



# Improved photovoltaic properties of the copolymers based on diketopyrrolopyrrole with broad absorption and high open-circuit voltage



Huan Guo, Chao Weng, Guo Wang, Bin Zhao, Songting Tan\*

College of Chemistry, and Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, Xiangtan, 411105, PR China

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## ABSTRACT

A series of donor–acceptor conjugated polymers based on the alkylthienyl-benzodithiophene (BDTT) as an electron-rich unit, and diketopyrrolopyrrole (DPP) incorporated in backbone or side chain as electron-deficient units have been synthesized and applied in polymer solar cells. Compared with the binary copolymers, random terpolymers exhibit a broader absorption range. By controlling the ratio of the electron-deficient units, both photophysical, electrochemical properties, lamellar distance,  $\pi$ – $\pi^*$  stacking distance and the photovoltaic properties of the random terpolymers were changed dramatically. Bulk heterojunction polymer solar cells based on the copolymers as the electron donors and (6,6)-phenyl-C<sub>61</sub>-butyric acid methyl ester as the acceptor were fabricated. The power conversion efficiency of 4.46% was obtained from the terpolymer (**PBDTT-DPP-TDPP**). Optimization via solution vapor annealing, the binary copolymer (**PBDTT-TDPP**) showed the best power conversion efficiency of 4.74% with a short-circuit current of 10.63 mA cm<sup>-2</sup>, a high open-circuit voltage of 0.88 V and a fill factor of 51.0%.

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## 1. Introduction

Conjugated polymers have been recognized as one of the most promising active materials of polymer solar cells (PSCs) because of various advantages such as lightweight, solution processability, flexibility, and low-cost [1–5]. Up to now, the power conversion efficiencies (PCE) of single junction PSCs surpass 10% [6]. Although progress has been impressive, the efficiencies of PSCs are still too low for their commercialization [7]. One of the most successful approaches to achieve high performance PSCs is to develop low bandgap polymers [8,9]. Synthesizing copolymers consisting of an electron-donating (D) and an electron-withdrawing (A) unit is an efficient approach to obtain a low bandgap polymer. This approach allows us to tune the absorption range and bandgap of conjugated polymer by choosing an appropriate combination of D and A units. Although many D and A units have been developed, only a few D–A alternating copolymers show the PCE over 9% in a single-junction device because of the lower short-circuit current density ( $J_{sc}$ ) [10–19]. Therefore, a goal is to enhance the device performance by

overcoming the limitation of low  $J_{sc}$  for D–A type copolymers.

The synthesis of copolymers with a broad and strong absorption in the visible to near-infrared region is an efficient strategy to obtain high  $J_{sc}$ . One potential strategy towards broadening the absorption of the solar spectrum is to synthesize random terpolymers which consist of one D unit and two A units (D–A–A) or two D units and one A unit (D–D–A). Among the electron-withdrawing units, diketopyrrolopyrrole (DPP) has emerged as an interesting material in paints, plastic, ink, thin-film transistors, and PSC applications [20,21]. It possesses a planar and well-conjugated electron-deficient lactam ring that gives rise to strong  $\pi$ – $\pi$  interactions, and results in strong intramolecular charge transfer (ICT) and a broad absorption spectrum ranging from the visible to near-infrared region, especially at 600–900 nm [22,23]. However, the open circuit voltage ( $V_{oc}$ ) of the devices from copolymers with DPP units is usually low due to elevation of the HOMO energy level.

Nowadays, most of the DPP-based copolymers are in main-chain D–A framework, which may suffer from low solubility due to the influence of acceptor units in the main chain. Compared to the main-chain D–A copolymers, the side-chain copolymers mainly possess some advantages. First, the highest occupied molecular orbit (HOMO) energy levels of the side-chain polymers can reside in

\* Corresponding author.

E-mail address: [tanst2008@163.com](mailto:tanst2008@163.com) (S. Tan).

a deeper position. Second, a two-dimensional like structural feature makes this class of polymers have better solubility. Finally, there exists an effective ICT behavior from the side-chain D–A structure, which can fine-tune the band gap ( $E_g$ ) of the resultant copolymers as well as promote an isotropic charge transport along the polymeric main chain [24]. As a result of these advantages, PSCs based on these side-chain D–A copolymers have a light prospect. Notably, the copolymers with the side chain containing diketopyrrolopyrrole (TTDPP) exhibited excellent properties, including good film-forming and a deep-lying energy level of the highest occupied molecular orbital (HOMO). More importantly, there is strong absorption at 300–700 nm. Based on the considerations above, the combination of DPP and TTDPP electron-deficient units in a polymer backbone could be ideal for complementary and broad light absorption.

