, 4.9 mmol) in conc. H_2SO_4 (15 mL) and H_2O (50 mL) was refluxed for 3 hours. Then, the mixture was slowly added into aqueous KOH, the pH value was then adjusted to ~8-9. The mixture was extracted with ethyl acetate twice. The organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the crude product was dried under vacuum and used directly without further purification (1.2 g, 78%). ^1H NMR ($CDCl_3$, 300MHz, δ): 7.49 (d, J = 7.29 Hz, 1H), 5.05 (s, 2H). GC-MS: (M+, $C_6H_3Br_2FN_2O_2$), cacld, 313.9; found: 314.

II-2-2-11. Synthesis of 2,5-dibromo-4-fluoro-5,6-benzenediamine (30)

To a solution of compound **30** (1.2 g, 3.8 mmol) in ethanol (15 mL) and conc. HCl (10 mL) was added $SnCl_2•2H_2O$ (6 g, 26 mmol) in several portions. The mixture was refluxed for 1 hour and stirred overnightat room temperature. Then, pH value of the mixture was adjusted to ~8-9 by adding aqueous KOH solution, and then the mixture was extracted with ethyl acetate three times. The combined organic phases were dried over anhydrous $MgSO_4$. Further purification was run by silica column to give an off-white solid (1.0 g, 72%). ^1H NMR ($CDCl_3$, 300MHz, δ): 6.84 (d, J = 8.01 Hz, 1H), 4.15 (s, 2H), 3.65 (s, 2H). ^{13}C NMR ($CDCl_3$, 125MHz, ppm): 154.33, 152.41, 135.93 (d, J = 3.27 Hz), 128.92 (d, J = 2.59 Hz), 109.61 (d, J = 11.35 Hz), 109.01 (d, J = 26.38 Hz), 96.95 (d, J = 24.14 Hz). GC-MS (M+, $C_6H_5Br_2FN_2$), cacld, 283.9; found:284.

II-2-2-12. Synthesis of 5,8-dibromo-2,3-didodecyl-6-fluoroquinoxaline (31)

The compound **31** (1.4 g, 4.9 mmol) and compound **23** (2.32 g, 5.9 mmol) were dissolved in acetic acid (60 mL). The mixture was refluxed overnight. After cooling to room temperature, the resultant mixture was poured into water and extracted with ethylacetate. After dried over $MgSO_4$ and purified by silica column with petroleum hexane to give a white solid of compound **32** (2.18 g, 75%). ^1H NMR ($CDCl_3$, 400MHz, δ): 7.80 (d, 1H, J = 8.08 Hz), 3.04 (m, 4H), 1.88 (m, 4H), 1.24-1.45 (m, 36H), 0.86 (t, 6H, J = 6.84 Hz). ^{13}C NMR ($CDCl_3$, 600MHz, ppm): 158.86, 157.65(d), 157.36, 139.39, 136.22, 123.79, 121.94, 107.88, 107.73, 34.75, 34.60, 31.92, 29.67, 29.65, 29.59, 29.51, 29.46, 29.36, 27.72, 22.69, 14.12.



Scheme 5. Synthetic route of acceptor monomer (FQx).

II-2-2-13. Synthesis of benzo[c][1,2,5]thiadiazole (33)

To the mixture of commercially available 10 g (92.47 mmol) of o-phenylenediamine in 300 mL of anhydrous MC was added 37.44 g (369.98 mmol) of triethylamine (TEA). After stirring the mixture to generate the homogeneous solution, thionyl chloride (SOCl) was added dropwise very slowly, and the mixture was refluxed for 4 h. The solvent was removed under reduced pressure, and 700 mL of water was added. Concentrated HCl was added to obtain the pH of 2. The desired compound was distilled by direct steam distillation after addition of water to the mixture. The steam-distilled mixture was extracted three times with 200 mL of MC, dried over MgSO4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography using 1:10 EA:HEX to give a white solid of needle type. Yield = 11.71 g (93 % based of 10 g of o-phenylenediamine). 1H NMR (300 MHz, CDCl3, ppm): δ 7.99 (dd, 2H), 7.57 (dd, 2H).

II-2-2-14. Synthesis of 4,7-Dibromo-2,1,3-benzothiadiazole (34)

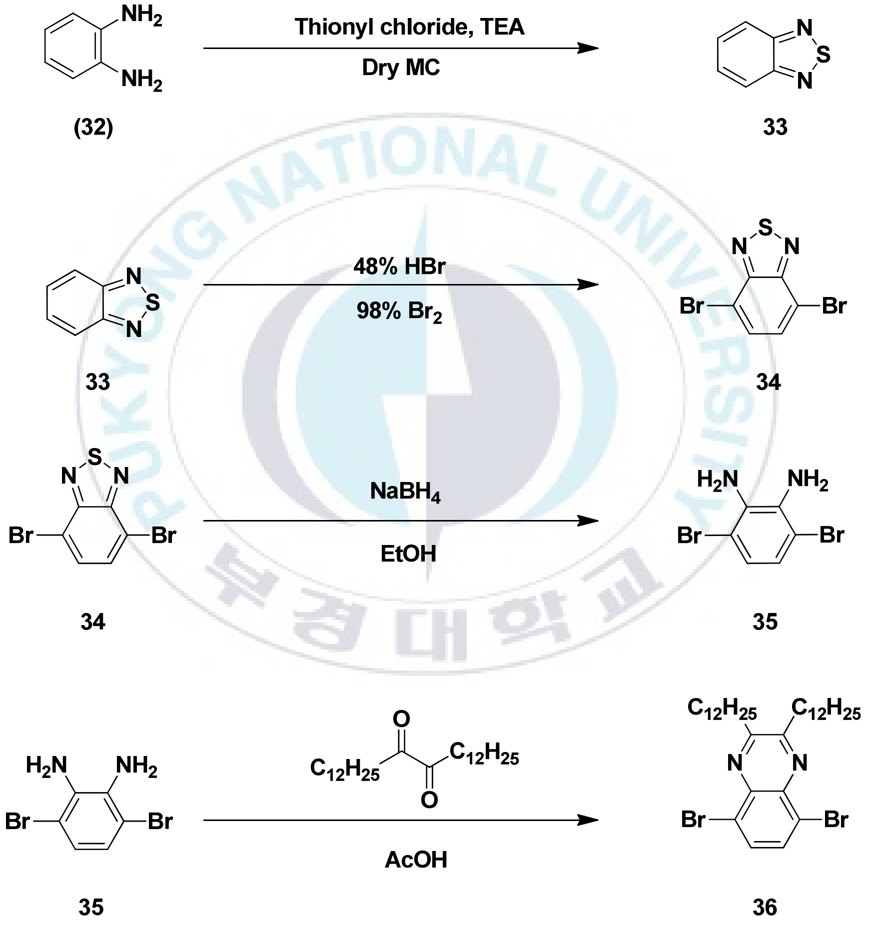
To the solution of compound **34** (10 g, 3.44 mmol) in 150 mL of HBr (48 %) was added dropwise a solution of Br_2 (35.21 g, 220.32 mmol) in 100 mL of HBr (48%) very slowly. After refluxing for 6 hours, an orange solid precipitated. The mixture was allowed to cool to RT, and saturated solution of $NaHSO_3$ was added to neutralize the residual amount of Br_2. The mixture was filtered and washed exhaustively with water. The solid was then washed once with cold Et2O and purified by flash chromatography to give a white solid of needle type. Yield = 20.51 g (95 %, based of 10 g of compound **34**). 1H NMR (300 MHz, CDCl3, ppm): δ 7.73 (s, 2H).

II-2-2-15. Synthesis of 3,6-dibromo-1,2-benzenediamine (35)

To a stirred solution of compound **35** (3.5 g, 11.91 mmol) in 400 mL of ethanol at 0 °C under argon (Ar) was added portion-wise (8.11 g, 214.31 mmol) of sodium borohydride ($NaBH_4$). After 10 min at 0 °C, the reaction mixture was stirred at room temperature for 3 hr. After cooling to 0 °C, the reaction mixture was treated with 100 mL of water. After removing the solvent under reduced pressure, the residue was diluted with 150 mL of ether, washed with 3 × 200 mL of water, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (60 × 150 mm column, SiO_2, EtOAc/hexane, 1:4) to give 3.05 g (96%) of compound **36** as a ivory solid. 1H NMR (300 MHz, CDCl3, ppm): δ 6.84 (s, 2H), 3.89 (br, 4H).

II-2-2-16. Synthesis of Synthesis of 5,8-dibromo-2,3-didodecylquinoxaline (36)

The compound **36** (1.3 g, 4.9 mmol) and compoun**d 23** (2.32 g, 5.9 mmol) were dissolved in acetic acid (60 mL). The mixture was refluxed overnight. After cooling to room temperature, the resultant mixture was poured into water and extracted with ethylacetate. After dried over MgSO4 and purified by silica column with petroleum hexane to give a white solid of compound **37** (2.11 g, 68.94%). ^{1}H NMR ($CDCl_3$, 400MHz, δ): 7.80 (s, 2H), 3.04 (m, 4H), 1.88 (m, 4H), 1.24-1.45 (m, 36H), 0.85 (t, 6H). ^{13}C NMR ($CDCl_3$, 600MHz, ppm): 158.26, 139.23, 131.92, 123.30, 34.75, 31.91, 29.51(m), 22.69, 14.12.



Scheme 6. Synthetic route of acceptor monomer (Qx).

II-2-2-17. Synthesis of 2,3-didodecyl-6,7-difluoro-5,8-di(thiophen-2-yl)quinoxaline (37)

To a solution of compound **23** (2.5 g, 3.8 mmol) and 2-tributylstannylthiophene (4.23 g, 11.4 mmol) in 60 mL *N,N'*-dimethylformamide (DMF) was added Bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$) (81 mg, 0.11 mmol) under argon and heated at 85~90 ^{o}C for 24 h. Water was then added, and then the mixture was extracted with dichloromethane (CH_2Cl_2). The organic phase was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the residue was recrystallized from ethanol to give compound **37** as a yellow solid (2.04 g, 81%). ^{1}H NMR ($CDCl_3$, 400MHz, δ): 7.98 (d, 2H, J = 2.96 Hz), 7.59 (d, 2H, J = 4.96 Hz), 7.21 (t, 2H, J = 4.56 Hz), 3.06 (t, 4H, J = 7.52 Hz), 1.96 (m, 4H, J = 7.45 Hz), 1.24-1.45 (m, 36H), 0.86 (t, 6H, J = 6.86 Hz). ^{13}C NMR ($CDCl_3$, 600MHz, ppm): 155.21, 149.62(d), 134.53, 131.01, 130.46, 130.41, 130.37, 129.52, 126.33, 117.51, 34.68, 31.92, 29.60(m), 28.14, 22.70, 14.14.

II-2-2-18. Synthesis of 5,8-bis(5-bromothiophen-2-yl)-2,3-didodecyl-6,7-difluoroquinoxaline (38)

Compound **37** (2.0 g, 3.0 mmol) was dissolved in THF (60 mL) under nitrogen atmosphere, and NBS (1.1 g, 6.0 mmol) was added. The mixture was stirred at room temperature overnight. After that water (100 mL) was added to quench the reaction, and then extracted with diethyl ether, washed with brine, and dried with anhydrous $MgSO_4$. The solvent was removed via rotary evaporation and subsequently purified by recrystallization to afford compound **38** as an orange solid (2.41 g, 95%). ^1H NMR ($CDCl_3$, 400MHz, δ): 7.75 (d, 2H, J = 4.00 Hz), 7.14 (d, 2H, J = 4.04 Hz), 3.08 (t, 4H, J = 7.66 Hz), 1.97 (m, 4H, J = 7.46 Hz), 1.23-1.46 (m, 36H), 0.85 (t, 6H, J = 6.84 Hz). ^{13}C NMR ($CDCl_3$, 600MHz, ppm): 155.42, 149.46(d), 133.58, 132.60, 130.35, 129.03, 118.56, 116.61, 34.75, 31.93, 29.63(m), 28.14, 22.70, 14.14.

II-2-2-19. Synthesis of 2,3-didodecyl-6-fluoro-5,8-di(thiophen-2-yl)quinoxaline (39)

To a solution of compound **31** (3.7 g, 5.7 mmol) and 2-tributylstannylthiophene (6.4 g, 17.2 mmol) in 70 mL *N,N'*-dimethylformamide (DMF) was added Bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$) (120 mg, 0.17 mmol) under argon and heated at 85~90 °C for 24 h. Water was then added, and then the mixture was extracted with dichloromethane (CH_2Cl_2). The organic phase was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the residue was recrystallized from ethanol to give compound **39** as a yellow solid (2.78 g, 75%). ^1H NMR ($CDCl_3$, 400MHz, δ): 7.82 (m, 3H), 7.5 (m, 2H), 7.19 (m, 2H), 3.04 (m, 4H), 1.97 (m, 4H), 1.24-1.45 (m, 36H), 0.86 (t, 6H). ^{13}C NMR ($CDCl_3$, 600MHz, ppm): 158.95, 157.28, 155.92, 154.27, 138.46, 137.55, 134.22, 132.03, 131.61, 131.54, 129.35, 128.58, 126.37, 126.13, 116.37, 115.64, 34.85, 34.67, 31.93, 29.62(m), 27.92, 27.87, 22.70, 14.13.

II-2-2-20. Synthesis of 5,8-bis(5-bromothiophen-2-yl)-2,3-didodecyl-6-fluoroquinoxaline (40)

Compound **39** (2.5 g, 3.85 mmol) was dissolved in THF (60 mL) under nitrogen atmosphere, and NBS (1.2 g, 7.7 mmol) was added. The mixture was stirred at room temperature overnight. After that water (100 mL) was added to quench the reaction, and then extracted with diethyl ether, washed with brine, and dried with anhydrous $MgSO_4$. The solvent was removed via rotary evaporation and subsequently purified by recrystallization to afford compound **40** as an orange solid (2.87 g, 92%). ^{1}H NMR ($CDCl_3$, 400MHz, δ): 7.80 (d, 1H, J = 13.72 Hz), 7.72 (m, 1H), 7.49 (d, 1H, J = 4.04 Hz), 7.10 (m, 2H, J = 4.03), 3.07 (m, 4H), 1.98 (m, 4H), 1.24-1.44 (m, 36H), 0.86 (t, 6H, J = 6.72 Hz). ^{13}C NMR ($CDCl_3$, 600MHz, ppm): 158.82, 157.14, 156.09, 154.46, 137.95, 137.30, 133.62, 133.18, 130.25, 129.72, 129.65, 129.58, 128.77, 128.72, 128.68, 125.27, 117.99, 117.45, 115.56, 113.93, 113.83, 113.73, 34.98, 34.78, 31.95, 29.72(m), 27.95, 27.79, 22.71, 14.15.

