Thesis for the Degree of Master of Engineering

Systematic Approach of π–Bridge to Propose One Method of High Efficiency OPV Development

by

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February2021

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(고효율 유기태양전지 개발을 위한 파이 브릿지를 적용하는 방법의 체계적인 접근)

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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 2021

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February 19,2021

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고효율 유기태양전지 개발을 위한 파이 브릿지를 적용하는 방법의 체계적인 접근

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요 약

과학기술이 발전함에 따라서 에너지 수요는 점점 더 증가하고 이에 따라 화석에너지 고갈과 온실가스에 의한 지구온난화 등 많은 문제가 발생하고 있다. 이를 해결하기 위하여 다양한 친환경 에너지가 연구되고 있고 이 중 태양전지는 무궁무진한 에너지원이며 추가적인 환경오염 부산물이 발생하지 않는 장점이 있다. 최근 많이 연구되는 유기태양전지는 액체상태로 작업이 가능하여 대량생산이 쉽고 이를 통해 낮은 가격으로 생산이 가능하단 장점이 있다. 이 논문에서는 유기태양전지의 광활성층 그 중에서 Donor 에 관한 연구로써 Donor 는 Push 유닛과 full 유닛의 Alternating 구조로 합성을 하였고 이 사이에 π-bridge 로 널리 사용되는 thiophene 의 위치와 수를 조절하며 합성함으로써 이 Thiophene bridge 가 유기태양전지에 어떠한 영향을 미치는지 체계적으로 접근하고 조사하였다.

Chapter I. Introduction

I-1. The Background of Organic Solar Cells (OSCs)

Nowadays, energy demands and consumption are growing rapidly. Researchers are predicting fuel will be eliminated within 100 years. The fossil fuel depletion will accelerate because of advances in oil production technology. Cause, eco-friendly energy is in the spotlight. Eco-friendly energy includes solar, geothermal, wind, hydro, and so on, among these eco-friendly energies, solar energy has many advantages that are infinite, pollution-free and no waste generation. scale.

Organic solar cells(OSCs) based on organic materials have drawn attraction in the people. Organic solar cells can apply solution processes. With this characteristics, organic solar cells use variety coating method. It cause mass production and inexpensive also the liquid does not have a fixed form so it can have characteristics of substrate such as flexibility. For the same reasons, Organic solar cells(OSCs) have been attracted attention of the world. Another important advantage of OSCs is the variety of the polymer structure. OSCs can adjust the variety backbone and side-chain as occasion demands.[1]

Organic solar cells are different inorganic solar cells. There are a lot of advantages, but disadvantages are clear. One is low efficiency then inorganic solar cells, the other is short life time because of organic compounds. To overcome these disadvantages organic solar cells have been studying a lot. Due to the many people's research, initially organic solar cells had low efficiency but it has recently shown high efficiency exceeding 18%.[2]

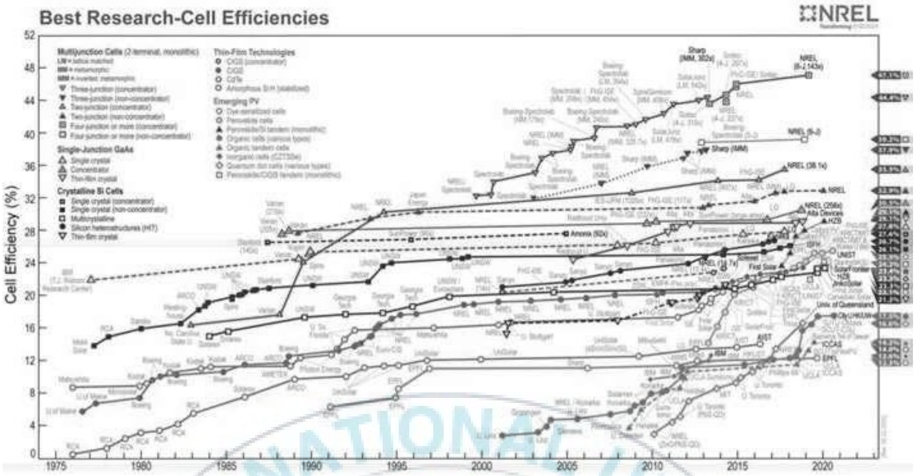


Figure 1 Organic solar cell performance table

I-2. Bulk Heterojunction Structure

Organic solar cells structure have similar or same structure at Figure2. Ordinary, Active layer is consist of two layer. First layer is donor and second layer is Acceptor layer.[3] But this structure is shown low charge mobility. Because exitons had short life time. Before reaching the surfaces of Acceptor layer, exitons are recombined it caused low current and performance. BHJ(Bulk Hetero Junction) method is used to solve this problem. The BHJ method is based on the liquidable characteristics of Organic solar cells. BHJ method is not two layer but one layer. Donor material and Acceptor material are mixed and dissolved. Two materials are mixed random and evenly distributed. By using this method, the distance between Donor and Acceptor has greatly decreased. Through this, Exitons life time are short but can reach Acceptor layer easily, the charge separation ratio has been increased and high Jsc and performance can be obtained.[4]

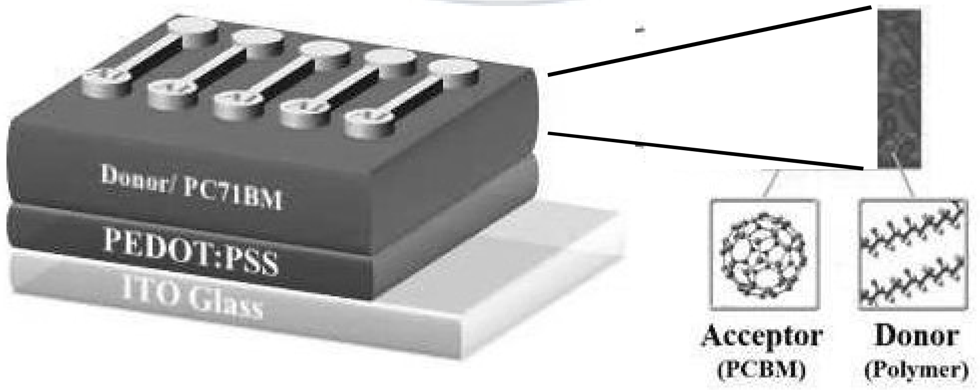


Figure 2 Device tructure of organic solar cell and bulk-heterojunction active layer

I-3. Efficiency of PSCs

There are three factors in an organic solar cell that determines efficiency. One is V_{oc} other is J_{sc} the other is FF. V_{oc} is affected the polymers HOMO value generally. V_{oc} is Open Circuit Voltage that means the maximum voltage theoretically when this circuit's resistance is max in this circuit. In generally V_{oc} is affected by HOMO energy level.[5] The deeper HOMO drawn higher V_{oc} value. J_{sc} is Short circuit Current.[3] J_{sc} means the maximum electron current theoretically when this circuit's electron current is max according to resistance is 0. J_{sc} is affected by electron. Many electron absorb energy, separation well, how much energy can absorb in this module. The sun emits more red wavelengths than blue wavelengths. Therefore, polymers have the smaller band gap, the more absorbs the red wavelength of light, it can be drawn high J_{sc} generally. FF is actually the product of the voltage and current value that this module has the highest value. FF is indicator of how well the electrons are moving and captured. FF is affected in combination by various factors such as crystallinity, morphology, charge carrier mobility, separation electron, ratio of recombination and so on.[6]

$$\eta = V_{oc} \times J_{sc} \times FF \qquad FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}}$$

Figure 3 equation of solar cell efficiency

I-3-1. Donor-Acceptor (D-A) Alternating Structure

One of the ways appropriate energy bandgap that came out to solve this contradiction is Donating-Accepting alternating structure. In polymer donor, the Donating-Accepting structure was one of the most promising tactics to improve the efficiency of the polymer solar cells.[7] The push and pull alternating copolymers composed of two monomers, one is pull electron using strong electron withdrawing group, and theother is electron rich unit. This structure helpful for achieve small band gap polymer by molecular orbital hybridization between Donating and Accepting units. The copolymer have four new orbital energy levels, higher-lying energy levels and lower-lying energy levels. The HOMO energy level is mainly affected by Donating unit and LUMO level is affected by Accepting unit. Among them, higher-lying HOMO and lower-lying LUMO led to narrow band gap energy levels. Thus, energy level can be narrow at the same time accepting structure's lower HOMO by using Donating-Accepting alternating copolymer.[8]

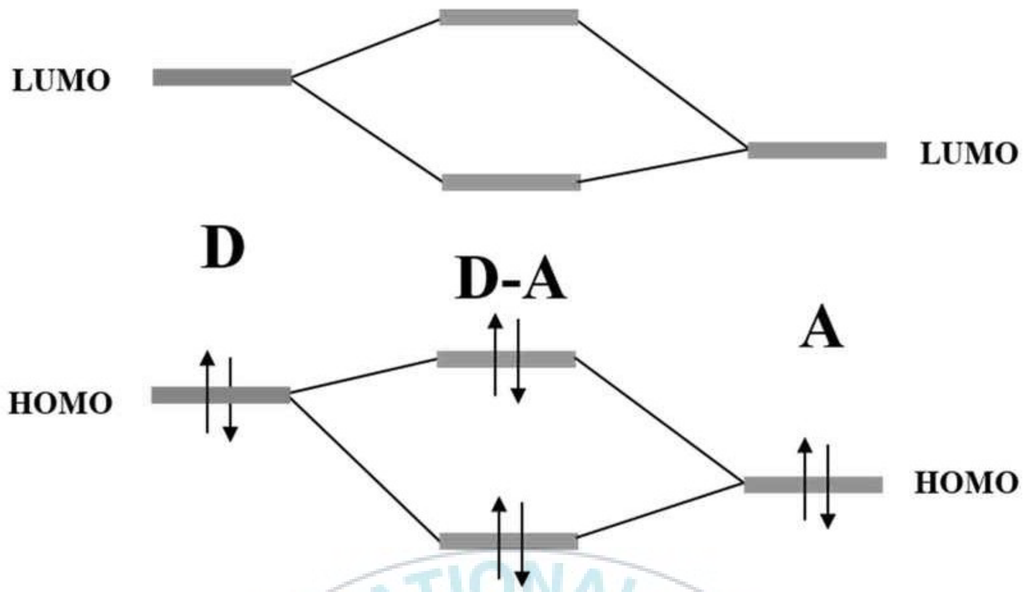


Figure 4 energy conversion of D-A alternating structure

I-3-2. Effect of functional group introduction

The other ways to appropriate energy bandgap that is used functional group. This method is also easily applicable because it is the case of organic solar cells that were used to synthesized material. Electron donating or withdrawing functional group can easily tune energy bandgap. Many paper used fluorine functional group. Fluorine has strong electron negativity so it can make deeper HOMO energy level easily. And Fluorine have small size atom so steric hindrance is minimize. Also functional group sometimes used aromatic group for high crystallinity, thermal durability. And used alkyl chain for high solubility. In these ways, by using various functional group, the properties of polymers change easily and thus used appropriate functional groups are important to achieve high performance organic solar cell.[9]

