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Synthesis and Characterization of Pentacene– and Anthradithiophene–Fluorene Conjugated Copolymers Synthesized by Suzuki Reactions

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ABSTRACT: We have synthesized new types of pentacene– and anthradithiophene–dialkylfluorene conjugated copolymer via Suzuki cross-coupling polymerization. The polymer chemical structures and molecular weights were characterized by ¹H NMR, ¹³C NMR, and gel permeation chromatography (GPC). Fundamental properties, such as electrochemical and optical behavior, were studied using cyclic voltammetry (CV) and UV–vis absorption (UV–vis) to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels as well as their optical bandgaps. Both polymers exhibit relatively low bandgaps and their high solubility in common halogenated organic solvents. They were successfully incorporated into photovoltaic cells, giving a power efficiency up to 0.68%. This is the first acene-containing conjugated polymer solar cell.

Organic semiconductors based on conjugated polymers are attractive candidates for applications, such as organic field effect transistors (OFETs),^{1,2} organic photovoltaic cells (OPVCs),³ and organic light-emitting diodes (OLEDs).⁴ In the past decade, regioregular polythiophene and its derivatives have been extensively investigated for FET^{2,5} and solar cell⁶ applications. Fused acenes and heteroacenes such as pentacene,⁷ anthradithiophene,^{8,9} and their derivatives have been extensively studied for OTFTs. They have also shown promising performance in OPVCs.¹⁰

However, few conjugated polymers based on these five-fused-ring acene systems have been reported due to their limited solubility and synthetic difficulties. Acene conjugated polymers may be particularly interesting for OPVCs. Low bandgap polymers can be readily achieved since the acene monomers already have a relatively low bandgap. For example, the optical bandgap for pentacene film is as low as 1.7 eV. By incorporating them into conjugated polymers, it is expected the bandgaps of the resulting polymers will be further reduced. Additionally, the large fused rings can potentially allow good π – π overlap between polymers for efficient charge transport.

Very recently, we have successfully synthesized alternating triisopropylsilylethynyl-substituted pentacene-based copolymers with dialkyldiethynylphenyl units by using a room temperature Sonogashira coupling reaction.¹¹ Those pentacene copolymers showed optical band gaps as small as 1.68 eV and improved air stability as compared to triisopropylsilylethynyl-substituted pentacene (**TIPSEP**), which in turn is 50 times more stable than pentacene.¹² Suzuki reaction,¹³ involving cross-coupling between an aryl halide and an arylboronic acid (or boronic ether), is another commonly used polymerization reaction for conjugated polymers.¹⁴ A variety of different monomers can be readily synthesized. It is therefore of great interest to investigate whether pentacene and anthradithiophene monomers can undergo Suzuki polymerization reactions. This would open up possibilities to synthesize a large variety of new conjugated polymers.

In this article, we report the synthesis and characterizations of new types pentacene– and anthradithiophene–dialkylfluorene conjugated copolymers having triisopropylsilylethynyl (**TIPSE**) substituents at the central positions of the pentacene and anthradithiophene core. The key polymerization step was carried out by using Suzuki coupling reaction.¹⁴ Dialkylfluorenediboron was chosen as the comonomer because it is commonly used for Suzuki polymerization. Despite our earlier report of incorporating **TIPSE** pentacene into conjugated polymers, anthradithiophene has never been incorporated into conjugated polymers. It is potentially an interesting monomer for conjugated polymer because it is more stable than pentacene, and the thiophene units on each end of the fused-ring molecule allow it to have a more coplanar structure with other conjugated units. We obtained polymers with relatively high molecular weights, good stability under ambient atmosphere, and good solubility in common halogenated organic solvents. To our knowledge, this is the first report to prepare an anthradithiophene-containing conjugated polymer.

