



# Tunable intrinsic semiconducting properties of diketopyrrolopyrrole-based copolymers with electron donating thiophene and electron accepting thiazole moieties

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## ABSTRACT

The *p*- and *n*-type semiconducting characteristics of four conjugated polymers, P(DPPBT), P(DPPBTz), P(TzDPPBT), and P(TzDPPBTz) with molecular energy levels that were systematically varied in a cascade manner, was investigated. The four polymers were synthesized using 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione or 3,6-bis(5-bromothiazol-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione monomers coupled with bithiophene or bithiazole monomers. By replacing the electron-rich thiophene with electron-deficient thiazole, the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were significantly lowered. Thin film transistors (TFTs) based on the four polymers were investigated to observe the effect of the polymer energy levels. The results demonstrate that DPP-based polymers have the potential to exhibit *p*-type or *n*-type semiconducting properties based on the number of thiazole units incorporated into the conjugated polymer structure.

## 1. Introduction

A number of  $\pi$ -conjugated polymers have been developed for the fabrication of semiconducting devices using solution-based processes at low temperatures and for achieving controlled optical and electronic properties based on various structures [1,2]. Intensive efforts have been expended in the exploration of the *p*-type semiconducting behavior of conjugated polymers. Highly crystalline conjugated polymers displaying hole mobilities in excess of  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  have been reported [3–6]. On the other hand, *n*-type semiconducting polymers exhibiting facile electron-transport characteristics under ambient conditions have rarely been reported [7–12].

These *n*-type conjugated polymers are known to exhibit poor electron transport properties under atmospheric conditions because the oxygen-water complex of the semiconducting polymer acts as an electron trap [13]. To increase the density of mobile electrons in the LUMO level, the LUMO levels of molecules or polymers should be lower than about  $-4.0 \text{ eV}$ . Electron-deficient molecules with relatively low LUMO levels are favorable as constituents of the conjugated polymer backbone to achieve efficient charge injection and stability under ambient conditions [14–17]. Therefore, steering the molecular energy levels is an effective emerging methodology for tailoring the properties of *n*-type

organic semiconductors. Although introducing electron-deficient atoms into conjugated molecules is very effective for lowering the LUMO level, the electron deficiency is not strongly related to the intrinsic charge carrier properties of the molecules [18]. It is well recognized that not only low-lying energy levels, but also a high degree of crystallinity, are essential for achieving high electron mobility for the development of high-performing *n*-type semiconducting polymeric materials [19].

Recently, the application of thiazole-based polymers has received attention as a potential method for effectively decreasing the LUMO energy level [20–22]. The thiazole moiety is classified as an electron-accepting moiety because it possesses a nitrogen atom in aromatic ring, which is a representative electronegative atom [23].

In many previous studies, diketopyrrolopyrrole (DPP)-based conjugated polymers have shown highly ordered crystalline structures owing to their fused aromatic rings and strong intermolecular interactions [24,25]. Owing to these merits, conjugated polymers containing the DPP moiety exhibit good charge transport behavior. To achieve both low-lying energy levels and a high degree of crystallinity for DPP-based copolymers, it is useful to employ thiazole as an electron withdrawing group instead of thiophene as an electron donating unit in the polymer backbone. Although some DPP-thiazole based polymers with