I-3-3. Selection of Donor and Acceptor Unit in Conjugated Polymer

In this research, push unit is fixed 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (BDT). The BDT unit is one of commonly used push units. The BDT backbone is consist of benzene with two fused thiophene. BDT has extended π-conjugated structures so can have high charge mobility. And the planar structure of BDT can have good crystallinity with pi-pi bond become stronger.[10] Phenazine is used as full units. The Phenazine structure is based on Quinoxaline (Qx). Qx has strong electron withdrawing effect becoming from C=N double bonds and good charge mobility carry out better photovoltaic properties. Phenazine is an extension of π-conjugation from Qx, take advantage of Qx and also have better charge mobility and strong π-π stacking effect becoming from more planer and extended backbone.[11]

I-4. Selection of research topics and contents to confirm

Many study use π bridge and studying about π bridge effect. They used various π bridge and also increase the number of π bridge like D-A, D-π-A-π, D- π-π-A- π, D-π-A-π-π and D-π-π-A-π-π. Research on the number of π bridge says that The π bridge adjacent to the backbone has a great influence on the properties of the polymer, but its influence decreases as this number increases. In this study, 3 type of fluoro substitute Phenazine units are compared. Each of polymer was made of thiophene bridge difference. Between Donor unit and Acceptor unit inserted zero or one or two thiophene bridge. So the form of three type polymers are D-A, D-A- π, D- π-A- π.

Chapter II. Experimental

II-1. Materials and Instruments

The monomer of (4,8-bis((2-ethylhexyl)oxy)-4,8-dihydrobenzo[1,2-b'4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) was purchased from Suna Tech Inc and 1,4-dibrom-2-fluorobenzene was purchased from Alfa aesar. Other were purchased from Aldrich, Acros, Alfa and used without further purification. Solvents were distilled with sodium under Argon atmosphere. 1H and 13C NMR spectra were recorded with a Delta JEOL JNM ECP-400 spectrometer and chemical shifts were recorded in ppm units with Tetra methyl silane as the internal standard. Gas chromatography/mass Spectrometer was recorded by using electron impact ionization method of 70eV. Liquid column chromatography was performed with Sk chemicals silica SL-60-60A (particle size 230-400 mesh ASTM) with hexane/ dimethyl chloride gradients unless otherwise indicated. Thin layer chromatography (TLC) was performed using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV 254nm. The UV-vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer. The CV analyze was performed with a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) 5mmol in acetonitrile 50ml at a scan rate of 100 mV/s at room temperature. Ag wire electrode was used as the reference parts. Pt wire electrode was used as the counter parts electrode. The energy level of $Ag/AgNO_3$ reference electrode was 4.80 eV below the vacuum level. It calibrated by the FC/FC$^+$ redox system. The formula for saving HOMO energy level is (E_{HOMO}= -([E_{onset}]$_{ox}$ + 4.80) eV) according to the empirical formula

II-2. Synthesis of Monomers

2-1. Synthesis of 1,4-dibromo-2-fluoro-5-nitrobenzene (2)

The compounds of (1) (5.0 g, 19.7 mmol), trifluoroacetic acid (9.05 mL, 118.16 mmol), and trifluoroacetic anhydride (16 mL, 118.16 mmol) and NH4NO3 (2 g, 25 mmol) was added to anhydrous dichloromethane (16 mL) at 0℃. Then, this solution was stirred at room temperature overnight. After that, the solution was poured into water at 0℃ then stirred 30min. And the solution was extracted with dichloromethane twice. The collected organic solution was dried over MgSO4. After removing the solvent, which afforded 5.61g (yield 95.31%) of a white powder as the product. 1H NMR (CDCl3, 400 MHz, δ) 8.21 (d, J = 6.36 Hz, 1H), 7.57 (d, J = 7.41 Hz, 1H).

2-2. Synthesis of 2,5-dibromo-4-fluoroanilline (3)

The compounds of (2) (5.61 g, 18.78 mmol) was added to Ethanol (55 mL), then HCl (50ml) and SnCl2·2H2O (16.95g, 75.12mmol) were added at 0℃. Then, this solution was stirred 1H at 80℃ then, stirred room temperature overnight. After that, the solution was poured KOH solution at 0 ℃ for adjust Ph Value 8~9 then stirred 30min. And the solution was extracted with Ethyl acetate twice. The collected organic solution was dried over MgSO4. the crude compound was purified by column chromatography using a solvent gradient of 30−50% dichloromethane in hexane as the eluent, which afforded 4.36g (yield 86.09) to give off white solid.1H NMR (CDCl3, 400 MHz, δ):8.62 (d, J = 6.66 Hz, 1H), 8.31 (s, 1H), 7.45 (d, J = 7.32 Hz, 1H).

2-3. Synthesis of 2,5-dibromo-4-fluorophenyl-2,2,2-trifluoroacetamide (4)

The compounds of (3) (4.36 g, 18.78 mmol) was added to Chloroform (80 mL), then Trifluoro acetic anhydride (46.24ml 20.88mmol) was added slowly at 0℃. Then, this solution was stirred 2H at room temperature. After that, the solution was poured NaHCO3 solution at 0℃ then stirred 30min. And the solution was extracted with Chloroform twice. The collected organic solution was dried over MgSO4. After removing the solvent, which afforded 5.28g (yield 89.23%) of a white powder as the product. 1H NMR (CDCl3, 400 MHz, δ):7.84 (s, 1H), 7.71 (d, J = 7.11 Hz, 1H).

2-4. Synthesis of 3,6-dibromo-4-fluoro2-nitrophenyl-2,2,2-trifluoroacetamide (5)

The compounds of (4) (5.28g, 16.76mmol) was added to three neck flask (500ml), then lower the temperature to -10℃ degrees. And solution of cool H2SO4 (60ml) and fuming HNO3 (30ml) are put into flask very slowly using dropping panel. The mixture was stirred at -10 ℃ for 2h and then poured into ice water. The resulting solid was filtered and purified by a column chromatography using a solvent gradient of 50%~60% dichloromethane in hexane as the eluent, which afforded 5.58g (yield 81.26) of a white powder as the product. 1H NMR (CDCl3, 400 MHz, δ):7.49 (d, J = 7.29 Hz, 1H), 5.05 (s, 2H).

2-5. Synthesis of 3,6-dibromo-4-fluoro2-nitroaniline (6)

The compounds of (5) (5.58g, 13.62mmol) was added to two neck flaks(250ml). Then diluted sulfuric acid (160ml) (40ml H2SO4 and 120ml water) is put into flask slowly. This solution stirred 3h at reflux condition. . Then, the mixture was slowly added into aqueous KOH in ice-water bath, the pH value was then adjusted to ~8-9. The mixture was extracted with ethyl acetate twice. The collected organic solution was dried over anhydrous MgSO4. After removing the solvent, which afforded 2.64g (yield 61.63) of a yellow powder as the product. 1H NMR (CDCl3, 400 MHz, δ): 6.84 (d, J = 8.01 Hz, 1H), 4.15 (s, 2H), 3.65 (s, 2H)

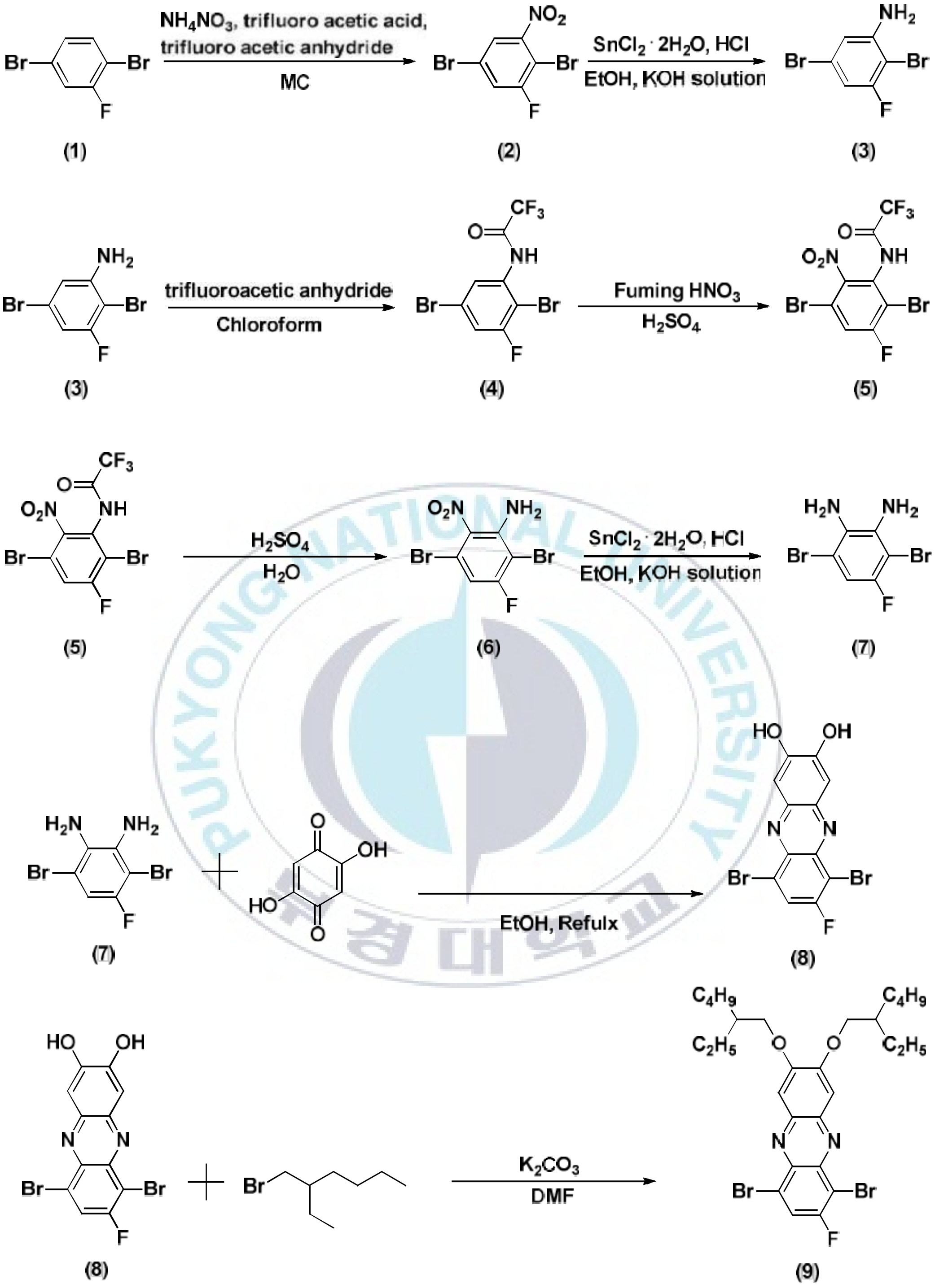
2-6. Synthesis of 3,6-dibromo-4-fluorobenzene-1,2-diamine (7)