II-2-2-21. Synthesis of 2,3-didodecyl-5,8-di(thiophen-2-yl)quinoxaline (41)

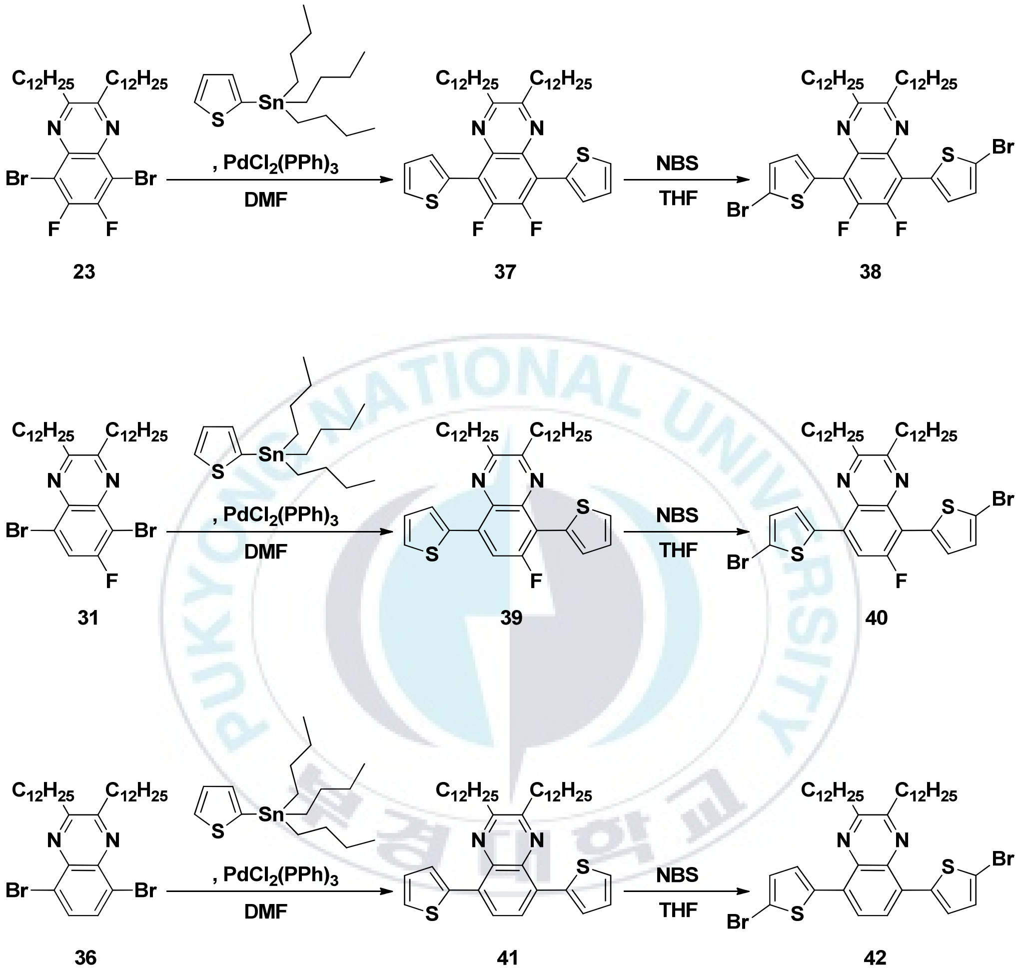
To a solution of compound **36** (2.37 g, 3.8 mmol) and 2-tributylstannylthiophene (4.23 g, 11.4 mmol) in 60 mL *N,N'*-dimethylformamide (DMF) was added

Bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$) (81 mg, 0.11 mmol) under argon and heated at 85~90 ºC for 24 h. Water was then added, and then the mixture was extracted with dichloromethane (CH_2Cl_2). The organic phase was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the residue was recrystallized from ethanol to give compound **41** as a yellow solid (2.45 g, 79.24%). %). ^{1}H NMR ($CDCl_3$, 400MHz, δ): 8.04 (s, 2H), 7.83 (dd, 2H), 7.46 (dd, 2H), 7.15(m, 2H), 3.07 (m, 4H), 2.00 (m, 4H), 1.24-1.47 (m, 36H), 0.86 (t, 6H). ^{13}C NMR ($CDCl_3$, 600MHz, ppm): 155.40, 139.01, 137.16, 130.80, 128.34, 126.39, 126.00, 125.85, 34.91, 31.92, 29.62(m), 27.89, 22.69, 14.13.

II-2-2-22. Synthesis of 5,8-bis(5-bromothiophen-2-yl)-2,3-didodecylquinoxaline (42)

Compound **41** (2.3 g, 3.64 mmol) was dissolved in THF (60 mL) under nitrogen atmosphere, and NBS (1.30 g, 7.29 mmol) was added. The mixture was stirred at room temperature overnight. After that water (100 mL) was added to quench the reaction, and then extracted with diethyl ether, washed with brine, and dried with anhydrous $MgSO_4$. The solvent was removed via rotary evaporation and subsequently purified by recrystallization to afford compound **42** as an orange solid (2.66g, 92.58%). ^{1}H NMR ($CDCl_3$, 400MHz, δ): 7.97 (s, 2H), 7.49 (d, 2H), 7.08 (d, 2H), 3.07 (m, 4H), 2.00 (m, 4H), 1.24-1.47 (m, 36H), 0.86 (t, 6H). ^{13}C NMR

($CDCl_3$, 600MHz, ppm): 155.62, 139.55, 136.15, 129.77, 128.68, 124.70, 124.04, 116.76, 34.96, 31.94, 29.72(m), 27.80, 22.71, 14.14.



Scheme 7. Synthetic route of acceptor monomer (DTDFQx, DTFQx, DTQx).

II-2-2-23. Synthesis of 3-hexylthiophene (46)

Magnesium (1.43 g, 59.29 mol) was introduced together with THF (25mL) in a flask and cooled to 0°C. A solution of bromo hexane (5.55 g, 38.75 mol) was added slowly. The resulting mixture was stirred under nitrogen for 2 h and then transferred to a dropping funnel fitted to a second flask containing 3-bromothiophene (3 g, 31.65 mol) and Ni(dppp)Cl_2 (0.34 g, 0.63mmol) in dry THF (25mL). After cooling with an ice bath, the Grignard reagent was added drop wise and the resulting adduct was allowed to warm to room temperature before being stirred for 3 days under nitrogen. The mixture obtained was poured onto dilute aqueous hydrochloric acid. The organic layer was washed three times with water, dried over $MgSO_4$, filtered and concentrated. The crude product was disted under reduced pressure. Colorless oil, yield 4.10g, 76.94%. ^{1}H NMR ($CDCl_3$, 400MHz, δ): 7.21 (m, 1H), 6.90-6.92 (m, 2H), 2.63 (t, 2H), 1.61 (m, 2H), 1.29 (m, 6H), 0.86 (t, 3H).

II-2-2-24. Synthesis of 4-hexylthiophen-2-yl)trimethylstannane (47)

To a round bottom flask loaded with dry THF (80 mL), 3-hexylthiophene (2 ml, 11.88 mmol) was added and the mixture was cooled to -78 °C by acetone/dry ice bath. n-BuLi in hexane solution (1.7M, 17.47 mL) was added dropwise. After stirring at -78 °C for 1hr, tributyl tin chloride (29.70 ml, 29.70 mmol) was added dropwise and removed the dry ice bath immediately. After three more hours, the reaction was then terminated by adding saturated $NaHCO_3$ solution (100 ml) into the flask. The solvent was removed by rotary evaporation. The remaining oil was diluted with diethyl ether and washed with brine several times. The collected organic layer was dried over $MgSO_4$ and the organic solvent was removed by rotary evaporation. The collected orange oil was dried under vacuum for another 3h and used directly for the next step. ^1H NMR ($CDCl_3$, 400MHz, δ): 7.17 (s, 1H), 6.99 (s, 1H), 2.62 (t, 2H), 1.66 (m, 2H), 1.23-1.36 (m, 6H), 0.86 (t, 3H).

II-2-2-25. Synthesis of 2,3-didodecyl-6,7-difluoro-5,8-bis(4-hexylthiophen-2-yl)quinoxaline (48)

To a solution of compound **23** (2.5 g, 3.78 mmol) and 2-tributylstannylthiophene (3.25 g, 9.81 mmol) in 60 mL N,N'-dimethylformamide (DMF) was added Bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$) (0.080 mg, 0.11 mmol) under argon and heated at 85~90 ^{o}C for 24 h. Water was added, and then the mixture was extracted with dichloromethane (CH_2Cl_2). The organic phase was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the residue was recrystallized from ethanol to give compound **48** as a yellow solid (2.90 g, 91.84%). ^1H NMR ($CDCl_3$, 400MHz, δ): 7.82 (s, 2H), 7.17 (s, 2H), 3.04 (t, 4H), 2.68 (t, 4H), 1.96 (m, 4H), 1.67 (m, 4H), 1.24-1.46 (m, 48H), 0.86 (m, 12H).

II-2-2-26. Synthesis of 5,8-bis(5-bromo-4-hexylthiophen-2-yl)-2,3-didodecyl-6,7-difluoroquinoxaline (49)

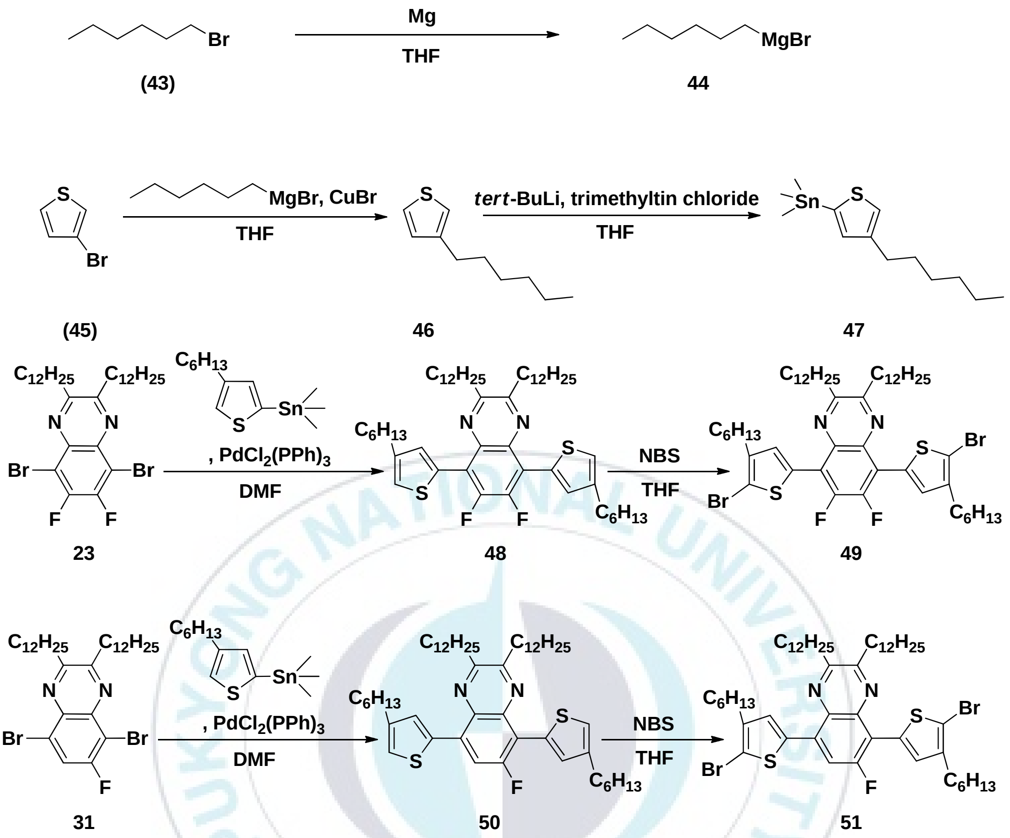
Compound **48** (2 g, 2.39 mmol) was dissolved in THF (60 mL) under nitrogen atmosphere, and NBS (0.86 g, 4.79 mmol) was added. The mixture was stirred at room temperature overnight. After that water (100 mL) was added to quench the reaction, and then extracted with diethyl ether, washed with brine, and dried with anhydrous $MgSO_4$. The solvent was removed via rotary evaporation and subsequently purified by recrystallization to afford compound **49** as an orange solid (1.78g, 74.87%). ^{1}H NMR ($CDCl_3$, 400MHz, δ): 7.68 (s, 2H), 3.04 (t, 4H), 2.61 (t, 4H), 1.96 (m, 4H), 1.61 (m, 4H), 1.24-1.52 (m, 48H), 0.86 (m, 12H).

II-2-2-27. Synthesis of 2,3-didodecyl-6-fluoro-5,8-bis(4-hexylthiophen-2-yl)quinoxaline (50)

To a solution of compound **31** (2 g, 3.11 mmol) and 2-tributylstannylthiophene (2.47 g, 7.47 mmol) in 60 mL N,N'-dimethylformamide (DMF) was added Bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$) (0.067 mg, 0.093 mmol) under argon and heated at 85~90 ^{o}C for 24 h. Water was then added, and then the mixture was extracted with dichloromethane (CH2Cl2). The organic phase was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the residue was recrystallized from ethanol to give compound **50** as a yellow solid (1.015 g, 39.93%). ^{1}H NMR ($CDCl_3$, 400MHz, δ): 7.85 (s, 1H), 7.80 (d, 1H), 7.69 (d, 1H), 7.10 (d, 2H), 3.04 (t, 4H), 2.67 (q, 4H), 1.97 (m, 4H), 1.68 (m, 4H), 1.25-1.47 (m, 48H), 0.87 (m, 12H).

II-2-2-28. Synthesis of 5,8-bis(5-bromo-4-hexylthiophen-2-yl)-2,3-didodecyl-6-fluoroquinoxaline (51)

Compound **50** (0.99 g, 1.22 mmol) was dissolved in THF (20 mL) under nitrogen atmosphere, and NBS (0.44 g, 2.43 mmol) was added. The mixture was stirred at room temperature overnight. After that water (100 mL) was added to quench the reaction, and then extracted with diethyl ether, washed with brine, and dried with anhydrous $MgSO_4$. The solvent was removed via rotary evaporation and subsequently purified by recrystallization to afford compound **51** as an orange solid (1.03g, 87.06%). %). ^1H NMR ($CDCl_3$, 400MHz, δ): 7.82 (dd, 1H), 7.67 (d. 1H), 7.45 (s, 1H), 3.05 (q, 4H), 2.61 (m, 4H), 1.98 (m, 4H), 1.61 (m, 4H), 1.23-1.47 (m, 48H), 0.87 (m, 12H).



