



3,7-Bis((*E*)-2-oxoindolin-3-ylidene)-3,7-dihydrobenzo[1,2-*b*:4,5-*b'*] dithiophene-2,6-dione (IBDT) based polymer with balanced ambipolar charge transport performance



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ABSTRACT

A novel acceptor building block, 3,7-bis((*E*)-2-oxoindolin-3-ylidene)-3,7-dihydrobenzo[1,2-*b*:4,5-*b'*] dithiophene-2,6-dione (IBDT), is developed to construct a donor-acceptor polymer **PIBDTBT-40**. This polymer has favorable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels for balanced ambipolar charge transport. Organic thin film transistors (OTFTs) based on this polymer shows well-balanced ambipolar characteristics with electron mobility of $0.14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and hole mobility of $0.10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in bottom-gate bottom-contact devices. This polymer is a promising semiconductor for solution processable organic electronics such as CMOS-like logic circuits.

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1. Introduction

Polymer semiconductors have been extensively studied as channel materials in organic thin film transistors (OTFTs) due to their good solution processability and mechanical robustness [1–3]. Different from unipolar p-type or n-type semiconductors, ambipolar semiconductors are able to transport both holes and electrons, allowing for certain new device designs such as single-component complementary metal oxide semiconductor (CMOS)-like circuits and ambipolar light emitting transistors [4–6]. The use of a single-component ambipolar polymer can significantly simplify the complicated patterning and fabrication processes for CMOS-like circuits [7]. Ambipolar light emitting transistors can integrate both the light-emission capability and the electrical current modulation in one single device architecture, which may enable the next generation of light-emitting devices [8]. For both single-component CMOS-like circuits and ambipolar light emitting transistors the semiconductor with balanced hole and electron charge transport characteristics is highly preferable [9]. To achieve balanced ambipolar charge transport characteristics, the frontier molecular orbital energy levels, i.e., the highest occupied molecular

orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the polymer semiconductor are crucial. First, the HOMO and LUMO levels of the polymer semiconductor should have small and similar differences against the Fermi energy of the source contact to minimize and balance the injection barriers for electrons and holes, respectively [10]. In this regard, it is desired that the polymer has a small band gap (the difference between the HOMO and LUMO levels), while the Fermi level of the source electrode sits in between the LUMO and HOMO levels. Second, the energy levels of the polymer need to be lower than ca. -5.0 eV [11,12] for the HOMO and ca. $-3.7\text{--}4.0 \text{ eV}$ [12–15] for the LUMO in order to achieve stable hole and electron transport, respectively. The common approach to delicately tune the energy levels of polymer semiconductors is to incorporate alternating donor-acceptor (D–A) structure in the polymer backbone, whereas the HOMO and LUMO levels of the polymers are primarily governed by an appropriate combination of the donor and acceptor building blocks, respectively [16,17]. However, available electron acceptor building blocks that are able to bring the LUMO level of polymers below ca. $-3.7\text{--}4.0 \text{ eV}$ for stable and efficient electron transport are rare [18–21]. Hence, extensive effort has been made to discover new electron acceptor building blocks [22–24].

Recently we developed a new strong electron acceptor building block, (3*E*,7*E*)-3,7-bis(2-oxoindolin-3-ylidene)-benzo[1,2-*b*:4,5-*b'*]

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difuran-2,6(3*H*,7*H*)-dione (IBDF, Fig. 1), for D-A polymers for OTFTs [15,18,25–29]. Due to their deep-lying LUMO levels, IBDF-based polymers showed n-type dominant charge transport behavior with high electron mobility up to $1.74 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [26]. By replacing the benzodifurandione (BDF) core in IBDF with a less electron-withdrawing benzodipyrroledione (BDP), we developed another electron acceptor, IBDP (Fig. 1). Opposed to the IBDF-based polymers, the IBDP-based polymers showed p-type dominant charge transport behaviors with hole mobility as high as $1.92 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [30,31]. In this work, we changed the core unit to benzodithiophenedione (BDT) to successfully develop another new acceptor building block in this series, 3,7-bis((*E*)-1-2-oxoindolin-3-ylidene)-3,7-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dione (IBDT, Fig. 1) and demonstrated that IBDT is a proper electron acceptor building block for making ambipolar polymers with well-balanced hole and electron mobilities.

2. Results and discussion

To probe how the sulphur atoms would impact the geometry and HOMO/LUMO levels of IBDT, we carried out a computational simulation on the model molecule, IBDT-Me with methyl substituents on nitrogen atoms (Figure S1, Supplementary Data). The calculated HOMO/LUMO levels are $-5.64 \text{ eV}/-3.46 \text{ eV}$, which are higher than those of IBDF-Me ($-6.11 \text{ eV}/-3.78 \text{ eV}$), but lower than those of IBDP-Me (and $-5.52 \text{ eV}/-3.44 \text{ eV}$) [30]. These results suggest that the IBDT-based polymers may exhibit ambipolar charge transport behavior. The simulations also gave the dihedral angle between the BDT core and the indolin-2-one ring to be $\sim 14^\circ$, which turned out to be larger than those of IBDF-Me ($\sim 8^\circ$) and IBDP-Me ($\sim 10^\circ$). This is attributed to the twisting of the cyclic thioester ring due to the larger sulphur atoms. A detailed discussion can be found in the footnote of Table S1 (Supplementary Data).