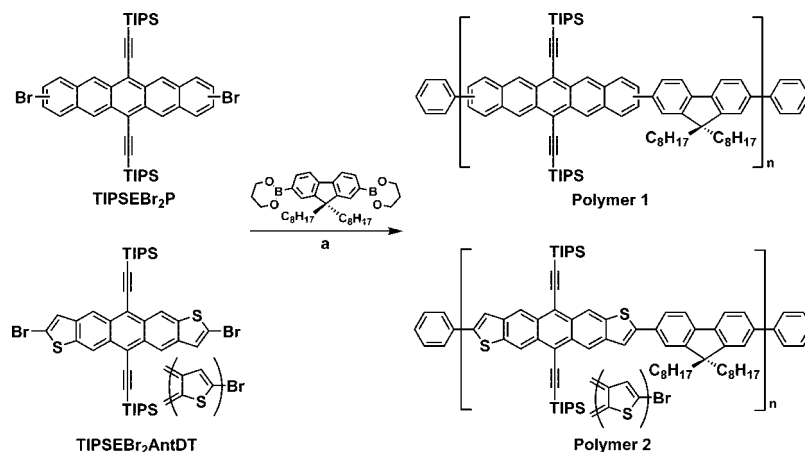
The synthesis of **TIPSE**-substituted dibromopentacene (**TIPSEBr₂P**) was reported previously.¹¹ The synthesis of **TIPSE**-substituted dibromoanthradithiophene (**TIPSEBr₂-AntDT**) from 2,3-thiophenedicarboxaldehyde took place in three steps including bromination, aldol reaction, and introduction of **TIPSE** substituent followed by reduction with a 25% overall yield after three steps (see Supporting Information).^{9,15} Both **TIPSEBr₂P** and **TIPSEBr₂-AntDT** were further purified by recrystallization prior to polymerization.

The polymerization reaction conditions are summarized in Scheme 1. The polymerization was carried out between the dibromo compounds and di-*n*-octylfluorene bispropylenediboron by using Suzuki coupling reaction followed by end-capping with phenylboronic acid and bromobenzene to obtain the desired pentacene- and anthradithiophene-containing alternating copolymers **1** and **2** in 92% and 83% yield, respectively, after washing with appropriate organic solvents such as methanol, acetone and hexanes in this order. The molecular weights of the polymers **1** and **2** were determined by gel permeation chromatography (GPC) using either tetrahydrofuran (THF) or

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Scheme 1. Polymerization and Reaction Conditions of Polymers 1 and 2^a

^a Conditions: (a) (1) Pd(PPh₃)₄, Aliquat 336, 2 M K₂CO₃ in water, toluene, 80–85 °C, for 2–3 days; (2) phenylboronic acid (5 mol amount), 80–85 °C, 2 h; (3) bromobenzene (5 mol amount), 80–85 °C.

Table 1. Electrochemical and Optical Properties of Polymers 1 and 2

| compounds | M_n^a | PDI | DP | $E_{red/onset}^b$ (V) | $E_{ox/onset}^b$ (V) | λ_{abs}/nm , λ_{onset}/nm | HOMO–LUMO gap/optical bandgap (eV) |
|-------------------|---------|------|----|-----------------------|----------------------|--|------------------------------------|
| 1 | 36 400 | 3.21 | 35 | –1.40 –1.89 | +0.24 | 675, 695 (<i>o</i> DCB) 670, 695 (film) ^c | 1.64/1.78 |
| 2 | 58 000 | 2.30 | 56 | –1.65 | +0.26 | 587, 607 (<i>o</i> DCB) 586, 626 (film) ^c | 1.91/1.98 |
| TIPSEP | | | | –1.54 | +0.24 ^d | 649, 667 (<i>o</i> DCB) 649, 668 (film) | 1.73 ^e /1.86 |
| TIPSEAntDT | | | | –1.70 | +0.33 | 559, 573 (<i>o</i> DCB) 560, 578 (film) | 2.10 ^e /2.15 |

^a Determined by GPC in THF (polymer **1**) or chlorobenzene (polymer **2**) with polystyrene as a standard. ^b These redox potentials were based on ferrocene. ^c Spin-coated from *o*-dichlorobenzene solution. ^d The HOMO level of **TIPSEP** was 5.20 eV vs vacuum.¹⁶ ^e See Supporting Information.

