제 39권 2호

# 2014 추계학술대회 연구논문 초록집

# PROCEEDINGS

The Polymer Society of Korea

2014. 10. 6[Mon] - 8[Wed] ICC JEJU

Annual Fall Meeting

한국고분자학회
The Polymer Society of Korea

Jeju CVB
Jeju Convention & Visitors Bureau

조새벽, 조길원† 포항공과대학교
Here, we demonstrate an efficient approach to dramatically enhance the photon harvesting in planar heterojunction solar cells by using highly oriented pentacene crystals grown on graphene. The quasi-epitaxial growth of pentacene significantly enhanced overall optoelectronic properties including light absorption, exciton diffusion, charge transport and interfacial energetics. The photovoltaic performance showed overall increment, leading to nearly 500% increment in maximum power conversion efficiency.

**3PS-274** 조성민

Surface engineering of paper substrate for the application of foldable organic devices

조성민, 윤대건, 진병두† 단국대학교
본 연구에서는 종이의 표면에 유/무기 다층막을 코팅하여 표면의 균일도 및 거칠기를 개선하였고, 접이식 전자소자에 적용 가능한 종이기판을 제작하였다. 종이기판의 상부에 고분자 계열[poly(4-vinylphenol) (PVP), poly(vinyl alcohol) (PVA), poly imide (PI), etc.]의 필름을 형성하여 표면의 거칠기를 완화시켰고, 박막의 금속 층을 형성하여 수분투습도 (WVTR)를 개선하였다. 종이기판의 상부에는 인쇄 공정 및 증착 공정을 이용하여 은 나노와이어, 은 나노와이어 와 graphene의 복합 전극을 제작하였으며 반복 접힘 테스트를 통해 접이식 전자소자에 적합한 조건을 선정하였다. 종이기판의 특성상 불투명 하기 때문에 전면유기발광다이오드(top emitting OLED, TOLED)를 제작하여 기존의 유리기반의 소자와 비교하였으며, 기존 소자와 비슷한 효율을 보임을 확인하였다.

**3PS-275** 조아라

Synthesis and properties of narrow band-gap small molecules for organic solar cells

조아라, 임은희† 경기대학교
Organic photovoltaic cells (OPV) are very promising sources in next generation because of low cost, flexibility, and renewable energy applications. Polymer-based OPVs show high performances due to good-film forming, broad absorption, and high charge mobility. However, polymer donors have difficulties in purification and poor reproducibility, such as polydispersity and molecular weight. Small molecule donors have some advantages, including facile synthesis and well-defined structure. Recently, fluorinated benzothiadiazole (F-BT) is used as an accepting unit for donor materials. The introduction of fluorine resulted in better open-circuit voltages in OPVs. Thiadiazolopyridine (TPy) also has higher electron affinity than thiadiazole due to the heterocycle in TPy. In this work, we adopted two units, F-BT and TPy, as accepting units in new small molecule donor materials. Their optical, electrochemical, and photovoltaic properties of small molecules will be systemically investigated.

**3PS-276** 조제웅

Comparison of two D-A type polymers with each being fluorinated on D and A unit for high performance solar cells

조제웅, 배승환[1], Feng Liu[2], Thomas P. Russell[2], 조원호[1,†] 서울대학교; [1]서울대학교 재료공학부; [2]UMASS, Amherst
Recently, polymers with fluorinated building block have recently attracted great interest because high power conversion efficiencies (PCEs) over 7% have been achieved by fluorination of A unit. In this work, we synthesized two kinds of D-A polymers with each being fluorinated on A and D unit, where quaterthiophene and benzothiadiazole are used as D and A unit, respectively, in order to investigate the effects of fluorination position on photophysical properties of polymers and their solar cell performances. Although the fluorination on either D or A unit effectively enhances intermolecular interaction and lowers energy levels, retaining a low bandgap of 1.58 eV, the polymer with fluorinated D unit exhibits a PCE of 7.10%, while the polymer with fluorinated A unit exhibits a PCE of 6.75%. Therefore it can be concluded that the fluorination on D unit in D-A polymer is a promising method for achieving high performance solar cells.

