Highly flattened donor-acceptor polymers based on fluoride-substituent acceptors for efficient heterojunction solar cells

Yuancheng Qin[*], Shuqiang Liu, Huihui Gu, Weili Dai, Xubiao Luo[*]

Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, PR China

ABSTRACT

For high performance polymer solar cells, the effects of planarity and alkyl chain steric hindrance are systematically examined in the polymer **poly[1-(4-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-6-methylbenzo[1,2-b:4,5-b′]dithiophen-2-yl)-6-methylthieno[3,4-b]thiophen-2-yl)-2-ethylhexan-1-one]** (**P4**) constructed with a **benzo[1,2-b:4,5-b′]dithiophene** (**BDT**) plane with symmetrical thiophene side chains, **poly[2-ethyl-1-(6-methyl-4-(6-methyl-4,4-dioctyl-4H-silolo[3,2-b:4,5-b′]dithiophen-2-yl)thieno[3,4-b]thiophen-2-yl)hexan-1-one]** (**P5**), composed of silaindacenodithiophene, **poly[2-ethyl-1-(6-methyl-4-(6-methyl-4-octyl-4H-dithieno[3,2-b:2′,3′-d]pyrrol-2-yl)thieno[3,4-b]thiophen-2-yl)hexan-1-one]** (**P6**), based on pyrrole moieties and the corresponding F-containing polymers, **poly[1-(4-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-6-methylbenzo[1,2-b:4,5-b′]dithiophen-2-yl)-3-fluoro-6-methylthieno[3,4-b]thiophen-2-yl)-2-ethyl-hexan-1-one]** (**P1**), **Poly[2-ethyl-1-(3-fluoro-6-methyl-4-(6-methyl-4,4-dioctyl-4H-silolo[3,2-b:4,5-b′]dithiophen-2-yl)thieno[3,4-b]thiophen-2-yl)hexan-1-one]** (**P2**), and **Poly[2-ethyl-1-(3-fluoro-6-methyl-4-(6-methyl-4-octyl-4H-dithieno[3,2-b:2′,3′-d]pyrrol-2-yl)thieno[3,4-b]thiophen-2-yl)hexan-1-one]** (**P3**). Except for **P1** and **P4**, the alkyl chain is directly linked to the main chain in the polymers. **P1** has a high degree of flatness because flanking thienyls can decrease the torsion angle between conjugated units. In addition, the introduction of fluorine (F) on the thienothiophene acceptors of **P4** reduces the dihedral angle between the **BDT** and thienothiophene, resulting in a more planar **P1**. Moreover, the introduction of short alkyl and thiophene side chains minimizes the intermolecular steric hindrance of **P1** and ensures strong inter-chain aggregation and π-π stacking. However, the introduction of F in **P2** and **P3** increases the dihedral angle relative to non-F-containing **P5** and **P6**. Finally, an efficiency of 7.1% is obtained for **P1**, leading to a 50% increase in power conversion efficiency (PCE) compared with P4. This work is a step towards enhanced polymer planarity and minimal intermolecular steric hindrance for the development of efficient polymer heterojunction solar cells.

1. Introduction

Solar energy is an environmentally friendly, inexhaustible energy that has been widely utilized (Cheng and Zhan, 2016; Cai et al., 2017; Collins et al., 2017; Kranthiraja et al., 2017; Xiao et al., 2017; Wright et al., 2017). Organic solar cells can convert light into electricity and have recently received much attention because of their low cost, low weight, and higher flexibility when compared with silicon materials (Duan et al., 2016). At present, small organic molecule donor materials and donor-acceptor (D-A) conjugated polymers composed of electron-rich and electron-deficient units are mainly used to build such cells. So far, the efficiency for heterojunction solar cells based on D-A conjugated polymers and fullerene systems has exceeded 10% (Cho et al., 2015; Jo et al., 2015; Nian et al., 2016; Fan et al., 2017; Zhao et al., 2017; Yin et al., 2017).

