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# Synthesis and characterization of solution-processable diketopyrrolopyrrole (DPP) and tetrathienothiophene (TTA)-based small molecules for organic thin film transistors and organic photovoltaic cells

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ABSTRACT

A series of new acceptor-donor-acceptor type conjugated small molecules with alkylated tetrathienoacene as donor and diketopyrrolopyrrole as acceptor moieties has been synthesized and characterized for solution-processed organic thin film transistor and organic photovoltaic applications. To investigate the effect of elongated conjugation on this system, thiophene and bithiophene units were systematically incorporated between the central core and end capped unit. In addition, the effect of alkyl chain substitution on diketopyrrolopyrrole was also examined. The thermal, optical, and electrochemical properties of these new molecules were investigated. The highest hole mobility of organic thin film transistor devices utilizing the solution sheared thin films of these compounds as an active layer is $1.0 \times 10^{-1}$ $cm^2$ $V^{-1}$ $s^{-1}$. Whereas organic photovoltaic cells based on these new molecules exhibited the power conversion efficiencies as high as 2.9% when blends with [6,6]-phenyl-$C_{71}$-butyric acid methyl ester. These performances are strongly correlated with their thin film morphologies.



## 1. Introduction

Designing new organic materials for both organic thin film transistors (OTFTs) and organic photovoltaics (OPVs) has received much interest due to a number of advantages over inorganic semiconductors, such as low cost, light weight, easy fabrication and solution processing, and compatibility with large-scale flexible substrates [1–5]. Solution processed small molecules in particular have attracted more attention due to their unique advantages of simple synthesis, easy purification, minimal batch-to-batch variation, high purity, and definite molecular structure, compared to their polymers. In fact, small molecular based organic semiconductors have recently demonstrated power conversion efficiencies of up to 10% in OPVs [6–9], and exhibited the highest hole mobilities up to 43 $cm^2$ $V^{-1}$ $s^{-1}$in OTFTs [10–12]. Typically, the structures of these reported organic electronic materials consist of some conjugated π-bridging donor cores, such as benzodithiophenes (BDT) [6,13], dithienosiloles (DTS) [14–16], thienothiophenes (TT) [10,17], dithienothiophenes (DTT) [18–22] and tetrathienoacenes (TTA) [4,23–28], which are then connected with some electron acceptors, such as alkyl cyanoacetates [13,29,30], 3-alkylrhodanines [6], and diketopyrrolopyrroles (DPP) [20,31–35]. Among these building blocks, fused-thiophenes such as TT, DTT, and TTA have been demonstrated to be attractive π-bridging cores,

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due to their strong intermolecular S···S interactions, extensive intramolecular π-conjugation and close intermolecular π–π stacking. At the same time, diketopyrrolopyrrole (DPP) moieties have been widely employed because of their strong electron-withdrawing ability, tunable solubility with proper alkyl side chains, excellent charge carrier motilities, strong light absorption and facile synthesis and structural modification [36]. As a result, several DPP and fused-thiophene based polymers and small molecules have been reported with good mobilities and power conversion efficiencies (PCE) for organic thin film transistors and organic photovoltaics, respectively. As shown in Fig. 1, carrier hole mobilities of up to 2 $cm^2 V^{-1} s^{-1}$and 0.94 $cm^2 V^{-1} s^{-1}$ have been reported for the polymers PTDPPTFT4 [37] and PDBT-c-TT [38], respectively. In particular, TTA-DPP-based polymer (PTTDPS) [39,40] achieved a high PCE of 4.5%. For small molecules, TT2DPP [41] showed hole mobility of 0.1 $cm^2 V^{-1} s^{-1}$and TT2DPP [42], while DTTDPP [20], (DPP)2PTA [43], and BDTDPP [44] demonstrated power conversion efficiencies of 4.0%, 2.2%, 2.39%, and 5.79%, respectively. Despite the promising features of the aforementioned DPP-fused-thiophene-based materials, small molecules based on the DPP-TTA system for OTFTs and OPVs were not explored until recently [4]. As such, new DPP-TTA-based small molecules deserve further investigation with regard to OTFTs and OPVs.

Herein, five conjugated acceptor-donor-acceptor (A-D-A) type organic semiconductors based on DPP (as acceptor) and TTA (as donor) were prepared to examine their structure-property relationships. To enhance the solubility of this system, two pentadecanyl chains are attached to the TTA core, and two alkyl side chains of 2-ethylhexyl and 2-decyltetradecyl on DPP are employed. To investigate the effect of elongated conjugation on this system, thiophene and bithiophene units were systematically introduced between the TTA core and DPP capped units. It is expected that the aforementioned TTA molecules will have better light harvesting ability (and hence the short circuit current density ($J_{sc}$)), via a further increase the conjugated lengths of this system. The introduction of different alkyl chains into the DPP unit and insertion of the thiophene or bithiophene units into the systems have important effects on the film crystallinity and miscibility with [6,6]-phenyl-$C_{71}$-butyric acid methyl ester ($PC_{71}BM$). The optical and electrochemical properties of these five small molecules are correlated to their molecular structures, their morphological variation of active layers (from AFM analyses), and thus associated with their performance in OTFTs and OPVs.

