Novel 2-hexylthieno[3,2-b]thiophene-containing conjugated molecules have been synthesized via a reduction reaction using tin chloride in an acidic medium. They exhibited good solubility in common organic solvents and good self-film and crystal-forming properties. The single-crystalline objects were fabricated by a solvent slow diffusion process and then were employed for fabricating field-effect transistors (FETs) along with thin-film transistors (TFTs). TFTs made of 5 and 6 exhibited carrier mobility as high as 0.10-0.15 cm²V⁻¹s⁻¹. The single-crystal-based FET made of 6 showed 0.70 cm²V⁻¹s⁻¹ which was relatively higher than that of the 5-based FET (μ = 0.23 cm²V⁻¹s⁻¹). In addition, we fabricated organic photovoltaic (OPV) cells with new 2-hexylthieno[3,2-b]thiophene-containing conjugated molecules and methanofullerene [6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM) without thermal annealing. The ternary system for a bulk heterojunction (BHJ) OPV cell was elaborated using PC₆₁BM and two p-type conjugated molecules such as 5 and 7 for modulating the molecular energy levels. As a result, the OPV cell containing 5, 7, and PC₆₁BM had improved results with an open-circuit voltage of 0.90 V, a short-circuit current density of 2.83 mA/cm², and a fill factor of 0.31, offering an overall power conversion efficiency (PCE) of 0.78%, which was larger than those of the devices made of only molecule 5 (η ~ 0.67%) or 7 (η ~ 0.46%) with PC₆₁BM under identical weight compositions.

Key Words: Anthracene, Semiconductor, Field effect transistor, Photovoltaic cell

Introduction

The recent, rapid development of novel organic semiconductors has resulted in the emergence of a number of high-performance organic field-effect transistors (OFETs) exhibiting high carrier mobilities. Soluble organic semiconductors have been used to fabricate single crystals (SCs) via solvent diffusion methods or to fabricate thin films via spin-coating or drop casting for field-effect transistors (FETs). They are all easily processable for desired electronic and optoelectronic applications. In particular, organic SC-based FETs have been studied intensely because they exhibit fully optimized semiconducting properties for each material due to their molecular structural perfection with a homogeneous spatial arrangement.

As new candidates, two-dimensional p-extended conjugated molecules have shown effective charge-transport properties as films, satisfying the requirement for soluble semiconducting materials. It is well recognized that the electronic structure, molecular structure, and morphology of thin films are important for enhancing carrier mobility in FET devices. When steering the band-gap energy and molecular energy levels of organic semiconducting molecules, varying the conjugation length of a molecule or introducing donor/acceptors into the p-conjugated molecular frames is often used for designing new semiconducting materials. A preferable method that is capable of changing the molecular energies in film states by only changing the position of peripheral substituents was reported in our group quite recently. Using this method, we demonstrated two new molecules bearing thienothiophene (TT) in an anthracene molecular skeleton. These molecules exhibited different molecular energies having substituents at different substitution sites (e.g. 2,6- and 9,10-positions in an anthracene ring). Therefore, we decided to synthesize highly soluble, low-bandgap anthracene-based molecules bearing TTs at the 9,10-position. They were employed to fabricate well-ordered, single-crystalline microplates and crystalline thin films owing to their high degree of intermolecular interactions. Two solution-processable molecules were employed to form FETs. The newly synthesized single-crystal-based FETs exhibited a high carrier mobility of 0.23-0.70 cm²V⁻¹s⁻¹ as well as promising high on/off current ratios.

Based on the promising hole mobility and crystallinity of the two molecules we synthesized, they could be exploited to fabricate organic photovoltaic (OPV) cells. Most OPV devices consist of single p-type semiconducting materials and methanofullerene [6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM) derivatives, with BHJ devices being notable so far. The HOMO level of the p-type semiconductor may not be matched with the HOMO level of poly(3,4-
ethylenedioxythiophene)/polystyrene sulfonate) (PEDOT: PSS) resulting in a poor short circuit current ($I_{sc}$) for the OPV cell. In addition, the relatively low open circuit voltage ($V_{oc}$) is another property we have to improve by changing the molecular energy level of the p-type semiconductor. The OPV devices we fabricated contained two different p-type conjugated molecules which were fairly miscible. Two X-shaped molecules used herein proved to be highly miscible to sustain individual specific aggregation in film states. 5.5’-(2,6-Bis[5-hexylthiophen-2-yl)ethynyl]anthracene-9,10-diyi]bis(ethyne-2,1-diyi]bis(2-hexyl thiieno[3,2-b]thiophene), 5 was employed to fabricate OPVs after mixing into a larger bandgap molecule, 5.5’-(9,10-bis[5-(hexylthiophen-2-yl)ethynyl]anthracene-9,2,6-diyi]bis(ethylene-2,1-diyi]bis[2-hexylthieno[3,2-b]thiophene), 7. The performance of the devices was then investigated. The OPV device made of 5, 7, and PC$_70$BM exhibited a relatively higher power conversion efficiency (PCE), which was larger than those for the devices made of only molecule 5 or 7 with PCBM under an identical weight composition.