Herein, we designed and synthesized a series of random terpolymers based on one electron-rich unit, 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (BDTT), and two electron-deficient units, 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP) incorporated in backbone or side chain (TTDPP), which have broad light absorption ranging from 300 to 900 nm. The much more broadened absorption of the copolymers gave a great potential for improving the PSC performance and provided an ideal system for studying the effect of composition on the PSC performances. To understand the effects of DPP and TTDPP on the non-linear compositional dependence of the PCE, the thermal, photophysical, electrochemical, and photovoltaic properties of these random terpolymers were systematically investigated. As well as optimization on device performance via THF vapor annealing are investigated, and the binary copolymer (PBDTT-TTDPP) obtained the best power conversion efficiency because the higher  $J_{sc}$  lead by improved morphology of the copolymer/PC<sub>61</sub>BM blend film.

## 2. Experimental section

### 2.1. Materials

The copolymers were synthesized according to Scheme 1. The materials, 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (DPP, **M1**), (4,8-bis(5-(2-

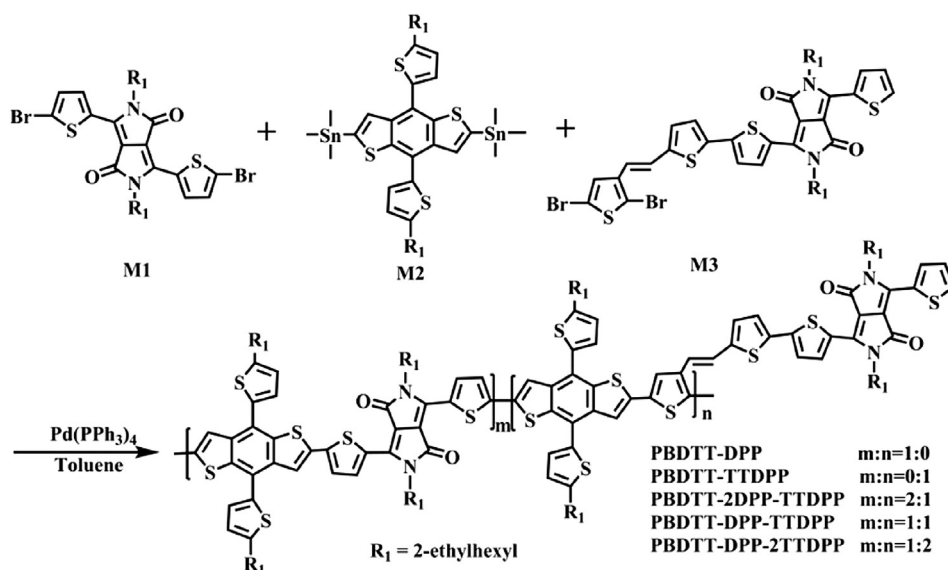
ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (BDTT, **M2**), tetrakis-(triphenylphosphine)palladium(0) [Pd(PPh<sub>3</sub>)<sub>4</sub>], PC<sub>61</sub>BM and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) were purchased from Derthon Optoelectronic Materials Science, Technology Co., Solenne BV and Bayer AG. (E)-3-(5'-(2-(2,5-dibromothiophen-3-yl)vinyl)-[2,2'-bithiophen]-5-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (TTDPP, **M3**) was synthesized according to the reported procedures [25]. Other reagents and solvents were purchased commercially with analytical-grade quality and used without further purification.

### 2.2. Characterization

Nuclear magnetic resonance (NMR) spectra were measured with Bruker AVANCE 400 spectrometer. UV–Visible–Near Infrared (UV–Vis–NIR) absorption spectra of the copolymers were conducted on a Perkin–Elmer Cary 100 UV–Vis–NIR spectrometer. The average molecular weight and polydispersity index (PDI) of the copolymers were determined using Waters 1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Thermogravimetric analysis (TGA) measurement was conducted on a Netzsch TG 209 analyzer under nitrogen at a heating rate of 20 °C min<sup>-1</sup>. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode configuration and an electrochemistry workstation (ZAHNER ZENNIUM) at a scan rate of 100 mV s<sup>-1</sup>. CV was conducted with the thin film on a Pt plate as the working electrode, Pt slice as the counter electrode, and Ag/Ag<sup>+</sup> (saturated 10 mmol L<sup>-1</sup> AgNO<sub>3</sub>) electrode as the reference electrode. The supporting electrolyte is 0.1 M *tetra-n*-butylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in anhydrous acetonitrile solution. Wide-angle X-ray diffraction (WAXRD) was obtained from Bruker d8 discover instrument. Atomic force microscopy (AFM) measurements were performed on a Veecomulty mode 8 in a tapping mode. Thicknesses of thin film were measured with AMBIOS XP-100.

### 2.3. Synthetic routes for copolymers

The synthetic routes of the copolymers were are in Scheme 1.



Scheme 1. Synthetic route for copolymers.

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