



High performance all-polymer solar cells employing systematically tailored donor polymers



Jianxia Sun, Jinan Gu, Jianyu Yuan, Zequn Cui, Kunyuan Lu, Shaohua Shi, Guanqun Ding, Wanli Ma*

Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, 199, Ren-Ai Road, Suzhou Industrial Park, Suzhou, Jiangsu, 215123, China

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ABSTRACT

We successfully designed and synthesized a series of BDT-Qx-T based polymers as the donor polymer used in all polymer solar cells (all-PSCs). Their properties were finely tuned by side-chain modification and the introduction of electron-withdrawing fluorine atoms to polymer acceptor unit. Then we systematically investigated the effect of molecular structure on the polymer morphology and photovoltaic properties in all-PSCs. We revealed that the fluorination can optimize polymer energy level and improve the polymer coplanarity, leading to enhanced intermolecular packing and balanced carrier transport. Meanwhile, the substitution of dodecyl for 2-ethylhexyl side chains can result in improved film morphology and hole transport. As a result of the synergistic effect between fluorination and side-chain modification, we achieved a high PCE of 5.35% for the optimized all-PSCs. More importantly, our approach may become a general and effective way to tailor the polymer molecular structure for achieving high performance all-PSCs.

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1. Introduction

In the past decades, the solution-processed polymer/fullerene solar cells have attracted the attention of many researchers because of their unique advantages, such as low-cost, light-weight, flexibility and semi-transparency [1–5]. In order to improve the power conversion efficiency (PCE), extensive research efforts have been devoted to the design, synthesis and characterization of new materials, morphology control, and the development of novel device architectures [6,7]. At present, PCEs about 10% and ~11% have been obtained for single-junction [8] and tandem [9] organic photovoltaic devices in laboratory, respectively. However, the widely used electron acceptor fullerene has weak absorption in the visible region, plus limited structure and energy level tunability, which have restricted further improvement of polymer/fullerene solar cells [10,11]. Therefore, non-fullerene acceptor materials including conjugated polymers and small molecules have been actively explored as the potential alternatives to replace fullerene in organic solar cells [12]. Especially, polymer/polymer blend solar cells are

attractive potential substitutes for polymer/fullerene systems [13,14]. The polymer acceptors exhibit numerous advantages, such as strong and broad absorption, as well as high tunability on energy level and chemical structure. In addition, their enhanced mechanical/thermal properties and superior film forming quality are critical to the solution-processed large-scale production of organic solar cells [15–17]. However, so far all-polymer solar cells (all-PSCs) still show relatively low PCEs of 3–8.27% [15–21]. It lags significantly behind that of polymer/fullerene systems (PCE exceeding 10%) [8,9], in which materials design and synthesis play a critical role in improving the PCEs [22,23]. Thus the performance of all-PSCs may also be significantly enhanced by designing suitable donor and acceptor copolymers [24] with well-aligned energy levels and complementary absorption [13,24,25]. Among all the materials, the polymers with two-dimensional (2D) conjugated structures have attracted many attentions due to their interesting properties and promising photovoltaic performance [26,27]. For example, BDT-Qx-T structure consist of popular BDT (Benzo[1,2-b:4,5-b']dithiophene) with conjugated side chains (2D-BDT) as the electron donor unit [28,29], strong electron-withdrawing quinoxaline as the acceptor unit [29,30] and a thiophene π bridge between them [31,32]. Side chain engineering can effectively affect the polymer performance [33,34]. The size and topology (e.g., linear, branched) of the alkyl

* Corresponding author.