**3PS-277** 조현아

Synthesis of thin silver nanowires using magnetic ionic liquids with PVP as a caping agent

조현아, 이은종, 김용희, 김진열† 국민대학교
One-dimensional (1-D) metallic nanostructures, silver nanowires (Ag NWs), have recently attracted a great deal of attention for their unique electrical, optical, magnetic, and thermal properties as a promising alternative to indium tin oxide (ITO) as an electrode material used in the fabrication of electronic devices. In this work, thin and long silver nanowires were successfully synthesized using the polyol method in the presence of magnetic ionic liquids (MILs), which served as soft template salts. The diameter of NWs was largely influenced by the type of IL, and their sizes could also be effectively and easily adjusted within a diameter range of 20 to 30 nm according to the ILs.

**3PS-278** 지찬혁

Enhancing performance of organic solar cells using B4PyMPM self-assembled nanostructures as n-type buffer layer on cathodes

오일수, 지찬혁, 임성빈, 오세용† 서강대학교
In the field of orgnic photovoltaic cells (OPVs), the electron transport(ETL) layer enhances power conversion efficeiency (PCE) through the incorporation of cathode interfacial layers. Here, we introduce [bis-4,6-(3,5-di-4-pyridylphenyl)-2-methylpyrimidine] (B4PyMPM) as an n-type buffer layer consisting of self-organized layer with a horizontal configuration in bulk hetero-junction(BHJ) OPVs. It is demonstrated that self-organization of this B4PyMPM compound in which molecules adopt a face to face orientation parallel to the organic semiconducting substrate induces a large local interfacial electric field that results in a significant enhancement of exciton dissociation. It is expected that the device using B4PyMPM as ETL layers has a significantly high short circuit current and good fill factor due to the stability of chemical reaction and low contact resistance leading to high power conversion efficiency.

**3PS-279** 지찬혁

Indium Tin Oxide Free Semitransparent Organic Photovoltaic Cells using Ytterbium as N-type Buffer Layer on Transparent Cathode Electrodes

지찬혁, 박지훈, 오세용† 서강대학교
We investigate Indium Tin Oxide (ITO) free semitransparent Organic Photovoltaic Cells (OPVs) with WO3/Ag/WO3 (W/A/W) layer as the transparent anode and Yb/BCP/Ag/WO3 (Y/B/A/W) layer as the transparent cathode. The both electrodes showed the low sheet resistance below 8.5 Ω/□ and observed the high transparency 90% (at λ=535nm). The semitransparent devices W/A/W/poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester(P3HT:PCBM)/Y/B/A/W recorded an average power conversion efficiency(PCE) of 2.2% estimated for 100 mW/cm$^2$ air mass 1.5 global illumination. Through our experimentation, we analyzed the effects of high PCE on the device physics of organic solar cells via Secondary Ion Mass Spectrometry and Ultra-Violet Photoelectron Spectroscopy.

**3PS-280** 진원용

Ultra-flat and Foldable Transparent Conducting Electrodes for Organic Photovoltaics Applications

진원용, 고금진, 장 미, 정은선, 강재욱† 전북대학교
We report a novel architecture to fabricate solution-processed foldable transparent conducting electrodes by using a combination of metal-grid embedded into flexible substrate and ultrathin transparent electrodes. The use of the silver metal grid and the PEDOT:PSS layer in combination resulted in an increase in conductivity without a reduction in the transmission and helped in overcoming the trade-off between them, leading to highly transparent (optical transmittance ≈ >85% at a wavelength of 550 nm), highly conducting (sheet resistance ≈ 20 ohm/sqr.) and extremely flexible (bending radius ≈ 200 um) electrodes with very flat surface (root-mean-square roughness ≈ 0.5 nm). These electrodes were used to fabricate foldable organic devices that exhibited performances similar to that of devices fabricated on glass substrate. In addition, these fabricated flexible devices did not show degradation in their performance even after being folded.

