



# Synthesis and photovoltaic properties of the copolymers based on 3-ethylrhodanine side group



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## ABSTRACT

Four conjugated copolymers (PBDT-TRD, PBDT-3TRD, PBDT-TTRD, and PBDT-3TTRD) based on 3-ethylrhodanine in the side chains have been designed and synthesized. The effects of the conjugated  $\pi$ -bridge and 3-ethylrhodanine unit on absorption spectra, energy levels, and photovoltaic properties of the copolymers have been investigated. These copolymers exhibit good thermal stabilities, broad absorption spectra, and deep highest occupied molecular orbital (HOMO) energy levels. The polymer solar cells have been fabricated by using these copolymers as the donors and [6,6]-phenylC<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as the acceptor. Among them, the devices based on PBDT-TRD and PBDT-TTRD demonstrated preferable power conversion efficiencies of 3.35% and 3.18% with high open-circuit voltages of 0.94 V and 0.85 V, respectively.

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## 1. Introduction

Bulk heterojunction polymer solar cells (BHJ-PSCs) have stimulated consistent attention recently due to their advantages of low cost, roll-to-roll production, good compatibility, flexible substrate, and mechanical flexibility versus conventional inorganic-based solar cells [1–5]. Nowadays, the power conversion efficiencies (PCEs) of BHJ-PSCs have exceed 10% due to the significant improvements of molecular structure, surface morphology, fabricating technique and the optimization in device configuration [6–10]. To pursue higher photovoltaic performances, it has been realized that an ideal polymer donor shall possess excellent film-forming ability with good solubility, broad and strong absorption spectrum, suitable energy level, and high hole mobility matching with the electron mobility of the fullerene acceptor. Recently, a lot of research efforts have been concentrated on the development of Donor–Acceptor (D–A) copolymers with narrow band gap, consisting of

electron-rich donor units and electron-deficient acceptor units. Some copolymers with narrow band gap have achieved great success in high-performance PSCs. Meanwhile, the other D–A copolymers with electron-withdrawing side chains have attracted considerable attention with the advantages of good solubility, relatively deep highest occupied molecular orbital (HOMO) energy level, and excellent film-forming ability [11–13].

We all know, the benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) is one of the most potential and effective donor units in D–A copolymers, because of the advantages of structural symmetry and conjugated planarity which can promote electron delocalization and intermolecular interaction [14–16]. Simultaneously, the HOMO energy levels of many BDT-based polymers are low-lying, which will be beneficial for obtaining high open-circuit voltage ( $V_{oc}$ ). 3-Ethylrhodanine has been investigated and used by Chen et al. as a strong acceptor unit in the solution-processed small-molecule (SM) BHJ solar cells [17–20]. The small molecules based on 3-ethylrhodanine units have shown the PCE values over 8%, which are among the highest efficiencies reported to date for small-molecule-based solar

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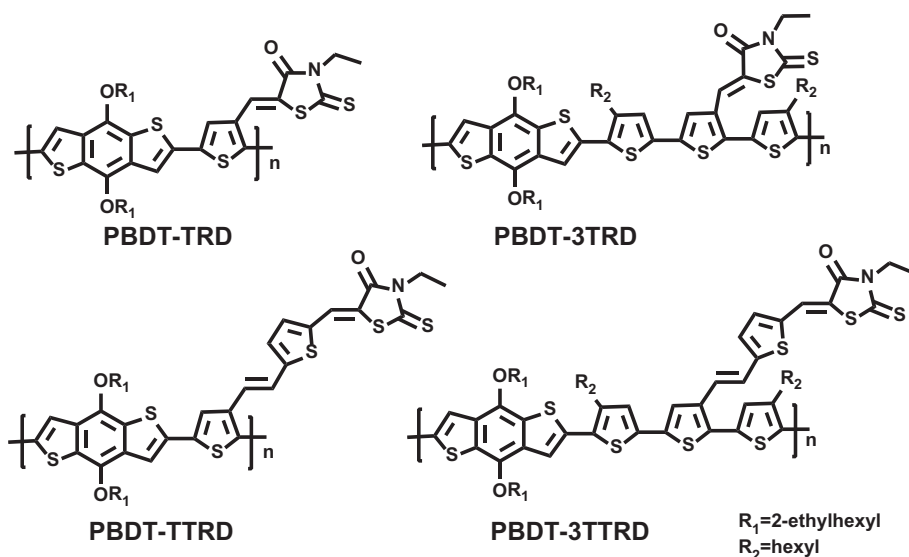