**Experiments**

**Synthesis.**

**Materials:** All commercially available starting materials and solvents were purchased from Aldrich, TCI, and Acros Co. and were used without further purification. 2,6-Bis((5-hexylthiophen-2-yl)ethynyl)trimethylsilane (3): A yellow liquid. Yield 4.5 g, 63%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.30 (s, H), 6.87 (s, 1H), 2.87 (t, $J$ = 7.4 Hz, 2H), 1.71-1.27 (m, 8H), 0.94-0.86 (m, 3H), 0.28-0.18 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.32, 139.82, 136.39, 125.14, 122.75, 116.43, 99.49, 98.48, 31.74, 31.59, 31.48, 28.95, 22.75, 14.27, 0.08. LR-MS (EI) m/z (M$^+$): Caled for C$_{70}$H$_{46}$Si: 320.11; found, 320.32. Anal. Caled. for C$_{70}$H$_{46}$Si: C, 63.69; H, 7.55; S, 20.00. found: C, 63.69; H, 7.45; S, 20.02.

2-Ethynyl-5-hexylthieno[3,2-b]thiophene (4): ((5-Hexylthieno[3,2-b]thiophen-2-yl)ethyl)trimethylsilane (4.5 g, 14.6 mmol) was dissolved in freshly distilled THF (30 mL) and methanol (100 mL) in a 250 mL, oven dried, mag.-stirred RBF. K$_2$CO$_3$ was added to the mother solution under nitrogen. The mixture was stirred at room temperature for 8 hours, and then quenched with water and HCl. After completing the reaction, the mixture was extracted with petroleum ether. The organic layer was washed with water and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated under vacuum. Further purification by silica-gel column chromatography (eluent: n-hexane) afforded the product as a dark yellow solid. Yield 4.5 g, 86%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.35 (s, 1H), 6.87 (s, 1H), 3.40 (s, 1H), 2.87 (t, $J$ = 10 Hz, 2H), 1.74-1.27 (m, 8H), 0.91-0.87 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.62, 139.96, 136.33, 125.65, 121.51, 116.41, 81.87, 77.97, 31.76, 31.62, 28.95, 22.78, 14.29. LR-MS (EI) m/z (M$^+$): Caled for C$_{71}$H$_{48}$Si: 248.07; found, 248.31. Anal. Caled. for C$_{71}$H$_{48}$Si: C, 67.69; H, 6.49; S, 25.82. found: C, 67.43; H, 6.46; S, 25.56.

2,6-Bis((5-hexylthiophen-2-yl)ethynyl)anthracene-9,10-dione (5): In a 50 mL, oven dried, mag.-stirred RBF, 2-ethynyl-5-hexylthieno[3,2-b]thiophene (1.5 g, 6.04 mmol) was dissolved in freshly distilled THF (50 mL). The solution was then cooled to –78 °C. n-BuLi (2.42 mL, 6.04 mmol, 2.5 M soln. in hexane) was then added dropwise over 15 minutes. This mixture was stirred for 30 min and 2,6-bis((5-hexylthiophen-2-yl)ethynyl)anthracene-9,10-dione (1.2 g, 2.01 mmol) were added at –78 °C. The mixture was then stirred for 12 hrs. After completing the reaction, the solution was poured into methanol to collect the precipitates. The crude solid was purified by recrystallization into ethanol. Yield 9.20 g, 60%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.32 (s, 2H), 8.23-8.25 (d, $J$ = 8.0 Hz, 2H), 7.81-7.89 (d, $J$ = 7.7 Hz, 2H), 7.16-7.17 (d, $J$ = 3.8 Hz, 2H), 6.69-6.70 (d, $J$ = 3.88 Hz, 2H), 2.82-2.88 (t, 4H), 1.64-1.71 (m, 4H), 1.28-1.41 (m, 12H), 0.87-0.90 (t, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 182.04, 150.38, 136.06, 133.72, 136.32, 132.13, 129.95, 129.89, 127.62, 124.78, 119.58, 91.57, 88.91, 31.72, 31.66, 30.50, 28.92, 22.76, 14.24. LR-MS (EI) m/z (M$^+$): Caled for C$_{30}$H$_{16}$O$_2$Si: 588.22; found (M$^+$ + H)$^+$, 589.2. Anal. Caled. for C$_{30}$H$_{16}$O$_2$Si: C, 77.51; H, 6.16; S, 10.89, found: C, 77.61; H, 5.90; S, 9.54.