Many strategies have been attempted to improve the PCE of D-A polymer solar cells, such as the introduction of high-mobility materials into the active layers as additives (Takeda et al., 2012; Liu et al., 2015) to overcome the low hole mobility. Other strategies include the conversion of binary batteries to ternary batteries (Zhao et al., 2017) with the addition of a third material to expand multiple charge transport channels, control of the morphology of the active layer through different solvents and heat treatment, adding a buffer layer between the electrode and the active layer, exploring new D-A materials with wide absorption bands and high charge mobility, and the introduction of electron-withdrawing substituents. By selecting a proper D and A structure or the introduction of electron-withdrawing substituents, the energy band gap for the material can be effectively adjusted, and the range of the absorption spectrum can be simultaneously widened. Thus, charge transfer performance can be improved. Moreover, the molecular

characteristics of D-A polymers can be tuned, such as the backbone planarity, molecular orientation at the interface, domain size and purity, intermolecular spacing, and miscibility with acceptors (Jo et al., 2015; Albrecht et al., 2012; Cho et al., 2012; Nketia-Yawson et al., 2015).

Recently, much attention has been focused on the introduction of a D monomer (benzodithiophene derivatives) into the high plane of the molecular skeleton, as well as fluorine substitution on the A monomer (benzodithiazole, benzotriazole, thienothiophene derivatives) (Nketia-Yawson et al., 2015). Building a planar molecular skeleton can ensure closer π-π stacking, which is propitious to internal aggregation, charge transfer, and molecular conjugation to produce a narrower band gap (Jo et al., 2015; Nketia-Yawson et al., 2015; Jo et al., 2015; Li et al., 2014). Pyrrole moieties are interesting for use as donor monomers, instead of the commonly used cyclopentadiene, because of efficient charge transport through tight inter-chain packing of the conjugated polymer chains. Such moieties also retain the ability to construct a planar molecule and, at the same time, strengthen the interaction between the molecules and charge transmission. To improve the charge transmission capacity, silicon-containing analogues have also been introduced. When the carbon–carbon bond of cyclopentadiene was replaced by a silicon–carbon bond, it exhibited improved charge transport properties because the silicon–carbon bond length was longer than the carbon–carbon bond length, which can, thus, support stronger intermolecular interactions and π-π stacking (Li et al., 2015). **BDTT**-based conjugated polymers show wide absorption bands and narrow band gaps leading to better energy conversion efficiency. **BDT** has a high degree of flatness and high charge transfer rates and is often used as a donor unit for the construction of conjugated polymers (Zhao et al., 2016). Many electron-withdrawing groups, especially fluorine, are introduced into A monomers to improve the electron affinity for D-A conjugated polymers. Fluorine is used to improve the open-circuit voltage because it leads to relatively deep **LUMO** energy levels without reducing the short-circuit current (Cho et al., 2012; Kim et al., 2013). It is also propitious to form an interconnected network with a nanoscale fibril structure, which is beneficial for generation of charge carriers (Yang et al., 2013). Despite the excellent properties of D and A monomers and the potential benefits of electron-withdrawing F, however, the twist angles for conjugation structures caused by F have been ignored. Therefore, the above monomers were selected as molecular skeletons and F substitution groups were examined in terms of how they affect molecular frameworks.

Six polymers composed of cyclopentadienyl-based derivative donor monomers and thiophene-thiophene derivative acceptor units were systematically studied. The main chemical structure is shown in Scheme 1. By introducing F atoms into the acceptor unit, the dihedral angle and molecular aggregation between adjacent monomers of the polymer could be improved. Theoretical calculations were used to investigate the effect of the lateral size of the molecule on inter/intra-molecular resistance and the effects of F atoms on polymer planarity. To ensure that this series of controls enhanced solar cell efficiency, a clear relationship was examined between the optical performance of the active layer and the molecular plane, steric hindrance, and molecular self-aggregation. The thiophene side unit was introduced into the BDT moiety to reduce steric hindrance within the molecule. The introduction of thienothiophene and units based on BDT led to an overall degree of molecular conjugation. **P1** exhibited strong aggregation in solution, strong π-π chain stacking, a planar molecular skeleton, and less molecular resistance. Ultimately, **P1** exhibited a power conversion efficiency of nearly 7.1%.