Scheme 8. Synthetic route of acceptor monomer (DTDFQx, DTFQx with alkyl group).

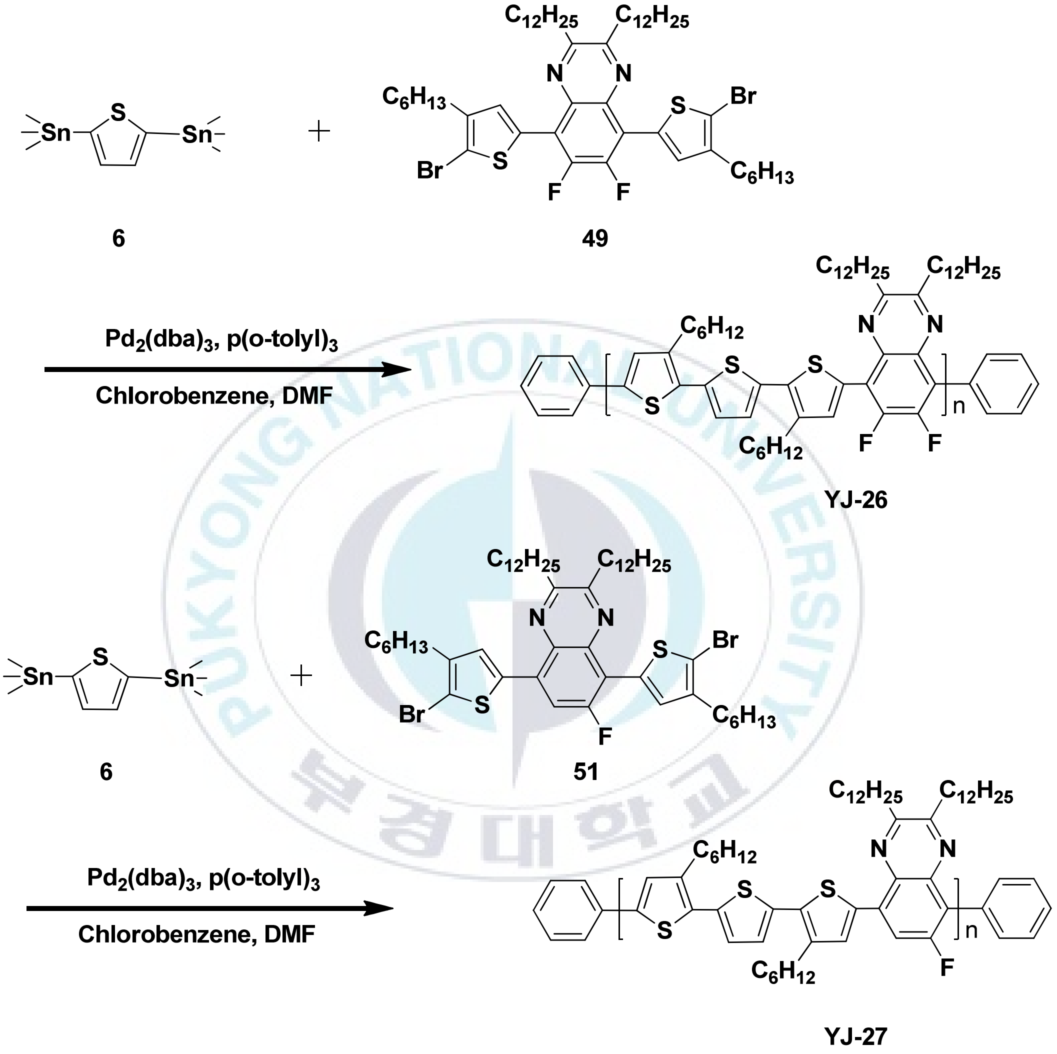
II-3. Synthesis of polymer

II-3-1. Synthesis of poly[2,3-didodecyl-6,7-difluoro-5-(3-hexyl-[2,2'-bithiophen]-5-yl)-8-(4-hexylthiophen-2-yl)quinoxaline] (YJ-26)

In a 25 mL dry flask, 2,5-bis(trimethylstannyl)thiophene (6) (0.2957 g, 0.7 mmol), 5,8-bis(5-bromo-4-hexylthiophen-2-yl)-2,3-didodecyl-6,7-difluoroquinoxaline (49) (0.6952 g, 0.7 mmol), were dissolved in a mixture of degassed chlorobenzene (7 mL) and *N,N'*-dimethylformamide (2 mL) under argon atmosphere. Tris(dibenzylideneacetone) dipalladium (0) ($Pd_2(dba)_3$) (32 mg, 0.035 mmol) and P(*o*-tolyl)$_3$ (85 mg, 0.28 mmol) were added. Then the mixture was vigorously stirred at 100~110 °C for 48~72 hr. After cooling down, the solution was poured into methanol. The polymer was collected by filtration and was Soxhlet-extracted in order with methanol, hexane and then with chloroform. The chloroform solution was concentrated to a small volume, and the polymer was precipitated by pouring this solution into methanol. Finally, the polymer was collected by filtration, dried under vacuum at 50 °C overnight and afforded YJ-26 (0.5473) in 85.22%

II-3-2. Synthesis of poly[2,3-didodecyl-6-fluoro-8-(3-hexyl-[2,2'-bithiophen]-5-yl)-5-(4-hexylthiophen-2-yl)quinoxaline] (YJ-27)

YJ-27 was synthesized with the procedure described for YJ-26. Copolymerization with monomer 2,5-bis(trimethylstannyl)thiophene (6) (0.2957 g, 0.7 mmol) and 5,8-bis(5-bromo-4-hexylthiophen-2-yl)-2,3-didodecyl-6-fluoroquinoxaline (51) (0.6826g, 0.7 mmol) gave YJ-27 (0.753g) in yield 95.68%.



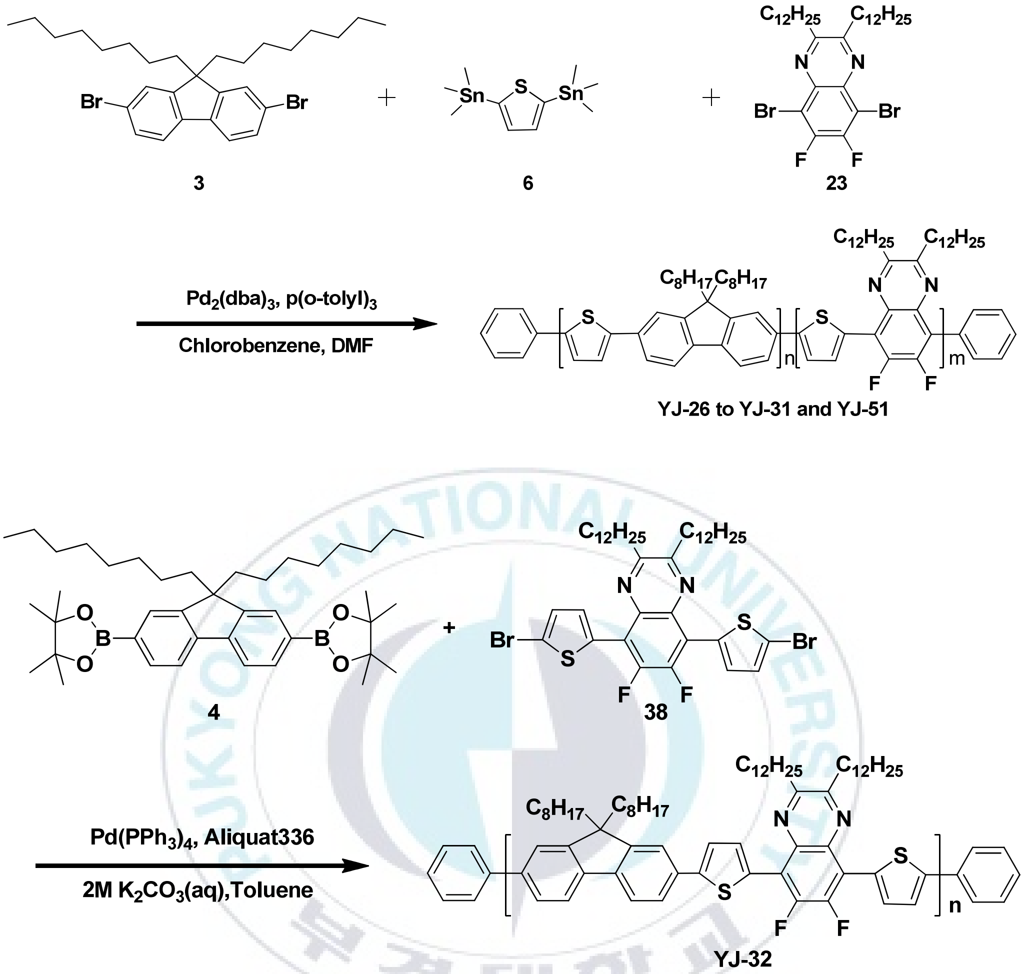
Scheme 9. Synthetic route of YJ-26 and YJ-27.

II-3-3. Synthesis of poly[2,7-dibromo-9,9-dioctyl-9H-fluorene-co-5,8-Dibromo-6,7-difluoro-2.3-didodecylquinoxaline] (YJ–28 to YJ-31 and YJ-51)

Carefully purified 2,7-Dibromo-9,9'-dioctyl-9H-fluorene (**3**), 2,5-bis(trimethylstannanyl)thiophene (6) and 5,8-dibromo-6,7-difluoro-2,3-didodecylquinoxaline (23), P(o-tolyl)3 (40 mol%)and $Pd_2(dba)_3(0)$ (5 mol%) were dissolved in a mixture of chlorobezene. The ratio of 2,5-bis(trimethylstannyl)thiophene (6) (1.4 equiv.) vs. 5,8-dibromo-6,7-difluoro-2,3-didodecylquinoxaline (23) and 2,7-Dibromo-9,9'-dioctyl-9H-fluorene (**3**) (1.4 equiv.) was kept always as (**6**):(**3** + 23) = 1:1. The comonomers feed ratios of **3** and 23 are 1:4, 2:3, 3:2, 4:1 and 1:1. The mixture was refluxed with vigorous stirring for 8 hr under argon atmosphere. After 36 hr, phenyltributylstannane was added to the reaction then 8 hr later, bromobenzene was added and the reaction mixture refluxed overnight to complete the end-capping reaction. The whole mixture was poured into methanol. The resulted solid was filtered and washed with acetone to remove oligomers and catalyst residues. This polymer was soluble in conventional organic solvents (chloroform).

II-3-4. Synthesis of poly[5-(5-(9,9-dioctyl-9H-fluoren-2-yl)thiophen-2-yl)-2,3-didodecyl-6,7-difluoro-8-(thiophen-2-yl)quinoxaline] (YJ-32)

In a 50 mL dry flask, 5,8-bis(5-bromothiophen-2-yl)-2,3-didodecyl-6,7-difluoroquinoxaline (38) and 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)-bis[4,4,5,5-tetramethyl-[1,3,2]dioxaborolane] (4) (0.5406 g, 0.7 mmol) were dissolved in a mixture of degassed toluene (10.5 mL) under argon atmosphere. $Pd(PPh_3)_4$ (5 mg,0.007mmol) and K_2CO_3 (2M, 3.5 ml) were added. Then the mixture was vigorously stirred at 100~110 ^{o}C for 48~72 hr. After cooling down, the solution was poured into methanol. The polymer was collected by filtration and was Soxhlet-extracted in order with methanol, hexane and then with chloroform. The chloroform solution was concentrated to a small volume, and the polymer was precipitated by pouring this solution into methanol. Finally, the polymer was collected by filtration, dried under vacuum at 50 ^{o}C overnight and afforded YJ-32 (686 mg) in yield 92.68%.



Scheme 10. Synthetic route of YJ-28 to YJ-32 and YJ-51.

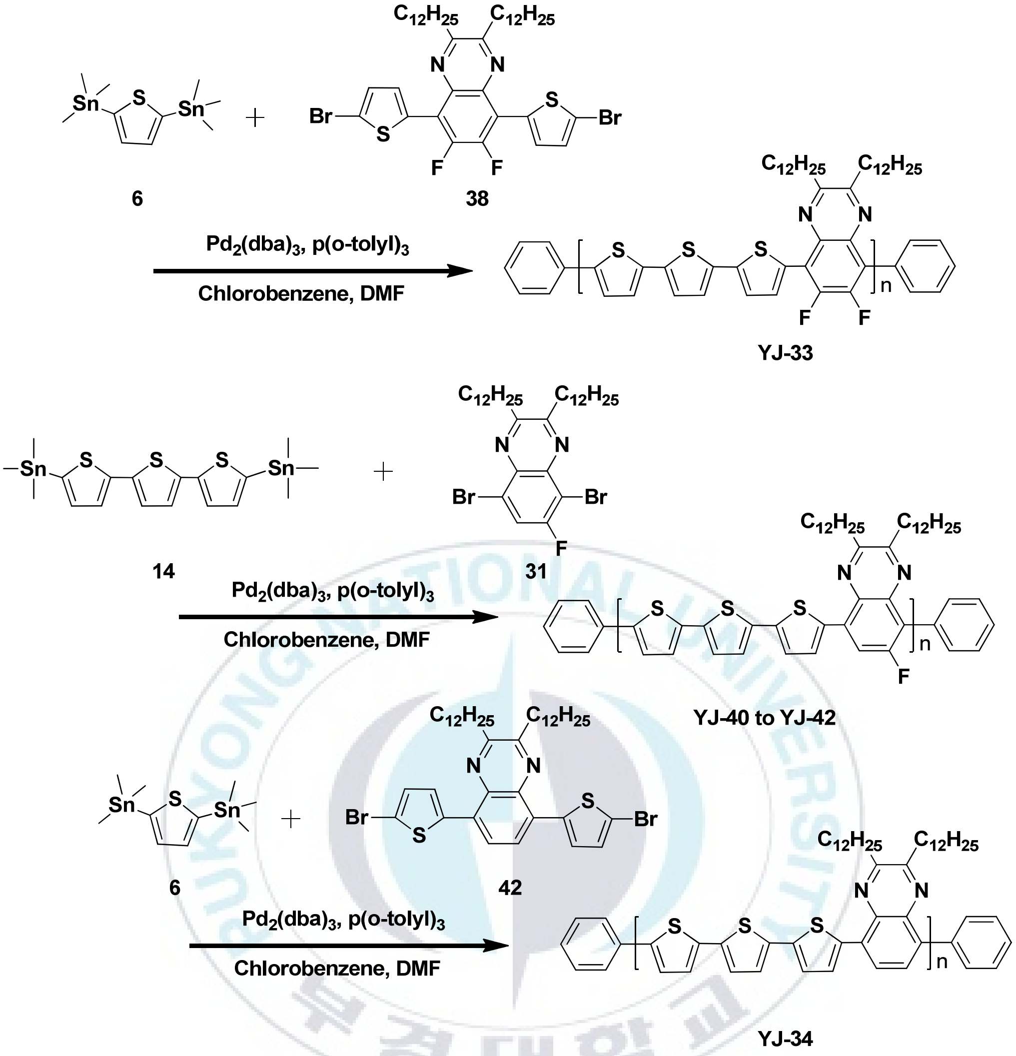
II-3-5. Synthesis of poly[5-([2,2':5',2''-terthiophen]-5-yl)-2,3-didodecyl-7-fluoroquinoxaline] (YJ-40 to YJ-42)

In a 50 mL dry flask, 2,5''-Bis(trimethylsilyl)-5,2',5',2''-terthiophene (14) (0.574g, 0.7 mmol) and 5,8-dibromo-2,3-didodecyl-6-fluoroquinoxaline (31) (0.4498g, 0.7 mmol) were dissolved in a mixture of degassed chlorobenzene (7 mL) and *N*,*N*'-dimethylformamide (2 mL) under argon atmosphere. Tris(dibenzylideneacetone) dipalladium (0) ($Pd_2(dba)_3$) (32 mg, 0.035 mmol) and P(*o*-tolyl)$_3$ (85 mg, 0.28 mmol) were added. Then, the resulted mixture was heated at 50 ^oC for 8 hr, 60 ^oC for 8 hr, 70 ^oC for 8hr, and 80 ^oC for 48 hr.(YJ-40) Then the mixture was vigorously stirred at 80 ^oC for 48~72 hr.(YJ-41) Then the mixture was vigorously stirred at 100~110 ^oC for 48~72 hr.(YJ-42) After cooling down, the solution was poured into methanol. The polymer was collected by filtration and was Soxhlet-extracted in order with methanol, hexane and then with chloroform. The chloroform solution was concentrated to a small volume, and the polymer was precipitated by pouring this solution into methanol. Finally, the polymer was collected by filtration, dried under vacuum at 50 ^oC overnight and afforded YJ-40, YJ-41 and YJ-42 (434, 421 and 301 mg) in yield 84.69, 82.12 and 58.81%, respectively.