((5-Hexylthieno[3,2-b]thiophen-2-yl)ethynyl)trimethylsilane (3): An oven dried, mag.-stirred, 100 mL RBF was charged with a solution of 2-bromo-5-hexylthieno[3,2-b] thiophene (7 g, 23 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.81 g, 1.15 mmol), and copper(I) iodide (0.22 g, 1.15 mmol) in a mixture of freshly distilled THF (40 mL), triethylamine (40 mL), and diisopropylamine (20 mL). Trimethylsilylacetylene (2.72 g, 27.6 mmol) was then added and the mixture was heated at 80 °C for 16 hrs. After completing the reaction, the mixture was extracted with petroleum ether. The organic layer was washed with water, dried over anhydrous Na$_2$SO$_4$ and the solvent was removed under vacuum. Further purification by using silica-gel column chromatography (eluent: n-hexane) afforded the product as a yellow liquid. Yield 4.5 g, 63%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.30 (s, H), 6.87 (s, 1H), 2.87 (t, $J$ = 7.4 Hz, 2H), 1.71-1.27 (m, 8H), 0.94-0.86 (m, 3H), 0.28-0.18 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.32, 139.82, 136.39, 125.14, 122.75, 116.43, 99.49, 98.48, 31.74, 31.59, 31.48, 28.95, 22.75, 14.27, 0.08. LR-MS (EI) m/z (M$^+$): Caled for C$_{70}$H$_{46}$Si: 320.11; found, 320.32. Anal. Caled. for C$_{70}$H$_{46}$Si: C, 63.69; H, 7.55; S, 20.00. found: C, 63.69; H, 7.45; S, 20.02.
137.17, 132.77, 131.57, 131.27, 130.31, 129.36, 127.45, 125.15, 124.58, 122.60, 121.99, 120.66, 117.90, 116.62, 104.99, 98.84, 97.56, 93.45, 90.94, 89.05, 85.87, 31.81, 31.79, 31.66, 31.61, 30.54, 29.04, 29.00, 22.82, 14.33. LR-MS (EI) m/z (M+): Caled for C_{50}H_{66}S_6: 1038.44; found, 1038.44. Anal. Calcd. C, 75.38; H, 6.33; S, 18.29.  

5.5'-([2,6-Bis(4-hexylphenyl)ethynyl]anthracene-9,10-diyl)bis(ethyne-2,1-diyl)bis([2-hexylthieno[3,2-b]thiophene] (6)): In a 250 mL oven dried, mag-stirred RBF, 2-ethynyl-5-hexylthieno[3,2-b]thiophene (2.5 g, 10.4 mmol) was dissolved in freshly distilled THF (70 mL). The solution was then cooled to −78 °C. n-BuLi (4.15 mL, 10.4 mmol, 2.5 M sol’n. in hexane) was then added dropwise over 20 minutes. This mixture was stirred for 30 min. and 2,6-bis([4-hexylphenyl]ethynyl)anthracene-9,10-dione (2 g, 3.45 mmol) were added at −78 °C. The mixture was stirred at room temperature for 3 hrs, and then quenched with water, SnCl_2, and HCl. After completing the reaction, the solution was poured into methanol to collect the precipitates. Yield 1.8 g, 50%. 1H-NMR (400 MHz, CDCl_3) δ 8.66 (s, 2H), 8.46 (d, J = 9.0 Hz, 2H), 7.66 (d, J = 9.0 Hz, 2H), 7.60 (s, 2H), 7.57 (d, J = 8.2 Hz, 4H), 7.21 (d, J = 8.2 Hz, 4H), 6.96 (s, 2H), 2.93 (t, J = 7.4 Hz, 4H), 2.65 (t, J = 7.4 Hz, 4H), 1.78–1.74 (m, 4H), 1.66–1.60 (m, 4H), 1.45–1.21 (m, 24H), 1.09–0.88 (m, 12H). 13C NMR (100 MHz, CDCl_3) δ 151.68, 143.97, 140.76, 140.34, 138.91, 137.17, 131.99, 131.69, 131.35, 130.64, 129.76, 128.76, 125.15, 122.58, 122.36, 120.45, 119.80, 117.95, 116.65, 97.51, 92.24, 90.98, 89.73, 36.23, 31.96, 31.81, 31.68, 31.62, 31.49, 29.95, 29.21, 29.04, 22.86, 22.83, 14.36 LR-MS (EI) m/z (M+): Caled for C_{70}H_{66}S_6: 1038.44; found, 1038.44. Anal. Calcd. C_{70}H_{66}S_6 for: C, 80.71; H, 6.83; S, 12.66.