**3PS-281** 차명주

A conjugated polyelectrolyte dipole layer induced at donor and acceptor interface in organic trilayer solar cells

차명주, 서정화†, Bright Walker[1] 동아대학교; [1]울산과학기술대학교
We report solution-processed organic trilayer solar cells consisting of P3HT, a CPE and PCBM, wherein the CPE exists as an interlayer within the donor-acceptor junction. The influence of interlayer thickness on device properties was investigated as well as the behavior of molecular dipoles in the trilayer solar cells when influenced by external electrical stimuli. We find that incorporation of an interlayer which is too thick results in decreased performance due to reduced JSC, VOC, and FF. However the VOC is found to increase slightly when a thin CPE layer is used in conjunction with an external electric field. These results provide an experimental approach for investigating the influence of interfacial dipoles on the on the solar cell parameters and behavior of charge separating organic donor/acceptor junctions, yielding fundamental information about the donor/acceptor interface in organic solar cells.

**3PS-282** 차효정

Development of Bulk Heterojunction Morphology by the Difference of Intermolecular Interaction Behaviors

차효정, 백장열[1], 안태규, 김슬옹[1], 권순기[1], 김윤희[1], 박찬언† 포항공과대학교; [1]경상대학교
The morphology of a bulk heterojunction can be controlled by adding a processing additive in order to improve its power conversion efficiency (PCE) in photovoltaic devices. The phase-separated morphologies of blends of PONTBT or P3HT with fullerene derivatives are systematically examined in the presence of processing additives that possess various alkane alkyl chain lengths or end-group electronegativities. We determined the morphologies of the bulk heterojunction layers by using atomic force microscopy (AFM) and grazing incidence wide angle X-ray scattering (GIWAXS). The photocurrent-voltage characteristics of the bulk heterojunction solar cells were found to be strongly dependent on the intermolecular interactions between the conjugated polymers, the fullerene derivatives, and the processing additives in the photoactive layer.

**3PS-283** 최미진

Pyridine containing polybenzoxazole gate dielectrics for solution processible metal-oxide semiconductor thin-film transistors

최미진, 장광석, 이미혜, 가재원†, 남선영 한국화학연구원
The wide variety of solution processes makes inorganic oxide semiconductors highly attractive and technologically advantageous for large-area, high throughput, and low-cost device production. Recently, solution processible metal-oxide precursors were widely investigated for high performance electronic devices such as portable electronics and flexible electronics. However, there have been some limitations for the utilization of organic gate dielectrics for flexible electronics with solution

**Comparison of two D–A type polymers with each being fluorinated on D and A unit for high performance solar cells**

조제웅[1], 배승환[1], Feng Liu[2], Thomas P. Russell[2], 조원호[1,*]

[1]서울대학교 공과대학 재료공학부

[2]Department of Polymer Science and Engineering, University of Massachusetts

Recently, polymers with fluorinated building block have recently attracted great interest because high power conversion efficiencies (PCEs) over 7% have been achieved by fluorination of A unit. In this work, we synthesized two kinds of D–A polymers with each being fluorinated on A and D unit, where quaterthiophene and benzothiadiazole are used as D and A unit, respectively, in order to investigate the effects of fluorination position on photophysical properties of polymers and their device performances of polymer solar cells. Although the fluorination on either D or A unit effectively enhances intermolecular interaction, exhibiting strong vibronic shoulder in UV–Visible absorption spectra, and lowers energy levels, retaining a low bandgap of 1.58 eV, the polymer with fluorinated D unit exhibits a PCE of 7.10%, while the polymer with fluorinated A unit exhibits a PCE of 6.75%. Therefore it can be concluded that the fluorination on D unit in D–A polymer is a very promising method for achieving high performance solar cells.

