Dyes and Pigments xxx (2016) 1–7

Contents lists available at ScienceDirect

Dyes and Pigments

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

# Nonfullerene acceptor with strong near-infrared absorption for polymer solar cells

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ARTICLE INFO

*Article history:*
Received 18 August 2016
Received in revised form
1 November 2016
Accepted 1 November 2016
Available online xxx

*Keywords:*
Polymer solar cells
Nonfullerene acceptor
Ternary blend
Indacenodithiophene
Diketopyrrolopyrrole
Rhodanine

ABSTRACT

A fused-ring electron acceptor based on indacenodithiophene was designed and synthesized. The nonfullerene acceptor shows strong absorption in 500–850 nm with extinction coefficient up to $1.4 \times 10^5\ M^{-1}\ cm^{-1}$ and relatively high lowest unoccupied molecular orbital energy level (−3.55 eV). As an electron-cascade acceptor and strong absorption material, the new acceptor was incorporated into poly(3-hexylthiophene): [6,6]-phenyl-$C_{61}$-butyric-acidmethyl-ester blend to fabricate ternary blend polymer solar cells. The introduction of the nonfullerene acceptor can not only broaden the light absorption of the active layer to the near-infrared region, but also increase the open circuit voltage due to the higher lowest unoccupied molecular orbital of the nonfullerene acceptor relative to the fullerene acceptor. Ternary blend devices with 20% of the nonfullerene acceptor exhibited an average power conversion efficiency of 3.84%, higher than those of the binary blends using the fullerene acceptor (3.30%) or the nonfullerene acceptor (1.42%).

## 1. Introduction

Solution-processed bulk heterojunction (BHJ) polymer solar cells (PSCs) have drawn considerable attention due to their advantages, such as low cost, light weight, flexibility, and large area fabrication [1–7]. Over the last few years, several methods have been proposed to improve the performance of PSCs, among which high performance narrow bandgap polymer donor materials have developed rapidly [8–13]. To date, power conversion efficiencies (PCEs) exceeding 11% have been achieved for PSCs based on a blend of narrow bandgap polymer donors and fullerene acceptors [14].

However, most of the narrow bandgap polymer donors are relatively expensive and complex to synthesize, which will be difficult to scale up. In contrast, poly(3-hexylthiophene) (P3HT) has some advantages, such as high crystallinity, good charge-transport property, easy synthesis and low cost [15]. More importantly, PSCs based on blends of P3HT and [6,6]-phenyl-$C_{61}$-butyric-acidmethyl-ester ($PC_{61}BM$) are a relatively mature and well-understood system. The active layer of the devices based on P3HT: $PC_{61}BM$ can be thick up to 200–300 nm, which is beneficial to fabricating large area solar cells [4,16]. Besides, the PCEs of the P3HT: $PC_{61}BM$ based large area devices can still reach 3% [17].

Nevertheless, the PCEs of PSCs based on P3HT: $PC_{61}BM$ are still relatively low due to weak and narrow light absorption as well as the high highest occupied molecular orbital (HOMO) energy level of P3HT. Recently, some efforts has been made to solve the inadequacy of P3HT: $PC_{61}BM$, among which ternary blend PSCs which contain one donor, one acceptor and a third component have received increasing attention [18–23]. Compared with the traditional binary blend, ternary blend PSCs present some advantages: stronger and broader absorption, more efficient charge transfer, more efficient charge transport pathways, more sufficient charge extraction at the electrodes and better stability [24]. On one hand, some research groups introduced some strong near-infrared (NIR) absorption materials including dyes, polymers and small molecules to enhance the absorption of the P3HT: $PC_{61}BM$ based active layers, which can improve the short-circuit current density ($J_{SC}$) [25–30]. On the other hand, some groups utilized some acceptor materials with higher lowest unoccupied molecular orbital (LUMO) energy levels

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http://dx.doi.org/10.1016/j.dyepig.2016.11.005
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Please cite this article in press as: Li T, et al., Nonfullerene acceptor with strong near-infrared absorption for polymer solar cells, Dyes and Pigments (2016), http://dx.doi.org/10.1016/j.dyepig.2016.11.005

like indene-$C_{60}$ bis-adduct to increase the $V_{OC}$ [31,32].

The Indacenodithiophene (IDT) unit has been widely used in the organic semiconductor field due to its excellent electron-donating and hole-transporting properties. Meanwhile, its energy levels can be tuned by using different end-capping electron-deficient groups [33–42]. Since the initial exploration by the Zhan group, many fused-ring electron acceptor materials based on IDT moiety have been synthesized and used in nonfullerene PSCs in the past three years, some of which yielded PCEs of 8–11% [43–46].

Here we have designed and synthesized a small molecule acceptor IDT-DPP-R with an "$A_1$-$A_2$-D-$A_2$-$A_1$" structure using IDT unit as the donor (D) core, diketopyrrolopyrrole (DPP) unit as the bridging acceptor ($A_2$) and rhodanine (R) unit as the end-capping acceptor ($A_1$) (Fig. 1). IDT-DPP-R exhibits strong NIR absorption and appropriate energy levels. As an electron-cascade acceptor and strong absorption material, IDT-DPP-R was incorporated into P3HT: $PC_{61}BM$ blend to fabricate ternary blend PSCs. The introduction of IDT-DPP-R can not only broaden the light absorption of the active layer to NIR region, but also increase the $V_{OC}$ due to the higher LUMO energy level of IDT-DPP-R relative to $PC_{61}BM$. Ternary blend devices with 20% IDT-DPP-R content exhibit an average PCE of 3.84%, higher than those of the P3HT: $PC_{61}BM$ (3.30%) and P3HT: IDT-DPP-R binary blends (1.42%).

