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Achieving high performance non-fullerene organic solar cells through tuning the numbers of electron deficient building blocks of molecular acceptors

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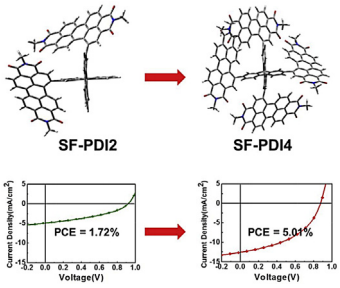
HIGHLIGHTS

- Two compounds, SF-PDI2 and SF-PDI4, were synthesized as electron acceptors.
- The effects of the electron deficient blocks on OPV performance were investigated.
- Increasing the numbers of PDI building blocks is beneficial to OPV performance.
- It is the first time to supply a useful strategy to achieve high OPV efficient.

GRAPHICAL ABSTRACT



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ABSTRACT

Two analogous dimer and tetramer compounds, SF-PDI2 and SF-PDI4, were designed, theoretically calculated, synthesized, and developed as electron acceptors for organic solar cells. The effects of the number of the electron deficient building blocks on the optical absorption, energy levels, charge transport, morphology, crystallinity, and photovoltaic performance of the molecules were investigated. In combination with two different donors, PTB7-Th and PffBT4T-2OD, the results showed that increasing the numbers of PDI building blocks is beneficial to photovoltaic performance and leads to efficiency over 5%.

1. Introduction

Organic solar cells (OSCs) have been attracting numerous attention for their advantages including low cost fabrication, flexibility and light-weight [1–3]. The bulk heterojunction configuration is most used for constructing the solar cell devices, which

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includes a blend with p-type donors and n-type acceptors [4]. Through tuning the parameters such as bandgaps, charge transport mobilities, and extinction coefficients, numerous p-type conjugated polymers have been designed and synthesized for donors to achieve high performance solar cells [5–10]. In comparison, the fullerene derivatives are dominant in n-type acceptors for years due to their triplet degeneration of LUMO [11], extremely fast charge split (~45 fs) [12], and excellent electron transport mobilities [13]. To date, the fullerene based single junction organic solar cells have achieved high efficiency over 10% [14–17]. However, the fullerene acceptors still have several intrinsic drawbacks. First, the visible light absorption of fullerene derivatives is weak due to symmetric forbidden. Second, the fullerene derivatives are costly partly due to their high energy consumption in production [18].

Recently, non-fullerene n-type organic semiconductors emerged as promising alternatives for fullerene derivatives due to their tunable bandgap, strong absorption in the visible region, and potential low cost production [19–22]. In combination with optimal p-type donors, the highest reported efficiency of non-fullerene n-type molecular acceptors based solar cells is over 7% [23–26]. Several important strategies have been proposed to design optimal non-fullerene molecular acceptor. First, electron deficient building blocks with extended π-conjugated backbone such as perylene diimide (PDI) [23–25,27–37], naphthalene diimide (NDI) [38], thiadiazole [39], diketopyrrolopyrrol [40,41], quinacridone [42] and others [43–50] were used to ensure the efficient charge delocalization and transport. Second, dimers or oligomers with same electron deficient units were designed and synthesized to achieve high density of states at the LUMO. For example, various dimeric and tetrameric PDI acceptors [23,24] were designed for high performance solar cells. However, to the best of our knowledge, direct comparison of oligomers with different numbers but same structure of electron deficient building blocks to probe the influence of the numbers of electron deficient building blocks on the solar cell performance has never been reported. Last, 3D structures were employed to enforce a nonplanar geometry and achieve optimal morphology for high efficient charge separation and transport. Twisted compounds with 3D configuration such as triphenylamine [51,52], tetraphenyl carbon group [34], tetraphenyl ethylene [53], spiro-bifluorene [28,30], indacenodithieno [3,2-b]thiophene [46,47] were employed as cores to connect electron deficient building blocks.