Fig. 1. Molecular structures of the copolymers.

cells [17,21]. It is noticed that incorporating 3-ethylrhodanine unit can improve the light absorption ability and increase short-circuit current ( $J_{sc}$ ) in SM-BHJ devices [22,23]. Theoretically, we can look forward to establishing a balance between high  $V_{oc}$  and high  $J_{sc}$ , thus achieving high photovoltaic performances for the resultant copolymers by combining the merits of BDT and 3-ethylrhodanine together.

On the basis of the considerations mentioned above, four alternating copolymers, namely PBBDT-TRD, PBBDT-3TRD, PBBDT-TTRD, and PBBDT-3TTRD (Fig. 1), have been designed and synthesized for application as donor materials in PSCs. To our best knowledge, it is the first time that 3-ethylrhodanine unit has been introduced into the side chains of the polymers for PSCs. To improve the solubility and increase the conjugation length of polymer backbone, 3-hexylthiophene is inserted between BDT and thiophene. Thienylene-vinylene serves to extend the  $\pi$ -conjugation and eliminate torsional strain between the polymer backbone and 3-ethylrhodanine side group.

## 2. Experimental section

### 2.1. Instruments and characterizations

NMR spectra were recorded on a Bruker AVANCE 400 spectrometer with deuterated chloroform as the solvent. Molecular mass of the compounds were measured by matrix assisted laser desorption–ionization time-of-flight mass spectrometry (MALDI-TOF MS) using a Bruker Aupoflex-III mass spectrometer. Thermal gravimetric analysis (TGA) was carried out on a Netzsch TG 209 analyzer. UV–Vis spectra were measured with a Perkin–Elmer Lamada 25 UV–Vis–NIR spectrometer. Cyclic voltammetry (CV) experiments were performed on an electrochemistry workstation (ZAHNER ZENNIUM) with the polymer film on Pt slice as the working electrode, Pt

slice as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The average molecular weight and polydispersity index (PDI) of the polymers were measured on Waters 1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. The atomic force microscopy was performed on a Digital Instruments Enviro Scope by using a tapping-mode.

### 2.2. Fabrication and characterization of solar cells

The devices were fabricated with a structure of glass/ITO/MoO<sub>3</sub> (20 nm)/Copolymer:PC<sub>61</sub>BM (~100 nm)/LiF(0.5 nm)/Al(100 nm). A thin layer (20 nm) of MoO<sub>3</sub> was deposited on a cleaned ITO glass by vacuum evaporation under  $5 \times 10^{-4}$  Pa, and then baked at 100 °C for 15 min. Subsequently, the active layer (~100 nm) was spin-coated from a blend *o*-dichlorobenzene solution of copolymers and [6,6]-phenylC<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) onto the ITO/MoO<sub>3</sub> surface. Then 0.5 nm LiF and 100 nm Al were successively deposited on the top of active layer under high vacuum of  $5 \times 10^{-4}$  Pa. The effective area of each cell was 3.8 mm<sup>2</sup> defined by the mask. The current density–voltage ( $J$ – $V$ ) curves were measured by a Keithley 2602 Source Meter under 100 mW cm<sup>-2</sup> standard AM 1.5G spectrum using a Sol 3A Oriel solar simulator. The incident light intensity was calibrated using a standard Si solar cell. The measurement of monochromatic incident photon-to-current conversion efficiencies (IPCE) was performed using a Zolix Solar Cell Scan 100 QE/IPCE measurement system.

### 2.3. Materials and synthesis

All the chemicals were purchased from Alfa Aesar and Chem Greatwall Chemical Company (Wuhan, China) and used without further purification. Column chromatography

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