**Instrumentation.** 1H NMR spectra were recorded on a Varian Mercury NMR 400 Hz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. 13C-NMR spectra were recorded using a Varian Inova-500 spectrometer. Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821 instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA/A50 (temperature rate 10°C/min under N_2). The redox properties of new molecules were examined by using cyclic voltammetry (Model: EA161 eDAQ). Thin films were coated on a platinum plate using methylene chloride (MC) as a solvent. The cyclic voltammetry of new molecules were examined by using cyclic voltammetry. The scan rate was 50 mV/s. Atomic force microscopy (Digital Instruments Multimode equipped with a nanoscope IIIa controller) operating in tapping mode with a silicon cantilever was used to characterize the surface topographies of the samples. The film samples were fabricated by spin-coating (1500 rpm) on n-octyltri chlorosilane (OTS)-treated silicon wafer followed by drying at 60 °C under vacuum (solvent: chloroform, conc. of the solution: 10 mg/mL). Absorption spectra of samples in a solution (chloroform, conc.: 1 × 10^{-6} mol/L), films, and crystalline microplates were obtained using a UV-VIS spectrometer (HP 8453, photodiode array type) in the wavelength range of 190–1100 nm. PL spectra of the solutions at room temperature were acquired on a Hitachi F-7000 FL Spectrophotometer.

**OFET Fabrication:** To fabricate the FET devices and characterize their performances, a bottom-gate top-contact device geometry was employed. For thin film transistors, spin-coated films of 5 and 6 were prepared on the heavily n-doped SiO_2/Si substrate with chloroform as a solvent. Surface modification of dielectric layer, SiO_2 was carried out with OTS to produce a hydrophobic dielectric surface. When fabricating the single-crystalline microplate FET devices, we grew the crystals directly on a SiO_2/Si substrate. The OTS-treated SiO_2/Si substrate was submerged into the chloroform solution (5 mg in 10 mL) and the vapor of MeOH (30 mL) was saturated in the closed vessel. In 3 days, the desired single-crystalline microplates were grown on the OTS-SiO_2/Si substrate and the grown microplates were dried under vacuum at 70 °C for 6 hrs. Source and drain electrodes were then thermally evaporated (100 nm) through a shadow mask with a channel width and length of 1500 and 100 μm for TFTs, respectively. The device performance was evaluated in air using 4200-5CS semiconductor characterization system in ambient conditions.

**OPV Device Fabrication:** The hole collecting electrode was 100-200 nm thick indium tin oxide (ITO) coated glass with resistance of 20.0 Ω/cm. ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 minutes in each solvent, sonification for 15 minutes in 50:50 isopropyl alcohol and acetone solution, and finally rinsed with de-ionized water. The cleaned ITO coated glass was treated with O_2 plasma and flattening ITO with a microwave-generated plasma reactor (Plasmatic Systems Inc., PLASMATIC-PREENII, 24 GHz) for 15 minutes. 30 nm thick PEDOT:PSS layer (Baytron P, 1 S cm⁻¹) was coated by spin coating stock solution at 2500 rpm for 30 seconds. PEDOT:PSS coating was heat-treated in the glove box at 200 °C for 5 minutes.

For control samples, the Device I was prepared with compound 5 and PCBM and the Device II was prepared with compound 7 and PCBM with 1:1 wt. ratio, respectively. When preparing the Device III, we first investigated the miscibility of molecules 5 and 7. The molecules 5 and 7 were mixed with 1:1 wt. ratio, which exhibits good miscibility and sustainability of specific aggregated structure. The mixture of two molecules and PCBM with 1:1 wt. ratio was dissolved in anhydrous o-dichlorobenzene. The thickness of a resulting photoactive layer was 80 nm and pre-annealed at 80 °C for 10 minutes. 150 nm thick aluminum was evaporated and deposited as an electrode. Current-voltage characteristics were measured with Keithley 2400 source-measure unit. 300 W Xe lamp was used as a light source to produce intensity of 100 mW/cm². To mimic
sun light, AM 1.5 filter (Oriel) was used and neutral density filter was used to reduce intensity as necessary. Intensity of incoming light power was measured with calibrated broadband optical power meter (Spectra Physics model 404).