The compounds of (6) (2.64g, 8.39mmol) was added to Ethanol (40 mL), then HCl (30ml) and SnCl2·2H2O (9.76g, 33.58mmol) were added at 0℃. Then, this solution was stirred 1H at 80 ℃ then, stirred room temperature overnight. After that, the solution was poured KOH solution at 0℃for adjust Ph Value 8~9 then stirred 30min. And the solution was extracted with Ethyl acetate twice. The collected organic solution was dried over MgSO4. the crude compound was purified by column chromatography using a solvent gradient of 30−50% dichloromethane in hexane as the eluent, which afforded 2.03g (yield 85.44) of a white powder as the product. 1H

NMR (CDCl3, 400 MHz, 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)

2-7. Synthesis of 1,4-dibromo-7,8-bis((2-ethylhexyl)oxy)-2-fluorophenazine (9)

The compounds of (7) (2.03g 7.17mmol) was added to Ethanol (120mL), then 1,2-dihydro quinone (1.18g 10.75mmol) put into flask. Then, the solution was stirred 24H at reflux condition. After that, the solution was dried under vacuum condition and collected red-dark powder (3.21g) was dissolved using dimethylformamide (100ml). Then put in 2-ethylhexylbromide (3ml) and K2CO3 (3.20g, 23.11mmol). This solution stirred 24h at reflux condition. After that, dried DMF and extracted with chloroform twice. The collected organic solution was dried over anhydrous MgSO4. After removing the solvent, purified by a column chromatography using a solvent gradient of0~10% dichloromethane in hexane as the eluent, which afforded 1.54g (yield 35.13) of a orange sticky solid the product. 1H NMR (CDCl3, 400 MHz, δ): 7.90 (d, 1H, J = 8.00 Hz), 7.40 (s, 1H), 7.39 (s, 1H) 4.11(d, 2H, J = 4Hz), 4.09(d, 2H, J = 4.00), 1.9~1.8(m, 2H), 1.63-1.42 (m, 8H), 1.41-1.28 (m, 8H), 0.968 (t, 6H, J = 8.00Hz), 0.90 (t, 6H, J=8.00Hz)



Scheme 1 Synthesis route of monofluoro ethylhexyl-oxy phenazine

2-8. Synthesis of 2-(Tributylstannyl)thiophene

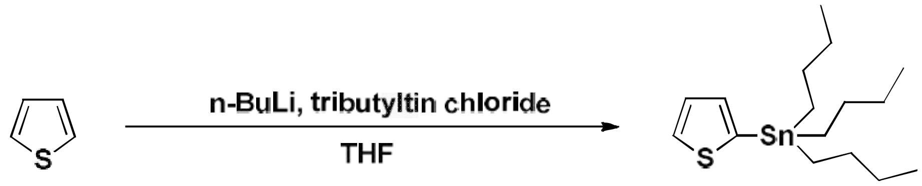
The thiophene (1.00g, 11.89mmol) was added to THF(20mL), then decreasing temprature at -72℃ using dry-ice bath. After 30minute, n-BuLi 1.6M solution (8.17ml, 13.1mmol) was ejected slowly using dropping panel. After 1hour, Tributyltin chloride (5.81g, 17.84mmol) was ejected slowly. This solution was stirred 1H at -72℃ then increase the temperature at room temperature. After that, enough water put into flask and extracted with Ethyl Acetate twice. The collected Organic solution was dried over $MgSO_4$. Removing the solvent, purified by a column chromatography using a solvent gradient 10% triethylamine in hexane as the eluent, which afforded 4.13g(yield 93.1%) of transparent sticky liquid the product.

2-9 Synthesis of 1-bromo-7,8-bis((2-ethylhexyl)oxy)-2-fluoro-4-(thiophene-2-yl)phenazine(10)

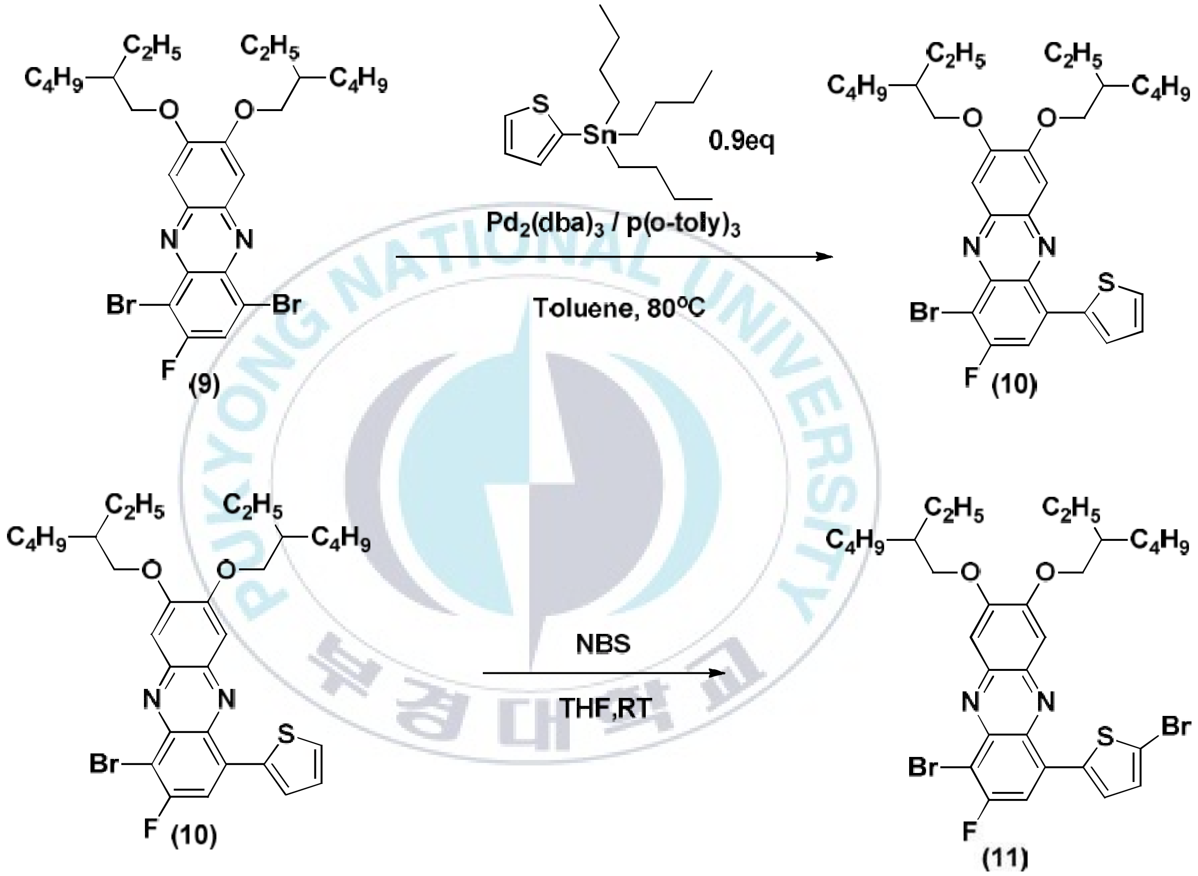
The compounds of (9) (1g, 1.64mmol) was added to toluene(100ml), then 2-(Tributylstannyl)thiophene (0.61g, 1.64mmol) and Pd catalyst that Tris(o-tolyl)phosphine (0.015g, 0.049mmol) and Pd2(dba)3 (0.045g, 0.0049mmol) put into flask. This solution was stirred 24H at reflux condition. After that, the solvent was dried and extracted with chloform twice. The collected Organic solution was dried over MgSO4. After removing the solvent, purified by a column chromatography using a solvent gradient 10~20% dichloromethane in hexane as the eluent, which afforded 0.72g (yield 60.4%) of a red sticky solid the product. 1H-NMR (400 MHz, CDCl3) δ 7.87-7.96 (2H), 7.35-7.60 (3H), 7.18-7.24 (1H), 4.09-4.14 (4H), 1.84-1.93 (2H)

2-10. Synthesis of 1-bromo-4-(5-bromothiophen-2-yl)-7,8-bis((2-ethylhexyl)oxy)-2-fluorophenazine(11)

The compounds of (10) (0.61, 0.99mmol) was added to Chloform(60mL), then NBS(0.34g, 1.98 mmol) ut into flask. Then, the solution was stirred 24H at rt condition. After that, the solution was extracted with chloform twice. The collected organic solution was dried over MgSO4. After removing the solvent, purified by a column chromatography using a solvent gradient 10~20% dichloromethane in hexane as the eluent, which afforded 0.66g (yield 94.9%) of a red-orange sticky solid the product. 1H-NMR (400 MHz, CDCl3) δ7.81-7.88 (1H), 7.54-7.57 (1H), 7.34-7.47 (3H), 7.12-7.16 (1H), 4.07-4.14 (4H)