# Comparison of Two D-A Type Polymers with Each Being Fluorinated on D and A Unit for High Performance Solar Cells

**Jea Woong Jo,[a] Seunghwan Bae,[a] Feng Liu,[b] Thomas P. Russell,[b] and Won Ho Jo*[a]**

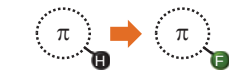
[a] Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

[b] Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, United States

## Introduction

### ❖ Fluorine atom substitution for high-performance solar cells

**Feature of fluorine atom**




✓ **Highest electronegativity**

| H | C | N | F |
|---|---|---|---|
| 2.55 | 3.05 | 3.44 | 3.98 |

Increase of electronegativity

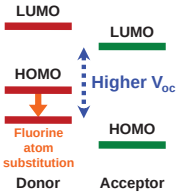
- Strong dipole
- C–F ···H (hydrogen bonding)

✓ **Small size**


- No deleterious steric effect

**Effect of fluorine atom substitution**

✓ **Deeper HOMO energy level**




*Nat. Photonics* **2009**, *3*, 649

✓ **Enhanced molecular ordering**

- Inter/intramolecular interaction with strongly induced dipole

*J. Am. Chem. Soc.* **2013**, *135*, 1806

✓ **Fast charge separation**

- Rate of exciton dissociation↑
- Lifetime of charge carriers↑

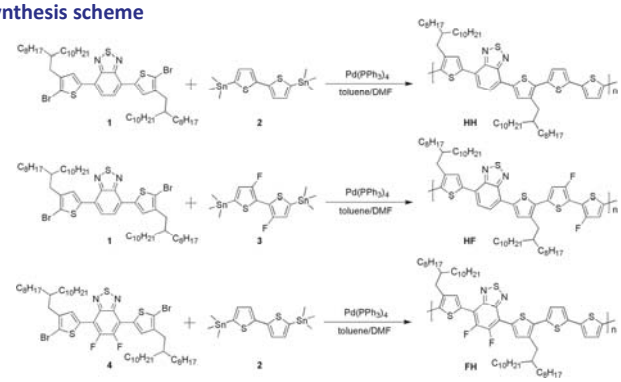
*J. Am. Chem. Soc.* **2011**, *133*, 20468

## Objectives

- To synthesize two types of fluorinated polymer, HF with fluorination on electron-donating unit and FH with fluorination on electron-accepting unit
- To clarify the effect of fluorination position on D-A type conjugated polymer on photophysical and photovoltaic properties

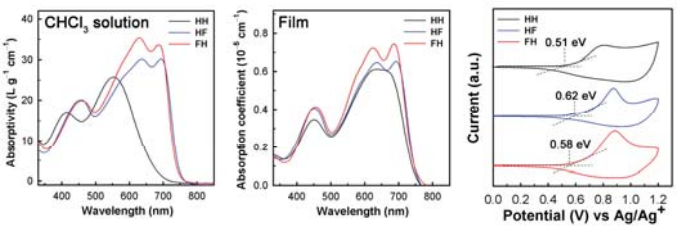
## Results

### ❖ Synthesis scheme




### ❖ Characterization of polymers

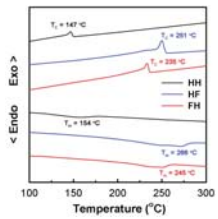
✓ **Absorption spectra and cyclic voltammogram**




| Polymer | $M_n$ [kg/mol] | PDI | $E_{g,opt}$[a)] [eV] | HOMO [eV] | LUMO[b)] [eV] |
|---|---|---|---|---|---|
| HH | 42 | 1.45 | 1.58 | −5.31 | −3.73 |
| HF | 58 | 1.92 | 1.58 | −5.42 | −3.84 |
| FH | 54 | 1.69 | 1.58 | −5.38 | −3.80 |

a) Determined from the onset of UV-Vis absorption spectra.
b) $E_{g,opt}$+HOMO.