Results and Discussion

Synthesis. We designed 2-dimensional (2-D) π-conjugated molecules that contained thienothiophene (TT) moieties at the periphery. Scheme 1 illustrates the synthetic routes for the two molecules and the structure of a known compound 7. 2,6-Dibromoanthracene-9,10-dione was synthesized using an established method. The synthesized 2,6-dibromoanthracene-9,10-dione went through a Sonogashira coupling reaction with 2-ethynyl-5-hexylthiophene and with 1-ethyl-1-y1-4-hexylbenzene to produce molecules 1 and 2, respectively in the presence of PdCl$_2$(PPh)$_3$, triethylamine, DIA, and copper iodide in freshly distilled THF. Then, 2-ethynyl-5-hexylthieno[3,2-b]thiophene, 4 was anchored into the dione group through reduction in the presence of n-BuLi and tin chloride. The two molecules 5 and 6 were successfully synthesized to be applied to the fabrication of thin film and crystal-based devices. Molecule 7 was already demonstrated in our previous report.

Four hexyl chains were substituted into the thiophene, benzene, and TT groups as solubilizing groups and crystallization-promoting groups. The identity and purity of the synthetic materials were confirmed by $^1$H NMR, $^{13}$C NMR, LR-MS, and elemental analysis. The compounds were found to have good self-film-forming properties and dissolved well in various organic solvents such as chloroform, xylene, MC, chlorobenzene, and THF.

Thermal Analysis. The thermal properties of the molecules were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TGA measurements were carried out at a heating rate of 10 °C/min under nitrogen. The measurements revealed that the molecules had good thermal stability indicated by the

![Scheme 1. Synthesis of the anthracene-based conjugated molecules 5 and 6. The structure of known molecule 7.](image-url)
high onset decomposition temperatures (~383-384 °C) (see Table 1).

DSC measurements were also performed at a heating (cooling) scan rate of 10 °C/min under nitrogen. Compounds 5 and 7 exhibited distinct crystalline-isotropic transition temperatures of 227 °C and 159 °C, respectively, including possible solid-solid crystal transitions. Although compound 5 exhibited crystallization temperature ($T_c$) of around 127 °C, the compound 7 did not show crystallization behavior during cooling cycle. The melting point of compound 6 was also determined to be 242 °C. No glass transition peaks of all compounds were observed in the measurement temperature range. Resulting from relatively higher melting points of compounds 5 and 6, it could be conjectured that the compounds bearing thienothiophene at 9,10-positions are likely to form more compact crystalline structures, which is attributed to higher extent of J-aggregation between the molecules.

The mixture of 5 and 7 at a 1:1 wt. ratio was scanned with changing temperature. The curve (c) showed a small enthalpy change at 152 °C, which indicates the existence of crystalline domain. This phenomenon can be supported by the results of absorption spectroscopy displaying robust J-aggregation behavior in the blend film sample.

**Absorption and Photoluminescence (PL) Spectroscopy.**
In order to study the optical absorption and emission properties of the molecules, samples in chloroform (conc. 1 × 10^{-5} mol/L), thin film, and single-crystalline microplates were prepared (see Figure 2). Figure 2 shows the UV-Vis absorption spectra of molecule 5. Very interesting chromic behavior was observed upon comparison of the spectra of the solution, film, and crystals. In a solution state, the absorption maxima appeared at around 500 and 540 nm. The cut-off wavelength was around 575 nm indicating an optical bandgap ($E_{g opt.}$) of 2.13 eV. The solution spectrum of molecule 5 exhibited an absorption maximum at 535(511) nm; however, bathochromic shifts and highly resolved vibronic peaks in the absorption spectra of the film and crystals were observed, indicating that strong intermolecular interactions were generated in the film and crystals. From the significant red-shift of $\lambda_{max}$, it was thought that localized J-aggregation behavior was predominant in the molecular film. This behavior was attributed to the formation of an ordered structure in a localized domain as a result of inter-molecular π-stacking. Similar behaviors were confirmed in our previous report by using single-crystal X-ray crystallography.\(^{30}\)

In the PL spectra, the difference between the solution and solid samples was more clearly observed. In particular, the emission spectrum of the single-crystalline microplate was exhibited to have a 15 nm red-shift in the emission maximum wavelength compared to the spectrum of the film.