Scheme 2 Synthesis route of 2-(Tributylstannyl)thiophene



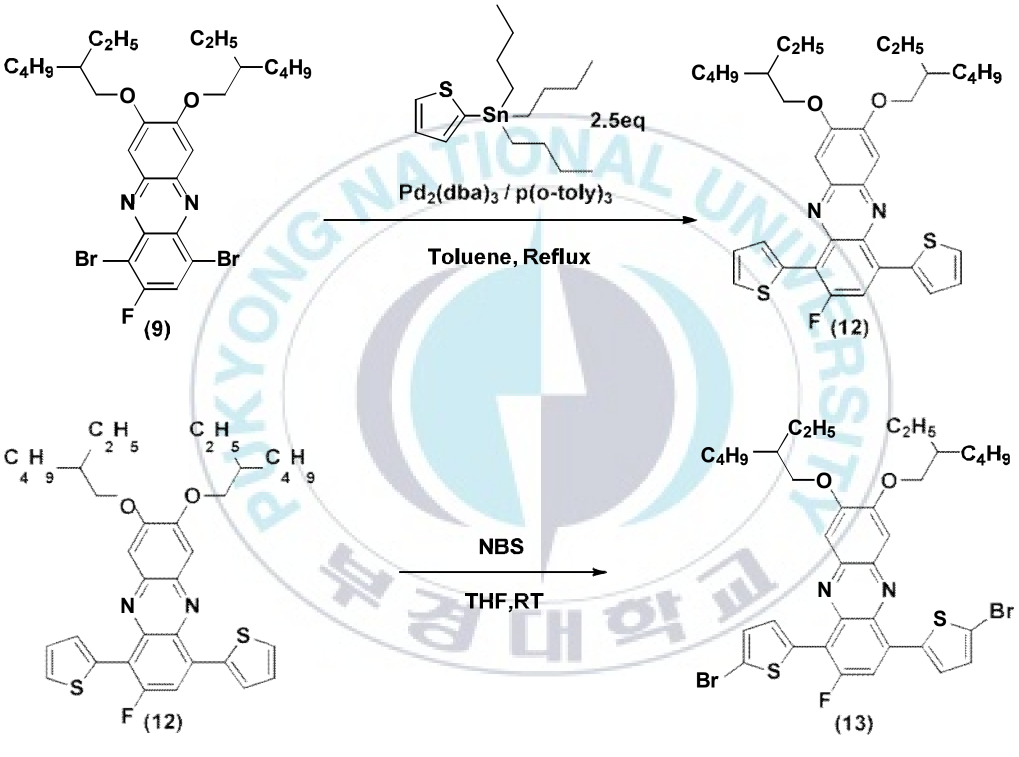
Scheme 3 Synthesis route of T-FPz

2-11. Synthesis of 7,8-bis((2-ethylhexyl)oxy)-1,4-di(thiophen-2-yl)-2-fluorophenazine(12)

The compounds of (9) (1g, 1.64mmol) was added to toluene(100ml), then 2-(Tributylstannyl)thiophene (1.83g, 4.92mmol) and Pd catalyst that Tris(o-tolyl)phosphine (0.045g, 0.138mmol) and Pd2(dba)$_3$ (0.135g, 0.0147mmol) put into flask. This solution was stirred 24H at reflux condition. After that, the solvent was dried and extracted with chloform twice. The collected Organic solution was dried over MgSO4. After removing the solvent, purified by a column chromatography using a solvent gradient 10~20% dichloromethane in hexane as the eluent, which afforded 0.89(yield 88.0%) of a red solid the product. 1H-NMR (400 MHz, CDCl3) δ 8.00-8.03 (1H), 7.93-7.99 (2H), 7.55-7.62 (2H), 7.37-7.41 (2H), 7.19-7.23 (1H), 4.08-4.16 (4H), 1.83-1.93 (2H)

2-12 Synthesis of 1,4-bis(5-bromothiophen-2-yl)-7,8-bis((2-ethylhexyl)oxy)-2-fluorophenazine(13)

The compounds of (11) (0.88, 1.41mmol) was added to Chloform(60mL), then NBS(0.73g, 4.23 mmol) put into flask. Then, the solution was stirred 24H at rt condition. After that, the solution was extracted with chloform twice. The collected organic solution was dried over MgSO4. After removing the solvent, purified by a column chromatography using a solvent gradient 10~20% dichloromethane in hexane as the eluent, which afforded 0.66g (yield 94.9%) of a red solid the product 1.07g (yield 93.0%) 1H-NMR (400 MHz, CDCl3) δ 7.82-7.89 (1H), 7.54-7.58 (1H), 7.36-7.44 (2H), 7.13-7.16 (1H), 4.08-4.20 (4H), 1.85-1.95 (2H)



Scheme 4 Synthesis route of DT-FPz

II-13. Synthesis of *N,N*-diethylthiophene-3-carboxamide (14)

Thiophene-3-carboxylic acid (5.00g, 39.02 mmol) was added to dichloro methane (100ml). The mixture was cooled using ice bath at half an hour, and then oxalyl chloride (39.02g, 78.04 mmol) was added slowly. The mixture was stirred 12hour at room temperature. After that, the solution (solvent and oxalyl chloride residue) dried under vacuum condition and collected white powder (5.61g) was dissolved usin dichloromethane (100ml). Then diehylamine (8.07ml, 78.04 mmol) solution in dichloromethane put in to flask slowly at ice-bath condition. All of the solution was added, removed the ice bath and stirred during 30 min at room temperature. After that, washed by water twice, and the organic layer was dried over anhydrous MgSO4. After removing solvent, purified by a column chromatography using a solvent gradient of 10~20% Ethyl acetate in hexane as the eluent, which afforded 5.26g (yield 73.55%) of a yellow oil the product 1H NMR (400 MHz, $CDCl_3$)δ 7.46 (d, 1H, *J* = 1.09 Hz), 7.30 (t, 1H, *J* = 1.09 and 4.94 Hz), 7.17 (d, 1H, *J* = 4.94 Hz), 1.18 (m, 10H)

II-14. Synthesis of *N,N*-diethylthiophene-3-carboxamide (15)

Compound 14 (5.60g 33.10mmol) was put into dried THF, then decreasing temperature at -72℃ using dry-ice bath. After 30minute, n-BuLi 1.6M solution

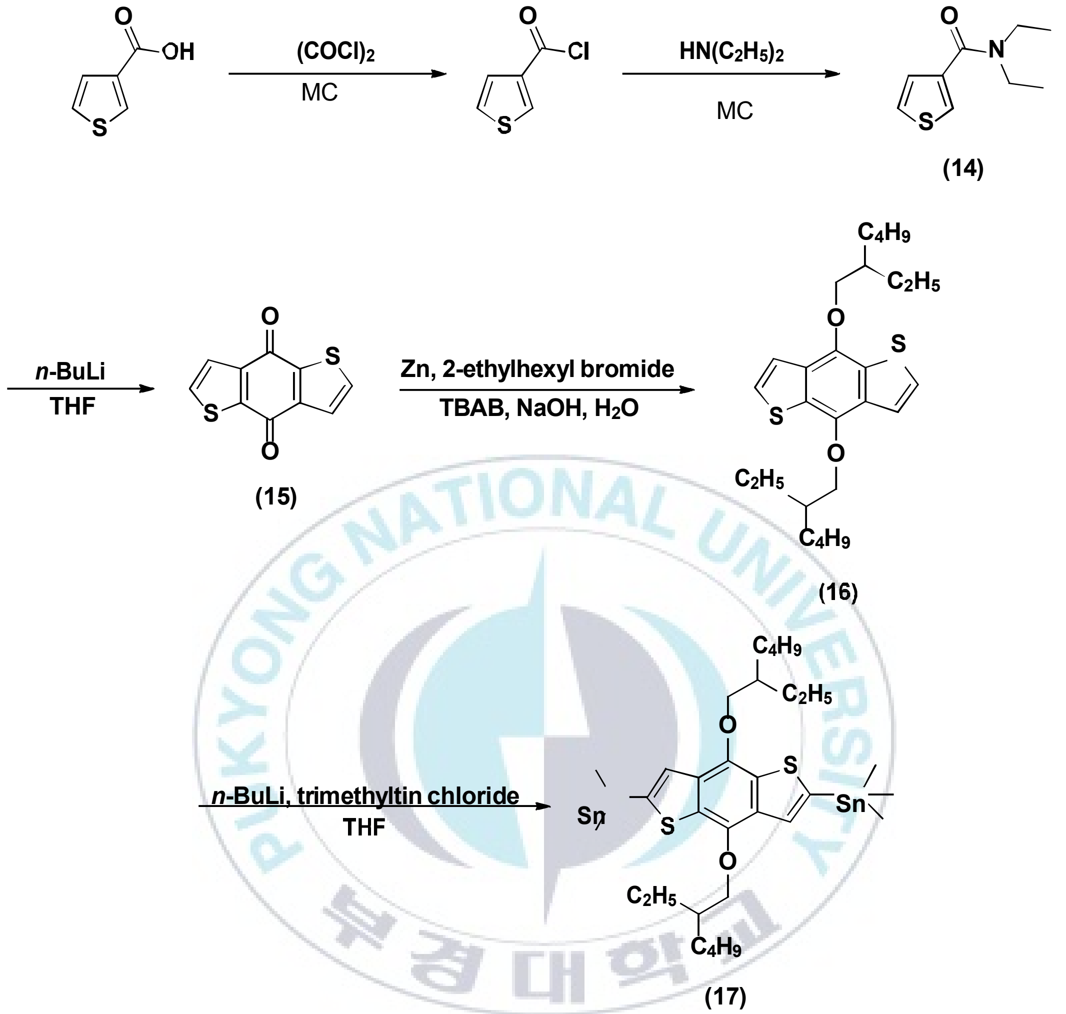
(24.83ml, 39.72mmol) was ejected slowly using dropping panel. After half an hour, the reaction was stirred at room temperature for 2 hour. The mixture was poured into ice water and stirred overnight. The formed yellow powder crystal was filterated and wash in order water methanol hexane and dry, which afforded 2.93g(yield 92.68%) 1H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, 2H, *J* = 4.94 Hz), 6.46 (d, 2H, *J* = 5.22 Hz)

II-15. Synthesis of 4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*']dithiophene (16)

The compounds of (15) (2.00g 9 mmol) and zinc powder (1.3 g, 20 mmol) was put into 20% NaOH aqueous solution (20 mL) and the mixture was stirred 3 hour at reflux condition. After 2-ethylhexylbromide (11.13 g, 27 mmol) and tetrabutylammonium bromide (0.45 g, 1.82 mmol) were put into the mixture solution after that stirred for 12 hr at reflux condition. The reaction mixture was extracted with ethyl acetate twice, and the organic layer was washed water and dried over anhydrous $MgSO_4$. After evaporating the solvent, the product was purified by column chromatography using hexane as the eluent, 3.44g (yield 84.45%) which afforded as a light yellow oil as the product. 1H NMR ($CDCl_3$, 400 MHz, δ 7.48(d, 2H, J = 5 Hz), 7.46 (d, 2H, J = 5 Hz), 4.18 (br, 4H), 1.78 (m, 2H), 1.73–1.25 (m, 16H), 0.92–1.03 (t, 12H, J = 7 Hz).