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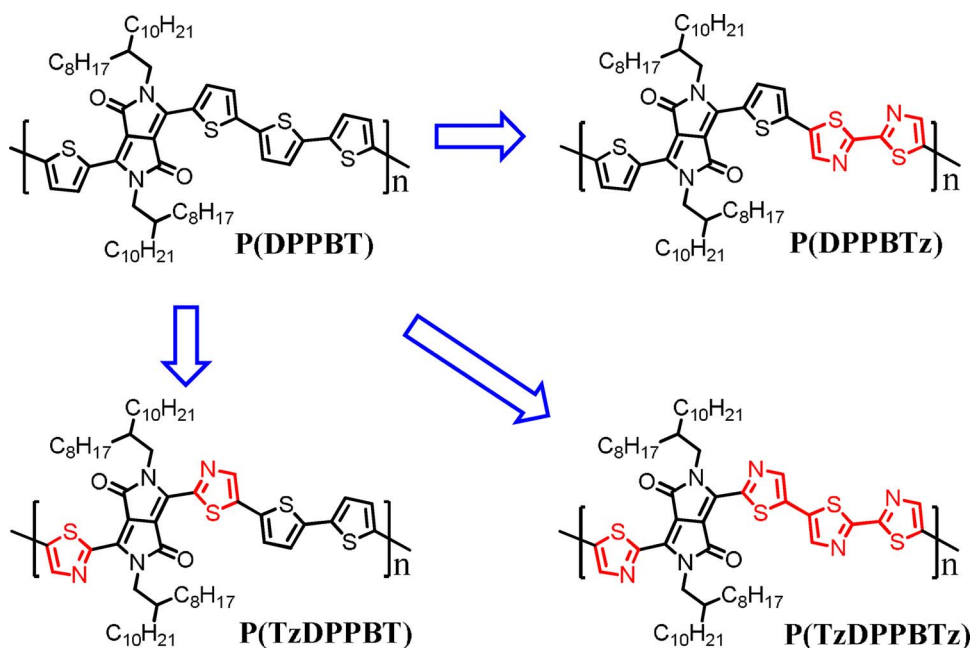
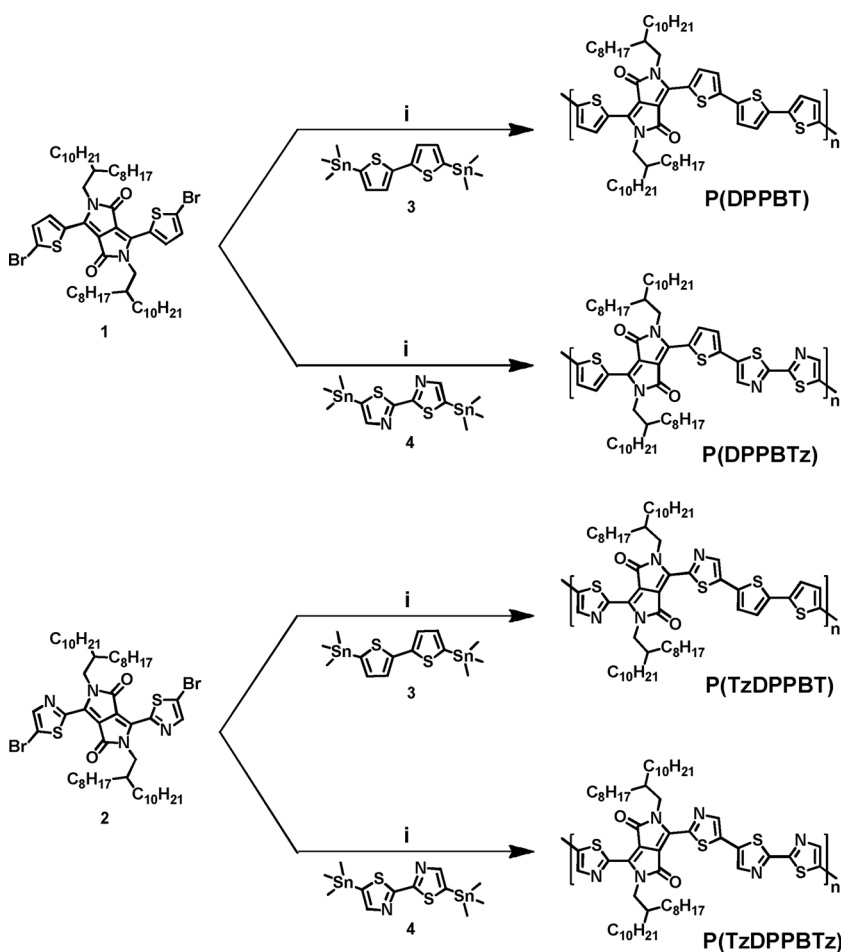


Fig. 1. Structures of four conjugated polymers: P(DPPBT), P(DPPBTz), P(TzDPPBT), and P(TzDPPBTz).



Scheme 1. Synthetic procedures of P(DPPBT), P(DPPBTz), P(TzDPPBT), and P(TzDPPBTz): i)  $\text{Pd}_2(\text{dba})_3$ ,  $\text{P}(\text{o-tol})_3$ , toluene, 100 °C.

ambipolar properties have been reported, there is no systematic study of their semiconducting properties by synthesizing polymers by replacing the electron donating moiety with an electron accepting moiety in a similar polymer backbone structure [26–29].

In this study, we explore the tunability of the energy levels and

related characteristics of four conjugated polymers, P(DPPBT), P(DPPBTz), P(TzDPPBT), and P(TzDPPBTz), the structures of which are shown in Fig. 1. The four polymers were synthesized by using dithienyldiketopyrrolopyrrole (DTPP) or dithiazolyldiketopyrrolopyrrole (TzDPP) monomers coupled with bithiophene (BT) or bithiazole (BTz)

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