In Figure 3, the absorption and PL spectra of compound 6 are displayed in solution, film, and crystalline objects. Identical spectral behaviors were confirmed in the spectral analysis of both absorption and emission resulting in the formation of J-aggregates in the solid samples, as expected.

In order to investigate the formation of J-aggregates in a representative molecule 5, we prepared the 5-doped poly(methylmethacrylate) (PMMA) films with the concentration. Then, the absorption spectra of three film samples were compared with that of the solution in chloroform. We dissolved 5 into PMMA to cast the film for taking their individual absorption spectrum. Doping 0.1 wt % of 5 into PMMA, the absorption spectrum was found to be quite
similar to that of the solution spectra. When increasing the concentration to 0.6 wt %, we could observe highly resolved peaks at 500, 540, and 590 nm separately. Finally, the spectrum with 2.0 wt % of 5 in PMMA (see Figure 4(d)) exhibited a well resolved absorption spectrum arising from J-aggregation mode, which is well evidenced from our previous results. At 2.0 wt % 5-doped PMMA film showed the identical spectrum as that of pristine film with molecule 5 only. The absorption band at 598 nm was assigned to the peaks from J-aggregation. The transformation of the spectrum from solution to solid film was manifestly observed in the spectral analysis. It indicated that the aggregation behavior was dependent on the concentration of molecule 5, which has a strong tendency for self-association via strong molecular interaction even under a very low concentration.

Electrochemical Analysis. Cyclic voltammograms (CVs) were recorded for the solution and film samples, and the potentials were obtained relative to an internal ferrocene reference (Fc/Fc⁺). The CV scans in the range of −1.2 V to +1.5 V (vs. Ag/AgCl) showed quasi-reversible oxidation peaks. Unfortunately, no reduction peaks were observed; therefore, we were unable to accurately estimate the energies of the lowest unoccupied molecular orbitals (LUMO) of the molecules directly from the CV measurements. In order to determine the LUMO levels, we combined the oxidation potential from the CV measurements with the optical energy bandgap (E_{g,opt}) resulting from the absorption edge in the absorption spectrum. The voltammograms of 5 and 6 in the film states showed their lowest oxidative waves at 0.96 and 1.16 V, respectively. As shown in Table 1, the highest occupied molecular orbital (HOMO) levels of molecules 5 and 6 have energies of −5.36 and −5.56 eV, and the LUMO energy levels lie in the region of −3.46 to −3.62 eV for 5 and 6.

Atomic Force Microscopy. XRD measurements can reveal the type of crystalline structure that is prevalent in the molecular films, while atomic force microscopy (AFM) observations can provide images of the top surface. A solution of each molecule was prepared and spin-coated on OTS-SiO₂/Si for each solution. The semiconducting films were dried completely, and two pristine films on OTS-treated SiO₂ were prepared. Micrographs of the two films were taken for each molecule as shown in Figure 5. Well-organized crystalline structures and a network of interconnected grains were observed in the as-cast films of both molecules. It is known that if the regions between the crystalline domains in 5 and 6 are more dense and ordered,

![Figure 3](image1.png)  
**Figure 3.** UV-Vis absorption (A) and photoluminescence (B) spectra of 6. (a) solution; (b) film; (c) single-crystalline microplate.

![Figure 4](image2.png)  
**Figure 4.** UV-Vis absorption spectra of 5-doped PMMA samples. (a) chloroform solution, (b) PMMA film doped with 0.1 wt % 5, (c) PMMA film doped with 0.6 wt % 5, (d) PMMA film doped with 2.0 wt % 5.

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<th>Molecule</th>
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<th>T_{c} (°C)</th>
<th>T_{d} (°C)</th>
<th>λ_{max,abs} (nm)</th>
<th>λ_{cut-off} (nm)</th>
<th>λ_{max,abs} (nm)</th>
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<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
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<td>388</td>
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</tbody>
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Table 1. Measured and calculated parameters of new molecules 5, 6, and 7.
charge transport should be easier as a result of the improvement in network connectivity and because the possibility of charge trapping within these regions will be lower\textsuperscript{31,32}. It was therefore expected that the improved connectivity and densely packed geometry between neighboring domains of the molecule should result in good charge transport in TFT devices with few charge traps.

Properties of OTFTs Made of Molecules 5 and 6.