II-16. Synthesis of 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:3,4-*b*']dithiophene (17)

The compounds of 16 (2 g, 2.5mmol) was put into dried THF (35 mL) then decreasing temperature at -72 ℃ dry-ice bath. After 30minute, n-BuLi 1.6M solution (3.19ml 5.1mmol) was ejected slowly using dropping panel. After half an hour increasing the temperature at room temperature for 30 min. After the mixture was cooled to -78 °C again at half an hour then 1M trimethyltin chloride solution (5.10 ml, 5.10mmol) was added. This solution increase the temperature at room temperature again and stirred for 12 hr. After quenching the reaction using water. The residue was extracted with hexane, and the organic layer was washed with brine, dried over anhydrous $MgSO_4$. The crude product was purified by recrystallization from acetone and methanol. The crystal was filterated and wash methanol and dried, which afforded white-yellow powder as the product 2.08g (yield 72.16%). 1H NMR ($CDCl_3$, 400 MHz, δ): 7.50 (t, 2H, J = 14.64 Hz), 4.17 (d, 4H, J = 5.36 Hz), 1.80 (m, 2H), 1.32-1.72 (m, 16H), 1.01 (t, 6H, J = 7.38 Hz), 0.93 (t, 6H, J = 7.12 Hz), 0.43 (m, 18H



Scheme 5 Synthe route of donor monomer that 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy) benzo[1,2-b:3,4-b′]dithiophene

2-18. Synthesis of poly 1-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-7,8-bis((2-ethylhexyl)oxy)-2-cyano-4-(thiophen-2-yl)phenazine(PBDT-FPz)

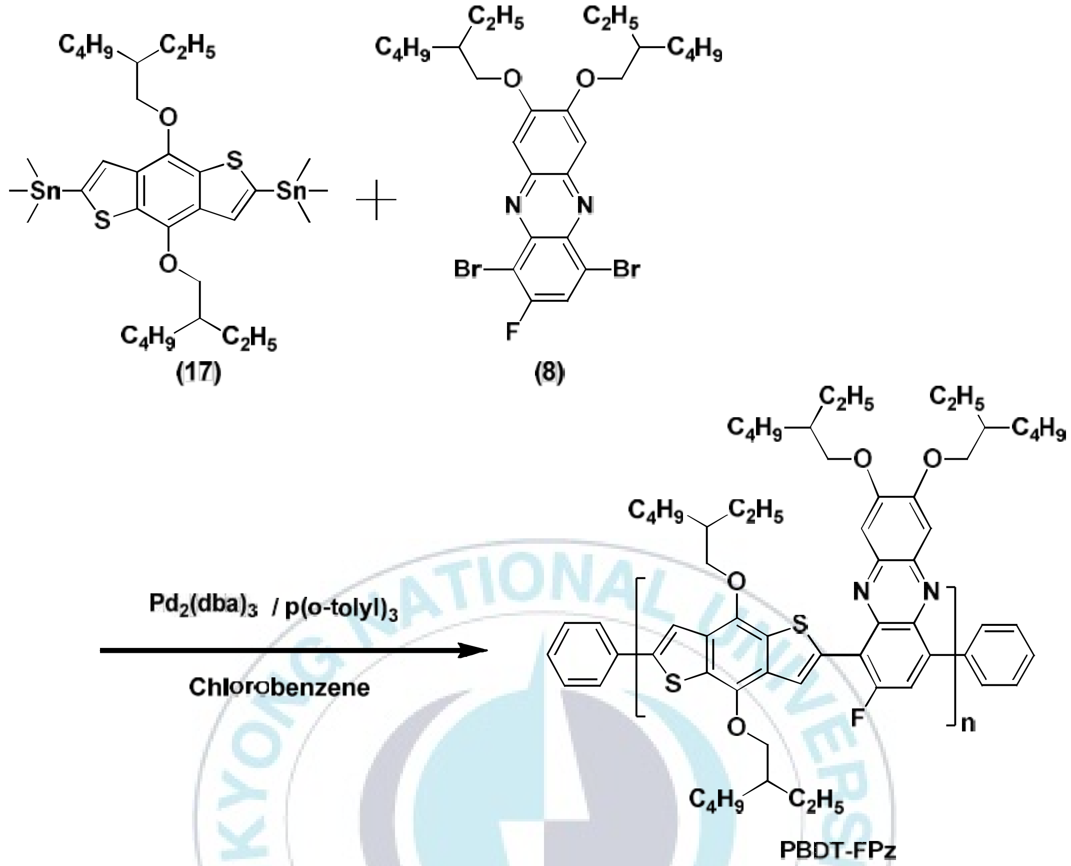
The compounds of (9) (0.3g, 0.492mmol) was added to chlorobenzene(20ml), then BDT (18) (0.38g, 0.492mmol) and Pd catalyst that Tris(o-tolyl)phosphine (0.080g, 0.0246mmol) and Pd2(dba)3 (0.0226g, 0.0246mmol) put into flask. This solution was stirred 48H at 100°C condition. After cooled to RT, this solution was put into stirred methyl alcohol at 0°C one by one. The polymer was filtered and washed with methanol. The collected polymer was soxhlet-extracted with methanol, acetone, chloroform, chlorobenze. Then, chloroform and chlorobenzene solutions were put into stirred methyl alcohol at 0°C to reprecipitation. Finally, the polymer was collected by filteration and dried under vacuum oven at 80°C over 24hr. PBDT-DT-DFPz was collected 0.303g.

2-17. Synthesis of poly 1-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-7,8-bis((2-ethylhexyl)oxy)-2-fluoro-4-(thiophen-2-yl)phenazine(PBDT-T-FPz)

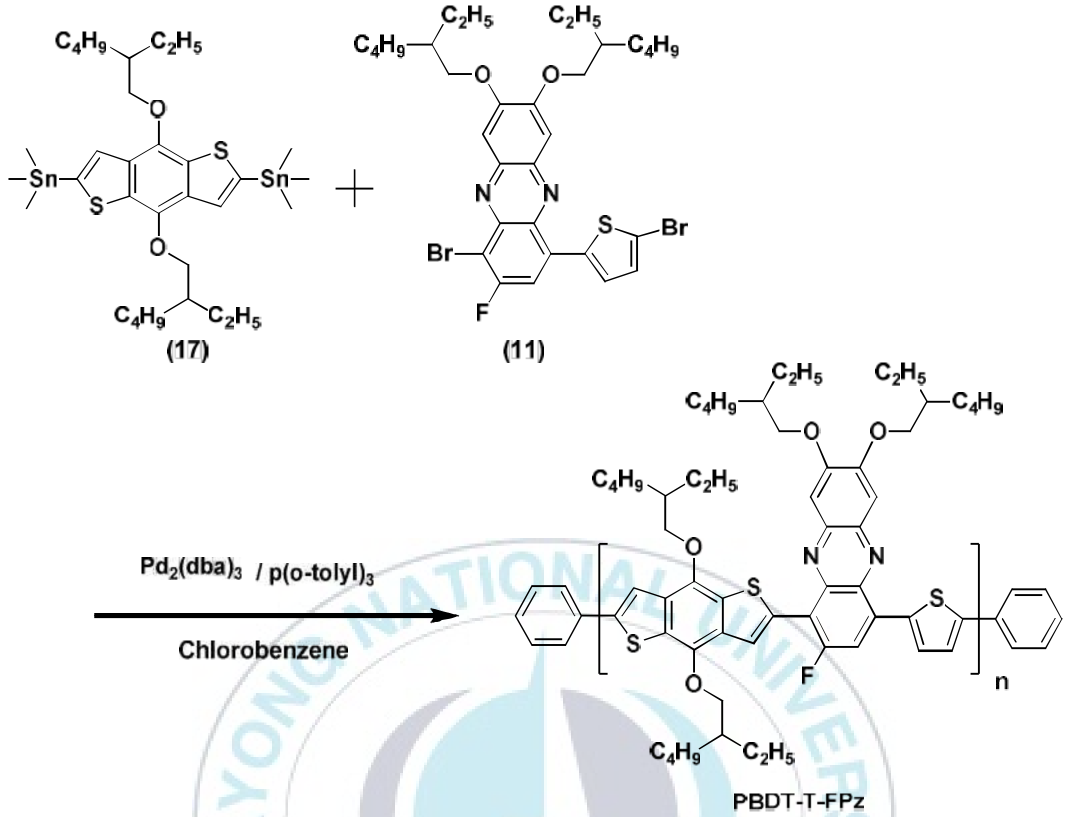
The compounds of (11) (0.3g, 0.492mmol) was added to chlorobenzene(20ml), then BDT (18) (0.38g, 0.492mmol) and Pd catalyst that Tris(o-tolyl)phosphine (0.080g, 0.0246mmol) and Pd2(dba)3 (0.0226g, 0.0246mmol) put into flask. This solution was stirred 48H at 100°C condition. After cooled to RT, this solution was put into stirred methyl alcohol at 0°C one by one. The polymer was filtered and washed with methanol. The collected polymer was soxhlet-extracted with methanol, acetone, chloroform, chlorobenze. Then, chloroform and chlorobenzene solutions were put into stirred methyl alcohol at 0°C to reprecipitation. Finally, the polymer was collected by filteration and dried under vacuum oven at 80°C over 24hr. PBDT-DT-DFPz was collected 0.303g.