✓ **DSC**

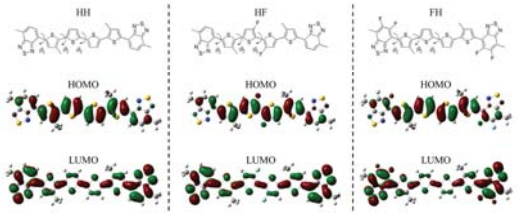



✓ **Dipole moments**

| Polymer | $\mu_g$ [D] | $\mu_{ex}$ [D] | $\Delta\mu_{ge}$[a)] [D] |
|---|---|---|---|
| HH | 3.26 | 22.5 | 19.7 |
| HF | 2.97 | 22.5 | 24.3 |
| FH | 2.82 | 23.5 | 26.3 |

a) $\Delta\mu_{ge} = [(\mu_{gx}-\mu_{ex})^2+(\mu_{gy}-\mu_{ey})^2+(\mu_{gz}-\mu_{ez})^2]^{1/2}$

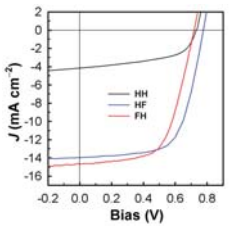
✓ **Torsion angles and energy levels of repeating units calculated by DFT**



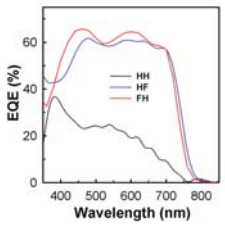

| Polymer | $\theta_1$ [Deg] | $\theta_2$ [Deg] | $\theta_3$ [Deg] | HOMO [eV] | LUMO [eV] |
|---|---|---|---|---|---|
| HH | 3.93 | −12.4 | −0.86 | −4.79 | −2.57 |
| HF | 2.08 | −8.99 | −0.48 | −4.85 | −2.63 |
| FH | 0.21 | 14.88 | -2.70 | −4.88 | −2.68 |

### ❖ Photovoltaic properties of the polymers

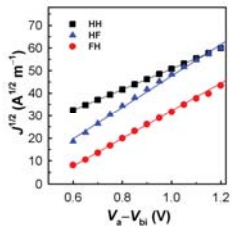
✓ ***J-V* curves**




✓ **EQE spectra**



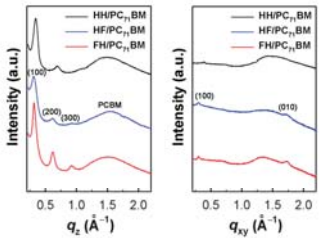

✓ **SCLC hole mobilities**



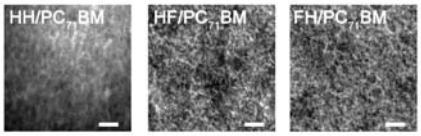

| Polymer | Polymer: $PC_{71}BM$ [w/w] | Thickness [nm] | $\mu_h$ SCLC [$cm^2$/V s] | $V_{OC}$ [V] | $J_{SC}$ [$mA/cm^2$] | FF [%] | PCE [%] |
|---|---|---|---|---|---|---|---|
| HH | 1:1 | 90 | $5.24\times10^{-4}$ | 0.73 | 4.15 | 54 | 1.64 |
| HF | 1:1 | 100 | $1.26\times10^{-3}$ | 0.78 | 14.0 | 65 | 7.10 |
| FH | 1:1 | 90 | $1.16\times10^{-3}$ | 0.72 | 14.6 | 61 | 6.41 |

### ❖ Morphologies of active layers in solar cells

✓ **GIWAXS**




✓ **TEM images (scale bar: 200 nm)**




## Conclusions

- Fluorinated polymers exhibit deeper HOMO energy level than non-fluorinated ones, leading to higher $V_{OC}$ in organic solar cells.
- Fluorinated polymers also exhibit enhanced molecular ordering as evidenced by vibronic shoulder in UV–Vis spectra, π–π scattering in GIWAXS and well-developed fibril structure in TEM.
- HF based solar cell shows a power conversion efficiency of **7.10%** at the 1:1 weight ratio of polymer and $PC_{71}BM$.