II-3-6. Synthesis of poly[5-([2,2':5',2''-terthiophen]-5-yl)-2,3-didodecyl-6,7-difluoroquinoxaline] and poly[5-([2,2':5',2''-terthiophen]-5-yl)-2,3-

didodecylquinoxaline] (YJ-33 and 34)

YJ-33, 34 was synthesized with the procedure described for YJ-42. Copolymerization with monomer 2,5-bis(trimethylstannyl)thiophene (6) (0.2957 g, 0.7 mmol), 5,8-bis(5-bromothiophen-2-yl)-2,3-didodecyl-6,7-difluoroquinoxaline (38) (0.5774g, 0.7 mmol) or 5,8-bis(5-bromothiophen-2-yl)-2,3-didodecylquinoxaline (42) (0.5522g, 0.7 mmol) gave YJ-33 and YJ-34 (0.753g) in yield 55.10% and 76.15%, respectively.



Scheme 11. Synthetic route of YJ-33, YJ-34, YJ-40, YJ-41 and YJ-42.

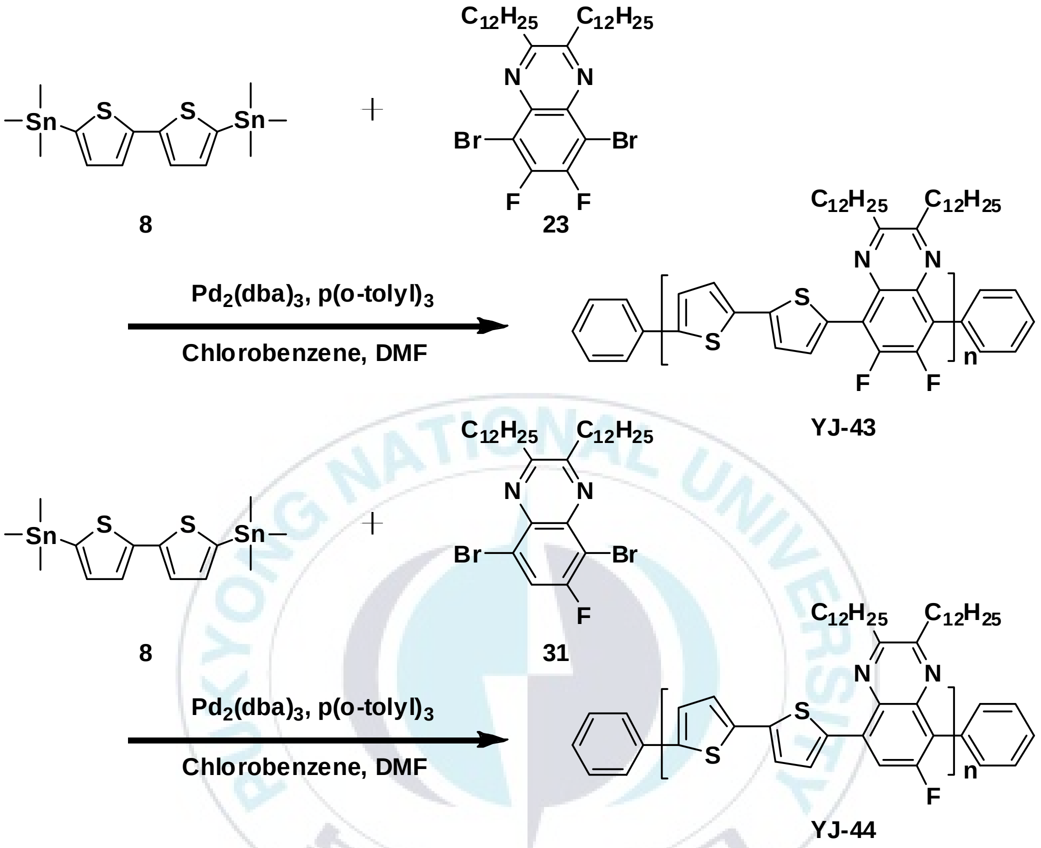
II-3-7. Synthesis of poly[5-([2,2'-bithiophen]-5-yl)-2,3-didodecyl-6,7-difluoroquinoxaline] (YJ-43)

In a 25 mL dry flask, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (8) (0.3443 g, 0.7 mmol), 5,8-dibromo-6,7-difluoro-2,3-didodecylquinoxaline (23) (0.4624 g, 0.7 mmol), were dissolved in a mixture of degassed chlorobenzene (7 mL) and *N,N'*-dimethylformamide (2 mL) under argon atmosphere. Tris(dibenzylideneacetone) dipalladium (0) ($Pd_2(dba)_3$) (32 mg, 0.035 mmol) and P(*o*-tolyl)$_3$ (85 mg, 0.28 mmol) were added. Then the mixture was vigorously stirred at 100~110 ^oC for 48~72 hr. After cooling down, the solution was poured into methanol. The polymer was collected by filtration and was Soxhlet-extracted in order with methanol, hexane and then with chloroform. The chloroform solution was concentrated to a small volume, and the polymer was precipitated by pouring this solution into methanol. Finally, the polymer was collected by filtration, dried under vacuum at 50 ^oC overnight and afforded YJ-43 (0.3022) in 64.72%.

II-3-8. Synthesis of poly[5-([2,2'-bithiophen]-5-yl)-2,3-didodecyl-7-fluoroquinoxaline] (YJ-44)

YJ-44 was synthesized with the procedure described for YJ-43. Copolymerization with monomer (5,5'-bis(trimethylstannyl)-2,2'-bithiophene (8) (0.4919g, 1.0 mmol) and 5,8-dibromo-2,3-didodecyl-6-fluoroquinoxaline (31) (0.6429g, 1.0

mmol) gave YJ-44 (0.622g) in yield 95.84%.



Scheme 12. Synthetic route of YJ-43 and YJ-44.

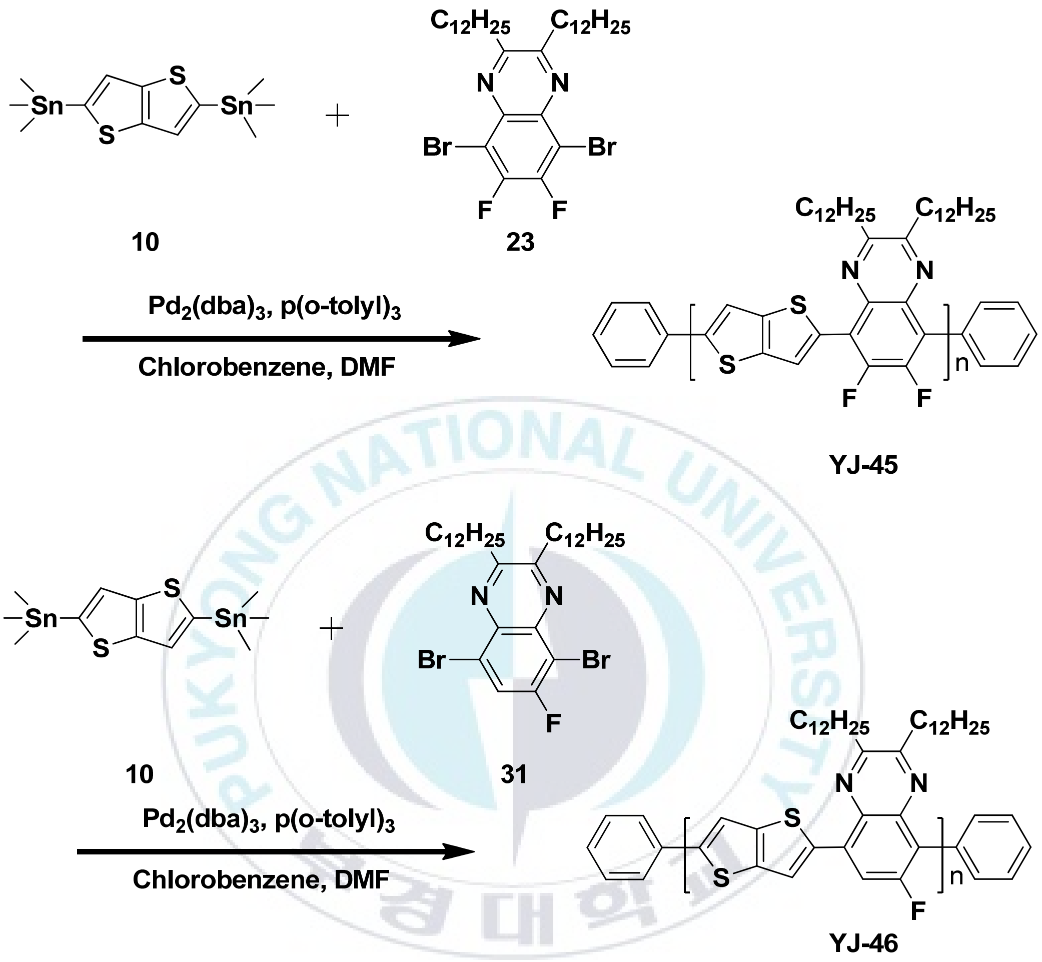
II-3-9. Synthesis of poly[2,3-didodecyl-6,7-difluoro-5-(thieno[3,2-b]thiophen-2-yl)quinoxaline] (YJ-45)

In a 25 mL dry flask, 2,5-bis-trimethylstannyl-thieno[3,2-b]thiophene (10) (0.4193 g, 0.9 mmol), 5,8-dibromo-6,7-difluoro-2,3-didodecylquinoxaline (23) (0.5945 g, 0.9 mmol), were dissolved in a mixture of degassed chlorobenzene (7 mL) and N,N'-dimethylformamide (2 mL) under argon atmosphere. Tris(dibenzylideneacetone) dipalladium (0) ($Pd_2(dba)_3$) (45 mg, 0.05 mmol) and P(*o*-tolyl)$_3$ (110 mg, 0.36 mmol) were added. Then the mixture was vigorously stirred at 100~110 ºC for 48~72 hr. After cooling down, the solution was poured into methanol. The polymer was collected by filtration and was Soxhlet-extracted in order with methanol, hexane and then with chloroform. The chloroform solution was concentrated to a small volume, and the polymer was precipitated by pouring this solution into methanol. Finally, the polymer was collected by filtration, dried under vacuum at 50 ºC overnight and afforded YJ-45 (0.5543g) in 96.08%.

II-3-10. Synthesis of of poly[2,3-didodecyl-7-fluoro-5-(thieno[3,2-b]thiophen-2-yl)quinoxaline] (YJ-46)

YJ-46 was synthesized with the procedure described for YJ-45. Copolymerization with monomer 2,5-bis-trimethylstannyl-thieno[3,2-b]thiophene (10) (0.4658g, 1.0 mmol) and 5,8-dibromo-2,3-didodecyl-6-fluoroquinoxaline (31) (0.6429g, 1.0

mmol) gave YJ-46 (0.732g) in yield 94.45%.



Scheme 13. Synthetic route of YJ-45 and YJ-46.