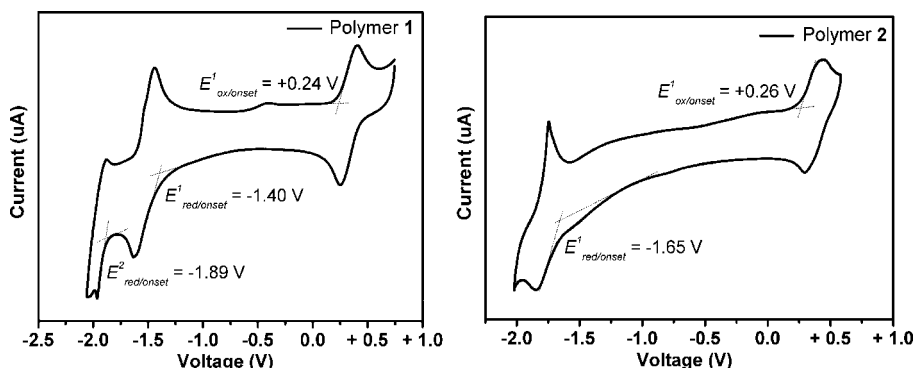


Figure 1. Cyclic voltammograms of polymers 1 and 2.

chlorobenzene as the eluent and polystyrene standards. Polymers **1** and **2** were found to have a number-averaged molecular weight (M_n) of 36×10^3 and 58×10^3 g mol^{–1} with a polydispersity index (PDI) of 3.21 and 2.30, respectively.

High solubility is important for characterizations and potential applications of these polymers. We have evaluated the solubility of polymers **1** and **2** in common organic solvents at ambient temperature. Both polymers **1** and **2** exhibited high solubility with halogenated benzenes (~5.0 mg/mL), while they are not soluble in hexanes and acetone (see Supporting Information).

The highest occupied molecular orbitals (HOMOs), lowest unoccupied molecular orbitals (LUMOs), and optical bandgaps were determined using cyclic voltammetry (CV) and UV–vis spectrometry (UV–vis) in both solution and thin film states. Table 1 summarizes the results as compared to those of TIPSE-substituted pentacene (**TIPSEP**) and anthradithiophene (**TIPSEAntDT**).

In terms of electrochemical properties, polymer **1** exhibited one reversible oxidation step and two reversible reduction steps, indicating that the oxidative and reductive species of polymer **1** are relatively stable in solution. On the other hand, polymer **2** showed one reversible oxidative step and one quasi-reversible reductive step under the same measurement conditions. The oxidation onset of polymer **1** is at the same potential as that of **TIPSEP** as a result of limited conjugation due to a twisted conformation between the terminal benzenes of pentacene and fluorene. In comparison, the oxidative onset of polymer **2** was 0.07 V lower than that of **TIPSEAntDT**. This is reasonable because the conjugation between anthradithiophene and fluorene is better due to less steric hindrance between them. From the first oxidative and reductive onsets, we have estimated HOMO and LUMO levels of of –5.20 and –3.56 eV for polymer **1** and –5.22 and –3.31 eV for polymer **2** using the HOMO level of **TIPSEP** as a reference.¹⁶ The HOMO–LUMO gaps were

