



# Synthesis and characterization of the fluorinated thieno[3,4-c]pyrrole-4,6-dione-based donor-acceptor polymers for organic solar cells

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## ABSTRACT

A new wide bandgap polymer (PC8TPD-F) has been synthesized via the Stille cross-coupling reaction between fluorine-substituted thieno[3,4-c]pyrrole-4,6-dione (TPD) and 4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b]dithiophene (BDTT). For structural comparison, the nonfluorinated TPD-based BDTT polymer (PC8TPD) was also synthesized with the same polymerization. The number average molecular weights ( $M_n$ ) of PC8TPD and PC8TPD-F were found to be 47,000 g/mol ( $\bar{D} = 2.1$ ) and 52,000 g/mol ( $\bar{D} = 1.8$ ) respectively. The HOMO levels of PC8TPD and PC8TPD-F were determined to be  $-5.56$  and  $-5.65$  eV respectively. The inclusion of the fluorinated TPD unit lowers the polymer's HOMO level. The SCLC mobilities of PC8TPD and PC8TPD-F were determined to be  $1.5 \times 10^{-4}$  and  $2.1 \times 10^{-4}$  cm<sup>2</sup>/V respectively. Polymer solar cell devices prepared with PC8TPD and PC8TPD-F as their active layers were found to exhibit power conversion efficiencies of 4.26% and 6.80% with open circuit voltages of 0.90 V and 0.95 V respectively.

## 1. Introduction

Polymer solar cells (PSCs) based on solution-processable organic molecules as donors have attracted intense attention as promising next-generation renewable energy sources [1,2]. Over the past decades, many strategies for the tuning of the optical and electrochemical properties of active materials have been developed with the aim of achieving high photovoltaic performances, such as the modification of donor–acceptor (D–A) structure and side chain engineering [3–6]. Of these strategies, the introduction of electronegative fluorine into donor-acceptor polymers is a very useful molecular design tool that enhances photovoltaic performance. The fluorination of a conjugated backbone is expected to lower both the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level without increasing the steric hindrance, which increases the open-circuit voltage ( $V_{OC}$ ) in the corresponding solar cell device [7–11]. Fluorinated D–A polymers exhibit higher molar extinction coefficients than their nonfluorinated counterparts, which enhances exciton formation and consequently increases the short circuit currents ( $J_{SC}$ ) of the associated solar cell devices [12,13]. Previous studies have mainly focused on the introduction of fluorine atoms onto the acceptor (A) units of D–A polymers with the aim of tuning their HOMO and LUMO levels and thereby improving their photovoltaic properties [7–13]. The electron acceptor thieno[3,4-c]pyrrole-4,6-dione (TPD) is an important

building block because it exhibits good electron delocalization in the solid state as a result of its relatively compact and planar structure [14–16].

In this study, we synthesized a new fluorinated wide-bandgap polymer (PC8TPD-F) comprising the 4,8-bis(5-hexylthiophen-2-yl)benzo[1,2-b:4,5-b]dithiophene (BDTT) donor unit and the fluorinated thieno[3,4-c]pyrrole-4,6-dione (TPD) acceptor unit. BDTT is the most commonly used donor unit in D–A polymer systems because of its planar molecular structure and facile  $\pi$ - $\pi$  stacking, which provide broad absorption and good photovoltaic performances. The fluorine atoms are attached directly to the TPD structure to ensure a low-lying HOMO level, broaden the absorption band, and increase the hole mobility of the resulting polymer, which thereby improves the  $V_{OC}$  and  $J_{SC}$  of the associated device. As a control, a nonfluorinated TPD-based BDTT copolymer (PC8TPD) was also synthesized with the same approach. The synthetic routes for the monomers and polymers are outlined in Scheme 1.

## 2. Experimental section

### 2.1. Materials

Compound 1–3 [17], 9 [18], and 10 [19] were synthesized according to previously published procedures.

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