2-15. Synthesis of poly 1-(5-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)thiophen-2-yl)-7,8-bis((2-ethylhexyl)oxy)-2-fluoro-4-(thiophen-2-yl)phenazine (PBDT-DT-FPz)

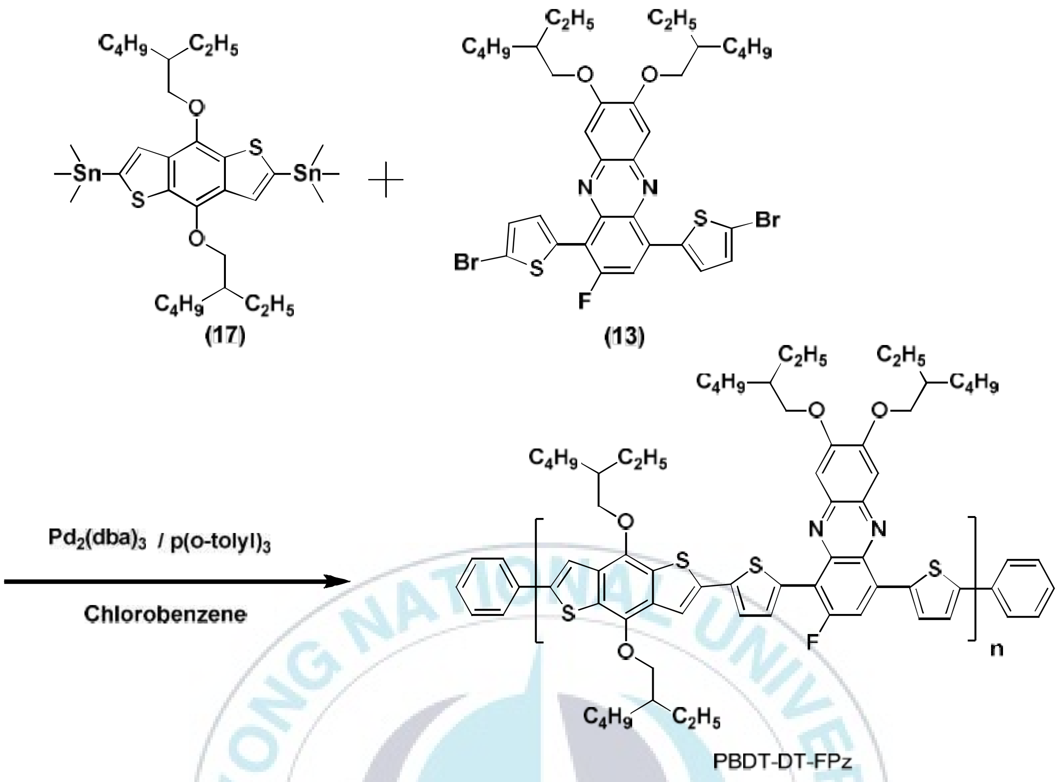
The compounds of (13) (0.3g, 0.492mmol) was added to chlorobenzene(20ml), then BDT (18) (0.38g, 0.492mmol) and Pd catalyst that Tris(o-tolyl)phosphine (0.080g, 0.0246mmol) and Pd2(dba)3 (0.0226g, 0.0246mmol) put into flask. This solution was stirred 48H at 100°C condition. After cooled to RT, this solution was put into stirred methyl alcohol at 0°C one by one. The polymer was filtered and washed with methanol. The collected polymer was soxhlet-extracted with methanol, acetone, chloroform, chlorobenze. Then, chloroform and chlorobenzene solutions were put into stirred methyl alcohol at 0°C to reprecipitation. Finally, the polymer was collected by filteration and dried under vacuum oven at 80°C over 24hr. PBDT-DT-DFPz was collected 0.303g.



Scheme 6 Synthesis route of PBDT-FPz



Scheme 7 Synthesis route of PBDT-T-FPz



Scheme 8 Synthesis route of PBDT-DT-FPz

II-3. Fabrication of photovoltaic device

For the EL experiment, the glass of ITO(Indium Tin Oxide) coted expose to O_3. For half an hour, make sure that hydrophilic solution is coated well through surface energy control.. After that PEDOT:PSS, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), aqueous in Isopropyl alcohol solvent that was coated as the hole-injection layer by using spin-coated method at 4500rpm. Then annealing 10minute at 145℃ for drying solvent. After that o-dichlorobenzene solution blended with polymer and PCBM at 20g/ml concentration solution are coated as active layer using spin-coated method in 1300rpm 40s.. This film was dried in hot plates. And aluminum were vacuum deposited on the top of device in the small molecule films as electrode through a mask by vacuum evaporation at pressures below 10^{-7}torr, yielding active areas of 4 mm^2.

Chapter III. Results and Discussion

III-1. Polymerization

These polymer series were measured molecular weight distribution by using GPC(Gell permeation chromatography) method at 80 ℃ as an dichlorobenzene eluent. PBDT-FPz and PBDT-T-FPz were measured molecule weight about 6000. But PBDT-DT-FPz was measured molecule weight about 22000. Through this results, thiophene bridge can attribute in polymer synthesis. It thought that BDT and Phenazine are adjacent without πbridge so it cause steric hindrance effect. For this reason, PBDT-FPz and PBDT-T-FPz had low molecule weight and PBDT-DT-FPz had appropriate molecule weight because thiophene bridge reduced the stereic hindrance between the two molecules by increasing the distance.[12]

Polymers	M_n	M_w	PDI
PBDT-FPz	5949	6425	1.08
PBDT-T-FPz	5149	6694	1.30
PBDT-DT-FPz	22152	30677	1.38

Table 1 Number-average molecular weight (Mn), weight-average molecular weight (Mw) and polydispersity of the polymers were determined by gel permeation chromatography (GP

III-2 Thermal Stability Analysis of Polymers by using TGA

In photovoltaic device need to enough thermal stability. Because it were exposed sunlight. The TGA(ThermoGraviMetric) was measured to check how stable this polymer is in the heat. TGA was measured in air condition, heated at 20 °C/min rate. Test results about TGA measuring, this polymers 5% weight loss temperature over 340°C . This data was shown suitable thermal stability for use photovoltaic device.

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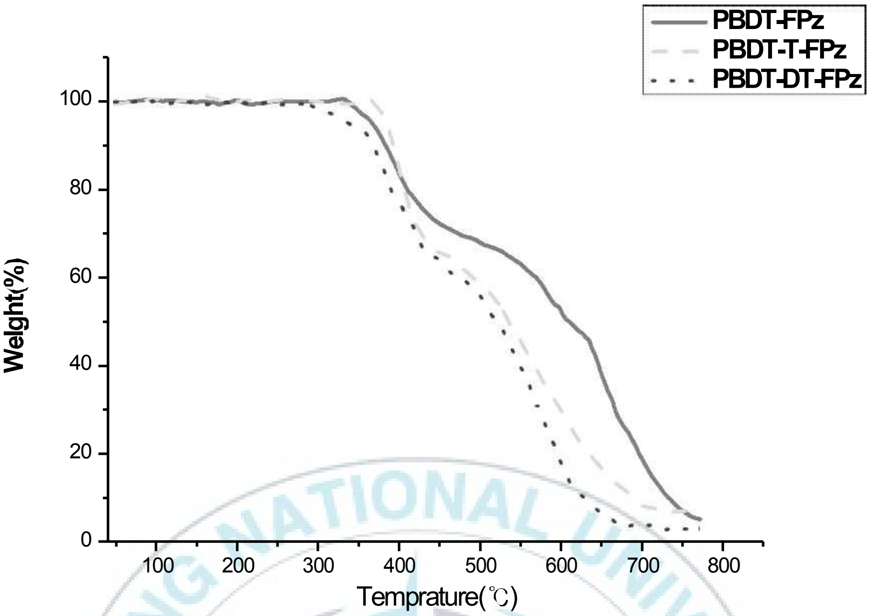

Figure 5 TGA analysis of PBDT-FPz, PBDT-T-FPz and PBDT-DT-FPz at air condition

Polymers	T_g
PBDT-FPz	368
PBDT-T-FPz	384
PBDT-DT-FPz	339

Table 2 Tg value of PBDT-FPz, PBDT-T-FPz and PBDT-DT-FPz

III-3. Optical Properties of Polymers

For check the polymers optical properties, two type of UV-Vis abs is measured. One is polymers solution's UV-Vis abs, the other is polymers film's UV-Vis abs. Polymer solution was made of CB solution and UV-Vis abs was measured. And Polymer film measured UV-Vis abs by spin-coated the polymer solution dissolved in CF onto the glass substrate. The absorption of three polymers have two absorption peak. It is in accordance with other D-A copolymers. One that peak at the red wavelength is attributed to intramolecule charge transfer the other that peak at the blue wavelength is π- π stacking. At red wavelength of the measurement about polymer solution, λ_{max} of PBDT-FPz is 609nm, λ_{max} of PBDT-T-FPz is 605nm and λ_{max} of PBDT-DT-FPz is 593nm. As increased the thiophene, the UV-Vis absorption spectra is shown blue shift tendency. In the case of polymer film, λ_{edge} of PBDT-FPz is 737nm and Eg opt is 1.64eV, λ_{edge} of PBDT-T-FPz is 744nm and Eg opt is 1.66eV and λ_{edge} of PBDT-DT-FPz in 753nm and E_g opt is 1.68eV. Optical bandgap also blue shift tendency as increase thiophene. Because distance of Donor unit and Acceptor unic is close. It occurred strong chain aggregation

Polymers	λ_{max} solution	λ_{max} film	λ_{edge} film	E_g opt
PBDT-FPz	609	653	753	1.64
PBDT-T-FPz	605	632	744	1.66
PBDT-DT-FPz	593	631	737	1.68