E-mail address: wлма@suda.edu.cn (W. Ma).

side chains connected with the thienyl moiety can affect the coplanarity, morphology and photovoltaic parameters of the polymers [30,35,36]. BDT-Qx-T based materials have shown excellent performance in conventional polymer/fullerene devices [30,37,38]. We thus expect that the BDT-Qx-T structure may also lead to superior performance in all-PSCs after fine tuning of its structures. Specifically, we introduced electron-withdrawing fluorine atoms to the periphery of quinoxaline. The strong electron-affinity nature of fluorine atom is useful to lower the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels to achieve high open circuit voltage (V_{oc}) in all-PSCs [28,39,40]. Meanwhile, the coplanarity of the conjugated backbone can be enhanced through F atom induced inter/intramolecular interactions, resulting in improved π - π stacking [37,41,42]. In addition, the small size of fluorine atom is expected to minimize the steric interactions, stabilizing the intermolecular packing of polymers [39,43]. Moreover, the electron-withdrawing fluorine atom can enhance the electron affinity of conjugated polymers to stabilize the formed radical anions on the polymer backbone. As a result, the improved polymer coplanarity and stabilized radical anions will facilitate the charge transport [15,42].

In this work, we successfully designed and synthesized a series of BDT-Qx-T based polymers PH-EH, PH-DO, PF-EH, PF-DO, P2F-EH and P2F-DO with different side-chain structure and fluorine atom numbers. Then we systematically investigated the effect of molecular structure on the morphology and photovoltaic properties of the all-PSCs. By using these polymers as the donor and Poly[*N,N'*-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5'-(2,2'-bithiophene)](P(NDI2OD-T2); Poly-*era*Activink N2200) [44] as the acceptor, we obtained decent PCEs for the corresponding all-PSCs. Especially, with optimal number of fluorine atoms in the quinoxaline and dodecyl (DO) side chain appended to the thienyl moiety, we obtained the highest PCE of 5.35% for P2F-DO based all-PSCs. It is worth noting that very recently, Hou group reported a high PCE of 5.8% for all-PSCs [19] using polymers also containing the same 2D-BDT block, while they focused more on morphology study. According to the best of our knowledge, systematical modifications on the chemical structure of the donor polymers have been rarely reported in all-PSCs. Our results suggest that the synergistic effect between polymer side-chain modification and fluorination is critical, which may become a general and effective approach to tailor the polymer molecular structure for enhancing the performance of current all-PSCs.

2. Experimental section

2.1. Characterization

UV-vis-NIR spectra were recorded on a Perkin Elmer model Lambda 750. Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer TGA4000. Tapping-mode AFM was obtained by using a Veeco Multimode V instrument.

2.2. General procedure for the synthesis of polymers

In a 50 mL reaction tube, compound BDT-TR (0.22 mmol), QX-T (M1, M2 and M3) (0.22 mmol) tri(*o*-tolyl)phosphine 10 mg, and $\text{Pd}_2(\text{dba})_3$ 5 mg were dissolved in 5 mL dry toluene under argon. After stirred at 110 °C for 24 h, the mixture was cooled to room temperatures and precipitated in methanol (100 mL). The precipitate was filtered and washed with methanol (24 h) and hexane (24 h) successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform (10 h). The chloroform fraction was concentrated and