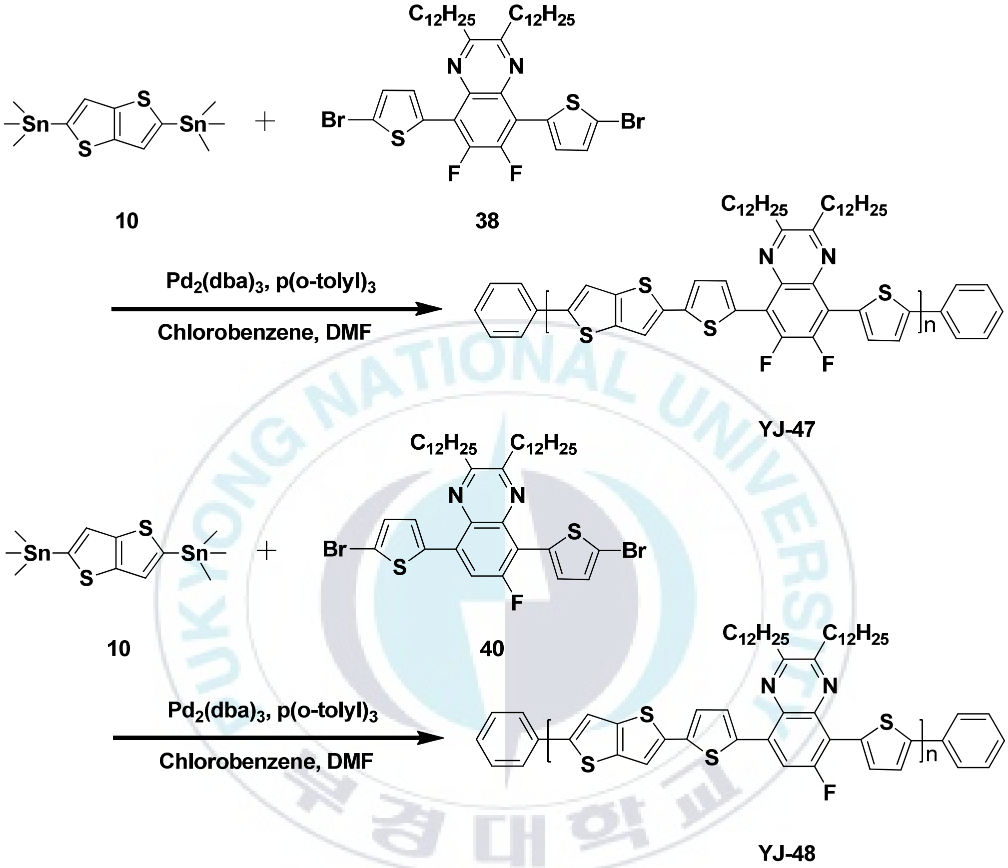
II-3-11. Synthesis of poly[2,3-didodecyl-6,7-difluoro-5-(5-(thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-8-(thiophen-2-yl)quinoxaline] (YJ-47)

In a 25 mL dry flask, 2,5-bis-trimethylstannyl-thieno[3,2-b]thiophene (10) ((0.4193 g, 0.9 mmol) and 5,8-bis(5-bromothiophen-2-yl)-2,3-didodecyl-6,7-difluoroquinoxaline (38) (0.7423 g, 0.9 mmol), were dissolved in a mixture of degassed chlorobenzene (7 mL) and N,N'-dimethylformamide (2 mL) under argon atmosphere. Tris(dibenzylideneacetone) dipalladium (0) (Pd2(dba)3) (32 mg, 0.035 mmol) and P(o-tolyl)3 (85 mg, 0.28 mmol) were added. Then the mixture was vigorously stirred at 100~110 ºC for 48~72 hr. After cooling down, the solution was poured into methanol. The polymer was collected by filtration and was Soxhlet-extracted in order with methanol, hexane and then with chloroform. The chloroform solution was concentrated to a small volume, and the polymer was precipitated by pouring this solution into methanol. Finally, the polymer was collected by filtration, dried under vacuum at 50 ºC overnight and afforded YJ-47 (0.301g) in 37.39%

II-3-12. Synthesis of poly[2,3-didodecyl-6-fluoro-8-(5-(thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-5-(thiophen-2-yl)quinoxaline] (YJ-48)

YJ-48 was synthesized with the procedure described for YJ-47. Copolymerization with monomer (5,5'-bis(trimethylstannyl)-2,2'-bithiophene (8) (0.4658g, 1.0

mmol) and 5,8-bis(5-bromothiophen-2-yl)-2,3-didodecyl-6-fluoroquinoxaline (40) (0.8068g, 1.0 mmol) gave YJ-48 (0.753g) in yield 95.68%.



Scheme 14. Synthetic route of YJ-47 and YJ-48.

Chapter III. Results and Discussion

III-1. Polymerization Results

YJ-26, YJ-27, YJ-28, YJ-29, YJ-30, YJ-31, YJ-32 and YJ-51 could dissolve completely in chloroform, toluene, chlorobenzene and 1,2-dichlorobenzene (o-DCB) at elevated temperature, YJ-43, YJ-44, YJ-45 and YJ-46 can dissolve partially in commonly organic solvent, but completely dissolve in the other solvents at elevated temperature. But YJ-33, YJ-34, YJ-40, YJ-41, YJ-42, YJ-43, YJ-47 and YJ-48 could almost not dissolve in chloroform, toluene chlorobenzene and 1,2-dichlorobenzene. Molecular weight of the polymers, weight-average molecular weight (M_w) and polydispersity (PDI) were measured by gel permeation chromatography (GPC) method using polystyrene as standard and chloroform as eluent (Table III-1).

Table III-1. Polymerization Results.

polymer	M_n [a]	M_w [a]	PDI[a]	polymer	M_n [a]	M_w [a]	PDI[a]
YJ-26	8998	11922	1.32	YJ-41	612	900	1.47
YJ-27	6261	7662	1.22	YJ-42	661	1013	1.53
YJ-28	35603	67626	1.90	YJ-43	580	777	1.34
YJ-29	18313	34199	1.87	YJ-44	738	1143	1.55
YJ-30	23886	44976	1.88	YJ-45	1859	14702	7.91
YJ-31	39076	153020	3.92	YJ-46	661	1204	1.82
YJ-32	1478	6378	4.32	YJ-47	622	954	1.53
YJ-33	461	531	1.15	YJ-48	515	644	1.25
YJ-34	811	1436	1.77	YJ-51	17912	27723	1.55
YJ-40	622	920	1.48				

[a] Number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity of the polymers were determined by gel permeation chromatography (GPC) in chloroform using polystyrene standards.

Thermal property of these polymers was measured by thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 20 °C min^{-1}. All polymers has excellent thermal stability with onset decomposition temperature corresponding to 5% weight loss at over 390 °C (Table III-2, Figure III-1 to Figure III-5). Because of fluorine atom effect, difluorinated quinoxaline indicated higher thermal stability than monofluorinated quinoxaline.

Table III-2. Decomposition Temperatures of polymers.

polymer	Td(°C)	polymer	Td(°C)
YJ-26	459.67	YJ-41	426.29
YJ-27	425.10	YJ-42	428.28
YJ-28	410.99	YJ-43	428.47
YJ-29	422.44	YJ-44	399.33
YJ-30	416.92	YJ-45	411.80
YJ-31	413.08	YJ-46	410.99
YJ-32	419.58	YJ-47	410.80
YJ-33	429.40	YJ-48	399.74
YJ-34	416.10	YJ-51	423.83
YJ-40	419.54		

Onset decomposition temperatures (T_d) (5% weight loss) measured by TGA under nitrogen.

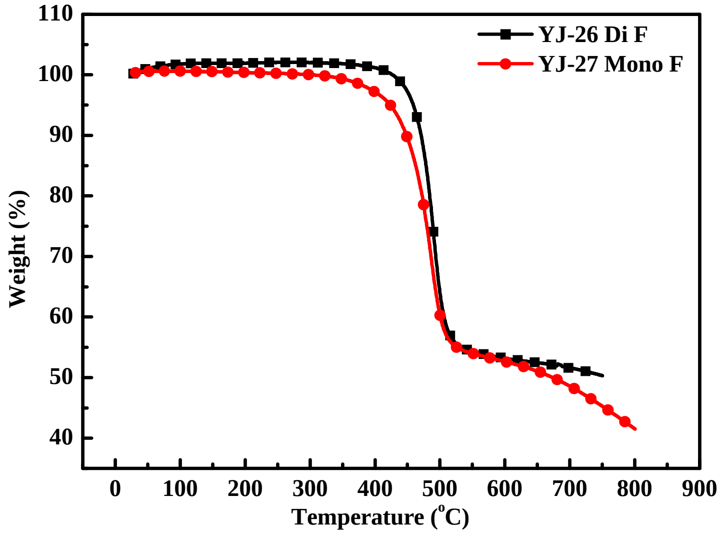


Figure III-1. Thermal gravimetric analysis of polymers (YJ-26 and YJ-27).

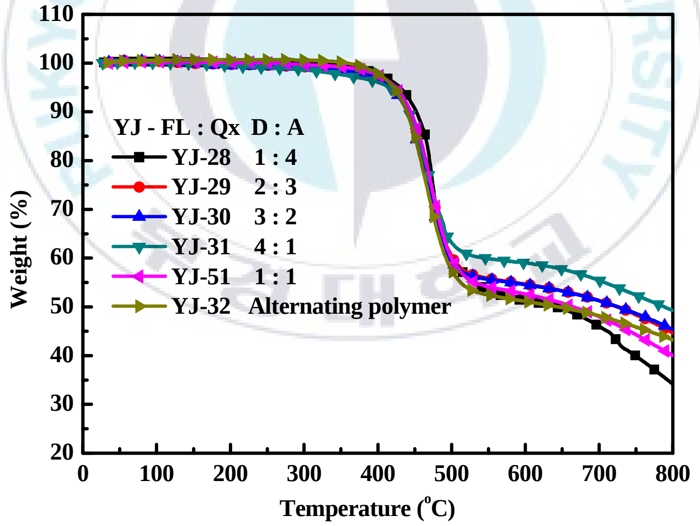


Figure III-2. Thermal gravimetric analysis of polymers (YJ-28 to YJ-32 and YJ-51).

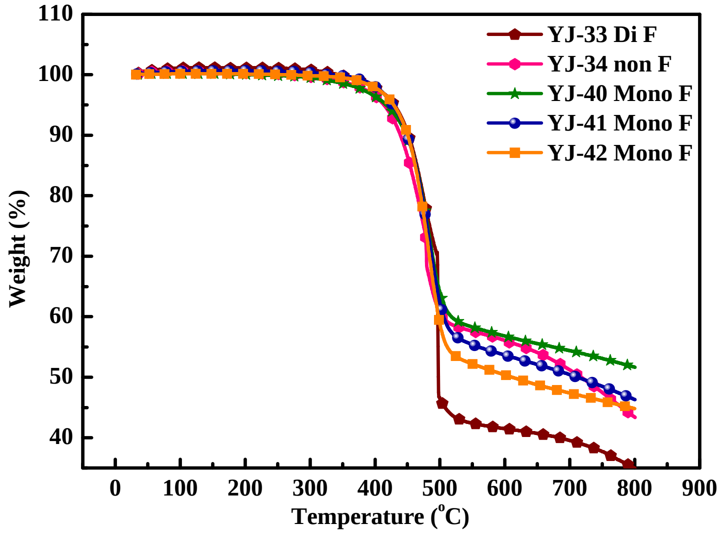


Figure III-3. Thermal gravimetric analysis of polymers (YJ-33, YJ-34 and YJ-40 to YJ- 42).

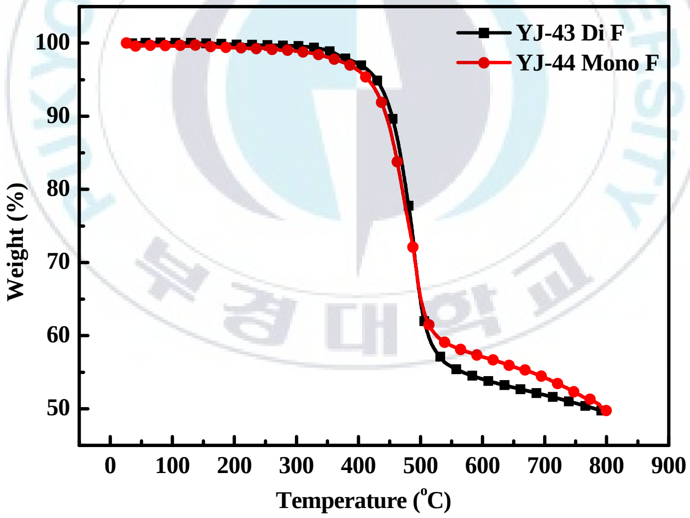


Figure III-4. Thermal gravimetric analysis of polymers (YJ-43 and YJ-44).

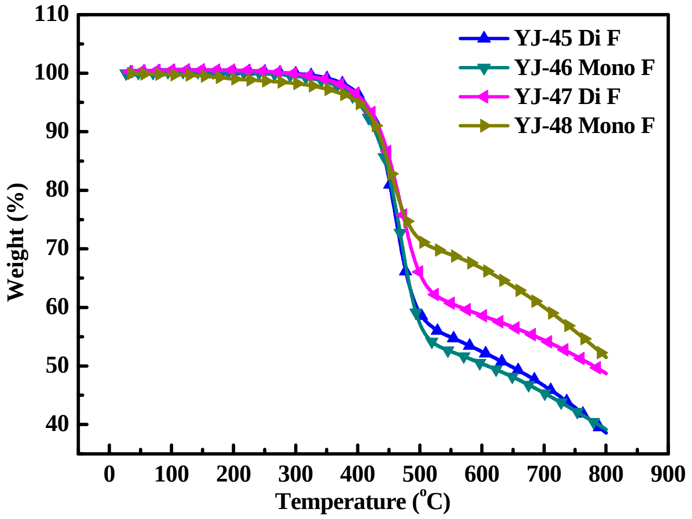


Figure III-5. Thermal gravimetric analysis of polymers (YJ-45 to YJ-48).

III-2. Optical Properties of Polymers

The UV-vis absorption spectra of all polymers in solution and in the solid state are summarized in Table III-3. The UV-vis absorption maxima (λ_{max}) spectra of FL based polymers showed from 443 to 496 nm in chloroform solution state (Figure III-8), however, the maximum absorption peaks in the films state exhibited from 460 to 540 nm (Figure III-9). The optical band gap showed in the range of 1.93 to 2.16. A polymers based on thiophene indicated λ_{max} at 515 to 641 nm in o-DCB solution(Figure III-6, 10, 12 and 14), whereas in the film state were observed from 519 to 644 nm(Figure III-7, 9, 11, 13, 15) and optical band gap from 1.79 to 1.84. The bathochromic shift in the film state exhibited an enhanced π-π stacking form and stronger electronic interaction between the polymer chains in the film state.

The polymers containing monofluorinated quinoxaline (YJ-27, YJ-40, YJ-41, YJ-42, YJ-44, YJ-46 and YJ-48) and indicated narrow optical band gaps compared with difluorinated quinoxaline polymers (YJ-26, YJ-33, YJ-43, YJ-45 and YJ-47). This can be partly attributed to a change in the polymer chain packing via the additional non-covalent interactions with a greater number of F atoms.[44]

Table III-3. Optical properties of polymers.

polymer	Abs.			
	solution	film		E_g^{opt}
	λ_{max} (nm)	λ_{max} (nm)	λ_{edge} (nm)	(eV)
YJ–26	521 [b]	631	685	1.81
YJ–27	534 [b]	595	693	1.79
YJ–28	496 [a]	540	641	1.93
YJ–29	487 [a]	526	623	1.99
YJ–30	450 [a]	460	606	2.05
YJ–31	443 [a]	461	593	2.09
YJ–32	486 [a]	503	574	2.16
YJ–33	633 [b]	635	683	1.82
YJ–34	576 [b]	577	681	1.82
YJ–40	515 [b]	563	686	1.81
YJ–41	536 [b]	567	685	1.81
YJ–42	570 [b]	574	687	1.80
YJ–43	626 [b]	627	675	1.84
YJ–44	637 [b]	638	688	1.80
YJ–45	641 [b]	644	703	1.76
YJ–46	588 [b]	625	706	1.76
YJ–47	625 [b]	638	688	1.80
YJ–48	633 [b]	637	694	1.79
YJ-51	457 [a]	519	574	2.16

[a] In CF solution and [b] in o-DCB solution.