Table 3 UV-Vis abs peak table of PBDT-FPZ, PBDT-T-FPZ and PBDT-DT-FPz

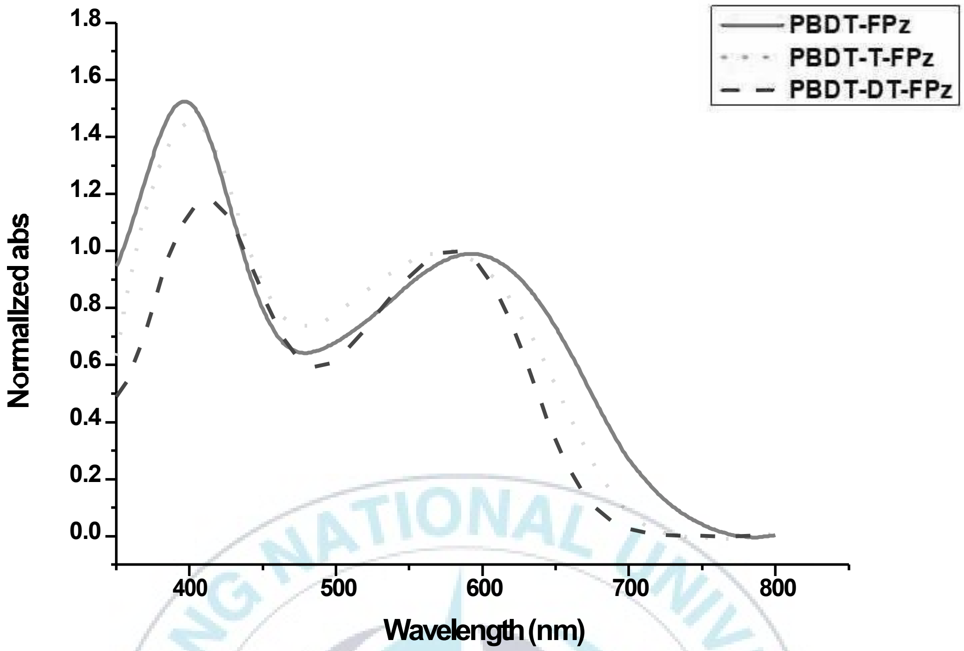

Figure 6 UV-VIs abs of PBDT-FPz, PBDT-T-FPz and PBDT-DT-FPz solution in Chlorobenzene

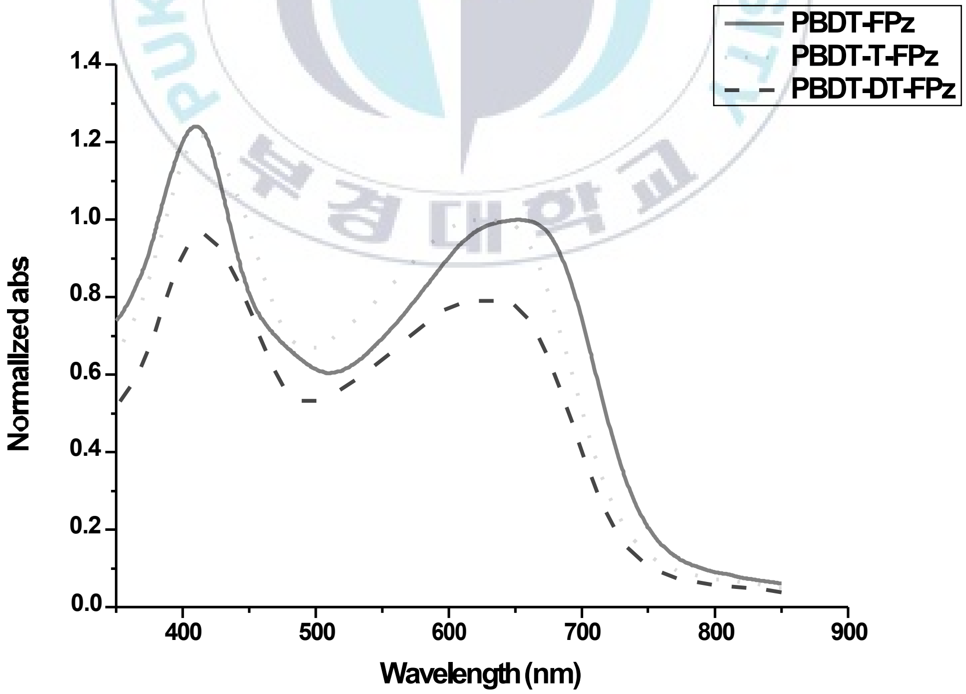

Figure 7 UV-VIs abs of PBDT-FPz, PBDT-T-FPz and PBDT-DT-FPz film by spin-coated

III-4. Electrochemical Properties of Polymers

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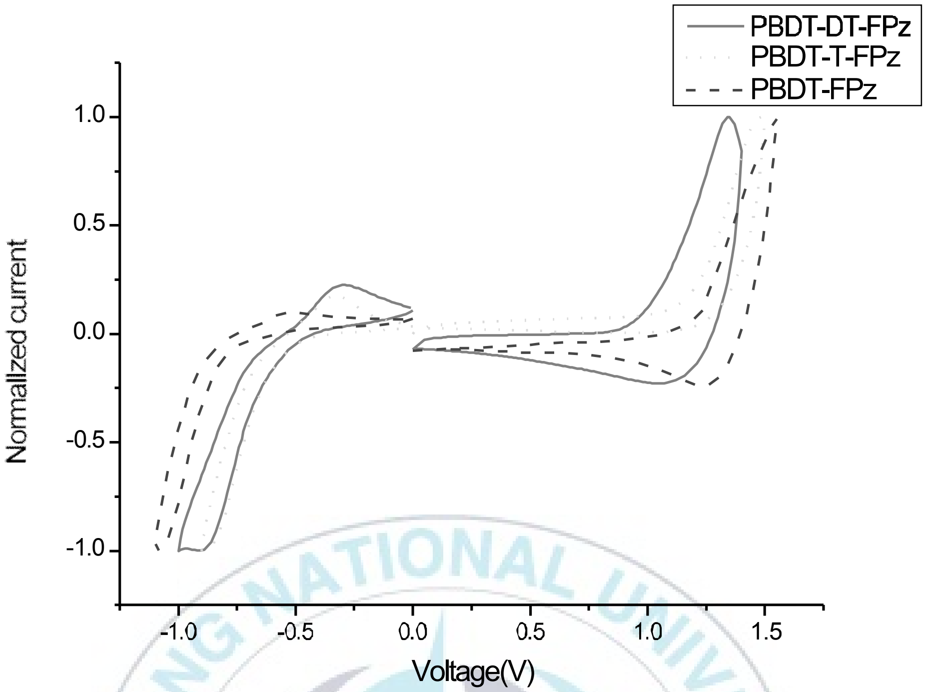

Figure 8 Cyclic voltammetry curves PBDT-DT-FPz, PBDT-T-FPz and PBDT-FPz in 0.1 M Bu¬4NPF6 acetonitrile solution at a scan rate of 100 mV/s at room temperature (vs an Ag quasi-reference electrode).

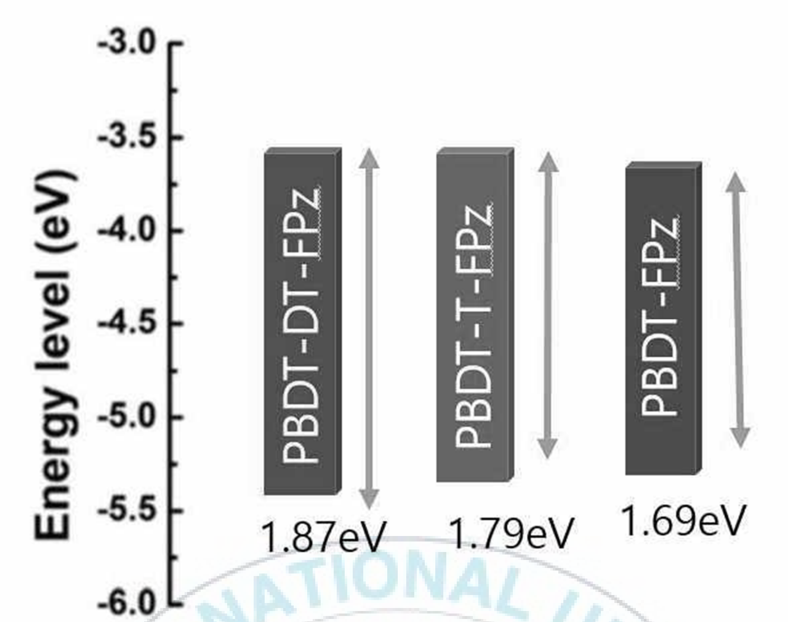

Figure 9 Energy diagram of polymers by measurement CV

Polymers	HOMO(eV)[a]	LUMO(eV)[a]	LUMO(eV)[b]	E_g[a]	E_g opt[b]
PBDT-FPz	-5.26 -3.55		-3.62	1.69	1.64
PBDT-T-FPz	-5.39 -3.57		-3.73	1.79	1.66
PBDT-DT-FPz	-5.45 -3.60		-3.77	1.87	1.68

Table 4 a) calculating HOMO and LUMO by using CV onset point b) by calculating bandgap using E_g opt

III-5. Photovoltaic Properties of Polymers

To check the photovoltaic properties of polymers, photovoltaic devices were fabricated using bulk-hetero junction active layer and spin-coated method. These polymer series could solve in chloroform at room temperature. But it is difficult in the process of creating a device. The polymers are soluble but the particles are too big. To solve this problem, process of creating a device use Dichlorobenzene.

Ratio of polymer donor to PC71BM is 1:1.5 and 3%DIO additives. The concentration is 22g/ml. The devices configuration of ITO/PEDOT:PSS/polymer:$PC_{70}BM$/Al. The PBDT-FPz device was not worked that 1.471ma/cm^2 of J_{sc}, 0.172V of V_{oc}, 0.280 of FF and 0.07% of PCE. Because the steric hindrance disorder of the polymer causes distortion so not blending the donor and acceptor. The other two polymers devices were worked normally. Devices based on PBDT-T-FPz and PBDT-DT-FPz showed the 0.67 and 0.59V of open circuit voltage(V_{oc}). Generally the HOMO energy level is consistent with polymers HOMO energy level.[14] PBDT-T-FPz and PBDB-DT-FPz showed the 3.642mA/cm^2 of and 5.117mA/cm^2 of J_{sc}. Generally the J_{sc} value is consistent of polymers band gap.[15] PBDT-T-FPz had smaller band gap than PBDT-DT-FPz. But this result was shown that thiophene's non bonding electron performed the charge transporter so PBDT-DT-FPz had broader bandgap but high Jsc value can achieve. The PBDT-T-FPz and PBDT-DT-FPz showed 0.412 and 0.549 of FF. PBDT-T-FPz had one thiophene bridge so steric hindrance was decreased that device could work.[12] But there was still a steric hindrance occurred, and for this reason, FF was low. It also can be checked about

Atomic Force Microscopy image. PBDT-T-FPz show a shape with domain connected, but PBDT-DT-FPz show well separated shape.