## 2. Experimental

### 2.1. Materials

All chemicals and solvents were of reagent grade and were obtained from Aldrich, Arcos, or TCI Chemical Co. Reaction solvents (toluene, and THF) were distilled under nitrogen from sodium/benzophenone ketyl, and halogenated solvents were distilled from $CaH_2$. Compounds **6**, **7**, **8** [4] and **12** [45] were prepared according to the procedures reported in the literature.

### 2.2. Instrumentation

$^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker 500 or a 300 instrument. Chemical shifts for $^1H$ and $^{13}C$ NMR spectra were referenced to solvent signals. Mass spectrometric data were obtained with a JMS-700 HRMS instrument. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 thermal analysis system using dry nitrogen as the carrier gas at a flow rate of 40 mL $min^{-1}$. The UV–Vis absorption was obtained using JASCO V-530 spectrometers. Differential pulse voltammetry (DPV)

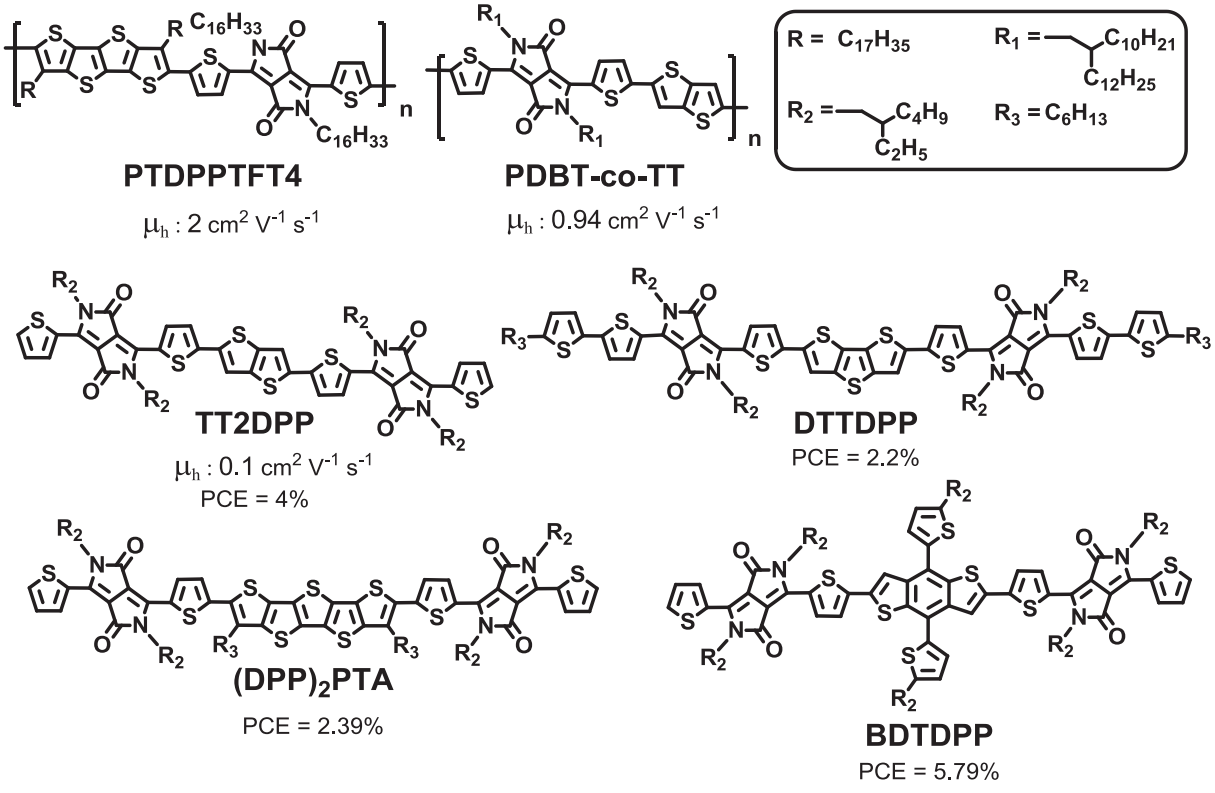


**Fig. 1.** Examples of fused thiophene-DPP semiconductors used in OTFTs and OPVs.