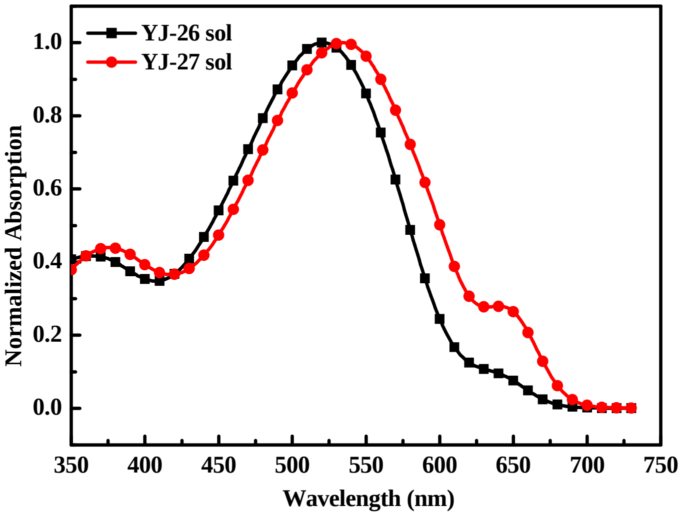


Figure III-6. UV-visible absorption spectra of polymers in chloroform solution (YJ-26 and YJ-27).

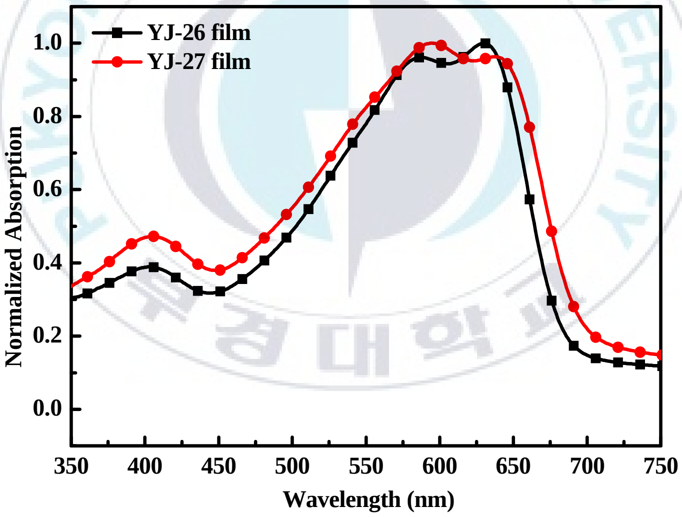


Figure III-7. UV-visible absorption spectra of polymers in a thin film formed via spin-cast from a solution in o-dichlorobenzene (1wt%).

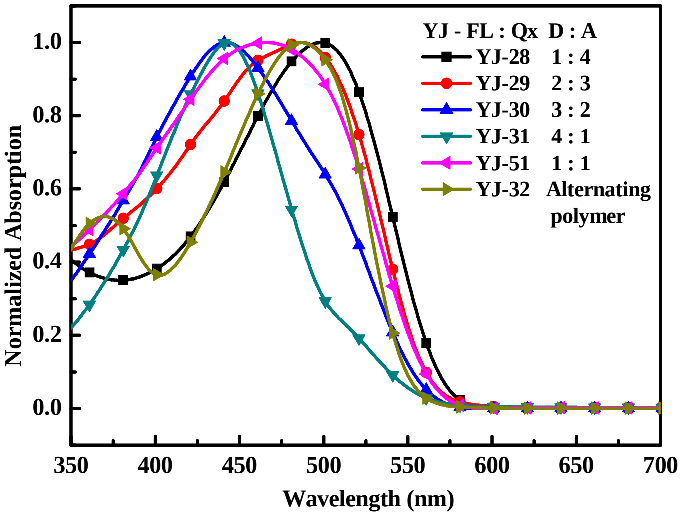


Figure III-8. UV-visible absorption spectra of polymers in o-dichlorobenzene solution (YJ-28 to YJ-32 and YJ-51).

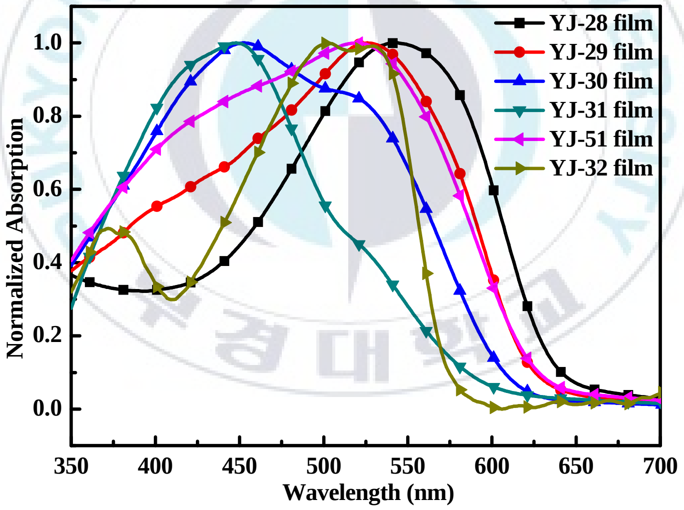


Figure III-9. UV-visible absorption spectra of polymers in a thin film formed via spin-cast from a solution in o-dichlorobenzene (1wt%).

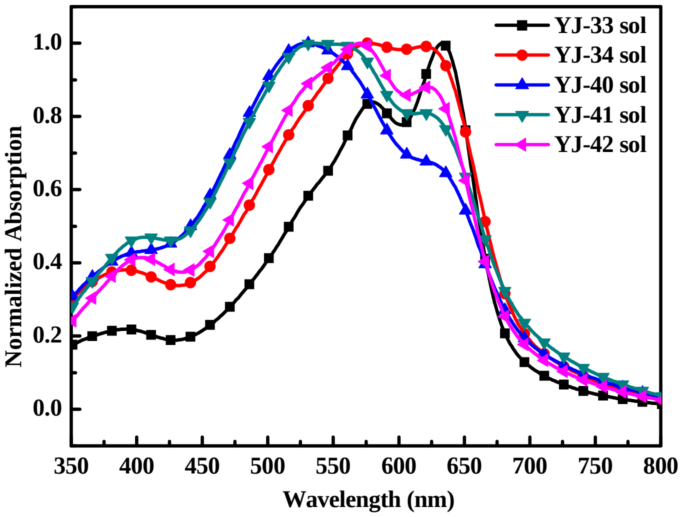


Figure III-10. UV-visible absorption spectra of polymers in o-dichlorobenzene solution (YJ-33, YJ-34 and YJ-40 to YJ-42).

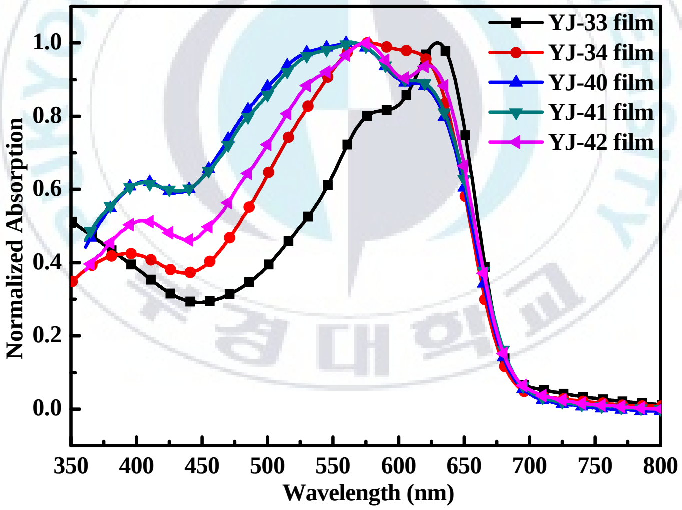


Figure III-11. UV-visible absorption spectra of polymers in a thin film formed via spin-cast from a solution in o-dichlorobenzene (1wt%).

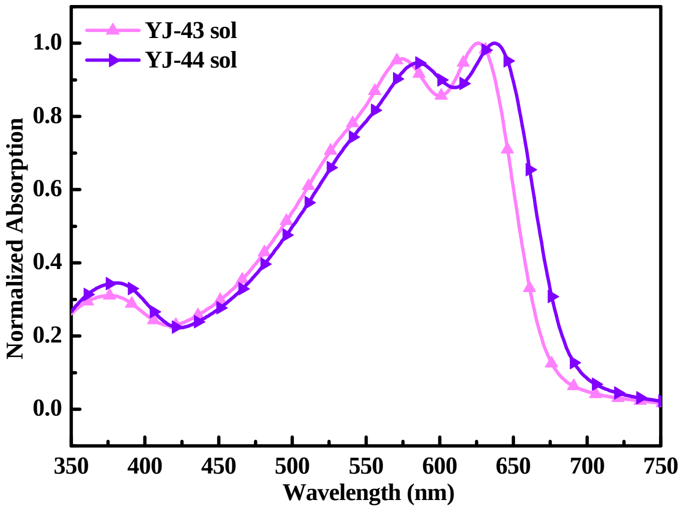


Figure III-12. UV-visible absorption spectra of polymers in o-dichlorobenzene solution (YJ-43 and YJ-44).

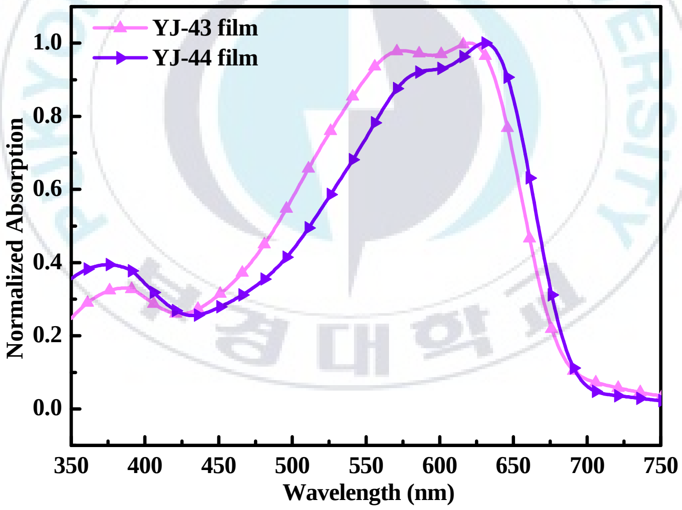


Figure III-13. UV-visible absorption spectra of polymers in a thin film formed via spin-cast from a solution in o-dichlorobenzene (1wt%).

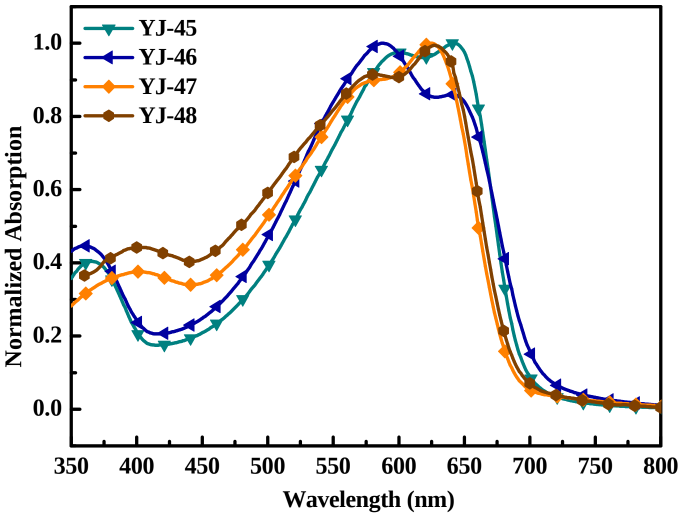


Figure III-14. UV-visible absorption spectra of polymers in o-dichlorobenzene solution (YJ-45 to YJ-48).

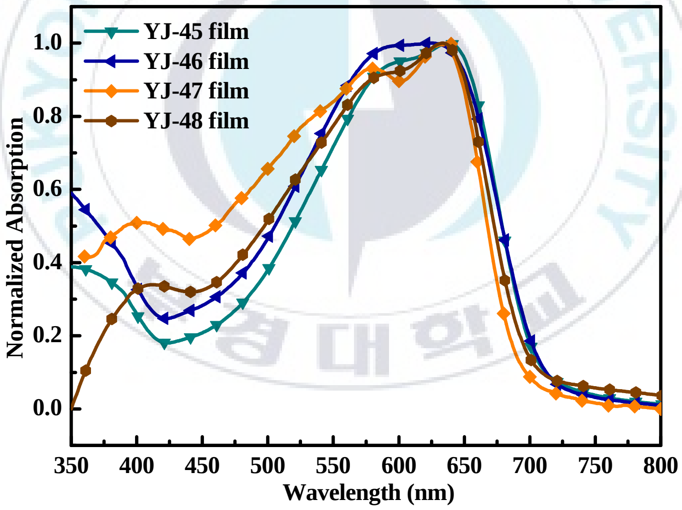


Figure III-15. UV-visible absorption spectra of polymers in a thin film formed via spin-cast from a solution in o-dichlorobenzene (1wt%).

III-3. Electrochemical Properties of Polymers

The HOMO energy levels of these polymers were investigated by cyclic voltammetry (CV). Figure 16 to 20 and table 4 to 8 indicated the CV of result using the sample film on the Pt working electrode in an acetonitrile solution of 0.1 mol/L. The HOMO and LUMO energy levels of the polymers were estimated according to the following equations.

$E_{HOMO} = -(E^{ox}_{onset} + Fc/Fc^{+} \text{ redox potential}) \text{ (eV)}$

$E_{LUMO} = (E_{HOMO} + E_g^{opt}) \text{ (eV)}$

According to the effect of fluorine atom pushing down HOMO energy levels, the polymers including difluorinated quinoxaline had lower HOMO levels compared to those containing monofluorinated quinoxaline. In this reason, these polymers based on difluorinated quinoxaline would be expected to obtain high V_{oc} compared to those based on monofluorinated quinoxaline. The polymers including difluorinated quinoxaline with fluorere especially indicated greatly lower HOMO energy levels by virtue of fluorene molecular and fluorine atom effect.

