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## Synthesis of new acenaphtho[1,2-c]thiophene-based low bandgap polymers for organic photovoltaics

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## ABSTRACT

Donor–acceptor conjugated polymers, PDTPDA and PDTPDT, composed of new acenaphtho[1,2-c]thiophene or thiophene as electron donors and 1,3-dithien-2-yl-thieno[3,4-c]pyrrole-4,6-dione (DTTPD) as the electron acceptor were synthesized by a Stille cross-coupling reaction. These polymers combine interesting properties such as good solubility and excellent thermal stability. The weight-averaged molecular weights ( $M_w$ ) of PDTPDA and PDTPDT were found to be 71,000 and 79,000 with polydispersity indices of 1.65 and 1.66, respectively. Photophysical studies revealed a low bandgap of 1.77 eV for PDTPDA and 1.72 eV for PDTPDT. The present study indicates that the combination of DTTPD and acenaphtho[1,2-c]thiophene building blocks can be a very effective way to lower the HOMO energy level and ultimately to enhance the Voc of polymer solar cells. The Voc reported here (up to 0.94 V) is one of the highest observed in polymer:PCBM bulk heterojunction devices, and a power conversion efficiency (PCE) of up to 3.28% was observed in the PDTPDA devices.

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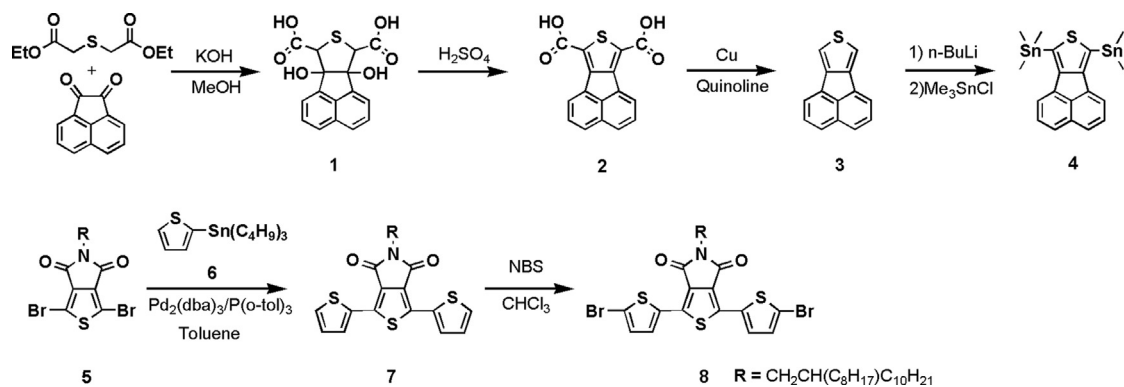
## 1. Introduction

The development of efficient organic photovoltaic (OPV) devices, such as bulk-heterojunction (BHJ) polymer solar cells (PSCs), has become an active area of research in recent years. Such devices show promise as economically competitive sustainable energy sources [1–3]. The most successful PSCs are based on a photoactive layer with a BHJ structure composed of a mixture of a conjugated polymer as an electron donor and a fullerene derivative as an electron acceptor. The morphologies of the films are optimized by controlling the preparation conditions. In this way, BHJ devices can be fabricated to have large material interfaces for exciton dissociation and interconnected networks within each domain for hole and electron transport to the electrodes [4,5]. Research relating to PSCs has mainly focused on the synthesis of new photovoltaic conjugated polymers and the development of device fabrication technologies. Novel conjugated polymers with low bandgaps, suitable energy levels, high charge carrier mobility, and absorption spectra that is both strong and broad are important for the development of high performance PSCs. The inclusion of