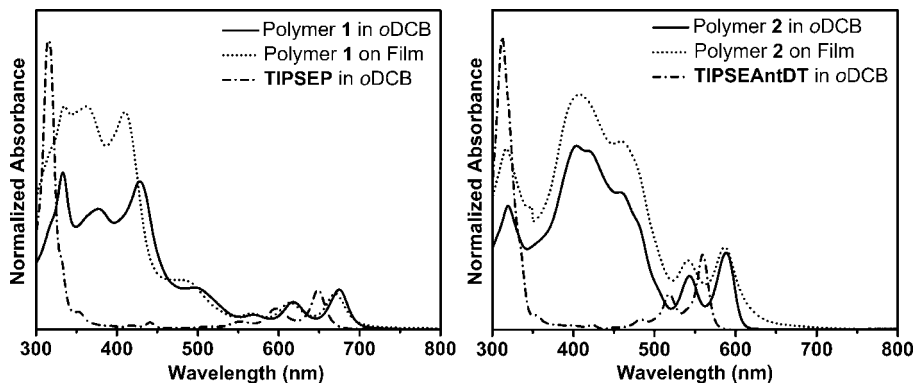


Figure 2. UV-vis spectra of polymers **1** (left) and **2** (right) in solution and thin film, together with **TIPSEP** and **TIPSEAntDT**.

calculated to be +1.64 and +1.91 eV for polymers **1** and **2**, respectively.

The CV experiments were performed under a stream of argon in a saturated solution of 0.05 M Bu_4NPF_6 as a supporting electrolyte, in anhydrous *o*-dichlorobenzene. The experiments were carried out using platinum electrodes at a scan rate of 100 mV s^{-1} against Ag wire as a pseudoreference electrode at room temperature. Ferrocene was used as a reference oxidation potential for both polymers **1** and **2**.

The UV-vis spectra for polymers **1** and **2** were measured in *o*-dichlorobenzene solution and as spin-coated thin films on glass. Both polymers easily formed smooth uniform films. For polymer **1**, its UV-vis spectrum in solution was red-shifted by 26 nm from that of **TIPSEP**. The thin film spectrum is similar to the solution spectrum indicating little aggregation between the polymer chains of polymer **1** due to the bulky **TIPSE** substituents on the polymer backbone and the presence of both the 2,9- and 2,10-substitutions on the pentacene. Polymer **2** also exhibited similar behavior with a 28 nm red-shifted in solution as compared to **TIPSEAntDT**. In the thin film spectrum, on the other hand, a broad tail appeared in the range of 600–700 nm, while its absorption maximum did not shift compared to solution spectrum. From the absorption edge for polymers **1** and **2**, the optical bandgaps were calculated to be 1.78 and 1.98 eV, respectively.

The thermal stability of polymers **1** and **2** in solid state was studied by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a stream of nitrogen. The degradation temperature for both polymers was around 400 °C, similar to those of pentacene–diethynylphenyl copolymers.¹¹ The analysis of the degradation of **TIPSEP** indicates that triisopropylsilyl ethynyl substituents might be removed at that temperature (see Supporting Information).

Successful bulk heterojunction solar cells have been fabricated using polymer **2** in a blend with [6,6]-phenyl C61-butyric acid methyl ester (PCBM) in a 1:3 ratio, while all attempts at using polymer **1** in a bulk heterojunction have led to poor performance and shorted devices. Initial results are promising yielding an open-circuit voltage of 750 mV, a short-circuit current of 2.35 mA/cm^2 , and a power conversion efficiency of 0.68%. We are currently aiming at gaining control of the blend morphology and trying these promising polymers with other electron acceptors.

In summary, we have synthesized new types of conjugated polymers containing pentacene or anthradithiophene by Suzuki polymerization reactions in good yields. This is the first report to synthesize alternating anthradithiophene-based copolymers.

Both polymers exhibited high molecular weights with optical bandgaps of 1.78 and 1.98 eV, respectively. In addition, they have high solubility in halogenated organic solvents (>5.0 mg/mL), making them good candidates for solution-processable device applications. We also have fabricated the first anthradithiophene-containing conjugated polymer solar cells and showed promising performance.

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Supporting Information Available: Details of experimental procedures, synthesis of all new compounds, UV-vis spectra, cyclic voltammograms, TGA, and DSC of polymers **1** and **2**, together with **TIPSEP** and **TIPSEAntDT**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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