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Benzodithiophene-based two-dimensional polymers with extended conjugated thienyltriphenylamine substituents for high-efficiency polymer solar cells

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ABSTRACT

Two novel donor–acceptor (D–A)-type two-dimensional (2-D) polymers of PTTPABDT-DTBT and PTTPABDT-DFDTBT were synthesized and characterized, in which extended conjugated side chained 4-thienyltriphenylamine benzo[1,2-*b*:4,5-*b*′]dithiophene (TTPABDT) as the donor unit, thiophene (T) as the π-bridge, benzo[*c*][1,2,5]thiadiazole (BT) and 5,6-difluorobenzo[*c*][1,2,5]thiadiazole (DFBT) as the acceptor units. Due to the introduction of the extended conjugated side chained TTPA, polymers exhibited good thermal stabilities, broad absorption spectra and narrow optical band gaps. The hole mobility of 2.15×10^{-4} cm^2 V^{-1} s^{-1} was obtained in the PTTPABDT-DFDTBT/PC$_{71}$BM blended film, which is two times higher than that of the PTTPABDT-DTBT/PC$_{71}$BM blended film. Finally, the PTTPABDT-DFDTBT/PC$_{71}$BM-based polymer solar cells presented the best power conversion efficiency (PCE) of 4.29% with a fill factor (*FF*) of 62.5%, while PTTPABDT-DTBT-based devices shown a PCE of 3.92% with a *FF* of 58.8%. The results indicate that the introduction of the extended conjugated TTPA side chain into the D–A-type 2-D polymers is an efficient approach to improve photovoltaic performances for its resulting polymers.

1. Introduction

Driven by the urgent need for a renewable energy supply, bulk heterojunction (BHJ) polymer solar cells (PSCs) have attracted considerable interests from both the academic and industrial communities over the past two decades, due to their distinctive potential for fabricating flexible, light weight, large-area, and low-cost devices through roll-to-roll coating process [1–4]. More encouragingly, the power conversion efficiencies (PCEs) of BHJ-PSCs have broken 10.5% [5,6]. However, in most studies of PSCs, the problem of low efficiency is still a challenging subject. So, to achieve highly efficient PSCs, the molecular design of new conjugated polymers is an important strategy [7,8]. Up to date, tremendous efforts have been focused on conjugated polymers with alternating electron-rich (donor/D) and electron-deficient (acceptor/A) units, due to this class of polymers has broad absorption spectra and high absorption coefficient in visible region resulting from intramolecular charge transfer (ICT) transitions [9–12].

Among the numerous reported donor units, benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) skeleton has been widely applied as a donor unit in D–A-type polymers, due to its highly planar nature and offers an easy way to link various substituents to further improve the backbone planarity and fine-tune the energy levels, and thus improves the photovoltaic properties of the devices [7]. Since Hou and Yang primarily reported the electronic and photovoltaic properties of BDT-based D–A-type polymers with alkoxy substituents [13], the alkylthienyl-substituted BDT-based D–A-type two-dimensional (2-D) polymers have come to the fore and become among the most frequently used donor materials in the PSCs [7,14–20]. For example, a PCE up to 9.48% was obtained in single layer BHJ solar cells with the BDT-based polymers [18]. More recently, many novel BDT-based polymers with the extend π-conjugated side group systems have garnered considerable interest because of the largely extended π-conjugation systems could enhance π-electron delocalization, thus facilitating to exhibit promising photovoltaic properties [21–26]. Some successful examples include a coupling of the 4-(2-ethylhexyl)phenyl substituted