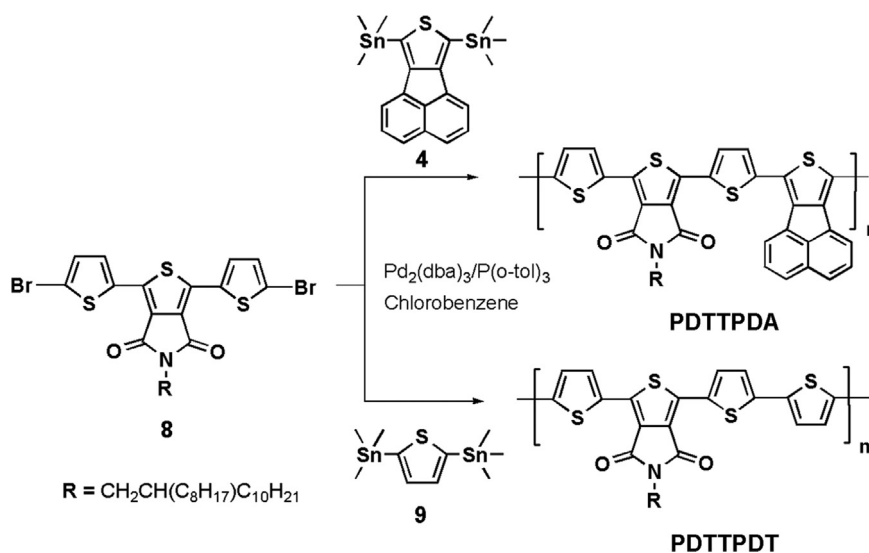
alternating electron donor and acceptor (D–A) units in a polymer main chain is a common approach to tuning the bandgap [6–8]. D–A copolymerization has proven to be an effective strategy for tailoring the properties of conjugated polymers for optoelectronic applications, including organic field effect transistors (OFET) and PSCs [9,10]. Besides alternating donor and acceptor units, the linker units are another factor to tuning optoelectronic property of the conjugated polymers [11,12]. The linker units between the donor and acceptor units change the  $\pi$ -conjugated systems and energy levels of the polymer backbone. High absorption coefficients ( $\alpha$ ) (ca.  $10^5 \text{ cm}^{-1}$ ) for the polymers are equally important for generating high photocurrents (i.e. high  $J_{sc}$ ) in solar cells [1]. The design and synthesis of new conjugated polymer donor materials with high absorption coefficients, broad absorption spectra, and low energy highest occupied molecular orbitals (HOMO) are the most important issues at present. The electron donating characters of thiophene and fused thiophene-based derivatives qualify the compounds as donor units for the construction of donor–acceptor (D–A) copolymers. Fused aromatic molecules have a rigidly enforced planarity that improves  $\pi$  electron delocalization, thereby providing two advantages to the design of conjugated polymers for use in organic photovoltaics. First, the HOMO energy levels of the polymers can be tuned by varying the identity of the fused aromatic moieties. Second, the improved  $\pi$ – $\pi$  interactions between polymer chains in thin solid films most likely enhances carrier mobility [13,14]. Here, we report the synthesis,

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Scheme 1. Synthetic routes for the monomers.



Scheme 2. Synthetic routes for PDTPDA and PDTPDT.

optical and physical properties, and the OPV performances of a new fused aromatic donor, acenaphtho[1,2-c]thiophene, containing a DTTPD copolymer (PDTPDA). Thiophene spacer thieno[3,4-c]pyrrole-4,6-dione (DTTPD) has emerged as a promising building block for use in low bandgap conjugated polymers in OFET and OPV applications. The highly conjugated structure of DTTPD yields strong intermolecular  $\pi$ - $\pi$  interactions and offers a degree of electron-accepting functionality for use in D-A low bandgap polymers due to its high electron deficiency [15]. As a control experiment, a thiophene donor containing a DTTPD copolymer (PDTPDT) was synthesized by the same polymerization method. The series of new DTTPD-based D-A polymers is shown in Schemes 1 and 2. To ensure the solubility of the polymers, unsubstituted thiophene and acenaphtho[1,2-c]thiophene were copolymerized with a DTTPD having long branched alkyl chains (2-octyldodecane). The PCE of the PDTPDA:PC<sub>71</sub>BM ([6,6]-phenyl C<sub>71</sub>-butyric acid methyl ester) blend in OPV devices was 3.28%, mainly due to a high  $V_{OC}$  (0.94 V) and a short circuit current density ( $J_{SC}$ , 8.72 mA/cm<sup>2</sup>). These  $J_{SC}$  and  $V_{OC}$  values were attributed to the higher absorption coefficient, film morphology, and lower HOMO energy level of PDTPDA.

## 2. Experimental

### 2.1. Instrumentations

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE 400 spectrometer, with tetramethylsilane as an internal reference.

Elemental analysis was done by using PerkinElmer 2400 Series II CHNS/O Analyzer. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were measured by a Shimadzu UV-3100 UV-vis-NIR spectrometer. The number- and weight-average molecular weights of polymers were determined by gel permeation chromatography (GPC) on Viscotek T60A instrument, using chloroform as eluent and polystyrene as standard. The differential scanning calorimetry (DSC) and thermal gravimetric analysis were made using TA Q100 instrument and operated under nitrogen atmosphere. Cyclic voltammetry was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in a solution of Bu<sub>4</sub>NBF<sub>4</sub> (0.10 M) in acetonitrile at a scan rate of 50 mV/s. Polymer film coatings on ITO anode electrode were formed by spin-coating method. Atomic force microscopy (AFM) was measured by tapping-mode using Multimode IIIa, Digital Instruments. Electrical characteristics of the TFTs were measured in ambient conditions using both Keithley 2400 and 236 source/measure units. For all measurements, we used channel lengths ( $L$ ) of 12  $\mu$ m and channel widths ( $W$ ) of 120  $\mu$ m. Field effect mobilities were extracted in the saturation regime from the slope of the source-drain current.

### 2.2. Materials

Tetrahydroacenaphthothiophene (**1**) [16], acenaphtho[1,2-c]thiophene-7,9-dicarboxylic acid (**2**) [16], acenaphtho[1,2-c]thiophene (**3**) [16], 1,3-dibromo-5-(2-octyldodecyl)thieno[3,4]pyrrole-4,6-dione (**5**) [17], 2-(tributylstannyl)thiophene (**6**) [18], and

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