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Fluorinated benzothiadiazole-based low band gap copolymers to enhance open-circuit voltage and efficiency of polymer solar cells

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ABSTRACT

Two donor–acceptor (D–A) copolymers containing dithienosilole (DTS) donor unit and unsubstituted benzothiadiazole (BT) or fluorinated benzothiadiazole (ffBT) acceptor unit, PDTSBT and PDTSffBT, were synthesized by Stille cross coupling polymerization and tested for application in polymer solar cells (PSCs). The new alternating copolymer (PDTSffBT) possesses both a low optical bandgap (E_g = 1.54 eV) and a deep highest occupied molecular orbital energy level (HOMO) (−5.46 eV). It was found that the introduction of the two electron-withdrawing fluorine atoms on the benzothiadiazole unit results in a decrease of the HOMO energy level with slight effect on the lowest unoccupied molecular orbital (LUMO) as observed through cyclic voltammetry (CV) analysis. Inclusion of fluorine atoms also leads to an increase in the interchain interaction in the PDTSffBT copolymer with respect to its analogue PDTSBT copolymer according to the X-ray diffraction measurements (XRD). When PDTSffBT:$PC_{71}BM$ blends are tested in bulk heterojunction (BHJ)-polymer solar cells, the cells display a short-circuit current (J_{SC}) of 8.82 mA/cm^2, a high open circuit voltage (V_{OC}) of 0.74 V, and a Fill Factor (FF) of 45%, giving an overall power conversion efficiency (PCE) of 2.93%, compared to 1.64% for the BT-containing cells prepared in parallel under identical conditions. The significant performance enhancement results from the higher V_{OC} and J_{SC} in the ffBT-containing cells. These results unambiguously indicate that the fluorination is an efficient method to modulate the energetic levels and improve the photovoltaic performances of the widely used benzothiadiazole-based low bandgap copolymers.

1. Introduction

Thanks to a great potential for low-cost, low-weight, flexibility and large-size processability, the new "plastic" photovoltaic cell is the major application of π-conjugated polymers. This new generation of solar cells could be an alternative to inorganics especially for transportable

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applications that not require high electrical power. Active layers of organic photovoltaic (OPV) solar cells are based on two organic materials [1], an electron donor (D) and an electron acceptor (A), such as π-conjugated polymers and fullerene C_{60} derivatives [2], respectively. Various architectures of the active layer are possible [3] such as bilayer [4] and bulk heterojunctions [5]. The global photovoltaic efficiency of OPV devices directly depends on the efficiencies of different processes involved in photovoltaic conversion: absorption, exciton diffusion, charge transfer and charge collection efficiencies [6,7]. These efficiencies are related to the intrinsic properties of D and A materials [8] and their arrangement in the active layer [9–11]. To improve the PV conversion efficiency, both intrinsic properties including absorption and transport properties, and morphology with maximal amount of D/A interface as well as continuous domains with size close to 10–20 nm must be optimized and controlled. Besides improving charge transport properties by increasing the interchain interactions via chemical modification, adequate alignment of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) electronic energy levels and decreasing the band gap energy (E_g) of D materials is required for an efficient OPV device [12,13].

Π-conjugated polymers are elaborated from organic chemical synthesis. Thus, their intrinsic and end-use properties can be controlled during elaboration phase. In this aim, various strategies have been developed, they included addition or substitution of an electron-rich or an electron-deficient functional group in the polymer backbone [14–16]. Another approach was using of low band gap polymers from regular alternating copolymerization of electron withdrawing and electron donating monomers as proposed by Havinga and coworkers [17]. Consequently, light absorption properties increased [18], with adequate HOMO and LUMO energy levels for efficient exciton dissociation, and the global PV efficiency is improved, which is due to increasing of both open-circuit voltage (V_{OC}) and short circuit current density (J_{SC}) [19].

In this work, our approach consists in designing a new low band gap donor copolymer with modulated HOMO and LUMO energy levels [20,21]. The aim is to enhance V_{OC} and increase the absorption efficiency in a large fraction of the solar spectrum by reducing the donor band gap [22]. V_{OC} can be increased by increasing the difference between HOMO and LUMO of D and A materials [21,23,24], respectively. Nevertheless, for an efficient exciton dissociation, an optimal difference close to 0.3 eV [20] between LUMO of D and A materials is required. For this, a widely used strategy consists in combination along the donor copolymer backbone [20] of D and A moieties functional groups such as dithienosilole (DTS) and benzothiadiazole (BT) [22,25–28] or their derivates, respectively. Optimization of ratio and electron-withdrawing strength of D and A units is required to obtain the appropriate HOMO and LUMO levels [28] and chemical stability [22] of the obtained copolymer. Among many available methods for modulation of electron-donating D unit and electron-withdrawing A unit, the most reported procedures are the followings: new combination of new D and A units [3,29–32], new combination of the existing units [33] or chemical modification of D and A units used in an existing combination [34]. This last solution is based on addition of some specific functional groups with covenant electron affinity, electro-negative [19,29,34–36] or electro-positive functional group [21,37].

In this work, the investigated low band gap polymer is an alternating copolymer resulting from combination of dithienosilole (DTS) and benzothiadiazole (BT) derivatives as D and A units (Fig. 1), respectively. This efficient combination was chosen because of interesting PV performances (5–6%) [33,38] of initial polymer (PDTSBT) based on alkylated DTS and unsubstituted BT patterns and their chemical stability [22]. An alkylated DTS with linear dodecyl side chains is used as donating-electron unit; the alkyl side chain should increase the solubility of the polymer without affecting the HOMO and LUMO energy levels [39,40]. Fluorinated BT is chosen as electron-withdrawing unit to obtain suitable HOMO and LUMO energy levels [34,41–49].

Aromatic hydrogen substitution of BT by fluorine leads to increase in electron-withdrawing and to decrease in both HOMO and LUMO energy levels [41,43–47,50–53]. This could increase V_{OC} as was highlighted by several authors [19,29,34–36,41–42,47,50,53–56]. Fluorine is the strongest electronegative element with slightly larger van der Waals radius than that of hydrogen, and smaller than CN and CF_3 groups currently used as electro-attractor substituents. In addition, besides π–π interactions between BT units [57], the fluorine atom often has a great influence on inter and intramolecular interactions [58] without hindering effect and could improve π-stacking effect [32,44,55,59] as well as the structuration with A material in the active layer [41,42,44,50,53,54]. As a consequence, J_{SC} could be improved [19,34–36,41–43,50,54–55].

Therefore, we synthesized a new polymer based on dithienosilole DTS and fluorinated benzothiadiazole (ffBT) as donor and acceptor patterns (Fig. 1), respectively. Thus, it is expected to increase the open-circuit voltage (V_{OC}) while conserving or improving UV–visible absorption and short circuit current density (J_{SC}). The originality of this present work lies in the chemical structure of the new easily accessible low band gap donor copolymer. Consequently, the chemical synthesis at large scale could be now considered. The solubility in common usual organic solvents and the interesting end-use properties exhibited by this new polymer highlight a potential wet-processability with existing technique (printing, roll-to-roll coating, etc.) for PV application.

2. Experimental section

2.1. Materials

All reactions involving air-sensitive reagents were carried out under dry nitrogen atmosphere using flame-dried glassware and conventional Schlenk techniques unless otherwise stated. Syringes which were used to transfer reagents or solvents were purged with nitrogen prior to use. 5,5′-Dibromo-3,3′-di-*n*-dodecylsilylene-2,2′-bithiophene (**3**) was purchased from Solarmer Materials, Inc. All other reagents, solvents and chemicals were purchased