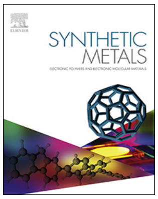
Synthetic Metals 245 (2018) 42–50

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Efficient heterojunction solar cells based on the synergy between planarity and dipole moment in fluorinated-thienothiophenes-based donor-acceptor polymers

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

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

ARTICLE INFO

Keywords:
Heterojunction solar cells
Dipole moment
Fluorinated
Planarity

ABSTRACT

Polymers consisting of benzodithiophene, dithienopyrrole derivative donor monomers and thiophene derivative acceptor units are synthesized. The effects of F on optical performance for several Donor-Acceptor conjugated polymer systems are investigated. The introduction of F is conducive to increasing the dipole moment of the molecule for effective intramolecular charge transmission. The incorporation of F in acceptor unit improves molecular planarity simultaneously. It is found that dipole moment and molecular planarity play a synergistic role in photovoltaic performance. Under the premise of ensuring the planarity, the dipole moment is enhanced, the charge transfer within the molecule can also be strengthened, thus, the short-circuit current is greatly increased. The theoretical calculations show and explain the effect of the F on the dipole moment. Finally, a *PCE* of 4% is achieved with a large short-circuit current density of 14.36 mA cm^{-2}. These results represent a synergy between planarity and dipole moment for improving the *PCE*.

1. Introduction

As flexible materials, organic photovoltaic materials can be processed using simple, low-cost solution processing techniques [1–10]. Despite its many advantages, the research on organic photovoltaic materials is still in infancy. The PCE of large-area organic solar cells is still much lower than inorganic solar cells, which limits its commercial development. Therefore, a wide range of research efforts have been focused on the design of new materials, as well as optimizing device fabrication conditions to achieve this goal [11,12].

One obvious defect of organic material is that the exciton lifetime is usually shorter. Thus, the maximum exciton diffusion length is generally about 3–10 nm [13]. In addition, the process of interfacial charge separation is more complex than the simplification model envisaged, and involves Coulomb bound electron-hole pairs, so there must be sufficient charge-separation driving force for the complete separation of electrons and holes. Likewise, there must be a suitable device structure to allow excitons to diffuse to the donor-acceptor interface. Finally, the polymer film must be thin enough to allow sufficient charge transfer to the electrode. Over the past decade, alternating conjugated copolymers consisting of electron donor (D) and electron acceptor (A) units are considered the most promising high molecular weight polymer solar cell [13–16]. The molecular weight of conjugated polymers is a key factor in determining their electrical, structural and properties. It has a great influence on the mobility of holes and electrons, once the molecular weight is too large, the polymer will be distorted due to the winding of the chain and self-aggregation, causing the cell defects and decreasing the migration between the molecular weight charge chains in the chain transport. Polymers with smaller molecular weight will have a significant blue shift and absorb less photon. Also, polymers with small molecular weight are not conducive to the redistribution of incident light due to the effect of light interference [17,18]. The energy level of the polymer can be effectively regulated by suitable D-A components. Apart from it, the molecular chain order, dipole moment, planarity of the polymer, solubility in organic solvents, compatibility and other molecular properties can also be fine-tuned by modifying the D and A building blocks, respectively [19,20].

The most effective way to induce charge difference in D-A polymer molecules is to introduce strong electron-withdrawing groups, such as F. With the introducing F in D-A photovoltaic materials, its power conversion efficiency has now exceeded to 10% [21,22]. As two types of D-A polymers often used for comparison, the F-containing D-A polymer always displays improved efficiency, although the factors for its efficiency increase are different. In some cases, the introducing F even lead to a drop in device efficiency, and its most obvious disadvantage is that it will cause the polymer to have a lower solubility

---

* Corresponding authors.
E-mail addresses: qinyuancheng@hotmail.com (Y. Qin), luoxubiao@126.com (X. Luo).

https://doi.org/10.1016/j.synthmet.2018.08.008
Received 22 May 2018; Received in revised form 30 July 2018; Accepted 12 August 2018

and exhibit a stronger aggregation tendency. However, lots of reasons account for positive effect of the introduction of F on device efficiency. Among them, the most common is that the introduction of electron-withdrawing groups F will downshift the Highest Occupied Molecular Orbital (**HOMO**) of the polymer, leading to an increase in the open-circuit voltage of the device, and also decrease the Lowest Unoccupied Molecular Orbital (**LUMO**) [23,24]. As long as the morphology is not changed, the increase of open circuit voltage will promote *PCE*. However, even if only one hydrogen replaced by F, the morphology of the polymer will undergo a large change, which will affect the fill factor [25,26]. Fluorination tends to greatly enhance polymerization, so blends of fluorinated polymers and fullerene acceptors generally have a larger domain size and a purer polymer-rich phase, which promotes effective charge collection [27,28]. However, the maximum amplitude of phase separation is limited by the diffusion length of excitons.

Although a great deal of work has been directed toward the study of fluorinated polymer donor material polymers [29–31], little is known about the impact of F on charge transport properties. The charge generation at the D/A interface is related to the interfacial dipole moment and planarity between the donor material and the acceptor material, as well as the internal dipole moment and planarity of donor materials. The former involves the efficient intermolecular charge transfer, while the latter is related to the effective intramolecular charge transport. In addition, for the conjugated polymer, once there is a large dipole moment, which likely helps suppress geminate recombination, and thus charge separation takes place effectively at the interface [32].