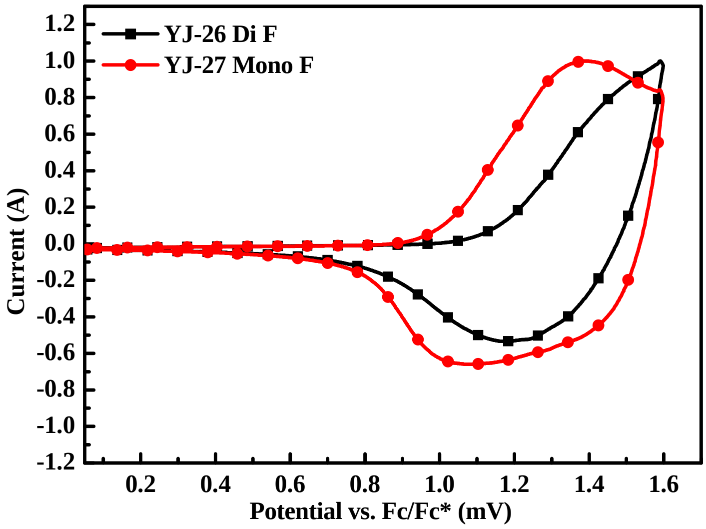


Figure III-16. Cyclic voltammogram of YJ-26 and YJ-27.

Table III-4. Electrochemical Properties of YJ-26 and YJ-27.

Polymer	CV		
	HOMO (eV)	LUMO (eV)	E_g^{cv} (eV)
YJ-26	-5.46	-3.65	1.81
YJ-27	-5.30	-3.51	1.79

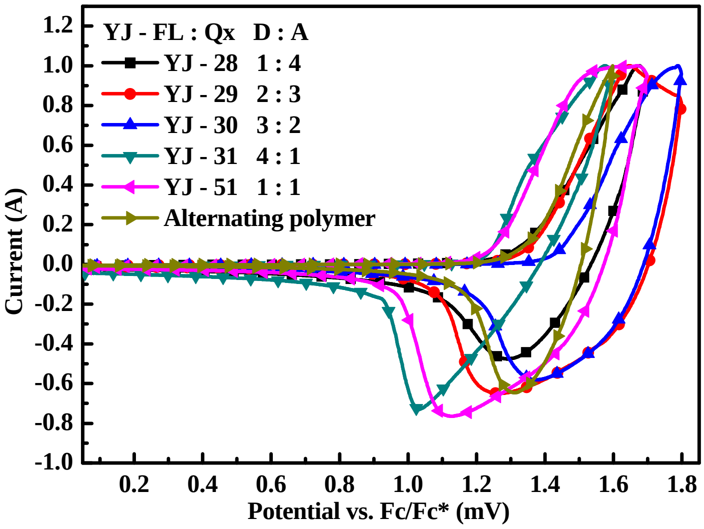


Figure III-17. Cyclic voltammogram of YJ-28 to YJ-32 and YJ-51.

Table III-5. Electrochemical Properties of YJ-28 to YJ-32 and YJ-51.

Polymer	CV		
	HOMO (eV)	LUMO (eV)	E_g^{cv} (eV)
YJ-28	-5.65	-3.75	1.93
YJ-29	- 5.63	-3.64	1.99
YJ-30	- 5.72	-3.67	2.05
YJ-31	-5.60	-3.51	2.09
YJ-32	-5.66	-3.50	2.16
YJ-51	-5.61	-3.63	1.98

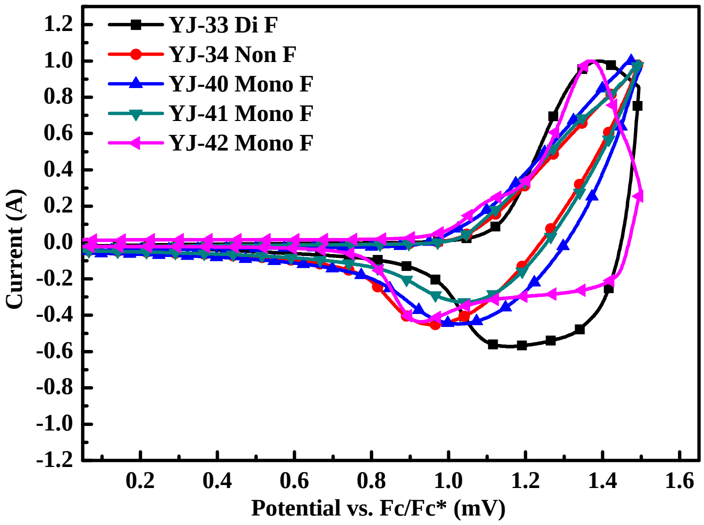


Figure III-18. Cyclic voltammogram of YJ-33, YJ-34 and YJ-40 to YJ-42.

Table III-6. Electrochemical Properties of YJ-33, YJ-34 and YJ-40 to YJ-42.

Polymer	CV		
	HOMO (eV)	LUMO (eV)	E_g^{cv} (eV)
YJ-33	-5.40	-3.58	1.82
YJ-34	-5.28	-3.46	1.82
YJ-40	-5.33	-3.50	1.81
YJ-41	-5.33	-3.52	1.81
YJ-42	-5.28	-3.50	1.80

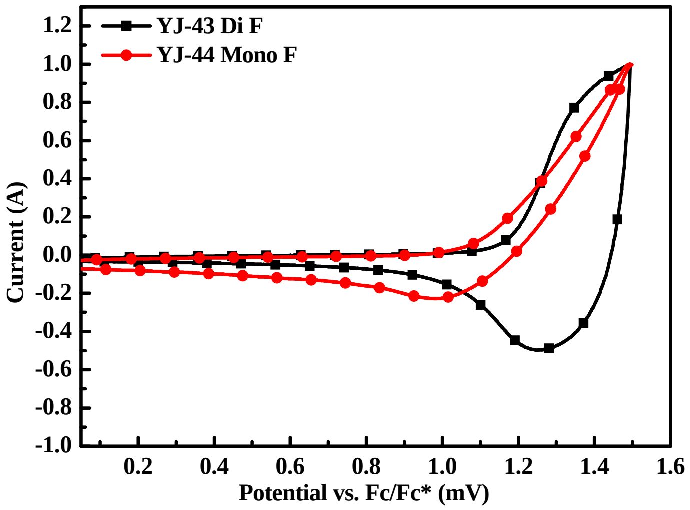


Figure III-19. Cyclic voltammogram of YJ-43 and YJ-44.

Table III-7. Electrochemical Properties of YJ-43 and YJ-44.

Polymer	CV		
	HOMO (eV)	LUMO (eV)	E_g^{cv} (eV)
YJ-43	-5.47	-3.63	1.84
YJ-44	-5.46	-3.66	-1.80

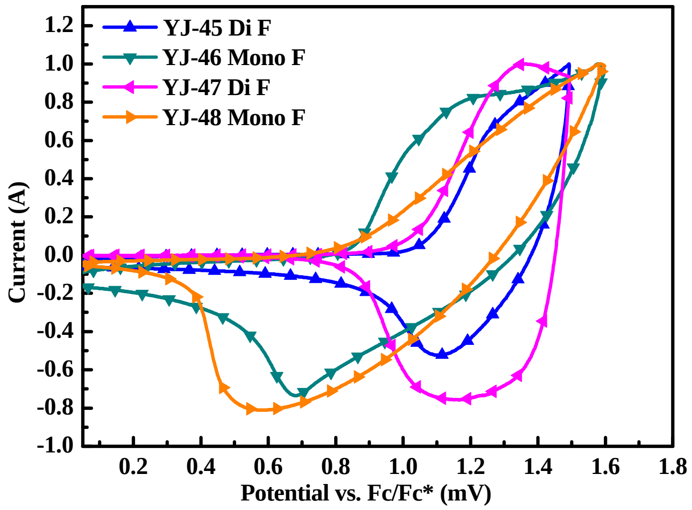


Figure III-20. Cyclic voltammogram of YJ-45 to YJ-48.

Table III-8. Electrochemical Properties of YJ-45 to YJ-48.

Polymer	CV		
	HOMO (eV)	LUMO (eV)	E_g^{cv} (eV)
YJ-45	-5.39	-3.63	1.76
YJ-46	-5.25	-3.49	1.76
YJ-47	-5.31	-3.51	1.80
YJ-48	-5.25	-3.79	1.79

III-4. Photovoltaic Properties of Polymers

In order to investigate the photovoltaic properties of the polymers, the polymer solar cells were fabricated with a general device structure of ITO/PEDOT:PSS/ polymer:PCBM/Al. The photoactive layer was composed of D/A blend with ratio(1:1.5) and added DIO 3% vol for enhanced morphology. The polymers containing fluorene with difluorinated quinoxaline indicated high V_{oc} due to effect of fluorine atom and property of fluorene, however those showed low J_{sc} because of narrow UV-vis absorption spectra and short wavelength absorption. Among fluorene based polymers (YJ-28 to YJ-32 and YJ-51), the best performance was achieved in YJ-28, monomer ratio of 1:4 (Donor:Acceptor) with V_{oc} 0.95, J_{sc} 6.37, FF 0.66 and PCE 3.98%, respectively. (Figure III-22, Table III-10) The most of polymers based on thiophene with difluorinated quinoxaline were difficult to fabricate device because those could almost not dissolve in common organic solvents. Therefore, these polymers usually indicated low PCE. The polymers using thieno[3,2-b]thiophene as donor could fabricate device because of excellent solubility than the other polymers (YJ-33, YJ-34, YJ-40 to YJ-48). As a result, among the polymers based on thiophene without alkyl group (YJ-33, YJ-34 and YJ-40 to YJ-48), the best performance was achieved in YJ-45 with V_{oc} 0.70, J_{sc} 5.51, FF 0.66 and PCE 1.53%, respectively. (Figure III-23 to 25, Table III-11 to 13) The thiophene substituting alkyl group synthesized to tackle this hurdle and polymerized with di or mono fluoro quinoxaline. These two polymers (YJ-26 and YJ-27) showed better solubility than non-alkyl thiophene series and displayed an optimal PCE of 3.25% (YJ-26) and 3.37% (YJ-27). (Figure III-21, Table III-9)

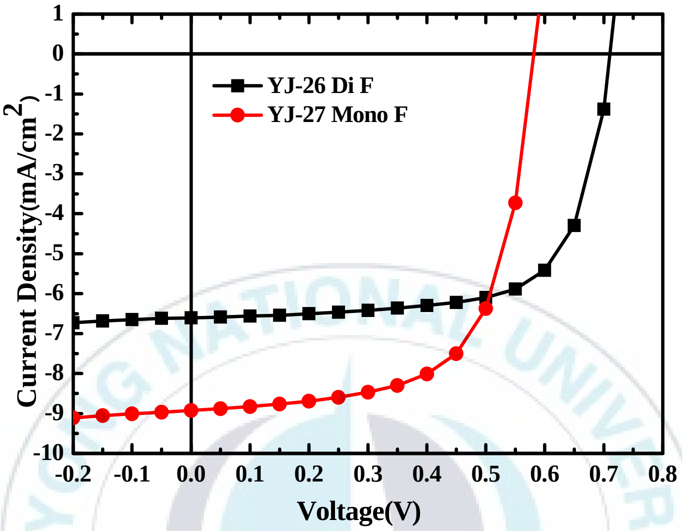


Figure III-21. J-V characteristics of the device based on YJ-26:PC$_{70}$BM and 27:PC$_{70}$BM blend.

Table III-9. Photovoltaic performance of devices based on YJ-26:PC$_{70}$BM and YJ-27:PC$_{70}$BM.

polymer	ratio (polymer:PCBM)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
YJ-26	1 : 1.5	6.60	0.71	0.69	3.25
YJ-27	1 : 1.5	8.93	0.59	0.64	3.37

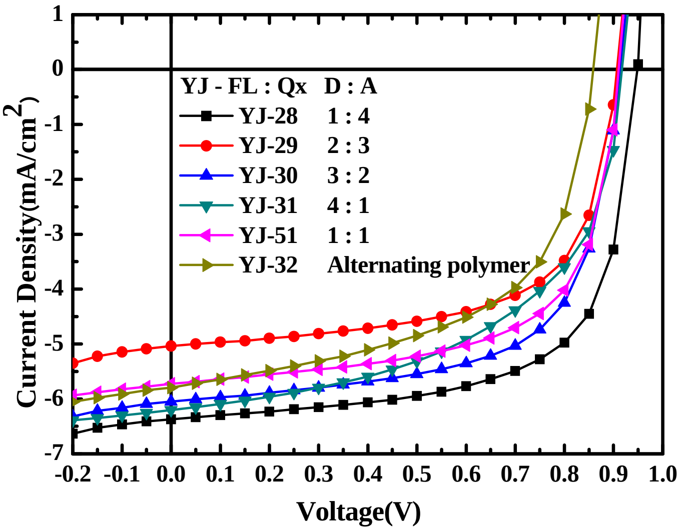


Figure III-22. J-V characteristics of the device based on YJ-28:PC$_{70}$BM to YJ-32:PC$_{70}$BM and YJ-51:PC$_{70}$BM blend.

Table III-10. Photovoltaic performance of devices based on YJ-28:PC$_{70}$BM to YJ-32:PC$_{70}$BM and YJ-51:PC$_{70}$BM blend.

polymer	ratio (polymer:PCBM)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
YJ-28	1 : 1.5	6.37	0.95	0.66	3.98
YJ-29	1 : 1.5	5.04	0.91	0.64	2.91
YJ-30	1 : 1.5	6.05	0.91	0.64	3.55
YJ-31	1 : 1.5	6.20	0.92	0.54	3.07
YJ-32	1 : 1.5	5.80	0.86	0.56	2.78
YJ-51	1 : 1.5	5.73	0.91	0.64	3.33

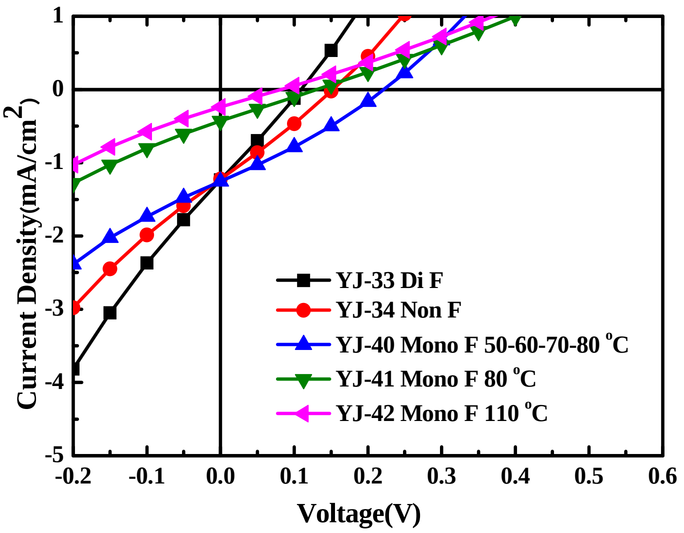


Figure III-23. J-V characteristics of the device based on YJ-33:$PC_{70}BM$, YJ-34:$PC_{70}BM$ and YJ-40:$PC_{70}BM$ to YJ-42:$PC_{70}BM$ blend.