Previously, SF-PDI2 with dihexyl chains was reported to be an excellent non-fullerene acceptor to achieve high performance solar cells [28]. At the same time, the two unfunctionalized phenyl rings afford the opportunity to further optimize the structure through molecular engineering. In this contribution, we connected two and four PDI building blocks with the highly twisted sprio-bifluorene core to achieve two novel dimeric and oligomeric n-type acceptors, 2,7′-di[N,N′-Bis(2-*octyl-dodecyl*)-perylene-3,4,9,10-tetracarboxylic diimide]-9,9′-spirobi[9H-fluorene] (SF-PDI2) and 2,2′,7,7′-tetrakis[N,N′-Bis(2-*octyl-dodecyl*)-perylene-3,4,9,10-tetracarboxylic diimide]-9,9′-spirobi[9H-fluorene] (SF-PDI4). We employed 2-octyldodecyl side chains for good solubility. Both acceptors exhibit 3D structures with a concentrated LUMO distribution on PDI planes, which facilitates charge split and transport. Two low bandgap conjugated polymers PTB7-Th [54,55] and PffBT4T-2OD [14] were chosen to construct organic solar cells due to their complementary optical absorptions to PDI analogues. The photovoltaic performances of both polymer:SF-PDI4 systems are superior to those of the corresponding polymer:SF-PDI2 systems. As the result, the PTB7-Th:SF-PDI4 based solar cells achieved efficiency over 5%. The charge transport ability, photoluminescence, morphology, and crystallinity of the blend films were investigated and consistent with the photovoltaic performances. During preparation of this manuscript, SF-PDI4 with different alkyl chains (dihexyl and 2-ethylhexyl) was reported independently as non-fullerene acceptor for OSCs by two groups [30,35]. Both of them afforded high efficiencies with 5.3% and 5.98%.

2. Experimental section

2.1. Characterization

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AVANCE NMR spectrometer. Mass spectra were measured on a Bruker Autoflex III Mass Spectrometer. Elemental analysis was recorded on a FLASH EA 1112 elemental analyzer. The electrochemical cyclic voltammetry (CV) was carried out in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) chloroform solution as the supporting electrolyte with a scan speed at 0.05 V/s. A Pt wire, glassy carbon discs, and Ag/AgCl were used as the counter, working electrode, and reference electrodes, respectively. A ferrocene/ferrocenium redox couple was used as an external standard. UV–vis absorption spectra were carried out using a Gary 60 UV–vis Spectrophotometer. All the film samples were spin casted on glass substrates. The morphology of blend films was observed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. All film samples were spin casted on ITO/ZnO substrates. The transmission electron microscopy (TEM) characterization was measured on a FEI Tecnai G2 F20. The scanning electron microscopy (SEM) characterization was measured on Quanta 250 FEG. GIWAXS characterization was performed at Xeuss 2.0 and samples were prepared on ITO/ZnO substrates using identical blend solutions as those used in devices. The incident angle was 0.14°. The scattered X-rays were detected by using a Dectris Pilatus 2 M photon counting detector. Thermogravimetric analysis (TGA) measurements were carried out using a Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were measured using a TA Instruments differential scanning calorimeter (Q2000) under nitrogen at a heating rate of 10 °C/min.

2.2. Fabrication and characterization of polymer solar cells

Inverted solar cells consisted of a stack of glass/ITO(110 nm)/ZnO(25 nm)/active layer(70–90 nm)/MoO_3(10 nm)/Ag(100 nm). ITO-coated glass substrates were first cleaned by ultrasonic agitation in detergent, deionized water, acetone, and isopropanol in sequence, followed by drying at 80 °C in an oven for an hour and then UV ozone treatment for 30 min. 25 μL of ZnO precursor solution was spin-coated on top of the pre-cleaned ITO (4500 rpm, 40 s). After coating, ZnO films were annealed at 200 °C for 30 min.

The photoactive layers were deposited in a glove box by spin coating. In the case of PTB7-Th, the chlorobenzene solution contains 10 mg/mL of the PTB7-Th, 15 mg/mL of small molecule and various concentrations of CN or DIO as additives. The solution was then spin-coated on the substrate at 2000 rpm for 1 min.

The solution was heat at 110 °C at least 3 h and spin-coated at 100 °C. After spin-coating, the substrate was annealed at 80 °C for 5 min. The thin films were transferred into a vacuum evaporator inside of the glove box. MoO_3 (10 nm) and Ag (100 nm) were deposited sequentially by thermal evaporation under 10^{-5} Pa. All device *J-V* characterizations were performed under AM1.5G using a Newport solar simulator. EQEs were measured using a Newport EQE system with a standard Si diode.

The device area was 0.04 cm^2.