Bottom-gate, top-contact OTFT devices were fabricated under ambient conditions. TFT-I was made of 5; TFT-II was made of 6. After spin coating the semiconductor solution on OTS-SiO\textsubscript{2}/Si, gold was deposited via thermal evaporation. All measurements were performed under ambient atmosphere.

The OTFTs of both molecules exhibited typical p-channel field-effect transistor characteristics. The mobilities were obtained from the source (S)-drain (D) current-voltage curves (\(I_{DS}\) vs. \(V_{DS}\)) in well-resolved saturation regions. The saturated field-effect mobility \(\mu_{FET}\) could be calculated from the amplification characteristics using known Eq. (1) describing field-effect transistors.

\[
\mu_{sat} = \frac{(2I_{DS})(W/C(V_G - V_0)^2)}{L^2}
\]  

where \(I_{DS}\) is the saturation drain current, \(C\) is the capacitance (~11.50 nF/cm\(^2\)) of the oxide dielectric, \(V_G\) is the gate bias, and \(V_0\) is the threshold voltage.

Even though the films were not thermally annealed, the TFTs made of 5 and 6 exhibited interestingly high carrier mobility around 0.1-0.15 cm\(^2\)V\(^{-1}\)s\(^{-1}\) with ~10\(^5\)-6 for current on/off ratio (see Figure 6). The high performance of the TFTs was attributed to the improved crystallinity and dense packed geometry, and continuous polycrystal-connectivity in the thin films.

For comparison with the TFTs, we investigated the FETs made of single-crystalline microplates using 5 and 6. The hexagonal microplates were formed in the solution by solvent diffusion methods successfully. Using slow diffusion of a THF solution over MeOH, we obtained microscopic crystalline objects. Analysis with scanning electron and
optical microscopes revealed that these crystalline objects were collections of rhombus plates of both 5 and 6 with sizes ranging from several micrometers to tens of micrometers. The insets in Figures 7(a) and 7(b) show optical microscope images of each crystalline microplate FET made of 5 and 6, where the channel length × width were 40 × 132 µm and 100 × 75 µm, respectively.

Rather than thin film transistors, organic field-effect transistors (OFETs) were the most promising electronic devices fabricated using well-defined SCs as charge-transporting layers. Molecules 5 and 6 with enhanced solubility were readily processed and the crystalline microplates were grown in the solution states. The transfer characteristics in the saturation regime at a constant source-drain voltage are presented on the right side of Figure 7. The fabricated crystalline device of 5 exhibited a mobility of $\mu = 0.23 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, whereas the device of 6 exhibited significantly higher mobility ($\mu = 0.70 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

Overall, the good performance of TFT devices might be a result of the presence of the TT fused rings and the triplet bond between TT and anthracene in the 9,10-positions, which support the more planar conformation of the molecules. In addition, TT units at the peripheries of 5 and 6 generate stronger intermolecular interactions and induce larger overlap between the $\pi$-orbitals of neighboring molecules, generating efficient channels for charge transport and resulting in higher carrier mobility.

**OPV Device Performances.** Finally, the potential of the newly synthesized molecules as photoactive materials in a PV cell was explored. All of the OPV devices were fabricated on glass substrates precoated with a 300 Å thick ITO anode. For BHJ type-OPV device fabrication, the solution-processable fullerene derivative, PC$_{61}$BM, is a typical electron acceptor that exhibits high optical absorption in the visible range. The device configurations are as follows: ITO/PEDOT:PSS/anthracene derivatives:PC$_{61}$BM (1:1 wt. ratio)/LiF/Al.

In Figure 8, the molecular energy levels and the configuration of the device are illustrated. After preparing blend films with 5 and 7, we first investigated their blending properties. It is important to display individual crystalline morphological characteristics which can be shown in absorption spectroscopy in order to utilize two different electronic properties in a blend sample together. As was shown previously, the thin films of 5 and 7 exhibited clear spectroscopic evidence of J-aggregation. In Figure 9, absorption spectra of molecule 5, 7, and their blend samples are illustrated both in solution and film states.
In Figure 9(a), in the solution state, molecule 7 showed hypochromic shift of the spectrum compared to that of molecule 5. As is typically known, the anthracene molecule bearing TT at the 9,10-position showed a lower bandgap energy than molecule 7. The spectrum of the blend sample was produced by simply adding the spectra of 5 and 7.

