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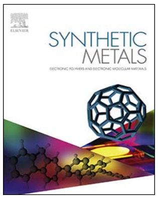

Energy levels modulation of small molecule acceptors for polymer solar cells

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ABSTRACT

Non-fullerene acceptor exhibits very promising prospect for the development of polymer solar cells (PSCs). It is necessary to carefully investigate the energy level matching between donor and acceptor to optimize the photovoltaic performance. In this paper, we have designed and synthesized two novel planar A-D-A type small molecular acceptors of IDT-RCN and IDT-CA with 2-(1,1-dicyanomethylene)rhodanine and cyanoacetate as the end groups, respectively. Compared to IDT-RCN with stronger electron-deficient end group, IDT-CA displayed 0.15 eV increase in LUMO level while almost the same HOMO level. PSC devices based on P3HT:IDT-CA show a power conversion efficiency (PCE) of 4.19% with V_{OC} of 0.84 V, J_{SC} of 7.77 mA cm^{-2} and FF of 0.64, which is much higher than that of P3HT:IDT-RCN mainly due to the higher V_{OC} value. This work indicates that end group modification is important for the modulation of PSC device parameters.

1. Introduction

Polymer solar cells (PSCs) has been paid intensive attentions in recent years for the potential of cost-effective, solution processable and flexible [1,2]. The power conversion efficiencies (PCEs) for a single junction PSCs have exceeded 10% with the investigation in materials design, interfacial modification and device fabrication [3,4]. In spite of this, the active layer materials are still far from demands for commercial utilization [5]. Among various active layer materials, regioregular poly(3-hexylthiophene) (P3HT) is the most representative donor material because it can be synthesized cost-effectively in large-scale and with good batch to batch reproducibility [6]. Conventionally, P3HT-based photovoltaic devices with fullerene acceptor such as PCBM ([6,6]-phenyl-C70-butyric acid methyl ester) could achieve a PCE of about 4% [7]. The fullerene derivatives are excellent acceptors for PSCs due to their good electron affinity and mobility. However, there are some drawbacks restricting their performance, such as low visible light absorption, difficulty in molecule modification, instability and so on. Therefore, it is not easy to further improve the photovoltaic performance of P3HT with PCBM as acceptor, especially the short-circuit current because of their limited optical absorption range in the wavelength of 300 nm to 650 nm.

In recent years, non-fullerene PSCs have developed very fast, especially with the emergence of A-D-A type small molecular acceptors (SMAs). High efficiencies of over 11% have been reported with several types of conjugated polymers as acceptors. However, these polymers are usually D-A type copolymers, which are much more tedious and poor reproducible in synthesis compared to P3HT. Therefore, it is important to develop non-fullerene acceptors coupled with P3HT as donor [8–11]. In 2014, McCulloch's group reported FBR as a new small molecule acceptor to couple with P3HT [12]. DFT calculation indicates the highest occupied molecule orbits (HOMOs) and LUMOs of this distorted A-D-A type molecule are determined by the central fluorene core and the external deficient units, respectively, which provides the possibility to conveniently tune energy level and bandgap of the material. The molecule also possesses controllable solubility and aggregation behaviors by means of the alkyl side-chains modification on the donor core. As the result, the photovoltaic devices provide the PCEs of 4.11%, which exceeds the control result from PC$_{61}$BM (3.53%), mainly attributed to enhanced open-circuit voltage (V_{OC}). In order to reduce the recombination loss of FBR induced by molecular distortion and expand the absorption spectrum, they introduced indacenodithiophene (IDT) as the replacement of fluorene [13]. As a result of the molecule structure improvement, they obtained the highest PCEs of 6.4% for P3HT-based non-fullerene PSCs. Professor Zhan and coworkers introduce peripheral tetrahexylphenyl group substituted IDT unit to construct another small molecule acceptor (IDT-2BR) to combine with P3HT. The phenyl modified IDT core can not only hold the main-chain flat, but also prevent the molecule from excessive aggregation [14]. As a result, high PCE of 5.12% was achieved in PSC device.

As is known, there is a trade-off between open circuit voltage (V_{OC}) and short circuit density (J_{SC}). The HOMO/LUMO level can be modulated carefully to reduce the energy gap (ΔHOMO and ΔLUMO) between donor and acceptor, which is beneficial for reduce the energy

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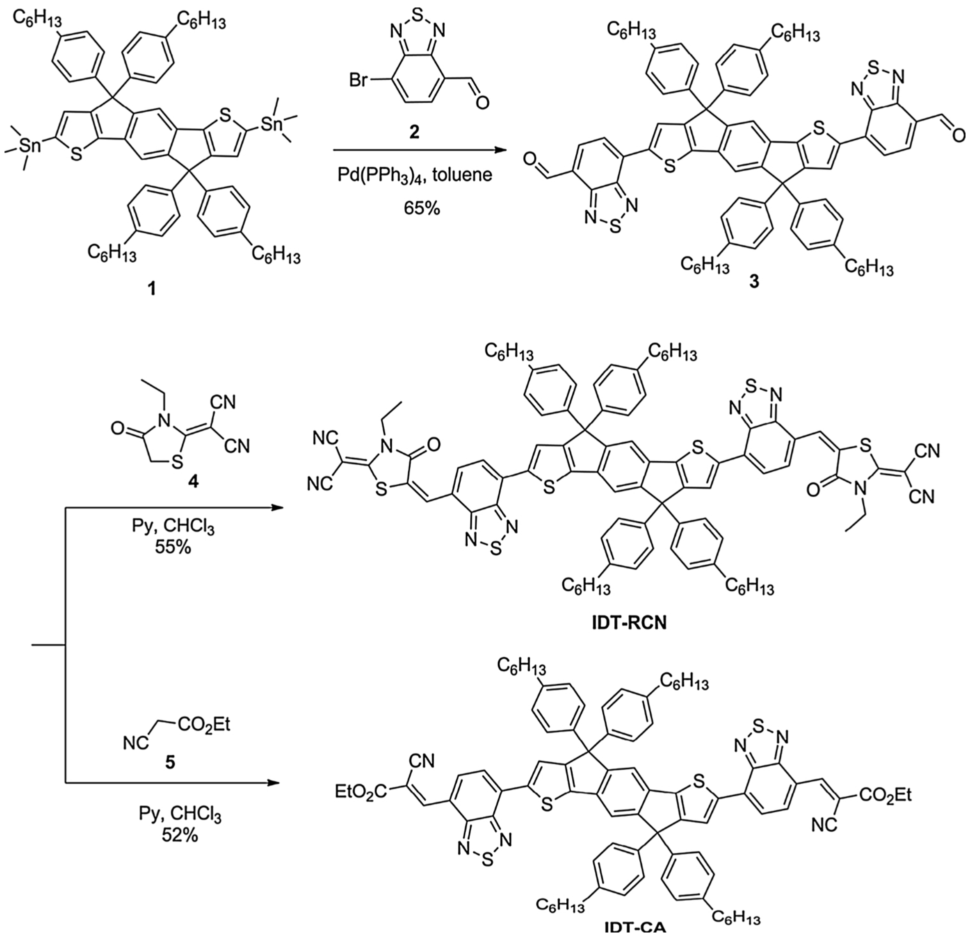

Scheme 1. Synthesis routes of IDT-RCN and IDT-CA.

loss during exciton dissociation process. As for the PSCs based on P3HT, there is still much room for improving V_{OC} and J_{SC} simultaneously through optimizing optical absorption, energy levels and crystallization property [15–17]. In this paper, we have designed two IDT-based small molecule acceptors IDT-RCN and IDT-CA with 2-(1,1-dicyanomethylene)rhodanine and cyanoacetate as the end groups, respectively. The LUMO levels vary from −3.75 eV to −3.64 eV and the HOMO levels keep almost unchanged. As a result, photovoltaic devices based on P3HT show PCEs of 3.42% and 4.19% for IDT-RCN and IDT-CA as acceptors, respectively. The devices performance show very good reproducibility, which is important for the further commercial application.

2. Results and discussion

2.1. Materials synthesis and characterization

The synthesis routes of compound IDT-RCN and IDT-CA are shown in Scheme 1. Organotin **1** reacted with bromide **2** by Stille coupling reaction affording key intermediate **3** in 65% yield. Then IDT-RCN and IDT-CA were synthesized through Knoevenagel condensation of aldehyde **3** with compound **4** and **5**, respectively in the yield over 50% [17,18]. IDT-RCN and IDT-CA are readily soluble at room temperature in common organic solvents, such as dichloromethane (DCM), chloroform (CF), tetrahydrofuran (THF) and so on. The thermal stability of IDT-RCN and IDT-CA were also studied by thermal gravimetric analysis (TGA) (Fig. 1S). The thermal decomposition temperatures of IDT-RCN and IDT-CA at 5% weight loss were 395 °C and 365 °C respectively, showing their good thermal stability for device fabrication [21].

2.2. Optical and electrochemical properties

The normalized UV–vis adsorption spectra of neat films and their blend films are shown in Fig. 1. Arising from strong intramolecular charge transfer, IDT-RCN and IDT-CA neat films show excellent absorption in the visible region with the main absorption peaks at 690 nm for IDT-RCN and 650 nm for IDT-CA, respectively [12,19]. It can be found that the absorption spectra of IDT-RCN and IDT-CA are both complementary to that of P3HT. Compared to the absorption onset of IDT-CA (745 nm), IDT-RCN shows about 60 nm red-shift, which is derived from stronger electron-withdrawing end groups of IDT-RCN. Accordingly, the optical band gap (E_g) of IDT-RCN and IDT-CA were calculated to be 1.54 eV and 1.66 eV, respectively. We also measured the absorption coefficient (α) in $CHCl_3$ solution as shown in Table 1, which are much higher than that of the PCBM in visible region [11,13,14].

The molecular energy levels of IDT-RCN and IDT-CA were calibrated via cyclic voltammetry (Fig. 1c). The HOMO and LUMO energy level are calculated from the onset of oxidation and reduction potential, assuming that the Fc/Fc^+ had an absolute energy level of −4.80 eV to vacuum. The onset oxidation potential/onset reduction potential of IDT-RCN and IDT-CA were 1.21 V/−0.66 V and 1.18 V/−0.77 V, respectively. Accordingly, the energy levels were calculated and listed in Table 1. It is obvious that the HOMO levels of two acceptors are nearly the same, while the LUMO levels are much different. The LUMO level of IDT-CA is −3.64 eV, which is about 0.11 eV higher than that of IDT-RCN (−3.75 eV). Compared with the HOMO/LUMO levels of P3HT, energy gaps between donor and acceptor are all larger than 0.3 eV, which can guarantee exciton dissociation in blend film [20]. It is observed that the electrochemical band (E_g^{EC}) gap is much larger than the optical band gap (E_g^{opt}), which is induced by the film delamination and