2. Experimental

2.1. Characterization

Nuclear magnetic resonance (NMR) spectra were acquired using a

Bruker ARX 400 NMR spectrometer. UV–Vis absorption spectra were recorded on a PerkinElmer Lambda 900 UV–Vis spectrometer at room temperature. All solution UV–Vis experiments used chloroform; films were recorded by $CHCl_3$ on glass. A BAS 100B instrument was used to perform cyclic voltammetry (CV) measurements at a scan rate of 50 mV/s. Tetrabutylammonium perchlorate (Bu_4NClO_4) in an anhydrous and nitrogen-saturated acetonitrile (CH_3CN) solution (0.1 mol/l) was used as the supporting electrolyte, with platinized platinum ($0.5\,cm^2$) counter electrodes. Polymers were coated onto the platinum plate working electrodes from dilute chloroform solutions. The Highest Occupied Molecular Orbital (**HOMO)** for the copolymers was calculated from the onset oxidation potential according to **HOMO** $= -(E_{onset}^{ox} + 4.32)\,eV$. The Lowest Unoccupied Molecular Orbital (**LUMO)** was calculated from the onset reduction potentials according to **LUMO** $= -(4.32 + E_{onset}^{red})\,eV$. Thermogravimetric analysis was carried out over the temperature range 50–1000 °C using a TGA Q600 at a heating rate of $10\,°C\,min^{-1}$ under a nitrogen flow rate of 100 mL/min. Gel permeation chromatography (**GPC**) was carried out using a Waters 515 GPC instrument using a THF eluent and polystyrenes as standards. The photocurrent–voltage (**J–V**) curves for the assembled **heterojunction solar cells** irradiated by simulated solar light from a 100 W xenon arc lamp in ambient atmosphere were recorded by Xe Lamp Oriel Sol3A™ Class AAA Solar Simulators (94023A, USA). Materials Studio7.0 is used to perform DFT calculations.

2.2. Polymer synthesis

The five monomers required for the polymer syntheses were obtained from Suna Tech Inc. (www.Suna Tech Inc.com): acceptor units (4,6-dibromothieno [3,4-b] thiophen-2-yl)-2-ethylhexan-1-one (A1), 1-(4,6-dibromo-3-fluorothieno [4-b] thiophen-2-yl)-2-ethylhexan-1-one (A2), donor units (4,8-bis (5-(2-Ethylhexyl) thiophen-2-yl) benzo [1,2-b: 4,5-b′] dithiophene-2,6-diyl bis(trimethylstannane) (**D1**), 4,4-dioctyl-(Trimethylstannyl)-4H-silolo [3,2-b: 4,5-b′] dithiophene (**D2**), 4-octyl-2,6-bis (trimethylstannyl)-4H-dithieno [3′-d] pyrrole (**D3**). Specific NMR data can be obtained from the support information. The general procedure adopted for synthesis was as follows: Different amounts of donor (**D1-D3**) and acceptor (**A1-A2**) mixtures were dissolved in 15 mL of degassed toluene in a 50-mL three-necked flask. Six polymers (**P1-P6**) were produced by the Stille coupling reaction. A corresponding amount of $Pd_2dba_3/CuO/P(o-tolyl)_3$ was then added to the solution, and the mixture was heated at 110 °C for 72 h in an inert gas atmosphere. The reaction mixture was allowed to cool to room temperature and precipitated by the addition of methanol (200–500 mL). The crude copolymer was collected by filtration and purified in a Soxhlet apparatus using methanol, hexane, and acetone. Finally, the polymer was extracted with chloroform. The chloroform solution was condensed and slowly added to methanol (200–500 mL). The solid was filtered and dried under vacuum to produce a dark purple solid with a yield of 45–75%.

P1: **A2** (0.3087 g, 0.6982 mmol), **D1** (0.6316 g, 0.6982 mmol), toluene (15 mL), and Pd_2dba_3(20.7 mg)/CuO(179.7 mg)/P(o-tolyl)$_3$(27.5 mg) were used to prepare **P1** according to the general procedure described above. A dark purple powder was obtained with a yield of 75%.^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.26 (br, 3H), 2.95 (br, 2H), 0.97–1.39 (br, 29H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 146.24, 136.99, 128.16, 125.07, 123.34, 41.32, 34.36, 32.71, 29.69, 28.96, 25.62, 23.12, 14.19, 10.93.

P2: **A2** (0.3087 g, 0.6982 mmol), **D2** (0.6316 g, 0.6982 mmol), toluene (15 mL), and Pd_2dba_3(20.7 mg)/CuO(179.7 mg)/P(o-tolyl)$_3$(14.5 mg) were used to prepare **P2** according to the general procedure described above. A dark purple powder was obtained with a yield of 65%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 6.67–7.84 (br, 38H), 2.84–3.91(br, 17H), 1.81(br, 54H), 1.24 (br, 362H), 0.87 (br, 184H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 197.78, 135.18, 133.75, 129.95, 128.66, 126.01, 70.47, 51.21, 33.68, 33.18, 31.88, 31.37, 29.62, 29.22,