In this paper, we systematically studied six polymers synthesized from benzodithiophene, dithienopyrrole donor units and thienothiophene derivative acceptor units. By introducing F into acceptor units, theoretical calculations were applied to investigate the planarity and molecular dipole moment changes between adjacent monomers. The theoretical results show that the dipole moment of the conjugated polymer is improved with the introduction of F. F-Containing polymers have lower electron-hole binding energy and are more effective for charge separation at the interface. Finally, it was proved by electrochemical experiments that the introduction of electron-withdrawing substituents reduced the HOMO and LUMO energy levels of F-containing polymers, and the J-V curve also showed that the introduction of F lead to the increase of the short-circuit current, confirming the more effective charge separation in F-containing polymers.

2. Results and discussion

The six polymers except for **QP-C** and **QP-F** showed good solubility in conventional solvents ($CHCl_3$, THF, DCB), benefiting from the introduction of alkyl side chains on thienothiophene units and D monomers. The molecular weight of conjugated polymers is a key factor in determining their electrical, structural and properties. So, the weight-average molecular weight (M_w) and polydispersity index ($PDI = M_w/M_n$) were measured by gel permeation chromatography (GPC). Polystyrene was used as a standard and tetrahydrofuran used as the mobile phase at room temperature. The polymer was tested three times under the same conditions and all had similar number average molecular weights and dispersion values. The molecular weights of these polymers are shown in Table 1. The molecular weights are 21.51, 9.81, 13.45, 19.38, 18.91 and 14.70 kg mol^{-1} for **QP-A**, **QP-B**, **QP-C**, **QP-D**, **QP-E** and **QP-F**, respectively. Generally, a high molecular weight is beneficial in promoting their intermolecular charge transport and enhancing the hole mobility due to the high inter-connectivity between the crystalline grains of the polymers thus improve device performance. [18,33] The results show that the trend of molecular weights variation is basically accord with the change of *PCE*. Thermogravimetric analysis (TGA) was used to carry out the thermal stability of the polymer. As shown in Fig. 1, **QP-A**, **QP-B**, **QP-C**, **QP-D**, **QP-E**, and **QP-F** have excellent thermal stability, with a 5% mass loss temperature (T_d) of 343 °C, 288 °C, 317 °C, 335 °C, 316 °C and 317 °C respectively. The six polymers all have excellent thermal stability, which are sufficient for the needs of solar cells. Thermal decomposition data for the polymers is summarized in Table 1.

Table 1
Decomposition temperature and molecular weight of polymer.

Polymers	M_n (kg. mol^{-1})	M_W (kg. mol^{-1})	*PDI*	T_d (°C)
QP-A	16.5	21.5	1.32	343
QP-B	7.8	9.8	1.26	288
QP-C	10.9	13.4	1.22	317
QP-D	16.7	19.4	1.16	335
QP-E	13.5	18.9	1.40	316
QP-F	12.5	14.7	1.17	317

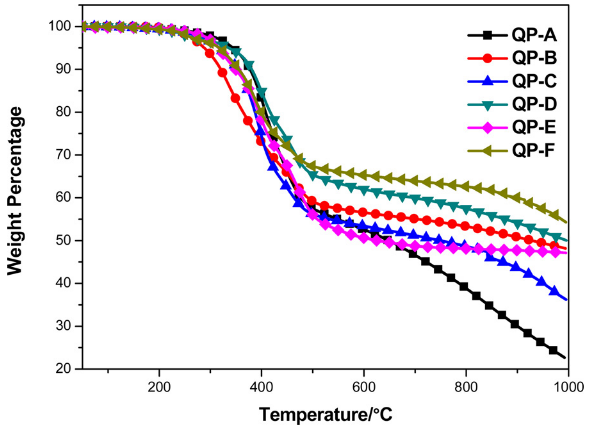


Fig. 1. Thermogravimetric curves of polymers.

To investigate the optical properties of the polymer **QP-A-F**, the UV–vis absorption spectra of the solutions and films were applied to study the ability of π stacking as well as the spectral response range and optical band gap. Despite people have already studied the effect of near infrared (NIR) on solar cells recently, [34,35] we consider the solar radiation is mainly concentrated in the UV–vis regions and the NIR is relatively weak. Therefore, we mainly measured the UV visible region (300–900 nm). [36,37] All the polymers exhibited superior optical absorption properties in terms of harvesting UV–vis solar photons. The solution and film optical absorption spectra are shown in Fig. 2. The relevant data are summarized in Table 2. Both **QP-A** and **QP-D** have two distinct characteristic peaks, 315 nm and 623 nm (**QP-A** solution), 329 nm, 640 nm (**QP-A** film); 326 nm, 644 nm (**QP-D** solution), 335 nm, 676 nm (**QP-D** film) respectively. The peak of 300–400 nm corresponds to the π-π* transition of the polymer backbone and 500–1000 nm corresponds to the effective internal charge transfer (ICT) interaction between rich and electron deficient units. Due to the tighter π-π stacking in the film, the UV–vis absorption in film undergoes a slightly red-shift around 1–34 nm with respect to that the solution, indicating that these polymers have a high concentration in film. It is found that the introduction of F and shorter alkyl chains result in a slightly blue-shift. Previous experiments have found that longer alkyl side chains weaken the distribution of the main chain electrons, causing blue shift [38]. However, shorter alkyl side chains still have the possibility of weakening the electron distribution of the main chain. At the same time, the blue shift occurs may be caused by the strong electronegativity of F and the electron density distribution of fluorine substitution weakening the π-conjugate of main chain. However, the absorption range of the polymer is still relatively wide, the absorption onset (λ_{onset}) exceeds 900 nm, generally use 900 nm as the absorption edge [39,40]. According to the formula [19]: