The influence of numbers of subunits on the photovoltaic performance of non-fullerene acceptors

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ABSTRACT

Two new small-molecular acceptors SF-2IIG and SF-4IIG were designed and synthesized to investigate the influence of the numbers of electron-deficient subunits of non-fullerene acceptors on the efficiencies of photovotaic devices. The studies showed that these two acceptors have different optical absorbption, energy levels, charge transport mobilities. As a result, the efficiencies of SF-4IIG based solar cells are significantly higher than those of SF-2IIG based ones.

1. Introduction

Organic solar cells (OSCs) have many advantages such as low-cost and large-area fabrication, light-weight, and flexibility comparing to inorganic solar cells [1,2]. Among the structures of organic solar cells devices, the most dominantis the bulk-heterojunction (BHJ) which possesses an active layer of donor polymers (p-type) and fullerene acceptors (n-type) [3]. The fullerene derivatives are the most common acceptors due to their triple similar LUMO energy levels to fill with up to six electrons, fast charge separation, and their spherical structure can enhance electron transport mobilities [4–12]. However, the fullerene derivatives also have many drawbacks such as weak absorption in the visible region and high-cost in the process of production [13–15]. Recently, non-fullerene acceptors have attracted much attention due to their merits. First, they poessess tunable energy levels and good absorbance in visible region. Also, the non-fullerene acceptors are low-cost in production [16–22]. However, the research of non-fullerene acceptors is still at the early stage.

Several strategies have been employed to design high-performing non-fullerene acceptors. First, a twist core is needed to form a spherical structure and prevent forming over-size domains. Second, subunits composed of large π-conjugated structures can facilitate intermolecular interactions and the charge transport. Third, the materials may contain two or more identical and electron-deficient subunits to enhance the density of the LUMO level. Previously, our group reported two small-molecular (SM) acceptors SF-PDI2 and SF-PDI4 with two and four

electron deficient groups, respectively [23]. The results showed that increase of the number of electron deficient group can significantly enhance the photovoltaic performances for PTB7-Th based systems.

In present, we reported two novel SM acceptor materials (SF-2IIG and SF-4IIG, see Fig. 1) with different numbers of electron-deficient building block isoindigo (IIG) and a highly twist spirobifluorene (SF) center [24,25]. IIG is a common subunit which is usually used in D-A polymers due to its strong electron-withdrawing character. Several reseaches shows that IIG-based moieties have good absorbance, electrochemical and photovoltaic properties [24,26–28]. Through varing the number of the electron-deficient groups, the physicochemical properties of the materials were tuned, which was supported with CV, UV-vis, TGA, DSC and DFT calculations. Furthermore, the photovoltaic performances of P3HT based solar cells were investigated to show that the efficiencies were significantly enhanced upon increase the number of the electron deficient building blocks, which was supported with the studies of charge transport mobilities and morphologies of blend films.

2. Experimental

2.1. Materials and characterizations

All raw materials were purchased from commercial sources and used without further purification. Toluene, H_2O, and THF were distilled before use. The reactions were carried under nitrogen condition. All ^{1}H NMR (300 MHz) spectra were characterized by a Bruker AVANCE NMR
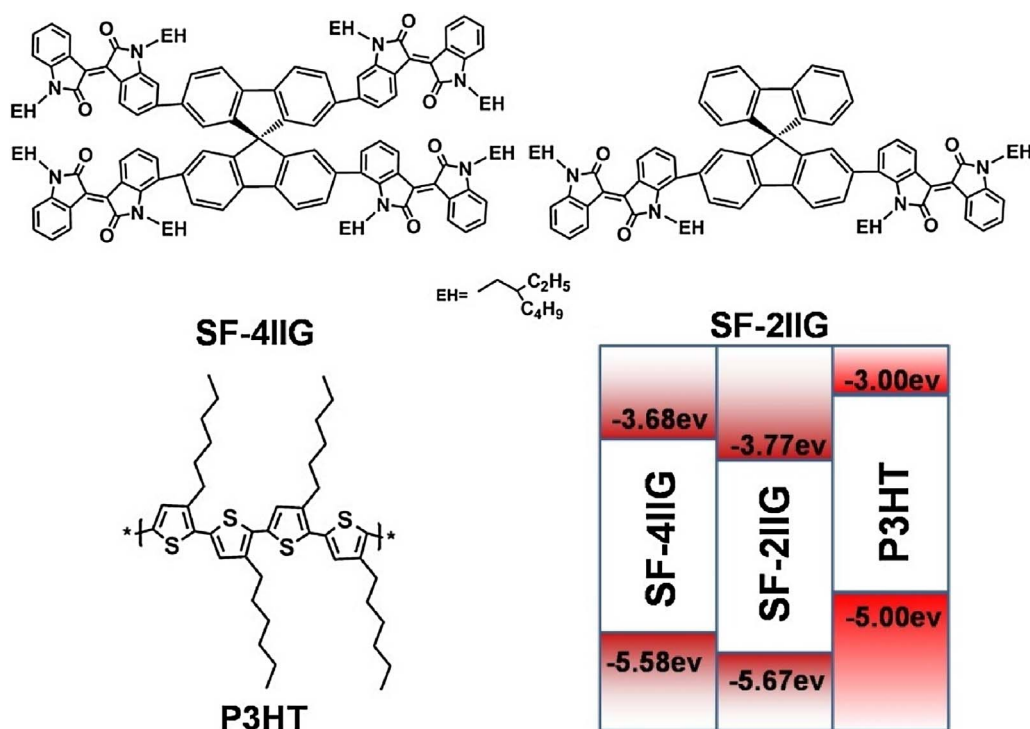
spectrometer. The cyclic voltammetry (CV) used a Pt wire, glassy carbon discs, and Ag/AgCl as the counter electrode, working electrode, and reference electrode, respectively. The results were measured in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The external standard used a ferrocene/ferrocenium (Fc/Fc^+) redox couple. UV–vis absorption spectra were measured using a Gary 60 UV–vis Spectrophotometer. All the film samples were spin casted on glass substrates. Thermogravimetric analysis (TGA) was measured with a Shimadzu Thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) were measured using a TA Instruments differential scanning calorimeter (Q2000) under nitrogen at a heating rate of 10 °C/min.