Table III-11. Photovoltaic performance of devices based on YJ-33:$PC_{70}BM$, YJ-34:$PC_{70}BM$ and YJ-40:$PC_{70}BM$ to YJ-42:$PC_{70}BM$.

polymer	ratio (polymer:PCBM)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
YJ-33	1 : 1.5	1.24	0.11	0.26	0.03
YJ-34	1 : 1.5	1.22	0.15	0.25	0.05
YJ-40	1 : 1.5	1.25	0.22	0.28	0.08
YJ-41	1 : 1.5	0.43	0.13	0.34	0.01
YJ-42	1 : 1.5	0.24	0.08	0.23	0.004

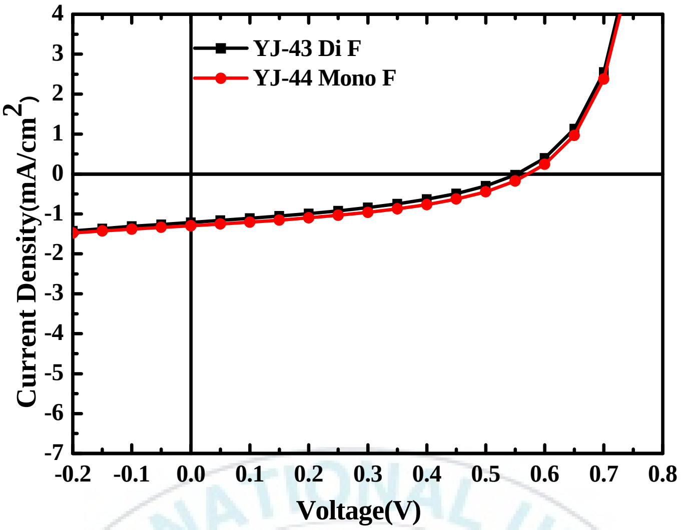


Figure III-24. J-V characteristics of the device based on YJ-43:PC$_{70}$BM and YJ-44:PC$_{70}$BM blend.

Table III-12. Photovoltaic performance of devices based on YJ-43:PC$_{70}$BM and YJ-44:PC$_{70}$BM.

polymer	ratio (polymer:PCBM)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
YJ-43	1 : 1.5	1.21	0.55	0.39	0.26
YJ-44	1 : 1.5	1.29	0.57	0.42	0.31

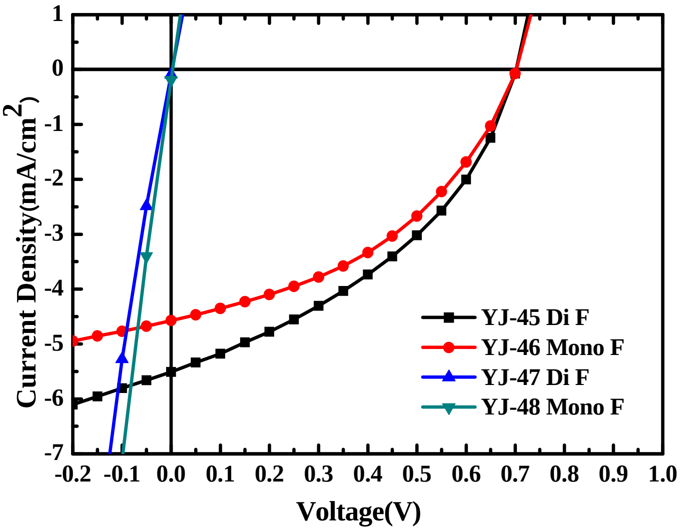


Figure III-25. J-V characteristics of the device based on YJ-45:PC$_{70}$BM to YJ-48:PC$_{70}$BM blend.

Table III-13. Photovoltaic performance of devices based on YJ-45:PC$_{70}$BM to YJ-48:PC$_{70}$BM.

polymer	ratio (polymer:PCBM)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
YJ-45	1 : 1.5	5.51	0.70	0.40	1.53
YJ-46	1 : 1.5	4.57	0.70	0.43	1.37
YJ-47	1 : 1.5	0.19	0.01	0	0
YJ-48	1 : 1.5	0.09	0.01	0	0

Chapter IV. Conclusions

In summary, we report the design, synthesis and properties of di, mono, non fluoro quinoxaline as acceptor with FL and thiophene derivatives as donor. Introducing electron-withdrawing functional group like fluorine atom, could achieve the lowered HOMO energy levels and FL molecular also was used for low HOMO energy levels. FL based polymers had a good solubility in common types of organic solvents like chloroform, chlorobenzene and o-dichlorobenzene but polymers based on thiophene derivatives usually showed bad solubility in organic solvents. All polymers exhibited good thermal stability mostly over 400 °C. YJ-28 to YJ-32 and YJ-51 polymers showed maximum absorption peak at 443 to 496 nm in chloroform solution and 460 to 540 nm in film state and optical band gap 1.93 to 2.16, with HOMO energy levels -5.60 to -5.72. Among the polymers, the best performance was achieved in YJ-28, monomer ratio of 1:4 (donor:acceptor) with V_{oc} 0.95V, J_{sc} 6.37mA/cm^2, FF 0.66% and PCE 3.98%, respectively. A polymers based on thiophene derivatives had λ_{max} at 521 to 641 nm in o-DCB solution and 563 to 644 nm in film state and optical band gap 1.76 to 1.84, with HOMO energy levels -5.25 to -5.47. Mostly, thiophene-based polymers could hardly fabricate device because those indicated low solubility in organic solvents. Therefore, the polymers based on thiophene showed low PCE. Among them, the polymers introducing alkyl group for enhance solubility (YJ-26, YJ-27) were possible to fabricate device. Among polymers based on thiophene derivatives, YJ-27 indicated the best efficiency, with V_{oc} of 0.59V, J_{sc} of 8.93 mA/cm^2, FF of 0.64% and PCE of 3.37%, respectively.

References

[1] C. W. Tang, Appl. Phys. Lett., 48, 183 (1986)

[2] T. T. Tsuzuki, J. Shirota, J. Rostalski, D. Meissner, Sol. Energy Mater. Sol. Cells 61, 1 (2000)

[3] J. X. Uchida, B. P. Rand, S. R. Forrest, Appl. Phys. Lett. 84, 4218 (2004)

[4] X. Zhou, J. Blochwitz, M. Pfeiffer, A. Nollau, T. Fritz, K. Leo, Adv. Funct. Mater. 11, 310 (2001)

[5] D. Wo¨hrle, D. Meissner, Adv. Mater. 3, 129 (1991)

[6] S. A. Jenekhe, S. Yi, Appl. Phys. Lett. 77, 2635 (2000)

[7] A. J. Breeze, A. Salomon, D. S. Ginley, B. A. Gregg, H. Tillmann, H. H. Hoerhold, Appl. Phys. Lett. 81, 3085 (2002)

[8] N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky, F. Wudl, Appl. Phys. Lett. 62, 585 (1993)

[9] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friends, S. C. Moratti, A. B.Holmes, Nature 78, 451 (1995)

[10] C. Winder, N. S. Sariciftci, J. Mater. Chem. 14, 1077 (2004)

[11] D. Gebeyehu, B. Maening, J. Drechsel, K. Leo, M. Pfeiffer, Sol. Energy Mater. Sol. Cells 79, 81 (2003)

[12] M. Hiramoto, H. Fujiwara, M. Yokoyama, Appl. Phys. Lett. 58, 1061 (1991)

[13] W. Geens, T. Aernouts, J. Poortmans, G. Hadziioannou, Thin Solid Films 403-404, 438 (2002)

[14] P. Peumans, S. Uchida, S. Forrest, Nature 425, 158 (2003)

[15] G. Yu, A. J. Heeger, J. Appl. Phys. 78, 4510 (1998)

[16] C. Y. Yang, A. J. Heeger, Synth. Met. 83, 85 (1996)

[17] M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. Brabec, J. Adv. Mater. 18 (6), 789-794 (2006)

[18] L. Yang, H. Zhou, W. You, J. Phys. Chem. C 114 (39), 16793-16800 (2010)

[19] A. Moliton, J.-M. Nunzi, Polym. Int. 55 (6), 583-600 (2006)

[20] B. C. Thompson, J. M. Fréchet, J. Angew. Chem. Int. Ed. 47 (1), 58-77 (2008)

[21] R. Kroon, M. Lenes, J. C. Hummelen, P. W. M. Blom, B. de Boer, Polym. Rev. (Philadelphia, PA, U. S.) 48 (3), 531-582 (2008)

[22] Havinga, E. E.; ten Hoeve, W.; Wynberg, H. Synth. Met.1993, 55 (1), 299−306.

[23] Ajayaghosh, A. Chem. Soc. Rev. 2003, 32 (4), 181−191.

[24] Zhou, H.; Yang, L.; Stoneking, S.; You, W. ACS Appl. Mater. Interfaces 2010, 2 (5), 1377−1383.

[25] Z. He, C. Zhong, X. Huang, W.-Y. Wong, H. Wu, L. Chen, S. Su and Y. Cao, Adv. Mater., 23, 4636-4643 (2011)

[26] Jenekhe SA, Osaheni JA. Excimers and exciplexes of conjugated

polymers.Science., 265:765-768 (1994)

[27] Grell M, Bradley DDC, Inbasekaran M, Woo EPA. Glass-forming conjugated main-chain liquid crystal polymer for polarized electroiuminescence applications. Adv. Mater., 9 798-802 (1997)

[28] Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, Chem. Rev., 109, 5868−5923 (2009)

[29] McCulloch I, Heeney M, Bailey C, Genevicius K, Macdonald I, Shkunov M, Nat Mater 5(4), 328-33 (2006)

[30] Bronstein H, Chen Z, Ashraf RS, Zhang W, Du J, Durrant JR, et al., J Am Chem Soc, 133(10), 3272-5 (2011).

[31] Pei-Yin Chao, Hung-Chin Wu, Chien Lu, Chian-Wen Hong, and Wen-Chang Chen, Macromolecules., 48, 5596－5604 (2015)

[32] Argiri Tsami,a Torsten W. Bu¨nnagel, Tony Farrell, Markus Scharber, Stelios A. Choulis,Christoph J. Brabec and Ullrich Scherf, J. Mater. Chem., 17, 1353–1355 (2007)

[33] Tianqi Cai , YiZhou , Ergang Wang, Stefan Hellstr¨oma, Fengling Zhang, ShiaiXu, OlleIngan¨as, Mats R.Andersson, T. Cai et al. / Solar Energy Materials & Solar Cells 94 1275–1281 (2010)

[34] C. Kitamura, S. Tanaka, Y. Yamashita, Chem. Mater., 8, 570 (1996)

[35] M. J. Edelmann, J.-M. Raimundo, N. F. Utesch, F. A. Diederich, C. Boudon,J.-P. Gisselbrecht, M. Gross, Helv.Chim.Acta,85, 2195 (2002)

[36] A. Tsami, T. W. Bunnagel, T. Farrell, M. Scharber, S. A. Choulis, C. J. Brabec, U. Scherf, J. Mater. Chem., 17, 1353 (2007).

[37] R. Duan, L. Ye, X. Guo, Y. Huang, P. Wang , S. Zhang, J. Zhang , L. Huo, J. Hou, Macromolecules., 45 , 3032 (2012)

[38] Y. Huang, M. Zhang, L. Ye, X. Guo, C. C. Han, Y. Li, J. Hou., J. Mater. Chem., 22, 5700 (2012)

[39] Delong Liu, Wenchao Zhao, Shaoqing Zhang, Long Ye, Zhong Zheng, Yong Cui, Yu Chen, Jianhui Hou macromolecules., 48, 5172-5178 (2015)

[40] R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu, J. M. J. Fréchet, M. F. Toney, Macromolecules, 38 (8), 3312- 3319 (2005)

[41] H. Zhou, L. Yang, S. Xiao, S. Liu, W. You, Macromolecules, 43 (2), 811-820 (2010)

[42] Espinet, P.; Echavarren, A. M. Angew. Chem. Int. Ed., 43, 4704-4734 (2004)

[43] Crabtree, R. H. The Organometallic Chemistry of the Transition Metals, 5th ed.; Wiley: New York (2009)

[44] Jonggi Kim, Myoung Hee Yun, Gi-Hwan Kim, Jungho Lee, Sang Myeon Lee, Seo-Jin Ko, Yiho Kim, Gitish K. Dutta, Mijin Moon, Song Yi Park, Dong Suk Kim, Jin Young Kim, and Changduk Yang, ACS Appl. Mater. Interfaces, 6, 7523-7534 (2014)

감사의 글

배움의 뜻만 가지고 무작정 찾아왔던 저를 받아 주시고 지금의 저를 있게 해주신 지도교수님 진영읍 교수님께 진심으로 감사하다는 말씀을 드리고 싶습니다. 그리고 지난 2년간 많은 도움을 주신 공업화학과 박진환 교수님, 이근대 교수님, 박성수 교수님, 문명준 교수님, 곽삼탁 교수님, 손민영 교수님 그리고 장동욱 교수님 정말 감사합니다. 측정을 도와주시고 조언을 해주신 박성흠 교수님, 김주현 교수님 감사합니다. 그리고 부산대 김주애 선배님도 감사합니다. 언제 어디서나 제가 하고 싶은 일들을 믿어주시고 이끌어주신 아버지 어머니 정말 감사합니다. 앞으로 더욱 열심히 노력해 멋진 모습들을 보여드리겠습니다. 그리고 하나밖에 없는 여동생 수진이도 항상 응원해줘서 고맙다. 실험실에서 생활하면서 성실한 연구자세를 몸소 보여주신 원준형님, 가끔 찾아오셔서 응원의 메시지와 맛있는 것을 사주신 은준, 동호형님, 나의 동기이자 격려도 많이 해주고 많은 도움을 준 지현이 모두 정말 감사합니다. 상하형님 제가 많이 도와 드려야 했는데 많이 못해드려서 죄송하고 남은 반년 마무리 잘하시고 민성형님은 성격도 활발하고 좋아서 남은 석사 생활도 잘할거라고 믿습니다. 이제 마무리이자 시작인 동욱아 박사 생활 열심히 하고 멋진 성과를 이루길 바란다. 민석이도 이제 1년 남았는데 마무리 잘하고 좋은데 취직했으면 좋겠다. 그리고 자주 만나지는 못했지만 언제나 옆에서 힘이 되어준 승준이, 창희, 영인이, 승엽이, 준원이, 준영이, 문성이, 규태, 규현이 나의 죽마고우 친구들아 모두 고맙다. 마지막으로 지면을 통해서 일일이 언급을 하지 못해서 죄송합니다. 그 동안 저를 아껴주시고 사랑해주시고 항상 응원의 메시지를 보내주신 모든 분들께 다시 한번 진심으로 감사드립니다.