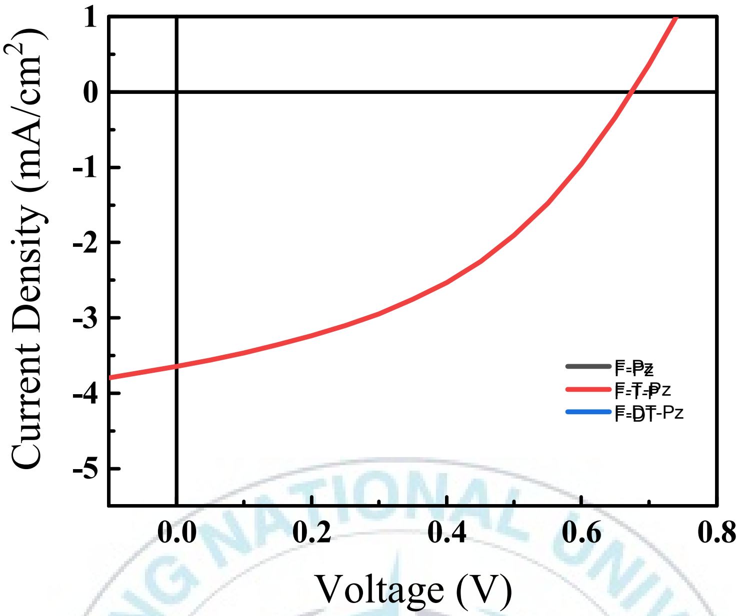

Figure 1 Characterstic J-V curves of the devices based on PBDB-PFz, PBDT-T-FPz and PBDT-DT-FPz under 100mW/cm^2 AM 1.5g illumination

Polymers	J_{sc} mA/cm^2	V_{oc} (V)	FF	PCE
PBDT-FPz	1.471	0.172	0.280	0.070
PBDT-T-FPz	3.642	0.674	0.412	1.011
PBDT-DT-FPz	5.117	0.592	0.549	1.664

Table 1 Photovoltaic Performance of Solar Cells Based on PBDT-FPz, PBDB-T-FPz and PBDB-DT-FPz

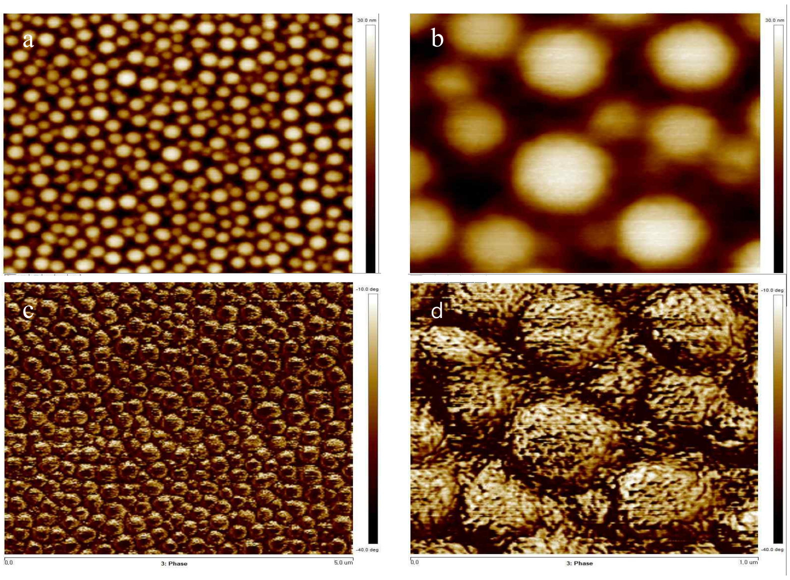

Figure 11 AFM images of PBDT-FPz a) height images(5 ㎛ x 5 ㎛) b) height images (1 ㎛ x 1 ㎛) c) phase images(5 ㎛ x 5 ㎛) d) phase images(1x㎛1) ㎛

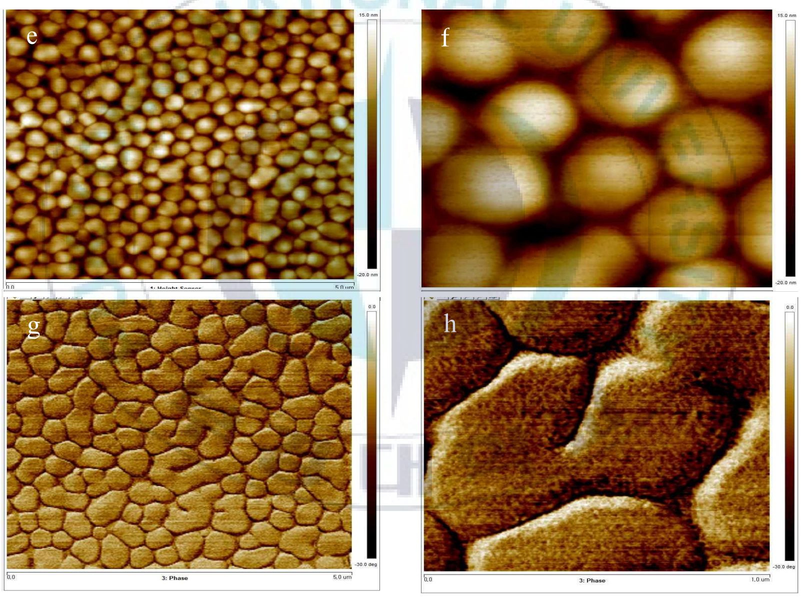

Figure 122 AFM AFM images of PBDT-T-FPz a) height images(5 ㎛ x 5 ㎛) b) height images (1 ㎛ x 1 ㎛) c) phase images(5 ㎛ x 5 ㎛) d) phase images(1 ㎛ x 1 ㎛)

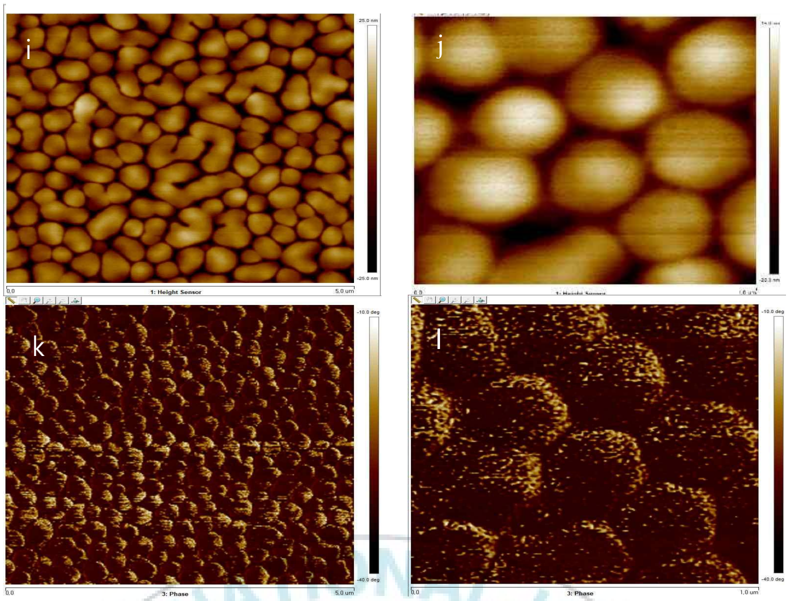

Figure 13 AFM images of PBDT-DT-FPz i) height images(5 ㎛ x 5 ㎛) j) height images (1 ㎛ x 1 ㎛) k) phase images(5 ㎛ x 5 ㎛) l) phase images(1 ㎛ x 1 ㎛)

Chapter IV. Conclusions

The results of this research, three type of D-A conjugated copolymers that were made of fluorinated phenazine with different number of thiophene and benzodithiophene were synthesized. Analyzed the result, thiophene performed reducing the steric hindrance by widening the distance between donor and acceptor monomer.

In polymerization result, polymer with either no or one thiophene had low molecular weight. The polymers uv-vis abs spectra was shown the two peak. One is red wavelength absorbance peak, the other is blue wavelength absorbance peak and blue wavelength absorbance peak is stronger than red wavelength absorbance peak. Through this results, intra molecule charge transfer is hard. It is shown that donor polymer aggregation is too strong instead the planar so not blended with acceptor well. In photovoltaic result, PBDB-FPz almost not worked because the FF is too low to work devices that 1.471ma/cm^2 of J_{sc}, 0.172V of V_{oc}, 0.280 of FF and 0.07% of PCE. The other two polymer worked normally that 3.642ma/cm^2 of J_{sc}, 0.671V of V_{oc}, 0.412 of FF and 1.011% for PBDB-T-FPz and 5.117ma/cm^2 of J_{sc}, 0.592V of V_{oc}, 0.549 of FF and 1.664% for PBDT-DT-FPz. Compared PBDB-T-FPz and PBDB-DT-FPz, PBDB-T-FPz had smaller bandgap but PBDB-DT-FPz achive higher Jsc. It is shown than thiophene's non bonding electron helps the charge transfer,[16] References

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감사의글

지난 3 년간 저의 연구뿐 아니라 연구외적인 많은 부분에서 저를 잘 이끌어 주 신 지도교수님 진영읍 교수님 진심으로 감사 드립니다. 그리고 지난 3 년간 저의 연구를 지지해주시고 도와 주신 공업화학과 이근대 교수님, 박성수 교수님, 문명준 교수님, 손민영 교수님, 조계용 교수님 그리고 장동욱 교수님 정말 감사합니다. 그리고 제 물질들 측정을 도와주신 물리과 박성흠 교수님과 양현석선생님 드린 것 없이 계속 부탁만 드린 것 같아 죄송하고 감사합니다. 2 년간 제가 하는 일 믿어주시고 지지해 주신 부모님 그리고 동생 감사합니다. 지난 3 년간 같이 생활했던 YJ- lab 식구들 저의 사수로써, 바른 생활의 표본 이셨던 지현이형 2 년간 많을 것을 배울 수 있었고, 그 마음가짐을 배움으로써, 무사히 졸업 할 수 있었습니다. 1 년 반 동안 선배 대접 잘 못해주고 많이 도와주지 못했던 진한이, 그리고 새로올 병윤이 앞으로 하는 일 다 잘되길 바란다. 너희도 1 년 6 개월동안 너희가 바라던 것 이상으로 실험실에서 얻어가길 바란다. 나중에 꼭 밥 사주러 올게. 그리고 종진이형 같이 대학원생활하면서 많이 못 도와줘서 미안하고 졸업하고도 좋은 결과 내길 바란다. 그리고 2 년간 석사 한다고 밥 사주고 응원하던 친구들 고맙다. 저를 지지해주고 도와주신 모든 분들께 다시 한번 감사의 말씀을 드립니다. 감사합니다..