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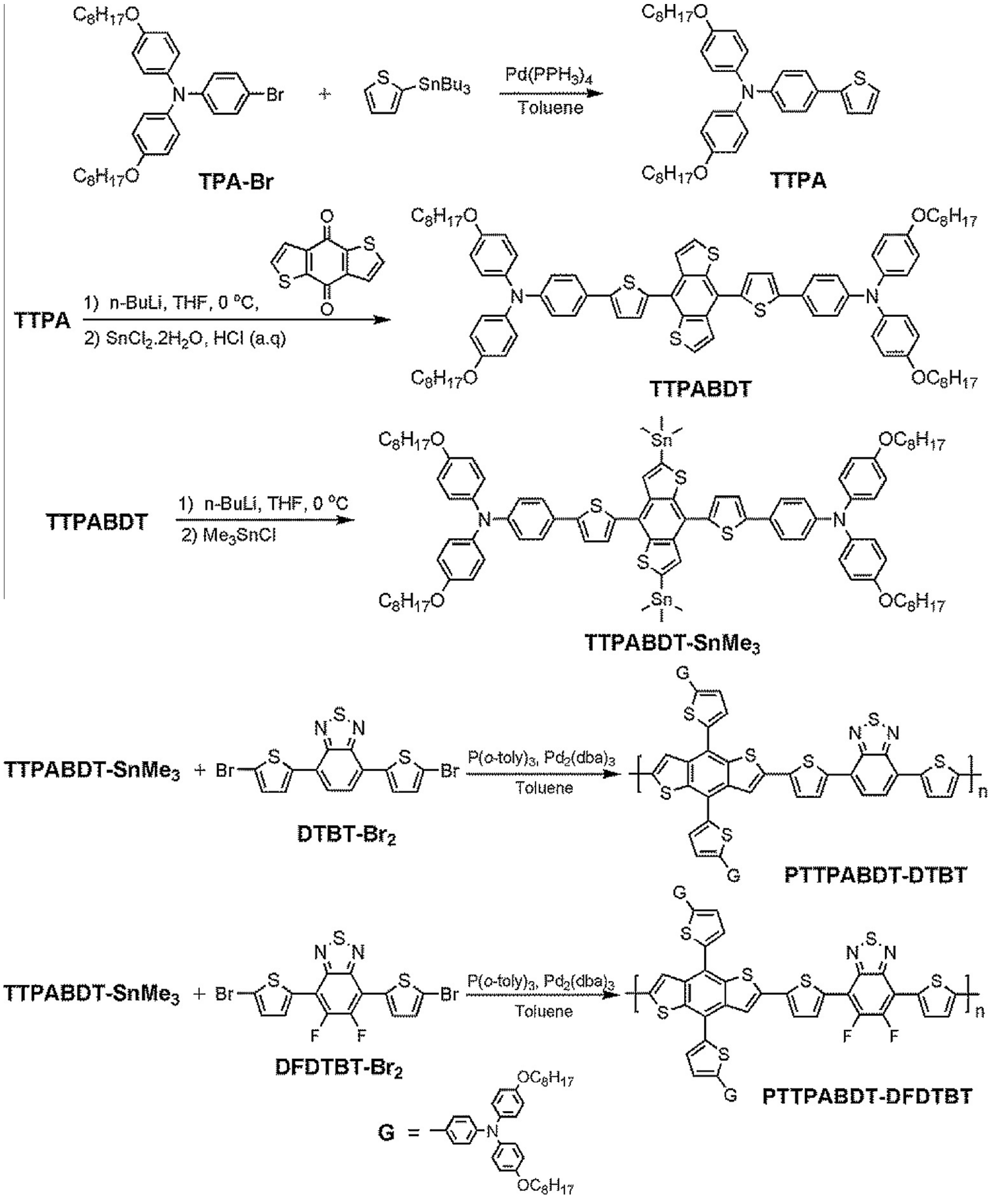

Scheme 1. Synthetic routes for PTTPABDT-DTBT and PTTPABDT-DFDTBT.

BDT unit with 4,7-di(4-(2-ethylhexyl)-2-thienyl)-2,1,3-benzothiadiazole giving a donor material that showed a PCE of 8.07% with a low HOMO level of −5.35 eV and a high *FF* of 70.9% [21]; a coupling of the extended conjugated 2,3-di(5-dodecylthiophen-2-yl)thienyl substituted BDT unit with 4,7-di(2-thienyl)-2,1,3-benzothiadiazole giving a donor material that showed a PCE of 3.57% with V_{oc} of 0.78 V [22]; and a new BDT monomer (TTBDT) by introducing two thieno[3,2-b]thiophene (TT) units onto the BDT unit exhibited a PCE of 7.44% for conventional PSCs and PCE of 7.71% for inverted PSCs [24]. Obviously, these previous work introducing conjugated 2-D side chains onto the BDT unit can increase the rigidity of the repeating unit and show excellent PSCs performance. From this perspective, extending π-conjugation side chains onto the BDT are promising candidates for designing new conjugated polymers for highly efficient electron donors for PSCs.

As is well known, triphenylamine (TPA) is one of the most popular organic optoelectronic groups due to its good electron-donating and hole-transporting performances [27,28], which has been widely used as donor groups to construct D–A-type photovoltaic materials for PSCs [29–31]. Meanwhile, benzothiadiazole (BT) units are the widely used acceptor units owing to its strong electron-withdrawing property, intense light absorption and good photochemical stabilities [32,33], which has been coupled with a variety of electron-rich groups to build low-band gap polymers [21–23].

Considering above merit, in this work, two novel D–A-type 2-D polymers of PTTPABDT-DTBT and PTTPABDT-DFDTBT were designed and synthesized, in which the extended π-conjugation by attaching a extended conjugated side chain of 4-thienyltriphenylamine (TTPA) onto the BDT (TTPABDT) as the donor unit, thiophene (T) as the π-bridge, BT and 5,6-difluorobenzo[*c*]-[1,2,5]thiadiazole (DFBT) as the acceptor units. The detailed synthetic routes for the monomers and the novel BDT-based 2-D conjugated polymers are outlined in Scheme 1. Their optical, thermal, electrochemical, charge-transporting and photovoltaic properties were investigated. As expected, two 2-D conjugated polymers show a high decomposition temperature (T_d), broad absorption range, small optical band gap and high hole mobility. The hole mobility of the PTTPABDT-DFDTBT/$PC_{71}BM$ blend (1:3, *w*/*w*) is 2.15×10^{-4} cm^2 V^{-1} s^{-1}, which is two times higher than