The synthetic route to a new dibrominated IBDT monomer **3** is outlined in Scheme 1. Synthesis of 3,7-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dione (**2**), the key precursor compound to the monomer **3**, was described only in one paper without much experimental details [32]. First benzo[1,2-*b*:4,5-*b'*]dithiophene was lithiated and then treated with tri-*n*-butyl borate to give **1**, which is essentially insoluble in common organic solvents. For the oxidation of **1**, we found that the amount of hydrogen peroxide and the reaction time are crucial. After optimization, compound **2** was obtained in a moderate yield of 61%. The aldol condensation of **2** with 6-bromo-1-(4-octadecyldocosyl)indoline-2,3-dione in refluxing toluene with a catalytic amount of *p*-toluenesulphonic acid afforded monomer **3** in 22% yield. Finally, an IBDT-based polymer **PIBDTBT-40** was synthesized via the Stille coupling reaction between **3** and 5,5'-bis(trimethylstannyl)bithiophene using $\text{Pd}_2(\text{dba})_3$ and $\text{P}(o\text{-tolyl})_3$ as the catalyst. The crude polymer was purified by Soxhlet extraction using acetone and hexanes to remove impurities

and oligomers, and finally dissolved with chloroform. Besides chloroform, **PIBDTBT-40** is soluble in several other common solvents such as toluene, *m*-xylene, chlorobenzene, 1,2-dichlorobenzene, and 1,1,2,2-tetrachloroethane. The molecular weight and polydispersity (PDI) of this polymer were determined by high temperature gel permeation chromatography (HT-GPC) at 140°C using 1,2,4-trichlorobenzene as the eluent and polystyrene as standards. A number averaged molecular weight (M_n) of 21.0 kDa and a polydispersity index (PDI) of 2.3 were obtained. The thermal stability of the polymer was characterized by thermogravimetric analysis (TGA) (Figure S5, Supplementary Data). A decomposition temperature of $\sim 300^\circ \text{C}$ for a 5% weight loss was found for **PIBDTBT-40**, which is lower than the analogues of IBDF- [26] and IBDP- [30] based polymers ($\sim 380^\circ \text{C}$). This could be attributed to the less stable thioester groups in IBDT [33].

The adsorption spectra of **PIBDTBT-40** in dilute solution ($\sim 10^{-5} \text{ M}$ in CHCl_3) and thin film are shown in Fig. 2a. Both absorption spectra showed a dual band absorption profile, where the high energy band originates from the $\pi\text{-}\pi^*$ transition of the IBDT unit and the low energy band can be attributed to the D-A intramolecular charge transfer (ICT) [34]. The wavelength of absorption maximum (λ_{max}) was slightly blue-shifted from 806 nm in solution to 794 nm in the thin film, which might be due to H-aggregation of polymer chains in the solid state [35,36]. By taking the absorption onset, the optical band gap of the polymer thin film was calculated to be 1.23 eV. Fig. 2b shows the cyclic voltammetry (CV) diagrams of **PIBDTBT-40**, which exhibits reversible redox processes. The oxidative and reductive peaks originate from the donor (bithiophene) and the acceptor (IBDT) units, respectively. Within the applied bias range from -1.3 V to 1.4 V there are two readily distinguishable peaks in the oxidation and reduction processes, respectively, indicating that distinct multiple redox sites exist within this polymer. The HOMO and LUMO levels of **PIBDTBT-40** were calculated from the oxidation and reduction onsets of the CV diagrams to be -5.60 eV and -4.06 eV , respectively (Fig. 2b), which are favoured for both stable hole and electron transport. Compared with the HOMO/LUMO levels of its analogues IBDF and IBDP polymers **PIBDFBT-40** ($-5.72 \text{ eV}/-3.88 \text{ eV}$) and **PIBDPBT-24/12** ($-5.60 \text{ eV}/-3.71 \text{ eV}$) (Fig. 1), the trends disagree with results predicted for their monomer compounds by computer simulations, where both HOMO and LUMO levels of IBDT-Me are located between those of IBDF-Me and IBDP-Me. Particularly the LUMO level of **PIBDTBT-40** is even lower than that of **PIBDFBT-40**, but IBDT is predicted to be a weaker electron acceptor than IBDF. The band gap of organic semiconductors obtained using the CV method is often larger than that obtained from the UV-vis measurement, which is due to the exciton binding energy (E_b) that has a value as high as ca. $0.4\text{--}1 \text{ eV}$ [37,38]. We noticed that E_b ($E_g^{\text{CV}} - E_g^{\text{opt}}$) for **PIBDTBT-40** ($1.46 \text{ eV} - 1.23 \text{ eV} = 0.23 \text{ eV}$) is much smaller than that of **PIBDFBT-40** ($1.84 \text{ eV} - 1.31 \text{ eV} = 0.53 \text{ eV}$) or **PIBDPBT-40**

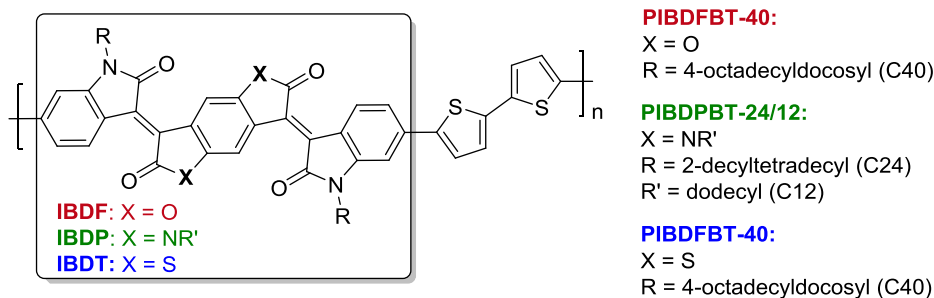


Fig. 1. IBDF, IBDP and IBDT building blocks and their polymers.

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