precipitated in methanol. The precipitate was filtered and dried in vacuum at 80 °C overnight. PH-EH: (138 mg, yield: 41%). GPC: $M_w = 74.8 \text{ kg mol}^{-1}$, PDI = 3.33. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) σ (ppm): 8.32–6.11 (br, 20H ArH), 4.23–3.61 (br, 4H), 3.41–2.66 (br, 4H), 1.65–1.32 (br, 2H), 0.59–1.24 (br, 18H). PH-DO: (218 mg, 68%). GPC: $M_w = 25.9 \text{ kg mol}^{-1}$, PDI = 2.02. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) σ (ppm): 8.23–6.51 (br, 20H ArH), 4.27–3.43 (br, 4H), 3.32–2.81 (br, 4H), 1.62–1.21 (br, 32H), 1.21–0.61 (br, 12H). PF-EH: (150 mg, yield: 44%). GPC: $M_w = 32.9 \text{ kg mol}^{-1}$, PDI = 2.84. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) σ (ppm): 7.99–7.32 (br, 7H ArH), 7.10–6.60 (br, 12H ArH), 4.06–3.44 (br, 4H), 3.18–2.75 (br, 4H), 1.99–1.06 (br, 22H), 1.05–0.63 (br, 18H). PF-DO: (162 mg, yield: 50%). GPC: $M_w = 11.8 \text{ kg mol}^{-1}$, PDI = 1.69. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) σ (ppm): 8.05–7.35 (br, 7H ArH), 7.17–6.45 (br, 12H ArH), 4.06–3.50 (br, 4H), 3.37–2.62 (br, 4H), 1.88–1.06 (br, 32H), 0.98–0.70 (br, 12H). P2F-EH: (140 mg, yield: 41%). GPC: $M_w = 25.2 \text{ kg mol}^{-1}$, PDI = 2.41. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) σ (ppm): 8.08–7.38 (br, 6H ArH), 7.08–6.16 (br, 12H, ArH), 4.04–3.36 (br, 4H), 3.15–2.71 (br, 4H), 1.86–1.06 (br, 22H), 1.05–0.50 (br, 18H). P2F-DO: (258 mg, yield: 78%). GPC: $M_w = 25.6 \text{ kg mol}^{-1}$, PDI = 2.08. $^1\text{H NMR}$ (CDCl_3 , 400 MHz) σ (ppm): 8.27–7.40 (br, 6H ArH), 7.23–6.08 (br, 12H ArH), 4.18–3.39 (br, 4H), 3.30–2.77 (br, 4H), 2.33–1.25 (br, 32H), 1.23–0.60 (br, 12H).

2.3. Device fabrication and testing

Patterned ITO glass substrates were cleaned by sequential ultrasonic treatment in detergent, acetone, deionized water and isopropyl alcohol. The organic residue was further removed by treating with UV-ozone for 10 min. All-PSCs were fabricated with a general structure of ITO/PEDOT-PSS (45 nm)/polymer:N2200/Al. A 40 nm thick topcoat layer of PEDOT-PSS was spin-coated onto the ITO substrate at a spinning rate of 4500 rpm (rotations per min) for 40 s and then dried in air at 150 °C for 10 min. A blend of polymers with different ratios was dissolved in chloroform, spin-coated at different speed (2000–3000 rpm) for 40 s and 100 nm. Al (2 Å/s) layers were then thermally evaporated on the active layer at a pressure of 1.0×10^{-6} mbar through a shadow mask (active area 7.25 mm²). The current density–voltage characteristics of the photovoltaic cells were measured using a Keithley 2400 (*I*-*V*) digital source meter under a simulated AM 1.5 G solar irradiation at 100 mW/cm² (Newport, Class AAA solar simulator, 94023A-U). The light intensity is calibrated by a certified Oriol Reference Cell (91150V) and verified with a NREL calibrated Hamamatsu S1787-04 diode. The external quantum efficiency (EQE) was performed using a certified IPCE equipment (Zolix Instruments, Inc, SolarCellScan100).

3. Results and discussion

3.1. Synthesis of monomers and polymers

The synthesis routes and structure of polymers are shown in Scheme 1. Stille cross-coupling reaction was performed between bis(trimethyl stannane) of BDT-TR and dibromides of Qx-T (M1, M2 and M3). The polymerizations of polymers with different side-chains and fluorine atoms were carried out under almost the same conditions. The weight-average molecular weight (M_w) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using THF as the eluent and polystyrenes as the internal standards, and the results are listed in Table 1. The M_w of PH-EH, PH-DO, PF-EH, PF-DO, P2F-EH and P2F-DO are 74.8 K, 25.9 K, 32.9 K, 11.8 K, 25.2 K and 25.6 K, respectively. EH and DO denote 2-ethylhexyl and dodecyl side chains respectively.

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