## 2. Experimental section

### 2.1. Measurements and characterization

$^1H$ NMR spectra were recorded using a Bruker AVANCE 400 MHz spectrometer. $^{13}C$ NMR spectra were recorded using a Bruker AVANCE 400 MHz spectrometer. Mass spectra were recorded using Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode. Elemental analysis was performed using a Flash EA1112 analyzer. The melting point was conducted on a SGW X-4 Microscopic melting point apparatus. Fourier transform infrared spectroscopy (FT-IR) was performed using a Bruker Tensor 27 with a thin KBr pellet. Photoluminescence spectra, fluorescence quantum yields ($\Phi$) and Stokes shifts ($\Delta_{ss}$) were measured by using a Hitachi F-4500 fluorescence spectrophotometer. $\Phi$ of the luminescent compounds were measured with rhodamine ($\Phi = 0.89$) in ethanol solution as a standard, $\lambda_{ex} = 495$ nm. UV–vis absorption (solution in chloroform, thin film using quartz substrate) was measured using a JΛSCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen in a solution of tetra-*n*-butylammonium hexafluorophosphate ($[^nBu_4N]^+[PF_6]^-$) (0.1 M) in $CH_3CN$ employing a computer-controlled CHI660C electrochemical workstation, glassy carbon working electrode coated with IDT-DPP-R film, a platinum-wire auxiliary electrode, and an Ag/AgCl reference electrode. The potentials were referenced to a ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple using ferrocene as an internal standard. Thermogravimetric analysis (TGA) measurements were performed using a Shimadzu thermogravimetric analyzer (Model DTG-60) under flowing nitrogen gas at a heating rate of 10 °C $min^{-1}$. The nanoscale morphology of the blended films was observed using a Bruker multimode ScanAsyst atomic force microscope (AFM) in the tapping mode. The grazing incidence X-ray diffraction (GIXRD) data were obtained at beamline 1W1A of the Beijing Synchrotron Radiation Facility (BSRF) at a wavelength of 1.54 Å. 1W1A is a beamline based on a bending mirror while a Si (220) bent crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about 0.7 × 0.4 $mm^2$ and the end station is equipped with a Huber 4-Circle diffractometers 424–511.1. A NaI scintillation detector was used for data collection. The transmission electron microscopy (TEM) characterization was carried out on a JEM-2100 transmission electron microscope operated at 200 kV. The samples for the TEM measurements were prepared as follows: The active layer films were spin-casted on ITO/PEDOT:PSS substrates, and the substrates with the active layers were submerged in deionized water to make the active layers float onto the air–water interface. Then, the floated films were picked up on unsupported 200 mesh copper grids for the TEM measurements.

### 2.2. Fabrication and characterization of the photovoltaic cells

Photovoltaic cells were fabricated with the structure of ITO/PEDOT: PSS/P3HT: IDT-DPP-R: $PC_{61}BM$/Ca/Al. The patterned indium tin oxide (ITO) glass (sheet resistance = 10 $\Omega\ \square^{-1}$) was pre-cleaned in an ultrasonic bath with acetone and isopropanol, and treated in an ultraviolet-ozone chamber (Jelight Company, USA) for 20 min. A thin layer (35 nm) of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT: PSS, Baytron PVP AI 4083, Germany) was spin-coated onto the ITO glass, and then baked at 150 °C for 20 min. A mixture of P3HT: IDT-DPP-R: $PC_{61}BM$ was dissolved in *o*-dichlorobenzene (*o*-DCB) solvent with stirring overnight. Then, the solution was spin-coated on the PEDOT: PSS layer, followed by thermal annealing at 140 °C for 15 min to form a photosensitive layer. The thickness of the photosensitive layer was measured on a Bruker DektakXT profilometer. The calcium layer (*ca.* 20 nm) and the aluminium layer (*ca.* 50 nm) were subsequently evaporated onto the surface of the photosensitive layer under vacuum (*ca.* $10^{-5}$ Pa) to form the negative electrode. The active area of the device was 4 $mm^2$. An XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70 × 70 $mm^2$ photobeam size) coupled with AM 1.5 G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW $cm^{-2}$. A 2 × 2 $cm^2$ monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The current-voltage (*J-V*) measurement of the devices was conducted using a computer-controlled Agilent B2912A Precision Source/Measure Unit (Agilent Technologies). The external quantum efficiency (EQE) spectrum was measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

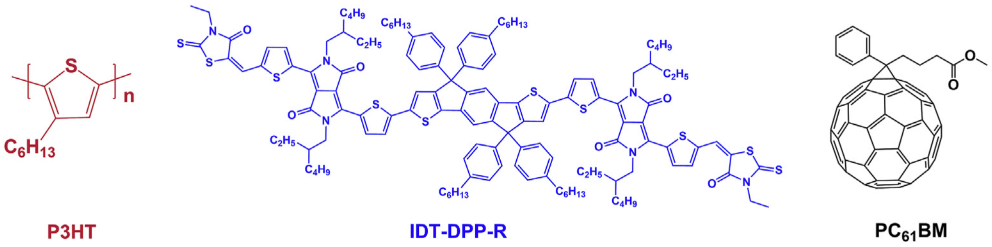

**Fig. 1.** Chemical structures of P3HT, IDT-DPP-R, and $PC_{61}BM$.

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