In Figure 9(b), for the film spectra, due to stronger molecular specific interaction between TTs at the 9,10-position, molecule 5 showed much larger bathochromic shift, which indicated the formation of J-aggregates. Molecule 5 has a lowest energy absorption band at 606 nm; molecule 7 has a 558 nm absorption maximum at long wavelength. When taking the absorption spectrum of the blend sample, we can observe two clear absorption bands both at 558 and 606 nm together. Usually, when mixing two different crystalline materials, the crystallinity or specific aggregation is often disrupted to become amorphous. In this case, the J-aggregates from each molecule were sustained firmly, and their unique crystalline domains were maintained.

The crystalline blend sample of 5 and 7 was employed as a host material for BHJ OPV devices. The main objective of this blend material was to minimize the energy barrier between the photoactive layer and PEDOT:PSS and to increase the open circuit voltage ($V_{oc}$). In the energy level diagram, from PEDOT PSS to molecule 7, an efficient cascade energy alignment could be observed. In addition, although molecule 5 has ~5.36 eV of HOMO energy level, molecule 7 acts as a molecule to lower the HOMO level of the blend resulting in the larger gap between the HOMO level for a p-type semiconductor and the LUMO level of PC$_{61}$BM. The higher $V_{oc}$ value could be anticipated from this blend technique.

We fabricated OPV devices using the molecular mixture with PC$_{61}$BM (1:1 wt ratio of 5 and 7). For comparison, we also fabricated the BHJs using each single molecule with PCBM. The performance characteristics of the devices were determined under identical conditions.

Figure 10 shows the current density-voltage characteristics of the devices under AM 1.5 G illumination. The maximum PCE of 5-based OPV Device I was found to be 0.67%, which was relatively higher than that of 7-based OPV Device II (see Table 2). As expected, we measured a lower $V_{oc}$ for Device I. The binary BHJ samples with 7 and PC$_{61}$BM (1:1 wt ratio) exhibited an open-circuit photovoltage of 0.86 V and a short-circuit current density of 1.88 mA cm$^{-2}$. The fill factor, a measure of the squareness of the J-V characteristics, was equal to 0.29. The PCE reached around 0.46%. However, when mixing molecules 5 and 7 with PCBM, higher $V_{oc}$ and $J_{sc}$ were measured, which was due to a higher HOMO level for the blend sample.

Finally, the PCE of Device III showed improved performance ($\eta$ ~ 0.78-0.80%) compared to the other two devices. Our strategy to use the miscible blend materials with p-type materials proved to be effective for improving device efficiency. However, the lower power conversion efficiency than we expected under the present device fabrication conditions might be due to microscopic phase segregation between X-shaped conjugated molecules and PCBM or disruption of J-aggregates in the crystalline structure of compound 5. More effort is being made to optimize the composition of the two p-type semiconducting molecules and to determine the effect of a semiconducting plasticizer for improving the PCE values.

### Table 2. Summary of anthracene molecule-based OPV device performance

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device I</td>
<td>0.80</td>
<td>2.53</td>
<td>0.34</td>
<td>0.67</td>
</tr>
<tr>
<td>Device II</td>
<td>0.86</td>
<td>1.88</td>
<td>0.29</td>
<td>0.46</td>
</tr>
<tr>
<td>Device III</td>
<td>0.90</td>
<td>2.83</td>
<td>0.31</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Device I: 5 and PCBM (1:1 wt ratio); Device II: 7:PCBM (1:1 wt ratio); Device III: (5 & 7) and PCBM (1:1 wt ratio)

**Conclusion**

We have successfully synthesized and characterized new anthracene-based 2-D conjugated molecules containing TTs at 9,10-positions that are solution processable. The molecules formed smooth films on large surfaces and also showed formation of crystalline microplates. Of the two molecules studied, TFTs made of 5 and 6 exhibited carrier mobility as high as 0.10 and 0.15 cm$^2$V$^{-1}$s$^{-1}$, and corresponding single-crystal-based FETs showed 0.23 and 0.70 cm$^2$V$^{-1}$s$^{-1}$, which were relatively higher than those in TFTs. These molecules can also be exploited in bulk heterojunction OPV cells in combination with PC$_{61}$BM. Such devices were prepared using individual p-type semiconductors 5 and 7 respectively with PC$_{61}$BM. Then, the blend with 5 and 7 was also employed as a p-type semiconducting material with PC$_{61}$BM. By taking the strategy of using a miscible blend, the PCE was improved by virtue of increasing the open circuit voltage ($V_{oc}$) and short circuit current ($J_{sc}$) under simulated AM1.5.

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References