2.2. Photovoltaic device fabrication

Devices were fabricated with the structure of ITO/ZnO/P3HT:SF-4IIG or SF-2IIG blend/MoO_3/Ag. The indium tin oxide (ITO) substrates were cleaned by deionized water, acetone and isopropanol and stored in an oven (80 °C), followed by UV ozone treatment (30 min). The 25 µL ZnO precursor solution, which is zinc acetate here, was spin-coated on the ITO substrates. Then the film was annealed at 200 °C for 30 min. The photoactive layers were stored in a glove box and span on the substrate. The active layer was a mixture of SF-based acceptors and P3HT. The concentrations of the acceptor and donor are 10 mg/mL and different amount of DIO or CN was added as additive. After the active layer was spin-coated, the thin films were moved into the vacuum evaporator which is inside of the glove box. MoO_3 and Ag were placed by thermal evaporation under 10^{-5} Pa condition.

2.3. Molecular modelling

The theoretical calculation was performed by density functional theory (DFT) calculations by Gaussian 09 software program using B3LYP hybrid functional with basis set 6-31G(d) [29,30]. Geometry optimizations were performed in gas phase without solvent effects and all the alkyl chains were replaced with methyl chains for simplification.

2.4. Mobility measurements

The electron and hole mobilities were measured with a device structure of (ITO/ZnO/polymer:accptor/Ca/Al and ITO/PEDOT:PSS/polymer:acceptor/MoO_3/Ag, respectively). The space charge limited current (SCLC) method was used to measure the mobility based on the equation as following [31],

$$J = 9\,\mu\varepsilon_0\varepsilon_r V^2/8L^3$$

where μ is the electron mobility, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_r is the relative permittivity of the material, V is the voltage drop across the device and L is the thickness of the film.

2.5. Materials synthesis

6-(N,N'-2-Ethylhexyl)-bromoisoindigo (1Br-IIG), 2,2′,7,7′-tetrakis (4,4,5,5- tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobi[fluorene] (4Bpin-SF), and 2,7′-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,90-spirobi[9H-fluorene] (2Bpin-SF) were synthesized according to the literatures [24,32,33].

2.5.1. Synthesis of SF-4IIG

4Bpin-SF (36 mg, 0.044 mmol), 1Br-IIG (120 mg, 0.193 mmol) and K_2CO_3 (60 mg, 0.44 mmol) were dissolved in a mixed solvent of THF (4 mL), water (4 mL) and toluene (4 mL). Then the mixture was degassed for 10 min. Pd(PPh$_3$)$_4$ (10 mg, 0.086 mmol) was added and degassed for 20 min again. The reaction was heated at 90 °C under microwave for 7 h. After reaction, the solvent was removed by rotary evaporation then extracted with CH_2Cl_2 and H_2O for three times. The organic layer was collected and dried by anhydrous $MgSO_4$. After filtration, the solution was concentrated and purified by silica column chromatography to afford a red solid after removing the solvent (72 mg, 72%).

^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ9.15 (dd, 8H), 8.05 (d, 4H), 7.75 (d, 4H), 7.34 (td, 4H), 7.14 (m, 8H), 7.04 (t, 4H), 6.86 (s, 4H), 6.77 (d, 4H), 4.06 (m, 16H), 1.59 (s, 8H), 1.3 (m, 32H), 0.88 (m, 24H).

Elem. Anal. Calcd.for $C_{89}H_{96}N_4O_4$: C, 83.14; H, 7.53; N, 4.36.Found: C, 882.84; H, 7.58; N, 4.28.